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*Research Article*

# Catalytic Synthesis of Glycerol tert-Butyl Ethers as Fuel Additives from the Biodiesel By-Product Glycerol

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Glycerol is a major by-product in the biodiesel production process. Every 100 kg of biodiesel produced generates approximately 10 kg of crude glycerol. As the biodiesel industry has expanded rapidly in recent years, finding new uses of the excess crude glycerol is important. Many studies have examined alternative uses of crude glycerol. One of them is the use of glycerol derivatives, such as glycerol tert-butyl ethers as fuel additives. In this paper, the etherification kinetics of glycerol with tert-butyl alcohol to glycerol tert-butyl ethers was studied using an Amberlyst catalyst. The influences of the catalyst type and loading, reaction time, molar ratio, and temperature were investigated in detail.

## 1. Introduction

Biodiesel is a renewable, clean-burning diesel replacement from biological sources that it is produced widely around the world. On the other hand, every 100 kg of biodiesel produced generates approximately 10 kg of crude glycerol. The glycerol market is influenced by the commercial availability of biodiesel. Therefore, how to use the surplus glycerol profitably is an important problem to solve in biodiesel production. Many applications of glycerol have been developed over the past few decades [1–4]. Despite these, new fields of glycerol use are needed to improve the economics of biodiesel production. Among the derivatives, glycerol tertiary butyl ethers (GTBEs) are excellent additives with large potential for diesel and biodiesel reformulation. In particular, a mixture of 1,3-di-, 1,2-di-, and 1,2,3-tri-tert-butyl glycerol, when incorporated in standard 30–40% aromatic-containing diesel fuel, leads to a significant decrease in the emissions of particulate matter, hydrocarbons, carbon monoxide, and unregulated aldehydes [5, 6]. The addition of glycerol ether additives results in a slight increase in $NO_x$ emissions; however, the use of sufficient known cetane improvers to increase the fuel cetane value by 5 to 10 units will reduce the $NO_x$ emissions to well below the level of the base reference fuel. Therefore, the production of GTBEs at low cost and high yield is an important research topic. By reacting of glycerol with isobutene could be obtained GTBEs in the presence of acid catalysts [7, 8]. On the other hand, its boiling point is −6.9°C, which means high pressure conditions are necessary to keep it in the liquid state. The most commonly used reactor is an autoclave, which can be adjusted to a high pressure about 1.5 MPa to keep isobutene in the liquid state. Despite this, the performance of the etherification process is strongly dependent on mass transfer between the two materials [9]. Compared to isobutene, tert-butyl alcohol (TBA) is more attractive for producing GTBE by the glycerol etherification reaction in a solid-liquid catalytic process [10]. TBA is a useful reactant in the etherification reaction to overcome the technological problems arising from the need to use solvents to dissolve glycerol. The etherification reaction is carried out at atmospheric pressure to optimize the reaction conditions. When the etherification reaction between glycerol and TBA takes place in the presence of an acid catalyst, some or all of the hydroxyl groups in the glycerol molecule are reacted to form five different types of alkyl glycerol ethers, as shown in Figure 1. Among the ethers, 3-tert-butoxy-1,2-propanediol and 2-tert-butoxy-1,3-propanediol have relatively high water solubility and are unsuitable as

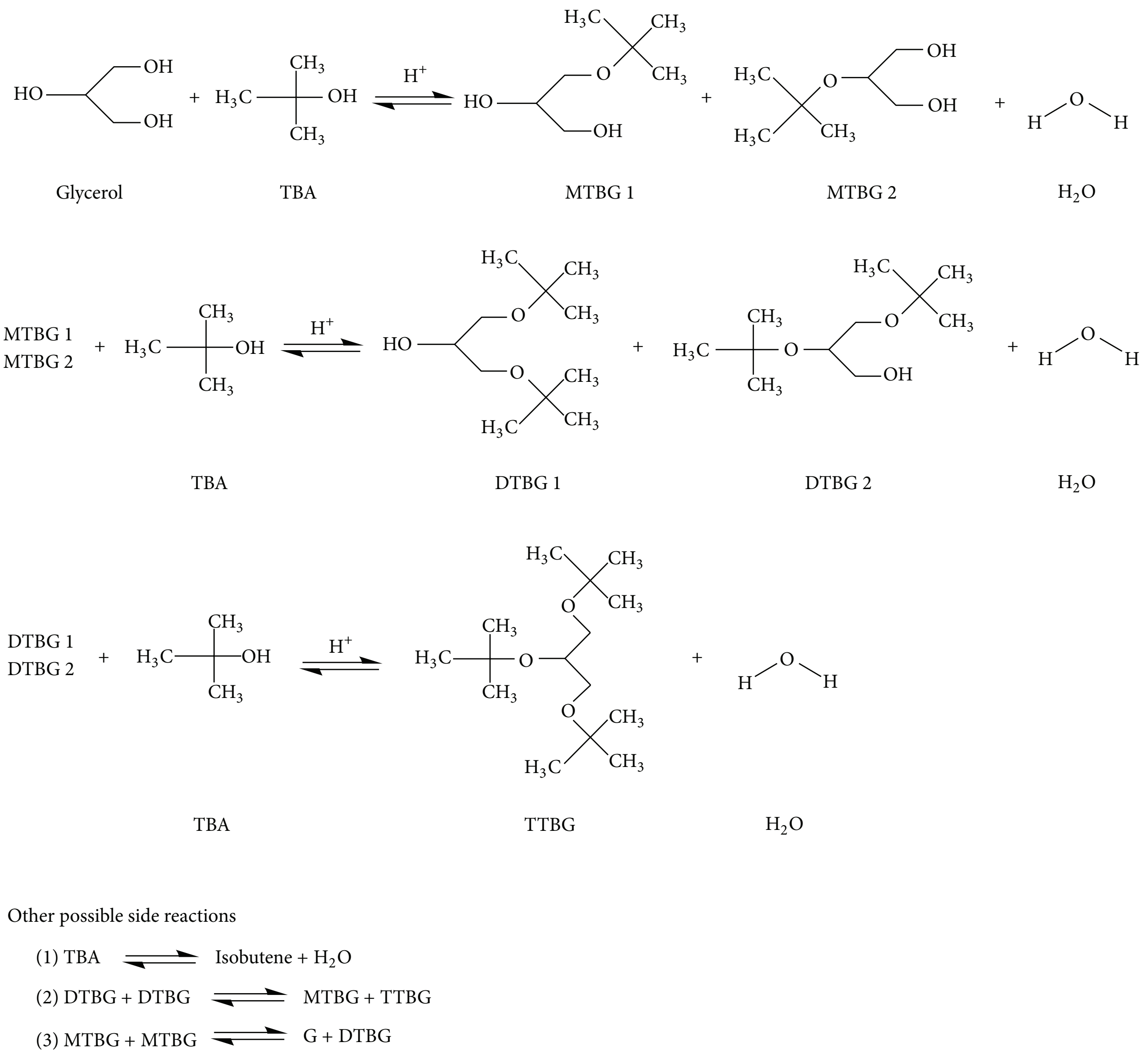

Figure 1: Tert-butylation of glycerol and side reactions.

diesel-blending agents whereas the higher ethers of glycerol, such as 1,3-di-tert-butoxy-2-propanol (DTBG1), 1,2-di-tert-butoxy-3-propanol (DTBG2), and 1,2,3-tri-tert-butoxy-2-propane (TTBG), have good solubility in biofuel, a high flash point, low water affinity, and negligible cetane reduction, making them a potential candidate fuel additive [10]. In this study, the etherification kinetics of glycerol with tert-butanol to glycerol tert-butyl ethers was examined using an Amberlyst catalyst. Amberlyst is a strongly acidic, sulfonic acid, macroreticular polymeric resin based on cross-linked styrene divinylbenzene copolymers. It is used in catalytic processes including etherification reaction. The influences of the catalyst type and loading, reaction time, molar ratio, and temperature were investigated in detail. The present study aims to produce as much DTBGs and TTBG as possible while minimizing the production of MTBGs.

## 2. Experimental

*2.1. Materials.* Glycerol (Extra Pure) and tert-butyl alcohol (Extra Pure) were used as the reactants in the etherification reaction. Both reagents were purchased from Duksan Reagents of Korea. Acetone (99.5%) (Duksan Chem. Co., Korea) was used as the analysis reagent. Industrial-grade, strongly acidic ion-exchange resins, such as Amberlyst 15 (Sigma-Aldrich Co.), Amberlyst 35 wet (Dow Chem. Co.), and Amberlyst 35 dry (Dow Chem. Co.) were used as the catalysts. Table 1 lists the typical properties of the catalysts used in this study.

*2.2. Experiment and Analysis Method.* The reactions were carried out in 150 mL glass reactors equipped with Graham condensers under pressure. All the reactors were settled in a water channel that was equipped with two temperature

Table 1: Characteristics of catalysts of catalysts used in this study.

| Characteristics | Amberlyst 15 | Amberlyst 35 dry | Amberlyst 35 wet |
|---|---|---|---|
| Physical form | Opaque beads | Opaque beads | Opaque beads |
| Concentration (eq/kg) | ≥4.7 | ≥5.0 | ≥1.9 |
| Surface area ($m^2$/g) | 53 | 50 | 50 |
| Average pore diameter (Å) | 300 | 300 | 300 |
| Total pore volume (mL/g) | 0.40 | 0.35 | 0.35 |

Table 2: GC retention time of each peak.

| Peak name | Retention time (min) |
|---|---|
| TBA | 2.41 ± 0.05 |
| TTBG | 6.31 ± 0.05 |
| DTBG 1 | 7.46 ± 0.05 |
| DTBG 2 | 8.20 ± 0.05 |
| MTBG 1 | 10.21 ± 0.05 |
| MTBG 2 | 11.26 ± 0.05 |
| Glycerol | 15.35 ± 0.05 |

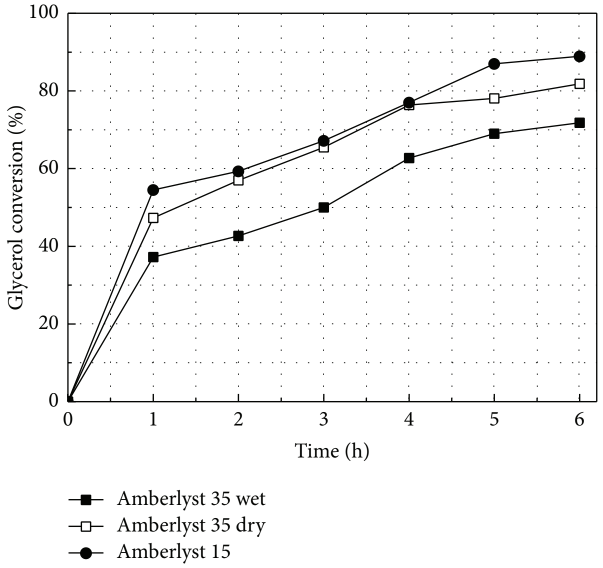

Figure 2: Influence of the different catalysts on glycerol conversion. Reaction conditions: 70°C, TBA to glycerol molar ratio = 4 : 1, catalyst loading = 7.5 wt.% to glycerol, and 8 hours.

controllers. In a typical experiment, sufficient water was added to the water channel and the temperature was set using a temperature controller. The reactants, catalysts, and stirring bar were placed in the reactors. TBA was first placed in the reactor followed by glycerol because the density of TBA was smaller than that of glycerol. By doing so the sequential reactant addition method can provide good mixing of the two reactants (stirring velocity 1000 $\text{min}^{-1}$). The samples obtained from the experiment were first treated by centrifugal separation to separate the catalyst from the reaction mixture. The reaction mixture was then diluted and mixed with the organic solvent, acetone ($(CH_3)_2CO$), and 1 $\mu$L was injected into a gas chromatograph for quantitative analysis [11]. The reaction samples were analyzed by gas chromatography (GC) using a DB-WAX column and a FID detector. Five abbreviations of the products are defined as follows: 3-tert-butoxy-1,2-propandiol or mono-tert-butyl ether of glycerol 1 (MTBG 1), 2-tert-butoxy-1,3-propandiol, or mono-tert-butyl-ether of glycerol 2 (MTBG 2), 1,3-di-tert-butoxy-2-propanol, or di-tert-butyl ethers of glycerol 1 (DTBG 1), 1,2-di-tert-butoxy-3-propanol, or di-tert-butyl ether of glycerol 2 (DTBG 2), and tri-tert-butoxy-propane or tri-tert-butyl ether of glycerol (TTBG). As shown in Table 2, retention times for the compounds are different, so they can be well separated. Since the area of each peak indicates concentration, the concentration of each compound could be calculated accurately with reference to its calibration data. Because MTBG1 and MTBG2 are isomers, it is possible to use the same calibration data to calculate their concentrations. In the case of DTBG and TTBG, response factors were extrapolated from that of MTBG [12]. TBA should be present in excess to glycerol because each step of the reaction consumes it, so glycerol was chosen as an indicator of reaction conversion. The glycerol conversion was defined as follows [13]:

$$\text{Glycerol conversion (\%)} = \frac{(\text{MTBGs} + \text{DTBGs} + \text{TTBG})\ \text{mmol/L}}{(\text{Glycerol remaining} + \text{MTBGs} + \text{DTBGs} + \text{TTBG})\ \text{mmol/L}} \times 100. \tag{1}$$

## 3. Results and Discussion

*3.1. Selection of Reaction Catalyst.* A number of Amberlyst catalysts are active in the reaction because of its large average pore diameter or in other words, its high cross-linked macroreticular structure. The large pore diameters allow relatively large glycerol molecules to access the inner surface of the catalyst to undergo a transformation. Klepáčová et al. [12] and Ozbay et al. [14] examined various kinds of Amberlyst type catalysts, such as Amberlyst 15, Amberlyst 16, Amberlyst 31, Amberlyst 35, Amberlyst 36, Amberlyst 39, and Amberlyst 119; both wet and dry forms were examined if they existed. The main difference between wet and dry form of Amberlyst 35 is the concentration of acid sites. The best results were obtained using Amberlyst 15 and Amberlyst 35, which are commonly used as catalysts for the transformation reaction of aliphatic ether oxygenates. They have a prominent large average pore diameter and surface area compared to the others.

To select the most efficient catalyst, comparative experiments were conducted under the same reaction conditions using Amberlyst 15, Amberlyst 35 dry and wet forms; the glycerol conversion from each reaction with the different catalysts was obtained. Although the mean pore diameters of these catalysts were the same, the surface area and pore volume of Amberlyst 15 are larger than those of dry and wet

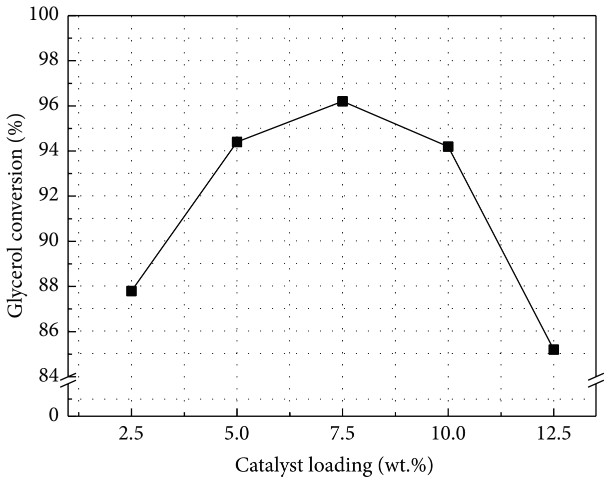

Figure 3: Influence of the catalyst loading on glycerol conversion. Reaction conditions: 70°C, TBA to glycerol molar ratio = 4 : 1, and 8 hours.

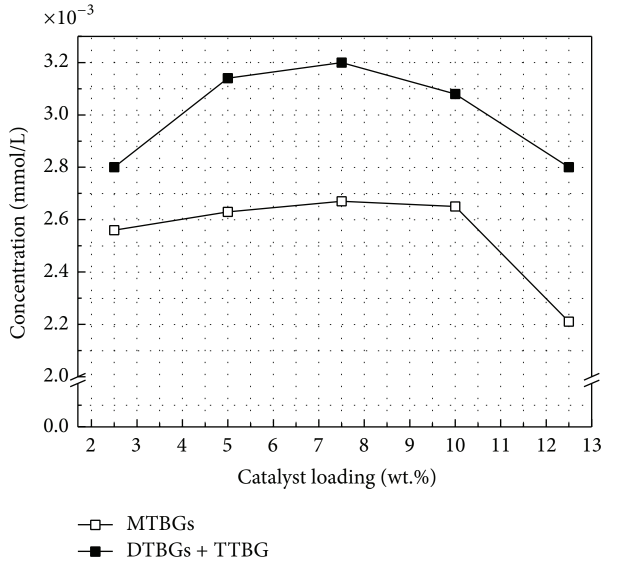

Figure 4: Influence of catalyst loading on product yield. Reaction conditions: 70°C, TBA to glycerol molar ratio = 4 : 1, and 8 hours.

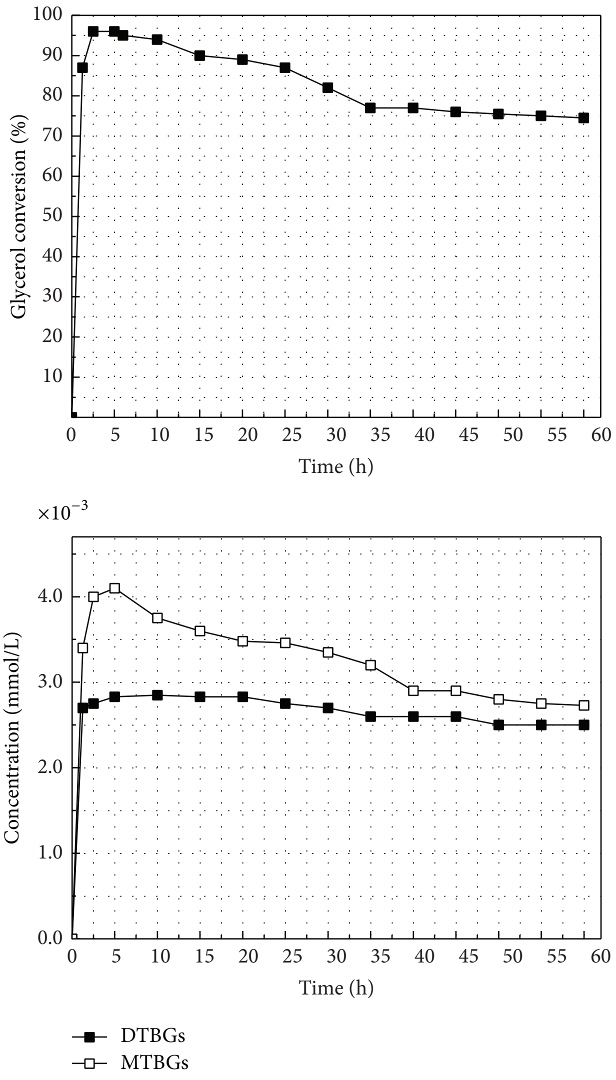

Figure 5: Glycerol conversion and products yields as a function of time. Reaction conditions: 70°C, TBA to glycerol molar ratio = 4 : 1; Amberlyst 15 catalyst = 7.5 wt.% to glycerol.

Amberlyst 35, providing a larger number of surface active sites. As shown in Figure 2, the conversion of glycerol in the presence of both dry and wet Amberlyst 35 was much lower than that of the Amberlyst 15 catalyst. Based on these results, Amberlyst 15 was selected as the catalyst for use in the subsequent experiments.

The effects of the catalyst amount were next assessed by varying the Amberlyst 15 loading in terms of the weight percentage of the glycerol weight. Figures 3 and 4 show the effects of the catalyst loading on the glycerol conversion and ether concentration, respectively; both the glycerol conversion and product yield were low at the lowest and highest catalyst loading levels tested, respectively. The best results were obtained at a 7.5 wt.% loading of glycerol. This pattern is in accordance with the previously published results [15]. On the other hand, the differences in conversion between 5.0% or 10.0% and 7.5% were not so significant; the highest glycerol conversion was 96% at 7.5 wt.% and around 94% at 5.0 wt.% and 10.0 wt.%. Similarly, the desired product (DTBGs and TTBG) yield was $2.69 \times 10^{-3}$ mmol/L when the catalyst loading was 7.5 wt.% and was $2.64 \times 10^{-3}$ mmol/L and $2.67 \times 10^{-3}$ mmol/L when loading was 5.0 wt.% and 10.0 wt.%, respectively. In conclusion, the catalyst loading was found to exert a relatively modest influence on the etherification reaction.

*3.2. Effect of the Reaction Time.* In this study, an etherification experiment was conducted for up to 60 hours to establish the reaction profile as a function of time and select the optimal reaction time. Figure 5 shows the conversion of glycerol and the concentrations of MTBGs and DTBGs.

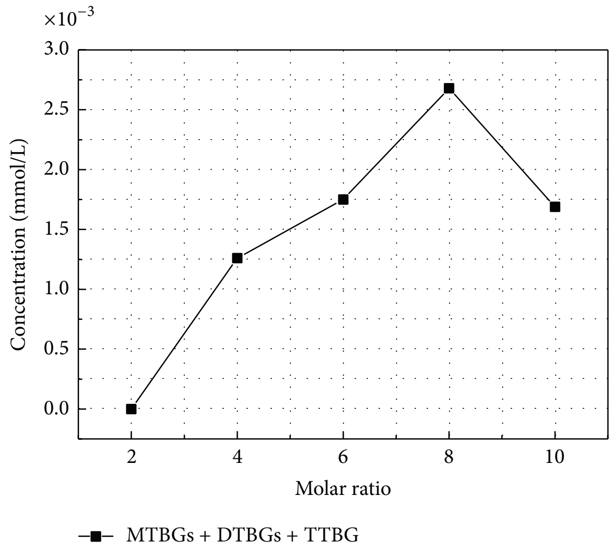

Figure 6: Influence of the molar ratio on the product yield. Reaction conditions: 70°C, Amberlyst 15 catalyst = 7.5 wt.% to glycerol, and 8 hours.

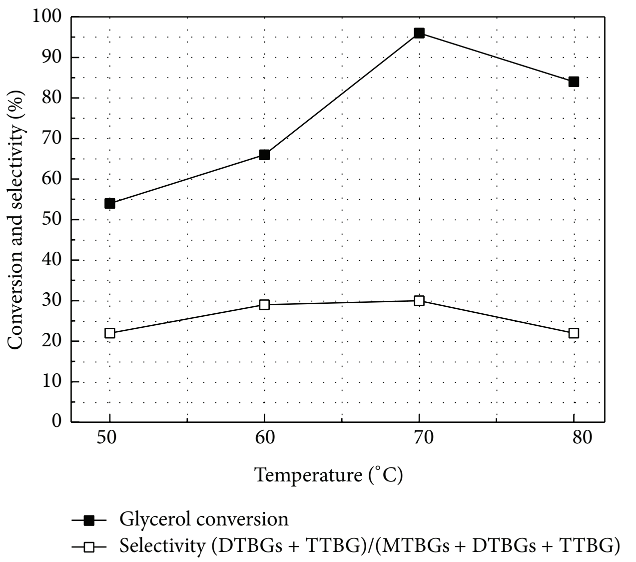

Figure 7: Influence of temperature on glycerol conversion. Reaction conditions: Amberlyst 15 catalyst = 7.5 wt.% to glycerol, molar ratio = 4 : 1, and 8 hours.

The reaction was quite fast in the first reaction hour and reached the highest conversion at approximately 6 hours; it then began to decrease thereafter. The highest conversion of glycerol was approximately 96.0% to 97.0% at 5 to 6 hours and approximately 80% at 60 hours; the products yields were highest at approximately 5 to 8 hours. After 6 hours, both the conversion and MTBGs concentration decreased. The concentration of DTBGs also decreased to 6 hours but remained constant until 60 hours. These results show that the reverse reaction and a third-side reaction shown in Figure 1 play a role in the reaction, causing one mol glycerol and one mol DTBG to be generated from two mole MTBGs after approximately 6 hours of reaction. This phenomenon led to a decrease in glycerol conversion after 6 hours of the reaction. Based on the results of this experiment, to obtain the maximum yield of the glycerol ethers, the reaction should be set between 5 and 8 hours. Systematic optimization studies will be conducted further to locate the optimal reaction time.

*3.3. Effect of Molar Ratio.* From the reaction mechanism, the formation of an ether molecule consumes 1 to 3 TBA molecules depending on the extent of the reaction, and the hydrolysis side reaction consumes 1 TBA molecule. Therefore, to enhance the yield of the desired higher ethers of glycerol, TBA should be present in excess compared to glycerol. Different TBA to glycerol molar ratios were tested to determine their effects on total concentration of ethers. As shown in Figure 6, an increase in the molar ratio leads to an increase in total concentration of ethers when the molar ratio is less than 8. Concentration of ethers was almost zero at the lowest molar ratio tested (TBA/glycerol = 2). The viscosity of the reaction mixture can explain the influence of the molar ratio on this reaction [11]. Given that these experiments were conducted under the same reaction conditions and the stirring speed was the same, the very low concentration was likely due to the higher viscosity of the reaction mixture. When the TBA/glycerol ratio was low, the higher viscosity led to less mass transfer between the phases. As the ratio was increased, mass transfer became easier and the highest concentrations were obtained when the molar ratio was 8. When the molar ratio was 10, more than two times the quantity of TBA was present. The surplus TBA enhanced the side reaction, having a negative influence on the ether concentration. In summary, the molar ratio affects the reaction in a positive way; it is essential to use large excesses of TBA to maximize total ether concentration. Therefore, the desired level of molar ratio should be set from 4 to 8, while more accurate assessments will be done with the design of the experiment approach.

*3.4. Effect of Temperature.* Glycerol conversion increased with increasing reaction temperature. At high temperatures, glycerol was not totally converted due to the occurrence of deetherification reactions, which became increasingly important as the reaction temperature was increased [10]. A higher temperature also enhanced the secondary reactions, such as the disproportionation of glycerol ethers [12], which can be observed from the decreased glycerol conversion and product yields. This also means that the activation energies in the side reactions are higher than those in the etherification reactions. In addition, in this study, one of the reactants, TBA, has a comparatively low boiling point of 82.4°C under a standard atmosphere. The evaporation near 80°C would become so serious that the reflux condenser would be unable to prevent a portion of the reaction mixture vapor from leaving the condenser, resulting in a large loss of TBA. This in turn would reduce the extent of glycerol conversion. On the other hand, the temperature also affected the reaction by its effect on the viscosity of the reaction mixture similar to the molar ratio. A higher viscosity can impede mass transfer and lower the selectivity. Figure 7 shows the effect of temperature on glycerol conversion and selectivity of DTBG and TTBG. The tert-butylation of glycerol was studied using Amberlyst 15 over the temperature range, 50 to 80°C. The conversion of glycerol increased with increasing temperature. On the other hand, as the temperature increased, the side reaction of the disproportionation of glycerol ethers would also occur, as shown in the mechanism section. The highest glycerol conversion was observed at 70°C (97.0%); the selectivities of DTBGs and TTBG were also highest at 70°C (30.3%). This pattern of temperature influence agrees with previous results [16]. In summary, temperature affected the reaction in the following aspects: enhancement of the side reactions; TBA evaporation; and changes in the viscosity of the reaction mixture. As mentioned previously, viscosity is also a function of the molar ratio. Therefore, further research will be needed to study the relationships between temperature and other factors.

## 4. Conclusions

The etherification reaction of glycerol and tert-butyl alcohol to GTBEs using Amberlyst as a catalyst was investigated to produce as much DTBGs and TTBG as possible while minimizing the production of MTBGs. Gas analysis by GC was performed. The influence of the catalyst type and loading, reaction time, molar ratio, and temperature on the etherification reaction was investigated in detail by calculating the conversion of glycerol and the selectivity of GTBEs. The experimental results showed that Amberlyst 15, which has large surface area and pore volume, was the best catalyst. The catalyst loading was found to have some influence on the etherification reaction. Based on the reaction time, the reaction should be set between 5 and 8 hours to obtain the maximum concentration of glycerol ethers. This might be caused by the reverse reaction of glycerol ethers. The molar ratio affected the reaction in a positive way. Therefore, it is essential to use large excesses of TBA to maximize the product yield. The highest glycerol conversion and the highest selectivity of DTBGs and TTBG were observed at 70°C.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

## Acknowledgment

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