The effects of durian skin ash concentration in methanolysis reaction of palm oil on fatty acid methyl esters concentration

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Abstract. Biodiesel is an alternative fuel made by methanolysis reaction of palm oil. Methanolysis reactions require a catalyst to accelerate the biodiesel formation reaction. The catalyst used in this study was the durian skin ash. This study was conducted to determine the effect of durian skin ash concentration on fatty acid methyl ester content that result in the reaction of palm oil methanolysis. Durian skin ash concentrations were varied to 1%, 2%, 3%, 4% and 5%. The methanolysis reaction was carried out by mixing palm oil, methanol and the ash of calcined durian skin at a temperature of 800°C for 5 hours. The reaction mixture was heated at a temperature of 50 to 70°C for 2 hours. The results of this study showed that the fatty acid methyl esters content increased with the concentration of durian skin ash up to 4% i.e. 90.03%. Fatty acid methyl esters content decreased on the durian skin ash concentration of 5% i.e. 85.66%. These results indicate that the fatty acid methyl esters reached the optimum content in 4% concentration of durian skin ash.

1. Introduction

One important requirement in human life is energy. Most of the energy is still supplied from petroleum, natural gas, and coal which are non-renewable natural sources [1] so that sooner or later they will be completely exhausted. Looking for renewable alternative energy continues to be done through various development of energy sources. Biodiesel is one of them [2], it is a type of fuel that is included in the biofuel group (BBN) [3].

Many types of researches are currently being developed to obtain biodiesel by methanolysis of vegetable oils or fats [4]. Catalyst is one of the factors that influence the production of biodiesel from vegetable oils. A catalyst is a substance that speeds up the reaction to reach equilibrium. The reaction will be slow and requires a large amount of cost and energy without a catalyst [5].

Homogeneous base catalysts are generally used in making biodiesel, namely NaOH and KOH. This is because they have a higher catalyst ability than other catalysts [2]. However, homogeneous catalysts have the disadvantage, they are unable to regenerate and recover, as well as the generation of hazardous liquid waste [6]. Making biodiesel using heterogeneous catalysts is now beginning to be used because it facilitates the process of purification and separation of biodiesel [7]. Durian skin ash can be used as a heterogeneous catalyst in the methanolysis reaction of palm oil which produces methyl esters of fatty acids (biodiesel) and glycerol [8].

Catalyst concentration is one of the factors that influence the methanolysis reaction of palm oils [9]. The use of catalysts with lower concentrations is not enough to complete the reaction [10]. Increasing the amount of catalyst after achieving optimum conditions does not result in increased biodiesel yield,
on the contrary, it will decrease further [11]. Therefore, it is necessary to conduct a study of the effect of durian skin ash concentration in the methanolysis reaction of palm oil to produce high content of methyl esters of fatty acids.

2. Methods

2.1. Materials and reagents
The materials and reagents used in this study were durian skin, methanol, palm oil, aquadest, filter paper, diethyl ether, formic acid, technical hexane, iodine crystal, thin layer chromatography (TLC), and pure fatty acid methyl esters.

2.2. Making of catalyst from durian skin ash
Durian skin was cut into small sizes then crushed and dried. After that, it was mashed into powder. Powder of durian skin was calcined in the furnace at 800°C for 5 hours. After the calcination process, the ash was put into a desiccator then stored in a closed container [12].

2.3. Methanolysis of palm oil
Variation of concentration of ash used was 1%, 2%, 3%, 4%, and 5% respectively by weight of oil. The ash catalyst was mixed with methanol with a ratio of oil and methanol 1: 6 at room temperature. The mixture of catalyst and methanol was then put into a three-neck flask that containing 25 grams of palm oil to carry out the methanolysis reaction (at a temperature of 50-70°C for 2 hours). The methanolysis reaction was stopped when the stirring time reached 2 hours. The catalyst and reaction products were separated by filter paper. The filtrate obtained was stored in a separating funnel until separation occurs between the biodiesel and glycerol. This acidification will produce 2 layers, namely the upper layer (raw biodiesel) and the lower layer (darker colour glycerol). The raw biodiesel obtained was then washed with warm aquadest (50-60°C) with a ratio of 1:1 (v/v) of aquadest and biodiesel by shaking. This process will cause a dissolve of methanol and soap into aquadest. After being shaken, the mixture was left to stand in a separating funnel and 2 layers will be formed namely the top layer of bright yellow (biodiesel) and the milky white bottom layer which was soap and methanol [11]. Washing was done up to the pH of the aquadest become neutral [13]. The biodiesel obtained was heated for 3 hours in an oven at 105°C to remove the aquadest from biodiesel [14].

2.4. Analysis of fatty acid methyl esters
Biodiesel products were analyzed using the TLC. A thin layer of adsorbent was made on the surface of a 4 x 8 cm aluminum plate with a thickness of 250 μm. A mixed mixture of separated compounds was dripped at about 1.5 cm from the bottom of the plate using a micropipette. The dripped sample was then eluted first with a mixture of hexane/diethyl ether/formic acid (80: 20: 2) based on v / v / v. Stain viewers used iodine crystals. Palm oil and fatty acid methyl esters were used as blanks. After staining, the fraction of the fatty acid methyl ester component was calculated (Equation 1) [15].

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\text{Fraction mass of methyl esters} = \frac{\text{stain mass of methyl esters}}{\text{stain mass total}} \times 100\%
\]  

(1)

3. Result and Discussion
The temperature of 800°C was used as the catalyst calcination temperature in determining the optimum concentration of durian skin ash catalyst with variations in concentrations (1%, 2%, 3%, 4% and 5%). The mass fraction of the methyl ester produced can be seen in figure 1.
Based on figure 1, it can be seen that the content of the highest fatty acid methyl esters was from 4% of catalyst concentration with a percentage of 90.14%. To find out whether there is an influence of catalyst concentration on the content of fatty acid methyl esters, a statistical test was obtained which can be seen in table 1.

**Table 1. Silica Content from the bottom and fly ash by extraction**

| Variance          | DB | Sum of square | Middle square | F<sub>count</sub> | F<sub>table</sub> 5% |
|-------------------|----|---------------|---------------|------------------|---------------------|
| Catalyst concentration | 4  | 154.85        | 38.712        | 98.50*           | 3.48                |
| Error             | 10 | 3.93          | 0.393         |                  |                     |
| Total             | 14 | 158.78        |               |                  |                     |

Note: * = significantly different (F<sub>count</sub> > F<sub>table</sub> 5%)

Due to the value of F<sub>count</sub> was greater than F<sub>table</sub>, the hypothesis (H<sub>1</sub>) was accepted which means there was an influence of catalyst concentration on the content of methyl esters of fatty acids received. Further tests were carried out to ensure the results obtained. The tests conducted were BNJ (Honestly Significant Difference) and the result was 1.678 which was greater than 0.05, this means that concentration affects the content of methyl esters of fatty acids.

Several factors that can be increased biodiesel production, namely reaction temperature, the ratio of methanol and oil, and catalyst concentration. In this study, the temperature used was 50-70°C. The higher the reaction temperature, the greater the yield of methyl esters obtained. When the reaction temperature is higher than the boiling point of methanol, bubbles will form which inhibit mass transfer on the surface of the phase [3, 16].

The ratio of the chosen oil and methanol mole was 1: 6 because the addition of methanol pushed the equilibrium to the right side so that it can result in the addition of the methyl esters obtained [9]. Too much methanol will cause glycerol dissolved in methanol and inhibits the methanolysis reaction [2].

The mass fraction of fatty acid methyl esters increased with increasing catalyst concentration up to 4% i.e. 90.03% and decreased at 5% of catalyst concentration i.e. 85.66. The addition of the amount of catalyst after the optimum conditions did not increase in the mass fraction of the methyl ester. This condition can occur due to increasing in the amount of ash which causes a greater concentration of potassium in the catalyst [17]. Increasing the catalyst concentration did not increase the content of...
methyl esters of fatty acids. According to [18], alkalis that function as catalysts can react with triglycerides to form soap. The use of excess catalysts can cause excessive emulsions due to the saponification reaction [17]. The formation of this soap can occur due to the conjugate acid, namely HCO$_3^{-}$ which is a very weak character. Consequently, the process of protonation of fatty acid esters becomes more difficult, on the contrary, the formation of ester salt (soap) is not influenced by the strength of the conjugate acid but the methoxy ion conjugate base, CH$_3$O$^{-}$. The nature of the methoxy ion as a conjugate base is very good, so more catalysts are added will form soap.

The formation of this soap is undesirable because it causes the acquisition of less fatty acid methyl esters. The saponification reaction takes a some of methyl esters formed and also other methyl esters may be trapped in the emulsion formed [17]. So that glycerol and soap are formed more than the methyl ester obtained [19].

The obtained results from the mass fraction of methyl esters of fatty acids in this study were still higher than the results of research conducted by [12] that making biodiesel using waste cooking oil with ash from banana stems calcined at 600°C and giving the acquisition of biodiesel by 76.8% by weight 8% catalyst.

These results indicate that the use of the durian skin ash catalyst was capable as a heterogeneous catalyst in the methanolysis reaction. This is because it can increase the yield of biodiesel. Similarly to [12], it was used cooking oil as the main ingredient in making biodiesel. Used cooking oil has high water content and free fatty acid (FFA) so it needs to be processed first through the reaction of esterification with H$_2$SO$_4$ before it is made into biodiesel. According to [20], waste materials such as unused cooking oil usually contain significant free fatty acids (FFA).

In research of oil as the main ingredient in making biodiesel, the oil has been processed before being used. But in this research, the esterification process is no needed because of the water content and free fatty acid content of the unused oil already following the standards for making biodiesel.

4. Conclusion

Based on the results of the study it can be concluded that the concentration of durian skin ash catalyst influences the contents of methyl esters of fatty acids in the methanolysis reaction of palm oil. The concentration of durian skin optimum is 4% that produces the best content of fatty acid methyl esters i.e 90.03%.

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