Kinetic Study of Glycerol Monolaurate (GML) Production from Glycerol with Lauric Acid Using a Dealuminated Zeolite Y Catalyst

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Abstract. This study aims is to study the ability of zeolite Y to produced higher yield of glycerol monolaurate. This study focused on dealumination zeolite synthesis Y applied on glycerol monolaurate synthesis and kinetic study of glycerol monolaurate synthesis. The stages of this research consisted of zeolite Y catalyst dealumination, synthesis of glycerol monolaurate and acid-base analysis of catalyst. The esterification process was carried out with 1: 7.5 mole ratio of reactant (glycerol/lauric acid) at 130°C and a stirring speed of 300 rpm. Data obtained from the experimental results show that the longer the time used, the greater the ability of the zeolite Y to synthesize the glycerol monolaurate. The esterification process was carried out by using 2nd order rate equation with R² about 0,9051 with ratio of the first reactant CA0≠CB0. The determination of k value was expressed by equation

\[ \ln \frac{M-xA}{M(1-xA)} = (C_{A0} - C_{A})kt. \]

Constant reaction rate value of glycerol monolaurate is 0,006805 L/mol.min.

Keywords: kinetic study; transesterification; dealumination; zeolite Y; glycerol monolaurate

1. Introduction

Glycerol is a by-product of biodiesel production from vegetable oil with 10% by weight of the yield product.¹ If biodiesel is produced on an industrial scale, the by-products of glycerol produced will be abundant. Unfortunately, glycerol produced from biodiesel production has not been optimally utilized, there is even no further processing so that it still has a low selling value. By converting glycerol to a derivative product such as glycerol monolaurate, it can increase the selling value of the product.

Glycerol monolaurate can be used for food additives, surfactants, pharmaceuticals, cosmetics and so on. Glycerol monolaurate can be used as a nutritional supplement because it is classified as a non-ionic surfactant containing hydrophilic and hydrophobic groups.² Glycerol monolaurate is made by reacting lauric acid and glycerol with a catalyst. The catalyst used can be an acid (H₂SO₄ and HCl) or a zeolite catalyst, where zeolite catalyst has a lot of advantages of usage.³,⁴,⁵,⁶,⁷ The esterification process in the glycerol monolaurate synthesis is usually carried out at high operating temperatures. The acid catalyst...
can reduce the temperature of the synthesis reaction. In addition, with the right reaction conditions, such as the mole comparison factor between lauric acid and glycerol, the reaction time and temperature, expected to produce monolaurin with high selectivity.4

The concentration of reactants affects rate of reaction catalyzed by zeolite Y. Previous study8 showed that the used of mole ratio of lauric acid with glycerol (1 : 7.5) was obtained 90.75% of glycerol monolaurate yield. This study is an advanced research that aims to study the activity of zeolite Y as the catalyst to produced higher yield of glycerol monolaurate. The dependent variables used were were the amount of catalyst, stirring speed, mole ratio of lauric acid and glycerol, time and temperature of process, while the independent variable used was the time of sample taken. To be able increasing the acidity of the zeolite catalyst and the efficiency of the catalyst itself, a dealumination process is carried out.8,9,10 This study determined the reaction order and the rate constant of the reaction of glycerol monolaurate synthesis in a batch reactor with a volume of 5 L.

2. Experimental

2.1. Materials

Zeolite Y was produced by Process Engineering Laboratory, Chemical Engineering, University of Diponegoro. H2SO4, aquadest, whatman filter paper, glycerol, and lauric acid were purchased in CV Indragiri, Semarang. The equipments used are a 5 liter batch reactor, which were equipped with heater and thermocouple, stative and clamp, erlenmeyer, three-neck flask, leibig condenser, thermometer, oven, and furnace.2 The stages of these research consisted of dealumination of Zeolite Y catalyst and glycerol monolaurate synthesis at 130°C of process temperature, process time of 4 h, and mole ratio of lauric acid: mole of glycerol is 1: 7.5 (with the mass of lauric acid is 1,009 g, and the mass of glycerol is 3,479 g).8

2.2. Methods

2.2.1. Dealumination of Zeolite Y Catalyst

The dealumination process was carried out by mixing 320 ml of H2SO4, 397 ml of aquadest, and 420 g of Zeolite Y into three neck flasks with a temperature of 60ºC for 4 h. Dealuminated Zeolite Y was dried in an oven at 110ºC for 1 h. Then put it in the furnace at a temperature of 500ºC for 3 h.8

2.2.2. Glycerol Monolaurate (GML) Synthesis

Glycerol and lauric acid in a ratio of 1: 7.5 (with the mass of lauric acid is 1,009 g, and the mass of glycerol is 3,479 g), and the zeolite Y catalyst is 424 g were mixed in the batch reactor with a volume of 5 L (figure 1) with stirring speed was 300 rpm, temperature was set on 130°C. The reaction time was 240 min that samples taken every 30 min then analyzed to obtain the free lauric acid content.

2.2.3. Acid Base Analysis

This stage aims to determine the levels of free lauric acid. The sample was put in Erlenmeyer and phenolphthalein (PP) was added into the Erlenmeyer, then titrated using 0.3 N KOH solvent. The addition of the titration solution into erlenmeyer was stopped when the color changes. This color change indicates the end point of titration has been reached.8,11,12

2.2.4. GC-MS Analysis

GC-MS is a method of separating organic compounds using two compound analysis methods, namely Gas Chromatography (GC) to analyze the quantity of compounds quantitatively and mass spectrometry (MS) to analyze the molecular structure of compounds. Retention time or retention volume of a solute is a quantity of a solute that can be used to determine a compound. Samples will be separated based on their retention time in the chromatograph column to be subsequently analyzed sequentially in a mass spectrometer.8 GC-MS analysis was carried out in the Organic Chemistry laboratory of FMIPA - Gajahmada University.8

2.2.5. Kinetic Modelling

The kinetic modeling of the reaction formation of Glycerol Monolaurate was performed by testing R2 on various types of reaction rate kinetics models. The model being tested is first and second order
irreversible reaction modeling. The reaction rate constant (k) was obtained by using the linear regression approach \( y = mx + c \) for 1st order using equation 1:

\[
\frac{-\ln \frac{C_A}{C_{A0}}}{c_{A0}} = kt
\]  

(1)

while for 2nd order using equation 2 is 8,13

\[
\ln \frac{M - XA}{M(1 - XA)} = (C_{B0} - C_{A0})kt
\]  

(2)

By processing the Glycerol Monolaurate conversion data, conversion vs. time graphs can be made based on experimental results and the tested models. From the graphical results obtained, the reaction modelling used is the model that best suits the experimental data. The selection of modelling can use R² testing where the reaction order modelling chosen is a graph that has the R² value closest to 1.

3. Results and Discussion

3.1. Qualitative Analysis of Glycerol Monolaurate Using GC

GC analysis is intended to determine the presence or absence of Glycerol Monolaurate content in the study sample. Analysis was carried out on samples with a 60-min time. The results were shown in Fig 1 and 2.

From the GC analysis results in Fig 1, the spectrum of GC analysis results in 30 mins shows that there is only one peak with a retention time of 15,226 which has an area of 10,369,200, this peak is the peak that shows glycerol, so that in 30 mins no glycerol monolaurate has formed yet. In Fig 2 the spectrum of GC analysis results at 60 mins obtained several peaks with different retention time values. Based on the above analysis, the retention time for glycerol monolaurate was shown at 41,683 with an area of 494,042 while the glycerol reactant was shown at 17,113 with an area of 33,861,094.
GCMS analysis carried out on samples with a reaction time of more than one hour did not have a peak at retention time 41 which according to the analysis results did not show the presence of glycerol monolaurate in the sample after one hour. In the reaction of glycerol synthesis with lauric acid using a zeolite catalyst which is realized to produce a further reaction to glycerol dilaurate and glycerol trilaurate.\(^8\)

Percent crystallinity affects the percent conversion of acid. In percent crystallinity above 50% causes decreased acid conversion percent. Similarly, the percentage of glycerol monolaurate and glycerol dilaurate also decreases with increasing crystallinity. The interesting thing is the percentage of glycerol trilaurate increases with increasing crystallinity.\(^2\)

3.2. Kinetic Modelling
In determining the reaction kinetics seen from the reaction order and the reaction speed constant value. This can be seen from the correlation between concentration and time. Measurement of lauric acid concentration is done by taking samples every 30 min for 4 h. The variable used is the operating temperature of 130\(^\circ\)C, with stirring 300 rpm as shown in table 1. Table 1 shown that the longer the time used, the greater the ability of the zeolite Y to synthesize the glycerol monolaurate.

Table 1. The results of lauric acid concentration measurements and reaction kinetics modeling

| Operation Variables | Temp (\(^\circ\)C) | Stirring speed (rpm) | Lauric Acid Concentration (CA) | Time (min) | 1\(^{st}\) Order | 2\(^{nd}\) Order |
|---------------------|-----------------|----------------------|-------------------------------|------------|----------------|----------------|
|                     | 130             | 300                  |                               |            | \(-\ln(CA/CA_0)\) | \(\ln(m-xa)/(m(1-xa))\) |
| 0                   | 0.144           | 0                    | 0                             | 0          | 0              | 0              |
| 30                  | 0.072           | 0.773190             | 0.698687                      |            |                |                |
| 60                  | 0.066           | 0.860201             | 0.780159                      |            |                |                |
| 90                  | 0.060           | 0.955511             | 0.869898                      |            |                |                |
| 120                 | 0.036           | 1.466337             | 1.358123                      |            |                |                |
| 150                 | 0.030           | 1.648659             | 1.534714                      |            |                |                |
| 180                 | 0.030           | 1.648659             | 1.534714                      |            |                |                |
| 210                 | 0.024           | 1.871802             | 1.752094                      |            |                |                |
| 240                 | 0.024           | 1.871802             | 1.752094                      |            |                |                |

The results obtained are shown in Fig 3 and Fig 4.

![Graph](image)

**Fig 3.** Graph of the correlation of reaction time to \(-\ln(CA/CA_0) = kt\)

From the graphs, it can be seen the reaction rate constant of GML for order 1 is 0.0073 / min with \(R^2\) equal to 0.8976, while for order 2 is 0.0068 L / mol. min with \(R^2\) value 0.9051. Determination of the
reaction order is based on the $R^2$ value which is close to 1, which indicates the value of the reaction kinetics modeling is close to the actual value.\textsuperscript{11} From the data obtained, the $R^2$ value for the 2\textsuperscript{nd} order reaction is closer to 1 where the 2\textsuperscript{nd} order modeling for the GML reaction in this study is considered more appropriate. Modeling is done by using the assumption $C_A0 \neq C_B0$, the $k$ value obtained is 0.006805 L/ mol.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{Graph of the correlation of reaction time to $\ln \left( \frac{M - X_A}{M(1 - X_A)} \right) = \left( C_{B0} - C_{A0} \right)kt$}
\end{figure}

4. Conclusion
Data obtained from the experimental results show that the longer the time used, the greater the ability of the zeolite Y to synthesize the glycerol monolaurate. The reaction of Glycerol Monolaurate formation from the esterification process of lauric acid and glycerol follows the equation of the second order reaction rate with an $R^2$ of 0.9051. The value of the reaction rate constant for the formation of glycerol monolaurate follows the second order equation with the ratio of the initial reactant - $C_A0 \neq C_B0$ so that to determine the value of $k$ the equation is used $\ln \left( \frac{M - X_A}{M(1 - X_A)} \right) = \left( C_{B0} - C_{A0} \right)kt$ The value obtained is 0.006805 L/ mol. mins. In GC-MS analysis, the glycerol monolaurate compound was obtained in a 60 min sample with a retention time of 41,683 which had an area of 494,042.

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