

Biodiesel Synthesis over Biochar-based Catalyst from Sengon (*Paraserianthes falcataria* L. Nielsen) Sawdust

by Arif Hidayat

Submission date: 29-Mar-2023 05:26PM (UTC+0700)

Submission ID: 2049870616

File name: yst_from_Sengon_Paraserianthes_falcataria_L._Nielsen_Sawdust.pdf (623.01K)

Word count: 2333

Character count: 13152

2
Biodiesel Synthesis over Biochar-based Catalyst from Sengon (Paraserianthes falcataria L. Nielsen) Sawdust using Palm Fatty Acid Distillate as Low-Cost Feedstock

Agus Taufiq¹, Sari Arista¹, Bachrun Sutrisno¹, Arif Hidayat^{1,*}

¹Department of Chemical Engineering, Faculty of Industrial Technology, Universitas Islam Indonesia, Yogyakarta 55584, INDONESIA

e-mail: arif.hidayat@uii.ac.id

Abstract. Biodiesel is mostly made from trans-esterification reaction using homogenous catalysts. Problems related to homogenous catalysts are the difficulty to separate the final product and the toxic that the waste contains. To prevent this negative effect, it is suggested to use heterogeneous catalysts. The heterogeneous catalysts have been considered to apply on biodiesel production associated with homogeneous catalysts limitations. Many advantages could be provided by heterogeneous catalysts including easily separated from reaction product, can be used repeatedly, generate less waste water, and environmentally friendly operations. In this paper, the Palm Fatty Acid Distillate (PFAD) esterification to form biodiesel was studied using biochar-based catalyst from sengon (*Paraserianthes falcataria* L. nielsen) sawdust as heterogeneous catalyst. Reaction parameters such as temperature, molar ratio of oil to methanol, and amount of catalyst percentage were varied to achieve the highest conversion. The highest free fatty acids (FFAs) conversion of 89.71%, was obtained by using 60°C of reaction temperature at 12:1 molar ratio of methanol to PFAD and 3% catalyst amount.

Introduction

The important factors encouraging efforts to look for renewable energy sources are the increasing of energy demand and the concerning of global warming in order to environmental pollution, greenhouse gases emission, and depletion fossil fuels supply. The promising renewable energy that considered as an alternative substitute for diesel fuel base petroleum is biodiesel. Biodiesel is a monoalkyl fatty acid ester which has many benefits, such as using renewable sources as raw materials, biodegradable, non-toxic, and contains neither sulfur nor aromatic compounds. Biodiesel can be produced through transesterifying of triglycerides or esterifying of free fatty acids with methanol by adding acid or alkaline catalyst.

The expensive raw material and the competition between food security and energy supply are the problems that associated with the biodiesel production. The utilization of inexpensive raw materials including edible oil and used cooking oils would be reduced the production cost and avoid the problems that occur in the food and energy supply. Thus, the biodiesel synthesis using non-conventional raw materials is necessary to be intensified. Palm oil refinery generates Palm Fatty Acid Distillate (PFAD) that contains high free fatty acids as by-products. The PFAD price is only 0.25 USD/liter which is much lower than the refined palm oil. Therefore, the application of PFAD as raw material for biodiesel production could be diminish the production cost and enabled to contend economically with petroleum-based fuel.

Currently, the biodiesel has been produced commercially by using homogeneous catalysts among them alkaline catalysts (NaOH or KOH) and acids catalysts (H₂SO₄ or HCl). Homogeneous catalysts have many shortcomings, including having to be neutralized after the reaction, difficult to separate from the product, cannot be reused, and lead to environmental problems. To solve the problems associate with the homogeneous catalysts, many reseachers have started to investigate the heterogeneous catalysts for biodiesel production. Usually, the high free fatty acid content on raw materials promotes the saponification reaction when using an alkaline catalyst. Therefore, the converting FFAs on PFAD to form methyl esters apply an acid catalyst.



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.

Different types of solid materials such as sulfated niobium oxide [1, 2], bituminous coal [3], metal oxide [4, 5], sulfonated-multiwalled carbon nanotubes [6] have been investigated as viable heterogeneous acid catalysts for esterification reaction. Carbon-based catalysts such as glucose [7], sucrose [8], carbohydrate-based catalysts [9], biomass waste [10-13], biochar [10, 13, 14], and activated carbon [15], were promisingly as as heterogenous acid catalysts in order to low cost, available abundantly, reusable, stable and have high porosity which promotes catalytic activity. The heterogenous acid catalyst which was synthesized from carbon materials is also prepared by simple procedure, including sulfonation using strong acid to attach SO₃H groups on carbon surface.

Based on literatur survey, the reported study on the utilization of sawdust biochar as heterogenous acid catalyst has not been investigated yet, for biodiesel synthesis from PFAD. In this paper, the esterification of PFAD to form biodiesel was studied using biochar-based catalyst from sengon (*Paraserianthes falcataria* L. nielsen) sawdust as heterogeneous catalyst. Reaction parameters such as oil to methanol molar ratio, temperature, and catalyst amount percentage were varied to achieve the highest conversion.

Experiment

Catalysts Preparation and Characterization

The sengon (*Paraserianthes falcataria* L. nielsen) sawdust were collected from sawmills in Sleman district, D.I. Yogyakarta province. Prior to use, the sawdust precursors were screened to get uniform size with diameter less than 100 mesh. The biochar was obtained by partially carbonization of sawdust in a furnace at 400°C using heating rate of 10°C/min for 4 hours. The resulted biochar was then sulfonated according to the following procedure: (i) biochar was mixed with H₂SO₄ p.a.; (ii) the mixture was agitated vigorously at 150°C for 12 h; (iii) after the sulfonation process was completed, the sulfonated biochar was filtered to be separated from the mixture; (iv) the sulfonated biochar was rinsed with hot distilled water and checked periodically to detect no remaining sulfate ions; and (v) the sulfonated biochar was dried in an oven at 110°C.

The measurement of N₂ adsorption at 77 K was carried out to analyze the porosity of characteristics. To determine the surface functional groups on solid surfaces, the FTIR spectroscopy analysis was conducted. The elements contained on materials were determined by X-Ray Fluorescence instrument. The standard acid-base back-titration was used to calculate the total acid density of the samples.

Results and Discussion

Catalysts Characterization

The biochar and biochar catalyst textural characteristics were analyzed using N₂ adsorption desorption technique to calculate the BET surface area, total pore volume, and average pore size diameter. The biochar catalyst and biochar textural characteristics were presented on Table 1. The reduction in BET surface area from catalyst to the catalyst catalyst indicates the successful of incorporating of SO₃H groups on surface. From Table 1, it also can be confirmed that the average pore size diameter was become wider after sulfonation process. Meanwhile, the total pore volume of biochar catalyst was smaller compared to the biochar. The back titration method was applied to measure the acid density of samples. The acid density of biochar catalyst dramatically increased after the sulfonation process which indicates the success of SO₃H groups anchoring on the surface.

Table 1. The biochar and biochar catalyst textural characteristics.

Samples	Specific surface area (m ² .g ⁻¹)	Average pore size	Total pore volume (cm ³ .g ⁻¹)	Acid Density	
				Total	SO ₃ H
Biochar	266	2.3	0.1631	0.19	n.a.
Bichar catalyst	196	2.5	0.1482	3.24	2.67

The identification of functionalized groups for both biochar and biochar catalyst surface were presented Figure 1. The $\text{-SO}_2\text{-}$ asymmetric and asymmetric stretching vibration bands were indicated at wavenumbers around 1035 and 1154 cm^{-1} . The band at 3431 cm^{-1} (biochar) and 3429 cm^{-1} (biochar catalyst) were ascribed to the phenolic OH groups and O-H stretching of the -COOH . Meanwhile, a wavenumber at 1704 cm^{-1} was correlated with the C=O stretching of COOH group. The content of sulfur in biochar catalyst was analyzed the Energy Dispersive X-ray (EDX) spectrometry analysis. The content of sulfur achieved 6.15% on the biochar catalyst. Based on the results, it can be confirmed that the anchoring of SO_3H groups into biochar catalyst surface was successful by sulfonation using H_2SO_4 concentrated.

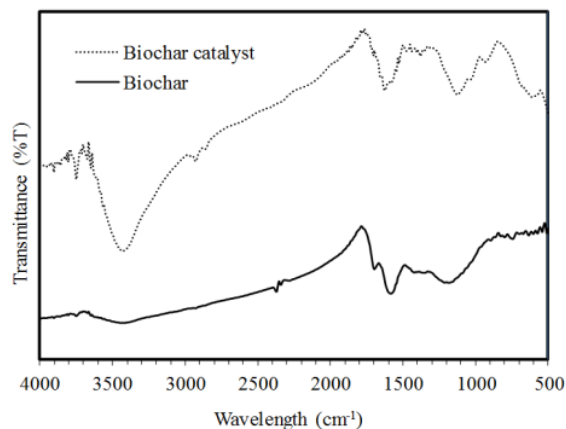


Figure 1. FT-IR Spectra of Biochar and Biochar Catalyst.

Activity Test

Effect of Mole Ratio

The FFA esterification reaction is limited by an equilibrium state. The equilibrium limitation should be shift to the formation of methyl esters by applying methanol excessively. One mole of methanol is needed to esterify one mole of FFAs. In this research, the mole ratio of oil to methanol was varied in the range of 1:4 to 1:10, while other reaction conditions were kept constant for 2 h at 60°C. As shown in Figure 1, the conversion of FFA was 71% at 1:4 of oil to methanol mole ratio. Furthermore, the conversion increased from 74% to 85% at 1:6 and 1:8 of oil to methanol mole ratio respectively. The maximum conversion at 89% was achieved at 1:10 of oil to methanol mole ratio.

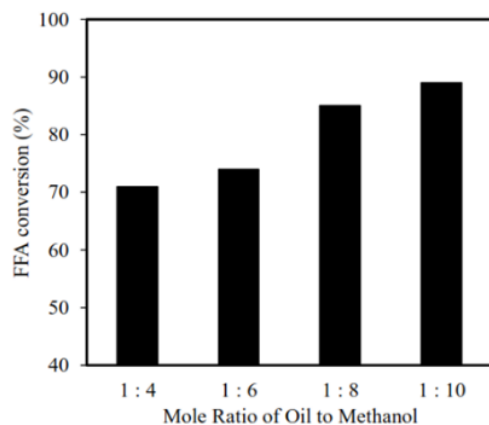


Figure 2. Mole Ratio Effect on FFA Conversion.

Reaction Temperature Effect

The investigation of reaction temperature effect on the FFAs conversion was studied at temperatures range of 30 to 60°C, while percentage of loading catalyst and the oil to methanol mole ratio were maintained stable at 10 wt. % of oil and 1:10, respectively. The reaction temperature effect on conversion was shown in Figure 2. As exhibited in Figure 2, the FFA conversion was 64% at a 30°C of reaction temperature. Subsequently, the conversion achieved 75 and 83% at reaction temperature of 40 and 50°C, respectively. The FFA conversion of 89% was obtained as maximum when the reaction temperature was 60°C.

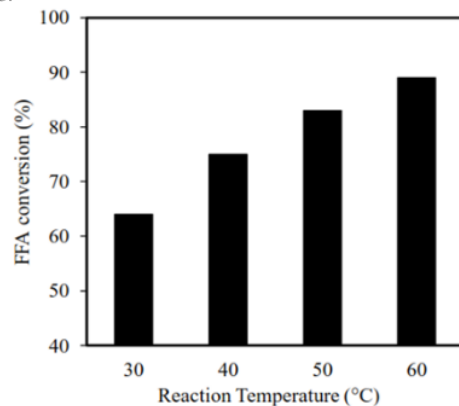


Figure 3. Reaction Temperature on FFA Conversion.

Catalyst Amount Effect

The catalyst amount effect on FFA conversion was investigated by varying the amount of catalysts within the range of 1 to 10 wt. % of oil. The effect of catalyst amount on FFA conversion is presented in Figure 2. From the results obtained as shown in Figure 2, increasing the catalyst amount results the enhancement of FFA conversion. The maximum conversion was obtained at 10 wt. % of oil catalyst amount.

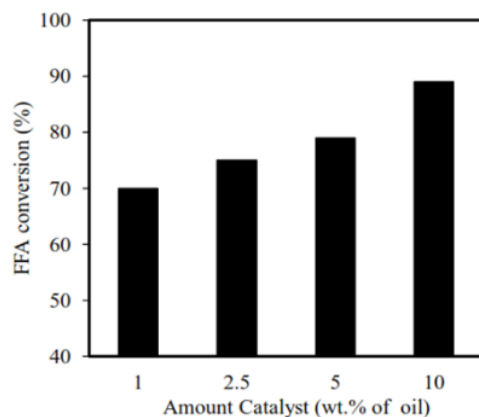


Figure 4. Catalyst Amount Effect on FFA Conversion.

Conclusions

The biochar-based catalyst from Sengon (*Paraserianthes falcataria* L. Nielsen) Sawdust was successfully synthesized by sulfonation process. The biochar-based catalyst was applied as heterogeneous catalyst for biodiesel production using Palm Fatty Acid Distillate. Reaction parameters such as temperature, oil to methanol molar ratio, and catalyst amount were varied to achieve the highest conversion. The highest free fatty acids (FFAs) conversion of 89.71%, was obtained by using 60°C of reaction temperature at 12:1 molar ratio of methanol to PFAD and 3% catalyst amount.

References

- [1] da Conceição LRV, Cameiro LM, Rivaldi JD, de Castro HF. Solid acid as catalyst for biodiesel production via simultaneous esterification and transesterification of macaw palm oil. *Industrial Crops and Products* 2016;89:416.
- [2] Alessio C, Ribeiro JS, Celante D, Brondani L, Castilhos F. Kinetics of methyl esters production with dimethyl carbonate over niobium phosphate. *Energy Conversion and Management* 2017;151:670.
- [3] Tang X, Niu S, Zhao S, Zhang X, Li X, Yu H, et al. Synthesis of sulfonated catalyst from bituminous coal to catalyze esterification for biodiesel production with promoted mechanism analysis. *Journal of Industrial and Engineering Chemistry* 2019;77:432.
- [4] Vieira SS, Magriotis ZM, Santos NAV, Saczk AA, Hori CE, Arroyo PA. Biodiesel production by free fatty acid esterification using lanthanum (La³⁺) and HZSM-5 based catalysts. *Bioresource Technology* 2013;133:248.
- [5] Park Y-M, Lee JY, Chung S-H, Park IS, Lee S-Y, Kim D-K, et al. Esterification of used vegetable oils using the heterogeneous WO₃/ZrO₂ catalyst for production of biodiesel. *Bioresource Technology* 2010;101:S59.
- [6] Shu Q, Zhang Q, Xu G, Wang J. Preparation of biodiesel using s-MWCNT catalysts and the coupling of reaction and separation. *Food and Bioprocess Processing* 2009;87:164.
- [7] Ayodele OO, Dawodu FA. Production of biodiesel from *Calophyllum inophyllum* oil using a cellulose-derived catalyst. *Biomass and Bioenergy* 2014;70:239.
- [8] Theam KL, Islam A, Lee HV, Taufiq-Yap YH. Sucrose-derived catalytic biodiesel synthesis from low cost palm fatty acid distillate. *Process Safety and Environmental Protection* 2015;95:126.
- [9] Lou WY, Zong MH, Duan ZQ. Efficient production of biodiesel from high free fatty acid-containing waste oils using various carbohydrate-derived solid acid catalysts. *Bioresource Technology* 2008;99:8752.
- [10] Mukti NIF, Sutrisno B, Hidayat A. Production of Biodiesel by Esterification of Free Fatty Acid

- over Solid Catalyst from Biomass Waste. IOP Conference Series: Materials Science and Engineering. 1 ed; 2018.
- [11] Farabi MSA, Ibrahim ML, Rashid U, Taufiq-Yap YH. Esterification of palm fatty acid distillate using sulfonated carbon-based catalyst derived from palm kernel shell and bamboo. *Energy Conversion and Management* 2019;181:562.
- [12] Pradana YS, Hidayat A, Prasetya A, Budiman A. Application of coconut-shell activated carbon as heterogeneous solid catalyst for biodiesel synthesis. *Defect and Diffusion Forum* 2018;382 DDF:280.
- [13] Hidayat A, Sutrisno B. Esterification free fatty acid in sludge palm oil using ZrO₂/SO₄²⁻ - Rice husk ash catalyst. *AIP Conference Proceedings*; 2017.
- [14] Hidayat A, Rochmadi, Wijaya K, Budiman A. Reaction kinetics of free fatty acids esterification in palm fatty acid distillate using coconut shell biochar sulfonated catalyst. *AIP Conference Proceedings*; 2015.
- [15] Pradana YS, Hidayat A, Prasetya A, Budiman A. Biodiesel production in a reactive distillation column catalyzed by heterogeneous potassium catalyst. *Energy Procedia*; 2017, p. 742.

Biodiesel Synthesis over Biochar-based Catalyst from Sengon (Paraserianthes falcataria L. Nielsen) Sawdust

ORIGINALITY REPORT

16%

SIMILARITY INDEX

12%

INTERNET SOURCES

15%

PUBLICATIONS

0%

STUDENT PAPERS

PRIMARY SOURCES

- 1 Wan Zairani Wan Bakar, Ismail Mohd Saaid, Husna Hayati Jarni, Noor Aqsa Nadeea Mat Isa et al. "An Investigation on The Effect of Silica Nanoparticle Concentration on Oil-based Mud Rheology and Fluid Loss Control Characteristic", IOP Conference Series: Materials Science and Engineering, 2020
Publication 7%
- 2 iopscience.iop.org
Internet Source 5%
- 3 repository.up.ac.za
Internet Source 3%
- 4 N. I. F. Mukti, B. Sutrisno, A. Hidayat. "Production of Biodiesel by Esterification of Free Fatty Acid over Solid Catalyst from Biomass Waste", IOP Conference Series: Materials Science and Engineering, 2018
Publication 2%

Exclude quotes On

Exclude matches < 2%

Exclude bibliography On