PALM KERNEL SHELL BIOCHAR CATALYST FOR BIODIESEL PRODUCTION FROM WASTE COOKING OIL

Widayat¹, A A A Fernanda² and E S Silvie³
¹ Professor and Lecturer, Chemical Engineering Department, Diponegoro University, Indonesia
² Student, Chemical Engineering Department, Diponegoro University, Indonesia
³ Student, Chemical Engineering Department, Diponegoro University, Indonesia

Email : yayat_99@yahoo.com

Abstract. Biodiesel is an alternative fuel and have properties similar to conventional diesel. The process of making biodiesel requires two stages of the process; namely esterification then proceed with the transesterification. But to keep the process efficient, the esterification and transesterification are carried out simultaneously. A new type of catalyst is being developed that comes from carbonization of incomplete natural products called biochar. Biochar has better catalyst performance for FFA esterification, and higher stability than other solid acid catalysts. The research procedure consist of stages: Pretreatment Palm Kernel Shell (PKS), Increasing Surface Size and Porosity, catalyst impregnation with H₂SO₄ and (NH₄)₂Fe(SO₄)₆.6H₂O, and the biodiesel manufacture. Weight variations of the catalyst (1% wt; 1.5 wt%; 2% wt, 2.5% wt; and 3% wt) and variations of temperature (50°C; 55°C; 60°C; 65°C; 70°C) to the %FAME biodiesel produced, is used in this research.

1. Introduction

Energy has an important role and cannot be separated from human life. The sustainable use of natural resources should be in line with the improvement of technology, when technology develops along with issues such as cleaner environments, processing of raw materials for oil manufacture, and others [1]. High oil price increases, due to the imbalance between fuel oil needs by the public against the availability of petroleum-based products. It has made the scientific community think of renewable alternative energy as a substitute for petroleum [2].

Biodiesel is an alternative fuel that can replace diesel. Biodiesel is a mixture of fatty acid methyl ester (FAME) produced from raw oil materials such as vegetable oils, oil that can not be consumed (non-edible oil), cooking oil, animal oil/fats that can be used in diesel engines without further modification [3]. The main reaction of biodiesel production is esterification and transesterification reactions. Biodiesel is generally obtained through a batch reaction using homogeneous catalysts such as potassium hydroxide, sodium hydroxide, as well as sodium methoxide [4]. The use of homogeneous catalysts has some weaknesses in both economic and efficiency. The already formed Biodiesel still requires a separation operation from its catalyst, so it required more cost. The use of a homogeneous catalyst is also less efficient as it can only be used once in production operation [5]. To avoid this problem, the use of a heterogeneous acid/base catalyst for transesterification reactions has been widely used because it is not too corrosive, easily separated and more environmentally friendly [6].

A new type of catalyst began to be developed derived from the carbonization of incomplete natural products called Biochar. Biochar has better catalyst performance for FFA esterification, and higher stability than other solid acid catalysts. The Biochar-based solid acid catalyst is the latest and most promising catalyst for its environmentally safe nature. With the presence of a heterogeneous solid acid catalyst, two-step biodiesel production (esterification and transesterification) can be carried out in one step at a time, thereby reducing further washing, neutralization, and Catalyst Solsification [2]. Biochar
has great potential to be used as a carbon catalyst or supporter in biodiesel synthesis due to its low price, functional surface, and high surface volume ratio [6].

This research will focus on manufacturing the Biochar catalyst from the PKS (Palm Kernel Shell) for the production of biodiesel from Waste Cooking Oil (WCO) with simultaneous esterification and transesterification methods. Inexpensive raw materials such as used cooking oil and animal fats have been used to replace refined vegetable oils to improve the economical feasibility of biodiesel [7].

The purpose of this study is to examine the process of creating a biochar catalyst from Palm Kernel Shell (PKS) and its characteristics through XRD and SEM analysis for the simultaneous production process of biodiesel, comparing the performance of the Biochar H₂SO₄ and (NH₄)₂Fe(SO₄)₂·6H₂O catalyst for biodiesel production and reviewing the impact of the best catalyst on used oil (% wt) and operating temperature (°C) on biodiesel products.

Based on previous research, the synthesis of biodiesel through two stages are esterification using acid catalysts and transesterification using a base catalyst. Therefore, at this research, in the production of biodiesel a heterogeneous catalyst of biochar from Palm Kernel Shell are used. To achieve maximum biodiesel results, the study was conducted with a weight variation of the Catalyst Biochar H₂SO₄ and the Catalyst Biochar (NH₄)₂Fe(SO₄)₂·6H₂O and also the variation in operating temperature in biodiesel production.

2. Materials and Methods

The main ingredients used in this research are Palm Kernel Shells, used cooking oil, aquadest, KOH, H₂SO₄, (NH₄)₂Fe(SO₄)₂·6H₂O, NaOH, HCl, and methanol. The tools used in this research are scales, glass beaker, measuring cup, oven, mixer, porcelain cup, triple neck flask, magnetic stirrer, hotplate stirrer, thermometer, condenser, static and water bath.

The fixed variables on this study are the comparison of mole oil : methanol (1:12), stirring speed (600 rpm), time (4 hours) and oil mass (100 gram). While the Independent variable are % weight catalyst (1% wt; 1.5% wt; 2% wt; 2.5% wt; 3% wt) and operating temperature (50 °C; 55 °C; 60 °C; 65 °C; 70 °C). Dependent Variables on this research are the % FAME, % FFA, density and viscosity.

Research is conducted on a laboratory scale. The stages of the process in this study consist of material preparation, increase of surface area and porosity, catalyst functionalization, catalyst characterization, biodiesel manufacturing process and biodiesel product analysis.

The preparation phase of raw materials starts from making charcoal from palm kernel shell. After carbon charcoal formed, then charcoal are mashed and sized by using sieving tool. The next stage is increasing the surface area and porosity via chemical activation method using KOH as a activating agent with a comparison of the carbon Mass : KOH (1:3). The dry carbon is impregnated in the solution of KOH and stirred for 2 hours followed by filtering and drying in the oven at a temperature of 110°C for 4 hours. The next stage is catalyst functionalization. The functionalization of the catalyst is performed using H₂SO₄ and (NH₄)₂Fe(SO₄)₂·6H₂O. For H₂SO₄ it is used a comparison of Biochar and H₂SO₄ 1 g : 6 mL. 5 grams of biochar and 30 mL sulfuric acid (85% wt) mixed in 100 mL flask and stirred for 1.4 hours. For (NH₄)₂Fe(SO₄)₂·6H₂O used 5% wt. That is by mixing 5 grams (NH₄)₂Fe(SO₄)₂·6H₂O with 95 grams of biochar, then dissolved with aquadest and stir for 1.4 hours. Then it is washed until the washing water is neutral, and then dried in the oven at 110°C for 4 hours. The next stage is a catalyst characterization with XRD (X-ray diffraction) to determine the level of crystallinity of the catalyst and the SEM (Scanning Electron Microscope) to find out the surface structure and pore distribution of the catalyst. The next phase is the biodiesel manufacturing process using the Biochar H₂SO₄ catalyst and the Biochar (NH₄)₂Fe(SO₄)₂·6H₂O catalyst with a catalyst weight variation (% wt) and the operating temperature (°C). Then the final stage is the analysis of biodiesel products. Biodiesel products that have been separated from catalysts are then analyzed using GCMS (Gas Chromatography Mass Spectrometry) for further assessment of the results obtained.

The data obtained from this research are catalyst morphological structures, crystallinity levels of catalysts, % FFA, % FAME, biodiesel density, and biodiesel viscosity.
3. Result and Discussion

3.1. Raw Material Characteristics

3.1.1. Characteristics of Waste Cooking Oil (WCO). WCO is used as a raw material for the research, the characteristics are shown below

| Material   | Density (kg/m$^3$) | Viscosity (cSt) | FFA (%) |
|------------|--------------------|-----------------|---------|
| WCO        | 910                | 7               | 5.35    |

The analysis result shows that the free fatty acid (FFA) content is 5.35%, because the FFA level of waste cooking oil (WCO) is above the level set by SNI (> 1%), it is necessary to carry out by 2-stage process, namely esterification and transesterification. Esterification is carried out first to convert FFA to methyl ester before the transesterification reaction is carried out. This is because if the FFA level is too high during transesterification, soap can form [8]. Viscosity that is too high can also impede the practical performance of biodiesel. Chemical and physical modifications have been studied to reduce the viscosity of biodiesel in order to appropriate standards, which is through the transesterification process [9]. So this research used the transesterification esterification process simultaneously.

3.2. Characteristic of Biochar Catalyst from Palm Kernel Shell

3.2.1. Analysis of Catalyst surface morphological structure. The surface morphological structure of activated carbon and biochar catalyst has been analyzed using SEM (Scanning electron microscope) with a magnification of 10,000x. The results of SEM observations for the surface of activated carbon and biochar catalyst are shown in Figure 1.

![Figure 1](image-url)

Figure 1. The results of the morphological appearance of biochar catalyst (a) carbon (b) carbon after KOH activation (c) (NH$_4$)$_2$Fe(SO$_4$)$_2$·6H$_2$O impregnation (d) H$_2$SO$_4$ impregnation

Figure 1 shows a picture of the morphological structure of carbon, activated carbon and biochar catalyst by impregnation. The morphological structure of carbon prior to activation (a), it can be seen
that on the carbon surface there are many pores with different diameters and these pores have not opened completely. This statement is also in accordance with the research of Ma et al. [10]. Carbon from coconut shells has pores with varying diameter sizes from small to large sizes, so it has the potential for high absorption power. Even though it has a high potential for absorption power, the carbon that is formed needs to be activated first with physical and chemical activation to get a more optimal pore size so that it can increase absorption power. The morphological structure for carbon after activation using KOH (b), it appears that many pores are formed on the carbon surface and with a cleaner surface. This is because during chemical activation, the KOH solution, which is a strong base, is mixed with carbon, which functions as an activating agent that will oxidize the carbon and damage the inner surface of the carbon. KOH solution can also function to remove impurities in carbon so that it makes carbon more porous and increases its absorption power [11]. The morphological structure of biochar with impregnation using \( (NH_4)_2Fe(SO_4)_2\cdot6H_2O \) (c) shows a smoother surface and some of the pores are closed even though there are still pores with a large diameter. This is due to the nature of Fe which is classified as metallic so that it has a larger active side in the carbon decomposition process and is easier to decompose, so that when added with a carbon catalyst support (Biochar) which also has active groups on its molecule, the carbon pore diameter is formed. become bigger [12]. The morphological structure for bichar with impregnation using \( H_2SO_4 \) (d), it can be seen that on the surface of the catalyst there are many pores with a smaller diameter than the pore size before impregnation. Some of the surface of the catalyst also appeared to be damaged. This is because \( H_2SO_4 \) is a strong and reactive acid so that it can damage the catalyst pores [13].

3.2.2. **XRD Analysis**. To determine the crystallinity of the catalyst used the X-ray diffraction method. In XRD analysis, the catalyst crystals diffract the X-rays sent from the source and received by the detector. The results of XRD analysis on the biochar catalyst can be seen in Figure 2.

![Figure 2](image-url)

**Figure 2.** XRD analysis results for impregnated biochar catalyst using \( (NH_4)_2Fe(SO_4)_2\cdot6H_2O \) and \( H_2SO_4 \)

**Figure 2.** shows the pattern of xrd analysis results in the form of a 2θ observed intensity point diffractogram for catalysts impregnated with \( H_2SO_4 \) which has the highest intensity located at peak 44,160. While the samples impregnated \( (NH_4)_2Fe(SO_4)_2\cdot6H_2O \) had the highest intensity at peak 64,410. The results of the structure detected from the XRD analysis results based on the match software, show the presence of an S atom peak which indicates the presence of \( SO_3H \) compounds as the active side of
the catalyst. This is in accordance with the research of Mo et al. [14] and Liu et al. [15] who stated that the S atom read in the XRD analysis was part of the –SO₃H group.

3.3. Effect of Catalyst Type on Biodiesel Production.

In this research, H₂SO₄ and (NH₄)₂Fe(SO₄)₂.6H₂O were used for catalyst impregnation. To compare the performance of the two types of catalysts on biodiesel production, the best biodiesel production from each catalyst is compared. Based on the research, it was found that the best results for H₂SO₄ catalyst produced 98.43% FAME at a concentration of 3% and a temperature of 60°C. Whereas on the catalyst (NH₄)₂Fe(SO₄)₂.6H₂O obtained the best results with 54.63% FAME at a concentration of 2% and a temperature of 60°C. The effect of the type of catalyst on biodiesel production is presented in Figure 3.

![Figure 3](image_url)

**Figure 3.** Comparison of the catalyst impregnation with H₂SO₄ and (NH₄)₂Fe(SO₄)₂.6H₂O

In the reaction, the triglycerides will be converted gradually into diglycerides, monoglycerides, and glycerol. Liu, et al. [1] used an acid magnetic catalyst to convert used cooking oil into biodiesel. The results of his research showed that the perfect triglyceride conversion rate to produce biodiesel was quite low, where in 1 hour the total FAME reaction produced was only 38%. This indicates that the transesterification reaction has not been completed completely. He concluded that it would take 9 hours to produce the optimal conversion using an acid magnetic catalyst.

3.4. Effect of Catalyst Concentration on Biodiesel Characteristics.

Biodiesel is made by using 1:12 mole ratio of waste cooking oil and methanol at 60°C for 4 hours with various concentrations of Biochar catalysts (1 gr, 1.5 gr, 2 gr, 2.5 gr and 3 gr) using H₂SO₄ catalyst. The biodiesel FAME is showed in Figure 4.
Figure 4. Effect of H$_2$SO$_4$ biochar catalyst concentration on FAME Biodiesel

Figure 4 shows the effect of catalyst concentration on FAME biodiesel produced. Where the more the catalyst concentration the tendency will increase. When the concentration of the catalyst is low, the active sites of the catalyst are not able to activate the reactants. Hence, when the concentration is higher, the active sites will increase at the specified condition [16]. The catalyst is known to decrease the activation energy required for the reaction to occur. So that an increase in the number of catalysts in the reaction system will shift the reaction to the product [17]. In this experiment, the results obtained are in accordance with the theory. The best catalyst was obtained at a concentration of 3% with% FAME of 98.43%. Meanwhile, the lowest yield was at a concentration of 1% with% FAME of 77.64%.

3.5. Effect of Using Various Temperature in Biodiesel Production .

Biodiesel is made using a mole ratio of used cooking oil and methanol of 1:12 for 4 hours with variations in operating temperature (50°C, 55°C, 60°C, 65°C and 70°C) using the best catalyst (H$_2$SO$_4$). Mainstream operating temperature against % FAME biodiesel shows in Figure 5.
Figure 5. Effect of temperature operation on FAME Biodiesel using H$_2$SO$_4$ Biochar Catalyst

Figure 5. shows the effect of temperature operation on the FAME of biodiesel production. Biodiesel production will increase to a certain point before declining. The higher temperature can decrease the viscosity of the oil and increase reaction rate. However, if temperature rises above the optimal temperature, biodiesel production will decrease because it can reduce the alcohol content when the alcohol evaporates. The range of optimal temperature is about 50-60°C [18]. At temperature of 50°C, it was found that% FAME is 95.41% which increased to 60°C with% FAME of 98.43%. Then at a temperature of 65°C there was a decrease where the %FAME is 86.22% and at 70°C% FAME is 85.16%.

3.6 Characteristic of Biodiesel Product

Table 2. Characteristic of biodiesel product

| Parameter | Result | SNI |
|-----------|--------|-----|
| Density (kg/m$^3$) | | |
| H$_2$SO$_4$ Catalyst | 866-877 | 850-890 |
| (NH$_4$)$_2$Fe(SO$_4$)$_2$.6H$_2$O) Catalyst | 867-879 | |
| Viscosity (cSt) | | |
| H$_2$SO$_4$ Catalyst | 4.36-5.81 | 2.3-6 |
| (NH$_4$)$_2$Fe(SO$_4$)$_2$.6H$_2$O) Catalyst | 4.79-5.73 | |
| FFA (%) | | |
| H$_2$SO$_4$ Catalyst | 1.15-1.92 | <1 |
| (NH$_4$)$_2$Fe(SO$_4$)$_2$.6H$_2$O) Catalyst | 1.38-1.94 | |

Based on Table 2. The higher amount of catalyst used, the density and viscosity values of the resulting product tend to decrease. The decrease in density value is due to the triglycerides in used cooking oil that will break down to form methyl esters and glycerol [19]. The resulting product has a density range of 0.866-0.879 gr / cm$^3$ and a viscosity of 2.6-6.6 at room temperature. The used cooking oil as raw material has an FFA value of 5.35% while the resulting product FFA has a range of FFA values of 1.15-1.92% for the H$_2$SO$_4$ variable and 1.13-1.94% for the variable (NH$_4$)$_2$Fe(SO$_4$)$_2$.6H$_2$O). According to SNI 7182-2015, biodiesel has a density value range of 0.85 - 0.9 gr / cm$^3$ and a viscosity of 2.8 - 6 cSt and FFA <1.

4. CONCLUSION

The conclusion of this study is that the biochar catalyst from Palm Kernel Shell can be used for simultaneous biodiesel production. H$_2$SO$_4$ biochar catalyst is the catalyst that produces the best %FAME than biochar (NH$_4$)$_2$Fe(SO$_4$)$_2$.6H$_2$O). The greater the concentration of catalyst added, the %FAME will increase. The increase in temperature causes %FAME to increase to the optimal temperature and then it will decrease at the use of higher temperatures.

5. REFERENCES

[1] Liu W, Jiang H and Yu H 2015 Development of Biochar-Based Functional Materials: Toward a Sustainable Platform Carbon Material Chemical Reviews, 115(22), 12251-12285
[2] Chellappan S, Nair V, Sajith V and Aparna K 2018 Chinese Journal of Chemical Engineering Synthesis, optimization and characterization of biochar based catalyst from sawdust for simultaneous esterification and transesterification Chinese Journal of Chemical Engineering, 2–11.
[3] Noiroj K, Intarapong P, Luengnaruemitchai A and Jai-In S 2009 A comparative study of KOH /Al2O3 and KOH/NaY catalysts for biodiesel production via transesterification from palm oil Renewable Energy, 34(4), 1145–1150.
[4] Theam K L, Islam A, Choo Y M and Taufiq-Yap Y H 2015 Biodiesel from low cost palm stearin using metal doped methoxide solid catalyst Industrial Crops and Products, 76, 281–289.
[5] Shajaratun et al 2014 Production of biodiesel from palm oil using modified Malaysian natural dolomites Energy Conversion and Management, 78, 738–744.
[6] Zhao C et al 2018 Biodiesel synthesis over biochar-based catalyst from biomass waste pomelo peel Energy Conversion and Management, 160(January), 477–485.
[7] Felizardo P et al 2006 Production of biodiesel from waste frying oils Waste Management, 26(5), 487–494.
[8] Nurhayati et al 2018 The Effects of Catalyst Weight and Mole Ratio of Oil-Methanol on Crude Palm Oil (CPO) Esterification using H₂SO₄ (3M)/ Clay Catalyst Journal of Physics : Conf. Series 1093(2018) 012006
[9] Lee D W, Park Y and Lee K 2009 Heterogeneous Base Catalysts for Transesterification in Biodiesel Synthesis Catal Surf Asia (2009) 13:63-77
[10] Ma Z et al 2017 Evolution of the chemical composition, functional group, pore structure and crystallographic structure of bio-char from palm kernel shell pyrolysis under different temperatures Journal of Analytical and Applied Pyrolysis, 127, 350–359.
[11] Taer E et al 2015 Impedance spectroscopic analysis of composite electrode from activated carbon/conductive materials/ruthenium oxide for supercapacitor applications Pakistan : Research Institute of Chemistry, University of Karachi
[12] Benhamed I, Barthe L, Kessas R and Julcour C 2016 Effect of transition metal impregnation on oxidative regeneration of activated carbon by catalytic wet air oxidation Applied Catalysis B: Environmental 187 (2016) 228–237
[13] Velasco U, Sierra I, Zudaire L and Ayastuy J L 2016 Preparation of a porous biochar from the acidactivation of pork bones Food and Bioproducts Processing 98 (2016) 341–353
[14] Mo X et al 2008 Activation and deactivation characteristics of sulfonated carbon catalysts Journal of Catalysis 254 (2008) 332–338
[15] Liu X 2010 Preparation of a Carbon-Based Solid Acid Catalyst by Sulfonating Activated Carbon in a Chemical Reduction Process Molecules 2010, 15, 7188-7196
[16] Widayat W et al 2020 Production of biodiesel from waste cooking oil using heterogeneous catalysts KI/γ-Al₂O₃ Journal of Environmental Engineering and Science 2020
[17] Dawodu F A et al 2014 Effective conversion of non-edible oil with high free fatty acid into biodiesel by sulphonated carbon catalyst Applied Energy, 114, 819–826.
[18] Leung D Y C, Wu X and Leung M K H 2010 A review on Production Using Catalyzed Transesterification Applied Energy 87:1083-1095
[19] Widayat et al 2020 Preparation of KI/Hydroxyapatite Catalyst from Phosphate Rocks and Its Application for Improvement of Biodiesel Production Molecules 2020 May 31;25(11):2565