Synthesis of Methyl Ester from Chicken Oil and Methanol Using Heterogeneous Catalyst of CaO-MgO as well as Characterization Its Potential as a Biodiesel Fuel

Aman Santoso*, Sumari, Agus Salim, Siti Marfu’ah
Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang, Jl. Semarang 5 Malang 65145, Indonesia

*Corresponding author’s email: aman.santoso.fmipa@um.ac.id

Abstract. The aim of this study was to synthesize methyl ester from chicken oil and methanol using catalyst of CaO-MgO as well as to characterize its potential as a biodiesel fuel. Synthesis methyl ester from chicken oil and methanol using CaO-MgO catalyst conducted through a trans-esterification reaction. Identification the methyl ester generated as a result of synthesis was used GC-MS. Characterization its potential as a biodiesel consisted of density, viscosity, refractive index, and acid number test. The results showed that methyl ester can be synthesized from chicken oil through trans-esterification with methanol using CaO-MgO catalyst with the yield of 81.32 wt%. The types of methyl esters resulted in this reaction were methyl palmitoleic (3.64 wt%), methyl palmitate (37.05 wt%), methyl linoleate (4.75 wt%) methyl oleate (40.90 wt%), and methyl stearate (2.28 wt%). The synthesized methyl ester has a density of 0.88 g/mL, a viscosity of 5.84 cSt, a refractive index of 1.45018, and the acid number of 0.69 mg KOH/g of methyl ester. Therefore, the methyl esters produced using chicken oil as a raw material meets the standard requirements for use as biodiesel fuel and has good prospects for use as a renewable energy source.

Keywords: Methyl ester, chicken oil, trans-esterification, CaO-MgO catalyst.

1. Introduction
The development of the economic level of society causes energy demand also increase. Indonesia is still heavily dependent on fossil energy while this kind of energy reserves are declining [1,2]. The fact is also followed by the absence of new reserve discoveries and the transition to alternative renewable energy sources is not yet running [3]. Therefore, alternative fuels instead of petroleum, especially diesel oil, can be used to reduce dependence of fossil fuels.

Biodiesel is an alternative fuel for diesel engines that are environmentally friendly and barely contain sulfur [4]. Biodiesel has advantages over diesel oils that is not emitting carbon monoxide, sulfur, hydrocarbons, and low burning fumes [5]. Biodiesel can be produced through the synthesis of vegetable oils such as palm oil or animal fats such as chicken fat or chicken oil.

Chicken is a relatively high-fat food in the body so that chicken fat is often separated and sold cheaply in the market even just thrown away as waste. This causes chicken fat has a low economic value. Chicken fat is in the form of liquid at room temperature. Chicken oil is a triglyceride composed of a series of saturated and unsaturated fatty acids where the largest fatty acid content is oleic acid...
which is unsaturated fatty acids [6]. The triglyceride could be reacted with an alcohol to form a potentially biodiesel alkyl ester by transesterification [7].

The biodiesel production through transesterification reaction is commonly used alcohol such as methanol or ethanol but methanol is more commonly used because it is more reactive and cheaper than that of ethanol [8]. The transesterification reaction is generally carried out using catalyst to speed up the reaction process. The most widely used catalysts are homogeneous catalysts such as NaOH and KOH [9]. The catalyst, however, has a weakness that is corrosive, hygroscopic, can cause saponification, and difficult to separate from the resulting product [10]. To overcome this problem, it has been developed the use of heterogeneous catalysts. This kind of catalyst has many advantages such as high activity, low reaction conditions, long life time, easily separated, reusable, and relatively cheap [11]. This fact leads to this study using heterogeneous catalysts. The transesterification reaction occurring between triglycerides and alcohols with the catalyst is shown in Figure 1

![Figure 1. Transesterification reaction occurring between triglycerides and alcohols with a catalyst.](image)

Heterogeneous catalysts like earth alkaline metal oxides such as CaO is often used. They are cheap, easily available, and less toxic [12] Calcium Oxide can be obtained from limestone, CaCO$_3$. When it is heated in a high temperature, the limestone limestone releases CO$_2$ and remaining CaO. The CaO catalyst has as a strong base but has a slightly weak activity when used as a catalyst to produce alkyl ester. One way to increase CaO activity is to combine it with magnesium oxide, MgO [7]. The MgO catalyst is obtained from MgCO$_3$ that is heated through a calcination process in a very high temperature to separate CO$_2$ from MgO. Therefore, the study of the coupling catalyst, CaO-MgO, in synthesis of methyl esters from chicken oil through transesterification reaction becomes interesting to do. What are the components resulted from transesterification dan its potential as a biodiesel are two interesting things to look at.

2. Materials and Methods

2.1 Preparation and Characterization of Chicken Oil

Chicken oil extraction was done by heating 450 g of chicken oil added 100 mL of distilled water in a Beaker glass. After heating for 3 to 4 hours will be obtained two layers. The top layer is chicken oil and the bottom layer is a water mixture with chicken fat impurities. The oil product is moved into a Beaker glass and heated to a temperature of 100 °C to remove residual water. Characterization of isolated chicken oil includes the properties of density, viscosity, refractive index, and acid number. Determination of free fatty acid content of chicken oil is done as the basis of whether transesterification can be done directly or need some stages of esterification.
2.2 Preparation of CaO-MgO Heterogeneous Catalysts
A total of 50.0 g of CaO and MgO catalysts were activated by calcination in the furnace for 2 hours at 825 °C. After cooling for a while, the heated catalyst was stored into the desiccator for ± 24 hours. A coupling catalyst of CaO and MgO are mixed with a weight ratio of 1: 1 to homogeneous before being used in methyl ester synthesis.

2.3 Synthesis of Methyl Ester with CaO-MgO Heterogeneous Catalyst
A total of 40.00 g of chicken oil is put into a three-neck flask. While heated slowly added methanol with a mole ratio of methanol: chicken oil (15: 1), which has added a catalyst mixture of CaO-MgO with a concentration of 5% of the sample weight. Heating with reflux at constant temperature between 60-65 ºC while stirring at 300 rpm. The reaction process was followed by analysis with Thin Layer Chromatography (TLC) to obtain Rf of the product of synthesis and compared with the initial sample. Eluent used in the TLC analysis was mixture of n-hexane, diethyl ether and formic acid with a ratio of 70: 30: 2.

After the reaction process is stopped, the synthesis mixture was centrifuged for 20 minutes at a rate of 3000 rpm. The mixture was poured into a separating funnel and allowed for two hours to obtain two layers where the top layer is expected of methyl ester while the bottom layer is glycerol. Top layer was separated and washed with warm aquadest. The resulting methyl ester was dried by adding an anhydrous Na₂SO₄ crystals. The yield of synthesis is determined by comparing the weight of the synthesis product with the weight of the theoretical results. The identification of methyl esters of the synthesis results was done by using GC-MS instrument.

2.4 Characterization.
Characterization of chicken oil and methyl esters as the result of synthesis consist of density, viscosity, refractive index, and acid number. Determination of the density was carried out picnometer, determination of the viscosity was carried out using Oswald viscosimeter, determination of the refractive index using Abbe refractometer, and determination of the acid number through titration using a 0.1 N KOH solution.

3. Results and Discussion

3.1 Chicken Oil Extraction and Characterization
Extraction results with water solvent, as much as 450 g of chicken fat obtained 171.15 g of oil (38.3%). The physical properties of chicken oil are liquid, clear yellow, specific odor. The character of chicken oil obtained were the density of 0.91 g/mL, the viscosity of 60.36 cSt, refractive index of 1.465, and the acid number 1.58 mL KOH/g of chicken oil. The fatty acid content of chicken oil is 1.64%. The free fatty acid content is less than 2.5%, so it can be directly done through transesterification reaction [13].

3.2 Activation of CaO-MgO Heterogeneous Catalyst
Preparation of CaO-MgO catalyst refers to a study conducted by Indah et a. [12]. Catalyst of CaO and MgO respectively of 50.00 g were activated by calcination in the furnace for 2 hours at 825 °C. Calcination can improve the active side of the catalyst. Calcination is also done to reduce the water content in the catalyst. The constant weight of CaO and MgO catalysts after each heating was 36.60 g and 43.02 g. The CaO and MgO catalysts are stored into desiccator for 24 hours.

3.3 Synthesis of Methyl Ester with CaO-MgO Heterogeneous Catalyst
Oil is a triglyceride or fatty acid ester of glycerol. Through the transesterification reaction of three glycerides from chicken oil can be converted to another ester form. The optimum condition of methyl ester synthesis of chicken oil with methanol (1:15) with a heterogeneous CaO-MgO catalyst at a concentration of 5% by weight of the sample at 65 °C for 2 hours. The concentration of the catalyst
refers from a study conducted. The reaction of the transesterification reaction with the CaO-MgO catalyst occurring is revealed in Figure 2.

![Diagram of transesterification reaction]

**Figure 2.** Transesterification reaction of three glycerides

Based on the stoichiometric reaction the mole ratio of three glyceride and alcohol was 1 : 3 and produced 3 moles of methyl ester. In this study excessive alcohols are used because of the reversible reaction properties to obtain product as much as possible. The transesterification reaction is reversible so that excess alcohol is required to obtain a maximum product [5]. The reaction is stopped after a change from oil to ester form can be tested by analysis with TLC showing difference Rf stain mixture of methyl ester with chicken oil. The result of synthesis of methyl ester by means of reflux can be seen in Figure 3.

![Image of synthesis of methyl ester]

**Figure 3.** Tormed two layers of liquid as a result of synthesis of methyl ester from chicken oil

The transesterification results form two layers where at the top is considered as a methylester and at the bottom is glycerol. Both layers were separated until the upper layer remains. The yield of methylester resulted at the synthesis using CaO-MgO catalyst was 81.39%.
3.4 Identification of Methyl Ester Using GC-MS

Methyl esters synthesized from chicken oil in this research identified using GC-MS yields a well-defined chromatogram as shown at Figure 4.

Figure 4. Chromatogram of Methylester Synthesized from Chicken Oil

Figure 2 shows there are 5 fairly large peaks that can be said there are five compounds making up the methylester mixture of the synthesis product. Each peak at chromatogram represents one compound. The total area shown in the chromatogram is proportional with percent composition of the compound in the mixture. The retention time and area of the five compounds making up the methyl ester mixture are listed in Table 1.

| Peak | Retention Time | Area   | Percent Area (%) |
|------|----------------|--------|------------------|
| 1    | 27.833         | 391036 | 3.64             |
| 2    | 28.683         | 3980858| 37.05            |
| 4    | 35.087         | 510951 | 4.75             |
| 5    | 35.263         | 4395149| 40.90            |
| 10   | 36.007         | 245343 | 2.28             |

The compounds in the mixture of methylester as the product of synthesis can be identified using mass spectroscopy analysis. One Example of the result of mass spectroscopy at with retention time (tR) of 27.833 min is shown in Figure 5.

Figure 5. Spectrum Peaks of Chromatogram of Methyl ester from Chicken Oil with Retention Time (tR) 27,833 Minutes
The mass spectra obtained are compared with the mass spectrum found in the WILEY7.LIB Library and searched for peaks of relatively equal position. Based on observations of the WILEY7.LIB Library entry number of 199160, it is presumed that the compound is methyl palmitoleate or methyl 7-hexadecenoate or methyl 7-hexadecenoate. It is reinforced by a fragmentation pattern whose peaks have m/z 41, 55, 69, 74, 96, 98, 123, 138 and 152. Peaks with m/z 152 and m/z 98 are thought to be obtained by breaking fragments is shown in Figure 6.

\[ \text{CH}_3(\text{CH}_2)_7\text{CH} = \text{CH}(\text{CH}_2)_4\text{CH}_2 \cdot \text{C} \rightarrow \text{[CH}_3(\text{CH}_2)_7\text{CH} = \text{CH}(\text{CH}_2)_4\text{CH}_2 \cdot \text{C} OCH}_3 \]
\[ \text{m/z 268} \]

\[ \text{CH}_3(\text{CH}_2)_7\text{CH} = \text{CH}(\text{CH}_2)_4\text{CH}_2 \cdot \text{C} \rightarrow \text{[CH}_3(\text{CH}_2)_7\text{CH} = \text{CH}(\text{CH}_2)_4\text{CH}_2 \cdot \text{C} OCH}_3 \]
\[ \text{m/z 237} \]

\[ \text{CH}_3(\text{CH}_2)_7\text{CH} = \text{CH}(\text{CH}_2)_4\text{CH}_2 \cdot \text{C} \rightarrow \text{[CH}_3(\text{CH}_2)_7\text{CH} = \text{CH}(\text{CH}_2)_4\text{CH}_2 \cdot \text{C} OCH}_3 \]
\[ \text{m/z 268} \]

\[ \text{CH}_3(\text{CH}_2)_7\text{CH} = \text{CH}(\text{CH}_2)_4\text{CH}_2 \cdot \text{C} \rightarrow \text{[CH}_3(\text{CH}_2)_7\text{CH} = \text{CH}(\text{CH}_2)_4\text{CH}_2 \cdot \text{C} OCH}_3 \]
\[ \text{m/z 237} \]

\[ \text{CH}_3(\text{CH}_2)_7\text{CH} = \text{CH}(\text{CH}_2)_4\text{CH}_2 \cdot \text{C} \rightarrow \text{[CH}_3(\text{CH}_2)_7\text{CH} = \text{CH}(\text{CH}_2)_4\text{CH}_2 \cdot \text{C} OCH}_3 \]
\[ \text{m/z 152} \]

Peak with m/z 123 allegedly obtained from fragments with m/z 268 as follows:

\[ \text{CH}_3(\text{CH}_2)_7\text{CH} = \text{CH}(\text{CH}_2)_4\text{CH}_2 \cdot \text{C} \rightarrow \text{[CH}_3(\text{CH}_2)_7\text{CH} = \text{CH}(\text{CH}_2)_4\text{CH}_2 \cdot \text{C} OCH}_3 \]
\[ \text{m/z 209} \]

\[ \text{CH}_3(\text{CH}_2)_7\text{CH} = \text{CH}(\text{CH}_2)_4\text{CH}_2 \cdot \text{C} \rightarrow \text{[CH}_3(\text{CH}_2)_7\text{CH} = \text{CH}(\text{CH}_2)_4\text{CH}_2 \cdot \text{C} OCH}_3 \]
\[ \text{m/z 208} \]

**Figure 6.** Fragmentation molecules of methyl ester of chicken oil.
Peaks with m/z 74 (base peak) and 55 are thought to be obtained via a molecular ion reconstitution of Mc Lafferty is shown in Figure 7.

Figure 7. Molecular ion reconstitution of Mc Lafferty

Peaks with m/z 41 are thought to be obtained by breaking the bonds on the molecular ions is shown in Figure 8.

Figure 8. Breaking the bonds on the molecular ions at m/z 41.

Based on spectral fragmentation analysis with a retention time of 27.835 min, it can be concluded that the compound is methylpalmitoleate like shown in Figure 9.

Figure 9. Methylpalmitoleate

Pattern analysis of mass spectrum fragmentation as a whole can be seen that the five main constituent components of methyl esters mixture of chicken oil are methyl palmitoleate (3.64%), methylpalmitate (37.05%), methyllinoleate (4.75%), methyloleate (40.90%), and methylstearate (2.28%).
3.5 Characterization of Methyl Ester as a Result of Synthesis

Characteristics of methyl esters of the synthesis include the density, viscosity, refractive index, and acid number.

| Parameter       | Methylester as a product of synthesis | Chicken oil |
|-----------------|---------------------------------------|-------------|
| Density (g/mL)  | 0.88                                  | 0.91        |
| Viscosity (cSt) | 5.84                                  | 60.36       |
| Refractive Index| 1.450                                 | 1.465       |
| Acid number (mg of KOH/ g of oil) | 0.69                             | 1.58        |

Data at Table 2 shows that the characters of Methyl ester product of synthesis are different with the character of chicken oil. As an example, there is a change of viscosity from 60.36 to 5.84, it means that there is a decline of 55 cSt. This data indicates that methyl esters have been successfully synthesized. Characteristics of methyl esters synthesized when compared with biodiesel characteristics as shown in Table 3.

| Parameter       | Methyl ester as a product of synthesis | Biodiesel Standard of SNI |
|-----------------|---------------------------------------|---------------------------|
| Density (g/mL)  | 0.88                                  | 0.850 – 0.890             |
| Viscosity (cSt) | 5.84                                  | 2.30 – 6.00               |
| Refractive Index| 1.450                                 | Max 1.45                  |
| Acid number (mg of KOH/ g of oil) | 0.69                             | Max 0.80                 |

The data show that the character of methyl ester as a result of synthesis approaches the biodiesel character according to SNI standard. Based on the results of the analysis, it can be concluded that the methyl ester of the synthesis has potential as biodiesel or fuel. This result is in line with the result of characterization of biodiesel produced from palm oil via base catalyzed transesterification [14].

4. Conclusion
Methyl esters can be synthesized from chicken oil using heterogeneous CaO-MgO catalyst at 5% concentration and obtained the yield of 81.32%. The selectivity each compound of methyl esters as the product of synthesis is methylpalmitoleate of 3.64%, methyl palmitate 37.05%, methyl linoleate of 4.75%, methyl oleate of 40.90%, and methyl stearate of 2.28%. The character of methyl ester resulted from synthesis shows the density of 0.88 g / mL, viscosity of 5.45 cSt, refractive index of 1.45018, and acid number of 0.69 mg KOH/ g methyl ester, so that the methyl ester has potentially as a biodiesel.

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