**Research Article**

# Transesterification of Waste Cooking Oil using Calcium Loaded on Deoiled Spent Bleaching Clay as A Solid Base Catalyst

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**Abstract**

Waste cooking oil has a high potential as a raw material in biodiesel production due to its abundant availability and cheapest among other feedstock. Hence transesterification reaction is carried out using waste cooking oil in this research. The objective of this study is to synthesize and characterize the catalyst. On the other hand, deoiled spent bleaching clay impregnated with 40% CaO utilized as a catalyst. Optimization was carried out on methanol to oil molar ratio (6:1-24:1), catalyst loading (3-10 wt.%) and reaction duration (2-10 h). The catalyst of deoiled spent bleaching clay doped with 40% CaO was prepared by wet impregnation method and calcined at 500 °C for 4 hours. The catalyst shows high activity under optimum condition of 5 hours of reaction time, 12:1 of methanol to oil molar ratio with 7 wt.% of catalyst. The transesterification yields 84.7% methyl ester. Therefore, this catalyst has potential to be used in the transesterification of waste cooking oil in producing biodiesel due to its high activity. Copyright © 2016 BCREC GROUP. All rights reserved

*Keywords*: Biodiesel; Waste cooking oil; Spent bleaching clay; Calcium oxide; Transesterification

## 1. Introduction

Biodiesel has been more attractive recent years because of its environmental benign and the fact that it is made from renewable resources [1, 2]. Increasing cost of petroleum and other environmental problems made researchers found an alternative to fossil fuel which is biodiesel which are derived from vegetable oils or animal fats with ethanol or methanol [3, 4]. Biodiesel does not need any engine modification (or little) and can be used in compression-ignition (diesel) engine due to its excellent properties as diesel engine fuel [5].

There is an alternative process to homogeneous catalysed transesterification for biodiesel production which is heterogeneous catalysed transesterification [6]. They have many advantages such as less wastewater generation and their ability to recycle or reuse [7, 8]. Hence,

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further development of heterogeneous catalysts must focus on enhancing, not only catalytic performance but also the reusability [9]. A large variety of heterogeneous catalysts have been investigated [10]. Among them, CaO has been received much interest since relatively cheap, it's mild reaction condition and less impact on environment [11]. Calcium oxide (CaO) has been reported recently as an active heterogeneous base catalyst for transesterification reaction. This is due to ease of handling, low solubility and its high basicity [12, 13]. The usage of CaO can be categorized into the group of neat CaO, doped CaO, waste CaO, mixed CaO and supported CaO [14, 15]. Until now, there has been limited work to prepare alkali metal based catalyst in macroscopic to catalyse the transesterification reaction for biodiesel production [16]. We need high surface area catalyst to work with transesterification reaction so that can increase the rate of reaction. Calcium oxide doped onto the deoiled spent bleaching clay has been chosen to be the catalyst as it is comparatively cheap and giving high methyl ester conversion compared to other the catalyst. Furthermore, calcium oxide has lower leaching effect in comparison with potassium oxide.

In this work, the transesterification of waste cooking oil with methanol has been investigated using deoiled-SBC loaded with 40% CaO as a catalyst including studied the structural and catalytic properties of the catalyst by several methods.

## 2. Materials and Methods

### 2.1. Material

The waste cooking oil is obtained from university cafeteria (UMP, Gambang) and spent bleaching clay is collected from Felda Global Venture in Kuantan. Commercial CaO (99.99% purity), chloroform (99.5% purity) and methyl heptadecanoate (as an internal standard) of chromatographic grade (99.5% purity) were obtained from Sigma-Aldrich (Switzerland), was used as an internal standard whereas methanol (99.5% purity), petroleum ether (90.0% purity) and hexane (≥99.0% purity) were purchased from Bendosen Laboratory Chemicals (Norway).

### 2.2. Catalyst preparation

De-oiled spent bleaching clay (25 g) was added into 100 mL distilled water and was placed into 250 mL flask held in an ultrasonic water bath for 3 hours. The Ca-functionalized D-SBC sample was prepared at 40 wt.% CaO (from D-SBC weight) where using the commercial CaO. It then was dried in an oven at 120 °C for 16 h. Upon drying, the D-SBC particle was calcined at 500 °C for 4 hour. Hammett indicators were used to test the basic strength of the catalyst. About 25 mg of sample were shaken with 1 cm$^3$ of a solution of Hammett indicator diluted in methanol and left to equilibrate for 2 h.

### 2.3. Transesterification reaction

Waste cooking oil that was obtained from local cafeteria contained comparatively high free fatty acid. Esterification is done first in order to reduce the high free fatty acid in the waste cooking oil. The transesterification of WCO was performed in a 50 mL 2-neck round bottom flask equipped with a reflux condenser and magnetic stirrer. The transesterification reaction between WCO and methanol was carried out in the liquid phase under atmospheric pressure, at 65 °C for 1 h with continuous stirring. The effect of the molar ratio of methanol to oil (6:1 - 24:1 wt.%), catalyst amount (3-10 wt.%) and reaction duration (2-10 h) on the reaction were investigated. After the transesterification, the reaction mixture was allowed to cool to room temperature. ME was isolated by centrifugation from the layers (ME, glycerol and catalyst), and then the excessive amount of methanol and water was evaporated before the chromatographic analysis. The reaction were carried out three times in order to reflect the precision and errors of the results.

### 2.4. Biodiesel Analysis

The European regulation procedure EN 14103 was used to determine the concentration of ME. In this study, GC–FID (Agilent Technologies,7890A GC-System) with capillary column DB-wax (length 60 × internal diameter 0.25 mm × film thickness 0.25 μm) using methyl heptadecanoate as an internal standard. The carrier gas is helium with a linear velocity of 40 cms$^{-1}$. The oven temperature was programmed at 190 °C, held for 2 min, then ramped at 10 °C per min until it reached 230 °C, and with a final hold time of 8 min. The sample volume of 0.6 μL was injected into GC-FID. The peaks of ME were identified by comparing them with their respective ME standards. Methyl esters peaks were identified by comparing with standards and to quantify the conversion, the following Equation (1) is used.

$$ME\ content = \frac{A_{Total} - A_{ISTD}}{A_{ISTD}} \times \frac{C_{ISTD} \times V_{ISTD}}{M_{Sample}} \times 100\%$$

(1)

Where: $A_{total}$ = Total area of methyl ester peak from C14:0 to C18:3; $A_{ISTD}$ = Area of internal standard; $C_{ISTD}$ = Concentration of internal standard in mg/mL; $V_{ISTD}$ = Volume of internal standard in mL; and $M_{sample}$ = Mass of sample in mg.

## 3. Results and Discussion

### 3.1. Catalyst characterization

The FT-IR spectra of D-SBC, CaO, and the catalyst are displayed in Figure 1. For the peak at 1050 cm$^{-1}$, it is due to siloxane bonds (Si–O–Si). Vibration of M$^+$–O bond is shown at peaks 486-779 cm$^{-1}$. In addition, FT-IR also displays a broad band at 1637, 3430 and a shoulder at 3250 cm$^{-1}$, due to the bending and stretching of bridging –OH. Peak was not found between 2800 and 3000 cm$^{-1}$ which indicated that there is no organic compound in the silica after the treatment [30]. The catalyst shows characteristics of strong base during Hammett indicators test which basic strength lies between $15 < H\_ < 18.4$. The field emission scanning electron micrograph of the catalyst is presented in Figure 2 (a) together with Energy Dispersive X-ray (EDX) depicted in Figure 2 (b). It shows nearly to a spherical shape. From the BET result shown in Table 1, CaO supported deoiled SBC shown as a mesoporous solid and the isotherm for this sample can be classified into type III of the IUPAC classification. Surface area of the catalyst slightly decreases due to CaO has filled the pores on the D-SBC surface.

### 3.2. Optimal process conditions

The conversion of biodiesel from triglycerides is depicted in Figure 3. Under optimize condition of 7 wt.% catalyst loading, 12:1 methanol to oil molar ratio, at methanol reflux-
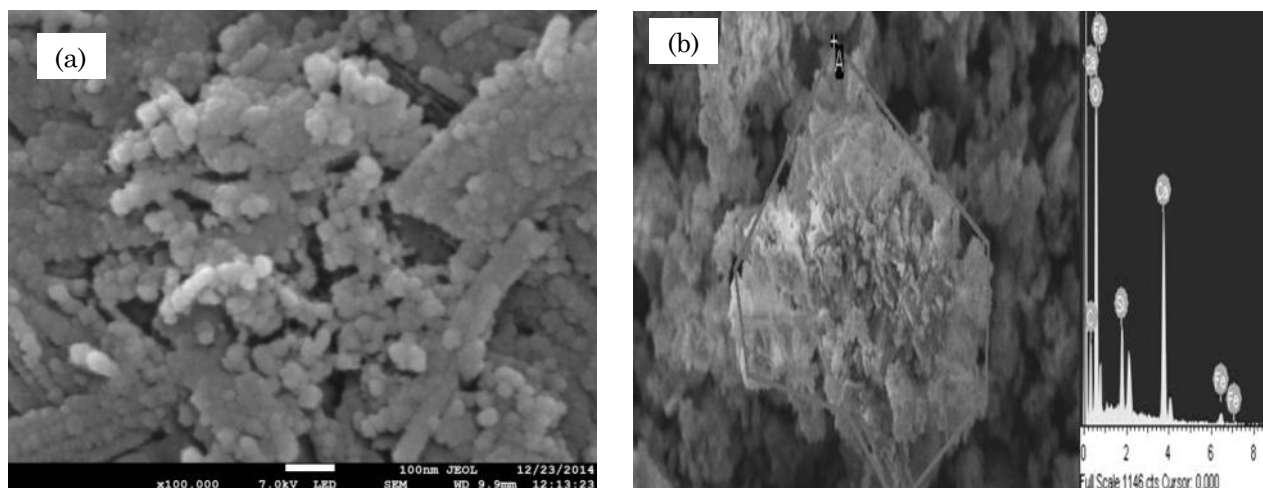


**Figure 2.** FESEM and EDX characterizations. (a). FESEM image of 40% CaO on D-SBC; (b). EDX of the catalyst
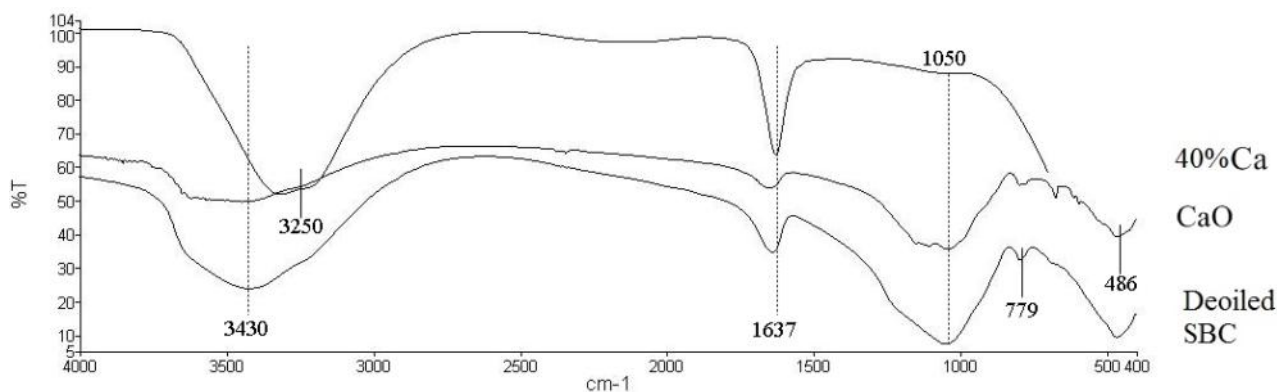


**Figure 1**. FTIR spectra of the catalysts

ing temperature about 65±2 °C and 5 h reaction duration, conversion of 84.7% methyl ester is produced. Hence this catalyst shows its efficiency towards transesterification reaction. Based on Figure 3(a), catalyst amount shows that 7% (based on waste cooking oil weight) is optimum for this reaction. The amount of catalyst was varied from 3-10 wt.%. The ME content reaches an optimal value when the catalyst amount reaches 7%. This is because the contact opportunity of the catalyst and the reactant, directly affect the reaction speed and the content. Instead, increasing the amount of catalyst did not affect the content profoundly. This is probably because of the demand of higher power consumption for an adequate stirring speed and the solution becoming more viscous or may because of the surface vacancies of support material were filled with metals of catalyst.

The catalyst is labeled as stronger than the indicator if exhibits a colour change and catalyst is said to be weaker than the indicator if not change the colour. This catalyst could change the colour of both phenolphthalein (H_ = 8.2) from colurless to pink and of 2,4-dinitroaniline (H_ = 15) from yellow to mauve but the colour of 4-nitroaniline (H_ = 18.4) is failed to change. As depicted in Figure 3 (b), reaction duration is varied from 2-10 h. The optimum duration for this reaction is shown to be 5 h. Moreover, it is interesting to note that for longer reaction duration the ME content decreases, possibility due to the reverse reaction, since transesterification, is a reverse reaction resulting in a loss of esters as well as causing more fatty acid to form soap. Methanol to oil molar ratio is carried out in range 6:1 - 24:1. Methyl ester conversion dropped after 12:1 because of too much methanol will disturb the transesterification reaction thus causing in dropping the biodiesel production. As we can see from Figure 3 (c), variation of methanol to oil molar ratio, 12:1 gives the highest ME conversion. Unfortunately the excess of methanol could be increasing the recycling cost of production; nevertheless the methanol is usually recovered and reused in the industrial process after purification. Therefore, the

**Table 1.** BET result of the catalysts

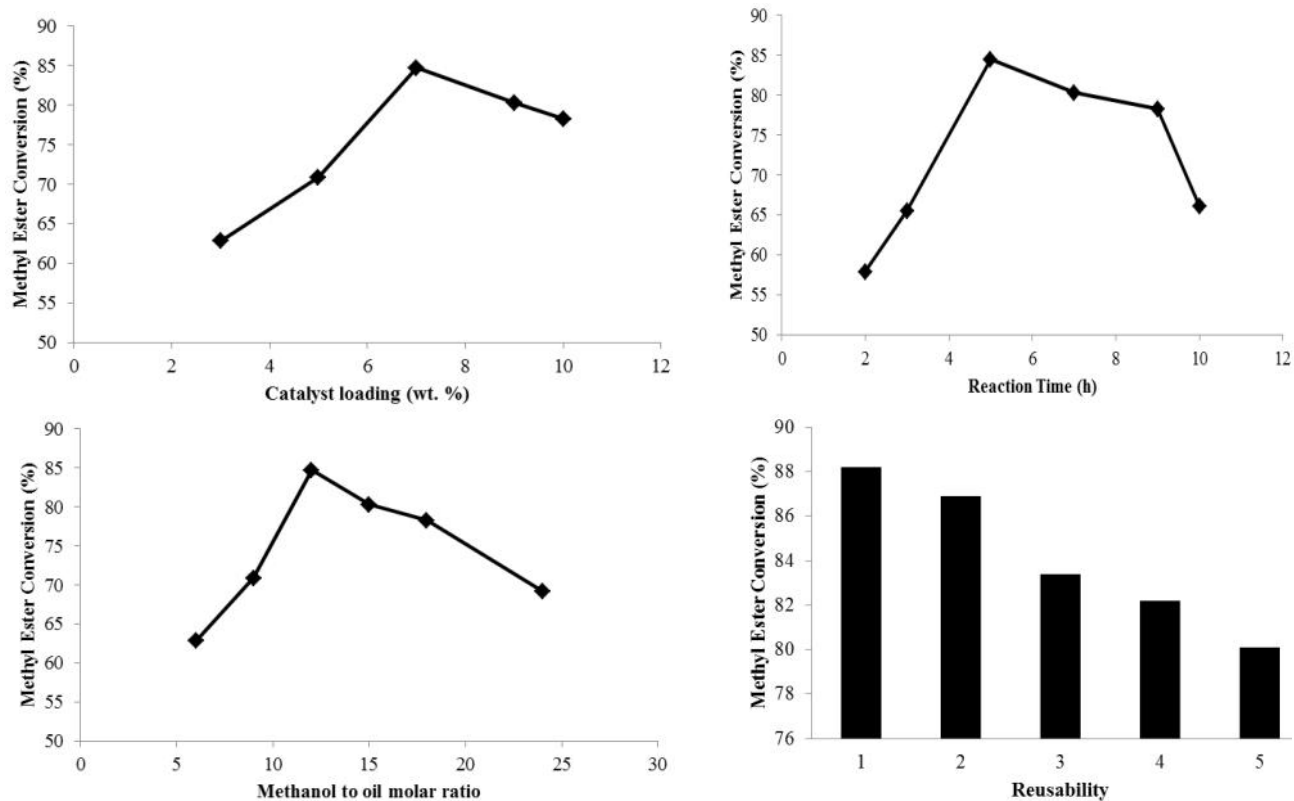| Sample | Surface area (m²/g) | Pore volume (cm³/g) | Pore size (Å) |
|---|---|---|---|
| Deoiled-SBC | 38.0212 | 0.243180 | 85.2033 |
| CaO with support | 36.9721 | 0.222066 | 233.6231 |



**Figure 3**. Effect of (a) catalyst loading, (b) reaction time, (c) methanol to oil molar ratio towards transesterification reaction (d) catalyst reusability under temperature 65±2 °C

choice of an optimal molar ratio has to take the increase in process expense into consideration.

Reusability is one of the factors in the economical application of heterogeneous base catalyst. The catalyst was reused without any further activation. The results provided in Figure 3(d) show that the catalyst can be used more than once by keeping the activity until five cycles with considerably high ME content, while this result is inline with other researchers [17]. After the transesterification reaction was completed, the catalyst was decanted with simple washing using methanol then n-hexane, and can be directly reused for the transesterification reaction. A ME content between 83-84% could be obtained even after the third cycle. The ME content was further reduced to 80-82% when the catalyst was reused for four to five cycles, which might be due to the leaching from the catalyst, thus it will reduce the ME content during the next run of the reaction due to the reduction in the number of active sites in the catalyst.

For the leachability study, the catalyst was stirred with methanol for 1 h (without feedstock). Then the reacted catalyst and the treated methanol was separated. The methanol-reacted solid catalysts were subjected to transesterification under the optimal conditions. Similarly, the treated methanol was also subjected to transesterification but without any catalyst. A considerable ME content were achieved under methanol-reacted solid catalyst (75-80%) whereas under the treated methanol (without any catalyst), a very low ME content (35-40%) was observed. The observation proves that there is no complete leaching of the alkali metals into methanol during reaction.

## 4. Conclusions

The catalyst which derived from spent bleaching clay and commercial CaO found to give a high performance towards waste cooking oil via transesterification reaction into methyl ester. The FT-IR and XRF show that the impregnation of CaO onto deoiled spent bleaching clay as a support is a success. When the reaction was carried out at reflux of methanol, with a molar ratio of methanol to waste cooking oil of 12:1, TG conversion catalysed by 7% catalyst (based on the waste cooking oil weight) reached 84.7% in 5 h. This catalyst can be used up to 5 cycles and has some leaching effect. The ME met several key specifications of European biodiesel standard (EN) 14214. Therefore, this catalyst has the potential to be used in the transesterification of waste cooking oil in producing biodiesel due to its high activity.

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