Dealumination and Characterization of ZSM-5 as Catalyst for Glycerol Conversion to Glycerol Monolaurate

Didi Dwi Anggoro*, Riko Rikardo Putra, Herawati Oktaviany, Lutfi Af’idatul Kamilah, and Fatma Tsaniya Chamdani

Department of Chemical Engineering, Faculty of Engineering, Diponegoro University
Jl. Prof. Soedarto, SH, Tembalang, Semarang 50275, Telp. (024)7460058

*Corresponding author: anggorophd@gmail.com

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Abstract

Glycerol Monolaurate (GML) is a fatty acid where widely used in food, cosmetics, and homeopathic supplements. Glycerol is a compound glycerides, a byproduct of biodiesel production from the transesterification process. Glycerol is converted to glycerol derivative product that has more value as Glycerol Monolaurate (GML). The catalyst used ZSM-5 dealumination change the acidity of the zeolite. The preparations of catalyst included dealumination of zeolite ZSM-5 using H₂SO₄, drying at 110°C for 1 hour, and calcination at a temperature of 550°C for 4 hours. Characterization catalyst to testing the acidity of the catalyst by absorption of ammonia and pyridine. ZSM affected in the acidity during deformalumized activity. Based on analysis by statistical, the temperature of dealumination and the time of dealumination is respectively 40-60°C and 2-5 hours. Our data reveal that the acidity have critical impact on glycerol monolaurate dealumination.

Keywords: dealumination; glycerol; glycerol monolaurate; ZSM-5

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INTRODUCTION

Glycerol is a glyceride compound, a by-product of the transesterification process of biodiesel. Glycerol with another name propane-1,2,3-triol, or glycerin, a liquid at room temperature has a clear as water color, viscous, hygroscopic with a sweet taste. One useful derivative product is glycerol monolaurate (GML). Glycerol Monolaurate is already listed in the HFA (Halal Food Authority) in the category of fatty acid esters, because GML is an emulsifier of monoglycerides produced by esterification of glycerin and lauric acid in natural raw materials (LPPOM MUI, 2014). GML has been widely applied in various products such as deodorants, lotions, and cosmetics. It is also widely available as a homeopathic supplement, and is extensively used as a food preservative and emulsifier (Zhang et al., 2016).

Glycerol Monolaurate can be prepared by an esterification process by reacting glycerol with lauric acid added with the aid of a catalyst (Nakamura et al., 2008). The esterification reaction in monolauric synthesis usually carried out at high temperatures. The use of an acid catalyst, can lower the temperature of the synthesis reaction. In addition, with the appropriate reaction conditions, such as the mole ratio between lauric acid and glycerol, reaction time and
temperature, is expected to produce a monolaurin with a high yield (Widiyarti and Hanafi, 2008).

One type of solid catalyst is often used in the manufacturing process Glycerol Monolaurate is a zeolite. Zeolite is a group of minerals produced from hydrothermal processes in alkaline igneous rocks. The objective of developments of zeolite synthesis was to produce of zeolite has physical and chemical properties similar to natural zeolite (Anggoro, 2017).

Acidity is one of the factors that influence the conversion of manufacture Glycerol Monolaurate from Glycerol. The higher the acidity, the faster the formation of Glycerol Monolaurate, because with higher acidity levels, the synthesis reaction temperature may decrease and decrease the activation energy (Widiyarti and Hanafi, 2008).

The resulting synthetic zeolite catalysts are sometimes not meet the specifications to be used as a catalyst to accelerate the reaction rate. Therefore, a catalyst characterization process is required to change the catalyst properties according to the required specifications (Wang et al., 2016). One process to change the nature of the catalyst is the dealumination process. Dealumination used for metal removal process aluminum in a zeolite by using acid solution (Xu et al., 2014). The purpose of the zeolite dealumination process is to increase the acidity of a zeolite catalyst and to increase the efficiency of the catalyst (Aishah et al., 2002; Müller et al., 2015). The objective of this is research to get optimum conditions of dealumination process on zeolite catalyst.

MATERIALS AND METHODS
Materials
The Zeolit ZSM-5 were purchased from Zeolite International, H₂SO₄ (sulfuric acid), Pyridine, Ammonia, Glycerol and Lauric acid from Merck (Germany) and aquadest is self-produced in the MeR-C laboratory (Membrane Research Center)

Research Design
The design model in this experiment to determine the effect of the variables on the desired main response is a centralized composite design (CCD) and using surface response method (RSM), this design is widely used for second order models (Yang et al., 2014). The experimental design used with the lowest, center and high value design for each factor such as the percentage of catalyst, temperature and processing time can be seen in Table 1.

| Factor       | Unit | Level       |
|--------------|------|-------------|
| Concentration (X₁) | %    | 3 5 7       |
| Temperature (X₂)  | °C   | 40 50 60    |
| Time (X₃)        | Hours | 2 3.5 5     |

Table 1. Experimental design for each variable

Catalyst Preparation
Twenty five grams of ZSM-5 was add to 3 or 7 M H₂SO₄ solution then heated at 40-60°C. The dealumination treatment was carried out in a three-neck flask with stirrer to mix sulfuric acid with ZSM-5 Zeolite for 2-5 hours. Dealuminated zeolite then dried at 110°C for 1 hour, and calcined for 4 hours at a temperature of 550°C.

GML Productions
Zeolite ZSM-5 which has dealuminated then tested to synthesize glycerol into glycerol monolaurate using 69 ml of glycerol and lauric acid weighing 25 grams. The deformed ZSM-5 zeolite used to synthesize was 4 grams for each sample. Catalyst performance was tested to synthesize by stirred the glycerol monolaurate. Weight 87.7 gram of purified glycerol, and lauric acid in a solid phase. The next step was weighing 25 grams and including a 4 g of dealuminated catalyst were reacted at atmospheric pressure and temperature of 130 °C for 4 hours. Reaction product is separated using Whatman filter paper.

Catalyst Characterization
The acidity characterization test performed by weighing 1 sample layer into 6 tray and weighed until reached same weight. Ammonia and pyridine were used as a comparison substance. Then contact it with the sample in the desiccator. Weigh the weight per day until gain constant weight. The total acidity and acidity of the cavity can be calculated by the following formula:

\[
\text{Total acidity} \left(\frac{\text{mmol}}{\text{g}}\right) = \frac{W_{\text{NH}_3}}{N_{\text{H}_3}} \times \frac{W_{\text{sampel}}}{N_{\text{sample}}} \times 100 \left(\frac{\text{mol}}{\text{mmol}}\right)
\]

\[
\text{Surface acidity} \left(\frac{\text{mmol}}{\text{g}}\right) = \frac{W_{\text{pyridine}}}{N_{\text{pyridine}} \times W_{\text{sampel}}} \times 100 \left(\frac{\text{mol}}{\text{mmol}}\right)
\]

\[
\text{The acidity of the pore} \left(\frac{\text{mmol}}{\text{g}}\right) = \text{total acidity} - \text{surface acidity}
\]

Analysis of Product
The GCMS analyzed will be performed to determine the molecular weight of the resulting Glycerol Monolaurate compound, and show the Glycerol Monolaurate purified from proceed of dealuminated ZSM-5 Zeolite catalyst.

RESULTS AND DISCUSSION
Glycerol Monolaurate reaction mechanism design due to the ion exchange on the surface of the catalyst ZSM - 5. The hydrogen ions to the catalyst is a cation that serves as an initiator in the esterification reaction. In the first stage of the reaction, the electrons of the oxygen element present in the laurate acid compound attack the hydrogen ion in the active site of the ZSM-5 catalyst, which causes the laurate acid compound to form carbon cations. the carbon cation is
attacked by electrons from the oxygen element in the glycerol compound, so that the laurate acids react with glycerol to form glycerol monolaurate, as in Figure 1 and if the reaction is not perfectly complete, the OH group present in glycerol is able to bind to a fatty acid group that can formed monoglycerol and diglycerides and water (Setiadi et al., 2016).

The result of acidity analysis of this deformunized ZSM-5 zeolite is listed in Table 2. Acidity is determined by the absorption of ammonia and pyridine alkaline by zeolites having acid sites in the skeleton. Therefore, the acidity of the zeolite is other than in the amount of mmol ammonia per gram of the catalyst as well as the amount of pyridine peroxide of the catalyst.

Molecular size ammonia (NH$_3$) is relatively smaller than the size of the zeolite cavity allowing it into the cavity and reach the acid sites. Therefore, this acidity is also called total acidity. Meanwhile, the pyridine size is much larger so it can not enter the zeolite cavity. As a result, this molecule reaches only acidic sites on the surface only. The difference in acidity between total acidity and surface acidity can be expressed as the acidity of the zeolite cavity (Trisunaryanti et al., 2005).

Figure 2 shows the effect of the temperature of the dealumination on the acidity produced. The higher the dealumination temperature will increase the acidity of the Zeolite ZSM - 5 is de-lumination. This is because the greater the temperature of dealumination, the crystallinity of the catalyst increases.

![Reaction Mechanism Diagram](image_url)

Figure 1. The reaction mechanism of esterification between outer acid and glycerol

| No | Dealumination Variable | Acidity (mmol/gram) |
|----|-----------------------|---------------------|
|    | X$_1$ | X$_2$ | X$_3$ | Total | Surface | Pore  |
| 1  | 3     | 40   | 2    | 1.099 | 0.105   | 0.994 |
| 2  | 3     | 40   | 5    | 0.688 | 0.128   | 0.560 |
| 3  | 3     | 60   | 2    | 1.082 | 0.159   | 0.923 |
| 4  | 3     | 60   | 5    | 1.128 | 0.065   | 1.063 |
| 5  | 7     | 40   | 2    | 1.549 | 0.011   | 1.538 |
| 6  | 7     | 40   | 5    | 2.844 | 0.272   | 2.573 |
| 7  | 7     | 60   | 2    | 0.412 | 0.073   | 0.339 |
| 8  | 7     | 60   | 5    | 0.810 | 0.109   | 0.701 |
| 9  | 5     | 50   | 3.5  | 0.911 | 0.118   | 0.794 |
| 10 | 1.4723 | 50   | 3.5  | 0.529 | 0.049   | 0.480 |
| 11 | 8.5276 | 50   | 3.5  | 0.297 | 0.023   | 0.273 |
| 12 | 5     | 32.3616 | 3.5 | 0.261 | 0.013   | 0.249 |
| 13 | 5     | 67.6383 | 3.5 | 0.705 | 0.061   | 0.644 |
| 14 | 5     | 50   | 0.8542 | 0.412 | 0.073   | 0.339 |
| 15 | 5     | 50   | 6.1457 | 0.522 | 0.026   | 0.496 |
| 16 | 5     | 50   | 3.5  | 0.727 | 0.035   | 0.692 |

Table 2. Results of catalyst acidity analysis of ZSM-5 dealumination
The greater crystallinity may increase the surface area of zeolite ZSM-5 catalyst. Increased surface area on this deformumized ZSM-5 indicates greater acidity. But at higher temperatures, the framework will become damaged and structural changes occur from zeolites, causing zeolite ZSM-5 crystallinity to decrease so that the acidity of zeolite decreases.

The influence of variables on the dealumination process

The products of Glycerol Monolaurate under difference variable of dealumination process are tabulated on Table 3.

| No | Variable Dealumination | Ye (%) |
|----|-------------------------|--------|
|    | X_1 | X_2 | X_3 |    |
| 1  | 3   | 40  | 2   | 62 |
| 2  | 3   | 40  | 5   | 34 |
| 3  | 3   | 60  | 5   | 51 |
| 4  | 3   | 60  | 5   | 58 |
| 5  | 7   | 40  | 2   | 73 |
| 6  | 7   | 40  | 5   | 89 |
| 7  | 7   | 60  | 2   | 39 |
| 8  | 7   | 60  | 5   | 57 |
| 9  | 5   | 50  | 3.5 | 59 |
| 10 | 5   | 50  | 3.5 | 54 |
| 11 | 5   | 50  | 3.5 | 43 |
| 12 | 5   | 32.3616 | 3.5 | 43 |
| 13 | 5   | 67.6383 | 3.5 | 47 |
| 14 | 5   | 50  | 0.8542 | 40 |
| 15 | 5   | 50  | 6.1457 | 56 |
| 16 | 5   | 50  | 3.5 | 64 |

X_1: concentration, X_2: temperature, X_3: time, Y_e: yield experiment.
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Figure 5. 3D graphic of acid concentration versus temperature dealumination

Figure 6. Contour surface of acid concentration versus temperature dealumination

Figure 7. 3D graphics of temperature versus time dealumination

Figure 8. Contour surface plot of temperature versus time dealumination

Figure 9. 3D graphics of acid concentration versus time of dealumination

Figure 5 and 6 show the interaction of H₂SO₄ concentration and the dealuminated temperature to the area or % yield of glycerol monolaurate produced. As the acid concentration change, it is followed by the greater % yield of GML produced. At a temperature range of 30-55°C, along with increasing the acid concentration, it will give a greater % GML yield. At a temperature range of 30-55°C, the use of a concentration of 7 M in the dealuminated process gives a greater % yield (residing in a red area) than using a 3 M acid concentration.

In this research, there is no result in the area of dark red color, it indicates that not yet reached optimum condition. If the concentration of H₂SO₄ is enlarged then it is likely to reach the optimum condition.

Figure 7 and 8 show the optimization graph and the surface contour of the interaction between temperature and time of dealumination to the yield % of GML produced. At temperatures above 35°C and 2-4.5 hour dealumination time range, a rise in the dealumination temperature will increase the % yield (glycerol monolaurate formed). As the temperature of dealuminated change, the acidity of the deformed ZSM-5 catalyst produced will increase as well. This is because the longer the dealumination process leads to Si/Al ratio.

However, at temperatures above 60°C, the temperature rise will decrease the yield % of GML produced. This is due to damage to some pores and catalyst framework that causes its ability in synthesis glycerol to Glycerol Monolaurate will decrease. Therefore, the optimum dealumination temperature of this process is in the range 35-60°C with optimum dealumination time of 2 to 4.5 hours.
An increase in Si/Al ratio leads to a skeletal change of the zeolite. Changing the zeolite framework will cause changes in the pores of the zeolite which will cause changes also to the surface area. This enhancement of acid sites on deodulated ZSM-5 enhances the catalyst ability in the process of synthesis of glycerol to GML.

Figure 9 shows a convex surface with the lowest point being at a concentration of 5 M acid and a 1.5 hour dealumination time. In figure 9 contour, it was observed that the highest yield occurred at 7 M acid concentration and 5 hour dealumination time. However, the graphs have not seen the results that are in the red area, which shows not yet achieved the optimum conditions in this study. Possible optimum conditions can be achieved by adding acid concentration and dealumination time.

![Figure 10. Contour surface plot of acid concentration versus time dealumination](image)

Figure 10. Contour surface plot of acid concentration versus time dealumination

![Figure 11. Effect of acidity of ZSM-5 terdealuminasi against yield of GML](image)

Figure 11. Effect of acidity of ZSM-5 terdealuminasi against yield of GML

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Increased Si/Al ratio can lead to increased activity of the catalyst. The increased activity of the catalyst is useful in lowering the activation energy of the reaction of a compound. This is what causes the conversion of glycerol to increased Glycerol Monolaurate (Machado et al., 2000).

### ANOVA and Mathematical Calculations

Analysis of Variance (ANOVA) is used to analyze Glycerol Monolaurate yield as shown in Table 4. The significance of each factor in Table 4 is tested using F-value and p-value. A high F-value value and a p-value < 0.05 indicates that the variable significantly affects the observed response. F-value shows the ratio between MSF (Mean Square of Factor) and MSE (Mean Squares of error). The effect of the operation variable can be seen in Table 4.

![Table 4. Analysis of Variance](image)

Based on ANOVA results for Glycerol Monolaurate yield, factor X1X2 is the most significant factor, indicated by F-value of 4.28745 and p-value of 0.083816. The objective function of the test results is used to determine the optimal value of acid concentration (X1), Dealumination Temperature (X2) and dealumination time (X3). The relationship between operating variables on the yield response of Glycerol Monolaurate can be expressed in the mathematical equations of polynomial of order 2 based on the equation 4.

\[
Y = -84.8479 + 24.1230X_1 - 0.6275X_1^2 + 4.7016X_2 - 0.0364X_2^2 - 16.6337X_3 - 1.1870X_3^2 - 0.4938X_1X_2 + 2.2917X_1X_3 + 0.3083X_2X_3
\]

Selection order can be determined by looking at the coefficient of determination, where the model with the highest determination koefisien is a recommended model. In this study, the coefficient of determination (R²) for the 2nd order polynomial mathematical equation has a value of 62.656.

In this research, the price of p-value for acid concentration (p = 0.569712), dealumination temperature (p = 0.417416) and dealumination time (p = 0.546010) showed that no variables had significant effect.

The regression line shows the best prediction of dependent variable (Y), against independent variables (X). However, in reality (if ever), very rarely can be perfectly predicted, and there is usually a substantial variation of the observed point, around the regression line (Figure 12). The deviation from a particular point of the regression line is called the residual value.
CONCLUSION

The acid concentration, temperature, and time variables in the dealumination process of ZSM-5 catalyst affect the acidity of the de-alumamized ZSM-5 catalyst also affect the yield of glycerol monolaurate produced from glycerol and lauric synthesis with de-alumamated ZSM-5 catalyst. The acidity of the ZSM-5 catalyst affected the yield of glycerol monolaurate produced from the synthesis of glycerol and lauric acid with an alduminated ZSM-5 catalyst. In the analysis using statistical software 10, obtained the optimum conditions in this study that is for the temperature of dealumination and the time of dealumination is respectively 40-60°C and 2-5 hours.

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