

The Use of Natural Zeolite as A Catalyst for Esterification Reaction Between Glycerol and Oleic Acid

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Abstract

Natural zeolite in Indonesia generally divided into 2 types, which are mordenite and clinoptilolite. As far the use of zeolites is very limited. This experiment tries to use both types of natural zeolites to find out its work. The purpose of this experiment is testing the performance of mordenite natural zeolite from Bayah-Indonesia and clinoptilolite from Lampung- Indonesia in the esterification reaction between glycerol and oleic acid integrated by several variable that affect the reaction. The experiment will be done by using three-neck rounded flask batch reactor. The result showed that modernite zeolite has a better performance compared to clinoptilolite zeolite. To get the oleic acid conversion of 70%, clinoptilolite zeolite needs 4% catalyst of glycerol weight and reactant ratio of 6:1 mole of glycerol/mole of oleic acid, Meanwhile the mordenite zeolite only needs 2% catalyst of glycerol weight with reactant ratio of 4:1 mole of glycerol/mole of oleic acid.

Keywords: *natural zeolite; glycerol; reaction; diffusion*

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INTRODUCTION

Indonesia is one of the country that has a lot islands and surrounded by many volcano, so it has abundance quantity of zeolite. Zeolite estimated made by the volcanic dust of volcano that interacted with the water and it turned into sediments which ultimately form like rocks (Setyawan, 2002). Based on Kusdarto (2008), Indonesia has 44,490,160 tons of zeolites, but by the result of characteristic test that has been done by the experimenters in reaction process or adsorption, natural zeolites in Indonesia are most likely mordenite and clinoptilolite (Kartika and Widyaningsih, 2012). Both, have different silica and aluminum ratio, which

are for modernite 4.3-5.3 and for clinoptilolite 4.0-5.1 (Zamroni and Las, 2002). Mordenite natural zeolites and clinoptilolite structurally have difference. This condition definitely will has an impact to the performance either as a catalyst or an adsorbent. Glycerol is an alcohol with a complex chain, so most of the time it called polyalcohol. From the size of the molecules, glycerol has 6.657 Å of molecule size (Root, 1998) and oleic acid has 20 Å of molecule size (Brohl et al., 2015). With that big of the size, it is difficult enough for glycerol and oleic acid to enter the active site that located inside of the zeolite if the zeolite isn't modified. The small size of the zeolite's pore and the

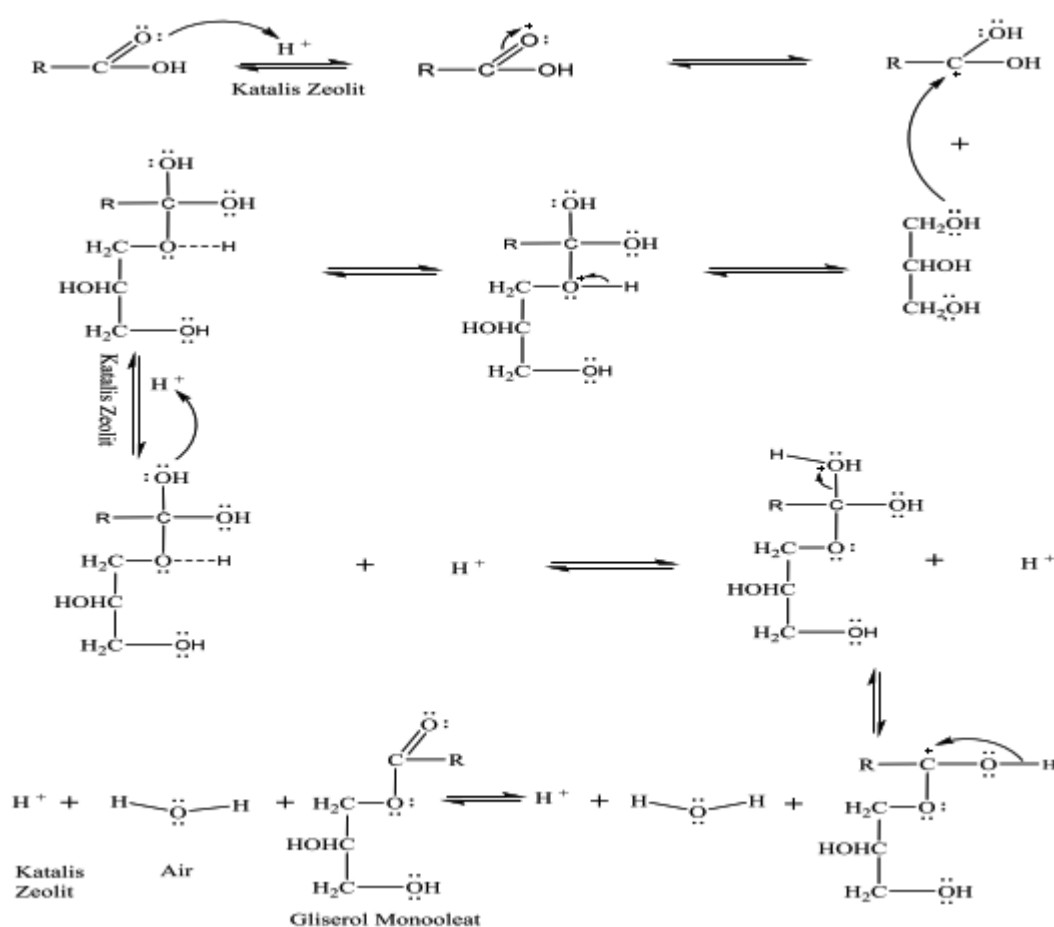


Figure 1. Reaction mechanism between glycerol and oleic acid

surface area of the natural zeolite is caused by the impurities (Nadiyah, 2018) that clog the pores of the zeolite that will inhibit the way of the substance to get into the active site. The result of the trial using the natural zeolite, whether it was a chemical reaction or adsorption shows that the percentage of reactant conversion and adsorption from non-modified zeolites are lower than the modified zeolite by acid (Subariyah et al, 2013). The observation result of isomerization reaction of xylene shows that the conversion of modified natural zeolite by activated was 44%, while without modification is only 4.5% (Arcoya, et al, 1993). At the other hand, which is the adsorption process with non-modified zeolite result 84.7% of conversion, while with modified zeolite result 90.42% of conversion (Subariyah et al, 2013). Based on literature review, so to make the reaction goes well in this experiment before using the natural zeolite, they modified the zeolite with acid, so the impurities goes off and the surface area will increase. Basically, the esterification reaction process between glycerol and oleic acid with zeolite catalyst that has been modified with acid provided in figure 1 (Setiadi et al, 2016).

In an effort to investigate the natural zeolite type of modernite and clinoptilolite, so this experiment use the natural zeolite from Lampung (clinoptilolite) and natural zeolite from bayah-Banten (modernite). The

purpose of this experiment was to test the performance of natural zeolite modernite-Bayah and clinoptilolite-Lampung in the esterification reaction between glycerol and oleic acid by integrated with several variable that has an effect to the chemical reaction. With a hope that one of the two natural zeolites can be used as an effective and efficient catalyst, so the natural resources in Indonesia, specifically natural zeolites will be used globally.

EXPERIMENTAL SECTION

Raw Materials

Chemicals

The main chemicals that used are glycerol (technical grade) produced by PT. WILMAR NABATI INDONESIA, before use it, it has been evaporated at $80\text{ }^{\circ}\text{C}$ so the purity increasing, and than analyzed by iodometric titration, with a result 87% of purity. Oleic acid (technical grade) produced by PT. TnT Chemical with 95% of purity.

Catalysts

Clinoptilolite zeolite from Lampung-Indonesia (ZAL) and modernite from Bayah-Indonesia (ZAB,) which are as catalysts. Both of them modified by strong acid. The zeolite has been crushed before, and has been screened to get the right size (60-60 mesh),

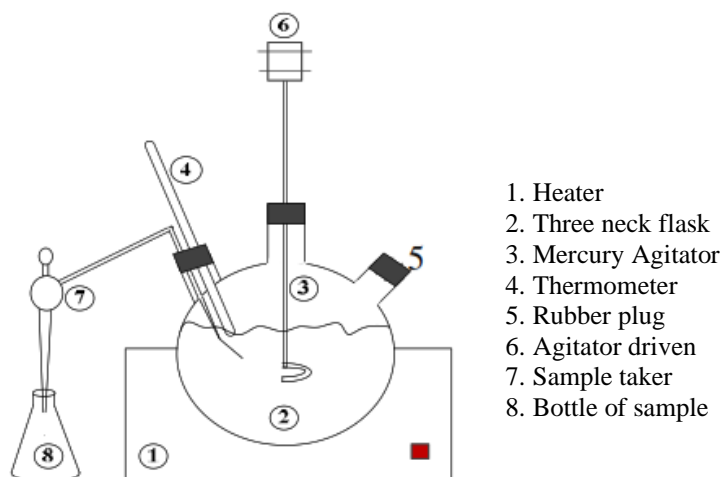


Figure 2. Experimental set up on esterification reaction between glycerol and oleic acid

Then it modified by strong acid solution which is chloride acid. After it modified by acid, then it washed by aquades for 4 times to make sure that the impurities and acid has get off from natural zeolite. The next stage is drying, put it in the oven at 110 °C for 2 hours (Nuryoto et al, 2017).

Experiments Apparatus

The esterification reaction experiments were conducted in 500 cm³ three neck-glass flask. A schematic of the experimental set up is described in figure 2.

Experiments Procedures

Reaction with ZAL as early reaction

Glycerol with the determined volume by refer to mole of reactants (4:1- 6:1 mole of glycerol/mole of oleic acid) added to the reactor, then heated until 160-180 °C. In separate way, oleic acid with determined volume heated until certain temperature in chemical glass, afterward added the oleic acid and glycerol to the reactor at once. The reactor heated to 160-180°C which is the temperature of the reaction, while the agitator is running, when the the reaction temperature reached, take the sample (Ao) to be analyzed for the oleic acid (Ao) by using acid-base titration method with 0.02 N NaOH. The catalyst added, after 90 minutes, the last sample was taken to be analyzed the purity of the last oleic acid (As). The trial repeated for all the variation. To know the tendency of the reaction for the reactant ratio variation, sample was taken every 30 minuets for 90 minutes

Reaction for the ZAB

The reaction that happen using ZAB is similar with the ZAL. The use of ZAB was just a comparassion, and to know which zeolite gives the better work as catalyst. The operation condition that has been done was a little different, fixed variable was just the reaction temperature and the speed of agitation. The changing variable were the reactant ratio and the

concentration of catalyst that needed to obtain the same conversion value of oleic acid between ZAL and ZAB.

RESULTS AND DISCUSSION

Effect of Agitation

Observation about the impact of 600 and 700 rpm agitation. Throughout the increase of agitation speed, there is the increase of oleic acid conversion which quite significant (see figure 3), which increase from 54,55% to 73,65% (the difference is about 19,11%). The increase of oleic acid conversion describe that the increase of the agitation speed has an impact on how smaller the external diffusion resistances of the catalyst – liquid (reactant) interfaces. Based on Ficks law, that condition impact on how faster the reactant mass transfer from bulk to the outside surface of catalyst (Bird et al., 2000; Fogler, 2006). While the mass transfer happens to the outside surface of catalyst increasing, the effect will be an increase of reaction rate, and the conversion of oleic acid increasing as well. On chemical reaction, mostly the speed of agitation to reduce external defense from one reaction to another are different, because it depends on the viscosity of the solution and reaction temperature itself.

As an example, on the esterification reaction between acetate acid and butanol, with 360 rpm agitation speed is enough to reduce the external resistances (Gangadwala et al, 2003), for electrolysis and benzyl acetate hydrolysis is about 700 rpm of agitation speed (Ali and Merchant, 2006), and on reaction between glycerol and solketal is about 600 rpm (Nuryoto et al., 2017). To solve viscosity issue actually can be solved by increasing the reaction temperature. On the different reaction temperature and with the same reactant, will result different viscosity. The higher of the reaction temperature, the viscosity of the solution is smaller. That also can decrease the external mass transfer resistances, and will increase the reactant mass transfer from bulk to the outside surface of catalyst (Bird et al., 2000). But the increasing the reaction

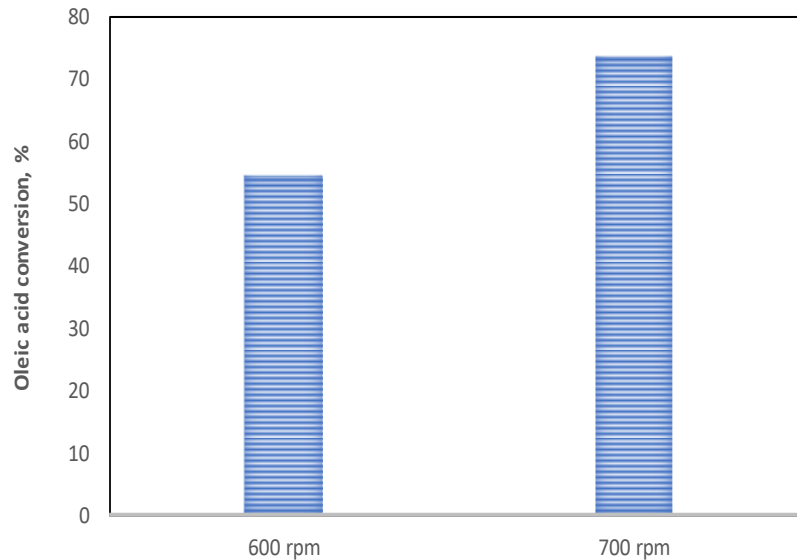


Figure 3. Effect of agitation speed on reactant ratio of 6:1 mole of glycerol/mole of oleic acid, reaction temperature of 180 °C, reaction time of 90 minutes, and ZAL catalyst size of 60 mesh

temperature is too high, on certain condition can caused the more possibility that the side product produced. So, it takes a really careful way. Based on the experiment that has been done by setiadi et al. (2006), 700 rpm of agitation speed is an optimum agitation speed to reduce the external resistances of reaction between glycerol and oleic acid. It is proven by the experiment of Setiadi et. al. (2016), when the agitation speed increase above 700 rpm, the value of oleic acid conversion result the same value which about 80%. The observation of agitation speed is really needed to get the optimum agitation speed, because if the speed is too high, not only affecting the process operational cost, it will give a negative effect to the process of the reaction. The catalyst will go with the fluid flow and the stagnation occurs (Fogler, 2006), so the turbulence and the reactant mass transfer to the outside surface of catalyst will get slower.

Effect of Reaction Temperatures

Technically, the reaction will happen if the minimum energy that needed to disconnect the molecular bond that the reaction has is reached. This statement is so often being called as activation energy. Arrhenius has formulated that the higher the reaction temperature, so the faster the reaction happen (Fogler, 2006). From Figure 4, it can see that on 160 to 170 °C, the conversion of oleic acid increasing from 54,55 to 73,52% (increase 18,97%). But, when temperature increased more, the conversion of oleic acid is only 73,65% (increase 0,14% from the conversion at 170 °C which 73,52%).

The result of this experiment, especially on the reaction temperature of 170 to 180 °C isn't quite significant the difference of the increase. So, it might be a possibility that it caused by internal mass transfer, which the transfer of the mass from the reactant from

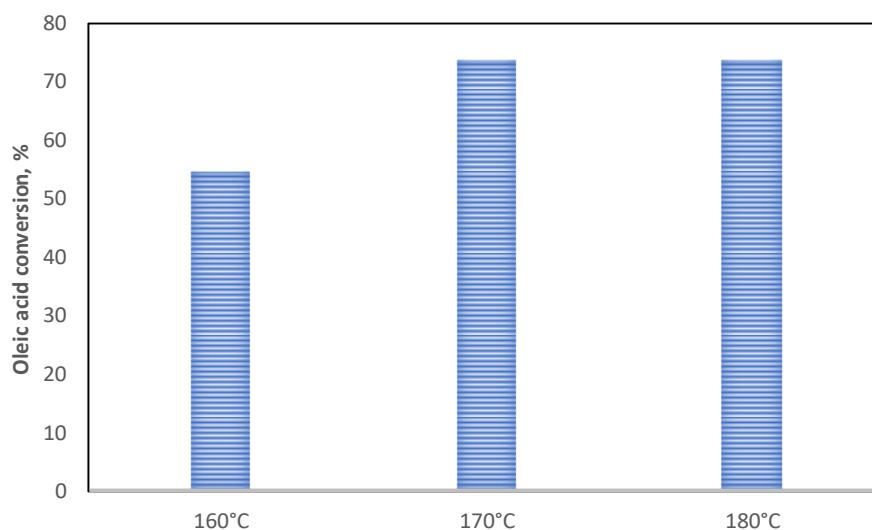


Figure 4. Effect of reaction temperatures on reactant ratio of 6:1 mole of glycerol/mole of oleic acid, agitation speed of 700 rpm, reaction time of 90 minutes, and ZAL catalyst size of 60 mesh

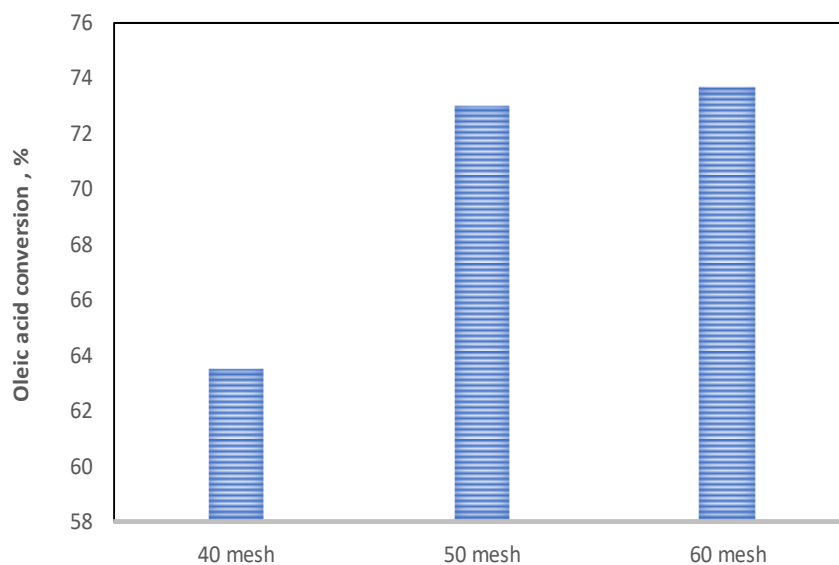


Figure 5. Effect of Catalyst size on reactant ratio of 6:1 mole of glycerol/mole of oleic acid, agitation speed of 700 rpm, reaction time of 90 minutes, and reaction temperature of 180°C

Table 1. Molecular size of glycerol, oleic acid, and pore size of ZAL

	Size, Å	Reference
Size of glycerol molecular	6.657	Root, 1988
Size of oleic acid molecular	20	Brohl, 2015
Size of modified ZAL pore	33.12	Subariyah et al., 2013

the outside surface of the catalyst to the active side of catalyst (a space where the reactant and catalyst interacted to react). On the reaction liquid-solid (liquid reactant and solid catalyst). Even though the reaction rate is one of the fast-reaction category, but when there is a problem with the internal mass transfer (there is resistance), so the internal diffusion rate will be bothered and the reaction process won't work at its best.

The size of the zeolite pores is relatively smaller than the size of the molecular, sometimes can be the reason why the increase of the external diffusion rate happens doesn't counterbalance with the increase of internal mass transfer. This condition is caused by the limited reactant molecular which can enter the active side of the catalyst. Automatically, the reaction rate tends to be very limited (which happens in this experiment at 170 and 180°C). From the pore size of ZAL at 33.12 Å, the molecular size of glycerol at 6.657 Å and oleic acid at 20 Å which is a big size (Table 1), the phenomenon at figure 4 becomes possible.

Effect of Catalyst size

In figure 5 shown that the increase of the zeolite size affects the increase of the result oleic acid conversion. In particular order, the result of oleic acid conversion is 63,50; 72,99; and 73,65 %.

By decreasing the size of catalyst, ideally will shorten the way and minimize the resistances occurred from the molecules that involved in the reaction to the active side of the catalyst (ZAL). This means, the internal diffusion rate will increase by the decrease of the catalyst size, and will be followed by the increasing of reaction rate too. When the size of catalyst has been reduced from 40 mesh (0,420 mm) to 50 mesh (0,297 mm), result a quite significant enhancement which is 9,49%. But when the size of the catalyst (ZAL) getting smaller, the enhancement only happened at 0,66%. Sometimes, reducing the size of the catalyst isn't something that gives an advantage to the work of the zeolite. This phenomenon happened by Prayitno et al (2006) and Gangadwala et al (2003). When the size of the catalyst is 25 mesh, the mole fraction of acetic acid getting lower quite well which from 0,5 to 0,21 (acetic acid converted 56%), but when the size of the catalyst get reduced become 72 mesh (about 0,21 mm) the decrease of the acetic acid mole fraction are same, and when it gets smaller to become 100 mesh (0,149 mm) the decrease only happened from 0,5 to 0,24 (acetic acid converted 52%) (Gangadwala et al., 2003). On the experiment of the absorption of Pb which has been done by Prayitno et al (2006), size 40+60 to -60+80 mesh the efficiency increase from 68% to 83%, however when the size of the zeolite reduced into -80+100 mesh the efficiency of Pb absorption decrease into 72%. So, there is an optimum point for reducing the size of the catalyst or absorber. If, size of the catalyst particles is too small, then there will be no shear stress between catalyst and fluid, so the catalyst will go with the fluid flow. When the catalyst particles go with fluid flow, the Reynolds number of the catalyst becomes so low and the Sherwood number equals 2. The consequence is a decrease of mass transfer and overall reaction rate. This is going to affect the reactant conversion or the result

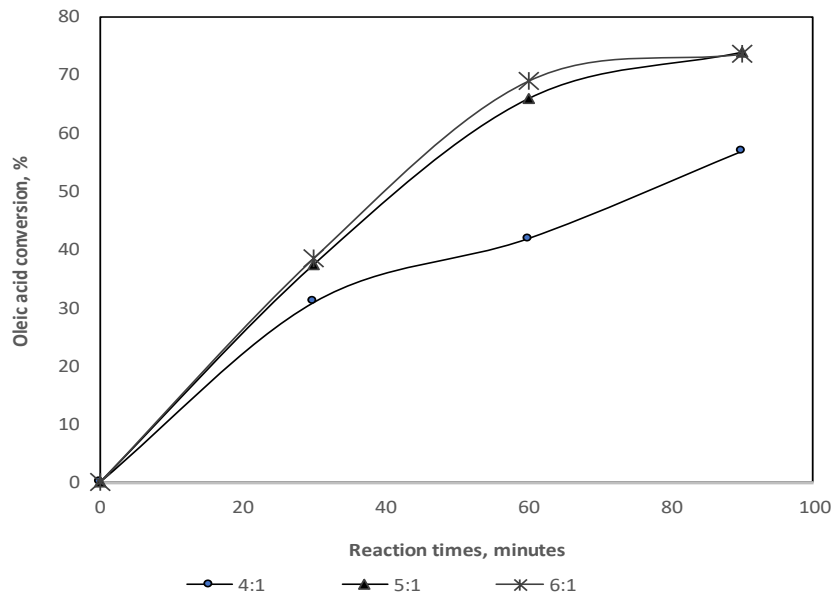


Figure 6. Effect of reactant ratio on catalyst size 60 mesh, agitation speed of 700 rpm, reaction time of 90 minuets, and reaction temperature of 180°C

of the absorption (Fogler, 2006; Perry and Green, 1997).

Effect of reactant ratio

To know how big the effect of the reactant ratio, shown in figure 6. On this observation, the sample is taken every 30 minuets to know the tendency of the reaction. Generally, oleic acid conversion increasing fast for 60 minuets, but at reactant ratio 5:1 and 6:1 mole of glycerol/mole of oleic acid at 90 minuets of reaction time shown at the graphic that it slightly decreasing. At 90 minuets, the highest increase happened at reactant ratio 4:1 to 5:1 mole of glycerol/mole of oleic acid which from 57,02 to 73,95% (increase 16,94%), while from 5:1 and 6:1

mole of glycerol/mole of oleic acid flat tendency and only increase a bit from 73,65 to 73,95% (increase 0,3%). At methyl acetate hydrolysis reaction produced methanol and acetate acid that has been done by Estheshami et al. (2006) had the same phenomenon in figure 6. The highest increase of methanol that produced is at reactant ratio 50,85:99,801 to 76,57 : 74,619 gram of methyl acetate/gram of water which increase 40% (from 8% to 11,2%), while at reactant ratio from 76,57 : 74,619 to reactant ratio.

The comparasion Between ZAL dan ZAB

They can see in figure 7, ZAB which is mordernite type (Suminta dan Las, 2006) has performance a little better than ZAL which is

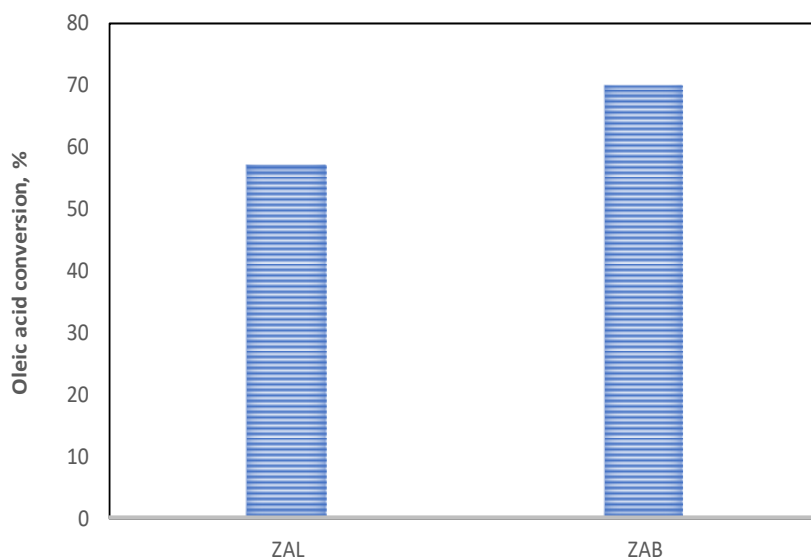


Figure 7. Performance test between ZAB and ZAL on reaction temperature of 180°C, and 4:1 mole of glycerol/mole of oleic acid

Table 2. Comparison of performance between ZAL and ZAB

Natural zeolites	Reactant ratio mole of glycerol/mole of oleic acid	170°C	180°C	200°C
ZAL, 1 N HCl	6:1	73.52	73.65	-
ZAB, 1 N HCl	4:1	-	70.00	75.09

clinoptilolite. At the same reactant ratio and reaction temperature which are 4:1 mole of glycerol/mole of oleic acid and reaction temperature of 180 °C, ZAB only need 2% concentration catalyst of glycerol weight, capable to reached 70% oleic acid conversion, but ZAL with the higher concentration of catalyst which is 4%, only capable to reached 57,02% (in figure 7). Based on XRF test by Ginting *et al.* (2006) from zeolite that has been modified, showed that Si/Al ratio (in cps/cps) of natural zeolite - Bayah and natural zeolite- Lampung are 16,86 and 14,7221. ZAB has the higher Si/Al ratio than ZAL, so ZAB will tend to be more hydrophobic than ZAL. Besides that, ZAB has a greater acid strength than ZAL. The greater the catalyst has acid strength, so the better the protonation works and the stronger the bond. While investigating the case, ZAL will have the same quality work as ZAB, if the reactant ratio increase to 6:1 mole of glycerol/mole of oleic acid (Table 2).

From the experiment, generally Indonesia natural zeolite has a good performance, but natural zeolite modernite (ZAB) has a better work than natural zeolite clinoptilolite (ZAL).

ZAL also has been analyzed by BET characterization analysis. Before the activation, ZAL has 38,050 m²/g of surface area, 0,037 cc/g of pore volume and 15,288 Å of pore radius. Right after ZAL has activated, it has 50,126 m²/g of surface area, 0,127 cc/g of pore volume and 15,279 Å of pore radius

CONCLUSIONS

From the result of the experiment, showed that natural zeolite modernite (ZAB) and natural zeolite clinoptilolite (ZAL) can be used as a catalyst of esterification reaction between glycerol and oleic acid. But natural zeolite modernite has a better performance as a catalyst than natural zeolite clinoptilolite. To get the same conversion of oleic acid which is 70%, natural zeolite clinoptilolite needs 4% concentration catalyst of glycerol weight and 6:1 reactant ratio mole of glycerol/mole of oleic acid, while natural zeolite modernite only need 2% concentration catalyst of glycerol weight with 4:1 reactant ratio mole of glycerol/mole of oleic acid.

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