



# **Biodiesel Synthesis from Waste Cooking Oil Using Periwinkle Shells as Catalyst**

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## **Authors' contributions**

*This work was carried out in collaboration among all authors. Author CCO designed the study, performed the statistical analysis and wrote the first draft of the manuscript. Authors CFOO and ICN wrote the protocol and managed the literature searches. Authors OCE and EIA managed the laboratory procedures and experimental data presentation. Authors CCO, CFOO and ICN managed the analyses of the study. All authors read and approved the final manuscript.*

## **Article Information**

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## **ABSTRACT**

Waste materials such as periwinkle shells (PS) and waste cooking oil (WCO) were considered as heterogeneous catalyst and renewable feedstock for biodiesel production respectively in line with the current search for alternatives of the environmentally unfriendly and gradually depleting fossil fuel. PS were size reduced and calcined at 673K for 4 hours to remove carbonaceous and volatile matter in the sample. Physicochemical analyses on the WCO revealed high FFA (2.81%) therefore the need for esterification (0.42%). One factor at a time (OFAT) results show that methanol to oil ratio, catalyst loading, reaction temperature and time had significant effect on the biodiesel yield. The transesterification reaction kinetics data was modelled using the zero-order, pseudo-first order and pseudo-second order models. The results presented from the error functions: root mean square error (RMSE), chi-square ( $\chi^2$ ), mean absolute error(MAE) and coefficient of determination ( $R^2$ ) adjudged that the pseudo-first order model best described the process. An activation energy of 16.47 KJ/mol was obtained. Gas chromatography result revealed that a biodiesel yield of 73.92% was achieved at 8:1 methanol to oil ratio, 1% catalyst loading, 300 rpm stirring speed, 333K reaction temperature and 90 minutes contact time. The findings suggest potentials of PS as a viable catalyst for biodiesel production.

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**Keywords:** Biodiesel; transesterification; kinetics; periwinkle shells; waste cooking oil.

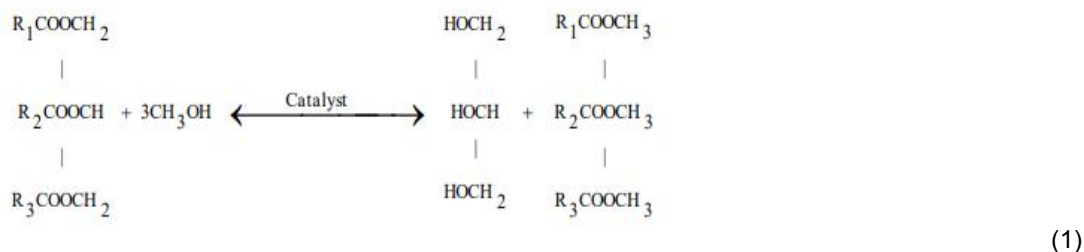
## 1. INTRODUCTION

Third world countries are faced with some challenges such as climate change, indiscriminate waste disposal, stunted economic growth, energy sustainability, etc. Obichukwu and Ausaji [1] reported that energy sources are the main drivers of economic growth and social development of a country. Myriad of deficiencies surrounding some conventional energy sources such as fossil fuel include: emission of oxides of sulfur and carbon, particulate matter and other gases which aggravate global warming challenges are detrimental to human health. These have stimulated research interest geared toward greener alternative sources of energy capable of meeting an increasing energy demand. One of the alternative fuels developed over a century ago is biodiesel [2].

Biodiesel, fatty acid methyl ester (FAME), is conventionally derived from transesterification reaction of oils or animal fats and alcohol in the presence of a homogeneous or heterogeneous catalyst. Acidic and basic heterogeneous catalysts have the benefits of cheap and simple separation and regeneration compared to homogeneous catalysts [3]. Generally, basic heterogeneous catalysts are preferred to acidic heterogeneous catalysts because of their higher activity [4,5]. Among the basic heterogeneous catalysts, calcium oxide (CaO) has drawn most attention owing to its high catalytic activity, regenerability/reusability. Numerous relatively inexpensive resources for CaO production include waste shells, egg shells, etc. Besides, CaO is not sensitive to small amounts of FFA and moisture, thus, suitable for waste cooking oils [4,6,7].

The efficiency of the transesterification process using heterogeneous catalysts depends on some process parameters such as temperature, catalyst, methanol to oil ratio, reaction time and agitation. Several types of alcohol can be used for transesterification namely methanol, ethanol and propanol [8]. Methanol and ethanol are most frequently used in the production of biodiesel but methanol is more preferred due to its low cost [9]. Traditional sources such as soya beans, rapeseed, palm/sunflower oils and other non-edible oils such as jatropha, karanja, waste cooking oils and animal fats were used as renewable feed stocks for biodiesel production. Selection of source for the biodiesel production also depends upon their availability in the particular area [5,10,11]. Waste cooking oil, a by-product from homes, eateries, hotels, vegetable oil refineries, etc, is easily accessible therefore was selected as a source of renewable feed stock for the current study.

Biodiesel burns cleaner than conventional diesel fuel, substantially reduces carbon monoxide, hydrocarbons, particulate matter and eliminates sulfur dioxide emissions. It contributes no net carbon dioxide to the atmosphere and reduces greenhouse gas emissions by 41% compared with diesel. In addition, biodiesel has high cetane number, high flash point, and excellent lubricity and miscibility with petroleum diesel at all ratios [12-14]. Transesterification reaction occurs between triglycerides and methanol leading to the production of FAME and glycerol as byproduct [4,11,15]. Transesterification reaction scheme is presented in equation 1 [4]. The  $R_1$ ,  $R_2$  and  $R_3$  indicate fatty acid at the stereo-specifically numbered -1, -2, and -3 positions, respectively [16,17].



The transesterification reaction kinetics is indispensable for the production process development, reactor design operation and scale-up. The understanding of the transesterification reaction kinetics is also necessary for development of mathematical models describing the reaction rate and the product yield [18]. Gurunathan and Ravi [10] reported that pseudo first order model with respect to triglyceride

best described the kinetics of biodiesel production from neem oil using copper doped zinc oxide heterogeneous nanocatalyst. A second order kinetics model was proposed by Ude et al. [19] for biodiesel production from refined cottonseed oil using calcium oxide as catalyst.

Producing renewable energies from low cost materials without affecting the food chain and reduction of greenhouse gases emanating from the usage of fossil fuels are subjects of primary concern. This work reports the conversion of waste to wealth in using waste cooking oil as a feedstock and thermally activated Periwinkle shells (TAPS) as catalyst for biodiesel production. TAPS as a catalyst for biodiesel production has barely been reported. The effect of reaction temperature, methanol-to-oil ratio, contact time and catalyst loading on the yield of biodiesel was investigated. Kinetics and thermodynamics for the biodiesel production was also examined.

## 2. MATERIALS AND METHODS

### 2.1 Materials

Waste cooking oil generated from Canola oil was obtained from an eatery in Nnamdi Azikiwe University, Awka. Periwinkle shells were obtained from a river bank in Rivers state. Reagents were supplied by Springboard Research Laboratories, Awka, Nigeria.

### 2.2 Methods

#### 2.2.1 Physicochemical analysis of the Waste Cooking Oil (WCO)

The physicochemical properties of the WCO were determined following these methodologies.

##### 2.2.1.1 Density

A known volume of the sample was weighed in a digital mass balance, the mass obtained was tabulated and divided using the same measured volume of the sample. The measurements were made in triplicate and then averaged.

##### 2.2.1.2 Determination of Free Fatty Acid (FFA) content

25 ml of isopropyl alcohol was added to 25ml of WCO in a beaker. 2-3 drops of phenolphthalein was introduced in the mixture as indicator and agitated afterwards. The content of the beaker was then titrated against 0.1M of KOH solution until a faint pink color which lasted for about 15secs was obtained. The process was repeated

3 times in order to determine the average titer value.

The acid value was calculated using equation 2:

$$\text{Acid value} \left( \frac{\text{mgKOH}}{\text{g}} \right) = \frac{56.1 \times V \times N}{W} \quad (2)$$

where: V (cm<sup>3</sup>) is the volume in of potassium hydroxide used in the titration, N (M) is the concentration of Potassium hydroxide, W (g) is the weight of the oil sample.

Free fatty acid (FFA) content is approximately half of the Acid value.

$$\text{FFA} = \frac{\text{Acid value}}{2} (\%) \quad (3)$$

##### 2.2.1.3 Determination of free fatty acid profile

2 g of the oil was first washed using 50 ml of n-hexane, 0.5 g sodium silicate and 1 g of magnesium trisilicate powder. The mixture was allowed to stand for 7 minutes in a separating funnel. The filtrate from the mixture was then collected and analyzed using gas chromatography (Buck scientific M910gas chromatograph).

##### 2.2.1.4 Determination of mono-, di- and triglycerides and FAME content of biodiesel

The method of standard solutions and sample preparation, quantification of glycerol, mono-, di- and triglycerides and FAME in biodiesel and chromatographic analyses were adopted from Dias et al. [20] and used in the present research. Stock solutions with 0.5 mg mL<sup>-1</sup> glycerol, 5 mg mL<sup>-1</sup> glycerides, 1 mg mL<sup>-1</sup> (S)-(-)-1,2,4-butanetriol and 8 mg mL<sup>-1</sup>tricaprin were prepared in pyridine. Different volumes of these solutions were used for the preparation of standard mixtures. 100 mg of sample was used. The standard mixtures and samples were silylated with 100 μL *N*-methyl-*N*-(trimethylsilyl) trifluoroacetamide and, after 20 min, 8 mL *n*-heptane were added.

The content in the samples was determined according to ASTM D6584. Analytical curves were constructed for glycerol, monoolein, diolein and triolein using the peak areas. The analytical

curve obtained from monoolein allowed the quantification of all monoglycerides; and the analytical curves from diolein and triolein allowed the determination of the diglycerides and triglycerides, respectively.

The chromatographic analyses were carried out using a Buck scientific M910 gas chromatograph, equipped with on-column injector, technique of simple on-column injection and flame ionization detector. An SGE HT-5 capillary column (25 m × 0.32 mm i.d., 0.1 μm film thickness) was used for the GC separation (Ringwood, VIC, Australia). Injection volume of 1 μL, hydrogen as carrier gas with linear velocity of 50 cm sec<sup>-1</sup> and flame ionization detector at 380 °C were used. The column oven temperature program was 50°C (1 min hold), 15 °C min<sup>-1</sup> up to 180°C, 7°C min<sup>-1</sup> up to 230°C; 30°C min<sup>-1</sup> up to 380°C (15 min hold); on-column injector with direct injection mode and temperature at 70°C (1 min hold), 20°C min<sup>-1</sup> up to 380°C (10.31 min hold).

### 2.2.2 Catalyst preparation

Periwinkle shells (PS) mainly composed of CaCO<sub>3</sub> [21] were size reduced and sieved with 75μm standard mesh. The sieved sample was thermally activated by calcination in a muffle furnace at 400°C for 4hrs to remove carbonaceous and volatile matters from the shells. The thermally activated Periwinkle shells (TAPS) was stored in an air tight container and subsequently used as catalyst in the transesterification reaction.

### 2.2.3 Pretreatment of Waste Cooking Oil (WCO)

WCO obtained from an eatery in Nnamdi Azikiwe University, Awka, was filtered to remove food particles from the oil. The filtered oil was heated to 100°C to remove any trace of water present in the oil. The oil was then poured into a tightly covered 4 litre gallon and stored at room temperature to prevent oxidation.

### 2.2.4 Reduction of free fatty acid (Esterification process)

Predetermined quantity of methanol (20% oil wt.) and sulphuric acid (5% wt of FFA present in oil) were mixed together in a conical flask to form a homogenous mixture. The oil sample was gradually added into the flask. A magnetic stirrer was introduced into the flask and its content was transferred onto a magnetic hot plate. The flask

was air tight to avoid vaporization of methanol. The mixture was heated for 60mins at temperature of 333K and 300 rpm stirring speed. The contents of the flask after heating was transferred to a separating funnel and allowed to stand for about 2-3 hours. The upper layer consists of a mixture of the ester (RCOOCH<sub>3</sub>), unreacted methanol (CH<sub>3</sub>OH), and the catalyst (H<sub>2</sub>SO<sub>4</sub>). The lower layer consists of the oil sample of reduced FFA which was carefully drained for further analysis.

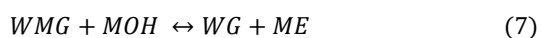
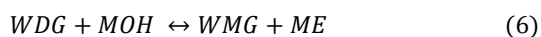
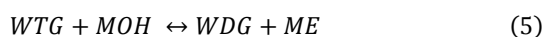
### 2.2.5 Transesterification reaction

The transesterification reaction was performed in a 500 ml two-neck glass reactor equipped with a reflux condenser to avoid alcohol evaporation, magnetic stirrer and a thermocouple. A defined amount of TAPS was measured and dissolved in a calculated quantity of methanol to form an alkoxide solution. A known quantity of the pretreated oil was then gradually added to the alkoxide solution in the reactor. The content of the reactor was heated with constant agitation (300rpm) at predetermined time and temperature. At the end of the reaction time, the product of the reaction was transferred to a separating funnel for about 4 hours. The product was then separated from glycerol. The product was first washed with acidified water to neutralize the mixture of esters, then with water only. Washing is carried out by spraying water over the biodiesel in a separating funnel with mild stirring to avoid foam formation. The mixture was left overnight to settle into two phases. The water (containing the impurities) phase was drained off from the funnel and properly disposed while the biodiesel layer was heated to about 383K to evaporate traces of remnant water molecules. The percentage of the biodiesel yield was determined by comparing the weight of biodiesel produced with the weight of WCO used.

$$\%Yield = \frac{\text{weight of biodiesel}}{\text{weight of WCO used}} \times 100 \quad (4)$$

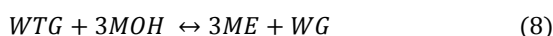
### 2.2.6 Reaction kinetics

The step-wise transesterification reaction is presented in equations 5 to 7:



where WTG, WDG and WG represent waste cooking oil triglyceride, waste cooking oil diglyceride and waste cooking oil glycerine. MOH and ME are methanol and methyl ester respectively.

The overall transesterification reaction is written in equation 8:



The relative rates of reaction of the various species in equation 8 are given by:

$$\frac{-r_{WTG}}{1} = \frac{-r_{MOH}}{3} = \frac{r_{ME}}{3} = \frac{r_{WG}}{1} \quad (9)$$

The rate of disappearance of triglyceride can be expressed by the rate law:

$$-r_{WTG} = \frac{-dC_{WTG}}{dt} = KC_{WTG}^a C_{MOH}^b \quad (10)$$

where a, b and  $C_{WTG}$ ,  $C_{MOH}$  are reaction orders and concentration at time t with respect to waste cooking oil triglyceride and methanol respectively.

The reaction was run in excess of methanol to drive the reaction to the product side thus the reaction (equation 10) was considered irreversible as presented in equation 11. Because methanol is in excess, the concentration of methanol at any time, t, is virtually the same as its initial concentration and the rate law is independent of the concentration of methanol ( $C_{MOH} \cong C_{MOH0}$ ) [22].

Therefore,

$$-r_{WTG} = \frac{-dC_{WTG}}{dt} = kC_{WTG}^a \quad (11)$$

Where

$$k = KC_{MOH}^b \quad (12)$$

$$C_{WTG} = C_{WTG0}(1 - X_{WTG}) \quad (13)$$

Substituting equation 13 in 11:

$$C_{WTG0} \frac{dX}{dt} = kC_{WTG0}^a (1 - X_{WTG})^a \quad (14)$$

The kinetics of the transesterification reaction was described by zero order, pseudo-first order

(PFO) and pseudo-second order (PSO) models. Zero order, PFO and PSO models were derived by integrating and rearranging equation 14 at a = 0, 1 and 2 respectively. The outcome of the integration is given in equations 15, 16 and 17.

$$X_{WTG} = \frac{k'}{C_{WTG0}} t \quad (15)$$

$$-\ln(1 - X_{WTG}) = k_1 t \quad (16)$$

$$\frac{1}{1 - X_{WTG}} = k_2 C_{WTG0} t \quad (17)$$

Where k',  $k_1$  and  $k_2$  are reaction rate constants for zero order, PFO and PSO, estimated from the plots of  $X_{WTG}$  vs t,  $-\ln(1-X_{WTG})$  vs t and  $1/(1-X_{WTG})$  vs t respectively. The suitability of the zero order, PFO and PSO models to describe the transesterification reaction was evaluated based on the calculated values of root mean squared error (RMSE), Chi square ( $\chi^2$ ), mean absolute error (MAE) and coefficient of determination ( $R^2$ ). The formulae for the error functions are presented in Table 1.

Activation energy of the reaction was calculated from Arrhenius equation

$$k_1 = A^{-E_a/RT} \quad (22)$$

Linearizing equation (22)

$$\ln k_1 = \ln A - \frac{E_a}{RT} \quad (23)$$

where A = pre-exponential factor,  $E_a$  = activation energy, R = universal gas constant and T = absolute temperature. Activation energy was computed from the slope of the plot  $\ln k_1$  against  $1/T$ .

### 3. RESULTS AND DISCUSSION

#### 3.1 WCO and Biodiesel Characterization

Table 2 presents the physicochemical characteristics of the WCO. The free fatty acid (FFA) value for WCO was observed to be 2.81%. A high FFA content (>%1) will lead to soap formation and the separation of products will be exceedingly difficult thus resulting to low yield of biodiesel [26,27]. Also, FFA can cause high losses of neutral oil due to saponification and emulsification during neutralization step [27]. These deficiencies justified the pretreatment (esterification) of the WCO to reduce the FFA

**Table 1. Error functions**

Error functions	Equations	References
Root mean square error	$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (y_{i,exp} - y_{i,pred})^2} \quad (18)$	[23]
Chi square ( $\chi^2$ )	$\chi^2 = \sum_{i=1}^n \frac{(y_{i,p} - y_{i,e})^2}{y_{i,p}} \quad (19)$	[24]
Mean absolute error	$MAE = \frac{1}{n} \sum_{i=1}^n  y_{i,exp} - y_{i,pred}  \quad (20)$	[25]
Coefficient of determination	$R^2 = \left( \frac{n(\sum y_{i,exp} \cdot y_{i,pred}) - (\sum y_{i,exp})(\sum y_{i,pred})}{\sqrt{[n \sum y_{i,exp}^2 - (\sum y_{i,exp})^2][n \sum y_{i,pred}^2 - (\sum y_{i,pred})^2]}} \right)^2 \quad (21)$	

**Table 2. Physicochemical characteristics of WCO**

Properties	WCO
FFA (%)	2.81 0.422 (Esterified)
Acid value	5.62mgKOH/g 0.884mgKOH/g (Esterified)
Density (g/cm <sup>3</sup> )	0.892

**Table 3. Gas chromatography result of the waste cooking oil**

Component	Symbol	Concentration	% Concentration
Linoleic acid	C18:2	20.207	39.9725
Lauric acid	C12	6.2695	12.4020
Palmitic acid	C16	0.0319	0.0631
Palmitic acid	C16	0.0345	0.0682
Myristic acid	C14	8.4175	16.6511
Eicosapentaenoic acid	C20:5	0.0018	0.0036
Oleic acid	C18:1	2.422	4.7911
Linoleic acid	C18:2	0.9345	1.8486
$\alpha$ -Linolenic	C18:3	12.1585	24.0514
$\alpha$ -Linolenic	C18:3	0.075	0.1484
Total		50.5522	100

**Table 4. Gas chromatography results of the biodiesel**

Component	Retention	Area	Height	External	Units	% comp
Triglyceride	0.143	561.4932	106.584	0.0754	ppm	0.4359
Alcohol	6.01	4474.9912	194.707	1.8127	ppm	10.4778
Monoglyceride	18730	3368.4132	145.83	0.8323	ppm	4.8109
FAME	26.76	3829.3396	166.36	12.7887	ppm	73.9214
Glycerol	36.133	2100.2272	91.433	1.4306	ppm	8.2692
Diglyceride	41.083	2936.0828	127.777	0.3606	ppm	2.0843
		17270.5472		17.3004		100

value before the transesterification reaction. The high FFA value may be due to the effect of frying time and temperature on the properties of the WCO. The quantity of heat to fry and

quantity of water in the cooking oil increases the hydrolysis of triglycerides, therefore leads to high percentage of FFA in the WCO [28].

Gas chromatography (GC) result showing the free fatty acid profile of the WCO is displayed in Table 3. The components of the fatty acid were identified by comparing the retention time of the sample with that of the standard (Accu standard USA). It is observed that linoleic acid (39.9725%),  $\alpha$ -Linolenic acid (24.0514%), myristic acid (16.6511%) and lauric acid (12.4020%) were the dominant components of the WCO while palmitic acid and eicosapentaenoic acid were found in traces. Table 4 reveals the GC result of the final product obtained at a temperature of 333K, 1% catalyst loading and 8:1 methanol to oil ratio and 90 minutes reaction time. The presence of residual amounts of triglycerides (0.4359%), diglycerides (2.0843%) and monoglycerides (4.8109%) in the final product as seen in Table 4 is a confirmation that transesterification reaction proceeds in 3 stages. The %Yield of fatty acid methyl ester (FAME) was recorded to be 73.9214 %. The amount of residual glycerol and alcohol were also found to be 8.2692% and 10.4778% respectively which are higher than the ASTM recommended standard for glycerol content (0.240% max) and alcohol content (0.2% max). Further purification techniques can be applied to improve the purity of the biodiesel and reduce the residual glycerol and alcohol contents.

### 3.2 OFAT Analysis

#### 3.2.1 Effect of Methanol Oil Ratio (MOR)

Fig. 1 shows the effect of methanol to oil ratio on the yield of biodiesel. At a reaction temperature of 333K, 1% catalyst loading, 300 rpm stirring speed and a contact time of 75 mins, the trend followed by the graph reveals initial increment on %biodiesel yield as MOR increases from 4:1 to 8:1. This might be a corroboration to the

hypothesis that excess methanol is required to ensure the equilibrium point lies so far to the product side. Methanol, ethanol, propanol, butanol and alkyl alcohol can be used in the transesterification reaction, amongst these alcohols methanol is applied more frequently as its cost is low and it is physically and chemically advantageous (polar and shortest chain alcohol) over the other alcohols [29]. An upward review of MOR above 8:1 displayed an observed negative impact on the response. Glycerol is soluble in alcohol, therefore increase in methanol beyond the observed limit may have increased the concentration of glycerol in the reaction mixture which can shift the equilibrium to the reactant side [30,31].

#### 3.2.2 Effect of catalyst loading

The effect of varying catalyst loading on the %Yield of biodiesel produced at constant temperature of 333K, 8:1 MOR, 300 rpm stirring speed and 75mins contact time was investigated to ascertain the least catalyst loading for maximal response (%yield). Fig. 2 shows a direct proportional relationship between %Yield (47.4% to 75.26%) and catalyst loading (0% to 1%). This behavior may be as a result of availability of more active sites which enhanced the production of biodiesel. The %Yield of biodiesel declined when catalyst loading was reviewed upwards above 1%. Increasing the catalyst loading beyond 1% possibly makes the reactant and catalyst mixture too viscous resulting to problems with mixing and poor diffusion of the reactants hence, the decrease in biodiesel yield. The decline may also be due to the attainment of mass transfer limitation (rate determining step) between the reactant and catalyst [28]. Therefore, 1% catalyst loading was chosen for further experiments.

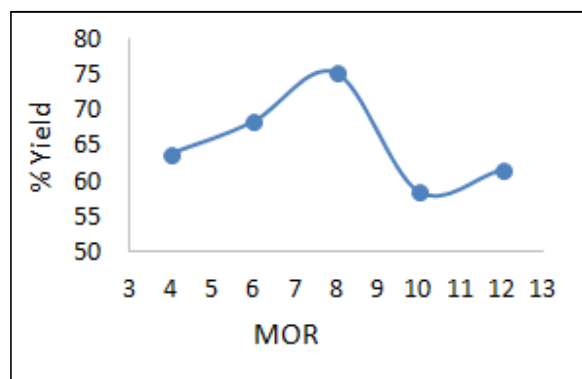


Fig. 1. Effect of MOR on % yield of biodiesel

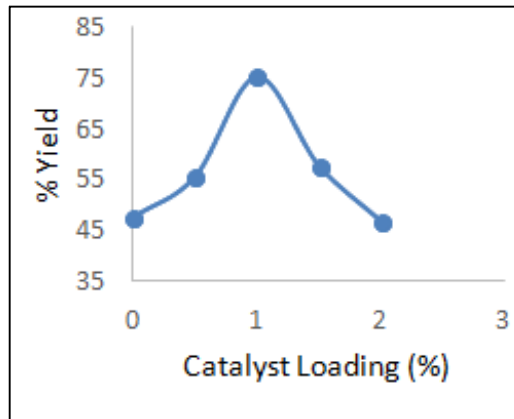


Fig. 2. Effect of cat. loading on %Yield of biodiesel

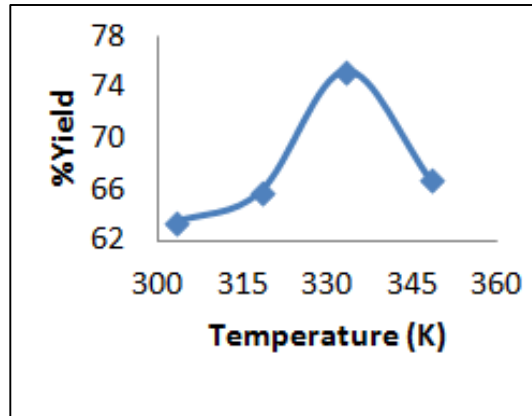


Fig. 3. Effect of temperature on % yield of biodiesel

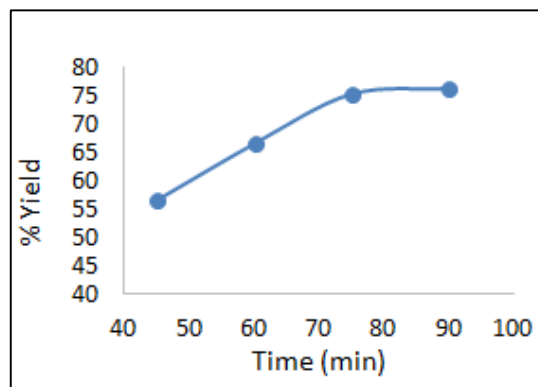


Fig. 4. Effect of contact time on % yield of biodiesel

### 3.2.3 Effect of reaction temperature

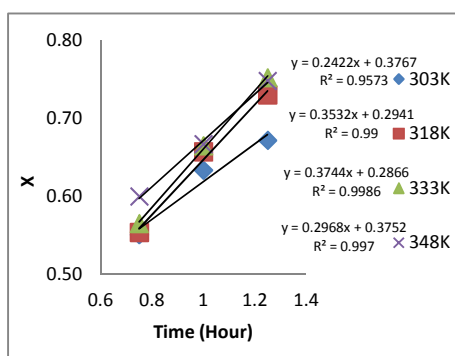
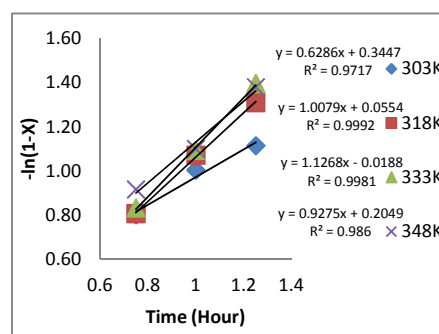
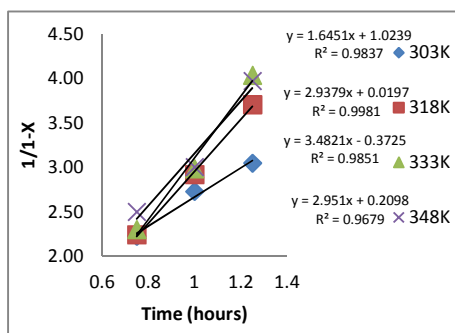
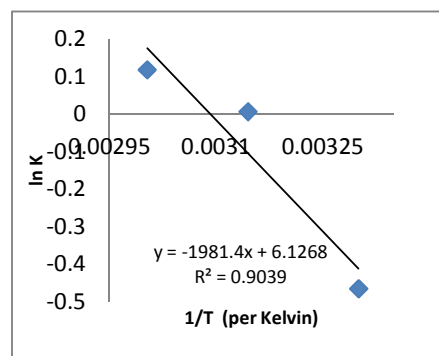
The optimum reaction temperature was evaluated by performing transesterification reaction at various temperatures (303, 318, 333 and 348)K, 1% catalyst loading, 300 rpm stirring speed, 8:1 methanol to oil ratio and a contact time of 75mins. Fig. 3 reveals that biodiesel yield

increases with temperature. Temperature increases the energy of the reacting molecules and also improves the miscibility of the alcoholic polar media into a non-polar oily phase, resulting in much faster reactions [32]. Optimum temperature was recorded at 333K above which an antagonistic effect was observed on biodiesel yield. Usually the transesterification reaction



**Table 5. Kinetics and statistical parameters**

Temperature	Model	$k_i$	RMSE	$\chi^2$	MAE	$R^2$
303	Zero-order	0.246	0.3771	1.8378	0.3769	0.9573
	PFO	0.628	0.1583	0.1722	0.1570	0.9737
	PSO	1.617	0.2672	0.8876	0.2539	0.9958
318	Zero-order	0.359	0.0901	0.7682	0.2943	0.9990
	PFO	1.007	0.0064	0.0022	0.0204	0.9992
	PSO	1.816	0.0015	0.0001	0.0042	0.9982
333	Zero-order	0.380	0.0879	0.6898	0.2870	0.9986
	PFO	1.126	0.0021	0.0002	0.0060	0.9982
	PSO	3.423	0.0128	0.0079	0.0390	0.9889
348	Zero-order	0.301	0.0914	0.7631	0.2980	0.9970
	PFO	0.927	0.0235	0.0318	0.0748	0.9855
	PSO	2.901	0.0099	0.0055	0.0259	0.9614

**Fig. 5. Zero-order kinetics plot for WCO transesterification reaction****Fig. 6. PFO kinetics plot for WCO transesterification reaction****Fig. 7. SO kinetics plot for WCO transesterification reaction****Fig. 8. PSO kinetics plot for WCO transesterification reaction**

temperature should be below the boiling point of alcohol in order to prevent the alcohol evaporation. The range of optimal reaction temperature may vary from 323K to 333K depending on the oils or fats used [33]. Therefore, the reaction temperature near the boiling point of the alcohol is recommended for faster conversion by various literatures. The

optimal temperature (333K) was just below the boiling point of methanol (337.7K). Evaporation of methanol at temperatures above the boiling point, may account for the decline in the yield of biodiesel at temperatures above 333K. Also, higher reaction temperature accelerates the saponification of triglycerides [33].

### 3.2.4 Effect of reaction time

The influence of reaction time on biodiesel yield was investigated at a temperature of 333K, 1% catalyst loading, 300 rpm stirring speed and 8:1 methanol to oil ratio as shown in Fig. 4. It is seen that biodiesel yield increased with increase in time up till 90 minutes. A closer observation reveals that %biodiesel yield margin recorded between 75 minutes (76.24%) and 90 minutes (75.26%) is statistically insignificant (approximately below 1.4%) when compared to approximately 18% obtained between 45 minutes and 60 minutes, and about 13% recorded between 60 minutes and 75 minutes. The researchers did not go beyond 90 minutes owing to the observed plateau after 75 minutes. Therefore, 90 minutes was selected as the optimum reaction time.

### 3.3 Reaction Kinetics

The kinetics of transesterification reaction of WCO and methanol in the presence of TAPS was analyzed by fitting the experimental data in zero order (equation 15), pseudo-first order (equation 16) and pseudo-second order (equation 17) models. From the slopes of Figs. 5, 6 and 7,  $k$ ,  $k_1$  and  $k_2$  at 303K, 318K, 333K and 348K were computed for zero order, PFO and PSO models. The suitability of the models in describing the kinetics data of the transesterification reaction was evaluated using some error functions: root mean squared error (RMSE), Chi square ( $\chi^2$ ), mean absolute error (MAE), coefficient of determination ( $R^2$ ). Table 5 summarized the kinetics and statistical parameters for the studied models. It was observed that the values presented for RMSE were  $\leq 0.38$ , 0.16 and 0.27,  $\chi^2 \leq 1.84$ , 0.17 and 0.89; MAE  $\leq 0.38$ , 0.16 and 0.25 for zero order, PFO and PSO respectively. Table 5 also shows that coefficients of determination values for PFO were closest to unity when compared with values for zero order and PSO. Based on these observations, PFO kinetics model best described the kinetics of the transesterification reaction considering its least recorded values for RMSE,  $\chi^2$  and MAE and overall closest to unity coefficient of determination values. Activation energy,  $E_a = 16.47\text{KJ/mol}$ , was calculated from the Arrhenius plot (Fig. 8) for the transesterification reaction of WCO using thermally activated periwinkle shell as heterogeneous catalyst.

## 4. CONCLUSION

Biodiesel, a promising alternative to fossil fuel was produced using basically inexpensive materials, periwinkle shells and waste cooking oil. The OFAT analyses indicated that methanol-to-oil ratio, catalyst loading, reaction temperature and time were significant on biodiesel yield. Gas chromatography result presented biodiesel yield of 73.92% achieved at 8:1 methanol to oil ratio, 1% catalyst loading, 333K reaction temperature and 90 minutes contact time. Based on the statistical indices investigated, the suitability of the models in terms of accuracy and precision was in the order: PFO>PSO>zero order model. Activation energy ( $E_a$ ) of the process was measured at 16.47 KJ/mol. The high coefficient of determination value recorded shows that the data conformed to Arrhenius equation.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

## REFERENCES

1. Obichukwu AC, Ausaji AA. Biodiesel production by transesterification of used vegetable oil. *Int J Innov Research Develop.* 2015;4:37-41.
2. Sani J, Samir S, Rikoto I, Tambuwal AD, Sanda A, Maishanu SM, Ladan MM. Production and characterization of heterogeneous catalyst (CaO) from snail shell for biodiesel production using waste cooking oil. *Innovative Energy & Research.* 2017;6(2):1-4.
3. Gaikwad ND, Gogate PR. Synthesis and application of carbon based heterogeneous catalysts for ultrasound assisted biodiesel production. *Green Process. Synth.* 2015;4:17-30.
4. Moradi GR, Mohadesi M, Ghanbari M, Moradi MJ, Hosseini Sh, Davoodbeygi Y. Kinetic comparison of two basic heterogeneous catalysts obtained from sustainable resources for transesterification of waste cooking oil. *Biofuel Research Journal.* 2015;6:236-241.
5. Endalew AK, Kiros Y, Zanzi R. Inorganic heterogeneous catalysts for biodiesel production from vegetable oils. *Biomass and Bioenergy.* 2011;35(9):3787–3809.
6. Veljkovic VB, Stamenkovic OS, Todorovic ZB, Lazic ML, Skala DU. Kinetics of

- sunflower oil methanolysis catalyzed by calcium oxide. *Fuel*. 2009;88:1554-1562.
7. Boey PL, Maniam GP, Hamid SA. Performance of calcium oxide as a heterogeneous catalyst in biodiesel production: A review. *Chem. Eng. J.* 2011;168:15-22.
  8. Babagana G, Shittu SB, Idris MB. Characterization and composition of *Balanite aegyptiaca* seed oil and its potential as biodiesel feedstock in Nigeria. *J Appl. Phytoch. Evn.I Sanit.* 2011;1(1):29-35.
  9. Onukwuli OD, Emembolu LN, Ude CN, Aliozo SO, Menkiti MC. Optimization of biodiesel production from refined cotton seed oil and its characterization. *Egypt. J. Petrol*; 2016.  
Available:<http://dx.doi.org/10.1016/j.ejpe.2016.02.001>
  10. Gurunathan B, Ravi A. Process optimization and kinetics of biodiesel production from neem oil using copper doped zinc oxide heterogeneous nanocatalyst. *Bioresource Technology*. 2015; 190:424-428.
  11. Taufiq-Yap YH, Lee HV, Hussein MZ, Yunus R. Calcium-based mixed oxide catalysts for methanolysis of *Jatropha curcas* oil to biodiesel. *Biomass Bioenerg.* 2011;35:827-834.
  12. Hanganu-Balkir Y. Green biodiesel synthesis using waste shells as sustainable catalysts with *Camelina sativa* Oil. *Journal of Chemistry*; 2016.  
Available:<http://dx.doi.org/10.1155/2016/6715232>
  13. Lin CY, Cheng HH. Application of mesoporous catalysts over palm-oil biodiesel for adjusting fuel properties. *Energ. Convers. Manage.* 2012;53:128-134.
  14. Yin X, Ma H, You Q, Wang Z, Chang J. Comparison of four different enhancing methods for preparing biodiesel through transesterification of sunflower oil. *Appl. Energ.* 2012;91:320-325.
  15. Sharma YC, Singh B, Korstad J. Latest developments on application of heterogeneous basic catalysts for an efficient and eco friendly synthesis of biodiesel: A review. *Fuel*. 2011;90:1309-1324.
  16. Bălănuță B, Stan R, Hanganu A, Iovu H. Novel linseed oil-based monomers: Synthesis and characterization. *UPB Scientific Bulletin, Chemistry and Materials Science, Series B.* 2014; 76(3):129-140.
  17. Sheila MI. Dietary triacylglycerol structure and its role in infant nutrition. *Adv Nutr.* 2011;2(3): 275-283.
  18. Ilgen O. Dolomite as a heterogeneous catalyst for transesterification of canola oil. *Fuel Processing Technology.* 2011;92:452-455.
  19. Ude NC, Amulu FN, Onukwuli DO, Amulu EP. *World Academy of Science, Engineering and Technology.* 2016;10(6):739-742.
  20. Dias AN, Kurz MHS, Fagundes CAM, Caldas SS, Clementin RM, D'Oca MCM, Primel EG. Evaluation of ASTM D6584 method for biodiesel ethyl esters from sunflower oil and soybean/tallow mixture and for biodiesel methyl esters from tung oil and soybean/tung mixture. *J. Braz. Chem. Soc.* 2014;25(7):1161-1165.
  21. Orangun CO. The suitability of periwinkle shells as coarse aggregate for structural concrete. *Matériaux et Constructions.* 1974;7(5):341-346.
  22. Fogler SH. *Elements of chemical reaction engineering.* New York: Prentice Hall; 1999.
  23. Pakravan P, Akhbari A, Moradi H, Azandaryani AH, Mansouri AM, Safari M. Process modeling and evaluation of petroleum refinery wastewater treatment through response surface methodology and artificial neural network in a photocatalytic reactor using polyethyleneimine (PEI)/titania (TiO<sub>2</sub>) multilayer film on quartz tube. *Appl Petrochem Res.* 2014;5:47-59.
  24. Maran JP, Sivakumar V, Thirugnanasambandham K, Sridhar R. Artificial neural network and response surface methodology modeling in mass transfer parameters predictions during osmotic dehydration of *Carica papaya L.* *Alexandria University Journal.* 2013;52:507-516.
  25. Betiku E, Odude VO, Ishola NB, Bamimore A, Osunleke AS, Okeleye AA. Predictive capability evaluation of RSM, ANFIS and ANN: A case of reduction of high free fatty acid palm kernel oil via esterification process. *Energy Conversion and Management.* 2016;124:219-230.
  26. Traore S, Magassouba S, Kourouma SY, Camara MA. Characteristics of *jatropha* oil and prospective for its valorization as feedstock for the development of biodiesel

- technology in Guinea. *International Review of Applied Sciences*. 2016;3(1):1-11.
27. Ridha B, Snoussi Y, Mounir B, Manef A. Waste frying oil with high levels of free fatty acids as one of the prominent sources of Biodiesel Production. *J. Mater. Environ. Sci.* 2015;6(4):1178-1185.
  28. Aworanti OA, Ajani AO, Agarry SE. Process parameter estimation of biodiesel production from waste frying oil (Vegetable and palm oil) using homogeneous catalyst. *J. Food Process Technol.* 2019;10(9):1-10.
  29. Hossain ABMS, Boyce AN. Biodiesel production from waste sunflower cooking oil as an environmental recycling process and renewable energy. *Bulgarian Journal of Agricultural Science*. 2009;15(4):312-317.
  30. Hsiao MC, Kuo JY, Hsieh PH, Hou SS. Improving biodiesel conversions from blends of high- and low-acid-value waste cooking oils using sodium methoxide as a catalyst based on a high speed homogenizer. 2018a;11(2298): 1-11.
  31. Hsiao MC, Hou SS, Kuo JY, Hsieh PH. Optimized conversion of waste cooking oil to Biodiesel using calcium methoxide as catalyst under homogenizer system conditions. 2018b;11(2622): 1-12.
  32. Ogbu IM, Ajiwe VIE. Biodiesel production via esterification of free fatty acids from *Cucurbita pepo* L. seed oil: Kinetic studies. *International Journal of Science and Technology*. 2013;2(8): 616-621.
  33. Mathiyazhagan M, Ganapathi A. Factors affecting biodiesel production, research in plant Biology: Review Article. 2011;1(2): 1-5.

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