Research Article

A Guinea Fowl Eggshells Derived Calcium Oxide Catalyst for Transesterification of Coconut Oil

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Abstract: The exponential rise in world population, the depletion of fossil fuels resources, and the severe environmental consequence of petroleum-based fuels have initiated an enormous search for renewable fuel as a substitute for petroleum fuel. In line with that, this study reports the use of a calcium oxide catalyst derived from waste guinea fowl eggshells in the transesterification of coconut oil for biodiesel production. The calcium oxide catalyst was prepared through the calcination of the eggshell at 950 °C for three hours and then characterized by Fourier Transform Infra-Red FTIR and basic back titration methods. The activity of the catalyst was evaluated in the transesterification of coconut oil with methanol by varying the reaction conditions to optimize the biodiesel conversion. The catalyst's Fourier Transform Infra-Red (FTIR) analysis revealed a peak equivalent to the Ca-O bond at 665 cm^{-1}, indicating eggshell conversion into CaO. This is justified by the appearance of a $Ca(OH)_2$ peak around 3640 cm^{-1} due to surface water attached to Ca^{2+}. While to the basic back titration yielded a value of 2.933 mmol/g, indicating a high number of basic sites. Consequently, the activity test for the catalyst signified that one hour reaction time, 1:18 oil to methanol molar ratio, 1% catalyst loading, and 60 °C reaction temperature gave the best yield, with a conversion of 85.81%.

Keywords: coconut oil, transesterification, calcination, heterogeneous catalyst

1. Introduction

The exponential increase in the global population and the excessive exploitation of fossil fuels has been a source of concern world wide. This is because oil reserves have been diminishing and less oil is being explored. These plus the injurious environmental effect associated with fossil fuels necessitated the search for alternative renewable sources [1]. In the past two to three decades, alternative sources of energy that can substitute or complement fossil fuels have been explored. Due to the renewable, biodegradable, and green nature of biodiesel, it is one of the promising alternatives to petroleum diesel [2-5].

However, the utilization of edible vegetable oils like sunflower, soya bean, rapeseed, corn, and canola for the production of biodiesel, makes the process expensive compared to petroleum diesel [6-8]. This is the due to the fact that edible vegetable oils are usually more expensive than petroleum diesel. Thus, non-edible oils, waste frying oil, and animal fats have been explored to lessen the price of biodiesel production [7, 9]. Furthermore, there is concern over food scarcity and a hike in food prices as more than 95% of the world's biodiesel is produced from edible oils [8]. This fear prompted researchers to shift attention to non-edible seed oils as well as waste cooking oils [10].Although waste

cooking oil is cheap, itis highly free of fatty acid that needs to be refined for efficient biodiesel production, and the high FFA makes the process tedious and expensive. The soap formation, if the high free fatty acid is not reduced, will affect the reaction rate and make product separation difficult [10, 11].

Biodiesel production utilizes oil or fat and short-chain alcohol in the presence of either homogeneous or heterogeneous catalysts. Heterogeneous catalysts have attracted greater attention due to, among others, there is no need to wash the biodiesel product to remove the catalyst, the possibility of catalyst regeneration, and the catalyst is non-corrosive and economical, giving them an advantage for industrial applications [12]. According to the Equations (1-3) of Trans-esterification of a triglyceride, for every one mole of triglyceride three moles of alcohol are required, but the equilibrium nature of the reaction obliges higher moles of alcohol to obtain high ester yields, depending on the reaction parameters; oil and catalyst type, reaction temperature, etc [9]. Lower molecular weight alcohols, methanol and ethanol are more frequently utilized in the transesterification process. As a result of its low-priced, polarity, high availability and its lowest viscosity, methanol is the most commonly used alcohol in biodiesel production. Alternatively, ethanol has the advantage of renewability, being a product for the fermentation of sugar and it is also cheap. Additionally, propanol, butanol, and octanol can be used but their cost is higher than that of methanol and ethanol [13].

$$Triglycerides + ROH \rightleftharpoons Diglycerides + RCOOR\ldots\ldots \qquad (1)$$

$$Diglycerides + ROH \rightleftharpoons Monoglycerides + RCOOR\ldots\ldots \qquad (2)$$

$$Monoglycerides + ROH \rightleftharpoons glycerol + RCOOR\ldots\ldots \qquad (3)$$

2. Experiments

2.1 Materials

The coconut oil was purchased from the Wudil market, and the guinea fowl eggshells were obtained from a cafeteria at Kano University of Science and Technology, Wudil, Kano State, Nigeria. 37% purity Hydrochloric acid (HCl), sodium hydroxide (NaOH), and methanol with purity greater than 99% were purchased from QRëCTM. Chemicals of analytical grade were used without further purification.

2.2.1 Preparation of Catalyst

The guinea fowl eggshells were carefully washed with tap water, rinsed well with distilled water, and dried in a hot air oven at 110 °C. The dried eggshells were crushed, sieved through 65 mesh, and transformed into CaO by calcination at 950 °C for three hours in a muffle furnace under static air conditions. The produced CaO catalyst was stored in a desiccator to prevent it from reacting with CO_2 and water vapor in the atmosphere.

2.2 Catalyst Characterization

2.2.1 Basic Back Titration

Exactly 10 ml of distilled water was measured into a centrifuge tube containing 0.15 g of the CaO catalyst and left for 24 hours. The mixture was then centrifuged, and to the separated supernatant solution, 10 mL 0.05 M HCl solution was added followed by three drops of methyl orange indicator, and the mixture was titrated with 0.02 M of NaOH solution.

2.2.2 FTIR Analysis

Horizontal attenuated reflectance Fourier transform infrared spectroscopy (FTIR-HATR Cary 630) was employed in the analysis of both uncalcined and calcined eggshells at frequencies ranging between 4000 cm^{-1} to 400 cm^{-1}. The sample preparation was by grinding and the ground sample was placed on the sample window for analysis.

2.3 Transesterification Reaction

Accurately 10 mL of the coconut oil was transferred into a conical flask and heated to 60 °C on a hot plate with a magnetic stirrer. Then 0.5wt% of calcium oxide catalyst was weighed and mixed with methanol in a1:9 oil: methanol molar ratio and mixed with the pre-heated oil under continuous stirring at 60 °C for one hour. The products were then allowed to cool and settle in a separation funnel overnight to remove the biodiesel from glycerol and settled catalyst. The procedure was repeated for the biodiesel optimization by varying the oil to methanol ratio: 1:12, 1:15, and 1:18; catalyst amount: 1%, 1.5%, and 2%; and time: one and a half hours, two hours, two and a half hours, and three hours. The percentage conversion was computed by comparing the acid value of biodiesel with that of oil using Equation (4) [14].

$$\% \; Conversion = 1 - \frac{AV_{Biodiesel}}{AV_{Oil}}$$

(4)

Where, $AV_{Biodiesel}$ and AV_{Oil} are acid value of biodiesel and oil, respectively

2.4 Free Fatty Acid (FFA) Determination

The FFA was determined by mixing about 1.5 g of the oil sample with 50 cm^3 of Propan-2-ol in a conical flask, followed by the addition of four to five drops of Phenolphthalein indicator, and titrated against a standardized 0.1 M KOH solution to the first permanent purple color. The titer value was recorded, and the acid value (AV) was evaluated using Equation (5) [14].

$$AV = \frac{M \times V \times 56.0}{W}$$

(5)

Where; M, V, and W stand for the concentration of KOH, the titer value of KOH, and the weight of the oil, respectively.

The value of the AV obtained from Equation (3) was used to calculate the free fatty acid (FFA) according to Equation (6) [14].

$$FFA = \frac{AV}{2}$$

(6)

3. Result and Discussion

3.1 Characterization of the Catalyst

The FTIR spectra for the uncalcined and calcined eggshells are presented in Figures 1 and 2, respectively. The strong bands at 1796 cm^{-1}, 881 cm^{-1},as well as 717 $cm^{-1}$are attributed to the out-of-plane bending vibration mode for CO_3^{2-} [15, 16]. The peaks at 881 cm^{-1}, and 771 cm^{-1}, respectively, due to C=C bending and C-O bending in CO_3^{2-} were found to disappear in the calcined eggshell spectrum. Furthermore, the characteristic peak for the Ca-O bond appeared around 665 cm^{-1} in the calcined sample suggesting the formation of CaO as a result of the decomposition of $CaCO_3$ [16]. The CaO formation was further authenticated by the appearance of a peak around 3640 cm^{-1} associated with O-H bond stretching vibration. This was ascribed to the hygroscopic nature of CaO that allows it to absorb moisture from the atmosphere to form $Ca(OH)_2$.
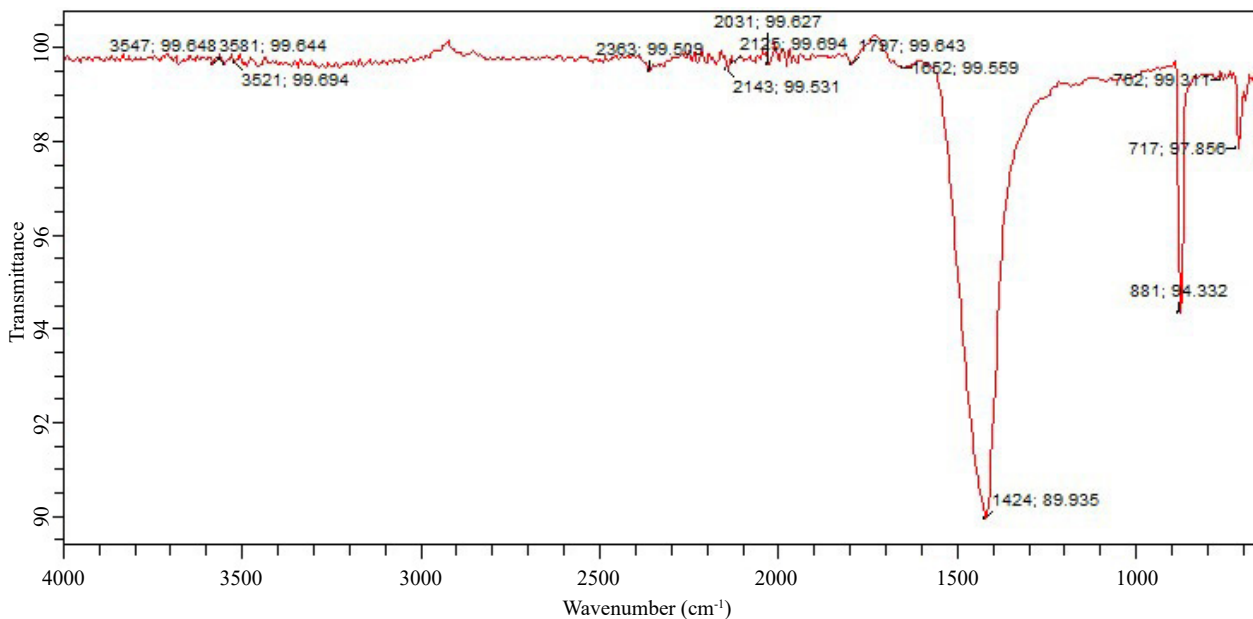
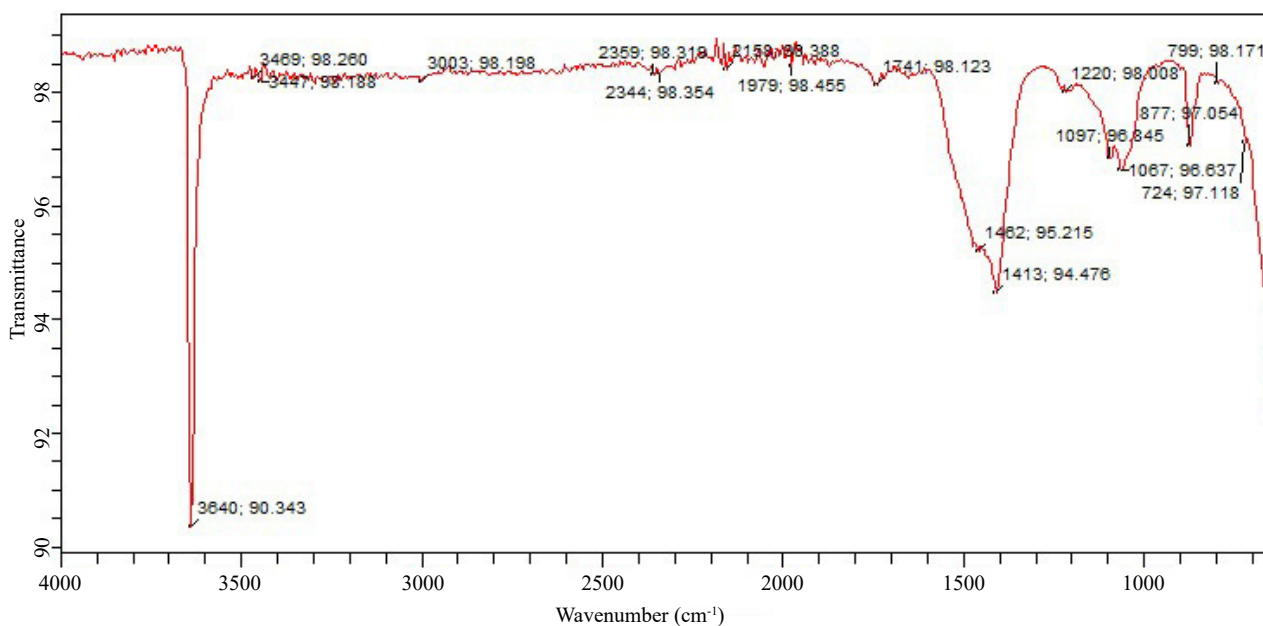**Figure 1**. FTIR of uncalcined guinea fowl eggshell

Figure 2. FTIR of calcined guinea fowl eggshell

From the basic back titration analysis performed on the calcined eggshell, up to 2.933 mmol/g was realized, signifying high basic sites for the eggshell-derived catalyst. For this reason, superior catalytic activity is highly probable when the CaO catalyst derived from eggshells is tested in a methanolysis reaction.

3.2 Transesterification Reaction

The transesterification reaction was carried out by varying reaction conditions; oil: methanol molar ratio, catalyst loading, in addition to reaction time as shown in Table 1. There was an increase in conversion with an increasing molar ratio, and the highest conversion of 81.20% was achieved with a 1:18 molar ratio. The observed insignificant

improvement in the FFA conversion after 100 mins for all molar ratios of methanol to oil was attributed to the esterification of FFA, consequently, water was probably produced and prevented further oil conversion.

Table 1. Biodiesel conversion at different oil: methanol molar ratio and catalyst amount

Oil: methanol /catalyst amount	1:9	1:12	1:15	1:18
0.5%	55.65%	38.00%	46.2%	79.90%
1.0%	59.80%	59.80%	68.36%	81.20%
1.5%	62.40%	62.30%	79.90%	59.80%
2.0%	70.00%	69.84%	81.15%	24.60%

It can be seen from Table1 that the coconut oil conversion to biodiesel increased with increasing catalyst amount from 0.5 to 2.0% with the methanol to oil ratio of 9:1, 12:1, and 15:1. However, for 18:1 it decreased beyond 1.0% catalyst amount. The observed increase in conversion may be attributable to the available active sites with increasing catalyst amounts. When the amount exceeded 1.0%, the catalyst might have overcrowded the reaction mixture, preventing the mass transfer process. The result suggested that the optimum catalyst loading for methanolysis of coconut oil is 1.0% with a conversion of 81.20%. When the catalyst is used in large excess, soap formation may result with consequence in emulsion and difficulty in the catalyst separation after the reaction. In addition, the soap formation would decrease the biodiesel yield as a result of the mislay of triglyceride molecules.

To further optimize the conversion, the reaction time was also varied from half of an hour to three hours, maintaining the methanol: oil molar ratio, amount of catalyst, and temperature at 18:1, 1 wt%, and 60 °C, respectively. The result is presented in Figure 3. The biodiesel conversion was found to increase slightly with increasing reaction time up to 85.81% within two hours, and then declined subsequently. This may be attributed to the equilibrium nature of the transesterification reaction that has been attained at two hours reaction time. The decline in biodiesel conversion afterward may be due to the reversal of the equilibrium process that favors the back reaction, hence the observed decrease in the conversion [17].
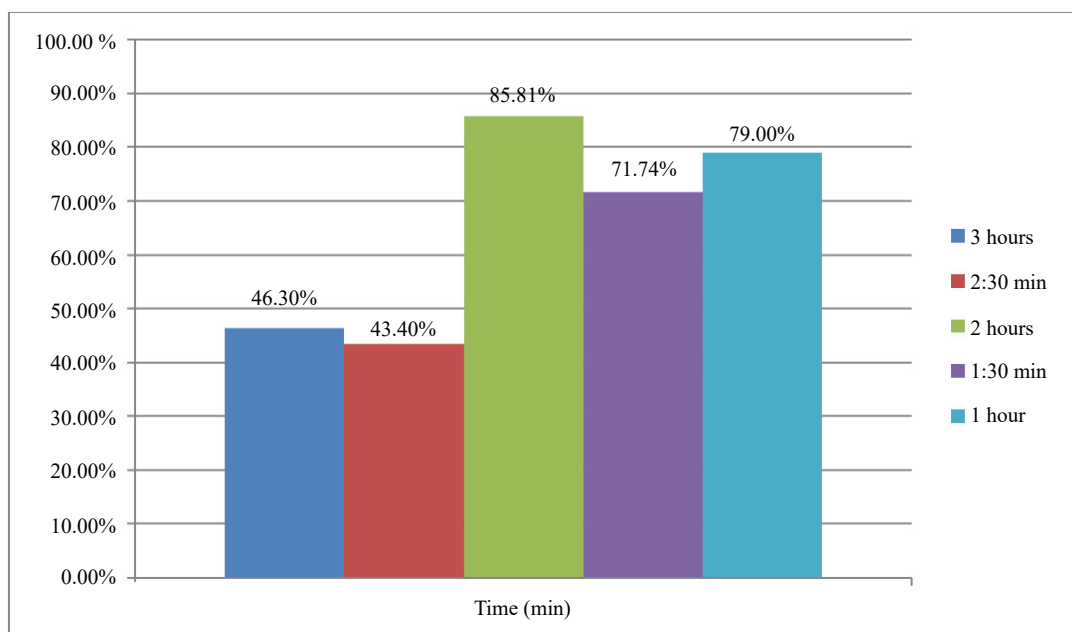

Figure 3. Biodiesel conversion at varying reaction time

Furthermore, there was a decrease in density with an increase in conversion. As a result, the highest conversion of 85.81% corresponded with the lowest density of 0.20 g/dm^3. Whereas the highest density of 0.77 g/dm^3 was achieved at the corresponding lowest conversion of 43.40%. Thus, it can be concluded that high conversion resulted in low density and vice versa. This concurs with the essence of the transesterification of oil or fats to reduce the density for proper application in the existing engines.

Table 2 compared some biodiesel properties; density, acid value, and free fatty acid, with that of ASTM D6751 and ASTM D975 standards, as well as the percentage conversion in this study with the previous study. The properties of the biodiesel in the present study agreed well with those of the standard and are even better than some studies in the literature.

Table 2. Comparison of biodiesel properties

Properties	ASTM D6751 standards for biodiesel fuel	ASTM D975 standards for diesel fuel	This study	Previous study [18]
Density	0.88	0.85	0.20	0.866
Acid Value (60 °C, g/dm³)	-	-	0.13	2.70
Free Fatty Acid (%)	-	-	0.066	1.35
Percentage Conversion (%)	-	-	85.81%	84.80

4. Conclusion

A CaO catalyst was derived from waste guinea fowl eggshells, and its successful synthesis was proved by the result from the FTIR analysis, with the FTIR spectrum revealing a peak at 665 cm^{-1} corresponding to the Ca-O bond. This is vindicated by the appearance of Ca(OH)$_2$ peak around 3640 cm^{-1}, due to surface water attached to Ca^{2+}. While from the basic back titration, a value of 2.933 mmol/g was obtained, indicating a high number of basic sites. Consequently, the activity test for the catalyst signified that one hour reaction time, 1:18 oil to methanol molar ratio, 1% catalyst loading, and 60 °C reaction temperature gave the best yield, with a conversion of 85.81%. The production of CaO catalyst from waste eggshells will not only help in curtailing environmental menace but also make the process economical and the biodiesel cheaper.

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