



UTILIZATION OF DE-OILED SPENT BLEACHING CLAY AS A CATALYST FOR TRANSESTERIFICATION OF PALM OLEIN

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ABSTRACT

Biodiesel fuel is produced catalytically by transesterification reaction where catches the researcher attention nowadays as it is a promising alternative diesel fuel. Edible oil industries produce spent bleaching clay (SBC) as their major wastes. In this work, an environmental friendly transesterification reaction using de-oiled spent bleaching clay (D-SBC) loaded with KOH is being developed. The catalyst loaded with 40% KOH on D-SBC using wet impregnation method followed by calcination at 600°C for 4 hours was seems to give highest basicity and the best catalytic activity for transesterification. The catalyst was undergoing characterization by means of FTIR, TGA, FE-SEM and Hammett indicator test. The effect of reaction parameters was then studied such as methanol to oil molar ratio, reaction time, and catalyst amount. The reaction conversion of 85.7% was achieved under the optimum condition. Utilization of D-SBC 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.

Keywords: supported catalyst, biodiesel, waste cooking oil, transesterification, spent bleaching clay.

1. INTRODUCTION

The awareness of fossil oil depletion, fluctuating oil price, and environmental concerns has intensified the search for an alternate fuel [1]. Fuel depletion and emission is the main issue to cater this energy needs [2]. Biodiesel fuel is produced catalytically by transesterification reaction where catches the researcher attention nowadays as it is a promising alternative diesel fuel [3]. Edible oil industries produce spent bleaching clay (SBC) as their major wastes [4]. Biodiesel is prepared via a catalytic reaction between triglycerides and alcohol [5]. Glycerol is the by-product of the reaction [6]. The reaction involves the breakage of the glycerol structure and exchanges of alkyl groups between the alcohol and ester part of the triglyceride molecule; as such, the reaction is known as transesterification [7]. Among the three major routes, transesterification seems to be the best compared to heating and micro emulsions for reducing the viscosity as well as minimizing engine complications [8]. Other than the transesterification pathway, esterification of free fatty acids (FFAs) with alcohols in the presence of acid catalysts also produces methyl esters or biodiesel [9].

One of the main reasons for the conceptualization of biodiesel is the environmental pollution, specifically CO₂ emission. Concerning the CO₂ emission, in 2005 the EU introduced an innovative cost-effective scheme termed the 'Emission Trading Scheme' (ETS), a scheme that Australia, New Zealand and the United States are keen to adopt in their long-term plan for dealing with greenhouse gases [10]. Over the years, extensive research have been carried out in transesterifying various type of oils such as palm oil, cottonseed oil, soybean oil, tobacco seed oil and tea seed oil using basic catalysts into biodiesel [11].

Bleaching clay is used in palm oil refinery to remove coloring matters, soap, gums, metals (iron, nickel), oxidized compounds, and polymers [12]. Reports indicated that bleaching clay retains 20-40% of oil and

importantly, the adsorbed oil represents the major part of bleaching cost. In Malaysia itself, with CPO production of 17.7 million tons in 2008, annually 177 000 tones of SBC is generated, at 1% clay dosage, which translates to nearly 50 000 tones 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 [13]. 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 feedstock's 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. In short, utilizing SBC for biodiesel production has many merits [14].

In this work, an environmental friendly transesterification reaction using de-oiled spent bleaching clay (D-SBC) loaded with KOH is being developed.

2. EXPERIMENTAL SET-UP

The reaction performed in a 50 ml 2-neck round bottom flask equipped with a reflux condenser and magnetic stirrer. The transesterification reaction between oil 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 (6:1-15:1 wt. %), catalyst amount (2-6 wt.%) and reaction duration (0.5-4.0 h) on the reaction were investigated. After the transesterification, the reaction mixture was allowed to cool to room temperature. ME was isolated by centrifugation to further separate the layers (ME, glycerol and catalyst), and then the excessive amount of methanol and water was evaporated before the chromatographic



analysis. The reaction was carried out three times in order to reflect the precision and errors of the results.

The impregnation of the 40 wt.% K 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 sample is prepared at 40 wt.% KOH. The 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.

The catalyst was examined by thermo gravimetric analysis (TGA) using Mettler Toledo TGA instrument, from 25 to 900 °C with 10 °C heating rate. A FTIR (PerkinElmer Spectrum 100) spectrophotometer was used to characterize the chemical structure of alkali metal silicate at 400-4000 cm⁻¹ range. The size and morphology of catalyst was observed by FE-SEM (JSM-7800F). The base strengths of the catalyst (H₋) were determined by using Hammett indicators. The following Hammett indicators were used: phenolphthalein (H₋ = 8.2), 2,4-dinitroaniline (H₋ = 15.0) and 4 nitroaniline (H₋ = 18.4). About 25 mg of catalyst was shaken with 5.0 mL of a solution of Hammett indicator diluted with methanol, and left to equilibrate for 2 h. After the equilibration, the colour change of the solution was noted.

The concentration of ME in the sample was 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 30 × diameter 0.25 mm × film thickness 0.25 μm) using methyl heptadecanoate as an internal standard. Helium was used as a carrier gas with a linear velocity of 40 cm/s. 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. The peaks of ME were identified by comparing them with their respective ME standards. Methyl ester peaks were identified easily by comparing with standards and the following Eq. (1) is used to quantify the conversion.

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

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. RESULT AND DISCUSSIONS

The catalyst loaded with 40% KOH on D-SBC using wet impregnation method followed by calcination at 600°C for 4 hours seems to give highest basicity and the best catalytic activity for transesterification. The catalyst was undergoing characterization by means of FTIR, TGA, FE-SEM and Hammett indicator test. FESEM image of the catalyst is clearly shown in Figure-1.

Potassium species could be found distributed on the surface of the support, which contributes to basicity of the catalyst. This structure also indicates that there is possible increase in contact between the catalyst and the substrates, which will lead in better efficiency of transesterification because the granules made up of smaller granules and porous netlike structure.

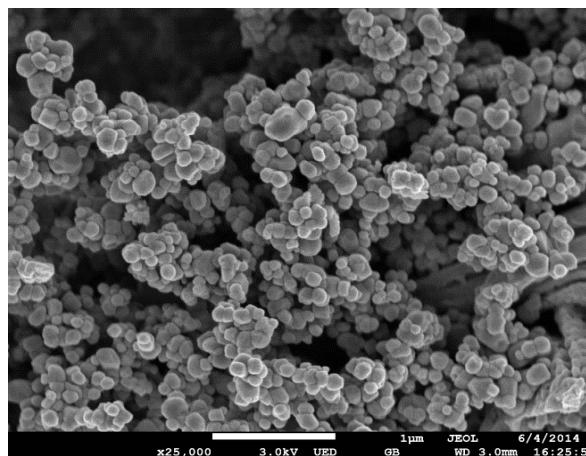


Figure-1. FESEM image of the catalyst.

The catalyst could change the color from colorless to pink (phenolphthalein) and from yellow to mauve (2,4-dinitroaniline) but failed to change the color of 4-nitroaniline. The basic strength is in the range of $15 < H_{-} < 18.4$. On the other hand, D-SBC has failed to change the color of all Hammett indicators. Therefore, it does not have basic properties and suitable to be used as a support material. The FTIR spectra of the catalyst together with potassium hydroxide and D-SBC are shown in Figure-2. The typical one, with the broadband at about 3410–3470 cm⁻¹ is due to the stretching vibration of the O–H bond from the silanol groups (Si–OH) and is due to the adsorbed water molecules on the silica surface, the band at 1654 cm⁻¹ is due to bending H–OH bond of adsorbed water molecules. The sharp peaks 1020–1100 cm⁻¹ are Si–O–Si bending. The bands at 786 and 973 cm⁻¹ are attributed to symmetric O–Si–O stretching and Si–O bending, respectively. The characteristic absorption peaks at 503–687 cm⁻¹ are attributed to the vibration of the K⁺–O bond structure, and the characteristic absorption band from deformation of Na+OH become Si–O–Na⁺ are shown at 865 and bands at 1440 cm⁻¹ is attributed to Si–O–Si stretching. Summarizing the FTIR results, it can be concluded that the potassium on D-SBC was successfully bound.

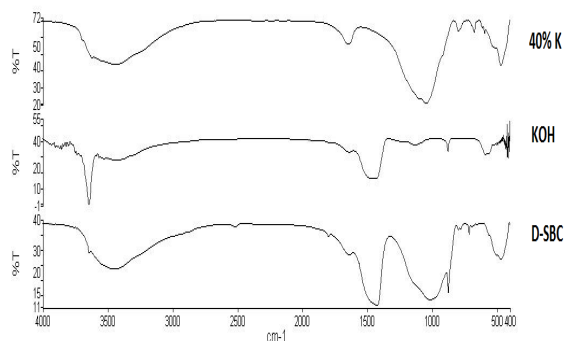


Figure-2. FTIR spectra for the catalyst.

The TGA curve is shown in Figure-3. In the first one, ranging from 50 to 175 °C, weight loss (4.25%) was attributed by the release of physically bound water on the surface of catalyst particles. The second region, the weight loss (4.66%) at temperature around 180–380 °C is attributed to the removal of organic compound from the D-SBC and the decomposition of potassium hydroxide. The third endothermic region ranging from 650 to 850 °C has a weight loss of 8.81%. The weight loss was attributed to water loss from the condensation of adjacent silanol group to form siloxane and silicate bond.

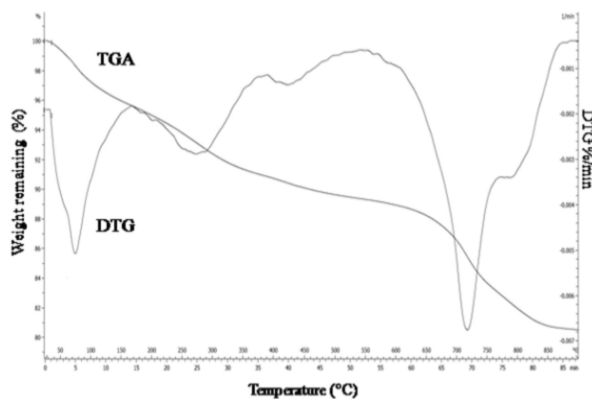


Figure-3. DTG/TGA of D-SBC with potassium.

The catalyst loaded with 40% KOH on D-SBC using wet impregnation method was studied for the transesterification of olein oil with methanol and the results are shown in Figure-4. The highest methyl ester conversion is achieved under 5% catalyst amount, 12:1 methanol to oil molar ratio and 2 hour reaction duration with temperature 65 ± 2 °C. Under this optimal condition, methyl ester conversion is 85.7%. The GC chromatogram in Figure-5 depicts the components of fatty acids, mainly consists of oleic acid (45.89%), followed by palmitic acid (39.57%), myristic acid (2.81%), lauric acid (0.98%) and others (10.75%).

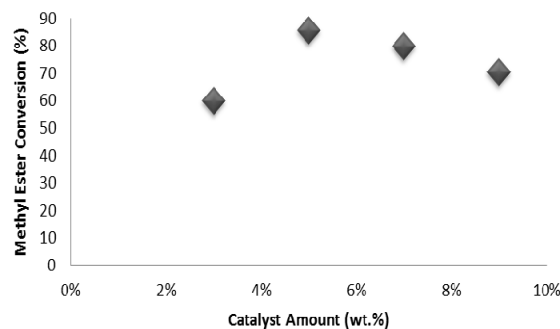


Figure-4. Methyl ester conversion under 2 hour reaction time, 12:1 methanol to oil molar ratio and temperature 65 ± 2 °C.

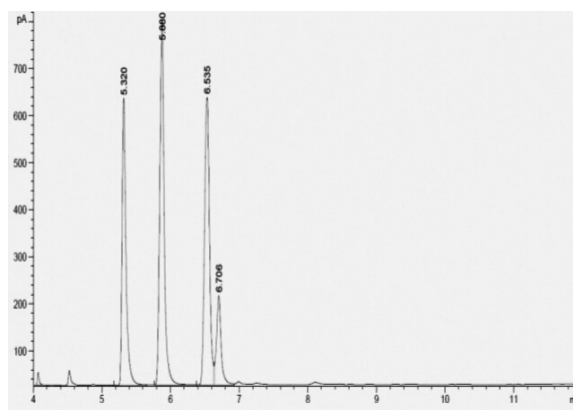


Figure-5. GC-FID chromatogram.

4. CONCLUSIONS

In this paper, KOH 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 D-SBC 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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REFERENCES

- [1] I. Nurfitri, G.P. Maniam, N. Hindryawati, M.M. Yusoff, S. Ganesan. 2013. Potential of feedstock and catalysts from waste in biodiesel preparation: a review. *Energy Conversion Management*. 74: 395-402.



- [2] M.M. Noor, A.P. Wandel, T. Yusaf. 2014. Effect of air-fuel ratio on temperature distribution and pollutants for biogas mild combustion. *International Journal of Automotive and Mechanical Engineering*. 10: 1980-1992.
- [3] W. Xie, D. Yang. 2012. Transesterification of soybean oil over WO_3 supported on $AlPO_4$ as a solid acid catalyst. *Bioresource Technology*. 119: 60-65.
- [4] A. Islam, Y.H. Taufiq-Yap, C.M. Chu, P. Ravindra, E.S. Chan. 2013. Transesterification of palm oil using KF and $NaNO_3$ catalysts supported on spherical milimetric $\gamma-Al_2O_3$. *Renewable Energy*. 59: 23-29.
- [5] M.V. Nagarhalli, V.M. Nandedkar, K.C. Mohite. 2010. Emission and performance characteristics of karanja biodiesel and its blends in a c.i. engine and its economics. *ARPN Journal of Engineering and Applied Science*. 5(2): 53-56.
- [6] A.C. Alba-Rubio, J. Santamaria-Gonzalez, J.M. Merida-Robles, R. Moreno-Tost, D. Martin Alonso, A. Jimenez-Lopez, P. Maireles-Torres. 2010. Heterogeneous transesterification process by using CaO supported on zinc oxide as basic catalysts. *Catalysis Today*. 149: 281-287.
- [7] M. Feyzi, G. Khajavi. 2014. Investigation of biodiesel production using modified strontium nanocatalysts supported on the ZSM-5 zeolite. *Industrial Crops and Products*. 58: 298-304.
- [8] P.L. Boey, S. Ganesan, S.X. Lim, G.P. Maniam, M. Khairuddean. 2011. Utilization of BA (boiler ash) as catalyst for transesterification of palm olein. *Energy*. 36: 5791-5796.
- [9] W. Xie, T. Wang. 2013. Biodiesel production from soybean oil transesterification using tin oxide-supported WO_3 catalysts. *Fuel Processing Technology*. 109:150-155.
- [10] N. Hindryawati, G.P. Maniam, M.R. Karim, K.F. Chong. 2014. Transesterification of used cooking oil over alkali metal (Li, Na, K) supported rice husk silica as potential solid base catalyst. *Engineering Science and Technology, an International Journal*. 17: 95-103.
- [11] G.P. Maniam, N. Hindryawati, I. Nurfitri, R. Jose, M.H.A. Rahim, F.A. Dahalan, M.M. Yusoff. 2013. Decanter cake as a feedstock for biodiesel production: A first report. *Energy Conversion and Management*. 76: 527-532.
- [12] N. Narkhede, V. Brahmkhatri, A. Patel. 2014. Efficient synthesis of biodiesel from waste cooking oil using solid acid catalyst comprising 12-tungstosilicic acid and SBA-15. *Fuel*. 135: 253-261.
- [13] P.L. Boey, S. Ganesan, G.P. Maniam, D.M.H. Ali. 2011. Ultrasound aided in situ transesterification of crude palm oil adsorbed on spent bleaching clay. *Energy Conversion and Management*. 5(5): 2081-2084.
- [14] C.S. Raj, S. Sendilvelan. 2010. Effect of oxygenated hydrocarbon additives on exhaust emissions of a diesel engine. *International Journal of Automotive and Mechanical Engineering*. 2: 144-156.