The Effects of Catalyst Weight and Mole Ratio of Oil-Methanol on Crude Palm Oil (CPO) Esterification using H₂SO₄ (3M)/ Clay Catalyst

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Abstract. This study aimed to synthesize biodiesel from CPO using heterogeneous clay catalyst activated with H₂SO₄ (3M) in the esterification step. The catalyst was synthesized by the method of reflux at a temperature of 85 °C. The catalyst was characterized using XRD and XRF. The synthesized catalyst was used to make biodiesel from CPO by esterification process with the variations of catalyst weight and the mole ratio of oil to methanol. The purity of biodiesel was analyzed using GC. The XRD results showed that sulfuric acid activated clay consisted of sharp intensities of silica and this was supported by XRF results in which the silica content was 87.05% while Al₂O₃ was 11.90%. Heterogeneous acid catalyst of H₂SO₄ / clay with 3M H₂SO₄ concentration could reduce a free fatty acid content of the oil as much as 85.2%, ie from 6.61% to 0.98%. The maximum Biodiesel yield after the process of transesterification using CaO catalyst from shells of blood cockle (anadara granosa) was 71.90%. The maximum Biodiesel yield was obtained at the optimum esterification reaction conditions that were the weight of the catalyst of 2%, the mole ratio (oil: methanol) 1:18 with a reaction temperature of 65 ± 2 °C for 3 hours.

Keywords: Clay catalyst, anadara granosa, oil-methanol, crude palm oil, esterification

1. Introduction

Biodiesel is an alternative diesel oil that is generally defined as a Fatty Acid Methyl Ester (FAME) of plant oil, or animal fat. Because of the increasingly low availability of petroleum fuels, biodiesel has attracted attention lately as it comes from renewable sources. Biodiesel may be obtained from the reaction of esterification and transesterification between oils with monohydric alcohols in an acidic and alkaline catalyst [1-4]. But the cost of production is higher than the production cost derived from petroleum fuel. To lower prices and make biodiesel compete with petroleum, the selection of cheaper materials and catalysts for biodiesel production needs to be taken into account.

Crude palm oil (CPO) has the best potential in the process of biodiesel synthesis because the available amount is abundant and its properties so it is worth more economically. According to the Minister of Industry, in 2013 the need for Indonesia Oil Palm (MGS) in 2013 was estimated to reach 5.22 million tons or an average of 435 thousand tons per month. CPO or unrefined palm oil is also much cheaper than refined cooking oil, however, it also contains high free fatty acids [1,3]. Free fatty acids contained in oil when reacting with an alkaline catalyst will produce soap, resulting in reduced...
biodiesel production. Thus, to increase the biodiesel yield processed from the oil it is necessary to do two synthesis steps, the first step is esterification of free fatty acid with an acid catalyst and followed by transesterification with base catalyst.

The synthesis of biodiesel by esterification process of CPO using homogeneous acid catalyst and continued with transesterification using CaO catalyst has been reported [1]. The use of the homogeneous acid catalyst (H₂SO₄) in esterification has high biodiesel yield, but it has some disadvantages, such as less economical because once used, it requires a lot of solvents to wash the biodiesel product. Promising alternatives are the use of heterogeneous acid catalysts.

The use of clay as a heterogeneous catalyst has several advantages, such as environmentally friendly, has a large surface and has a high cation exchange capability. Several studies have been conducted to activate the natural clay and used as a heterogeneous catalyst in the transesterification process [4,5]. Activation natural clay with a strong acid such as sulfuric acid (H₂SO₄) is expected to increase the acidity and surface area of the clay, and it can be used as a heterogeneous acid catalyst for the esterification process in biodiesel synthesis. According to Michelle and Angelo, the acid treatment of a Brazilian natural clay gave excellent catalytic properties and provided good conversion in the esterification of fatty acids [4]. In addition, H-Mordenite (Al/Si ratio = 19) treated with phosphoric acid is an efficient alternative to a homogeneous acid catalyst for esterification of free fatty acid in neem oil [5]. Therefore, in this study biodiesel synthesis was done by two stages, esterification using heterogeneous acid catalyst activated with sulfuric acid (H₂SO₄ / Clay) and transesterification using CaO catalyst from the shell of blood cockle (anadara granosa).

2. Materials and Methods

2.1. Instrumentation and materials

The instrumentation used in this research was analytical balance (Mettler Toledo AL204), oven (Heraeus Instrument D-63456), desiccator, furnace (Naberthem type L31R), crucible, mortar, hotplate stirrer (RSH-IDR), magnetic stirrer (spin bar), three-neck flask, condenser, thermometer, separating funnel, Ostwald viscometer, pycnometer, Cleveland flash point tester and other glassware. The materials used were crude palm oil (CPO), natural clay from Maredan Village, isopropyl alcohol (IPA), phenolphthalein indicator, KOH 0.1 N, potassium hydrogen phthalate, acetone, HCl 0.5 N, CCl₄, reagent wjs, KI, Na₂S₂O₃, and starch solution.

2.2. Procedure

2.2.1. Activation and characterization of clay heterogeneous acid catalyst

The Maredan natural clays were washed several times to remove the impurities, then they were dried overnight in an oven at 105 °C. Chemical activation of natural clay was carried out by adding 300 ml of H₂SO₄ (3M) to 30 grams of clay, then the mixture was refluxed for 1 hour at a temperature of 85 °C. The resulting catalyst was heated to 105 °C, washed several times, dried and calcined at 500 °C for 3 hours.

2.2.2. Biodiesel synthesis

The esterification process was carried out by mixing the catalyst of H₂SO₄ (3M)/clay and methanol refluxed while stirring at 70 °C for 3 hours. After reacting, the mixture was inserted into the separating funnel and washed with warm water. The bottom wash water was removed and the top was inserted into a three-neck flask for the transesterification process [1]. The transesterification process was done using CaO heterogeneous catalyst derived from anadara granosa [1, 9] calcined at 900 °C for 10 h.
3. Results and Discussion

3.1. Catalyst Characterization

Characterization of mineral content and chemical composition on catalyst clay activated with sulfuric acid (3M) analyzed using X-ray diffraction (XRD) and XRF respectively. The XRD results were compared to JCPDS (Join Committee Powder Diffraction Structure) standard by Markgraf and Reeder [6]. The XRD data of the H$_2$SO$_4$/clay heterogeneous catalyst are shown in figure 1.

The XRD pattern on the activated Maredan clay of 3 M sulfuric acid (H$_2$SO$_4$) shows some peaks kaolinite loss. The main peak appear was non-mineral (Quartz) which was found at 2 thetas of 26.61°, 20.84° and 50.09°. The peak characterization of muscovite can be seen from the diffraction peak at 2θ of 36.52, 68.3 and 42.43, and this is in accordance with the research that has been done by Bhattacharyya and Gupta [7]. Furthermore, from the result of chemical composition analysis using XRF (Table 1), it can be seen that the main content of catalyst H$_2$SO$_4$ (3M)/ clay catalyst was silica (SiO$_2$) of 87.05%, followed by alumina (Al$_2$O$_3$) of 11.91%.

![Figure 1](image)

**Figure 1.** XRD patterns of (a) natural clay and (b) H$_2$SO$_4$ (3M)/ natural clay

| Elements | Concentration (%) |
|----------|------------------|
| Al       | 10.229           |
| Si       | 87.502           |
| P        | 0.422            |
| K        | 0.607            |
| Ca       | 0.119            |
| Ti       | 0.581            |
| Cr       | 0.008            |
| Fe       | 0.374            |

3.2. Catalyst effect on biodiesel analysis

In biodiesel synthesis by esterification process, free fatty acid content was always controlled (determined). This was done to find out how much free fatty acid (FFA) was reduced in the process. This is due to the transesterification process (continued from the esterification process) the FFA content in oil should not exceed 2%. If a sample has free fatty acid content and water content > 1% then when reacted with the catalyst will form an emulsion that can cause the formation of soap. The soap formation will affect the biodiesel separation process. Therefore, before the transesterification
process, esterification process was firstly done to convert fatty acid into methyl ester while the oil having water content of <1% can be directly carried out by transesterification reaction [8].

Table 2 shows the results of biodiesel synthesis with variations in catalyst weight (1, 2, and 3%) and the mole ratio of oil to methanol (1: 6, 1:12, and 1:18). From the table, it shows that the content of FFA decreased from 6.61% to 0.98 %. The optimum biodiesel yield was obtained at 71.90% found when the catalyst weight of 3M H_2SO_4/clay was 2%, the mole ratio of oil to methanol 1:18 and the reaction temperature of 65 ± 2 °C for 3 hours. When compared to the biodiesel yield using catalyst natural Maredan clay (64.04%), biodiesel yield using H_2SO_4(3M)/clay catalyst showed greater results.

| Catalyst weight | Molar ratio oil: Methanol | FFA after esterification (%) | Water content (%) | Biodiesel yield (%) |
|-----------------|--------------------------|------------------------------|------------------|---------------------|
| 1%              | 1:6                      | 1.83                         | 0.07             | 55.37              |
|                 | 1:12                     | 1.70                         | 0.06             | 50.82              |
|                 | 1:18                     | 1.96                         | 0.06             | 31.95              |
| 2%              | 1:6                      | 1.40                         | 0.05             | 43.75              |
|                 | 1:12                     | 1.40                         | 0.08             | 49.35              |
|                 | 1:18                     | 1.83                         | **0.05**         | **71.90**          |
| 3%              | 1:6                      | 1.40                         | 0.07             | 42.67              |
|                 | 1:12                     | 0.98                         | 0.06             | 45.92              |
|                 | 1:18                     | 1.28                         | 0.06             | 31.95              |

From the Table 2, it can be seen that when the number of catalysts increased the number of molecules formed would increase and the rate of reaction would also increase until it reached the maximum state (2%). The addition of the catalyst further does not increase the yield of biodiesel but otherwise, the biodiesel yield decreases. This is because a certain amount of catalyst can react with triglycerides and methanol. When the use of a catalyst with excess amounts then the mass transfer between the catalyst and the reactants will decrease so that the interaction decreases and the biodiesel yield is reduced. In addition. By adding an excess amount of catalyst will cause the catalyst to accumulate in the glass reactor wall and will affect the equilibrium of the reaction. so that at the end of the reaction will produce more by products such as soap formation [10].

3.3. Characterization biodiesel by GC analysis
GC analysis was used to determine the compound of methyl ester of biodiesel produced. The chromatogram of GC results can be seen in Figure 2 which shows the presence of 12 peaks detected as methyl esters at the first peak with an area of 26.95% with a retention time of 33.848 minutes (pentadecanoate acid/methyl myristate). The second largest area followed by pale eleven with area of 21.00% with a retention time of 39.951 min (hexadecanoic acid / methyl palmitate). and the third largest area at the fourth peak of 18.90% with retention time of 35.78 min (9 octadecanoic acid/methyl oleate).
Figure 2. The chromatogram GC of biodiesel

4. Conclusion

The synthesis of biodiesel was done by esterification process using H$_2$SO$_4$ (3M)/clay of heterogeneous catalyst and transesterification process using CaO catalyst from blood cockle shell calcined at 900 °C for 10 hours. The mineral types in H$_2$SO$_4$ (3M)/clay heterogeneous catalysts were kaolinite and muscovite while non-mineral type was quartz. with silica (SiO$_2$) content was 87.05% and alumina (Al$_2$O$_3$) was 10.229. The heterogeneous acid catalyst could reduce free fatty acid CPO by 85% from 6.61% to 0.98%. The maximum yield of biodiesel after going through two stages (esterification and transesterification) was 71.90% obtained under optimum esterification conditions with a heterogeneous catalyst H$_2$SO$_4$ (3M)/clay 2% w/w and a mole ratio of oil to methanol was 1:18.

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