

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

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(Received: March 15, 2018; Accepted: June 2, 2018)

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 dealumination 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

How to Cite This Article: Anggoro, D.D., Putra, R.R., Oktavianty, H., Kamilah, L.A., and Chamdani, F.T., (2018), Dealumination and Characterization of ZSM-5 as Catalyst for Glycerol Conversion to Glycerol Monolaurate, Reaktor, 18(2), 110-116, <http://dx.doi.org/10.14710/reaktor.18.2.110-116>

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.

Table 1. Experimental design for each variable

Factor	Unit	Level		
		-1	0	+1
Concentration (X ₁)	%	3	5	7
Temperature (X ₂)	°C	40	50	60
Time (X ₃)	Hours	2	3.5	5

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 deormal ZSM-5 zeolite used to synthesize was 4 grams for each sample. Catalyst performance was tested to synthesize by stirred the glycerol monolaurat. 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:

$$\text{Total acidity} \left(\frac{\text{mmol}}{\text{g}} \right) = \frac{W_{NH_3(g)}}{NH_3 \left(\frac{\text{g}}{\text{mol}} \right) \times W_{\text{sampel}} (g)} \times 100 \left(\frac{\text{mol}}{\text{mmol}} \right) \quad (1)$$

$$\text{Surface acidity} \left(\frac{\text{mmol}}{\text{g}} \right) = \frac{W_{\text{pyridine}} (g)}{\text{pyridine} \left(\frac{\text{g}}{\text{mol}} \right) \times W_{\text{sampel}} (g)} \times 100 \left(\frac{\text{mol}}{\text{mmol}} \right) \quad (2)$$

$$\text{The acidity of the pore} \left(\frac{\text{mmol}}{\text{g}} \right) = \text{total acidity} - \text{surface acidity} \quad (3)$$

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 there is glycerol to bind to a fatty acid group that can form monoglycerol and diglycerides and water (Setiadi *et al.*, 2016).

The result of acidity analysis of this dealuminated 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 (NH₃) 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-luminated. This is because the greater the temperature of dealumination, the crystallinity of the catalyst increases.

Table 2. Results of catalyst acidity analysis of ZSM-5 dealumination

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

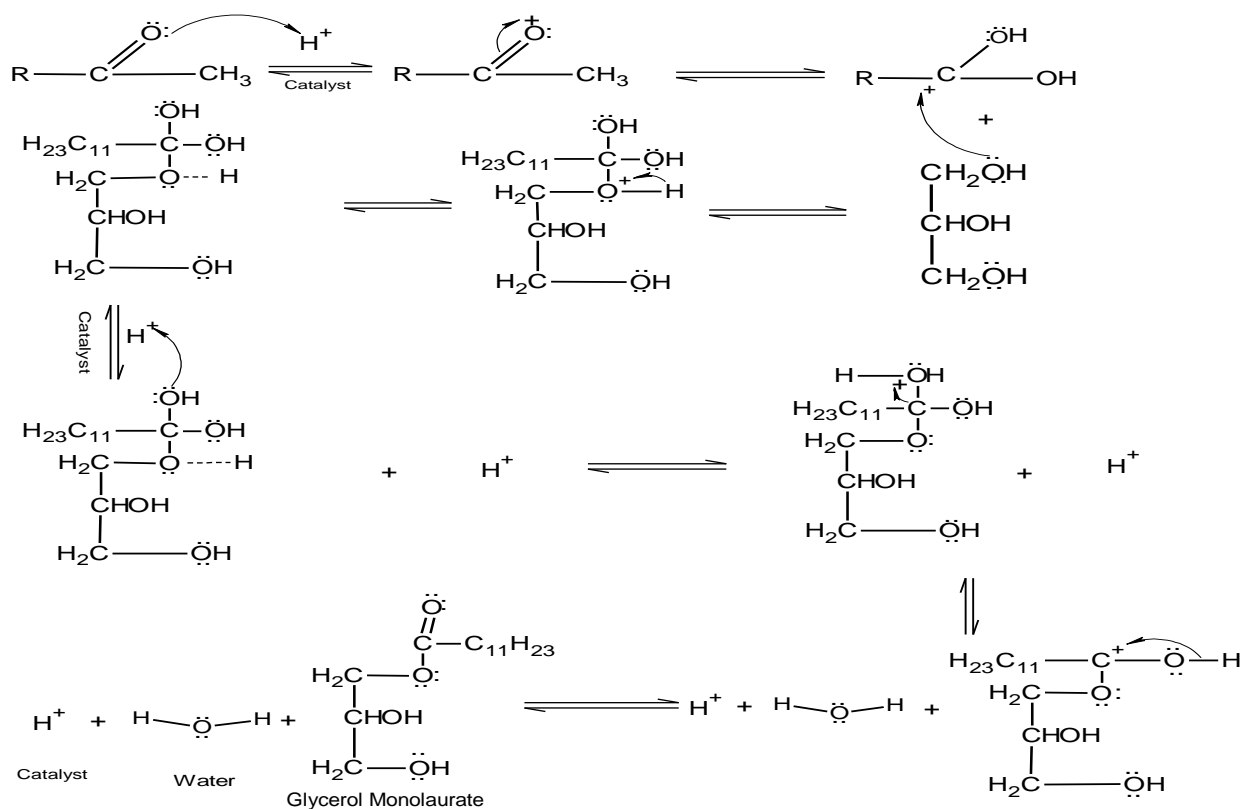


Figure 1. The reaction mechanism of esterification between outer acid and glycerol

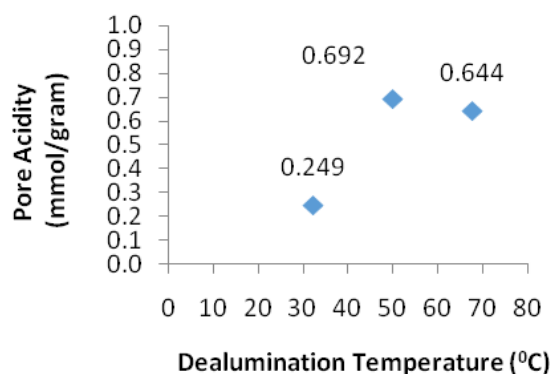


Figure 2 Correlation between temperatures of dealumination with pore acidity

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.

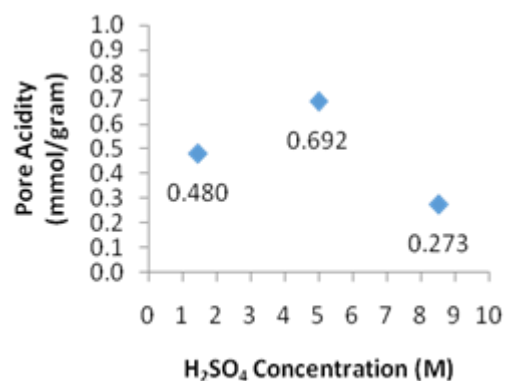


Figure 3 Relationship between the concentration of H₂SO₄ with acidity cavities

Figure 3 show the higher concentration of H₂SO₄ will increase the acidity of the Zeolite ZSM-5 is deformumized. This is because the greater the concentration of H₂SO₄, the aluminum metal that is detached from the zeolite increases, causing an increase in Si/Al ratio. Comparison between silica and high aluminum causes increased adsorption ability. The acidity of a catalyst is defined as the ability of the catalyst to adsorb base. So the greater the ability of the catalyst adsorption the greater the acidity site (Satterfield, 1991). Based on research (Ertan and Cakicioglu-ozkan, 1999) states that the use of acid concentration is too high to cause damage to the crystal structure so that the crystallinity of the ZSM-5 will decrease. The decreasing of crystallinity caused the decreasing acidity of zeolite.

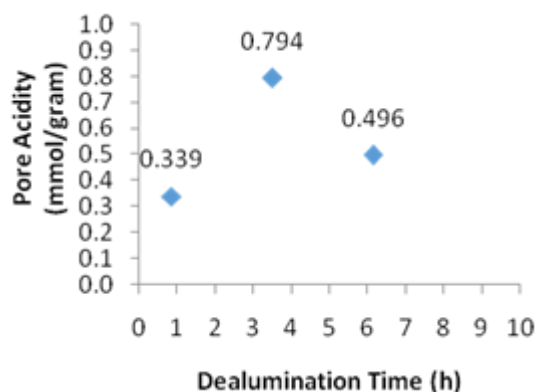


Figure 4. Relationship between time dealumination with pore acidity

Figure 4 shows that the longer the dealumination time increases the acidity. This is because the longer the dealumination process leads to Si/Al ratio. An increase in Si/Al ratio leads to a framework structure 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. However, if the dealumination time is increased, the silica and aluminum compounds will follow soluble. This causes the value of Si/Al ratio decreased resulting in the pore surface area becomes smaller (Aishah *et al.*, 2002).

The Influence of Variables on the Dealumination Process

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

Table 3. Result of GCMS% yield GML

No	Variable Dealumination			Y _E
	X ₁	X ₂	X ₃	
1	3	40	2	62
2	3	40	5	34
3	3	60	2	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	1.4723	50	3.5	54
11	8.5276	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

X₁: concentration, X₂; temperature, X₃; time, Y_E; yield experiment.

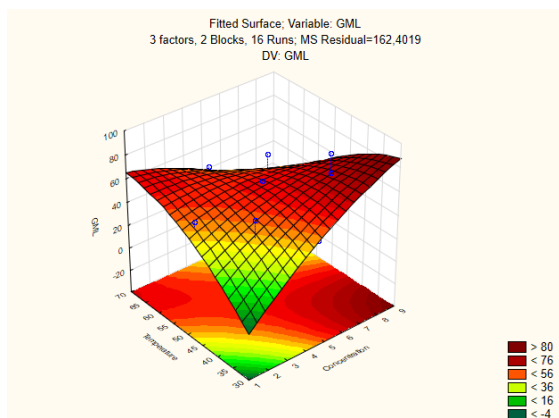


Figure 5. 3D graphic of acid concentration versus temperature dealumination

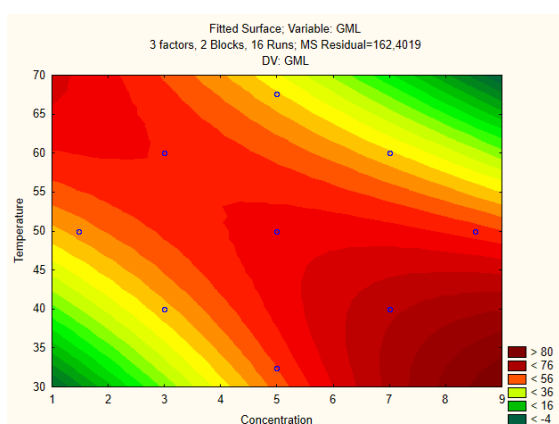


Figure 6. Contour surface of acid concentration versus temperature dealumination

Figure 5 and 6 show the interaction of H_2SO_4 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 H_2SO_4 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.

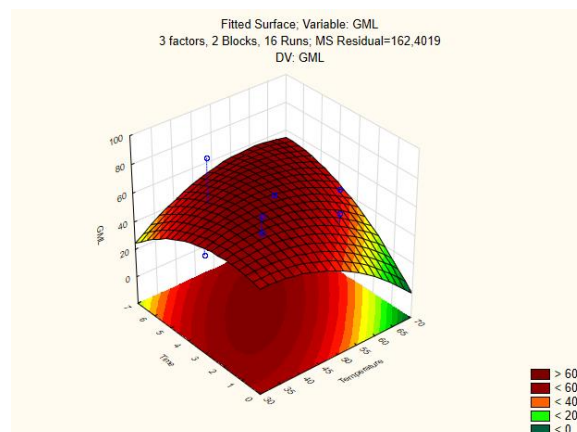


Figure 7. 3D graphics of temperature versus time dealumination

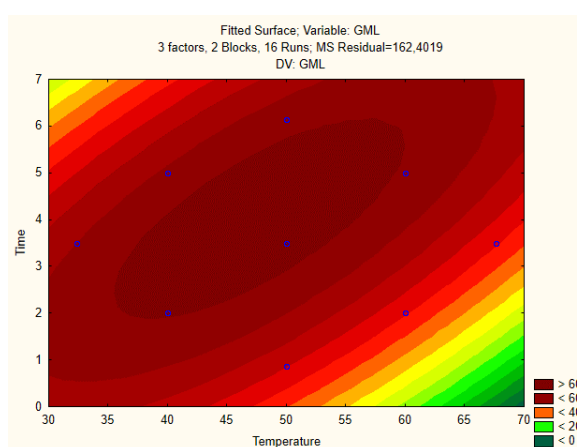


Figure 8. Contour surface plot of temperature versus time dealumination

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.

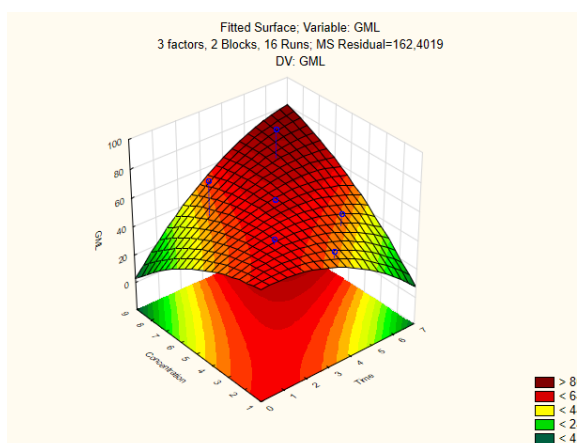


Figure 9. 3D graphics of acid concentration versus time of dealumination

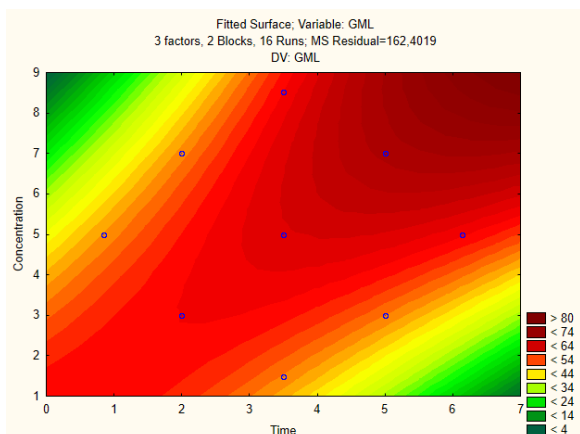


Figure 10. Contour surface plot of acid concentration versus time dealumination

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 dealuminated 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.

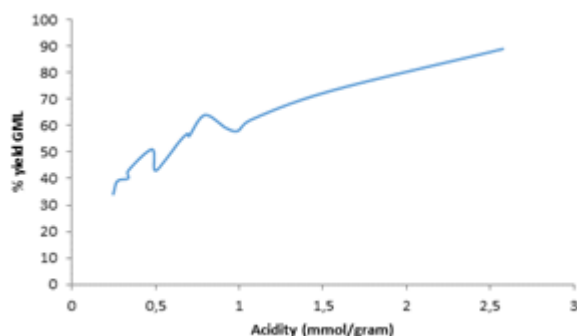


Figure 11. Effect of acidity of ZSM-5 terdealuminasi against yield of GML

Figure 11 can be concluded that the higher the acidity of zeolite the higher the % yield of Glycerol Monolaurate can be. This is because the increase in acidity is due to an increase in Si/Al ratio and dissolution of CaO impurities. 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

Variant	Koefisien	F-Value	DF	p-value
X0	-84.8479			
X1	24.1230	0.436204	1	0.533481
X1 ²	-0.6275	0.361433	1	0.569712
X2	4.7016	0.815713	1	0.401241
X2 ²	-0.0364	0.758024	1	0.417416
X3	-16.6337	0.656616	1	0.448695
X3 ²	-1.1870	0.409199	1	0.546010
X1X2	-0.4938	4.287450	1	0.083816
X1X3	2.2917	2.078118	1	0.199510
X2X3	0.3083	0.940477	1	0.369608

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.

$$Y = -84.8479 + 24.1230X_1 - 0.6275X_1^2 + 4.7016X_2 - 0.0364X_2^2 - 16.6337X_3 - 1.1870X_3^2 - 0.4938X_1X_2 + 2.2917X_1X_3 + 0.3083X_2X_3 \quad (4)$$

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.

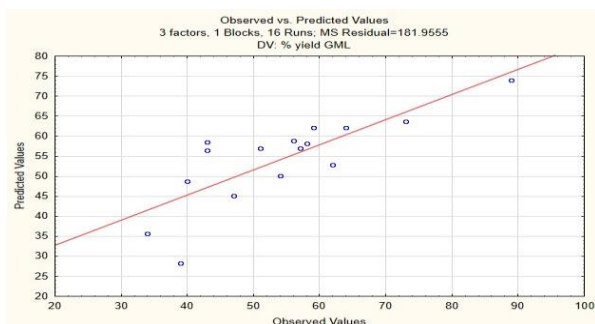


Figure 12. Correlation of predicted and observed value and yield of GML

CONCLUSION

The acid concentration, temperature, and time variables in the dealumination process of ZSM-5 catalyst affect the acidity of the dealuminated ZSM-5 catalyst also affect the yield of glycerol monolaurate produced from glycerol and lauric synthesis with dealuminated 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 dealuminated 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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