Effect of K-Silica heterogeneous catalyst in transesterification reaction of crude palm oil

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Abstract. Crude Palm Oil (CPO) is a raw material form of vegetable oil that cannot be consumed anymore and where the availability is very large. The purpose of this study was to observe the use of crude palm oil in the manufacturing of biodiesel by using a catalyst of bamboo ash leaves catalyst impregnated with KOH to get in the best yield of various reaction variables performed. The transesterification process reacted oil and methanol to produce methyl esters and glycerol. The methyl ester was produced at the top layer and it was separated from the glycerol and then washed. The effects of various process variables such as the type of the catalyst, the amount of catalyst, and time of reaction were observed in this experiment. The properties of biodiesel such as ester content, density, and kinematic viscosity, were evaluated and compared with Standard Nasional Indonesia (SNI). Under the best conditions, the maximum yield of biodiesel was 92.58\% and 99.76\% FAME methyl ester was 99.76\% obtained using a molar ratio of oil: methanol of 1: 9 at 65°C with a reaction time of 2 hours and 4\% catalyst. The results obtained in this study indicated that the K-Silica catalyst of KOH impregnated ash bamboo leaves is suitable as a catalyst to produce biodiesel.

1. Introduction

In recent years, studies on biodiesel were mostly conducted to find environmentally friendly alternative fuels. However, biodiesel is different from fossil fuels because it is biodegradable and free from toxic substances and sulfur [1]. Biodiesel is one of the energy sources that can be used as an alternative fuel for diesel engines. Demonstrates the global awareness of the limitations of fossil fuel and the quest for new energy alternatives. The common feedstocks for biodiesel are vegetable oils and animal fats. Thus, it can be said that the major lipid for biodiesel production comes from edible oils. However, feedstock alone accounts for approximately 80\% of the operational cost [2].

Alternatively, crude palm oil (CPO) can be used as the raw material in the manufacture of high-quality biodiesel [3, 4]. Indonesia is one of the largest producers of crude palm oil in the world. It is great potential as the main ingredient in the production of biodiesel. Nowadays, Indonesia is the country with the largest area of palm oil in the world with more than 7 million hectares of plantations. In 2009 and 2010, Indonesia’s palm oil production has increased by 1.20402 million tons [5]. Therefore, using palm oil as the raw material in the manufacturing of biodiesel can be considered because its production keeps increasing every year.

The production of biodiesel by transesterification method using solid catalysts has become more favorable compared to the other method. It has been scaled up to industrial scale. Solid base catalyst
bring several advantages, where the catalyst can be easily be separated from the advantages, such as the catalyst can be easily separated from the reaction mixture, no washing is required, easy regeneration, the less corrosive character of the product, low in cost and as a more environmental-friendly approach [6]. A study by Hindryawati et.al (2014) used cooking oil as the raw material and impregnation method to alkali metal silicate (Li, Na, K). The optimum reaction conditions were catalyst 3%, methanol to oil ratio 9:1, reaction temperature 65 °C with ME content 96.5% [7].

The synthesis, characterization, and performance of silica impregnated with calcium oxide as a heterogeneous catalyst in biodiesel production resulted in 87.5% yield FAME yield 87.5% with catalyst 3%, methanol to oil ratio 20:1 at reaction temperature 60 °C. An important focus of this work is to present the application of bamboo ash leaves to be used to obtain get a low-cost material as a basic heterogeneous catalyst in biodiesel production.

2. Materials and Methods

2.1 Material
The raw material used in this study was crude palm oil (CPO) obtained from PT Perkebunan Nusantara IV. The alcohol used was methanol purchased at PT E-Merck, K-silica which was synthesized from bamboo leaves impregnated with KOH. The transesterification reaction was carried out at a stirring speed of 600 rpm, with a reaction temperature of 65 °C, and a reaction time of 2 hours with the following process variables such as type and amount of catalyst:

- A1 = Catalyst obtained from calcination at a temperature of 500°C with a K: SiO2 molar ratio (2.5: 1) certain amount of K: SiO2: 10.9 - 31.10%.
- A2 = Catalyst obtained from calcination at a temperature of 600°C with a K: SiO2 molar ratio (2.5: 1) certain amount of K: SiO2: 12.2 - 26.7%.
- A3 = Catalyst obtained from calcination at a temperature of 700°C with a K: SiO2 molar ratio (2.5: 1) certain amount of K: SiO2: 12.1 - 32.40%.
- A4 = Catalyst obtained from calcination at a temperature of 800°C with a K: SiO2 molar ratio (2.5: 1) a certain amount of K: SiO2: 10.7 - 31.10%

2.2 Transesterification of Palm Oil
Transesterification for a certain amount of CPO, methanol, and K-Silica was prepared. CPO was heated to the reaction temperature the catalyst was added into methanol: CPO at a predetermined ratio, the temperature was kept constant for a reaction time of 2 hours. After that, the reaction mixture was filtered using a filter paper to separate K-Silica. The analysis was carried out after the preparation of methyl esters. Methanol and CPO, at a certain molar ratio, were poured into an Erlenmeyer placed on a heater. The temperature was measured using a thermometer until it reached the specific temperature, and then a shaker was used to homogenize the mixture for a certain duration [8]. After that, the reaction mixture was filtered using a filter paper to separate K-Silica. The analysis was carried out after the preparation of methyl esters.

2.3 Product Analysis
Biodiesel product produced was analyzed for the content of methyl ester using by the GC-MS Shimadzu-2010 gas chromatograph. The viscosity, density, and ester content of biodiesel were analyzed using the SNI standard.

3. Results and Discussion

3.1 Analysis of Water Content and FFA to Crude Palm Oil (CPO)
The CPO moisture content used in this study was analyzed using the Ca 2c-25 AOCS test method while the FFA levels were analyzed using the AOCS Ca 5a-40 test method.
Table 1. Water content and FFA on CPO

| Content | Percentage (%) |
|---------|----------------|
| Water   | 3.90 %         |
| FFA     | 4.45 %         |

Table 1 shows that in the synthesize of biodiesel, both water content and FFA can have a negative impact on the results of the transesterification reaction if they are too high because these two things can lead to the formation of soap, increase the number of catalysts needed, reduce the effectiveness of catalysts, and cause low conversion and production of yield [9].

3.2 The Effect of Type and Amount of Catalyst on Biodiesel Yield.

In this study, the catalyst used consists of several types namely catalyst types A1, A2, A3, and A4, with each type of catalyst carried out in the transesterification reaction to CPO as raw materials.

Figure 1. The effect of type and amount of catalyst on biodiesel yield

Figure 1 shows that the greater the amount of catalyst used for all variations of catalyst type K: SiO2 ratio, the yield of biodiesel would increase up to a certain point then decreases. From Figure 1, it can be explained that if the catalyst exceeds 4%, it caused the mixture to become thicker, which increased the viscosity so there would be difficulties as collisions occurred between molecules that are not free weak interaction between molecules can decrease the yield of methyl esters.

Figure 1 also shows the amount of potassium in each catalyst A2 and A3 had the highest potassium content. The highest yield was produced with A4 catalyst, which did not have high potassium content. So this explained that potassium levels are not the only determining parameter of success in catalyzing this reaction. When viewed from the silica content, the type of catalyst with the highest silica content is owned by was in type A3 catalyst by 32.40%, so that there was a role for silica in this reaction and produced different results. However, high silica content does not produce high yield and methyl ester content. While the type of catalyst A3 and A2 catalysts with different Si content and similar potassium content produced a low yield. Catalyst A4 gave the highest yield conditions. So from the explanation catalyst, A4 with a ratio of 1:3 gave the highest yield compared to A1 (1:2), A2 (1:2) A3 (1:2).
3.3 The Effect of Reaction Time and Type of Catalyst in Transesterification to Methyl Esters Production of mono, - di, and Triglycerides.

The relationship between reaction time to triglycerides, monoglycerides, diglycerides, and methylesters with type A₂ and A₄ catalyst in this study is shown in Figure 3.

![Figure 3](image)

**Figure 2.** (a) Effect of reaction time on mono composition, - di, and triglycerides in catalyst a₂ (b) effect of reaction time on mono, - di composition, triglycerides on a₄ catalyst type.

The data above shows that the A₂ catalyst at the last minute monoglycerides was still much restrained so that the stages of monoglyceride reaction into esters contaminated the reaction rate of triglycerides to esters. In the A₄ catalyst type, monoglyceride conversion took place slower so that the conversion of diglycerides to monoglycerides controlled the rate of diglyceride reaction to become an ester.

In the transesterification reaction, the reaction initially formed 2 phases of a liquid system. In this state the reaction is controlled by fusion (mass transfer), while diffusion was only slightly produced between 2 phases which did not dissolve so that the reaction starts slowly at first. When the ester was formed, it acted as a mutual solvent for the reactants so that the liquid phase waiting system was formed. The formation of the ester began after 1-2 minutes. A sudden change in the rate of formation of the ester product against the point when the ester was concentrated was relatively maximum. This maximum concentration was formed by an intermediate reaction which was a reversible reaction type. This has proven that the unidirectional or irreversible reaction in this study could be accepted [10]. From Figure 2 it can be explained that in different conditions, namely the types of catalysts A1 and A4 with A₂ (K-Si: 10.9 - 31.10%) and A₄ (K-Si (10.7 - 31.10%) respectively with a catalyst number of 3% with A1 and A4 (different catalyst type conditions affected the weight % of mono, di, and triglycerides). Which each type of catalyst would not give a maximum conversion of 100% if it has the same conditions, and changed the equilibrium position but only accelerated the achievement of equilibrium.

3.4 The Effect of Purity on Biodiesel Density from Each Type of Catalyst

Density can be a parameter of the success in the transesterification reaction. Density is the main characteristic of a fuel that directly affects engine performance characteristics, such as cetane numbers and heat values [11]. The biodiesel density should range from 0.850 to 0.900 g / cm³ [11]. The relationship between density and purity of biodiesel with various types of catalysts can be seen in table 2.
Table 2. Biodiesel Purity and Density of each Type of Catalyst.

| Type of catalyst | Ester Content(%) | Density(kg/m$^3$) |
|------------------|------------------|-------------------|
| A₁               | 99.21            | 876               |
| A₂               | 98.77            | 878               |
| A₃               | 99.18            | 882               |
| A₄               | 99.78            | 886               |

From table 2 the relationship between purity and density can be explained with the amount of catalyst, 4%, type A₁ catalyst. the purity of 99.21%, the density was 876 kg/m$^3$ A₂ catalyst purity decreased by 0.44%, and the density also lower. Catalyst type A₁ A₂ and A₃ continued to experience increases in purity and caused density to increase as well. From table 2, the correlation value of 0.91 was obtained which indicated that the correlation was very strong with a positive correlation between purity and density in each type of catalyst. This means that the greater the purity obtained, the greater the density.

Table 3 explained that the difference in the density of biodiesel was related to the composition of fatty acids and the level of purity of biodiesel. The density will increase with the decrease in the length of the carbon chain and the increase in double bonds [12]. Besides, the more unsaturated oil was used, the density would be ill the higher and, the longer the reaction time was used, the smaller the density would be longer reaction time would reduce the purity of the biodiesel produced and affect the density. This was due to the breaking of glycerol from triglycerides so that compounds with smaller molecular sizes were formed [12].

3.5 The Effect of Purity on Viscosity Kinematic Biodiesel from Each Type of Catalyst

Viscosity can be classified into dynamic viscosities that have centipoise units, and kinematic viscosity associated with fluid density and has centistokes. The viscosity of biodiesel is an important factor in the performance of a machine where high and low viscosity has a negative effect on engine performance [13]. The relationship between kinematic viscosity and biodiesel purity with various types of catalysts can be seen in Table 3.

Table 3. Kinematic purity and viscosity of biodiesel

| Type of Catalyst | Ester Content(%) | Viscosity Kinematic(cSt) |
|------------------|------------------|--------------------------|
| A₁               | 99.21            | 4.233                    |
| A₂               | 98.77            | 4.231                    |
| A₃               | 99.18            | 4.231                    |
| A₄               | 99.78            | 4.544                    |

Table 3 can be explained that the relationship between purity and density with the amount of catalyst 4%, where the type A₁ catalyst gets had a purity of 99.21%, the density was 4.233 kg / m$^3$. While type A₂ catalyst purity decreased by 0.372%. Kinematics viscosity kinematics also decreased from catalyst type A₁ to A₃ and experienced an increase in A₄ for purity and density. From table 3, the correlation value of 0.891 was calculated which indicated a very strong and positive correlation between purity and density in each type of catalyst. This means that the greater the purity obtained, the greater the kinematic viscosity would be.

Kinematic viscosity ($\mu$) is an important physical property of biodiesel. The kinematic viscosity of biodiesel correlated with the number of carbon atoms, the number of double bonds, and temperature [14]. Kinematic viscosity increased with the increasing chains of either fatty acids or alcohol in hydrocarbons, and an increase in kinematic viscosity of several carbon atoms was smaller than the increase in kinematic viscosity of a straight-chain hydrocarbon.
4. Conclusion
Each type of catalyst obtained by K-Si: 10.7 - 31.10% has the highest yield in this study at 92.91% and conversion of 99.76% with 1:3 ratio K-Silica compared to the other three types of catalyst. Crude Palm Oil which is used as a raw material in the production of biodiesel without pre-treatment (processed) with the help of the K-Silica catalyst produced relatively good results. K-Silica catalyst had very good catalytic properties where the equilibrium of the reaction could be achieved in a short time and was able to produce a high product yield.

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