Production of Biodiesel by Esterification of Free Fatty Acid over Solid Catalyst from Biomass Waste

N. I. F. Mukti, B. Sutrisno and A. Hidayat
Chemical Engineering Department, Universitas Islam Indonesia
Jalan Kaliurang km 14,5 Yogyakarta 55584, Indonesia
nurindah_fm@uii.ac.id

Abstract. Recently, low cost feedstocks have been utilized to replace vegetable oils in order to improve the economic feasibility of biodiesel. The esterification of free fatty acid (FFA) on Palm Fatty Acid Distillate (PFAD) with methanol using solid catalyst generated from bagasse fly ash is a promising method to convert FFA into biodiesel. In this research, the esterification of FFA on PFAD using the sulfonated bagasse fly ash catalyst was studied. The performances of the catalysts were evaluated in terms of the reaction temperatures, the molar ratios of methanol to PFAD, and the catalyst loading. The effects of the mass ratio of catalyst to oil (1-10%), the molar ratio of methanol to oil (6:1-12:1), and the reaction temperature (40-60°C) were studied for the conversion of PFAD to optimize the reaction conditions. The results showed that the optimum conditions were methanol to PFAD molar ratio of 12:1, the amount of catalyst of 10%wt. of PFAD, and reaction temperature of 60°C. The reusability of the solid acid carbon catalysts was also studied in this work. The catalytic activity decreased up to 38% after third cycle. The significant decline in catalyst esterification activity was due to acid site leaching. The physico-characteristics and acid site densities were analyzed by Nitrogen gas adsorption, surface functional groups by Fourier transform infrared spectroscopy (FT-IR), elemental analysis using X-ray fluorescent (XRF), and acid-base back titration methods for determination of acid density.

1. Introduction
Increased demand for energy, global warming due to emission of greenhouse gases, environmental pollution, and fast diminishing supply of fossil fuels are the major key factors leading to search for alternative sources of energy [1, 2]. Biodiesel is considered a promising alternative substitute for petroleum diesel fuel. Biodiesel, defined as monoalkyl fatty acid ester preferentially methyl and ethyl esters, has several advantages over petroleum diesel, such as it is biodegradable, non-toxic, originates from renewable sources and contains no sulphur or aromatic compounds and would therefore, contribute to the reduction of emissions from diesel engines [3]. Biodiesel is generally synthesized by the transesterification of vegetable oils or animal fats, which is carried out by acid or base catalysis. Biodiesel can be also produced by esterification of free fatty acids, which are present in animal fats (ex. lard or tallow), with methanol over acid catalysts [4].

The problems related to biodiesel production are high cost feedstock and the conflict of interest between energy crisis and food security. The use of low cost feedstocks such as waste cooking oils and non-conventional seed oils can reduce biodiesel production cost and increase supply while avoiding the food versus fuel problem. Therefore, it is necessary to search for non-conventional feedstocks for biodiesel production. Palm Fatty Acid Distillate (PFAD), which has high content of free fatty acids, is by-product of palm oil refinery. Compared to the expensive refined palm oil (1 USD per Liter), PFAD costs only 0.3 USD per liter. Thus, the utilization of PFAD for biodiesel production via esterification

Published under licence by IOP Publishing Ltd
Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
reaction would reduce the production cost of biodiesel, and would consequently enable it to compete economically with petroleum-based fuel. Commercial biodiesel production employs homogeneous alkali catalysts. The homogeneous catalysts for biodiesel production are alkaline catalysts (such as sodium hydroxide, potassium hydroxide, and alkali metal hydroxides) and acids catalysts (such as sulfuric acids or hydrochloric acid) [5]. Conventional homogeneous catalysts are no longer feasible for biodiesel production. The homogeneous catalysts are generally corrosive to equipment, have to be usually neutralised after reaction, cannot be regenerated and recycled, also give rise to serious environmentally problems. These problems can be overcome by the use of solid acid catalysts. A literature survey shows that esterifications of free fatty acids to produce biodiesel involve use of different heterogeneous catalysts such as, clays [6], zeolite [7], ion exchange resin [8], carbon based material [9], metal oxides as well as sulphated metal oxides [10], WO3/ZrO2 [11], propylsulphonic acid functionalized mesoporous silica [12], heteropolyacids [13] and heteropolyacids supported on to different supports such as zirconia [14], activated carbon, silica [15] and tantalum pentoxide [16].

A novel catalyst which has not been fully explored is carbon based catalysts. Carbon supported catalysts have several distinct advantages over alumina or silica supported systems; they are stable under acidic basic conditions, can have very high surface area (200–1500 m²/g), renewable biomass sources can be used to generate the carbon, and the non-polar nature of the support matrix may reduce adsorption of polar molecules (e.g., water or glycerol) that can deactivate the catalyst [17]. Sulfonated carbons are the most promising solid acids and their use have been demonstrated in many acid catalyzed reactions including that of FFAs esterification as well as cellulose hydrolysis [15,16]. Such catalysts are generally produced by sulfonation of incompletely pyrolyzed biomass, such as sucrose[17], glucose [18], starch [19], glycerol [20] or biochar [21]. Carbon precursors are directly pyrolyzed and sulfonated in concentrated H2SO4 at high temperatures. However, this simple process usually produces sulfonated carbons with low specific surface area, low acid density and poor reusability. In this research, the esterification of PFAD using the sulfonated bagasse fly ash catalyst was studied. The performances of the catalysts were evaluated in terms of the reaction temperatures, the molar ratios of methanol to PFAD, the catalyst loading and the reaction times. The reusability of the solid acid carbon catalysts was also studied in this work.

2. Experiment

2.1. Catalysts Preparation
Bagasse fly ash used as raw materials were obtained from Bantul regency, D.I. Yogyakarta province. The starting materials were manually chosen, cleaned with deionized water, and dried at 110°C for 48 h. Prior to use, bagasse fly ash were crushed and sieved to obtain particles with sizes less than 1 µm. Sulfonation was carried out at 15°C for 12 h by immersed and stirred 10 g activated carbon in 100 ml concentrated sulfuric acid (98%). The sulfonated sample was filtered water washed with hot distilled water (>80°C) until the sulphate ions were no longer detected in the wash water. Then the sulfonated catalyst was dried at 110°C for overnight in a oven to remove water.

2.2. Catalyst Characterization
The specific surface area and pore structure characteristic of prepared activated carbons were determined by nitrogen adsorption at −196°C. The BET surface area was calculated using the BET equation; total pore volumes were estimated to be the liquid volumes of N2 at a high relative pressure (~0.99). The surface functional groups and structure were studied by Fourier transform infrared spectroscopy (FTIR). The FTIR spectra of the raw material and the resulting activated carbons were recorded from a wavenumber of 4000–400 cm−1. Elemental analysis was used to determine the composition of the catalysts. The sulphur contents of the catalyst were determined by elemental analysis. The total acid density of the catalysts was determined using the standard acid-base back-titration.

2.3. Catalyst testing
Esterification of PFAD using the prepared catalysts was performed in batch runs on a hot plate with a magnetic stirrer at different process conditions. The samples were analyzed by titration procedure for the evaluation of free residual acidity. Once the sample was taken from the reactor, it was washed with
water in order to stop the reaction and separates the catalyst and the alcohol from the oil phase. A weighted amount of the sample was dissolved in ethanol and sulfuric ether in order to be able to make the titration analyses, and some drops of phenolphthalein as indicator were added to the solution to be able to measure the conversion. The titration was done with a 0.05 mol/L KOH solution. The acid value was calculated using the following equation:

\[
AV = \frac{56.1 \times C \times V}{M}
\]

(1)

where \(AV\) is the acid value of the sample (mg KOH.g\(^{-1}\)), \(V\) is volume of KOH consumed for titration (mL), \(C\) is concentration of the KOH used for titration (mol/L), \(m\) is the weight of the sample (g), and 56.1 is the molecular weight of KOH. The conversion of free fatty acid was calculated using the following equation:

\[
X_r = \left(1 - \frac{AV_2}{AV_1}\right) \times 100
\]

(2)

where \(X_r\) is the FFA conversion, \(AV_1\) is the initial acid value of the mixture and \(AV_2\) is the acid value of mixture after reaction. To study the effect of the catalyst amount on FFA conversion, the reaction was carried out at four different catalyst loadings of 1, 2.5, 5, and 10%wt. of PFAD. Each reaction was carried out at 60°C for 4 h using molar ratio of methanol to oil of 12:1. In this study the molar ratio of methanol to PFAD was varied from 6:1 to 12:1. At the end of each experiment, the catalyst was filtered from the reaction mixture, washed with fresh methanol, dried at 100°C for 2 h, and then reused in the next cycle of experiments. The esterification reaction was carried out at temperature of 60°C with a 6:1 molar ratio of methanol to oil and a 10 wt.% PFAD of catalyst amount.

3. Results And Discussions

3.1. Catalysts Characterization

Nitrogen isotherms of biochar and catalyst at −196°C are presented in Figure 1.

![Figure 1. Nitrogen Adsorption Isotherm at −196°C.](image-url)

The shape of adsorption isotherm can provide preliminary qualitative information about the adsorption mechanism as well as the pore structure of activated carbons. These isotherms show that the biochar from bagasse fly ash has type IV isotherm which is an indication of mesoporous carbon. Catalyst, on the other hand, also has type IV isotherm. The characterization of biochar and catalyst presented in Table 1. It can be seen that sulfonation process change the carbon characterization. Moreover, the pore volumes and surface area of mesopore were increased by sulfonation process. Pore size distribution of the biochar and catalyst obtained from BJH model is presented in Figure 2. As expected from N\(_2\) adsorption isotherms (Figure 1), all samples showed that has type IV isotherm which is an indication of mesoporous carbon. However, the PSDs calculated using BJH model which is related to the
fundamental assumptions on describing the porous structure and/or mechanism of adsorption for mesoporous structure.

### Table 1. Characterization of Carbons.

| Sample   | S, m²/g | Sₘₑₛ, m²/g | % | V, cm³/g | Vₘₑₛ, cm³/g | % | Dₐᵥₚ, nm |
|----------|---------|-------------|---|----------|--------------|---|----------|
| Biochar  | 65.96   | 25.02       | 37.93 | 0.060   | 0.04         | 66.00 | 3.46     |
| Catalyst | 70.60   | 35.19       | 49.84 | 0.061   | 0.04         | 68.76 | 3.64     |

**Figure 2.** Pore Size Distribution using BJH Model.

3.2. **Catalyst Testing**

The esterification reaction is affected by various factors depending upon the reaction conditions used. Further experiments for investigating the influence of different reaction parameters such as catalyst loading, reaction time, methanol to oil molar ratio and reaction temperature on the conversion of FFA. Figure 3 shows the effect of catalyst loading on FFA conversion. Based on these results, it can be clearly seen that, when the amount of catalyst was increased from 1 to 10%, conversion of FFA was found to be increased.

**Figure 3.** Effect of catalyst loading on FFA conversion (reaction conditions: reaction temperature 60°C, stirring speed 800 rpm, and molar ratio of PFAD to methanol 1:12).
The highest conversion of 82.5% was obtained at catalyst loading of 10%wt. of PFAD. When the catalyst amount was increased, the total number of available active sites increased resulted in faster reaction rate to reach reaction equilibrium, with more catalyst addition [17]. Molar ratio is one of the important factors affecting the conversion of FFA. Theoretically, the esterification of FFA requires one moles of methanol per mole of FFA. Since the esterification of FFA is a reversible reaction, the excess of methanol shifts the equilibrium towards the direction of fatty acid methyl ester formation. In addition to this, usage of excess methanol is one of the better options to improve the rate of the esterification reaction catalyzed by heterogeneous catalysts. In this study the molar ratio of methanol to PFAD was varied from 6:1 to 12:1. Figure 4 shows the effect of methanol to oil molar ratio on the conversion at the end of 4 h reaction time at 60°C in the amount catalyst of 10%wt. of PFAD. It can be clearly seen from Figure 4, when the molar ratio was increased from 6:1 to 12:1, the conversion was found to increase from 68% to 82.5%. The highest conversion was found at molar ratio of 12. Further increase in the methanol amount has not showed any significant improvement in the conversion.

![Figure 4. Effect of oil to methanol molar ratio on FFA conversion (reaction conditions: reaction temperature 60°C, stirring speed 800 rpm and catalyst loading 10% wt. of PFAD).](image)

The influence of temperature was studied in the esterification of FFA applying methanol to oil molar ratio of 12:1 and using amount catalyst of 10%wt. PFAD by varying the reaction temperature from 40 to 60°C. Figure 5 illustrates the influence of temperature on the conversion of FFA. Figure 5 shows that the FFA conversion increases from 61 to 83% as the temperature increases from 40 to 60°C. The increased of FFA conversion due to the effect of increase of the reaction rate by increasing temperatures. Some improvement of the mass transfer limitation between reactant and catalyst when the temperature increase also effect on the FFA conversion. As the reaction temperature is increased, all reactant molecules will gain more kinetic energy that will eventually accelerate the mass transfer rate among the oil–methanol–catalyst phases that resulted in the formation of more FAME [17]. Reusability of the catalyst in the esterification of FFA, under the optimum condition, was studied. The catalyst recovered after the reaction by filtration and directly used for another reaction. The results are presented in Figure 6. It can be seen that the catalyst's esterification activity was reduced to 38% at the end of 3rd cycle. This decay could be due to the leaching of active sites to the reaction media.
4. Conclusions
The sulfonated carbon catalyst derived from biomass waste were studied for esterification of the free fatty acid on PFAD. The effects of the mass ratio of catalyst to oil (1–10%), the molar ratio of methanol to oil (6:1–12:1), and the reaction temperature (40–60°C) were studied for the conversion of PFAD to optimize the reaction conditions. The results showed that the optimum conditions were methanol to PFAD molar ratio of 12:1, the amount of catalyst of 10 wt.% of PFAD, and reaction temperature of 60°C. The catalytic activity decreased up to 38% after third cycle.

Acknowledgments
This work is fully financially supported by the Direktorat Riset dan Pengabdian Masyarakat, Direktorat Jenderal Pendidikan Tinggi, Kemenristekdikti, Republik Indonesia.

References
[1] Kawentar W A and Budiman A 2013 Energy Proc. 32 190-199.
[2] Fatimah, Hidayat A and Setiawan K H 2010 Asian J. Chem. 22 5 3793-3801.
[3] Budiman A and Ishida M 1997 J. Chem. Eng. Japan 30 5 966-969.
[4] Budiman A, Sutijan and Sawitri D R 2011 Int. J. Exergy 8 4 477-493.
[5] Kusumaningtyas R D, Rochmadi, Purwono S and Budiman A 2014 Int. J. Exergy 14 447-467.
[6] Do Nascimento L S, Tito L M Z, Angelica R S, Da Costa C E F, Zamian J R and Da Rocha G N Filho 2011 Appl. Catal. B: Environ. 101 3-4 495–503.
[7] Chung K H and Park B G J 2009 Ind. Eng. Chem. 15 388–392.
[8] Kiss A A, Dimian A C and Rothenberg G 2006 Adv. Synth. Catal. 348 1-2 75–81.
[9] Okuhara T 2002 Catal. Today 73 167–176.
[10] Wang Y, Liu Y and Liu C 2008 Energy Fuels 22 4 2203–2206.
[11] Park Y M, Lee J Y, Chung S H, Park I S, Lee S Y, Kim D K, Lee J S and Lee K Y 2010 Bioresour. Technol. 101 1 S59–S61.
[12] Melero J A, Bautista L F, Morales G, Iglesias J and Briones 2009 Energy Fuels 23 1 539–547.
[13] Silva V W G, Laier L O and Da Silva M J 2010 Catal. Lett. 135, 207–211.
[14] Oliveira C F, Dezaneti L M, Garcia F A C, De Macedo J L, Dias Silva J A, Dias C L and Alvim K S P 2010 Appl. Catal. A: Gen. 372 153–161.
[15] Caetano C S, Fonseca I M, Ramos A M, Vital J and Castanheiro J E 2008 Catal. Commun 9 1996–1999.
[16] Xu L, Wang Y, Yang X, Yu X, Guo Y and Clark J H 2008 Green Chem. 10 746–755.
[17] Hidayat A, Rochmadi, Wijaya K, Hinode H and Budiman A 2013 Asian J. Chem. 25 3 1569-1575.
[18] Toda M, Takagaki A, Okamura M, Kondo J N, Hayashi S and Domen K 2005 Nature 438 178.
[19] Okamura M, Takagaki A, Toda M, Kondo J N, Domen K and Tatsumi T 2006 Chem. Mater. 18 3039–3045.
[20] Guo F, Xiu Z L and Liang Z X 2012 Appl. Energ. 98 47–52.
[21] Hidayat A, Rochmadi, Wijaya K, Nurdiawati A, Kurniawan W, Hinode H, Yoshikawa K and Budiman A 2015 Energy Proc. 75 969-974.