Production of biodiesel based on moringa seed oil at varied reaction times by using CaO catalyst from chicken eggshells

Ruslan*, J Hardi, H Sosidi, A Ridhay and A Y Agus
Chemistry Department, Tadulako University, Palu, Indonesia

*Email: ruslan_abdullah66@yahoo.co.id

Abstract. Moringa seed oil has many long-chain fatty acid contents that very potential transformed become fatty acid methyl ester or biodiesel. CaO material that was obtained from calcinating of chicken eggshells can be used as a heterogeneous catalyst at biodiesel production from Moringa seed oil. The purpose of this research was to determine the reaction time that produced biodiesel with the highest mass fraction of fatty acid methyl esters and also to determine the characteristics of biodiesel. Biodiesel was made through a transesterification reaction by using CaO catalyst at a mole ratio of oil: methanol of 1:6 for 1, 2, 3, and 4 hours. Transesterification reaction for 2 hours resulted in a methyl ester mass fraction of 82.69%. GC-MS analysis result has shown that methyl oleate had the highest concentration of 86.56% at a retention time of 37.62 minutes. The characteristics of biodiesel including the acid number of 0.09 mg KOH/g, saponification number of 356.4 mg KOH/g, iodine number of 0.635 g iod/100g, cloud point of 13°C, pour point of 20°C, and cetane number of 61.45.

1. Introduction
Biodiesel is an alternative fuel made through transesterification reaction between vegetable oil with alcohol [1]. Biodiesel fuel has advantages including biodegradable, non-toxic, low emissions of CO₂ and sulfur gas (SOₓ), and very environmentally friendly [2]. The raw materials for making biodiesel oil include used cooking oil and palm oil [3], pangi seed oil [4], coconut oil [5], and Moringa seed oil [6]. Moringa seed oil can be extracted using n-hexane solvent and is able to produce oil of 38 - 40% [7].

Production of biodiesel requires a catalyst, either a homogeneous catalyst or a heterogeneous catalyst. Heterogeneous catalysts have advantages over homogeneous catalysts because they are easily separated and can be used repeatedly, such as CaO [8] and zirconia-pillared clay [9]. CaO from chicken eggshells can be used in making biodiesel from Moringa seed oil. Chicken eggshell is one of the household wastes that contains a lot of CaCO₃ (calcium carbonate) as much as 94% [10]. Arifin et al. produced biodiesel from used cooking oil with CaO catalyst from snail shells and produced 63% biodiesel [11]. The purpose of this study was to obtain the best reaction time in biodiesel production from Moringa seed oil by utilizing CaO catalyst from chicken eggshells. Biodiesel from coconut oil using a CaO catalyst 2%, temperature of 60°C, and an 8:1 mole ratio of methanol to oil for 1.5 hours has been studied with yield of 75.02% [8].

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 sodium sulfate (Merck). Moringa seed oil was extracted from Moringa seed powder that used the
maceration method for 3 days and it used n-hexane solvent at a ratio of seed powder : solvent of 1: 8 (w/v). The oil was passed to anhydrous Na₂SO₄ 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 1100°C for 2 hours.

2.1. **Biodiesel production**

CaO catalyst with concentration of 3% (base on mass of CaO catalyst/oil) was mixed with methanol at room temperature. This mixture was reacted with moringa seed oil (mole ratio of methanol: oil = 6: 1) at a temperature of 50-70°C for 1, 2, 3, and 4 hours. Once the metanalysis reaction completed, the catalyst was separated by filtering. The filtrate was collected in a separating funnel and left standing until it forms two layers. The glycerol layer at the bottom was removed, while the crude biodiesel was washed by using warm distilled water (50-60°C) with a ratio of biodiesel/aqueduct of 1: 1 (v/v). The biodiesel was separated from side product 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). The highest mass fraction of biodiesel was analyzed for its compound components using a GC-MS GC17A MSQP 5000 Shimadzu.

\[
\text{Mass fraction of biodiesel (\%) = \frac{\text{mass of biodiesel spot}}{\text{mass of all spot}} \times 100}
\]

(1)

2.2. **Characterizations of biodiesel**

Characterization of biodiesel used fourier transform infrared (FT-IR Spectrophotometer 8201PC Shimadzu). The quality of biodiesel is determined by analyzing the moisture content, acid number, saponification number, iodine number, cloud and pouring points, and cetane number. The cetane number was determined as a function of the iodine number (IV) and the saponification number (SN) according to equation 2 [12].

\[
\text{CN} = 46.3 + \frac{5458}{\text{SN}} - 0.255 \times \text{IV}
\]

(2)

3. **Results and discussion**

3.1. **Biodiesel from transesterification at various reaction times**

The use of 2 hours reaction time resulted in the highest mass fraction of methyl ester or biodiesel of 82.69%. The mass fraction of the methyl ester decreased at the reaction time of 3 and 4 hours (Figure 1).

![Figure 1. Mass fraction of biodiesel at various reaction times](image-url)
3.2. GC-MS spectrum of biodiesel

Profile of methyl ester was identified by by GC-MS analyzing. MS spectra showed fragmentation at (m/z) of 264, 222, 180, 137, 98, 69, 55, and 41 (Figure 2). At the peak of the fragmentation of 264 (m/z) was methyl oleate (C_{19}H_{36}O_2). The existence of a double bond is shown in the addition of the fractional series of the C_{n}H_{2n-1}^+ 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 CH_3-CH=CH^+ ions.

![Figure 2. MS spectrum of biodiesel (A) and methyl ester oleic acid (B)](image)

GC-MS analysis produced one dominant peak, namely peak 3 (Figure 3). Methyl oleate was thought to be detected at the retention time of 37.62 minutes with a peak area of 86.56% (Table 1). 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 [6].

![Figure 3. GC spectrum of biodiesel](image)

| Peaks | Time retention (minute) | Peak area (%) | Prediction of compounds in biodiesel |
|-------|-------------------------|---------------|-------------------------------------|
| 2     | 33.96                   | 4.63          | Methyl laurate                      |
| 3     | 37.62                   | 86.56         | Methyl oleate                       |
| 4     | 37.94                   | 4.09          | Methyl stearate                     |
| 6     | 41.56                   | 0.86          | Methyl palmitate                    |
| 7     | 44.92                   | 2.21          | Methyl tetracosanoate               |
3.3. 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). 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 1165.00 cm\(^{-1}\) shows the C-O ester group (Figure 4). The absorption band at the number 2924.09 cm\(^{-1}\) shows the C-H functional group. In this spectrum there is no broad peak found at wavenumber > 3000 cm\(^{-1}\) which indicates the absence of O-H groups or the free fatty acid impurities are very small.

3.4. Characteristic of biodiesel
Characteristics of biodiesel including acid number of 0.09 mg KOH/g, saponification number of 356.4 mg KOH/g, iodine number of 0.635 g iod/100g, cloud point of 13\(^\circ\)C, pour point of 20\(^\circ\)C, and cetane number of 61.45. The cetane number is an important parameter which shows how fast the diesel engine fuel that is injected into the combustion chamber can burn spontaneously [15]. Several parameters have fulfilled ASTM, such as the acid number with a value of <0.5 mg KOH / g, the saponification number with a value of <370 mg KOH/g, and cetane number more than 47 [7]. Cloud point, pour point, iodine value, and cetane number have also fulfilled Standar Nasional Indonesia (SNI). SNI requires maximum value of iodine value of 115 gr iod/100 gr, cloud point of 18\(^\circ\)C, pour point of 28\(^\circ\)C, and minimum value of cetane number of 51. Based on the cloud point and pour point values, the biodiesel produced can be used in tropical countries because paraffin crystals in the fuel line will not formed.

4. Conclusion
Transesterification of Moringa seed oil with methanol was able to produce a mass fraction of methyl ester or biodiesel of 82.69% at a reaction time of 2 hours. The results of GC-MS analysis showed that the dominant compound was methyl oleate with a percentage of 86.56%. The characteristics of biodiesel including the acid number of 0.09 mg KOH/g, saponification number of 356.4 mg KOH/g, iodine number of 0.635 g iod/100g, cloud point of 13\(^\circ\)C, pour point of 20\(^\circ\)C, and cetane number of 61.45 or according to ASTM and SNI standards. But it is necessary to optimize the treatment in order to obtain a mass fraction with the quantity more than 90%.

Acknowledgement
Thanks to the Faculty of Mathematics and Natural Science, Tadulako University who has funded this research so that this research can be done smoothly.
References

[1] Szybist J P, Taylor J D, Boehman A L and Mc Cormick R L 2005 Journal Fuel Processing Technology 86 1109-1126
[2] Marchetti J M and Errazu A F 2008 Fuel 87 3477-3480
[3] Miskah S, Anugrah A and Gunadi 2016 Jurnal Teknik Kimia 22 54-61
[4] Efendi S, Hamzah F H and Ali A 2018 Jurnal Faperta 5 1-12
[5] Putri S K, Suprianto and Sudiyono R 2012 Jurnal Rekayasa Proses 6 20-25
[6] Rashid U, Anwar F, Moser B R and Knothe G 2008 Bioresource Technology 99 8175-8179
[7] Azad A K, Rasul M G, Khan M M K, Sharma S C and Islam R 2015 Procedia Engineering (6th BSME International Conference on Thermal Engineering) 105 601 – 606
[8] Padil, Wahyuningsih S and Awaluddin A 2010 Journal Natur Indonesia 13 27-32
[9] Ruslan, Khairuddin, Hardi J and Mirzan M 2020 AIP Conference Proceedings (The 8th International Conference of The Indonesian Chemical Society) 2243 030022 1-6
[10] Stadelman W J and Cotteril O J 2000 Food Products Press: An Imprint of the Haworth Press. Inc.
[11] Arifin Z, Rudyianto B and Susmiati Y 2016 Jurnal Rotor 9 100-104
[12] Azam M M, Waris A and Nahar N M 2005 Journal Biomass dan Bioenergy 29 293-302
[13] Affandi R D N et al. 2013 Jurnal Teknik Kimia USU 2 1-6
[14] Santoso H, Kristianto I, Setyadi A 2013 Research Report - Engineering Science 1
[15] Sundaryono A 2011 Jurnal Teknologi Industri Pertanian 21 34-40