



Full Length Article

Methanolysis of CaO based catalyst derived from egg shell-snail shell-wood ash mixed for fatty acid methylester (FAME) synthesis from a ternary mixture of *Irvingia gabonensis* -*Pentaclethra macrophylla* - *Elais guineensis* oil blend: An application of simplex lattice and central composite design optimization

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ABSTRACT

Considering the large number of wastes produced as wood ash, snail and eggshells around the globe, CaO based catalyst was derived from the thermal treatment of carbon carbonate obtained from the mixture of these wastes for methanolysis synthesis of FAME from the ternary mixture (33:33:34) of *Irvingia gabonensis*, *Pentaclethra macrophylla*, and *Elais guineensis* oil was carried out in this study. Calcined blend catalyst (CBC) was well characterized by SEM, EDX-ray, FTIR and BET analysis. The strength of the basicity of the catalyst was tested by catalyst recyclability via methanolysis of CaO transesterification of ternary blend oil to FAME. Results showed a maximum FAME yield of 98.00 (wt%) with the statistical optimization prediction of 97.33 (wt%) at a reaction time of 64.71 min, catalyst amount of 4.5 wt%, reaction temperature of 61.61 °C, and methanol/oil molar ratio of 8:1 (ml/ml), the predicted value was validated in triplicate to obtain an average FAME of 97.22 (wt%). Catalyst reusability was stopped at the 3rd cycle due to decrease in its activity. Statistical optimization through analysis of variance further confirmed the remarkable significant effects of the independent variables with p -value < 0.0001. Physicochemical properties of the FAME conformed with biodiesel recommended standard. Results also show that the CaCO₃ contained in the mixture of wood ash, snail and eggshells is a promising source for CaO catalyst production for industrial application.

1. Introduction

Energy resources come with them abundant socioeconomic potential, providing financial progress for people and energy facilities for indigenous economies. Nevertheless, the infrastructure which brings energy services can cause disruption in energy accidentally, often cause damages, and energy mortalities, with many systems often deaths will happen even when the systems are working as intend (Silva *et al.*, 2013) [1]. Meanwhile, the greatest energy mortalities that resulted from energy generation by humankind are the creation of air pollution. The most deadly of which, generated from the burning of fossil fuels and biomass is estimated to cause deaths annually (Silva *et al.*, 2013) [1].

According to the recent reports by US Environmental Protection Agency (EPA), in each year, between 2.96 million and 4.21 million premature deaths occur due to fossil (coal, oil and natural gas) fuels. In

the US alone, it has been reported that there are 194,000 annual deaths due to these causes, while a country like China sees 1.6 million deaths, India reportedly sees 692,000 deaths, Africa has the largest mortalities compare with other continents. Worldwide, fossil-fuel-related emissions account for about 65% on the excess mortality with an additional of 1.94 million early deaths occur as a result of air pollution from other sources, including domestic energy and agricultural activities (Lelieveld *et al.*, 2019) [2].

Meanwhile, the international agreement on limiting emissions (2015 Paris Agreement) has purposes to limit global warming in the 21st century to 1.5–2 °C. A total phase-out of fossil fuel is obligatory to avoid temperatures from rising beyond the internationally agreed goal. By doing this, the rainfall increase by 10–70% over densely populated regions (India, China, Central America, West Africa, and the Sahel region), that have been suffering from long-lasting food scarcities caused

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by economic crises, poverty, desertification and climate changes since the 70 s (WHO). One way to achieve this goal is by removing carbon dioxide from the atmosphere that occurs through the use of fossil fuels, and replaces it with a promising renewable and sustainable green diesel (biodiesel).

Biodiesel is a fuel obtained via the trans-esterification reaction in the presence of acidic, basic, or acid/base homogeneous catalysts, such as NaOH, KOH, H₂SO₄, or methoxides. Although biodiesel has been reported as a potential for replacement of petro-diesel, much of its production involves the use of homogeneous catalysts. The use of homogeneous catalysts, however, comes with various disadvantages, such as additional cost incurred due to wastewater generated during washing, highly corrosive, non-reusability, phase separation, difficulty in separating glycerol from biodiesel, and high reaction time required for total conversion (Viriya-empikul et al., 2012; Eleonice et al., 2015; Hadiyanto et al., 2016; Trisupakitti et al., 2018; Nor-Azyan et al., 2018; Subramaniapillai et al., 2019; Minakshi et al., 2020) [3–9]. Alternatively, heterogeneous catalysts have been developed to overcome these problems.

Recently, the use of ecofriendly heterogeneous catalysts derived from animal shells, agricultural wastes, cement clinker, hydrated lime, and quicklime as a bio-based catalyst at the different reactions, feedstocks, and calcination temperature conditions for conversion of oil to biodiesel have been tested and reported (Table 1). Meanwhile, the use of blend oil in the ratio of 7:3, 1:1, 1:2, 1:3, 3:2, and 2:3, have been

reportedly exploited for biodiesel synthesis, and the reports recorded high FAME conversion yield (Joana et al., 2008; Khalil et al., 2017; Qiu et al., 2011; Yathish et al., 2013; Milano et al., 2018) [10–14], but, the researchers adopted the use of a blend of two oil via methanolysis of homogeneous catalyst (KOH/NaOH) for transesterification process apart from the work reported by Subramaniapillai et al. (2019) [8] and Falowo et al., (2019) [15], where heterogeneous based the catalyst used was derived from elephant ear tree pod husk and *Donax deltoideis* shells in the production of biodiesel. A more innovative work was recently reported by Falowo et al. (2020) [24], where biodiesel was synthesized from the blend of Honne-Rubber-Neem oil via methanolysis of mesoporous base catalyst synthesized from a mixture of three agrowastes. No single report has ever utilized the blend of *Irvingia gabonensis* (Dikanut)- *Pentaclethra macrophylla* (Ukpaka) – *Elais guineensis* (Palm kernel) oil for biodiesel synthesis.

Due to increase in the world production rate of *Irvingia gabonensis* based on consumption and the used in the health industry, about 1.2 billion tons are traded annually in Nigeria, 70.79 tons were traded in South Cameroon with the value of sales up to \$70,000 within 29 weeks (FAOSTAT, 2011) [25]. But, there exist waste along the part that needs to be converted to useful energy. Meanwhile, the inedible nature of *Pentaclethra macrophylla* oil used for the production of condiments in Africa, due to the existence of some anti-nutritional factors such as undigestible oligosaccharides and phytate, has necessitated the choice for its energy production feedstock. *Elais guineensis*, one the most quickly

Table 1
Earlier reports conditions on developed heterogeneous catalysts.

Feedstocks	Heterogeneous Catalysts Source	Major mineral content	Calcination condition	FAME reaction conditions	FAME yield %	Authors
Palm olein oil	Egg shells, golden apple snail, meretrix venue	CaO 98.6% 99.0% 99.2%	800 °C, 2 h	T: 60 °C, C: 10 wt% MeOH/OMR: 9:1	94.1% 93.2% 92.3%	Viriya-empikul et al. (2012) [3]
Calophyllum inophyllum-waste cooking oil	Donax deltoideis shells	CaO 70.87%	105 °C, 24 h	T: 65 °C, C: 7.5 wt% MeOH/OMR: 63.8%	96.5%	Subramaniapillai et al. (2019) [8]
Waste oil and <i>Scenedesmus obliquus</i>	<i>Carica papaya</i> stem	K = 56.71%	700 °C, 4 h	T: 60 °C, C: 2 wt% MeOH/OMR: 9:1	95.23% 93.33%	Minakshi et al. (2020) [9]
Palm oil	<i>Anadara granosa</i> and CaCO ₃ shells	CaO 57.31% 43.26%	800 °C, 2 h	T: 70 °C, C: 2.6–10% MeOH/OMR: 12:1	94.71% 92.5%	Hadiyanto et al. (2016) [5]
Waste oil	DM waste treatment Mussel shells	CaO 50.85% 69.83%	900 °C, 2 h	T: 70 °C, C: 9.08–12 wt% MeOH/OMR: 22.5:1	92.65%	Moradi et al. (2015) [16]
Lucky nut oilseed	Pearl spar	CaO 58.48%	700 °C, 5 h	T: 50 °C, C: 2.5 wt% MeOH/OMR: 2.5:1	92.87%	Adepoju et al. (2018a) [17]
Waste oil	Brette pearl spar	K = 56.94%	700 °C, 6 h	T: 60 °C, C: 6 wt% MeOH/OMR: 5.5:1	98.46%	Adepoju et al. (2018b) [18]
Neem oil	Cocoa pod husk	K = 59.2%	700 °C, 3 h	T: 65 °C, C: 0.65 wt% MeOH/OMR: 0.73 v/v	99.3%	Betiku and Ajala, (2015) [19]
Kariya oil	Kola nut husk	K = 47.4%	500 °C, 6 h	T: 65 °C, C: 3 wt% MeOH/OMR: 6:1	98.67%	Osakwe et al. (2018) [20]
<i>Ceiba pentandra</i> oil	Banana peduncle	K = 68.3%	700 °C, 4 h	T: 60 °C, C: 1.16 wt% MeOH/OMR: 9.2:1	98.69%	Balajii et al. (2020) [21]
Sunflower oil	Palm kernel shell biochar	CaO = 78.5%	850 °C, 2 h	T: 65 °C, C: 3 wt% MeOH/OMR: 9:1	99%	Milan et al. (2016) [22]
Rubber seed oil	Cement clinker	CaO 96.9%	700 °C, 2 h	T: 65 °C, C: 5 wt% MeOH/OMR: 4:1	96.9%	Gimbun et al. (2013) [23]

C = Catalyst, T = Temperature, MeOH/OMR = methanol/oil molar ratio.

Table 2
Five level three factors experimental design for oil blend.

Variable	Units	Symbol	Levels				
			−2	−1	0	1	2
PKSO	(ml)	X_1	0	0.16667	0.3333	0.66667	1.00
USO	(ml)	X_2	0	0.16667	0.3333	0.66667	1.00
DNO	(ml)	X_3	0	0.16667	0.3333	0.66667	1.00

growing crops in the tropics. From the early 80 s, the worldwide land capacity under oil palm production has tripled; it attained almost 20 million hectares in 2009 and accounted for 12% of the world's permanent cropland (Okeke and Oluka, 2017) [26]. Most of its kernel in any part of the world exists as wastes, hence the need for diversification as valuable raw material for biofuel production.

Hence, this work focus on the production of a novel based heterogeneous catalyst derived from the methanolysis mixture of wood ash (WA), eggshells (ES), and snail shell (SS), applied to the transesterification of *Irvingia gabonensis* (Dika nut) - *Pentaclethra macrophylla* (Ukpaka) - *Elaeis guineensis* (Palm kernel) ternary oil blend to biodiesel. Details characterization of the developed catalyst was also carried out using SEM, BET, FTIR, and XRD to establish its catalytic potential. Process parameters optimization for the transesterification process was carried out using response surface methodology; while the physico-chemical properties of FAME produced were carried out using AOAC standard method with a view to determining its potential use as a replacement for petro-diesel.

2. Experimental

2.1. Materials

Palm kernel seed (PKS), Ukpaka seed (US), and Dika nut (DN) were collected from a nearby locality. Wood ash and the eggshells were obtained from nearby bakery, while the snail shell was obtained from eatery, Eket, Nigeria. The seeds were washed with distilled water, sun-dried for three days and then oven-dried to constant weight were milled into powder of small sizes for oil extraction.

All chemicals used in this work were of analytical grades purchased from Terasson Chemical Venture Nig., Ltd., and used without any further purification.

The egg and the snail shells were washed with ionized water, dried to constant weight, then mill into fine powders and then sieved. The wood ash collected from the bakery was manually separated from the dirt's and sieved into powder of the same size with eggshells powder. The shells powder and the wood ash were transformed into calcium oxide catalysts through thermal treatment. The powders (eggshell, snail shell, wood ash, and the blended powder) were calcinated at the temperature of 900 °C for 3 h. All calcined catalysts (CESC, CSSC, and CWAC, and CBC) were kept in close containers to avoid exposure to the atmosphere. CESC, CSSC, CWAC and CBC is the abbreviation for calcined eggshell catalyst, calcined snail shell catalyst, calcined wood ash catalyst, and calcined blend catalyst.

2.2. Oils extraction

Extraction of oils from the purified, milled powder of PKS, US, and DN was carried out using a solvent extraction method with n-hexane as solvent. A four-phase-heating mantle equipped with 1000 ml capacity soxhlet extractor was used to mass-produce the oils at an extraction temperature of 70 °C with a known volume of n-hexane and powder sample. Details step by step procedure was as described by Betiku *et al.* (2012) [27] with little modifications. The residuals cakes after extraction were kept as a supplement for animal feeds; excess N-hexane in oils was recovered through the rotary evaporator. The clean oils (PKSO,

USO, and DNO) were collected and kept in a separate jar before blends. Qualities of the oils and the blend were examined using recommended AOAC (1997) standard test and Agilent 5973N GCMS instrument control and data storage to examine its constituent of the volatile matter, long and branched-chain hydrocarbons, esters and alcoholic acids.

2.2.1. Oils blend

To blend the oil, it is worthwhile to know that the action of oil is increased by mixing several oils together, but, the order in which the oil is blended must be factor properly. Lighter with smaller molecules produce less viscous oils with high volatility while heavier and larger molecules produce high viscous oils with low volatility. To obtained oil with low viscosity, low density, and good volatility, a need for proper blending to allow for a synergistic effect within the blend. A guess mix reported by few researchers in their work cannot be ascertained as a proper synergistic effect within the blend. Hence, there is a need for experimental design for the proper mixing ratio of the oils.

2.2.2. Experimental design for oil blend ratio

To carry out a proper mix ratio, a design expert 6.0.8 trial version was used. The design is about the mixture of three oil samples, a mixture with simplex lattice design was chosen, where all components must have the same range and there are no constraints on the design space. The point's chosen are the pure points and there are enough points between those to estimate the polynomial chosen. A- three-factors (mixtures)-five levels design was used (Table 2) which generated thirteen (16) experimental runs and were carried out.

2.3. Catalysts characterization

The CESC, CSSC, CWAC, and CBC were characterized using standard methods such as Scanning Electron Microscopy (SEM), used to view the surface morphology of the catalysts, Energy Dispersive Spectroscopy (EDS) used to determine the elemental analysis of the samples and the quantitative composition of the catalysts, X-ray diffraction analysis (XRD) equipped with $K\alpha$ and Cu radiation source, accelerated at 20 mA and 30 kV, used to confirm the angular scanning electron performed in the range of $20^\circ < 2\theta < 80^\circ$ at speed of $2^\circ \text{C min}^{-1}$, Fourier transform infrared spectroscopy (FTIR), used to confirm the presence of functional group and verify the presence of characteristic absorption bands of CaO. Brunauer-Emmett-Teller (BET) isothermal sorption (QUANTACHROME, 1 KE), used to determine the surface area of the catalysts through N_2 -adsorption. The basicity was determined using a CO_2 TPD thermal.

2.4. Synthesis of biodiesel

The predicted acid value (1.59 mg KOH/g oil) validated as 1.562 (mg KOH/g oil) of a ternary mixture of the blended oil (TMBO) containing 33:33:34 of PKSO: USO: DNO mix meet the require synthesis of biodiesel by transesterification with catalyzed methanolysis of CBC. The procedure for production was the step by step procedures earlier reported by Minakshi *et al.* (2020) [7] with little modifications. A three-necked-reactor was used to carry out the biodiesel synthesis, four factors with five-level was considered viz. reaction time of 50–70 min, CBC amount 3.0–5.0 (wt.%), reaction temperature of 50–70 °C and MeOH/OMR of 4:1–8:1, respectively. Furthermore, 100 ml of the oil was preheated at 60 °C for 1 h, a measured catalyst amount was added to known methanol in 250 ml flask, heated at 65 °C for 20 min, and was added to the preheated oil in the reactor, and the reaction was monitored until it reaches completion. At the end of the reaction, the catalyst was separated by decantation and the biodiesel phase was separated from the ethanol phase by separating funnel. The leached catalyst in the biodiesel was removed by washing with a mixture of 2.0 g NaCO_3 and 40 ml ethanol thermally heated for 2 h under agitation. The mixture was filtered, washed with distilled water twice before the separation

Table 3
Experimental design for FAME synthesis.

Variables	Units	Symbol	Levels				
			−2	−1	0	1	2
Reaction time	(min)	K_2	50	55	60	65	70
CBC amount	(wt.%)	K_2	3.0	3.5	4.0	4.5	5.0
Reaction temp.	(°C)	K_3	50	55	60	65	70
MeOH/OMR	(ml/ml)	K_4	4	5	6	7	8

MeOH/OMR = Methanol/oil molar ratio, CBC = Calcined blend catalyst.

of biodiesel through gravity settling was carried out. The washed biodiesel was then dried over anhydrous Na_2SO_4 and then separated by filtration to obtain pure biodiesel (FAME). The CBC used was recycled for reuse at the end of the reaction with reduction in the 4th, 5th and 6th cycle. Hence, the catalyst reusability were stopped after 3rd usage. These processes was repeated based on experimental runs generated by design expert.

2.4.1. Experimental design for biodiesel synthesis and its statistical analysis

Table 3 showed the five-level four-factors considered for the experimental design of biodiesel synthesis. A central composite design was used to generate a total of 30 (thirty) experimental runs, which includes the plus and minus axial points, plus and minus factorial points and the central-point with factors low and high entered in terms of alpha. For every combination of categorical factor levels, CCD was duplicated.

For statistical analysis, the transformation which selected-response model and chooses transformation was used. The model for response surface and the interaction was evaluated by fit summary. The model order, significant effects, and desired terms were evaluated by model effects. ANOVA was used to analyze the chosen model and view results, while the diagnostic evaluate the model fit and transformation choice with the graph to interpret and evaluate the model. Furthermore, process optimization was carried out by determining the p-value, the f-value the df, and the VIF, respectively. The coefficient of determination (R^2), the predicted coefficient of determination (R^2_{pred}), the adjusted coefficient of determination (R^2_{adj}), and the adequate precision were also evaluated to confirm the model suitability. Graphing a function with two inputs (K_1K_2 ; K_1K_3 ; K_1K_4 ; K_2K_3 ; K_2K_4 or K_3K_4) and one-dimensional output (FAME) required plotting points in three-dimensional spaces for a perfect interactive effect among the variables was carried out. The second-order model equation that relates the relationship between the FAME and the independent variables is mathematically expressed as in Eq. (1).

Table 4a
Experimental runs with the response variables.

SR	PKSO	USO	DNO	PKSO	USO	DNO	Viscosity (mm^2/s)	Acid value (mg KOH/g oil)	Density (kg/m^3)
1	1.00	0.00	0.00	100	0.00	0.00	3.22	2.46	900
2	0.66667	0.33333	0.00	66.6667	33.333	0	3.22	2.39	879
3	0.66667	0.00	0.33333	66.6667	0.00	33.333	3.17	2.46	874
4	0.33333	0.66667	0.00	33.333	66.6667	0	3.35	2.25	873
5	0.33333	0.33333	0.33333	33.333	33.333	33.333	3.14	2.43	885
6	0.33333	0.00	0.66667	33.333	0.00	66.6667	3.50	2.51	870
7	0.00	1.00	0.00	0.00	100	0	3.58	2.04	883
8	0.00	0.66667	0.33333	0.00	66.6667	33.333	3.23	2.33	882
9	0.00	0.33333	0.66667	0.00	33.333	66.6667	3.43	2.52	884
10	0.00	0.00	1.00	0.00	0.00	100	4.19	2.60	890
11	0.66667	0.17	0.16667	66.6667	16.6667	16.6667	3.13	2.44	883
12	0.16667	0.66667	0.16667	16.6667	66.6667	16.6667	3.24	2.23	882
13	0.16667	0.16667	0.66667	16.6667	16.6667	66.6667	3.45	2.52	883
14	1.00	0.00	0.00	100	0	0	3.22	2.46	900
15	0.00	1.00	0.00	0	100	0	3.58	2.04	883
16	0.00	0.00	1.00	0	0	100	4.19	2.60	890

$$\text{FAME (wt. \%)} = \vartheta_0 + \sum_{i=1}^k \vartheta_i K_i + \sum_{i=1}^k \vartheta_{ii} K_i^2 + \sum_{i < j}^k \vartheta_{ij} K_i K_j + \epsilon \quad (1)$$

where FAME is the response (biodiesel) in percentage, ϑ_0 is the intercept, ϑ_i is the linear coefficient, ϑ_{ii} is the interaction coefficient, ϑ_{ij} is the quadratic coefficient terms, K_i, K_j are the four factors and ϵ is the residual error.

2.4.2. Physicochemical properties of FAME

The quality of FAME produced determines its suitability as fuel for industrial application, therefore, the properties of FAME were determined using recommended standard methods (AOAC, 1997). The results were compared with biodiesel recommended standards (EN 14214 and ASTM D6751) in a view to determine its suitability as a replacement for conventional diesel (petrol-diesel).

3. Results and discussion

3.1. Optimization of the oil blend

Based on the simplex lattice experimental design employed for the oil blend, 16 experimental results were obtained according to three factor-five level experimental designs on the response values. The response values were acid value, density, and viscosity as the important parameters for FAME feedstock. Presented in Table 4a are the value for sixteen experimental designs and the responses obtained. The statistical optimization predicted an acid value of 2.44 mg KOH/g oil, a viscosity of 3.15 (mm^2/s), and a density of 884.91 (kg/m^3) at ternary point of 33:33:34 (Fig. 1) as depicted in Table 4b. These predicted values were validated in triplicate by mixing the oils in the ternary point ratio; the mixture was placed on a magnetic shaker heated at 40 °C for proper homogeneous mixing. And the density, viscosity and the acid value were determined in triplicate. Average mean values of 2.40 mg KOH/g oil for acid value, 3.20 mm^2/s for viscosity, and density 885 kg/m^3 , were respectively obtained. The final equations in terms of the pseudo, real and actual components are represented in Eqs. (2)–(4) for the density, viscosity, and the acid value. This shows that the order in which the oils are blend was factor properly. The resultant mix produced oil with less viscous and high volatility with proper synergistic effect within the blend. The blended oil was successively converted to FAME via transesterification reaction with methanolysis of the derived heterogeneous catalyst.

$$V = 3.2190x_1 + 3.5818x_2 + 4.185x_3 - 0.51804x_1x_2 - 1.65701x_1x_3 - 2.48388x_2x_3 \quad (2)$$

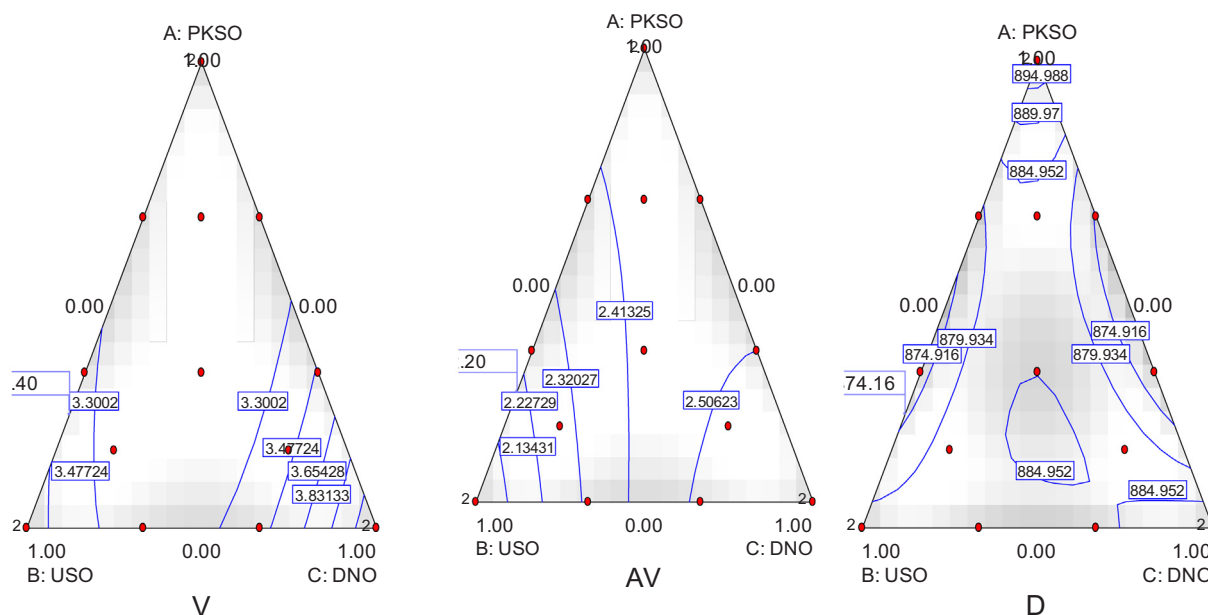


Fig. 1. Viscosity, Density and Acid value ternary plots.

$$AV = 2.4564x_1 + 2.0413x_2 + 2.5992x_3 + 0.33797x_1x_2 - 0.20067x_1x_3 + 0.48325x_2x_3 \quad (3)$$

$$D = 900.00579x_1 + 882.60492x_2 + 889.75040x_3 - 68.83477x_1x_2 - 99.81106x_1x_3 - 14.85417x_2x_3 + 391.25000x_1x_2x_3 \quad (4)$$

3.2. Characterization of catalyst and elemental analysis

Table 4c showed the result of the BET surface, basicity, total pore volume, and the percentage composition of CaO obtained by EDX-nitrogen adsorption- CO_2 TPD. The Bet-surface of the CBC is higher than the CSSC, CESC, and CWAC, but the surfaces displayed by CESC and CWAC are of the same value ($0.90 \text{ m}^2\text{g}^{-1}$). This observation could be attributed to the nature of the catalysts involved, as snail shell has higher surface area than the eggshell and the wood ash; however, the resultant blending (CBC) surface is higher than the individual surface due to proper mixing which increased the surface area after thermal treatment, thereby increase the rate of reaction during transesterification. Based on CO_2 -TPD results, the CBC showed a higher weak and strong basic site with a value of the basic amount of 12 and 162 ($\mu\text{mole.g}^{-1}$) than the value obtained by the individual catalysts. This proved that the CBC with the highest basic amount corresponds to FAME with high conversion yield. Although the CSSC, CESC and CWAC also exhibited an active value for a strong basic site, it appears to be less active to the reaction compared with the CBC catalyst.

The percentage CaO present is high for a single methanolysis base conversion of oil to biodiesel, but the CaO obtained through blends

produced a higher base which resulted in higher FAME formation. Fig. 2a shows the angular SEM images through the CBC(D) at a different magnification of $1500\times$, $1000\times$, $500\times$, and $350\times$, respectively, performed in the range of $20^\circ < 2\theta < 80^\circ$ at speed of $2^\circ \text{C min}^{-1}$. The images obtained after calcinations for 3 h at 900°C indicated that the calcined powder were of diverse shape, non-uniform in size and less porous at $1500\times$ and $1000\times$ than at $500\times$ and $350\times$. The number of aggregates structural displayed showed the glossy nature, permeability and spongy nature of the particles present in the catalyst. Further observation shows that the calcination also resulted in the sintering of small mineral aggregates and agglomerated particles responsible for the squishy nature of the catalysts. The SEM image promptly shows an abundance of calcium and oxygen after calcination which proved that no carbon remains after the thermal treatment due to gaseous formation of CO_2 at 900°C . Infrared spectroscopy (FTIR) was used to analyze the materials in detecting both organic and inorganic materials present in the developed CBC catalyst. The FTIR works to convert the raw data from the broad-band light source to obtain the absorbance level at each wavelength. The FTIR results of CBC calcined at 900°C for 3 h are displayed in Fig. 2b with the infrared spectrum, which plots the intensity of infrared spectra. The peaks, (absorbance bands), correspond with the various vibrations of the sample's atoms when it's exposed to the infrared region of the electromagnetic spectrum. The transmittance and the wavelength observed from 1036.2 ; 44.952 cm^{-1} 1442.5 ; 76.401 cm^{-1} stretches indicated the presence of aldehyde/ketone and ester (below 1500 cm^{-1} in the infrared spectrum). The spectrum stretching from 1636.3 ; 65.145 cm^{-1} – 2922.2 ; 74.179 cm^{-1} indicated the presence of two functional groups CH_2 and $\text{C}=\text{O}$ (above

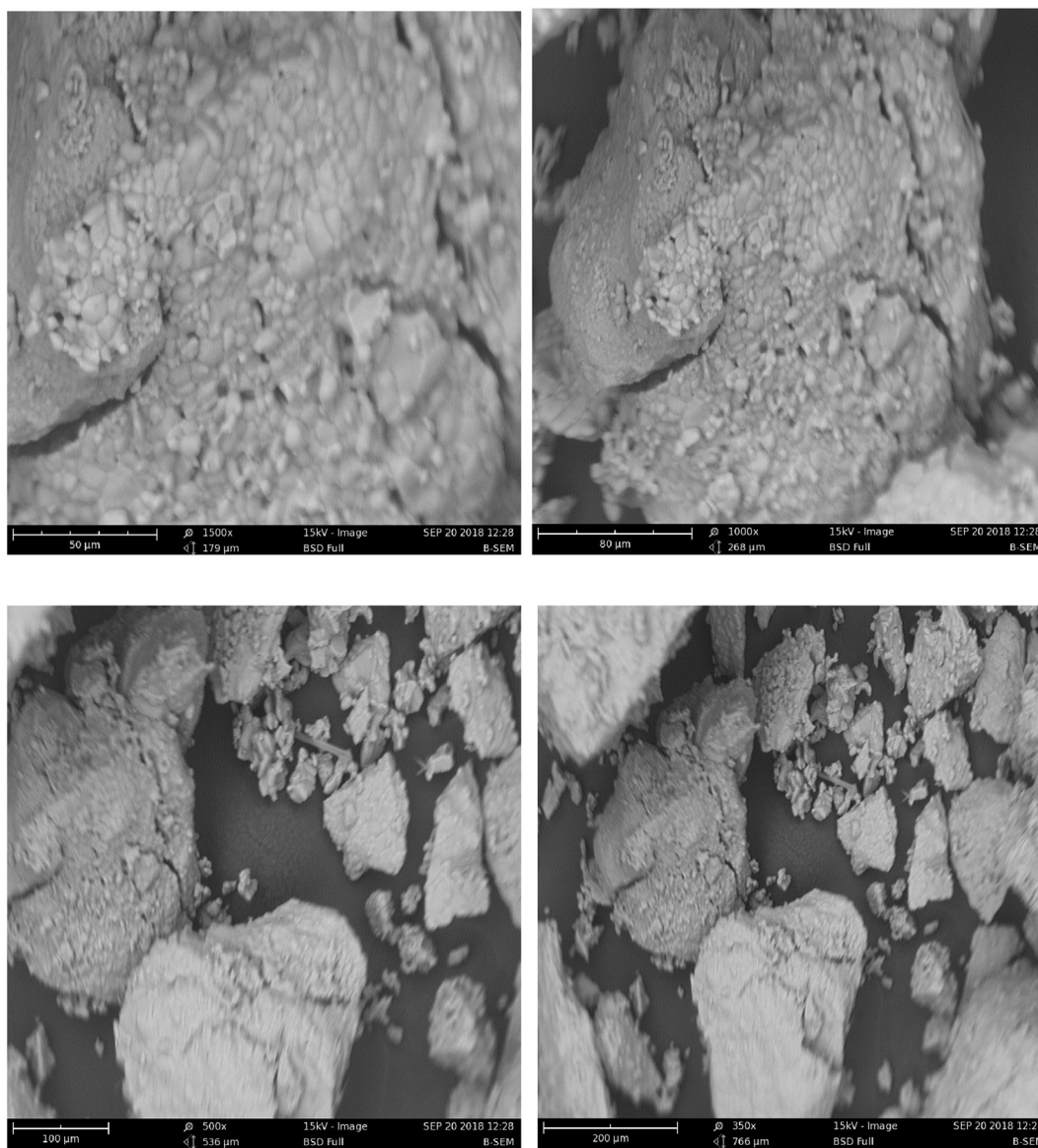
Table 4b
Predicted-Ternary Level.

Name	Prediction	SE Mean	95% CI low	95% CI high	SE pred	95% PI low	95% PI high
Viscosity	3.14546	0.00	3.15	3.15	0.00	3.15	3.15
Acid value	2.43522	0.00	2.44	2.44	0.00	2.44	2.44
Density	884.914	0.00	884.91	884.91	0.00	884.91	884.91
Component	Name	Level	Low level	High level	Std Dev		
A	PKSO	0.33	0.00	1.00	0.00		
B	USO	0.33	0.00	1.00	0.00		
C	DNO	0.34	0.00	1.00	0.00		

Table 4c

Pro-catalytic activity of catalysts calcined at 900 °C for 3 h.

Catalysts	S_{BET} (m^2g^{-1})	Total pore volume (cm^3g^{-1})	%CaO	BS ($\mu\text{mole.g}^{-1}$)	Weak	Medium	Strong	< 450 °C	> 450 °C	> 650 °C	TBS	BSD ($\mu\text{mole.m}^{-2}$)
CWAC	0.90	6×10^{-3}	94.10	5			40		130		175	194.4
CESC	0.90	6×10^{-3}	92.83	4			42		122		168	186.7
CSSC	1.10	6×10^{-3}	94.25	4			32		140		176	160.0
CBC	1.30	6×10^{-3}	98.50	12			40		162		224	172.31

BS = Basic site, TBS = Total basic site, BSD = Basic site density = TBS/ N_2 -AA.**Fig. 2.** a: SEM images through the CBC at different wavelengths. 2b: FTIR analysis.

$1,500\text{ cm}^{-1}$ in the infrared spectrum). However, the broad absorption displayed within the range 3339.7 ; 53.157 cm^{-1} suggested the absence of amide, catalytic acid, and O–H present.

The elemental analysis results of the CBC using EDX-ray showed that at the temperature of 450 °C , the main compound is a carbonate of calcium, an increase in thermal temperature to 550 °C , decomposition of calcium carbonate to form calcium (II) oxide was observed. It was observed that the thermal decomposition of CaCO_3 to complete CaO occurred at a higher temperature above 750 °C than reported temperature observed by Viriya-empikul *et al.* (2012) [3] and Subramaniapillai *et al.* (2019) [8]. The undistorted structure of mixed

catalyst transformed into a porous clumsy like structure indicates that calcination at a higher temperature is appropriate for complete transformation of CaCO_3 to complete CaO (Subramaniapillai *et al.*, 2019) [8]. This observation may be related to the presence of some functional groups present in the shells and wood plant during the growth period which occurred as a result of carbon growth inhibition. But, due to the abundance of calcium in the CBC other metals that may be present were of no concern, but could also aid biodiesel synthesis (Helwania *et al.*, 2009; Zabeti and Daud, 2009) [28,29].

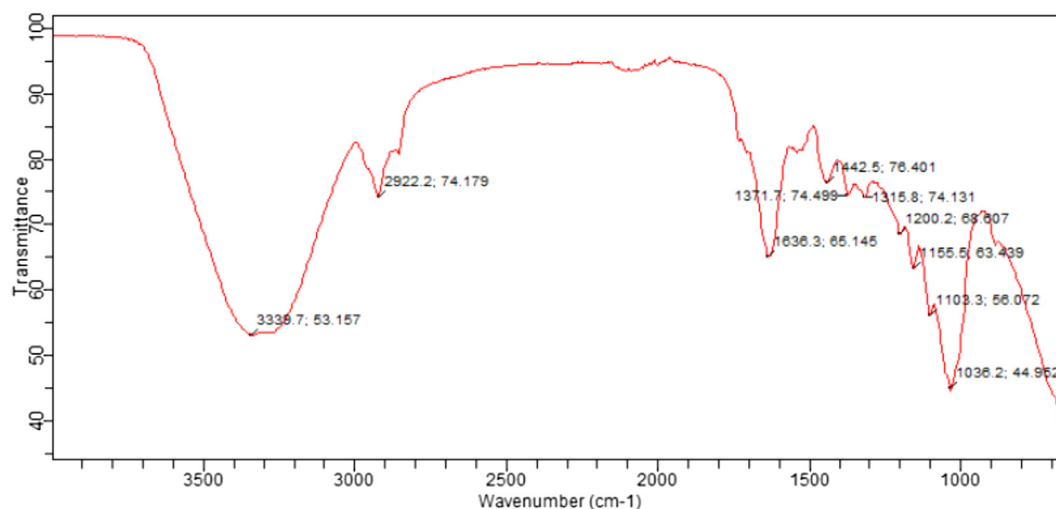


Fig. 2. (continued)

3.3. FAME synthesis

3.3.1. Statistical optimization of methanolysis of CBC for FAME synthesis

Table 5 showed the results of the 30 runs-experimental yield obtained, the predicted and the residual value as obtained by CCD in coded four factors-five level variables: K_1 (50–70 min), K_2 (3.0 wt%, 5.0 wt%), K_3 (40 °C, 60 °C), and K_4 (4:1, 8:1) (ml/ml). Observation from the table showed the highest FAME obtained was 98.00 (wt. %) at run 13 while the lowest FAME produced was 79 (wt. %) at run 27. The statistical optimization showed that the predicted value by the software was 97.33 (wt. %) at K_1 of 64.71 min, K_2 of 4.5 wt%, K_3 of 61.61 °C, and K_4 of 8:1 (ml/ml) at the desirability of 96.5%, at the same condition, the predicted value was validated in triplicate and an average mean value of FAME 97.22 (wt. %). The value showed that methanolysis of CBC derived from wood ash, egg and snail shell successfully converts

PKSO-DNSO-USO blend to biodiesel.

Meanwhile, the positive and the negative coefficients' in equation the direct measure of influence of variables are the coefficient value, the K_3 (reaction temperature) with f -value = 960.58, the sum of squares = 135.71 (p -value < 0.0001) is the most significant variable among the second order polynomial was used to generate the regression coefficients and significance of response surface quadratic equation. Presented in Eq. (5) is the final second-order polynomial input factor. Also, Table 6 shows the ANOVA used to determine the level of significant for statistical analysis. The high model with sum of squares = 619.62, f -value = 313.27 with p -value < 0.0001 indicated significant model term. Based on probability value and respected f -value, all the variables, their interaction and their quadratic forms were significant except the

The final equation in term of coded

Table 5

FAME result of experimental run, predicted and the residual value.

Std	Run	Block	K_1	K_2	K_3	K_4	FAME(wt%)	Predicted FAME (wt. %)	Residual
1	12	1	−1.000	−1.000	−1.000	−1.000	84.00	84.05	−0.052
2	3	1	1.000	−1.000	−1.000	−1.000	84.10	84.05	0.045
3	6	1	−1.000	1.000	−1.000	−1.000	88.30	88.39	−0.086
4	30	1	1.000	1.000	−1.000	−1.000	88.00	88.05	−0.052
5	28	1	−1.000	−1.000	1.000	−1.000	88.40	88.56	−0.16
6	2	1	1.000	−1.000	1.000	−1.000	90.20	90.09	0.11
7	29	1	−1.000	1.000	1.000	−1.000	92.01	91.91	0.10
8	4	1	1.000	1.000	1.000	−1.000	93.00	93.11	−0.11
9	22	1	−1.000	−1.000	−1.000	1.000	85.00	85.04	−0.038
10	19	1	1.000	−1.000	−1.000	1.000	88.60	88.83	−0.23
11	11	1	−1.000	1.000	−1.000	1.000	91.30	91.54	−0.24
12	20	1	1.000	1.000	−1.000	1.000	95.00	94.99	0.012
13	23	1	−1.000	−1.000	1.000	1.000	85.00	85.08	−0.075
14	1	1	1.000	−1.000	1.000	1.000	90.34	90.40	−0.058
15	8	1	−1.000	1.000	1.000	1.000	90.40	90.59	−0.19
16	5	1	1.000	1.000	1.000	1.000	95.50	95.58	−0.075
17	7	1	−2.000	0.000	0.000	0.000	83.30	83.07	0.23
18	10	1	2.000	0.000	0.000	0.000	88.10	88.06	0.041
19	27	1	0.000	−2.000	0.000	0.000	79.00	78.91	0.091
20	14	1	0.000	2.000	0.000	0.000	88.60	88.42	0.18
21	15	1	0.000	0.000	−2.000	0.000	90.00	89.82	0.18
22	26	1	0.000	0.000	2.000	0.000	95.00	94.91	0.090
23	18	1	0.000	0.000	0.000	−2.000	94.20	94.24	−0.037
24	13	1	0.000	0.000	0.000	2.000	98.00	97.69	0.31
25	25	1	0.000	0.000	0.000	0.000	94.50	94.95	−0.45
26	21	1	0.000	0.000	0.000	0.000	95.00	94.95	0.050
27	24	1	0.000	0.000	0.000	0.000	94.60	94.95	−0.35
28	17	1	0.000	0.000	0.000	0.000	95.10	94.95	0.15
29	16	1	0.000	0.000	0.000	0.000	94.50	94.95	−0.45
30	9	1	0.000	0.000	0.000	0.000	96.00	94.95	1.05

Table 6
Test of significance for every regression coefficient.

Source	Sum of squares	df	Mean Square	F-value	P-value
Model	619.62	14	44.26	313.27	< 0.0001
K ₁	37.33	1	37.33	264.20	< 0.0001
K ₂	135.71	1	135.71	960.58	< 0.0001
K ₃	38.89	1	38.89	275.26	< 0.0001
K ₄	17.91	1	17.91	126.74	< 0.0001
K ₁ K ₂	151.00	1	151.00	1068.85	< 0.0001
K ₁ K ₃	218.33	1	218.33	1545.42	< 0.0001
K ₁ K ₄	11.46	1	11.46	81.11	< 0.0001
K ₂ K ₃	1.76	1	1.76	12.49	0.0030
K ₂ K ₄	0.11	1	0.11	0.81	0.3834
K ₁ ²	2.35	1	2.35	16.62	0.0010
K ₂ ²	14.35	1	14.35	101.54	< 0.0001
K ₃ ²	0.97	1	0.97	6.83	0.0195
K ₄ ²	4.68	1	4.68	33.10	< 0.0001
Residual	19.96	1	19.96	141.27	< 0.0001
Lack of Fit	37.33	1	37.33	264.20	< 0.0001
Pure Error	135.71	1	135.71	960.58	< 0.0001
Cor Total	38.89	1	38.89	275.26	< 0.0001
Fits statistics					
R squared	0.996				
Adjusted R squared	0.9934				
Predicted R squared	0.9919				
Adequate precision	70.673				

$$\begin{aligned} \text{FAME} = & +94.80 + 1.25X_1 + 2.38X_2 + 1.27X_3 + 0.86X_4 - 0.084X_1 \\ & X_2 + 0.38X_1X_3 + 0.950X_1X_4 - 0.25X_2X_3 + 0.54X_2X_4 - 1.12X_2 \\ & X_3 - 2.35X_1^2 - 2.82X_2^2 - 0.65X_3^2 + 0.25X_4^2 \end{aligned} \quad (5)$$

interaction of K₁K₂ with lowest sum of the squares = 0.11, p-value = 0.181 with f-value = 0.3834 > 0.05, that is a non-significant interactive term. The Lack of fit f-value of 0.14 with p-value 0.9956 > 0.05 implies non-significant lack of fit. There is a 99.56% chance that a “Lack of fit f-value” this large could occur due to noise, though this is required for model accuracy (Adepoju *et al.*, 2018a) [17].

Still, on the table, based on fit and model comparison statistics, the coefficient of determination (R²) which showed the proportion of the variances in the dependent variable that is predictable from independent variable was obtained as 0.9966%, the predicted coefficient of determination (pred. R²) of 0.9919% is in reasonable agreement with the adjusted R² of 0.9934 with adequate precision of 70.673 greater than 4 for satisfactory model navigation of the space. Fig. 3(a) shows the comparative evaluation of experimental FAME and predicted results, a straight line was observed that passed through the origin with nearly all points indicating that the residual values known as an error, are so small to be neglected, while Fig. 3(b), shows the residual SS vs. the Lambda with the current at 1 and best value at 0.1, given a low and high confident level (CI) at −1.11 and 1.41, respectively. Furthermore, the effects of variable interactions on the FAME were further confirmed by the three-dimensional-contour plots of 3D's plots (Fig. 4(a-f)). From the figures, it was observed that the highest mutual interaction was observed in K₃K₄ (Fig. 4f), followed by K₁K₄ (Fig. 4c), and then K₂K₄ (Fig. 4e). The lowest interaction was observed in

K₁K₂ (Fig. 4a), but the interaction of K₂K₃ (Fig. 4d) was greater than that of K₁K₃ (Fig. 4b) which is high than K₁K₂ (Fig. 4a). These showed that there were perfect interactions between variables on the response, the effects were only varied based on the impact.

3.4. Catalyst reusability

The reactor wall accumulated about 0.15 wt% catalyst, during the reaction, this reduced the surface area and effectually lowered catalyst activity. Hence, the need to carry out catalyst reusability on the catalytic activities CBC under different experimental conditions, the result in Fig. 5 revealed that the catalytic activities continue stable upon successive reuse from cycle 1 to cycle 3 with little decreased from 93.01% to 91.30%. However, a significant decreased was noticed at 4th and 5th cycle, this occurred due to transitional products formed during the reaction, such as monoglyceride and diglyceride, which obstructed the holes of catalysts (Wong *et al.*, 2015; Trisupakiti *et al.*, 2017) [30,6], as well as water-oxygen reacted at the catalyst surface hereby reduce

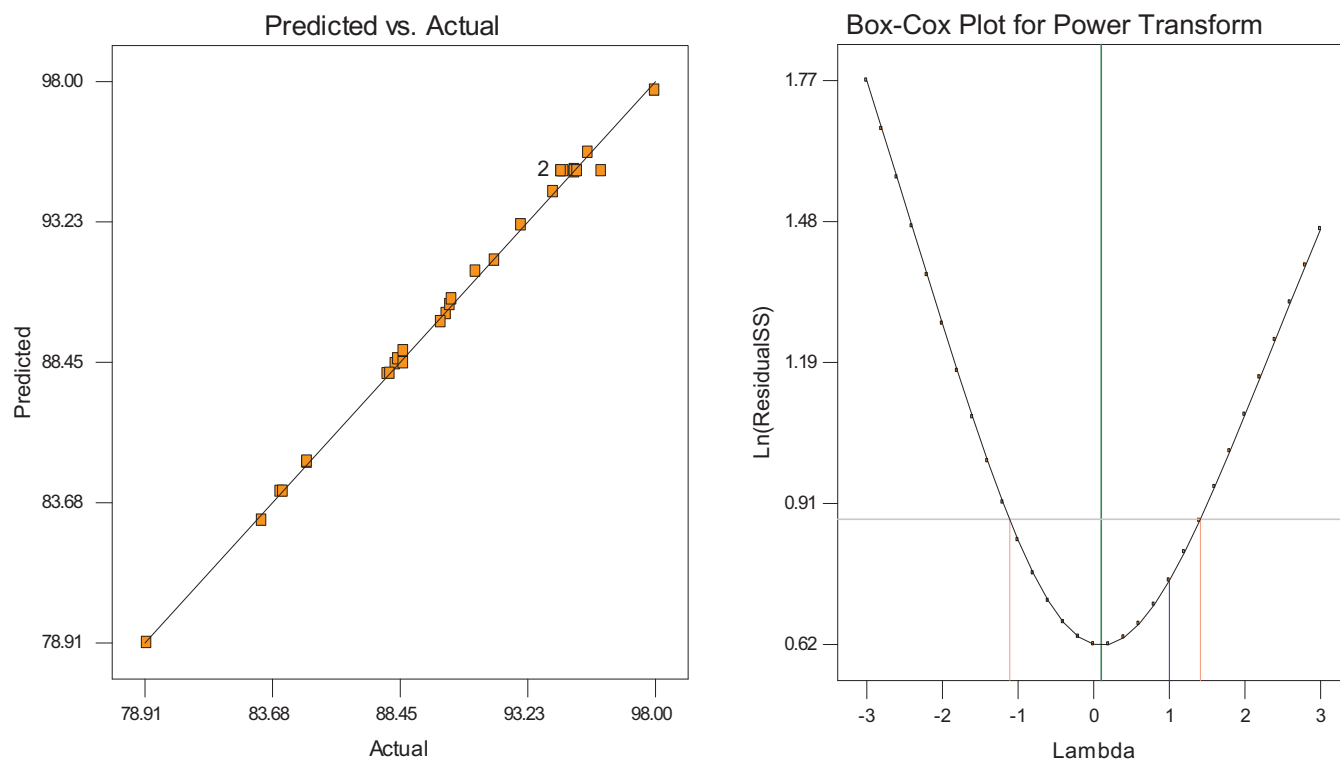


Fig. 3. (a) Predicted vs Actual; (b) Residual vs, Lambda.

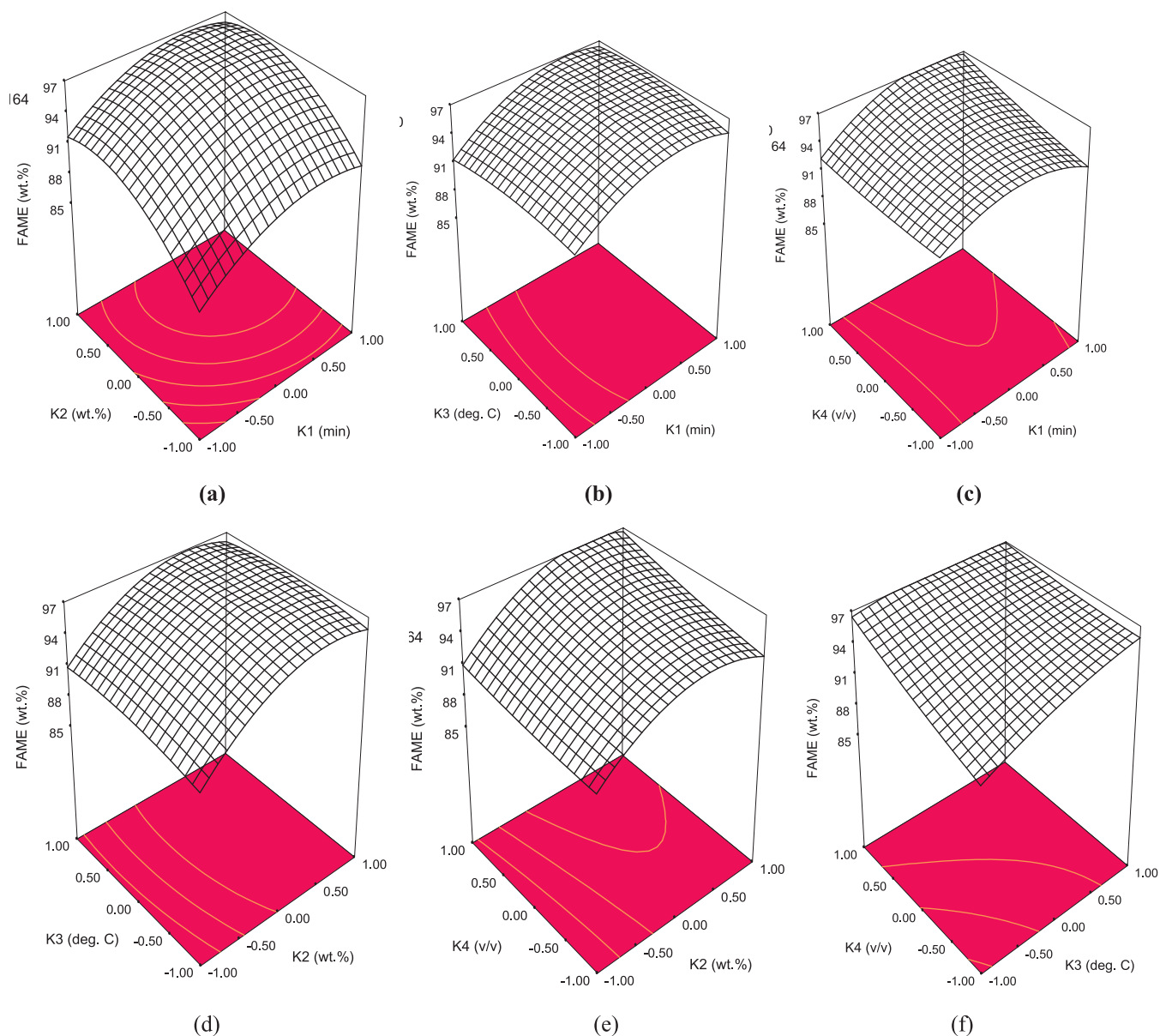


Fig. 4. (a-f): Three dimensional plots.

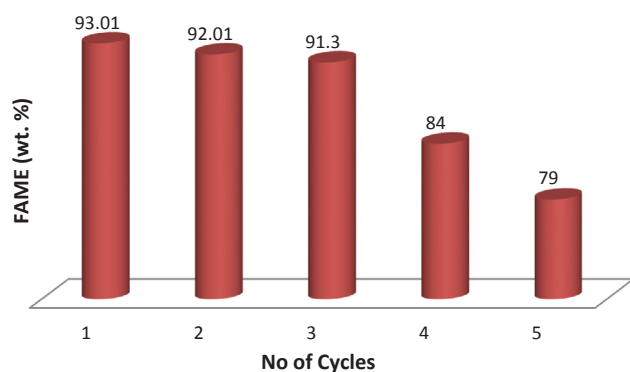


Fig. 5. Catalyst reusability test.

the catalyst sensitivity. Hence, catalyst reusability was stopped at the 3rd cycle. Catalyst purification and reusability analysis of the reaction mixture was carried out using a built-in heating system vacuum centrifuges/concentrators operated at 4000 revolutions per minute (rpm),

Table 7
Properties of TMBO and FAME.

Parameter	TMBO	FAME	ASTM D6751	EN 14214
<i>Physicochemical properties</i>				
Density (kg/m ³) @ 25 °C	885	865	–	860–900
Viscosity @ 40 °C/(mm ² /s)	3.20	1.64	1.9–6.0	3.5–5.0
Physical state @ 27 °C	Yellowish	Brownish	–	–
Moisture content (%)	0.003	0.001	< 0.03	0.02
%FFA (as oleic acid)	1.20	0.157	0.40 max	0.25 max
Acid value (mg KOH/g oil)	2.40	0.314	0.80 max	0.5 max
Iodine value (g I ₂ /100 g oil)	92.54	76.12	–	120 max
Saponification value (mg KOH/g oil)	168.90	134.50	–	–
Peroxide value (meq O ₂ /kg oil)	8.50	10.20	–	12.85
HHV (MJ/kg)	41.12	42.77	–	–
Cetane number	63.42	69.75	57 min	51 min
API	28.39	32.08	39.95 max	–
Diesel index	74.19	83.00	50.4 min	–

and washed with --OH to remove the unwanted impurity. The recoverable catalyst was oven-dried at 150°C for 2 h and then cooled to room temperature before reused.

3.5. Properties of TMBO and FAME

The quality of the TMBO and the synthesized FAME were carried out and the results are as presented in Table 7. The density, viscosity, the moisture content, acid value, the iodine value, and the peroxide value of TMBO were higher than the FAME values confirming that the synthesized product is consistent with biodiesel and that the conversion of TMBO to FAME was complete with negligible resistance to flow and reduce internal drag in engine. The moisture content of the FAME was well within the range stated by ASTM D6751 and EN 14214. This value indicated that the produced FAME is of high quality which accounts for its high cetane number (69.75). The low acid value (0.314 mg KOH/g oil) obtained in this study as compared with the recommended standard values explained the higher yield of FAME recorded in this work (98.00 wt%). FAME with an acid value greater than 0.8, will produce low ester yield and increase base consumption for neutralization. Peroxide value reported that the increase in its value in FAME increased the cetane number and the ignition time reduction (Zuleta *et al.*, 2012) [31]. The value obtained in this study for FAME (10.20 meq O_2/kg oil) takes into account the high cetane number (69.75) obtained. The higher heating value of FAME is higher than the TMBO indicating a higher heat of vaporization of water in the combustion FAME. American petroleum institute (API) gravity, used to determine the weight of oil/petroleum in comparison with water, the value > 31.1 indicates light oil, the value of API gravity obtained in this work (32.08) showed clearly that the FAME is of lighter quality. Diesel index which denotes the efficiency of the FAME, as well as the ignition properties, was well within the required standard for biodiesel.

4. Conclusion

The statistical approach to a mixture of oil produced TMBO of low viscosity, low density, and low acid value. A calcination temperature of 900°C for 3 h was found to be an optimum condition for preparing CaO based catalyst derived from a mixture of CSSC, CESC, and CWAC. The catalytic activity noticed during transesterification depended more on the basicity of the basic site present in the CBC. The maximum FAME yield obtained was 98.00 (wt%) at run 13, but the statistical optimization predicted value of 97.33 (wt%) at a reaction time of 64.71 min, catalyst amount of 4.5 wt%, reaction temperature of 61.61°C , and methanol/oil molar ratio of 8:1 (ml/ml), under the same condition, the predicted value was validated in triplicate and an average mean value of FAME of 97.22 (wt%) at the desirability of 96.5% was obtained. A significant decrease was noticed at the 4th and the 5th cycles due to transitional products formed during the reaction, obstructing the holes of catalyst and reduce the catalysts sensitivity, hence, catalysts reusability was stopped at the 3rd cycle. Produced FAME from a ternary blend of synthesized oils via methanolysis of calcium oxide-based catalyst derived from mixed powders calcined egg, snail shells and wood ash conformed with biodiesel recommended standard.

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CRediT authorship contribution statement

T.F. Adepoju: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data curation, Writing - original draft, Supervision. **M.A. Ibeh:** Formal analysis, Investigation, Resources, Data curation, Methodology, Software. **E.O.**

Babatunde: Methodology, Software, Validation, Formal analysis, Methodology, Investigation, Resources. **A.J. Asquo:** Formal analysis, Investigation, Resources, Data curation, Methodology.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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