Synthesis of Biodiesel from Vegetable Oil over Hydrotalcite Solid Catalyst

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Abstract. Biodiesel as an alternative fuel was produced by transesterification of vegetable oil with hydrotalcite catalysts. Hydrotalcite was prepared by co-precipitation method using NaOH solution with the Mg to Al molar ratio 1 : 1, 2 : 1, 3 : 1 and 4 : 1 at 65 °C. Transesterification of vegetable oil were performed in 5 : 1, 10 : 1 and 15 : 1 methanol to vegetable oil molar ratio at 65 °C for 12 hours. Gas chromatography was used to determine the fatty acid methyl ester (FAME) contents in the produced biodiesel. Data obtained showed that 15 : 1 methanol to vegetable oil molar ratio gave the highest biodiesel amount (% yield : 72.53%).

Keywords: biodiesel, hydrotalcite, transesterification, methanol

INTRODUCTION

Globally, the awareness of energy issues and environmental problems associated with burning fossil fuels has encouraged many researchers to investigate the possibility of using alternative sources of energy instead of oil and its derivatives. Among them, biodiesel seems very interesting for several reasons: it is highly biodegradable and has minimal toxicity, it can replace diesel fuel in many different applications without major modifications and small decrease in performances is reported, almost zero emissions of sulfates, aromatic compounds and other chemical substances that are destructive to the environment, a small net contribution of carbon dioxide (CO₂) [1, 2]. Compared to diesel fuel, biodiesel produces no sulfur, no net carbon dioxide, less carbon monoxide, particulate matters, smoke and hydrocarbons emission and more oxygen. More free oxygen leads to the complete combustion and reduced emission [3, 4]. Biodiesel has viscosity similar to diesel fuel derived from petroleum and has a higher cetane number [5].

Biodiesel is generally produced by transesterification of vegetable oils or animal fats with short-chain alcohols (generally methanol) in the presence of catalysts. The reaction is shown in Fig. 1. Methanol is generally preferred because it is cheaper and more easily obtained [6-8]. If the alcohol used is methanol produced biodiesel is a fatty acid methyl ester [5]. The conventional catalysts for this transesterification reaction are homogeneous strong bases (such as alkali metal hydroxides and alkoxides) and homogeneous acids (such as H₂SO₄). However, alkaline catalysts are generally corrosive to equipment and also react with free fatty acid to form unwanted soap by-products that require expensive separation; the small amount of water will be produced from the reaction of the hydroxide with alcohol although it has been used vegetable oil and alcohol-free water. The presence of water can cause the resulting ester hydrolysis and causes the separation of reaction products (ester and glycerol) become one obstacle. The homogeneous acid catalysts are difficult to recycle and operate at high temperatures, and also give rise to serious environmental and corrosion problems. Therefore, the development of solid catalysts that can act as heterogeneous catalyst has recently gained much attention in view of their ease of separation and lack of corrosion or toxicity problems [5, 9-10].

Hydrotalcite is a heterogeneous catalyst that has been used for the base catalyzed reaction for metanalysis of soya bean oil. The molar ratio of soybean oil and methanol is 15 : 1, 9 hours of reaction time and the amount of catalyst of 7.5% and soybean oil conversion yield reached 67% [11]. The relationships between structure and reactivity hydrotalcite Mg Al have been studied on synthesis reaction of glyceryl tributyrte biodiesel with methanol [8]. The increasing of the concentration of Mg, the reaction rate increased which the Mg₂₉₈₆Al content is the most active catalyst and 10 times more active than pure. The hydrotalcite has attracted much attention during the development of new environmentally friendly catalysts. Hydrotalcite material is a mixed metal hydroxide groups
that are generally formulated as \([\text{M}^{2+}_{x}\text{M}^{3+}_{y}(\text{OH})_{z}]\left[\text{A}^{m-}\right]_{\text{n}}\cdot\text{nH}_{2}\text{O}\). The chemical composition can be represented by the general formula \([\text{M}^{2+}_{x}\text{M}^{3+}_{y}\text{X}_{z}](\text{Ax/}\text{y})_{n}\cdot\text{nH}_{2}\text{O}\), where \(\text{M}^{2+}\) and \(\text{M}^{3+}\) are divalent and trivalent metal cations respectively, \(\text{A}^{m-}\) is an \(n\)-valent anion, and \(x\) usually has a value between 0.25 and 0.33. The structure of hydrotalcites is based upon layered double hydroxides with brucite-like \((\text{Mg(OH)}_{2})\) hydroxide layers containing octahedrally coordinated \(\text{M}^{2+}\) and \(\text{M}^{3+}\) cations [12-13]. Many studies have been reported the effects of different parameters involved in the reaction, such as using different oils and alcohols, alcohol to oil molar ratio, types and amount of catalysts, reaction time or temperature [14–17].

In this work, biodiesel is produced by transesterification vegetable oil with methanol in the presence of hydrotalcite as solid catalyst. The properties of biodiesel obtained are measured and compare to SNI standard for biodiesel.

![Fig 1. Transesterification reaction of triglycerides and alcohol.](image)

**METHODS**

**Materials.** \(\text{Mg(NO}_{3}\text{)}_{2}\cdot6\text{H}_{2}\text{O}, \text{Al(NO}_{3}\text{)}_{2}\cdot9\text{H}_{2}\text{O}, \text{NaOH}, \text{Na}_{2}\text{CO}_{3}\) and methanol were purchased from Merck in analytical grade. The vegetable oil sample was bought from market in Banda Aceh and gas chromatography analysis revealed that lauric acid was the main component.

**Preparation of Hydrotalcite Catalyst.** Hydrotalcites catalysts were prepared by co-precipitation methods. An aqueous solution (200 ml) containing 0.75 mole \(\text{Mg(NO}_{3}\text{)}_{2}\cdot6\text{H}_{2}\text{O}\) and 0.375 mole \(\text{Al(NO}_{3}\text{)}_{2}\cdot9\text{H}_{2}\text{O}\) (the ratio of \(\text{Mg}\) to \(\text{Al} = 2 : 1\)) was added slowly to 60 ml \(\text{Na}_{2}\text{CO}_{3}\) 0.9 M solution under vigorous stirring. The addition took nearly 2 h and the \(\text{pH}\) of solution was maintained at 10 by adding 2.25 M of \(\text{NaOH}\) solution. The mixture was kept at room temperature for 2 h under stirring, after which the gel product was left for 6 h at 338 K. The white gel was filtered, washed with demineralised water to eliminate the alkali metal ions and the nitrate ions until the \(\text{pH}\) of the washing water was 7. The formed hydrotalcite was dried for 18 h at 383 K. The sample was calcined at 723 K for 3 h and designated as HT21. The catalyst with different Mg/Al ratios denominated as HT11, HT31 and HT41 were obtained by using 0.5 mole \(\text{Mg(NO}_{3}\text{)}_{2}\cdot6\text{H}_{2}\text{O}\) and 0.5 mole \(\text{Al(NO}_{3}\text{)}_{2}\cdot9\text{H}_{2}\text{O}\), 0.75 mole \(\text{Mg(NO}_{3}\text{)}_{2}\cdot6\text{H}_{2}\text{O}\) and 0.25 mole \(\text{Al(NO}_{3}\text{)}_{2}\cdot9\text{H}_{2}\text{O}\) separately.

**Characterization.** The powder XRD measurement of hydrotalcites were recorded on a Philips Analytical XRD B.V using \(\text{Cu K}\alpha (\lambda = 1.5405 \text{ Å in 2θ range of 10 – 90°})\) with a step size of 0.02°. The operating voltage and the current were 40 kV and 30 mA. The phases were identified using the powder diffraction file (PDF) database (JCPDS).

**Transesterification of Vegetable Oil.** Transesterification of vegetable oil was performed in a three-neck round-bottom flask equipped with a magnetic stirrer and water cooling condenser at various molar ratios of vegetable oil to methanol 1: 5, 1: 10 and 1: 15. The catalyst amount was 1 gram and the mixture was refluxed at 65°C for 12 hours. After completion of the reaction, the catalyst was separated from the liquid phase by filtration. The filtrate was added with \(n\)-hexane to separate the organic phase (which contained biodiesel as transesterification product reaction) from inorganic phase. Anhydrous \(\text{Na}_{2}\text{SO}_{4}\) was added to organic phase in order to remove the remaining inorganic phase. The mixture was filtered and \(n\)-hexane was separated from the organic phase via rotary evaporation. The liquid was analyzed using a Hewlett Packard 5890 Series II gas chromatography with a HP 5 column and flame ionization detector.
Analysis. Fatty acid composition of vegetable oil and the methyl ester content of biodiesel were analyzed by gas chromatography equipped with HP 5 column and used nitrogen gas as the carrier gas. The yield of the biodiesel production was calculated by using the following equation [18]:

\[
\text{Yield (\%)} = \frac{\text{Total weight of methyl esters}}{\text{Total weight of oil in the sample}} \times 100
\]

(1)

\[
\text{Acid Value} = \frac{A \times N \times 56.1}{G}
\]

(2)

Where A = volume of KOH needed in titration (mL), N = Normality of KOH solution, G = massa of sample and 56.1 was molecular weight of KOH.

\[
\text{Iodine Value} = \frac{(B - S) \times N \times 12.69}{G}
\]

(3)

Where B = volume of Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} needed in titration of blank (mL), S = volume of Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} needed in titration of sample (mL), Normality of Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} solution, G = massa of sample and 12.69 was atomic weight of Iodine/10.

**RESULT AND DISCUSSION**

**Catalysts Characterization.** Fig. 2 shows powder XRD patterns of hydrotalcite obtained in this study. The XRD patterns of four samples are almost similar in peak positions to the typical pattern of commercial hydrotalcite and presented in previous study [19-20]. Fig. 2 also showed the transformation of the hydrotalcite into a mixed oxide with MgO like structure and the crystallinity of sample increases with Mg/Al molar ratio increase. All the hydrotalcite samples showed characteristic peaks of mixed oxides that can act as basic catalysts for transesterification reaction. The MgO peaks shift from higher to lower \(2\theta\) values as the Mg/Al molar ratio increases (pure MgO PDF No. 45-946 at 43° and 66°, HT11 at 45.67° and 63.01°, HT21 at 43.34° and 63.01, HT31 at 43.30° and 62.70°, HT41 at 42.99° and 62.41°). Two weak peaks at about 37.50° and 66.73° observed in the patterns of HT11 was attributed to Al\textsubscript{2}O\textsubscript{3} (PDF No. 29-63), but the second peak was not appeared in the patterns of HT21, HT31 and HT41. This is suggested that the amount of Al\textsuperscript{3+} cations incorporated into the bulk lattice of the hydrotalcite sample decreases accordingly [21-22].

**Transesterification Reaction.** Transesterification of vegetable oil was performed using hydrotalcite with the Mg to Al molar ratio 1 : 1 (HT11) and the methanol to vegetable oil molar ratio 5 : 1, 10 : 1 and 15 : 1. The lauric acid is the mayor fatty acid of vegetable oil used in this work, followed by myristic acid and palmitic acid. The alcohol to vegetable oil molar ratio is one of the most important factors that can affect the yield of esters [14]. Table 1 shows the yield of transesterification of vegetable oil at 65 °C for 12 hours.

<table>
<thead>
<tr>
<th>Methanol to vegetable oil molar ratio</th>
<th>Yield (%)</th>
<th>Boiling Point (°C)</th>
<th>Acid Value</th>
<th>Iodine Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>5: 1</td>
<td>47.86</td>
<td>120</td>
<td>0.50</td>
<td>52.65</td>
</tr>
<tr>
<td>10: 1</td>
<td>60.26</td>
<td>133</td>
<td>0.44</td>
<td>55.80</td>
</tr>
<tr>
<td>15: 1</td>
<td>72.53</td>
<td>132</td>
<td>0.34</td>
<td>55.15</td>
</tr>
</tbody>
</table>

When a 5 : 1 ratio of methanol to oil was used in this study, a very small conversion for transesterification reaction was reached. The yield increased with an increase in methanol to vegetable oil molar ratio. The transesterification
process consists of a sequence of three consecutive reversible reactions in which the triglyceride is successively transformed into diglyceride, monoglyceride, and finally into glycerine and fatty acid methyl esters. The molar ratio of methanol to oil is an important factor that affects the conversion to methyl esters. Stoichiometrically, 3 mols of methanol are required for each mole of triglyceride, but in practice a higher molar ratio is employed in order to shift the reaction toward methyl esters products production. In heterogeneous catalysis, mass transfer and reactant adsorption on the catalyst are very important; thus, a molar ratio higher than the stoichiometric molar ratio of methanol is needed to shift the equilibrium for the reaction [20].

Fig. 2. XRD patterns of hydrotalcite a) HT41, (b) HT31, (c) HT21 and (d) HT11
Fig. 3. Mass spectrum of (a) Methyl laurate, (b) Methyl myristate and (c) Methyl Palmitate

A 2.5% 1377.3
B 6.1% 3346.0
C 14.3% 7632.7
D 100.0% 54720.0
E 9.0% 4941.5

Fig. 4. $^1$H NMR spectrum of (a) Vegetable oil and (b) Biodiesel from vegetable oil

A 1.2% 498.5
B 8.2% 3460.9
C 4.0% 1698.6
D 15.12% 6366.6
E 100.0% 42202.9
F 12.2% 5169.5
The mass spectra of biodiesel from vegetable oil are shown in Fig. 3. The molecular ion peaks of methyl laurate, methyl myristate and methyl palmitate were observed at 214, 242 and 270 respectively as expected. All the fatty acid methyl ester detected in the biodiesel from vegetable oil show CH_{3}OC(=OH')CH_{2} fragment and appears at m/z = 74 as the base peak (100%) [23]. The $^1$H NMR spectrum of vegetable oil and biodiesel from vegetable oil are shown in Fig. 4. A singlet signal at $\delta$ 3.70 ppm is representing methoxy protons of the ester functionality of the biodiesel which was not observed on $^1$H NMR spectrum of vegetable oil. The triplet signal at $\delta$ 2.20 ppm represents the $\alpha$-methylene protons to ester (-CH$_2$-CO$_2$CH$_3$). The singlet signals at $\delta$ 1.20 is expected for the protons of backbone methylenes of the long fatty acid chain. The terminal methyl protons (C-CH$_3$) at $\delta$ 0.80 ppm appear as a multiplet. The $^1$H NMR spectrum and chemical shift of biodiesel produced in this study was in accordance with previous study [23].

**Iodin and Acid Value.** The iodin value was dependent on the origin of the vegetable oil. The iodin value of biodiesel were about 52 – 55 because of the lauric acid major content of vegetable oil used in this study. The iodin value showed as acceptable values based on the national biodiesel standard of Indonesia (SNI 04-7182-2006). The iodin value of the conventional diesel fuel was about 10 [24] and was 115 based on national biodiesel standard of Indonesia. The high iodin value showed the high degree of unsaturation. When heating unsaturated fatty acids, polymerization of glyceride will occur, which may lead to the gum formation [25].

The acid value is defined as the milligrams of potassium hydroxide necessary to neutralize the free acid in 1 g of sample [25]. The suggested ASTM standard for pure biodiesel and the national standard of Indonesia (SNI 04-7182-2006) set the maximum acid value at 0.8 mg KOH/g. The acid value of biodiesel obtained in this study varied from 0.34 to 0.5 mg KOH/g.

**CONCLUSION**

Hydrotalcites with Mg to Al molar ratio 1 : 1, 2 : 1, 3 : 1 and 4 : 1 have been successfully synthesized and were used as heterogeneous catalyst for transesterification of vegetable oil. The effect of methanol to vegetable oil molar ratio on biodiesel production was investigated on 5 : 1, 10 : 1 and 15 : 1. As the molar ratio of methanol to vegetable increases the amount of methyl ester produced increased. The acid and iodin value of the produced biodiesel were measured and showed as acceptable values based on the national biodiesel standard (SNI 04-7182-2006).

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