The Synthesis of Biodiesel from Crude Palm Oil (CPO) using CaO Heterogeneous Catalyst Impregnated H₂SO₄, Variation of Stirring Speed and Mole Ratio of Oil to Methanol

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Abstract. Biodiesel is a diesel engine fuel produced from renewable material and contains fatty acid alkyl ester from triglyceride or oils through transesterification reactions with short chain alcohols and catalysts. In this study biodiesel was synthesized using crude palm oil (CPO) using CaO catalyst from blood cockle shells calcined at 900 °C for 5 hours and impregnated with H₂SO₄ (1, 2 and 3M). The catalyst was characterized by XRD and XRF. The biodiesel was synthesized with variation of stirring speed (300, 400, 500, 600 rpm) and mole ratio of oil to methanol (1:6, 1:9, 1:12, 1:15 and 1:18). The maximum biodiesel results obtained on a H₂SO₄ (3M)/ CaO catalyst with a stirring speed of 500 rpm and mole ratio of oil to methanol was 1:12 at the transesterification reaction stage and using a CaO catalyst calcined at 900 °C for 5 hours produced a yield of 96.69%. The characteristics of biodiesel produced was water content 0.05%, specific gravity 890 kg/m³, viscosity 4.46 mm²s⁻¹, carbon residue 0.05% and acid number 0.5 mg KOH g⁻¹. It can be concluded biodiesel, meets the quality requirements of SNI 7182-2015

1. Introduction

The world energy crisis and global warming are two big problems caused by increasing population growth, industry and increasing use of fossil fuels. This causes the need for renewable energy potential as an energy source [1]. Biodiesel is known as an environmentally friendly material that has the potential as an alternative to replace fuel derived from diesel. As a renewable energy source, biodiesel is non-toxic, biodegradable, produces less pollution and has lower sulfur and aromatic content compared to fossil fuels [2].

The biodiesel manufacturing process generally uses a transesterification process of plant oil with short chain alcohol, using a homogeneous catalyst of acid or base, namely H₂SO₄, NaOH, and KOH. The process of making biodiesel has several disadvantages, which are sensitive to the content of free fatty acids (FFA) contained in oil, the complexity of separating biodiesel products produced by catalysts, the formation of by-products in the form of soap, the presence of alkaline waste which requires quite complex follow-up processes and requires quite high energy and ultimately increases production costs. This weakness can be overcome by using heterogeneous catalysts. The advantages of using heterogeneous catalysts including easy separation of biodiesel products from catalysts, catalysts can be regenerated and reused, so that the cost of biodiesel production becomes more economical [3]. Heterogeneous catalysts that can be used in biodiesel production are blood cockle shells (Anadara granosa) because they contain CaCO₃ which when calcined at temperatures > 800°C produces CaO
[4].

The raw material for producing biodiesel used in this study is crude palm oil (Crude Palm Oil) because Indonesia is the world’s largest supplier of palm oil, reaching 42,869,429 tons/year. The main centers of palm oil production in Indonesia are Riau, North Sumatra, Central Kalimantan, Sumatra Selatan and Jambi provinces with annual production of 8,864,883; 5,623,054; 6,279,857; 3,767,108 and 37,939 tons/year respectively [5]. Based on these data it can be concluded that palm oil (CPO) has the potential as a raw material for making biodiesel. However, CPO has a relatively high free fatty acid (FFA) content of > 5% [4]. The high FFA content can influence to the catalyst performance in the reaction, reduce biodiesel yield and can trigger saponification reactions or soap formation.

The synthesis biodiesel from CPO has already been done through two reaction stages, namely the esterification stage which converts free fatty acids into methyl esters and the transesterification stage which is carried out separately [6,7]. CPO produced through a two-stage process (esterification and transesterification) has high purity, and the biodiesel yield was 71.90% [6]. However, a two-stages reaction was less efficient and consumed a lot of energy, so it is necessary to modify the catalyst to save energy in biodiesel synthesis [8]. Istadi, et all [9] used an impregnated sulfuric acid at ZnO catalyst for transesterification in the biodiesel synthesis process and obtained yield of methyl esters was 80.19%. The addition of $\text{SO}_3\text{H}-\text{ZnO}$ increased the active acid site on the surface of the catalyst. For this reason, the use of calcium oxide (CaO) heterogeneous catalyst impregnated with sulfuric acid ($\text{H}_2\text{SO}_4$) is expected to be the best solution to improve catalyst performance and to be a solution to prevent the occurrence of saponification or soap formation.

In this study the synthesis of CaO catalyst impregnated by Sulfuric Acid from a shell of BCS was calcined at 900 °C for 5 hours. Sulfuric acid impregnation in base catalysts (CaO) aims to make this catalyst capable of catalyzing FFA and triglycerides into methyl esters simultaneously (esterification and transesterification) in one stage of the transesterification reaction and to prevent the saponification reaction or the formation of soap caused by high free fatty acids on the methyl ester together transesterification process. According to Nurhayati [4] on calcination 900 °C for 5 hours, CaO has been formed which is sufficient to provide active catalysts in the reaction, so that it can reduce energy consumption and time and licensing the biodiesel synthesis process.

Stirring affects the reaction speed due to the mass transfer between the oil and the catalyst, besides the variation of the stirring speed of the CaO catalyst has never been done so that in this study biodiesel synthesis carried out variations in the stirring speed in the transesterification reaction stage using CaO catalyst impregnated with Sulfuric Acid 1, 2 and 3 M. This research also studies the effect of the mole ratio of oil to methanol (1: 6, 1: 9, 1: 12:1: 15, 1:18). The use of excess oil to methanol mole ratio is expected to be able to shift the reaction towards product formation, resulting in maximum biodiesel yield conversion.

2. **Methodology**

2.1. **Instrumental and Materials**

In this research, we used Mortar martyr, sieve 100 and 200 mesh (rathest), an oven (Gallenkamp), furnace (nabertherm series 400-1), squash the neck three complete with a condenser, crussible, hotplate (rsh-idr), a stirrer magnetic, a separating funnel, a stopwatch, water pump, the alcohol thermometer, buret, viscometer ostwald, pycnometer 10 ml, desiccator, analytic balance (mettler AE), surface area analyzer and other study glassware. The materials used in this study are crude palm oil (CPO) taken at PT. Wilmar City Dumai, blood clam shells (*Anadara granosa*), methanol (Merck), isopropyl alcohol, $\text{H}_2\text{SO}_4$ (Smart Lab Indonesia), phenolphthalein indicator, potassium hydrogen phthalate (PHP), ethanol 96%, HCl (Merck), CCl₄ (Merck) , KI, Na₂S₂O₃, hexane, ordinary filter paper, Whatman 42 filter paper, aquades, aqua DM and asetic acid 2%.
2.2. Catalyst Preparation and Characterization

The catalyst preparation begin with calcination of blood clam shells (Anadara granosa) at 900°C for 5 hours, crushed and sieved until they pass through a 100 mesh sieve and were held at 200 mesh. Preparation of CaO catalyst impregnated with H₂SO₄ using the wet impregnation method. Calcined BCS samples (100 g) were added 500 ml of H₂SO₄ solution with variations of H₂SO₄ concentration (1, 2 and 3M), drop by drop using a burette while stirring using a stirring rod, and the mixture was stirred using magnetic stirrer for 6 hours. Then it was dried in the oven at 105 °C for ±24 hours continued by calcination at a temperature of 300 °C for ±3 hours. The H₂SO₄-CaO catalyst was characterized by FTIR to identify functional group of catalyst (Anadara granosa), and X-ray fluorescence (XRF) to analyse the chemical composition.

2.3 Biodiesel synthesis

100 g of CPO was heated to 105 ± 5 °C and stirred using a magnetic stirrer for 30 minutes. After being heated, the CPO is then cooled to a temperature of 50 °C. In a 500 mL three neck flask, mixed 3 g of H₂SO₄/CaO catalyst with concentrations of H₂SO₄ 1, 2 and 3M (before use, the catalyst is heated in an oven at 105 °C for at least 30 minutes) and 47.66426 g of methanol (mole ratio of oil: methanol 1 : 12) refluxed for 1 hour. CPO (temperature 50 °C) was added to the catalyst-methanol mixture and stirred for 3 hours at a stirring speed of 300, 400, 500 and 600 rpm at 60 °C. After reacting, the mixture is put into a separating funnel and left overnight to separate crude biodiesel from the catalyst and the glycerol formed. Repetition is carried out for catalysts that have been impregnated with H₂SO₄ with variation of mole ratio of oil: methanol (1:6, 1:9, 1:12, 1:15 and 1:18). The synthesized methyl ester was characterized including acid number, water content, specific gravity, viscosity, carbon residue and the results were compared to biodiesel standard ASTM D6751.

3. Result and Discussion

3.1. Catalyst characterization

CaO and H₂SO₄/CaO catalysts 1, 2 and 3 M were analyzed using X-Ray Fluorescence (XRF) which is a test tool that qualitatively provides information on the types of elements contained in the material being analyzed. The results of the analysis with XRF can be seen in Table 1. The chemical composition of the CaO catalyst calcined at 900 °C for 5 hours contains the highest CaO of 97.834% and the elements Ag₂O, Al₂O₃, SrO and MgO in the least amount.

| Chemical Composition | Concentration (%) |
|----------------------|-------------------|
| CaO                  | 97.834            |
| H₂SO₄(1M)/CaO        | 58.426            |
| H₂SO₄(2M)/CaO        | 43.719            |
| H₂SO₄(3M)/CaO        | 33.248            |
| Al₂O₃                | 0.425             |
| Ag₂O                 | 0.599             |
| SrO                  | 0.197             |
| SO₄                  | -                 |
| Fe₂O₃                | 0.021             |
| MgO                  | 0.392             |

The functional group of CaO catalyst from the shells of blood clam (Anadara granosa) and CaO impregnated H₂SO₄ were analyzed using Fourier Transform Infra Red (FTIR) spectroscopy. The results of the analysis can be seen in Figure 1. Based on the results of the analysis, it was obtained several wave numbers at 3641,72 cm⁻¹, 3642,73 cm⁻¹, 3642,73 cm⁻¹ and 3336,18 cm⁻¹ which were the O-H stretching vibration from Ca(OH)₂. This indicated that CaO has been hydrated with air. The CaO surfaces absorbed air very quickly when it comes in contact with air during the catalyst test. In addition, wave number at 1452,46; 1444,75 and 1444,75 cm⁻¹ appeared on the CaO catalyst without H₂SO₄ impregnation, H₂SO₄(1M)/CaO and H₂SO₄(2M)/CaO which where accompanied to symmetric stretching vibration from CO, which was strengthened by the appearance of a wave number at 874,76
cm\(^{-1}\) which was the bending vibration of C-O.

According to Ruiz et al., 2016 [10] the wave number at 1456-1409 cm\(^{-1}\) was related to symmetrical stretching vibration of C-O from monodentate. However, on catalyst H\(_2\)SO\(_4\) (3M)/CaO it was shown that no symmetrical stretching vibration and bending vibration of C-O appeared. The higher the concentration of H\(_2\)SO\(_4\) impregnated on CaO, the intensity of C-O decreased. According to Ruiz et al. [10] and Liu et al., [11]. From the FTIR spectrum, it also shown the presence of S=O functional group at 1170-1126 cm\(^{-1}\).

3.2. The biodiesel results

Crude palm oil (CPO) has high Free Fatty Acid (FFA). Crude palm oil (CPO) which has FFA content below 2% can be directly processed by transesterification to be biodiesel without going through the esterification process. The transesterification process begins by reacting the CPO with methanol which CaO/H\(_2\)SO\(_4\) 1, 2 and 3M added as a catalyst. The reaction takes place at 60 °C for 3 hours on a three-neck flask. The results of transesterification with a variation of stirring speed was obtained data as in Figure 2.

![Figure 1. FTIR Spectrum of catalyst (a). CaO, (b). H\(_2\)SO\(_4\) (1M)/CaO, (c). H\(_2\)SO\(_4\) (2M)/CaO, (d). H\(_2\)SO\(_4\) (3M)/CaO](image)

![Figure 2. The effect of stirring speed on the biodiesel yield](image)
From the variation of the stirring speed seen in figure 2, that the higher the stirring rate the higher the biodiesel conversion is due to the reaction process, the speed of contact between reactants greatly influences the conversion of the result. The greater the contact rate between reactants will increase the reaction or increase the conversion. However, each reaction has an optimum condition, where in the process of transesterification of this cooking oil, 500 rpm stirring speed gives an optimum result with the volume conversion reaches 91.16%. The increased of stirring speed after equilibrium does not increase biodiesel conversion, the reaction which continues and the stirring speed that is too high after achieving equilibrium will result in a backlash so that the acquisition of biodiesel yield decreases [13].

In addition to stirring speed, the effect of mole ratio of oil to methanol on the biodiesel yield was also studied. This synthesis was carried out under reaction condition with a catalyst weight of 3%, a reaction temperature of 60°C for 3 hours and stirring speed of 500 rpm (Figure 3). The increasing of the oil :methanol mole ratio from 1:6 to 1:12 will increase the yield of biodiesel, however after reaching an optimum condition (at 1:12) the resulting biodiesel yield decreased. This is because excessive use of methanol will lead to increased glycerol formation. It is understood that glycerol will dissolve in excess methanol and then inhibits the methanol reaction, thereby influential to the separation of glycerol which in turn will decrease the biodiesel conversion by shifting the equilibrium in the opposite direction [14]. The optimum biodiesel yield is 96.69%, with a mole ratio of oil: methanol 1:12, using H$_2$SO$_4$ (3M) / CaO catalyst.

![Figure 3. The effect of mole ratio of oil: methanol on the biodiesel yield](image)

### Table 2. Characteristics of biodiesel from crude palm oil (CPO)

| Parameters          | Unit          | Biodiesel this study | SNI Biodiesel |
|---------------------|---------------|----------------------|---------------|
| Water content       | % vol         | 0.02                 | Maks.0.05*    |
| Density (40 °C)     | kg/m³         | 886                  | 850-890       |
| Viscosity (40 °C)   | mm²/s (cSt)   | 4.75                 | 2.3 – 6.0     |
| Carbon residue      | % berat       | 0.05                 | Maks. 0.05    |
| Acid number (N$_A$) | mg-KOH/g      | 0.46                 | Maks. 0.5     |
From biodiesel characteristics, for density, viscosity, carbon residue and acid number are in accordance with the quality requirements of SNI 7182-2015. Determination of biodiesel characterization in this study was conducted to determine the quality of the biodiesel produced. Characterization of biodiesel produced must meet SNI-04-7182-2015, so that the engine can work well and be more durable.

The water content contained in biodiesel can be seen in Table 3 that in biodiesel using \( H_2SO_4 (3M)/CaO \) obtained by 0.02%. The water content in the fuel must be considered so that the engine can operate properly. If the fuel contains excess water it can cause the hydrolysis process in the fuel so that the acid number will rise, the pH decreases and is corrosive in the engine [16]. Biodiesel washing that can draw water, soap and glycerol which is in biodiesel affects the low value of the water content produced. So the results obtained are in accordance with the water content standard based on SNI 7182-2015 (maximum 0.05%).

Specific gravity shows the ratio of mass per volume. The biodiesel synthesized using the catalyst has a specific gravity of 886 kg m\(^{-3}\). This biodiesel specific gravity in accordance with SNI-04-7182-2015. Biodiesel which has a specific gravity exceeding the provisions will produce incomplete combustion, increase emissions and damage to the engine used [17]. Biodiesel which has a large specific gravity value is affected by the presence of glycerol compounds so that the separation is not perfect. Viscosity is very important because it affects the working of the injector on the engine. Viscosity of biodiesel in this study can be seen in Table 3 that biodiesel has viscosities of 4.75 mm\(^2\) s\(^{-1}\) and this is in accordance with SNI-04-7182-2015 viscosity values that are too low result in the formation of very fine grains and cannot enter further into the combustion cylinder so that the fuel rich zone is formed which causes soot formation [17].

In addition, biodiesel carbon residues in this study were obtained at 0.05, using catalyst impregnated with CaO / \( H_2SO_4 \) 3 M. This value indicates that the carbon residual parameters of CaO/\( H_2SO_4 \) 3 M, is in accordance with SNI 7182-2015 (maximum 0.05%). Determination of acid numbers is an indicator to determine the content of free fatty acids in biodiesel by dissolving an amount of oil or fat. The acid numbers obtained in this study can be seen in Table 3. That in biodiesel synthesized using \( H_2SO_4 \) 3 M /CaO 3 M catalysts of biodiesel acid numbers in accordance with SNI-04-7182-2015. Biodiesel which has a high acid number will be corrosive and can cause deposits on the engine injector [17].

4. Conclusion
Based on the results of the research conducted, several conclusions can be obtained as follows: Heterogeneous catalyst \( H_2SO_4/CaO \) has been successfully synthesized by reflux method with concentrations of Sulfuric Acid 1, 2 and 3 M. The results of the characterization with XRF obtained the composition of CaO on each catalyst of 58.426; 43.719 and 33.248% and \( SO_3 \) composition in each catalyst were 38.609; 53.682 and 65.037%. Optimal biodiesel results obtained on a \( H_2SO_4 \) (3M)/CaO catalyst with a stirring speed of 500 rpm and mole ratio of oil to methanol was 1:12 at the transesterification reaction stage and using a CaO catalyst calcined at 900 °C for 5 hours produced a yield of 96.69%. The characteristics of biodiesel produced was water content 0.05%, specific gravity 890 kg/m\(^3\), viscosity 4.46 mm\(^2\) s\(^{-1}\), carbon residue 0.05% and acid number 0.5 mg KOH g\(^{-1}\). In general the characteristics of biodiesel were in accordance to SNI 7182-2015 requirements.

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