

## **Biodiesel from Adsorbed Waste Oil on Spent Bleaching Clay using CaO as a Heterogeneous Catalyst**

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### **Abstract**

Oil-laden spent bleaching clay (SBC) is currently under-utilized by dumping it in landfills without any attempt to recover the oil. Therefore, effort has been made to extract the waste oil using different solvents (methanol, ethanol, petroleum ether, and hexane), and utilize the oil in transesterification reaction. Cleaner oil (free from polar components and least acid content) of  $28.2 \pm 0.6$  wt.%, a significant amount susceptible to be converted to biodiesel, was extracted using non-polar solvent. However, the relatively high free fatty acid content leads to yield loss through saponification under homogeneous base-catalyzed reaction. As such, in the present work, heterogeneous base-catalyzed transesterification has been proposed using CaO. Parametric study has been conducted and the optimal conditions was found to be: methanol/oil mass ratio 0.5:1; catalyst amount 6 wt.%, and reaction temperature of 65°C. The highest purity of  $98.6 \pm 0.8$  % was achieved within 2.5 h. Biodiesel yield under the solid catalyst was quantified as 90.4% as compared to 45.5% and 61.0%, respectively for classical NaOH, and KOH homogeneous catalysts.

**Keywords:** Biodiesel, Spent bleaching clay, Transesterification, Methyl ester

### **1. Introduction**

The awareness of fossil oil depletion, fluctuating oil price and environmental concerns has intensified the search for an alternate fuel. Vegetable oil and animal fats are found to be the best candidates as an alternate energy source. Their direct use, however, is limited due to two main reasons; high viscosity and low volatility (Knothe, 2005). To counter these limitations, vegetable oil or animal fats are reacted with simple alcohol to produce fatty acid methyl ester (FAME) or known as biodiesel. There are few methods to do such conversion; namely pyrolysis, microemulsion, and transesterification and among

them transesterification was found to be the best route with minimal engine complications (Knothe, 2005; Pryde, 1984).

Biodiesel is found to be the best substitute of petro-diesel fuel not only for its comparable calorific value but also for its several other advantages such as biodegradable, low toxic emission, higher flash point, excellent lubricity, carbon neutral, and environmentally acceptance fuel (Knothe, 2005; Wedel, 1999). Triglyceride for biodiesel production comes from various sources; edible oil, inedible oil, waste/used oil, animal fats (Haas & Foglia, 2005), and recently from microorganisms (Meng et al, 2009). However the use of edible sources comes under heavy criticism since 'fuel-for-food' concept is regarded as an unethical by many quarters. Alternatively, the use of waste edible oil could be a better solution as it is available in abundant (Gui et al, 2008). In view of this situation, in current work the use of waste crude palm oil (CPO) from spent bleaching clay (SBC) is proposed. Bleaching clay is used in palm oil refinery to remove colouring matters, soap, gums, metals (iron, nickel), oxidized compounds and polymers. Reports indicated that bleaching clay retains 20-40% of oil and importantly, the adsorbed oil represents the major part of bleaching cost as reported by Ong (1983). In Malaysia itself, with CPO production of 17.7 million tonnes in 2008 (Malaysian Palm Oil Board), annually 177 000 tonnes of SBC is generated, at 1% clay dosage, which translates to nearly 50 000 tonnes of adsorbed oil (at 28% oil retention). This oil-laden SBC is currently under-utilized by dumping it in landfills without any attempt to recover the oil. In addition to the oil wastage, dumping the oil-laden SBC undoubtedly creates environmental complications. On the other hand, Tyson (2005) has indicated that the feedstock cost is one of the greatest challenges in producing biodiesel. As such any effort to utilize the adsorbed waste oil reduces bleaching cost, add value to SBC as well as environmental gain. The other advantage of using SBC oil is that its abundant availability at one single location (at oil refineries), whereas those other reported feedstocks are scattered around and relatively, in smaller quantity. The cost and hassle to collect and transport the feedstock is much avoided in the case of SBC oil. In addition to that, the deoiled clay can be reused as reported by Tsai, Chen, Hsieh, Sun and Chien (2002), and Al-Zahrani and Daous (2002). In short, utilizing SBC for biodiesel production has many merits.

Although the oil extraction from SBC have been worked previously by many (Ong, 1983; Hong, 1983; Lee et al, 2000) but the study to transesterify those extracted oils via heterogeneous-catalyzed route is very limited. Transesterification is a catalyzed process by both homogeneous and heterogeneous catalysts, although the former reaction is widely used by industries for its faster kinetic. However, the use of oil with high free fatty acid (FFA) and moisture content in base-catalyzed reaction comes at the expense of product loss through saponification (Scheme 1), time loss in product separation and purification, and environmental issues via wastewater generation. On the other hand, the use of heterogeneous base catalysts has many merits; higher activity, mild reaction conditions, tolerance to FFA and moisture content; long catalyst lifetimes, and low catalyst cost (Ebiura et al, 2005; Liu et al, 2008). The use of CaO in transesterification has been around for many years (Peterson & Scarrah, 1984), but transesterifying waste SBC oil using CaO is very limited. As such, present work focus on transesterifying the high FFA content waste SBC oil aided by CaO as a heterogeneous base catalyst. Biodiesel yield profile of CaO-catalyzed reaction has also been presented against classical NaOH- and KOH-catalyzed homogeneous reactions.

**Scheme 1:** Saponification reaction of free fatty acid



## 2. Experimental

### 2.1. Materials

Spent bleaching clay was supplied by Carotino Sdn. Bhd., Johor, Malaysia. Fatty acids composition of the extracted oil was analyzed by comparing their standards and consisted of lauric acid 0.2%, myristic acid 1.2%, palmitic acid 44.5%, stearic acid 3.9%, oleic acid 39.1%, linoleic acid 9.8%, arachidic acid 0.8% and traces of other acids. FAME standards and internal standards were obtained from Sigma-Aldrich (Switzerland) and of chromatographic grade. Methanol, ethanol, petroleum ether and hexane were purchased from ChemAR. All solvents were of analytical reagent grade. Transesterification reagent was prepared as mentioned in literature (Cvengros & Cvengrosova, 1984). Acidity of the extracted oil was determined by AOCS 5a-40 method.

### 2.2. Catalyst

Calcium oxide (minimum 96.0% assay) was obtained from R&M Chemicals (Essex, UK). The catalyst was treated in a furnace at 900 °C for 2 h prior the use. The basic strength of the catalyst was tested using Hammett indicators: phenolphthalein ( $H_- = 8.2$ ), 2,4-dinitroaniline ( $H_- = 15$ ) and 4-nitroaniline ( $H_- = 18.4$ ). The catalyst was examined by thermogravimetric analysis (TGA) and thermogravimetric coupled with Fourier transform infra red analysis (TGA-FTIR) using Mettler Toledo TGA/SDTA 851e instrument, from 30°C to 900°C with 20°C/min heating rate, under N<sub>2</sub> environment; surface analysis using Micromeritics ASAP 2000. The sample was degassed at 105°C prior to analysis and the adsorption of N<sub>2</sub> was measured at -196°C. Surface area was calculated using BET equation over the pressure range  $P/P_0 = 0.01-0.30$ , where a linear relationship was maintained; scanning electron microscopy (SEM) were obtained using Leo Supra 50VP Field Emission SEM system with 5 kV accelerating voltage; particle size of the catalyst was determined by transmittance electron microscopy (TEM) using Philips CM12 equipped with analySIS Docu ver 3.2 image analysis system; and X-ray diffraction (XRD) was measured on a Siemens Diffraktometer D5000 using Cu K $\alpha$  radiation,  $2\theta$  range from 5° to 40° with step size of 0.05° at 1 min<sup>-1</sup> scanning speed.

### 2.2. Oil Extraction

Adsorbed oil in SBC was extracted using Soxhlet set-up using various polar and non-polar extracting solvents; methanol, ethanol, petroleum ether, and hexane. In each experiment, the extraction solvent was collected and swapped with fresh solvent after every two solvent-cycle until there was no further increase in weight of extracted materials. Each solvent-cycle lasts for about 8 min. at extraction rate of 200 drops min<sup>-1</sup>, approximately.

### 2.3. Reaction

Transesterification reactions were performed in a 25 mL glass reactor with a condenser, immersed in water bath. In a typical reaction, 10.0 g of non-polar extracted SBC oil was added onto the mixture of 0.6 g catalyst (calcined CaO) and 5.0 g methanol. The contents were refluxed under magnetic stirring. Several reaction parameters (methanol/oil mass ratio, catalyst amount and reaction temperature) were studied to find out the optimum reaction conditions. Sample was drawn at every 10 min interval for analysis of methyl ester content. Then the reaction mixture was allowed to cool, resulting glycerol to separate by gravity. Centrifuge was used to further separate the layers (methyl ester and glycerol) and the residual methanol in methyl ester layer was evaporates out using rotary evaporator at 80 °C before washing with lukewarm water to separates the residual catalysts and finally drying over sodium sulphate to obtain pure methyl esters. It should be noted that, although water washing step is not necessary for CaO-catalyzed reaction, but for the purpose of comparison, it was followed.

## 2.4. Gas Chromatography Analysis

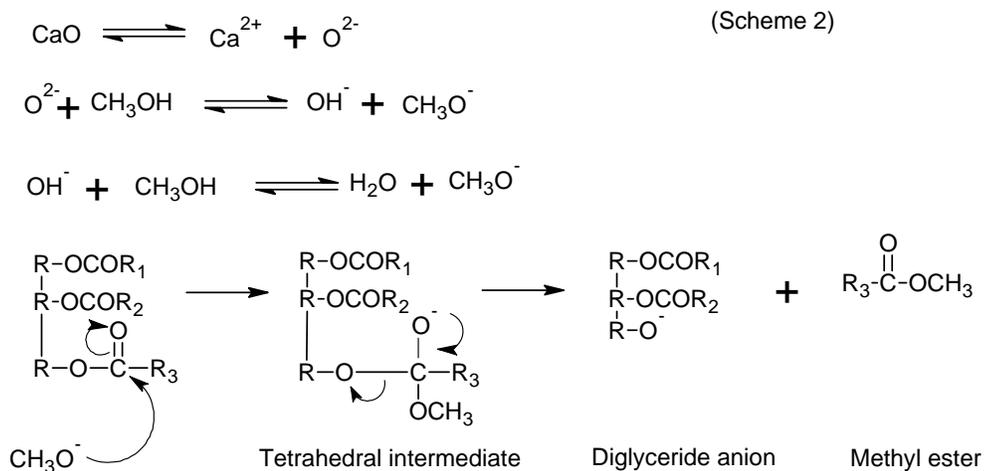
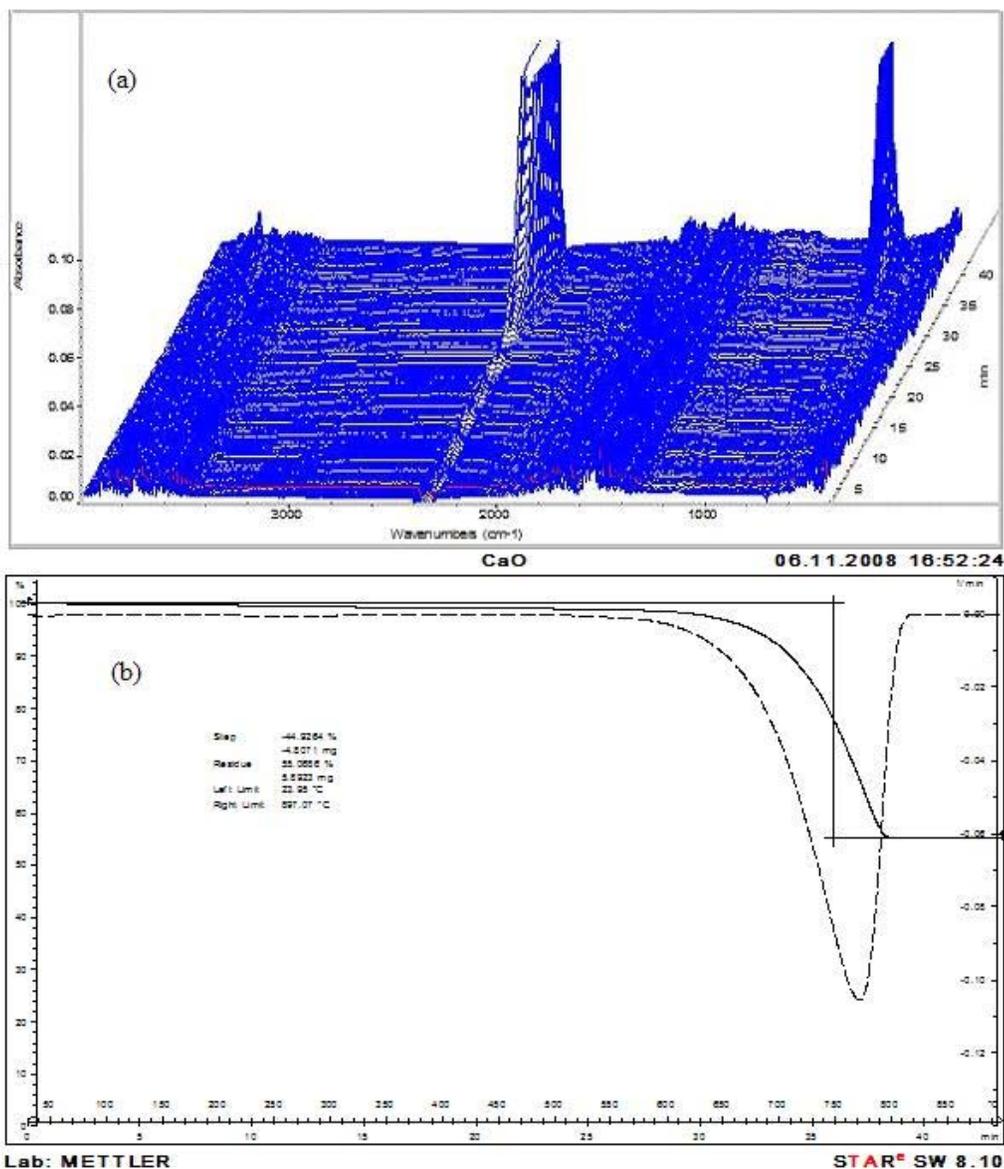
Standard materials and samples were analyzed by a gas chromatography (Perkin Elmer, Clarus 500) fitted with flame ionization detector (FID). The fatty acid methyl esters (FAME) content was determined by following the European regulation procedure EN 14103 with a polar capillary column (Supelco Wax, 30 m x 0.25 mm i.d. x 0.25  $\mu\text{m}$ ) using methyl heptadecanoate as an internal standard. The methyl esters peaks were identified by comparing them with their respective standards.

## 3. Results and Discussion

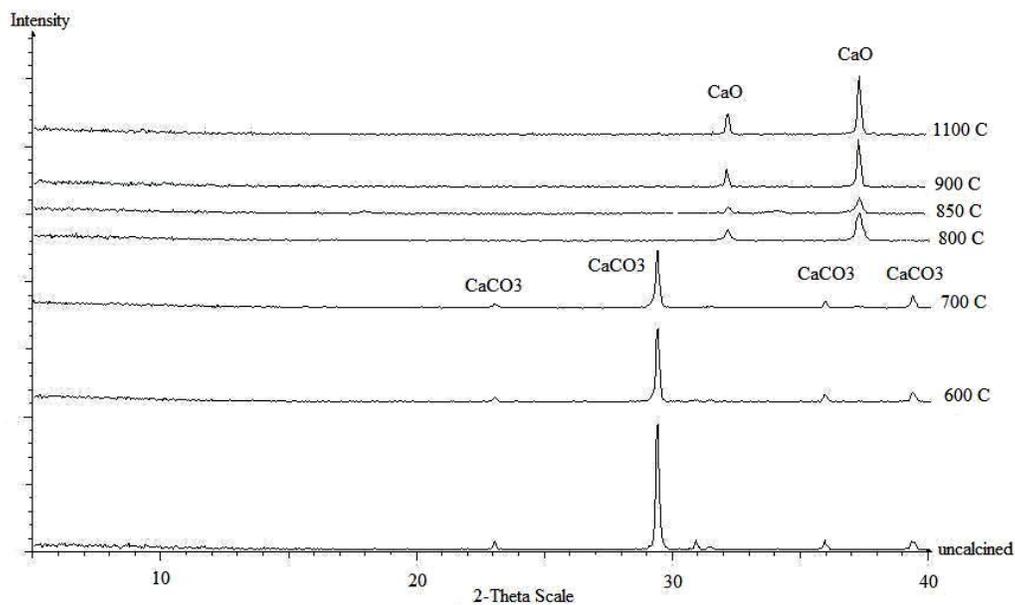
### 3.1. Catalyst

The basic strength of the catalyst was tested using Hammett indicators. About 25 mg of sample were shaken with 1  $\text{cm}^3$  of a solution of Hammett indicator diluted in methanol and left to equilibrate for 2 h (Watkins et al, 2004). If the indicator exhibits a colour change then the catalyst is labeled as stronger than the indicator and if not then the catalyst was said to be weaker than the indicator. The catalyst could change the colour of both phenolphthalein ( $H_- = 8.2$ ) from colourless to pink and of 2,4-dinitroaniline ( $H_- = 15$ ) from yellow to mauve but failed to change the colour of 4-nitroaniline ( $H_- = 18.4$ ). Therefore the catalyst basic strength were assigned as  $15 < H_- < 18.4$ , and regarded as a strong base for transesterification reaction. BET surface area was found to be  $21 \text{ m}^2\text{g}^{-1}$  versus  $5 \text{ m}^2\text{g}^{-1}$  for treated and untreated catalysts, respectively. This is in accordance with SEM images at 20,000 magnifications (not shown here) in which pores are clearly visible for treated catalyst, and not seen in untreated catalyst. TGA-FTIR profile is shown in Fig. 1(a), indicating two major decompositions at around 700 and 2500  $\text{cm}^{-1}$  wavenumbers. These degradations were attributed to the evolving of adsorbed  $\text{CO}_2$  on the catalyst. The  $\text{CO}_2$  evolving temperature window (from around 600°C to around 830°C) was matched with the results obtained from TGA, as depicted by Fig. 1(b), and XRD (Fig. 2). XRD diffractogram indicates that the uncalcined catalyst was saturated with  $\text{CO}_2$  until 700°C. Above the temperature, presence of CaO peaks signaling the evolution of  $\text{CO}_2$  gas from the catalyst. Narrow, and high intense CaO peaks (at  $2\theta = 32.2^\circ$ ,  $37.4^\circ$ , and  $53.9^\circ$ ) were noted for the treated catalyst at 900 °C for 2 h. This was further confirmed by separate FTIR analysis, as depicted by Fig. 3(a); the complete absence of  $\text{CaCO}_3$  signatory peaks at 712, 1798, and 2514  $\text{cm}^{-1}$  for the calcined catalyst. The presence of a unusual peak at 3644  $\text{cm}^{-1}$  for calcined catalyst, may related to the alcohol adsorption during sample preparation, which is absence in uncalcined catalyst as the pores are well saturated with  $\text{CO}_2$ . TEM image as shown in Fig. 3(b) quantified the particle size of calcined catalyst was in the range of 10-50 nm, with mean value of  $22 \pm 9.6$  nm.

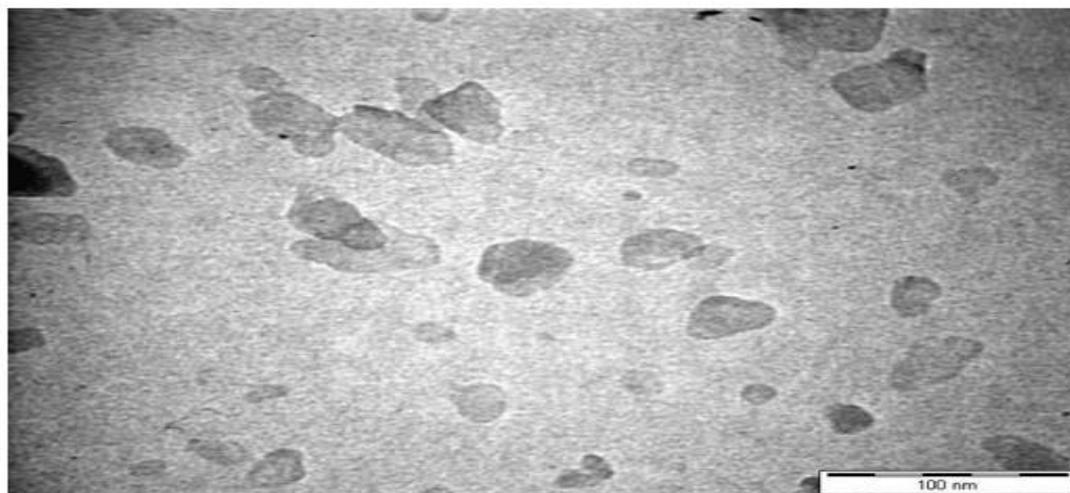
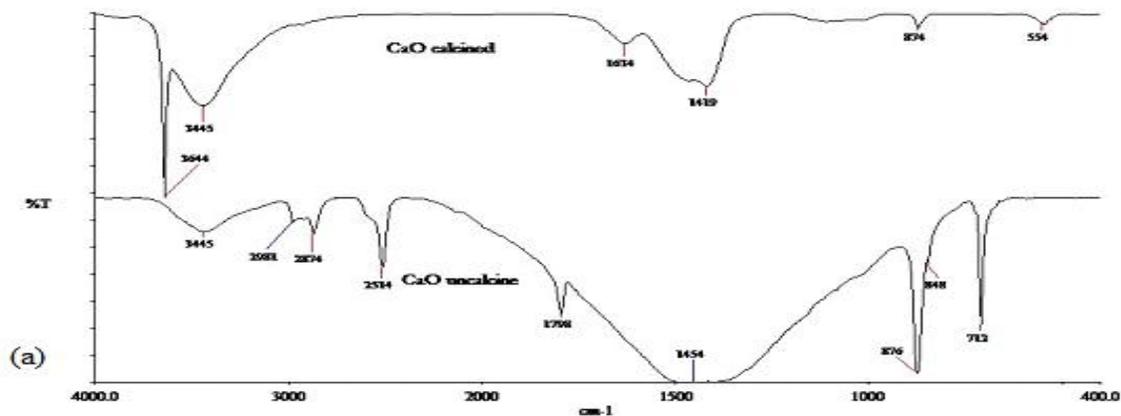
As shown in Scheme 2, the mechanism of CaO in transesterification reaction starts with disassociation of CaO and methanol (Step 1 and Step 2). Then the formation of methoxide anion resulted from the reaction between methanol and hydroxide ion (Step 3). The anion later attacks carbonyl carbon of triglyceride to form tetrahedral intermediate. Then the rearrangement of the intermediate molecule forms a mole of methyl ester and diglyceride, as shown by Step 4 (Granados et al, 2007). Then the methoxide attacks another carbonyl carbon atom in diglyceride, forming another mole of methyl ester and monoglyceride. Finally another methoxide attacks on monoglyceride produces a total of three moles of methyl esters and a mole of glycerol. Other mechanism routes have also been recognized in previous literatures (Liu et al, 2008; Kouzu et al, 2008).

**Scheme 2: Mechanism of CaO-catalyzed transesterification****Figure 1:** (a) TGA-FTIR profile, and (b) TGA decomposition curve of as-received catalyst

**Figure 2:** Powder XRD patterns of untreated and treated catalyst at different calcinations temperatures.



**Figure 3:** (a) FTIR comparison spectra between calcined and uncalcined catalysts, and (b) TEM image of calcined catalyst at microscope magnification of 22K

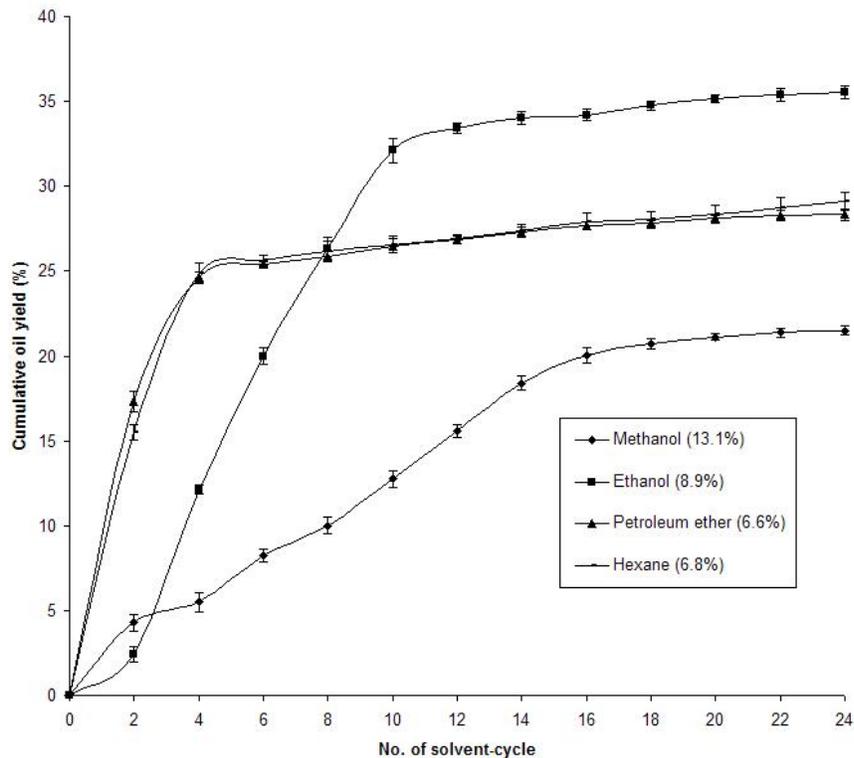


(b)

### 3.2. Oil Extraction and Quality

Accumulated oil yields extracted with different solvents were presented in Fig.4. Ethanol extraction yields more extracts than methanol and non-polar solvents, in agreement with previous work by Lee, Seng, and Liew (2000). Both non-polar solvents have shown a very similar extraction trend. The poor extraction performance by methanol defines that CPO is less soluble in it than in ethanol. In addition, the wide polarity difference between them (since methanol is the simplest alcohol) has also contributes to the low performance. Although ethanol extraction gives higher yield, but cleaner and clearer oil was only obtained through non-polar solvents extractions. The colour of polar extractions was darker (brown) than that of the non-polar extractions (light yellow). The development in colour can related to the presence of polar components from CPO. The other most noticeable feature other than the color is the acidity. Acidity (as palmitic acid) of the extracted oil with different solvents, shows that methanol extract recorded the highest FFA content of 13.1%, followed by ethanol (8.9%), then hexane ( 6.8%) and petroleum ether (6.6%).

**Figure 4:** Cumulative oil yield extracted with different solvents. Value in parentheses denotes FFA content of the corresponding solvent extract



In order to confirm the deoiled clay is free from any residual oil and to quantify any other retained substances in the clay, polar-deoiled clay was subjected to second extraction with non-polar solvent and vice versa, using the combinations of all the mentioned solvents. In each experiment, the second extracted residual matters were weighted and in order to confirm the presence of oil, it was treated with the prepared transesterification reagent before subjected to GC analysis. As presented in Table 1, the weight of second extracts was highest when methanol deoiled clay was subjected to re-extraction with hexane and petroleum ether. GC results confirmed that, for both cases, the second extractions were mainly consists of triglycerides, which was not completely extracted in first extraction. High FFA content in methanol extract further confirmed that FFA is the major constituent in the first extraction and not the triglycerides. In contrast, the weight of second extracts was lowest when ethanol deoiled clay was subjected to re-extraction with petroleum ether and hexane; indicates

most of the triglycerides as well as polar components have been extracted completely in the first extraction. The very small residue after re-extraction was mainly triglycerides, confirmed by the presence of methyl esters traces in chromatogram.

For the case of both petroleum ether and hexane deoiled clays, around 6% extracts were recorded if methanol is used for re-extraction and about half of the value was afforded with ethanol as re-extract solvent. All these second extracts were shown negative for the presence of triglycerides; deduces that triglycerides have been completely extracted with non-polar solvents in the first extraction, and only polar components were extracted in the second extraction with methanol extracts more polar matters (nearly double) than that of ethanol.

**Table 1:** Data on residual amount of re-extracted clay with different solvent combinations

1 <sup>st</sup> Extraction	Extracts <sup>a</sup> (wt. %)	2 <sup>nd</sup> Extraction <sup>b</sup>	Extracts <sup>a</sup> (wt.%)	Methyl Esters <sup>c</sup>	Total Extracts <sup>a</sup> (wt.%)
Methanol	21.5 ± 0.3	Petroleum ether	11.7 ± 0.9	Yes	33.2
		Hexane	12.0 ± 0.7	Yes	33.5
Ethanol	35.6 ± 0.4	Petroleum ether	0.6 ± 0.05	Traces	36.2
		Hexane	0.7 ± 0.07	Traces	36.3
Petroleum ether	28.2 ± 0.6	Methanol	6.3 ± 0.5	No	34.5
		Ethanol	3.1 ± 0.7	No	31.3
Hexane	28.8 ± 0.5	Methanol	6.0 ± 0.7	No	34.8
		Ethanol	3.4 ± 0.8	No	32.2

<sup>a</sup>Based on clay weight.

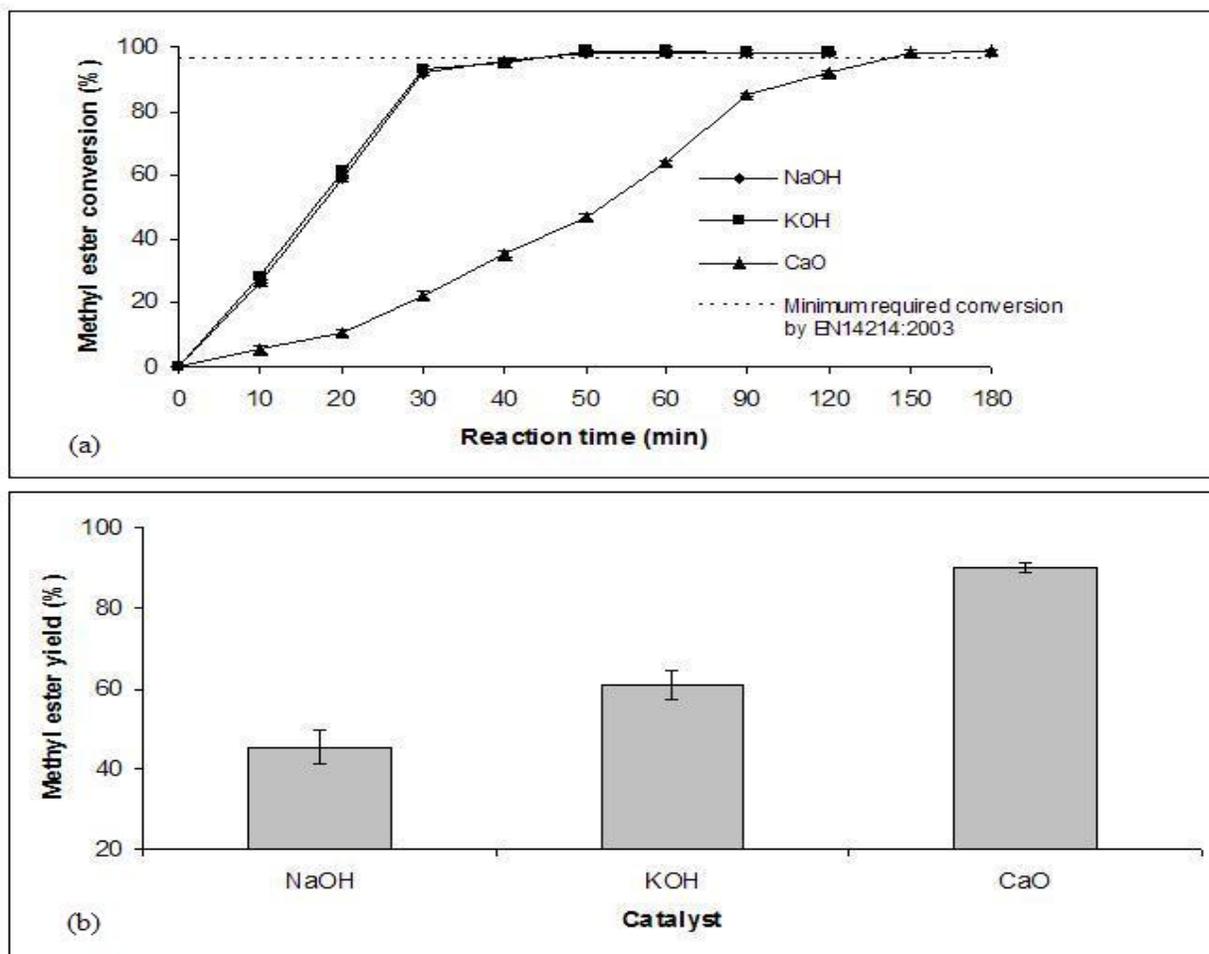
<sup>b</sup>Deoiled, dried clay from 1<sup>st</sup> extraction is subjected to 2<sup>nd</sup> extraction with the listed solvents

<sup>c</sup>Determined by GC after treated with transesterification reagent

### 3.3. Reaction

Parametric study was performed on CaO-catalyzed reaction and the optimal conversion was achieved through the following conditions; methanol/oil mass ratio 0.5:1; catalyst amount 6 wt.%, and reaction temperature of 65°C. For NaOH- and KOH-catalyzed reactions, optimal conditions found to be; methanol/oil mass ratio 0.25:1; catalyst amount 1 wt.%, and reaction temperature of 65°C. As depicted by Fig. 5(a), conventional catalysts were achieved near 99% conversion in less than an hour as compared to 2.5 h for CaO-catalyzed reaction; as a result, experiment with conventional catalysts was not continued after 2 h. Expectantly, at reaction time of 30 min., the conversion differences between them were as high as 70% defines the faster kinetics of hydroxide catalysts. For CaO-catalyzed reaction, in the first 20 min. only 10% conversion was achieved (vs. 60% for classical catalysts); but a more rapid conversion was observed thereafter until reached plateau after 150 min. Although the reaction time was longer for heterogeneous reaction, but the time was well compensated by the elimination of few processes such as neutralization, washing, drying, treating large amount of wastewater, and tedious product separation which are unavoidable steps in homogeneous reaction.

**Figure 5:** (a) Conversion of SBC oil to methyl esters as a function of time, for different catalysts, and (b) Influence of different catalysts on the methyl esters yield. Reaction conditions are as mentioned in the text



### 3.4. Biodiesel Yield

Under optimized conditions, biodiesel yield was quantified by calculating the ratio of the weight of methyl esters (from GC) to the weight of oil used. Regardless the type of catalysts, methyl esters purity was found close to 99% at equilibrium, much higher than the minimum requirement of 96.5% by EN 14214:2003 procedures. But as for the yield, as described by Fig. 5(b), highest yield was only recorded with CaO as compared to the other two classical homogeneous catalysts. The highest yield differences between them was as much as 45%, a significant amount, and the loss is attributed to the saponification reaction (Scheme 1), in which FFA reacts with alkali hydroxides to form alkali salts and water. The produced soapy alkali salt emulsion not only reduces methyl esters yield but also complicates the separation of methyl esters and glycerol (Haas et al, 2003), which is well reflected by the higher standard deviations (about 4%) for the both hydroxide catalysts. The more loss in NaOH-catalyzed yield as compared to KOH is probably due to the higher mol of NaOH. At equal mass, NaOH delivers higher mol (1.4 times) than KOH due to their differences in molecular weight. On an industrial scale, the formed emulsion could easily choke the pipelines and complicates the product separation. Hence, it looks impractical technically and uneconomical to use homogeneous alkali catalysts to transesterify oil with high FFA content. On the other hand, heterogeneous catalysts offer simpler process with relatively higher biodiesel yield. Although more methanol and catalyst was used in the latter reaction, but the excess methanol is always can be recovered while the catalyst (CaO) is capable to be reused for several more cycles (Liu et al, 2008).

#### **4. Conclusion**

As a summary, among the solvents, only ethanol is capable to extract both polar components and triglyceride in a single run. As the consequent, cleaner clay is obtained through ethanol extraction. However for the purpose of transesterification, oil without polar components is wanted. As such, non-polar extracts are preferred, which are not only clean from polar constituents but also with least FFA content. The extracted waste oil was successfully converted to biodiesel with higher yield using CaO as compared to that of conventional catalysts. The use of classical homogeneous catalysts resulted in higher yield loss through saponification as well as from the complicated separation process due to soap formation. Although the reaction time is longer with CaO, but the elimination of few processes and less waste generation compensates the delay well, in additional to higher yield and the possibility of catalyst reusable. Since non-polar solvents could extract triglyceride well and polar solvents could extract polar components better, the study can extend to investigate the clay reusability, after a pair of extractions with polar and non-polar solvents.

#### **Acknowledgement**

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