Use of Mg-Al/hydrotalcite Catalyst in Biodiesel Production from Avocado Seed Oils: A Preliminary Study

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Abstract

Biodiesel production from avocado seed oils has been carried out using the heterogeneous catalyst of Mg-Al/hydrotalcite. Transesterification process was conducted by varying temperature reaction and oil-methanol molar ratio. The reaction temperature was 30, 40, 50, and 60°C, whereas the oil-methanol molar ratio was 1:3, 1:6, 1:9, and 1:12, respectively. The as-synthesized Mg-Al/hydrotalcite catalyst was characterized using X-ray diffraction and FTIR. Meanwhile, the biodiesel was analyzed their density, viscosity, water content, and 1H-NMR analysis. The results showed that optimum condition in biodiesel production was the oil-methanol molar ratio of 1:6 at a reaction temperature of 60°C for 60 minutes and catalyst quantity of 2% yielding biodiesel conversion percentage was approximately 15.90%. However, these preliminary findings showed that Mg-Al/hydrotalcite was able to convert the avocado seed oils into biodiesel even if still need further analysis and research so that produces a higher percentage of biodiesel conversion.

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1. INTRODUCTION

Nowadays, the increase of human population in line with high demand and use of energy resources have decreased the non-renewable fossil-energy reservation [1]. Notably, it was predicted that can only exist in less than 50 years later [2]. Therefore, the limited availability of those has forced researches and industry players around the world searching for new and renewable energy for the energy needs in the near future. Renewable energy such as biodiesel is one of the alternatives and green fuels which was widely explored and investigated because of its raw material availability; environmental friendly; low-pollution emission; a consideration in green-fuels for climate change prevention; in vehicles, an unwanted modified of machine was not required; well-performance because of high cetane number; no need lubricant addition for high purity grade of biodiesel; more efficient than fossil resources based fuels [3].

Biodiesel is defined as long-chain of monoalkyl ester of fatty acid derived from renewable fat. It was similar to vegetable and animal fat [4]. In addition, Santoso et al. [5], it is a mixture of monoalkyl ester of fatty acid and vegetable and animal fat. As-reported raw materials for biodiesel production have been established such as plant or vegetable [6,7], animal fat [8-10], macro- and microalgae [11,12], wastes [13-18], and so on. However, plant oil-based biodiesel synthesis has promising
and attracting the researches to explore deeply. Plant oil from non-edible feedstock has considered a raw material alternative to minimize the use of edible feedstock as well as affordable cost and food security in biodiesel production [19]. The oil produced from avocado seed extract is one of feedstock that recently used to produce biodiesel. In Indonesia, the avocado seed was found in by-products that are rarely used and thrown away. However, about 25.15% of oil could be extracted per 50 grams of avocado seeds and potential to be utilized as biodiesel feedstock [20]. Moreover, Djenar et al. [21] also reported that avocado seed oils can be used and converted into biodiesel with a yield of about 83.46%.

Besides, the catalyst is also important especially to enhance the quantity and the quality of biodiesel production simultaneously [22]. Hydrotalcite is one catalyst that used in biodiesel production. Hydrotalcite has known as anionic loam consisted positive-charged layers and water within interlayer [23], with general structure of \[\text{MII}_x\text{MIII}_y(\text{OH})_z\] and \[x\cdot\text{nH}_2\text{O}\] where MII, MIII and A\text{m} were divalent (such as Mg\text{2+}, Zn\text{2+}, etc.), trivalent (such as Al\text{3+}, Fe\text{3+}, etc.) and organic or inorganic anionic, respectively [24]. Salmao et al. [25] stated that hydrotalcite is derived from brucite structure [Mg(OH)\text{2}]. The as-reported heterogeneous catalyst of Mg-Al/hydrotalcite has used in biodiesel production from jatropha oils yielding ~83.32% [26], and ~94.17% [27], respectively. Nonetheless, Mg-Al/hydrotalcite catalyst is still open to be investigated. In addition, biodiesel production from avocado seed oils using Mg-Al/hydrotalcite catalyst has not been reported previously. Therefore, herein we synthesized and characterized biodiesel from avocado seed oils using the heterogeneous catalyst of Mg-Al/hydrotalcite. As-synthesized catalyst of Mg-Al/hydrotalcite was characterized using X-ray diffraction and FTIR. The transesterification has been conducted by mixing avocado seed oils with the variation of oil-methanol molar ratio and reaction temperature, respectively. The as-resulted methyl ester from the transesterification process was investigated using 1H-NMR. Finally, biodiesel characteristics were presented and explained in this research.

2. EXPERIMENTAL SECTION

2.1. Materials

Materials were commercial natural zeolite, Na\text{2}CO\text{3}, AlCl\text{3}, MgCl\text{2}·6H\text{2}O, n-heksane, HCl, NaOH, AgNO\text{3}, Na\text{2}SO\text{4}, methanol (p.a), ethanol 95%, alcohol 95% and avocado seed oils.

2.2. Method

2.2.1. Preparation of ZAH catalyst

Preparation of catalyst follows Kartika et al. [28] which 200 gr of natural zeolite was crushed and filtered with 100 mesh filter. Then, added into HCl 6 M, mixed with a magnetic stirrer for 24 hours. Subsequently, the sample was washed with aquadest until reaches neutral conditions of pH. The sample was dried and calcined at 120°C and 400°C, respectively. The catalyst was filtered using 100 mesh filter and named as ZAH.

2.2.2. Preparation of Mg-Al/hydrotalcite

Preparation of Mg-Al/hydrotalcite follows Rao et al. [29] which 0.2 moles of MgCl\text{2}·6H\text{2}O and 0.05 mole of AlCl\text{3} were dissolved into 200 mL aquadest. Then, added into 400 mL of 0.40 moles Na\text{2}CO\text{3} with the rate of addition was 5 mL/min. During this step, the solution was mixed using stirrer magnetic and keep it at a pH of 10 (by adding some droplets of NaOH solution). Subsequently, the suspension was stirred at 60-63°C for 1 hour. The solution was stored for 18 hours in controlled temperature without mixing treatment. The precipitate was washed with aquadest until the Cl ion-free precipitate resulted. Cl ion in solution could be removed by adding AgNO\text{3} into the filtrate. Cl ion-free precipitate then was dried in the oven at 80 °C for 16 hours. Finally, the as-resulted white-solid precipitate was analyzed using XRD and FTIR.

2.2.3 Esterification

The esterification process follows Nisa [30]. The esterification of avocado seed oils has been carried out in 500 mL three-neck flask integrated with electrical heating instrument, thermometer, magnetic stirring, and cooling system. The
esterification process was conducted under reaction condition that was reaction temperature of 60°C, stirring speed of 700 rpm, ZAH quantity of 2% (w/w%), the oil- methanol molar ratio of 1:3 and reaction time of 60 minutes. Then, the solution was transferred into separating funnel and stored for 24 hours until oil and methyl ester were clearly separated. The as-resulted methyl ester was dried under room temperature to eliminate successive methanol.

2.2.4 Transesterification

The transesterification of as-resulted methyl ester follows Kartika and Widyaningsih [31] which the oil transferred into 500 mL three-neck flask and then heated at 30, 40, 50, and 60°C, respectively. Subsequently, the oil was introduced with methanol and Mg/Al hydrotalcite under controlled-temperature and stirring speed of 700 rpm for a reaction time of 60 minutes. Noted that in this research Mg/Al hydrotalcite catalyst was wrapped in a paper filter so it is easy to use again or separate it from suspension. Then, the transesterification was continued with the varied oil-methanol molar ratio that is 1:3; 1:6; 1:9; and 1:12 (oil weight) under optimum reaction temperature, catalyst weight of 2% and stirring speed of 700 rpm. The reaction was stopped by soaking the three-neck flask in ice water. The oil from transesterification subsequently was transferred into separating funnel and deposited for 24 hours until oil and catalyst residue were clearly separated. Bottom and top layers were glycerol and biodiesel product, respectively. The mixture was washed 2-4 times using aquadest until the washing solution was neutral. The top layer was collected and added with Na2SO4. Then, oil was filtered using Buchner funnel and dried under room temperature.

2.2.5 Density analysis of biodiesel (ρ)

The density analysis of biodiesel follows Nisa [30]. The pycnometer was cleaned up using HCl and then washed for 3 times with aquadest (with alcohol once). Subsequently, it was dried in the oven for 5 minutes, stored into desiccator. Then, porcelain (W1) was added 5 grams of oil, weighed (W2) and dried for 4 hours at 110°C. The cup was allowed cooling down in desiccator and weighed (W3). The water content was calculated by the formula as follows: water content = ((W2 - W3)/Wsample) x100% where W2 and W3 are porcelain cup and methyl ester weight before and after heating (in gram), respectively.

2.2.6 Viscosity analysis of biodiesel (η)

The viscosity analysis follows Atkins [32]. The Ostwald viscometer was cleaned up with acetone solution. Pure biodiesel of about 2 mL was pumped up to boundary mark on the tube of the Ostwald viscometer. Biodiesel was allowed to drain along the tube and passed through the other boundary mark at the temperature condition of 40°C. The time used for the sample passed through the boundary mark was recorded. Viscosity was determined by comparing the consumed-time for sample (t1) and viscosity (ρ1) to the reference (t1 and ρ1). The viscosity was calculated by the formula as follows: (η/η2) = (t1.ρ1)/(t2.ρ2) where η1 and η2, t1 and t2, ρ1 and ρ2 are the viscosity, consumed-time, and density of sample and reference, respectively.

2.2.7 Water content determination of biodiesel (η)

The water content determination of biodiesel follows Nisa [30] which porcelain cup was dried in an oven for 15 minutes, then stored into the desiccator. Then, porcelain (W1) was added 5 grams of oil, weighed (W2) and dried for 4 hours at 110°C. The cup was allowed cooling down in desiccator and weighed (W3). The water content was calculated by the formula as follows: water content = ((W2-W3)/Wsample) x100% where W2 and W3 are porcelain cup and methyl ester weight before and after heating (in gram), respectively.

2.2.8 1H-NMR analysis

The percentage of methyl ester conversion was analyzed using 1H-NMR.

3. RESULT AND DISCUSSION
3.1. Characterization of catalyst

A solid precipitate of Mg-Al/hydrotalcite catalyst was synthesized using facile-precipitation method by reacting the precursor of MgCl\(_2\)-6H\(_2\)O and AlCl\(_3\) with Na\(_2\)CO\(_3\) under base condition. The anion along CO\(_3\)\(^{2-}\) interlayer has chosen because it can bind immediately and strong enough within a brucite structure-like positive-charged layers so it was not needed hindering the unwanted contaminant in synthesis process [33]. The initial mole ratio of Mg/Al was 4:1 where has a high crystallinity [34]. The as-synthesized Mg-Al/hydrotalcite catalyst has a white color and small particle-cob as shown in Figure 1.

![Figure 1](image1.png)

**Fig. 1.** X-ray diffraction (XRD) and an inset picture of as-synthesized heterogeneous catalyst of Mg-Al/hydrotalcite; a white-solid cob.

Figure 1 shows the XRD pattern of the as-synthesized Mg-Al/hydrotalcite catalyst. Based on Figure 1, Mg-Al/hydrotalcite showed high crystallinity with an apparent sharp peaks on the diffractogram attributed to JCPDS No. 22-700 [35]. However, there are some new peaks within hydrotalcite diffraction. It might be the impurity or another phase besides the hydrotalcite phase. Star sign (*) could be attributed as Mg\(_5\)(CO\(_3\))\(_4\)(OH)\(_2\)-4H\(_2\)O or hydromagnesite phase [36]. In addition, the three highest peaks of Mg-Al/hydrotalcite catalyst has observed in 2θ of 11.20, 22.60 and 34.45° with d-spacing of 7.88, 3.93, and 2.62 Å respectively, that are characteristic of a layered structure [37]. Notably, it was similar to previous research [38, 39].

![Figure 2](image2.png)

**Fig. 2.** FTIR spectra of as-synthesized heterogeneous catalyst of Mg-Al/hydrotalcite.

Figure 2 shows the FTIR spectra of Mg-Al/hydrotalcite catalyst. As shown in Figure 2, the stretching and bending vibration was observed in 3400-3500 cm\(^{-1}\) and 1644 cm\(^{-1}\) attributed to the O-H functional group and a water molecule (OH group) within interlayers of Mg-Al/hydrotalcite catalyst, respectively [40, 41]. The infra-red absorption of 1371 cm\(^{-1}\) was attributed to the symmetry stretching of O=C-O group [42], whereas stretching vibration of Al-O and Mg-O appears on the adjacent peaks of 503 and 449 cm\(^{-1}\), respectively [37, 43]. Septiyaningrum et al. [44] reported that the Al-O and Mg-O could observe in distinctly region yet the increase of mole variation of hydrotalcite catalyst, the peak of Mg-O and Al-O are presumably difficult to be identified as shown in Figure 2.

3.2. Biodiesel Characteristics

3.2.1. Density of biodiesel

Density is defined as a value of the weight comparison per volume units [45]. Table 1 and Figure 3, shows temperature and oil-methanol molar ratio towards biodiesel density. Based on Table 1 and Figure 3, temperature influences the biodiesel density of about 0.9074-0.9587 g/cm\(^3\). A similar trend was also observed in oil-methanol molar ratio with the range of 0.9084-0.91012 g/cm\(^3\).

Based on SNI 7182:2015 (Standar Nasional Indonesia) biodiesel density standard at 40°C is around 0.85-0.89 g/cm\(^3\). However, the as-synthesized biodiesel from avocado seed oils was slightly higher neither temperature nor oil-
methanol molar ratio than SNI’s biodiesel requirement. But, as we saw in Table 1 showed that temperature and oil-methanol molar ratio were 60°C and 1:6 have biodiesel density is 0.9074 and 0.9084, respectively. It was close to the SNI’s requirement than other varied-temperature and oil-methanol result.

Table 1. Summary data of biodiesel characteristics

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Temperature (°C)</th>
<th>Oil-methanol molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>1:3</td>
<td>1:6</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>0.9</td>
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<tr>
<td></td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Viscosity (cSt)</td>
<td>15.34</td>
<td>16.02</td>
</tr>
<tr>
<td></td>
<td>16.02</td>
<td>16.52</td>
</tr>
<tr>
<td></td>
<td>16.52</td>
<td>12.638</td>
</tr>
<tr>
<td>Water content</td>
<td>2.5</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>1.9</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>1.9</td>
<td>1.4</td>
</tr>
</tbody>
</table>

The reaction temperature was maintained at 60°C that close to the maximum temperature of methanol (at 1 atm) which correspond to its normal boiling point [36]. This was estimated that the intensity of collisions between methanol and triglyceride have enhanced each other and reached optimum condition, significantly. Moreover, the varied temperature in this research was not set at a higher reaction temperature (more than 60°C) is a plausible reason to restrict the methanol evaporation to the air. In addition, Sihombing et al. [46] stated that reaction temperature higher than 60°C can decrease the methanol concentration in suspension. Therefore, the lack of methanol in the liquid phase decreases the collisions between methanol and substrate as same as decreases the reaction rate.

In the oil-methanol molar ratio, higher molar ratio slightly increased the biodiesel density. This might be caused by an excess of water in suspension as same as biodiesel impurities. Water density is higher than biodiesel, hence an excess of water could increase the biodiesel density [47]. In addition, Verma et al. [48] stated that the optimum molar ratio of alcohol has an important role in biodiesel yield. The lower and higher molar ratio of alcohol would give the effect in conversion ability of triglyceride into methyl esters and down the biodiesel yield attributing to the backward reaction through emulsification of polar groups of glycerol, respectively. Therefore, the optimum oil-methanol ratio in suitable biodiesel density was reached in 1:6.

3.2.2. Viscosity of biodiesel

Viscosity is defined as the value of resilience of fuel to flow. The viscosity of biodiesel was influenced by an unreacted-triglyceride content and their constituent of fatty acid composition. Based on Table 1 and Figure 3, temperature influences the biodiesel viscosity of about 12.638-16.5253 cSt. The effect of varied oil-methanol molar ratio was also observed in biodiesel viscosity. It was about 12.9348-14.9707 cSt.

Based on SNI 7182:2015, biodiesel viscosity standard at 40°C is around 2.3-6.0 cSt. It showed that temperature and oil-methanol molar ratio have a higher viscosity than SNI’s standard. However, temperature and oil-methanol molar ratio were 60°C and 1:6 have biodiesel viscosity of 12.638 and 12.934, respectively where is slightly lower than other varied temperature and oil-methanol molar ratio. A higher biodiesel density could also be caused by unsuccessful
conversion from triglyceride to methyl ester that has a lower density than triglyceride [49]. At certain biodiesel concentrations (lower concentration), a hydroxy group of mono- or diglyceride caused a strong hydrogen bond formation so increases the viscosity between triglyceride molecules as same as increases the biodiesel density [50]. Therefore, the optimum condition was conducted in temperature and oil-methanol molar ratio were 60°C and 1:6.

3.2.3. Water content of biodiesel

Water content is one of the important parameters that determined the quality of avocado seed oils. However, Murniash [51] reported that higher water content could accelerate the triglyceride hydrolysis process to produce free-fatty acid and glycerol. Water content in biodiesel is shown in Figure 3 and Table 1. Based on Table 1, the reaction temperature and oil-methanol molar ratio influence the water content of about 1.7195-2.5718 %v/v and 1.4041-2.8845 %v/v, respectively. Based on SNI 7182:2015, water content requirement at 40°C is 0.05 %v (%v max). However, the water content in this research was highest than SNI’s standard. In addition, temperature and oil-methanol molar ratio were 60°C and 1:6 have a water content of 1.7195 and 1.4041, respectively were lower than other varied temperature and oil-methanol molar ratio.

The highest water content in biodiesel synthesis attributing to the remaining water as same as biodiesel impurities when washing treatment was carried out. Moreover, the higher molar ratio of oil-methanol (1:12) diluted more water in suspension so the increase of oil-methanol molar ratio also increases the water content as shown in Figure 3 and Table 1. Even though, an excess amount of methanol is required to restrict the backward reaction because of the reversible reaction of the transesterification mechanism [48]. Therefore, the oil-methanol molar ratio was achieved in 1:6 although requires further purification.

3.3. Percentage of biodiesel conversion

Fig. 4. 1H-NMR result of avocado seed oils (a) and biodiesel product (b), respectively.

Determination of the biodiesel conversion percentage was carried out by using 1H-NMR. The avocado seed oils and biodiesel product are shown in Figure 4 (a) and (b), respectively. Figure 4 (a), pure or untreated avocado seed oils showed a peak in 4.2 ppm corresponded to the glyceride compound. Moreover, the presence of methyl ester was not found at around 3.7 ppm. Conversely, the presence of methyl ester was observed in Figure 4 (b) with esterification and transesterification process at around 3.5 ppm with the integration of about 0.39. In addition, glycerol compound could be detected at around 4.2 ppm with the integration of 1.14 [10]. Finally, based on calculation, the biodiesel conversion could be determined that is approximately 15.90%. We guessed that the low-biodiesel percentage due to the decrease in surface contact between catalyst and substrate. These because of Mg-Al hydrotalcite catalyst wrapping in filter paper. However at this stage, the heterogeneous catalyst was successfully carried out to convert avocado seed oils become biodiesel, although the low-biodiesel conversion is needed to be optimized by varying time reaction, catalyst weight, stirring speed, catalysis system, etc. to
produce high quality and quantity of biodiesel [18,31].

4. CONCLUSION

Biodiesel production from avocado seed oils using the heterogeneous catalyst of Mg-Al/hydrotalcite was successfully carried out with the percentage of biodiesel conversion is approximately 15.90%. The characteristics of as-resulted biodiesel were optimum under reaction temperature and oil-methanol molar ratio were 60°C and 1:6 (with catalyst concentration and time reaction were 2% and 60 minutes), respectively. Although it was not meet SNI 7182:2015 standards, this result showed preliminary findings of the use of Mg-Al/hydrotalcite catalyst in biodiesel production from avocado seed oils and potentially can be explored and investigated for other raw materials.

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