



## IN-SITU TRANSESTERIFICATION OF SPENT BLEACHING CLAY USING CaO SUPPORTED ON ZnO AS A BASIC CATALYST

Intan Shafinaz Abd Manaf<sup>1</sup>, Nurul Hajar Embong<sup>1</sup>, Mohd Hasbi Ab. Rahim, and Gaanty Pragas Maniam<sup>1,2</sup>

<sup>1</sup>Faculty of Industrial Sciences & Technology, University Malaysia Pahang, Lebuhraya Tun Razak, Kuantan, Pahang, Malaysia

<sup>2</sup>Central Laboratory, University Malaysia Pahang, Lebuhraya Tun Razak, Kuantan, Pahang, Malaysia

E-Mail: [gaanty@hotmail.com](mailto:gaanty@hotmail.com)

### ABSTRACT

Shrinking fossil fuels sources, accelerating prices and the effect of its usage on the environment have indicate to the exploration for alternative fuels for diesel engines. This study focus on *in-situ* transesterification using barnacle shell supported on ZnO as a basic heterogeneous catalyst and spent bleaching clay as feedstock. The catalyst was characterized using XRD, FTIR, BET, FESEM and basicity. The optimum conditions for the process were: time 4 h; catalyst amount 2% (SBC weight); methanol to oil molar ratio 150:1; and co-solvent (petroleum ether to hexane, 1:1 mass ratio) with highest methyl ester content at 77 wt.%.

**Keywords:** biodiesel, catalyst, *in-situ* transesterification, spent bleaching clay.

### 1. INTRODUCTION

Instead of becoming as a product for export, biodiesel already act as a source domestic energy, has been started recently in Malaysia. Transportation meets a crucial role in globalization and economy. As known, industry sector in Malaysia has recently outstripped many sectors but transportation still is a major energy consumer in Malaysia. Hence, biodiesel can be announcing as most reliable and desirable renewable energy because of the sources area and demand of energy. Generally, biodiesel feedstock can be divided into four main categories as edible oil, non-edible vegetable oil, waste or recycled oil, and animal fats [1, 2]. From those four categories of feedstock, waste oils from industry such as spent bleaching clay as raw materials are an appropriate idea despite of there are many advantages for using waste feedstock for biodiesel. The catalysts from waste sources, especially from the shell (calcium oxide) gave more advantages: (i) abundant supply (ii) easily separated (iii) reusable (iv) less corrosive (v) cost effective and (vii) environmental friendly. The catalyst synthesized with the waste shells gave opportunity for renewable catalyst and at the same time recycles the waste created [3].

Previously, the conventional transesterification process had been used widely in biodiesel production. Today, another alternate process for biodiesel, which is considered to have the potential of reducing the processing units and costs of the fuel conversion process, is the '*in-situ*' transesterification method. This process simplifies the conversion of the feedstock oil to methyl ester directly from the oil bearing, by excluding the solvent extraction procedure. Hence, costs effective process can be done by subtracting the other step and low consumptions of solvents, energy, and time. Moreover, this method will reduce waste and pollution matter. *In-situ* process is highly probable to recover the oil in the spent bleaching earth by using *in-situ* method for biodiesel production [4]. This research aimed to reveal the utilization of palm oil refinery waste (spent bleaching clay, SBC) as feedstock; and mixed

oxide (B-CaO·ZnO) from waste marine waste (barnacle shell) as a catalyst. The study of *in-situ* transesterification methods with conventional method also was studied. The optimization of methanol to oil ratio, catalyst amount and time was investigated.

### 2. METHODS

#### 2.1. Materials

Spent bleaching clay (SBC) was collected from refinery palm oil Felda Vegetable Oil Sdn. Bhd, Kuantan, Malaysia and the barnacle shell were collected at Pantai Gelora beach Kuantan, Pahang, Malaysia. Methyl heptadecanoate of chromatographic grade, obtained from Sigma-Aldrich (Switzerland), was used as an internal standard, whereas zinc oxide, methanol, petroleum ether (PE) and hexane of analytical grades were purchased from Bendosen Laboratory Chemicals (Norway).

#### 2.2. Catalyst preparation and characterization

The barnacle shell supported by ZnO was prepared using the ball milling procedure with the ratio of 1:1-1:5 with stoichiometrically required addition of water was used as starting materials for mechanochemical treatment. Milling was done for 1 h and subsequently for 2 h with angular velocities of basic disc, measured by tachometer. Calcination of mechanochemically prepared precursor was performed at 400 °C for 3 h in air atmosphere [5]. The catalyst was characterized by X-ray diffraction (Rigaku) with Cu Ka as a source, 2θ range from 25 °C to 125 °C with step sizes of 0.1°, at a scanning speed of 1° min<sup>-1</sup>. Surface analysis of the catalyst was examined by using Micromeritics ASAP 2000. Prior to the analysis all the samples were degassed at 105 °C and the adsorption of N<sub>2</sub> was measured at -196 °C. The morphology of catalyst was observed by FESEM with electron dispersive X-ray (EDX) (JSM-7800F).



### 2.3. In-situ transesterification reaction

The content of SBC to methyl ester (ME) was performed in a 50 ml 2-neckround bottom flask equipped with a reflux condenser and magnetic stirrer. The *in-situ* transesterification reaction between SBC and methanol was carried out in the liquid phase under atmospheric pressure, at 65 °C for 4 h with continuous stirring 5 g SBC (1.3 g oil, at oil content 26 wt. %), 2 wt.% catalyst [based on SBC weight], 7.62 g of methanol to give approximately 1:150 oil to methanol molar ratio and 2.5 g co-solvents (PE and hexane in equal ratio) to give 1:1 co-solvents:SBC mass ratio. Then, the sample was transfer into the test tube and centrifuged at 1000 rpm for 5 min. Four layers were formed; the top was co-solvents, followed by methanol, SBC and catalyst layer at the bottom. The co-solvents and methanol layers were pipetted out separately, then about 3ml of each PE and hexane were added into the test tube, homogenized and centrifuged, then the resultant top co-solvents layer was added to the portion of co-solvents that was pipetted out earlier. The step was repeated twice to obtain a total amount of about 14 ml of accumulated co-solvents. Upon solvent evaporation using rotary evaporator, pure ME was obtained. The resultant ME was subjected to chromatographic analysis for quantification using GC-FID (Agilent 7890A) following the European procedure EN 14214 with polar capillary.

## 3. RESULTS AND DISCUSSION

### 3.1. SBC characterizations

From the composition Table-1, noted that palmitic acid is the major fatty acid in the SBC oil (44.1%), the acidity is reported in respect of the palmitic acid. The results show similar to [6] where is the palmitic acid is about 44.1%. Higher acidity is predictable as crude palm oil (CPO) commonly contains high free fatty acid (FFA). The fatty acid distribution of SBC oil has slightly higher saturated components and unsaturated fatty acids. Generally, CPO has saturated and unsaturated fatty acids in about a 50:50 ratio. However, the SBC oil used in this experiment has higher lauric acid content (4.5%, Table-1). In contrast, CPO generally contains less than 1% of lauric acid. This inconsistency may arise due to the adulteration of the SBC in the refinery with palm kernel oil. Commonly, palm kernel oil content of 4.0-8.0% of lauric composition.

### 3.2. Catalyst characterization

X-ray diffraction (XRD) was used to determine the crystal structure of the B-CaO-ZnO, which is shown in Figure-1. The diffractograms of B-CaO-ZnO showed the processes of precursor preparation [ball milled Ca(OH)<sub>2</sub> and ZnO powders either with the addition of water) leads to the formation of CaO and ZnO mixture, with other phase[s] being undetectable. It is very likely that fine CaO particles are embedded in ZnO matrix, proposing that ZnO actually denotes the support for CaO.

Table-1. Composition of fatty acid in SBC oil.

Fatty acid	Composition (%)	
	Present work	Previous work [6]
<b>Saturated</b>		
Lauric (C <sub>12:0</sub> )	4.0	4.5
Myristic (C <sub>14:0</sub> )	2.2	2.6
Palmitic (C <sub>16:0</sub> )	44.1	41.1
Stearic (C <sub>18:0</sub> )	4.5	4.6
Sub total	48.8	52.8
<b>Unsaturated</b>		
Oleic (C <sub>18:1</sub> )	35.0	37.5
Linoleic (C <sub>18:2</sub> )	10.2	9.7
Arachidic (C <sub>20:0</sub> )	traces	traces
Sub total	45.2	47.2
<b>Total</b>	<b>100.0</b>	<b>100.0</b>

In Figure-2, the FTIR peaks show hydroxyl ions are characterized by sharp bands appearing between 3700 and 3500 cm<sup>-1</sup>. Therefore, two sharp bands at 3615 and 3505 cm<sup>-1</sup>, which can be seen at Figure-2 are assigned to ν [OH] stretching vibrations. The stretching bands at 3150, 3034 and 2880 cm<sup>-1</sup> are attributed to the O-H groups from H<sub>2</sub>O molecules [7]. The increase amount of carbonates was determined for the samples of catalysts obtained by ball-milling. The band at 1070 cm<sup>-1</sup> attributed to the Zn-O-H bending vibration is observable for B-CaO-ZnO catalyst. The wide band that is observed in the region of 3400–3100 cm<sup>-1</sup> is caused by the stretching of water molecules.

Surface area and pore structure analyses were done using BET method. The B-CaO has total surface area is 6.0528 [m<sup>2</sup>/g] and pore volume is 0.016646 cm<sup>3</sup>/g. The supported metal may have collapsed in the surface area and pore volume of calcined B-CaO-ZnO (3.6198 m<sup>2</sup>/g and 0.007366 cm<sup>3</sup>/g, respectively). The micrographs of B-CaO and B-CaO-ZnO have shown in Figure-3. The B-CaO-ZnO presented the existence of large, plate like particles of hexagonal shape. It appears that better dispersion is achieved when ball milling procedure for catalyst preparation was used, and this is the most pronounced in this case where small round particles of CaO entirely covered ZnO crystals [8]. Smooth, polygonal plates observed calcined B-CaO-ZnO catalysts appear to be ZnO crystals with small particles of CaO dispersed on them. It appears that better dispersion is achieved when ball milling procedure for catalyst preparation was used where small round particles of CaO entirely covered with ZnO crystals. While the major element is CaO, the mixture of metal oxides could also contribute to basicity of the catalyst.

### 3.3. In-situ transesterification

The conversion of adsorbed CPO to methyl esters, under the conditions described in Section 2.3, was found to be 77 wt. %. The molar ratio of methanol to oil is one of the important variables which affect transesterification reaction. Stoichiometrically, the reaction requires three moles of methanol for each mole of oil (MeOH:oil = 3:1), and with excess methanol it would



shift the equilibrium towards the direction of ME production. Too much methanol could dilute the oil and as a result slows the reaction rate [9], which in turn, lowers conversions. In addition, a higher mass ratio of alcohol to oil increases the solubility of glycerol, and as a consequence, the separation of glycerol becomes more difficult and retards the forward reaction by promoting the backward equilibrium. The relatively larger amount of methanol was used in this work mainly to cater for the solvent-absorbing and solvent-retaining characteristics of the SBC during reaction. Nevertheless, the excess of

methanol can be readily recovered at the end of the reaction. The ME content reaches the highest value at the catalyst amount of 2 wt.%, due to the contact opportunity between catalyst and the reactants hence propels the reaction kinetics. Based on the oil weight, the amount of catalyst used in this work seems to be higher due to several reasons; part of the catalyst could be entrapped in the clay matrix; this portion of the catalyst may not have contributed to catalytic activity.

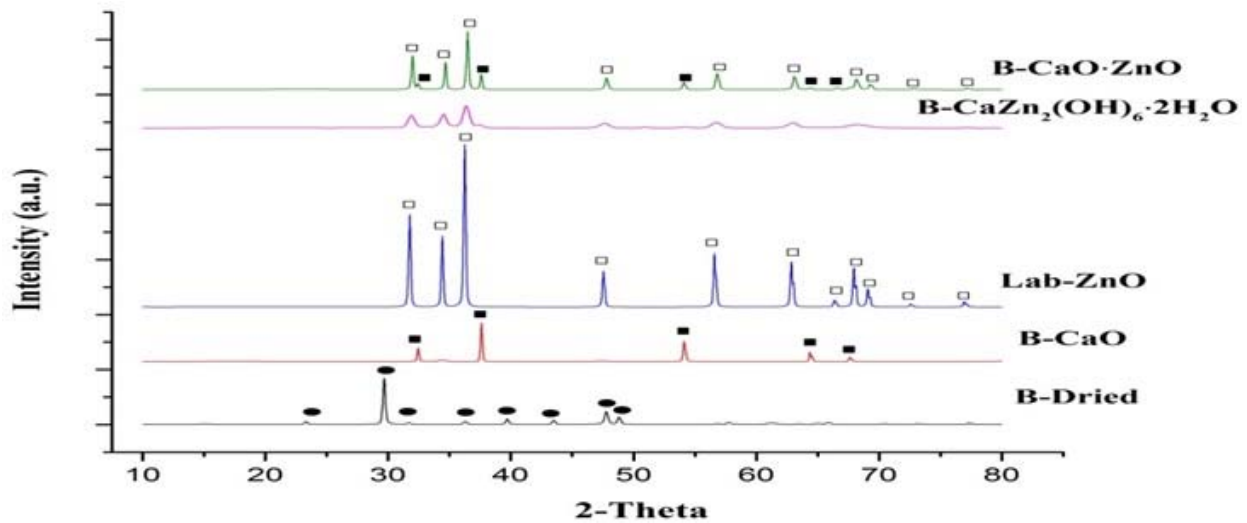


Figure-1. Diffractogram for mechanochemical compound.

●  $\text{CaCO}_3$ , ■  $\text{CaO}$ , □  $\text{ZnO}$ .

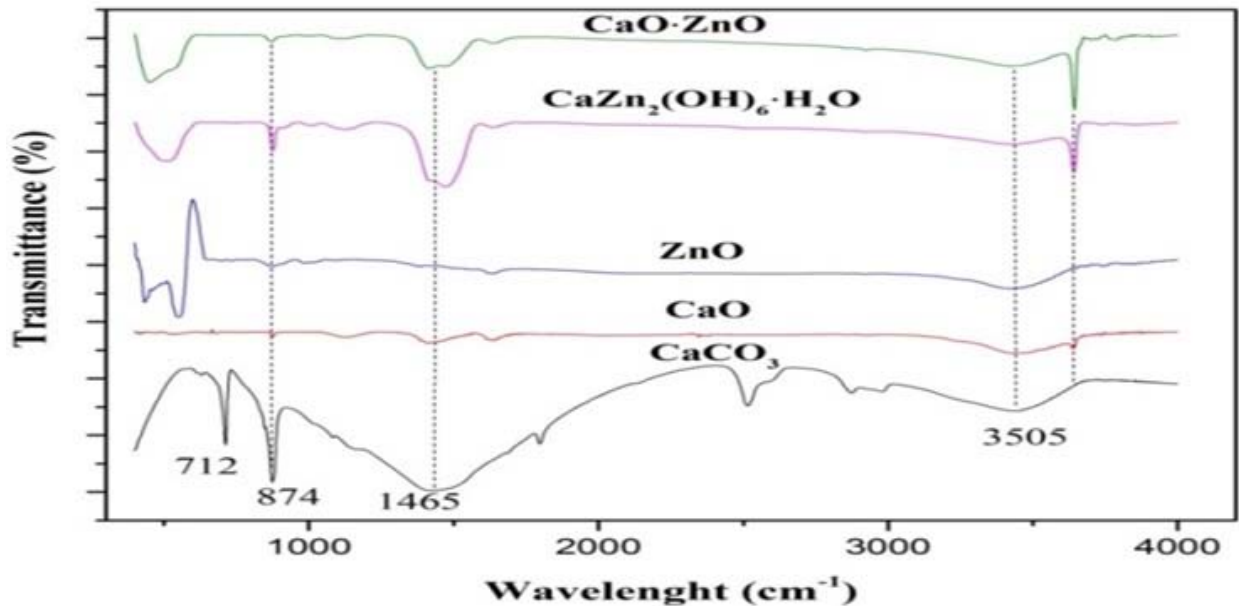
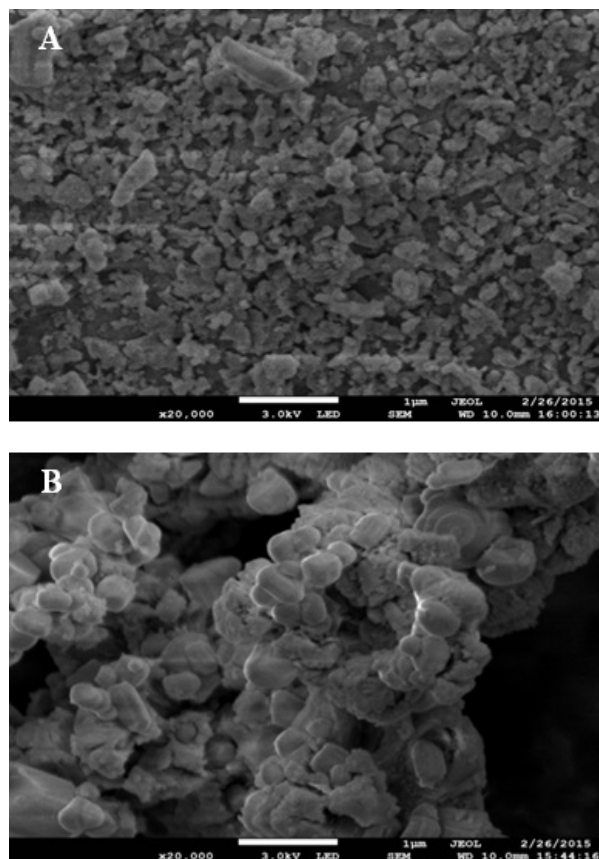


Figure-2. FTIR analysis for B-CaO·ZnO catalyst.



**Figure-3.** FESEM images for (A) B-CaO (900 °C, 2 h)  
(B) B-CaO·ZnO (400 °C, 3 h).

In addition, a part of the catalyst (basic nature) is also used to neutralize the acids in CPO. The in-situ transesterification using magnetic stirrer makes methanol to cavitate, thus disperse as nano droplets into the oil, forming a fine emulsion of methanol in oil. This increases the contact surface between the reactants dramatically and consequently accelerating the reaction. The cavitation bubbles also help in the release of oil from SBC so that transesterification reaction can take place. The use of magnetic methods processing not only can provide energy for the reaction, but can achieve better mixing, more rapid separation and thus not disturb the reaction.

#### 4. CONCLUSIONS

In this work, spent bleaching clay was successfully utilized as a low-cost feedstock to produce methyl ester (biodiesel) via in-situ transesterification. Highest ME content of 77 wt. % was obtainable in 4 hour reaction time at 65°C. Optimization of reaction parameters revealed that MeOH:oil, 150:1 molar ratio; catalyst, 2 wt.% (based on SBC weight) and co-solvents to SBC mass ratio of 1:1 as the optimal reaction conditions. Materials

derived from waste sources, as used in this work, should be given a priority for sustainable production of biodiesel.

#### REFERENCES

- [1] S. Silitonga, A. E. Atabani, T. M. I. Mahlia, H. H. Masjuki, I. A. Badruddin and S. Mekhilef. 2011. A review on prospect of jatropha curcas for biodiesel in Indonesia. *Renewable and Sustainable Energy Reviews*. 15(8): 3733–3756.
- [2] E. Atabani, A. S. Silitonga, I. A. Badruddin, T. M. I. Mahlia, H. H. Masjuki and S. Mekhilef. 2012. A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *Renewable and Sustainable Energy Reviews*. 16(4): 2070–2093.
- [3] J. Boro, D. Deka, and A. J. Thakur. 2012. A review on solid oxide derived from waste shells as catalyst for biodiesel production. *Renewable and Sustainable Energy Reviews*. 16(1): 904–910.
- [4] R. Mat, O. S. Ling, A. Johari and M. Mohamed. 2011. In situ biodiesel production from residual oil recovered from spent bleaching earth. *Bulletin of Chemical Reaction Engineering & Catalysis*. 6(1): 53–57.
- [5] Lukić, Ž. Kesić, S. Maksimović, M. Zdujić, H. Liu, J. Krstić and D. Skala, 2013. Kinetics of sunflower and used vegetable oil methanolysis catalyzed by CaO·ZnO. *Fuel*. 113: 367–378.
- [6] P. Lim, G. P. Maniam and S. A. Hamid. 2009. Biodiesel from adsorbed waste oil on spent bleaching clay using cao as a heterogeneous catalyst. *European Journal of Scientific Research*. 33(2): 347–357.
- [7] T. Lin, M. Y. A. Mollah, R. K. Vempati and D. L. Cocke. 1995. Synthesis and characterization of calcium hydroxyzincate using x-ray diffraction, ftir spectroscopy and scanning force microscopy. *Chemistry Materials*. 1974–1978.
- [8] Ž. Kesić, I. Lukić, D. Brkić, J. Rogan, M. Zdujić, H. Liu and D. Skala. 2012. Mechanochemical preparation and characterization of CaO·ZnO used as catalyst for biodiesel synthesis. *Applied Catalysis A: General*, 427-428: 58–65.
- [9] Y. C. Leung, X. Wu and M. K. H. Leung. 2010. A review on biodiesel production using catalyzed transesterification. *Applied Energy*. 87(4): 1083–1095.