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# PRODUCTION OF BIODIESEL FROM PALM OIL USING EGG SHELL WASTE AS HETEROGENEOUS CATALYST

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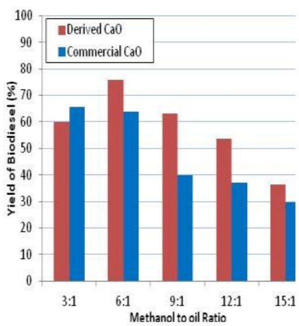
**Graphical abstract**




## Abstract

Egg shell waste was investigated in a triglyceride transesterification with a view to determine its viability as a solid catalyst for the biodiesel production. The utilization of egg shell as a catalyst not only reduces its environmental effects, but also reduces the price of biodiesel to make it competitive with petroleum diesel. In this study, egg shell waste was ground and the powder produced was calcined at 900˚C for 4 hours in a furnace. The physical properties of the catalyst were characterized by using the Fourier Transform-infrared (FTIR) spectroscopy and the biodiesel conversion was determined by the Gas Chromatography-Mass Spectrometry (GC-MS). 4wt% of catalyst dosage was fixed throughout the experiment. The results obtained indicated that CaO derived from egg shell waste was comparable with the commercial CaO. The maximum percentage yield of biodiesel by using derived CaO is 75.85% under optimum conditions of 6:1 methanol to oil ratio after 3 hours at 65˚C, while for commercial CaO, 74.97% yield of biodiesel with 3:1 methanol to oil ratio after 3 hours at 60˚C.

*Keywords*: Biodiesel, transesterification, egg shell derived catalysts, palm oil

## Abstrak

Sisa kulit telur telah dikaji dalam transesterifikasi trigliserida untuk menentukan daya maju penggunaannya sebagai mangkin pepejal dalam pengeluaran biodiesel. Penggunaan kulit telur sebagai mangkin bukan sahaja dapat mengurangkan kesan pencemaran alam sekitar, malahan juga dapat mengurangkan harga biodiesel agar mampu berdaya saing dengan petrol diesel. Dalam kajian ini, sisa kulit telur telah dikisar dan serbuk yang dihasilkan telah dikalsinkan pada suhu 900˚C dalam masa 4 jam di dalam relau. Ciri-ciri fizikal pemangkin telah dicirikan dengan menggunakan Spektroskopi Fourier Pengubah Inframerah (FTIR) dan penukaran biodiesel telah ditentukan dengan menggunakan Spektroskopi Jisim Gas Kromatografi (GC-MS). 4wt% daripada dos pemangkin telah ditetapkan sepanjang eksperimen. Keputusan yang diperolehi menunjukkan bahawa CaO yang dihasilkan dari kulit telur adalah setanding dengan CaO komersil. Hasil peratusan maksimum biodiesel yang mengunakan CaO kulit telur adalah 75.85% pada keadaan optimum nisbah methanol kepada minyak adalah 6:1 selepas 3 jam pada suhu 65˚C, manakala keadaan optimum bagi CaO komersil untuk menghasilkan 74.97% biodiesel adalah pada keadaan nisbah methanol kepada minyak 3:1 selepas 3 jam pada suhu 60˚C.

*Kata kunci*: Biodiesel, transesterifikasi, pemangkin dari kulit telur, minyak sawit

## 1.0 INTRODUCTION

The search for alternative energy resources to supplement or replace fossil fuels has been intensifying in the recent years because of the increase in environmental concern, energy security and fast depletion of fossil fuel resources [1]. In this respect, biodiesel is an emerging alternative to diesel fuel derived from renewable and locally available resources which is biodegradable, nontoxic and environmentally friendly [2]. Currently, biodiesel is industrially produced by the transesterification of triglycerides in methanol. This is a well-established industrial process that is carried out using a homogeneous catalyst such as NaOH, KOH or their methoxides [3]. The most widely recognized feed stocks utilized for biodiesel production are vegetable oils inferred from edible plants, such as rapeseed, palm, soybean, sunflower, and different oleaginous harvests [4]. In Malaysia, palm oil is a major raw material for biodiesel production [5]. Other than oil, alcohols also are feed stocks of biodiesel productions. Methanol and ethanol are utilized more frequently in biodiesel production, particularly methanol because of its low cost and its physical and chemical preferences (polar and shortest chain alcohol). Other than oil and alcohol, catalyst also is one of main materials in the production of biodiesel [6]. There are a few types of catalyst such as homogeneous, heterogeneous and enzyme catalysts. However, the homogeneous catalytic process suffers from drawbacks; complicated process of post treatments and inevitable production of wastewater from washing process of catalyst residues [7]. Based on these drawbacks, the use of heterogeneous catalyst could be an attractive solution [8].

A heterogeneous catalyst like calcium oxide has numerous points of interest, for example, being non corrosive, environmentally benign, and showing fewer disposal problems. These catalysts are additionally much easier to separate from liquid products and they could be intended to give a higher activity and selectivity and have longer catalysts lifetimes [9]. Therefore, in this study, the CaO derived from egg shell waste had been used as heterogeneous catalyst to produce the biodiesel from palm cooking oil.

## 2.0 METHODS

### 2.1 Materials

Palm oil and anhydrous methanol are the main materials in the biodiesel production for this study. The egg shell waste was washed thoroughly with tap water to remove any unwanted material adhered to its surface and then rinsed twice with distilled water. The washed shells then were dried in a hot air oven at 100°C for 24 hours. It was then grounded and crushed and the powder was sieved. The size of egg shell powder was fixed at 250 µm. Then, the dried egg shell waste was calcined at 900°C in a muffle furnace under static air with a heating rate of 2.5°C/min for 2 hours. All calcined samples were kept in a closed vessel to avoid the reaction with carbon dioxide ($CO_2$) and humidity air before use.

### 3.2 Characterizations of Catalysts

Fourier Transform Infrared (FTIR) spectroscopy was performed to determine the presence of functional group in a CaO derived from egg shell waste and then compared with the functional group present in commercial CaO.

### 3.3 Reaction Procedures

Transesterification was carried out in laboratory scale in a round bottom flask with condenser on electric heater and magnetic stirrer. The reaction was performed to obtained the maximum yield and the best conditions of biodiesel by varying the operation variables such as methanol/oil ratio ( 3:1, 6:1, 9:1, 12:1 and 15:1), reaction temperature ( 30, 40, 50, 60, and 65˚C) and reaction time (1, 2, 3, 4, and 5h). After the reaction was completed, the solid catalysts were separated by filtration. Then the solution was transferred into separatory funnel until two layers form which are the top layer is biodiesel product and the bottom layer is glycerol. The percentage yields of biodiesel were calculated and the samples taken from the oil phase were analyzed using Gas Chromatography-Mass Spectrometry (GC-MS).

## 3.0 RESULTS AND DISCUSSION

### 3.1 Characterization of Catalysts

The IR spectra of the commercial CaO and derived CaO from egg shell waste are shown in Figure 1. The bottom spectrum represents the derived CaO from egg shell waste while the upper represents spectrum of commercial CaO.

The spectra band at 3639.68 $cm^{-1}$ is detected over two catalysts that can be assigned to the presence of 0-H stretching vibrations of $Ca(OH)_2$ due to the moisture absorption on the surface of the pellets.[10] While peak at 1413 $cm^{-1}$–1436 $cm^{-1}$ corresponds to the bending vibration of Ca-O stretching.

Besides that, from the FTIR result, it can be said that all $CaCO_3$ component in the egg shell waste was converted into CaO because no peak appeared for the $CaCO_3$ component. Moreover both types of CaO catalyst have the same characteristics as shown in the IR spectra. Hence, it can be said that the derived CaO which is the egg shell has the same potential as the commercial CaO to be a catalyst in the biodiesel production.

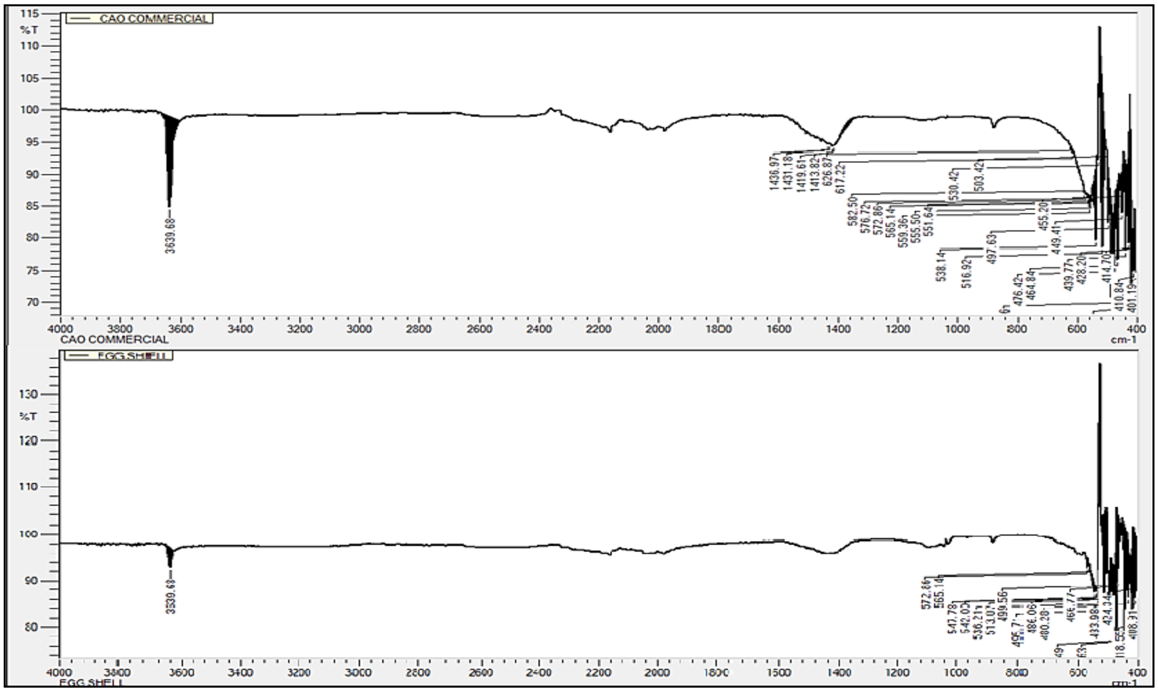



**Figure 1** IR pattern for commercial CaO and derived CaO

### 3.2 Effect of Methanol to Oil Ratio

The alcohol to oil ratio is one important factor that affects the reaction. The stoichiometric ratio for transesterification requires 3 moles of methanol for each mole of oil to yield 3 moles of fatty acid methyl ester and one mole of glycerol. Since the transesterification is a reversible reaction, excess methanol is required to drive the reaction towards the product. Figure 2 shows the comparison between commercial CaO and the derived CaO catalyst. From the result, it can be observed that the more preferable ratio for derived CaO from egg shell waste and commercial CaO is 6:1 and 3:1 since it gives the maximum biodiesel yield which is at 75.85%, and 74.97% respectively. From the bar chart in Figure 2, after the reaction reaches the maximum yield, the trend starts to decrease for both types of catalyst. This is due to the dilution effect of too much alcohol that slightly affects to the yield of FAME. Moreover, too high an amount of methanol will slow down the separation of the methyl ester and glycerine phases [10].

### 3.3 Effect of Reaction Temperature

The reaction and yield of biodiesel are strongly influenced by the reaction temperature used. The effect of varying the temperature from 30˚C to 65˚C was studied. The methanol to oil molar ratio used for commercial CaO is 3:1 while derived CaO is 6:1 which was found to be the maximum yield found from a study. The reaction time is 3 hours and the result for this study is illustrated in Figure 3. Generally, the formation of biodiesel increases with temperature. However, by increasing the temperature beyond the methanol boiling point may burn the methanol and may influence the saponification reaction of triglycerides [11-13]. From Figure 3, the maximum percentage yield of biodiesel obtained at 65°C is 75.85% for derived shell catalyst and at 60°C is 73.95% for the commercial CaO catalyst. However, the yield obtained for both catalysts will be decreased after 65°C due to the vaporization of methanol [13].

### 3.4 Effect of Reaction Time

Other than the effect of methanol to oil ratio and the effect of reaction temperature, the effect of reaction time also is influenced in the production of biodiesel. The result of this effect is shown in Figure 4 by varying the reaction time from 1 to 5 hours and fixing the methanol to oil ratio and reaction temperature at 3:1 and 60˚C for commercial CaO and 6:1 and 65˚C for derived CaO from egg shell waste. As can be seen, the maximum yields of 73.95% and 67.56% were obtained in 3 hours for derived and commercial CaO respectively. In the early stage of transesterification reaction, the production of methyl esters gradually increased and the rate diminished and finally started to decrease after about 3 hours. This is because transesterification reaction between oil and alcohol will form soap due to the reversible reaction when the reaction time increased [14].

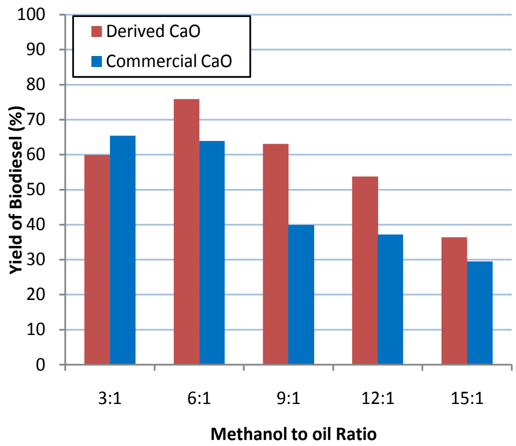



**Figure 2** Percentage of biodiesel yield towards the effect of methanol to oil ratio (reaction time: 3hr; reaction temperature: 60˚C and catalyst loading: 4wt %)

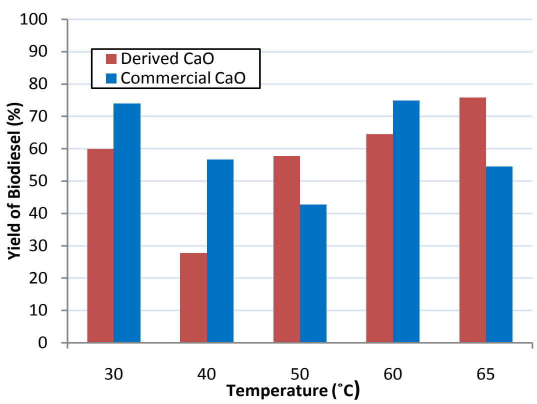



**Figure 3** Percentage of biodiesel yield towards the effect of reaction temperature

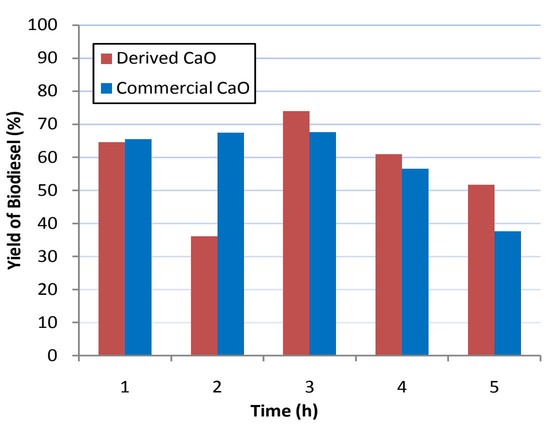



**Figure 4** Percentage of biodiesel yield towards the reaction time

## 4.0 CONCLUSION

The characteristics of derived CaO and commercial CaO are the same as showed by FTIR result. Hence, it proves that commercial CaO can be substituted by derived CaO from egg shell waste as a catalyst in the biodiesel production. In order to achieve a high yield of biodiesel, the optimum conditions for commercial CaO and CaO derived from egg shell waste were found to be slightly different. For commercial CaO, the optimum conditions to produce biodiesel were at 3:1 methanol to oil ratio at 60˚C and 3 hours reaction time while for derived CaO, the optimum conditions were at 6:1 methanol to oil ratio, 65˚C and also at 3 hours. In conclusion, the results show that CaO derived from egg shell waste can be used as a catalyst in the production of biodiesel and hence minimizes the cost of production.

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