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Appraisal of CaO derived from waste fermented-unfermented kola nut pod for fatty acid methylester (FAME) synthesis from *Butyrospermum parkii* (Shea butter) oil

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ABSTRACT

Fatty acid methylester (FAME) synthesis from *Butyrospermum parkii* (Shea butter) oil using a CaO derived catalyst derived from waste kola nut pod as a heterogeneous catalyst was examined in this study. Due to the high free fatty acid of the oil, the oil was first esterified with acidic catalyst before transesterified with CaO. In both reactions, response surface methodology was used to model and optimized the reaction conditions. The rendering method adopted produced oil with low viscosity and density. Based on ANOVA, the effect of reaction time, catalyst amount, and methanol/oil molar ratio on acid value reduction were significant. The high free fatty acid of 10.76 mg KOH/g oil was reduced significantly to 0.37 mg KOH/g oil via statistical optimization in seventeen experimental runs. Submerged fermentation of waste kola nut pod before thermal treatment of the powder increased the calcium and potassium content of the catalyst. Decreased in catalyst reusability was noticed in the 4th and 5th cycles. The optimum reaction conditions ensuring the best FAME content of 95.30 (wt. %) are found to be catalyst amount of 2.5 wt.%, the reaction time of 55 min, reaction temperature of 50 °C, and methanol/oil molar ratio of 5:1 (ml/ml). The produced FAME quality is within the biodiesel standard (ASTM D6751 and EN 14214).

1. Introduction

With the latest awareness to increase biofuel production in the United States and European Union (EU) member states by 2019–2030, countries around the globe have injected millions of euros to meet up with Safety Data Sheet (SDS) level. China, India, Brazil, and the Association of Southeast Asian Nations (ASEAN) countries have widened the permitted feedstock base for biofuel and introduced subsidies to expand production capacity. Europe is currently the largest producer of biodiesel but Brazil was on the high increase in production rate in the past years (IES, 2019). The main advantages of biofuel are 50% less particulate, 80% less CO₂, 70% less H–C, high flash point, and high cetane number when compare to conventional fuel (Kiss et al., 2012). Therefore, for a global presence, working towards a secure, sustainable future for all through biofuel production is the technology roadmap.

Shea butter (*Butyrospermum parkii*) oil is a vegetable fat extracted from the kernel of what is known as the *Vitellaria paradoxa* (shea tree). This particular tree belongs to the family of *Sapotaceae* and mainly indigenous oil producing wild plants spontaneously growing in Savanna

including West Africa and Uganda. This plant can be grown in another part of the world by the hybrid process. Although, the trees do not reach maturity until 20 to 45 years, but can continuously produce shea nuts for up to 200 years in commercial quantities. *B. parkii* is very cheap, the rich vegetable extract contains fatty acids, phytosterol, and unsaponifiable matter used for varieties of purposes including raw material for the production of biofuel.

B. parkii fruit like other fruits has three layers, the green epicarp (the outer part); a fleshy mesocarp (pulp), and a relatively hard endocarp containing embryo known as shea kernel (Olaniyan and Oje, 2007). Both oil and solid wastes can be generated in a great percentage in shea oil processing. The effluent obtained from thermal treatment, grinding, extraction, oil recovery, and drying of shea oil processing is discharged as underground water. The shea nut cake after extraction can be used to make animal feeds and as a substitute for maize in the diets of growing gilts (Abdul-Mumeen et al., 2013).

In the agricultural sector, tons of wastes are generated yearly and they are always ignored which later resulted in environmental pollution and anesthetic effect (Ubalua, 2007). These wastes pose a disposal

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problem and will even be more problematic with the increase in industrial production without turning the wastes into a useful form. Among these wastes is *Cola nitida* (Kola nut) pod (KNP), a by-product of the kola nut fruit with great environmental concerns. KNP constitutes 60–75% by weight of the fruits since it is similar to cocoa (Cruz et al., 2012). Considering the large amounts of solid waste that KNP constituted to the fruit, there is a need for the process of recycling/recovery. Direct burning of wastes does not decompose easily and substantial furnace modifications are usually required if they are to be used as firewood or fuel oil (Alireza et al., 2015). It has been reported that using fermented KNP before furnace modifications over unfermented KNP increases the calcium, potassium, phosphorous, and magnesium contents (Fabunmi and Arotupin, 2015) enough to produce energy.

Nevertheless, the biodiesel production route depends solely on the free fatty acid (FFA) value of the oils. Oils with high acid value need acid-catalyzed esterification before transesterification with a solid base catalyst. In acid esterification, hydrogen tetraoxosulphate (IV) is preferable than hydrochloric acid owing to its high acidic strength (Dias et al., 2012; Yaakob et al., 2012; Chang et al., 2013; Silitonga et al., 2013; Adepoju et al., 2018a). The use of solid acid catalysts and ionic liquid has also been tested (Gan et al., 2010; Zhang et al., 2010; Hayyan et al., 2011; Thiruvengadaravi et al., 2012; Man et al., 2013) to reduce high acid value before transesterification with solid base coupled with different operating conditions to arrive at optimum yield.

Operating conditions of biodiesel production are usually modeled and optimized via statistical methods. Box Behnken, central composite design, fussy logic, genetic algorithms, tanguchi design, Minitab response surface, factorial design, etc. have been tested and confirmed as good optimization software (Adepoju 2020; Adepoju et al., 2020a, 2020b, 2020c; Ramadhas et al., 2006; Karnasuta et al., 2007; Tiwari et al., 2007; Canakci et al., 2009; Schinas et al., 2009; Khan et al., 2010; Goyal et al., 2012; Suwito et al., 2012; Muazu et al., 2013).

Optimization of process condition of *B. parkii* oil for biodiesel production through acid-alkaline catalysis has been reportedly carried out (Ing Samuel et al., 2018). Ajala et al. (2017) used H_2SO_4/KOH for the production of biodiesel from shea butter and its optimization using RSM. In another attempt, Betiku et al. (2015) optimized the process condition of shea butter to produce biodiesel, only to end up using H_2SO_4/KOH as catalysts. As far as authors' awareness, fermented and unfermented KNP have not been investigated as a catalyst for biodiesel production yet. Hence, this work, the use of fermented and unfermented powder residues obtained after thermal treatment are tested for base catalyst production. The operating conditions were modeled and optimized using Box Behnken experimental design. Physicochemical analysis of the *B. parkii* oil and its FAME were also determined using AOAC (1990) and (1997) standard methods.

2. Materials and methods

2.1. Materials

2.1.1. Shea butter (*Butyrospermum parkii*) oil

B. parkii was obtained from a named market, Oja- Oba in Kwara State, Nigeria. The butter was made into a liquid by dry-rendering method through heating in a batch reactor at 110 °C for 60 min (Dias et al., 2009). Kola nut pod was collected from the Ete market in Ikot Abasi Local Government Area, Akwa Ibom State, Nigeria.

2.1.2. Chemicals

All chemicals used were of analytical grade and need no further purification. 99.5% pure methanol, 36 wt% HCl, HPLC grade n-hexane, chloroform, sulphuric acid, acetic acid etc., were all purchased from Finelab Nig. Ltd.

2.2. Methods

2.2.1. Oil preparation and quality characterization

The rendered fat oil was subjected to quality characterization by determining its physicochemical properties to ascertain its usefulness for energy production. Properties such as viscosity using NDJ-5S viscometer, density using Sigma-Aldrich density bottle, moisture content using moisture analyzer or drying oven (thermogravimetric approach), acid, peroxide and saponification values were determined using AOAC (1990) standard methods, iodine value using Wij's method, cetane number and higher heating value using ASTM D2015 method and mean molecular mass using method cited by Adepoju et al. (2018b). The constituent of the volatile matter, long and branched-chain hydrocarbons, esters and alcoholic acids, and others were determined using complete Agilent 5973 N gas chromatography-mass spectrometry instrument control and data storage, with the system programmed as follows: Column Elite-1 fused with silica capillary column (30 mm x 250 μ m x 0.25 μ m) composed of 5% phenyl methyl siloxane, operated in 1329.412 eV; 99.99% of helium used as carrier gas at a constant flow rate of 1.5 mL/min with an injection volume of 1 μ l employed in a split ratio of 10:1. The injector and ion-source temperatures were 150 °C and 250 °C, respectively. The oven temperature was programmed from 35 °C (isothermal for 5 min), with an increase of 4 °C/min, to 150 °C, for 2 min, then 2 °C/min to 250 °C. Mass spectral were taken at an average velocity of 44.297 cm/sec; a hold time of 1.1287 min, pressure of 11.064 psi, and frequency of 50 Hz. Gas chromatography-mass spectrometry running time was 45 min (Adepoju and Eyibio, 2016).

2.2.2. Catalyst preparation

Two samples of KNP were prepared as follows: each sample weighing 100 g in a cleaned container was washed with deionized water to remove unwanted materials. One sample was oven-dried to constant weight while the other was submerged in distilled water and covered for 10 days for fermentation to take place. The fermented sample after 10 days was filtered, washed, and then filtered before oven-dried to constant weight. These samples were milled to powder and then calcined at a temperature of 700 °C for 4 h in a muffle furnace. UCKNP is the abbreviation for unfermented calcined kola nut pod while SFCKNP is the abbreviation for solid fermented calcined kola nut pod.

2.2.3. UCKNP and SFCKNP characterization

The surface morphology of the UCKNP and SFCKNP catalysts were viewed by using the Scanning Electron microscope (SEM), model 6300F by JEOL solution for innovation, USA. The BET isothermal sorption method (QUANTACHROME, 1KE) was used to determine the surface area of the UCKNP and SFCKNP catalysts through N_2 -adsorption. The basicity was determined using a CO_2 TPD. The elemental analysis of the samples and the quantitative composition of the samples were determined to reveal the elemental composition of the catalyst using Energy dispersive x-ray (EDX-ray), model NEX CG, made by Rugaku, Austin, USA. The presence of calcium oxide was confirmed using XRD equipped with $K\alpha$ and Cu radiation source, accelerated at 30 mA and 40,000 V with angular scanning electron performed in the range of $10^\circ < 2\theta < 70^\circ$ at a rate of 2 min^{-1} using the method earlier adopted by Alireza et al. (2015).

Fourier Transform Infrared Ray (FTIR) is an amazingly useful materials analysis technique, assisting in detecting both organic and inorganic materials. It measures a sample's absorbance of infrared light at different wavelengths to decide the material's structural and molecular composition. The FTIR works to convert the raw data from the broadband light source to obtain the absorbance level at each wavelength. Hence, the FTIR model 3,116,465, made in Japan, was also used to confirm the presence of the functional group.

2.2.4. Esterification of *B. parkii* oil (acid treatment)

Since the acid value of the *B. parkii* oil was >1.5 as earlier

determined, esterifying the oil with a strong acid is essential. Hence, the method adopted by Adepoju et al. (2018a) was used with little modification. The experiment was carried out in a three-necked batch reactor, placed on a hot magnetic plate fitted with a condenser and magnetic stirrer. A known volume (70 ml) of oil was transferred to the reactor and the hot plate with temperature control was heated. H_2SO_4 of the known volume was properly mixed with a known volume of methanol in a separate flask and then transferred to the heated oil in a batch reactor. The reaction time between 40 and 60 min was sufficient to complete the reaction. The resultant product was transferred to a separating funnel for phase separation. The methanol-oil phase was washed with deionized water to remove methanol. The washed esterified oil was then dried over a hygroscopic substance (anhydrous Na_2SO_4) to remove unwanted water. The Na_2SO_4 was recovered by filtration. The acid value of esterified oil was determined using an official standard method of AOAC (1990). The experimental procedures were repeated based on the number of experimental runs produced by a design expert.

2.2.5. Experimental design for *B. parkii* oil (BPO) esterification

Three variable factors were considered during the experimental procedures for this stage, namely; the acid amount (H_2SO_4), the methanol/oil ratio, and the reaction time. Since Box Benken Design (BBD) produce seventeen (17) experimental runs, to increase the number of experimental runs, generate new extremes for all factors, generate more star points, provides higher quality predictions over the entire design space, increase in the interactive effects among the variables, and to increase the chances of more acid value reduction, Central Composite Design (CCD) with three levels was used which produced twenty (20) experimental runs. Table 1 showed the experimental factor, units, and levels of each variables factor considered for esterification of BPO.

2.2.5.1. Process optimization of experimental design. To determine the extreme (suboptimal) acid value for the esterification process, the coefficient of the quadratic model of the response fitting (acid value: AV) and multiple regression were used (design expert: SEDE.12.0.4. x86/x64). The regression parameter and test of significance were obtained by setting the optimized variable factor in Table 1 to its minimum value and the response fitting to suboptimal using the response surface. Model testing and estimation were carried out using Eqs. (1–3). The quality of the fitted model that correlated the response fitting with the variables, intercept, and the residual values (minima errors) were estimated using analysis of variance in Eq. (4).

$$RMSE = \sqrt{\frac{\sum (AV_{i,cal} - AV_{i,exp})^2}{NOER}} \quad (1)$$

$$R_{adj}^2 = 1 - \sum_{i=1}^n \left(\frac{AV_{i,cal} - AV_{i,exp}}{AV_{avg,exp} - AV_{i,exp}} \right)^2 \quad (2)$$

$$R_{pred}^2 = 1 - \left\{ \frac{(1 - R_{pred}^2)(NOER - 1)}{NOER - (NOIV + 1)} \right\} \quad (3)$$

Table 1

Process variable factors for CCD esterification and BBD transesterification of SBO.

Esterification Variable	Units	Symbol	Levels				
Reaction time	(min)	ω_1	40	0	+1 (high)	-alpha	+ alpha
H_2SO_4	(ml)	ω_2	1.0	50	60	33.1821	66.8179
Methanol/oil molar ratio	(ml/ml)	ω_3	3	1.5	2.0	0.6559104	2.3409
Transesterification							
Reaction time	(min)	X_1	50	55	60	41.4776	66.8179
Reaction temperature	(°C)	X_2	40	50	60	33.1821	66.8179
MeOH/oil molar ratio	(ml/ml)	X_3	3	5	7	1.63641	8.36359
Catalyst amount	(g)	X_4	2	2.5	3	1.09094	1.63641

with RMSE is the root mean square error, R_{adj}^2 is the adjusted R-square, R_{pred}^2 predicted R-square, $AV_{i,cal}$ calculated acid value, $AV_{i,exp}$ experimental acid value, NOER is the number of experimental runs, $AV_{avg,exp}$ average experimental acid value, NOIV is the number of independent variables.

$$Y = \beta_0 + \sum_{i=1}^k \beta_i \omega_i + \sum_{i=1}^k \beta_{ii} \omega_i^2 + \sum_{i < j} \beta_{ij} \omega_i \omega_j + \epsilon \quad (4)$$

where Y is the response, β_0 is the intercept, β_i is the linear coefficient, β_{ii} is the factor interactive coefficient, β_{ij} is the quadratic coefficient terms, ω_i, ω_j are the factors and ϵ is the residual error.

2.3.1. Transesterification of esterified oil (UCKNP and SFCKNP treatment)

Transesterification was carried out in the same three-necked reactor used for the esterification process. This time, the methanol/oil molar ratio, catalyst amount, reaction temperature, and reaction time were the four variable factors considered. Both UCKNP and SFCKNP were used for production consecutively. The reaction procedure was as described elsewhere (Milan et al., 2016). The biodiesel phase was separated through gravity settling and then dried over anhydrous calcium chloride (anhydrous $CaCl_2$) which was filtered to obtain pure biodiesel (FAME). The leached catalyst in the biodiesel was recycled for reuse at the end of the reaction. Catalyst purification and reusability analysis of the reaction mixture was carried out using a built-in heating system vacuum centrifuges/concentrators operated at 4000 rpm (rpm) 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. It was observed that there were reductions in the 4th and 5th cycles. The catalyst reusability was stopped after the 3rd cycle. These processes were repeated majorly for the experimental runs with the same reaction conditions based on experimental runs generated by design experts.

2.3.2. Experimental design for transesterification (FAME production)

For the optimization of transesterification of esterified BPO to biodiesel, three- levels- four factors were considered namely; reaction time (min), reaction temperature (°C), catalyst amount (g), and methanol/oil ratio (ml/ml). Since the reduction of acid value was carried out by comparing the mass transfer rate between the oil, the methanol, and the catalysts, UCKNP, and SFCKNP were examined consecutively for FAME production. For the sake of a well-designed experiment, a higher number of runs, interactive effects among the variables, and greater room for duplication, Box Behnken design was adopted and the number of experimental runs (29 runs) generated was carried out. Table 1 showed the experimental factor, units, and levels of each variable factor.

2.3.3. Statistical analysis for FAME production

Eq. (4), also represent the model fitting that correlates the relationship between the response variable and the independent variables factor in Table 1. The regression parameter and test of significance were

obtained by setting the optimized variable factor in Table 1 to its minimum value and the response fitting to maximum value via BBD. Again, statistical analysis was carried out step by step through the test of significance, regression analysis, and three-dimensional plots of response against the interaction of variables. Process optimization was further carried out by determining the significance of probability test value (p -value < 0.05), F -distribution (f -test), variance inflation factor (VIF), and the degree of freedom (df). The adequacy of the model was confirmed by determining the adjusted R -square (R_{adj}^2) and predicted R -square (R_{pred}^2) values.

2.3.4. Biodiesel qualities

The properties of the produced biodiesel were determined by using the AOAC (1997) standard method as earlier stated in oil properties determination. These qualities of the biodiesel were compared with the standard recommended values (ASTM D6751 and EN 14214) to determine its suitability as fuel in the internal combustion engine for industrial applications.

3. Results and discussion

3.1. Physicochemical-fatty acid properties of *B. parkii* oil (BPO)

Presented in Table 2 are the properties and fatty acid compositions of BPO. For comparative purposes, the literature data on properties and fatty acid compositions from other researchers were also presented. The fatty acid present in BPO in descending order of compositions are oleic acid (57.20%) > stearic acid (26.65%) > palmitic acid (6.88%) > linoleic acid (6.34%) > linolenic acid (2.24%). Observation shows that more than 80% of the fatty acid composition is oleic and stearic acids. This relative proportion of duo acids affects the *B. parkii* consistency. The stearic acid indicates its solid stability while the oleic acid influences how soft or hard the *B. parkii* is based on the ambient temperature. The high oleic acid obtained in this study and low value of stearic acid when compared with other researcher's reports (Table 2) indicated a hard Africa *B. parkii* oil with minimum stability obtained within West Africa region-Nigeria (Steven et al., 2004).

The density and viscosity of the oil are lesser than those reported by other researchers (Betiku et al., 2015; Eweremadu and Alamu, 2010). This observation may be due to the dry-rendering method adopted. It

has been reported that dry-rendering of oil produces low viscous oil with low density (Dias et al., 2009). The low density of 0.91 kg/m³ reported by Eweremadu and Alamu, (Eweremadu and Alamu, 2010), could also be attributed to the low measuring temperature (viscosity measured at 25 °C). The acid value and the %FFA obtained in this study is higher than the earlier reported results on the same oil. This also can be attributed to the storage conditions and duration, different agro-climatic conditions, and species-genus of the shea butter (Meher et al., 2006). The *B. parkii* used in this study before purchased was stored in an open bucket placed in a cool mud house under uncontrolled temperature and moisture. Thus, a high FFA content of BPO could be attributed to the triacylglycerols hydrolysis during the storage process to produce free fatty acids and glycerol.

The high iodine value (124.90 g I₂/100 g oil) and high peroxide value (20 meq O₂/kg oil) obtained in this study showed the oil is of a higher degree of unsaturation (polyunsaturated) which can be attributed to the *B. parkii* nut plants belonging to the species-genus *Vitellaria paradoxa* categorized by high iodine value and high autoxidation.

3.2. Catalyst characterization and elemental analysis

The result of the chemical compositions, BET surface, and basicity, obtained by EDX, nitrogen adsorption, and CO₂ TPD, are presented in the appendix. It was observed that the BET-surface of the SFCKNP is higher than that of UCKNP, the difference could be attributed to the fermentation process adopted which increased the surface area after thermal treatment, thereby increasing the rate of reaction during transesterification. Based on CO₂-TPD results, the SFCKNP showed a stronger basic site (BS > 550) with the value of the basic amount of 175 (μmole.g⁻¹) at high temperature, than the FAME produced by UCKNP catalyst with a low surface area of 0.8 (m²g⁻¹) at BS of 140 (μmole.g⁻¹). This proved that having a high basic amount corresponds to the high FAME conversion. Though the UCKNP also exhibited an active value for a strong basic site, it appears to be less active to the reaction compared with the SFCKNP catalyst. Meanwhile, the corresponding pore size distribution curves are presented in SF8, this figure further confirmed that the SFCKNP catalyst is highly mesoporous than the UCKNP composite. Furthermore, the angular SEM images through the UCKNP and SFCKNP ranges from approximately different wavelengths (100 μm – 536 μm; 200 μm-766 μm) performed in the range of

Table 2
Physicochemical and fatty acid composition of SBO/PBO.

Parameters	PBO	SBO	SBO	SBO	SBO	SBO	SBO	SBO
							Mean	Min Max
Physicochemical properties								
Density (kg/m ³) @ 40 °C	840	901	0.91	–	–	–	–	–
Viscosity @ 40 °C/ (mm ² /s)	3.82	41.76	39.98	–	–	–	–	–
Physical state @ 27 °C	yellowish	–	–	–	–	–	–	–
Moisture content (%)	0.081	0.065	0.037	–	1.37%	–	–	–
%FFA (as oleic acid)	5.38	4.10	–	–	1.9125	–	–	–
Acid value (mg KOH/g oil)	10.76	8.20	3.62	–	3.825	–	–	–
Saponification value (mg KOH/g oil)	171.11	–	190	–	196.90	–	–	–
Iodine value (g I ₂ /100 g oil)	124.90	58.34	59.5	–	43.27	–	–	–
Peroxide value (meq O ₂ /kg oil)	20.00	–	12.15	–	12.85	–	–	–
HHV (MJ/kg)	40.54	42.20	–	–	–	–	–	–
Cetane number	75.20	58.23	–	–	–	–	–	–
Diesel index	90.56	81.02	–	–	–	–	–	–
Fatty acid properties (%)								
Oleic acid (C18:1)	57.20	54.26	49.6	45	N	46.4	37.1	62.1
Linoleic acid (C18:2)	6.34	7.80	7.80	6.0	–	6.6	–	10.8
Palmitic acid (C16:0)	6.88	5.93	5.4	4.0	–	4.0	0.6	8.4
Stearic acid (C18:0)	26.65	30.47	35.7	42	75.03-n	41.5	2.6	50.2
Linolenic (C18:3)	2.24	0.66	–	–	–	–	25.6	–
Others	0.69	0.88	1.3	3.0	–	–	–	–
References	This study	Betiku et al. (2015)	Enweremadu and Alamu, (2009)	Alander, (2009)	Chukwu and Adgidzi, (2008)	Steven et al. (2004)		

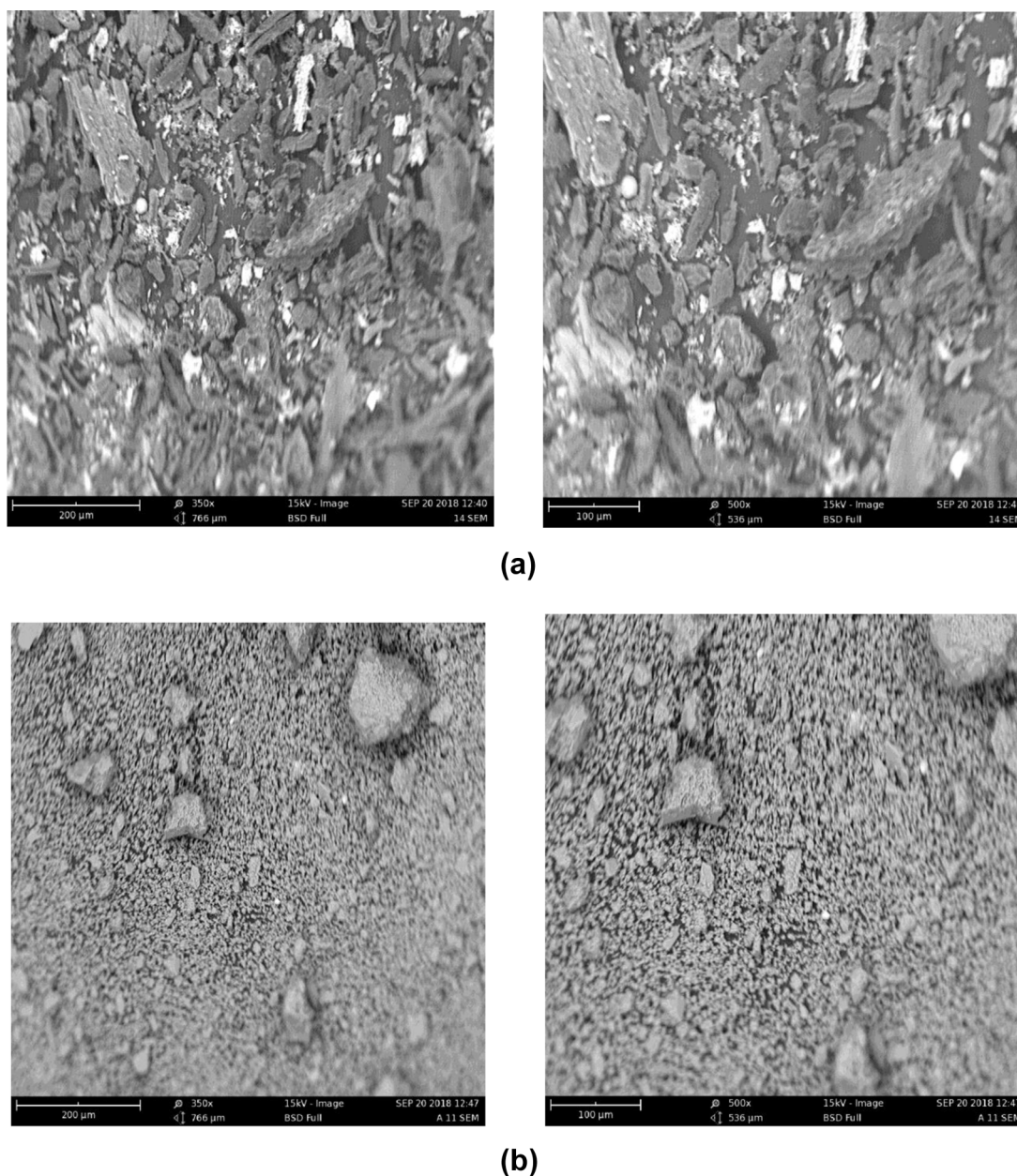


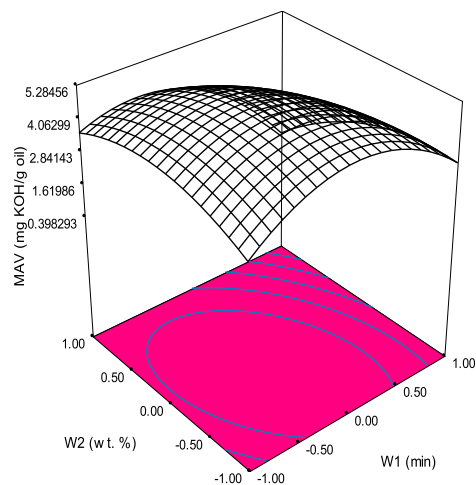
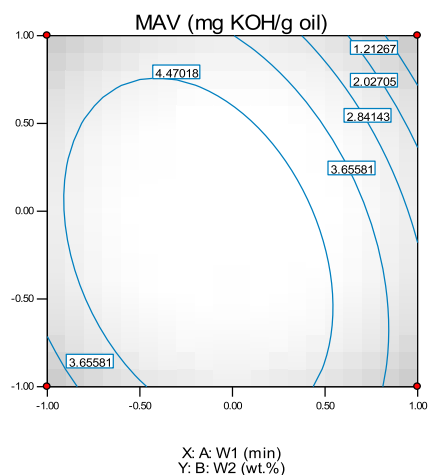
Fig. 1a. UCKNP at various SEM magnifications 350x and 500x.

$10^\circ < 2\alpha < 70^\circ$ at a rate of 2 min^{-1} are displayed in Fig. 1(a-b). The images obtained after calculations for 4 h at 700°C indicated that the calcined powders were of diverse shape, non-uniform in sizes, and less porous. The number of aggregates with the microscopic structure of SEM taken at the resolutions, showed the glossy nature, permeability, and spongy nature of the particle present. Further observation shows that the calcination also resulted in the sintering of small mineral aggregates and agglomerated particles responsible for the squishy nature. The structural outlook of the SEM images also revealed the gaseous evolution of CO_2 from CaCO_3 after calcination which proved that no carbon remains after the heat treatment due to gaseous formation of CO_2 via decomposition with CO_2 desorption monitored in the temperature range of $60 - 650^\circ\text{C}$.

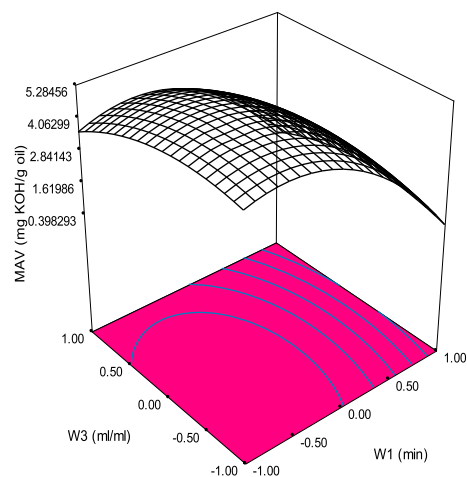
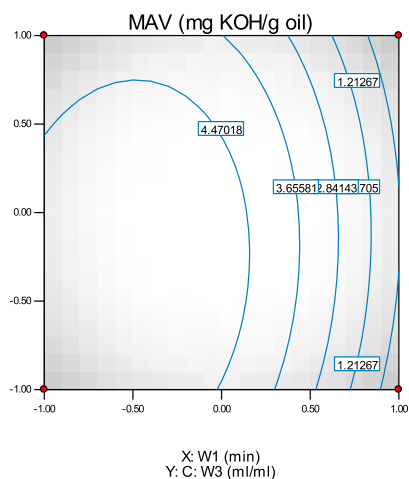
The FTIR results of UCKNP and SFCKNP calcined at 700°C for 4 h are displayed in the appendix with the infrared spectrum, which plots the intensity of infrared spectra. The peaks, (absorbance bands), correspond with the various vibrations of the sample's atoms when it's exposed to the infrared region of the electromagnetic spectrum. The

spectrum shows numerous adsorption bands. The wavelength observed from $711.9\text{--}1401.5 \text{ cm}^{-1}$ stretches indicated the presence of aldehyde/ketone and ester (below 1500 cm^{-1} in the infrared spectrum). The spectrum stretching from 1640 to 2512 cm^{-1} indicates the presence of two functional groups CH_2 and C=O (above 1500 cm^{-1} in the infrared spectrum). However, the broad absorption displayed within the range $3000\text{--}3500 \text{ cm}^{-1}$ indicated the absence of amide, catalytic acid, and O-H functional group (FTIR of UCKNP). Similarly, FTIR of SFCKNP shows the wavelength band from $711.9\text{--}1397.8 \text{ cm}^{-1}$ stretches indicated the presence of aldehyde/ketone and ester. The spectrum stretching from $1796.6\text{--}2516 \text{ cm}^{-1}$ indicates the presence of two functional groups CH_2 and C=O , above the wavelength suggest the absence of amide, catalytic acid, and O-H present.

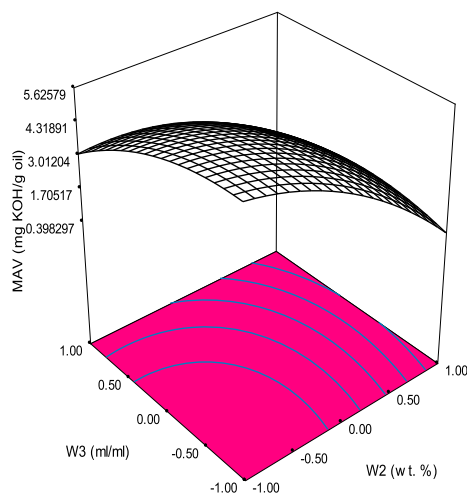
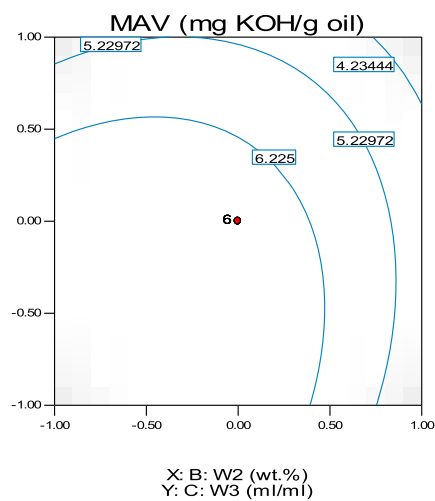
The elemental analysis results of the UCKNP and SFCKNP using Energy dispersive x-ray (EDX-ray) were obtained and recorded in the appendix. At the temperature of 450°C , the main compound is a carbonate of calcium, an increase in thermal temperature to 550°C , decomposition of calcium carbonate to form calcium (II) oxide was



(a)



(b)



(c)

Fig. 1b. SFCKNP at various SEM magnifications 350x and 500x.

observed. It was observed that the thermal decomposition of calcium carbonate to calcium II oxide occurred at a lower temperature than that observed by (Ar and Dogu, 2001; Alizera et al., 2015; Betiku et al.,

2015; Adepoju et al., 2018b). This observation may be related to the presence of some functional groups present in the *B. parkii* plant during the growth period which occurred as a result of carbon growth

Table 3

Actual, coded, mean acid values, predicted and residual values.

Std Run	Actual			Coded			Acid values		MAV	PAV	Residual
	ω_1	ω_2	ω_3	ω_1	ω_2	ω_3	AV ₁	AV ₂			
1	40	1	3	−1	−1	−1	7.00	7.20	7.10	6.68	0.42
2	60	1	3	1	−1	−1	5.30	5.50	5.40	5.62	−0.22
3	40	2	3	−1	1	−1	4.40	4.40	4.40	4.78	−0.38
4	60	2	3	1	1	−1	0.62	0.63	0.625	0.66	−0.037
5	40	1	7	−1	−1	1	3.45	3.43	3.44	3.16	0.28
6	60	1	7	1	−1	1	3.69	3.69	3.69	3.07	0.62
7	40	2	7	−1	1	1	4.00	4.00	4.00	3.54	0.46
8	60	2	7	1	1	1	0.22	0.23	0.2205	0.40	−0.18
9	33.1821	1.5	5	−1.682	0	0	3.42	3.42	3.42	3.76	−0.34
10	66.8179	1.5	5	1.682	0	0	0.21	0.25	0.23	0.23	0.0042
11	50	0.659104	5	0	−1.682	0	5.65	5.65	5.65	6.19	−0.54
12	50	2.3409	5	0	1.682	0	2.54	2.54	2.54	2.34	0.20
13	50	1.5	1.63641	0	0	−1.682	6.50	6.72	6.61	6.37	0.24
14	50	1.5	8.36359	0	0	1.682	2.40	2.80	2.60	3.18	−0.58
15	50	1.5	5	0	0	0	6.30	6.50	6.40	6.81	−0.41
16	50	1.5	5	0	0	0	7.10	7.10	7.10	6.81	0.29
17	50	1.5	5	0	0	0	6.40	6.60	6.50	6.81	−0.31
18	50	1.5	5	0	0	0	6.88	7.12	7.00	6.81	0.19
19	50	1.5	5	0	0	0	6.40	7.00	6.70	6.81	−0.11
20	50	1.5	5	0	0	0	7.10	7.10	7.20	6.81	0.39

AV₁ = 1st acid value; AV₂ = 2nd acid value; MAV = mean acid value; PAV = predicted acid value.

inhibition. Owing to the abundance of calcium in the UCKNP and SFCKNP, other metals (Na, K, Mg, Zn, P, Fe) are less discussed, but could also help the transesterification reaction process (Helwanian et al., 2009; Zabetti and Daud, 2009).

3.3. Synthesis of FAME from BPO

The BPO produced contained high acid value (10.76 mg KOH/g oil) which was not suitable for direct methanolysis-base-catalyzed biodiesel production. Therefore, an acid-catalyzed esterification step of BPO is required to reduce the acid value to the required standard (FFA < 1.5) as prescribed by ASTM limits followed by base-catalyzed methanolysis of the esterified oil to produce biodiesel.

3.3.1. Acid-catalyzed esterification of BPO

3.3.1.1. *Statistical optimization of acid-catalyzed esterification.* Esterification of BPO using H₂SO₄ acid was examined at different reaction time (40, 60 min), H₂SO₄ amount (1.0 wt.%, 2.0 wt.%), and methanol/oil molar ratio (3, 7 ml/ml). Table 3 reported the experimental matrix with coded and actual values of variable factors together with the obtained mean acid value and the predicted minimum acid values obtained at 60 °C. The mean acid value experimental results were fitted by the process order (2nd-order) and the model type (polynomial) via regression coefficients and significance of response surface quadratic equation. The second-order polynomial equations derived were based on actual factors (Eq. 5) and coded factors (Eq. (6)).

Final equation in term of actual

$$Y = -33.43464 + 1.64958\omega_1 + 1.970478\omega_2 + 0.28669\omega_3 - 0.038153\omega_1\omega_2 + 0.012159\omega_1\omega_3 + 0.14267\omega_2\omega_3 - 0.017011\omega_1^2 - 0.22464\omega_2^2 - 0.17956\omega_3^2 \quad (5)$$

Final equation in term of coded

$$Y = +6.81 - 1.05\omega_1 - 1.148\omega_2 - 0.95\omega_3 - 0.76\omega_1\omega_2 + 0.24\omega_1\omega_3 + 0.57\omega_2\omega_3 - 1.70\omega_1^2 - 0.90\omega_2^2 - 0.72\omega_3^2 \quad (6)$$

However, the coefficient indicates the direct measurement of contributions of each factor on the acid value, H₂SO₄ amount with coefficient 1.97047 is the most positively significant variable among the selected factors.

The statistical model and the fitness of the quadratic equation together with the interactive effects of the variables were analyzed using the test of significance and analysis of variance (ANOVA) in the appendix. The quality of the model was evaluated by *f*-value, *p*-value, and the lack of fit. The model *F*-value of 105.81 with *p*-value < 0.0001 implied significant model. In this case, ω_1 , ω_2 , ω_3 , $\omega_1\omega_2$, $\omega_2\omega_3$, ω_1^2 , ω_2^2 , ω_3^2 are significant model terms, except $\omega_1\omega_3$ with *p*-value = 0.1963 > 0.05, that was not significant. The Lack of fit, *f*-value of 3.36 with *p*-value > 0.05 implies the Lack of Fit is not significant relative to the pure error. There is a 9.76% chance that a Lack of fit *f*-value this large could occur due to noise. Non-significant lack of fit is good (Adepoju et al., 2018a). Based on fit statistics and model comparison statistics, the Predicted *R*² of 0.9772 is in reasonable agreement with the adjusted *R*² of 0.9567; since the difference is less than 0.200. Adequate Precision accounts for the signal to noise ratio. A ratio greater than 4 is required. The ratio of 16.11 indicates an adequate signal.

The plots of predicted versus actual acid values in the appendix, and normal% probability vs external studentized residuals in the appendix, shows there is perfect agreement among the variables considered with high *R*² of 0.9772 further proved the variables mutual interactions. Meanwhile, Fig. 2(a) shows the mean acid value (MAV) as a function of reaction time and H₂SO₄ amount at constant methanol/oil molar ratio of 7 (ml/ml) in form of contour and 3-dimensional plot based on second-order CCD. Based on the graph, a higher H₂SO₄ amount with higher reaction time produced lower MAV while higher H₂SO₄ amount with lower reaction time produced high acid value. The contour and the 3D's plots showing the MAV as a function of reaction time and methanol/oil molar ratio at a constant H₂SO₄ amount of 5 wt.% are presented in Fig. 2b. Higher reaction time and higher methanol/oil molar ratio favoured the low MAV. Fig. 2c. shows the mutual interaction among the H₂SO₄ amount and methanol/oil molar ratio at a constant reaction time of 60 min as a function of acid value. Low variables interaction also favoured low MAV. Furthermore, the acid values at optimum variables obtained through statistical solutions from 73 combinatorial ways powered by ramps are depicted in the appendix. It was observed that the optimum reaction conditions ensuring the lowest acid value (0.37 mg KOH/g oil) of the esterified BPO were obtained at a temperature of 60 °C were reaction time of 60 min, H₂SO₄ amount of 2.0 (wt.%), and methanol/oil molar ratio of 7:1 (ml/ml). These values were used for a successive transesterification with base.

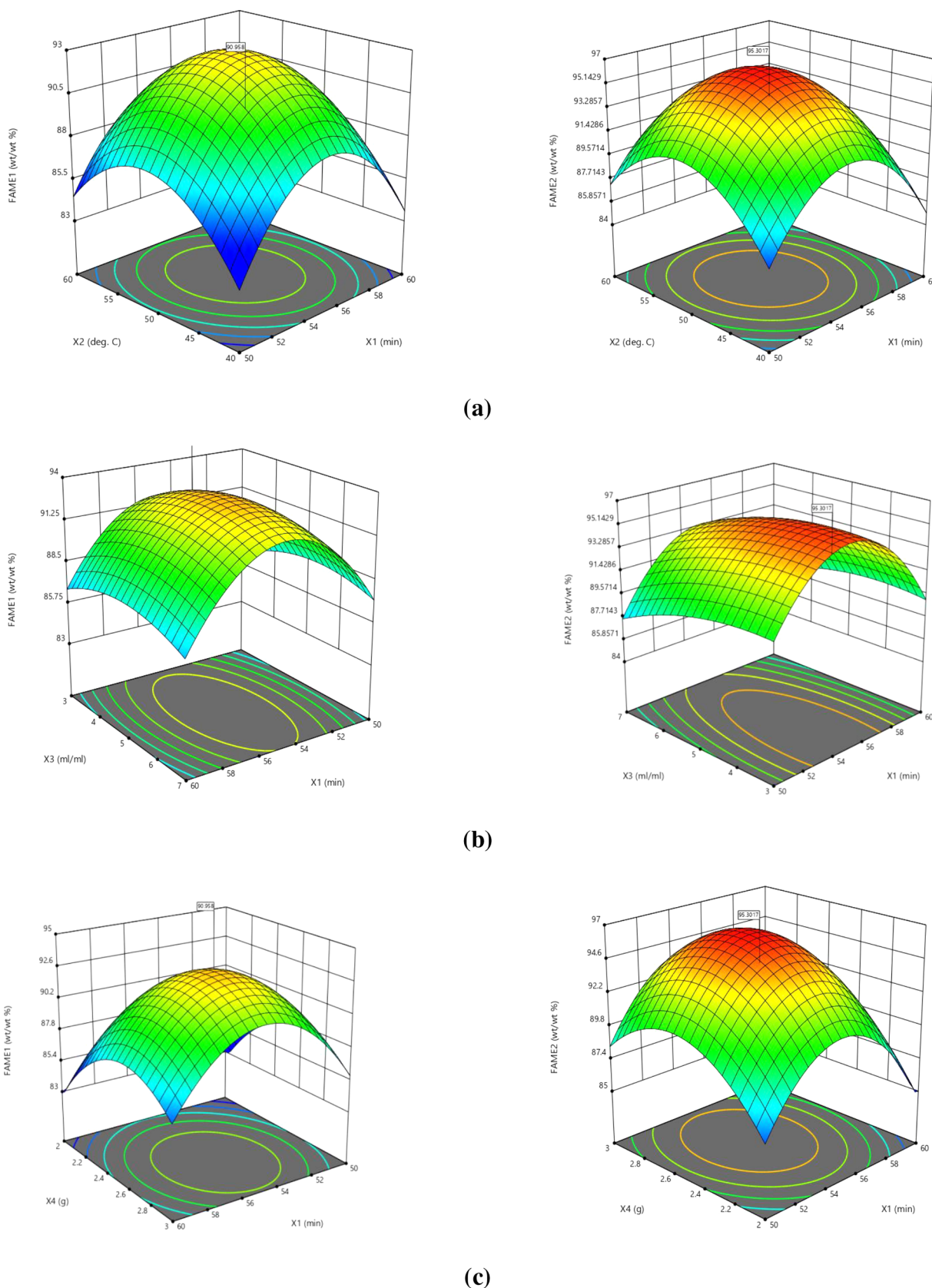


Fig. 2. a.c. Contours and the 3-D's plots of variable factors as a function of acid value (mg KOH/g oil).

3.3.2. Base catalyzed transesterification of esterified BPO

3.3.2.1. Statistical optimization of base-catalyzed transesterification.

Transesterification of the esterified BPO was carried out using

Box Behnken experimental design. Four factors-three levels variable were examined namely: reaction time (50, 60 min), reaction temperature (40 °C, 60 °C), methanol/oil molar ratio (3:1, 7:1) (ml/

Table 4

Results of transesterification of esterified oil using UCKNP and SFCKNP as base catalysts.

Std. Runs	X ₁	X ₂	X ₃	X ₄	UCKNP FAME1	PFAME1	SFCKNP FAME2	PFAME2
1	50	40	5	2.5	85.00	85.30	85.84	85.84
2	60	40	5	2.5	85.40	85.37	85.80	85.78
3	50	60	5	2.5	86.40	86.64	86.62	86.68
4	60	60	5	2.5	85.78	85.70	85.29	85.33
5	55	50	3	2	88.60	88.46	91.54	91.56
6	55	50	7	2	90.40	90.46	90.34	90.37
7	55	50	3	3	92.50	92.65	94.60	94.61
8	55	50	7	3	88.00	88.35	90.00	90.02
9	50	50	5	2	85.78	85.70	86.67	86.68
10	60	50	5	2	85.10	85.33	85.48	85.49
11	50	50	5	3	87.20	86.80	87.54	87.55
12	60	50	5	3	86.40	86.31	87.32	87.33
13	55	40	3	2.5	89.50	89.50	91.73	91.72
14	55	60	3	2.5	91.03	91.06	92.76	92.75
15	55	40	7	2.5	89.27	89.07	89.63	89.66
16	55	60	7	2.5	89.35	89.18	88.98	89.01
17	50	50	3	2.5	89.00	88.97	91.78	91.76
18	60	50	3	2.5	88.90	88.89	90.30	90.31
19	50	50	7	2.5	88.20	88.17	88.18	88.12
20	60	50	7	2.5	87.40	87.39	88.20	88.16
21	55	40	5	2	87.50	87.45	87.85	87.84
22	55	60	5	2	86.30	86.28	86.80	86.73
23	55	40	5	3	86.50	86.48	87.88	87.89
24	55	60	5	3	89.30	89.31	89.43	89.38
25	55	50	5	2.5	94.70	94.80	96.36	96.37
26	55	50	5	2.5	95.00	94.80	96.43	96.37
27	55	50	5	2.5	94.70	94.80	96.35	96.37
28	55	50	5	2.5	94.60	94.80	96.34	96.37
29	55	50	5	2.5	94.80	94.80	96.35	96.37

Where: X₁ = Reaction time, X₂ = Reaction temperature X₃ = MeOH/oil molar ratio, X₄ = Catalyst amount, PFAME1 = predicted fatty acid methylester using UCKNP, FAME1 = fatty acid methylester using UCKNP, FAME2 = fatty acid methylester using SFCKNP, PFAME2 = predicted fatty acid methylester using SFCKNP.

ml), and catalyst amount (2.0 wt.%, 3.0 wt.%). A total of 29 experimental runs were obtained and were carried out consecutively via methanolysis of UCKNP and SFCKNP as an active base catalyst. Table 4 shows the results of the experimental runs carried out and the predicted values by the design. From the table, the highest experimental FAMEs obtained using UCKNP and SFCKNP were 95.00 (wt.%) and 96.43 (wt.%), respectively at reaction time of 55 min, reaction temperature of 50 °C, methanol/oil molar ratio of 5:1 (ml/ml), and catalyst amount of 2.5 (wt.%). The predicted values by the software were 94.80 (wt.%) and 96.37 (wt.%) at the condition of the same variables. The predicted values were validated in triplicate (by carried out three experiments under these conditions) and the average optimum FAMEs produced were 90.56 (wt.%) and 95.30 (wt.%). These values showed that using both UCKNP and SFCKNP as a base catalyst after successive esterification step produced a high yield of FAME, but FAME produced using SFCKNP produced the highest yield. This observation showed that truly, fermentation increase energy production without oxygen. Meanwhile, the catalyst the wall of glass accumulates about 0.5 wt.% catalyst, this reduced the surface area during the reaction and effectively lowered catalyst activity (Buasri et al., 2012).

Again, the results of experimental FAMEs and the selected factors were fitted 2nd-order polynomial through regression coefficients and significance of response surface quadratic equation. The second-order polynomial equations are presented in coded factors as in Eqs. (7) and (8).

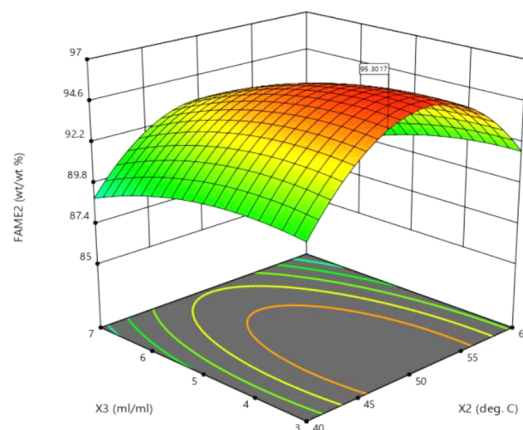
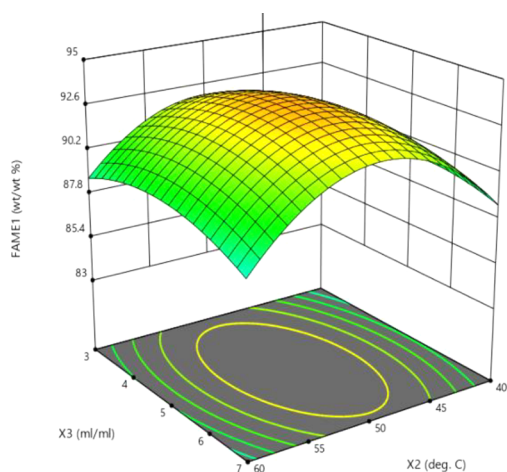
Final equation in terms of coded

$$FAME_{UCKNP} = +94.80 - 0.2167X_1 + 0.4158X_2 - 0.5758X_3 + 0.5183X_4 - 0.2550X_1X_2 - 0.1750X_1X_3 - 0.0300X_1X_4 - 0.3625X_2X_3 + 1.0X_2X_4 - 1.58X_2X_3 - 5.20X_1^2 - 3.85X_2^2 - 1.25X_3^2 - 3.57X_4^2 \quad (7)$$

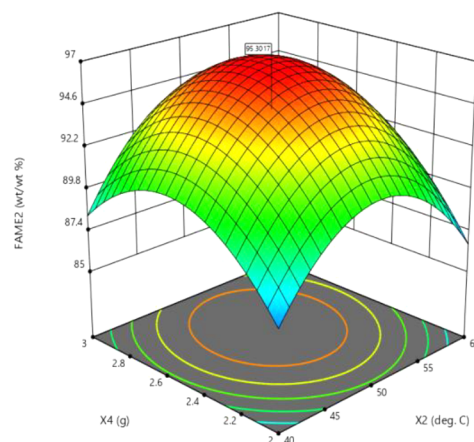
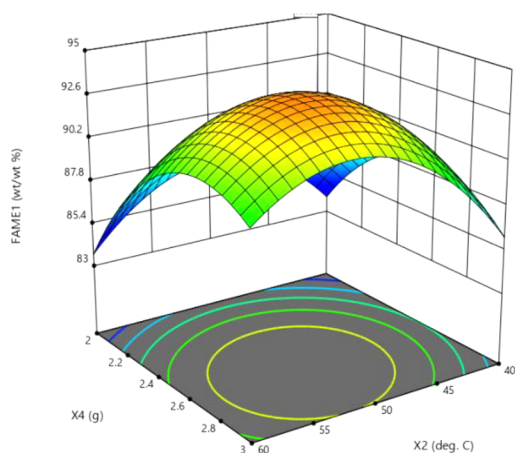
$$FAME_{SFCKNP} = +96.37 - 0.3533X_1 + 0.0958X_2 - 1.45X_3 + 0.6742X_4 - 0.3225X_1X_2 + 0.3750X_1X_3 + 0.2425X_1X_4 - 0.4200X_2X_3 + 0.65X_2X_4 - 0.85X_2X_3 - 5.83X_1^2 - 4.63X_2^2 - 0.9513X_3^2 - 3.78X_4^2 \quad (8)$$

Nevertheless, the coefficient is the direct measure of influence of each variable on the response (FAME), therefore, X₃ (MeOH/oil molar ratio) with *f*-value = 81.30 (*p*-value < 0.0001) is the supreme significant variable among the selected factors when UCKNP (FAME1) was used as a catalyst, this same variable was also the supreme significant variable among the selected factors when SFCKNP (FAME2) was used (*f*-value = 12.521.17; *p*-value < 0.0001). Though, the significance effects of X₃ were higher with SFCKNP as a catalyst than the corresponding counterpart. From the table, the statistical model and the suitability of the equations 7&8 together with the interactive effects of the variables were analyzed using ANOVA. The model *F*-value of 13,524.43 and 420.53 with *p*-value < 0.0001 inferred significant models. Further analysis proved that all the selected variables considered for FAMEs production using the two catalysts were significant except the X₁ × X₃ (*p*-value = 0.1360) and X₁ × X₄ (*p*-value = 0.7902) that are non-significant interactive terms. The Lack of fit *f*-value of 4.17 and 1.72 with *p*-value > 0.05 implies the Lack of Fit is not significant relative to the pure error. There is a 10.50% chance that a Lack of fit *f*-value this large could occur due to noise. Non-significant lack of fit is good (Adepoju et al., 2018a). Based on fit statistics and model comparison statistics, the coefficient of determination (*R*²) of 99.76% and 99.99% obtained showed the proportion of the variances in the dependent variable that is predictable from the independent variable. Predicted *R*² of 98.72% and 99.96% were in reasonable agreement with the adjusted *R*² of 99.53% and 99.99%; meanwhile, the difference is less than 0.200 with adequate precision greater than 4 (SF3). The standard deviation obtained was 0.2212 for FAME 1, and 0.0448 for FAME 2, with a mean value of 89.06 and 90.08, respectively.

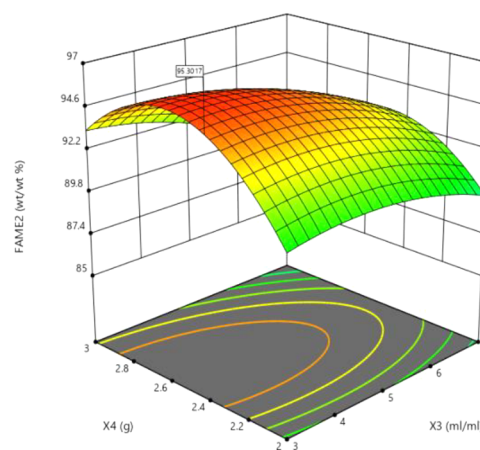
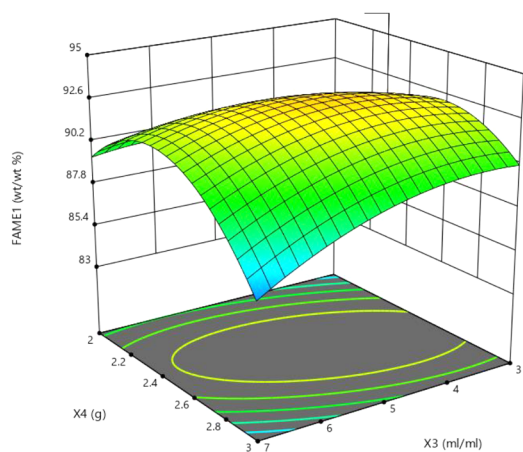
The validity of the experimental results of the FAMEs was confirmed by the close values of predicted, and these were demonstrated through the predicted versus actual plots. The straight lines passing through the points indicated that there were negligible errors between the predicted and experimental results. Furthermore, the 3D's plots showing the interactions among the selected variables on the FAMEs yield are shown in Fig. 3(a-f) while keeping other factors constant. The plots of interaction between the reaction time and reaction temperature are depicted in Fig. 3(a) while keeping other factors constant (FAME1; X₃ = 3.00002 ml/ml, X₄ = 2.31212 g; FAME2; X₃ = 3.00005 ml/ml, X₄ = 2.37535 g). The plots of interaction between the reaction time and MeOH/oil molar ratio are portrayed in Fig. 3(b) while keeping other factors constant (FAME1; X₂ = 45.3671 °C, X₄ = 2.31212 g; FAME2; X₂ = 46.825 °C, X₄ = 2.37535 g). Fig. 3c illustrates the plots of reaction time and catalyst amount while keeping other factors constant (FAME1; X₂ = 45.3671 °C, X₃ = 3.00002 ml/ml; FAME2; X₂ = 46.825 °C, X₃ = 3.00005 ml/ml), while the plots of reaction time and MeOH/oil molar ratio are shown in Fig. 3(d) while keeping other factors constant (FAME1; X₁ = 53.0009 min, X₄ = 2.31212 g; FAME2; X₁ = 53.4159 min, X₄ = 2.37535 g). The 3-dimensional plots showing the interactive effects between reaction time and catalyst amount are displayed in Fig. 3(e) while keeping other factors constant (FAME1; X₁ = 53.0009 min, X₃ = 3.00005 ml/ml; FAME2; X₁ = 53.4159 min, X₃ = 3.00005 ml/ml), whereas the plot indicating the relationship between the MeOH/oil molar ratio and catalyst amount are demonstrated in Fig. 3(f) while keeping other factors constant (FAME1;



(d)



(e)



(f)

Fig. 3. a-f. 3D's plots showing the interactions among the selected variables on the FAMES yield.

$X_1 = 53.0009$ min, $X_2 = 45.3671$ °C; FAME2; $X_1 = 53.4159$ min, $X_2 = 46.825$ °C), respectively. From the plots, it was observed that the most perfect interaction was found in Fig. 3a, (c&e) mutual interaction

was better than that noticed in Fig. 3(b&d), but the lowest interaction was found in Fig. 3f. These show that concerning the quadratic equation of second order, single variables played major roles in FAMES

Table 5
Properties of FAME produced from SBO.

Parameters	Other research works				
<i>Physicochemical properties</i>					
Density (kg/m ³) @ 25 °C	848	858	865.18	–	860–900
Viscosity @ 40 °C/ (mm ² /s)	2.82	4.77	2.17	1.9–6.0	3.5–5.0
Physical state @ 27 °C	Brownish	–	–	–	–
Moisture content (%)	0.005	0.001	–	< 0.03	0.02
%FFA (as oleic acid)	0.12	0.175	0.14	0.40 max	0.25 max
Acid value (mg KOH/g oil)	0.24	0.35	0.28	0.80 max	0.5 max
Iodine value (g I ₂ /100 g oil)	117.14	39.04	36.42	–	120 max
Peroxide value (meq O ₂ /kg oil)	18.60	–	–	–	12.85
HHV (MJ/kg)	41.00	38.31	37.93	–	–
Cetane number	53.49	54.88	58.00	57 min	51 min
Diesel index	60.40	62.66	–	50.4	–
References	This work	Betiku et al. (2015)	Samuel et al. (2018)	ASTM D6751	EN 14,214

production than the quadratic and the interactive variables. The two catalysts produced FAME > 94% at 55 min, but the FAME produced by SFCKNP catalyst is high (96.43%) with the higher surface area (1.2 m²g^{−1}) having the smaller particle size compared with the FAME of 95.00% produced by UCKNP with the low surface area (0.8 m²g^{−1}), having the larger particle size.

3.3.2.2. Catalyst reusability. The test on catalyst reusability was conducted on the catalytic activities of SFCKNP and UCKNP under the same experimental conditions. The result revealed that the catalytic activities continue to be stable upon successive reuse with FAME yield greatly reduced with catalyst recycled after 4 and 5 cycles (R4&R5). Various conversion of FAME yield after each cycle of methanolysis of esterified shea butter oil using calcination catalysts are presented in supplementary file 9 (SF9). The decrease in effectiveness after 3rd cycle was 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), as well as water-oxygen reacted at the catalyst surface hereby reduce the catalyst sensitivity.

3.3.4. Properties of FAME produced from BPO

Table 5 shows the physicochemical properties of FAME produced from BPO, the low density with low viscosity indicated that the conversion of oil to ester 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 14,214, but higher than what was reported by Betiku et al. (2015). This value indicated that the FAME produced is of high quality which accounts for its high Cetane number (53.49). The lowest acid value obtained in this study when compared with other reported values explained the higher yield of FAME recorded in this work. Meanwhile, higher iodine value (117.41 g I₂/100 g oil) indicated the higher quality of double bonds in FAME. The value obtained is well within the range reported by EN 14214. Peroxide value, which has been reported that the increase in its value in FAME increased the cetane number and the ignition time reduction (Zuleta et al., 2012). The value obtained to take into account the high cetane number obtained.

4. Conclusion

The rendered oil fatty acid composition was predominately oleic and stearic acids. The optimum reaction conditions ensuring the lowest acid value (0.37 mg KOH/g oil) of the esterified BPO were obtained at a temperature of 60 °C were reaction time of 60 min, H₂SO₄ amount of 2.0 (wt.%), and methanol/oil molar ratio of 7:1 (ml/ml). Kola-nut pod used as catalyst served as good agricultural waste material for transesterification of esterified BPO to FAME, but the fermented calcined kola nut pod as base catalyst improved its efficient conversion of the high FFA *B. parkii* oil to FAME. The statistical analysis predicts the

effects of reaction time, catalyst amount, reaction temperature, and methanol/oil molar ratio were statistically significant during the reaction processes. Based on the XRD analysis result, calcium is the predominant constituent element. The quality of FAME produced is within the specification limits of the biodiesel standard.

CRedit authorship contribution statement

T.F. Adepoju: 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, Investigation, Resources. **A.J. Asuquo:** Formal analysis, Investigation, Resources, Data curation, Methodology. **G.S. Abegunde:** .

Declaration of Competing Interest

None.

Acknowledgment

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.sajce.2020.07.008>.

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