Utilizing of CaO catalyst from chicken eggshells at several concentrations to produce biodiesel based on moringa seed oil

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Abstract. Chicken eggshells contain a high concentration of CaCO$_3$ compounds, which are potentially transformed to CaO by calcination method. CaO has been used as a heterogeneous catalyst for biodiesel or fatty acid methyl ester production from Moringa seed oil. The purpose of this study is to determine the percentage of CaO which produces the highest methyl ester mass fraction and to find out the characteristics of the biodiesel. Biodiesel was made through a transesterification reaction by using a CaO catalyst that has been calcined at 900°C for 2 hours. This study was conducted using a completely randomized design (CRD) with the independent variable in the form of CaO mass percentages consisting of 5 levels (1, 2, 3, 4, and 5%). CaO catalyst at 3% concentration resulted in a mass fraction of methyl ester of 57.1%. Characteristics of the biodiesel contained water content of 0.3%, acid number of 0.03 mg KOH/g, saponification number of 6.93 mg KOH/g, iodine number of 5.49 g iod/100g, cloud point of 18°C, and pour point of 16°C. Some of the characteristics have fulfilled the standardizations of ASTM and SNI.

1. Introduction

Biodiesel production generally uses a homogeneous catalyst, such as acid (H$_2$SO$_4$) and alkaline (NaOH or KOH). But the use of this catalyst has drawbacks, such as the separation of the catalyst from the product is quite complicated and increases the consumption of the catalyst in the methanolation reaction [1]. Therefore, many studies have been developed using heterogeneous base catalysts such as CaO [1] and K$_2$CO$_3$ [2]. Heterogeneous catalysts have a different phase from the reactant phase, so they can be easily separated by filtering. Heterogeneous catalysts such as CaO are more stable, very low effect of corrosion on equipment, environmentally friendly, and more economical because they can be used repeatedly [3]. Heterogeneous CaO catalysts have been obtained from various sources such as blood clam shell ash [3], chicken bones [4], snail shells [5], eggshells [6]. Especially for eggshells, the highest chemical compound content is CaCO$_3$ as much as 94% [7]. CaCO$_3$ compounds from eggshells can be converted into CaO through a calcination process [8] which is very potential to be used as a heterogeneous base catalyst in making biodiesel or fatty acid methyl esters.

In the production of biodiesel from Moringa seed oil, CaO has never been used as a heterogeneous catalyst. The aim of this study is to determine the mass fraction and properties of fatty acid methyl esters in various CaO catalyst concentrations that were obtained from chicken eggshells. In previous research, biodiesel from coconut oil using a CaO catalyst with a concentration of 2%, a temperature of 60°C, and an 8:1 mole ratio of methanol to oil for 1.5 hours has been resulted the yield of 75.02% [1].

2. Materials and methods

The materials used are dry moringa seeds, chicken eggshells, n-hexane, HCl 0.4944 N, aquadest, methanol (Merck), TLC silica gel G60 plate size 20 x 20 cm, diethyl eter, formic acid and anhydrous

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sodium sulfate (Merck). Moringa seed oil was extracted from Moringa seed powder by maceration method for 72 hours using n-hexane solvent at a ratio of 1: 8 (w/v). The oil is passed to anhydrous Na$_2$SO$_4$ and followed by a degumming process at 90°C for 30 minutes, then washed with 60°C water. Eggshells were made into 100 mesh powder and then calcined at 900°C for 2 hours. The results of the calcination were analyzed using an X-Ray Diffractometer.

2.1. Biodiesel production

CaO catalyst with a concentration of 1, 2, 3, 4, and 5% on the basis of a percent (%) of CaO catalyst to oil was mixed with methanol at room temperature. The mixture was reacted with oil (mole ratio of methanol: oil = 6:1) at a temperature of 60±5°C for 3 hours [1]. After the methanolsis reaction is complete, the catalyst is separated by filtering. The filtrate is collected in a separating funnel and left to stand until it forms two layers. The glycerol layer at the bottom is removed, while the crude biodiesel is washed using warm aquadest (±60°C) with a ratio of biodiesel/aquadest of 1:1 (v/v). The biodiesel is separated from the emulsion and methanol residue by passing it over anhydrous sodium sulfate. The mass fraction of fatty acid methyl ester or biodiesel was determined using Thin Layer Chromatography (TLC). The eluent mixture that used in the chromatography process is hexane/diethyl ether/formic acid of 8: 2: 2 (v/v/v). The spot on the TLC plate was cut and weighed to determine the mass fraction of biodiesel using Equation 1.

$$\text{Mass fraction of biodiesel (\%) } = \frac{\text{mass of biodiesel spot}}{\text{mass of all spot}} \times 100 \tag{1}$$

The highest mass fraction of biodiesel was analyzed for its compound components using a GC-MS.

2.2. Characterizations of biodiesel

Characterization of biodiesel used fourier transform infrared (FTIR). The quality of biodiesel is determined by analyzing of moisture content, acid number, saponification number, iodine number, cloud and pouring points.

3. Results and discussion

3.1. Characteristics of a CaO catalyst from eggshells

The results of characterization analysis with XRD on CaO catalyst from eggshells showed the formation of CaO compounds at 2θ = 33.8° and 54.1° with total intensities of 1109 and 187, respectively (Figure 1). Mohadi et al. reported that CaO from chicken eggshells formed at 2θ = 32.3° and 54°, while at 2θ = 47.2° and 50.9° the compound Ca(OH)$_2$ was formed [9]. Tang et al., (2011), reported that Ca(OH)$_2$ shows a peak at an angle of 2θ = 46.9° and 50.7° [10]. Ca(OH)$_2$ is formed because CaO has strong alkaline properties due to the presence of oxygen anions on its surface, so that if CaO interacts with air (H$_2$O or water vapor) it will produce Ca(OH)$_2$ [11]. The remaining CaCO$_3$ is found at an angle of 2θ = 29.1° and 30.4° with a total intensity of 104 and 248, respectively (Table 1).

![Figure 1. XRD pattern of CaO from chicken eggshells](image-url)
Table 1. XRD analysis of CaO from chicken eggshells

| Compounds       | Research result | Tang et al. [10] | Mohadi et al. [9] |
|-----------------|-----------------|------------------|-------------------|
| CaO             | 33.8 and 54.1   | 32.1, 37.3, and 53.9 | 32.3 and 54       |
| Ca(OH)₂         | 46.9 and 50.5   | 46.9 and 50.7     | 47.2 and 50.9     |
| CaCO₃           | 29.1 and 30.4   | 29.2              | 29.1              |

3.2. Biodiesel from transesterification at various concentration of CaO catalyst

The results showed that the highest methyl ester mass was obtained of 57.1% when using a catalyst concentration of CaO 3% (Figure 2). The methyl ester fraction (biodiesel) has increased in the addition of catalyst concentration to 3%, but decreased at a concentration of 4%-5%. This was due to the use of excessive catalyst causing soap formation or a saponification reaction. This reaction took amount of methyl esters that have formed as well as other methyl esters which might be trapped in the emulsion formed [12].

![Figure 2. Mass fraction of biodiesel at various concentration of CaO catalyst](image)

The results obtained from this study were still lower than the research by Haryono et al. which produced fatty acid methyl esters from used cooking oil using 3% CaO catalyst from eggshells with a 1:12 mole ratio of oil and methanol which yielded the mass fraction of fatty acid methyl ester of 77.76% [11].

3.3. Profile of methyl ester

Profile of methyl ester was identified by by GC-MS analyzing. MS spectra showed fragmentation at (m/z) of 264, 222, 163, 137, 97, 69, 55, and 41 (Table 2). At the peak of the fragmentation of 264 (m/z) was methyl oleate (C₁₉H₃₆O₂). The existence of a double bond is shown in the addition of the fractional series of the CₙH₂n⁺ ion series with fragmentation (m/z) of 69, 55, and 41. The base peak appears at fragmentation (m/z) is 55, namely the absorption of CH₃-CH=CH⁺ ions.

GC-MS analysis produced two dominant peaks, namely peaks 2 and 3 (Figure 3). Methyl oleate was thought to be detected at the retention time of 43.413 minutes with a peak area of 45.60%, while methyl elaidate was thought to be detected at the retention time of 42.534 with a peak area of 19.47% (Table 3). In a study on the transesterification of castrol oil, methyl oleate compounds were detected at a retention time of 43.02 minutes [13]. In the transesterification reaction of oil with methanol, it still contains oil composed of oleic acid, as evidenced by the mass fraction of methyl ester which is still carried 60%. Rashid et al. reported that the composition of the fatty acid methyl esters analyzed using GC was methyl palmitate, methyl behenic, methyl stearate, methyl oleate, methyl linoleate and methyl arachydrate [14].
### Table 2. Fragmentation of biodiesel

| Compound                      | Fragmentation (m/z) |
|-------------------------------|---------------------|
| Research result               | 41 55 69 - 87 97 - 137 163 222 264 - |
| Methyl ester oleate (WILEY229.LIB, entry:12554, SI:91%) | 41 55 69 74 - 97 123 137 - 222 264 296 |

### Table 3. Prediction of compounds in biodiesel

| Peaks | Time retention (minute) | Peak area (%) | Prediction of compounds in biodiesel |
|-------|-------------------------|---------------|---------------------------------------|
| 1     | 39.783                  | 14.67         | Methyl palmitate                      |
| 2     | 42.534                  | 19.47         | Methyl elaidate                       |
| 3     | 43.413                  | 45.60         | Methyl oleate                         |
| 4     | 45.326                  | 10.96         | 9-octadecenal                         |

#### 3.4. FT-IR spectrum of biodiesel

The FT-IR spectrum results show that there is a wave number of 1743.65 cm\(^{-1}\) which is the absorption of the C = O group of fatty acid methyl esters (Figure 4). This data is inline with the research that the biodiesel spectrum at wave number 1743.09 cm\(^{-1}\) indicates the presence of a carbonyl group (C = O) of the ester compound [6]. The absorption at wave number 1712.79 cm\(^{-1}\) is the C = O absorption of free fatty acids which is still contained in the reaction product, while the absorption band at wave number 1157.29 cm\(^{-1}\) shows the C-O ester group (Figure 4). Similar results were also found the C-O ester group of biodiesel at wave numbers 1170.16 cm\(^{-1}\) [6]. The absorption band at the number 2924.09 cm\(^{-1}\) shows the C-H functional group. In the spectrum there is also an absorption band at wave number 3294.42 cm\(^{-1}\) which indicates the presence of an O-H group, so there is still free fatty acids.

#### 3.5. Characteristic of biodiesel

Characteristics of biodiesel including the water content of 0.3%, acid number of 0.03 mg KOH/g, saponification number of 6.93 mg KOH/g, iodine value of 5.49 g iod/100g, cloud point of 18°C, and pour point of 16°C. Several parameters have fulfilled ASTM D6751 for biodiesel fuels, such as the acid number with a value of <0.5 mg KOH/g and the saponification number with a value of <370 mg KOH/g. Low acid numbers can reduce the saponification reaction [15]. The evidence of this reason is that the saponification number obtained was very low. Cloud point, pour point, and iodine value have fulfilled Standar Nasional Indonesia (SNI). SNI requires maximum value of iodine value of 115 gr iod/100 gr, cloud point of 18°C, and pour point of 28°C. The cloud point value can still be reduced by optimizing the transesterification reaction. The low cloud point and pour point can increase the acceleration of a diesel engine at low temperatures [16].
4. Conclusion

Utilizing of CaO catalyst with a concentration of 3% resulted in the highest mass fraction of biodiesel of 57.1%. Biodiesel from Moringa seed oil which was resulted from transesterification reaction has a methyl oleate content of up to 45.60%. Characteristics of biodiesel including the water content of 0.3%, acid number of 0.03 mg KOH / g, saponification number of 6.93 mg KOH/g, iodine number of 5.49 g iod/100g, cloud point of 18°C, and pour point of 16°C. It is necessary to optimize the production of Moringa seed oil biodiesel using a CaO catalyst from chicken eggshell to obtain a higher mass fraction of biodiesel.

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