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To cite this article: D D Anggoro *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **578** 012027

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## Dealumination of ZSM-5 as catalyst to convert glycerol to glycerol monostearate

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**Abstract.** This study aims to improve the acidity of the ZSM-5 catalyst as a catalyst that can produce the highest yield of glycerol monostearate from conversion of glycerol to glycerol monostearate. This study consisted of three stages: dealumination ZSM-5 Zeolite using H<sub>2</sub>SO<sub>4</sub>, catalyst characterization using ammonia absorption for acidity analysis and pyridine analysis for basicity catalyst, and GC-MS for Glycerol Monostearate molecular weight and purity analysis. Zeolite was dealuminated and then dried at a temperature of 110<sup>0</sup>C for 1 hour, then calcined at a temperature of 550<sup>0</sup>C for 4 hours. The dealumination variables used are acid concentration, temperature and time of dealumination. The test results obtained the optimum condition to produce the highest total acidity and the highest surface acidity at 7M of acid concentration, temperature of 60<sup>0</sup>C, and 2 hours of dealumination time. The optimum conditions of the dealumination variables to produce monoglycerides as product respectively, 3.5-6.5 M of acid concentration, temperature of dealumination at 40-60<sup>0</sup>C and 0.85-2 hours of dealumination time. This study also found other product namely glycerin, with high % yield on two catalyst samples which have the lowest total acidity.

### 1. Introduction

Glycerol monostearate is an ester compound produced from the esterification reaction between glycerol and stearic acid. The manufacture of glycerol stearic is carried out in a temperature range of 140<sup>0</sup>-190<sup>0</sup>C with the time used for the experiment is 8 hours, the optimal conditions are produced at a temperature of 180<sup>0</sup>C with a reaction time of 8 hours which is obtained 94.58% ester, catalyst used acid catalyst (HCl) and base (KOH) with a concentration of 0.75% [1]. The use of this GMS (glycerol monostearate) product is for non-ionic surfactants in the oleochemical industry, this GMS is used in shampoos as pearlizing agents, emulsifiers and lotions, and in the food industry (ice cream, butter, etc.) as an opacifier.

Zeolite is defined as a group of crystalline aluminosilicate materials (less than 2 nm), composed of tetrahedral units of SiO<sub>4</sub> and AlO<sub>4</sub> which are interconnected with each other [2]. Zeolite is a type of aluminosilicate where the aluminosilicate type material has three main characteristics, namely a good and regular crystal structure, the ion in the framework structure can be easily exchanged with other ions, and ion exchange in the framework greatly affects the properties of zeolite. Zeolites have a unique structure, because they have cavities or pores with molecular dimensions which



are part of the structure of the crystalline. Having a microscopic cavity, zeolites can be compared to enzymes, which have certain catalytic groups [3].

Zeolite has been widely used in the reaction of important chemical industries, such as for cracking (hydrocracking) and isomerization [4]. Kadja et al. [2] research zeolite that has been used in various fields, such as sorbent [5; 6; 7], cation exchange agents [8; 9; 10], as well as catalysts [11; 12; 13; 14; 15]. Further use of zeolite has also been rampant, such as optical-electronic materials [16; 17], and membranes [18; 19; 20]. However, until now the most commonly used zeolite utilization is as a catalyst.

Gu et al [21] conducted synthesis of Glycerol Monostearate from stearic acid and glycerol as the main material with the help of N, N-dimethylformamide (DMF) / toluene as a solvent, and  $H_3PW_{12}O_{40}/MCM-41$  with weight ratio of  $H_3PW_{12}O_{40}$  are 10% ,30%, and 50% as a catalyst. A mixture of glycerol and stearic acid with DMF solvent was stirred at 800 rpm and heated using oil.  $N_2$  gas with steady flow is passed over the mixture, then the catalyst is added to the reactant when the desired temperature has been reached. In the results, it was found that 30%  $H_3PW_{12}O_{40}/MCM-41$  was more active than 10%, 50% of  $H_3PW_{12}O_{40}/MCM-41$ . Stearic acid conversion at 30%  $H_3PW_{12}O_{40} /MCM-41$  as catalyst increased from 80% to 98% with the selectivity of glycerol monostearate 91%. This is related to higher catalytic activity due to acid strength and amount of acid. When the amount of  $H_3PW_{12}O_{40}$  acid is too small, the activity of the catalyst is weak so it cannot direct the synthesis of diglycerides or triglycerides, whereas if the amount of  $H_3PW_{12}O_{40}$  acid is too large then the large granules of  $H_3PW_{12}O_{40}$  will form, the granules will block the pores, where monoglycerides will form more in pores diglycerides and triglycerides. The Si/Al ratio of the ZSM-5 Zeolite (obtained from International Zeolite in  $NH_4$  form) is 30. Increased Si /Al ratio has an impact on catalytic activity due to acid strength and the amount of acid. The dealumination process can increase the Si/Al comparison ratio so that the catalyst is more acidic, and can increase zeolite activity and can produce high Glycerol Monostearate conversion.

This study was used three stages, namely the process of chemical treatment/dealumination, washing process and calcination process. Variables used in the dealumination process are temperature variables, time variables and acid solution concentration variables. This research is expected to get the optimum operating conditions of the dealumination process on zeolite catalysts.

## 2. Experimental

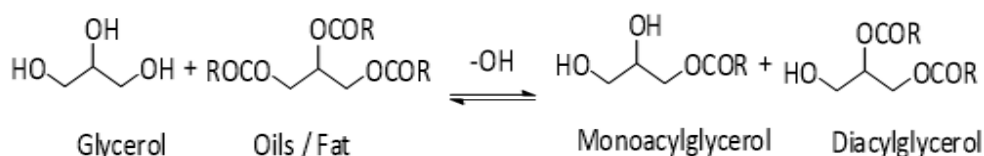
The experiment was held in Process Laboratory, Chemical Engineering, Diponegoro University. ZSM-5 catalyst came from Zeolit International, was dealumination using  $H_2SO_4$  solution (Merck). The  $H_2SO_4$  solution was done by making a solution of  $H_2SO_4$  (3-8 M) which is dissolved in 25 ml of distilled water then 10 grams of ZSM-5 is put into the mixture. The dealumination process is carried out over time variation (2-5 hours) with temperature of dealumination range of  $40^0-60^0C$ . The mixture is filtered with a suction filter. The filtered sediment was dried in an oven at  $110^0C$  for 4 hours. Modified catalysts, calcined with  $550^0C$  for 3 hours. Monostearate synthesis is carried out by inserting glycerol and stearic acid into a three-neck flask, then adding 20% tetradecane w/w, and ZSM-5 catalyst. Heat and set the stirring speed to 800 rpm. Flow nitrogen gas into a three-neck flask, set the flow rate to 10 ml / minute and do the synthesis for 6 hours.

Catalyst acidity test is done by smoothing the calcined catalyst first. Weigh the initial weight of each sample. Pour ammonia and pyridine into the container and place it into a different desiccator. Enter the sample into each desiccator. Weigh the weight of sample on the first day, second day, and so on until it reaches 3 times constant. The results of the ZSM-5 dealumination catalyst process were used for glycerol synthesis with stearic acid. GC-MS analysis will be carried out to determine the molecular weight of the compounds produced, and show the purity of the compounds produced using the dealuminated ZSM-5 catalyst [22].

### 3. Results and Discussion

#### 3.1 Effect Variables of Dealumination Process on Monoglycerides Yield

In this study, ZSM-5 which has been dehydrated with H<sub>2</sub>SO<sub>4</sub> solution was used as a catalyst to synthesize glycerol and stearic acid into monoglycerides. The mechanism of monoglyceride formation reaction is as follows:



**Figure 1.** Mechanism of Monoglycerides Formation Reaction

The reaction between glycerol and fat will produce monoglycerides and diglycerides. Adding a base catalyst to the glycerolysis reaction will help break the OH bond in glycerol to form monoglycerides and diglycerides. Table 1 shows GCMS analysis of monoglycerides yield for 16 runs and also shows the glycerin product that obtained.

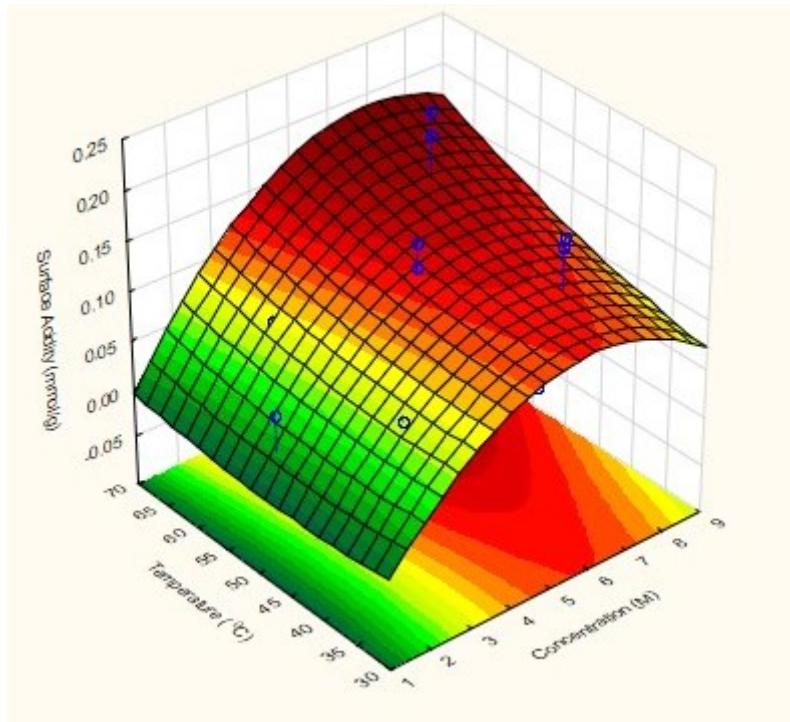
**Table 1.** GCMS Analysis of % Yield of Monoglycerides

Run	Dealumination Variables			% Monoglycerides	% Glycerin
	Acid Concentration (M)	Temp (°C)	Time (hour)		
1	3	40	2	7.23	7.24
2	3	40	5	8.62	10.82
3	3	60	2	20.97	26.23
4	3	60	5	4.42	7.52
5	7	40	2	21.07	12.05
6	7	40	5	3.85	2.78
7	7	60	2	4.08	6.27
8	7	60	5	4.12	7.04
9	5	50	3.5	18.7	0
10	1.4723	50	3.5	1.81	1.81
11	8.5276	50	3.5	0	0
12	5	32.3616	3.5	0	100
13	5	67.6383	3.5	0	5.34
14	5	50	0.854249	0	99.15
15	5	50	6.145751	10.09	0
16	5	50	3.5	0	0

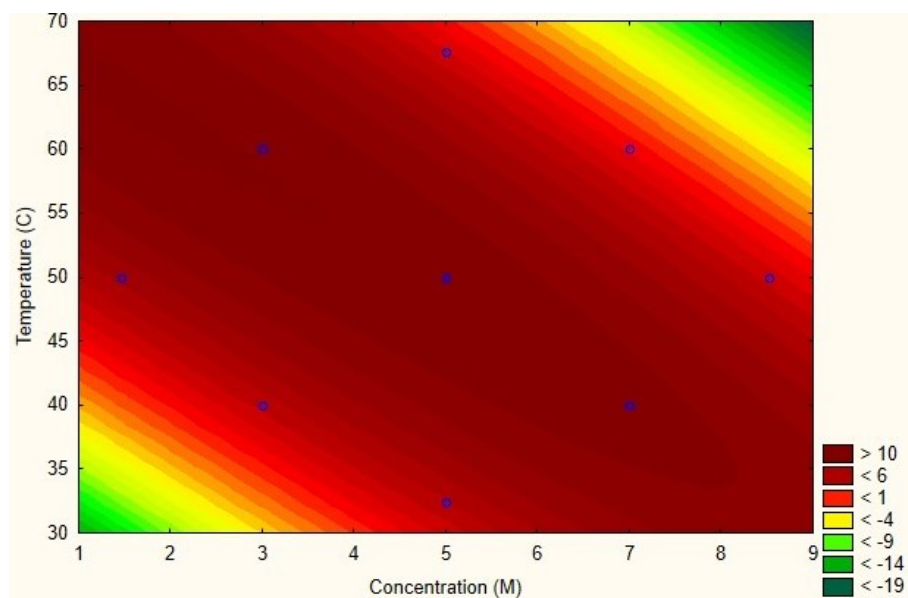
#### 3.2 Effect of Acid Concentration and Temperature of Dealumination on Monoglycerides Yield

Figure 2 and Figure 3 show the interaction of H<sub>2</sub>SO<sub>4</sub> concentration and the dealumination temperature on the % area or % yield of Monoglyceride produced. Along with the increasing concentration of acid, it is followed by the greater% yield of the monoglyceride produced. In the temperature range of 40<sup>0</sup> - 60°C, along with the increasing concentration of acid it will give a higher% yield of Monoglyceride as well. In the temperature range of 40<sup>0</sup>- 60°C, the use of 7 M concentration in the dealumination process gives a greater % yield (in the dark red area) than the use of 3 M acid concentration (in the red area). This is because the greater the concentration of H<sub>2</sub>SO<sub>4</sub>, the more aluminum metal released from zeolite will cause an increase in the Si/Al ratio. The high ratio between silica and aluminum causes increased adsorption capability. The acidity of a catalyst is defined as the ability of a catalyst to adsorb bases. So that the greater the ability of catalyst adsorption, the greater the acidity site, this happens because of the large number of zeolite pores that are exposed and the surface of the solid being wider due to Al

being released from the zeolite. The increase in surface area of the dealuminated ZSM-5 shows a greater level of acidity thus increasing the ability of the catalyst in the synthesis of glycerol to become Monoglycerides.

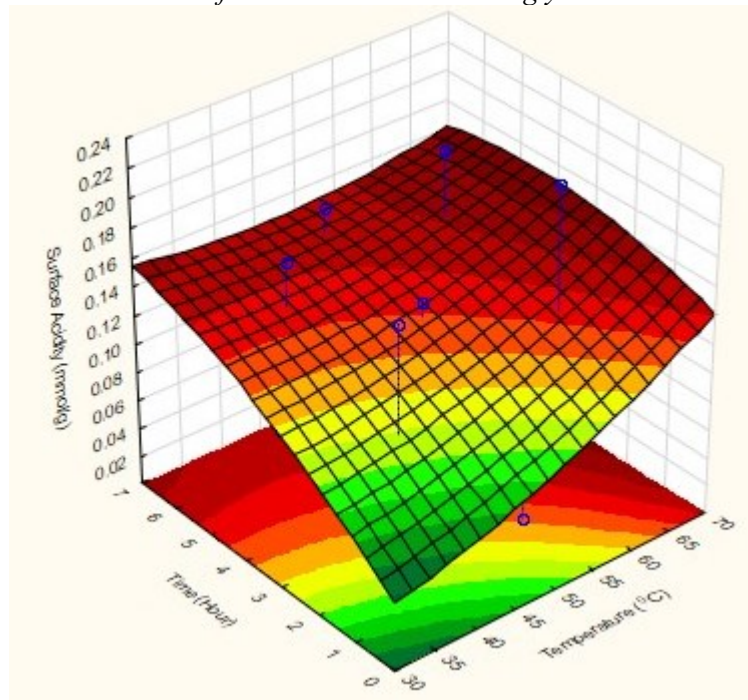


**Figure 2.** 3D Surface of Acid Concentration vs Dealumination Temperature

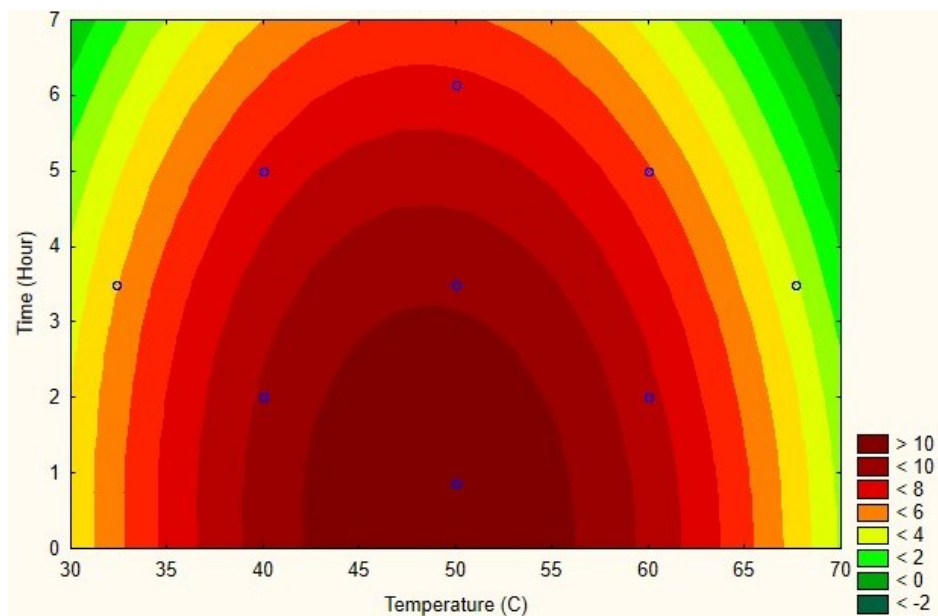


**Figure 3.** Contour of Acid Concentration vs Dealumination Temperature

### 3.3 Effect of Temperature and Time of Dealumination on Monoglycerides Yield



**Figure 4.** 3D Surface of Temperature vs Time of Dealumination



**Figure 5.** Contour of Temperature vs Time of Dealumination

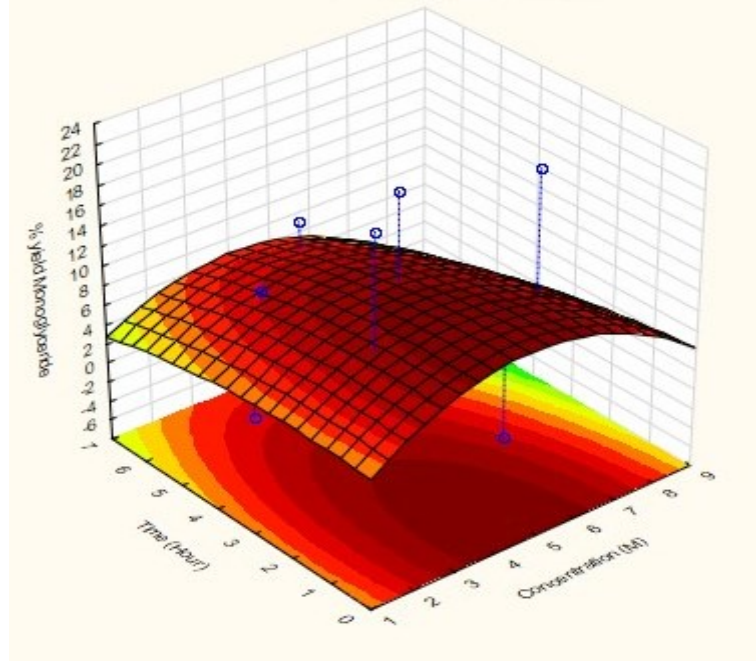
Figure 4 and Figure 5 show the interaction between temperature and time of dealumination on the % yield of Monoglyceride produced. In the temperature range between 40<sup>o</sup>-50<sup>o</sup>C and dealumination time range 0.85-2 hours, the dealumination temperature increase will increase the yield% formed (Monoglyceride formed). Where the dealumination temperature is increasing, the acidity of the resulting dealuminated ZSM-5 catalyst will also increase. This is because the longer the dealumination process causes the Si/Al ratio to rise. The increase in the Si/Al ratio causes a change in the skeleton of the zeolite. Changes in the zeolite framework will cause changes in the pores of the zeolite which will



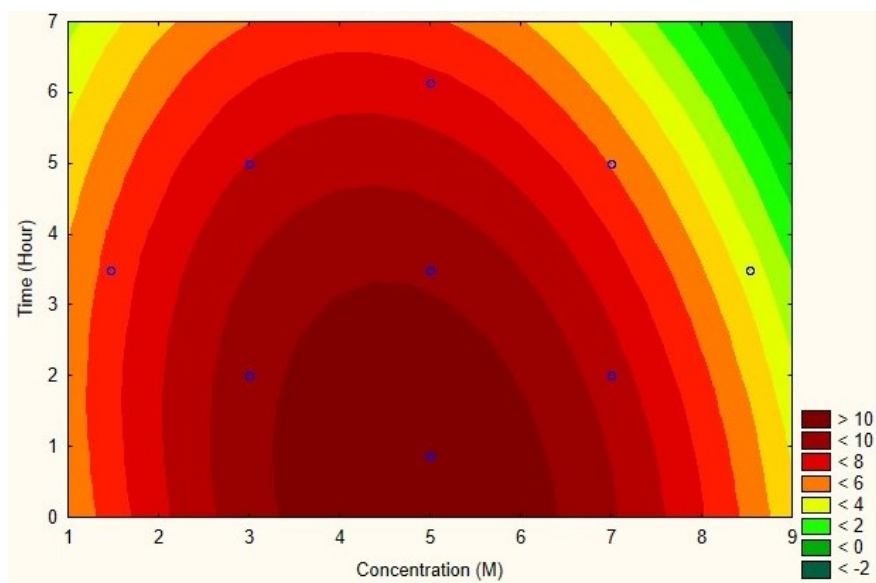
also cause changes in surface area. The increase in surface area of the dealuminated ZSM-5 shows a greater level of acidity thus increasing the ability of the catalyst in the synthesis of glycerol to become Monoglycerides.

But at temperatures above 60°C, a rise in temperature will reduce the % yield of the Monoglyceride produced. This is caused by damage to some of the pores and catalyst framework so that it will decrease its ability to synthesize glycerol to Monoglyceride. Therefore the optimum dealumination temperature of this process is in the range of 40<sup>0</sup>-50°C with optimum dealumination time of 0.85 to 2 hours.

### 3.4 Effect of Acid Concentration and Time of Dealumination on Monoglycerides Yield



**Figure 6.** 3D Surface of Acid Concentration vs Time of Dealumination

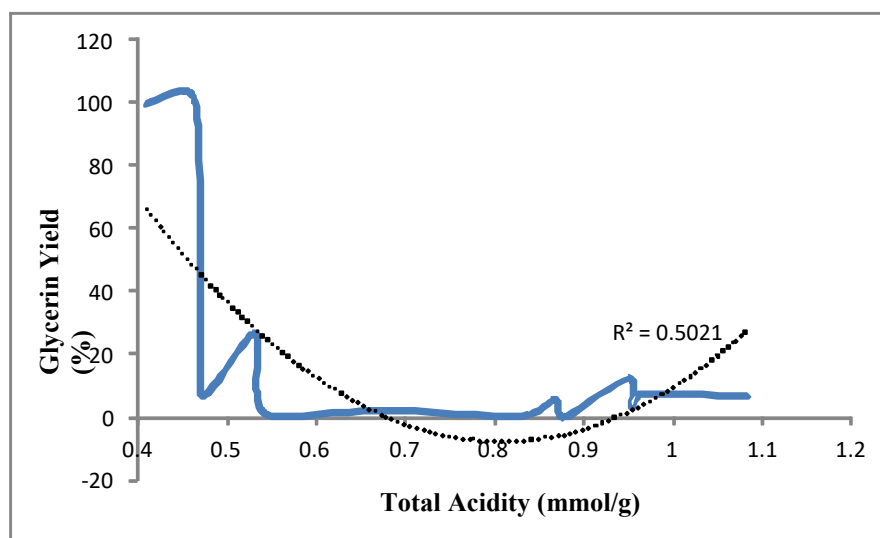


**Figure 7.** Contour of Acid Concentration vs Time of Dealumination

Figure 6 and Figure 7 show the interaction of concentration and time of dealumination on the % yield of the Monoglyceride produced. In the range of  $\text{H}_2\text{SO}_4$  concentrations between 3.5-6 M and the dealumination time range for up to 3 hours, an increase in  $\text{H}_2\text{SO}_4$  concentration will increase the % yield formed (Monoglyceride formed). Where the longer the dealumination time is, the acidity of the resulting dealuminated ZSM-5 catalyst will also increase. This is because the longer the dealumination process causes the Si/Al ratio to rise. The increase in the Si/Al ratio causes a change in the skeleton of the zeolite. Changes in the zeolite framework will cause changes in the pores of the zeolite which will also cause changes in surface area. The increase in surface area of the dealuminated ZSM-5 shows a greater level of acidity thus increasing the ability of the catalyst in the synthesis of glycerol to become Monoglyceride.

But at concentrations of  $\text{H}_2\text{SO}_4$  above 7 M, the increase in  $\text{H}_2\text{SO}_4$  concentration will reduce the % yield of Monoglyceride produced. This is caused by damage to some of the pores and catalyst framework so that it will decrease its ability to synthesize glycerol to Monoglyceride. Therefore, the optimum  $\text{H}_2\text{SO}_4$  concentration of this process is in the range of 3.5-6 M with optimum dealumination time a maximum of 3 hours.

In this study, another product was found besides monoglyceride, glycerin. The effect of the detected ZSM-5 acidity on % monoglyceride yield can be seen from Figure 8. From Figure 8, it can be concluded that the higher the acidity of zeolite, the lower % yield of Glycerin can be obtained. Acidity increasing is caused by an increase in the Si/Al ratio and dissolution of CaO impurities. Si/Al ratio increasing can cause increased activity of the catalyst. The activity increasing of catalysts is useful in reducing the activation energy of the reaction of a compound [23]. This is what causes the conversion of glycerol to Glycerine decreases with increasing acidity because glycerol is converted into other compounds.



**Figure 8.** Effect of Acidity of Dealuminated ZSM-5 on Glycerin Yield

#### 4. Conclusion

Acid concentration, temperature, and time in the ZSM-5 catalyst dealumination process affected the acidity generated from the dealuminated ZSM-5 catalyst. The total acidity of the ZSM-5 catalyst which has the most optimum results was found in sample 7 with a variable acid concentration of 7 M, temperature of 60 °C, and the processing time of catalyst for 2 hours. The surface acidity of the ZSM-5 catalyst which has the most optimum results was found in sample 7 with 7 M acid concentration variable, temperature 60 °C, and dealumination time of catalyst for 2 hours. The optimum conditions for producing Monoglyceride products are when the acid concentration variable is 3.5-6.5 M with dealumination temperature 40-60 °C and dealumination processing time for 0.85 to 2 hours. Glycerin



products were found with% yield of 100% and 99.15% in two catalyst samples which had the lowest total acidity.

### Acknowledgements

The authors gratefully acknowledge the financial support received in the form of a research grant from KEMENRISTEKDIKTI Indonesia No: 101-76/UN7.P4.3/PP/2018.

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