

# Combusted Molluscs Shell as Solid Base Catalyst for Transesterification to Produce Biodiesel

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## Abstract

Calcium oxide (CaO) catalyst was synthesized thermally from molluscs shell. The raw material was calcined at temperature between 500 to 1000°C. Both commercial CaO and CaO from combusted cockle shell were used as catalyst in the transesterification reaction. The transesterification reaction was conducted in a mixture of methanol:oil (12:1, v/v) and 8 wt % catalyst for the required reaction time was used. The content was refluxed in ultrasonic bath at 65°C for 15 minutes. The non-ultrasonic reaction was performed using magnetic stirrer for 3 hours. Combustion of cockle shells at 500, 600, 700 and 800°C showed no significant difference in XRD patterns and the XRD patterns are similar to calcium carbonate (CaCO<sub>3</sub>). The peaks correspond to CaO ( $2\theta = 32.2^\circ$  and  $37.4^\circ$ ) appeared in the XRD pattern of combusted cockle shell at 900 °C and 1000 °C, respectively. However, a peak corresponds to CaCO<sub>3</sub> ( $2\theta = 29.4^\circ$ ) disappeared at 900°C. These results indicate CaCO<sub>3</sub> transformed to CaO by combustion at or above 900°C. The percentage conversion for CaO from commercial and cockles via mechanical stirring were 96.65% and 96.77%, respectively and 88.40% and 93.33%, respectively, *via* ultrasonic irradiation. The percentage yield of fatty acid methyl esters (FAMES) from both sources of CaO were found to be comparable with percentage yield of CaO from cockles which were 27.0% and 29.3% for mechanical stirring and ultrasonic irradiation, respectively. CaO from cockles shell combusted at above 900°C provides a better catalyst than commercial CaO for transesterification reaction due to the higher calcite purity.

## Introduction

The production of biodiesel can significantly reduce harmful emissions and contributing to domestic energy security (Eevera *et al.*, 2009). For the production of biodiesel, triglycerides, the major component of vegetable oils undergoes transesterification with alcohol to form esters in basic conditions (Van Garpen *et al.*, 2004). However, Kouzu *et al.* (2008) suggest that the common base used for such reaction such as potassium hydroxide (KOH) and sodium hydroxide (NaOH) can lead to massive wastewater discharge to wash the dissolved alkali-hydroxide. They suggest the use of calcium oxide (CaO) which is milder. Although the transesterification reaction rate of CaO is lower

than KOH and NaOH, the catalytic activity can be improved by calcination process (Grandos *et al.*, 2007). Ultrasonic energy can also improve transesterification reaction using CaO as catalyst (Stavarache *et al.*, 2006). It was also reported that ultrasonic field can accelerate transesterification reaction due to effective emulsification compared to the conventional mechanical stirring condition (Hanh *et al.*, 2009). This is because ultrasonic irradiation can produce emulsions of immiscible liquids thus increasing the reaction area (Mason & Philip, 2002).

In Malaysia, the shellfish industry flourish with the support of the government and it was estimated that the industry to produce 130 000 tons per year mainly in the form of cockles (Rashid & Anwar, 2008). With that estimation, the problem for shell disposal can be predicted. The need to dispose of molluscs shells from the food industry namely oyster shell lead to researchers to investigate its usage as transesterification catalyst for biodiesel production (Nakatani *et al.*, 2009). Molluscs shell such as oyster and cockles also have high content of calcite (Yoon *et al.*, 2003). Thus, calcium oxides can be produced from combusted molluscs shell (Nakatani *et al.*, 2009). Commercially available calcium oxides are usually produced from combusted calcium carbonate stones.

Therefore, it is the intention of this paper to study the effectiveness of combusted cockle shell as transesterification catalyst.

## Methodology

### *Materials*

Commercial cooking palm oil (Vesawit, Malaysia) was purchased from a local market and used without any further purification. The analytical reagent grade methanol was used in the transesterification reaction. Reference standards such as methyl arachidate, methyl behenate, methyl linoleate, methyl lonilenate, methyl myristate, methyl palmitate and methyl stearate were obtained from SUPELCO.

### *Catalyst Preparation*

The shells were washed with tap water and dried naturally to remove sands and seaweeds deposited on the shell surface. The shells will be roughly crushed using a hammer. The crush shells were dried at 110°C for 2 h and stored in desiccators. Combustion of the crush shells were transformed to CaO catalyst by thermal synthesis. The raw materials were calcined at designated temperatures ranging from 500°C to 1000°C. All catalyst was kept in the close vessel to avoid the reaction with CO<sub>2</sub> and humidity in air before used (Salamatina *et al.*, 2010).

### *Catalyst Characterization*

X-ray powder diffraction (XrD) patterns for combusted mollusks shell at different temperature and calcium oxide were analyzed using XrD equipment.

### *Transesterification Reaction Procedure*

Both commercial CaO and CaO from combusted cockle shell are used as catalyst in the transesterification reaction. The setup for the transesterification process consisted of a two-neck glass reactor partially submerged in a water bath to regulate the temperature. A condenser was fitted to the reaction vessel to return the evaporated methanol back to the reaction vessel. The palm oil 50 cm<sup>3</sup> was added onto the mixture of catalyst and methanol. The content was reflux under ultrasonic reactions at 65°C for 15 minutes. The non-ultrasonic reactions were performed using magnetic stirrer. The palm oil 50 cm<sup>3</sup> in a 100 cm<sup>3</sup> round-bottom flask equipped with a reflux condenser was stirred at 65°C for 3 hours. The transesterification reaction was conducted under 12:1 MeOH to oil ratio and catalyst amount of 8 wt % for the required reaction times. To finish the reaction, the catalyst was separated from biodiesel product by centrifugation, and the excessive amount of methanol was evaporated before analysis of % FAME. After the products were centrifugated, it formed three phases, the upper layer was biodiesel, the middle layer was glycerol, and the lower layer was a mixture of solid CaO and a small amount of glycerol. The biodiesel was collected for chromatographic analysis.

### *Determination of % FAME*

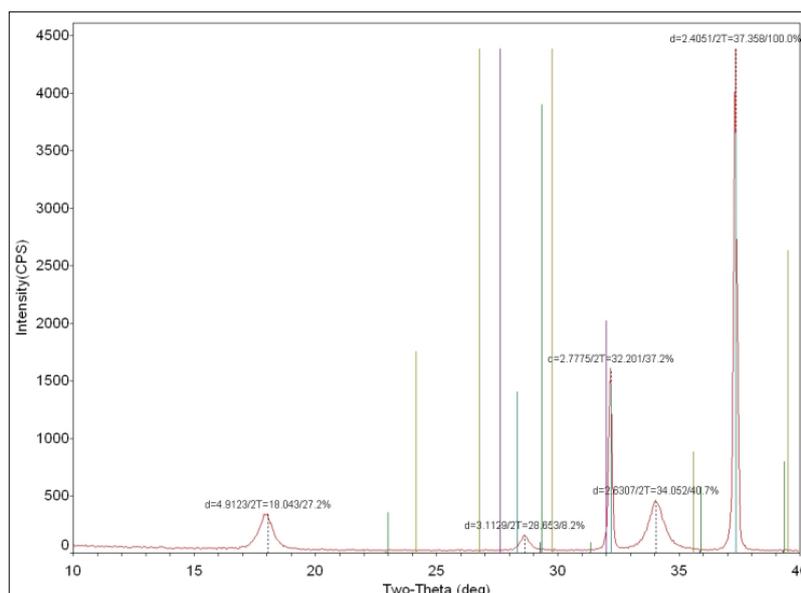
Analysis of fatty acid methyl esters was performed on Shimadzu gas chromatograph equipped with Shimadzu GCMS-QP2010 PLUS Series mass spectrometer and BPX-5 capillary column (29.5 m x 0.25 mm x 0.25 µm film thickness). The operating conditions of the gas chromatographic technique were as follows: the column temperature was initially set at 90°C for 5 min and then increased to 300°C at the rate of 3.5°C/min where it was held constant for 10 min. The injection temperature was kept at 260°C with a split ratio of 1:20. The sample injected was 1 µl with helium used as a carrier gas. Individual fatty acids were identified and quantified by comparison with retention times and peak areas of fatty acid methyl ester standards which were prepared and run under similar conditions as those of the real samples. Methylnonadecanoate and methylpentadecanoate was used as internal standard for quantification. The biodiesel content was represented in term of % FAME as a function of time. Methylnonadecanoate and methylpentadecanoate was used as internal standard for quantification. The biodiesel content was represented in term of % FAME as a function of time.

## **Result and discussion**

### *Effect of the combustion temperature of cockle shell on the formation of calcium oxide*

Combustion of cockles shells at 500 °C, 600 °C, 700 °C, and 800 °C shows no difference in XRD patterns and similar to the XRD patterns of CaCO<sub>3</sub>. Meanwhile, peaks corresponding to CaO (2θ = 32.2° and 37.4°) appeared in the XRD pattern of cockle shell combusted at 900°C and 1000°C (Figure 1). On the other hand, peaks corresponding to CaCO<sub>3</sub> (2θ = 29.4°) disappeared. These results indicate calcium carbonate transformed to calcium oxide by combustion at or above 900 °C. Similar report on

transformation of combusted cockles shell at temperature 900 °C was also reported by (Boey *et al.*, 2011).



**Figure 1** : Powder X-ray diffraction (XRD) patterns of the combusted cockle shells at 900 °C

#### *Effect of Commercial CaO and Prepared CaO from Cockle Shells on Transesterification via Ultrasonic Irradiation and Mechanical Stirring*

A set of experiments was carried out to see the effect of CaO from two sources. The first was commercially available CaO and the second was CaO obtained from cockles shell combusted at 900 °C. Transesterification reactions of both sources of CaO were also studied under the influence of ultrasonic irradiation at 40 kHz and the conventional mechanical stirring.

Mechanical stirring of the transesterification was done for 2 hours with the temperature maintained above 65°C which is the optimum condition for transesterification *via* mechanical stirring (Kouzu *et al.*, 2008). Meanwhile, the transesterification *via* ultrasonic irradiation was done for 15 minutes with temperature above 65 °C. Previous studies suggest that transesterification *via* ultrasonic irradiation was found to reach maximum at 15 minutes (Hanh *et al.*, 2009). The data obtained are shown in Table 1.

The data shows that the percent FAME conversion of both types of CaO sources was comparable. The percent conversion for CaO from commercial and cockles was at 96.65% and 96.77% *via* mechanical stirring and 88.40% and 93.33% *via* ultrasonic irradiation. Although the percent of conversion *via* ultrasonic was lower than mechanical stirring, it should be noted that the time for the reaction was much lower for ultrasonic method at 15 minutes compared to 120 minutes for mechanical stirring. It was reported that for similar level of conversion, the ultrasonic irradiation method consumes less energy than mechanical stirring, around 1/3 less energy (Lifka & Ondruschka, 2004) and at the same reaction time duration of 40 minutes, the percent conversions of FAME was almost double *via* ultrasonic than mechanical stirring (Hingu *et al.*, 2010).

**Table 1:** Percent conversion and yield of transesterification *via* mechanical stirring and ultrasonic irradiation using commercial CaO and CaO from cockles

Method	Commercial CaO		Cockles CaO	
	% FAME Conversion	% yield	% FAME Conversion	% yield
Mechanical stirring	96.65	23.9	96.77	27.0
Ultrasonic irradiation (40 kHz)	88.4	25.4	93.33	29.3

The percent yield of FAME from both source of CaO was also found to be comparable with percent yield from cockles shell CaO to be slightly higher at 27.0% and 29.3% for mechanical stirring and ultrasonic irradiation respectively. We suggest that the cockles shell contain higher purity of calcite than limestone, a common source to produce commercial CaO. Higher purity of calcite will produce higher purity CaO.

It was also found that the percent yield of biodiesel was slightly higher *via* ultrasonic irradiation than mechanical stirring for both source of CaO. It was suggested that mechanical stirring produces more soap than ultrasounds which hinders the separation of some esters trapped in the soap micelles, thus the lower yield (Stvarache *et al.*, 2006).

### Conclusion

We conclude that the CaO from cockles shell combusted at above 900°C provides a better catalyst than commercial CaO for transesterification reaction due to the higher calcite purity. We also conclude that ultrasonic irradiation method to produce FAME is efficient, more economical and fast compared to mechanical stirring. Ultrasonic irradiation method produces comparable percent conversion of FAME and higher percent yield at shorter time.

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