Waste-ram-fat as a Feedstock for Biodiesel Production using Heterogeneous Catalyst of Kaolinite-clay Impregnated Calcium-oxide from Chicken Eggshell

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ABSTRACT: Synthesis of a catalyst (AKC-CE) from activated kaolinite clay (AKC) and chicken eggshells (CE) for biodiesel production using waste-ram-fat (WRF) was undertaken in this study. Characterisation studies of AKC, CE, and AKC-CE samples were investigated using various equipment such as X-ray fluorescence (XRF), X-ray diffraction (XRD), and High-resolution scanning electron microscope (HR-SEM) incorporated with Energy-dispersive X-ray spectroscopy (EDAX). The catalyst produced was tested for biodiesel production using WRF in a one-factor-at-a-time study of the process parameters. The XRD analysis showed that the main components of $Al_2(Si_2O_5)(OH)_4$, SiO_2, and CaO are present in the AKC-CE catalyst. These compounds are commonly used as catalysts for biodiesel production. The AKC-CE catalyst's morphology also demonstrated a significant cavity containing irregular crystals, with numerous white flaky crystals. These characteristics show that the catalyst would be efficient for WRF transesterification for biodiesel production. The highest biodiesel yield of 81.33% was obtained at process parameters of MeOH: WRF molar ratio of 18:1, reaction time of 4 h, catalyst loading of 10% (w/w), and temperature of 70°C. The biodiesel produced with the developed catalyst has properties within the ASTM standard. The AKC-CE catalyst is effective for producing biodiesel from WRF. Using WRF and chicken eggshells as materials for sustainable energy may not pose more threat to food availability in the biodiesel production that meets the ASTM standard as established in the Nigerian Biofuel Policy. Therefore, an increase in the use of non-edible feedstock for biofuel production is recommended.

KEYWORDS: Waste-ram-fat, Biodiesel; Catalyst; Calcium-oxide; Kaolinite-clay

[Received Nov. 22, 2024; Revised Dec. 9, 2024; Accepted Dec 27, 2024] Print ISSN: 0189-9546 | Online ISSN: 2437-2110

I. INTRODUCTION

Waste Ram Fat (WRF) is a potential low-cost feedstock for biodiesel production. However, the less desirable high moisture content and free fatty acid of WRF favours soap formation consequently resulting in low biodiesel production (Ajala *et al*., 2020). The use of suitable heterogeneous catalysts can overcome these challenges associated with the WRF for biodiesel production. Other advantages of the use of heterogeneous catalysts for biodiesel production are easy recovery from product mixture, reusability for many cycles, and regenerative ability with high catalytic activity (Ajala *et al*., 2019). Various heterogeneous catalysts have been reported in the literature for biodiesel production, including alkaline earth metal oxides (CaO and MgO), acid zirconia, alumina-based catalysts, hydrotalcite, and immobilised lipase (Toldra-Reig *et al*., 2020). Other examples are KOH/NaY, Al_2O_3–SnO, La/zeolite beta, Al_2O_3/KI, carbon-based solid acid, $CaZrO_3$, KF/CaO–Fe_3O_4, KOH/Al_2O_3, and KF/γ–Al_2O_3/honeycomb ceramic catalyst (Hajra *et al*., 2015). The aforementioned researchers developed their heterogeneous catalysts from chemical feedstock, which could be expensive and difficult to handle. It is worth noting that numerous elemental compositions found in biomass, the earth's crust, and organic waste materials are suitable as raw materials for catalyst development for biodiesel production. These materials are appropriate as alternatives and could replace chemical stocks for catalyst production.

Recently, CaO/MgO-based catalysts were developed from dolomite and calcite for biodiesel production using palm kernel oil (Ajala *et al*., 2019a; Ajala *et al*., 2019b). Waste-based materials are also being utilised to develop heterogeneous catalysts due to their availability, low cost, and environmental benefits (Betiku & Ajala, 2014). Examples include chicken eggshell (Odetoye *et al*., 2021), anthill-chicken eggshell (Yusuff *et al*., 2018), and calcium carbide (Ajala *et al*., 2020). Chicken eggshells were reported to contain mainly calcium carbonate, an important ingredient in heterogeneous catalysts for biodiesel production (Odetoye *et al*., 2021). However, the adsorption of water molecules and carbon dioxide on the active sites of CaO suppresses the esterification and transesterification reactions of WRF (Kwong & Yung, 2015). This shows that not all heterogeneous catalysts are effective for triglycerides with high FFA and moisture content, such as WRF.

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doi: http://dx.doi.org/10.4314/njtd.v21i4.3104

Catalyst support is necessary to overcome the effect of high FFA and moisture content in some triglycerides, to reduce leaching, and to improve the reusability of CaO in biodiesel production. Albuquerque *et al*. (2008) reported that supporting CaO on silica and alumina can improve the thermal resistance of the catalyst and prevent the lixiviation of the active phase in methanol. This is because the silica and alumina components in the catalyst act as a molecular filter, facilitating esterification and transesterification processes while enhancing the catalyst's reusability (Syukri *et al*., 2020). The implication is that kaolinite clay-based catalysts, abundant in alumina and silica, are highly compatible with high moisture content and high FFA triglyceride such as WRF, thus facilitating efficient biodiesel production.

Furthermore, it is important to note that kaolinite clay is readily accessible at a comparatively affordable price and does not interfere with food resources or contribute to the production of industrial waste. Although a Ca/Si/Al/Fe catalyst derived from local clay and chicken eggshells was effectively used to synthesise biodiesel, a low FFA (0.45%) commercial palm oil was utilised (Syukri *et al*., 2020). The authors did not utilise their catalyst for biodiesel production using high FFA triglyceride in a single-step reaction, nor did they use local clay from Ilorin to develop their catalyst, thus emphasising the novelty of this study.

Therefore, this study aimed to develop a heterogeneous catalyst from chicken eggshells and kaolinite clay, for biodiesel production from WRF. The catalyst developed was characterised to determine their efficacy for biodiesel production. The functionality of the catalyst was also investigated for biodiesel production using high FFA WRF. The properties of the biodiesel were determined to ascertain its quality by comparing it with the ASTM standard. The study also examined the Nigerian Bio-fuels Policy *vis-a-vis* the challenges of biofuel production and its sustainability.

II. MATERIALS AND METHODS

A. Materials

The kaolinite clay used in this study was obtained from *Akerebiata* Ilorin, Kwara State, Nigeria, and was beneficiated to remove impurities. The waste chicken eggshells (WCE) used in this research were acquired from various local restaurants in *Tanke* Area, Ilorin. The WRF was collected from a local abattoir along *Sango* Road, Ilorin. The reagents used for this experiment were methanol and sodium hydroxide which were analytical grades acquired from Merck, India.

B. Samples Preparation and Characterisation

The procedure described by Ajala *et al*. (2022) was considered for the beneficiation of the clay through the sedimentation process to obtain a fraction of <300 mm particle size. This was done by weighing 3 kg of milled clay sample and dispersing it in 10 L of de-ionised water in a plastic container. The mixture was vigorously stirred and allowed to stay for 24 h for proper intercalation of the clay structure by water molecules. It was then sieved with a 300 mm sieve diameter and allowed to settle in the containers for another 24 h. The clay slurry was decanted, sun-dried until constant weight, and oven-dried at 100°C for 1 h. The dried clay was pulverised and sieved with a 0.25 mm diameter sieve, to obtain a beneficiated kaolinite clay (BKC) sample and kept in a desiccator (Ajala *et al*., 2022).

The WRF was cleaned using deionised water to eradicate any presence of microscopic bone and flesh particles. It was melted at 70°C to filter suspended insoluble fats to produce the WRF sample. The sample was then stored in an airtight glass bottle to prevent air and moisture absorption before biodiesel production.

BKC (20 g) was weighed and mixed with 40 ml of 0.4 M NaOH in a 250 mL glass beaker. The mixture was stirred and heated at 65ºC for 6 h to produce a precipitate. The precipitate was filtered through filter paper and thereafter rinsed with distilled water until the pH of the water was neutral. The sample was oven-dried at 110ºC for 3 h, crushed, and screened using a 180 µm sieve. Subsequently, the modified BKC sample was calcined at 500ºC for 6 h in a muffle furnace, labelled as activated kaolinite clay (AKC), and stored in a desiccator.

The WCE was extensively washed with deionised water to eliminate the membrane, surface impurities, and other organic constituents. The sample was oven-dried at 110°C for 1 h, pulverised with a mortar and pestle, sieved through a 90 µm sieve, and calcined for 5 h at 800ºC in a muffle furnace. The sample was identified as calcined chicken eggshell (CCE) and kept in a desiccator for characterisation and further use.

The AKC sample was impregnated with the CCE sample in a wet process of ratio 1:1 (w/w), to synthesise Ca/Si/Al/Mg/Ti-based catalyst for biodiesel production. The modified procedure described in the literature was followed to develop the catalyst (Syukri *et al.*, 2020). The AKC (10 g) and CCE (10 g) were measured in 100 ml deionised water in a 500 ml conical flask. The mixture was stirred for 24 h at 65ºC using a magnetic stirrer and filtered with filter paper. The residue was oven-dried at 100ºC for 2 h and then calcined at 800ºC for 6 h in a muffle furnace, to obtain the catalyst identified as AKC-CE catalyst.

The AKC, CEC, and AKC-CE samples were characterised for their elemental composition using X-ray fluorescence (Thermo Scientific Niton; Model XL3t XRF). The functional groups present in the samples were also analysed by a Fourier transforms infrared spectroscopy (FT-IR Shimadzu, 8400S). The samples were pelletised with potassium bromide, and the spectra were obtained from the accumulation of 32 total scans in the range of wave numbers 4000–450 cm^{-1} with a resolution of 4 cm^{-1} (Ajala *et al*., 2020). Also, the chemical compositions of the samples were investigated using X-ray diffraction (XRD), Model Bruker AxSD8. The operating conditions as described by Ajala *et al*. (2020) were followed for the XRD analysis.

Table 1: Metal oxides of samples by XRF analysis

Sample	Metal oxides (wt%)													
	Fe_2O_3	MnO	TiO_2	CaO	K_2O	P_2O_5	SiO_2	Al_2O_3	MgO	Na_2O	SrO	ZnO	*LOI	Total
AKC	1.40	0.02	2.80	15.30	0.68	0.10	61.02	17.97	0.49	0.42	-	-	0.29	100.48
CEC	11.22	0.14	-	71.31	1.30	0.06	2.01	-	6.20	6.34	0.04	1.10	0.22	99.93
AKC-CE	7.20	0.11	0.15	48.13	0.26	0.24	27.61	11.03	2.99	2.42	-	-	0.01	100.16

*LOI = Loss on ignition

High-resolution scanning electron microscope (HR-SEM) incorporated with Energy-dispersive X-ray spectroscopy (EDAX) (Zeiss Auriga) was used to characterise the surface micrograph and elemental composition of AKC, CEC, and AKC-CE samples.

C. Biodiesel production from WRF using AKC-CE catalyst

A 500 ml three-neck flask equipped with a water-cooled reflux condenser, thermometer, and magnetic stirrer was used for the biodiesel production. The effect of variables on the yield of biodiesel in a one factor at a time (OFAT) was undertaken for methanol: oil molar ratio (MeOH: oil ratio) (12:1 - 18:1); reaction time (1 - 5 h), catalyst loading (5 - 20, w/w), and temperature (50 - 90^{o}C). The MeOH: oil (WRF) ratio (12:1, 13:1, 14:1, 15:1, 16:1, 17:1, or 18:1) was charged into the flask with AKC-CE catalyst (5, 10, 15 or 20%, w/w) and the mixture was set up by continuously stirring at 600 rpm for reaction time of 1, 2, 3, 4, or 5 h at a temperature of 50, 60, 70, 80, or 90°C. Subsequently, the catalyst was recovered through filtration using filter paper and the liquid phase was transferred into a 150 ml separating funnel for 24 h. This enhances the separation of the lower glycerol layer from the upper FAME, biodiesel. The excess methanol was recovered from the upper layer through a rotary evaporator and the biodiesel yield was calculated using Equation 1:

$$\%Yield\ of\ biodiesel = \frac{Weight\ of\ biodiesel\ recovered}{Weight\ of\ WRF\ used}\ x\ 100 \quad (1)$$

III. RESULTS AND DISCUSSION

A. Characterisation of samples and catalyst

XRF analysis

The elemental composition of the AKC, CEC, and AKC-CE samples obtained from the XRF are presented in Table 1. From the table, the AKC sample has chemical compositions of SiO_2, Al_2O_3, and CaO in the major proportion of 61.02wt%, 17.97wt%, and 15.30wt%, respectively, which is typical of kaolinite clay (Jamo & Abdu 2014; Kumar & Lingfa 2020). Other metal oxides of Fe_2O_3, MnO, TiO_2, K_2O, P_2O_5, MgO, and Na_2O, are present in traces and served as minor impurities in the AKC sample, which correspond to the findings in the literature (Bello *et al*., 2021; Dewi *et al*., 2018). The XRF analysis of the CEC sample shows a major quantity in wt% for CaO, Fe_2O_3, Na_2O, and MgO as 71.31, 11.22, 6.34, and 6.20, respectively. This result justified that the CEC contains mainly CaO as it represents about 71wt% of the total composition of the sample. This implies that the chicken eggshell is an attractive source of high-purity CaO for basic oxide catalyst for biodiesel production (Kamkum *et al*., 2015). The presence of other metal oxides in the CEC, though recessive, supports the good catalytic behaviour of the sample in the transesterification reaction.

The XRF analysis of the AKC-CE catalyst, as presented in the table, indicates the existence of a combined metal oxide derived from the AKC and CEC samples. This occurrence is attributed to their impregnation process. It was seen that the AKC-CE catalyst is composed of essential metal oxides suitable for transesterification reaction which include Fe_2O_3 (7.20 wt%), CaO (48.13 wt%), SiO_2 (27.61 wt%), Al_2O_3 (11.03 wt%), MgO (2.99 wt%), and Na_2O (2.42 wt%). This finding suggests that the impregnation of the two samples is responsible for the percentage distribution of the metal oxides in the catalyst.

FT-IR analysis

Figure 1 (a-c) illustrates FT-IR spectra of the AKC, CEC, and AKC-CE samples at a wavenumber range of 4000–400 cm^{-1}. It could be seen from Figure 1a that the AKC shows bands at 3693 cm^{-1}, 3652 cm^{-1}, 1640 cm^{-1}, 1114 cm^{-1}, 1002 cm^{-1}, 909 cm^{-1}, 782 cm^{-1}, 749 cm^{-1}, and 682 cm^{-1}. The two medium sharp bands at 3693 cm^{-1} and 3652 cm^{-1} could be assigned to Al-O-H stretching of the inner surface hydroxyl group and Al-OH-Si of the hydroxyl group that lies within lamellae in a plane common to both the tetrahedral and octahedral sheets (Ibrahim *et al*., 2014). The absorption peak observed at 1640 cm^{-1} is associated with the -OH buckling vibrations trapped in the crystal lattice of kaolinite clay (Dewi et al., 2018). The characteristic bands at 1114 cm^{-1} and 1002 cm^{-1} are suggestive of quartz interference in the samples which were identified as Si-O stretching of anhydride (longitudinal mode) and in-plane Si-O stretching, respectively (Oyebanjo *et al*., 2018). The sharp band of 909 cm^{-1} and 782 cm^{-1} are associated with the Al-Al-OH and Al-Mg-OH stretching respectively, in which the latter is the hydroxyl group deformation linked to Al and Mg. The medium sharp band of 682 cm^{-1} is due to Si-O-Al stretching (Kumar & Lingfa, 2020).

Also, the FTIR spectra of CEC as shown in Figure 1b revealed the identification of absorption bands at 3600 - 2600 cm^{-1}, 1385 cm^{-1}, 1037 cm^{-1}, 870 cm^{-1}, 710 cm^{-1}, 548 cm^{-1}, and 451 cm^{-1}, which are typical of eggshell. From the spectra, the bands in the range of 3600 - 2600 cm^{-1} though very weak, indicate the presence of an OH group which according to Sabir *et al*. (2021) could be the absorption of the $Ca(OH)_2$ in the sample.

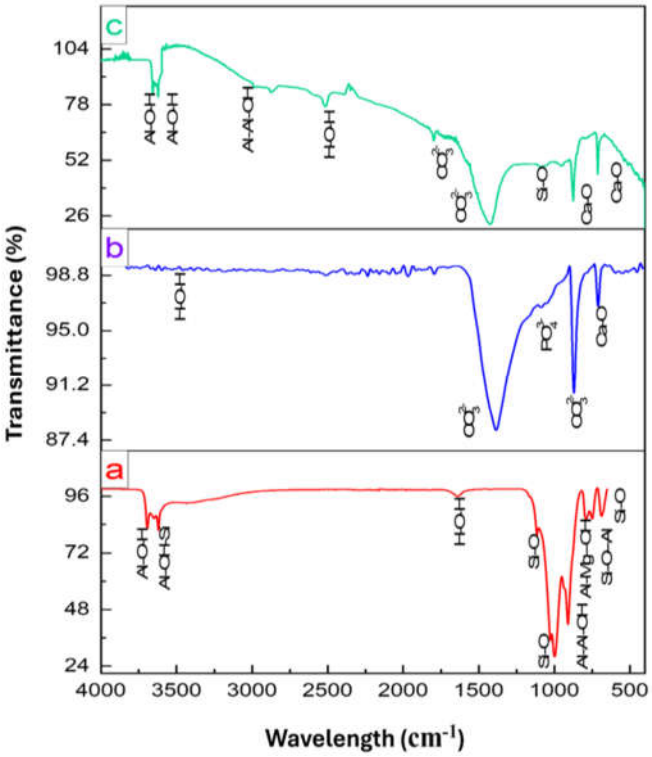

Figure 1: FTIR samples of (a) AKC, (b) CEC, and (c) AKC-CE

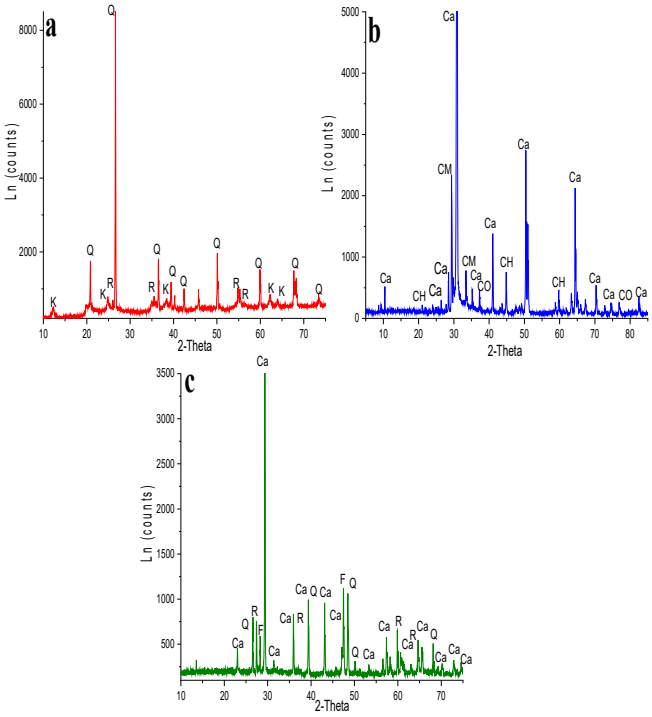

Figure 2: XRD samples of (a) AKC, (b) CEC, and (c) AKC-CE

The presence of OH in the sample could be due to the moisture content in the CEC, as the water may be filling the cavities of the CaO crystal lattice. The absorption band that appears at 1385 cm^{-1} may be assigned to carbonate (CO_3^{2-}) group. The band observed at 1037 cm^{-1} corresponds to the phosphate (PO_4^{3-}) groups (Khalid *et al*., 2022). The appearance of absorption spectra in the range of 900 – 4000 cm^{-1} is the confirmation of CaO metal oxide in the sample which is typical of $CaCO_3$; the CaO group is a characteristic peak of asymmetrical vibrations of PO_3 (Mohadi *et al*., 2016; Sabir *et al*., 2021).

The FTIR of the AKC-CE catalyst developed from the impregnation of AKC and CEC samples is shown in Figure 1c. After the impregnation of the two samples, the intensity of the initial bands shifted to a lower frequency and new bands also appeared. The potential cause of this phenomenon could be attributed to the disruption of hydrogen bonds within the kaolinite layers, resulting in the creation of new peaks. The process usually involves the inner surface OH group by changing the intensities of bands assigned to vibrations of these groups (Ibrahim *et al*., 2014). From the FTIR measurement of the AKC-CE catalyst as shown in the figure, absorption bands of 3693 cm^{-1}, 2980 cm^{-1}, 2879 cm^{-1}, 2515 cm^{-1}, 1799 cm^{-1}, 1419 cm^{-1}, 1099 cm^{-1}, 954 cm^{-1}, 874 cm^{-1}, and 710 cm^{-1} were observed. The bands may be assigned to different functional groups as seen in the AKC and CEC samples. For instance, the 3693 cm^{-1} band is assigned to the Al-OH-Si hydroxyl group in the kaolinite clay. The small band at 1799 cm^{-1} and broadband at 1419 cm^{-1} are assigned to symmetric stretching of CO_3 deformation, and asymmetric stretching of the CO_3^{2-} group in the chicken eggshell.

The band at 1099 cm^{-1} is assigned to Si–O stretching vibrations in kaolinite clay, and the band at 954 cm^{-1} is attributed to OH-bending vibrations (Zunino & Karen, 2021).

XRD analysis

The XRD spectra of the AKC, CEC, and AKC-CE samples are shown in Figure 2. The figure illustrates the mineral composition and compares the peak intensity position (2θ) in each of the samples using XRD gram with the Joint Committee for Powder Diffraction Standards (JCPDS). The AKC sample displayed in Figure 2a showcases both monoclinic and hexagonal structures, corresponding to quartz and kaolinite compounds (Bello *et al*., 2021). Sixteen prominent spectra are spotted at 2θ of 12.07°, 20.84°, 24.57°, 26.62°, 36.53°, 37.28°, 42.43°, 45.77°, 50.11°, 55.06°, 59.95°, 62.23°, 63.98°, 64.43°, 68.01°, and 73.50° which are indexed to hkl of (0 0 1), (1 0 0), (0 0 2), (1 0 1), (-2 0 1), (1 1 0), (0 0 3), (1 1 1), (-2 0 3), (0 2 1), (1 1 2), (3 0 0), (2 1 1), (0 6 0), (2 1 2) and (0 1 4) respectively. The appearance of the peaks at 2θ of 12.07°, 24.57°, 37.28°, 45.77°, 55.06°, 62.23°, 63.98° and 64.43° correspond to kaolinite minerals. While the peaks at 2θ of 20.84°, 26.62°, 36.53°, 42.43°, 50.11°, 59.95°, 68.01° and 73.50° are the quartz minerals (Dewi et al., 2018). Another compound present in the sample is rutile titanium with only four diffraction patterns at 2θ of 28.44°, 36.24°, 54.84°, and 57.07°. The lower content of rutile titanium in this sample is also a characteristic of kaolinite clay (Syukri *et al*., 2020). This could be attributed to the occurrence of titanium in probably authigenic rutile that could be dissolved and adsorbed by the kaolinite clay (Abayazeed *et al*., 2019). The XRD result corroborates the XRF result obtained for the AKC in this study, which confirmed that the sample comprised kaolinite

($Al_2(Si_2O_5)(OH)_4$) and quartz (SiO_2) minerals. Hence, kaolinite clay has important properties suitable for catalyst development in biodiesel production (Kumar & Lingfa, 2020).

Figure 2b shows the XRD of the CEC sample with eighteen conspicuous spectra that consist of calcium oxide (CaO), calcium hydroxide ($Ca(OH)_2$), dolomite ($CaMg(CO_3)_2$), and calcite ($CaCO_3$) which are characteristics of chicken eggshell (Ajala *et al*., 2018; Ok *et al*., 2011). The spectra appear at 2θ of 10.05º, 27.81º, 29.41º, 31.42º, 35.97º, 43.15º, 48.51º, 65.60º, 70.24º, 76.30º, 83.77º which correspond to hkl index of (0 1 1), (1 0 1), (1 0 4), (0 0 6), (1 1 0), (2 0 2), (1 1 6), (0 0 12), (0 2 10), (2 2 0), and (1 3 4), respectively. These spectra could be assigned to the CaO of JCPDS card number 00-005-0586. This shows the conversion of $CaCO_3$ which is the dominant compound in the chicken eggshell to CaO due to the thermal treatment (Dwiwedi *et al*., 2018; Naemchan *et al*., 2008). The diffraction pattern and JCPDS card number obtained for this sample confirm the formation of CaO crystalline product which is similar to those reported for calcined chicken eggshells in the literature (Awogbemi *et al*., 2020; Dwiwedi *et al*., 2018; Minakshi *et al*., 2019). Apart from the CaO diffraction pattern seen in the XRD, the figure also shows the characteristic $Ca(OH)_2$ pattern with lower diffraction intensity of three peaks at 2θ of 23.02º, 45.07º, and 60.31º. This observed diffraction pattern though minimal, could be formed due to the interaction of CaO with water vapour in the air (Mohadi *et al*., 2016). Other diffraction patterns in the sample include $CaMg(CO_3)_2$ at 2θ of 28.51º and 33.76º, and $CaCO_3$ at 2θ of 37.15º, and 77.18º. The presence of these two compounds in the sample was suspected to be from the incomplete thermal decomposition during the calcination of the chicken eggshell (Awogbemi *et al*., 2020).

The diffraction patterns of the AKC-CE catalyst, produced from AKC and CEC samples by wet impregnation, are presented in Figure 3c. The figure revealed that the XRD diffraction patterns were consistent with the combination of AKC (Figure 2a), and CEC (Figure 2b). This showed that the AKC-CE catalyst consists of the main components, that is, $Al_2(Si_2O_5)(OH)_4$, SiO_2, and CaO present in the kaolinite clay and chicken eggshell (Setiadji *et al*., 2018). These results suggest that the functional groups identified through FTIR analysis correspond to specific elements present in the sample, as determined by XRD analysis. The abundant presence of $Al_2(Si_2O_5)(OH)_4$, SiO_2, and CaO in the AKC-CEC catalyst is a good development as they have been recognised as active and efficient compounds in the catalytic transesterification process for biodiesel production (Awogbemi *et al.*, 2020; Sivaprakash *et al*., 2020).

HR-SEM/EDX analysis

The HR-SEM (i) and EDAX (ii) of the AKC, CEC, and AKC-CE samples are shown in Figure 3(a–c), respectively. Each sample shown in the figure has a size range of 0.1 - 1 μm. According to Figure 3ai, the morphological structure of the AKC corresponds to that of kaolinite clay reported in the literature (Dewi *et al*., 2018). The micrograph revealed a flattened plate-like shape of a pseudo-hexagonal crystal of kaolin clay that contains compartments of alumino-silicate substance with strong interactions among its molecules (Mudi *et al*., 2018; Senoussi *et al*., 2016). Also, the image shows a dominant content of distinctive kaolinite structure with a heterogeneous outlook having a large quantity of quartz mineral (Dewi *et al*., 2018). The presence of alumino-silicate and quartz in the morphology of AKC corroborates the findings in the FTIR and XRD. Both analyses also revealed the dominance of the two compounds in the sample. The EDAX data also supported this claim as presented in Figure 3aii. The result indicated that the AKC sample predominantly consisted of the elements C, O, Al, and Si, with weight percentages of 33.52%, 18.56%, 13.28%, and 21.09%, respectively. This data obtained by the EDAX for the AKC sample is in close agreement with the report in the literature for kaolinite clay (Mudi *et al*., 2018; Senoussi *et al*., 2016). Figure 3bi shows the morphology of the CEC sample having irregular crystal shapes of particles in the form of spherical, rod-like, and dumbbell (Chingakham *et al*., 2019). The irregular shape obtained may be attributed to the formation of CaO particles as a result of the decomposition of $CaCO_3$ through the calcination process (Mmusi *et al*., 2021). The particles were also observed to have bonded together and formed large agglomerations which could be due frittage effect (Lani et al., 2020). To evaluate the surface composition of CEC, the EDAX was investigated and the result is presented in Figure 3bii. The figure showed that the chicken eggshell yielded a high concentration of CaO which is expected. Also, the elemental composition from the EDAX data showed that O, Mg, Si, and Ca were present in percentages of 53.02, 13.1, and 1.46. and 32.42%, respectively. This result agrees with other studies reported in the literature on chicken eggshell decomposition to produce CaO by the calcination process (Lani *et al*., 2020; Mmusi *et al*., 2021; Yusuff & Popoola, 2019).

Figure 3c(i) depicts the morphology of the AKC-CEC catalyst obtained after the wet impregnation of the AKC with the CEC sample. The image presents a bee-hive-like structure with large cavities similar to the CaO/kaolin catalyst reported in the literature (Setiadji *et al*., 2018). The large cavities with irregular crystal shapes could also depict large specific surfaces which may contribute to the catalytic activity of the AKC-CEC (Liu *et al*., 2016). The image shows many amorphous white flaky crystals which are characteristics of kaolinite clay (Iorliam *et al*., 2021). The figure also revealed the presence of a regular pattern of particles which is a characteristic of CEC morphology (Figure 3b(i)). These particles were well dispersed on the pseudo-hexagonal crystal of the AKC sample (Figure 3a(i)) to form the new hybrid AKC-CEC (Figure 3c(i)). This suggests that the CaO in the chicken eggshell was successfully immobilised on the surface of the alumino-silicate compound in the kaolinite clay which agrees with the literature (Lani *et al*., 2020). The AKC-CEC catalyst was subjected to EDAX analysis, to assess the sample's elemental composition, as depicted in Figure 3c(ii).

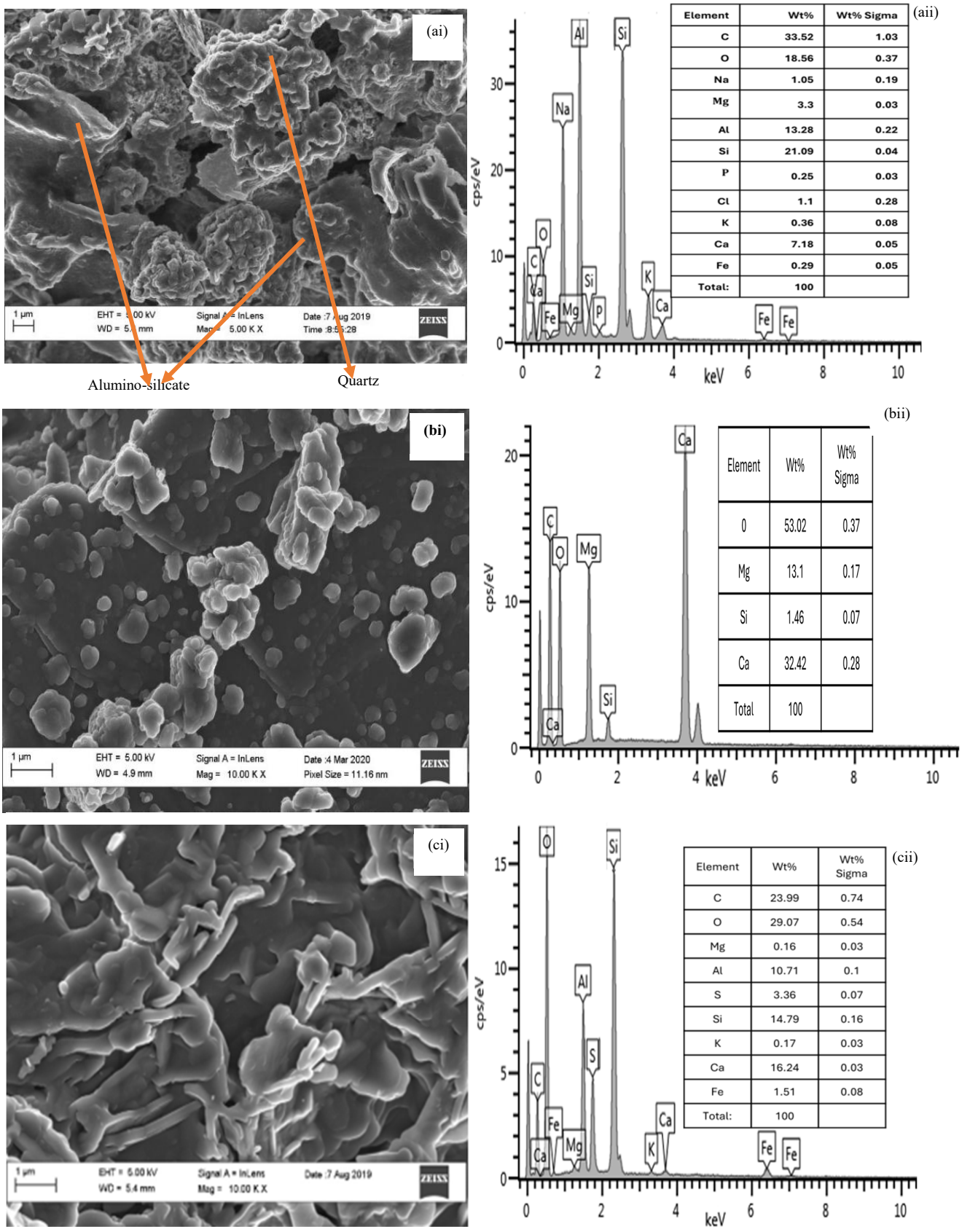

Figure 3: HR-SEM (i) and EDAX (ii) analyses of (a) AKC, (b) CEC, and (c) AKC-CE

The figure reveals that the AKC-CEC catalyst is composed of mainly C (23.99%), O (29.07%), Al (10.71%), Si (14.79%), and Ca (16,24%) which are similar to the previous research (Setiadji et al., 2018). The result of the EDAX further corroborates the XRD and confirms that the CaO in the chicken eggshell immobilised on alumino-silicate in the kaolinite clay (Albuquerque *et al*., 2008; Iorliam *et al*., 2021; Mmusi *et al*., 2021). The Al, Si, and Ca are abundant in the AKC-CEC catalyst which are the elements that enhance the catalytic activity during the transesterification process (Munir *et al*., 2019). The other elements observed in traces in the sample could also be characteristics of either chicken eggshell or kaolinite clay (Senoussi *et al*., 2016).

B. AKC-CE catalyst for biodiesel production using WRF

Figure 4a shows the effect of MeOH: WRF molar ratio (12:1 - 18:1) on the %yield of biodiesel at a constant reaction time of 4 h, catalyst loading of 10% (w/w), and temperature of 90^{o}C. The figure revealed that the biodiesel yield increases steadily as the MeOH: WRF molar ratio increases and attained 81.33% at a ratio of 18:1. This is because the higher methanol concentrations promote oil solubility and thus, increase the biodiesel yield (Ajala *et al*., 2020).

Figure 4b reveals the effect of reaction time on %yield of biodiesel at a constant MeOH: WRF molar ratio of 18:1, catalyst loading of 10% (w/w), and temperature of 90^{o}C. The figure showed a significant increase in the biodiesel yield from 34.8% to 72.53% when the reaction time was increased from 1 h to 2 h. An increase in the reaction time from 2 h to 4 h steadily increases the biodiesel yield to 81.33%. Further increase in the reaction time beyond 4 h showed a marginal decline in the biodiesel yield to 79.00%. This observation is consistent with the literature (Hassan & Nageswara, 2018).

Figure 4c presents the effect of catalyst loading on the %yield of biodiesel at a constant MeOH: WRF molar ratio of 18:1, reaction time of 4 h, and temperature of 90^{o}C. It was seen from the figure that the increase in the catalyst loading from 5% (w/w) to 10% (w/w) increases the biodiesel yield from 69.6% to 81.33%. The linear relationship of the catalyst loading to biodiesel yield can be associated with an increase in the number of active sites available for the transesterification of WRF to biodiesel (Ajala *et al*., 2020). However, further increases in the catalyst loading to 15% (w/w), and 20% (w/w) significantly reduced the biodiesel yield to 66.22%, and 64.71%, respectively.

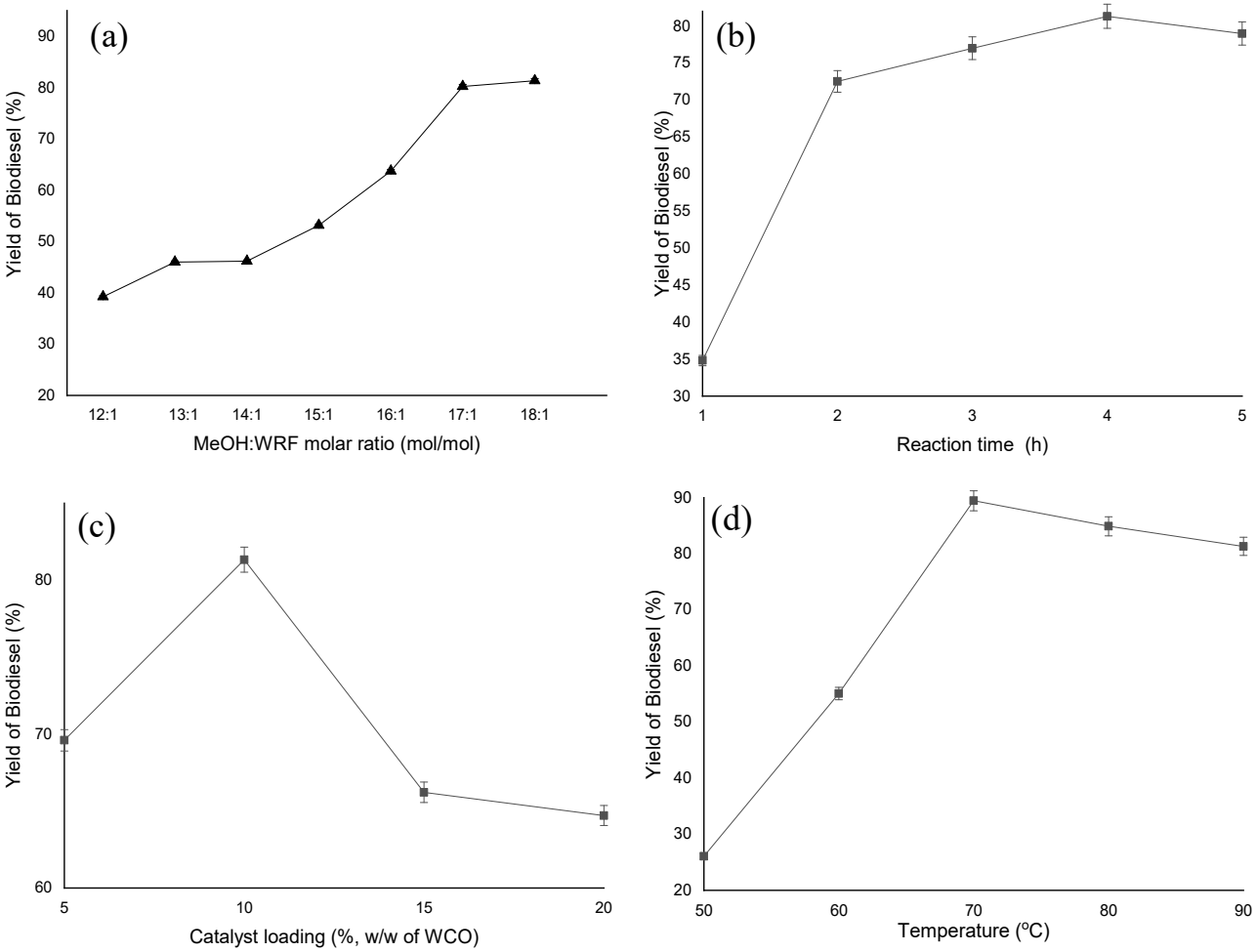

Figure 4: Effects of (a) MeOH: WRF molar ratio, (b) Reaction time, (c) Catalyst loading, and (d) Temperature on the biodiesel yield

This indicates that the catalyst loading above the required quantity for the reaction could result in undesirable effects. The excess catalyst loading could enhance the viscosity of the mixture and hamper the effectiveness of the mass transfer of WRF into AKC-CE leading to a decrease in the biodiesel yield (Xie & Wang, 2020).

Figure 4d shows the effect of reaction temperature (50ºC - 90ºC) on the %yield of biodiesel at a constant MeOH: WRF molar ratio of 18:1, reaction time of 4 h, and catalyst loading of 10% (w/w). As can be seen from the figure, the %yield of biodiesel increased continuously as the temperature increased from 50 to 70ºC. This supports the idea that a higher temperature enhances reactant activation, increases oil miscibility, and decreases reactant viscosity by speeding up the trans-esterification reaction rate through a shift in reaction equilibrium (Ajala *et al*., 2020). A further increase in the reaction temperature beyond 70°C reveals a decline in biodiesel yield, this implies that the reaction is moving in the reverse direction. Therefore, in this investigation, the reaction temperature of 70°C can be selected as an appropriate temperature for the maximum biodiesel yield.

Conclusively, the highest biodiesel yield of 81.33% was obtained at a MeOH: WRF molar ratio of 18:1, reaction time of 4 h, catalyst loading of 10% (w/w), and temperature of 70ºC. Therefore, the maximum %yield of biodiesel obtained in this study confirms the functionality of the AKC-CE.

C. Fuel Properties of the Biodiesel

Table 2 shows the physiochemical properties of the WRF, biodiesel from the WRF using AKC-CEC catalyst, and the range of ASTM standards for biodiesel. From the table, the values of density, kinematic viscosity, flash point, cloud and pour points, and cetane number obtained for the biodiesel are 0.868 g/cm^3, 2.5 mm^2/s, 138ºC, +3ºC, -1ºC, and 62.43, respectively. These results revealed a positive deviation from the properties of the WRF (Table 2), indicating the catalyst's effectiveness in yielding biodiesel. The properties of the biodiesel also fall within the range of the ASTM standard (Table 2) which justifies the fuel quality obtained from the WRF using the AKC-CEC catalyst. According to (Kumar & Lingfa, 2020), the values obtained for these properties confirmed the possibility of using WRF biodiesel produced by the AKC-CEC catalyst as an alternative to diesel.

D. Examining the Nigerian Bio-fuels Policy *vis-a-vis* Challenges of Bio-fuel Production

In the quest for an effective legal framework for biofuel production as an alternative to fossil fuel, the Federal Government issued a Bio-fuel Policy and Incentives in 2007 to create a favourable investment climate for the entrance (Ohimain, 2013a). This was according to an August 2005 government directive on an Automotive Biomass Programme for Nigeria, which gave the Nigerian National Petroleum Corporation the mandate to create an environment for the take-off of a domestic fuel ethanol industry. This is to gradually reduce the nation's dependence on imported gasoline and environmental pollution while at the same time creating a commercially viable industry that can precipitate sustainable domestic jobs (Ohimain, 2013b). The policy includes the establishment of the Bio-fuels Energy Commission and Bio-fuels Research Agency, with a target of

Table 2: Physiochemical properties of WRF, and biodiesel samples

S/N	Parameters	Unit	WRF	Biodiesel	ASTM standard
1	Density (15ºC)	(g/cm^3)	0.969	0.868	0.820 – 0.900 D4,052
2	Kinematic viscosity (40ºC)	(mm^2/s)	26.5	2.5	1.9 – 6.0 D 445
3	Flash point	℃	156	138	≥130 D 93
4	Cloud point	℃	+28	+3	-3 to 12 D 2,500
5	Pour point	℃	+18	-1	-15 to 10 D 97
6	Cetane number		32.73	62.43	>47 D 613

producing biofuels consumed in the country from domestic production. Under the policy, the Bio-fuels Energy Commission is responsible for implementing the strategies for bio-fuels in the country. At the same time, the Bio-fuels Research Agency shall act as the central coordination body for bio-fuel research in the country. The Bio-fuels Energy Commission (the Commission) shall be a corporate body with perpetual succession and common seal, having the power to own property and to sue and be sued in its corporate name. Specifically, the Commission shall register all Bio-fuel Plants/Projects in the country; issue licenses to Bio-fuel operators for the production of fuel ethanol and bio-diesel in Nigeria; formulate and recommend fiscal, financial and other incentive policies for the bio-fuel industry; review and assess the economic, technical, environmental and social impact of the use of bio-fuels; monitor the supply and utilisation of bio-fuels and bio-fuel blends and recommend appropriate measures to the Department of Petroleum Resources in case of a shortage in the supply of bio-fuels or feedstock; review and adjust the minimum mandated bio-fuel blends as it deems appropriate; determine and put in place industry stabilisation mechanisms; designate and oversee the activities of the investment bank appointed to manage the Bio-fuel Industry Equity Fund; establish and support the Bio-fuels Research Agency established under the Bio-fuels Programme; monitor intra-industry commerce; present quarterly reports and briefings on the status of the Bio-fuel Industry to the National Assembly; disseminate and share information with investors and other interested members of the public; liaise with the Energy Commission of Nigeria in the formulation, revision and implementation of the National Energy Policy; liaise with the National Sugar Development Council as may be required;

and liaise with government ministries, agencies, parastatals, research institutes or other bodies charged with responsibility for the development of biofuel feedstock.

Under the Policy, the Bio-fuels Research Agency (the Agency) shall collaborate with the Ministry of Agriculture and Ministry of Science and Technology to provide direction for research in crop production, industry technology, and processes about the production of biofuels. The Agency shall coordinate the allocation of funds set aside for biofuel research for mandated national research organisation. In the Policy, bio-fuels are defined as fuel ethanol bio-diesel, and other fuels made from biomass and primarily used for automotive, thermal, and power generation, according to quality specifications stipulated by the Standards Organisation of Nigeria (SON), Department of Petroleum Resources (DPR), and any other competent government agency (Ohimain, 2013a).

The Biofuel programme constitutes a major and unique attempt to integrate the agricultural sector of the economy with the downstream petroleum sector. The use of Biofuels in Nigeria is anticipated to make a significant impact on petroleum product quality enhancement given the current limitations of fossil-based fuels which have not kept pace with the increasing demand for environmentally friendly fuel. Other anticipated benefits of Bio-fuel Programme include additional tax revenue for the government from the economic activities attributable to the industry; job creation in terms of increase in economic development and empowerment of rural communities; agricultural benefits in terms of improved farming techniques, increase in agricultural research and crop demand resulting from activities in the industry; energy benefits resulting from co-generation benefits; and environmental benefits from reduction in tailpipe emissions and ozone pollution, reduction in particulate emission, and replacement of toxic octane enhancers in gasoline.

The objective of the programme is to firmly establish a thriving fuel ethanol industry utilising agricultural products as a means of improving the quality of automotive fossil-based fuels in Nigeria. The Policy shall link the agricultural and the energy sector, with the underlying aim of stimulating development in the agricultural sector. In broad terms, the policy aims: (a) to promote job creation, rural and agricultural development, and technology acquisition and transfer; (b) to provide a framework that is capable of attracting foreign investment in the bio-fuels industry; (c) to streamline the roles of the various tiers of government to ensure the orderly development of the biofuels industry in Nigeria; and (d) to involve the oil and gas industry in more purposeful development of other sectors of the nation's economy.

Despite the extant policy on biofuel production, the implementation of the policy *vis-à-vis* bio-diesel production is faced with so many glaring challenges. The major challenge has been its promotion, especially regarding subsidies (Aliyu *et al*., 2017). Since the production involves huge investment, the private sector may not be able to finance the entire project. Therefore, government needs to stimulate the interest of both private and public sectors, especially the collaborative effort of the two in research and development. Thus, there is a need for a public-private partnership approach (Oniemola & Sanusi, 2009). Another challenge of the policy is its impact on food prices as it may have to compete with farmland, technological development, and infrastructure (Aliyu *et al*., 2017). This challenge lies in improving farming practices to enhance the quality and yield of feedstock and provision of enabling infrastructures like power, good roads, and usable water to boost feedstock production (Odetoye *et al*., 2019). There is also the challenge of fiscal and regulatory policies that will attract investors, and fund research on bio-fuel development from biomass feedstock. High cost of production which will ultimately determine the price is another challenge of bio-fuel or bio-diesel production at the commercial level. Nigeria is one of the countries faced with high fuel prices. The price of biodiesel may be diametrically higher than fossil fuels (diesel and gasoline) if not properly managed. The various production processes are, therefore, steps that must be carefully taken to reduce the cost of biodiesel production.

The various feedstocks used for bio-diesel production may pose more threat to food availability. Therefore, mass production of non-edible feedstock such as waste-ram-fat needs to be encouraged. Thus, priorities should be given to feedstocks and their standardisation. To enhance bio-diesel production yield, technological advancement in the areas of its feedstock processes and production is required. This can be done by engaging in rigorous research in biotechnology, plant agronomy, and precision agriculture techniques (Odetoye *et al*., 2019). To achieve success in feedstock production, the government must provide local farmers with the money to start the industry. This is the only way Nigeria could use bio-diesel or bio-fuels to improve the standard of living of its citizens.

The willingness of the public to switch to bio-fuels or bio-diesel from gasoline fuel in the transportation sector is also of paramount concern in ensuring the success of the implementation. This is because failure of public support towards bio-fuel implementation will create an adverse effect which may lead to production failure. Campaigns and public awareness of the importance and benefits of biofuels must be embarked on. The use of biofuel is a promising approach to reduce dependence on gasoline fuel, thereby alleviating global warming. Moreover, the development of the biofuel industry in Nigeria is an important milestone in achieving sustainable energy development, especially in the transport sector. However, the current bio-fuel production activities in Nigeria are still at a low scale and need motivational approaches to be put in place and enforced, to ensure that the public and environment derive maximum benefits from the venture.

IV. CONCLUSION

In this study, a heterogeneous catalyst of AKC-CEC was developed from AKC and CCE for the transesterification of WRF for biodiesel production. Based on the characterisation studies, it was confirmed that the AKC-CE consists of the main components of $Al_2(Si_2O_5)(OH)_4$, SiO_2, and CaO which are present in the AKC and CCE samples. These are the compounds that enhance the catalytic activity during the transesterification process. The micrograph also confirmed the successful immobilisation of the CaO in the CEC on the surface of the alumino-silicate compound in the AKC to form the new hybrid of AKC-CEC catalyst. The highest biodiesel

yield of 81.33% was obtained at a MeOH: WRF molar ratio of 18:1, reaction time of 4 h, catalyst loading of 10% (w/w), and temperature of 70ºC. The biodiesel produced via the AKC-CEC catalyst is within the ASTM standard. For Nigeria to achieve its ambition for sustainable development in bio-fuel production, it must take a holistic approach to meet the challenges of massive investment in biomass feedstock research and appropriate institutional and policy frameworks. Further studies on computer-aided scale-up simulation, process design, and economic feasibility of biodiesel production using the developed catalyst are recommended.

AUTHOR CONTRIBUTIONS

E.O. Ajala: Conceptualisation, methodology, analysis, manuscript writing - original draft and revision. **M.A. Ajala:** Methodology, analysis, manuscript writing - original draft and revision. **F.D. Afolabi:** Methodology, analysis, manuscript writing - original draft. **J.O. Ajala:** Methodology, analysis, manuscript writing - revision. **S. Opawoye:** Analysis, manuscript writing - review and editing. **D.A. Ariyoosu:** Manuscript writing - original draft and revision.

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