Esterification glycerol (by product in biodiesel production) with oleic acid using mordenite natural zeolite as catalyst: study of reaction temperature and catalyst loading effect

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Abstract. In the heterogeneous system, reaction temperature and catalyst loading are very affected to the fluid diffusivities and molecular interaction in the active sites of catalyst. Theoretically, increasing both of them ensued to increases the chemical reaction rate. The aim of this research was to know how the effect of reaction temperature and catalyst loading to reaction rate in esterification of oleic acid with glycerol, based on oleic acid conversion result. The experiments were Carried out in a batch reactor by the reaction temperature from 160 to 200°C, catalyst loading of 0.5 to 2 wt% of solution, the reactants glycerol ratio of 3 mole / mole of oleic acid, reaction time of 80 minutes, agitation speed of 600 rpm, and mordenite natural zeolite as a catalyst. Observation result Showed that increasing the reaction temperature and catalyst loading were Accompanying by increases of oleic acid conversion. The highest conversion to reach at reaction temperature of 200°C and a catalyst loading of 2 wt% that was 75.09%.

1. Introduction
The reaction temperature and catalyst concentration generally affect the reaction rate. The reaction rate can be seen from the result of the reactants conversion, or reaction rate constants. The greater the reactant conversion and reaction rate constants generated, then the reaction rate will increased. Basically the increasing reaction temperature will have an impact on the improvement of the translation and rotation of molecules reacting substances, and reduce the viscosity of the fluid, thereby increasing the diffusion rate of the reactants to the active site of the catalyst. This condition will increase the collisions between the reacting substances [1]. On the other hand, increasing the concentration of the catalyst will increase the collisions between the reactant - catalyst that will going to affect the process of protonation of reactant by the catalyst. The right reaction temperature and concentration of the catalyst will affect the effectiveness and efficiency of the reaction process. The results of the literature review showed that the reaction process is done above boiling point, it will resulting a decrease of the reaction product [2]. In reaction ketalisation of acetone and glycerol, the reaction temperature of 70 °C will produce a higher product than the temperature of 80°C (which is from 70% to 60%). Therefore, increasing the reaction rate by increasing the reaction temperature needs to be done carefully so that the chemical reaction can take place properly. Giving excessive catalysts will not be a proportional impact on the reaction rate and the acquisition of a reaction product since each catalyst has certain characteristics and specific. So when the contact process has already reached the maximum, the addition of another catalyst would not affect the acceleration of chemical
reactions that occur. The study of glycerol reaction sealed ketalisation with zirconia catalyst at a catalyst concentration of 1 to 5% by mass of glycerol [3] and SnO2 catalyst at a catalyst concentration of 1 to 7% by mass of glycerol [4], showed that with increasing concentrations of the catalyst, followed by an increase in the conversion of glycerol produced. The highest glycerol conversion catalyst is produced at a concentration of 5% by mass of glycerol (Reddy et al., 2011), and 7% by mass of glycerol (Mallesham et al., 2014), respectively by 98% and 91% [3, 4]. But the trial Kirbaslar (2001) on the esterification of acetic acid and ethanol were performed at a concentration of 1.08 catalyst; 3.30; 5.40; and 10.08 grams show different results. At a concentration of 1.08 to 5.40 grams of acetic acid conversion has increased from 55 to 60%, but the catalyst concentration of 5.40 to 10.08 grams of conversions resulting fixed at 60% [5]. This means that increasing the conversion of reactants by increasing the supply of catalyst to the reaction system actually has a limit.

This study tried to observe how phenomena that occur esterification reaction between glycerol and oleic acid with temperature and catalyst concentration as a variable parameter. The catalyst used in this study is a natural zeolite type mordenite of Bayah-Banten (Indonesia) [6]. The selection of the esterification reaction between glycerol and oleic acid as the observation process is based on anticivation or preparatory steps alternative processing technologies glycerol which is a byproduct of biodiesel. From the literature mentions that glycerol generated in the process of making biodiesel is equal to 10% of the mass of the biodiesel production capacity itself [7, 8], so that the development of biodiesel production will be followed by the increase of byproducts such as glycerol. If there are not enough alternative technologies, while glycerol continues to increase, the market will bestow glycerol and glycerol price impact will be very cheap. the policy of large countries (America, China, Canada, and Brazil) Against fossil energy transition to renewable energy continues encouraged [4]. America as a country with the largest energy consumer in the world, in the range of 2011-2012 itself has increased its production of biodiesel significantly by 30 million pounds in 2011 to 120 million pounds in 2012 [9]. The abundance of glycerol byproduct of biodiesel is a serious challenge for further resolved, while the use of glycerol in the industry is still limited [10]. So, to anticipate that, alternative technologies for utilization of glycerol as intermediate products is necessary, so that the glycerol uptake will remain high. This study aims to study the impact of temperature and catalyst concentration affect the conversion of the reactant (oleic acid), and how it impacts the rate of reaction.

2. Research Methods

2.1. Materials research

The raw materials used are technical glycerol were purchased from PT. WILMAR VEGETABLE INDONESIA grading analysis results of 87%, technical oleic acid was purchased from PT. TnT Chemical with levels of 95%. Catalysts used are zeolite mordenite of Bayah, Banten (ZAB) which has been activated with sulfuric acid 1 N, sized 40 mesh. The washing process that has been modified acid zeolite using distilled water 4 times to ensure the impurity that has been released and the rest of the acid solution is no longer attached to the natural zeolite and heating it in the oven for 2 hours at a temperature of 110°C [6].

2.2. Research equipment

Observations were made using a stirrer batch reactor, as presented in Figure 1.
2.3. The course of the reaction
Glycerol with volumes that have been adjusted calculation (3 mol glycerol/mol oleic acid) are each heated in a separate place, and then inserted into the reactor. Heating the reactor to adjust the heating mantle button until close to the reaction temperature (160-200°C), while stirring run. When the temperature has been reached, take a sample to be analyzed early oleic acid (Ao) using an acid-base titration of 0.1 N NaOH. The catalyst is added, and every 20 minutes for analysis of samples taken for the rest of the oleic acid (As). The experiment was stopped until the reaction time of 80 minutes.

3. Result and discussion

3.1. Effect of temperature reaction
Increased reaction temperatures made a significant impact on the increase in the conversion of oleic acid (Figure 2). At the same reaction ranges of 0, 20, 40, 60 and 80 minutes, to the reaction temperature of 160 to 180°C an increase in the conversion of oleic acid from 0; 8.49; 17.76; 27.03; and 51.35% to 0; 10.44; 26.52; 47.39; and 70% (increase: 0; 1.95; 8.76; 20.36; and 18.65%), while at 200°C to 0; 43.43; 65.33; 70.07; and 72.26% (increase: 0; 32.99; 38.81; 22.68; and 2.26%).

![Figure 1](image1.png)
**Figure 1.** Scheme reactor at the esterification reaction of glycerol and oleic acid [6]

![Figure 2](image2.png)
**Figure 2.** Effect of reaction temperature on the conversion of oleic acid at a concentration of 1% by mass glycerol catalyst.
In this case, when the conversion has reached around 70%, the increase is very small, only an increase of 2.26%, namely by increasing the reaction temperature from 180 to 200°C. This means at that condition it has approached the equilibrium point condition. Because of that, the increase in temperature made almost no change any more, or because of the large molecular size of the reactants. When the reaction temperature is raised, in theory, the diffusion rate of reactants to the active site of the catalyst contained on the inside of the catalyst increases. But due to the large size of reactant molecules [11,12] and the limited pore size of the catalyst, the rate of diffusion is held and the number of molecules that diffuse into the interior of the catalyst is limited. Under these conditions, the reaction rate will be determined by how many reactant molecules are able to enter the active site of the catalyst. The results in Figure 2 have the same tendency as the study conducted by Anggara et al., 2019 in the same study using natural zeolite clinoptilolite from Lampung, where the increase in reaction temperature carried out no longer had a significant impact on the acquisition of the resulting conversion. At reaction temperatures from 160 to 170 °C the resulting conversion from 54.55 to 73.53%, but when the temperature is increased to 180°C the resulting oleic acid conversion results in only 73.65% [6]. This means that the natural zeolite catalyst is only able to convert oleic acid into a product in the esterification reaction between glycerol and oleic acid, only around 70%.

3.2. Effect of catalyst concentration

As shown in Figure 3, the increased concentration of catalyst has a positive effect on the acquisition of oleic acid conversion. The increase is quite significant when the catalyst concentration is increased from 0.5 to 1%, but when increased to 2%, the changes that occur are quite small. The result of oleic acid conversion produced in a row is 0; 37.45; 59.18; 66.29 and 67.42% (for concentrations of 0.5% mass of glycerol), 0; 43.43; 65.33; 70.07; and 72.26% (for concentrations of 1% mass of glycerol), and 0; 50.52; 66.44; 70.93; and 75.09% (for concentrations of 2% mass of glycerol). The data shows that the addition of catalyst to increase contact between reactants and their active site has a maximum limit. When the maximum conditions are exceeded, the addition of the catalyst to the reaction system will no longer have a significant impact.

![Figure 3. Effect Concentration catalyst to the conversion of oleic acid at the reaction temperature of 180°C.](image-url)

The results of this research has some similarities with the trial of Ali and Merchant 2009 on research related to the hydrolysis of benzyl acetate. In these experiments, when the catalyst concentration increased from a concentration of 10 to 30 grams / liter of reactant conversion increased quite good, but when it increased again 30 to 50 grams / liter of benzyl acetate conversion is only
increased by 4.2% (from 53.5 to 57.7 %). At the time of the catalyst concentration is increased again from 50 to 60 grams/liter of benzyl acetate conversion is generated tends to remain [13].

To illustrate the phenomena that occur during a reaction, a kinetics study of the reaction is carried out, namely by determining the reaction rate constants and the reaction order. The reaction rate and order constants are useful for the design of pilot plant and operational scales. The data used for kinetics studies are data on temperature variations. If referring to Figure 2, the possibility of a suitable model is to describe the phenomenon that occurs is homogeneous pseudo. In simple terms the esterification reaction between Glycerol and oleic acid is as follows:

\[
A + G \xleftrightarrow{} \text{GMO + W} \tag{1}
\]

A : Oleic acid
G : Glycerol
GMO : Glycerol monooleate
W : Water

The assumptions used for the kinetics study are:
- The reaction rate is only affected by changes in oleic acid. This assumption is based on the number of moles of glycerol tend excess 3 time compared to oleic acid, so it is assumed to remain.
- The reaction is a reaction in the same direction and not back and forth, because the reactants (glycerol) made very excessive

Referring to these assumptions, the reaction rate of Equation (1) can be elaborated and simplified as in Equation (2).

\[-r_A = k C_A^n \tag{2}\]

With,
\[-r_A = \text{The rate of reaction of oleic acid, (molar} / \text{min)} \ n\
 k = \text{reaction rate constant, 1 minute}
 C_A = \text{Concentration of oleic acid, the molar}
 n = \text{order of the reaction}

a. Trial : n = 1

\[-r_A = - \frac{dc_A}{dt} = kC_A \tag{3}\]

In integral be:

\[-\ln \frac{c_A}{c_{Ao}} = k t \tag{4}\]

b. Trial : n = 2

\[-r_A = - \frac{dc_A}{dt} = kC_A^2 \tag{5}\]

In integral be:

\[\left(\frac{1}{c_A} - \frac{1}{c_{Ao}}\right) = k t \tag{6}\]
From the experimental data and the calculation results of the mathematical models presented in Figure 4, Figure 5, Table 1 and Table 2 it appears that the first-order mathematical model is better than the second-order to describe the phenomenon of the reaction between glycerol and oleic acid. This is evident from the price of $R^2$ generated. Price $R^2$ order one larger base than the second-order, even though the price of $R^2$ is still less than 1. In these conditions, there will be deviations between real data and use models when predicting the conversion of oleic acid produced. By making the deviation as a correction factor, then the usage of mathematical models that will be very helpful to predict the conversion of oleic acid at the reaction temperature range will be very helpful for future operations and design.

**Table 1.** Results of the calculation of the mathematical model approach order 1

| Temperature, deg.C | k. 1 / minutes | R2  |
|--------------------|----------------|-----|
| 160                | 0.007          | 0.8204 |
| 180                | 0.0124         | 0.8839 |
| 200                | 0.0191         | 0.8386 |

**Figure 4.** Relationship between versus time at various temperatures $\frac{\ln{C_A/C_{Ao}}}{\text{Times, min.}}$

**Figure 5.** Relationship between versus time at various temperatures $\frac{1/C_A - 1/C_{Ao}}{\text{Times, min.}}$
Table 2. Results of the calculation of the mathematical model approach of order 2

| Temperature, deg.C | 160 | 180 | 200 |
|--------------------|-----|-----|-----|
| k. 1 / minutes     | 0.002 | 0.0043 | 0.0073 |
| R2                 | 0.7692 | 0.7599 | 0.9376 |

4. Conclusion
From the experiments, ZAB (Alam Bayah Natural Zeolite) that has modified with 1 N H$_2$SO$_4$, showing a good performance. Increasing concentrations of the catalyst and the reaction temperature, followed by increasing the conversion of oleic acid were obtained. The highest conversion was obtained at the reaction temperature 200°C and catalyst concentration 2 wt% with a conversion of 75.09% oleic acid. The mathematical model approach better to approach a homogeneous pseudo-first-order at a price of R$^2$ average of 0.848.

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