Effect of Reaction Time on Biodiesel Production from Palm Fatty Acid Distillate by Using PTSA as a Catalyst

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Abstract. This study aims to determine the effect of reaction time on the production of biodiesel (methyl ester) from palm fatty acid distillate (PFAD) by using para-toluene sulphonic acid (PTSA) as a catalyst. The reaction carried out is the esterification reaction which reacts PFAD with methanol to produce methyl esters and water. In this study, the molar ratio of methanol to PFAD is 6:1 and the reaction is carried out at 65 °C. The amount of PTSA catalyst used is 5%, 10%, 15%, and 20% of the amount of fatty acids. Acid value observation is carried out at the reaction time of 60 minutes, 75 minutes, 90 minutes, 105 minutes, and 120 minutes. The results obtained indicate that the optimum conditions for producing biodiesel from PFAD are with a reaction time of 105 minutes and a catalyst amount of 15%. The acid value obtained does not decrease again or the amount of fatty acids converted to methyl esters does not increase again when the reaction time and the amount of catalyst are increased. The lowest acid value at this optimal condition is 13.37 mg KOH/g, and in this condition, 95.84% of the fatty acid is converted to methyl ester.

1. Introduction
Biodiesel or methyl esters are alternative fuels to replace fossil fuels. Generally, biodiesel is made from plant seeds or animal fat [1,2], but biodiesel production in Indonesia is generally still made from palm oil [3]. Some plants in Indonesia are very potential to be used as raw material for making biodiesel such as jatropha and coconut [4,5]. Biodiesel has advantages and disadvantages compared to diesel oil derived from fossils. One of the disadvantages of biodiesel is the price is more expensive than fossil diesel and its production is still limited in number, while the advantages are more environmentally friendly and simpler production. At present, one of the challenges of biodiesel production is that it cannot be made on a large scale because raw materials are limited.

At present, one of the main problems in making biodiesel is the high cost of production, both the cost of raw materials and the cost of the manufacturing process, such as the cost of catalysts used [6–11]. The use of inexpensive catalysts has the potential to increase the ability of biodiesel to compete with fossil diesel. In this research, biodiesel from palm fatty acid distillate (PFAD) is made by using inexpensive catalysts, para-toluene sulphonic acid (PTSA) [8,12,13]. PTSA is a material that is easily obtained and as a catalyst has been successfully used in protein production [14]. The use of PFAD as a raw material has advantages compared to other raw materials such as olein or stearin, namely biodiesel formed has a lower melting point so that it will be able to be used at lower temperatures. So far, one of the shortcomings of biodiesel is its use at low temperatures, especially in areas that have 4 seasons.
PTSA is a strong acid containing sulfur compounds and is easily soluble in water and alcohol. In this research, PTSA will be dissolved in methanol to catalyze PFAD into biodiesel. The reactions that occur can be seen in equation (1).

$$\text{RCOOH} + \text{CH}_3\text{OH} \xrightarrow{\text{PTSA catalyst}} \text{RCOOR} + \text{H}_2\text{O}$$

(1)

In this esterification reaction, because the raw material is fatty acids, the acid value is used as an indicator of the amount of PFAD converted to biodiesel, meaning that the smaller the acid value indicates that more PFAD is converted into a product. Based on this, this research conducted a study of the effect of reaction time and reactant molar ratio as variables that affect the acid value obtained.

2. Methods

PFAD is the raw material used in this study. The characteristics of PFAD include acid value is 336 mg KOH / g, density is 0.904 /cm$^3$, Iodine Value is 4.36 g I$_2$/100 g, sulfur is 2.05 ppm, and water content is 0.02 %. Based on the analysis using gas chromatography, the majority of fatty acid content in PFAD consists of caprylic acid (32.1471%) and capric acid (64.3952%), the others are caproic acid (0.0279%), lauric acid (0.3498 %), myristic acid (0.0792 %), palmitic acid (0.0099%), and linolenic acid (0.0193%). Other main ingredients used are methanol 99% (Merck Chemicals Ltd) and PTSA monohydrate (Navdeep Chemicals Pvt Ltd).

The making of biodiesel is carried out in a reactor using a 100 mL glass beaker that is heated to a temperature of 65 $^\circ$C above the hot plate and is stirred at a speed of 300 rpm. PFAD is first put into the beaker glass, then a mixture of methanol and PTSA is added with a molar ratio of 6:1. This molar comparison is based on Idris’s research (2016) which states that if using methanol, the best ratio of reactants is 6:1, while if using ethanol, the best ratio of reactants is 9:1 [15]. The amount of catalysts used are 5%, 10%, 15%, and 20% of the amount of PFAD. Acid value measurements are made at the reaction time of 60 minutes, 75 minutes, 90 minutes, 105 minutes, and 120 minutes. The amount of PFAD converted to biodiesel is calculated using equation (2) [10,16].

$$x \, (\%) = \frac{AV_0 - AV_1}{AV_0} \times 100\%$$

(2)

where $x$ is the conversion of PFAD into biodiesel, $AV_0$ is the initial acid value of PFAD, and $AV_1$ is acid value of esterification at specific reaction time.

3. Results and Discussion

Figure 1 shows the acid value obtained at various reaction times and catalyst concentrations. In Figure 1 it can be seen that the reaction time is very influential on the acid value obtained. The amount of catalyst also significantly influences the acid value. The decrease in acid value occurred from the reaction time of 60 minutes to the reaction time of 105 minutes, but at the reaction time of 105 minutes and the reaction time of 120 minutes, the acid value obtained is almost the same. The reaction time of 105 minutes can be concluded as the best reaction time because after 105 minutes the acid value does not increase again.

In Figure 1, it can be seen that the effect of the amount of catalyst 5% gives an acid value that is close to the amount of catalyst 10%, while the amount of catalyst 15% gives an acid value which is close to the amount of catalyst 20%, so the results given in Figure 1 form 2 groups, namely groups 5% and 10%, and groups 15% and 20%. At the reaction time of 60 minutes to 90 minutes, the amount of catalyst 5% and 10% gives the same acid value, but after the reaction time of 90 minutes, the value of the acid value given is different. This is in contrast to the use of catalysts of 15% and 20%, in the reaction time of 60 minutes to the reaction time of 105 minutes, the two catalyst amounts give different acid values, but after the reaction time of 105 minutes, the amount of catalyst 15% and 20% gives same acid value. So it can be concluded that the optimal amount of catalyst in this reaction is 15%, which can produce an acid value of 13.37 mg KOH / g with a reaction time of 105 minutes. So
in this esterification reaction, the reaction time and the amount of catalyst are not directly proportional to the amount of biodiesel produced, but there is an optimum point reached.

Figure 1. Effect of reaction time and catalyst concentration on acid value

Figure 2. Effect of reaction time and catalyst concentration on PFAD conversion to biodiesel

Figure 2 is the effect of reaction time and catalyst concentration on PFAD conversion to biodiesel. Figure 2 is the result of the calculation of the acid value reduction in Figure 1 by using equation 2. The acid value of the raw material is 336 mg KOH / g as measured by the AOCS (American Oil Chemists' Society) test method Te 2a-64. The reaction that takes place at a certain time with the help of a catalyst will convert PFAD to biodiesel, and the acid value in the product will be used to measure the amount of converted PFAD. In Figure 2 it can be seen that the highest PFAD conversion is obtained at the use
of catalysts of 15% and 20% at the reaction time of 105 minutes. PFAD conversion on the use of these two catalysts is balanced, which is equal to a conversion of 95.84%. These results obtained are equivalent to those of other researchers [16]. So, it can be concluded that the best condition in this study is the reaction time of 105 minutes and the amount of catalyst is 15% of the amount of PFAD.

4. Conclusion

Biodiesel production from PFAD using PTSA catalysts at a molar ratio of methanol and PFAD 6:1 has an optimal reaction time of 105 minutes and an optimal amount of catalyst is 15% of the amount of PFAD. The reaction time is longer than 105 minutes and the amount of catalyst more than 15% does not give a decrease in acid value anymore, or the amount of biodiesel formed from PFAD does not increase again. The lowest acid value at the reaction time was 105 minutes and the amount of catalyst 15% was 13.37 mg KOH/g, and the amount of PFAD converted to biodiesel under this condition is 95.84%. It can be concluded that the reaction time and the amount of catalyst are not directly proportional to the amount of biodiesel produced, but there is an optimum point in this esterification reaction.

Acknowledgements

This research is supported by the Ministry of Research and Technology/National Research and Innovation Agency of Republic Indonesia for Research Grant, under Thesis Research of Magister Scheme, 2020.

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