

**ALKALINE EARTH METALS LOADING ON WASTE DEOILED-SPENT BLEACHING
CLAY AS CATALYSTS IN TRANSESTERIFICATION REACTION**

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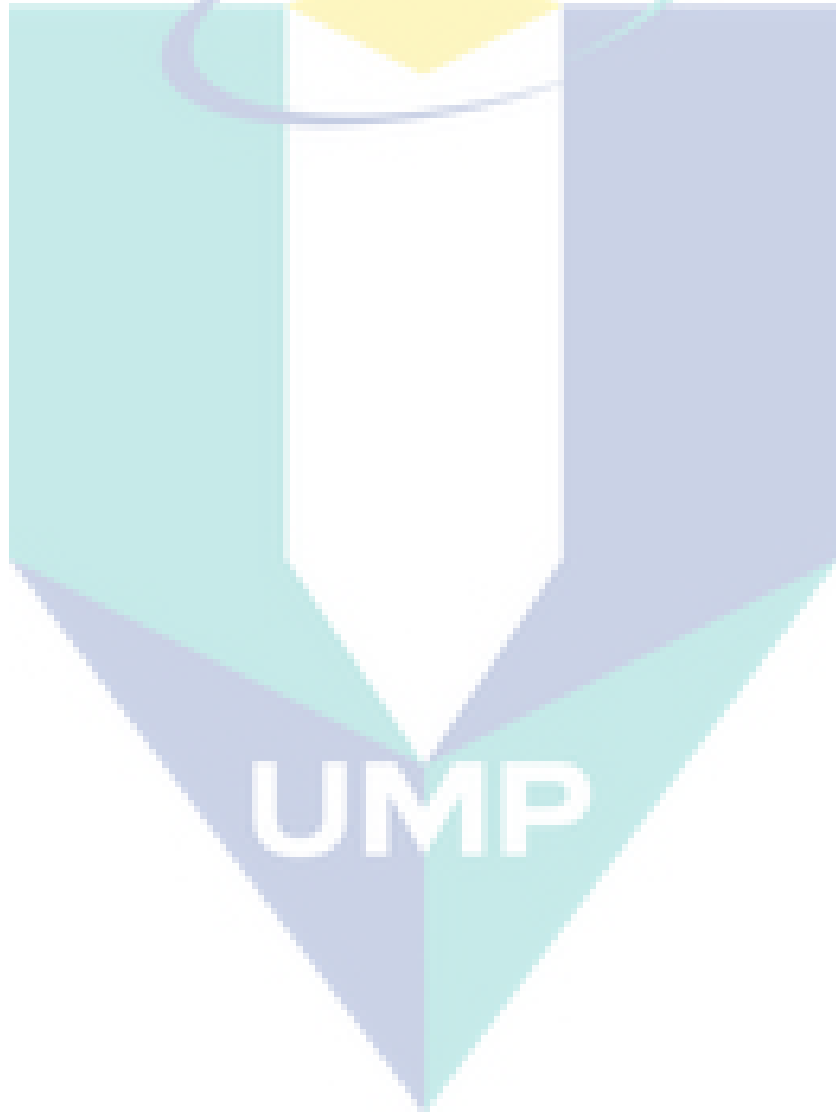
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ABSTRACT

**ALKALINE EARTH METALS LOADING ON WASTE DEOILED-SPENT BLEACHING
CLAY AS CATALYSTS IN TRANSESTERIFICATION REACTION**

(Keywords: Spent bleaching clay, transesterification, biodiesel, catalyst)

In the present work, waste sources, namely spent bleaching clay, has been successfully utilized as solid catalysts support in the transesterification of refined, bleached and deodorized palm olein (RBD-PO), waste palm cooking oil (WPCO) and spent bleaching clay oil (SBC) to produce methyl esters (biodiesel). Energy plays an important role in social, economy, development of the country as well as our daily life. Biodiesel is one of the alternative ways to replace fossil fuels as the energy source. It is renewable and environmental friendly. Biodiesel are usually made from the reaction between triglycerides and alcohol under presence of catalyst through transesterification reaction. The triglycerides source from waste source such as WPCO and SBC can help to reduce the production cost and do not cause food issue. In order to enhance the catalytic activity, the deoiled SBC had been calcined at 500 °C for 10 h and doped with KOH, CaO and La₂O₃. The catalyst was characterized with TGA, FTIR, XRD, XRF, BET, FESEM and Hammett indicators (phenolphthalein, 2,4-dinitroaniline and 4- nitroaniline). The optimal reaction conditions found to be: for transesterification of RBD-PO using K-DSBC was 3 wt.% catalyst amount while for Ca-DSBC and La- DSBC were 5% catalyst (based on oil weight) and 9:1 methanol to oil molar ratio for 2 h reaction period producing 99.0%, 98.8% and 96.2% methyl ester conversion respectively. Meanwhile in transesterify WPCO, K-DSBC was 3 wt.% catalyst amount while for Ca-DSBC and La-DSBC were 5% catalyst (based on oil weight) and 9:1 methanol to oil molar ratio for 3 h reaction period producing 97.2%, 85.5% and 83.1% methyl ester conversion respectively. Transesterification of SBC oil using K-DSBC was 3 wt.% catalyst amount while for Ca-DSBC and La-DSBC were 5% catalyst (based on oil weight) and 9:1 methanol to oil molar ratio for 4 h reaction period producing 88.9%, 80.2% and 76.6% methyl ester conversion respectively.. All catalysts undergo transesterification at the reflux temperature of methanol (65 °C). Furthermore, the regenerated of the catalytic activity was investigated, and found that all the three catalysts could be reused up to five times, when maintaining methyl esters content above 90%. In addition, the catalysts exhibit tolerance towards the presence of water at 1.75% and 2.0% and free fatty acid at 1.75% and 1.75%, respectively, with over 80% of methyl esters content.

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ABSTRAK

Dalam kajian ini, bahan buangan tanah liat pelunturan telah digunakan sebagai penyokong mangkin pejal dalam proses transesterifikasi menggunakan minyak sawit tulen (RBD-PO), minyak masak sawit terpakai (WPCO) dan minyak tanah liat pelunturan (SBC) bagi menghasilkan metil ester (biodiesel). Tenaga memainkan peranan penting dalam social, ekonomi, pembangunan negara dan juga kehidupan seharian. Biodiesel adalah salah satu cara alternatif bagi menggantikan bahan api fosil sebagai sumber tenaga. Ia bersifat boleh diperbaharui dan mesra alam sekitar. Biodiesel biasanya diperolehi melalui reaksi antara minyak dan alcohol dengan adanya mangkin melalui proses transesterifikasi. Sumber minyak daripada bahan terbuang seperti WPCO dan SBC boleh membantu mengurangkan kos dan tidak menimbulkan isu terhadap pemakanan. Dalam usaha untuk meningkatkan aktiviti mangkin, tanah liat pelunturan yang telah dibuang minyak telah dikalsin pada suhu 500 °C selama 10 jam dan ditambah dengan KOH, CaO dan La₂O₃. Kesemua mangkin diuji dengan menggunakan TGA, FTIR, XRD, XRF, BET, FESEM dan penunjuk Hammett (phenolphthalein, 2,4- dinitroaniline and 4-nitroaniline). Keadaan optimum tindak balas untuk transesterifikasi daripada RBD-PO menggunakan K-DSBC sebagai mangkin adalah 3% manakala Ca- DSBC dan La-DSBC adalah sebanyak 5% (berdasarkan berat minyak) dan 9:1 nisbah molar metanol kepada minyak, selama 2 jam menghasilkan 99.0%, 98.8% dan 96.2% metil ester. Untuk transesterifikasi dengan menggunakan WPCO, mangkin K-DSBC digunakan 3%, Ca-DSBC dan La-DSBC adalah sebanyak 5% (berdasarkan berat minyak), 9:1 selama 3 jam mencatat 97.2%, 85.5% dan 83.1% metil ester. Transesterifikasi minyak SBC menggunakan K-DSBC adalah 3% manakala Ca-DSBC dan La-DSBC adalah sebanyak 5% (berdasarkan berat minyak) dan 9:1 nisbah molar metanol kepada minyak, selama 4 jam menghasilkan 88.9%, 80.2% dan 76.6% metil ester. Kesemua mangkin menjalani transesterifikasi pada suhu refluks metanol (65 °C). Keberkesanan penggunaan semula mangkin dikaji dan didapati bahawa ianya boleh digunapakai semula sebanyak 5 kali dengan kandungan metil ester lebih dari 90%. Tambahan pula, mangkin masing-masing menunjukkan toleransi terhadap air pada 1.75% dan 2.0 % dan asid lemak bebas pada 1.75% dengan kandungan metil ester lebih dari 80%..

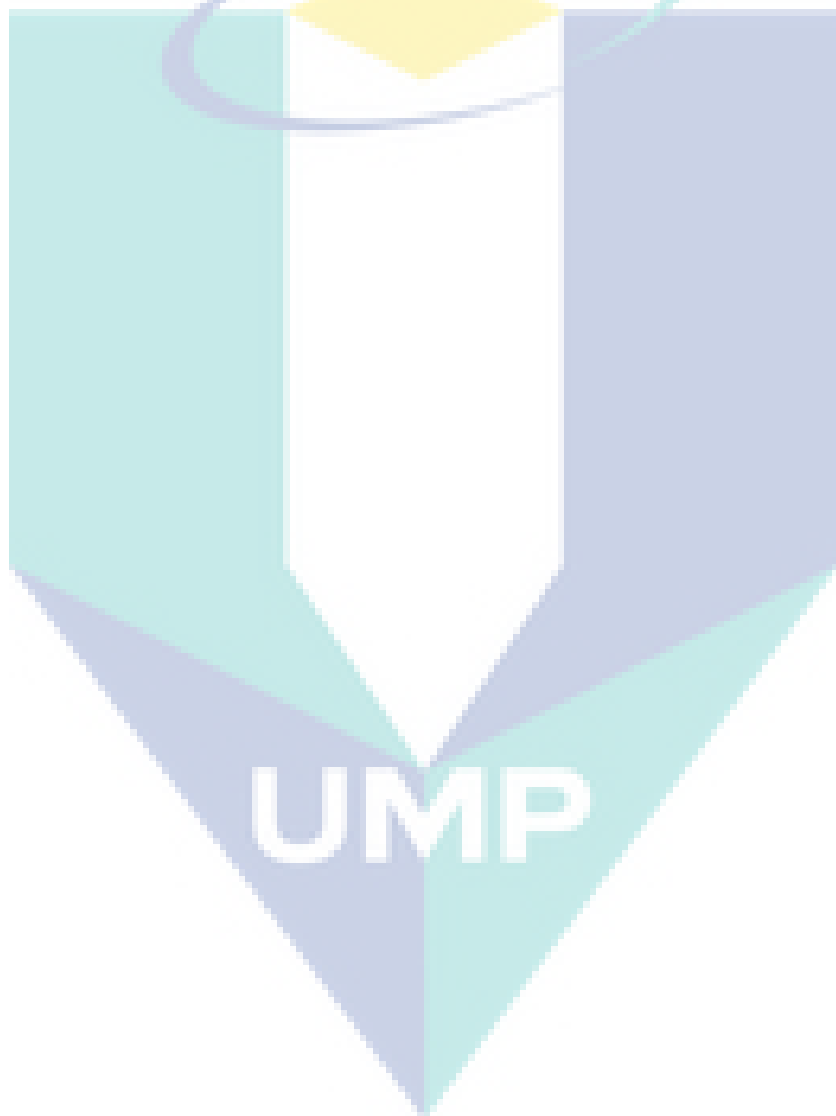
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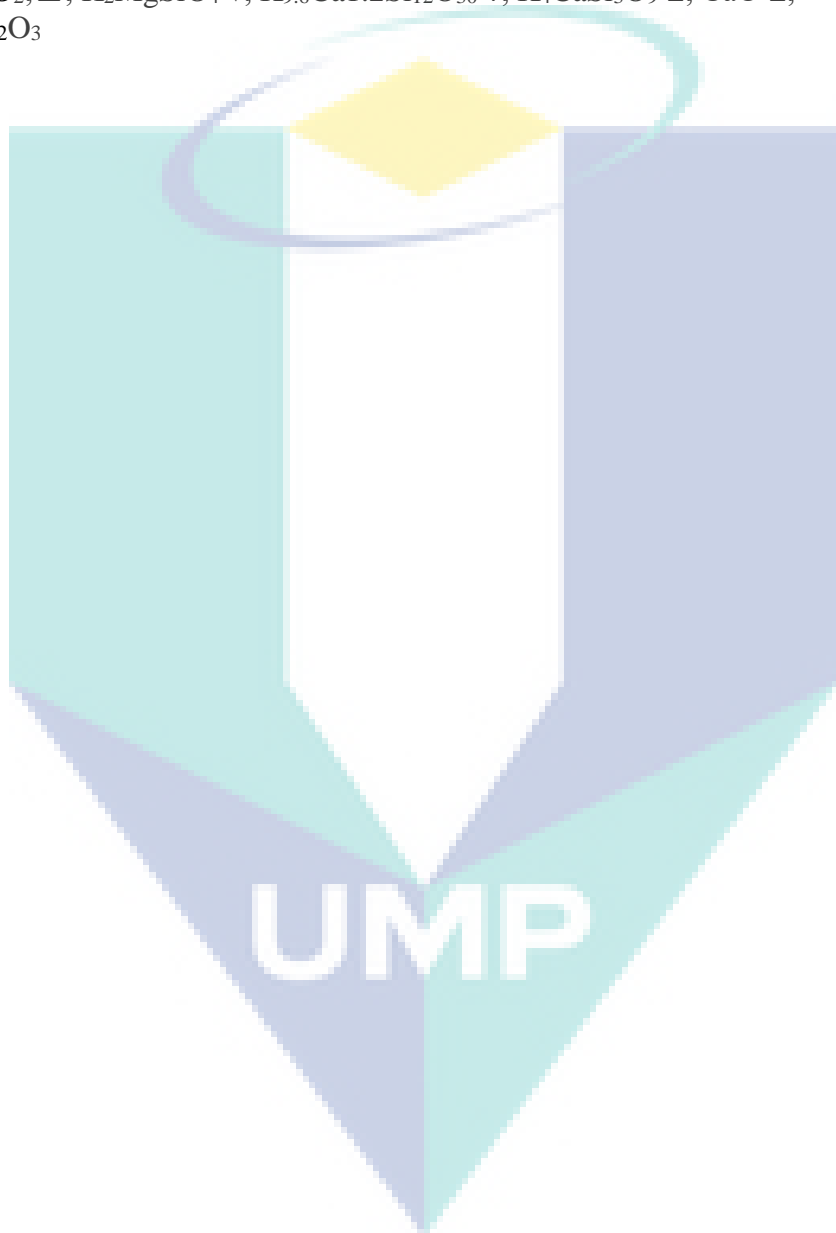
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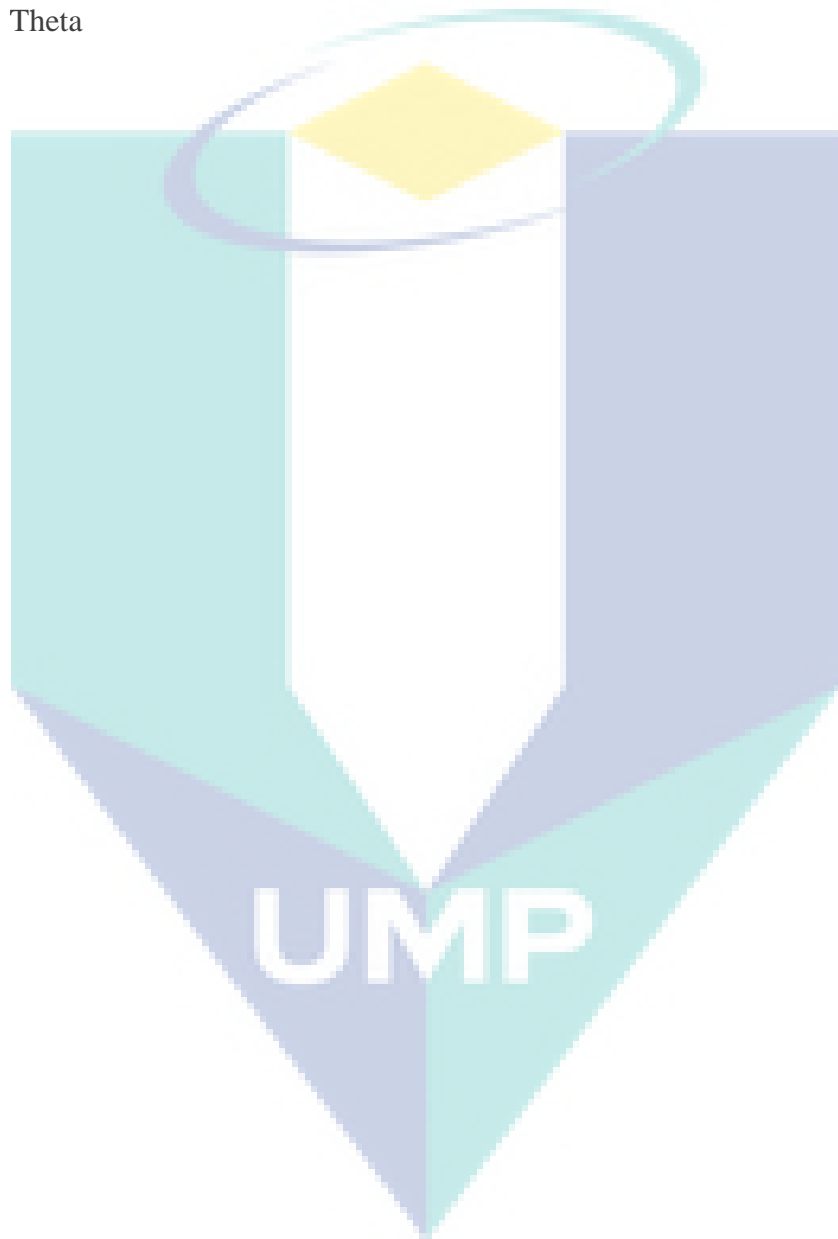
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LIST OF SYMBOLS

%	Percentage
°C	Degree celsius
θ	Theta



Chapter 1

Introduction

The disposal of SBC has become increasingly unacceptable due to the potential environmental hazards and the rising cost of disposal. This has prompted urgency in innovating practical and economical ways in utilizing SBC. Aziz and Shareef [6] utilize deoiled-SBC as an adsorbent of phenol in aqueous medium. Deoiled-SBC has mixed layer and high porosity, from that properties, loading of K^+ , Ca^{2+} and La^{3+} in the layer deoiled-SBC by impregnation and solid state need to be investigate. How the effects of the loading of single metal and combined metal on structure and properties of deoiled-SBC by measuring basicity, structure and surface analysis by TPD, Hammett indicator test XRD, BET, FTIR and FE-SEM. In addition the catalytic activities of compound in transesterification need to be evaluated. Furthermore, new catalyst from the waste of the very same transesterification reaction and capable to transesterify low-quality oils (and as an adsorbent too). As such, SBC acts as source for oil and as a catalyst. So far no study has been initiated on the use of metal loaded D-SBC (deoiled-spent bleaching clay) as a catalyst. Palm refineries having chances to reutilize their industrial waste both as oil source and a catalyst.

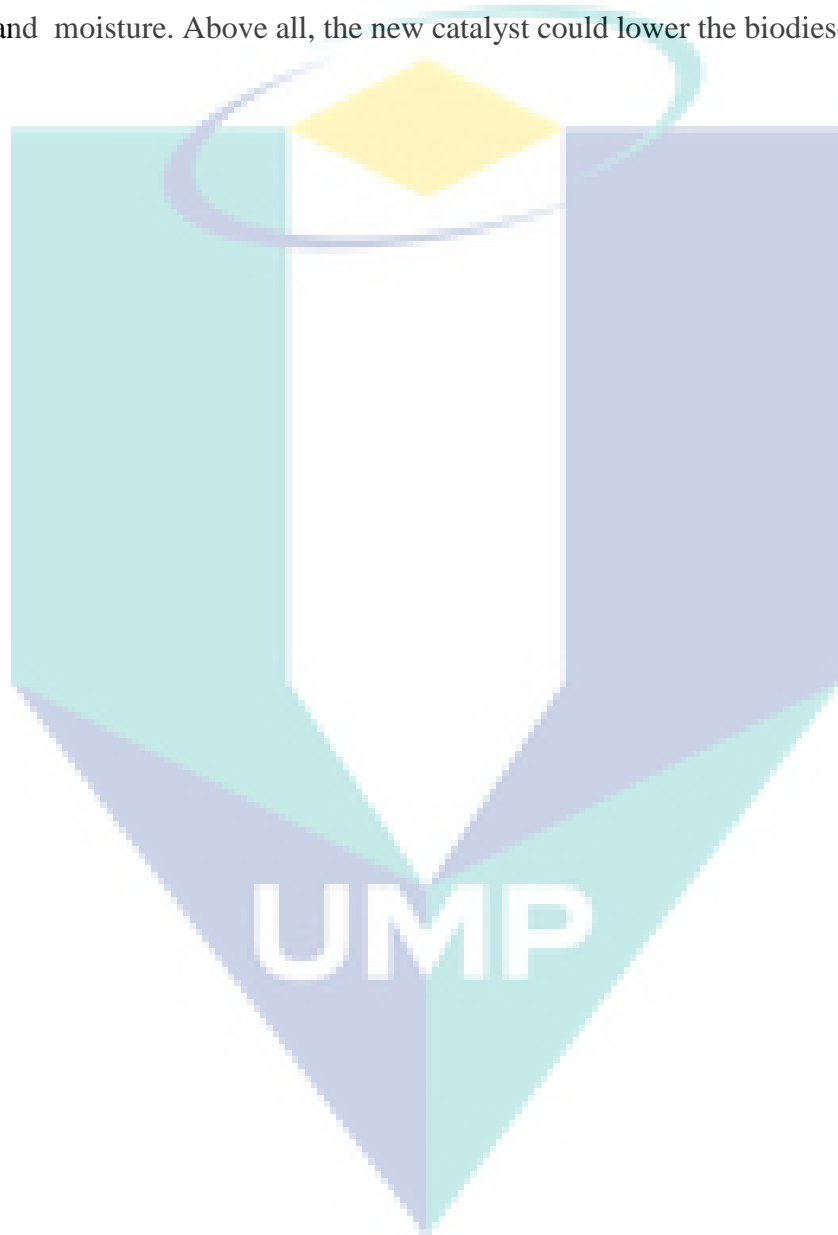
Chapter 2

Literature Review

Spent bleaching clay (SBC) is one of the major wastes from the edible oil industry. In Malaysia alone, with an annual production of about 18 million tonnes of crude palm oil (CPO), more than 100,000 tonnes of SBC is generated yearly [1,2]. The most common way of disposing of the oil laden SBC is by dumping into landfill. Using SBC as a feedstock in biodiesel production has been reported [2,3], but again, the deoiled-spent bleaching clay (D-SBC) is a waste without any appreciable use. Bleaching clay is mainly composed of smectite, an aluminosilicate mineral with variable net negative charge, which is balanced by Na, Ca, Mg and, or, H adsorbed externally on interlamellar surfaces. The native metal is very low in content and in unstructured pattern. When D-SBC is acid-activated, hydrogen ions attack the aluminosilicate layers via the interlayer region. This attack alters the structure, chemical composition and physical properties of the clay [4,5]. The hydrogen ion on interlayer could exchange by substitution of metal. As such, the metals presence can be designed in more structural manner and in desired amount. No one has reported the use of D-SBC as a catalyst.

In this work, a novel approach is proposed where the D-SBC will be used as a catalyst in the very same reaction of transesterification where SBC is used as a source of oil. Heterogeneous catalysts have the potential to address the disadvantage issues created by the conventional caustic homogeneous catalysts as they provide easier separation techniques, leave the product free of catalyst impurities and exclude the requirement for product neutralization and purification steps. Furthermore, the lesser consumption of heterogeneous catalysts with reusability could potentially lead to economical production costs of biodiesel. The optimization of catalyst preparation methods (wet impregnation and solid state) plays an important role in term of catalytic stability and the activity. The high surface area of the supports also allows a good dispersion of the metal oxide and thus increasing the catalytically active surface. Metal loading (Be, Mg, Ca and Ba ions) onto activated clay will catalyze the transesterification reaction

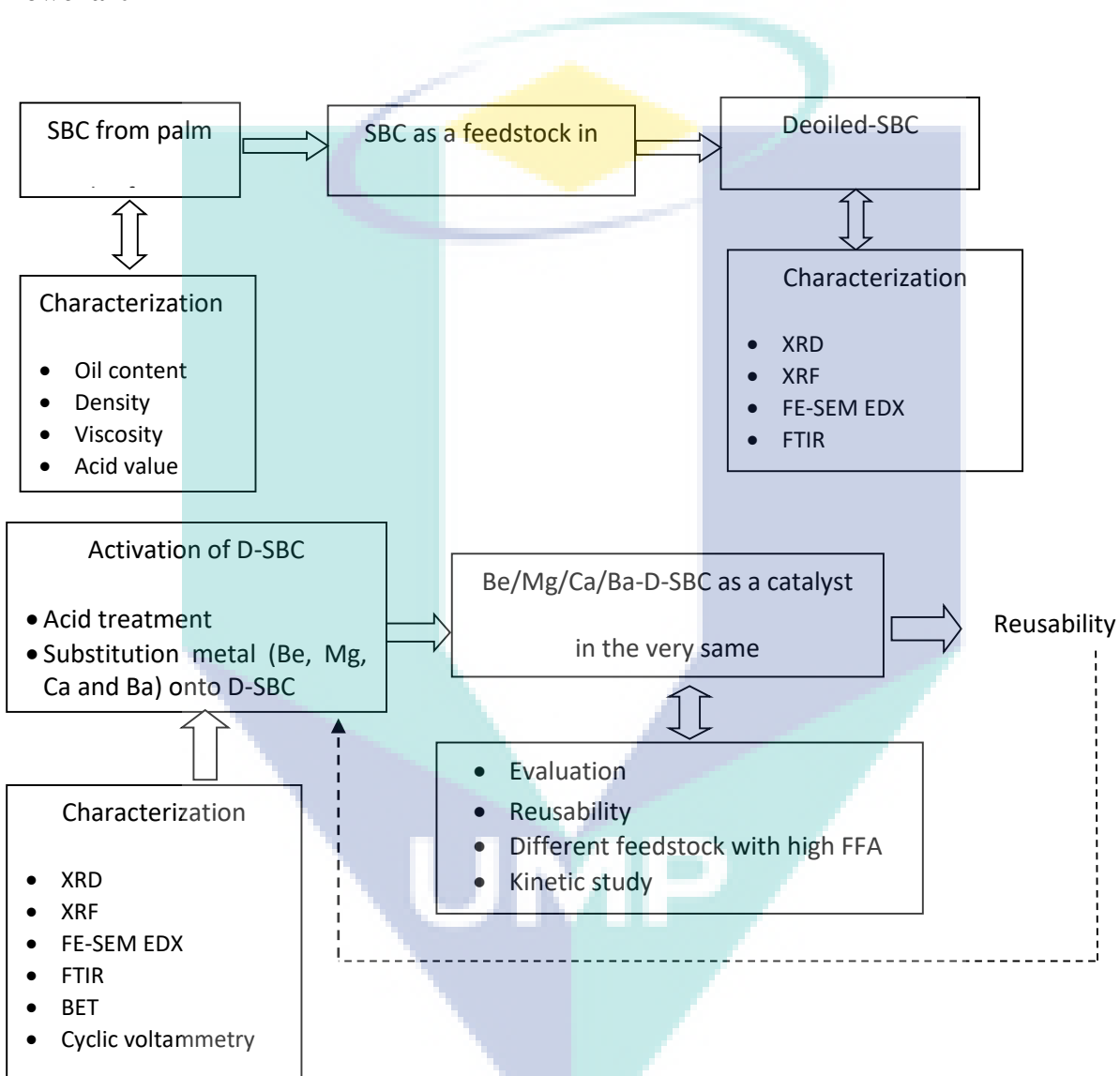
more promisingly. Research on the use of clays such as bentonite and zeolite as catalysts or catalyst supports has attracted attention in recent years [6–8]. However, there is no report available on the use of deoiled-spent bleaching clay as a catalyst support for transesterification, in spite of its industrial importance. Moreover, the new catalyst is capable in transesterifying low-cost oil which is high in FFA content and moisture. Above all, the new catalyst could lower the biodiesel production cost.



Chapter 3

Methodology

3.1 Flowchart



3.2 Description of Methodology

De-oiling of spent bleaching clay

The SBC is drying in an oven at 105 °C for 2.5 h. Subsequently, the dried SBC is ground and sieved to get a smaller particle size. The oil content is determined by extracting 2 g dried SBC with 20 g of co-solvents (PE and hexane in equal ratio). The above mixture is immersed in an ultrasound water bath (Bransonic at a working frequency of 42 kHz and the power supply of 235 W) at a temperature of 55 ± 2 °C for 30 min. The sonicated mixture is centrifuge at 1000 rpm for 5 min. The yellow-brown supernatant layer is transfer into a pre-weighed flask. The process is repeated two times and the accumulated supernatant solution.

Regeneration of deoiled- spent bleaching clay

The deoiled- SBC is treated with 20% H_2SO_4 at room temperature for 5 h before washing with distilled water until the pH of the filtrate is neutral, and then subject to heat treatment at 400°C for 10 h.

Activation by metals loading on deoiled-spent bleaching clay

Impregnation method: The typical procedure for the impregnation of the (40 wt.% K, Ca, and La) sample is involving the placement of 3 g of deoiled-SBC into a 250 ml flask held in an ultrasonic water bath. The K-functionalized D-SBC samples will be prepared at 10, 20, 30 and 40 wt.% KOH. The same procedure will be used for the preparation of D-SBC samples upon impregnation of 40% by weight of $\text{Ca}(\text{OH})_2$ and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in functionalized D-SBC.

D-SBC particles will be dried in a vacuum oven at 120 °C for 16 h. Upon drying, the D-SBC particles are calcined at 500 °C for 4 h.

Solid state method: To prepare K/Ca/La-DSBC using solid state method, first, KOH and DSBC is adding in the agate tank and then well mixed by ball-milling with same ratio that use in impregnation

method, which was performed in a planetary ball mill (ZKX-2B, Nanjing) under air atmosphere at a speed of 300 rpm for 4 h. The resulting mixture was calcined at 500 °C for 2.5 h in a muffle furnace in air, mesoporous K/Ca/La-DSBC can be obtained. The same procedure will be used for the preparation of CaO and La₂O₃. For comparison, combined K/Ca/La-DSBC is also prepared via the same process. The stability of catalyst is prepared with different temperature (300-800 °C).

Transesterification

The content of waste palm cooking oil (WPCO) to ME is done in a 50 ml 2-neck round bottom flask equipped with a reflux condenser and magnetic stirrer. The transesterification reaction between oil and methanol will carry 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 (6:1-20:1 wt.%), catalyst amount (1-8 wt.%), reaction duration (0.5-5.0 h), and reaction temperature (35-75 °C) on the reaction are investigated. After the transesterification, the reaction mixture is allowed to cool to room temperature. ME is isolated by centrifugation to further separate the layers (ME, glycerol and catalyst), and then the excessive amount of methanol and water will evaporate before the chromatographic analysis. The reactions are carried out three times in order to reflect the precision and errors of the results. The concentration of ME in the sample will be determined by following the European regulation procedure EN 14103. In this study, GC- MS (Agilent Technologies, 7890A GC-System) with capillary column DB-wax (length 30m x diameter 0.25mm x film thickness 0.25µm) using methyl heptadecanoate as an internal standard. Helium is used as the carrier gas with a linear velocity of 40 cm/s. The oven temperature is programmed at 190 °C, held for 2 min, then ramped at 10 °C per min until it reached 230 °C, and with a last hold time of 8 min. The sample volume of 0.6 µL injected into GC.

Chapter 4

Results & Discussion

4.1 XRD Analysis of the Catalysts

The XRD analysis was employed to observe the crystal structure of the catalyst, shown in Figure 4.1. The diffractograms of DSBC showed a minor amorphous structure; with silicon dioxide as a dominant structure and other silicates (Yang et al., 2008). XRD analysis is carried out for D-SBC and the metal impregnated catalyst (K, Ca, La) in order to demonstrate that D-SBC is a good support material for metals to produce catalyst for transesterification. In the XRD pattern of D-SBC show that it contains high amount of SiO₂ proved that it is suitable to become the support for catalyst. After impregnation of the K⁺, Ca²⁺ and La³⁺ species, the crystallinity of the catalyst increased. For D-SBC, the intense peak found at 21.014 ° and 26.838 °. SiO₂ appear at miller indices of (100) and (011) which are at 21.014° and 26.838 °. For K-DSBC, the intense peak found at 20.04 °, 26.73 °, 29.04° and 40.368 °. SiO₂ appear at miller indices of (20-2) which are at 21.01 °. As depicted in Figure 4.4, K₂MgSiO₄ can be seen as it shows at 20.04 °. On the other hand, K₄CaSi₃O₉ appears at miller indices (20-2) at 29.04 ° and K_{9.6}Ca_{1.2}Si₁₂O₃₀ is (-312) at 40.37 °. The calcined KDSBC contains K₂O (potassium oxide) because of the KOH molecules were transformed into K₂O. K₂O believed as the significant molecule which play an important role during transesterification (Kusuma et al., 2013). Next, Ca-DSBC and La-DSBC illustrates CaO and La₂O₃ peaks which give evidence to the metal impregnated onto DSBC. It is very likely that fine CaO and La₂O₃ particles are embedded in DSBC matrix, proposing that DSBC actually denotes the support for CaO and La₂O₃ as well as K₂O.

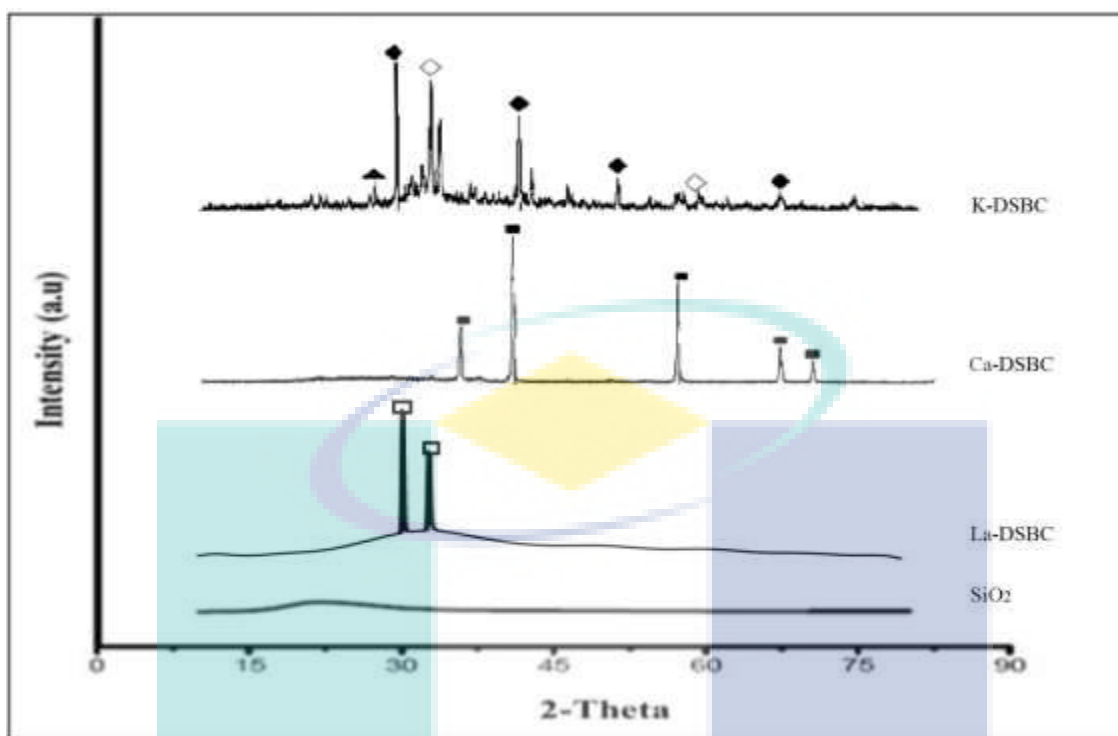


Figure 4.1: Powder XRD patterns of K-DSBC, Ca-DSBC, La-DSBC and SiO₂; ▲, K₂MgSiO₄ ♦, K_{9.6}Ca_{1.2}Si₁₂O₃₀ ◇, K₄CaSi₃O₉ ■, CaO □, La₂O₃

4.2 Basicity Analysis of the Catalysts using Hammett Indicators

The Hammett indicator test for all of the waste catalysts (K-DSBC, Ca-DSBC and La-DSBC) is provided in Table 4.2. All of the metal doped onto DSBC catalysts showed changes in both the colour of phenolphthalein ($H_{\text{c}} = 8.2$) from colourless to pink and the colour of 2,4-dinitroaniline ($H_{\text{c}} = 15$) from yellow to mauve. However, the colour of 4-nitroaniline ($H_{\text{c}} = 18.4$) remained unchanged. This means that the basic strength of this catalyst in the series of $15 < H_{\text{c}} < 18.4$. The calcination does not affect to the strength of the catalyst itself. On the other hand, different case for D-SBC was observed. It showed positive result to phenolphthalein and negative results to both 2,4-dinitroaniline and 4-nitroaniline. The basic strength of them, by the Hammett scale is between 8.2 and 15.0 ($8.2 < H_{\text{c}} < 15.0$) which is weak base.

Table 4.2: Basicity of catalyst towards Hammett indicators

Waste Catalysts	Basicity(mmol/g)		
	Phenolphthalein ^a H = 8.2	2,4 dinitroaniline ^b H = 15.0	4-nitroaniline ^c H = 18.4
D-SBC	√	X	X
K-DSBC	√	√	X
Ca-DSBC	√	√	X
La-DSBC	√	√	X

Colour change for indicator is ^acolourless to pink, ^byellow to mauve and ^cyellow to orange) √, colour changed and X, no colour changed

4.3 Catalyst Activity

In order to study the effect of catalyst activity from the three catalysts (K-DSBC, Ca-DSBC and La-DSBC), experiments using different catalysts were conducted under the optimal reaction conditions. The reaction time and catalyst amount have influence on catalytic activity of transesterification. From Table 4.3, it can be seen that the lower catalyst amount at 3 wt.% and reaction time of 1 h gave maximum catalytic activity of 0.55 mol/gcat.s⁻¹ using K-DSBC catalyst. While for both Ca-DSBC and La-DSBC with catalyst amount of 5 wt.% and reaction time 3 h, the catalytic activity were calculated as 0.11 mol/gcat.s⁻¹. This is in line with reports of Bond et al. (2006) where the kind of reaction by various types of solid catalysts is determined by the ability of surface to convert the reactants into product. In addition, the activity of the catalyst is defined as the rate of reactant(s) consumption, where the maximum rate will be achieved with combination effects of reactant and the catalyst.

Table 4.3: Catalytic performances of waste catalysts

Catalyst	ME content (%)	TOF (mol/g _{cat} .s ⁻¹)
K-DSBC	98.9 ± 0.3	0.55 ± 0.002
Ca-DSBC	95.6 ± 0.4	0.11 ± 0.0005
La-DSBC	93.1 ± 0.4	0.11 ± 0.0003

^a Reaction conditions: t = 1h, W_{cat} = 3%

^b Reaction conditions: t = 3h, W_{cat} = 5%

4.4 Physical Properties of Methyl Ester

Properties of biodiesel from K-DSBC, Ca-DSBC and La-DSBC using RBD-PO as a feedstock are tabulated in Table 4.4. It shows that the ester content of the final products was determined following EN 14103 standard. The density and viscosity of the fuels affect the start of injection, the injection pressure, and the fuel spray characteristic, so that they influence the engine performance, combustion and exhaust emissions. Many performance characteristics such as cetane number and high heating value (HHV) are related to the density. In addition, since the diesel fuel injection systems measure the fuel by volume, the fuel density will influence engine output power due to a different mass of fuel injected (Bahadur et al., 1995). Viscosity is also of among the important properties of methyl ester, as viscosity gives effect to the fuel atomization and engine deposits (Knothe, 2001). By transesterification process, the viscosity can be reduced drastically, so it could be suitable for diesel engine. The biodiesel has flash point greater than petroleum diesel, makes biodiesel as much safer substance than petroleum diesel. The cold point is the temperature, when crystals form in the fuel, the cold point biodiesel higher than petro diesel. The HHV is one of the important analyses in the production biodiesel, measured using bomb calorimeter. The cold point and HHV is among the physical important parameters in ignition of biodiesel. According to the Demirbas (2008), density of biodiesel has values between 848 kg/m^3 to 885 kg/m^3 . An increase in density up to 885 kg/m^3 for biodiesel will highly increase the viscosity. The viscosity values of ME decreases sharply after transesterification process (vegetables oils are between 57.2 and 64 cP). The viscosity value in biodiesel is due to the presence of hydroxyl groups to form hydrogen bonding in fatty acid molecule or sometimes ME associated with unreacted triglycerides in the fuel (Okullo et al., 2012). Due to the structural differences in the fatty acids constituent of catfish oil and SBC oil, the properties of both show different results. Palm oil is predominantly made of palmitic acid (C16:0), a saturated fatty acid that is associated with higher energy content than unsaturated acids (Okullo et al., 2012).

Table 4.4: Properties of the prepared biodiesel with different catalysts

Property	Method (Specification)	K-DSBC	Ca-DSBC	La-DSBC	Unit
Ester content	EN 14103 (96.5 Min.)	99.0 ± 0.4	988.8 ± 0.4	97.2 ± 0.3	% (m/m)
Density (15 °C)	EN ISO 3675 (860 – 900)	882	880	887	kg/m ³
Viscosity (25 °C)	EN ISO 3104 (3.5 – 5.0)	4.3	4.2	4.0	cP
Flash Point	ASTM D93 (>130 °C)	156	156	168	°C
Cold Point	ASTM D2500 (-)	10	8	8	°C
HHV	ASTM D240 (35 Min.)	38.0	38.6	39.2	MJ/kg
Sulfur content	D 5453 (0.05 Min.)	0.04	0.045	0.045	% (mass)

Reaction conditions K-DSBC: Catalyst amount, 3 wt.%; MeOH:oil molar ratio, 9:1 for 2 h. Reaction conditions Ca-DSBC and La-DSBC: Catalyst amount, 5 wt.%; MeOH:oil molar ratio, 9:1 for 2 h.



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Chapter 5

Conclusion & Recommendation

In this work, Be, Mg, Ca and Ba has been successfully loaded onto D-SBC as a catalyst in transesterification of palm olein. Optimized conditions found to be 12:1 methanol to oil molar ratio; 2h reaction time and 5 wt.% catalyst amount achieving 85.7% conversion. Utilization of DSBC as an eco-friendly and cheap solid support is a promising. Therefore, progress should be made on doping more other metals on D-SBC for transesterification of oil with methanol.



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