Journal of Sustainability Science and Management
Volume 13 Number 1, June 2018 : 133-146
ISSN: 1823-8556

A COMPARISON OF THE EFFECTS OF PREPARATION VARIABLES ON ACTIVITY OF COMPOSITE ANTHILL-CHICKEN EGGSHELL CATALYST FOR BIODIESEL PRODUCTION

ADEYINKA SIKIRU YUSUFF[1,3*], AFEEZ OLAYINKA GBADAMOSI[2], OLALEKAN DAVID ADENIYI[3], MOSES ADEREMI OLUTOYE[3] AND UDUAK GEORGE AKPAN[3]

[1]Department of Chemical and Petroleum Engineering, College of Engineering, Afe Babalola University, Ado-Ekiti, Nigeria. [2]Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310, Johor Bahru, Malaysia. [3]Department of Chemical Engineering, School of Engineering and Engineering Technology, Federal University of Technology, Minna, Nigeria.

**Corresponding author: adeyinkayusuff@yahoo.com*

Abstract: This study is initiated to develop a composite catalyst from naturally occurring and waste materials. The catalyst preparation conditions which include activation temperature (600-1000^{o}C), activation time (2-4 h) and mixing proportion of anthill to eggshell (1:1.5-1:4) were investigated using central composite design (CCD) of response surface methodology (RSM) in design expert software. A model that correlates the three process parameters to the response (biodiesel yield) was established. The model reliability was evaluated using analysis of variance (ANOVA). The catalyst prepared under the optimum conditions was characterized using scanning electron microscopy (SEM), Fourier transform infrared radiation (FTIR) spectroscopy and X-ray Diffraction (XRD) technique. From the ANOVA, both the predicted and experimental biodiesel yields agreed well with each other with correlation coefficient ($R^{2)}$ of 0.9806. The optimum composite anthill-eggshell catalyst preparation conditions were obtained as follow, activation temperature of 1000^{o}C, 4 h activation time and anthill/eggshell mixing ratio of 1:4, which provided biodiesel yield of 70.92%.

Keywords: Biodiesel, composite catalyst, characterization, transesterification, waste cooking oil

Introduction

Due to the double crises of fossil hydrocarbon depletion and environmental deterioration, the search for renewable fuel that contributes less to carbon cycle is ongoing. Out of the alternative fuels discovered so far, biodiesel has been regarded as the most attractive, because it can be produced from renewable resources and the fact that it reduces greenhouse gas emission (Felizardo *et al.,* 2006). From the technical point of view, biodiesel, a form of fatty acid methyl esters (FAME), is usually synthesized from plant oils or animal fats. Generally, it is produced via the transesterification process in which triglyceride contained in those aforementioned feedstocks react with simple alcohol (methanol precisely) using liquid (homogeneous) or solid (heterogeneous) catalyst, to produce FAME and glycerin (Olutoye *et al.,* 2016). However, homogeneous catalyst is often used in commercial production of biodiesel and this is due to the fact that it is cheap and also provides higher biodiesel yield. Meanwhile, homogenous catalysis is associated with problems such as effluent generation, difficulty in reusing catalyst and high production cost. In this regard, biofuel might not be able to contest with fossil hydrocarbon fuel. Recent research has proven that the employment of suitable heterogeneous catalysts could provide solution to these problems (Basumatary, 2013).

Several heterogeneous catalysts, such as single metal oxides (Vujicic *et al.,* 2010), mixed metal oxides (Sun *et al.,* 2010) and sulphated/metal oxides (Chen *et al.,* 2007) have been used in synthesizing biodiesel. Catalytic behaviour of pure CaO for conversion of sunflower oil to biodiesel has been reported (Vujicic *et al.,* 2010). More so, the use of TiO-MgO as catalyst in transesterification of cotton seed oil has been investigated (Wen *et al.* 2010). The use of heterogeneous catalysts derived from agricultural waste (Tan *et al.,* 2015), naturally occurring materials (Olutoye and Hammed,

2013), industrial waste (Olutoye and Hameed, 2011) and domestic waste (Sulaiman *et al.,* 2010) have also been reported. Tan *et al.* (2015) investigated the catalytic conversion of waste cooking oil using calcined ostrich and chicken eggshells as catalysts, while Olutoye *et al.* (2015) had made use of Ba/montmorillonite clay as catalyst for converting waste cooking palm oil to its biodiesel. The majority of these materials are cheap sources of active mixed metal oxides and can also reduce the cost of biodiesel production (Lam & Kee, 2011). Although derivation of solid catalysts from those materials is still ongoing, to the best of our knowledge, no literature on the use of anthill as a potential starting material of a catalyst in transesterification reaction process has been reported (Yusuff, 2017). Moreover, detailed studies on the catalytic activity of mixed naturally occurring (anthill) and waste (eggshell) materials for biofuel synthesis have not been reported. In the present study, however, the composite catalyst was synthesized from anthill and chicken eggshell for the conversion of waste cooking oil (WCO) to biodiesel. An anthill, according to Henne (2009) is a fire clay, which is formed at the entrances of anthill colonies. It has numerous industrial usefulness, including ceramic, cement, bricks, and sand-cast making (Akinwekomi *et al.,* 2012) and adsorbent synthesis (Yusuff, 2017).

Chicken eggshells are agricultural wastes that pose threat to the environment. Eggs are commonly consumable product worldwide because of its nutritional values (Sharma *et al.,* 2010). In Nigeria, eggs are often consumed by citizens because of series of awareness being created by the ministry of health and Poultry Association of Nigeria (PAN). However, over 90% by weight of dried eggshell is calcium carbonate. Thus, it is possible to synthesize from waste eggshell calcium oxide (CaO) based catalyst. Several researchers have synthesized CaO-based catalysts from eggshells of different birds for biodiesel synthesis (Tan *et al.,* 2015; Sharma *et al.,* 2010).

According to Tan *et al.* (2008), the use of suitable statistical experimental design in verifying the impact of treatment on quality attributes is necessary. However, among the various optimization and statistical tools in design expert software, RSM has been regarded as most powerful in that it could identify and quantify interactions between variables (Mahalik *et al.,* 2010; Karacan *et al.,* 2007). It has been widely employed in numerous chemical engineering operations including extraction, catalysis, photocatalytic degradation, hydrolysis, fermentation, adsorption and biodiesel production processes (Tan *et al.,* 2008; Ölmez & Akbas, 2009; Giwa *et al.,* 2012; Igbokwe *et al.,* 2016). Among the reported catalysis studies found in using RSM to investigate the influence of catalyst preparation conditions are palladium-supported alumina (Pd/Al_2O_3) (Alshaibani *et al.,* 2014), red mud loaded Cobalt (Li *et al.,* 2013), Copper/activated carbon (Amanpour *et al.,* 2013), Zeolite-A/sodium (Matob *et al.,* 2012), Platinum-gold/Carbon (Pt-Au/C) (Osman *et al.,* 2014). Thus, in this study, the preparation condition for composite anthill-eggshell was optimized using response surface methodology. The model equation that correlates the independent variables (activation temperature, activation time and mixing ratio of anthill/eggshell) to dependent variable (biodiesel yield) was developed and analyzed by ANOVA to evaluate the reliability of the model. Moreover, the chemical and morphological properties of both raw and thermally treated optimal composite anthill-eggshell (CAE) catalyst were determined using characterization techniques such as SEM, FTIR and XRD.

Materials and Methods

Materials

The anthill harvested for the purpose of this study is situated behind the Works and Project Department, Afe Babalola University (ABUAD), Ado-Ekiti, Nigeria. Waste cooking oil (WCO) and chicken eggshell were collected from the

cafeteria of postgraduate students, ABUAD, Ado-Ekiti, Nigeria. The free fatty acid (FFA) content of the WCO was determined to be 1.987 wt%. The methanol used was GC grade (99.9%). Propylene acetate (internal standard) used for biodiesel analysis in gas chromatography (GC) analyzer and hexane (solvent) were bought from Nizo-chem Enterprise, Akure, Nigeria.

Catalyst Preparation

Preparation of Anthill and Waste Eggshell-derived powders

The procedure employed in synthesizing CAE catalyst was directed to my previous study (Yusuff, 2017). The anthill was first crushed to obtain it in powder form and was then sieved to the required particle size (< 0.3 mm). It was then kept in a covered plastic container. The chicken eggshell was thoroughly washed to remove white membrane and impurities from it and was then heated up at 110^{o}C in an oven overnight in order to remove the water. The dried eggshell was ground with the aid of a mechanical grinder, sieved to required particles size and then kept in a covered plastic container.

Preparation of CAE Catalyst

As suggested by CCD (Table 2), the anthill powder with varied mass ratio to the eggshell powder was dissolved in 100 mL of distilled water and then stirred at room temperature for 2 h. The obtained slurry was heated up at 125^{o}C in an oven overnight in order to remove excess water. Finally, raw CAE at various mixing ratios of anthill to eggshell were calcined at various temperatures (600-1000^{o}C) and corresponding time in the range of 1-4 h using a muffle furnace with heating rate of 10^{o}C/min. The calcined CAE samples were kept in a desiccator containing silica pellet in order to prevent moisture contamination.

Characterization of Composite Anthill-Eggshell catalyst

The SEM analysis was conducted to study the surface texture of raw and activated CAE catalysts prepared under optimum conditions by using SEM analyzer (JEOL-JSM 7600F). FTIR spectroscopy (FTIR-IR Affinity-1S Shimadzu, Japan) applied on the uncalcined and calcined optimal CAE catalysts to determine the surface functional groups, and the spectra were recorded from 4000 to 500 cm^{-1}. The crystalline phases in the optimal catalyst were identified using a GBC eMMA XRD analyzer. A Cukα radiation (1.54051 Å) was employed to generate diffraction patterns at ambient temperature in the scanning angle 2Θ of 5-70 ^{o}.

Experimental Design

In this study, CAE catalyst was prepared by incipient wetness impregnation-calcination method. The catalyst preparation variables studied were activation temperature, T ^{o}C, activation time, t h and mixing proportion of anthill to eggshell, M. CCD was applied to study the effects of the three variables towards response of biodiesel yield (Y). As suggested by CCD (Table 2), a total of twenty (20) experimental runs were conducted, including eight (2^3 = 8) factorial points, six (6) axial points and six (6) replicate at the center point. The replicate at the center point was employed to assess the experimental error. The response considered was the biodiesel yields obtained from transesterification of WCO. The empirical model was proposed for the response which correlated the biodiesel yield with three CAE preparation variables by applying second degree polynomial equation as given by Equation 1 (Kafuku *et al.* 2010).

$$Y = a_0 + a_1T + a_2t + a_3M + a_{12}Tt + a_{13}TM + a_{23}tM + a_{11}T^2 + a_{22}t^2 + a_{33}M^2 \quad (1)$$

where a_0 is the constant coefficient, a_1, a_2 and a_3 are the linear term coefficients, a_{12}, a_{13} and a_{13} are the interaction term coefficients and a_{11}, a_{22}, and a_{33} are the quadratic term coefficients.

Catalyst Activity Study

Waste cooking oil (WCO) was converted to biodiesel via transesterification at optimum reaction conditions obtained from our preliminary experiment (60°C reaction temperature, 2 h reaction time, 3 wt% catalyst loading and methanol/WCO molar ratio of 6:1) using various CAE catalysts prepared under different conditions. The whole experiments were performed in a 250 mL glass reactor coupled with condenser and magnetic stirrer placed on a temperature controlled heating mantle. 30 mL of WCO was heated up to 60°C in an oven, after which a mixture of methanol and catalyst with a required amount was added to the heated oil. The reaction mixture was stirred at a speed of 350 rpm for 2 h. After the reaction was completed, the catalyst was separated from the product mixture (biodiesel and glycerol) by cloth filtration. The biodiesel collected from product mixture was stored in a sample bottle for methyl esters characterization. A gas chromatograph-mass spectroscopy (Varian 4000 GC/MS/MS system) equipped with a Flame Ionization Detection (FID) and Agilent J&W capillary column (60 mm x 0.320 mm x 1.8 μm) with helium as the carrier gas was used to determine the methyl esters composition in the biodiesel samples.

The biodiesel yield (Y) was evaluated using mathematical expression given in equation (2)

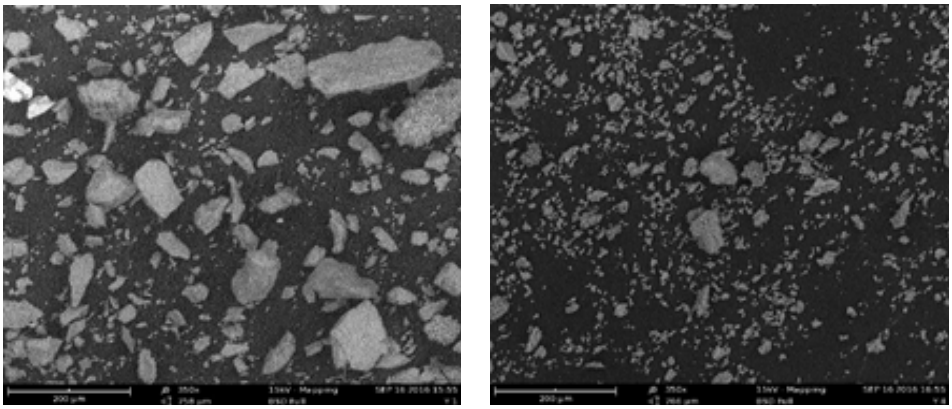
$$\text{Biodiesel yield, } Y\,\% = \frac{(weight\ of\ internal\ standard) \times (peak\ area\ of\ biodiesel\ sample)}{(weight\ of\ biodiesel\ sample) \times (peak\ area\ of\ internal\ standard)} \times 100\% \quad (2)$$

Results and Discussion

Characterization of Optimal CAE Catalyst

Scanning Electron Microscopy (SEM)

The SEM analysis result shown in Figure 1 presents the surface images of uncalcined and calcined optimal CAE catalysts. As can be seen in Figure 1(a), the raw catalyst possessed irregular and undefined particles with larger size. The method of preparation adopted in this study might be responsible for this observation. Meanwhile, upon calcination the larger particles contained in the raw CAE split into smaller particles. This might be due to transformation of raw CAE catalyst to mixed metal oxide with closed interaction and CO_2 (Olutoye & Hameed 2013; Tan *et al.,* 2015), therefore, causing clear pores opening (Leofanti *et al.,* 1997). The present result is in agreement with the finding reported by Tan *et al.* (2015).



(a) (b)

Figure 1: SEM images of (a) uncalcined CAE; (b) calcined CAE.

Fourier Transform Infrared Radiation (FTIR) Spectroscopy

The major FTIR spectra obtained for raw and calcined optimal CAE catalysts are shown in Figure 2 and Table 1. Some of the peaks in raw CAE shifted and new peaks were formed after calcination process. The difference in FTIR spectrum obtained for the raw and activated CAE is an indication that there was transformation of the components into a new phase of active mixed oxides as also corroborated by XRD analysis (Olutoye and Hameed, 2013).

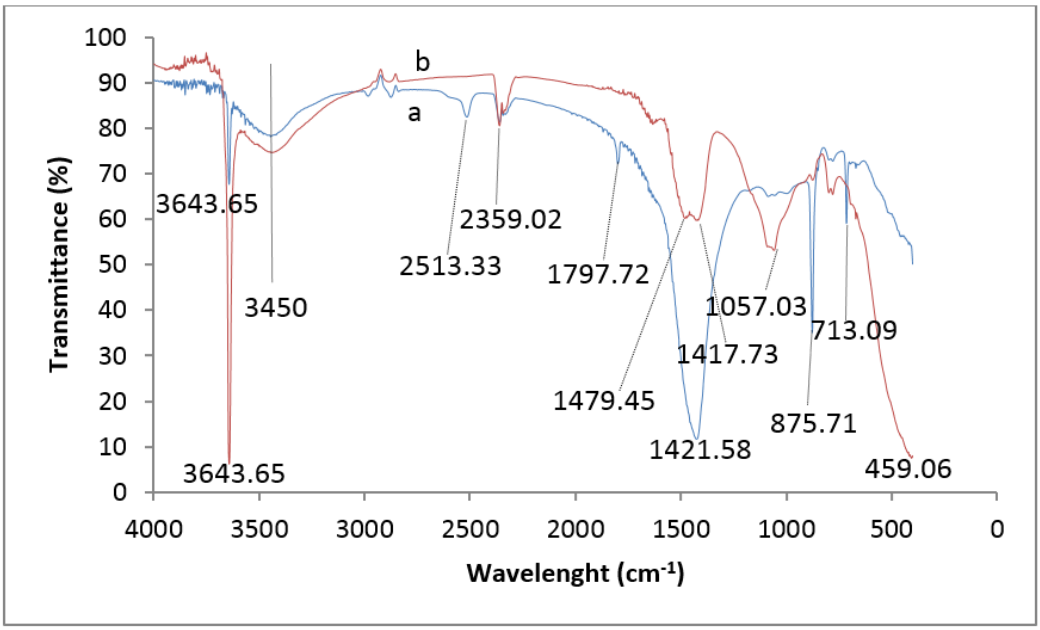


Figure 2: FTIR spectra for (a) raw CAE, (b) Calcined CAE.

Table 1: FTIR bands of CAE catalyst.

Peak	Wavelength cm^{-1}		Assignment
	Raw catalyst	Calcined catalyst	
1	3643.65,3450	3643.65, 3450	O-H stretching vibration in absorbed water
2	2513.33	-	It has not been interpreted definitely, but confirms the existence of $CaCO_3$.
3	-	2359.02	P-H stretching
4	1797.72	-	C=O antisym stretch
5	-	1479.45	CH_3 antisym deformation or CH_2 scissors vibration
6	1421.58	-	C-O asymmetric stretching mode of CO_3^{2-} from $CaCO_3$
7	-	1417.73	C-N stretching band
8	-	1057.03	Al-Al-OH vibration of clay
9	875.71	-	Out of plane bend of C-O
10	713.09	-	In plane bend of C-O
11	-	459.06	Presence of CaO vibration/Si-O in the silica octahedral plates

X-ray Diffraction (XRD) analysis

The result of XRD analysis shown in Figure 3 revealed the crystal phase/structure of CAE. The characteristic peaks which were displayed by the diffraction pattern at 2θ equal to 20.85°, 26.7° and 59.95° corroborate the presence of silica (SiO_2). The first two peak values show patterns for crystal phase, while third peak value is for tridymite. Hassani *et al.* (2014) in their investigation reported the same observation. This implied that SiO_2 constitutes larger percentage in anthill. Meanwhile, the peaks occurred at 2θ equal to 28.7°, 32.3°, 37.45°, 54.0°, 67.6° and 68.2° are all attributed to calcium oxide (CaO), while those peaks at 18.1°, 34.3° and 47.3° corresponded to $Ca(OH)_2$ which might have formed as a result of reaction between CaO and atmospheric moisture. This is corroborated by the FTIR result. However, the presence of CaO in the activated CAE catalyst is as a result of complete decomposition of calcium carbonate contained in chicken eggshell into CaO and CO_2. The detection of SiO_2 and CaO suggested that the calcined composite anthill-eggshell is a supported catalyst (Boey *et al.,* 2011).

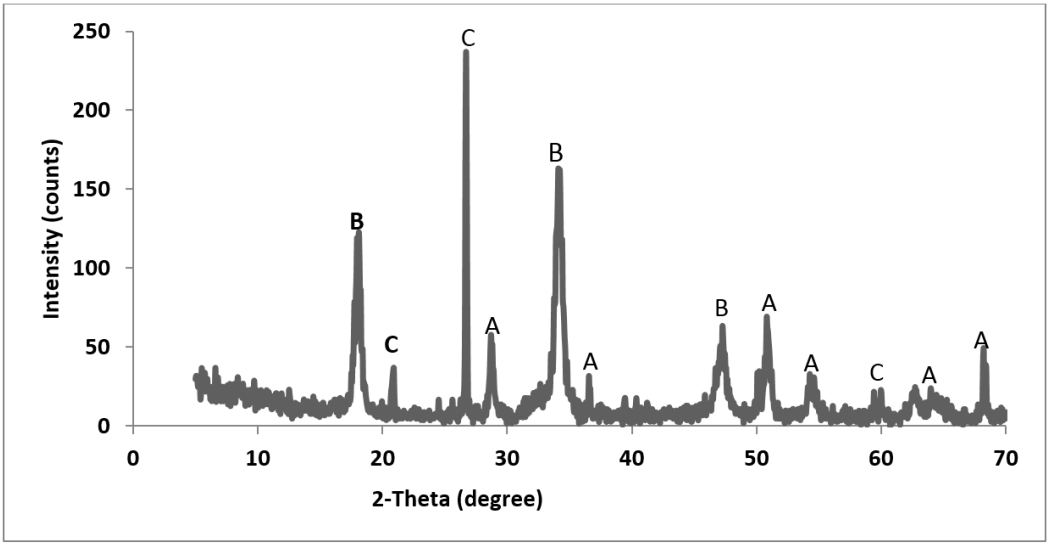


Figure 3: X-ray Diffraction Spectra of the Calcined CAE Catalyst. The Crystalline Phases are also Correspondingly Labeled as: (A) CaO, (B) $Ca(OH)_2$, (C) SiO_2.

Regression model development

Table 2 shows the controlled experimental variables in both coded and actual values as well as their corresponding measured responses (biodiesel yields). The correlation between catalyst preparation variables and the response was developed using central composite design (CCD). Based on the operation of CCD, several models were suggested and a quadratic model was selected because of its level of significance. However, the overall mathematical model equation comprising of actual variables for biodiesel yield (Y) is given in Equation (3).

$$Y = 93.89 - 0.15T - 30.12t + 2.47M - 1.38E - 003Tt - 9.00E - 004TM - 0.34tM + 1.37E - 004T^2 + 7.11t^2 - 0.02M^2 \quad (3)$$

Table 2: CAE preparation process parameters in coded and actual values with biodiesel yields (responses) from the experimental results.

Run No.	Levels			Composite anthill-eggshell catalyst preparation parameters			Biodiesel yield, *Y* (%)	
				Activation temperature, *T* (°C)	Activation time, *t* (h)	Anthill/ eggshell mixing proportion, *M*	Predicted yield	Experimental yield
1	0	0	0	800.00	3.00	30:70	42.08	39.7
2	+1	+1	+1	1000.00	4.00	40:60	53.91	53.5
3	0	0	0	800.00	3.00	30:70	42.08	44.2
4	0	0	+2	800.00	3.00	46.82:53.18	36.37	34.8
5	0	0	0	800.00	3.00	30:70	42.08	43.5
6	0	+2	0	800.00	4.68	30:70	63.72	65.5
7	0	0	0	800.00	3.00	30:70	42.08	42.7
8	0	-2	0	800.00	1.32	30:70	61.65	59.9
9	-2	0	0	463.64	3.00	30:70	43.99	45.6
10	+1	-1	+1	1000.00	2.00	40:60	60.58	62.0
11	+1	-1	-1	1000.00	2.00	20:80	61.4	60.3
12	+2	0	0	1136.36	3.00	30:70	68.18	70.6
13	-1	-1	-1	600.00	2.00	20:80	39.86	41.2
14	-1	-1	+1	600.00	2.00	40:60	46.75	44.8
15	0	0	0	800.00	3.00	30:70	42.08	43.1
16	0	0	-2	800.00	3.00	13.18:86.82	39.0	41.6
17	-1	+1	+1	600.00	4.00	20:80	46.68	42.7
18	+1	+1	-1	1000.00	4.00	20:80	63.93	70.8
19	0	0	0	800.00	3.00	30:70	42.08	39.5
20	-1	+1	-1`	600.00	4.00	20:80	48.99	47.5

The model validity was examined by considering correlation coefficient (R^2) value obtained from experimental data analysis with the principle that the model would predict accurate response, if the value of R^2 for Eq. 3 is approximately equal to one (Yusuff *et al.,* 2017). The value of R^2 (0.9806) obtained herein implies that the model is adequate enough to predict responses (biodiesel yields) that will agree with the experimental values. Thus, it is adequate to validate the fit. Furthermore, ANOVA was employed to justify the model adequacy and also estimate the model statistical features. According to ANOVA result (Table 3), the model F-value was 56.21 and according to Yi *et al.* (2010), the model and its terms are said to be significant, if the F-value magnitude and corresponding probability of error (p-value) are larger and less than 0.05, respectively. Thus, the obtained model was significant.

Table 3: ANOVA table for the model and its terms.

Source	Sum of squares	Degree of freedom	Mean square	F-value	Prob > F
Model	2,288.37	9	254.26	56.21	<0.0001
T	925.82	1	925.82	204.69	<0.0001
t	17.86	1	17.86	3.95	0.0750
M	58.38	1	58.38	12.91	0.0049
Tt	0.6	1	0.60	0.13	0.7222
TM	25.92	1	25.92	5.73	0.0377
tM	93.84	1	93.84	20.75	0.0011
T^2	432.78	1	432.78	95.68	<0.0001
t^2	727.77	1	727.77	160.90	<0.0001
M^2	34.88	1	34.88	7.71	0.0196
Residual	45.23	10	4.52	-	-
$R^2 = 0.9806$; $Adj\text{-}R^2 = 0.9632$					

As shown in Table 3 as well, those significant model terms were *T, M, TM, tM,* T^2, t^2, M^2, while, the other terms were insignificant. However, statistical analysis revealed that the model was appropriate in predicting the responses (biodiesel yields) within the value range of variables considered. As can be observed in Figure 4, the error between the predicted and experimental biodiesel yield is quite small, thus, indicating better correlation between the CAE catalyst preparation process variables and biodiesel yield.

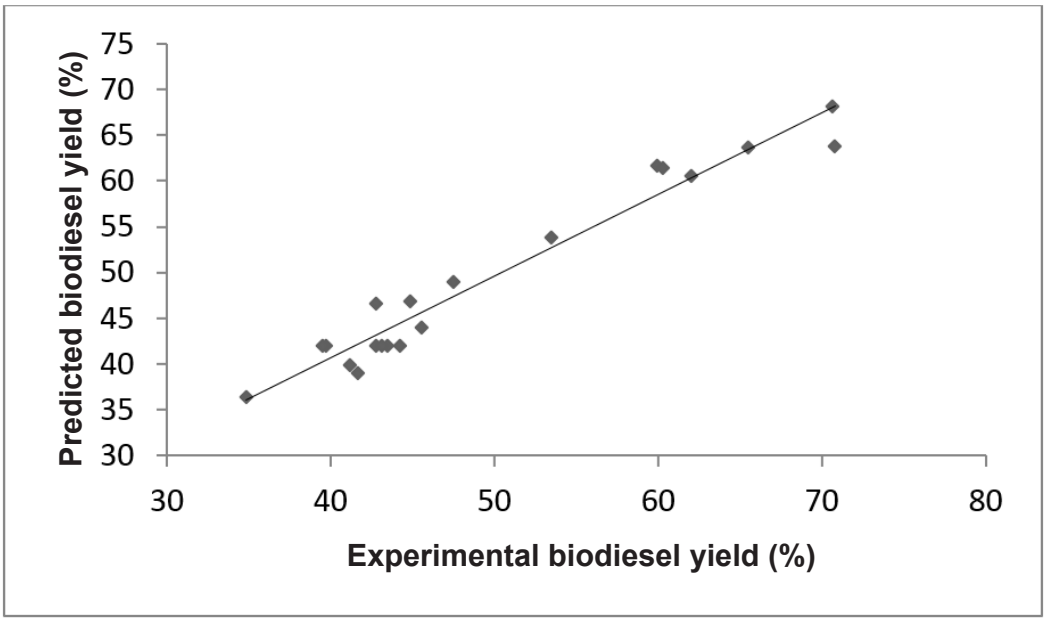


Figure 4: Plot of Predicted value vs. experimental value for biodiesel yield from reduced surface quadratic model.

Influence of individual and interactive effects of preparation variables on biodiesel Yield

As revealed by the ANOVA, the most influential factors on the biodiesel yield are activation temperature (*T*) and mixing proportion (*M*). Activation temperature (*T*) has largest F-value of 204.69 compared to other variables which indicates that it is mostly correlated to biodiesel yield. The effect of anthill/eggshell mixing ratio (*M*) is as well quite significant on the biodiesel yield, with F-value of 12.91 compared to activation time which was smaller. Besides, the quadratic effects of the variables studied, as well as interaction effects of *TM* and *tM* were less than 0.05 as can be seen in Table 3, which indicated that they were relatively significant. This research output revealed the beauty of using design of experiment in examining the interaction among variables that influence the response.

The Figures 5(a) depicts the 3D-plot to display the effects of activation temperature (T) and mixing proportion (M) on biodiesel yield (Y) while keeping activation time constant (t) at 3 h. The plot shows that at 1000°C activation temperature and anthill/eggshell mixing ratio of 2:3, the maximum biodiesel yield was obtained. This observation agreed with the model. It is obvious that thermal treatment of the catalyst at higher temperature brings about solid rearrangement and creation of pores on its surface, thus, paving the way for methanol adsorption (Hattori, 2004). Increasing the anthill content in CAE catalyst from 20% to 40% reduces the biodiesel yield. This indicates that at lower quantity of anthill, there could be better performance of CAE in transesterification reaction. This observation is appropriate because the role of anthill in CAE catalyst is to serve as a support, which should be less than eggshell. This is corroborated by Zabeti *et al.* (2009) who found that anchoring the catalyst active ingredient onto a support significantly reduces leaching.

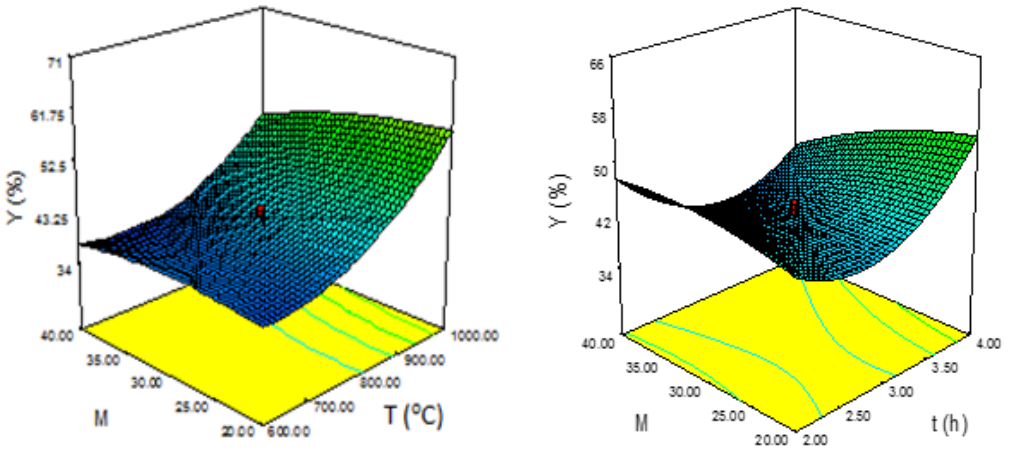


Figure 5: 3D surface plotted for interaction effect of (a) activation temperature (T) and mixing proportion (M); (b) mixing proportion and activation time (t).

Figure 5(b) shows combined effect of activation time (t) and mixing proportion of anthill to eggshell (M), while keeping activation temperature (T) constant at 800°C. The plot shows that the maximum biodiesel yield (Y) at 59.9% occurs when CAE sample (30% anthill-70% eggshell) treated at 800°C for 3 h was used as catalyst in converting WCO to biodiesel. However, it is evidently clear that decreasing the anthill content in CAE catalyst and increasing the activation time result in high biodiesel yield. This is attributed to the presence of CaO (active ingredient) obtained from eggshell, which dominates the catalyst surface

(Olutoye *et al.,* 2016).

There is no doubt that all the three catalyst preparation process variables considered in this study have close interaction and combined effects on the response (biodiesel yield). This is actually expected, because for any material to be used as catalyst such material must pass through a series of preparation stages, including washing, drying, mixing with precursor and calcination. However, to have basic sites exposed on the catalyst surface, calcination at elevated temperature or time is required (Refaat, 2011). This enhances the methanol adsorption (Chorkendorff & Niemantsverdriet, 2003). Meanwhile, there is a maximum limit of activation temperature or time above which agglomeration of particles would set in (Yusuff *et al.,* 2017), whereas, lower activation temperature or time could only partially remove adsorbed gases (CO_2 and SO_2) which occupy and fill up the catalyst pores (Olutoye & Hameed, 2013). Blending proportion of supporting particles to active ingredient in supported catalyst like composite anthill-eggshell plays an important role in the catalyst performance. According to Olutoye *et al.* (2016), if best mixing proportion of composite catalyst constituents is adopted, lixiviation of active ingredient into reaction media will not occur. However, presence of anthill in the prepared catalyst could serve as a support to active ingredient in eggshell, because research has proven that there are large silica (SiO_2) and alumina (Al_2O_3) contents in anthill (Henne, 2009). These metal oxides are regarded as catalyst supports due to their thermal stability (Furuta *et al.,* 2004) and therefore, could prevent the active phase (CaO) in the CAE catalyst from be leached. Thus, study on regeneration and reusability of CAE catalyst needs to be conducted to investigate its stability during reuse.

Composite Anthill-Eggshell Catalyst Preparation Process Optimization

Having established the factors that mostly influence the activity of the CAE catalyst, the optimum condition of CAE preparation process was determined using numerical optimization feature of the RSM. The optimum predicted variables obtained are given in Table 4. Biodiesel yield of 70.72% could be predicted when CAE sample mixed in anthill/eggshell ratio of 1:4 was treated at 1000 ^oC for 4 h. In a bid to ascertain whether the predicted biodiesel is in agreement with the experimental value or not, transesterification reaction was conducted at the same reaction conditions previously used. The experimental biodiesel yield was obtained to be 70.92%, which was close to the predicted value with a slight error of 0.28%.

Table 4: Model validation and optimum condition of CAE catalyst preparation process.

Activation temperature (^oC) (T)	Activation Time (h) (t)	Anthill-eggshell mixing ratio (M)	Biodiesel yield (%)	
			Predicted	Experimental
1000.00	4.00	1:4	70.72	70.92

The activity of the optimal CAE sample for transesterification reaction is quite good as it provided 70.92% of biodiesel yield. However, the low biodiesel yield recorded is as a result of high FFA content in the feedstock used. This indicates that prepared optimal catalyst could be regarded as an effective solid catalyst as it converted high FFA content feedstock to biodiesel via single step transesterification. Moreover, the reaction process conditions adopted in the study were constant throughout. However, further research such as optimization of biodiesel production process is recommended in order to establish favourable reaction conditions and also, enhance the biodiesel yield by considering a two-step transesterification process.

Conclusion

A composite catalyst from naturally occurring and waste materials has been successfully synthesized and utilized for the production of biodiesel from WCO. The characterization results discussed revealed that CAE can serve as a cheap source of supported catalyst in heterogeneous catalyzed reaction. The optimal condition established for the CAE preparation was activation temperature of 1000^{o}C, activation time of 4 h and anthill to eggshell mixing proportion of 1:4. The optimized condition was validated with the actual biodiesel yield of 70.92%. Statistical optimization of CAE preparation parameters revealed that activation temperature and mixing proportion of anthill to eggshell mostly affected the response (biodiesel yield). The prepared CAE catalyst exhibited slow but good performance in conversion of WCO to its biodiesel. Thus, catalyst modification may be required and tested with various biodiesel feedstocks.

Acknowledgements

Our profound appreciation goes to Professor A.I. Igbafe (Head, Chemical Engineering Department, ABUAD Ado-Ekiti, Nigeria) and Dr. M. Abdulkadri (Head of Chemical Engineering Department, FUTMINNA, Minna, Nigeria, for their unlimited support and encouragements.

References

Akinwekomi, A.D., Omotoyinbo, J.A., Folorunso, D. (2012). Effect of high alumina cement on selected foundry properties of anthill clay. *Leonardo Electronic Journal of Practices and Technology,* 1(21), 37-46.

Alshaibani, A., Yaakob, Z., Ghaleeb, A. (2014). Optimization of sunflower oil hydrogenation on Pd-B/ γ-Al_2O_3 catalyst. *Oriental Journal of Chemistry,* 30(1), 161-180.

Amanpour, J., Salari, D., Niaei, A., Mousari, S.M., & Panahi, P.N. (2013). Optimization of Cu/activated carbon catalyst in low temperature selective catalytic reduction of NO process using response surface methodology. *J. Environ. Sci. Health. A Tox Hazard Subst Environ. Eng,* 48(8), 879-886.

Basumatary, S. (2013). Transesterification with heterogeneous catalyst in production of biodiesel. A Review. *Journal of Chemical and Pharmaceutical Research,* 5(1), 1-7.

Boey, P.L., Mariam, G.P., Hamid, S.A., Ali, D.M.H. (2011). Utilization of waste cockle shell (Anadara granosa) in biodiesel production from palm olein optimization using response surface methodology. *Fuel,* 90, 2353-2358.

Chen, H., Peng, B., Wang, D., Wang, J. (2007). Biodiesel production by the transesterification of cottonseed oil by solid acid catalyst. *Frontier of Chemical Engineering in China,* 1(1), 11-15.

Chorkendorff, I., & Niemantsverdriet, J.W. (2001). *Concepts of modern catalysis and kinetics:* Weinhem, Germany: Wiley-VCH press.

Felizardo, P., Neiva Correia, M.J., Raposo, I., Mendes, J.F., Berkemeier, R., & Bordado, J.M. (2006). Production of biodiesel from waste frying oils, *Waste Management,* 26, 487–494.

Furuta, S., Matsuhashi, H., & Arata, K., (2004). Biodiesel fuel production with solid amorphous zirconia catalysis in fixed bed reactor. *Biomass & Bioenergy,* 30(10), 870-873.

Giwa, A., Akpan, U.G., & Hameed, B.H. (2012). Optimization of photocatalytic degradation of an anthraquinone dye using design of experiment. *Journal of Engineering Research,* 17(3), 20-31.

Hassani, M., Najafpour, G.D., Mohammadi, M., & Rabiee, M. (2014). Preparation, characterization and application of zeolite-

based catalyst for production of biodiesel from waste cooking oil. *Journal of Scientific & Industrial Research*, 73, 129-133.

Hattori, H. (2004). Solid Base Catalysts: Generation, characterization, and catalytic behavior of basic sites. *Journal of the Japan Petroleum Institute,* 47 (2), 67-81.

Henne, G.A. (2009). Anthill as a resource for ceramics. A Dissertation submitted to the School of Graduate Studies, Kwame Nkrumah University of Science and Technology.

Igbokwe, P.K., Idogwu, C.N., & Nwabanne, J.T. (2016). Enzymatic hydrolysis and fermentation of plantain peels: Optimization and kinetic studies. *Advances in Chemical Engineering and Sciences,* 6(2), 216-235.

Kafuku, G., Lam, K.T., Kanselo, J., Lee, K.T., & Mbarawa, M. (2010). Heterogeneous catalyzed biodiesel production from Moringa oleifera oil. *Fuel Processing Technology,* 91(11), 1525-1529.

Karacan, F., Ozden, U., Karacan, S. (2007). Optimization of manufacturing conditions for activated carbon from Turkish lignite by chemical activation using response surface methodology. *Applied Thermal Engineering,* 27, 1212–1218.

Lam, M.K., Lee, K.T. (2011). Application of sulphated tin oxides in transesterification waste cooking oil. An optimization study. *International Conference on Bioenvironment, Biodiversity, and Renewable Energies,* 1-4.

Leofanti, G., Tozzola, G., Padovan, M., Petrini, G., Bordiga, S., & Zecchina, A. (1997). Catalyst characterization: characterization techniques. *Catalysis Today*. 34, 307-327.

Mahalik, K., Sahu, J.N., Patwardhan, A., & Meikap, B.C. (2010). Statistical modeling and optimization of hydrolysis of urea to generate ammonia for the flue gas conditioning. *Journal of Hazardous Materials,* 182, 603-610.

Matob, A., Kamarudin, R.A., Jubri, Z., & Ramli, Z. (2012). Response surface methodology for optimizing Zeolite Na-A synthesis. Arabian Journal for Science and Engineering, 37(1), 27-40.

Ölmez, H., & Akbas, M.Y. (2009). Optimization of ozone treatment of fresh-cut green leaf lettuce, *Journal of Food Engineering,* 90(1), 487–494.

Olutoye, M. A., Hameed, B. H., (2011). Synthesis of fatty acid methyl ester from used vegetable cooking oil by solid reusable $Mg_{1-x}Zn_{1+x}O_2$ catalyst. *Bioresource Technology.* 102, 3819-3826.

Olutoye, M.A & Hameed, B.H., (2013), "A highly active clay-based catalyst for the synthesis of fatty acid methyl ester from waste cooking palm oil". *Applied Catalysis A: General.* 450, 57-62

Olutoye, M.A., Adeniyi, O.D, & Yusuff, A.S. (2016). Synthesis of biodiesel from palm kernel oil using mixed clay-eggshell heterogeneous catalysts. *Iranica Journal of Energy and Environment,* 7(3), 308-314.

Olutoye, M.A., Wong, S.W., Chin, L.H., Asif, M., & Hameed, B.H. (2015). Synthesis of fatty acid methyl esters via transesterification of waste cooking oil by methanol with a barium-modified montmorillonite K10 catalyst. *Renewable Energy,* 86(10), 392-398.

Osman, O., Erdogan, A., & Ali, A. (2014). Optimization of catalyst preparation conditions for direct sodium borohydride fuel cell using RSM. *Energy,* 67, 97-105.

Refaat, A.A. (2011). Biodiesel production using solid metal oxide catalysts. *International Journal of Environmental Science and Technology.* 8(1), 203-221.

Sharma, Y.C., Singh, B., & Korstad, J. (2010). Application of an efficient nonconventional

heterogeneous catalyst for biodiesel synthesis from pongamia pinnata oil. *Energy Fuels,* 24, 3223-3231.

Sulaiman, S., Khairudin, N., Jamah, P., Alam, M.Z., Zainudi, Z., & Azmi, S. (2014). Characterization of fish bone catalyst for biodiesel production. *International Journal of Biological, Food, Veterinary and Agricultural Engineering,* 8(5), 464-466.

Sun, H., Ding, Y., Duan, J., Zhang, Q., Wang, Z., Lou, H., & Zheng, X. (2010). Transesterification of sunflower oil to biodiesel on ZrO2 supported La2O3 catalyst. *Bioresource Technology,* 101(3), 953-958.

Tan, I.A.W., Ahmed, A.L., & Hameed, B.H. (2008). Preparation of activated carbon from coconut husk: Optimization study on removal of 2, 4, 6-trichlorophenol using response surface methodology. *Journal of Hazardous Materials,* 153, 709-717.

Tan, Y.H., Abdullah, M.O., Hipolito, C.N., & Taufiq-Yap., Y.H. (2015). Waste ostrich and chicken-eggshells as heterogeneous base catalyst for biodiesel production from used cooking oil: catalyst characterization and biodiesel yield performance. *Applied Energy,* 2, 1-13.

Vujicic, D.J., Comic, D., Zarubica, A., Micic, R., & Boskovic, G. (2010). Kinetics of biodiesel synthesis from sunflower oil over CaO heterogeneous catalyst. *Fuel,* 89(8), 2054-2061.

Wen, Z., Yu, X., Tu, S. T., Yan, J., & Dahlquist, E. (2010). Synthesis of biodiesel from vegetable oil with methanol catalyzed by Li-doped magnesium oxide catalysts. *Applied Energy,* 87(3), 743-748.

Yi, S., Su, Y., Qi, B., & Wan, Y. (2010). Application of response surface methodology and central composite rotatable design in optimization; the preparation condition of vinyltriethoxysilane modified silicate/ polydimethylsiloxane hybrid pervaporation membranes. Separation and Purification Technology. 71, 252-262.

Yusuff A.S., (2017). Synthesis and characterization of anthill-eggshell-Ni-Co mixed oxide composite catalysts for the production of biodiesel from waste frying oil. PhD Thesis, School of Postgraduate Studies, Federal University of Technology, Minna, Nigeria.

Yusuff, A.S. (2017). Preparation and characterization of composite anthill-eggshell adsorbent: optimization study of heavy metals adsorption using response surface methodology. *Journal of Environmental Science and Technology,* 10(3), 120-130.

Yusuff, A.S., Adeniyi, O.D., Olutoye, M.A., & Akpan, U.G. (2017). Performance and emission characteristics of diesel engine fuelled with waste frying oil derived biodiesel-petroleum diesel blend. *International Journal of Engineering in Africa,* 32, 100-111.

Yusuff, A.S., Olateju, I.I., & Ekanem, E.S. (2017). Equilibrium, kinetic and thermodynamic studies of the adsorption of heavy metals from aqueous solution using thermally treated quail eggshell. *Journal of Environmental Science and Technology,* 10, 245-257.

Zabeti, M., Wan Daud, W.M.A., & Aroua, K. (2009). Activity of solid catalysts for biodiesel production: A review. *Fuel Processing Technology,* 90(6), 770-777.