



## Evaluation of Shell-Derived Calcium Oxide Catalysts for the Production of Biodiesel Esters from Cooking Oils

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### Abstract

Due to the high cost of feedstock and catalyst in biodiesel production, the viability of the biodiesel industry has been dependent on government subsidies or tax incentives. In order to reduce the cost of production, food wastes including eggshells and oyster shells have been used to prepare calcium oxide (CaO) catalysts for the transesterification reaction of biodiesel synthesis. The shells were calcined at 1000 °C for 4 hours to obtain CaO powders which were investigated as catalysts for the transesterification of waste cooking oil. The catalysts were characterized by Fourier Transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), X-ray powder diffraction (XRD) and X-ray fluorescence (XRF) spectroscopy. Reaction parameters such as methanol-to-oil molar ratio, CaO catalyst concentration, and reaction time were evaluated and optimized for the percentage conversion of cooking oil to biodiesel esters. The oyster-based CaO showed better catalytic activity when compared to the eggshell-based CaO under the same set of reaction conditions.

**Keywords:** Biodiesel production; Calcium oxide; Calcination of oyster and egg shells; Catalyst characterization; Transesterification; biodiesel composition; Catalytic conversion of triglycerides into fatty acid methyl esters.

## 1. Introduction

The increase in global energy demand, diminishing fossil fuel reserves, awareness of climate change issues, and environmental pollution resulting from the excessive use of fossil fuels, have in the recent past triggered serious interest among researchers in investigating alternative energy sources which can supplement or substitute fossil fuels.

Vegetable oils are mainly esters of fatty acids and glycerol, which can be converted to fatty acid methyl esters (FAME), also known as biodiesel [1]. Much attention has been focused in the last few decades on utilizing heterogeneous catalysts for biodiesel production instead of the homogeneously catalyzed transesterification of vegetable oil. The pure CaO or CaO mixed with some other metal oxides, with its low solubility in methanol, FAME and glycerol, low cost and availability, is one of the most promising among the proposed heterogeneous catalysts [2].

Biodiesel has been identified as a suitable alternative to petroleum diesel due to its advantages including biodegradability, renewability, negligible toxicity, higher flash point, higher cetane number, and higher combustion efficiency [3, 4]. Although biodiesel has many advantages over the traditional petroleum diesel, the commercial acceptance of biodiesel has been limited due partly to the high production cost and the dependence on government subsidies to make biodiesel cost-competitive with petroleum diesel [5, 6]. The high cost of production is mainly attributed to the high cost of feedstocks and catalyst consumption. Approximately 70 – 95% of the overall production cost of biodiesel is expended on raw material purchase [7]. Effective ways to reduce the cost of production involve the use animal fats or waste cooking oil (WCO) as feedstocks. The use of WCO as biodiesel feedstock is of interest to researchers because it utilizes waste products thereby eliminating the need for their disposal. Using alternative feedstock like WCO can effectively reduce the cost of raw material by 60 – 70 % [8].

Transesterification is the most advanced and the commonest technique used in biodiesel production. This process is often reliant on a catalyst to improve the surface contact between the alcohol and the triglyceride. Currently, biodiesel synthesized for commercial purpose via transesterification of triglycerides generally makes use of inexpensive homogeneous base catalyst like potassium hydroxide or sodium hydroxide. However, the application of homogeneous catalyst in biodiesel synthesis is usually accompanied with some purification and separation processes that require more equipment which ultimately add to the overall production cost. Also, large amounts of

wastewater are usually generated in the purification step [9]. Another major disadvantage of homogeneous catalyst is non-reusability. For these reasons, heterogeneous catalysts have emerged to overcome some of these challenges. Heterogeneous catalysts are reusable and can be applied to continuous processes without necessarily regenerating the catalyst. Unlike homogenous catalysts, the use of heterogeneous catalysts does not require water washing. The purification of the products is simplified and a very high ester yield is obtained [10]. Most alkaline earth metal oxides with high basic strength can be utilized as heterogeneous catalyst for the transesterification of triglyceride to produce biodiesel. Calcium oxide (CaO) is one of the most promising heterogeneous catalyst under this category. It can be obtained readily by calcination of limestone and/or renewable sources like shell materials which contain mainly calcium carbonate (CaCO<sub>3</sub>). In line with that, [11], investigated microwave assisted transesterification of palm oil catalyzed by calcined egg shell and obtained optimum yield of fatty acid methyl ester (FAME) of 96.7% at 4 min reaction time, methanol-to-oil molar ratio of 18:1, 900 W microwave power and 15% catalyst loading. Tan, *et al.* [12], reported that waste ostrich and chicken eggshells can be utilized as heterogeneous base catalyst for transesterification of used cooking oil. These studies revealed that waste shell materials can be used as potential catalysts for low-cost production of biodiesel. Whereas many eggshell based calcium oxides had been reported in literature, this present study tend to compare the catalytic activities of the calcium oxides derived from sea animal (oyster) and a terrestrial animal (chicken eggshell) in the transesterification of waste cooking oil. The efficiency of calcination is characterized by X-ray powder diffraction (XRD) and thermogravimetric analysis (TGA). The influence of process parameters such as methanol-to-oil molar ratio, percentage by mass of catalyst, and reaction time on biodiesel yield is evaluated and optimized. The percentage conversion of the synthesized biodiesel is determined by <sup>1</sup>H NMR.

## 2. Material and Method

### 2.1. Biodiesel Feedstocks and Reagents

Both Great Value vegetable oil (Walmart, Bentonville, Arkansas, USA) and waste cooking oil (WCO) were used to produce biodiesel for comparison. The waste cooking oil was procured from the university cafeteria at no cost. Before use, oil was heated to 110 °C for 1 hour to remove water contents and subsequently filtered in order to remove food debris. Anhydrous methanol of analytical grade was purchased from Sigma-Aldrich and used as received. Chicken eggshells were obtained from Waffle House Restaurant in Murfreesboro, Tennessee whereas the oyster shells were obtained from a local restaurant in Nashville, Tennessee, USA.

### 2.2. Catalyst Preparation

The shells were thoroughly washed with deionized water to remove impurities and subsequently dried in an electric oven at 110 °C for 24 hours. They were crushed into smaller pieces using porcelain mortar and pestle and then reduced into fine powder with the aid of a mechanical grinder. Thereafter, the fine powder was calcined in a muffle furnace at 1000 °C at a heating rate of ~16 °C/min for 4 hours to yield calcium oxide (CaO) as a transesterification catalyst. After calcination, the CaO powder was transferred immediately into an airtight container and allowed to cool slowly in a desiccator to prevent contact with atmospheric moisture and carbon dioxide which can cause unwanted side reactions.

### 2.3. Catalyst Characterization

A Model Q500 thermogravimetric analyzer (TA Instruments, New Castle, Delaware, USA) was used to analyze the decomposition and phase transition of the shell-derived CaCO<sub>3</sub> powder. A heating rate of 11 °C/min was used to analyze the loss of sample mass from about 10 mg of finely ground eggshell or oyster shell powders. A MiniFlex 600 X-ray powder diffractometer (Rigaku, Tokyo, Japan) was used to confirm the crystalline phases of the calcined shell powders using CuK<sub>α</sub> radiation over a 2θ range from 5° to 80° with a step size of 0.02° at a scanning speed of 5°/min. A Niton XL3t X-ray fluorescence analyzer (Thermo, Billerica, Massachusetts, USA) was used to characterize the elemental composition of the shell-derived CaO catalysts loaded onto the sample holders covered with a thin polypropylene film.

### 2.4. Procedures of Biodiesel Synthesis

The transesterification reaction of the WCO oil and methanol was performed in a three-neck round bottom flask of about 250 mL capacity equipped with a water-cooled reflux condenser and a thermometer for regular temperature measurement. The third neck was used as the sampling outlet. Known amounts of the catalyst and methanol were mixed together and heated at 60 °C for 30 minutes to form the methoxide. The methoxide was added into a round-bottom flask which contains a known quantity of a preheated oil at 60 °C. The mixture was constantly stirred with a magnetic stir bar at 65 °C for the reaction times under review. Reaction conditions such as methanol-to-oil molar ratio, catalyst concentration, and reaction time on biodiesel yield were varied and optimized. At the end of the reaction, the catalysts were separated from the mixture by centrifugation. The upper layer was decanted into a separating funnel and allowed to settle for 24 hours. Excess methanol was evaporated via hot-plate heating of the samples before the analysis of the final product by gas chromatography-mass spectrometry (GC-MS).

## 2.5. Biodiesel Conversion Percentage and Biodiesel Ester Analysis

The percentage conversion was analyzed by a 300 MHz  $^1\text{H}$  NMR spectrometer (JEOL, Tokyo, Japan). Replicate experiments were conducted for more reliable results. The percentage conversion (C %) was calculated according to the following equation developed by Knothe [13].

$$C \% = 100 \times \frac{2A(\text{OCH}_3)}{3A(\alpha\text{CH}_2)} \quad (\text{Equation No. 1})$$

where  $A(\text{OCH}_3)$  = Integration value of the methoxy protons of the methyl esters

and  $A(\alpha\text{CH}_2)$  = Integration value of the  $\alpha$ -methylene proton

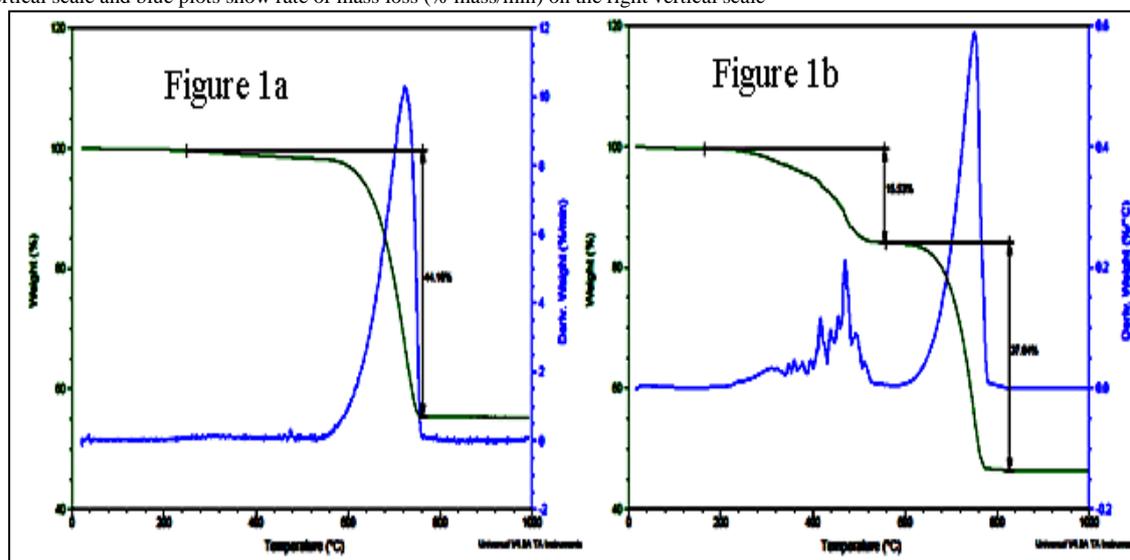
The distribution of fatty acid methyl esters in the biodiesel was analyzed by a Shimadzu QP2010 gas chromatograph coupled to mass spectrometer (Kyoto, Japan) with electron impact ionization at 70 eV. A 30-meter Zebtron ZB-5 GC column (Phenomenex, Torrance, California, USA) with a stationary phase of 95 % polydimethylsiloxane with 5% phenyl substitution was used.

## 3. Results

### 3.1. Catalyst Characterization

The curves from thermogravimetric analysis (TGA) were used to investigate the decomposition behavior of the shell materials when heated in a regulated environment. Figure 1a and 1b shows the decomposition behavior of oyster shell powder and eggshell powder, respectively. The oyster shell powder (Figure 1a) experienced just a single step weight loss starting at 570 °C, reaching a maximum rate of mass loss at 570 °C, and ending at a stable mass 760 °C. A loss of 44.2 % of the original mass of the shell powder is due to the evolution of  $\text{CO}_2$  (molar mass  $\approx 44 \text{ g}\cdot\text{mol}^{-1}$ ) from  $\text{CaCO}_3$  (molar mass  $\approx 100 \text{ g}\cdot\text{mol}^{-1}$ ). The single step decomposition of the oyster shell implied that there were minimal organic impurities found in the oyster shell structure. At above 800 °C, the sample mass remained constant which is indicative of complete decomposition to CaO. The TGA curve of eggshell powders indicates a two-stage weight loss. The weight loss recorded at 230-520 °C can be attributed to loss of organic impurities present in the shell powder. This corresponds to about 15.5 % of the total weight loss shown by the sample which has a molar mass of  $\sim 100 \text{ g}\cdot\text{mol}^{-1}$ . At the temperature range of 560-800 °C, a significant weight loss was observed in both samples due to the release of carbon dioxide from the decomposed calcium carbonate. For the chicken eggshell powder, the 37.6 % weight loss as seen in the second stage is attributed mainly to the loss of  $\text{CO}_2$ . The calcination temperature should be above 800 °C to ensure the complete conversion of the eggshell to CaO. This is consistent with the work published by Viriya-Empikul, *et al.* [14], who reported temperature above 800 °C as the optimum calcination temperature for the production of CaO from shell materials.

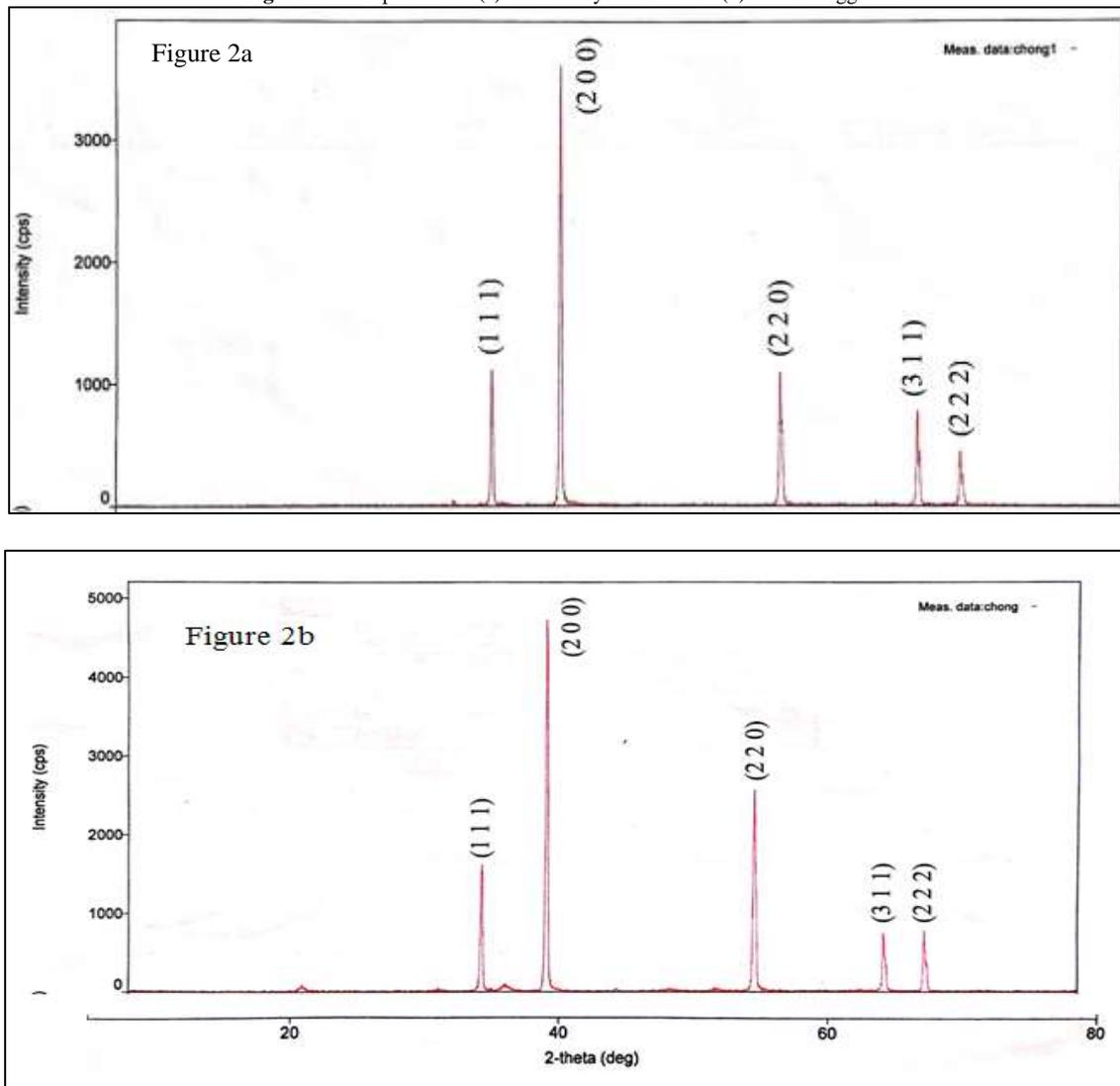
**Figure-1.** TGA curves of (a) uncalcined oyster shell powder and (b) uncalcined eggshell powder. Green plots show percentage mass loss on the left vertical scale and blue plots show rate of mass loss (% mass/min) on the right vertical scale



The XRD patterns of the calcined shell powders revealed that CaO was the major component of the calcined shell powders. The diffraction peaks were indexed using the Joint Committee on Powder Diffraction Standards (JCPDS) file. The presence of sharp XRD reflections with (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) orientations as shown in Figures 2a and 2b implied that the calcined shell powders were highly crystalline after the heat treatment process at a temperature of 1000 °C [11]. The main diffraction peaks for both calcined shell powders appeared at  $2\theta$  angles of 32.9°, 38.1°, 54.5°, 64.8° and 68.0°. The characteristic peaks for calcium hydroxide phase were also observed in the calcined eggshell pattern at  $2\theta$  angles of 18.7° and 34.7°. The XRD patterns of the calcined powders were compared to the patterns of the original uncalcined powders of oyster shells and eggshells containing calcium carbonate. There were no traces of calcium carbonate found in both the calcined shell powders of oysters and chicken eggs. For the XRD pattern of calcined egg-shell powders, there were five additional tiny diffraction peaks below the  $2\theta$  angles of 54.5° compared to the calcined oyster shell powders that lacked these XRD signals. It is

likely that these weak XRD signals are related to the calcined products of eggshells formed at the temperature of 230-520 °C during the heat treatment as indicated in the TGA data discussed above.

**Figure-2.** XRD patterns of (a) calcined oyster shell and (b) calcined eggshell



The trace elements of the calcined shell powders were analyzed to determine if they play a role in affecting the catalytic efficiencies of the catalysts. In Table 1, Sr was the next most abundant element after calcium, and it was three times higher in the calcined oyster shells relative to eggshells. Both Fe and Mn were found in the calcined oyster shells but they were below limit of detection (i.e. <LOD) in eggshells.

**Table-1.** XRF data showing elemental composition of oyster shells and eggshells

Sample	Uncalcined Oyster Shells	Calcined Oyster Shells	Uncalcined Egg Shells	Calcined Egg Shells
Sr	1063±10 ppm	1715±22 ppm	268±5 ppm	465±9 ppm
Fe	159±28 ppm	310±53 ppm	56±22 ppm	< LOD
Mn	130±38 ppm	276±81 ppm	60±33 ppm	< LOD
Cr	64±23 ppm	< LOD	< LOD	60±32 ppm
Ca	(50±0.27%)	(70±0.41%)	(40±0.25%)	(70±0.41%)

### 3.2. Effect of Catalyst Concentration

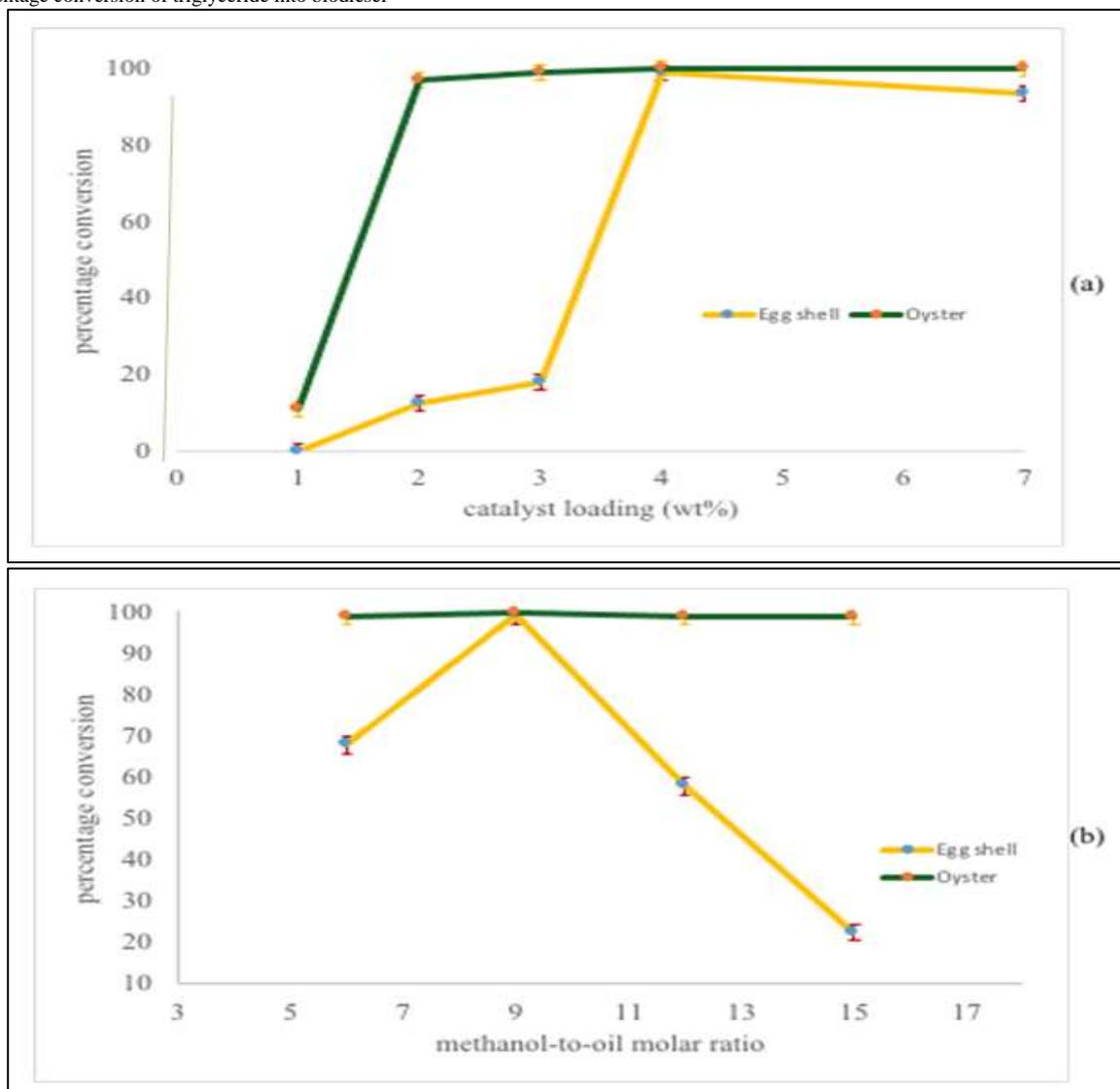
The optimal mass loading of catalyst for transesterification depends on the nature of the catalyst and the type of oil. The catalytic activities of the shell-derived CaO in transesterification of WCO and methanol were investigated by varying the loading of catalyst from 1.0 to 7.0 wt. % (based on oil volume). The dependence of biodiesel conversion on catalyst loading is shown in Figure 3a for the reaction performed using 9:1 methanol-to-oil molar ratio at 65 °C for 2 hours. As the mass of the catalyst was increased from 1.0 to 4.0 wt. %, the percentage of conversion via transesterification increased until the maximum values of 99.3 % and 99.8 % were attained for the egg and oyster shell catalysts, respectively. This trend in catalytic activity is attributed to increased number of active sites and surface area in contact with reactant molecules as the catalyst loading was increased. When the concentration of the catalyst was increased beyond 4.0 wt. %, the percentage conversion slightly dropped for both catalysts due to

increased viscosity of the reaction mixture which offered resistance to mass transfer in the liquid-liquid-solid system [12]. The 4.0 wt. % loading was chosen as the optimal level of catalyst loading.

### 3.2.1. Effect of Methanol-to-Oil Molar Ratio

The molar ratio of the reactants plays an important role in determining the extent of conversion. Generally, the reactions proceed in three sequential and reversible reactions, wherein triglycerides are converted to diglycerides, monoglycerides, and glycerol by releasing one mole of fatty acid methyl esters (FAMES) at every step of the reaction. Stoichiometrically, the transesterification reaction requires three moles of methanol to convert one mole of triglyceride into three moles of esters. In practice, however, excess methanol is utilized to shift the equilibrium position in favor of the alky esters formation [3]. The effect of methanol-to-oil molar ratio was probed at 4.0 wt. % catalyst, 2.00 h reaction time, and reaction temperature of 65 °C. The results are shown in Figure 3b. For both catalysts, the percentage conversion of biodiesel increased as the methanol-to-oil molar ratio was increased from 6:1 to 9:1 with the more drastic increase shown in the eggshell-derived CaO catalyst. This is because, in addition to the increased rate of the ester formation, excess methanol tends to remove product molecules adhered to the catalyst surface thereby regenerating the catalytic site for more activities [15]. Additional increase beyond the 9:1 methanol-to-oil molar ratio however led to a decrease in percentage conversion. Researchers reported that glycerol tends to dissolve in excess methanol thereby delaying the separation of glycerol and ester leading to the decreased yields for reactions with methanol-to-oil molar ratios of greater than 9:1 [12]. At both the 12:1 and 15:1 molar ratios, there was significant decline in the biodiesel conversion percentages for the eggshell-based CaO catalyst whereas the oyster-derived CaO yielded consistently high conversion percentages of greater than 97% for the biodiesel product.

**Figure-3.** (a) Effect of catalyst loading on percentage conversion of triglyceride into biodiesel (b) Effect of the methanol-to-oil molar ratio on percentage conversion of triglyceride into biodiesel

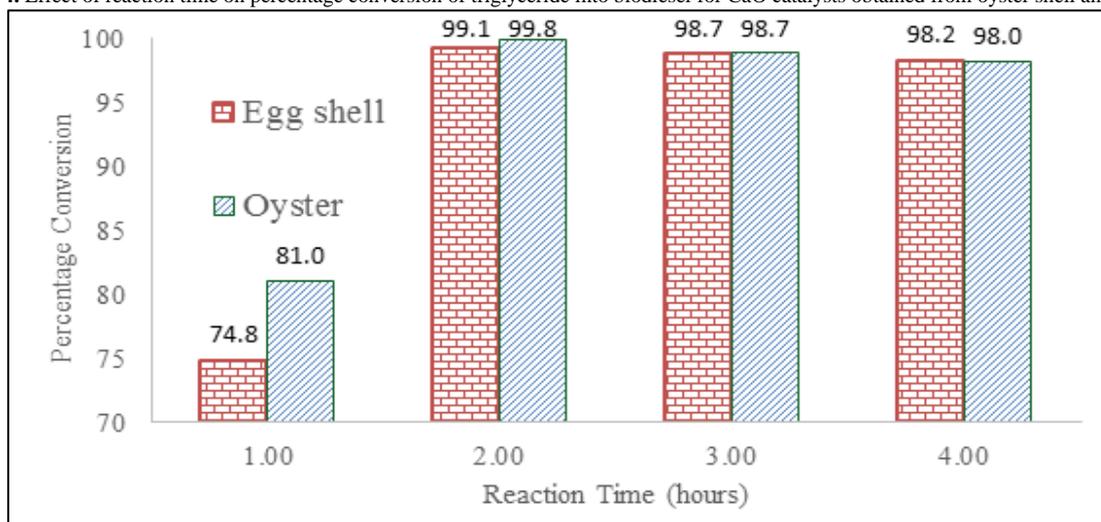


### 3.2.2. Effect of Reaction Time

When using heterogeneous catalyst for biodiesel production, reaction time is an important parameter to consider due to the mass transfer limitation that exists in the reaction mixture. Figure 4 shows the effect of reaction time on percentage conversion of biodiesel. Both catalysts showed increase in percentage conversion with the increase in the

reaction time for the transesterification reaction. The maximum conversions of 99.8% and 99.1% were achieved for the CaO catalysts prepared from the shells of oysters and chicken eggs, respectively, based on 2.00 hours of reaction time, 9:1 methanol-to-oil molar ratio, 4.0 wt. % catalyst loading, and reaction temperature at 60 °C. Beyond 2.00-hr reaction time, saponification reaction occurred which caused a slight decrease in conversion percentages.

**Figure-4.** Effect of reaction time on percentage conversion of triglyceride into biodiesel for CaO catalysts obtained from oyster shell and eggshell

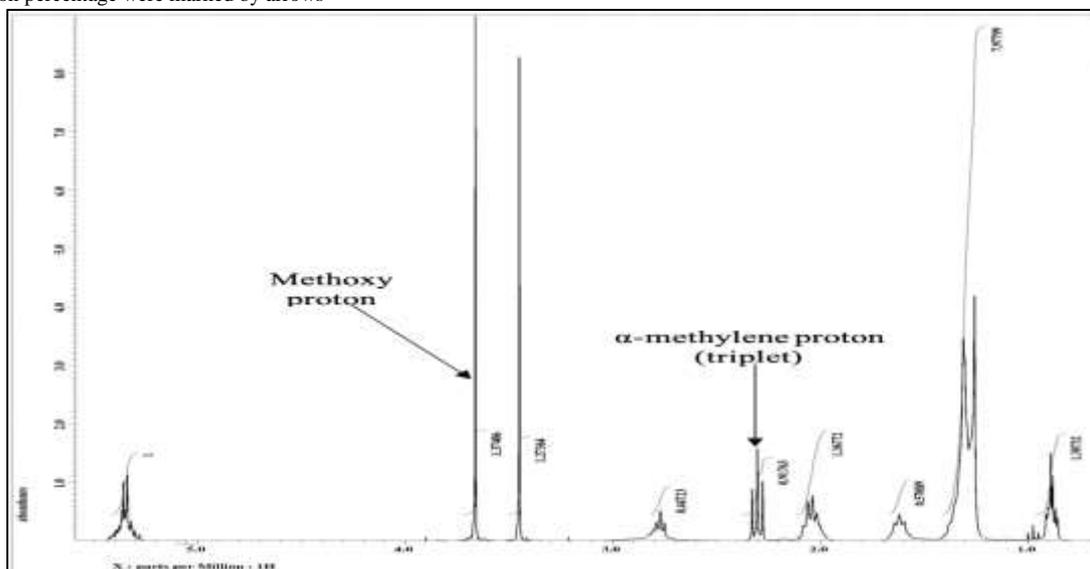


### 3.3. Biodiesel Conversion Yields and Analysis of Fatty Acid Methyl Esters

A comparative study of the catalytic activity of the shell-based calcium oxide revealed that the calcined oyster shells generally have better catalytic activity than the eggshell under the same reaction conditions. The difference in activity could be related to the morphology, basic strength or chemical composition of the trace elements in the polycrystalline CaO materials. The catalytic efficiency is measured by the percentage conversion of synthesized biodiesel as estimated by two specific proton signals of the NMR spectrum indicated in Figure 5. The characteristic methoxy and  $\alpha$ -CH<sub>2</sub> protons appear as a singlet and a triplet respectively at 3.68 ppm and 2.32 ppm in both samples. These two distinct sets of peaks were used as confirmatory signals for the formation of methyl ester. Equation (1) was used to calculate the percentage conversion (C%) of triglyceride to methyl esters based on the peak area fractions of methoxy hydrogen (-OCH<sub>3</sub>) relative to methylene hydrogen at the  $\alpha$ -carbon position (A $\alpha$ CH<sub>2</sub>). The oyster shell-derived CaO gave percentage conversion of 99.8 $\pm$ 0.5 % whereas the eggshell-based CaO gave a 99.3 $\pm$ 0.5 % conversion under the same optimal reaction conditions of 4.0 wt. % catalyst, 2.00 hours of reaction time, 9:1 methanol-to-oil molar ratio, and transesterification reaction temperature of 65 °C. These conversion percentages are very close to the traditional biodiesel production methods using 0.5 wt. % sodium hydroxide catalyst at the methanol-to-oil molar ratio of 6:1 or 9:1.

The other proton signals of the biodiesel esters are assigned, using a detailed NMR study of biodiesel [16], as follows in the NMR spectrum: 5.35ppm (vinyl CH=CH), 2.78 ppm (bisallylic, CH=CH-CH<sub>2</sub>-CH=CH), 2.04 ppm (allylic, CH<sub>2</sub>CH=CH), 1.62 ppm (CH<sub>2</sub>-CH<sub>2</sub> C=O); as well as 1.25 ppm and 1.30 ppm (long alkyl chain, (CH<sub>2</sub>)<sub>n</sub>), 0.98 ppm and 0.89 ppm (terminal CH<sub>3</sub> of long alkyl chain unsaturated and saturated fatty acids, respectively). The appearance of C18:2 is indicated by their characteristic signals at 2.78 ppm.

**Figure-5.** <sup>1</sup>H NMR spectrum of soybean oil biodiesel produced using calcined oyster shell powder. The two peak clusters used in calculating conversion percentage were marked by arrows



The GC-MS results are consistent with the NMR data showing near complete conversion of vegetable oil or triglycerides into esters. The major FAMES detected include C16:0, C18:2, C18:1 (Z isomer), C18:1 (E isomer), and C18:0 in the ascending order of increasing GC retention times. The MS match indices using the NIST mass spectral database of the methyl palmitate, methyl oleate isomers, and methyl linoleate peaks are all above 90.

## 4. Discussion

### 4.1. Properties of the Calcined CaO Catalyst

The potential uses of diverse types of discarded shells from edible seafoods presents an attractive and yet challenging problem for chemists. Although shells are generally recognized as being composed of  $\text{CaCO}_3$  that can be calcined to form CaO for use as catalysts, their performance characteristics are different for each type of shells. The reasons for their unique catalytic properties include the presence of other concomitant elements besides calcium, the inclusion of organic moieties, and the existence of the polymorphic forms of  $\text{CaCO}_3$  such as calcite, aragonite, and vaterite [17]. It is necessary to employ more sophisticated analytical tools such as Raman microscopy, X-ray photoelectron spectroscopy, and secondary ion mass spectrometry to unravel the intricate structural differences of both the shells and the calcined products in order to select the best shell materials for conversion into CaO catalysts.

### 4.2. Performance of CaO in Transesterification

The significant difference of the catalyst performance for calcined materials prepared from eggshells and oyster shells is intriguing. There are three possible explanations that need further investigation to understand why oyster shells is a better starting material than eggshells for preparing calcined CaO catalyst. First, the CaO catalyst prepared from oyster shells seems to yield larger crystalline powders that are more resistant to absorbing moisture in the ambient air or water impurities or by-products from transesterification. This is manifested in the presence of small XRD signals of  $\text{Ca}(\text{OH})_2$  at the  $2\theta$  angles of  $18.7^\circ$  and  $34.7^\circ$  in Figure 2b.  $\text{Ca}(\text{OH})_2$  is more soluble than CaO in the reaction mixture and therefore led to the saponification problem that resulted in low yields of eggshell-derived CaO relative to CaO prepared with oyster shells as shown in Figure 3b. Second, the smaller crystalline CaO particles prepared from eggshells could have residual carbonized residues that precluded their catalytic function. Chicken eggshells likely contain more organic moiety than oyster shells as indicated by the evolution of gases in the TGA characterization in Figure 1b. The weight loss recorded at  $230\text{--}520^\circ\text{C}$  could be due to the conversion of organic components of eggshell powder such as proteins into partially carbonized CaO powder. Since the oyster-based CaO catalyst was devoid of the organic components, the CaO catalyst loading of 2.0-7.0 wt. % for the oyster-based catalyst yielded >95% conversion compared to chicken egg-based CaO that required at least 4.0 wt. % to achieve similar performance and yield unacceptable conversion rates at 1.0, 2.0, and 3.0 wt. % of catalyst loading. Third, the trace metal oxides found in the oyster-based CaO may have worked in synergy with the CaO more effectively in boosting the catalytic strength; this is mentioned in several review articles that mixed metal oxides can enhance the catalytic performance of CaO [18-20]. Three elements, namely, strontium, iron, and manganese, were found to be higher in oyster-based CaO catalysts based on XRF analysis. More work needs to be done in using more sensitive techniques like inductively coupled plasma combined with optical emission spectrometry or mass spectrometry techniques to quantify trace metals in the shell-based catalysts. The difference in activity could be related to the morphology, basic strength or chemical composition of the trace elements in the polycrystalline CaO materials.

### 4.3. Utilization of Waste Materials in Biodiesel Production

The idea of using waste materials including waste cooking oils, animal fats, and discarded shells as material inputs for producing biodiesel is inherently attractive. Although biodiesel is a clean-burning transportation fuel compared to petroleum diesel in terms of emissions of sulfur dioxide, carbon monoxide, particulate matter, and many volatile organic compounds, its widespread is limited by the higher production costs associated with the oil feedstocks, catalysts, and the inadequacy of government subsidies based on the credit of biodiesel for reducing carbon emission. Several recent studies have aimed at promoting the use of biodiesel through new research findings on the use of low-cost feedstocks [6, 9, 21, 22].

## 5. Conclusion

The research results show that it is technically feasible to use shell-derived CaO catalysts to successfully convert cooking oils or vegetable oils into biodiesel esters. However, more research needs to be carried out to identify the best shell materials to use for calcination and to develop the best treatment conditions for converting the waste shells into highly efficient transesterification catalyst. More research needs to be carried out to evaluate the durability of the catalysts and how many times they could be recycled for transesterification without losing catalytic efficiency. The possibility of controlling the calcination atmosphere to reduce carbonization should be investigated. In addition, it is necessary to control the CaO crystallite size by choosing the milling, sieving, and calcination conditions. Lastly, there should be future endeavors in exploring the engineering aspects of scaling up the production of CaO catalyst via calcination of waste shells.

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