Free Fatty Acid Removal on Sludge of Palm Oil using Heterogeneous Solid Catalyst Derived from Palm Empty Fruit Bunch

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Abstract- This research investigated the activity of catalysts from biomass waste derived from Palm Empty Fruit Bunch (PEFB). An important factor for assessing the feasibility of biodiesel production is related to its economic evaluation. The sludge of Palm Oil (SPO) is generated from palm oil processing industry. SPO was potential as biodiesel feedstock due to its low price. The investigation of free fatty acid esterification reactions on SPO with methanol was conducted in this research. A new strategy for preparing a heterogeneous solid catalyst from biomass wastes has been developed. The investigation was carried out by varying several parameters, i.e.: the molar ratio of methanol to SPO catalyst to oil (8:1 - 14:1), the amounts of catalyst (0.5 - 5 wt. % SPO), and the reaction temperatures (40 - 60 °C). It is concluded that the optimum conditions of esterification reactions were acquired at molar ratio of methanol to SPO catalyst to oil 14:1, the amounts of catalyst 5 wt. % of SPO, and the reaction temperature of 60 °C.

Keywords Biodiesel, sludge of palm oil, palm empty fruit bunch, biomass waste, esterification, free fatty acid

1. Introduction

The fossil fuel combustion processes emit CO_2 emission which is responsible for climate problem. Many attempts have been conducted to find the renewable energy source for achieving friendly environment [1]. In this regard, biodiesel was considered as a potential candidate for sustainable energy source. Biodiesel was defined as monoalkyl fatty acid ester which can be possibly extracted from animal fat and vegetable oil. It has many benefits compared to fossil fuel such as non-toxic, using renewable feedstock and reduces sulfur compound on exhaust gas. Palm oil [2, 3], palm fatty acid distillate [4], sunflower [5], peanut [6], corn [7], soybean [8], and rapeseed [9] is commonly used as biodiesel feedstock. To produce biodiesel, vegetable or edible oils [3], as well as waste animal fats [10], were reacted with methanol by applying base catalyst. In addition, biodiesel can be obtained through esterification of raw materials with high free fatty acid. The acid catalysts were introduced when esterification reaction was done. The high cost of feedstock was the main constraint associated with biodiesel production. In addition, the edible oil as the biodiesel feedstock competes with the food supply. The production cost of biodiesel can be suppressed by reducing feedstock cost. Some types of feedstock including waste cooking oil [11], non-edible oil [12] and by-products of palm oil industry [13, 14] are receiving more interest due to the economic reasons.

Indonesia has vast palm oil plantations. The palm oil industries generate huge amounts of liquid wastes such as Sludge of Palm Oil (SPO). The SPO price is about a quarter of the price of refined palm oil. SPO considered as feedstock for biodiesel production because it contains fatty acids that allow it to be converted into methyl esters by facilitating the esterification reactions. The utilization of low-cost SPO as feedstock will make biodiesel more competitive as fuel in term of production cost. Meanwhile, reusing by-products will reduce the negative impact of palm industry, at once it will become an opportunity to increase the value of these biomass wastes and realize the environmental sustainability.

Many literatures had studied many materials such as, alkaline earth oxides [15], metal oxides [16], modified polymer [17], zeolites [2,18-19], heteropolyacids [20], Amberlyst-15 [21], heteropolyacid ($H_3PW_{12}O_{40}.6H_2O$) [22], tungsten oxide zirconia (WO_3/ZrO_2) [23], hydrotalcite [24], ion exchange [25], carbon based material [13], metal phosphate [26], and metallic zinc and zinc acetate [27] as solid catalysts for esterification reaction. Some common problems that faced by using the conventional heterogeneous acid catalysts have been: the complexity of catalyst synthesis, high cost production and hydrophilic properties of the materials.

The development of novel heterogeneous catalysts using carbon materials from biomass wastes has been intensively studied in last few years. Toda et al. (2005) conducted research on sulfonation of carbon material from sugar. Then, many studies performed research on producing solid catalyst derived from carbon materials such as sugar [29], various carbohydrate [30], glucose - starch [31], glycerol [32], biochar [33], or rice husk ash catalyst [14], coconut-shell activated carbon [34]. The sulfonated carbon-based catalysts have polycyclic carbon atoms that formed a strong chemical bond with the solid surface as active sites. Indeed, the esterification reactions are mainly promoted by the active sites. The existence of functional groups such as carboxyl, phenolic or sulfonic on the carbon surface is capable of incorporating several hydrophilic molecules, for instance, methanol and water [35]. The catalyst activity will increase given the reactant easy to bond with sulfonic groups the hydrophilic molecules on the catalyst surface. The catalyst activity will increase as the reactants bonded easily to the sulfonate group that formed from the incorporation of several hydrophilic properties on a solid surface.

In this study, the preparations of solid catalyst from Palm Empty Fruit Bunch (PEFB) biochar for the esterification reaction of FFAs on SPO were carried out. The characteristics of the PEFB catalyst were analyzed in terms of porosity, FT-IR, the total number of acid sites and elemental analysis. Many parameters, i.e. the reaction temperatures, the molar ratio of methanol to SPO, and the amount of catalyst were investigated to study the catalyst activity. To our best of knowledge, the use of Palm Empty Fruit Bunch biochar as heterogeneous catalysts in biodiesel production is still rare.

2. Material and Methods

2.1. Catalyst synthesis

Palm Empty Fruit Bunch (PEFB) used as raw materials were collected from palm oil plantation in Jambi area, Indonesia. PEFB was first cleaned using distilled water and put in the oven at 110 ºC overnight to remove the moisture content. Then, the materials were crushed into small particles and sieved to have uniform size at less than 50 µm. A muffle furnace was used to obtain PEFB biochar by carbonization process. The samples were carbonized under nitrogen flow at atmospheric pressure. The rate of heating was 20 °C/min and the carbonization process was maintained at 800 °C for 4 h. At the end of the carbonization process, the furnace was naturally brought to ambient temperature. Thereafter, the catalyst was synthesized by preparation of EFB biochar through impregnation method. As the precursor of Zirconia metal, in this research used Zirconium (IV) oxychloride octahydrate ($ZrOCl_2.8H_2O$). In concise, the biochar that obtained from carbonization of PEFB was mixed with a solution of $ZrOCl_2.8H_2O$. Hereafter, the mixture was heated up to reflux conditions while constantly stirring for 6 hours. Subsequently, the prepared PEFB catalyst was removed from the metals solution using filtration method. To remove the remaining of the solution in the pore of catalyst, the PEFB catalyst was dried at 120 °C for 24 h on the oven. To attach the sulfonic group in solid surface, a certain mass amount of ammonium sulfate ($(NH_4)_2SO_4$) were milled in the porcelain mortar with the PEFB catalyst. The mass ratio of ammonium sulfate to PEFB catalyst was 5 to 2. Then, the sulfonated PEFB catalysts were placed on vacuum desiccator for 12 h at atmospheric temperature. Finally, the sulfonated PEFB catalyst was kept in a furnace at 500 °C for 4 h for calcination process.

From the nitrogen adsorption isotherm data, the surface area of the catalyst was measured using the Brunauer–Emmet–Teller (BET) method. The Barret-Joyner-Halenda method (BJH) method was used to estimate total volume and average pore diameter. Analysis of functional groups on the PEFB biochar and catalyst surface was conducted out using FTIR spectroscopy instrument. The compositions of Zr, C, H, O and S molecules on PEFB biochar and catalyst were analyzed by elemental analysis using X-Ray Fluorescence. The Boehm titration sequence was used to calculate the acid strength of the catalyst.

2.1. Catalytic Activity

In the present study, a flat bottom flask (250 mL) was used as the batch reactor. a hot plate and a magnetic stirrer were installed in the reactor for heating the reactor and maintaining the homogeneity of the mixture, respectively. In addition, a condenser and a thermometer were installed in the batch reactor. The reactor was kept in a water bath to maintain the temperature at the constant given reaction temperature. The esterification reaction was conducted initially by pouring the SPO on the reactor. Then the temperature of SPO was raised up to 60 °C. When the temperature of 60 °C was achieved, methanol was added to the reactor followed by the PEFB catalyst. The mixture was stirred vigorously in order to obtain uniform mixing. After 4 hours, the esterification reaction was stopped and the reactor temperature was lowered to the ambient condition. The product of esterification reaction was removed from the PEFB catalyst by filtration method. Then, the liquid mixture was poured in glass funnel followed by adding distilled water. Furthermore, the mixture was settled overnight to allow the separation of biodiesel product from aqueous phase perfectly. The upper layer was fatty acid methyl ester (FAME) compounds (biodiesel product). The remaining methanol was removed by evaporation to obtain pure biodiesel product by using a rotary vacuum evaporator. After that, the product was kept in the storage for further analysis. To study the parameters that influenced the free fatty acids conversion, the molar ratio of methanol to SPO was varied in this research included the amounts of catalyst (0.5 - 5 wt. % of SPO), and reaction temperatures (40 - 60 °C) were studied. To investigate the ability of PEFB catalyst to be used repeatedly, the esterification reaction was performed in three sequent runs using the same catalyst under the optimum reaction conditions. Before reuse, the PEFB catalyst was regenerated by washed repeatedly using n-hexane to remove organic compounds in the pores of solids. Finally, the catalyst was dried in the oven at 80 °C overnight.

2.2. Analysis of the Sample

The acid value of biodiesel product was determined by an acid-base titration standard procedure. Prior to titration analysis, the water by-product and remaining methanol were evaporated from the sample. Then the purified sample was weighted accurately and dissolved to neutralized ethanol by heating. The indicator that employed in this titration analysis was phenolphthalein. The mixture was stirred until completely dispersed. Then, the mixture was titrated with potassium hydroxide solution so that pink colour can be observed. When the pink color in the mixture persists for at least 10 second, the titration was finished. The acid value (*AV*) was defined bellow:

$$AV = \frac{56.1 \times V \times N}{m} \qquad (1)$$

where:

V = volume of the consumed potassium hydroxide solution titrant in mL
N = exact normality of the titrant (potassium hydroxide solution)
m = mass of the analyzed sample in gram

The conversion of free fatty acid (X_F) was determined by equation as follows:

$$X_F = \left(1 - \frac{AV_t}{AVi}\right) \times 100 \qquad (2)$$

where AVi is the acid value of the mixture initially and AV_t is the acid value of mixture after reaction.

3. Material and Methods

3.1. Characterization of catalyst

The physical properties as well as acid density of PEFB biochar and PEFB catalyst are presented in Table 1. The textural properties of the sample including surface area, total pore volume and mean pore size diameter were calculated based on the nitrogen adsorption – desorption data. Table 1 depictes the BET surface area of PEFB biochar was 179.961 m^2/g, meanwhile for the PEFB catalyst was 75.852 m^2/g. The decreasion of BET surface area was due to the filling of internal solid pores by zirconia and sulfonate group. It shows the succesfull of impregnation and sulfonation to form active site on the surface of PEFB biochar. The same result also had seen on the total pore volume. The total pore volume of PEFB biochar was 0.2539 cm^2/gram which lower compared to PEFB catalyst (0.2580 cm^2/gram). Meanwhile, the mean pore size diameter was increased after the PEFB biochar was to synthesize as a solid catalyst. The mean pore size diameter was widening from 2.82 to 6.81 nm that indicate the pore was in mesopore range. Enlargement of catalyst pores will allow reactant molecules to penetrate into the internal catalyst. In addition, the method as described by Boehm was used to determine the quantity of acid site (i.e., sulfonate, carboxyl and phenols functional groups) on the surface of both PEFB biochar and catalyst. The Boehm method was carried out by acid–base back titration. As can be observed in Table 1, the amounts of total acidic groups before and after sulfonation were 1.1 and 4.6 mmol.g^{-1} respectively. The increasing of total amount of acid groups was due to successful of the sulfonation process which had attached the sulfonate, carboxylic and phenolic functional groups on the surface. Futhermore, the elemental analysis was performed to calculate the amount of Sulfur atoms attached on the surface of materials. The percentage of contained Sulfur on PEFB catalyst was 4.3% and its significantly larger compared to PEFB biochar. A significant increase in sulfur content on PEFB catalyst indicates that the sulfonic groups are successfully linked to the catalyst surface.

FTIR spectroscopy was used to investigate the existence of various functional groups on the catalyst surface. The spectra of FTIR on PEFB biochar and catalyst were depicted on Fig. 1. As shown in Fig. 1, the bands appearing at 1040 cm^{-1} attributted to S=O symmetric stretching vibration while S=O asymmetric stretching vibration was shown at wavelength of 1080 cm^{-1}. Meanwhile, the vibrational bands at 1397 cm^{-1} confirm the asymmetric SO_2 stretching in sulfonate functional groups. The appearance of those vibrational bands on FTIR spectra was proving the introduction of sulfonate functional groups during catalyst synthesis. Furthermore, the band found at 1719 cm^{-1} was attributed to the C=O stretching on carboxyl functional groups. In the other hand, at wavelength of 1610 cm^{-1}, there is clearly visible the C=C stretching vibration for aromatic structure. The O–H stretching vibrational band on phenolic groups was shown at 3440 cm^{-1}. The analysis of FTIR spectra had confirmed that the PEFB catalyst consist of acidic group such as sulfonate, phenolic, and carboxyl functional groups.

Table 1. Characteristics of PEFB biochar and PEFB catalyst.

Sample	BET surface area (m^2 g^{-1})	pore size (nm)	total pore volume (cm^3 g^{-1})	Acid density (mmol g^{-1})			
				SO_3H	COOH	OH	Total
PEFB biochar	179.961	2.82	0.2539	-	0.5	0.6	1.1
PEFB catalyst	75.852	6.81	0.2580	1.9	0.4	2.3	4.6

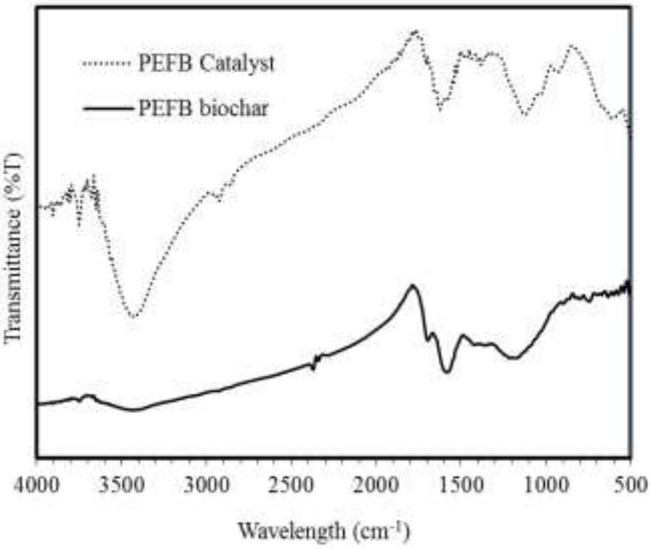

Fig. 1. FTIR Spectra of PEFB biochar and PEFB catalysts.

3.2. Catalytic activity

The Effect of Molar Ratio on FFA Conversion

The esterification reaction is a reaction involving methanol and fatty acids to generate methyl ester as the main product. This reaction runs reversible and every mole of free fatty acid requires one mole of methanol, stoichiometrically. The maximum conversion of the free fatty acids can be achieved by shifting the reaction toward the formation of the product by using excessive reactants. One of the variables that influenced the free fatty acids conversion is the molar ratio of the reactant. The molar ratio of the reactants is the ratio of the moles amounts of reactants involved in the reaction. The molar ratio of methanol to SPO used in this experiment was used between the values of 8:1 to 14:1. Fig. 2 depicts the influence of molar ratio on FFA conversion. It is clearly shown in Fig. 2 that FFA conversion elevated from 75.1 to 80.4% by increasing the molar ratio from 8:1 to 10:1. Furthermore, the molar ratio of methanol to SPO of 12:1, the FFA conversion was 84.8% while the FFA conversion of 87.2% was achieved at the methanol to SPO molar ratio of 14:1. It is concluded that the increase of the molar ratio of methanol to SPO has a positive effect on the FFA conversion.

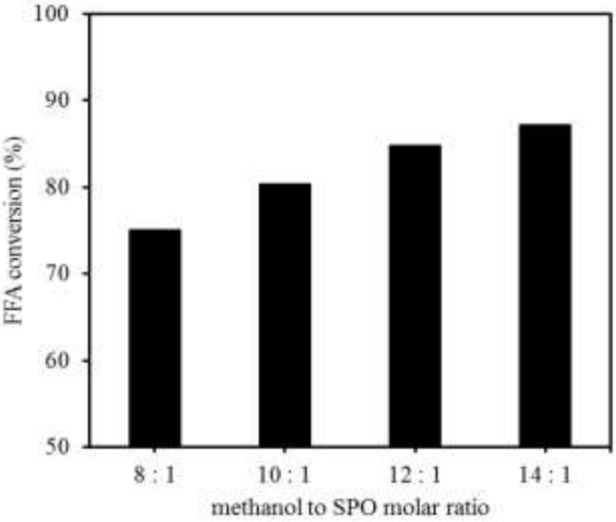

Fig. 2. The effect of molar ratio methanol to SPO on the FFA conversion (reaction temperature was 60 °C, the reaction time 4 h and catalyst amount of 5 wt. % of SPO).

The Influence of Catalyst Amount

The catalyst that loaded was varied from 0.5 to 5 wt. % of initial SPO mass. Fig. 3 exhibits the influence of catalyst amount on FFA conversion. As shown in Fig. 3, using 0.5 wt. % of initial SPO mass, the FFA conversion achieves 66.8%. When the amount of catalyst was elevated from 1 to 2.5 wt. % of initial SPO mass, the FFA conversion increased from 76.3 to 87.2 %. Further increases of catalyst amount up to 5 wt. % gives FFA conversion attained to 87.2%. From the data, it was concluded that the FFA conversion increases with the addition of catalyst to the reactant mixture. The increasing activity was due to the enhancement of active sites on the surface because of the rise of catalyst amount. Thus, it can be summarized that the highest FFA conversion was reached at the catalyst amount of 5 wt. % of initial SPO mass.

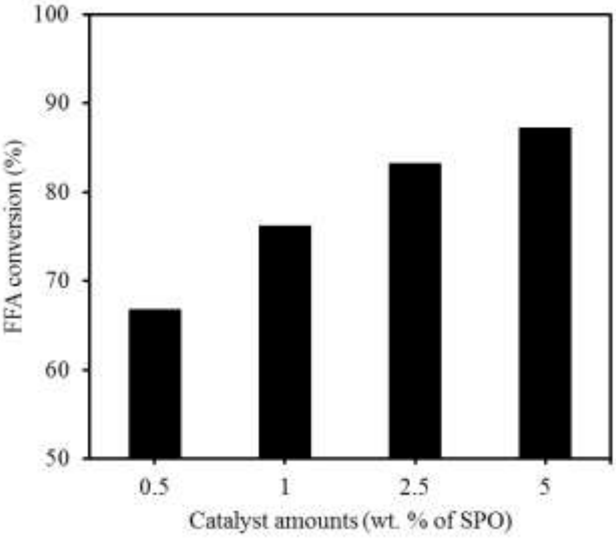

Fig. 3. The Influence of catalyst amounts on the FFA conversion (the reaction temperature was 60 °C, molar ratio of methanol to SPO of 12:1, and reaction time 4 h).

The Effect of the Reaction Temperature

Another important variable that has a strong influence on FFA conversion is reaction temperature. It is worth noting that the reaction temperature was kept below the boiling point of the methanol to avoid the reactants evaporation. Various reaction temperatures were chosen to study the influence of the reaction temperature on FFA conversion i.e. 40, 50, and 60 °C. Fig. 4 depicts the experimental data results of the influence of reaction temperature on FFA conversion.

It can be clearly seen in Fig. 4, the FFA conversion was 71.5% at reaction temperature of 40 °C. Furthermore, when the reaction temperature augmented to 50 °C, the FFA conversion increases to 78.7%. When reaction temperature of 60 °C the highest FFA conversion was achieved at 87.2%. It can be concluded that the rise in reaction temperature would increase the activity of the catalyst and shortened reaction time. Moreover, the esterification reaction is endothermic, so that the reaction temperature also has a strong effect on the FFA conversion.

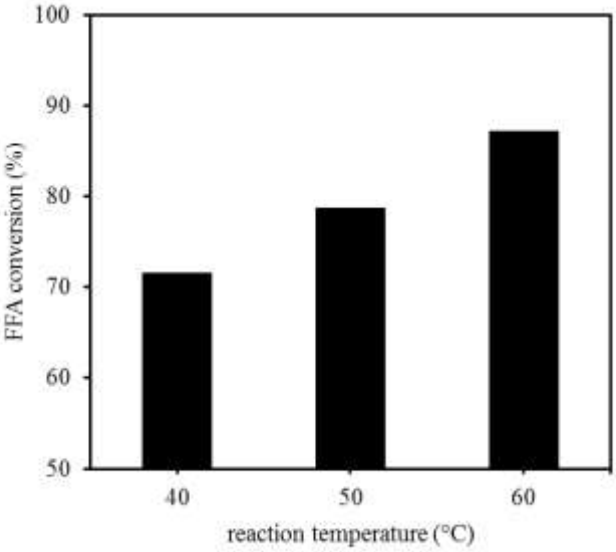

Fig. 4. The effect of reaction temperature on the FFA conversion (molar ratio of methanol to SPO of 14:1, the reaction time 4 h and catalyst amount of 5 wt. % of SPO).

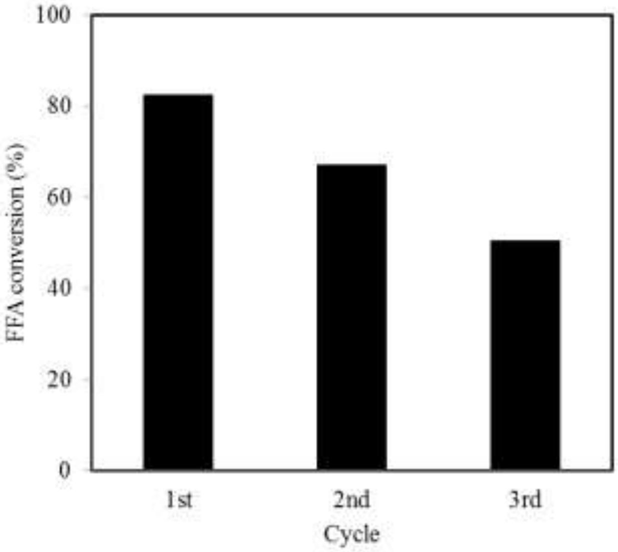

Fig. 5. Comparison of the activity of the PEFB catalyst during three reaction cycles at three different catalyst amounts (the reaction temperature was 60 °C, methanol to SPO molar ratio was 14:1, catalyst amount of 5 wt. % of SPO and reaction time 4 h).

Reusability

The ability of PEFB catalysts was examined by conducting a series of successive esterification reactions under the same operating conditions. Prior to be used on the subsequent reaction, the PEFB catalyst was removed from the product by filtration. Then the PEFB catalyst was washed using n-hexane to separate the remaining organic compound on the internal pore. Finally, the PEFB catalyst was dried in the oven overnight at 110 °C. The reusability of catalyst was carried out on three consecutive reactions. During the ~~reaction~~ process, the reaction time was maintained at 4 hours, the molar ratio of methanol to SPO was kept at 14:1, the reaction temperatures was remained constant at 60 °C and 5 wt. % of initial SPO mass of catalysts was used. Fig. 5 presents the results of FFA conversion after the catalyst was used repeatedly for three times. As indicated in Fig. 5, the conversion of FFA decreases to 66.4 and 51.3% in the second and third reactions. The decreasing of catalyst substantially was caused by leaching of active site from solid surface.

In Table 2, recently reported literatures on esterification reaction of FFAs using several heterogeneous catalysts with different feedstocks. From the table, the Zirconia/natural zeolite catalyst introduced in the present work is comparable to other research works in term of reaction temperature, alcohol to oil ratio and catalyst amount. In addition, it can be concluded that esterification reaction of FFA using the Zirconia/natural zeolite catalyst gives a high FFA conversion.

Table 2. Comparison several catalysts on esterification reaction of FFAs using different feedstocks.

Feedstock	Catalyst	Optimum reaction conditions	Conversion (%)	Reference
Palm fatty acid distillate using	Sulfonated sugarcane bagasse	T = 60 °C, t = 4 h, Methanol/oil = 12:1, Catalyst amount= 10wt.%	92	[4]
Palm fatty acid distillate using	Sulfonated coconut shell biochar	T = 60 °C, t = 4 h, Methanol/oil = 12:1, Catalyst amount= 7wt.%	87	[13]
Palm oil sludge	ZrO_2/SO_4^{2-} - Rice husk ash	T = 60 °C, t = 4 h, Methanol/oil = 12:1, Catalyst amount= 10wt.%	83.1	[14]
Waste cooking oil	CaO/SiO_2 based on eggshell/PEFB	T = 60 °C, t = 1,5 h, Methanol/oil = 14:1, Catalyst amount= 8% w/w	96	[36]
Jatropha curcas	Palm empty fruit bunch (PEFB) impregnated with KOH	T = 65°°C, t = 45 mins, methanol to oil ratio= 15:1, 15 wt.% of KOH doped on PEFB ash	>98	[37]
Palm oil sludge	Sulphuric acid (H_2SO_4)	T = 60 °C, t = 1 h, Methanol/oil = 8:1, Catalyst amount= 0.75% wt/wt of H_2SO_4	83.72	[38]
Palm oil sludge	Zirconia/natural zeolite	T = 60 °C, t = 4 h, Methanol/oil = 14:1, Catalyst amount= 7wt.%	87.2	This study

4. Conclusion

In this work, the performance of PEFB catalyst has been investigated on the esterification of SPO with high FFA. The PEFB catalyst activity was significantly sensitive to (1) the molar ratio of methanol to SPO, (2) the amounts of PEFB catalyst, and (3) reaction temperature. The highest activity of the PEFB catalyst was observed when the reaction was conducted at 60 °C, the methanol to SPO molar ratio of 14:1 and the amounts of PEFB catalyst of 5 wt. % of initial SPO mass. The significant decrease in PEFB catalyst activity was found after three consecutive reactions due to leaching of acid sites. The PEFB as catalysts was an alternative technology to suppress biodiesel production cost and as a strategy to replace the acid homogeneous catalysis in the synthesis of biodiesel.

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References

[1] M. A. Adnan, H. Susanto, H. Binous, O. Muraza and M. M. Hossain, "Enhancement of hydrogen production in a modified moving bed downdraft gasifier – A thermodynamic study by including tar", *International Journal of Hydrogen Energy*, vol 42, pp. 10971-85, April 2017.

[2] P. Intarapong, A. Luengnaruemitchai, S. Jai-In "Transesterification of palm oil over KOH/NaY zeolite in a packed-bed reactor", *International Journal of Renewable Energy Research*, Volume 1, No. 4, pp. 271-280, 2011.

[3] Y. S. Pradana, A. Hidayat, A. Prasetya, and A. Budiman, "Biodiesel production in a reactive distillation column catalyzed by heterogeneous potassium catalyst", *Energy Procedia*, vol. 143, pp. 742-747, December 2017.

[4] V. A. S. Augustia, R. A. Djalal, B. Sutrisno, and A. Hidayat, "Kinetic study of free fatty acid in Palm Fatty Acid Distillate (PFAD) over sugarcane bagasse catalyst", *IOP Conference Series: Earth and Environmental Science*, vol. 105(1), pp. 012065, January 2018.

[5] A. J. Lopez, I. J. Morales, J. S. Gonzalez and P. M. Torres, "Biodiesel production from sunflower oil by tungsten oxide supported on zirconium doped MCM-41 silica", *Journal of Molecular Catalysis A: Chemical.*, vol. 335, pp. 205-209, February 2011.

[6] E. G. S. Junior, E. Simionatto, V. H. Perez, O. R. Justo, N. A. H. Zarate and M. C. Vieira, "Potential of Virginia-type peanut (Arachis hypogaea L.) as feedstock for biodiesel production", *Industrial Crops and Products*, vol. 89, pp. 448-454, October 2016.

[7] M. Sirajuddin, M. Tariq and S. Ali, "Organotin(IV) carboxylates as an effective catalyst for the conversion of corn oil into biodiesel", *Journal of Organometallic Chemistry*, vol. 779, pp. 30-38, March 2015.

[8] S. Nasreen, H. Liu, D. Skala, A. Waseem and L. Wan, "Preparation of biodiesel from soybean oil using La/Mn oxide catalyst", *Fuel Processing Technology*, vol. 131, pp. 290-296, March 2015.

[9] B. Wang, S. Li, S. Tian, R. Feng and Y. Meng, "A new solid base catalyst for the transesterification of rapeseed oil to biodiesel with methanol", *Fuel*, vol. 104, pp. 698-703, February 2013.

[10] D. Kumar and M. C. Math, "Application of Response Surface Methodology for Optimization of Biodiesel Production by Transesterification of Animal Fat with Methanol", *International Journal of Renewable Energy Research*, Volume 6, No. 1, pp. 74-79, 2016.

[11] S. Gunawardena, D. H. Walpita, M. Ismail, "Method for Quantification of Methanol and Sulfuric Acid Required for Esterification of High Free Fatty Acid Oils in Biodiesel Production", *International Journal of*

Renewable Energy Research, Volume 7, No. 4, pp. 1639-1645, 2017.

[12] H. Venkatesan, G. John, S. Sivamani, Cotton Seed Biodiesel as Alternative Fuel: Production and its Characterization Analysis using Spectroscopic Studies, *International Journal of Renewable Energy Research*, Volume 7, No. 3, pp. 1333-1339, 2017.

[13] A. Hidayat, Rochmadi, K. Wijaya and A. Budiman, "Removal of free fatty acid in Palm Fatty Acid Distillate using sulfonated carbon catalyst derived from biomass waste for biodiesel production", *IOP Conference Series: Materials Science and Engineering*, vol. 105(1), pp. 012026, January 2016.

[14] A. Hidayat, and B. Sutrisno, "Esterification free fatty acid in sludge palm oil using ZrO^2/SO_4^{2-} - Rice husk ash catalyst", *AIP Conference Proceedings*, Volume 1840, pp. 050001, May 2017.

[15] G. Arzamendi, E. Arguinarena, I. Campo, S. Zabala and L.M. Gandia, "Alkaline and alkaline-earth metals compounds as catalysts for the methanolysis of sunflower oil", *Catalysis Today*, vol. 133-135, pp. 305-313, April–June 2008.

[16] N. Pasupulety, G. L. Rempel and F. T. T. Ng, "Studies on Mg-Zn mixed oxide catalyst for biodiesel production", *Applied Catalysis A: General*, 489, pp. 77-85, January 2015.

[17] R. A. Soldi, A. R. S. Oliveira, L. P. Ramos and M. A. F. Cesar-Oliveira, "Soybean oil and beef tallow alcoholysis by acid heterogeneous catalysis", *Applied Catalysis A: General,* vol. 361, issues 1-2, pp. 42-48, June 2009.

[18] W. Xie, X. Huang and H. Li, "Soybean oil methyl esters preparation using NaX zeolites loaded with KOH as a heterogeneous catalyst", *Bioresource Technology*, vol. 98, issue 4, pp. 936-939, March 2007.

[19] A. Brito, M.E. Borges and N. Otero, "Zeolite Y as a heterogeneous catalyst in biodiesel fuel production from used vegetable oil", *Energy Fuels*, vol. 21 (6), pp. 3280-3283, October 2007.

[20] A. Alsalme, E. F. Kozhevnikova, and I. V. Kozhevnikov, "Heteropoly acids as catalysts for liquid-phase esterification and transesterification", *Applied Catalysis A: General*, vol. 349, pp. 170-176, October 2008.

[21] M. M. Rahman Talukder, J. C. Wu, S.K. Lau, L. C. Cui, G. Shimin and A. Lim, "Comparison of Novozym 435 and Amberlyst 15 as heterogeneous catalyst for production of biodiesel from palm fatty acid distillate", *Energy Fuels*, vol. 23 (1), 1-4, December 2008.

[22] X. Zhang, J. Li, Y. Chen, J. Wang, L. Feng and X. Wang, "Heteropolyacid nanoreactor with double acid sites as a highly efficient and reusable catalyst for the transesterification of waste cooking oil", *Energy Fuels*, vol. 23 (9), 4640-4646, July 2009.

[23] Y. M. Park, J. Y. Lee, S. H. Chung, I. S. Park, S. Y. Lee, and D. K. Kim, "Esterification of used vegetable oils using the heterogeneous WO_3/ZrO_2 catalyst for production of biodiesel", *Bioresource Technology,* vol. 101, issue 1, pp. S59-S61, January 2010.

[24] Y. T. Wang, Z. Fang, F. Zhang and B. J. Xue, "One-step production of biodiesel from oils with high acid value by activated Mg–Al hydrotalcite nanoparticles", *Bioresource Technology*, vol. 193, pp. 84-89, October 2015.

[25] N. S. Kitakawa, K. Hiromori, T. Ihara, K. Nakashima and T. Yonemoto, "Production of high quality biodiesel from waste acid oil obtained during edible oil refining using ion-exchange resin catalysts", *Fuel*, vol. 139, pp. 11-17, 2015.

[26] M. D. Serio, M. Cozzolino, R. Tesser, P. Patrono, F. Pinzari, B. Bonelli and E. Santacesaria, "Vanadyl phosphate catalysts in biodiesel production", *Applied Catalysis A: General*, vol. 320, pp. 1-7, March 2007.

[27] P. Felizardo, J. Machado, D. Vergueiro, M. J. N. Correia, J. P. Gomes and J. M. Bordado, "Study on the glycerolysis reaction of high free fatty acid oils for use as biodiesel feedstock", *Fuel Processing Technology*, vol. 92, pp. 1225-1229, June 2011.

[28] M. Toda, A. Takagaki, M. Okamura, J.N. Kondo, S. Hayashi and K. Domen, "Green chemistry: biodiesel made with sugar catalyst", *Nature*, vol. 438, pp. 178, November 2005.

[29] M. H. Zong, Z. Q. Duan, W. Y. Lou, T. J. Smith and H. Wu, "Preparation of a sugar catalyst and its use for highly efficient production of biodiesel", *Green Chemistry*, vol. 9, issue 5, pp. 434-437, February 2007.

[30] W. Y. Lou, M. H. Zong and Z. Q. Duan, "Efficient production of biodiesel from high free fatty acid-containing waste oils using various carbohydrate derived solid acid catalysts", *Bioresource Technology*, vol. 99, issue 18, pp. 8752-8758, December 2008.

[31] G. Chen, and B. Fang, "Preparation of solid acid catalyst from glucose–starch mixture for biodiesel production", *Bioresource Technology*, vol. 102, issue 3, 2635-2640, February 2011.

[32] B. L. A. P. Devi, K. N. Gangadhar, P. S. S. Prasad, B. Jagannadh and R. B. N. Prasad, "A glycerol- based carbon catalyst for the preparation of biodiesel", *ChemSusChem.*, vol. 2, issue 7, pp. 617-620, July 2009.

[33] A. Hidayat, Rochmadi, K. Wijaya and A. Budiman, "Reaction kinetics of free fatty acids esterification in palm fatty acid distillate using coconut shell biochar sulfonated catalyst", *AIP Conference Proceedings*, vol. 1699, pp. 050005, December 2015.

[34] Y. S. Pradana, A. Hidayat, A. Prasetya, and A. Budiman, "Application of coconut-shell activated carbon as heterogeneous solid catalyst for biodiesel synthesis", *Defect and Diffusion Forum,* volume 382, pp. 280-285, January 2018.

[35] M. Hara, "Biodiesel Production by Amorphous Carbon Bearing SO_3H, COOH and Phenolic OH Groups, a Solid Brønsted Acid Catalyst", *Topics in Catalysis,* vol. 53, issue 11–12, pp 805–810, July 2010.

[36] M.D. Putra, Y. Ristianingsih, R. Jelita, C. Irawan and I.F. Nata, "Potential waste from palm empty fruit bunches and eggshells as a heterogeneous catalyst for biodiesel production", *RSC Advances*, Issue 87, pp. 55547-55554, December 2017.

[37] Z. Yaakob, I.S.B. Sukarman, B. Narayanan, S.R.S.Abdullah, M. Ismail, "Utilization of palm empty fruit bunch for the production of biodiesel from

Jatropha curcas oil”, *Bioresource Technology*, Volume 104, pp. 695-700, January 2012.

[38] A. Hayyan, Md.Z. Alam, M.E.S.Mirghani, N.A. Kabbashia, N.I.N.M Hakimi, Y. M. Siran, S. Tahiruddin, “Reduction of high content of free fatty acid in sludge palm oil via acid catalyst for biodiesel production”, *Fuel Processing Technology*, Volume 92, Issue 5, pp. 920-924, May 2011.