



## Degradation of Glycerol to Ethanol Using x/Y Zeolite Catalyst (x=H, Ni, Mo, NiMo) by the Sonication Method

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**Abstract:** The performance of the Y Zeolite (YZ) catalyst can be improved by metal impregnation. The purposes of this study were to determine the characteristics and effectiveness of the H/YZ, Ni/YZ, Mo/YZ, and NiMo/YZ catalyst, and the effect of the time of sonication on the glycerol degradation reaction to ethanol using the sonication method. The study began with the preparation and activation of YZ using NH<sub>4</sub>Cl 1M solution. The activated YZ was then impregnated with nickel metal, molybdenum metal, and their mixtures. Catalyst characterization using XRD, XRF, acidity test, and surface area test. As a result, (a) nickel and molybdenum metals successfully impregnated into YZ, (b) H/YZ, Ni/YZ, Mo/YZ (Predictable), and NiMo/YZ (Predictable) catalysts had a crystalline phase, (c) the highest catalyst acidity value was NiMo/YZ of 1.0810 mmol/gram, (d) the largest catalyst surface area was H/YZ of 110.321 m<sup>2</sup>/g. The NiMo/YZ catalyst is more effective than the H/YZ, Ni/YZ, and NiMo/YZ, because it produced the highest %yield ethanol both at 4 hours (4.49%) and 6 hours (27.33%). The time of sonication greatly influenced the percentage of ethanol yield in the glycerol degradation reaction. The longer the time of sonication, the higher % the yield of ethanol produced.

**Keywords:** Glycerol, ethanol, impregnation, sonication, Y Zeolite.

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### 1. INTRODUCTION

The demand for fossil fuels increased economic growth and population in the world. In recent years, fossil fuels not balanced with petroleum reserves. Therefore, the government is currently promoting the use of biodiesel as an alternative fuel to replace fossil fuels (1). Increasing biodiesel production will be a big problem because biodiesel synthesis produces by-products (glycerol) by 10% of the weight of biodiesel (2). As biodiesel production increases, the amount of by-product (glycerol) also increases.

So far, glycerol waste from the biodiesel industry has become a useless material because of impurities and its complex purification process, so the amount is abundant. On the other hand, The utilization also resulted in a decrease in the selling price of glycerol from \$ 0.33 to \$ 0.04 per kilogram (3). The availability of glycerol could be a support for the

development and transformation of glycerol into a product. Previous study, the degradation of glycerol was carried out under supercritical water conditions at 450 °C, 300 bar, and 30 minutes to produce methanol (4). The degradation of glycerol by hydrothermal process was carried out at 150 °C, 50 bar, and a 2 hours assisted by microwaves to produce ethanol 7.4% (5). In addition, the degradation of glycerol assisted by ultrasonic waves using a ZAA catalyst was produce ethanol of 3.7% (6). Several studies showed that ethanol can be obtained through glycerol degradation, but it still requires high temperature and pressure that is less safe. Therefore, one potential method to the degradation of glycerol is sonication method (7).

The sonication method is a method using ultrasonic waves. The use of ultrasonic waves can accelerate reaction times and increase product yield (8). Furthermore, an increasing sonication time can increase degradation yields (9). Besides using the

sonication method, the degradation reaction also need a heterogeneous catalyst, because it is easily separated from the reaction mixture, has a large surface area, is easily regenerated, and has a high acidity level (10). One type of heterogeneous catalyst is the metal-impregnated catalyst. Y Zeolite is one type of synthetic zeolite that is widely developed in improving catalyst performance (11).

Y zeolite is a hydrated aluminosilicate mineral containing alkali or alkaline earth cations that can be exchanged with other cations, and can be modified to increase its activity and selectivity (12). The Y zeolite has several advantages including regular crystal structure, uniform pore size, large surface area, and thermal stability reaching 793 °C (13) i. The catalyst activity of the Y Zeolite can be increased by purging the metal into the zeolite pores. The catalyst is synthesized by by impregnation metal into the zeolite producing the zeolite as a bifunctional catalyst (11). Metals that can be impregnated in zeolites are usually included in transition metals such as Pt, Pd, Ni, Mo, and others (14).

In this study, Ni and Mo metals are potentially used because they have unpaired electrons in d orbitals which can provide Lewis acid sites capable of adsorbing reactants on the catalyst surface. Ni and Mo metals have good catalytic properties (15), so they can be used as active catalysts. Cahyono has synthesized Ni/ZAA as a catalyst in the esof degradation of glycerol to ethanol (16). Furthermore, synthesized Mo/ZAA was used as a catalyst in the es of glycerol to ethanol (17). ZAA was known as a natural zeolite that has impurities. So, industrial zeolite like Y zeolite is a potential alternative to replace ZAA as the support material. There is no reported study of Y Zeolite-supported Ni and Mo metals. Other studies report the success of NiMo supported on titania (18), NiMo/Al<sub>2</sub>O<sub>3</sub>-HY, and NiMo/Beta (19).

On the basis the above research, it can be seen that the Ni and Mo metals have been successfully impregnated into the natural zeolite type as catalyst in the degradation of glycerol to ethanol, but they have never been impregnated into the Y zeolite. Therefore, the effectiveness of the degradation of the glycerol using a synthesized catalyst under sonication method is very interesting to study. he purposes of this study are (1) to determine the characteristics of Y Zeolite which vehave been modified with Ni, Mo and their mixtures, (2) to determine the eeffectiveness of catalyst of H/YZ, Ni/YZ, Mo/YZ, and NiMo/YZ in the degradation of glycerol to ethanol by sonication method, (3) to analyze the effect of sonication time on the eeffectiveness of the H/YZ, Ni/YZ, Mo/YZ and NiMo/YZ catalyst on the degradation of glycerol to ethanol.

## 2. EXPERIMENTAL SECTION

The instruments used include: Mortar and pestle, 60 Mesh softene, glass and ceramic tools, analytical balance (Durascale), spatula, shaker, oven, hot plate stirrer, water bath shaker, desiccator, furnace

(Thermolyne), Spectronic-20 (Ganesys 20), Ultrasonic devices (Branson 1510), X-Ray Diffraction (XRD) (PANalytical X'Pert PRO), X-Ray Fluorescence (XRF) (PANalytical Minipal 4) and Gas Chromatography (GC) (HP 5890). The materials used in this study include Y Zeolite, NH<sub>4</sub>Cl 1 M solution, 100 ppm blue methylene solution, ammonia p.a, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O salt, (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O salt, technical glycerol, distilled water, and aqua-demineralization.

### 2.1. Preparation and Activation of Y Zeolite with NH<sub>4</sub>Cl Solution 1 M

Y Zeolite was mashed and sieved with 60 Mesh sieve sieve. The Y Zeolite was dried at 100 °C for 2 hours. The Y Zeolite was activated by mixing 10 grams of the Y Zeolite with 100 mL NH<sub>4</sub>Cl 1 M. The precipitate was filtered and washed with distilled water to a neutral pH. The precipitate was then dried at a of 120 °C for 6 hours and calcined at 500 °C for 2 hours.

### 2.2. Impregnation of Active Y Zeolite with Ni, Mo, Ni-Mo Metals

Ni/YZ: 4.75 grams of the Y Zeolite mixed with nickel nitrate solution (1.2380 grams of nickel nitrate salt in 100 mL of water). The mixture was stirred using a water bath shaker for 24 hours at 65 °C with 130 rpm. The precipitate was filtered and washed with distilled water to a neutral pH. The precipitate was then dried at 120 °C for 6 hours and calcined at 500 °C for 2 hours. Mo/YZ: the same procedure as Ni/YZ, with a specific solution of ammonium heptamolibdat (0.46 grams of ammonium heptamolibdate salt in 100 mL of water). NiMo/YZ was synthesized by co-impregnation, i.e.: a) the same procedure of Mo/YZ synthesis with ½ grams of ammonium heptamolibdate salt, and it continued with b) the same procedure of Ni/YZ synthesis with ½ grams of nickel nitrate salt.

### 2.3. Characterization of The Catalysts

The synthesized catalysts were characterized by XRD and XRF. Also, the physical characterization is as follows:

#### 2.3.1. The analysis of acidity level

0.300 g of the catalyst of was put into a desiccator which was saturated with ammonia vapor. The catalyst was left in contact with ammonia vapor for 24 hours. The catalyst was carefully weighed to a constant weight.

#### 2.3.2. The analysis of the catalyst surface area

The analysis of the Surface Area Analysis was carried out using the Langmuir Isotherm Method: (1) maximum wavelength ( $\lambda$  max), 10 ppm methylene blue was absorbed at a wavelength of 600-700 nm using Spectronic-20, and (2) adsorption of standard solutions, standard solutions were prepared by dilution of standard 100 ppm methylene blue with variations in concentration of 1, 2, 3 and 4 ppm. Each solution was measured absorbance at the maximum wavelength ( $\lambda$  max) (3) surface area of catalysts: 0.01 gram of the catalyst was mixed with 20 mL of 18 ppm methylene blue. The mixture was then stirred using a shaker at 150 rpm for 30 minutes. The

catalyst precipitate was filtered. The filtrate was then analyzed at the maximum wavelength.

### 2.5. Glycerol Degradation

5 mL of Glycerol was mixed with 20 mL of distilled water in Erlenmeyer. The catalyst about 5% of the mass of glycerol was put into the Erlenmeyer. The mixture was sonicated with variations in time of 2, 4, and 6 hours with 60 °C at 42 kHz. The filtrate was then analyzed using GC.

## 3. RESULTS AND DISCUSSION

### 3.1. Preparation and Activation of Y Zeolite

The Y Zeolite sample used in this study has a white solid with a coarse grain texture. Therefore, the Y Zeolite needs to be prepared to obtain a smoother texture with a larger surface area. Generally, the Y Zeolite is composed of two components, namely the main metal component and the impurity metal component. The presence of these impurity metal components can cover the active sites of the Y Zeolite. The Y Zeolite needs to be activated to eliminate impurities and evaporate the water trapped in the pores of zeolite (20).

The Y Zeolite can be in two ways, i.e: physical and chemical activation. Physical activation is referred to grinding the Y Zeolite to get a smaller particle size. The refined Y Zeolite is then sieved using a 60 Mesh sieve and dried at 100 °C for 2 hours intending to increase the surface area of the Y Zeolite Y and eliminate increase the surface area of the Y Zeolite Y and eliminate increase surface area of the Y Zeolite Y and eliminate the water content trapped in the Y Zeolite framework. Chemical activation is carried out by mixing the Y Zeolite with  $\text{NH}_4\text{Cl}$  solution 1 M. Chemical activation occurs through cation exchange reactions. The  $\text{NH}_4^+$  cation is a cation that is easily absorbed by zeolite minerals because it has a high absorption selectivity for zeolites in the order  $\text{NH}_4^+ > \text{Pb} > \text{Ag} > \text{Ba} > \text{Na} > \text{Sr}$  (21). This cation exchange is based on equilibrium reactions and depends on the magnitude of the concentration of the solution, where the the concentration of  $\text{NH}_4\text{Cl}$  solution, the more  $\text{Na}^+$  cations can be replaced with  $\text{NH}_4^+$  cations (22). Based on the activation process, an H/YZ

catalyst was obtained in the form of a white solid with a fine powder texture. This H/YZ is an active Y Zeolite and can be used as a catalyst in the degradation of glycerol to ethanol.

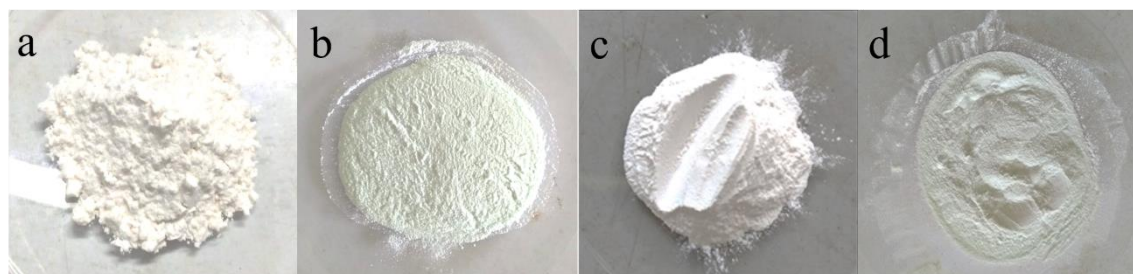
### 3.2. Impregnation of Y Zeolite with Ni, Mo Metals and its Mixtures

In this study, metals impregnated into the pores of the Y Zeolite are Ni, Mo, and mixture. This impregnation aims to distribute Ni and Mo metals evenly into the pores or surfaces of the Y Zeolite, where they can act as active catalyst sites. Ni/YZ and Mo/YZ catalysts were prepared by wet impregnation. The metal impregnation process, a cation exchange reaction between  $\text{H}^+$  ions with  $\text{Ni}^{2+}$  ions and  $\text{Mo}^{6+}$  ions. Chemically, cation exchange in the impregnation method is caused by the weak interaction of dipole ions between the Y Zeolite and  $\text{H}^+$ , so that it is easily replaced by  $\text{Ni}^{2+}$  and  $\text{Mo}^{6+}$  cations. Generally, cation exchange can be affected by the amount of ion charge. The greater the charge of ions, the easier it is to replace the position of other ions in a molecule.  $\text{Ni}^{2+}$  and  $\text{Mo}^{6+}$  ions have a higher charge than  $\text{H}^+$  ions, consequently,  $\text{Ni}^{2+}$  and  $\text{Mo}^{6+}$  ions can easily replace  $\text{H}^+$  positions of the Y Zeolite through cation exchange.

The coimpregnation method was then carried out. First, H/YZ is mixed with  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  solution to impregnate Mo metal in the Y Zeolite. After forming Mo/YZ, the  $\text{Ni}(\text{NO}_3)_2$  solution is mixed with Ni solution for Ni metal impregnation. Zeolites that have been impregnated with Ni and Mo metals have different colors. Ni/YZ and NiMo/YZ catalysts were greenish-white powders while Mo/YZ catalysts were white powders. Physically, greenish-white Ni/YZ and NiMo/YZ indicated that the nickel metal impregnated into the Y Zeolite. The impregnated Y Zeolite was used as a catalyst in the degradation of glycerol. The catalysts formed up to this process are H/YZ, Ni/YZ, Mo/YZ, and NiMo/YZ shown in Figure 1.

### 3.3. Characterization of Catalysts

The results of the XRF on the initial Zeolites Y, H/YZ, Ni/YZ, Mo/YZ, and NiMo/YZ are shown in Table 1.



**Figure 1:** (a) H/Zeolite Y, (b) Ni/Zeolite Y, (c) Mo/Zeolite, (d) NiMo/YZ

**Table 1:** The results of the XRF of YZ, H/YZ, Ni/YZ, Mo/YZ dan NiMo/YZ.

Element	Content (%)				
	Y Zeolite	H/YZ	Ni/YZ	Mo/YZ	NiMo/YZ
Al	30.1	30.9	27.3	31.0	26
Si	64.3	64.7	44.6	64.9	41.9
P	1.7	1.6	0.96	1.4	0.91
K	0.4	-	-	-	-
Ca	2.0	1.5	0.75	1.4	0.83
Cr	0.15	0.12	0.078	0.12	0.092
Sc	-	-	0.01	-	-
Sr	-	0.01	-	-	-
Fe	0.82	1.03	0.48	0.78	0.49
Cu	0.16	0.16	-	0.14	-
Yb	0.2	-	-	0.2	-
Ni	0.16	-	25.8	-	28.2
Mo	-	-	-	Not detected	Not detected

Table 1 shows that the Y Zeolite containm Si of 64.3% and Al of 30.1%, so it can be calculated the mole ratio of Si/Al on the Y Zeolite of 2.2. This was consistent with a literature by that the mole ratio owned by the Y Zeolite ranges from 1.5 – 3 (23), so it can be said that the sample of zeolite used in this study was the Y Zeolite. Besides the Si and Al content, the XRF analysis results indicate the presence of other components which are impurities. The presence of these impurities will reduce the activity of the Y Zeolite as both an adsorbent and catalyst. Therefore activation is needed using  $\text{NH}_4\text{Cl}$  solution to remove these metal impurities.

Table 1 shows that the levels of impurities have decreased significantly and that even some impurities have disappeared after activation. Some impurities still stick to the Y Zeolite, but the levels are much lower than before the activation process. After activation, the Y Zeolite is impregnated with Ni, Mo metal and their mixture to increase the active site as a catalyst. The success of the impregnation of Ni and Mo metals can be seen in Table 1. On the basis the XRF test, it can be seen that Ni metal was successfully impregnated into the Y Zeolite because it was successfully detected by XRF instruments, while Mo metal was not detected by XRF. This is

because the level of Mo impregnated into the Y Zeolite was too small at 5% in Mo/YZ and 2.5% in NiMo/YZ. Due to the undetectability of Mo metal, further analysis is needed to determine the presence of molybdenum in the Y Zeolite using XRD analysis.

XRD analysis was carried out on the Y Zeolite samples before and after being activated and impregnated with Ni, Mo metals, and their mixtures. The Y Zeolite sample can be analyzed by matching the  $2\theta$  data and d-spacing between the synthesized Y Zeolite and the standard Y Zeolite in JCPDS No. 38-0240. Based on the comparison of  $2\theta$  and d-spacing between the Y Zeolite and the standard Y Zeolite, it can be seen that there was a peak of  $2\theta$  are  $14,01^\circ$ ,  $19,86^\circ$ ,  $22,20^\circ$ ,  $24,38^\circ$ ,  $28,25^\circ$ ,  $31,65^\circ$ ,  $34,77^\circ$ ,  $37,67^\circ$ ,  $42,97^\circ$ ,  $45,45^\circ$ ,  $47,74^\circ$  which similar to the peak  $2\theta$  the Y Zeolite standard in JCPDS No. 38-0240 (24). Based on the similarity of the 11 data, it can be interpreted that the zeolite sample used in this study was correctly the Y Zeolite. After it was proven that the sample used was the Y Zeolite, then the Y Zeolite was activated and impregnated with Ni, Mo metals and their mixture to enhance its active side as a catalyst. The XRD analysis results of the H/YZ, Ni/YZ, Mo/YZ, and NiMo/YZ catalysts are shown in Figure 2.

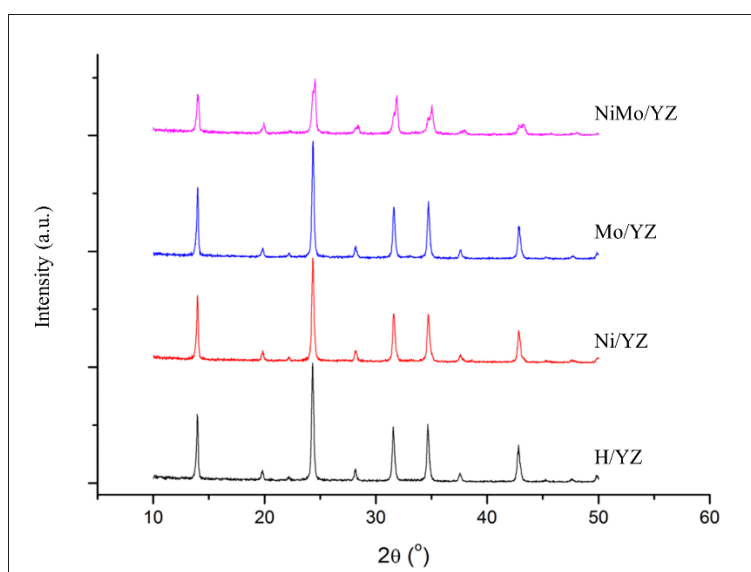
**Figure 2:** Diffractogram of H/YZ, Ni/YZ, Mo/YZ and NiMo/YZ.

Figure 2 showed that the catalyst formed has a crystalline phase which was indicated by the appearance of sharp peaks. However, the NiMo/YZ chromatogram slightly experienced a broad (decreased intensity). The decrease in catalyst intensity can occur due to the impregnation of two metals in zeolites (25). Based on Figure 2, the four catalysts have the same diffractogram pattern (not significantly different) so it can be said that the

presence of activation and impregnation does not damage the structure of the Y Zeolite. The successful impregnation of Ni and Mo metals can be seen based on the match of  $2\theta$  data from the analysis with  $2\theta$  data of NiO standard on JCPDS No. 73-1519 and  $2\theta$  data of MoO<sub>3</sub> standard in JCPDS No. 05-0508. The comparison of  $2\theta$  data between Ni/YZ and Mo/YZ with  $2\theta$  NiO and MoO<sub>3</sub> is shown in Table 2.

**Table 2:**  $2\theta$  Ni/YZ, Mo/YZ, and NiMo/YZ toward NiO and MoO<sub>3</sub> standards.

Ni/YZ $2\theta$	Mo/YZ $2\theta$	NiMo/YZ $2\theta$	NiO Standard $2\theta$	MoO <sub>3</sub> Standard $2\theta$
13.98	13.98	14.11	-	-
19.83	19.82	19.93	-	-
22.20	22.18	24.32	-	-
24.39	24.35	24.53	-	-
28.19	28.18	28.40	-	-
31.60	31.61	31.67	-	-
34.70	34.71	35.02	-	34.30
37.58	37.59	37.93	37.34	-
42.85	42.86	42.84	43.38	42.00
45.40	45.38	43.25	-	-
47.62	47.71	48.02	-	-
49.98	49.90	-	-	-

Based on Table 2, showed that the Ni and Mo metals have been successfully impregnated into the Y Zeolite was evidenced by the appearance of peaks of 37.58° and 42.85° on Ni/YZ which indicated the presence of NiO. The appearance of peaks of 34.71° and 42.84° on Mo/YZ did not surely indicate the presence of MoO<sub>3</sub>. In co-impregnation, the mixture of Ni and Mo metals was not surely impregnated into the Y Zeolite. This was evidenced by the appearance of peaks of 37.93° and 42.84° which indicated the presence of NiO while the peaks of 35.02° and 42.84° indicated the presence of MoO<sub>3</sub> in the Y Zeolites. In this study, the term Mo/YZ and NiMo/YZ is considered predictable material, because no specific peaks of Molybdenum species appeared.

### 3.5. Acidity Level and Surface Area of The Catalyst on Glycerol Degradation

The determination of the acidity of the catalyst is based on the adsorption of ammonia gas by the gravimetric method. The acidity of the catalyst is the amount of base mmol adsorbed per gram of catalyst. The amount of base mmol adsorbed is equivalent to the amount of acid mmol in the Y Zeolite.

Table 3 shows that the acidity level of the Y Zeolite after being impregnated with Ni and Mo metals has increased. The presence of metal impregnation can increase the total acidity of the catalyst (25) because these metals can form Lewis acidic sites. The acidity level of the catalyst is related to the Brønsted and Lewis acid sites. The number of Brønsted and Lewis acid groups present on the surface is the total amount of acid contained in the catalyst. Based on the catalyst, the acidity level from highest to lowest respectively is NiMo/YZ > Ni/YZ > Mo/YZ > H/YZ. NiMo/YZ catalyst has the highest level of acidity because two metals form the Lewis acid site, so more

free-electron pairs from the ammonia base can be adsorbed by the catalyst.

The surface area of the catalyst can be determined by adsorbing methylene blue. This adsorption is a type of Langmuir isotherm, where only a monolayer layer will be formed at the time of maximum adsorption on the surface of the catalyst (26). Based on Table 3, the surface area of the catalyst before and after impregnation with Ni and Mo metals has decreased. The order of the catalyst surface area from largest to smallest is H/YZ > Ni/YZ > Mo/YZ > NiMo/YZ. The surface area of a catalyst will decrease with the presence of metal because these metals can cover a single layer of the Y Zeolite (27).

### 3.6. Degradation of Glycerol to Ethanol

In this study, the degradation of glycerol was carried out assisted by ultrasonic waves at a time variation of 2, 4, and 6 hours at 60 °C with the desired ethanol product. Glycerol degradation was carried out with glycerol:water ratio of 1:4.

The process of degradation will break the OH bond in glycerol to form a 2-propene-2,3 diol compound. Furthermore, the compound 2-propene-2,3 diol undergoes tautomerization to form acetol where, under the influence of ultrasonic waves, acetol will break apart to form methanol and ethanone radicals. Ethanone radicals can react again with H radicals obtained from the breakdown of water molecules to form acetaldehyde, ethanol, and 2,3-butanediol compounds. The advantage of using ultrasonic waves is that the degradation process will be faster and more products will be produced with a high %yield (7). After the filtrate was obtained, it was then tested using GC to determine the ethanol content. The results of the degradation product analysis are shown in Table 3.

**Table 3:** Physical characterization of catalyst acidity.

Catalyst	Acidity (mmol/gram)	Surface Area (m <sup>2</sup> /g)	Ethanol Yield by GC (%)		
			2 hours	4 hours	6 hours
H/YZ	0.5120	110.321	0	1.99	26.74
Ni/YZ	0.7755	105.701	0	2.25	25.87
Mo/YZ	0.5361	105.235	0	1.66	20.08
NiMo/YZ	1.0810	104.874	0	4.49	27.33

Table 3 showed that the % yield of ethanol increased with the time duration of sonication. Based on GC results, it can be seen that the biggest %yield was formed within 6 hours. The longer the reaction time, the longer the contact between ultrasonic waves and glycerol (28), so the degradation yield also increases. GC results showed that the highest catalytic activity in the glycerol degradation was the NiMo/YZ catalyst. The catalytic activity correlated with the highest acidity and the lowest surface area. This proves that the impregnation of two metals can increase zeolite activity as a catalyst, so the %yield produced is also greater. Without sonication and catalyst in the degradation of glycerol, the %yield of ethanol will be lower (7). Therefore, the order of ethanol product at 6 hours reaction was: NiMo/YZ > H/YZ > Ni/YZ > Mo/YZ. Also, the order of ethanol product at 4 hours reaction was: NiMo/YZ > Ni/YZ > H/YZ > Mo/YZ.

#### 4. CONCLUSION

The catalysts formed in this study were H/YZ, Ni/YZ, Mo/YZ, and NiMo/YZ. The results of the analysis of catalyst characteristics include: (a) Ni and Mo metals were successfully impregnated into the Y Zeolite as indicated by the XRF and XRD results, (b) catalysts H/YZ, Ni/YZ, Mo/YZ, and NiMo/YZ have crystalline phase, (c) the acidity levels of catalyst H/YZ, Ni/YZ, Mo/YZ, and NiMo/YZ were 0.5120, 0.7754, 0.5362 and 1.0810 mmol/gram, (d) the surface area of catalyst H/YZ, Ni/YZ, Mo/YZ, and NiMo/YZ were 110.321, 105.701, 105.235 and 104.874 m<sup>2</sup>/gram, respectively. Based on the research, it can be seen that the NiMo/YZ catalyst had the highest catalytic activity because it produced the highest %yield of ethanol both at 4 hours (4.49%) and 6 hours (27.33%). Through the degradation process with time variations, it can be seen that the longer the time sonication, the higher % the yield of ethanol produced. The further study will evaluate the metal leaching during the catalytic reaction, and the decomposition product (by-product) of glycerol after the catalytic reaction.

#### 5. CONFLICT OF INTEREST

The authors declare no conflict of interest.

#### 6. ACKNOWLEDGEMENTS

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