



Analysis of the effect of temperature on the morphology of egg shell calcium oxide catalyst: Catalyst production for biodiesel preparation

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Abstract. The increasing number of studies on the usage of egg-shell-derived Calcium Oxide (CaO) as a catalyst for biodiesel production highlights the need to investigate the effects of temperature on the calcination of egg shells. To this end, the present study investigates the calcination of chicken and duck egg shells exposed to different temperatures of 800°C, 900°C, and 1000°C for one hour. The synthesized CaO was characterized by X-Ray Diffraction (XRD), Fourier-Transform Infrared spectrometry (FT-IR), Scanning Electron Microscope (SEM), and Energy Dispersive X-ray analysis (EDX). This study showed that there were changes in the distribution and formation of calcium, oxides, and the naturally occurring substance carbon during calcination of the samples. It was observed in both chicken and duck egg shells that 800°C was a decent temperature for calcinating egg shells to produce calcium oxide catalyst.

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1. Introduction

Alarmed by the increasing pollution created by conventional diesel engines [1], researchers have identified biodiesel production trends and accordingly, proposed allocating more capital investment to searching for a better source of biofuel. Numerous studies have shown that biodiesel could be produced from various sources such as edible oils, non-edible oil, waste fat of fish and animals, alcohols [2], waste tyre and plastics [3,4], waste cooking oils, microalgae [5–12], etc. In the conventional process of biodiesel production, a process

commonly known as transesterification is used to reduce the viscosity and density of the raw biofuel. The process usually involves heat treatment of biofuel with alcohol, preferably ethanol/methanol, in the presence of a catalyst at about 50 to 75°C for a certain time period. The process is deemed completed after removing glycerol from the conical flask, purifying the leftover esters, and washing off any alcohol or catalyst. Normally, KoH or NaOH was used as a catalyst for the transesterification process. However, in an attempt to reduce costs and minimize the damaging impacts on the environment, an eco-friendly catalyst was developed. Amongst the widely used catalysts, Calcium Oxide (CaO) is highly outstanding. In a search for sourcing and producing CaO in much cheaper ways, researchers have conducted various experiments to extract CaO from renewable sources. For instance, a study was conducted on sourcing and producing CaO from Scallop waste shell which was further used as a catalyst

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for biodiesel production. Another similar trend of synthesized CaO includes solid ostrich, chicken egg shells, river snail shells, and others used as catalysts, as reported by other studies. These studies have reported that the application of eggshell-based CaO catalysts had a recognizable methyl ester conversion rate, compared to those using KOH or NaOH [13–17]. Researchers have also reported use of homogeneous catalysts such as commercial KOH for methanolysis of Canola oil using response surface methodology. They obtained a conversion rate of 84.42%, which was in good agreement with the already predicted value of 89.15% [18]. They also stressed the significance of biofuels (bioethanol) to internal combustion engine research [19]. Many studies regarding the catalysts have suggested that there are various effects of temperature on the morphology and chemical and physical characteristics of the catalyst deemed substances. For instance, a study reported that the surface area of the alumina catalyst was drastically reduced when the temperature reached 1100°C (14 m²/g) from its initial 800°C (265 m²/g) [20]. Preparation of nanocatalyst by the microemulsion method was demonstrated through the use of (H₂O + H₂PtCl₆)/*n*-heptane/Triton X-100/2-butanol and (HCl(aq) + H₂PtCl₆)/*n*-heptane/Triton X-100/2-butanol. The study concluded that the content of HCl had an important effect on the activity and shape of the nanocatalyst [21]. Excellent yield of catalyst was also reported through the condensation of amines, aldehydes, and unmodified ketones under solvent-free conditions in the presence of ZnI₂. The study also concluded that the same approach would be inapplicable with chiral catalyst [22].

The possibility of using washed cells of *Lactobacillus plantarum* PTCC 1058 and *Lactobacillus plantarum* subsp. *Plantarum* PTCC1745 as the catalysts used for producing linoleic acid from castor oil was previously reported in a study. The reactions were further optimized and the researchers concluded that *Lactobacillus plantarum* PTCC 1058 was a better catalyst since it had a higher production yield of 36% in 121 hr at 15% (w/v) cell [23]. Use of catalyst through impregnation method for methanation of carbon dioxide was successful. The study showed that conversion of 86.82% CO₂ and 61.94% CH₄ was achieved at a reaction temperature of 200°C while using Ru/Mn (30:70)-Al₂O₃ catalyst (calcinated at 1000°C) [24]. On the contrary, researchers have introduced sodium alginate as an effective and renewable biopolymer catalyst [25]. Heterogeneous catalysts such as MoO₃/CuMoO₄ were prepared as selective nanoparticle catalysts for epoxidation of olefins. The study revealed higher selectivity and activity of the catalyst during the reaction [26]. Other studies suggested that the catalyst prepared by the addition of aluminium nitrate in the paste of boehmite, δ -alumina, polyethylene glycol 400, and

nitric acid as a peptizing agent resulted in an increase in lateral crushing strength by up to 50% (622 N/cm²) [27]. Yet, the problem which hinders the applicability of such sophisticated catalysts is the matter of availability and cost. The effectiveness of the catalyst is proportionate to the cost of the catalyst. Hence, many researchers hold the view that the use of easily accessible materials, which are cheap and highly reusable, must be encouraged as catalysts [28]. Nanocatalyst can also be successfully prepared using microemulsion route in hydrogenation reactions [29]. Another study emphasized that addition of CuO to FAZ-X (fly ash derived zeolite-X) would significantly improve the catalytic activity and reusability of the waste-derived catalyst. Similarly, other researchers proposed the application of environmentally friendly and highly reusable catalysts to carrying out reactions [30–34]. The necessity of this issue is evident since biodiesels have better characteristics in emission during combustion from internal combustion engines [35–39]. Other researchers have emphasized the need to study the effect of temperature on materials which have the capability to act as catalysts [40–47].

Following a close review of the literature and other related researches, the authors did not find a significant correlation between the formation of CaO-based heterogeneous catalyst and the effect of calcination temperature. In many of the reported works, the researchers failed to illustrate the effect of the calcination temperature on the formation of CaO from egg shells. Hence, they made efforts to bridge the knowledge gap in understanding the effect of the calcination temperature to the formation of CaO from egg shells. The present study considers two samples, chicken and duck egg shells, which are widely available as waste material, and they are calcinated to form CaO at different temperatures (700°C, 800°C, and 900°C). The calcinated samples were characterized using X-Ray Diffraction (XRD), Fourier- Transform Infrared (FT-IR) spectrometry, Scanning Electron Microscope (SEM), and Energy Dispersive X-ray analysis (EDX).

2. Material and method

2.1. Material collection

Among the widely consumed poultry products, egg is considered to be a healthy source of protein and other nutrients. Hence, it is pretty easy to collect the leftover egg shells as they are thrown away in large quantity from numerous homes, hotels, and shops. Apart from chicken eggs, duck eggs are also considered to be delicate due to their intense flavour and thus, obtaining duck egg shells is not a problem for researchers. A batch of chicken and duck egg shells (250 gm each) was collected from the National Institute of Technology Manipur, Imphal, India



Figure 1. Chicken and duck egg shells measured on an electronic scale of accuracy ± 0.005 g.

(24.832° N & 93.914° E, 785 m above sea level). The collected samples are shown in Figure 1.

2.2. Preparation of CaO catalyst

The egg shells were preheated at 80°C in an electric oven for few hours (2–3 hr) to ensure that the samples were fully dried [13,47] of any leftover moisture. Afterward, a mild force was applied to the egg shell samples to coarsely crush them in order to determine the size of 10–20 mm (approx.) smaller samples. The samples were then weighed using an electronic scale and by using a stainless-steel cup, they were exposed to different temperatures of 700°C, 800°C, and 900°C by an electric muffle furnace for about an hour. After exposure, the samples were cooled inside the insulated electric oven for about 4–5 hr. They were finely crushed using a mortar and then, kept within closed cups for easy storage.

2.3. Characterization of CaO catalyst

For characterization, the CaO samples were exposed to XRD for recording the diffraction patterns using a Bruker AXS (D8-Advanced) with 1.5406 Å of Cu-K α radiation in the 2θ range of 20° to 80°. The samples were then exposed to Perkin Elmer (spectrum two) FT-IR spectrometer and the corresponding values were recorded using instrument-equipped Spectrum 10TM software with LiTaO₃ detector. The chemical morphology of the samples was studied using Nova NanoSEM (1.0 nm@30 kV resolution, 5x to 1,000,000 x magnification) with Bruker SDD-EDS detector attached to EDX analyzer. The techniques and methodology placed by AOAC (1998) [46] were followed for determining the properties of chicken and duck egg shells.

3. Results and discussion

By following the procedures laid down by AOAC (1998) and after performing the experiments five times, the mean values of ash and moisture of the samples were observed to be 4.28 ± 0.034 g/100 g and 3.04 ± 0.028 g/100 g (chicken egg shells) as well as 5.05 ± 0.051 g/100 g and 2.96 ± 0.021 g/100 g, respectively (duck egg shells). Again, calcium and magnesium contents (dry basis) of the samples were

found 65.7 mg/100 g and 61.76 mg/100 g as well as 59.4 mg/100 g and 63.8 mg/100 g for chicken and duck egg shells, respectively.

3.1. XRD pattern of the samples

Figure 2a and 2b shows the XRD of the synthesized CaO from the calcinated chicken and duck egg shells. In both of the cases of chicken and duck egg shells, the diffractions peaks corresponding to (111), (222), and (220) of the face centred cubic phase were observed to be at about 29°, 33°, and 47°, respectively, at all temperatures. Less intense peaks were also noticed at around 35°, 39°, and 53° in the diffraction patterns. This is in agreement with the findings of other researchers [6,13,17]. It can be noted that the exposure of the samples to higher temperatures in both of chicken and duck egg shells resulted in rapid decline of calcium ions and homogenous nucleation of calcium, thus allowing the formation of smaller size CaO. This result is consistent with the reported work of other researchers [40–42,45,47].

3.2. FT-IR spectroscopy of the samples

Similar observations to the findings of the XRD were found in FT-IR results. The IR spectra for the calcinated CaO samples of chicken and duck egg shells are shown in Figures 3a and 3b, respectively. The figure shows the infra-red spectra at 400–2000 cm⁻¹ wavenumbers. The exhibition bands of 1474 cm⁻¹ and 869 cm⁻¹ define the asymmetric stretching of C=O for carbonaceous group, which may be explained by the chemisorption of CO₂ from the atmosphere on the surface of the synthesized CaO. The extra stretching of Ca-O at about 406 cm⁻¹ and 407 cm⁻¹ displays the formation of CaOs during the calcination process at all of the exposed temperatures. This phenomenon is explained by the vibrations of Ca-O lattice of pure CaO [43]. The findings of the present study are consistent with the reported work of other researchers [44]. The absorption was reduced with an increase in calcination temperature. Although there were few changes in the spectra of chicken egg shells and variations in the calcination temperature, higher fluctuations in the absorption of the duck egg shell CaO

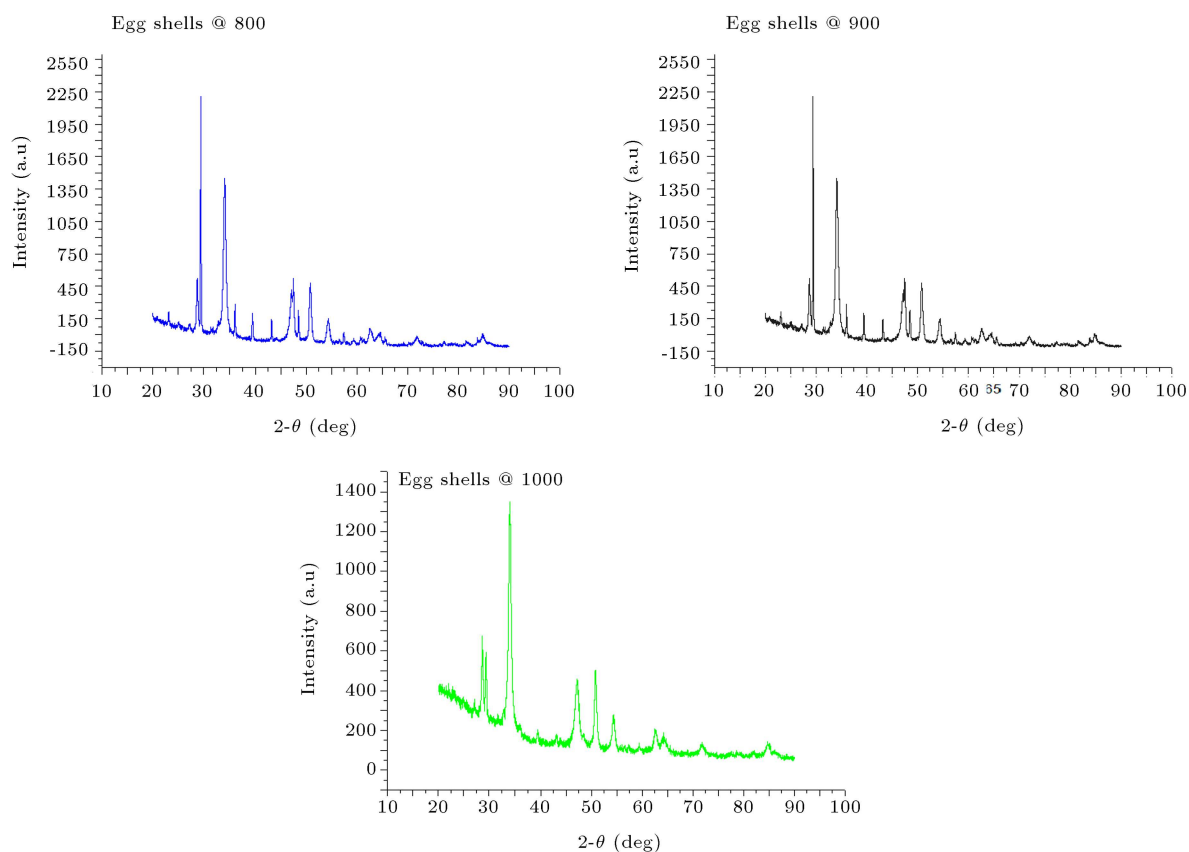


Figure 2a. X-Ray Diffraction (XRD) findings of the calcinated chicken shell CaO.

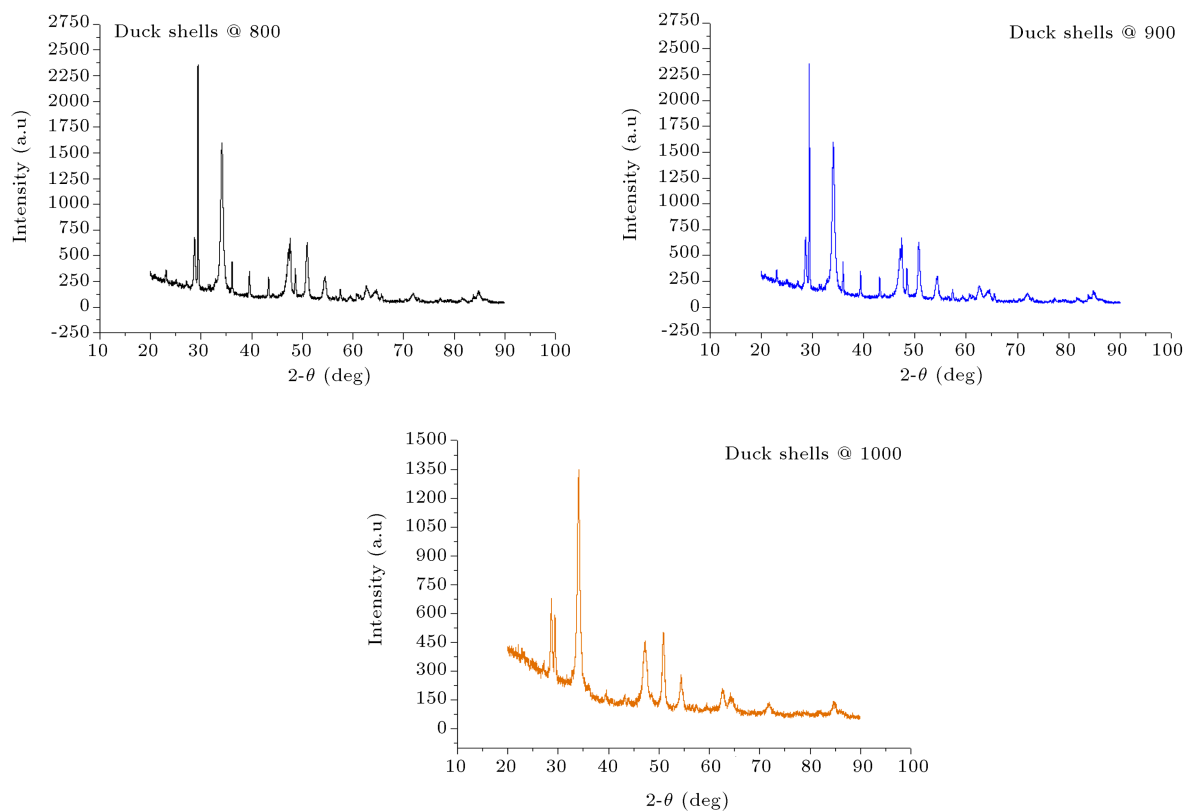


Figure 2b. X-Ray Diffraction (XRD) findings of the calcinated duck shell CaO.

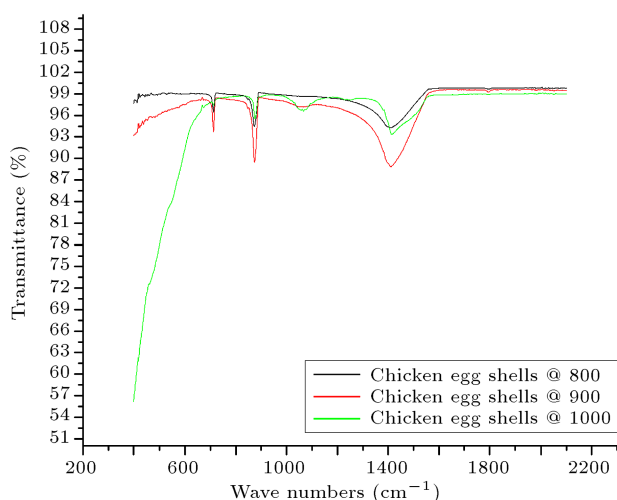


Figure 3a. Fourier-Transform Infrared (FT-IR) findings of the calcinated chicken shell CaO.

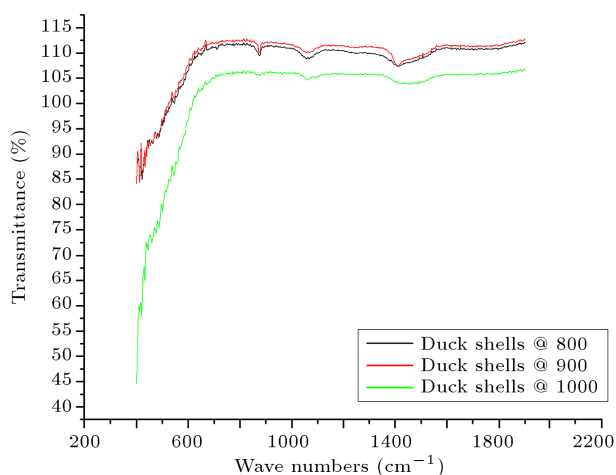


Figure 3b. Fourier Transform Infrared (FT-IR) findings of the calcinated duck shell CaO.

were observed. The transmittance of the duck egg shell CaO was reduced with an increase in the calcination temperature (1000°C), although fewer changes at tem-

peratures 800°C and 900°C were observed.

3.3. Scanning electron microscopy of the samples

The morphology of the synthesized CaO (50000 x magnification) from chicken and duck egg shells after their exposure to different temperatures of (a) 800°C, (b) 900°C, and (c) 1000°C is shown in Figures 4 and 5, respectively. The figure shows that the grains of CaO are asymmetrical and are of varying sizes. This might have been caused by the exposure of the samples to varying temperatures. Due to the exposure to higher temperatures, the grains were seen to be agglomerated with tremendous permeable nature. Therefore, an EDX analysis was conducted to show the elemental composition of the samples. Figure 6(a) and (b) shows EDX of the synthesized CaO from chicken and duck egg shells, respectively.

3.4. EDX characterization of the samples

From the EDX results presented in Figure 6, the composition of CaO in its elemental state comprising calcium (Ca), oxide (O) and naturally occurring substance, carbon (C) can be observed. In the case of chicken egg shells with CaO shown in Figure 6(a), the sample exposed to 900°C had more C and O with less Ca, while at 800°C, the composition of C in the sample decreased and there was an increase in Ca and O. At 1000°C, the carbon content of the sample suddenly escalated, while the amount of O and Ca was almost similar to CaO at 800°C. Thus, the temperature of 800°C was found to be better in terms of Ca and O composition with lower C content. Increase in the temperature from 800°C to 900°C and then to 1000°C was unfavorable as it increased the content of carbon in the sample, which is evidently seen in the figure.

Similarly, in the case of duck egg shell with CaO, shown in Figure 6(b), the CaO obtained at 800°C was found to be quite suitable as it contained a large quantity of Ca and O with less C. Increase in the

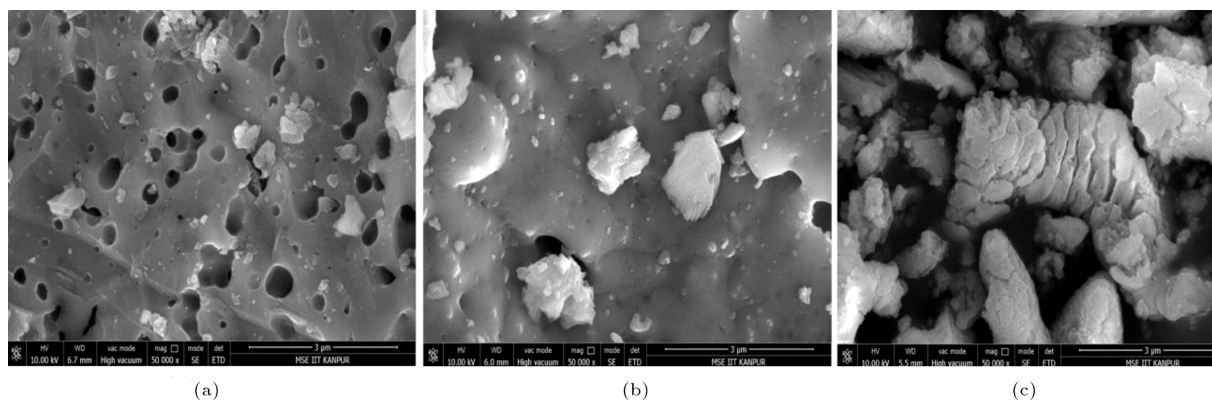


Figure 4. Scanning Electron Microscope (SEM) image showing the surface morphology of chicken egg shell with CaO at (a) 800°C, (b) 900°C, and (c) 1000°C.

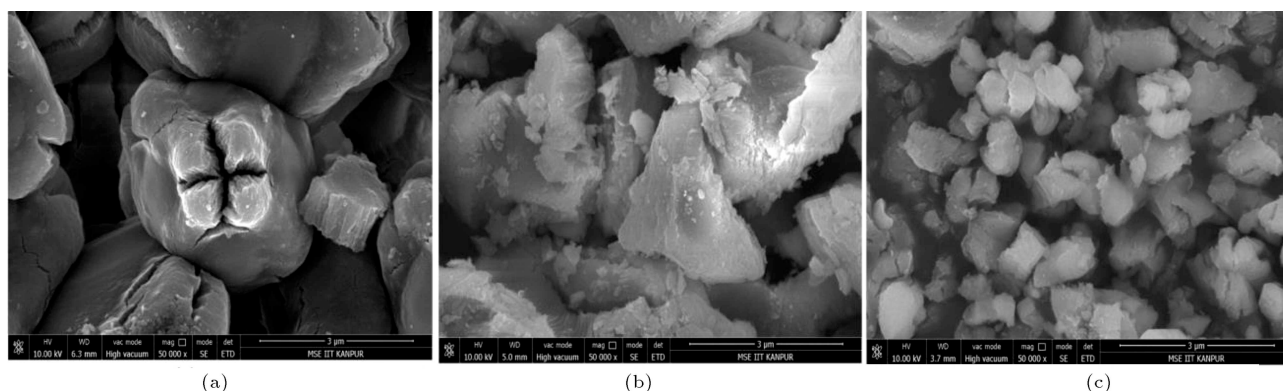


Figure 5. Scanning Electron Microscope (SEM) image showing the surface morphology of duck egg shell with CaO at (a) 800°C, (b) 900°C, and (c) 1000°C.

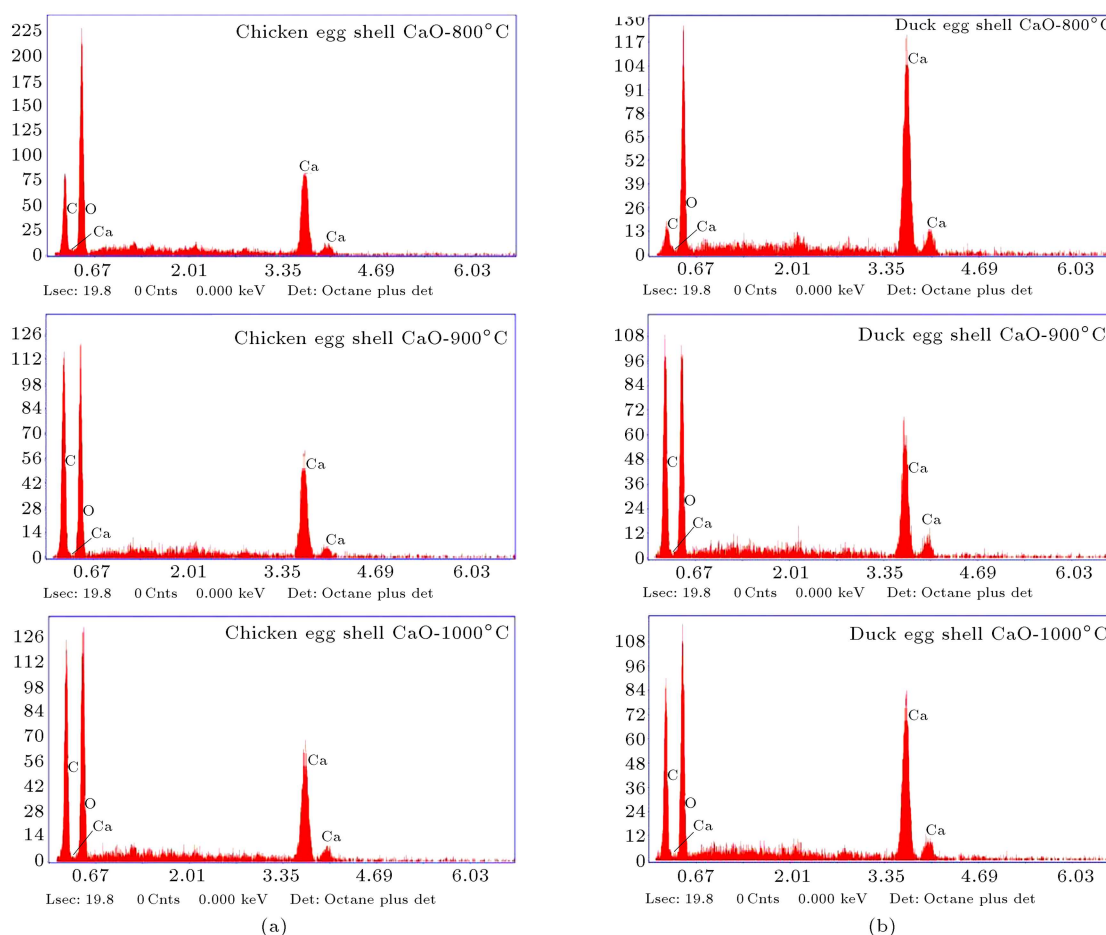


Figure 6. Energy Dispersive X-ray analysis (EDX) of (a) chicken egg shell with CaO and (b) duck egg shell with CaO.

calcination temperature had a negative effect on the distribution of Ca and O in the samples. Increasing the calcination temperature to 900°C was found to lower the Ca distribution in the sample, while an extensive increase in C was observed. Further increase in the temperature to 1000°C resulted in a slight decrease in C distribution in the sample with slight Ca enhancement.

4. Conclusion

A parametric study of the effect of temperature on the morphology of CaO synthesized from chicken egg shells and duck egg shells at varying calcination temperatures of 800°C, 900°C, and 1000°C was carried out. The samples were prepared and the following observations were found:

- The ash and moisture content of chicken and duck egg shells were 4.28 ± 0.034 g/100 g and 3.04 ± 0.028 g/100 g as well as 5.05 ± 0.051 g/100 g and 2.96 ± 0.021 g/100 g, respectively;
- The X-ray diffraction patterns of all the samples at 29° , 33° , and 47° showed the formation of CaO at all temperatures corresponding to the (111), (200), and (220) of the face centered cubic phase;
- Fourier Transform Infrared (FT-IR) spectrometry showed extra stretching of Ca-O at about 406 cm^{-1} and 407 cm^{-1} at all exposed temperatures. Exhibition bands of 1474 cm^{-1} and 869 cm^{-1} defined the asymmetric stretching of C=O for the carbonaceous group;
- Grains were observed to be asymmetrical and of varying sizes. Energy Dispersive X-Ray analysis (EDX) showed that greater amount of Calcium (Ca) and Oxygen (O) was detected at 800°C for both chicken and duck egg shells.

It can be concluded that 800°C is quite suitable and favorable as it contains acceptable amounts of Ca, O and less C in both of the CaO samples obtained from chicken and duck egg shells. The authors hope that the present findings provide a reference study for the researchers working in the area of catalyst synthesis using egg shells for biodiesel production.

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