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Characterization of Eggshells Nanocatalyst: Synthesized by Bottom-Up Technology

Jeremiah O. Masime*[1], Eric Ogur[2], Betty Mbatia[3], Austin O. Aluoch[1] and Geoffrey Otieno

[1] Department of Chemical Sciences and Technology, The Technical University of Kenya, P.O. Box 52428 – 00200, Nairobi-Kenya
[2]Department of Mechanical and Mechatronic Engineering, The Technical University of Kenya, P.O. Box 52428 – 00200, Nairobi-Kenya
[3]United States International University-Africa School of Pharmacy and Health Sciences, P.O. Box 67881-00200, Nairobi Kenya

*Corresponding author: masimejo@yahoo.com

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Abstract

The sol-gel technique was used to prepare the nanocatalyst from waste egg shells for the production of yellow oleander biodiesel. In this study, the physicochemical and catalytic properties of the nanocatalysts were investigated using: X-ray fluorescence spectrometry (XRF), transmission electron microscopy (TEM), the Barrett-Joyner-Halenda (BJH) model to quantify the pore structure of the samples, and Brunauer-Emmett-Teller (BET) to calculate the exact surface area were the techniques used. The results of the EDX, and XRF analysis showed that the synthesized nanocatalyst was majorly CaO. At 90.46 ± 1.73%, this was higher than the control for incinerated eggshells. From TEM images the particles were spherical in shape with particle sizes ranging from ≈ 7 to 41 nm. BET analysis results indicated that the nanocatalyst was mesoporous with surface area, average pore diameter, and pore volume was; 5.54 ± 0.48 m^2/g, 18.57 ± 2.16 nm, and ≈ 0.016 ± 0.0 – 0.017 ± 0.0 cm^3/g, respectively. The surface area to volume ratios were 3.27 ± 10^8 m^{-1}, 2.52 ± 10^8, and 1.95 ± 10^8 m^{-1}, respectively. Incinerated eggshells highest followed the synthesized nanocatalyst and CaO, respectively. The synthesized eggshell nanocatalyst was found to be a potential nanocatalyst.

Keywords: *Synthesized nanocatalyst; waste eggshells; physicochemical properties*

Introduction

The growing world population has led to the depletion of fossil resources, which has led to a growing demand for fuel from developing countries (Santos *et al.,* 2019). Biodiesel has since been chosen as one of the alternative fuels and is renewable, biodegradable, (Bet-Moushoul *et al.,* 2016) non-toxic, and environmentally friendly (Jeevanandam *et al.,* 2018; Mavridis 2013). Biodiesel was chosen as one of the alternative fuels because it is renewable, biodegradable, non-toxic, and environmentally friendly (Tan *et al.,*2015). Homogeneous catalysts have been used in the production of biodiesel. However, they have some disadvantages as they are corrosive, toxic, hygroscopic and easily soluble in reaction mixtures. They also cause poor product quality. These catalysts can cause saponification reactions that require large amounts of fresh water for washing (Manuscript 2016). This can lead to a reduction in biodiesel yield and also generates a large amount of waste water (Diamantopoulos 2015). Homogeneous catalysts can also cause inevitable corrosion of the reactor. These result in the overall production costs being high (Hossain *et al.,*2019).

The heterogeneous catalyst is environmentally friendly, inexpensive, readily available, biodegradable, environmentally safe, reusable, and more competitive in biodiesel production. Most heterogeneous catalysts used in biodiesel production are alkali or alkaline earth metal oxides (Solomon *et al.,* 2018). They have a large reaction surface and molecules attach themselves to the surface of the catalyst. Separating the biodiesel and cleaning it is quite easy and reduces the amount of wastewater (Degirmenbasi *et al.,* 2015). Production costs can also be reduced by reusing the catalyst (Galchar 2017; Tan *et al.,* 2015).

Solid wastes from mussel shells and chicken egg shells are useful in the preparation of heterogeneous catalysts. Eggshell CaO is a promising green catalyst in biodiesel production (Da Silva Castro *et al.,* 2019). Among the various food wastes, eggshells have many bioactive compounds exhibiting high economic benefits (Birol 2019). Internationally, about 250,000 tons of eggshell waste is released annually (Faridi and Arabhosseini 2018). Waste egg shells are among useful agricultural biowaste materials that have the following properties; they are biodegradable, recyclable and biocompatible (Pedavoah *et al.,* 2018). Egg shells are mainly composed of calcium carbonate ($CaCO_3$), which accounts for about 93.6% by weight, followed by calcium triphosphate (0.8%), which accounts for about 10% of a hen's egg (Neunzehn, Szuwart, and Wiesmann 2015). The main component of eggshells is calcium carbonate, $CaCO_3$, which converts to calcium oxide and carbon dioxide when burned. It is therefore an excellent biomass resource for green CaO (Tan *et al.,* 2015). Green heterogeneous catalysts can be prepared from it (Faridi and Arabhosseini 2018; Oulego *et al.,* 2020). Nanocrystalline CaO has a specific surface area that is 1.54 times higher than commercially available calcium oxide (Bharti, Singh, and Dey 2019). It has a large specific surface area and high catalytic activities, making it an efficient catalyst for the production of biodiesel with high yields (Santos *et al.,*2019).

Researchers have studied the preparation of heterogeneous nanocatalysts using top-down or bottom-up techniques (Mohammadlou, Maghsoudi, and Jafarizadeh-Malmiri 2016). It controls the size, shape, composition, and architecture (Khan, Saeed, and Khan 2017; Patra and Baek 2014; Tandon 2015) In the bottom-up process, nanoparticles can be integrated using substances by assembling atoms into new nuclei, which evolve into a nanoscale particle. In the top-down method, nanoparticles are produced by crushing bulk material into fine particles (Shah *et al.,*2015). The bottom up is the cost effectiveness, scalability, and generally controlled shape and size of the product. The selection of the respective method depends on the chemical composition and the desired properties of the nanoparticles (Awan *et al.,*2016). Recently, many researchers have switched from bottom-up synthesis techniques to utilizing nature-based biogenic materials to synthesize calcium carbonate nanoparticles, which is generally a top-down approach (Mohd Abd Ghafar, Hussein, and Abu Bakar Zakaria 2017). Ahn *et al*., (2019), studied the FE-SEM images of calcium oxide nanoparticles prepared from waste eggshells by the sol-gel method and found that the particles were nearly spherical in shape. The nanoparticles had an average particle size of 198 nm. They also suggested using a higher temperature in the synthesis of the nanoparticles to improve the result and this is the reason for this study.

The synthesized eggshell nanocatalyst was characterized using different methods. X-ray fluorescence (XRF) analysis was also used to determine the chemical constituents of the generated nanoparticles, transmission electron microscopy (TEM) was used to examine the crystalline properties of the catalyst, and catalytic properties were also analyzed using BET and BJH.

Methodology

Materials

Waste egg shells were collected from the Kenya University of Technology cafeteria, washed with tap water until the albumen was completely removed, and dried in an oven at 100. Clean and dried eggshells were broken into small pieces and ground to a fine powder in a china mortar and stored in desiccators at room temperature. The resulting powder was burned in a furnace at a temperature of 1000°C for 3 hours. The generated CaO was stored in a desiccator container for later use (Salame, Pawade, and Bhanvase 2018).

Chemicals and Instruments

All chemicals were of analytical grade (Merck, > 99% purity), Ammonium carbonate, iso-octane, cetyl trimethyl ammonium bromide (CTAB), methanol n-butanol, n-butanol, and chloroform were purchased from Kobian Chemicals. These chemicals were used directly without any purification, and distilled water was also used in all experiments.

Synthesis of eggshells nanoparticles

The synthesis of metal oxide nanoparticles by the sol-gel method has four basic sequential processes: preparation of a homogeneous solution, formation of sol by hydrolysis, formation of a gel by condensation, and drying of the formed gel (Habte *et al.,* 2019). The synthesized nanocatalyst was prepared using a modified Sharma and Virk procedure reported elsewhere (Sharma and Virk 2009). The product from the microemulsion was incinerated at 1000°C separately for 3 hrs. Details are given in the next section.

Calcination process

After the synthesis of the nanocatalyst, as explained in 2.3. A laboratory muffle furnace (Linn High Thermo GmbH, LM 412.27, model DC021032 with a thermocouple type K, NiCr-Ni) was used to incinerate the samples at 1000 °C. Eggshell nanoparticles samples were incinerated in an alumina crucible at a heating rate of 10 °C/min for 3hours to ensure complete the decomposition of $CaCO_3$ in the eggshell to CaO, which is catalyst rich (Ayodeji *et al.,*2018). Calcination temperature and time are critical factors in the developing the active sites, structural and catalytic properties. (Banković-Ilić *et al.,*2017). The eggshells decomposed into the respective oxides; $CaCO_{3\,(s)} \rightarrow CaO_{\,(s)} + CO_{2\,(g)}$ and $MgCO_{3\,(s)} \rightarrow MgO_{\,(s)} + CO_{2\,(g)}$ (Correia *et al.,*2017).

Catalysts Characterization

The synthesized nanocatalyst was characterized by the X-ray fluorescence (XRF), transmission electron microscopy (TEM), and Brunauer-Emmer-Teller (BET) surface. Chemical compositions were obtained using X-ray fluorescence (XRF) (Philips, model PW 2400) at a tube current of 1000 A with an acquisition lifetime of 30 s (Ayodeji *et al.,*2018). Samples for analysis using Transmission electron microscopy (TEM) were prepared by placing a drop of the nanoparticle suspension on a copper grid (Ted Pella, CA) and air drying it overnight. Imaging was done using a JEOL 123 microscope operated at 80 kV (JEOL, USA) (Michen *et al.,* 2015; Zhou, Bennett, and Keller 2012). BET (Brunauer, Emmett, and Teller) surface area of the catalyst samples were obtained in a Micromeritics TriStar 3000 Surface Area and Porosity System analyzer by the low-temperature N_2 adsorption method. Prior to analysis, the samples were degassed at 120°C overnight (12 h) under a continuous flow of N_2 gas to remove the adsorbed contaminants and moisture from the surface and pores of the material (Chinthakuntla *et al.,*2014; Kumar, Some, and Kiriamiti 2014). ASTM C1274-12 Standard Test Method for

Advanced Ceramic Specific Surface Area by Physical Adsorption was used (Brame and Griggs 2016).

Result and Discussion

Characterization of the nanocatalyst

XRF Spectroscopy

The chemical composition of incinerated eggshell and the synthesized nanocatalyst were obtained using X-ray fluorescence analysis. The calcium oxide content in the synthesized eggshells catalyst calcined at 900 °C for 3 hours is approximately 95.52 % w/w of CaO. However, the rest of the elements and compounds amounted to only 4.48 % w/w. This means that the synthesized eggshells' thermal treatment transforms the chemical composition from calcium carbonate ($CaCO_3$) to calcium oxide almost entirely. The major component of synthesized eggshells nanocatalyst are CaO 95.516 ± 2.04 %, P_2O_5 - 2.102 ± 0.09, Al_2O_3-1.637 ± 2.57 %, and MgO - 0.087 ± 0.02 %, respectively. The composition of CaO in the incinerated eggshells was lower at 90.457 ± 1.73 %. It also contained small amounts of Mg - 0.087 ± 0.02%, P_2O_5 - 2.102 ± 0.09%, Sr - 0.018 ± 0.01%, Ti - 0.057± 0.06%, Fe - 0.232 ± 0.02%, Cu - 0.018 ± 0.01%, and Zn -0.019 ± 0.01%. The EDX spectrum of the synthesized eggshell catalyst samples shows that calcium and oxygen were the main element compositions. However, the presence of P_2O_5, Al_2O_3, and MgO was not registered.

Mmusi *et al.*, (2021) studied the SEM images of CaO-NPs derived from eggshells and found that the percentage atomic compositions were 38.18, 45.56, 6.05, and 0.01% for calcium (Ca), oxygen (O), carbon (C), and magnesium (Mg), respectively. These results confirmed that indeed CaO was present.

Tahvildari *et al.,* (2015), produced biodiesel from cooking oils using CaO and MgO nanoparticles. They discovered that CaO nanoparticles showed a significant increase in biodiesel yield compared to MgO nanoparticles. They also concluded that various metal oxide nanocatalysts are the most efficient heterogeneous catalysts in biodiesel production from different feedstocks. Another research found that the gel-combusted CaO nanocatalyst improved surface area, porosity, basic site, and higher catalytic performance (Kesic *et al.,*2016). The elements present in the synthesized eggshell nanocatalyst have potential catalytic activities essential in producing yellow oleander biodiesel.

TEM Spectroscopy

The TEM images of incinerated eggshells and synthesized eggshells nanocatalyst samples are in Figures 1 A and 1 B respectively

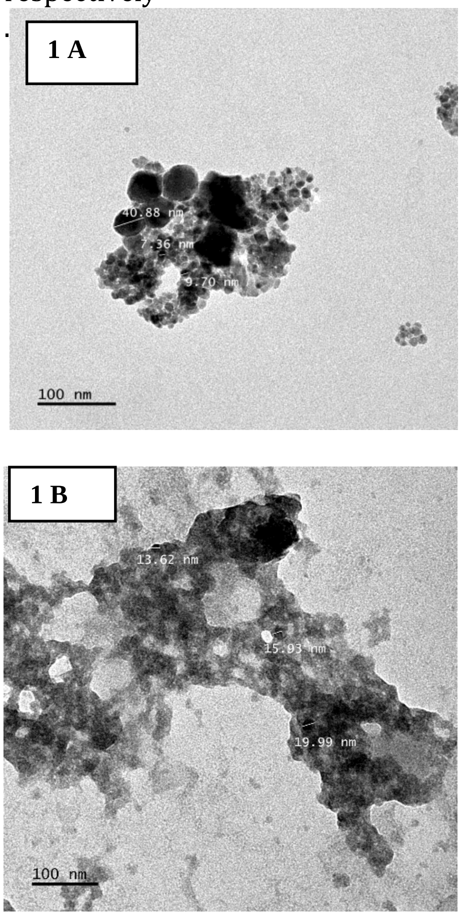

Figure 1 (A & B): TEM images of incinerated eggshells and the synthesized nanocatalyst

Figure 1 confirmed that the CaO particles from incinerated eggshells are majorly spherical, approximately ≈7 to ≈ 41 nm in diameter. Furthermore, Habte *et al.*, (2019) studied the synthesis of nano-calcium oxide from waste eggshells by the Sol-Gel Method. Using FE-SEM image, they found spherical polycrystalline nanoparticles agglomerated to each other. The mean size of CaO nanoparticles was ≈ 198 nm. The effect of the bottom-up technique on the synthesis of synthesized eggshells nanocatalyst observed using the TEM and selected area electron diffraction (SAED) images.

The TEM images showed that the synthesized eggshell nanocatalyst had irregular agglomerates with particle sizes ranging from ≈ 13 to ≈ 48 nm. However, the porosity of the synthesized eggshells nanocatalyst was higher than that of incinerated eggshells. This was due to the CO_2 released from inside the structure during calcination (Ahmad *et al.,* 2021). Venkatesh *at al.,* (2018) studied the TEM image of CaO nanocatalyst and its application for biodiesel production using *Butea monosperma* oil. They found the NP agglomerates, with their sizes ranging from ≈ 10 to 15 nm; they also exhibited NP a cone-like structure.

BET-BJH Analysis

The catalyst's surface area and pore diameter are two key characteristics to be evaluated in all catalysts. Therefore, the nanoparticles' surface areas were determined using the Brunauer–Emmett–Teller (BET) equation (Brame and Griggs 2016). This research used the Barrett– Joyner–Halenda (BJH) method to calculate the pore size distribution and pore volume from the adsorption isotherm at $\frac{P}{P_\circ} = 0.996$ (Correia *et al.,* 2017).

The results for BET analysis for the incinerated eggshells and the synthesized nanocatalyst. The synthesized nanocatalyst had a higher surface area of 5.54 ±0.48 m^2/g than the incinerated eggshells, 4.44 ± 0.38 m^2/g. This indicates that the synthesized nanocatalyst is a better catalyst.

The average adsorption pore size (4 V/A after BET) was 15.69 ± 2.63 nm for the incinerated eggshells compared to 10.04 ± 0.98 nm and the synthesized nanocatalyst. Similar results were obtained by BJH analysis; the average pore size of BJH adsorption (4V/A) was 23.10 ± 2.17 nm for the incinerated eggshells compared to 10.87 ± 2.61 nm for the synthesized nanocatalyst. The average pore size of BJH desorption was 22.93 ± 2.94 nm for the incinerated eggshells compared to 10.72 ± 1.71 nm for the synthesized nanocatalyst. These were applied to the incinerated eggshell and the synthesized nanocatalyst, respectively. An increase in the pore diameter leads to a reduction in the pore volume. In all of these cases, the incinerated eggshells are relatively more porous than the synthesized nanocatalyst. As a result, the incinerated eggshells would be more efficient during the catalytic process.

Bharti *et al.,* (2021) studied the BET analysis of the synthesized CaO nanocatalyst for biodiesel production. They found that the specific surface area of the synthesized CaO nanocatalyst was 67.781 $m^2\ g^{-1}$. At the same time, the average pore diameter was 3.302 nm. The surface area of commercial CaO has been reported as 13 $m^2\ g^{-1}$, which is significantly lower than that of the synthesized nano-CaO. They also reported that a high specific surface area and smaller pore diameter impart mesopores in the catalyst, making it suitable for reaction through adsorption. A high surface area indicates high porosity and high functionality of the catalyst and the availability of a greater number of active sites. Pandit & Fulekar, (2017) studied the egg shell waste as heterogeneous nanocatalyst for biodiesel production and found that the newly synthesized nano-CaO had specific areas of 16.4 $m^2\ g^{-1}$ with average pore diameter and pore volume of 5.07 nm and 0.0207 cm^3/g respectively.

Effects of reaction variables on the performance of nanocatalysts

The following reaction variables: Surface area/volume ratio of the nanocatalysts, reaction time, amount of catalyst, methanol: oil ratio, and reaction temperature were investigated. This study examined the catalytic performance using these variables in the transesterification reaction of yellow oleander oil to find the optimum reaction condition.

The surface-area-to-volume ratio of the nanocatalysts

Nanocatalysts yield a tremendous surface-area-to-volume ratio, which account for their versatility and effectiveness (Chaturvedi, Dave, and Shah 2012). The nanocatalysts' surface area to volume ratio are in Table 1 below.

Table 1. Surface area/volume ratio of the nanocatalysts

Nanocatalyst	SA/Vol ratio (m^{-1})
Incinerated eggshells	2.52×10^8
synthesized eggshells nanocatalyst	3.27×10^8
CaO	1.95×10^8

The results indicate that the synthesized eggshells nanocatalyst samples possessed a surface area to volume ratio of 3.27×10^8 m^{-1}. Meanwhile, the Incinerated eggshells and CaO nanocatalyst samples had a lower surface area/volume ratio. These were 2.52×10^8 and 2.52×10^8 m^{-1}, respectively. Making the synthesized eggshell nanocatalyst a better heterogeneous phase for the production of yellow oleander biodiesel. These results confirm that the synthesized eggshell nanocatalyst is a better heterogeneous phase for the production of yellow oleander biodiesel. It has been found to have many active chemical sites caused by its large surface area. Reducing the particle size to the nanoscale increases the surface/volume ratio, favouring high chemical reactivity and high catalytic activity (Erchamo *et al.,* 2021). BET and BJH analysis results confirmed that the samples analyzed were nanoparticles and had low porosity. There was also a general decrease in particle size, surface area, and pore volume. This was caused by agglomeration at high temperatures during the calcination step (Gaber *et al.,* 2014). El-Gendy *et al.*, (2015) recorded a total pore volume of 0.058 cm^3/g for the mesoporous biocatalyst. Nasrollahzadeh *et al.*, (2016) studied the BET/BJH analysis of Cu/eggshell and Cu/Fe_3O_4/eggshell nanocomposites. They found that surface area, average pore volume, and pore diameter of eggshell were ≈ 0.84 m^2/g, ≈ 0.0049 cm^3/g, and ≈ 3.22 nm, respectively. These results indicated that natural eggshells possessed low porosity.

Effect of catalyst loading on biodiesel production

Catalyst loading is another important parameter that needs to be optimized to improve the FFA conversion. Figure 2 gives the effect of catalyst loading on biodiesel yield.

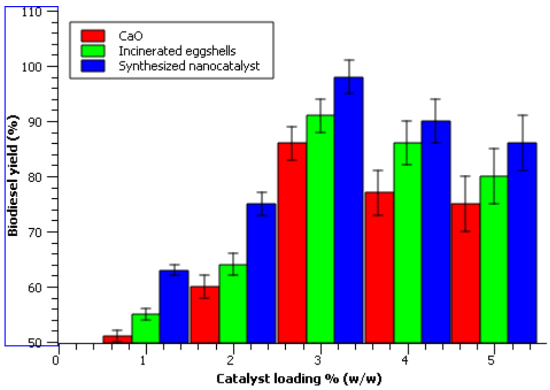

Figure 2. The effect of catalyst loading on biodiesel production

The catalyst loading in the oil varied from 1% to 5% (w/w). According to the recorded results, biodiesel conversion increased significantly with nanocatalyst loading, to a level where higher loading no longer increased biodiesel conversion. The total number of available active sites increased with increasing nanocatalyst loading. On the other hand, further increasing the nanocatalyst loading beyond the optimal 3% ratio increased the viscosity of the liquid mixture, resulting in reduced biodiesel production. In CaO, incinerated eggshells, and synthesized nanocatalysts, the biodiesel yield is 86.3 ± 4.76, 91.3 ± 6.71, and 98.2 ± 1.23%, respectively. However, with catalytic loading, the biodiesel production yield decreased from 3 to 5 wt%. Increasing the catalyst loading led to particle cohesion and aggregation, resulting in a decreased active surface area. These also increased the viscosity of the solution, thereby reducing the biodiesel production yield. Kifli *et al.,* (2018) studied the synthesis of alumina-CaO-KI catalyst to produce biodiesel from rubber seed oil. They found that the yield increased with increasing catalyst loading from 0 to 2% for all catalysts. The highest biodiesel yield with alumina CaO-KI, alumina-KI, and alumina-CaO were 91.6%, 90.7%, and 63.5%, respectively. They also observed that the optimal catalyst loading was at 2.0%, and biodiesel yield decreased with a further increasing amount of catalyst. As expected, alumina-CaO-KI gave the highest yield of biodiesel. This is due to a combination of factors; the high basicity of alumina-KI catalyst.

Compared to homogeneous catalysts such as NaOH, heterogeneous catalysts offer a number of advantages including ease of separation, recyclability, and reusability. In addition, solid catalysts consume less energy, are less corrosive, less toxic, and have minimal corrosion. Therefore, solid catalysts offer a productive and cost-effective way to produce biodiesel. Because of their insolubility in methanol and their low toxicity, alkaline earth metal oxides are among the best-studied catalysts for biodiesel synthesis. MgO, CaO, SrO and BaO are the alkaline earth metal oxides with the highest basicity. The transesterification reaction is essentially unaffected by magnesium oxide. CaO is the alkaline earth metal, oxide most commonly used in the manufacture of FAME because it is non-toxic, inexpensive, strongly basic, and insoluble in alcohol (Changmai *et al.,* 2020).

Effect of the reusability of nanocatalyst on the biodiesel yield

This study tested the reusability of the nanocatalysts in the transesterification of yellow oleander oil. Repeated use of a heterogeneous catalyst reduces the chemical reaction's overall processing cost (Kaur and Ali 2014). Figure 3, shows the results for the reused nanocatalyst.

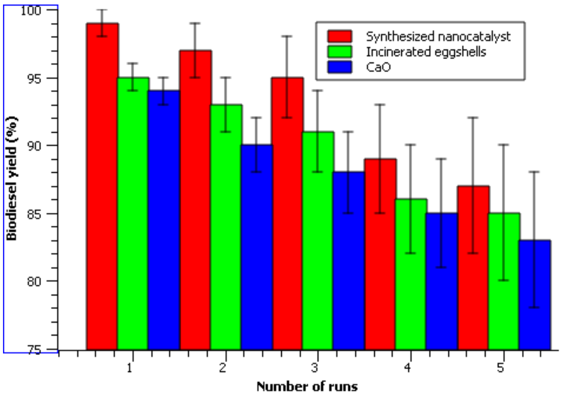

Figure 3. Effect of the reusability of nanocatalysts on the biodiesel yield

The synthesized nanocatalyst, the incinerated eggshells, and the CaO nanocatalysts were reused five times, and the biodiesel yields were 94.2 ± 4.73, 95.3 ± 3.72, 99.4 ± 3.11 %, respectively. However, most research results reported the reusability of CaO-based catalysts up to five cycles (Bet-Moushoul *et al.,*2016). Banković-Ilić *et al.*, (2017) studied the optimization of biodiesel production from waste vegetable oil using eggshell ash. They found that the catalyst obtained can only be reused up to 10 times without affecting the activity. CaO showed sustained activity after being recycled and reused 10 times. The biodiesel yield was relatively constant at 91% during these repeated uses. Beyond this, the yield was reduced to 30% when used for the 18th time.

Conclusion

In this research, an active synthesized heterogeneous CaO catalyst was successfully synthesized from incinerated waste eggshells. The eggshell CaO nanocatalyst was synthesized by using the bottom-up technology and thermally treated at 900 °C for 3 h to produce mesoporous CaO catalysts that have high basicity, high surface area, and active sites density with good morphology responsible for the catalytic activity. The spectral characterizations of the synthesized nanocatalyst were investigated using XRF, TEM, BET, and BJH spectrographic techniques. The results reveal the presence of mesopores uneven particle surfaces with a low surface area, average pore diameter, and pore volume of 5.54 ± 0.48 m^2/g, 18.57 ± 2.16 nm, and ≈ 0.016 ± 0.0 – 0.017 ± 0.0 cm^3/g, respectively, and presented a uniform pore size. Therefore, the thermal decomposition of eggshells and the synthesized catalyst led to the formation of CaO.

Acknowledgement

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