

Impregnation of K^+ over deoiled spent bleaching clay (SBC) as a catalyst in transesterification

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Abstract— World energy demand expected to increase as a result of blossoming urbanisation, better living standards and rising human population. Biodiesel becomes an important alternative energy as the price and demand of fossil fuel in the global market is increasing each day. It has become obvious that biodiesel can create a generous contribution to the future energy demands as it brings less pollution to environment if compared to fossil fuels. There are many different types of potential feedstock and catalyst for biodiesel production. Compared to edible oil and non-edible vegetable oils as a feedstock, natural waste is very much considered as a biodiesel feedstock because of the huge demand for edible oils as a food source. Moreover, the uses of natural waste oils as a feedstock and catalyst from wastes are more cost effective. Therefore, production of biodiesel from natural waste is the best way to overcome all the associated problems with edible oils. In this present study, waste cooking oil (WCO) and impregnation of K^+ over deoiled spent bleaching clay (SBC) as a catalyst (K^+ impregnated DSBC) were attempted. In this study, K^+ impregnated DSBC was obtained from impregnation of 60 % potassium hydroxide (KOH) into deoiled SBC, dried in oven at 100 °C for 16 hours and finally calcined on furnace at 500 °C for 4 hours. The prepared catalyst is characterized by several methods such as TGA, XRD, XRF, FESEM and FTIR. Result from transesterification showed that highest methyl esters (ME) content was at 91.8 % with 5 h reaction duration at 65 ± 2 °C. Optimization of reaction revealed that 12:1 methanol to oil ratio and catalyst amount of 7 wt.% as optimal reaction conditions. Furthermore, catalyst can be reused up to 5 times while maintaining ME conversion at 70 ± 0.2 %.

Keywords— *biodiesel; spent bleaching clay; impregnation; waste cooking oil; transesterification*

1. INTRODUCTION

The economic uses of fatty acid methyl esters (biodiesel) equally as a diesel alternate start in Europe in the late 1980s. Biodiesel become a basis of continual substitute to fossil fuels due to its renewable properties as fossil fuel is getting reduced day by day [Mutreja et al., 2014]. Biodiesel fuel (BDF) is produced from organic sources for example vegetables oils, animal fats, edible oils, non-edible oils, and waste/ used oils and from microorganisms [Boey et al., 2010].

The main problem regarding the use of vegetables oil and animal fats is the biological sources cannot be used directly in internal combustion engine due to two main reasons: low volatility and high viscosity [Carillo et al., 2010]. However, there

are some methods that could be executed to reduce viscosity and increase volatility. Those techniques are pyrolysis, micro-emulsification, transesterification and direct use and blending method. Among them, transesterification method is discovered as the best technique with minimum energy complications [Pryde, 1984]. Transesterification with oil and methanol is a typical way of producing methyl esters (biodiesel) from triglycerides by switching the alkoxyl group of an ester compound with alcohol [Soetaredjo et al., 2011].

Feedstock and catalyst are the major contributing factors in biodiesel production cost. Some examples for alternative feedstock are waste cooking oil (WCO), decanter cake (DC), spent bleaching clay (SBC), vegetable oil and animal fat. Zabeti et al. (2009) reported that about 4.1 kg of waste cooking oil (WCO) is produced per person in a year. Disposal of WCO is a major problem due to the possible pollution of the land resources and water and these indicate that waste cooking oil is one of the best options to be used for biodiesel production. However, these kinds of feedstock contain high moisture content and free fatty acids (FFAs). Heterogeneous catalysts could accept water and FFA much well than the homogeneous catalyst [Ho et al., 2012]. The study will be focusing on the transesterification of the waste cooking oil using potassium impregnated heterogeneous catalyst which is deoiled spent bleaching clay (SBC).

2. MATERIALS AND METHOD

WCO is collected from cafeteria KK1, Universiti Malaysia Pahang. SBC is collected from palm oil refinery at Felda Vegetable Oil Product Sdn. Bhd., Gebeng. FAME standard (methyl heptadecanoate) is obtained from Sigma-Aldrich. Potassium hydroxide, sulphuric acid (to wash the catalyst), methanol, and n-hexane, were obtained from Merck. Phenolphthalein ($H_{\text{pH}} = 8.2$), 2, 4-dinitroaniline ($H_{\text{pH}} = 15.0$), 4-nitroaniline ($H_{\text{pH}} = 18.4$) (as Hammett indicators), methyl esters standards, palmitic and oleic acid are purchased from Sigma (Deisenhofen, Germany) are chromatographically pure. All the chemicals mentioned above were analytical reagent grade. Thin Layer Chromatography (TLC) aluminium sheets are purchased from Merck (Darmstadt, Germany).

Waste cooking oil was kept for about 2-3 days to equilibrate the impurities. Filtration is being applied to eliminate food deposits and solid precipitous in the oil. The filtered oil was added with warm water and shake vigorously. Then the mixture is poured into centrifuge tube and centrifuged. Then water layer is removed together with other particles. Oil is centrifuged many times until no water layer shown. Then oil is heated until all water is evaporated. WCO is furthered for transesterification process. About 50 mL of oil is kept for characterization. [Hindryawati et al., 2014]. Oil characterization involves determining its acid value, density, viscosity, moisture content, saponification value and iodine value. Viscosity, density, and moisture content tests are conducted at Central Laboratory, Universiti Malaysia Pahang (UMP), meanwhile saponification value, acid value and iodine executed in Faculty of Sciences and Technology laboratory.

Spent bleaching clay is being washed with 20% sulphuric acid to remove any impurities and organic matter after the extraction. 25 g of de-oiled spent bleaching clay (D-SBC) was added into 250 ml beaker containing 100 ml distilled water. It then proceeds with adding 60% KOH (loading based on D-SBC weight) by wet impregnation method. The mixture was held in an ultrasonic water bath for 3 h (Bransonic at a working frequency of 42 kHz with 235 W power supply). The K-functionalized D-SBC (K-DSBC) sample was prepared at 60 wt.% KOH. It then was dried in oven at 120 °C for 16 h. After drying, the K-DSBC particles were calcined at 500 °C for 4 h.

Methyl esters peaks from GC-FID were identified easily by comparing with standards and the following Formula 1 is used to quantify the conversion.

$$\text{Conversion (\%)} = \frac{A_{\text{Total}} - A_{\text{ISTD}}}{A_{\text{ISTD}}} \times \frac{C_{\text{ISTD}} - V_{\text{ISTD}}}{M_{\text{Sample}}} \times 100\% \quad (1)$$

Where

- A_{total} = Total area of methyl ester peak from $C_{14:0}$ to $C_{18:3}$
- A_{ISTD} = Area of internal standard
- C_{ISTD} = Concentration of internal standard in mg/ml
- V_{ISTD} = Volume of internal standard in ml
- M_{sample} = Mass of sample in mg

3. RESULTS AND DISCUSSION

The data from XRF in Table 1 shows that the catalyst is suitable for transesterification reaction since it contain high amount of potassium which can act as base catalyst. Meanwhile silica, the main active compound in DSBC act as the support for the catalyst.

Table 1: XRF data of K^+ impregnated SBC

Parameter	Result (%)
Potassium Oxide (K ₂ O)	40.40
Silicon dioxide (SiO ₂)	25.31
Aluminium Oxide (Al ₂ O ₃)	3.80
Iron oxide (Fe ₂ O ₃)	2.15
Calcium oxide (CaO)	1.66

From the results that have obtained, the XRD patterns for deoiled SBC shows the intense diffraction peaks of the element and indicate that it is in crystalline form. It contains silica oxide (SiO₂) and it can react easily in the formation of new catalyst. As the KOH loading ratio increased, the crystallinity of the catalyst increased. For the calcined, K⁺ impregnated over deoiled SBC, the XRD patterns show more crystalline form than deoiled SBC. Potassium, phosphorus, gamma-Fe, calcium and cyclo-18-sulphur are the elements that have been found in calcined, K⁺ impregnated over deoiled SBC. Since deoiled SBC contains silicate, it can act as support material in the formation of basic catalyst. The intense diffraction peak for deoiled SBC can be found at Miller index of (2,2,-1) which is 29.14°. Meanwhile for calcined, K⁺ impregnated over deoiled SBC, the intense diffraction peaks are at 8.51°, 20.00°, 25.53°, 26.72°, 35.05°, 42.63°, 50.51°, 54.96°, 61.82° and 68.56°.

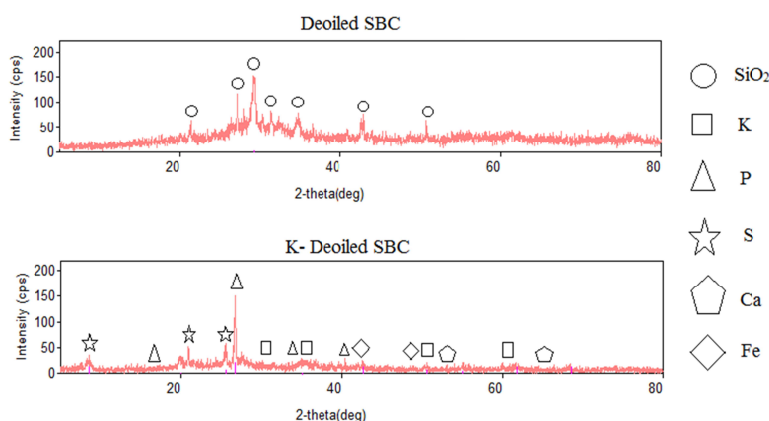


Figure 1: Diffractogram of deoiled SBC and calcined, K⁺ impregnated over deoiled SBC catalyst

FTIR is conducted to determine the bonding that exists in the compound. The FTIR spectrum of the deoiled SBC reveals the presence of functional groups such as Al(Mg)–O–H stretching (3443.92 cm⁻¹), H–O–H bending (1645.76 cm⁻¹), Si–O–Si stretching (1046.95 cm⁻¹), Si–O stretching (797.58 cm⁻¹), C–O–H bending (674.76 cm⁻¹) and C–O–C bend (470.98 cm⁻¹). FTIR analysis showed that the addition of KOH affected the structure of the deoiled SBC network. The intensity of the Al(Mg)–O–H stretching group increased with an increased KOH loading.

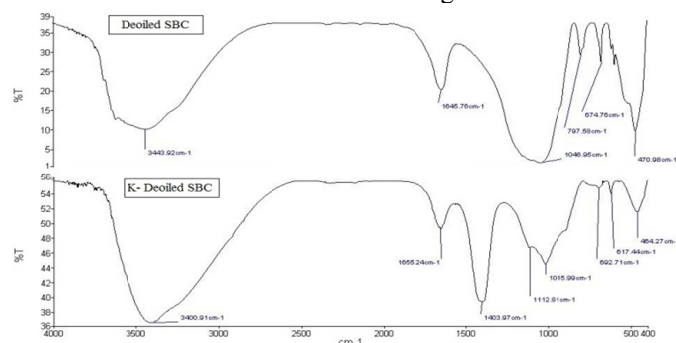


Figure 2: FTIR spectra for deoiled SBC and calcined, K⁺ impregnated over deoiled SBC

Electron image EDS spectra and atomic concentration of various elements in K⁺ impregnated over deoiled SBC catalyst. The deoiled SBC catalyst is impregnated by KOH is shown by the surface area attached by round and oval shape. Electron image is used to capture one of the molecules in the catalyst and identify elements present in the molecule. FESEM-EDS spectra and atomic concentration of various elements result from electron image and its show the impregnation of potassium ion in the catalyst. There is C-K, O-K, Mg-K, Al-K, Si-K and K-K element in catalyst. This explained that there is impregnation of K⁺ in each element of deoiled SBC.

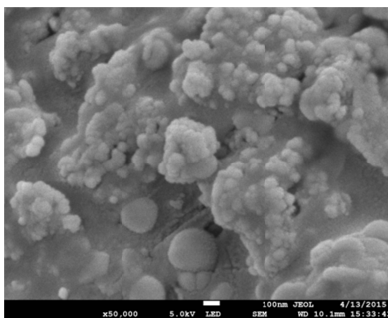


Figure 3: FESEM image of K^+ impregnated over deoiled SBC catalyst

TGA was conducted on calcined, K^+ impregnated over deoiled SBC catalyst. The TGA curve shows three separate degradation stages. The first stage was observed in the temperature range of 40 to 130 °C. The weight loss of 3.0 % (99.-96.5) occurs at this stage. The loss of weight consisted of the loss of water and small molecular substance. The water was present either because of the quantity added during the impregnation of the catalyst or as a result of condensation [Dias et al., 2012]. Aldehydes and hydrocarbons constituted the major part of the small molecular substances.

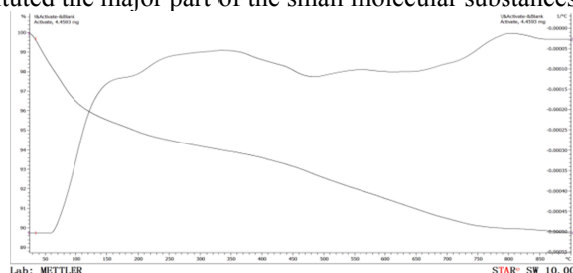


Figure 4: Thermogram of calcined, K^+ impregnated over deoiled SBC catalyst

Catalyst was varied from 3-12wt.%. Under reaction condition of methanol to oil molar ratio 12:1, 5h and 65 ± 2 °C, 7 wt.% of catalyst is the most efficient which producing 91.8% methyl ester. From that, we could conclude that the optimum time reaction for the catalyst is 5 h. The conversion drops after 5 h might be due to reverse reaction is taken place and difficulties in separation of final product [Taufiq-Yap et al., 2014].

The methanol to oil molar ratio was varied from 6-18:1 to find the optimum condition for biodiesel conversion. Methyl ester conversion increased from 6:1 until 12:1 but then decreased until 18:1. This shows the low amount of methanol did not enough to enhance the reaction while excessive amount of methanol proves to disturb the reaction [Rashid and Anwar, 2008]. ME conversion is poor at low methanol to oil molar ratio. It is suggested by reduction of collision frequency of the reactant with catalyst that inhibits the reaction rate. Variation of methanol to oil molar ratio 12:1 gives the highest ME conversion. Methyl ester conversion dropped after 12:1 due to excess methanol which negative effect on biodiesel yield. Higher amount of methanol will cause difficult separation of ME and glycerol thus difficulting the separation process.

The cost of catalyst influences biodiesel production cost. In this part, reusability study of the catalyst in transesterification is investigated. In order to test the catalyst, transesterification was carried out by repeated batch experiments under optimized conditions (reaction temperature of 65 °C, methanol to oil molar ratio of 12:1, catalyst content of 7 wt.% and reaction time of 5 h). Without calcination, the catalyst was reused after been washed by methanol and n-hexane in order to remove the glycerol and cleanse the residual oils. It then dried at 130 °C for 4 h. The reusability study shows that this catalyst can be used up to 5 cycles and can maintain its activity at considerable ME content (70 ± 0.2 %). In order to assess the leachability of the catalyst, the catalyst was stirred with methanol for 5 h without SBC oil. Next, the treated methanol and the reacted catalyst were separated. Without catalyst, the treated methanol was subjected to transesterification. Next we found that for the reaction with treated methanol without catalyst, a low ME content was recorded. Leaching was checked with ICP-MS found out that there is 3240 ppm potassium leaching. In the case of alkali metal supported by deoiled-spent bleaching clay, the solubility of metal could be influenced from the type of support and the atomic size of alkali metal. The type of support affects the amount of leaching of the active species to the methanol.

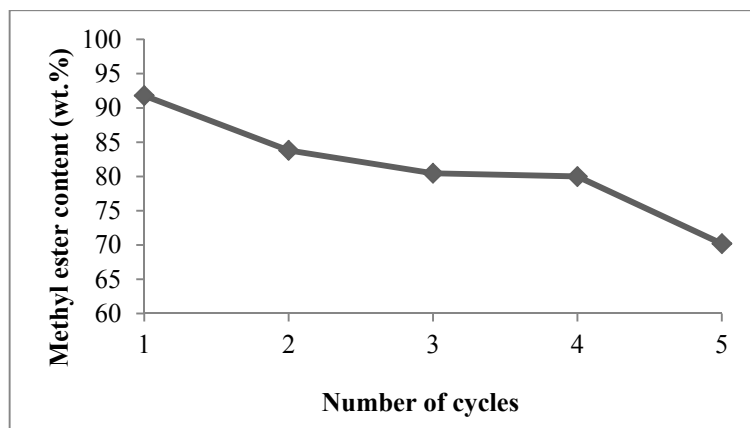


Figure 5: Cycles vs Methyl ester content (wt.%). Reaction conditions: 5 h, 7 wt. % catalyst amount and 12:1 methanol to oil ratio (wt/wt)

4. CONCLUSION

The catalyst show 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 91.8% methyl ester. Methyl ester was then analyzed using gas chromatography flame ionization detector (GC-FID). Therefore, magnetic composite catalyst is able to reuse 5 times and maintaining its activity at considerable ME content (70 ± 0.2 %).

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