

## Effectiveness of Fly Ash Heterogeneous Catalyst (FA-SO<sub>3</sub>H) on Biodiesel Synthesis from PFAD by Batch Reactor

Sudrajat Harris Abdulloh<sup>1</sup>, Eko Andrijanto<sup>1</sup>, Saripudin<sup>1</sup>, Anindya Indrita Putri<sup>1</sup>, Dhea Nurul Amalia<sup>1</sup>, Lidya Elizabeth<sup>1\*</sup>

<sup>1</sup>Department of Chemical Engineering, Politeknik Negeri Bandung, Indonesia

\*Email: lidya.elizabeth@polban.ac.id

### ARTICLE INFORMATION

Received 14 July 2023

Accepted 11 May 2024

[doi.org/10.35313/fluida.v17i1.5286](https://doi.org/10.35313/fluida.v17i1.5286)

**Keywords:**  
Biodiesel  
FA-SO<sub>3</sub>H  
PFAD  
Batch reactor

### ABSTRACT

The increasing fossil fuel consumption, along with the decline in the production of petroleum exploration activities, encourages efforts to find alternative fuels, one of which is biodiesel from Palm Fatty Acid Distillate (PFAD). Biodiesel from PFAD using Fly ash (FA)-SO<sub>3</sub>H catalyst, which is a heterogeneous catalyst, can synthesis through esterification. FA used in this study was wet impregnated using 6M sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) for 24 hours so that the highest acid concentration was obtained at a calcination temperature of 500 °C of 1.1654 mmol/gram. The research was conducted with the Response Surface Method (RSM) with the Box Behnken Design model in Design Expert 13 software, and 13 runs were obtained. The resulting model from RSM was obtained as optimum conditions at catalyst loading (%-w) 5-10, methanol: PFAD molar ratio (n/n) 10:1-30:1, reaction time 3-5 hours, and temperature 60 °C. Based on the experimental results and ANOVA, the high conversion is influenced by the high catalyst loading and methanol: PFAD ratio (n/n), with the conversion obtained of 72.89% at a catalyst loading of 10%-w, methanol: PFAD molar ratio of 20 (n/n) and time for 5 hours.

### INTRODUCTION

Supplies of fossil fuels are dwindling. One of the national energy development strategies is to increase energy diversification activities by developing the utilization of new and renewable energy. However, until the end of 2021, the renewable energy mix will still be 12.1% of the total national energy, which is targeted to reach 23% by 2025. If new sources are not found, then petroleum will run out in a short period. One of the utilizations of new renewable sources is Palm Fatty Acid Distillate (PFAD) with a Free Fatty Acid (FFA) content of >80% as a raw material for biodiesel synthesis through an esterification process due to its abundant amount of about 0.21 million tons per year [1].

However, the esterification process of PFAD into biodiesel needs to involve an appropriate acid heterogeneous catalyst to lower reversible reactions so that there is a decrease in Free Fatty Acids with increased

conversion in biodiesel. The esterification process was chosen because it is suitable for high FFA levels (acidic number >5 mg-KOH/g [2]). In addition, heterogeneous catalysts have become the appropriate choice for catalysts because of the ease of catalyst separation, product purification, and simple manufacturing process [3]. One of the heterogeneous catalyst materials derived from waste is Fly ash (FA). Fly ash was chosen because of the SO<sub>3</sub> content that can be responsible for catalyzing esterification reactions and the porous size of fly ash, which shows a specific surface area (m<sup>2</sup>/g) of 4.56 ± 0.40 with a particle size distribution (µm) of 20-70 [4].

Based on previous research, FA catalysts have been used with various treatments to elevate biodiesel yield. Research by Munoz et al., converted waste cooking oil into biodiesel using only FA catalysts without any treatment, resulting in a yield of 78.1%-w [4]. Hidayati et al., treated FA catalysts with calcination and acidification through impregnation using

H<sub>2</sub>SO<sub>4</sub> for 43-48% eugenol esterification [5]. Lathiya et al., analysed the performance of FA catalyst that has been sulfonated into sulphated fly ash for biodiesel conversion from corn oil and produced a yield of 98.25%-w [6].

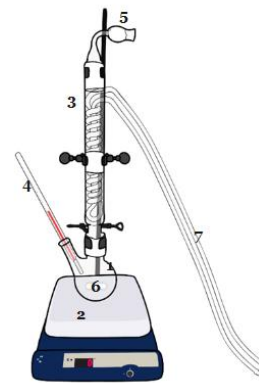
In this study, fly ash heterogeneous catalyst will be made with treatment in the form of acidification through wet impregnation and calcination to improve the quality of the catalyst in assisting the esterification reaction of PFAD as a biodiesel source. Wet impregnation is chosen because it can penetrate the material's pores better to reach deeper areas than dry impregnation. The calcination temperature range of 400 – 800 °C was obtained from the results of Andrijanto and Rob research on sulphated zirconia catalysts, which showed that temperatures > 700 °C caused the decomposition of sulphate groups which cause reduced active sites on the catalyst [3]. The selection of temperature of 400°C was chosen because sulphated fly ash, through impregnation with H<sub>2</sub>SO<sub>4</sub> at a calcination temperature of 400°C caused an increase in surface area from 5 m<sup>2</sup>/g to 49.05-70.13 m<sup>2</sup>/g [5]. Therefore, based on the previous study, the research aims to investigate the effectiveness of Fly ash Heterogeneous Catalyst (FA-SO<sub>3</sub>H) in Biodiesel Synthesis from Palm Fatty Acid Distillate.

## METHODS

This research consists of 2 stages, namely preparation of the FA-SO<sub>3</sub>H catalyst and the synthesis of biodiesel with this catalyst. In catalyst preparation, fly ash was wet-impregnated and calcined at a temperature range of 400-800 °C. Each of these catalysts was used in biodiesel synthesis, and the results were analyzed.

### Material

Fly ash (FA) was from PT PLN Nusantara Power, and Palm Fatty Acid Distillate (PFAD) was from PT Tunas Baru Lampung. H<sub>2</sub>SO<sub>4</sub> 98%, Methanol 99% purity, and Natrium hydroxide and potassium hydroxide pro analyst were purchased from Merck Chemical. The series of esterification equipment is presented in **Figure 1**.



**Figure 1.** Esterification Apparatus

## Methods

### FA-SO<sub>3</sub>H Catalyst Impregnation

Preparation of FA-SO<sub>3</sub>H catalyst was done through wet impregnation to fill the pores of FA with H<sub>2</sub>SO<sub>4</sub> solution based on research [8]. Fifty grams of FA was soaked with 100 mL of H<sub>2</sub>SO<sub>4</sub> solution (6 M) for 24 hours, then oven at 110 °C for 2 hours to dry. Then calcination was carried out at various temperatures (400, 500, 600, 700, 800 °C) for 3 hours. The solid phase of the catalyst obtained was then washed with distilled water until the pH was neutral. Next, it was oven again at 110 °C for 1 hour to remove the water content. The final step was to grind the catalyst.

### Synthesis of Biodiesel from PFAD with FA-SO<sub>3</sub>H Catalyst

The biodiesel synthesis was carried out based on research [7], starting with assembling the esterification equipment, as shown in Figure 1. Then, 20 gr of PFAD was heated separately at 60°C [8]. After heating, methanol was put into the flask, and the solution was heated until it reached the desired temperature. After that, take samples for FFA analysis through the titration method using 0.1 N KOH. Furthermore, a fly ash catalyst was added to the reactor with continuous stirring. The mixture was refluxed for the appropriate time at 60°C. Every 1 hour, a sample of 1 gram was taken to calculate the decrement of FFA content. Finally, the biodiesel was separated from the catalyst using a syringe filter before analyzing the FFA content.

The experimental design using the Response Surface Methodology by Design Expert software is shown in **Table 1**.

**Table 1. Experimental Design**

Run	Ratio Methanol : PFAD (n/n)	Catalyst Loading (%-w)	Time (hour)
1	30	7,5	5
2	20	10	3
3	10	7,5	5
4	20	10	5
5	20	5	5
6	20	7,5	4
7	30	10	4
8	20	5	3
9	30	7,5	3
10	10	7,5	3
11	30	5	4
12	10	5	4
13	10	10	4

The data obtained from biodiesel synthesis is the conversion of PFAD fatty acids into biodiesel. The effect of methanol to PFAD ratio, catalyst loading, and reaction time was calculated statistically by analyzing its significance, namely at p-value <0.05.

#### FA-SO<sub>3</sub>H Catalyst Analysis

Analysis of FA-SO<sub>3</sub>H catalyst concentration was carried out by titration method [3]. A total of 1 gram of catalyst sample was stirred for 1 hour in 30 mL of 0.1 M NaOH solution, then filtered. A total of 10 mL of filtrate in Erlenmeyer was dripped with 3 drops of PP indicator and titrated with 0.1 M HCl. The volume of HCl used was recorded, and the titration was performed in duplicate. The FTIR test of FA-SO<sub>3</sub>H catalyst was carried out using Shimadzu Type: Prestige 21.

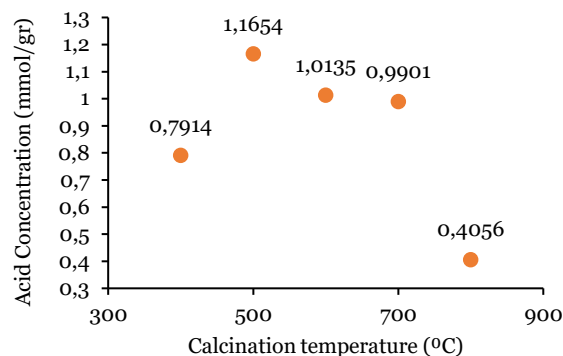
#### Data Biodiesel Analysis

Biodiesel analysis carried out was FFA concentration (mg-KOH/g) (analysis method based on SNI 7182:2015), density and viscosity.

## RESULT AND DISCUSSION

In this study, the analysis of acid concentration was carried out at various calcination temperatures with temperatures of 400 °C, 500 °C, 600 °C, 700 °C and 800 °C to determine the effect of calcination temperature on acid concentration. Calcination activates the FA-SO<sub>3</sub>H catalyst because it can increase its catalytic activity. The calcination process

triggers structural and compositional changes in FA-SO<sub>3</sub>H, altering its surface properties and catalytic activity. In addition, it can increase the ability of FA-SO<sub>3</sub>H as a catalyst because the impregnated acid will be covalently bound.



**Figure 2.** The Effect of Calcination Temperature to Acid Concentration Catalyst

**Figure 2** shows the effect of calcination temperature on the concentration of active sites on the catalysts. The concentration of acid in FA-400 and FA-500 increases as the calcination temperature increases. This is because, the higher the temperature, sulfuric acid can dissociate more into hydrogen ions H<sup>+</sup> and sulphate ions (SO<sub>4</sub><sup>2-</sup>). However, at FA-600, FA-700, and FA-800, the acid concentration decreased significantly. This is because, at 600°C, the catalyst loses sulphate groups due to decomposition and is responsible for the loss of acidity [3].

At temperatures starting from 600 °C, thermal decomposition occurs, which causes the fly ash to become unstable, and a chemical reaction occurs. Leliana et al., research shows that in the TGA results of fly ash, there is a decrease in mass in the temperature range of 600-680 °C where the decomposition of CaCO<sub>3</sub> into CaO occurs [9]. Research by Murzyn et al., shows that thermal process of fly ash at temperatures above 800 °C, the dominant reaction produces oxygen and sulphur dioxide emissions which are the decomposition of sulfur trioxide (redox reaction) [10]. Therefore, figure 2 also shows the acid concentration decreases drastically at a temperature of 800 °C. This

can happen because of the decomposition of  $\text{SO}_3$  into  $\text{SO}_2$ .

FA- $\text{SO}_3\text{H}$  catalysts at various calcination temperatures are shown in **Figure 3**.

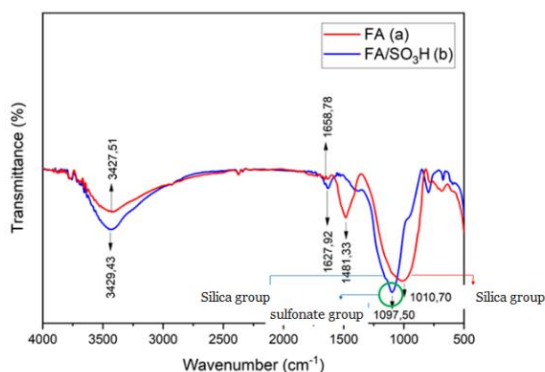


**Figure 3.** FA- $\text{SO}_3\text{H}$  Catalyst

**Figure 3** shows that FA after calcination, where the results have different colors, from light brown to brownish red. This is due to the crystallization of hematite ( $\text{Fe}_2\text{O}_3$ ) from the amorphous part of FA, which involves the oxidation reaction of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ .

#### FTIR Test Results of FA and FA- $\text{SO}_3\text{H}$ Catalysts

The FA- $\text{SO}_3\text{H}$  catalyst at 500 °C with the highest acid concentration was analysed using FTIR to compare fly ash before and after impregnation and identify sulphate groups attached to fly ash. The FTIR analysis is shown in **Figure 4**.



**Figure 4.** FTIR Results of FA and FA- $\text{SO}_3\text{H}$  Catalysts

Based on **Figure 4** and **Table 2**, the fly ash before impregnation showed the absence of the  $\text{SO}_3$  group. However, after activation in the form of impregnation, **Figure 4(b)** shows the appearance of O=S=O ( $\text{SO}_3$  stretching) groups in  $\text{SO}_3$  at a wavenumber of  $1097.5 \text{ cm}^{-1}$  with a transmittance of 14.272%T showing symmetrical and asymmetrical O=S=O stretching modes - $\text{SO}_3$ .

**Table 2.** Functional Group Description in FTIR

Function Groups	Fly Ash		FA- $\text{SO}_3\text{H}$	
	Peak	%T	Peak	%T
Si-O-Si	1010,7	16,713	-	-
O=S=O	-	-	1097,5	14,272
C=O	1629,85	92,397	1627,92	86,542
	1658,78	91,933		
O-H	3427,51	67,952	3429,43	57,817

This is confirmed by the  $\text{SO}_3$  peak at wavelengths of  $1160 \text{ cm}^{-1}$  and  $1030 \text{ cm}^{-1}$  in FT-IR [9]. The presence of - $\text{SO}_3$  and O=S=O stretching modes confirmed the successful attachment of sulphate groups to the fly ash skeleton as active sites for esterification reactions.

#### Catalyst Effectiveness Analysis through Esterification

##### Statistical Analysis

The results of the study were carried out statistical analysis of the Response Surface Methodology (RSM) method and obtained regression to analyse the research data. Research data processing with RSM produces a model with the reaction conversion formula as follows:

$$Y = -147 + 6.72 X_1 + 8.5 X_2 + 23.5 X_3 \quad (1)$$

Description:

Y = biodiesel conversion (%),  $X_1$  = methanol ratio: PFAD (n/n),  $X_2$  = catalyst loading (%-b),  $X_3$  = time (hours).

The results of the study were subjected to statistical analysis of the RSM (Response Surface Methodology) method, which aims to determine the variables that have a significant effect on biodiesel conversion. **Table 3** shows the results of the analysis using Design Expert software.

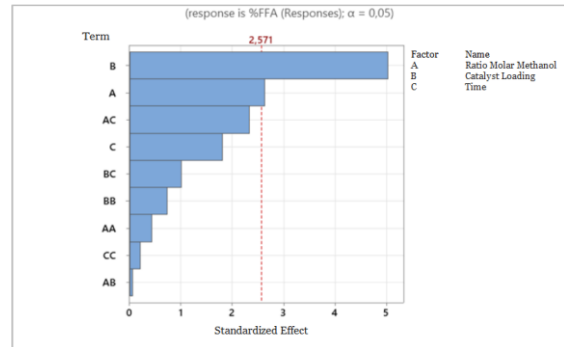
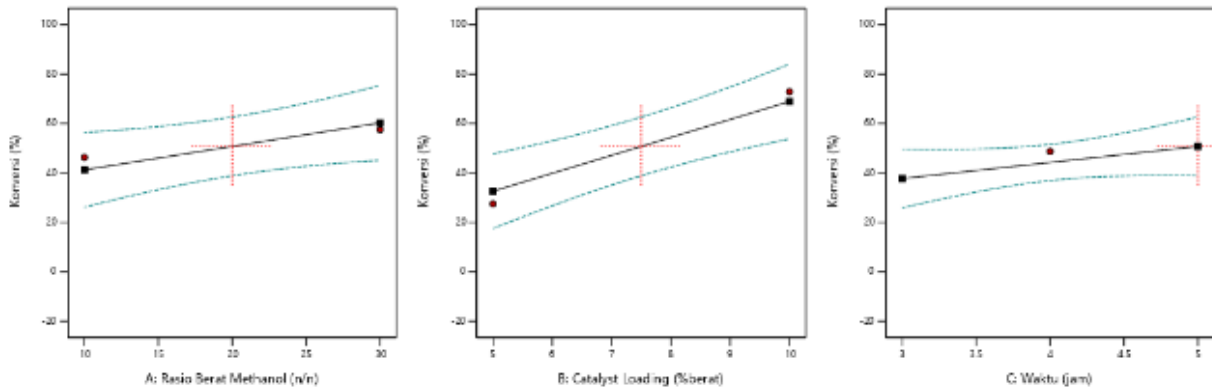
Based on the ANOVA analysis obtained in Table 3, which uses an alpha value ( $\alpha$ ) of 0.05, it shows that catalyst loading has the most significant effect (statistically) among the other 2 variables.

**Table 3.** ANOVA Research Results

Source	F-value	p-value
<b>Significant</b>		
Model	9,00	0,0045
A-methanol: PFAD ratio (n/n)	5,28	0,0472
B-Catalyst Loading (%-b)	19,25	0,0018
C-reaction time (hour)	2,48	0,1499

In addition to the effect of catalyst loading, the performance of conversion is also influenced by the methanol: PFAD ratio, which shows a p-value below the alpha value of 0.0472. However, the time variable was not met. The effect values of the independent variables of the study. The

most influential variables are catalyst loading and methanol ratio, as shown in **Figure 5-6**.

**Figure 5.** Pareto Chart of Research Results**Figure 6.** Graph of the Effect of 3 Variables on Biodiesel Conversion

#### *Interaction of Catalyst loading (%-w) and time (h) on Biodiesel Conversion*

**Figure 7** shows that the esterification time variable did not affect the conversion significantly. It is explained that at 5%-w and 6%-w catalyst loading with variable time from 3-5 hours, the conversion is constant below 30% and 40%. In addition, at 7%-w and 8%-w catalyst loading there was a 1 level increase in conversion at a given time from the range of 40-50% and 50-60%, respectively. An increase in conversion every time occurred in catalyst loading 9%-w and 10%-w but the optimum conversion occurred when the catalyst and time were maximum. From this explanation, catalyst loading plays a very important role in the increase in conversion. This interaction certainly requires a longer time so that the active

sites of the catalyst can increase the contact between the catalyst and the material (vegetable oil). This shows that the diffusion by the reactants to the catalyst surface is faster, thus reducing the time needed to reach the catalytic site. A faster diffusion process accelerates the overall reaction.

#### *Interaction of Methanol Ratio: PFAD (n/n) and Time (Hour) on Biodiesel Conversion*

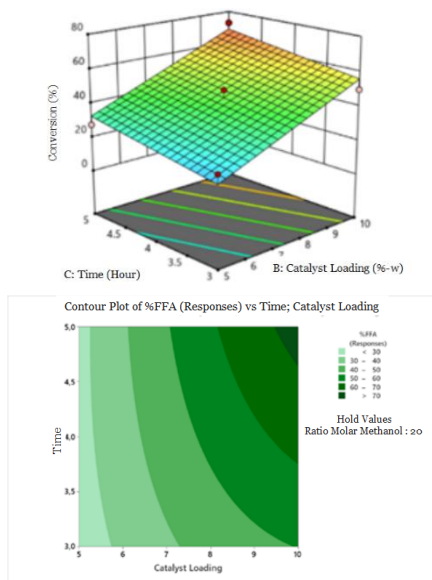
**Figure 8** shows that the ratio of methanol: PFAD 10 (n/n) alone has increased the conversion to a maximum of more than 60%. This also occurs at a molar ratio of methanol: PFAD 15 (n/n) and 20 (n/n). Whereas, at a molar ratio of methanol: PFAD 25 (n/n), the conversion is constant in the range of more than 60% with respect to time. However, at the ratio of methanol:

PFAD 30 (n/n), there is a decrease in conversion to the range of 40-50%. This is because if the mole of methanol used is too high, it can increase by-products in the form of H<sub>2</sub>O. In addition, when viewed from the time variable, increasing esterification time increases the possibility of contact between molecules, which is beneficial for the interaction between particles, which causes the esterification reaction to run toward the product [11].

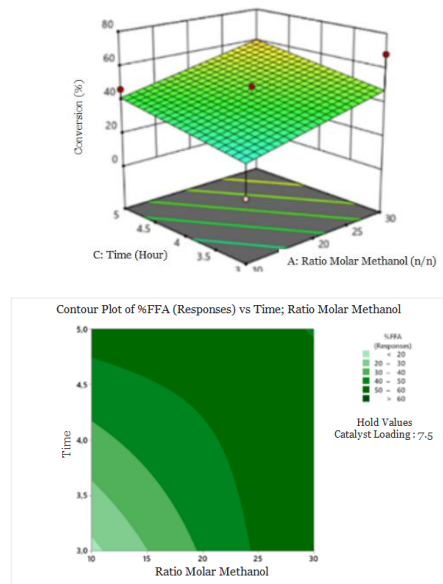
*Catalyst loading (%-w) and Methanol Ratio: PFAD (n/n) on Biodiesel Conversion*

Based on Figure 9, shows that if the ratio of methanol: PFAD ratio is a maximum of 30

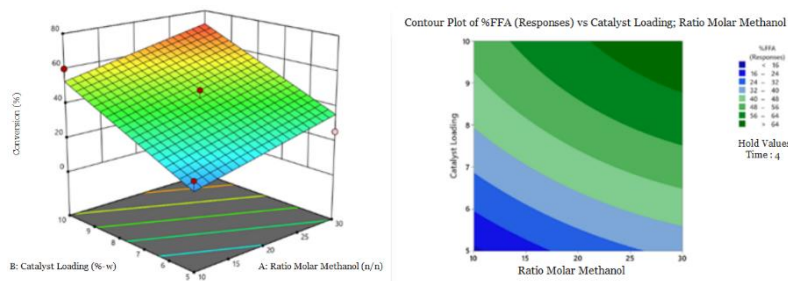
(n/n) with a minimum catalyst loading of 5%-w, the conversion is 32-40%. This value is smaller than the ratio of methanol: PFAD ratio of 10 (n/n) with a maximum catalyst loading of 10%-w, resulting in a conversion of 40-56%. This is because the larger amount of catalyst increases the number of active sites that methanol-soluble PFAD molecules can access. However, if the molar ratio is insufficient, the chance that the molecules can interact with the active sites of the catalyst to initiate the reaction is reduced, resulting in lower conversion.



**Figure 7.** Visualization of the Interaction of Catalyst Loading (%-w) and time (h)



**Figure 8.** Visualization of Interaction of Methanol Molar Ratio: PFAD (n/n) and Time (Hours)



**Figure 9.** Visualization of Interaction of Methanol Molar Ratio: PFAD (n/n) and Catalyst Loading (%-w)

The optimization of operation condition to obtain optimum biodiesel conversion are shown in **Table 4**.

**Table 4.** Biodiesel Conversion Optimization

Parameter	Optimization	Research
1.Methanol: PFAD ratio	14,24	20
2.Catalyst Loading (%-b)	10	10
3. Reaction time (hour)	5	5
4.FFA conversion (%)	74,36	72,89

In Table 4, the results of statistical data processing show that optimization to obtain the highest FFA conversion can be carried out at a methanol to PFAD ratio of 14.24 with an FFA conversion of 74.36%. This condition is more efficient than the research results that have been achieved, namely a methanol to PFAD ratio of 14.24, resulting in an FFA conversion of 72.89%, which is improved the FFA conversion.

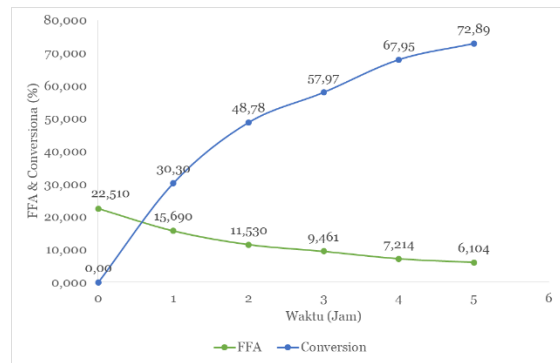
Characteristics of Biodiesel produced are shown in **Table 5**.

**Table 5.** Characteristics of Biodiesel produced

Parameter	Research	SNI
Density (gr/cm <sup>3</sup> )	0,86	0,85-0,89
Kinematic Viscosity (mm <sup>2</sup> /s)	2,38	2,3-6
Acid number (mg KOH/g)	0,13	Maks. 0,4

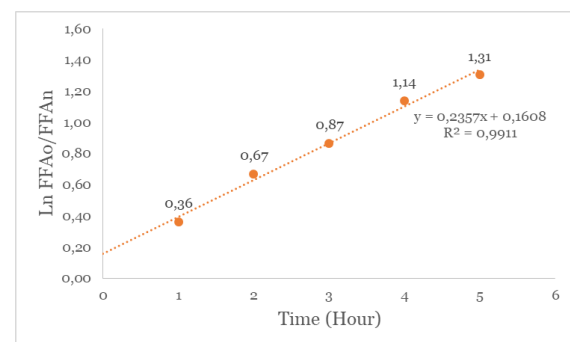
### Kinetics Reaction Study

The kinetics study was conducted in Run 4, which is esterification held at 60 °C, methanol to PFAD ratio 20, catalyst loading 10% and reaction time 5 hours. This run gave the highest conversion in the FA-SO<sub>3</sub>H catalyst. Figure 10 shows the decrease in FFA of the PFAD and the increase in biodiesel conversion.

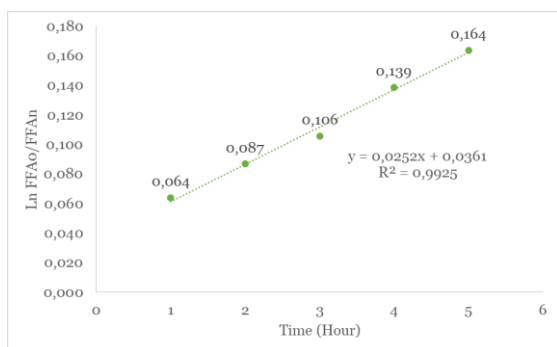


**Figure 10.** Esterification Results on Run 4

Adsorption could be physical (physisorption) or chemical (chemisorption). Physical adsorption results from weak, short-range electrostatic attractive forces arising from a dipole moment (Van Der Waals), and chemisorption involves bond formation between the adsorbate and the adsorbent [12]. In this research, catalyst FA-SO<sub>3</sub> is an adsorbent, and PFAD is an adsorbate. Catalysis reactions follow the adsorption isotherm kinetics, which is considered a reversible process between the adsorbent and the adsorbate. There are two constant rates: the adsorption and desorption rate constant. The most common practice to determine adsorption kinetic parameters or to model the adsorption process is to use linearized models [13]. Therefore, this research's kinetic study compares pseudo-first order (PFO) and pseudo-second order (PSO) reaction kinetics, which are presented in **Figures 11-12**.



**Figure 11.** Pseudo-First-Order Reaction Kinetics on RUN 4



**Figure 12.** Pseudo-Second-Order reaction Kinetics on RUN 4

Based on the comparison of reaction kinetics addressed by Figure 11 and Figure 12 between order 1 and order 2, there is a small difference in R-value or linearity of 0.14%. However, the value of the reaction rate constant of PFO is greater than that of PSO. Therefore, an approach was taken through order 1, which also refers to Saimon et al., and Tang, based on several assumptions, namely (1) Biodiesel production involves only esterification reaction, (2) methanol concentration is constant due to excess methanol used, (3) non-catalytic reactions can be ignored (4) reaction mixture is considered homogeneous without mass transfer limitation with high agitation intensity and a good mixture of methanol with PFAD (5) reverse reaction can be ignored due to excess methanol [14]-[15].

Zappi et al. summarized that, in the adsorption systems they analyzed, PSO kinetics provided the best correlation of experimental data. The superiority of PSO was also reflected by the fact that some studies (around 12%) never bothered to test PFO in their modeling and solely applied PSO for adsorption kinetic parameter determination. In addition, many adsorption studies do not achieve equilibrium, which makes linear PFO modeling unsuitable for direct parameter estimation and only suitable for PSO [13]. Even though the value of the reaction rate constant of PFO is greater than that of PSO, R-squared values are relatively the same (0.9911 for PFO and 0.9925 for PSO). Therefore, the esterification-reaction of PFAD and methanol catalyzed by a fly ash heterogeneous acid catalyst could follow not only linear PFO but also PSO. Further research must be conducted to prove this

kinetic reaction.

## CONCLUSION

Based on the research data that has been obtained, fly ash Heterogeneous Catalyst (FA-SO<sub>3</sub>H) is effective in Biodiesel synthesis from Palm Fatty Acid Distillate, obtaining 72.89% FFA conversion with the operating conditions of Catalyst Loading (10%-w), Methanol: PFAD Ratio (20 n/n) and Time (5 hours). It resulted from (FA-SO<sub>3</sub>H), which was calcinated at 500°C and resulting an acid concentration of 1.1654 mmol/gram. The most significant variable in the biodiesel synthesis process using FA-SO<sub>3</sub>H heterogeneous catalyst based on statistics is Catalyst Loading (%-w).

The kinetics constant of the 1st order reaction in the study was 0.2357 h<sup>-1</sup> from pseudo-first-order kinetic. However, the esterification-reaction of PFAD and methanol catalyzed by a fly ash heterogeneous acid catalyst could follow not only linear PFO but also PSO reactions. Further research must be carried out to establish the kinetics of this reaction.

## ACKNOWLEDGEMENT

The authors are grateful for the support from the Department of Chemical Engineering, Politeknik Negeri Bandung.

## REFERENCES

- [1] D. E. Putri, Y. Azis, and C. D. Alfarisi, "Sintesis Biodiesel Dari Palm Fatty Acid Destillate (PFAD) Menggunakan Katalis Cu-Hap Dengan Variasi Kecepatan Pengadukan Dan Waktu Reaksi," *Jom FTEKNIK*, vol. 5, no. 2, pp. 1–15, 2018.
- [2] H. K. Gurdeep Singh *et al.*, "Five-lump kinetic approach on biofuel production from refined rubber seed oil over Cu/ZSM-5 catalyst via catalytic cracking reaction," *Renew Energy*, vol. 171, pp. 1445–1453, Jun. 2021, doi: 10.1016/j.renene.2021.02.085.
- [3] A. Eko and B. Rob, "The effect of calcination temperature of sulfated zirconia catalyst for simultaneous reactions in biodiesel production," *Research Journal of Chemistry and*



- Environment*, vol. 22, no. Special issue II, pp. 157–162, 2018.
- [4] R. Muñoz *et al.*, “Fly ash as a new versatile acid-base catalyst for biodiesel production,” *Renewable Energy*, vol. 162, pp. 1931–1939, 2020, doi: 10.1016/j.renene.2020.09.099.
- [5] N. Hidayati, T. Pujiati, E. B. Prihandini, and H. Purnama, “Synthesis of solid acid catalyst from fly ash for eugenol esterification,” *Bulletin of Chemical Reaction Engineering and Catalysis*, vol. 14, no. 3, pp. 683–688, 2019, doi: 10.9767/bcrec.14.3.4254.683-688.
- [6] D. R. Lathiya, D. V. Bhatt, and K. C. Maheria, “Sulfated Fly-Ash Catalyzed Biodiesel Production from Maize Acid Oil Feedstock: A Comparative Study of Taguchi and Box-Behnken Design,” *ChemistrySelect*, vol. 4, no. 14, pp. 4392–4397, 2019, doi: 10.1002/slct.201803916.
- [7] A. Hidayat, S. C. Faizah, and R. Trisnaningtyas, “Sintesis Metil Ester dari Minyak Dedak Padi Menggunakan Katalis Kalium dengan Pengmban Zeolit Alam,” *Teknoin*, vol. 23, no. 1, pp. 19–28, 2017.
- [8] N. H. Embong, N. Hindryawati, P. Bhuyar, N. Govindan, M. H. A. Rahim, and G. P. Maniam, “Enhanced biodiesel production via esterification of palm fatty acid distillate (PFAD) using rice husk ash (NiSO<sub>4</sub>)/SiO<sub>2</sub> catalyst,” *Applied Nanoscience (Switzerland)*, vol. 13, no. 3, pp. 2241–2249, 2021, doi: 10.1007/s13204-021-01922-4.
- [9] N. Fitria Apriliani, W. Artha Wirawan, S. Widi Astuti, A. Puspitasari, and A. Leliana, “Thermal Stability of Fly Ash by TGA Analysis for the Development of Composite Railway Brake Blocks,” 2022, doi: 10.2991/978-94-6463-126-5\_31.
- [10] W. Wons, K. Rzepa, M. Reben, and P. Murzyn, “Thermal studies of fly ashes expansion,” *J Therm Anal Calorim*, vol. 143, no. 4, pp. 2883–2891, Feb. 2021, doi: 10.1007/s10973-020-09566-2.
- [11] D. Yu *et al.*, “Study on the Deacidification of Rice Bran Oil Esterification by Magnetic Immobilized Lipase,” *Catalysis Letters*, vol. 150, no. 5, pp. 1256–1267, 2020, doi: 10.1007/s10562-019-02939-9.
- [12] M. Musah, Y. Azeh, J. Mathew, M. Umar, Z. Abdulhamid, and A. Muhammad, “Adsorption Kinetics and Isotherm Models: A Review,” *Caliphate Journal of Science and Technology*, vol. 4, no. 1, pp. 20–26, Feb. 2022, doi: 10.4314/cajost.v4i1.3.
- [13] E. D. Revellame, D. L. Fortela, W. Sharp, R. Hernandez, and M. E. Zappi, “Adsorption kinetic modeling using pseudo-first order and pseudo-second order rate laws: A review,” *Cleaner Engineering and Technology*, vol. 1. Elsevier Ltd, Dec. 01, 2020. doi: 10.1016/j.clet.2020.100032.
- [14] N. N. Saimon, M. Jusoh, N. Ngadi, and Z. Y. Zakaria, “Kinetic study of esterification of palm fatty acid distillate using sulfonated glucose prepared via microwave-assisted heating method,” *Chemical Engineering Transactions*, vol. 78, pp. 403–408, 2020, doi: 10.3303/CET2078068.
- [15] Z. E. Tang, “Synthesis of Corncob Based Carbon Acid Catalyst By Arylation of 4-Benzenediazonium Sulfonate for Biodiesel Production Tang Zo Ee Master of Engineering Science Lee Kong Chian Faculty of Engineering & Science Universiti Tunku Abdul Rahman,” no. January, 2019.