Synthesis of Methyl Tertiary Glycerol Ether (MTGE) from glycerol and Tertiary Butyl Alcohol (TBA)

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Abstract. Glycerol is a by-product of the biodiesel industry which can be further processed into a product that has economic value. One of them is becoming a fuel additive. Glycerol was reacted with TBA (Tertiary Butyl Alcohol) to produce MTGE (Methyl Tertiary Glycerol Ethers) by using HZSM-5 as catalyst. The experiment was conducted within 2 hours, a pressure of 1 atm, using batch reactor. This research was studied of effect temperature, catalyst concentration, and reactant molar ratio to conversion of glycerol. The product of reaction was analyzed by GC-MS (Gas Chromatography-Mass Spectrometry). The product was contained like as Butane, 1-(2-methoxyethoxy)-CAS or 1-Butoxy-2-methoxyethane or 2, 5-dioxanonane amounted to 29.98% and 19.74% and Propane, 1-(1,1-dimethylethoxy)-2-methyl (CAS) or 1-tert-Buthoxy-2-methylpropane by 6.66% and 1.86% for the ratio of 4:1 and 1:1. The results of the experiment have shown the effect of single variable effect on the conversion of glycerol as follows: temperature (X1), reactant molar ratio (X3), and catalyst concentration (X2). The interaction variable affected in etherification reaction followed temperature-molar ratio (X1X3), temperature-catalyst concentration-molar ratio (X1X2X3), catalyst concentration-molar ratio (X2X3), and temperature-catalyst concentration (X1X2).

1. Introduction
Glycerol (propane-1,2,3-triol) is a type of alcohol trihydroxyle commonly known as glycerine which is widely used in the food industry, pharmaceutical, polymer and fuel industry [1]. Glycerol can be produced as a by-product from biodiesel production of using transesterification reaction. The amount of glycerol produced about 10% by weight of the total production of biodiesel [2]. Biodiesel production increased sharply in almost all countries. Thus the amount of glycerol produced is also increased with increasing biodiesel production. It is estimated that the production of glycerol in the world in 2020 will reach about 41.9 billion litres [3]. Therefore, it is necessary to further processing to the glycerol in order to become something more valuable in the market.

Glycerol has three hydroxyl groups, this resulted glycerol cannot be directly added to the fuel at low levels of warming. There are several kinds of processes that can be used to synthesize glycerol in order to be additive in fuels such as by reaction between glycerol and acetic acid through the process of acetylation or the esterification process. The reaction between glycerol and ether substrate through etherification as well as the reaction between glycerol and acetone or anhydrous acid through the process of acetylation. In the process of glycerol into fuel additives, there are several things to note are...
the physical properties, reaction mechanisms, the design of catalyst used, the operating conditions such as temperature, pressure and the addition of solvent during the process. Etherification is a reaction that is widely used, including for the production of Methyl Tertiary Glycerol Ether (MTGE). MTGE is additive to the fuel that has commercial value which is quite a lot of them as a reformulation of biodiesel, improving cold properties, reducing the number of contaminant emissions such as particulates, hydrocarbons, carbon monoxide (CO) [4] and lower the viscosity of the fuel, increasing the octane number (octane boosters) [5], alternatives to MTBE and ETBE, reduce the cloud point of diesel fuel when mixed with biodiesel [6], and good solubility when mixed into fuel [7].

Glycerol etherification with Tert-Butyl Alcohol (TBA) has also been discussed in the literature. [8] observed the process of etherification with tert-butyl alcohol using silica catalyst. The study was conducted at a pressure of 1.0 MPa in a batch reactor with a temperature of about 303-363 K with a frequency of 1200 rpm stirring, to limit the influence of external mass transfer phenomena. The reaction time ranges from 1 to 30 hours, and the ratio of TBA / glycerol from 2 to 5 and using the catalyst weight ratio of 0.3 to 7.5 w%. In addition to silica catalysts, ion-exchanger resin A-15 was used to evaluate the effect of the level of acidity in the reaction. The reaction mixture analyzed by gas chromatography (HP 6890N). From the results of the analysis showed that the conversion of glycerol increases with the reaction temperature and the conversion of alkyl ethers were achieved by 95% within 6 hours with the catalyst A-15. Alkyl ether formed by the reaction of etherification. Observations regarding the amount of catalyst used, the result that an increase in the formation of glycerol ethers with a significantly increased amount of catalyst from 0 to 7.5 wt%. With increasing reaction time, the concentration of mono-ether produced decreases while the concentration of di-ether formed increases. In addition, the observations obtained from the number of isobutene, which is thought to originate from the reaction of tert-butanol dehydration.

Generally, the catalyst used in etherification is almost the same as the catalyst used for the esterification process. The catalyst used may be homogeneous catalysts mineral acids such as H2SO4, HCl, HF, etc. [9]. Nevertheless, the use of homogeneous catalysts is rarely used in an industry, because it is corrosive, it is difficult to separate the catalyst with the final product, as well as other harmful effects on the environment. Therefore the use of other alternative is by using a heterogeneous catalyst such as Amberlyst-15, Amberlyst-36, Montmorillonite K-10, zeolite HZSM-5, etc. [10]. In the presence of such catalysts are expected to accelerate the reaction, and improve conversions and product selectivity.

In this paper described the results of research that aims, in general, to make MTGE method etherification between glycerol and tertiary butyl alcohol by using a catalyst of zeolite HZMS-5, while specifically to study the effects of temperature, catalyst concentration, and the molar ratio of the response (conversion of glycerol) using Factorial Design. Hopefully, with this study, further processing can be done against a by-product of biodiesel is glycerol into a fuel additive that has the same level with ETGE or MTGE and can explain the effect of temperature, catalyst concentration, and the molar ratio of the glycerol conversion.

2. Materials and methods

2.1. Materials
The materials that used in this study were glycerol and TBA (Tertiary butyl alcohol). Glycerol has industrial grade specification and TBA found from Merck Ltd. The catalyst of HZSM-5 was from industry grade. The tools that used in this study was three-neck flask equipped with magnetic stirrer as reactor as shown in the figure 1. The etherification product was analyzed by using GC-MS (Gas Chromatography-Mass Spectrometry) TQ8030 Shimadzu Serial No. 0207051 00187 to determine the composition of the product.
2.2. Procedure
TBA, glycerol, and HZSM-5 catalyst were mixed with the specific composition which has been predetermined. TBA was heated until the temperature 40°C and then mixed with glycerol and the catalyst. The compound was stirred evenly into the reactor (three-neck flask). The etherification product was sampling during the process 5 ml at t0 and t. These samples will be analyzed and then observed the influence of the time, the catalyst concentration, and the molar ratio of the glycerol on conversion of the etherification product. Composition of the product was determined by using GC-MS TQ8030 Shimadzu Serial No. 0207051 00187. Column RTX-1. Column oven temperature 65°C, injection temperature 250°C, pressure 74.5 kPa. Flow control mode lineair velocity, column flow 1.2 ml/min and total flow 602.4 ml/min. Rate temperature for 65°C hold time 8 min and rate temperature for 250°C was 4 and hold time 20 min.

3. Result and Discussion

3.1. Time of the Reaction
In the early stages of conducted the experiments to determine the operation time. In this case, we conducted an experiment for each ratio of reactants (TBA / glycerol) which is 4: 1 and 1: 1. Experiments carried out at the operating temperature of 75°C with the catalyst such as HZSM-5 of 1.5 w% (4.5 grams) within 7 hours. For 7 hours, the samples were taken about 5 ml per hour. Results of the study are presented in the graph of conversion with time, as presented in Figure 2.
Based on the chart, it appears that the conversion of glycerol with a ratio of TBA: glycerol = 4:1 is greater than the ratio of TBA: glycerol = 1:1. This is consistent with the theory that the greater the mole ratio of reactants than the possibility of reactants to react to form products are also getting bigger, thus conversion will also increase [11]. [2] studied the effect of the difference between the initial molar ratio of tert-butanol and glycerol on the conversion and selectivity of the reaction. They get the result that the molar ratio of tert-butanol / glycerol was higher than 3 glycerol conversion yield of 72.3%. This occurs because of the greater the amount of glycerol in the mixture, the greater the viscosity of the solution which is an impact on the mass transfer between phases and the catalyst. Moreover, a small initial of molar ratio will generate a low selectivity and enable to develop unwanted reactions [2].

Figure 2 shows that the conversion of glycerol on the reactant ratio of 4:1 was 54.24% achieved within one hour, while the ratio of reactants to 1:1 was 56.87% achieved within 2 hours. The fluctuation conversion for the molar ratio 1:1 of glycerol and TBA because of the equilibrium reaction reached in a longer time than conversion for the molar ratio 4:1. These results were supported by research conducted by [9] regarding the optimization of the molar ratio of reactants to selectivity. From these experiments showed that the molar ratio of reactants higher, the products they want appear within 10 minutes of reaction, much faster than the lower molar ratio [9]. Therefore, it can be concluded that the greater the ratio of reactants, the reaction time required will be smaller, in accordance with the theory that the greater the mole ratio of reactants then the possibility of reactants to collide will increase too, so that the time required to reach equilibrium is also getting smaller [12]. Thus, we determine the best operating time for etherification reaction between TBA and glycerol is 2 hours.

3.2. Qualitative Analysis

In an experiment that required analysis of both qualitative and quantitative. For this study, our analysis is used in the form of qualitative analysis. Qualitative analysis, the analysis is meant to determine the content of the compound contained in a sample. This analysis can be done using an instrument. The products produced in the process of etherification of glycerol and TBA is an ether compound that is non-polar. Therefore, the chosen method of analysis GC-MS to determine the type of the compound contained in the product. Basically, GC-MS is a combination of tools instrument GC (gas chromatography) and MS (mass spectrometry). GC-MS is used to separate a compound into its constituent components by gas as a mobile phase. Separation of compounds by GC-MS is based on the volatility of the analyzed substance. From the analysis using GC-MS were obtained the following results:

Table 1. GC-MS analysis results for the ratio of TBA: Glycerol = 4: 1 at t = 7 hours

| R Time | Name                                                                                   |
|--------|----------------------------------------------------------------------------------------|
| 2,195  | Propane, 1-(1,1-dimethylethoxy)-2-methyl-(CAS : 33021-02-2)                             |
| 3,087  | Butanamide, 3,3-dimethyl-(CAS : 926-04-5)                                              |
| 5,129  | 1,2,3-Propanetriol (CAS : 56-81-5)                                                    |
| 5,25   | Cyclohex-1,4,5-triol-3-one-1-carbocyclic acid                                           |
| 9,72   | Butane, 1-(2-methoxyethoxy)-(CAS : 13343-98-1)                                          |
Figure 3. TBA etherification chromatogram graph and glycerol with a molar ratio of TBA:
Glycerol = 4: 1

Table 2. GC-MS analysis results for the ratio of TBA: glycerol = 1: 1 at t = 7 hours

| R Time | Name                                                                 |
|--------|----------------------------------------------------------------------|
| 2.195  | Propane, 1-(1,1-dimethylethoxy)-2-methyl-(CAS: 33021-02-2)            |
| 3.090  | Butanamide, 3,3-dimethyl-(CAS: 926-04-5)                              |
| 5.176  | 1,2,3-Propanetriol (CAS: 56-81-5)                                    |
| 5.222  | 2,3-Dihidroxy-1,4-dioxan-(CAS: 4845-50-5)                             |
| 5.278  | 1,2,3-Propanetriol (CAS: 56-81-5)                                    |
| 5.301  | 1,2,3-Propanetriol (CAS: 56-81-5)                                    |
| 5.330  | 2,3-Dihidroxy-1,4-dioxan-(CAS: 4845-50-5)                             |
| 5.355  | 1,2,3-Propanetriol (CAS: 56-81-5)                                    |
| 5.385  | 1,2,3-Propanetriol (CAS: 56-81-5)                                    |
| 9.716  | Butane, 1-(2-methoxyethoxy)-(CAS: 13343-98-1)                         |

Figure 4. TBA etherification chromatogram graph and glycerol with a molar ratio of TBA:
Glycerol = 1: 1

Figure 3 is the result of chromatography experiments for the ratio of TBA: Glycerol = 4: 1, which is converted glycerols amount to 41.5%. For TBA ratio: glycerol = 1: 1, which is converted glycerol amount to 38.7% in the graph chromatography Figure 3.3. Based on GC-MS analysis can then be seen that for a molar ratio of TBA: glycerol = 4: 1, ether compounds that are formed in the form Propane, 1- (1,1-dimethyl ethoxy) -2-methyl (CAS: 33021-02-2 ) by 6.6% in retention time 2.195 and Butane,
1- (2-methoxy ethoxy) - (CAS: 13343-98-1) amounted to 29.98% at retention time of 9.72 while the ether compounds that are formed to a molar ratio TBA : glycerol = 1: 1 was Propane, 1- (1,1-dimethyl ethoxy) -2-methyl (CAS: 33021-02-2) of 1.86% on the retention time 2.195 and Butane, 1- (2-methoxy ethoxy) - (CAS: 13343-98-1) amounted to 17.54% at retention time 9.716. As for the other compounds as shown in table 1 and table 2.

Here are the specifications of ether compounds produced are:

**Propane,1-(1,1-dimethylethoxy)-2-methyl-(CAS : 33021-02-2)**

![Propane molecule]

- Molecular Formula: \(\text{C}_8\text{H}_{18}\text{O}\)
- Average mass: 130.227905 Da
- Monoisotopic mass: 130.135757 Da
- Systematic name: 2-Methyl-1-[(2-methyl-2-propanyl)oxy]propane

**Butane,1-(2-methoxyethoxy)-(CAS : 13343-98-1)**

![Butane molecule]

- Molecular Formula: \(\text{C}_7\text{H}_{16}\text{O}_2\)
- Average mass: 200699 Da
- Monoisotopic mass: 132.115036 Da
- Systematic name: 1-(2 M ethoxy ethoxy)butane

### 3.3. Statistics Analysis

In this study, the factorials design used for statistical analysis the result of the experiment. Design of study was \(2^3\) (3 factors and 2 levels). The selected response was the conversion of the glycerol. The purpose of the selected method was to know the interaction between the selected variable, due to all the selected variable was to work together with the response or not. From the table 3, the high level variable symbolized (+) and the low level was (-), for T, C and MR was unit for temperature, the concentration of the catalyst and ratio of the reactant. \(X_1\), \(X_2\), and \(X_3\) are symbolized for temperature, the concentration of the catalyst and ratio of the reactant.

| run number | coded designs level | real values | Conversion |
|------------|---------------------|-------------|------------|
|            | \(X_1\) \(X_2\) \(X_3\) | T (°C) C (% wt) MR |           |
| 1          | - - -               | 60 1 1     | 26.295     |
| 2          | + - -               | 90 1 1     | 10.698     |
| 3          | - + -               | 60 2 1     | 48.846     |
| 4          | + + -               | 90 2 1     | 20.478     |
| 5          | - - +               | 60 1 4     | 9.24       |
| 6          | + - +               | 90 1 4     | 14.681     |
| 7          | - + +               | 60 2 4     | 93.703     |
| 8          | + + +               | 90 2 4     | 37.156     |
From table 3, we can get equation 1 for calculate the main effect and interaction effect against conversion of the glycerol.

\[ Y_{\text{glycerol}} = 42.76 - 44.02X_1 + 14.57X_2 + 32.36X_3 + 1.56X_1X_2 - 22.04X_1X_3 - 1.59X_2X_3 + 7.95X_1X_2X_3 \]  

(1)

The most influential effect was the variable with the high value without seeing the negative and positive symbol. From the method, the negative and positive were code for synergies response and antagonist response. From equation 1, we can calculate the value of the determinant coefficient (R2) was 0.9307. This value showed that conversion of the glycerol was influenced with all of the variables and 0.0693 from the total variance was not identified in the equation. So that, there was the other variable that influence of the glycerol conversion.

From the picture 5, showed there was point T, R and TR that the farthest point in the graph. It was symbols for temperature, molar ratio and temperature-molar ratio. All of the points were variables which give the main effect for the response variable.

![Figure 5. Graphic for Normal Probability](image)

**Table 4. Comparison between Y_{practical} and Y_{theoretical}**

| Run | X_T | X_MR | X_TMR | Y_{practical} | Y_{theoretical} | Deviation |
|-----|-----|------|-------|---------------|-----------------|-----------|
| 1   | -   | -    | +     | 26.29         | 26.21           | 0.09      |
| 2   | +   | -    | -     | 10.70         | 10.62           | 0.08      |
| 3   | -   | -    | +     | 48.85         | 48.76           | 0.09      |
| 4   | +   | -    | -     | 20.48         | 20.39           | 0.09      |
| 5   | -   | +    | -     | 90.24         | 90.15           | 0.09      |
| 6   | +   | +    | +     | 14.68         | 14.58           | 0.11      |
| 7   | -   | +    | -     | 93.70         | 93.62           | 0.09      |
| 8   | +   | +    | +     | 37.16         | 37.07           | 0.09      |

Thus, we can conclude that to increase the glycerol conversion from etherification reaction between TBA and glycerol, there are 3 factors which must have attention. The factor is temperature and ratio of the reactant for a single effect, and temperature-molar ratio for the double effect. [10] has been done identified the effect of temperature to glycerol conversion on the etherification process. From that
study, the higher temperature of the reaction, time to complete the reaction was to fast due to increasing of the kinetic reaction, so that the conversion of the glycerol was higher too [10].

4. Conclusion
The operating time required to achieve the greatest conversion in both etherification reaction to a molar ratio of 4: 1 or 1: 1 is for two hours. Based on the results of the GC-MS analysis, the type of ether contained in the sample is Butane, 1-(2-methoxy ethoxy) -CAS or 1-Butoxy-2-methoxypentane or 2,5-dioxanonane amounted to 29.98% and 19.74% and propane, 1-(1,1-dimethyl ethoxy) -2-methyl (CAS) or 1-tert-Buthoxy-2-methylpropane amounted to 6.66% and 1.86% for the ratio of 4: 1 and 1: 1.

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