

# Calcium Oxide Derived from Egg Shells: A Low Cost Catalyst for Biodiesel Production

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The decrease in fossil fuels reserves triggers the need for alternative sources of energy. One renewable energy source that may be considered as a substitute for traditional fossil fuels is biodiesel. Biodiesel is synthesized from waste cooking oil by transesterification with a CaO catalyst derived from egg shells. The chicken egg shells were treated by calcination in a furnace at a temperature of 900 °C for 3 hours with a flow rate of 10 °C/min. The egg shells were completely converted into CaO catalyst, as characterized by XRD. BET analysis revealed that the catalyst is mesoporous with a surface area of 1.1152 m<sup>2</sup>/g and an average pore diameter of 78.2 nm. CO<sub>2</sub>-TPD analysis revealed that the CaO catalyst has strong basic active sites with a basic amount of 630 μmol/g. SEM images show that the catalyst's morphology is more regular, and the size of its particles decreased after calcination. Results showed the percentage of FFA was 0.4%. The effects of catalyst loading, methanol/oil ratio, temperature, and reaction time on the transesterification of waste cooking oil were investigated. The results obtained showed that 2 wt.% of catalyst, 15:1 of methanol/oil molar ratio, and reaction at 65 °C for 5 hours are the optimum parameters, with a biodiesel yield of 80%. This study revealed that CaO derived from chicken egg shells has good catalytic activity in the transesterification of waste cooking oil into FAME.

**Key words:** Biodiesel; chicken egg shell; transesterification; waste cooking oil

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Fossil fuel consumption is rising worldwide due to industrialization and an ever-increasing population. The world depends a great deal on fossil fuels such as petroleum, natural gas and coal [4], which are essential for transportation, heating and electrical power. In addition, fossil fuels are known to be a major source of greenhouse gases and other airborne contaminants such as NO<sub>2</sub>, SO<sub>2</sub>, CO, particulate matter and volatile organic compounds which cause global warming, acid rain and depletion of the ozone layer [11]. One of the renewable sources of energy that could be considered as a substitute for traditional fossil fuels is biodiesel. From previous research, biodiesel is eco-friendly due to its biodegradability and low effusion of carbon dioxide, as well as its sulphur-free and nontoxic nature [6]. Biodiesel also possesses physicochemical properties similar to fossil fuels including a high cetane number and a high flash point [15]. Biodiesel should be commercialized in order to overcome the challenges of possible future depletion of world fuel reserves. The prime barrier to the manufacturing of biodiesel on a commercial scale is cost, as it is more expensive compared to fossil fuels [3]. Its high cost of production is due to the cost of raw materials and labour. Aside from this, the lack of raw

materials and an efficient catalytic system are the leading problems facing commercialization of biodiesel to fulfil global demand. In order to solve these problems, the synthesis of biodiesel from transesterification of waste cooking oil derived from egg shells is being studied. In this work, the CaO commonly used for the transesterification of palm oil is derived from chicken egg shells. However, the utilization and the potential of this catalyst is yet to be determined for waste cooking oil which has a low fatty acid content. It is known that basic catalysts could cause a saponification problem if waste cooking oil with high free fatty acid (FFA) content is used as the feedstock [13-14]. Waste cooking oil that has a low FFA value potentially could substitute for the expensive feedstock as it has received excellent reviews as an alternative option for low cost feedstock for biodiesel synthesis.

## MATERIALS AND METHODS

### 1. Preparation of Catalyst

The egg shells were washed with distilled water to remove impurities and then dried in an oven at 120 °C

for 6 hours. The dried egg shells were ground to a fine powder in a blender for 5 minutes. The fine powder was then calcined in a furnace at a temperature of 900 °C for 3 hours with a flow rate of 10 °C/min to eliminate any form of carbon and to achieve complete conversion of CaCO<sub>3</sub> to CaO [10]. The obtained CaO was stored at room temperature in a glass vial sealed with paraffin film.

## 2. Catalyst Characterization

The characteristics of the catalyst were assessed using X-ray diffraction spectroscopy (XRD) and scanning electron microscopy (SEM). XRD analysis was carried out on a Bruker D8 diffractometer equipped with a Cu anode. The analysis of the powdered catalyst's crystallinity was performed at 40kV and 30mA using Cu K $\alpha$  radiation as suggested by a previous study [5]. The data was collected in the 2 $\theta$  range from 10° to 90° (2°/min). Nitrogen adsorption/desorption isotherms generated for each sample were analyzed using the sorption analyser (Micrometrics ASAP 2020). Adsorption isotherms were recorded at 77 K after degassing at 150 °C. The adsorption isotherms were then used to calculate the BET surface area. Desorption isotherms were used to calculate pore volumes and pore size distributions.

## 3. Acid Value Determination

An acid value determination was conducted on the waste cooking oil. 30 mL of 95% ethanol was added into 2.0 g oil in a conical flask. The mixture was heated in a water bath for 2 minutes and left to cool to room temperature. 1 mL of phenolphthalein was poured into the conical flask and titrated with 0.1 N of potassium hydroxide until a very pale pink colour was observed. The acid value (AV) and percentage of free fatty acids (FFA) in the waste cooking oil were calculated by using the formula below:

$$AV \text{ (mg KOH/g)} = \frac{56.1 \times N \times V}{w}$$

Where;

N = normality of KOH

V = volume in mL of KOH consumed

w = weight in g of waste cooking oil

## 4. Transesterification Reaction

The transesterification reaction was performed in a 250 ml three-neck round-bottom flask fitted with a water-cooled condenser and a thermometer. The catalyst was first activated by dispersing it in methanol at 50 °C with constant stirring for 5 minutes. 15.0 g of pre-treated oil in which the methanol to oil ratio was 15:1 was added into the reactor and the reaction was carried out using 2 wt. % of catalyst at 50°C for 2 hours. The mixture was refluxed with stirring at 400 rpm. After the reaction

ended, the product was transferred into a separatory funnel and left overnight to obtain two distinct phases. The lower layer of glycerol was discarded, while the upper layer of biodiesel was purified by washing with boiled water three times. All the processes were repeated with different temperatures (55 °C, 60 °C, 65 °C and 70 °C) and reaction times (3, 4, 5 and 6 hours).

## 5. Analysis of Biodiesel

The biodiesel (methyl ester) produced from the transesterification reaction of WCO was analysed with gas chromatography (GC-FID), (model type FID-ECD 6890N-AGILENT) with a flame ionization detector (GC-FID) and a HP-5 capillary column (30 m  $\times$  0.25 mm internal diameter, 0.25  $\mu$ m film thickness). The carrier gas used was helium with a flow rate of 30 mL/s. The temperature of the injector was 250 °C and the detector 250 °C. The split mode was applied during injection with a split ratio of 40:1.

20 mg of FAME mix (C8-C24) was diluted with 10 mL hexane to produce 2000 ppm stock solution. Methyl heptadecanoate was used as an internal standard and prepared by dissolving 1 g of methyl heptadecanoate with 1000 mL of hexane. 5 mL of FAME stock and methyl heptadecanoate were then mixed (total volume of 10 mL) to inject into the GC-FID. Then, a response factor (RF) for each methyl ester (linolate, myristate, stearate and palmitate) was calculated using the formula shown in Equation 1:

$$RF = \frac{A_{IS} \times C_{IF}}{A_{IF} \times C_{IS}} \quad (1)$$

Whereby:

A<sub>IS</sub> = Area of internal standard, from GC-FID chromatogram

A<sub>IF</sub> = Area of individual FAME, from GC-FID chromatogram

C<sub>IF</sub> = Concentration of individual FAME, ppm

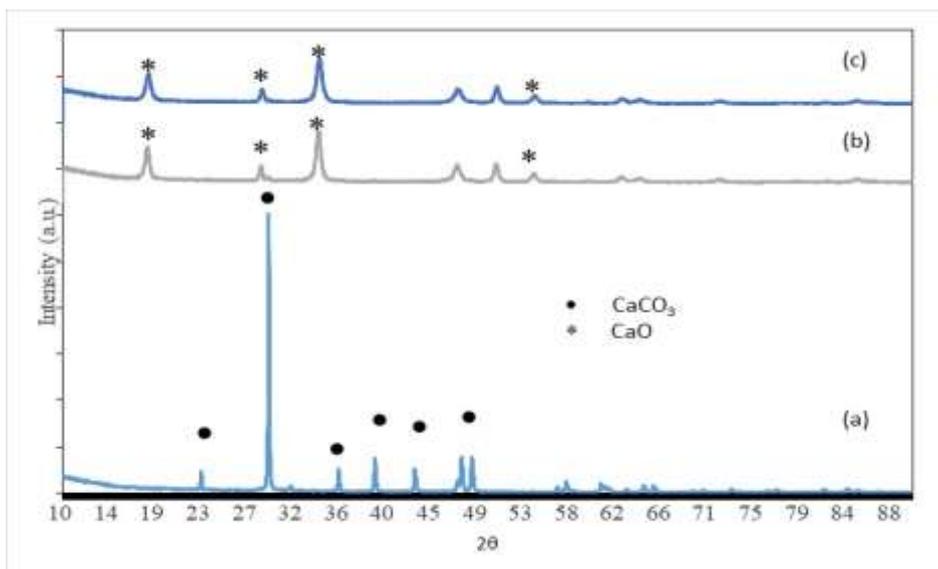
C<sub>IS</sub> = Concentration of internal standard, ppm

## RESULTS AND DISCUSSION

### 1. Catalyst Characterization

#### 1.1. XRD Analysis

The synthesized CaO catalyst was analyzed with X-ray diffraction (XRD). The results of the analyses of egg shell samples before and after calcination are shown in Figure 1. A standard of CaO was also analyzed as a comparison.



**Figure 1.** XRD pattern of (a) egg shells before calcination, (b) standard CaO and (c) CaO from calcined egg shells

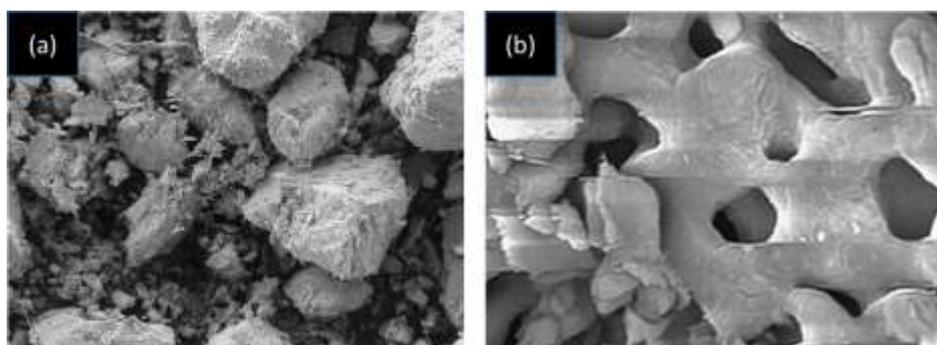
Based on the XRD analysis, the calcined egg shells were totally converted to CaO. The spectrum obtained from the calcined egg shells was indistinguishable from the spectrum obtained from the standard CaO. Furthermore, the peaks present in the original egg shell powder were not present in CaO. The changes in the XRD pattern are caused by the removal of CO<sub>2</sub> from the egg shells as CaCO<sub>3</sub> decomposed to CaO. In previous studies, egg shells were calcined at a temperature range of 200 °C – 1000 °C and it was reported that CaO was successfully formed at temperatures above 900 °C [9,16]. The results showed that egg shells calcined above 800 °C resulted in the most active catalyst. The diffraction patterns of egg shells calcined at temperatures < 800 °C were characteristic of CaCO<sub>3</sub>, and contained CaCO<sub>3</sub> as the major phase and CaO as a minor phase. Conversely, egg shells calcined at temperatures > 800 °C displayed diffraction patterns characteristic of CaO. Thus in this experiment, a CaO catalyst was

successfully derived from egg shells which were calcined at 900 °C.

## 1.2. SEM Analysis

The powdered egg shells were characterized by scanning electron microscopy (SEM) before and after calcination to determine its morphological characteristics. The SEM images in Figure 2 show that the egg shells before and after calcination have different morphologies and particle sizes.

Before calcination, the egg shells showed an irregular crystal structure. Based on a previous study, the particle shape of catalysts derived from egg shells became more regular and the particle size decreased after calcination [9]. Furthermore, the catalyst particles should be cracked with high porosity. The morphological changes may be due to the change in composition.

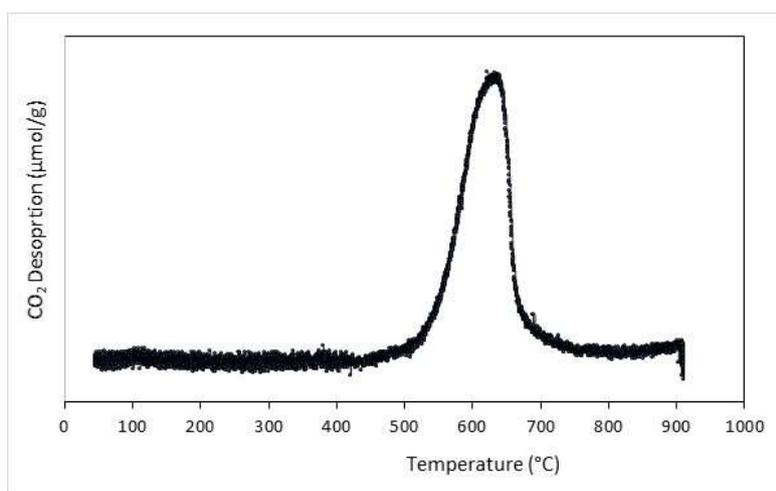


**Figure 2.** SEM images of (a) egg shells before calcination and (b) egg shells after calcination

### 1.3. TPD-CO<sub>2</sub> Analysis

CO<sub>2</sub> temperature-programmed desorption (TPD) analysis was employed to study the basic properties of the prepared catalyst, and the results are shown in Figure 3. CaO is a highly basic oxide catalyst that produces two hydroxide ions (OH<sup>-</sup>) in aqueous solution [2]. Figure 3 clearly demonstrates that the egg shell-derived catalyst calcined at 900 °C possesses broad peaks at the temperature range of 500–700°C, showing the existence of strong basic sites on the surface of catalyst. This peak can be ascribed to CO<sub>2</sub>

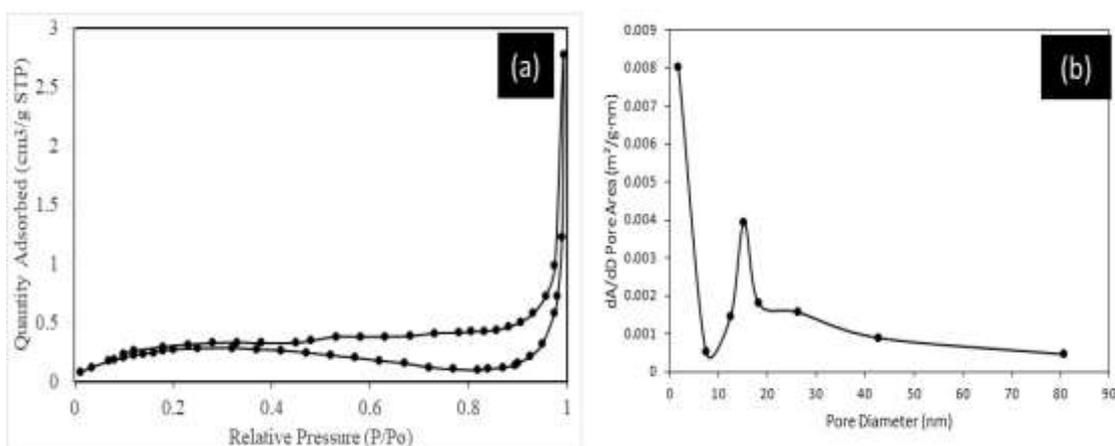
desorption due to the interaction of CO<sub>2</sub> with the strong basic sites. The basic amount of CaO catalyst derived from chicken egg shells was 630 μmol/g. This is similar to results from previous studies which analyzed calcined ostrich and chicken egg shells [12,17]. Those studies showed that both samples exhibited a desorption peak at approximately 600 °C. The calcined ostrich and chicken egg shells provided strongly basic sites with basic amounts of 595 μmol/g and 205 μmol/g respectively. These experimental results indicate that the basicity of the catalyst surface correlates to the activity of the catalyst.



**Figure 3.** Temperature programmed desorption of CO<sub>2</sub> of CaO egg shells

**Table 1.** BET results for CaO from egg shells

Physical property	This study	[12]
BET surface area	1.1 m <sup>2</sup> g <sup>-1</sup>	2.3 m <sup>2</sup> g <sup>-1</sup>
Pore volume	0.0042 cm <sup>3</sup> g <sup>-1</sup>	0.0134 cm <sup>3</sup> g <sup>-1</sup>
Average pore diameter	16.6 nm	11.6 nm



**Figure 4.** N<sub>2</sub> adsorption isotherm linear plot of CaO from egg shells (a) and pore size distribution (b)

#### 1.4. BET Analysis

BET surface area analysis was used to calculate the surface area, pore volume and pore diameter of the catalyst, and the results are summarized in Table 1. The BET surface area, pore volume and average pore diameter of CaO derived from chicken egg shells are  $1.1 \text{ m}^2/\text{g}$ ,  $0.0042 \text{ cm}^3/\text{g}$  and  $16.6 \text{ nm}$  respectively, indicating that the active sites are present at the external surface of the catalyst. This is expected to lead to better and quicker interaction between the catalyst and the feedstock. The results obtained were found to be similar to a previous study [8] as shown in Table 1. The average pore diameter obtained was  $16.6 \text{ nm}$  which is characteristic of mesoporous materials because their average pore diameter is between  $7$  and  $50 \text{ nm}$ , and this is further confirmed by the type IV isotherm linear plot as shown in Figure 4.

### 2. Effect of Different Parameters on Biodiesel Production

#### 2.1. Effect of Catalyst Loading

Production of biodiesel from triglycerides involves a catalyst which speeds up the rate of reaction by producing an alternative pathway. The amount of catalyst may affect the yield of biodiesel. The effect of catalyst loading (wt.%) on the transesterification reaction was investigated using five different amounts of catalyst from  $1 \text{ wt.}\%$  to  $3 \text{ wt.}\%$  based on the weight of the catalyst per volume of waste cooking oil. Figure 5 shows that the yield of biodiesel increased from  $54.2\%$  to  $77.0\%$  with an increase in catalyst concentration from  $1 \text{ wt.}\%$  to  $2 \text{ wt.}\%$ .

This result indicates that increasing the amount of catalyst increases the contact between the catalyst and the reactants, which then affects the reaction rate.

However, when more catalyst (more than  $2 \text{ wt.}\%$ ) was used, the yield of biodiesel slightly decreased because the number of active sites were fully occupied. Therefore,  $2 \text{ wt.}\%$  of CaO catalyst from egg shell was found to be the optimum amount of catalyst to achieve a high yield of biodiesel in 2 hours. This result was similar to recent research [1] that reported  $2 \text{ wt.}\%$  of KOH catalyst produced a biodiesel yield of  $77\%$  while  $2.5 \text{ wt.}\%$  of KOH produced a biodiesel yield of  $55\%$ .

#### 2.2. Effect of Methanol to Oil Molar Ratio

Aside from the catalyst concentration, the methanol/oil molar ratio is also one of the parameters that should be optimized to obtain a good yield of biodiesel through transesterification. Figure 6 shows the effect of five different methanol/oil molar ratios ( $9:1$ ,  $12:1$ ,  $15:1$ ,  $18:1$  and  $21:1$ ) on the percentage of biodiesel yield. The result shows that increasing the methanol/oil molar ratio from  $9:1$  to  $15:1$  led to an increase in biodiesel yield of up to  $80\%$ . However, the biodiesel yield decreased with higher methanol to oil ratios from  $15:1$  to  $21:1$  due to an excess of methanol. A possible reason for this is that the polar  $-\text{OH}$  group of the excess methanol may cause the product to solidify and form a gel that is difficult to separate [8].

The percentage yield of biodiesel is directly proportional to the methanol to oil molar ratio for the egg shell catalyst. In general, the molar ratio for methanol/oil is  $3:1$ . Excessive methanol is necessary to shift the equilibrium to obtain a higher biodiesel yield. However, when the ratio of oil to methanol is too high, it could have an adverse effect on the yield of biodiesel because the concentration of glycerol increases due to the excess methanol in the reaction mixture. A previous study has also reported similar results, where a maximum biodiesel yield of  $89\%$  was reached by using  $15:1$  of the methanol to oil ratio [5].

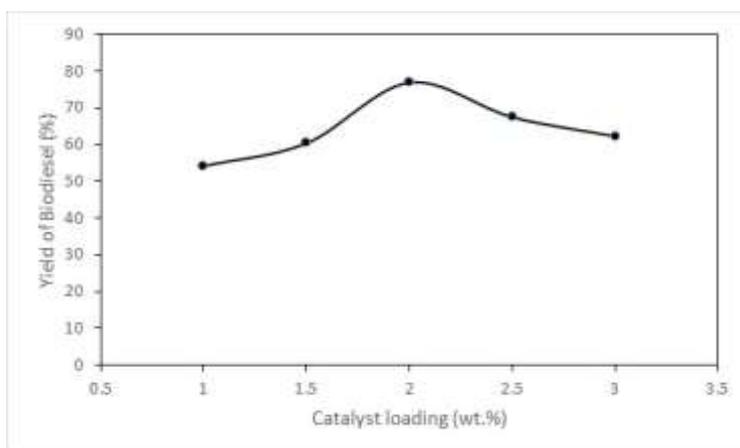


Figure 5. The effect of catalyst loading on biodiesel yield

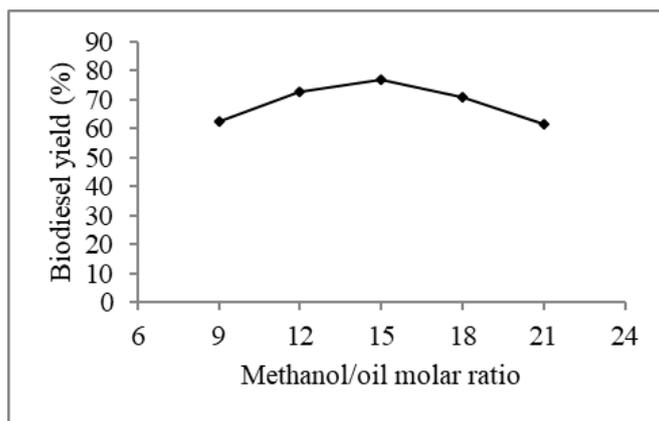


Figure 6. The effect of methanol to oil ratio on the biodiesel yield

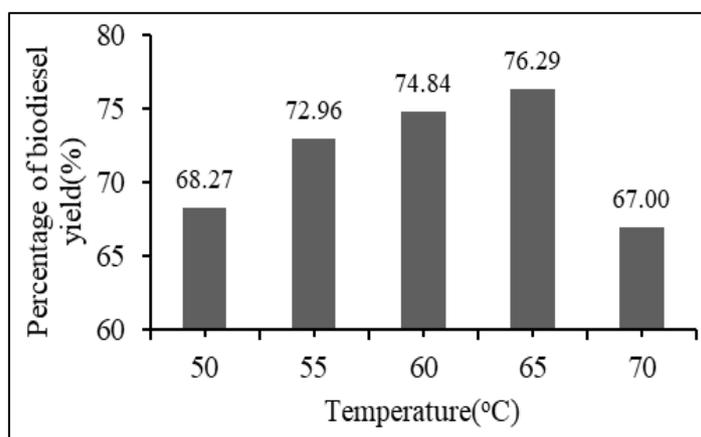


Figure 7. Effect of temperature on biodiesel yield

### 2.3. Effect of Temperature

Transesterification can occur at different temperatures depending on the oil used and temperature is a crucial parameter as it influences the reaction rate and yield of methyl esters. In order to determine the effect of reaction temperature, experiments were conducted at 50, 55, 60, 65 and 70 °C. Other reaction conditions are kept constant, such as the oil to methanol ratio (1:15), reaction time (2 hours) and catalyst loading (2 wt.%). The effect of temperature on biodiesel yield is shown in Figure 7.

This study showed that the biodiesel yield increases as the reaction temperature increases, and the optimum temperature at which the biodiesel yield is highest (76.29%) was 65 °C. However, the yield decreased when the temperature was raised above 65 °C. At temperatures above its boiling point

of 65°C, methanol evaporates quickly. As a result, the reaction will not proceed due to an insufficient amount of methanol present [13]. Hence, 65 °C was found to be the optimum reaction temperature.

### 2.4. Effect of Reaction Time

The effect of reaction time on biodiesel yield was studied by varying the reaction time from 2 hours to 6 hours. Figure 8 shows the effect of reaction time on biodiesel yield. Based on the graph, the biodiesel yield increases as the reaction time increases. The longer the reaction time, the greater the amount of oil that can react with the methanol. The optimum reaction time is 5 hours with 88.50% yield, as beyond this the biodiesel yield becomes constant. Transesterification is a reversible reaction, therefore the yield remains constant because both the reverse reaction and forward reaction have achieved an equilibrium.

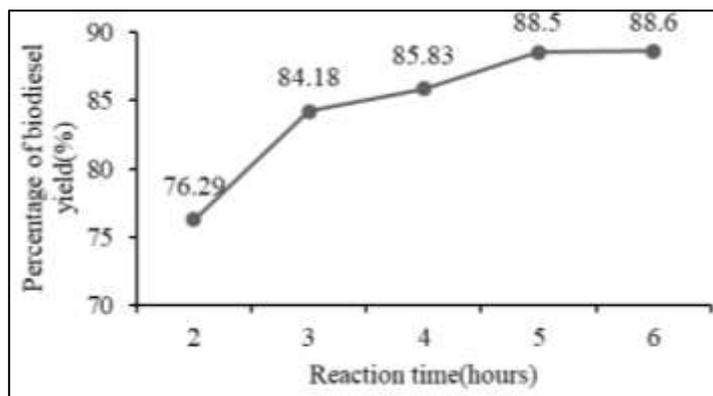


Figure 8. Effect of reaction time on biodiesel yield

Table 2. Comparison of the catalytic activity of CaO derived from waste egg shells for biodiesel production

References	FAME (%)	Feedstock	Reaction Parameter			
			Catalyst loading (wt.%)	Time	Temperature (°C)	Methanol oil ratio
[2]	93.4	<i>Chlorella pyrenoidosa</i>	2.06	180 min	60	10:1
[12]	92.0	<i>Chlorella Vulgaris</i>	1.39	3 hrs	70	10:1
[10]	92.0	Waste frying oil	9.00	4 hrs	60	9:1
This study	80.0	Waste cooking oil	2.00	5 hrs	65	15:1

Table 2 shows the catalytic activity of CaO compared to other studies for biodiesel production using CaO derived from egg shells. The results shows that CaO used in this study is reliable and has good potential as a basic catalyst for biodiesel production.

### CONCLUSION

A low cost, green and efficient CaO catalyst for biodiesel production was successfully synthesized from chicken egg shells. XRD analysis shows that calcination of chicken egg shells at 900 °C resulted in the CaCO<sub>3</sub> completely decomposing into CaO with a crystallite size of 24.43 nm and possessing strong basic sites with total basicity of 630 μmol/g. The obtained CaO catalyst exhibited high catalytic performance for production of biodiesel via transesterification of waste cooking oil. An 80% yield of fatty acid methyl esters (FAME) was achieved under the optimum conditions of 15:1 of methanol/oil molar ratio, 2wt.% of catalyst loading, and 5 hours of reaction time at a temperature of 65 °C.

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