



Research article

Modification and characterization of chicken eggshell for possible catalytic applications

Omojola Awogbemi^{*}, Freddie Inambao, Emmanuel I. Onuh*Discipline of Mechanical Engineering, University of KwaZulu-Natal, Durban 4041, South Africa*

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ABSTRACT

Researchers have shown considerable interest in finding a sustainable, low cost, and readily available substitute for the commercial calcium oxide (CaO) catalyst. In this work, raw chicken eggshell was modified by boiling and calcination at 900 °C for 3 h. The x-ray diffraction characterization revealed that while the proportion of CaCO₃ in the raw and boiled samples was found to be 79.3 % and 99.2 % respectively, the CaCO₃ had been converted to 63.8 % CaO and CO₂ in the calcined sample. This was due to the thermal decomposition during calcination. The outcome of the infrared spectroscopy showed that the raw and boiled chicken eggshell presented a similar absorption profile with peaks at 1 394 cm⁻¹, 873 cm⁻¹, and 712 cm⁻¹, which were as a result of the presence of asymmetric stretch, out-of-plane bend, and in-plane bend vibration modes. The major peaks presented by the calcined sample at 3642 cm⁻¹ can be attributed to the OAH stretching vibration and bending hydroxyl groups present in Ca(OH)₂. The Brunauer-Emmett-Teller surface areas for the raw, boiled and calcined chicken eggshell were found to be 2.33 m²/g, 3.26 m²/g, and 4.6 m²/g respectively, indicating increased catalytic activity of the calcined sample. Overall, boiling was found to have a negligible effect on the chicken eggshell, while high-temperature calcination greatly affected the pore size, surface area, composition, and thermal decomposition profile of the chicken eggshell sample.

1. Introduction

Increased population growth, change in lifestyles, urbanization, and many other reasons, have precipitated an upsurge in the global demand for energy in the last few decades. This increased demand for energy, environmental concerns, depletion in fossil fuel reserves, instability in the global oil price, continuous increases in the price of fossil-based petroleum products, high cost of exploration, and unacceptable combustion and performance of fossil-based fuels in internal combustion engines has led to an urgent search for sustainable alternative fuel to substitute fossil-based fuel [1]. Among the biofuel family, biodiesel appears to have gained considerable informed attention. Biodiesel, because of its renewability, biodegradability, non-toxicity, and ease of handling and transportation, has gained prominence as one of the leading candidate alternative fuels for compression ignition engines.

The catalyzed transesterification reaction is an easy and commonly used technique for biodiesel synthesis. The transesterification process is achieved with the help of homogeneous and heterogeneous catalysts. The application of a homogeneous alkali catalyst has been found to engender high conversion efficiency with reduced reaction time, moderate

temperature, and at approximately atmospheric pressure. The difficulties in catalyst separation, corrosion of refining infrastructure, high energy consumption, generation of wastewater, and soap formation have, however, made this catalyst less attractive [2]. The use of solid heterogeneous catalysts is not only environmentally benign, less corrosive, reduces environmental challenges, avoids difficult catalyst separation problems, allows recoverability and reusability, is highly stable, has less leaching effect, and is easily disposed of, but also cost-effective [3, 4]. In order to ensure that biodiesel production is more cost-effective, the conversion of some household wastes into a form of catalyst to replace the commercially available catalysts has been proposed. A good example of such waste material is chicken eggshell, which is a proven source of CaO for biodiesel synthesis.

Chicken eggshell is obtained when eggs are broken for consumption and after hatching of an incubated egg [5]. Chicken eggs belong to the animal product category and consist of yolk, white, and a protective shell. Chicken egg is a common food item that is rich in protein, minerals, and vitamins. Chicken eggs are consumed in scrambled, boiled, or fried forms and are used in households, restaurants, bakeries, confectionary outlets as well as for other social, industrial, and religious purposes. China, The

^{*} Corresponding author.

E-mail address: jolawogbemi2015@gmail.com (O. Awogbemi).

United States of America (USA), and India were among the leading chicken egg producers in 2018, producing 458, 109, and 95 billion eggs respectively [6]. Per capita annual chicken egg consumption in the USA is projected to increase from 242.8 per person in 2010 to 289.9 in 2020 [7]. According to statistics released by the United Nations Food and Agricultural Organization (FAO), the average per capita egg consumption for most countries, computed in kilograms per year (shell weight) has continued to increase over the years. Figure 1 shows the average per capita egg consumption of some selected countries from 2010 to 2017.

Shells of these eggs constitute an environmental nuisance and end up in dumpsites. A chicken eggshell weighs 5 g–6 g on average and contains about 85 %–95 % calcium carbonate (CaCO_3), 1.4 % magnesium, and other elements in trace percentages. Among the numerous types of food waste, eggshells possess many bioactive composites and other valuable minerals of proven commercial significance, but which can become hazardous if not appropriately handled and disposed of [9]. Chicken eggshells can be treated and modified to improve their value and efficiency. Investigations have revealed that chicken eggshells which hitherto have been considered as dumpsite waste can be recovered, reused, and regenerated to enhance their applications. Various researchers have experimented with the utilization of chicken eggshells as an environmentally friendly catalyst for transesterification reactions with good and encouraging outcomes [10, 11, 12, 13].

With an increased interest in the utilization of chicken eggshells to catalyze a transesterification reaction, the pertinent question to ask, which forms the motivation for the current investigation, is how well has chicken eggshell been modified and characterized. The techniques adopted for the modification of the chicken eggshell were boiling and calcination. Calcination stimulates catalyst generation and modification by way of the enhancement of key catalytic fingerprints and other performance criteria including basic/acidic site densities, surface area, pore volume, molecular and crystalline structure [11, 13, 14]. The present study aimed to modify and characterize chicken eggshells to gain more insight into the behavior of chicken eggshells when subjected to various characterization techniques. In the present effort, calcium oxide (CaO) was synthesized from raw, boiled, and calcined waste chicken eggshell powder and subjected to characterization. The outcome of the characterization was analyzed, compared, and discussed.

2. Materials and methods

2.1. Materials collection

Chicken eggshells were gathered from restaurants and bakeries within the central area of the city of Durban, KwaZulu-Natal province, South Africa. The spent shells were accumulated from daily use and

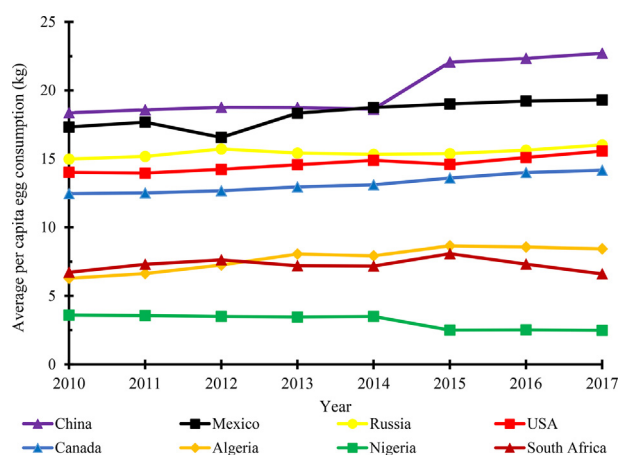


Figure 1. Average per capita egg consumption, 2010 to 2017 (kg) (in shell weight). Adapted from [8].

transported to the laboratory in a sealed plastic bag. Figure 2 shows the waste chicken eggshells as gathered from the bakeries and restaurants.

2.2. Preparation

The waste chicken eggshells were washed in hot (40 °C) tap water to remove any dirt and other foreign objects adhering to the body of the shells. The internal white membrane in the shell was detached and the shell was thoroughly rinsed with ionized water. The clean eggshells were divided into three portions. The first portion was dried in an oven maintained at 100 °C for 3 h to eliminate any left-over water in the eggshell. The dried eggshells were manually crushed using pestle and mortar and mechanically pulverized using a laboratory grinder. The powder was passed through a 75 μm sieve mesh, poured into a dry clean bottle, sealed, and marked as the raw sample.

The second portion was boiled for 30 min using tap water and an electric stove. The boiled shells were oven-dried at 100 °C for 3 h thus removing any left-over moisture in the boiled eggshell. The boiled eggshells were dried in the oven maintained at 100 °C for 3 h, manually crushed into smaller pieces then pulverized into fine particles by a laboratory mechanical grinder, and sieved using a 75 μm mesh. The pulverized boiled eggshell powder was poured into a glass vial, sealed tightly, and labeled appropriately.

The third portion was dried in the oven maintained at 100 °C for 3 h, ground manually in a mortar, pulverized in a mechanical grinder into a fine powder, and sieved using a 75 μm screen mesh. The sample was thereafter calcined in a furnace maintained at 900 °C for 3 h to allow for the total breakdown of the CaCO_3 in the eggshell into CaO [15], according to Eq. (1). The calcined sample was cooled to room temperature before withdrawing it from the furnace, and poured into a glass vial, sealed firmly, and labelled appropriately. The raw, boiled, and calcined samples were kept in closed glass bottles away from contamination with water and carbon dioxide [15, 16, 17]. The three samples were subjected to characterization by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA)/Derivative thermogravimetric (DTG), scanning electron microscope (SEM), and Brunauer-Emmett-Teller (BET). Figure 3 shows the raw, boiled, and calcined chicken eggshell powder before being poured into sealed glass vials. The flowchart for the preparation of the samples is illustrated in Figure 4.



2.3. Characterization

The three chicken eggshell samples were characterized by XRD, SEM, TGA/DTG, FTIR, and BET.



Figure 2. Chicken eggshell as received.



Figure 3. Sample of (a) raw, (b) boiled, (c) calcined chicken eggshell powder.

2.3.1. Thermal analysis

The thermal behaviours of the three chicken eggshell samples were analyzed by a DTG (DTG-60AH, Shimadzu) and TGA (TA-60WS, Shimadzu) thermal analyzer. About 10 mg of dry powder of each sample was scanned between the temperature range of 20 °C to 1000 °C, the heating rate 20 °C/min, and under nitrogen atmosphere at a flow rate of 20 ml/min in a simultaneous TGA and DTG analyses. The data were analyzed using a TA-60 ch 1 DTG-60AH workstation.

2.3.2. Spectroscopic analysis

In order to obtain a recognizable absorption spectrum, the dilution and homogenization of the dried chicken eggshell samples with KBr (spectroscopic grade), were carried out with additional grinding and mixing in an agate mortar. Discs (12.7 mm ID and ≈1 mm thick) were prepared in a manual hydraulic press (model 15.011, Perkin Elmer Co., USA) at about 10 tonnes for a pressing time of 30 s–60 s. The spectrum was measured and recorded from 300 cm⁻¹ to 4000 cm⁻¹ on a

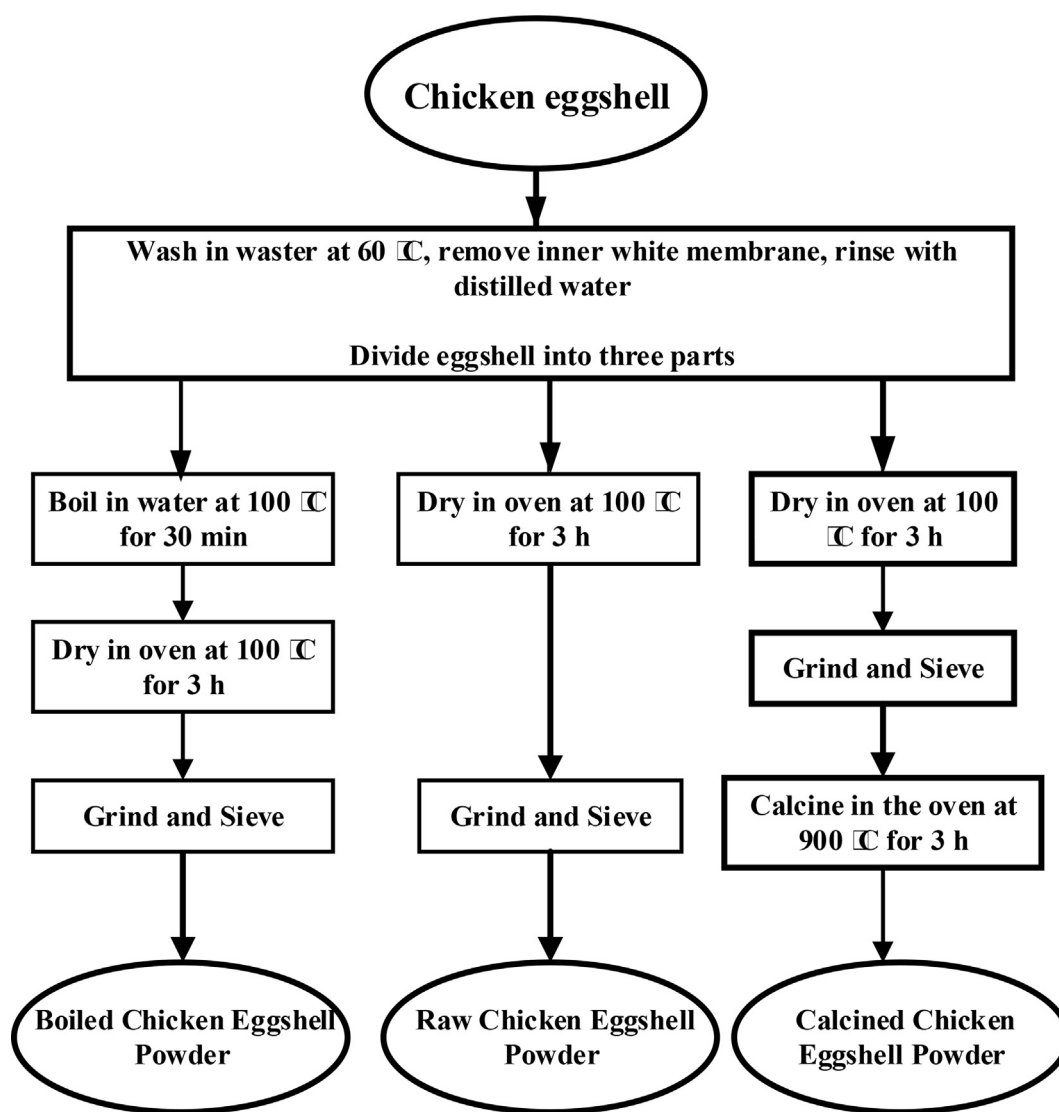


Figure 4. Flowchart of modification of chicken eggshell.

spectrometer (model system 1000 FTIR, Perkin Elmer Co., USA) with a resolution of 2.0 cm^{-1} .

2.3.3. XRD analysis

The samples were prepared on a Quorum Q150A ES sputtering machine and coated with a thin, electric conductive gold film at a density of 19.32 g/m^3 using nitrogen as a carrier gas before analysis. The XRD analysis was performed on a PANalytical Empyrean diffractometer with High Score Plus software version 3.0d. The porous properties of the three chicken eggshell samples were determined from the measurement of N_2 adsorption-desorption isotherm.

2.3.4. SEM analysis

The SEM analysis was carried out on an Ultra Plus Field Emission Gun Scanning Electron Microscope. The samples were affixed via carbon tape to the SEM sample holders and vacuum-coated with a 20-nm layer of platinum. SEM was performed at 15 kV and room temperature. The average pore size was calculated with image analysis software (Zeiss Ultra Plus).

2.3.5. BET analysis

The textural properties of the eggshell samples were obtained through BET analysis by a Quantachrome Instrument (Autosorb-1 Model No. ASIMP.VP4, USA) using N_2 adsorption-desorption isotherms at $-196\text{ }^\circ\text{C}$. The BET surface area (m^2/g), total pore volume (cm^3/g at STP), and average pore radius (\AA) were thus obtained by the N_2 adsorption data. The pore size distribution was calculated based on the differential pore volume of Barrett-Joyner-Halenda (BJH) adsorption-desorption. About 0.35 g of the dry eggshell powder was degassed prior to analysis. All measurements were carried out in duplicates.

3. Results and discussions

Upon physical examination, while both the raw and boiled chicken eggshell powder appeared white, the raw sample appeared greyish compared to the boiled eggshell sample. The grey colour can be ascribed to the existence of calcite (CaCO_3) in the samples. The CaCO_3 is converted to CaO during calcination and CO_2 is given off in the process according to Eq. (1). This explains the change of color of the calcined sample to light white [18, 19]. The outcomes of the characterization of the samples by XRD, SEM, TGA/DTG, FTIR, and BET are presented.

3.1. SEM analysis

The effects of boiling and high-temperature calcination on the surface morphology of chicken eggshell powder were performed by SEM analysis. The result is shown in Figure 5. The SEM images of raw and boiled chicken eggshell samples displayed identical particle morphology. Both samples comprised of particles of irregular sizes and shapes. The boiled samples, however, presented more irregularly shaped particles in

comparison with the raw chicken eggshell sample. This can be attributed to the impact of the boiling on the sample. The modification of the raw chicken eggshell by boiling marginally spread the particles of the boiled sample. As a result of boiling, the particles became more scattered and irregular in shape than the particles of the raw chicken eggshell sample. The sizes of the eggshell particles became smaller and the particle shapes more smoothly arranged and cemented together after the calcination process. This might be due to the calcined sample being in the oxide state as evidenced by the presence of CaO. The changes in the structure of the calcined sample, when compared to those of the raw and boiled samples, can be as a result of the change in its composition. During calcination, the CaCO_3 in the raw and boiled samples was thermally decomposed to CaO and CO_2 [20]. Tan et al. [15] reported that calcination plays an important role in the morphology of chicken eggshell powder. They posited that calcined eggshell consists of small size particles and therefore larger total surface area. In comparison with CaO derived from waste chicken eggshells, commercial CaO presents wider particle size distribution while impregnated commercial CaO offers a more exfoliated morphology, which can translate to higher catalytic activities [21, 22].

3.2. XRD analysis

Figure 6 and Table 1 depict the XRD profile and XRD concentrations of raw, boiled, and calcined chicken eggshell samples. There is no significant difference in the profile of the raw sample and the boiled sample while the calcined sample presented a remarkably distinct XRD profile. The proportion of CaCO_3 in the raw and boiled sample was found to be 79.3 % and 99.2 % respectively with both samples having no CaO. In the calcined sample, the CaCO_3 was converted to CaO and Ca(OH)_2 . It can be seen that calcined waste chicken eggshell consists mainly of CaO and Ca(OH)_2 . The peaks indicating the formation of Ca(OH)_2 in the XRD profile are minimal. The conversion of CaCO_3 to CaO is as a result of the thermal treatment, represented by high-temperature calcination. The existence of Ca(OH)_2 in the calcined sample could be due to the outcome of the reaction of the CaO with air during packaging and analysis [23]. The conversion of CaCO_3 to CaO and Ca(OH)_2 in the calcined sample will improve its catalytic activity and efficiency in biodiesel production [24]. Due to incomplete thermal decomposition during calcination, 0.4 % CaCO_3 was recorded in the calcined sample. The presence of 20.2 % calcite magnesium in the raw sample can be traced to the contamination of calcite with magnesium [25, 26]. The peaks of the XRD profile of CaO derived from waste chicken eggshell, commercial CaO, and impregnated CaO appeared at the vicinity of 2θ value of 35 which confirms the presence of CaO [21, 27].

3.3. BET analysis

The textural properties, which consist of the surface areas, pore volume, and micropore volume of the eggshell samples, were determined using BET analysis. The results are presented in Table 2. It is clear that the

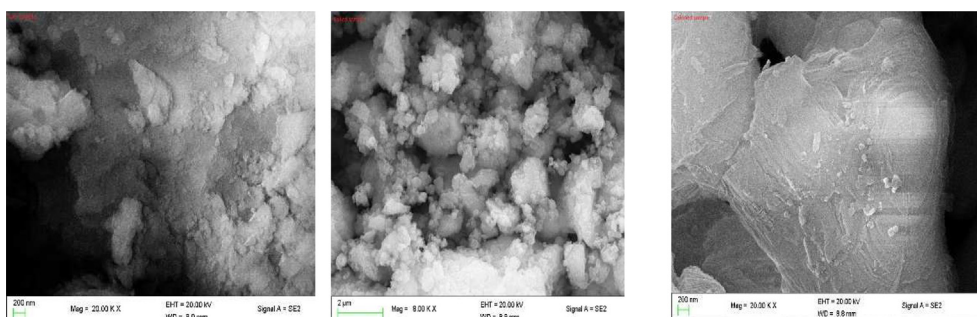


Figure 5. SEM images for (a) raw (b) boiled (c) calcined chicken eggshells.

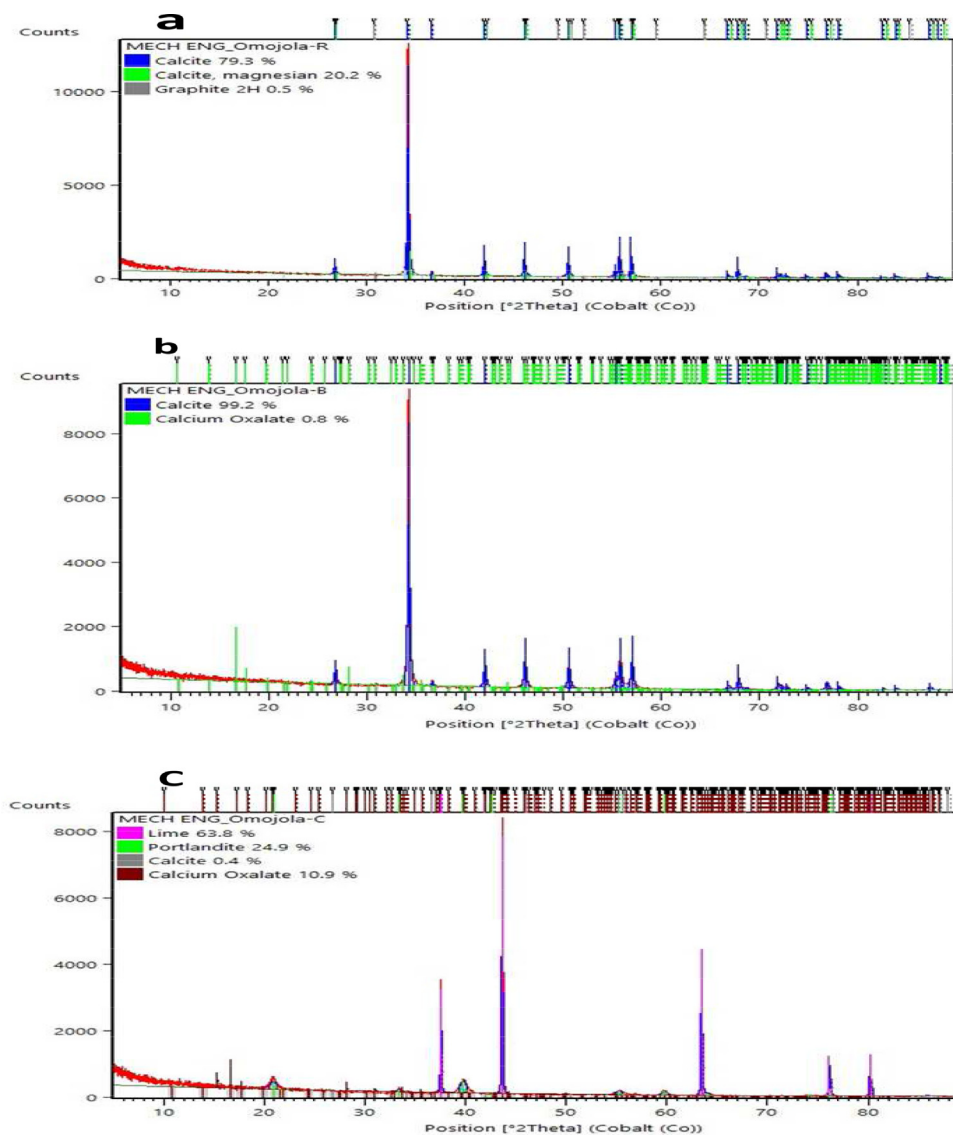


Figure 6. XRD profile of (a) raw, (b) boiled, and (c) calcined chicken eggshells.

Table 1. XRD composition of the samples.

Compound	Chemical formula	Chicken eggshell samples concentration (%)		
		Raw	Boiled	Calcined
Lime	CaO	-	-	63.8
Portlandite	Ca(OH) ₂	-	-	24.9
Calcite	CaCO ₃	79.3	99.2	0.4
Calcium oxalate	C ₂ H ₂ CaO ₅	-	0.8	10.9
Calcite magnesium	CaCO ₃ Mg	20.2	-	-
Graphite	C	0.5	-	-

BET surface area and the external surface area of the calcined chicken eggshell were greater than those of the uncalcined samples. Also, the BET surface area and the external surface area of boiled chicken eggshell powder was greater than that of raw chicken eggshell. It can, therefore, be concluded that modification techniques such as boiling and calcination of chicken eggshell powders lead to an increase in both the BET surface area and the external surface area [15]. The higher surface area of the boiled and calcined chicken eggshell compared to the raw and boiled samples is posited to have a direct encouraging effect on the catalytic activity of the eggshell powder as a transesterification process catalyst

Table 2. Textural parameters of the samples.

Properties	Chicken eggshell samples		
	Raw	Boiled	Calcined
BET surface area (m ² /g)	2.33	3.26	4.6
External surface area (m ² /g)	2.49	3.49	4.57
Average pore radius (Å)	115.67	138.28	116.06
Pore volume (cm ³ /g)	0.013473	0.029482	0.026708
Micropore volume (cm ³ /g)	-0.000105	-0.000204	-0.000004

[28]. The pore volume of the samples was discovered to be 0.013473 cm³/g, 0.029482 cm³/g, and 0.026708 cm³/g for the raw, boiled, and calcined sample respectively, indicating that the active site is near the external surface of the powder. This is expected to lead to better and quicker interaction between the catalyst and the feedstock. Commercial CaO has been found to be non-porous and presented BET surface area of 1.5 m²/g [29]. On the other hand, commercial CaO impregnated with aqueous potassium iodide solution and calcined was found to have a BET surface area of 5.66 m²/g. This is lower than the BET surface area of 2.33 m²/g, 3.26 m²/g, and 4.6 m²/g presented by CaO derived from raw, boiled,

and calcined chicken eggshells respectively. This is expected to make CaO derived from chicken eggshell to possess more catalytic properties than the commercial CaO. The high value of the pore radius suggests that the particle size of the eggshell powder should be further pulverized from the current 75 μm and reduced to nano-size for better catalytic activity. However, commercial CaO impregnated with aqueous potassium iodide solution and calcined was found to have BET surface area of 5.66 m^2/g [27] while commercial CaO modified with bromooctane/hexane solution recorded 68.6 m^2/g [22]. This was attributed to better surface exfoliation when compared with CaO derived from waste chicken eggshells. Impregnated CaO has been found to demonstrate a higher surface area than commercial one [21].

3.4. FTIR analysis

FTIR was used to examine the structure and the functional group of the samples. FTIR analysis was performed and compared for the raw, boiled, and calcined chicken eggshell powders as presented in Figure 7. The raw and boiled eggshell samples presented similar spectra which were remarkably different from the spectra from the calcined eggshell sample. The major absorption bands of the raw and boiled chicken eggshell samples, which were uncalcined, appeared at 1394 cm^{-1} , 873 cm^{-1} , and 712 cm^{-1} . This can be traced to the presence of asymmetric stretch, out-of-plane bend and in-plane bend vibration modes, respectively, for CO_3^{2-} molecules as expressed by Jazie et al. [30] and Laska et al. [31]. The absorption bands of the organic matter visible at 2513 cm^{-1} and 1795 cm^{-1} disappeared after calcination of the raw eggshell samples. The slight difference between the raw chicken eggshell and the boiled chicken eggshell samples was noticed in the absorption band appearing at 1071 cm^{-1} and 1092 cm^{-1} for the raw and boiled eggshell samples respectively. The calcined chicken eggshell showed a sharp stretching band at 3642 cm^{-1} which can be attributed to the existence of the OH^{-1} group [32]. Tan et al. [15] and Roschat et al. [33] also reported the formation of an absorption peak for calcined eggshell at 3642 cm^{-1} , corresponding to OAH stretching vibration and bending hydroxyl groups present in $\text{Ca}(\text{OH})_2$. During thermal treatment by calcination, the carbonate in the chicken eggshells is broken down to CaO and the absorption bands of CO_3^{2-} molecules can be seen to have migrated to higher energy as represented by 1403 cm^{-1} , 1065 cm^{-1} , 878 cm^{-1} , and 529 cm^{-1} . The reduction in the mass of the functional group attached to the CO_3^{2-} ions is believed to be responsible for this development. Available data from literature showed that commercial CaO witnessed spectral bands at 867 cm^{-1} and 1477 cm^{-1} comparable to that witnessed by CaO synthesized from waste chicken eggshell which was assigned to the vibration modes of mono and bidentate

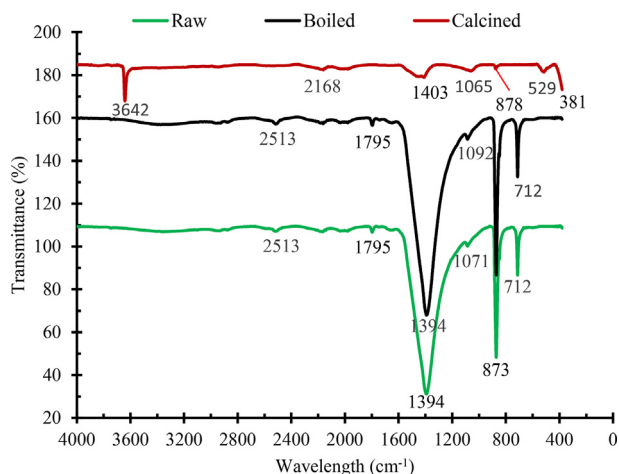


Figure 7. FTIR spectra for the chicken eggshells samples.

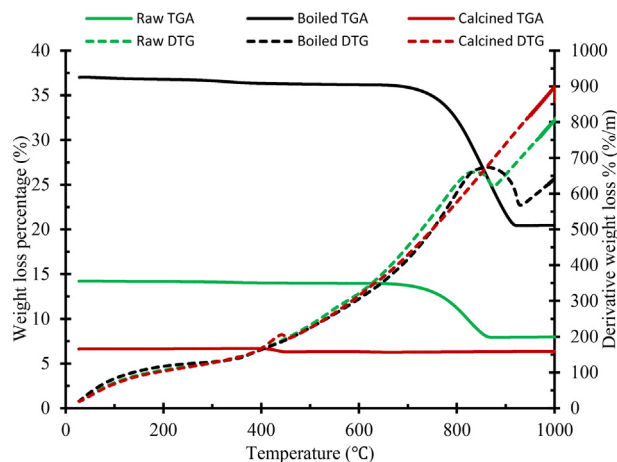


Figure 8. TGA/DTG curves for chicken eggshells.

carbonates. The calcined chicken eggshell witnessed the peak band at 3642 cm^{-1} as compared with the 3460 cm^{-1} presented by commercial CaO as reported by Tang et al. [22].

3.5. TGA/DTG analysis

TGA/DTG curves, shown in Figure 8, illustrate and compare the thermal behavior of the three samples when subjected to thermal decomposition in a regulated space. The raw and boiled chicken eggshell powder showed similar TGA curves and exhibited a single-stage decomposition. The uncalcined samples started to decompose at approximately 700 $^{\circ}\text{C}$, the raw chicken eggshell ended its thermal decomposition at 850 $^{\circ}\text{C}$, while the boiled chicken eggshell powder ended its decomposition at around 900 $^{\circ}\text{C}$. No weight loss was noticed after these temperatures. This confirms that a temperature of not less than 850 $^{\circ}\text{C}$ is required for thermal decomposition of CaCO_3 present in the chicken eggshell into CaO [3, 34]. The minor change at the end of the thermal decomposition can be ascribed to the effect of boiling on the raw chicken eggshell. The insignificant decomposition witnessed by the calcined chicken eggshell occurred at around 400 $^{\circ}\text{C}$ was due to the conversion of CaCO_3 into CaO and CO_2 . The DTG curves confirm only a slight pattern in the decomposition of raw chicken eggshell and boiled chicken eggshell, whereas the calcined samples presented a remarkably different decomposition pattern. In contrast to CaO synthesized from waste chicken eggshells, commercial CaO modified with bromooctane/hexane solution was reported to witness two stages of thermal degradation between 400 $^{\circ}\text{C}$ and 700 $^{\circ}\text{C}$. This was attributed to the loss of water and CO_2 from hydrated and carbonated CaO. The DTG curve of modified commercial CaO also witnessed two broad peaks at 450 $^{\circ}\text{C}$ and 700 $^{\circ}\text{C}$ which corresponded to the decomposition of $\text{Ca}(\text{OH})_2$ and CaCO_3 [22,35]. These contrasted with single-stage thermal decomposition and at higher temperatures witnessed by waste chicken eggshells which suggest that their higher thermal stability over commercial CaO.

4. Conclusions

The desire to find a green, eco-friendly, nonpoisonous, and readily available catalyst to replace commercial CaO has led to increased research interest in the investigation of chicken eggshell as a possible sustainable catalyst for possible biodiesel generation. In this present work, waste chicken eggshell has been modified by boiling and calcination and subjected to characterization. After characterization, boiling was found to have little effect on the chicken eggshell but calcination at 900 $^{\circ}\text{C}$ increased the surface area, pore size, and aided the thermal degradation of CaCO_3 .

The outcome of the characterization of modified chicken eggshell suggests that calcined chicken eggshell powder has the potential for better catalytic activity than the raw and boiled chicken eggshell powder. The conversion of waste chicken eggshell to catalyst will not only help in waste recycling and the proper disposal of the large quantity chicken eggshell generated by bakeries and restaurants, minimize the cost of waste disposal, and reduce landfill waste, but also substantially reduce the reliance on synthetic commercial CaO for catalytic biodiesel production and other industrial applications.

Going forward, more targeted investigations are needed on the viability of combined boiling and calcination of chicken eggshell as a viable source of CaO. The availability and sustainability of chicken eggshell to meet the demand of anticipated biodiesel production needs to be investigated as the world moves to implement more biodiesel in the energy mix.

Declarations

Author contribution statement

Omojola Awogbemi: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Freddie Inambao & Emmanuel I. Onuh: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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