Effect of Calcination Temperature on the Structural and Catalytic Efficiency of APSR-DerivedCaOfor Biodiesel Production

Abstract

This study aimed to investigate the effect of varying the calcination temperature of calcium oxide (CaO) based biocatalysts for biodiesel production from low-cost feedstock (African Periwinkle Shell Residue, APSR). The synthesized APSR-derived biocatalyst was characterized through Energy Dispersive X-ray spectroscopy (EDX), Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), and Fourier Transform Infrared spectra (FTIR). The catalytic strength was examined via catalyzed transesterification of soybean oil. The results indicate thatthe mass fraction of the main element (Calcium, Ca) present in the APSR, increased with temperature. Likewise, the morphological composition and percentage composition of crystalline phases (CaO, SiO_2 and calcite) of the derived biocatalyst increased with the increase in calcination temperature. Catalytic testing showed that the biodegradation of triglycerides in soybean oil was able to aid the conversion of oleic acid to biodiesel. The results of this study suggest that the composition and efficiency of CaO are dependent on the calcination temperature.

Keywords: Calcination temperature, African periwinkle shell, characterization, catalytic efficiency, biodiesel yield

1. Introduction

Growing concerns about environmental pollution, fuel security and sustainability have driven immense interest in biodiesel as a renewable alternative fuel. Biodiesel is a non-toxic, biodegradable fuel that can be produced from plant oils and animal fats through processes such as supercritical methanol, micro-emulsion, and catalytic transesterification(Oloyede et al., 2022). However, transesterification is the most widely used method. In the transesterification reaction, triglycerides in the oil react with an alcohol like methanol or ethanol in the presence of a catalyst to form fatty acid alkyl esters, commonly known as biodiesel, and glycerol as a byproduct(Pathak et al., 2018).Calcium oxide (CaO) is a promising heterogeneous base catalyst that has been extensively studied for biodiesel production through transesterification from various biomass residues due to its advantages over homogeneous catalysts(Odude et al., 2017). The CaOdisplays high catalytic activity and reusability. However, its catalytic activity and efficiency can be influenced by factors related to the preparation and treatment of the CaOfeedstock.

A Calcination temperature is the exact temperature at which amaterialsheated, which causesthermaldegradation,phase transition, or removal of volatilecomponents and usually resultsin the formation of oxidesandother stable forms. In preparation of green heterogeneous catalyst from agricultural residues or waste, calcination of biomaterials over a range of temperature has been an effective approach(P. U. Okoye et al., 2019). The calcination temperature at which CaO is heated during synthesis from agricultural residue source has been shown to significantly impact its surface properties and catalytic behavior.Previous researcherssuch as Okoye et al.(2019) andOloyede et al.(2023)hadsynthesized CaOfrom periwinkle shell over a range of temperatures from 300°C to 800°C. Results indicate catalytic activity is affected by calcination temperature up to an optimal point due to improved surface properties like basicity and porosity. However, the specific calcination temperature that maximizes the catalytic efficiency of CaO for biodiesel transesterification has not been definitively established and may depend on reaction parameters. Furthermore, characterizing how calcination temperature influences physiochemical properties like surface area, morphology and crystallinity could provide insights into structure-activity relationships.

This study aimed to systematically investigate the effect of varying the calcination temperature ofCaO-based catalysts from 900°C and 1000°C for biodiesel production from low-cost feedstock (African Periwinkle Shell Residue, APSR). The findings seek to determine the optimal calcination temperature for maximizing biodiesel yields and provide knowledge to rationally design CaO biocatalysts with enhanced activity. Optimized heterogeneous catalysts could help advance the commercial viability and scale-up of biodiesel as a renewable transportation fuel.While CaO-based biocatalyst derived from periwinkle shell had shown promise as an effective heterogeneous base catalyst for biodiesel production via transesterification, the factors influencing its catalytic activity and efficiency have not been fully elucidated. In particular, the calcination temperature used in the synthesis of CaO-based biocatalysts may strongly impact the catalyst's physicochemical properties and performance, yet the optimal temperature for maximizing catalytic efficiency remains uncertain. Determining the calcination temperature that yields a CaO biocatalyst with the highest activity is important for developing an economically viable biodiesel manufacturing process. However, the relationship between calcination temperature, catalyst structure and activity has not been thoroughly studied.

2. Materials and methods

2.1 Sample Collection and Preparation

African Periwinkle shell residue (APSR) was sourced for from one of the regions (Ebute-pare, $6^{o}21^{1}$N $4^{o}47^{1}$E) in Ondo State, because of their abundance in these region. The residue was washed with water to remove dissimilar materials and then sundried for three days. The sundried residue was oven dried at 100^{o}C until a constant weight was obtained(Oloyede et al., 2022). The sample was milled into powder via an attrition mill and sieved using a sieve with aperture size of 150 μm in laboratory mechanical shaker machine. The sieved sample was kept in air tight container for further analysis (Falowo et al., 2019).

2.2 Synthesis of CaO biocatalyst from APSR

The CaO was synthesized from APSR via calcination of 200 g each of a milled APSRsample at two different calcination temperatures of 900 and 1000 □, respectively in a muffle furnace (Fig. 1a) with retention time of 4 hours. This is to remove carbonaceous and volatile matter from the milled APSR and obtain a fine ash (CaO). The calcined ash sample

(Fig. 1b) was kept in a desiccator and then in Ziploc bag(an air tight bag) for further studies(Oladipo & Betiku, 2020):(Oloyede et al., 2023).

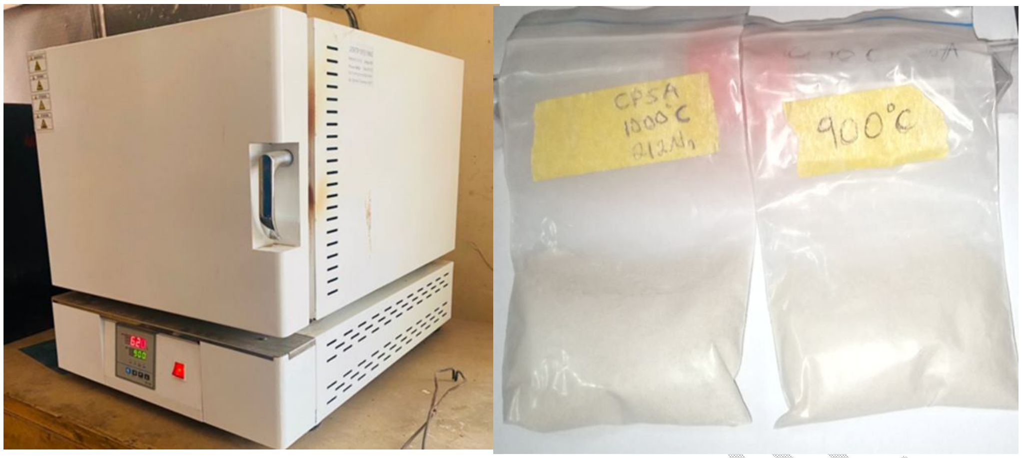


Figure 1: (a) Smokeless Muffle furnace (b) Synthesized CaO biocatalyst in ziploc bags.

2.3 Characterizationof APSR Derived CaO Biocatalyst

The synthesized APSR derivedCaO biocatalyst at the two varying calcination temperatures were characterized through Energy Dispersive X-ray spectroscopy (EDX), Scanning electron microscopy (SEM), X-ray diffraction analysis (XRD), Thermogravimetric analysis (TGA), and Fourier Transform Infrared spectroscopy (FTIR). These were done to test for the elemental composition, morphology, crystalline structures, thermal stability, and active surface functional group presents in the catalyst sample follow the procedure reported byBetiku et al.(2017) andEtim et al.(2018). The SEM-EDX was done using scanning electron microscope instrument (JEOL JSM-7600F, Japan) with a Gatan alto 2500 Cryo system. Rigaku Miniflex 600 (Miniflex, Japan) was used to determine the crystalline structure of each catalyst. The XRD was measure over Cu-Kα_2 radiation at a wavelength of 1.5444 □, 45 kV voltage and 40 mA current. The samples were scanned at a speed of 5°/min in the 2θ range of 5 – 76°. The catalyst active surface functional were determined using FTIR spectrophotometer (Thermo-Nicolet iS10) measured in the wavelength range of 4000-400 cm^{-1}. The FTIR spectral of the samples were obtained in the wavelength range of 4000-400 cm^{-1}. The catalyst characterization was carried out at the National Research Institute for Chemical Technology (NARICT) laboratory, Zaria, Nigeria.

2.4 Catalytic strength of the APSR derived CaO Biocatalyst

The catalyzed transesterification of soybean oil was used to examine the strength of the APSR derived CaO biocatalysts. The transesterification of the oil was conducted in a three necked round bottom flask of 500 ml equipped with a reflux condenser, heating source controller, thermometer, and magnetic stirrer (Fig.2a) The transesterification procedure was carried out under the reaction condition with a methanol-to-oil ratio at 1:6, catalyst concentration at 7.0 wt.%, reaction temperature at 60 °C and reaction time of 60 minutes at an agitation of 750 rpm. At the end of the reaction, the catalyst was recovered through filtration using Wartman filter paper (100 microns)(Oloyede et al., 2023). The mixture was then poured into a separating funnel and allowed to separate into two distinct layers, with the top layer being the biodiesel and the lower layer being glycerol (Fig.2b).

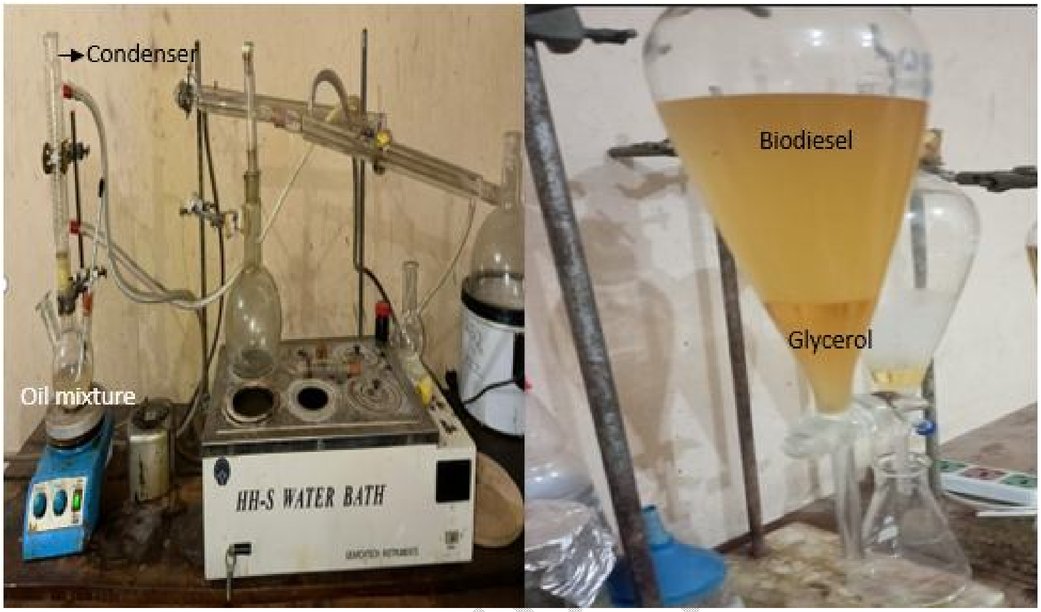


Figure 2. (a) Transesterification set-up, (b) Biodiesel mixture

2.5 Determination of Biodiesel Yield

The biodiesel yield obtained from the catalytic testing of the APSR derived CaObiocatalysts was calculated using equation 1(Etim et al., 2020).

$$B_y\ (\%) = \frac{W_b}{W_o} \times 100 \qquad 1$$

Where: B_y = *Biodiesel yield*
W_b = *Weight of biodiesel produced*
W_o = *weight of oil used*

2.6 Data Analysis

The SEM micrograms were analyzed using Imagej software and the data obtained were statistically analyzed using frequency distribution in Origin software(Version 2021) to show the occurrence of particle sizes in relation with calcination temperatures. The graphs were also drawn using Origin software.

3. Results and Discussions

3.1 Effect of calcination temperatures on elemental composition of APSR derived CaO biocatalyst

The effect of calcination temperatures (900 and 1000□) on the elemental composition of the CaO-based biocatalyst is presented in Fig. 3. It was observed from the Figure that as calcination temperature increased, the percentage mass fraction of calcium (Ca), increases.

The mass fraction of Ca increased from 94.31 to 95.50 $wt.\%$ at 900 and 1000℃, respectively. The Figure also detailed that the raw sample of APSR contained 92.23 $wt.\%$ of Ca. The increase in mass fraction of Ca, in the calcined ash sample (CaO derived catalyst) of APSR from 94.31 to 95.50 $wt.\%$ could be attributed to the removal of organic matter and volatile impurities during the calcination process, leading to a higher concentration of calcium in the remaining material.Okoye et al.(2020) stated that at higher calcination temperatures, there might be enhanced decomposition of organic components, further concentrating the Ca content in the sample. The other metallic element such as Sodium (Na), Magnesium (Mg), and Aluminum (Al) were present as trace elements. Thus, shown that Ca is the main metal present in the calcined APSR. Oloyede et al. (2022) reported similar mass fraction of 60.60 $wt.\%$ for calcined African periwinkle shell derived ash catalyst at 800℃.

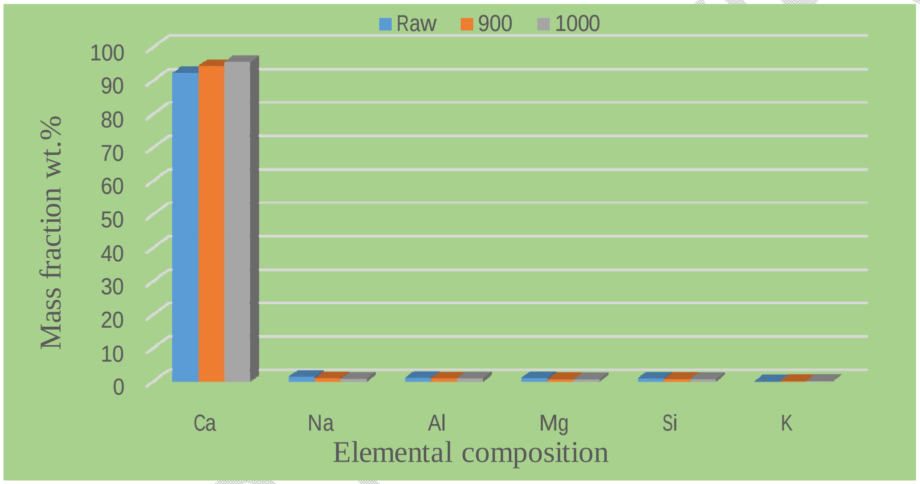


Figure 3: Effect of calcination temperature on elemental composition of raw and calcined ash samples of APSR.

3.2 Effect of calcination temperature on morphological analysis of APSR derived CaO biocatalyst

The effect the calcination temperature on morphological character of the synthesized CaO-based biocatalyst was explained using the particle sizes and their nature. The relationship between the calcination temperature and the size of the CaO-based biocatalyst is statistically given in Figures 4. It was observed from the Figures that the particle size in term of length ranged between 0-100 μm is higher at calcination temperature of 1000℃ than at 900℃. At both temperatures, the occurrence of the particle sizes ranged between 100-200 μm are similar. While no particle size observed for between 200-500 μm, however, particles having size of 500 μm at frequency between 0-1.0 occurred at 900℃. This implies that the particle size in the micrograms changes with increase in temperature. Also, the particles area as observed in Fig. 5 increased with increased in temperature. The occurrence of the particle area decreased from 58 to 3 with corresponding particle area of 0 to 1000 $\mathbf{\mu m^2}$ as calcination temperature increased from 900 to 1000□. At frequency of 2.0, the constant particle area between 2000 to 4000 $\mu\mathbf{m}^2$ was observed in the CaO-based biocatalyst. It was similarly observed that the morphology at both temperatures exhibits a microporous nature. Moreover, increasing the calcination temperature to 1000°C further enhances the particle area of the biocatalyst. Thus, elevating the calcination temperature within the examined range results in a more developed porous network structure and enhanced micro-porosity or crystallinity in the resulting CaO-based biocatalyst. Nath et al.(2019)reported similar morphological observation for *Brassica nigra* derived biocatalyst for transesterification of soybean oil which showed particle agglomeration and the presence of layered spongy stringy microstructures in the derived catalyst.

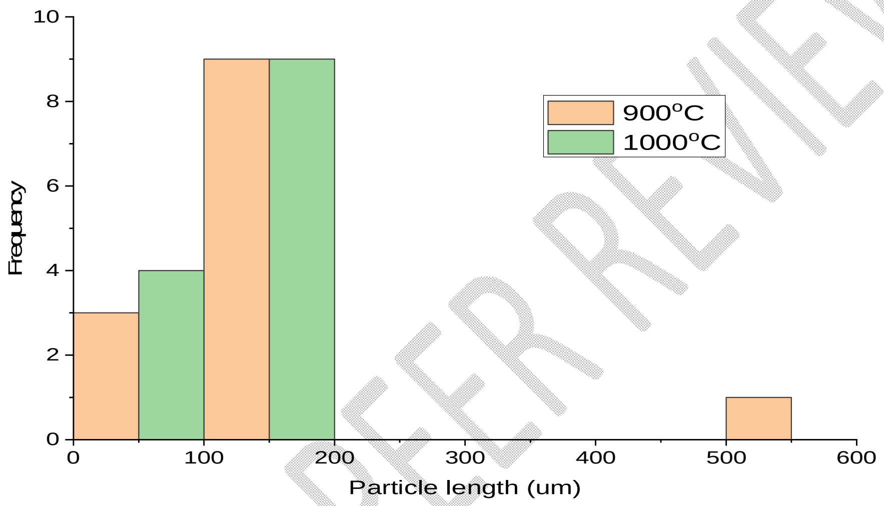


Figure 4: Effect of calcination temperature on particle length.

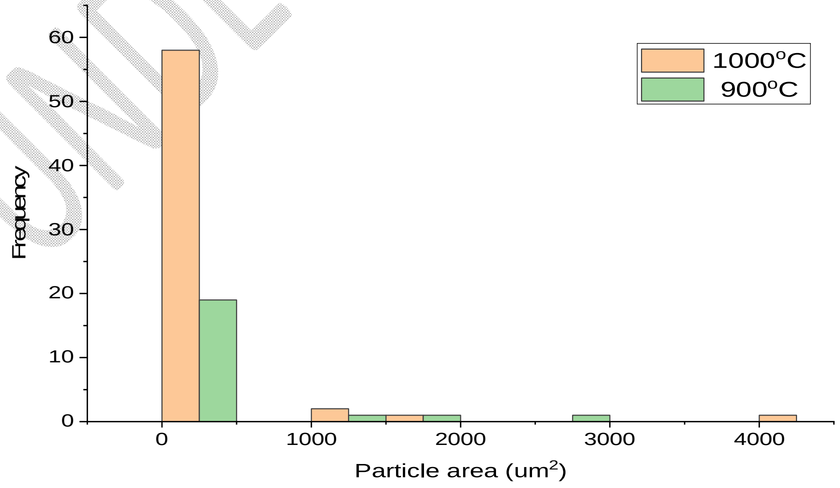


Figure 5: Effect of calcination temperature on particle area.

3.3 Effect of calcination temperature on Crystalline phase of APSR derived CaO-based biocatalyst

The Figure 6 presented the effect of calcination temperature on crystalline structures of the APSR derivedCaO biocatalyst.As shown from the figure, the crystalline phases of CaO (lime) present in the derived catalyst (CaO) increased with the increased in calcination temperatures. The percentage occurrence (88.3%) of the CaO phase was higher at 1000℃ than at 900℃ which has percentage occurrence of 85% for CaO. This implies that increase in calcination temperature led tocrystalline phase of CaO. However, the histogram shown that there is no much significant difference between the two temperatures. The crystalline phases of aragonite (C_aCO_3 and S_iO_2) present in the derived catalyst were also affected by calcination temperature. The $CaCO_3$ and SiO_2 decreased with an increased in temperature with percentage occurrence of 2 and 13.2% at 900℃ and 1.2 and 10.5% at 1000℃. Oloyede et al. (2022) obtained similar composition of phases for APS calcined as 800℃ with percentage occurrence of 61.1%. Suryaputra et al.(2013) reported similar phases of CaO and calcite in Capiz shell calcined at 900 ℃. This shows that the crystalline structure of the derived CaO biocatalyst is temperature dependent.

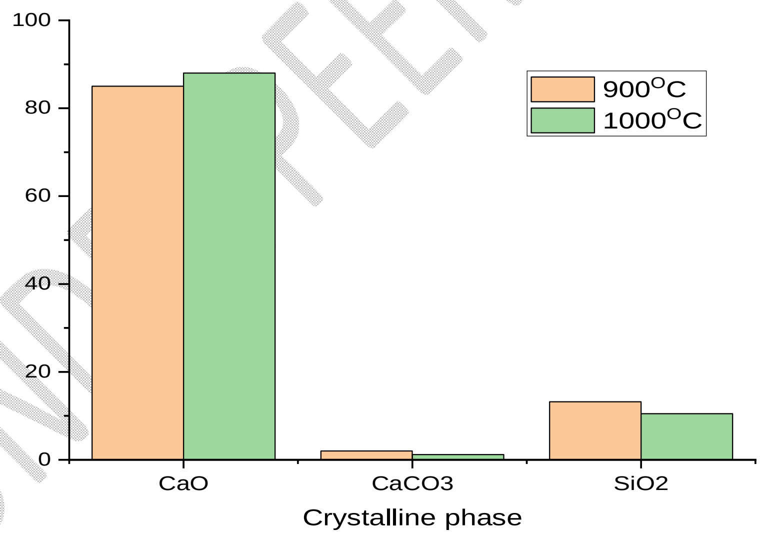
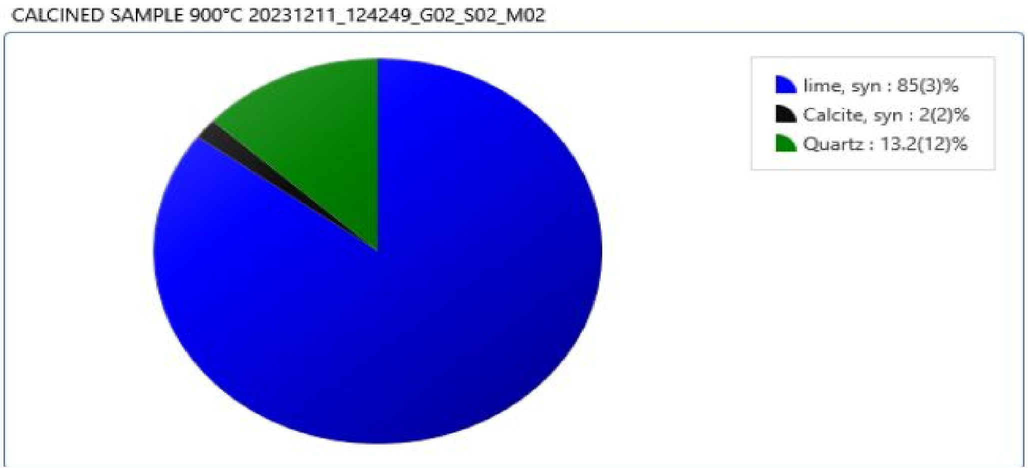
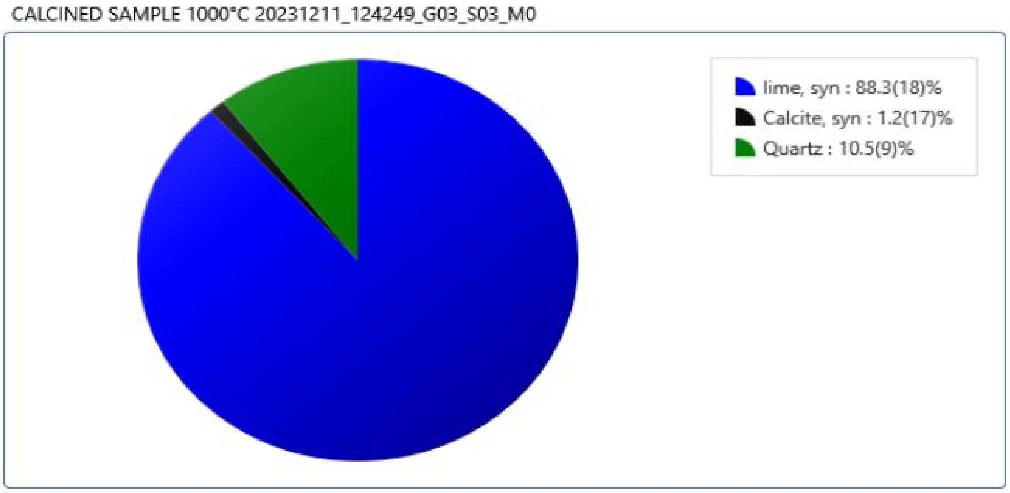


Figure 6: Effect of calcination temperature on crystalline phase of CaO-based biocatalyst.

Figure.7 Pie chart showing concentration of calcined sample





3.4 Effect of calcination temperature on functional group present inAPSR derived CaO-based biocatalyst

The FTIR pattern of the derived CaO-based biocatalyst at calcination temperature of 900 and 1000℃ were presented inFig.8a-b, respectively. The strong peak at 3041.0$cm^{-1}$for the two temperatures revealed band that represent the C=O group in CO_3^{2-}. Boonyuen*et al.* (2018) also identified the presence of C=O group in the raw sample of *Turbo jordani*shells. The othercharacteristics absorption peaks positioned at 2974.4, 2117.1, 1408.9, 1066.0, and 875.9 cm^{-1} represent the stretching vibrations of C-O group also in CO_3^{2-} and Ca-O which suggests the presence of CaO and aragonite. This implies that calcination temperature did not significantly affect the position of functional group present in the synthesized biocatalyst. Oloyede et al. (2022) also reported similar stretching vibrations for calcined APSR at 800℃ for peaks at 721.05, 897.35 and 1600.65cm^{-1} that are due to the stretching vibrations of Ca-O and Na-O bonds suggesting the presence of CaO and Na_2O in the calcined ash sample derived catalyst. Similar observation was detailed by Nath et al. (2019) for the calcined *Brassica nigra* ash catalyst which shown the stretching vibration of Ca-O and K-O bonds at infrared peak of 624 cm^{-1}.

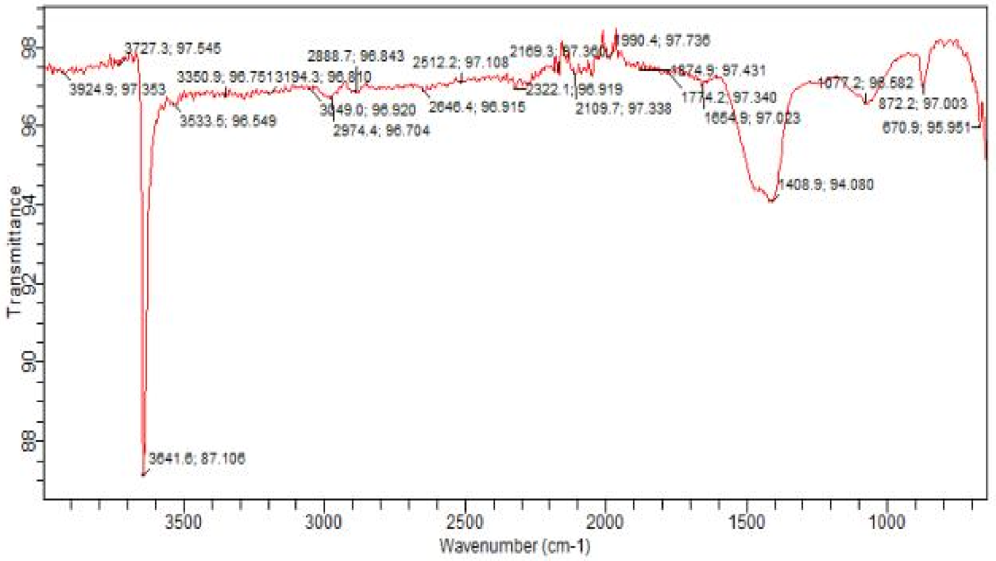


Figure 8a: The FTIR spectra of derived APSR CaO biocatalyst at 900□.

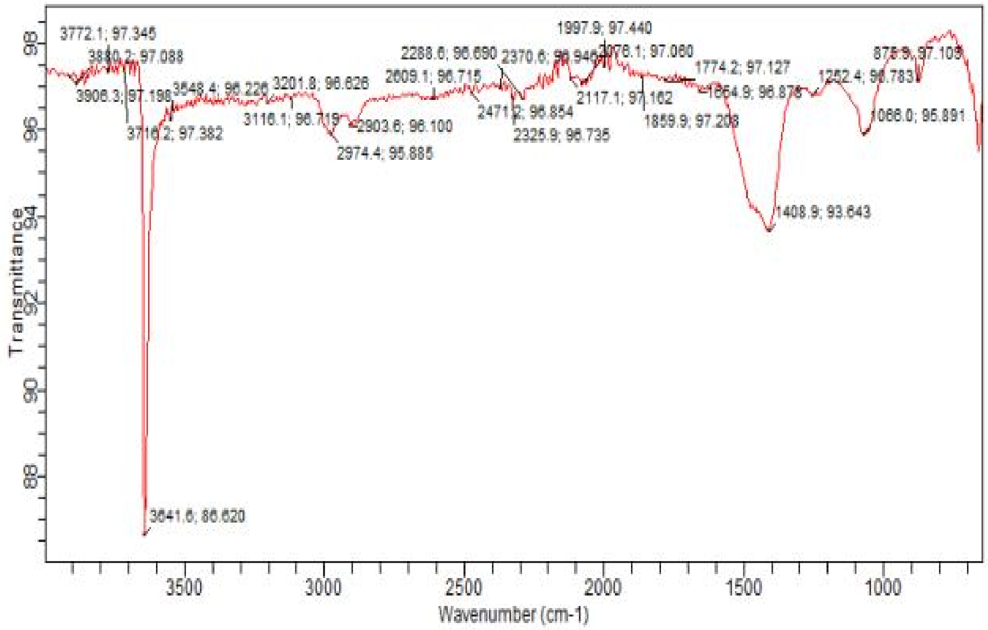


Figure 8b: The FTIR spectra of APSR derived CaO biocatalyst at 1000□.

3.5 Effect of calcination temperature on catalytic efficiency of synthesized CaO-based biocatalyst

The catalytic strength of the APSR derived CaO biocatalyst at the calcination temperature(900 and 1000□), was examined through transesterification of soybean oil. It was observed that the APSR derived biocatalyst was able to aid the conversion of triglycerides in soybean oil to biodiesel (Fig2). The biodiesel yield was 92.4 and 95.2 wt.%at 900 and 1000□, respectively. This shown that the biodiesel yield increased with an increase in calcination temperature. The increase in biodiesel yield maybe as a result of the percentage occurrence of CaO phase in the APSR derivedCaObiocatalyst as contained in XRD at temperature of 1000□. The yield of biodiesel at the two temperatures are greater than the reported yield by Okoye et al. (2019) when calcined periwinkle shell at 500□ was used to produce biodiesel. Comparing the biodiesel yield obtained using APSR derivedCaO biocatalyst with the one produced using KOH(homogeneous catalyst) which has a yield of 96.3 wt.%. It was observed that there is no much significant difference between the yields of biodiesel produced using synthesized CaO biocatalyst and that of KOH.

4. Conclusion

This study examined the effect of calcination temperatures on characterization of synthesized CaO-based biocatalyst from African periwinkle shell residue for biofuel production. The following conclusions were drawn, based on the experimental results:

i. The increase in calcination temperature affects the mass fraction of the elemental composition present in the APSR derivedCaO-based biocatalyst and Ca being the major element present in the sample. Likewise, the biocatalyst morphological composition, and crystalline phases, were affected with increase in calcination temperature. However, the calcination temperature has no effect on the functional group present in the synthesized biocatalyst.

ii. Catalytic testing showed the synthesized APSR CaO biocatalyst effectively convert soybean oil to biodiesel via catalysed transesterification. The biodiesel yield increased with increased in calcination temperature.

iii. Hence, the study concludes that the composition and efficiency CaO derived biocatalyst is dependent on the synthesized calcination temperature. Likewise, to develop a green CaO for APSR, an optimum calcination temperature of 1000□ is recommended. Moreover, further studies on the stability of APSR CaO derived biocatalyst is also recommended.

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