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PREPARATION AND CHARACTERIZATION OF COW HORN NANO CATALYST FOR PRODUCTION OF BIODIESEL USING NEEM SEED OIL

***Jude Edogbo Eneche[ab], Iliya Ibrahim Nkafamiya[a], Buba Ardo Aliyu[a], Tari Joel Honda[c] Jim-Ezetulugo, Arinze Bob[b] and Meyanga Hassan Ijuwa[d]**
[a]Department of Chemistry, Modibbo Adama University, Yola, Nigeria.
[b]Department of Science Laboratory Technology, Federal Polytechnic Ohodo, Enugu State, Nigeria
[c]National Center for Technology Management (NACETEM), Nigeria
[d]Department of Agricultural technology The Federal Polytechnic Damaturu, Yobe State, Nigeria

***Abstract**: This study focused on developing a novel cow horn nanocatalyst (CHNC) and aluminum impregnated cow horn nancocalyst (Al-CHNC) for transesterification reaction of neem seed oil to biodiesel. The cow horns were obtained from a popular Yola abattoir, Yola South LGA Adamawa state. The cow horns were washed to removed impurities, sun dried for two weeks before taking to the laboratory mill for grinding. After grinding it to powdery form; the cow horn was placed in the oven at 70 °C for 7 hours to ensure moisture had completely removed from the cow horn powder. The powdered was calcined at two different calcined temperature (700 °C and 800 °C) in order to know at which temperature give optimum CaO yield. The result of XRF revealed that calcination temperature of 800 °C gave higher yield of CaO in the cow horn. The Impregnation technique was employed to dope the cow horn with aluminum nitrate to form Al-CHNC. The FTIR analysis was conducted to affirmed chemical interaction in the aluminum doping cow horn catalyst (Al-CHNC). Both CHNC and Al-CHNC were subjected to activity test by deploying them in transesterification reaction of neem seed oil of which Al-CHNC have a higher yield of biodiesel (91.8%) compare to CHNC (67.5%). The BET analysis carried out on the CHNC and AL-CHNC revealed higher surface area of Al-CHNC (354.769 m^2/g) which is responsible for the better catalytic activity compare to the CHNC (247.087m^2/g). Also, XRD, XRF and SEM analyses were carried out on the Al-CHNC before transesterification and after transesterification.*

***Keywords**: Cow horn, transesterification, neem seed oil, nanocatalyst.*

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1.0 Introduction

The global population has placed so much demand on energy. According to Obidike *et al.,* (2022), the average world energy usage is expected to increase by 34% between 2014 and 2035. Fossil fuel happened to be the major means of harnessing energy for global consumption. Agarwal (2007) reported that fossil fuels are needed for transportation, the production of petrochemicals and plastics, asphalt for road construction, packaging materials, and some medical equipment. Regrettably, fossil fuel applications have suffered setbacks due to their environmental pollution and poor sustainability (Demirbas, 2003). Onimisi *et al.,* (2021) reported that oil fields are experiencing a decline in oil reserves coupled with the severe aftermath of combustion on both public health and the environment. This is further corroborated by Atabani, *et al.,* (2012) that combustion of fossil fuels is the leading cause of climatic change, such as greenhouse effects and ozone layer depletion. Acid rain is also one of the many negative consequences of climate change. Also, Maulidiyah *et al.,* (2022) reported that fossil fuels release harmful substances such as carbon dioxide (CO_2), sulphur oxides (SOy) and hydrocarbon volatile solvents (HCs). This negative consequence of fossil fuel has necessitated research into alternative bio-based feedstocks to produce bio-fuel.

According to Abdul-Wahab and Takase (2019), biofuel is an alternative fuel made from renewable resources such as vegetable oils, animas such as animal fats, and once used cooking oils. Gidigbi and Abubakar (2023) reported that biodiesel, which is one of the important components of biofuel, is a renewable resource that can be produced in any country of the world. Van Gerpen *et al.,* (2004) explained that biodiesel is a liquid obtained chemically from chemical reactions between either vegetable oils or animal fats and an alcohol. Apart from being environmentally benign, production of biodiesel has several advantages over petroleum-diesel, such as zero toxic emissions (Wan Ghazali *et al.,* 2015); smooth engine operation (Puagsang *et al.,* 2021), biodegradable (Yusuff *et al.,* 2017) , ease of production and transportation (Datta and Mandal, 2016), least concern of health risk (Romano and Laborde, 2006); higher flash point (above 100 ^oC) (Romano and Sorichetti, 2011), much more stable than fossil-diesel and can be blended readily with fossil-diesel (Azeez *et al.,* 2016).

Several studies have highlighted different approaches to biodiesel production, but Obidike *et al.,* (2022) argued that biodiesel made via the chemical process of transesterification has been the best of all the chemical processes. Gidigbi and Abubakar (2023) explained that transesterification of vegetable oils with low molecular weight simple alcohols has been established as the best option to reduce the, low volatility, high viscosity, heavy engine deposits, and toxic substance formation associated with the direct use of vegetable oils.

The transesterification process (otherwise known as alcoholysis) involves the displacement of alcohol from ester by another alcohol. This is further explained by Abdul – Wahab and Takase, (2019); Parthiban *et al.,* (2021) that production of biodiesel via transesterification involves the use of alcohols, usually the first and second members of the alcohol group (methanol and ethanol), in a chemical reaction with vegetable oil or animal fats in the presence of an alkaline catalyst to form a long chain of fatty acids of methyl ester (FAME). Methanol is easily accessible and affordable. Romano and Sorichetti (2011), affirmed that biodiesel formulated with methanol is reported to have desired and improved physicochemical parameters such as high reactivity and high yield. While ethanol is eco-friendly, and can be synthesized from sugarcane molasses, bio-diesel formulated using ethanol easily forms emulsions, which make it difficult to separate end products (especially with waste or used oils) (Reyero *et al.,* 2015).

Catalyst plays an important role in the transesterification process, as reported by Yasodhara *et al.,* (2021) who observed that catalyst reduces the activation energy involved in the transesterification process, thereby increasing the rate of conversion, which leads to a high yield of biodiesel. Gidigbi and Abubakar (2023) affirmed that the choice and quantity of catalyst affected both the transesterification process and the yield. Also, Yusuff *et al.,* (2017) reported that using nanocatalysts in transesterification reactions favors conversion rate due to an increase in surface area, as more area is available on the catalyst surface for the reaction to take place. Recent studies are now directing on synthesizing catalysts from renewable and waste materials in line with sustainable and environmental management. This minimizes cost and puts the waste to reuse thereby protecting the environment.

Large volumes of cow horn are generated annually in Nigeria as a byproduct of cow processing to produce meat, and because they have no current purpose, they litter the environment, causing pollution (Ezeh *et al.,* 2020). There is interest in using this material as a precursor for the creation of solid catalysts since it contains elements and chemicals that confer catalytic activity (Ezeh and Onukwuli, 2020). Cow horn has been reviewed for possible synthesis of cow horn nanocatalyst (CHNC) due to the presence of elements and compounds that have catalytical capabilities. Therefore, this study ia aimed at preparation and characterisation of cow horn nano catalyst for production of biodiesel using neem seed oil.

2.0 Materials

Methanol (99.5 % purity), sulphuric acid (98% BDH), Aluminum Nitrate, distilled water, crucibles, Electric digital precision weighing balance (Ohaus, Adventurer, model AR 3130), muffle furnace, heating mantle and Magnetic stirrer, rotary evaporator, thermometer, beakers, separating funnel, sample bottles, 150µm sieve, conical flask.

2.1. Extraction and Esterification of Neem seed oil

Neem seed used were gotten from the neem trees at Modibbo Adama University, Yola. The neem seeds were sun dried for 7 days. The neem seed oil was extracted from the neem seeds using soxhlet extraction method. Esterification reaction (reduction of free fatty acid) was carried out using sulphuric acid (H_2SO_4) according to the method described by Gidigbi and Abubakar (2023). The neem seed oil was heated first at 60 ^oC for 20 mins to remove residue moisture. Then, 60ml of methanol was introduced into a 500 ml conical flask containing 200 ml of preheated neem seed oil and 0.3 ml of H_2SO_4 was subsequently introduced. The mixture was placed on a hot plate with magnetic stirrer for 60 minutes at 50 ^oC. The mixture was separated by separating funnel with glycerine at lower layer, and esterified oil at upper layer and percentage yield was determined using the equation.

$$\%\ Oil\ yield = \frac{wei \qquad of\ the\ oil\ (g)}{weight\ of\ the\ dried\ sample\ (g)}\ X\ 100 \tag{2.1}$$

$$\%\ Oil\ yield = \frac{20.5}{50}\ X\ 100$$

$$\%\ Oil\ yield = \ 41\%$$

2.2. Preparation of the Cow Horn and Aluminum Impregnated Cow Horn Nanocatalyst

The cow horn catalyst was prepared according to the method described by Amenaghawon *et al.,* (2021). The cow horns were collected from Yola abattoir in Yola South Local Government Area of Adamawa State, Nigeria; thoroughly washed with tap water and sun dried for two weeks. The cow horn was crushed and grinded using laboratory mill and consequently sieved to obtain particles of 150 µm size. The powder obtained was further dried in an oven for 7 hours at 70 ^oC until constant weight.

Calcination of the powdered cow horn was carried out in a muffle furnace at 800 ^{o}C for 3 hours according to the method described by Amenaghawon *et al.,* (2021). The calcined cow horn was removed and immediately placed in a desiccator to prevent atmospheric interaction. The calcined Cow horn sample was hydrated at 60 ^{o}C for 6 hours. After that, it was strained and oven-dried at 105 ^{o}C for 24 hours. The calcined-hydrothermal-dehydrated Cow horn samples was further re-calcined at 900 ^{o}C for 3 hours for conversion of the calcium hydroxide formed ($Ca(OH)_2$) into a highly porous nano-sized catalyst particles, Subsequently, the dried cow horn were crushed which were referred to as cow horn nano-catalyst (CHNC). The CHNC sample was cooled in a desiccator and kept in a sealed container to prevent interaction of the catalyst from humidity before use. The Aluminium cow horn nano catalyst was prepared via wet impregnation method using Aluminium nitrate as a precursor according to the method described by (Deraz ,2018).

2.3. Characterisation of the Cow Horn Nanocatalyst Catalyst

The cow horn catalyst characterisation was carried out using FTIR, BET, XRD, XRF and SEM.

2.3.1 X-ray diffraction analysis of catalysts

The x-ray diffraction (XRD) characterization of the catalysts was performed on a Empyream (panalytical model) based generator x –ray diffractometer, the analysed material was finely ground to pass through 63 microns homogenized, and average bulk composition was determined. The powdered sample was prepared using the sample preparation block and compressed in the flat sample holder to create a flat on the sample smooth surface that was later mounted on the sample stage in to XRD cabinet. The sample was analyzed using the reflection transmission spinner stage using the theta-theta settings 20 starting position was 0.00483 and end at 75.000 with a 20 step of 0.0026 at 3.57 seconds per step. Tube current was 40 mA and the tension was 45 VA. Fixed divergent ship size of 1^{o} was used and the goniometer reading was 240mm.

2.3.2 Scanning electron microscopy analysis of catalysts

Scanning election microscopy provides a high-resolution image of the surface of a material (topographical information) over a length scale from nanometer up to several hundred micro meters. It provides information concerning catalysts particle morphology, active phase, homogeneity and composition near surface regions of the material. The morphologies of the freshly prepared catalysts and the coke deposited on the used catalysts were studied using a Hitachi SU8230 scanning electron microscope (SEM), which was operated at 2 kV and working distance of 3 mm.

2.3.3 X-ray florescence analysis of catalysts

X-ray florescence is an important analytical technique which is generally utilized in the determination of chemical composition of a given sample. Catalyst sample was prepared to a reduced particled size of less than 63 microns using a Tema vibrating mill. The agate meter in the mill crushes the sample before sieving it to pass through 63 microns. Beads used for the major elemental analysis expressed in oxides weight percent was prepare by first drying the catalyst in an oven at 110 ^{o}C for 24 hours to remove the moisture in the prepared catalyst powder.

About 5.0g of dry sample powder was weighed in the silica crucible and then ignited in the finance at 1000 °C for 2 to 3 hours for the calcination of impurities in the sample. The sample was removed from the furnace and allows cooling at room temperature in a desiccator. The ignited sample was weighed again to determine the Weight of the calcinated impurities which was H_2O and CO_2.

1.0g of the stored ignited sample powder was weighed and exactly 5 time of flux (X-ray Flux-types 66.34% (66.0% lithium Tetra borate: 34% lithium Metaborate)) was added to lower the verification temperature of the sample powder. The weigh mixture was mixed properly in a platinum dish and ignited in the pre-set furnace (Eggon 2 Automatic fuse bead maker) at 1500 °C for 10 minutes to form glass bead. The glass bead was slotted into the computerized XRF (Epsilon 5 panalytical model) for major elemental analysis.

Trace elemental analysis was carried out using compressed powder pellets. These pellets were prepared by weighing 3.0g of oven dried powder sample and 3.0g flux (cellulose-powder) was added as abrader and dispensary agent and shaking in a small plastic container for 12 minutes. The mixed mixture was then compressed by applying pressure of 1500 kg m^{-2} using both manual and electronic compressor. The pellets were placed in the computer-program XRF and the condition for trace elemental set to give the result in elemental form.

2.3.4 Brunauer-Emmett-Teller (BET) method

The BET specific surface area was measured by nitrogen adsorption performed at 77 K with a Micromeritics ASAP2000 system; the sample preparation was carried out with a degassing temperature of 200 °C and time 8 hours. The specific surface area was calculated with the Brunauer-Emmett-Teller (BET) method.

2.4. Transesterification of Neem Seed oil

Three neck 500 ml glass and a reflux condenser were filled with a known amount of neem seed oil. It was then placed on a hot plate magnetic stirrer and heated to the temperature required by the experiment. The heated oil was mixed with methanol. After adding the heterogeneous catalyst to the reactor, the reaction was allowed to continue for the predetermined amount of time, as stipulated by the experimental design (El-Gendy *et al.,* 2014). Upon completion of the reaction, the mixture was centrifuged to separate the solids. In a separating funnel, the residual liquid was left to separate for the entire night. After that, the bottom layer, which contained glycerol and some leftover solid catalyst, was separated from the upper layer, which contained biodiesel and unreacted methanol. Warm distilled water was used three times to wash the recovered biodiesel in order to eliminate any leftover methanol, glycerol, and catalyst. To remove any remaining moisture, the refined biodiesel was further dried. After that, it was maintained for characterization and kept in a bottle.

3.0 RESULTS AND DISCUSSION

3.1. Biodiesel yield

The yields of biodiesel from both catalysts are 67.5% for calcined catalyst and 91.8% for impregnated catalyst.

3.2. Characterisation of Cow-horn Catalysts

3.3. BET analysis for the catalysts

The calcined cow horn and impregnated cow horn catalysts were subjected to BET analysis (BJH method adsorption) in order to study the possible catalytic activities on their surfaces. The surface areas and pore sizes of the catalysts were assessed and the results are presented in table 3.1.

According to the BET analysis, the surface area of calcined cow horn catalyst (CHNC) was recorded to be 247.087 m^2/g, while that of Aluminium impregnated cow horn catalyst (Al-CHNC) was recorded to be 354.769 m^2/g. Zabeti *et al.,* (2009) reported that high surface area and pore volume contribute to high catalytic activity of solid catalysts. Therefore, the higher surface area observed in Al-CHNC is responsible for its higher catalytic activities (high biodiesel yield) as more active sites are available on the surface of the catalyst for chemical interaction and adsorption with the reactants. Also, larger pore size witnessed in the Al-CHNC also suggests higher adsorption capacity of reactants from the medium which led to higher rate. Also, both catalysts have lower pore diameter, which showed better dispersion of active sites in the catalyst, but the smaller value for Al-CHNC means more dispersion of active site. Some researchers such as Madai *et al.,* (2020) have also reported very high surface areas of 411.2 m^2/g and a pore size of 3.01 nm and pore volume of 0.628 cm^3/g for banana peel ash functionalized with mixed metal oxide ($Li–CaO/Fe_2(SO)_4)_3$ for catalysts prepared for biodiesel production.

Table 3.1. Brunauer, Emmett and Teller (BET) surface area and pore size analysis for the catalysts

Sample	S_{BET} (m^2/g)	Pore volume (cc/g)	Average Pore diameter (nm)
Cow-horn Catalyst (CHNC)	247.087	0.120	2.118
Al- Cow-horn nanocatalyst (Al-CHNC)	354.769	0.175	2.453

3.4. FTIR for the Al-CHNC catalyst before and after biodiesel production

After establishing that Al-CHNC has higher catalytic activities due to the presence of high surface area, the FTIR study was carried out to assess the chemical structure before and after transesterification procedure. Figure 3.1 shows the FTIR spectra of the Al-CHNC catalyst before transesterification and after. The peaks that are indicative of the presence of functional groups can be clearly seen. The broad peak at around 3412.85 and 3408.54 cm^{-1} is due to OH stretching vibrations and similar peak was reported by Amenaghawon *et al.,* (2021). The peak which is broader in the spectrum of the calcined catalyst after esterification, could be ascribed to the formation of a new phase of Al-CHNC compound. The peaks at 2934.50 and 2937.36 cm^{-1} are due to CH stretching vibrations. These peaks are slightly narrower in the spectrum of the calcined catalyst after esterification, which suggests that some of the organic material has been removed from the catalyst during use. The peak at 1704.75 and 1717.86 cm^{-1} are due to C=O stretching vibrations. These peaks are slightly larger in the spectrum of the calcined catalyst after transesterification, which suggests that there is more carbonyl-containing material on the surface of the calcined catalyst after esterification. The peaks at 1442.52 and 1460.66 cm^{-1} are due to CH bending vibrations. These peaks are similar in the spectra of the egg shell/ant hill-based catalyst reported by Yusuff *et al.,* (2019).

The FTIR analysis suggests that the calcined catalyst (after transesterification) has undergone some changes from the used catalyst (before transesterification). There is more hydrogen bonding in the calcined catalyst (after transesterification), and some of the organic material has been removed from the surface which is in accordance to the work reported by Mallah and Sahito (2020). There is also more carbonyl-containing material on the surface of the calcined catalyst after esterification. These changes could be due to the reaction of the catalyst with the neem oil or with the products of the biodiesel reaction as reported by Vinayaka *et al.,* (2021).

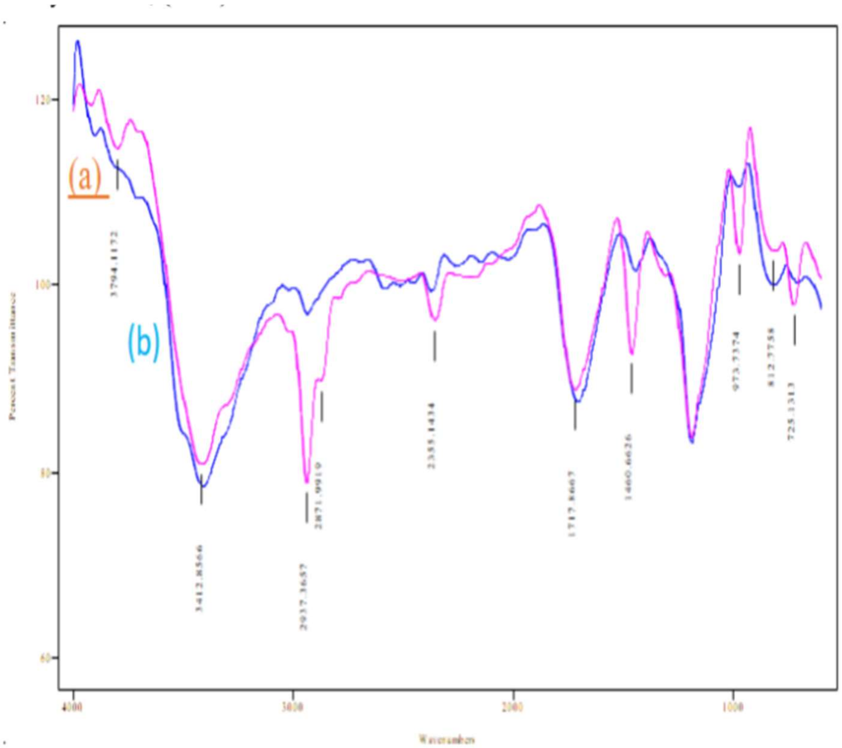


Figure 3.1. FTIR Al-CHNC catalyst (a) before transesterification (b) after transesterification

3.5. X-ray Diffractometry of the Al-CHNC catalyst

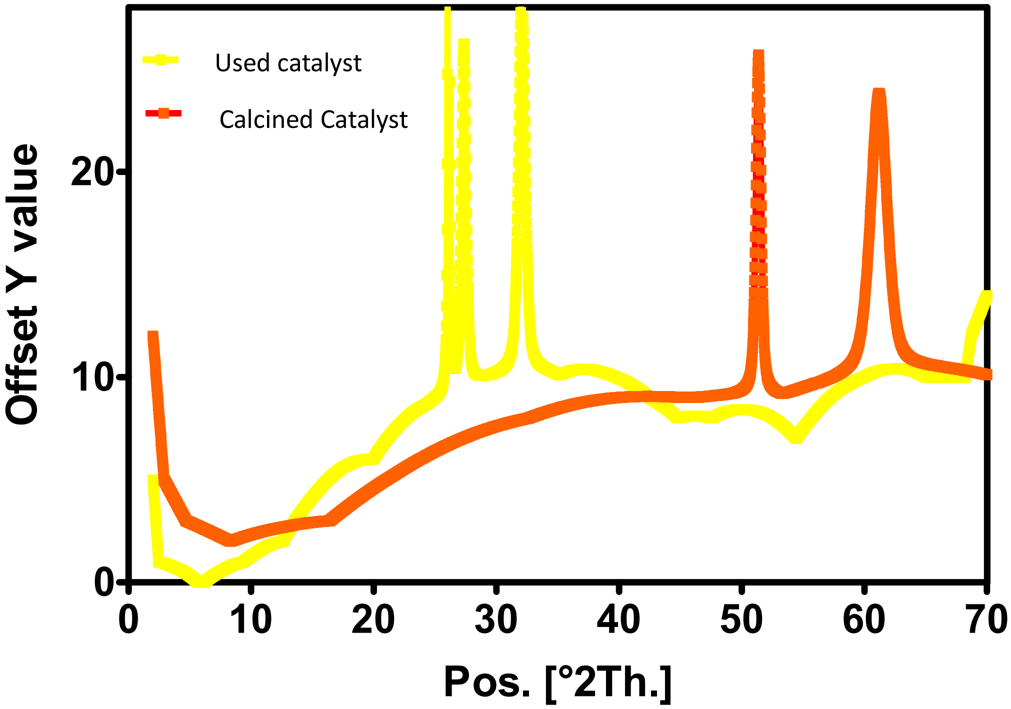


Figure 3.1. XRD spectra of calcined and unused catalyst

Figure 3.2 compares the crystallographic structure of calcined (before reaction) and used catalysts (after reaction) in the production of biodiesel from neem seed oil. The XRD patterns exhibit differences that can be attributed to changes in the catalyst's structure after use. The calcined catalyst (before reaction) shows higher intensity peaks compared to the used catalyst (after reaction), particularly around 52° and 63° and 27°, 28° and 34° at 2θ. This indicates a more crystalline structure in the calcined catalyst. The used catalyst's peaks are less intense, suggesting a reduction in crystallinity after the catalytic process this is in line with Chaudhary *et al.,* (2022). There are slight shifts in the peak positions between the calcined and used catalysts.

The XRD analysis reveals significant structural changes in the catalyst after being used in the biodiesel production process. The calcined catalyst starts with a highly crystalline structure, which is advantageous for catalytic activity due to the availability of active sites this is in agreements with the findings of Inayat *et al.,* (2021). However, after usage, the catalyst's crystallinity decreases, as evidenced by the broadening and reduction in peak intensities. This can be attributed to the reduction in the activities of the catalyst and it could be caused by attrition during reaction which is capable of wearing off active sites of the catalyst as reported by Pandit and Fulekar (2017).

The changes in peak positions and the emergence of new peaks suggest that the catalyst undergoes chemical reactions during the biodiesel production, leading to the formation of new compounds or phases. This can result from interactions between the catalyst and the feedstock

or products, leading to fouling or coking, which covers the active sites and reduces catalytic efficiency. Additionally, the reduced crystallinity in the used catalyst indicates structural degradation, likely due to high temperature and chemical reactions during the process. This degradation can lead to the loss of surface area and active sites, reducing the catalyst's effectiveness over time as reported by Chaudhary (2022).

The XRD analysis demonstrates that the calcined catalyst possesses a well-defined crystalline structure that degrades after use in the biodiesel production process. The reduction in crystallinity and the formation of new phases in the used catalyst suggest that the catalyst's activity may decline with usage, necessitating regeneration or replacement for sustained biodiesel production efficiency.

3.6. X-ray Florescence (XRF) Characterisation for both CHNC and Al-CHNC

The X-ray fluorescence is a non-destructive analytical technique that has been widely used to study the composition of materials such as metals; rocks, soil, cement etc. The XRF was used to study the calcination temperature for cow horn catalyst at 700°C and 800°C. This is to ascertain the calcination temperature with the best yield of calcium oxide (CaO).

Table 3.2: XRF analysis of Cow horn catalyst at 700 °C and 800 °C

Major constituents of Cow horn catalyst	Composition (%) at 700 °C	Composition (%) at 800 °C
SO_3	35.334	20.780
CaO	40.758	41.644
SiO_2	8.114	17.395
ZnO	4.375	4.455
Al_2O_3	1.999	2.941

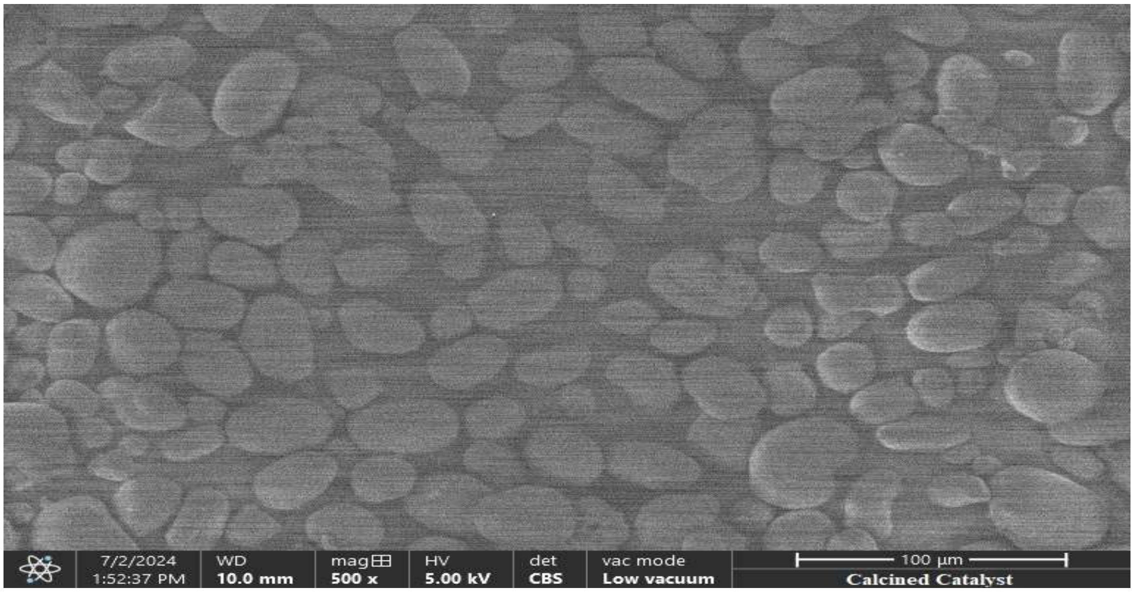
Table 3.3. XRF analysis of CHNC, Al-CHNC before and after transesterification

Major Constituents	CHNC (%)	Al-CHNC before transesterification (%)	Al-CHNC after transesterification (%)
SO_3	20.780	21.150	19.258
CaO	41.644	43.164	40.062
SiO_2	17.395	14.318	12.770
ZnO	4.455	4.614	3.573
Al_2O_3	2.941	5.662	4.663

The calcination of cow horn catalyst at 800 ºC yielded more calcium oxide (41.644%) compared to at 700 ºC (40.758%) as shown in table 3.2. Therefore, since CaO is the targeted compound, calcination at 800 ºC was adopted for cow horn catalyst (CHNC) and Aluminium doped cow horn catalyst (Al-CHNC). Aluminium Oxide was another metallic oxide present in significant quantity. This supports the fact that these dominant elements (Ca and Al) were contributed respectively by the Al doping and cow horn which makes up the catalyst for the study. Also, the loading of Aluminium metal on cow horn catalyst was confirmed by XRF which reported it as (5.66%) in table 3.3. The CaO is a desired base catalyst for biodiesel production because of its low toxicity and high reactivity (Kouzu and Hidaka, 2012). Therefore, both components contributed significantly to the reaction process, providing the capacity for catalyst bi-functionality. The other constituents included SO_3, SiO_2, SO_3, ZnO, etc, have been reported by Sani *et al.,* (2017) as active materials for catalyzing transesterification. The reduction in CaO observed at the aftermath of transesterification process is indicative of the fact that some active metal sites of catalyst were involved in the transesterification reaction, and may need to be reactivated for catalyst reuse.

3.7. SEM for Al-CHNC

The morphology of the catalyst before and after use, as seen in the SEM images at magnifications of 500, 1000, and 1500 (Fig. 3.7a, b, c), reveals an irregular shape morphology, this could be as a result of the impregnation method as particles of aluminum can agglomerate on the surface of calcined cow horn resulting to irregular shape morphology as reported by Sharma *et al.,* (2013). Comparing the SEM images of the calcined catalyst with those of the used catalyst, it is evident that the catalyst's porous structure diminishes after use, suggesting a decrease in surface area. This reduction in surface area may be due to the occupation of some active sites by reacting species during the reaction. Continuous use of the catalyst could lead to reduced activity and deactivation of its active sites Amenaghawon *et al.,* (2013). The observed changes in the structure, activity, and porosity of the catalyst indicate its role during the reaction, similar to findings reported by Amenaghawon *et al., (*2021).



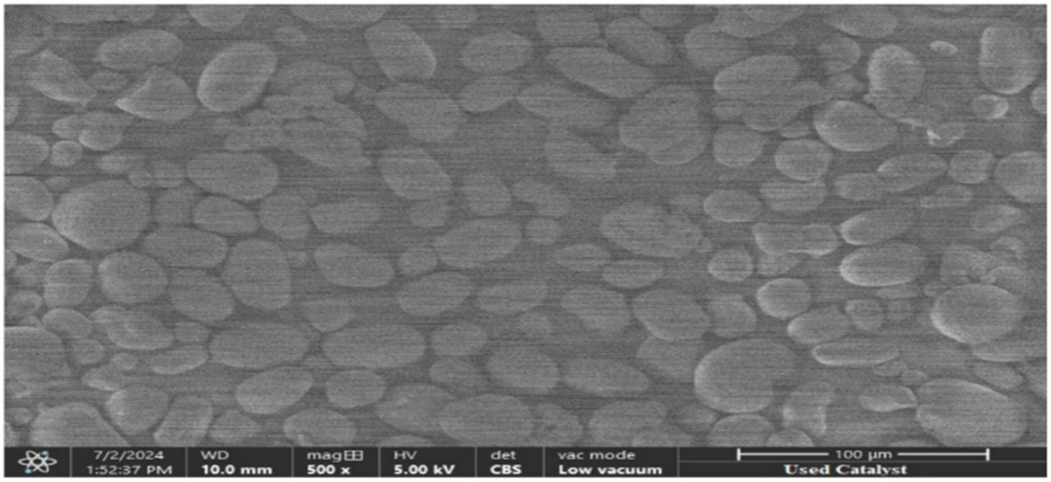
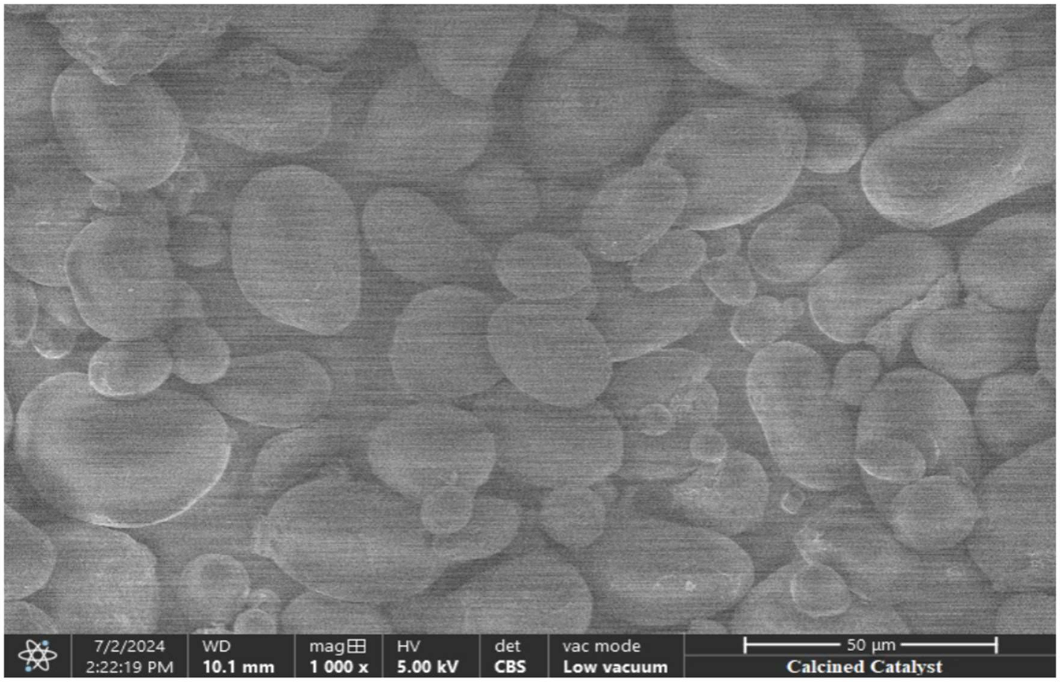


Figure 3.3a: Surface morphology of the Al-CHNC at 500 magnification



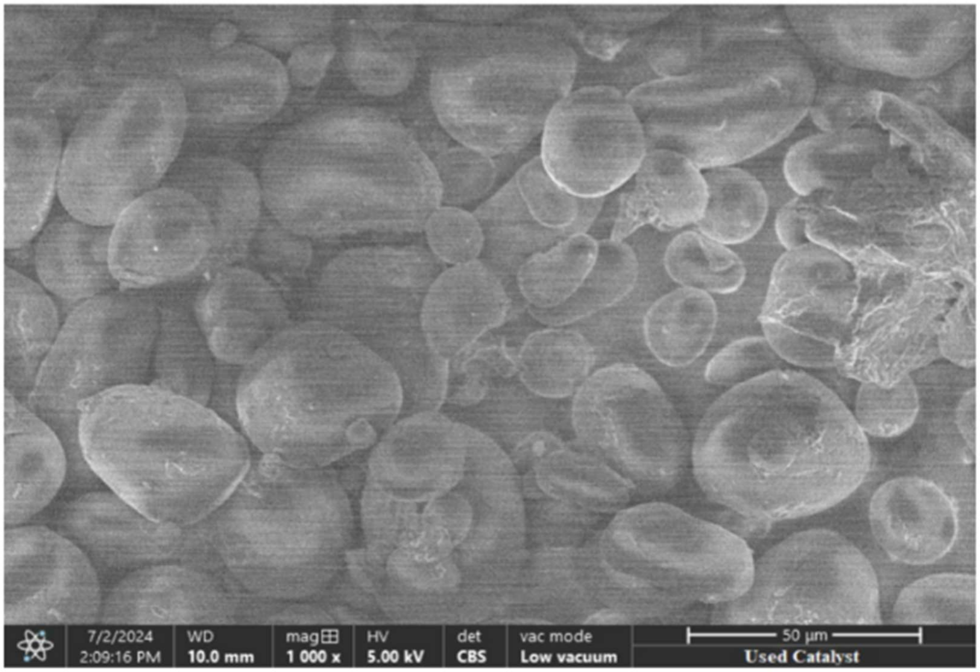
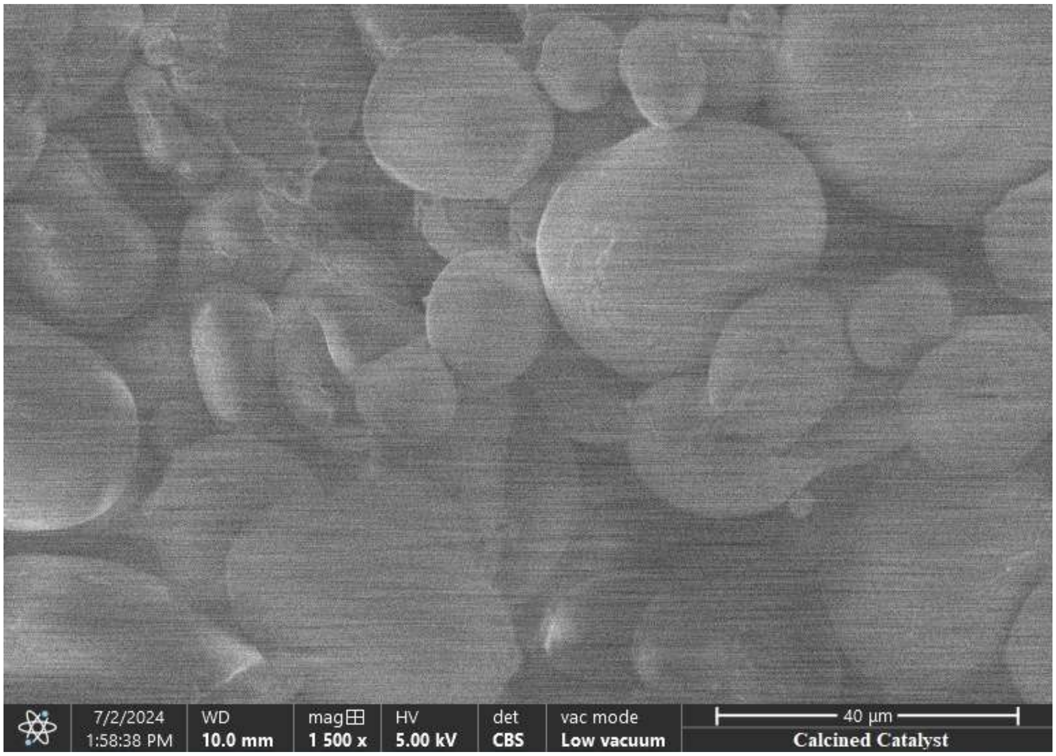


Fig. 3.3b: Surface morphology of the Al-CHNC at 1000 magnification



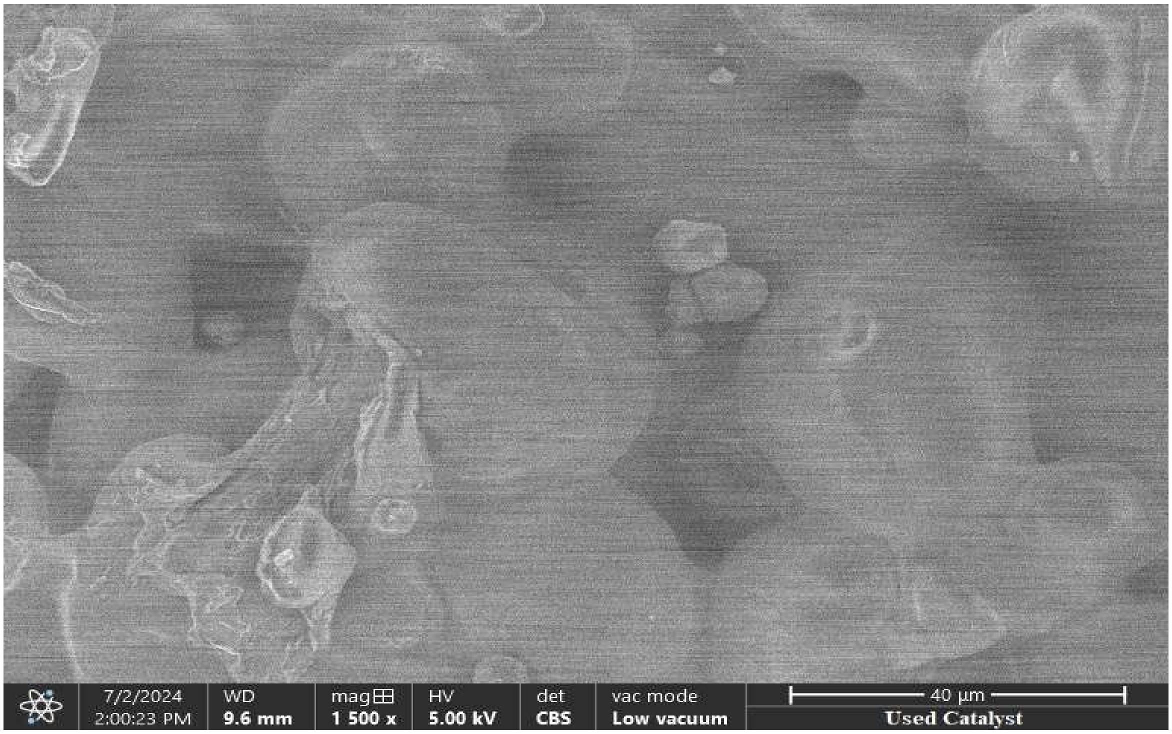


Fig. 3.3c: Surface morphology of of the Al-CHNC at 1500 magnification

4.0 Conclusion

The novel Aluminium cow horn nanocatalyst (Al-CHNC) was successfully prepared with higher surface area when compared with conventional cow horn catalyst (CHNC) via BET analysis. The catalyst demonstrated higher catalytic activity in the transesterification reaction of non-edible neem seed oil to biodiesel. XRF analysis for calcination of cow horn catalyst at 800 °C yielded more calcium oxide (41.644%) compared to at 700 °C (40.758%). The SEM analysis also revealed well dispersed Aluminium on the surface of cow horn. Also, the XRD revealed a crystalline nature of the novel Al-CHNC.

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