# Biodiesel Production of Palm Oil Mill Effluent by Using Hydrotalcite Catalyst

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**ABSTRACT**

Biodiesel is currently preferred for consumption and has been widely used as a substitute for diesel. This study aimed to determine the effect of various methanol-to-oil ratios in the esterification process and also the effect of hydrotalcite catalyst weight on the transesterification product. The catalyst was characterized with SEM, XRD, FTIR, and TG-DTG-DTA. The esterification process was operated at various oil-to-methanol ratios, i.e., 1:12–1:36 and the transesterification was performed using several catalyst weights, 0.5%–2.5%. The results showed that the optimum conditions of esterification were at the 1:30 molar ratio of oil-to-methanol, which decreased the amount of acid number by 95.75%, while the optimum condition of transesterification was at 1.5% catalyst weight. The characteristics of biodiesel using 0.5–2% hydrotalcite catalyst (acid number, total glycerol, free glycerol, ester levels, viscosity, density, oxidation stability) have met the Indonesian biodiesel standard of SNI-04-7182-2012.

**Keywords:** biodiesel, esterification, transesterification, hydrotalcite.

## INTRODUCTION

Indonesia is an archipelagic country with abundant natural resources which are used as a source of energy for survival. However, over time, the availability of natural resources has started running out, making it necessary to develop new and renewable energy as an alternative energy source. This source is environmentally friendly, because it is obtained from sustainable natural processes such as sunlight, wind, water, biofuels, and geothermal. Biodiesel is one of the biofuels currently developed as a renewable energy source in Indonesia. It

is an environmentally friendly alternative fuel that has the potential to reduce the energy needs from petroleum in Indonesia and also the world and it can be alternative energy sources (Senthilkumar et al., 2019). This is because it is non-toxic, sulfur-free, and biodegradable. Biodiesel is a fatty acid ester that is produced from the transesterification of a triglyceride with the use of an alcohol, either methanol or ethanol. It is also produced from pure vegetable oil, rapeseed, canola, etc. However, the manufacturing process from these raw materials is considered less efficient, because of their relatively high cost (Pathak et al., 2019).

Biodiesel, as a low-emission substitute fuel for petroleum diesel, can be produced from renewable resources (Silva et al., 2017) and derived from animal fat (Rashid et al., 2009). Biodiesel is a mixture of alkyl esters obtained in the transesterification of triglycerides (Botella et al., 2014). Biodiesel is fatty acid methyl esters produced from reaction of oils and fats with an alcohol in the presence of a catalyst (Putra, 2021). Catalysts are used in biodiesel processing to make the process run faster under low operating conditions (Kolakaningrum et al., 2021).

Recently, the economic aspect has been a major concern in the manufacture of biodiesel, because of the high cost of raw materials compared to the relatively low price of fossil fuels. The calculated cost to produce biodiesel is around 60–75% greater than fossils. On the other hand, Indonesia is being projected to become the largest Crude Palm Oil (CPO) exporting country in the next ten years. Therefore, using palm oil as a substitute for fuel is envisioned to be profitable. Furthermore, biodiesel does not only function as a controller of Indonesia's CPO stock, it also reduces the dependence on fossil fuels and strengthen national energy security (Zuhri, 2018).

Moreover, during the manufacturing of biodiesel, a catalyst is also needed, to increase the rate of reaction towards the product and to ease the conversion of chemicals by bypassing some reaction processes. Two types of catalysts are often used in the manufacturing of biodiesel, namely homogeneous and heterogeneous. The heterogeneous catalysts are usually preferred because of their numerous advantages, namely being environmentally friendly, non-corrosive, reusable; moreover, they increase the purity of the product by eliminating some unnecessary side reactions (Riniati, 2013). One of the heterogeneous catalysts that are widely used is hydrotalcite. It is anionic clay with a derivative of the brucite structure. The general formula for hydrotalcite is $Mg_6Al_2CO_3(OH)_{16} \cdot 4H_2O$. It has been widely used as a catalyst in heterogeneous catalytic processes, because it is characterized by large surface area, easy preparation, easy separation, minimization of reaction waste, and the possibility of regeneration.

These characteristics make the hydrotalcite material quite promising to be applied as a catalyst (Handayani et al., 2009). Moreover, the percentage of catalysts that are added during the production process is directly proportional to the biodiesel produced. However, when the catalyst used

exceeds the optimum quantity, it causes a decrease in the amount of biodiesel produced, because the excess catalysts experience saponification reaction to form an emulsion (Pahlevi et al., 2015).

Esterification is the process of reacting free fatty acids with alcohol to form methyl esters and water. However, the water and free fatty acids are still too high (>2%), leading to saponification of the acid catalyst. Therefore, during the biodiesel production, this process is only carried out as a prelude to reduce the levels of free fatty acids. Transesterification is the process of reacting oil or fat with alcohol to produce methyl ester and glycerol. This is a common process in which the vegetable oils are converted into alkyl esters (Liu et al., 2017). This procedure is performed after esterification to produce methyl ester products, which are commonly called biodiesel. It is also usually carried out in the presence of a catalyst which serves to accelerate the rate of reaction. This study used heterogeneous catalyst because it is non-corrosive, environmentally friendly, reusable and increases the purity of the product by eliminating the side reactions. The examples of heterogeneous catalysts usually utilized in the transesterification process are CaO, $CaCO_3$, $Na_2O$, and hydrotalcite. This study aimed to determine the effect of various ratios of methanol and oil on the esterification process and the effect of catalyst weight on the characteristics of transesterification product, i.e., biodiesel.

## MATERIALS AND METHODS

### Materials

The materials used in this study were Aquadest, Hydrochloric Acid (HCl), Hydrotalcite, Methanol, PP indicator, and the raw material for the oil used is oil extracted from the cooling pond wastewater.

### Methods

#### Preparation of hydrotalcite as a trans-esterification catalyst

This preparation begins by adding a source of aluminum ($AlCl_3$) with the initial mole ratio between Mg and Al is 2 to 4. The next process is the addition of 0.10 M $Na_2CO_3$ to obtain a pH of 10 and then this solution is stirred and heated for 1 hour at a temperature of 60–70°C. The

synthesized material is calcined at a temperature of 450°C for 3 hours (Gao et al., 2010). Half of the calcined HTlc oxide product was directly used for transesterification, while the other half was mixed with KF compounds in a ratio of 20, 40, 60, 80 and 100% w/w HTlc with the addition of a few drops of water. The paste from this mixture was then dried at a temperature of 65°C for one night. The hydrotalcite catalyst was characterized with SEM-EDX, XRD, FTIR, and TG-DTG-DTA.

*Esterification procedure*

The esterification process was carried out to reduce the amount of free fatty acids in the oil and to obtain additional methyl esters. In the esterification process, 500 mL of oil was placed in a three-neck flask and a magnetic stirrer was inserted into it, then it was connected to a condenser. The series of three-neck flasks were heated on a hot plate at 65°C. Afterwards, the speed of the magnetic stirrer was adjusted to bring about a faster heat transfer. HCl acid catalyst (approximately 1.5% of the volume of oil) was mixed with various molar ratio of methanol and stirred evenly in different containers. The HCl and methanol solutions were mixed into different three-neck flasks slowly and were tightly covered with a cork.

The mixture was refluxed using a stirrer, while the temperature was kept constant at 65°C for 120 minutes and the results were recorded every 20 minutes as a time variable t1 as the stirring was maintained. The reaction products were placed in a separator flask and allowed to stand for ± 60 minutes. After it had settled, the top layer of the mixture was separated into different containers. The top layer was weighed on an analytical balance. The bottom layer of the mixture was kept in a glass beaker as the main ingredient in the transesterification process. These steps were repeated with different oil to methanol molar ratio.

*Transesterification procedure*

The transesterification process was carried out to reduce fats or oils into methyl esters and glycerol. The catalyst used in this process was heterogeneous one. In the transesterification process, 70 g of the esterified oil was poured into a three-neck flask and a magnetic stirrer was inserted into it, then it was connected to a condenser. The series of three neck flasks were heated on a hot plate at 65°C for ± 60 minutes. Furthermore, the agitation speed on the magnetic stirrer was adjusted to cause a faster

heat transfer. Hydrotalcite base catalyst (0.5% of oil volume) was mixed with methanol and stirred evenly in different containers. The hydrotalcite and methanol solutions were mixed into various three-neck flasks slowly then tightly corked. The solution was refluxed using a stirrer, while the temperature was kept constant at 65°C for 60 minutes. The reaction products were placed into a separatory funnel and allowed to stand for ± 60 minutes. Then, biodiesel was washed with water that had been heated to 40°C. Then, the washing water was placed in a separatory funnel and was allowed to stand until two layers were formed.

The biodiesel from the washing results was separated and placed into a glass beaker; then, it was heated at 110°C until all the water had evaporated. The biodiesel that had been washed was cooled; after that, the solution was centrifuged to separate the product from the catalyst. After the catalyst was separated, the biodiesel obtained was weighed and then placed into a bottle that was tightly corked. The previous procedure steps were repeated with different weight and time variables.

## RESULTS AND DISCUSSION

### Hydrotalcite catalyst characterization

Characterization using FTIR was carried out to determine the functional groups of hydrotalcite. The FTIR spectra of hydrotalcite in Figure 1 show that the broad peak at 3224.98 cm$^{-1}$ was associated with the hydroxy group (O-H) stretching of Mg-OH and Al-OH. A lower absorption band 1662.84 cm$^{-1}$ was associated with the O-H bending of water molecules trapped in the hydrotalcite layer (Vreysen & Maes, 2008). The peaks of 1365 cm$^{-1}$ and 879.54 cm$^{-1}$ were associated with symmetric CO strain mode and a deformation mode in the outer plane, respectively (Olszówka et al., 2019).

The strong peak at 1417.68 cm$^{-1}$ indicates the presence of CO strain from the carbonate anion in the hydrotalcite interlayer region (Rodriguez-Chiang et al., 2016). According to (Ma et al., 2016), the strong band appears due to the positive charge on the surface of the newly formed $Al(OH_3)$, attracting negatively charged anions during the formation of hydrotalcite. The weak peaks at 453.27 cm$^{-1}$ and 677.01 cm$^{-1}$ were associated with Mg-O and Al-O stretching vibrations, respectively. According to (Velázquez-Herrera et al., 2018), the peak appeared between 400–900
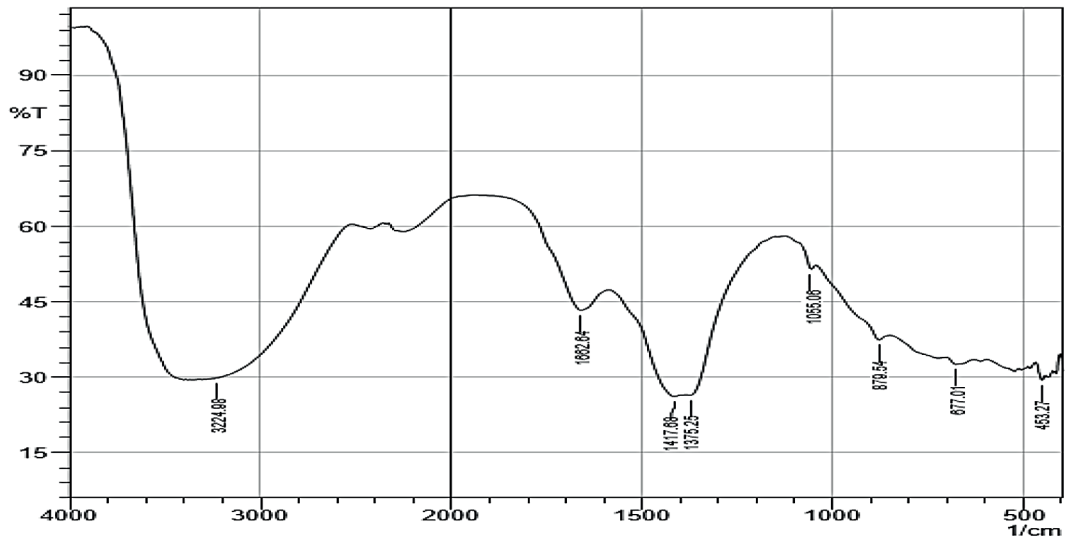
**Figure 1.** FTIR spectra of hydrotalcite

cm$^{-1}$ were associated with the presence of $M^{2+}$ and $M^{3+}$ cations. Similar findings were reported by a previous study (Dahdah et al., 2021).

Characterization using XRD was carried out to determine the structural properties of hydrotalcite. The XRD diffractogram of hydrotalcite in Figure 2 shows characteristic of hydrotalcite diffraction peaks at 11.25, 23.03, 34.62, 38.32, 46.95, 61.3, and 62.14, which could be attributed to (003), (006), (009), (015), (018), (110), (113) crystal planes, respectively. This peak was identified according to JCPDS card 22–0700, ascribed to Mg-Al hydrotalcite (Dahdah et al., 2021).

There was no additional crystalline phase identified that verifies the purity of the hydrotalcite. Similar found have been reported by a

previous study (Ma et al., 2016). Furthermore, the two reflections (110) and (113) can be clearly distinguished, indicating that the hydrotalcite structure with high crystallinity (Zeng et al., 2014).

Characterization using SEM was carried out to determine the surface morphology of hydrotalcite. The particle size distribution of hydrotalcite was also analyzed. The SEM image of hydrotalcite in Figure 3a shows the agglomeration of particles with a coarse structure that is relatively irregular and hollow. The surface morphology of hydrotalcite is consistent with a previous study (Santosa & Astuti, 2021). According to (Velázquez-Herrera et al., 2018), the surface morphology of hydrotalcite usually consists of irregular flakes piled up and forming heterogeneous
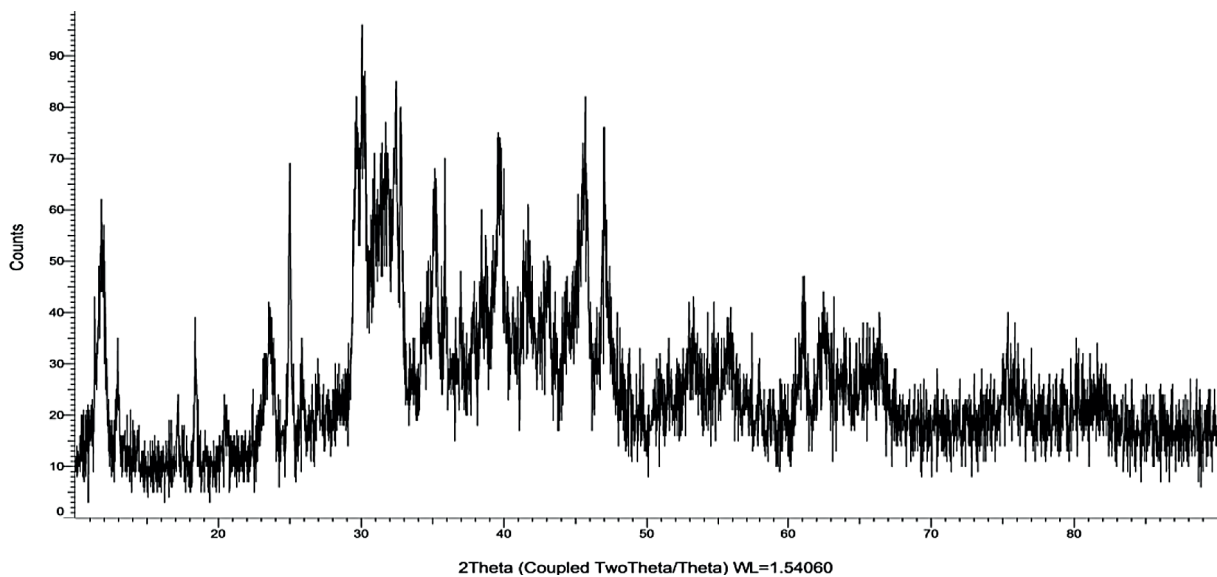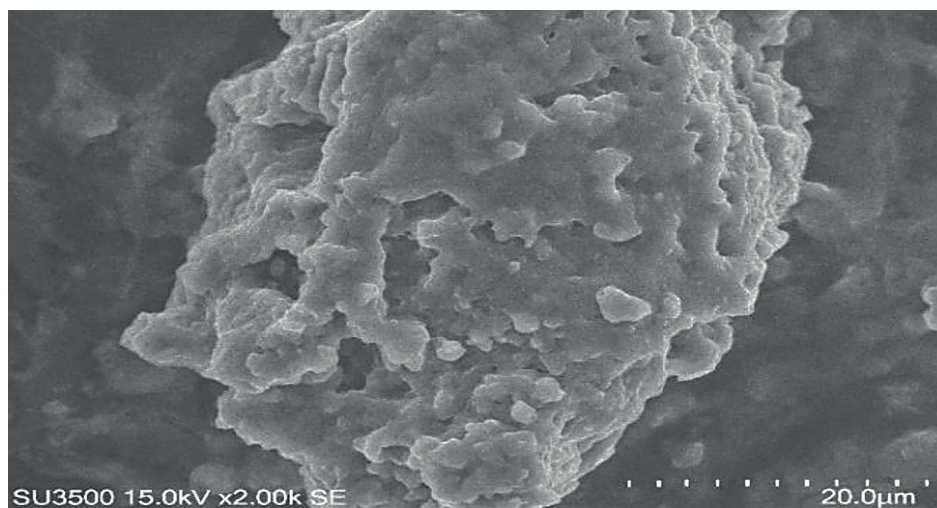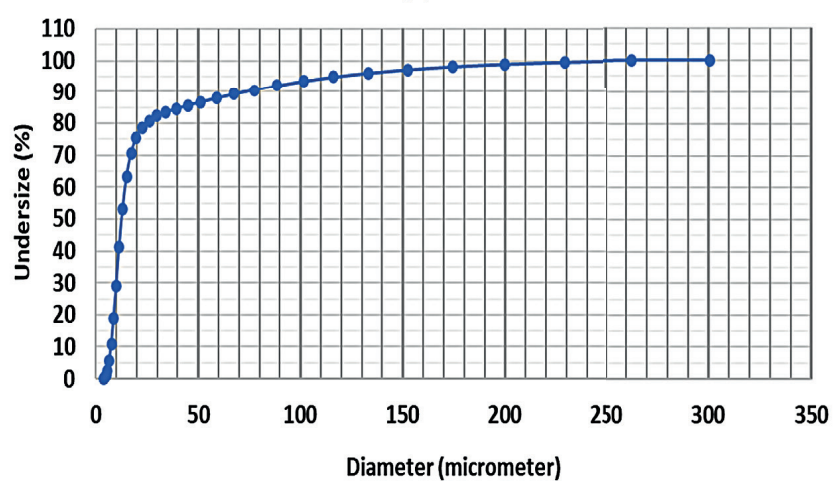


**Figure 2.** XRD diffractogram of hydrotalcite

(a)



(b)

**Figure 3.** (a) SEM image of hydrotalcite at 2000 times of magnification
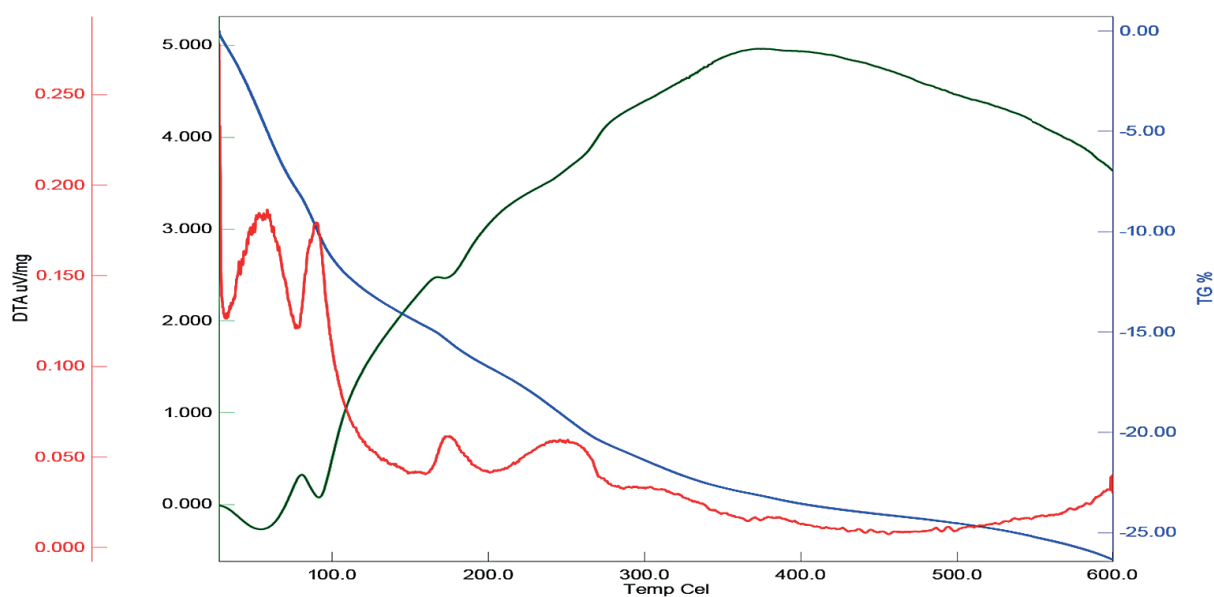(b) Particle size distribution of hydrotalcite



**Figure 4.** TG-DTG-DTA curve of hydrotalcite

sections. The particle size distribution of hydrotalcite in Figure 3b shows that the average size of hydrotalcite obtained with a diameter of 27.13 μm. Similar found was reported by (Ogawa & Kaiho, 2002) with hydrotalcite particles of 25 μm with a relatively narrow particle size distribution. According to (Harju et al., 2020), particle size not only affects the distribution of the product, but also greatly affects the stability of the catalyst.

Characterization using TGA/DTA was carried out to determine the thermal properties of hydrotalcite. There are three curves, namely TGA, DTG, and DTA, each with a different color shown in Figure 4.

Two typical decomposition stages occur each with the first stage from 50°C to 150°C and the second stage occurring from 200°C to 300°C; thus, two peaks of weight loss were observed around 150°C–300°C. The first decomposition step was related to the elimination of physically adsorbed water on the hydrotalcite surface and water interlayer without changing the hydrotalcite layer structure (Silva et al., 2017). The second decomposition step was related to the hydroxylation of the OH group in hydrotalcite and the release of the $CO_3^{2-}$ interlayer as $CO_2$ (Ma et al., 2016).

According to (Navarro et al., 2018), in the temperature range from 200 to 345°C, dehydration of the OH group coordinated with $Al^{3+}$ and $Mg^{2+}$ ions could occur in the hydrotalcite layer, and at a higher temperature than 350°C, elimination of the cation-bound carbonate anion occurs in the inter-laminar space. This process was endothermic and consistent with previous study (Barbosa et al., 2017).

## Effect of oil to methanol ratio on acid number decrease in the esterification process

Figure 5 shows that the esterification time affected the acid number produced. It means that the longer the esterification process, the lower the acid number produced. It was also observed in Figure 5 that by using the 1:12 oil to methanol ratio, the highest acid number of 10.01 mg KOH/g was obtained at 20 minutes of esterification, while the lowest acid number value of 3.66 mg KOH/g was achieved after 120 minutes.

Furthermore, when the ratios of oil-to-methanol were 1:30 and 1:36, there was no further significant decrease of the acid number after 40 minutes of esterification process. This is due to the presence of excess methanol which had increased the solubility of the product, leading to a decrease in yield. However, by using the oil-to-methanol ratio of 1:30, the lowest acid number of 0.75 mg KOH/g was obtained after 120 minutes; while by using the oil-to-methanol ratio of 1:36, the lowest acid number of 2.35 mg KOH/g was attained after 120 minutes of esterification process.

Therefore, ratio of oil-to-methanol in the esterification process affected the acid number produced. The greater the ratio used, the higher the percentage of compounds with lower acid numbers produced. The highest percentage of 95.75% of low acid number compound generated was obtained when using 1:30 oil-to-methanol ratio while the lowest percentage of 70.71% was obtained when using 1:12 oil-to-methanol ratio.

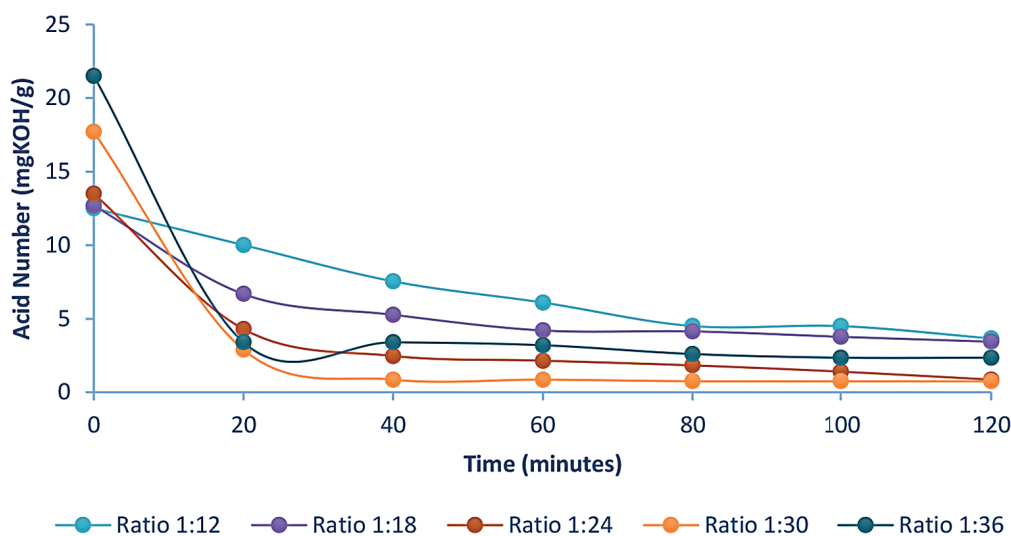The results were in accordance to (Prawoko, 2009) where the esterification process was



**Figure 5.** Effect of esterification time on acid number by various oil to methanol ratio

**Table 1.** Characteristics of biodiesel production by using hydrotalcite catalyst

| Test parameter | SNI 04-7182-2012 | Unit | % Hydrotalcite catalyst | | | | |
|---|---|---|---|---|---|---|---|
| | | | 0.5% | 1.0% | 1.5% | 2% | 2.5% |
| Acid number | 0.8 | mg KOH/g | 0.16 | 0.16 | 0.10 | 0.10 | 0.10 |
| Total glycerol | Max 0.24 | %-w | 0.240 | 0.233 | 0.231 | 0.243 | 0.236 |
| Free glycerol | Max 0.02 | %-w | 0.0189 | 0.0197 | 0.0218 | 0.0274 | - |
| Ester content | Min. 96.5 | %-w | 97.79 | 97.91 | 97.95 | 97.84 | 97.89 |
| Viscosity | 2.3–6.0 | mm$^2$/S | 4.73 | 4.09 | 4.22 | 4.27 | 4.70 |
| Density | 0.85–0.89 | kg/m$^3$ | 0.8836 | 0.8797 | 0.8786 | 0.8786 | 0.8819 |
| Oxidation stability | 6 | hour | 28.89 | 20.78 | 15.72 | 8.96 | 1.03 |

carried out to reduce the acid number of oil. In this study, when 1:15 oil-to-methanol ratio was applied, with 1% HCl as catalyst, a 76% decrease in the acid number was observed. The acidity value of the oil before esterification was approximately 17 mg KOH/g and after the process it decreased to 4 mg KOH/g.

**Biodiesel transesterification results by using hydrotalcite catalyst**

According to the SNI-04-7182-2012 the maximum acid number for biodiesel is 0.8 mg KOH/g. it can be seen in Table 1, that the acid number produced by using 0.5–2.5% hydrotalcite catalyst has fulfilled the Indonesian standard for biodiesel. Other parameters, namely total glycerol, free glycerol, ester content, viscosity, and density has also accomplished the standard.

Furthermore, the oxidation stability of biodiesel should take minimum of 6 hours based on the SNI. Meanwhile, the results showed that

the analysis of oxidation stability with the use of 0.5–2% hydrotalcite catalyst took more than 6 hours. It shows that the usage of catalyst within that range was in accordance with the standard of biodiesel oxidation stability.

Figure 6 depicts the comparison of the biodiesel obtained through the transesterification method by using different hydrotalcite catalyst percentage. It can be concluded that the greater the percentage of hydrotalcite catalyst utilized, the shorter the oxidation stability of biodiesel obtained. However, the use of hydrotalcite catalyst of 2.5% did not satisfy the standard which may be caused by the high-water content. The factors influencing biodiesel oxidation often become the focus of the study in many countries. One of the causes of decrease in oxidation stability was the water content. The production process that uses water for washing as a purification step, increases the water content in biodiesel, in addition to dissolved water in the raw materials (Oliveira et al., 2012).
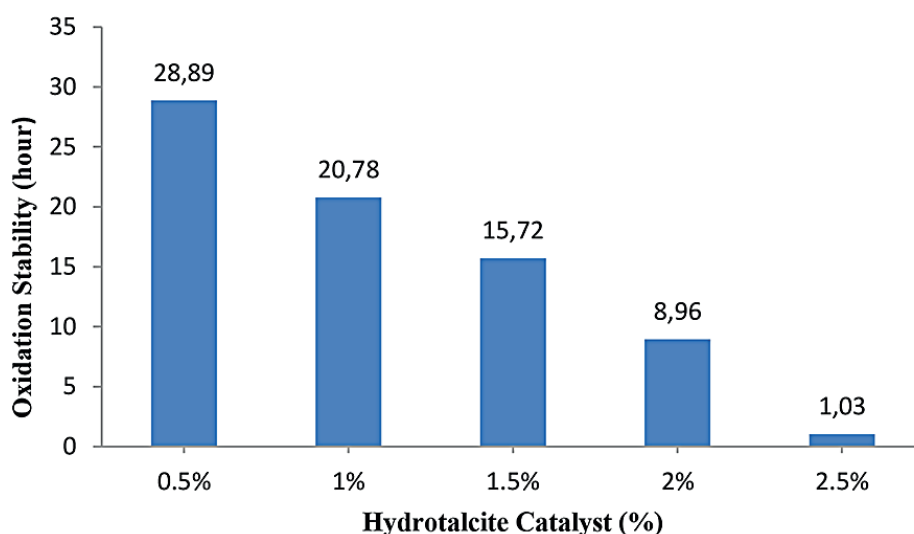


**Figure 6.** Effect of hydrotalcite catalyst percentage on oxidation stability of biodiesel

Over time, changes in the acid number usually occur in biodiesel samples due to the oxidation reaction that occurs, which produces more acidic compounds. The increase in acid number is also affected by temperature. This is because an increase in temperature directly increases the rate of the oxidation reaction. This reaction consists of several stages, where the primary reaction involves the formation of hydroxy peroxide compounds. Meanwhile, hydroxy peroxide is an unstable compound that undergoes several secondary reactions at once. The secondary reaction produces aldehydes and radicals, which undergo the final oxidation to form acids and aldehydes. Depending on the type of secondary and tertiary reactions which occur, the final products of the oxidation reaction vary widely (Flitsch et al., 2014).

Therefore, the biodiesel oil yield by utilized 2.5% of hydrotalcite catalyst is not suitable for oxidation stability. This is because hydrotalcite is hygroscopic, i.e., the greater the amount of catalyst used, the more moisture it absorbs from the air. Lapuerta et al., 2012 stated that the two main causes of oxidation are exposure of biodiesel to high temperatures (thermal oxidation), and the presence of an oxidizing agent. It was concluded that the percentage of hydrotalcite catalyst influences the oxidation stability of the biodiesel results (Lapuerta et al., 2012). The factors that affect the oxidation stability of biodiesel during storage in Canada were investigated by Yang et al. (Yang et al., 2013). The results showed that the use of antioxidant additives can improve the oxidation stability, and the tank materials which inhibited oxidation were steel and aluminum alloys. However, solvent content, such as methanol, water, and acetone do not contribute significantly to oxidation stability. Therefore, it was concluded that under favorable conditions, the biodiesel with good quality is still able to fulfil the required quality limits for oxidation stability for a 3-month storage period.

## CONCLUSIONS

The biodiesel characteristics (acid number, total glycerol, free glycerol, ester levels, viscosity, density, and oxidation stability) produced by using 0.5–2% hydrotalcite catalyst have met the Indonesian National Standard (SNI-04-7182-2012) for biodiesel. The smaller the percentage of hydrotalcite catalyst utilized, the better the biodiesel made from the transesterification process. It was discovered that the greater the ratio used, the greater the percentage of compounds with lower acid number produced. This was shown when the highest percentage of 95.75% of lower acid number compound formed was observed when using 1:30 oil to methanol ratio. The optimum conditions to produce biodiesel were discovered to be during the use of 1.5% hydrotalcite catalyst where the biodiesel produced fulfilled the SNI parameters. The product had 0.1 mg KOH/g of acid number, total glycerol of 0.02%, free glycerol of 0.02%, esters content of 97.9%, viscosity of 4.22 mm$^2$/S, density of 0.87 kg/m$^3$, and oxidation stability of 15.7 hours.

## Acknowledgements

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