A Comparison of Palm Fatty Acid Distillate (PFAD) Esterification using Sulphated Alumina versus Sulphuric Acid Catalyst

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Abstract. The selection of raw materials is the cost-wise strategy for biodiesel to compete with diesel. The raw material used in the second generation of biodiesel production is non-edible oil which contains high free fatty acids (FFA). Palm Fatty Acid Distillate (PFAD); the by-product of crude palm oil (CPO) industry has a high potential as the amount is abundant in Indonesia. The objective of this study is to compare the catalytic activity of esterification reaction using self-synthesized sulphated alumina and a sulphuric acid catalyst against the reduction of FFA. The reaction was carried out in a three-necked flask, at a temperature of 60°C, 7 hours of reaction time and rotation speed of 400 rpm. The results showed that the maximum FFA conversion of PFAD esterification reactions over sulphated alumina was 84%, achieved at methanol to oil ratio of 1.7 (v/v), catalyst to PFAD ratio of 12 % (w/w) and reaction time of 7 hours. Meanwhile, the optimum conditions for PFAD esterification using sulphuric acid catalyst are methanol to oil volume ratio of 1.5; catalyst to PFAD ratio of 7.4 wt.% and 3 hours of reaction time. 99.34% of FFA conversion was achieved with the homogeneous catalyst.

1. Introduction
The biodiesel produced from non-edible oils is said to be the second-generation biodiesel[1]. In Indonesia, the availability of these non-edible oil resources such as castor oil (Ricinus communis), polanga (Calophylluminophyllum), rubber seed oil (Hevea brasiliensis), sea mango seed oil (Cerberamanghas L), and palm fatty acid distillate (PFAD) is very abundant. Palm fatty acid distillate is a by-product of the palm oil industry (crude palm oil, CPO) with up to 3.25% of PFAD is yielded from every tonne of CPO processed. As the largest producer of palm oil, Indonesia produced 32.5 million tons of CPO in 2015 [2]. Thus, the PFAD generated was 1,056,250 tons. This suggests that the development of the biodiesel industry in Indonesia over PFAD as raw material is substantial. Currently, the majority of PFAD is exported to overseas market as the source of vitamin E in the cosmetics industry, animal feed and raw materials for the oleo-chemical industry. On the contrary, in Indonesia PFAD utilization has not been explored. PFAD comprise mainly of free fatty acids (FFA) ranged from 85 to 100%. An acid-catalyzed esterification pre-treatment, both homogeneous and heterogeneous, is the most suitable initial step to lower the FFA content. Heterogeneous catalysts have always been preferred over homogeneous
catalysts due to their easy separation from products and reusability, lesser purification steps, resulting in less water consumption.

Few numbers of heterogeneous catalysts application in PFAD esterification have been reported. PFAD esterification in the presence of modified Zr-based catalysts, i.e. $\text{SO}_4\text{ZrO}_2$, $\text{WO}_3\text{ZrO}_2$, and $\text{TiO}_2\text{ZrO}_2$ has investigated [3]. Among the three types of catalysts, $\text{SO}_4\text{ZrO}_2$ catalyst generated the highest biodiesel yield of 93.7% which was carried out at 80°C for 2 hours with 6:1 methanol to PFAD molar ratio and catalyst loading of 1 wt.%. A similar investigation was reported [4]. It was concluded that the maximum methyl ester production of 81% was carried out in the presence of $\text{WO}_3\text{ZrO}_2$ at 250°C for 1 minute. Furthermore, the study on mixed Cr : W : Ti oxides catalysts with different mass ratio has been studied [5]. The highest methyl ester content of 83% was obtained at a mass ratio of Cr : W : Ti = 1:1:1 using 2:1 methanol/PFAD molar ratio and increase in temperature until 170 °C for 3 hours. Another PFAD esterification by Shuit and Tan [6] using a multi-walled carbon nanotubes catalyst in a pressurized reactor was performed. The reaction was conducted at 170°C for 3 hours, methanol to PFAD mole ratio of 20 and catalyst loading of 2 wt.%. It was found that the multi-walled carbon nanotubes catalyst prepared via the inset polymerization of poly (sodium-4-styrenesulphonate) gave a biodiesel yield of 93.4%. Moreover, Olutoye et al. compared the performance of three different solid acid catalysts ($\text{ZrFeTiO}$, $\text{ZrFeO}$ and $\text{FeTiO}$) prepared using the sol-gel method [7]. The highest PFAD conversion of 96.45% was observed for the $\text{ZrFeTiO}$ catalyst at a temperature of 170°C, 5 hours of reaction time, methanol to PFAD molar ratio of 3:1 and 3 wt.% catalyst loading. The activities of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ supported on SiO$_2$, MCM-41 and ZrO$_2$ have been studied [8]. The highest reactivity and stability of the catalyst was obtained using $\text{Cs}_{1.5}\text{H}_{1.5}\text{PW}_{12}\text{O}_{40}$ supported with 20 wt.% MCM-41. Methyl ester obtained was 92% at temperature of 85°C, 4 hours of reaction time, 12 wt.% catalyst amount and methanol to PFAD molar ratio of 15. The polymeric mesoporous SO$_3\text{H-ZnAl}_2\text{O}_4$ catalyst prepared at a sulfonation temperature of 100°C and the molar ratio of Al/(Zn + Al) equal to 1 has reported [9]. Resulted in 94.65% of methyl ester obtained [9]. This biodiesel recovery is achieved at a reaction temperature of 100°C, reaction time of 60 min, methanol to PFAD molar ratio of 9:1, and catalyst concentration of 1 wt.%. In light of the foregoing, the application of sulphated alumina as a catalyst in the esterification of PFAD has not been well explored. The performance of sulphated alumina catalyst in esterification of rubber seed oil and used cooking oil has studied [10]. As reported by this research, the sulphated alumina catalyst has a large specific surface area and pore size in addition to high thermal stability. The maximum conversion of 97% rubber seed oil was achieved under the optimum reaction conditions; methanol to oil volume ratio of 1.8; concentration of catalyst/oil of 1.67% (w/v); 7 hours of reaction time and a temperature of 70°C. Meanwhile, 89.97% of used cooking oil conversion was obtained at the optimum reaction conditions; methanol to oil concentration of 1% (w/v); 1 hour of reaction time and temperature of 60°C [11]. Accordingly, the objective of this research was to study the activity of self-synthesized sulphated alumina catalyst, the optimum operating conditions (ratio of methanol to PFAD and catalyst loading) in addition to performance comparison of the catalyst to homogeneous sulphuric acid catalyst.

2. Materials and Method

2.1 Materials

Palm fatty acid distillate (PFAD) used in this research was obtained from PT. Incasi Raya-Padang which contains 95.23 wt.% of free fatty acids (FFA). The chemicals used were including boehmite (from PT. Pertamina-Indonesia), HNO$_3$ (67%, Merck), NH$_3$ (25%, Merck), in addition to sulphuric acid (precursor of sulphated alumina catalyst) and methanol used for esterification reaction (technical grade) supplied by Bratachem, Inc., Indonesia. Meanwhile, alcohol (99%, Merck); phenolphthalein (Merck), and sodium hydroxide (technical grade) were used in FFA analysis.
2.2. Catalyst synthesis
Sulphated alumina catalyst synthesis has been reported [10]. The catalyst was prepared in two stages; gamma-alumina catalyst synthesis followed by wet impregnation with concentrated sulphuric acid.

2.3. Esterification reaction
The esterification reaction was conducted in a batch-wise system using 500 mL three-necked glass flask equipped with hot plate, magnetic stirrer, thermometer and coupled to a condenser to avoid alcohol loss. In all experiments, approximately 25 g (30 mL) of PFAD was weighed and heated at 60°C. Different methanol to PFAD volume ratio in the range of 1.1:1 to 1.7:1, and catalyst loading (12.0 wt.% to 28.0 wt.% of PFAD) were used to investigate their influences on esterification reaction of PFAD. After heated, methanol and catalyst were added into melted PFAD. Following completion of the reactions, the mixture was cooled, discharged and centrifuged. The FFA conversion was determined by the following (AOCS 5a-40) standard method as Eq. (1), where AV<sub>f</sub> and AV<sub>p</sub> were assigned for the acid value of feedstock and product, respectively.

\[
\% \text{FFA} = \frac{AV_f - AV_p}{AV_f} \times 100\%
\]  

(1)

3. Results and Discussion
Changes in textural properties (i.e. surface area, pore diameter and pore volume) of alumina caused by impregnation of concentrated sulphuric acid into γ-Al<sub>2</sub>O<sub>3</sub> for 3 hours have been reported. The pore diameter increases, but the surface area and pore volume of the sulphated alumina decreases with the increase of sulfate loading [11]. The surface area, pore volume and pore diameter of self-synthesized catalyst were 76.387 m<sup>2</sup>/g; 0.11 cm<sup>3</sup>/g and 63.64 Å, respectively.

In addition to the type of catalyst, other factors affecting the FFA conversion are the ratio of methanol to raw materials, catalyst loading, reaction time and temperature along with the stirring speed. In this study, the reaction temperature was set at 60°C and stirrer speed of 400 rpm. Earlier research has shown that methyl ester generated from PFAD esterification reaction was obtained at 7 hours of reaction time.

3.1. PFAD esterification using self-synthesized sulphated alumina solid catalyst

3.1.1. Effect of methanol to oil volume ratio
Catalyst loading used in this experiment was 12 wt.%. Figure 1 depicts a significant increase of FFA conversion with respect to methanol/PFAD volume ratio ranged between 1: 1.3 to 1: 1.7.

![Figure 1. Effect of methanol to PFAD volume ratio on FFA conversion (T = 60°C, catalyst loading 12 wt.% and 7 hours)](image)
An excess amount of methanol as reactant was added to shift the reaction towards the product, in principle, because esterification is a reversible reaction, according to the following stoichiometric equation.

\[ R - \text{COOH} + R'\text{–OH} \leftrightarrow R\text{–CO–CH}_2\text{–R'} + \text{H}_2\text{O} \quad (2) \]

However, this method is not effective where higher methanol to oil ratio will no longer increase FFA conversion [12]. This lack of a significant increase in the esterification reaction, which thus reacted with the PFAD and, therefore pushed the reaction backwards. In this study, the optimum methanol/oil volume ratio was 1.7 (shown in Figure 2).

![Figure 2. Effect of methanol to PFAD volume ratio on FFA conversion (T = 60°C, catalyst loading 28 wt.% and 7 hours)](image)

3.1.2. Effect of catalyst loading

The effect of sulphated alumina catalyst loading on FFA conversion was also investigated (Figure 3). In contrast to the amount of methanol, FFA conversion decreases with the increase of sulphated alumina catalyst loading. FFA conversion of 84% was obtained when methanol/PFAD volume ratio of 1:1.7 and sulphated alumina catalyst loading of 12 wt.% were used. Nevertheless, the conversion was decreased by approximately 3.6% at catalyst loading of 20 wt.. These results demonstrated PFAD esterification reactions limited by mass-transfer in addition to the equilibrium that has been established [13].

![Figure 3. Effect of catalyst loading on FFA conversion (volume ratio methanol to PFAD of 1.7, T = 60°C, and 7 hours)](image)
3.2. **PFAD esterification using homogeneous sulphuric acid catalyst**

### 3.2.1. Effect of methanol to oil volume ratio

This study also investigated the catalytic activity of PFAD esterification using a sulphuric acid homogeneous catalyst. The effect of the methanol/PFAD volume ratio on FFA conversion was observed in the range of 1: 0.9 to 1: 1.5. The reaction was conducted at 60°C with the amount of sulphuric acid catalyst of 7.4 wt.%, magnetic rotation speed of 400 rpm and 3 hours of reaction time. As the amount of methanol in the PFAD esterifications reaction increases, the FFA conversion also increases as shown in Figure 4. FFA conversion of more than 99% was achieved at methanol to PFAD volume ratio of 1.5 and the next experiments will be carried out under these conditions.

![Figure 4. Effect of methanol to PFAD volume ratio on FFA conversion (T = 60°C, catalyst loading 7.4 wt.% and 3 hours)](image)

### 3.2.2. Effect of catalyst loading

25 g of PFAD was used in this study and after melting at 40°C the volume obtained was 30 ml. the volume of sulphuric acid observed was 0.7; 1.0 and 1.3 ml (the density of concentrated sulphuric acid is assumed to be 1.84 g/ml), thus the catalyst/PFAD weight ratio is 5.2%; 7.4% and 9.6%. From Figure 5 it is concluded that an appropriate amount of sulphuric acid catalyst is needed to achieve optimum FFA conversion. The optimum FFA conversion was achieved at sulphuric acid loading of 7.4 wt.%. Increasing the sulphuric acid catalyst loading to 9.6 wt.% did not significantly increase the PFAD esterification reaction. This result showed that the equilibrium has been reached.

![Figure 5. Effect of catalyst loading on FFA conversion (volume ratio methanol to PFAD of 1.5, T = 60°C and 7 hours)](image)
3.2.3. Effect of reaction time
Optimum reaction time was essential to achieve maximum FFA conversion allowing sufficient contact between catalyst, methanol and PFAD. Figure 6 showed that FFA conversion increase on 1–3 hours. Several investigations [14,15] concluded if the reaction time is set longer, the reaction can shift toward the reactants because the esterification reaction is a reversible reaction.

A side from high conversion of FFA catalyzed using sulphuric acid, the acid condition of reaction can cause corrosion of equipment. Furthermore, after reaction was completed, the mixture resulting from the esterification reaction need to be washed to avoid environmental contamination. Accordingly, the use of sulphuric acid homogeneous catalysts was shifted to the acid heterogeneous catalysts [3-6]. As stated previously in the introduction, the optimum temperature for the conversion of FFA from PFAD using a solid catalyst over 90% was achieved at temperatures above 60 °C. In this study, the reaction was carried out at a temperature of 60 °C.

4. Conclusions
The optimum conditions for the esterification reaction catalyzed by sulphated alumina and sulphuric acid were different, and so does the FFA conversion achieved. Heterogeneous sulphated alumina catalyst requires higher optimum parameters than the sulphuric acid catalyst, but allowing lower product generated. The maximum FFA conversion of 84% was obtained using sulphated alumina catalyst at methanol to PFAD volume ratio of 1.7, catalyst loading of 12 wt.% and 7 hours of reaction time. Meanwhile, the optimum parameters for PFAD esterification using a sulphuric acid catalyst are volume ratio of methanol/PFAD volume ratio at 1:1.5 with 7.4 wt.% catalyst loading and 3 hours giving a 99.34% reduction in FFA.

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References
[1] Bikkavolu J and Swarna K 2019 Recent Advances in Material Sciences 693-709
[2] Nazratul Z A K, Gaanty P M, Mohd HAR and Mashitah MY 2017 J Clean Prod 143 1-9
[3] Mongkolbovornkij P, ChampredaV, SutthisripokW and Laosiripojana N 2010 Fuel Process. Technol.911510-16
[4] Laosiripojana N, Kiatkittipong W, Sutthisripok W and Assabumrungrat S2010 Bioresour. Technol.1018416-23
[5] Wan Z and Hameed B H 2014 Energy Convers. Manag.88 669-676
[6] Shuit S H and Tan S H 2014 *Energy Convers. Manag.* 88 1283-89
[7] Olutoye M A, Wong C P, Chin L H and Hameed B H 2014 *Fuel Process. Technol.* 124 54-60
[8] Trakarnpruk W 2013 *Mendeleev Commun.* 23 46-48
[9] Soltani S, Rashid U, Yunus R and Taufiq-Yap Y H 2016 *Fuel* 178 253-262
[10] Ulfah M and Subago 2016 *Reaktor* 16(3) 109-115
[11] Ulfah M, Firdaus, Octavia S, Suherman H and Subagjo 2018 *IOP Conf. Ser. Mater. Sci. Eng.* 543:012007
[12] Konwar L J, Das R, Thakur AJ, Salminen E, Mäki-Arvela P, Kumar N., Mikkola, J-P and Deka D 2014 *J. Mol. Catal. A: Chem.* 388–389 167–176
[13] Yujaroen D, Motonobu G, Sasaki M and Shotipruk A 2009 *Fuel* 88(10) 2011-16
[14] Akinfalabi S-I, Rashid U, Yunus R and Taufiq-Yap Y H 2017 *Renew. Energy* 111 611-619
[15] Syazwani O N, Rashid U, Mastuli M S and Taufiq-Yap Y H 2019 *Renew. Energy* 131 187-196