Effect of dealumination on the acidity of zeolite Y and the yield of glycerol mono stearate (GMS)

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HIGHLIGHTS

- The catalytic dealumination process can change the strength of zeolite Y catalyst acid.
- Dealumination variables such as acid concentration, temperature and time of dealumination affect the surface acidity of Zeolite Y.
- The strength of the catalyst acid can increase the yield of Glycerol Monostearate.
- Statistica software can be used to determine the optimum conditions of dealumination zeolite.

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ABSTRACT

Research on the production of Glycerol Monostearate from glycerol using dealuminated Zeolite Y catalysts has been carried out. Optimization of the dealumination process is conducted using the help of statistical software 10, where the variables used are acid concentration (5–7 M), temperature of dealumination (55–70 °C) and time of dealumination (2–6 h). The acidity characterization test of dealuminated Zeolite Y using ammonia and pyridine solution. Glycerol Monostearate yield was obtained by GC-MS test that was carried out on 2 samples zeolite Y catalyst with the highest value of total and surface acidity of zeolite Y which produced 2.18% and 4% yield of Glycerol Monostearate. The two samples showed that the greater the acidity, the GMS yield was also greater. Compared to previous studies it was found that ZSM-5 catalyst has a higher acidity value than zeolite Y so that the yield of Glycerol Monostearate is higher with the use of ZSM-5 than Zeolite Y.

1. Introduction

Increase in population growth causing increase in fuel consumption too, especially fossil fuels. Biodiesel is a renewable alternative energy that can be used to replace fossil fuels that are low in pollution. This has caused a massive increase in biodiesel production. This biodiesel manufacturing process produces two main results, namely methylester and glycerol. Glycerol, in other words propane-1,2,3-triol at room temperature in the form of liquid has a clear color like water, thick, hygroscopic with a sweet taste. One of the glycerol derivatives is glycerol monostearate and has uses as an emulsifier in the food, pharmaceutical, and cosmetics industries. Glycerol monostearate is produced from the esterification process which reacts glycerol with stearic acid.

In the glycerol monostearate production used catalyst that serves to speed up the reaction and increase the yield of glycerol monostearate. The catalyst is a chemical that can increase the rate of reaction and is involved in chemical reactions even though the substance does not react. Catalysts can be divided into 3 parts, homogeneous catalysts, heterogeneous catalysts, enzyme catalysts (Istadi, 2011). One type of catalyst used in the manufacture of glycerol monostearate is zeolite.

The resulting synthetic zeolite catalyst sometimes does not meet specifications to be used as a catalyst in accelerating the reaction rate. Therefore, the catalyst characterization process is needed to change the properties of the catalyst in accordance with the required specifications (Wang et al., 2015). One of the catalyst

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characterization processes is dealumination. Dealumination is the process of removing metals found in a zeolite, one of which is by using an acid solution. The dealumination method is very important to improve the characteristics of the catalyst and increase acidity. The advantage of the dealumination method is that it does not require sophisticated equipment, as well as products that are soluble in water (Borges and Macedo, 2016).

Previous research by Anggoro et al. (2019) carried out synthesis of glycerol monostearate from glycerol and stearic acid as the main material with the help of ZSM-5 as a catalyst. ZSM-5 catalyst was dealuminated in order to increase the surface area of the catalyst. The acidity of a catalyst is defined as the ability of a catalyst to adsorb bases which can be adjusted by modifying Si/Al ratio. The optimum conditions with 7 M acid concentration variable, temperature 60 °C, and dealumination time of catalyst for 2 h resulted a glycerol monostearate yield of 21.07%. (Anggoro et al., 2019).

This research carried out the effect of acidity of zeolite Y on Glycerol Monostearate yield. This study uses three stages, namely the process of chemical treatment/dealumination, washing, drying/calcination process. The variable that we will use in this dealumination process is the temperature, stirring time and H_2SO_4 normality. This research is expected get the optimal operating conditions of the dealumination process on the zeolite catalyst.

2. Materials and methods

2.1. Dealumination process

This experiment was held in Process Laboratory, Chemical Engineering, Diponegoro University. Zeolite Y was obtained from Zeolyst International, H_2SO_4 solution used was Merck. Dealumination process was prepared by dissolving H_2SO_4 solution (variables: 7−9 M) in 25 ml of distilled water then mixed with 10 g of Zeolite Y. After that dried with a temperature of 110 °C for 1 h. Then, calcinate in the temperature range of 500−600 °C for 4 h. Zeolite Y then tested for its acidity to obtain the best operating conditions to produce a Zeolite Y catalyst to obtain glycerol monostearate with the highest yield.

2.2. Acidity characterization

The acidity characterization test is carried out by weighing 1 sample layer in 6 containers of the same weight. The bases used are ammonia and pyridine. Then contact the base with the sample in the desiccator. Weigh the weight per day to a constant weight (Trisunaryanti et al., 2010).

2.3. GC-MS analysis

GC-MS analysis will be carried out to determine the molecular weight of the resulting Glycerol Monostearate compound, and to show the purity of the Glycerol Monostearate using dealuminated Zeolite Y catalyst (Anggoro et al., 2019).

2.4. Experimental design

Experimental design of glycerol monostearate synthesis using dealuminated zeolite Y catalyst was done by determining important parameters such as concentration of acid, dealumination temperature and dealumination time. These parameters were chosen because they are considered the most important in the dealumination process. Experimental matrix design (experimental design/DOE) uses central composite design by response surface methodology. Experimental Design (DOE) was designed in a number of 16 trial runs consisting of 8 factorial points (1-8), 6 axial points (9-14), and 2 repetitions at the center point (15,16). The second-order model was created to test the interaction of independent variables on response. The basis for the formation of the polynomial equation is shown in equation (1), where Y is the response, β_0 is the intercept, β_1 is a linear coefficient, β_{ii} is the quadratic coefficient, β_{ij} is the interaction coefficient, and X_iX_j is the independent variable (Sing, 2019).

$$Y = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \ldots\ldots \sum_{i<j} \beta_{ij} X_i X_j \quad (1)$$

3. Results

In this study, Zeolite Y was used as a catalyst and was dealuminated with sulfuric acid (H_2SO_4) solution which using variables such as acid concentration, temperature and time of dealumination, and then characterized the zeolite Y. The characterization test including the acidity of dealuminated Zeolite Y using ammonia and pyridine solution. The results of the acidity analysis of the dealuminated Zeolite Y are listed in Table 1.

Determination of acidity is done by absorption of ammonia and also the absorption of pyridine which are alkaline, by zeolites which have acidic sites in their structure. Therefore the zeolite acidity is expressed in addition to the amount of ammonia per gram of catalyst per mmol as well as the amount of pyridine per gram of catalyst. It appears that the acidity expressed as mmol ammonia is always greater than the acidity of pyridine. Ammonia (NH_3) molecular size is relatively smaller than the size of the zeolite cavity, allowing it to enter the cavity and reach existing acidic sites. So ammonia interacts not only with acidic sites on the surface, but also with acidic sites in the cavity. Therefore, this acidity is also called total acidity.

Meanwhile, pyridine size is much larger so that it cannot enter the zeolite cavity. As a result, this molecule only reaches the acidic sites on the surface. The difference in acidity between total acidity and surface acidity can be expressed as the zeolite cavity acidity (Trisunaryanti et al., 2010). The total acidity and acidity of the cavity can be calculated using the following equations:

Table 1
Dealuminated zeolite Y catalyst acid analysis results.

Sample	Dealumination Variables			Acidity (mmol/g)	
	Acid Concentration (M)	Temp (°C)	Time (h)	Total	Surface
1	3	40	2	0.0039	0.0006
2	3	40	5	0.0251	0.0007
3	3	60	2	0.0075	0.0013
4	3	60	5	0.0101	0.0015
5	7	40	2	0.0074	0.0012
6	7	40	5	0.0095	0.0017
7	7	60	2	0.0131	0.0015
8	7	60	5	0.0109	0.0013
9	5	50	3.5	0.0110	0.0012
10	1.4	50	3.5	0.0103	0.0008
11	8.5	50	3.5	0.0272	0.0016
12	5	32.3	3.5	0.0067	0.0009
13	5	67.6	3.5	0.0079	0.0008
14	5	50	0.8	0.0097	0.0009
15	5	50	6.1	0.0094	0.0011
16	5	50	3.5	0.0098	0.0012
Without dealumination				0.0021	0.0004

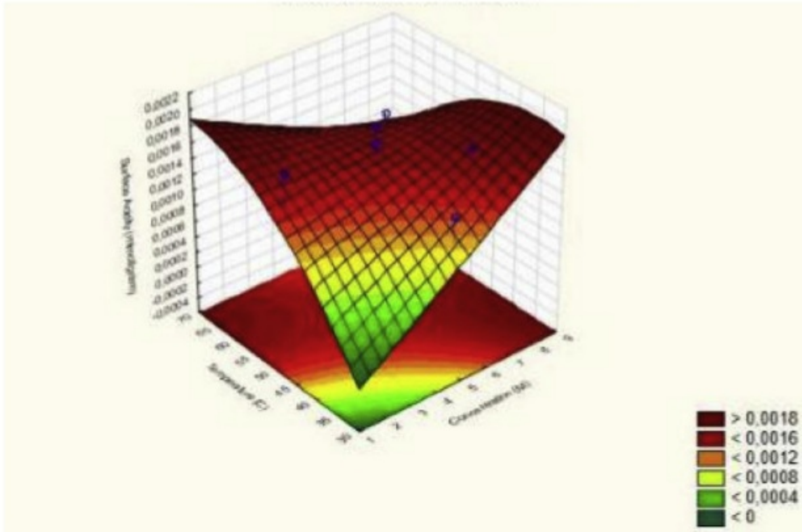

Fig. 1. 3D Optimization Chart of Acid Concentration vs Dealumination Temperature.

$$total\,acidity\left(\frac{mmol}{g}\right)=\frac{W\,NH_3\,(g)}{MW\,NH_3\,(\frac{g}{mol})\,x\,W\,sample\,(g)}x\,1000\frac{mmol}{mol} \quad (2)$$

$$surface\ acidity\left(\frac{mmol}{g}\right)=\frac{W\ Pyridine\ (g)}{MW\ Pyridine\ (\frac{g}{mol})\ x\ W\ sample\ (g)}\ x\ 1000\frac{mmol}{mol} \quad (3)$$

$$surface\ acidity\left(\frac{mmol}{g}\right)=\frac{W\ Pyridine\ (g)}{MW\ Pyridine\ (\frac{g}{mol})\ x\ W\ sample\ (g)}\ x\ 1000\ \frac{mmol}{mol} \quad (4)$$

Figs. 1 and 2 show the interaction of H_2SO_4 concentration and dealumination temperature with the resulting surface acidity. The higher concentration of H_2SO_4 will increase the acidity of dealuminated Zeolite Y. It can be seen in the graph, that 8.53 M H_2SO_4 concentrations have higher acidity compared to 1.47 M H_2SO_4 concentrations and 5 M H_2SO_4 concentrations. This is because the greater the concentration of H_2SO_4, the aluminum metal released from zeolite more and more, causing an increase in the ratio of Si/Al. A high ratio of silica and aluminum causes the adsorption ability to increase (Satterfield, 1991). In this study the optimum conditions occur in dark red areas, with an acid concentration of 7 M - 9 M and a dealumination temperature of 55–70 °C.

Figs. 3 and 4 show the interaction between temperature and dealumination time on the % yield of Glycerol Mono Stearate produced. The higher the temperature of the dealumination will increase the acidity of the dealuminated Zeolite Y. It was proven that at 50 °C the acidity was greater than 32.2 °C. This was caused by the

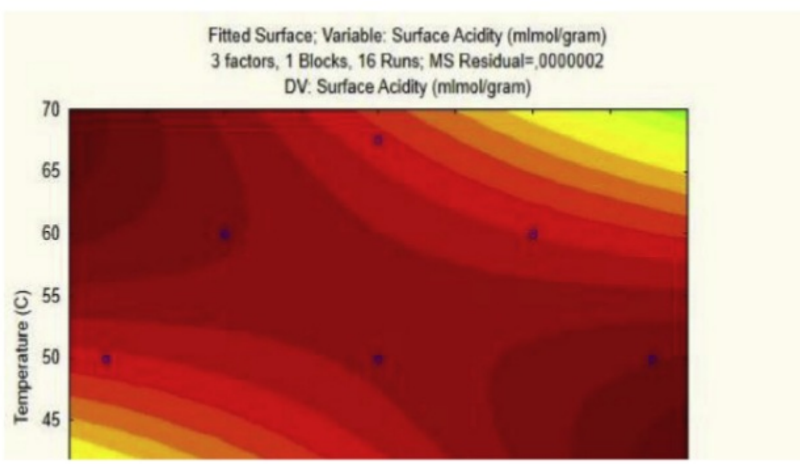

Fig. 2. Contour of Acid vs. Dealumination temperature.

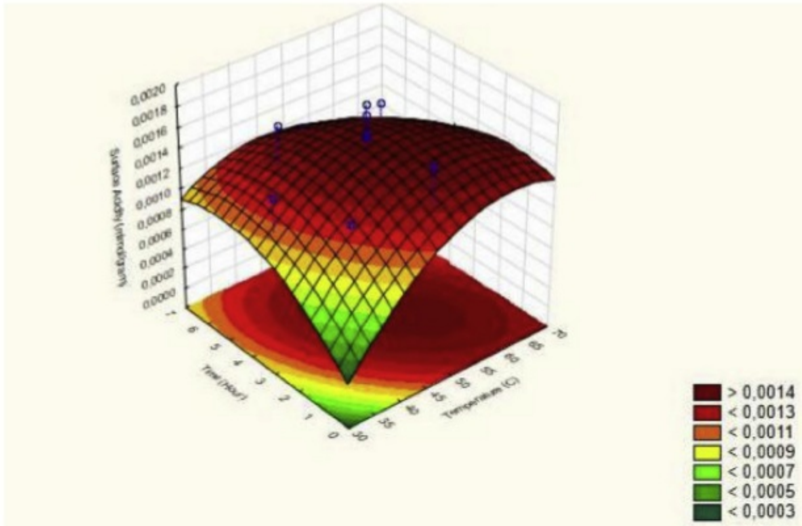

Fig. 3. 3D Optimization Chart of Temperature vs Time of Dealumination.

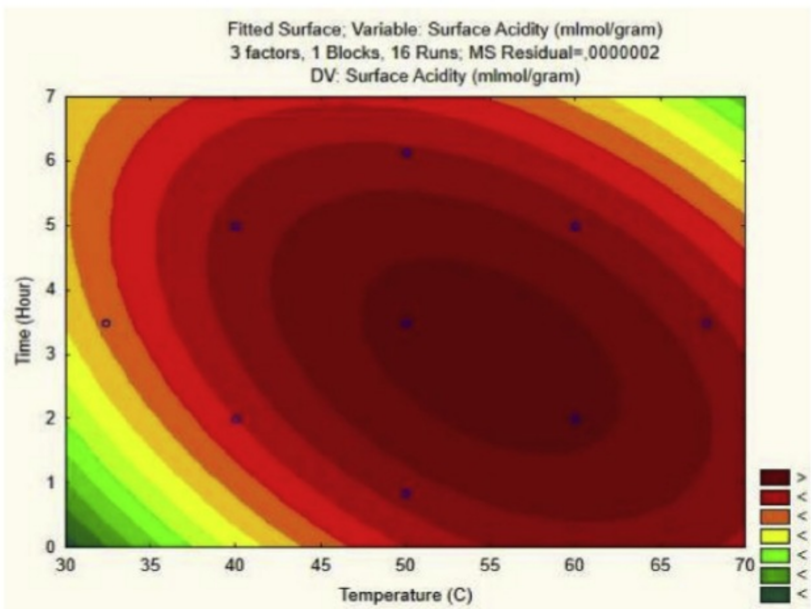

Fig. 4. Contour Graph of Temperature vs. Time of Dealumination.

greater of the dealumination temperature, the crystallinity of the catalyst increased. The catalyst crystallinity is the degree of ability of the crystal side to maintain its crystal structure (Hamdan, 1992).

But at higher temperatures, the framework will become damaged and changes in the structure of zeolites, which cause the crystallinity of Zeolite Y will decrease (Bagas et al, 2017), so that the acidity level of zeolites decreases. It can be seen in the graph that with the addition of temperature to 67.6 °C the acidity obtained is lower than the temperature of 50 °C.

Figs. 5 and 6 show the interaction between acid concentration and dealumination time with the resulting acidity. In this study, the optimum conditions occur in dark red areas. With a concentration of 7–9 M and 2–5 h of dealumination time. it shows that the longer the dealumination is, the acidity increases. It was proven that at 0.85 h there was a lower acidity compared to 3.5 h. This is because the longer the dealumination process causes the Si/Al ratio. An

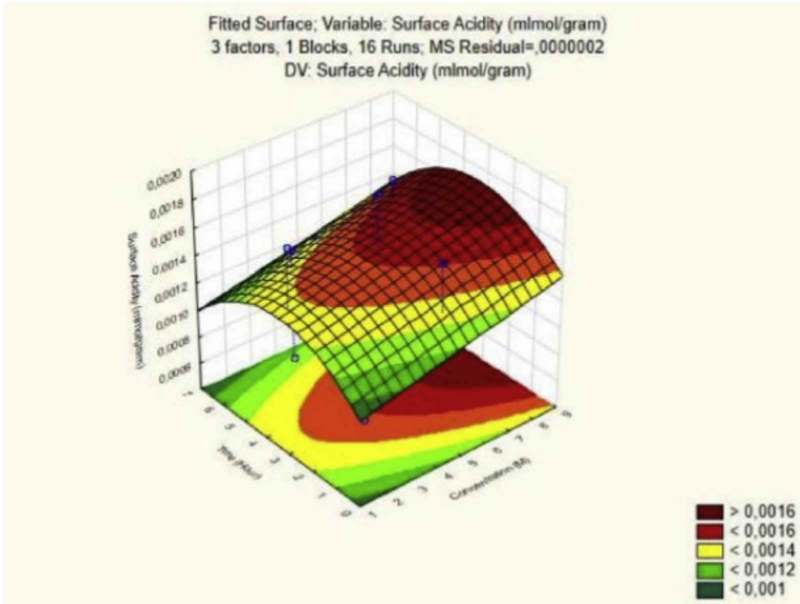

Fig. 5. 3D Optimization Chart of Acid Concentration vs Time of Dealumination.

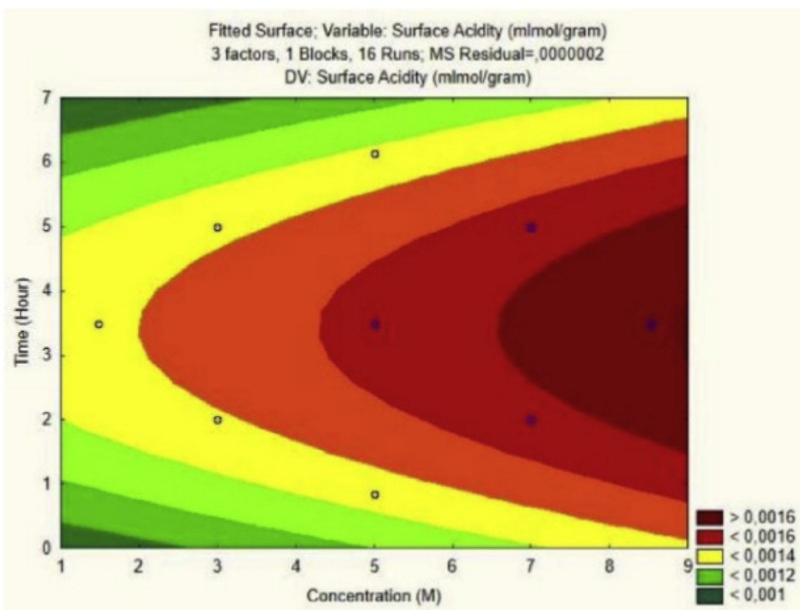

Fig. 6. Contour Graph of Acid Concentration vs. Time of Dealumination.

increase in the Si/Al ratio causes a framework change from zeolites. Changes in the zeolite framework will cause changes in the pores of zeolites which will cause changes in the surface area. Acid treatment will increase the surface area, this is in accordance with the results of research by Boveri et al. (2006) and Chung (2008).

But if the dealumination time is increased, the silica and aluminum compounds will dissolve. From the graph it can be seen, at a time of 6.2 h the acidity is lower than the time of 3.5 h. This is due to the longer time the dealumination of the silica component also dissolves, so the Si content becomes smaller. This causes the value of the Si/Al ratio decreases which results in smaller pore surface area (Widayat, 2010).

Table 2
Analysis of variance.

Variant	Koefisien F-Value DF p-value			
X0	4.0060034			
X1	−1.303380	0.580662	1	0.474931
$X1^2$	−0.835281	0.000005	1	0.998335
X2	0.7620117	0.558880	1	0.482971
$X2^2$	0.7475829	0.697694	1	0.435552
X3	−0.488769	0.004157	1	0.950685
$X3^2$	−0.476371	0.226929	1	0.650662
X1 X2	−0.447700	1.698812	1	0.240220
X1 X3	0.002175	0.000000	1	1.000000
X2 X3	0.000000	0.238895	1	0.642355

3.1. ANOVA test and development of mathematical models

$$Y = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \ldots\ldots \sum_{i<j} \beta_{ij} X_i X_j \qquad (2a)$$

Analysis of Variance (ANOVA) is used to analyze acidity as shown in Table 2. The significance of each factor in Table 2 is tested using the F-value and p-value. A high F-value and a p-value <0.05 indicate that the variable significantly influences the observed response. F-value shows the ratio between MSF (Mean Square of Factor) and MSE (Mean Squares of error). The effects of operating variables can be seen in Table 2.

The objective function of the results of this test is used to determine the optimal value of the concentration of acid (×1), temperature of dealumination (X2) and time of dealumination (X3). The relationship between operating variables to the acidity response can be expressed in a 2nd order polynomial mathematical equation based on the following equation:

$$\begin{aligned} \text{Acidity} = {} & 4.0060034 - 1.30338X_1 - 0.835281X_1^2 \\ & + 0.7620117X_2 + 0.7475829X_2^2 - 0.488769X_3 \\ & - 0.476371X_3^2 - 0.4477X_1X_2 + 0.002175X_1X_3 \end{aligned}$$

The selection of order can be determined by looking at the value of the coefficient of determination, where the model with the highest efficiency of determination is the recommended model. In this study, the coefficient of determination value (R^2) for the 2nd order polynomial mathematical equation has a value of 0.40201.

3.2. Effect of zeolite Y Acidity on Glycerol Monostearate yield

The yield of glycerol monostearate was obtained by analyzing GC-MS where only zeolites Y with the highest acidity were sampled. The 2 samples with the highest acidity values of zeolite Y for GC-MS testing are shown in Table 1.

Fig. 7 showed that in terms of Total Acidity and Surface Acidity have the same phenomenon that is the higher the acidity of zeolites, the higher the Glycerol Monosterate yield obtained. Increased acidity is caused by an increase in the Si/Al ratio and the dissolution of CaO impurities. Increased Si/Al ratio can cause increased activity of the catalyst. Increased catalyst activity is useful in reducing the activation energy of the reaction of a compound. This is what causes the conversion of glycerol to glycerol monostearate to increase. Compared to previous studies it was found that ZSM-5 catalyst has a higher acidity value than zeolite Y so that the yield of Glycerol Monostearate is higher with the use of ZSM-5 than Zeolite Y (Anggoro et al., 2019).

4. Conclusions

This study showed the optimization of the dealuminated Zeolite Y catalyst using statistica 10 software, where the variables used in the dealumination process are acid concentration, dealumination temperature and dealumination time. GC-MS test was carried out on 2 samples zeolite Y catalyst with the highest value of total and surface acidity of zeolite Y which produced 2.18% and 4% yield of Glycerol Monostearate. The two samples showed that the greater the acidity, the GMS yield was also greater. This results showed that the use of Zeolite Y carried out lower of Glycerol Monostearate yield compared to the use of ZSM-5 catalyst in previous study. This is due to the fact that zeolite Y has a low total and surface acidity value so that the catalyst capability to synthesize glycerol to Glycerol Monostearate is also low. Therefore, further research is needed on the use of ZSM-5 catalysts for synthesis of Glycerol Monostearate with different operating conditions.

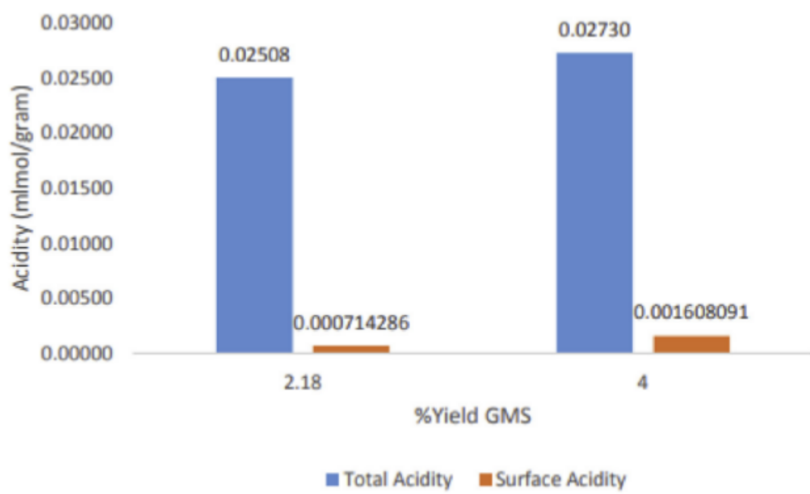

Fig. 7. Effect of Dealuminated Zeolite Y Acidity on Glycerol Monostearate yield.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Didi Dwi Anggoro: Conceptualization, Methodology, Software. **Herawati Oktavianty:** Data curation, Writing - original draft, Writing - review & editing. **Setia Budi Sasongko:** Visualization, Investigation. **Luqman Buchori:** Software, Validation.

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References

Anggoro, D.D., Sasongko, S.B., Buchori, L., Oktavijaya, A., Oktavianty, H., 2019. Dealumination of ZSM-5 as catalyst to convert glycerol to glycerol monostearate. IOP Conf. Ser. Mater. Sci. Eng. 578, 1–8.

Borges, L.D., Macedo, J.L., 2016. Solid – state dealumination of zeolite Y: structural characterization and acidity analysis by calorietric measurements. Microporous andMesoporous Materials 236, 85–93.

Boveri, M., Márquez-A' lvarez, C., Laborde, M.A., Sastre, E., 2006. Steam and acid dealumination of mordenite characterization and influence on the catalytic performance in linear alkylbenzene synthesis. Catal. Today 114, 217–255.

Chung, K.H., 2008. Dealumination of Mordenites with Acetic Acid and Their Catalytic Activity in the Alkylation of Cumene. Microporous Mesoporous Materials 111 (1–3), 544–550. https://doi.org/10.1016/j.micromeso.2007.08.031.

Hamdan, H., 1992. Introduction to Zeolites: Synthesis, Characterization, and Modification. Universiti Malaysia, Malaysia.

Istadi, 2011. Teknologi Katalis Untuk Konversi Energi. Graha Ilmu, Yogyakarta.

Satterfield, C.N., 1991. Heterogeneus Catalysis in Industrial Practice. 2nd. McGraw Hill Book Company, New York.

Sing, R.S., et al., 2019. Statistical optimization of solid-state fermentation for the production of fungal inulinase from apple pomace. Bioresource Technology Reports 9. https://doi.org/10.1016/j.biteb.2019.100364.

Trisunaryanti, W., Triyono, Putranto, A., Purwono, S., 2010. Hydrocracking of waste lubricant oil into liquid fuel fraction using NiO2/NbO2-HCl activated natural zeolite catalyst : effect of contact time and reaction temperatures. In: The 2nd International Conference on Chemical Science. Yogyakarta.

Wang, Y., et al., 2015. Dealumination of Organic Structure-Dirceting Agent (OSDA) Free Beta Zeolite for Enhancing its Catalytic Performance in N-Hexane Cracking, 220. Microporous and Mesoporous Materials.

Widayat, et al., 2010. Pengaruh Waktu Dealuminasi Dan Jenis Sumber Zeolit Alam Terhadap Kinerja H-Zeolit Untuk Proses Dehidrasi Etanol. Reaktor 51–57. https://doi.org/10.14710/reaktor.13.1.51-57.

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