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The Synthesis of Glycerol Carbonate from Biodiesel By product Glycerol and Urea over Amberlyst 15

Reviana Inda Dwi Suyatmo, **Hary Sulistyo, Wahyudi Budi Sediawan**

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Departemen Teknik Kimia, Fakultas Teknik, Universitas Gadjah Mada, Jl. Grafika No. 2, Yogyakarta,

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Abstract

The growing utilization of biodiesel as a renewable fuel has generated a large surplus of glycerol as a major byproduct. The prices of glycerol continue to drop in such an oversaturated market. Therefore, new uses are being developed for glycerol to produce value-added chemicals. Among those chemicals, glycerol carbonate has many application in various fields. Glycerol carbonate is mostly used as a solvent in cosmetic and pharmacheutical industries due to its low toxicity, high boiling point, and low vapor pressure. The synthesis of glycerol carbonate from glycerol and urea using Amberlyst15 as a catalyst was being conducted in this study. The reaction was carried out using a batch reactor for 5 hours with the condition of the reaction temperature was around 120°C, mole ratios of reactant of urea:glycerol were 0.8:1, 0.9:1, 1:1, and 1.2:1 , catalyst concentrations were 2%, 2,5%, 3%, and 4%, and mixing speeds were 370 rpm, 525 rpm, and 700 rpm. It is found that the optimum conversion of glycerol was obtained at 120°C with 5 hours of reaction using an equimolar amount of glycerol and urea with catalyst load of 3%. Mixing speed did not affect glycerol conversion. Amberlyst15 as catalyst was also stable enough to be reused at least for three times.

INTRODUCTION

Along with the depletion of petroleum, renewable energy sources are needed. Biodiesel is a promising alternative source of renewable energy. Biodiesel or fatty acid methyl ester compounds are generally prepared by transesterification of vegetable oils with methanol, forming glycerol as a byproduct. The amount of glycerol produced is about 10% (weight) of biodiesel production (Knothe et al., 2005; Yang et al., 2012). Glycerol production continues to increase every year by about 2.8% (Pagliaro & Rossi, 2008). In Indonesia, the production of glycerol from the biodiesel industry in 2013 reached 724,000 tons (Direktorat Jenderal Industri Agro, 2014). Before the development of biodiesel industry, the price of crude glycerol was around Rp 21.000 / kg, but now the price is only about Rp 1,500 - Rp 7,500 / kg (Hansen et al., 2009). This low selling price of glycerol can be overcome by the utilization of glycerol as a raw material for the manufacturing of value-added chemicals.

One of the interesting possibilities of glycerol utilization is as raw material of glycerol carbonate. Glycerol carbonate is a material with high boiling point, low vapor pressure, low toxicity, low flammability, and good moisturizing ability. Glycerol carbonate is widely used as a solvent and intermediate (Nunes et al., 2013). One of the high-value chemicals that can be synthesized from glycerol carbonates is glycidol which is widely used in the textile, plastics, pharmaceutical, and cosmetic industries (Yoo et al., 2001).

Glycerol carbonates can be synthesized from glycerol, as the source of OH, and carbonate

Corresponding author:
Departemen Teknik Kimia, Fakultas Teknik, Universitas Gadjah Mada
Jl. Grafika No. 2, Yogyakarta, 55281
E-mail: reviana_suyatmo@yahoo.co.id

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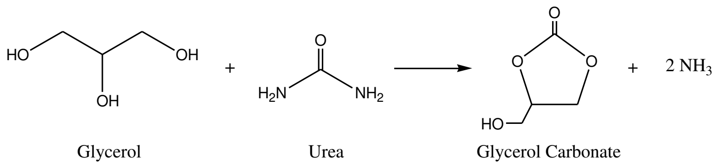

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group sources, such as phosgene, alkyl carbonate, alkylene carbonate, CO and O_2, CO_2, and urea. Glycerol carbonates were initially made by using phosgene but this process was very hazardous because phosgene was a toxic substance (McKetta & Cunningham, 1984). Glycerol carbonates could be synthesized by oxidative-carboxylation reaction between glycerol, CO, and O_2 by using Cu as a catalyst (Teles et al., 1994). However, this route had limitation in production costs, because CO was a toxic material whose safety in the laboratory and industrial scale was quite difficult. Research of Aresta et al. (2006) on carboxylation reactions between glycerol and CO2 by using n-Bu2SnO as a catalyst resulted in a low (<10%) yield of glycerol carbonate due to the low solubility of CO_2 in glycerol. Ochoa-Go'mez et al. (2012) concluded that transesterification of ethylene carbonate or dimethyl carbonate using CaO catalyst resulted in a high conversion of glycerol carbonate, above 90%. However, CaO was deactivated rapidly in the first use and the regeneration was expensive. The route of glycerol carbonate synthesis through transesterification of alkylene carbonate is also used by Huntsman company to produce glycerol carbonate by reacting glycerol and propylene carbonate in the presence of catalyst at 100-150 ° C and 33 mmHg (Huntsman Corporation).

The glycerol carbonate synthesis route that is currently stealing the attention is glycerolysis using urea. The advantage of this reaction is that urea as a reactant is a material whose availability quite a lot and the price is not that expensive. In addition, the ammonia formed can be converted back into urea. Climment and Corma (2010) performed a synthesis of glycerol carbonate from glycerol and urea using MgO, CaO, Al / Mg, and Al / Ca catalysts. The results showed that the optimum catalyst was Al / Ca with 72% glycerol carbonate yield. Rahim et al. (2012) conducted research using gold and palladium as a catalyst. In addition to the expensive price, this catalyst also required a long reaction time.

In the synthesis of glycerol carbonate by using glycerol and urea, the use of solid base catalyst produced a high yield (Wang et al., 2011; Hammond et al., 2011). However, this catalyst had poor stability after being recycled. According to Kumar et al. (2012), the solid acid catalyst was a good catalyst in the reaction between glycerol and urea. The selectivity of glycerol carbonate reached maximum at 140 ° C and decreased at temperatures above 150 ° C (Aresta et al., 2009; Kim et al., 2011; Seemann & Kaszonyi, 2011; Jagadeeswaraiah, 2014). This might be due to the decomposition of glycerol carbonate into glycerol.

Acidic catalysts have been used in various studies on glycerol carbonate synthesis. Ochoa-Gómez et al. (2012) formed glycerol carbonate from glycerol and dimethyl carbonate by using Amberlyst39wet acid catalyst and resulted in a 33.9% glycerol conversion. Meanwhile, Vieville et al. (1998) conducted a study on the reaction glycerol and CO_2 by using cationic resin catalyst K2411 resulting in glycerol conversion of 8.2%. The use of an acidic catalyst in the reaction of glycerol and urea may activate the carbonyl group in urea which further reacts with glycerol to form glycerol carbonate.

In this study, the utilization of glycerol as a raw material for synthesis of glycerol carbonate was done by reacting it with urea by using Amberlyst15 as a catalyst. Amberlyst15 is a cation resin that provides the acid site that is needed. The highest operating temperature for Amberlyst15 is 120ºC. With the use of Amberlyst15 as a catalyst, it is desirable to obtain a high enough glycerol conversion with a relatively low operating temperature.

MATERIALS AND METHODS

Materials

The main materials used in this study were technical glycerol (95.78%), urea (98.57%), Amberlyst15, and $Na_2S_2O_3$ for titration.

Experimental Setup

Experimental setup used in this research is shown in Figure 1.

Synthesis of Glycerol Carbonate

Glycerol and Amberlyst15 were inserted into a three-neck flask, the cooling water was flowed, the

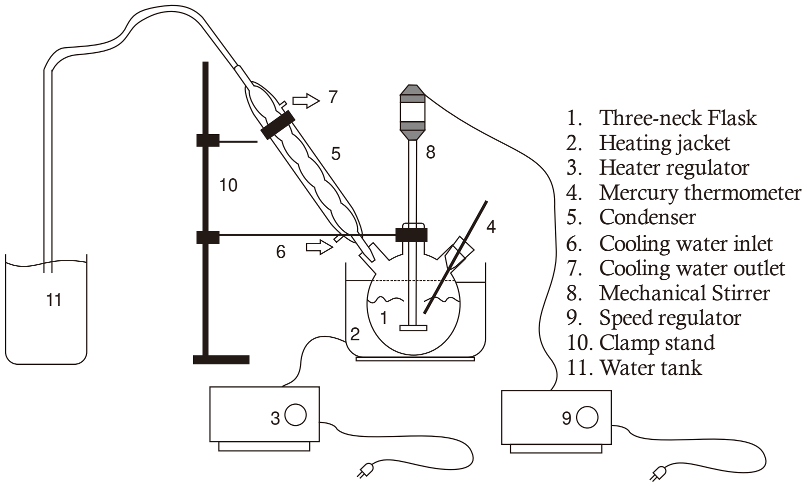


Figure 1. Experimental setup of glycerol carbonate production

mechanical stirrer was adjusted to rotation scale according to the variable, and then the heater was adjusted at 150 ° C. Urea was introduced when the temperature in the reaction flask reached 120°C and reaction time was recorded as t = 0. After urea was inserted, the temperature inside the reaction flask would drop to about 90 ° C, and would continue to rise until it reached a constant temperature (at about 120°C). The changes of temperature were recorded every 15 minutes and the samples were taken every 1 hour. The reaction run for 5 hours. Samples were analyzed by titration method to determine the level of glycerol. The qualitative analysis of glycerol carbonate in the reaction sample was carried out using GC-MS (Gas Chromatography-Mass Spectrometry). The variations in the study were the reactant molar ratio (urea/glycerol) of 0.9, 0.8, 1, and 1.2, mixing speed of 370 rpm, 525 rpm, and 700 rpm, and catalyst concentration of 2%, 2.5%, 3 %, And 4% (glycerol weight). Using the catalyst that was already used, the experiment was repeated to see the reusability of the catalyst.

RESULTS AND DISCUSSION

Variations of reactant molar ratio, mixing rate, catalyst concentration, and the reuse of catalysts were performed in this study. Through these variations, we could know the optimum conditions of glycerol carbonate synthesis by looking at the increase of glycerol conversion. Stability of the catalyst could be known through the reuse of it.

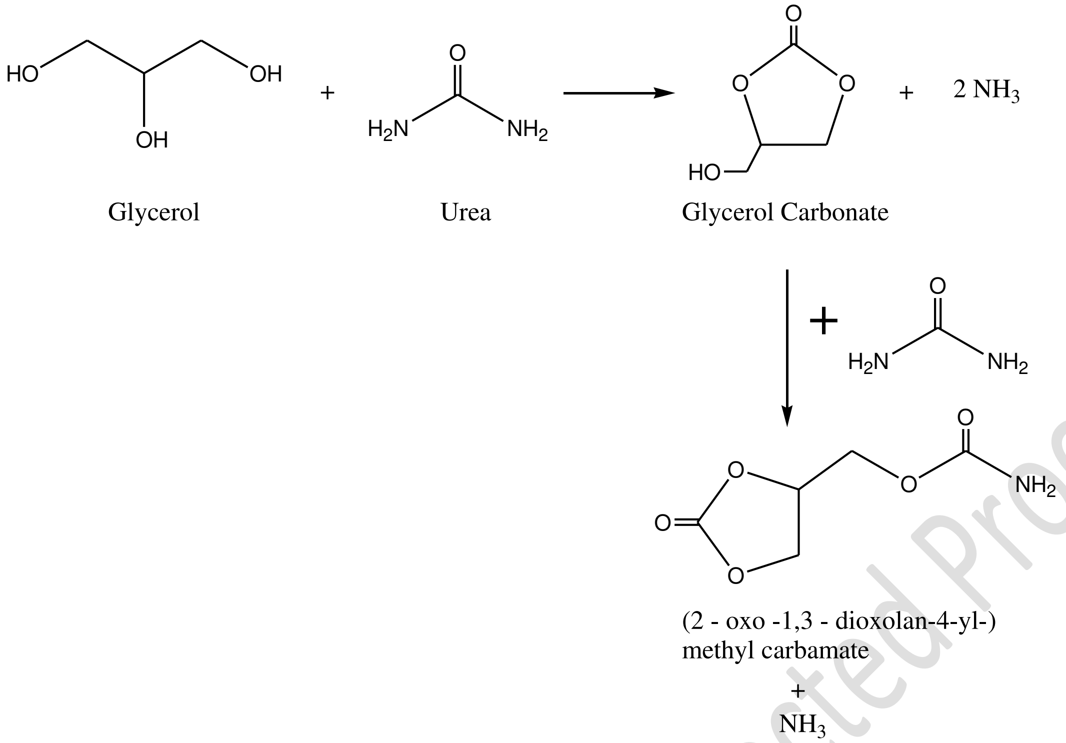
Effect of Reactant Molar Ratio

The molar ratio of reactants is an important factor in chemical reactions. The speed of the reaction is influenced by the concentration of the reactants, although they are not always the same for each reactant and for each reaction. In general, the higher concentration will increase the reaction rate because of the possibility of collision between the reactant particles will be greater. However, not always every collision will ensure the ongoing reaction. The effect of the reactant molar ratio on the increase of glycerol conversion can be seen in Figure 2. The stoichiometric molar ratio yielded the highest glycerol conversion of 58.49%. A study conducted by Jagaadeeswaraiah (2014) also showed the same result that the molar ratio of glycerol to urea 1: 1 was the optimum ratio for obtaining high selectivity of glycerol carbonate.

The lowest glycerol conversion of 34.92% was achieved by the ratio 1,2: 1. This was similar to Zhang & He (2014) which stated that the excess of urea would cause a side reaction to form methyl carbamate. Methyl carbamate was formed by the reaction between glycerol carbonate and urea. The occurrence of the reactions between urea and glycerol carbonate would reduce the possibility of collisions between urea and glycerol molecules thereby resulting in smaller glycerol conversion. The molar ratio of 1: 1 (stoichiometric) resulted in the highest conversion of glycerol so that this molar ratio was considered to be the most optimum ratio.

Effect of Mixing Speed

Stirring in chemical reactions aims to increase the likelihood of occurrence of collisions between reactant molecules. Stirring is closely related to external mass transfer or mass transfer from the main body of the liquid to the outer surface of the catalyst. If the stirring speed is increased, it will add turbulence which will cause the film layer



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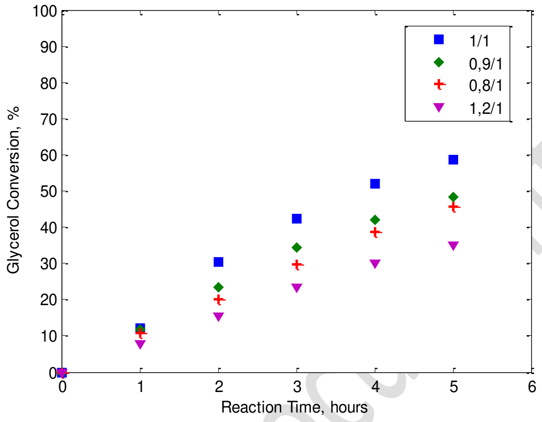

Figure 2. Effect of Reactant Molar Ratio (Glycerol/Urea) on Glycerol Conversion.

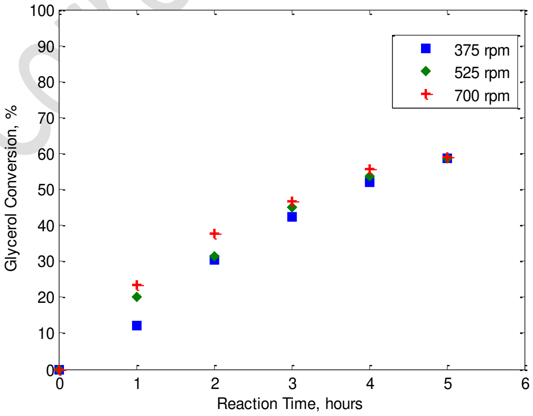

Figure 3. Effect of Mixing Speed on Glycerol Conversion.

to decrease so that the external mass transfer resistance will be smaller (Fogler, 2006).

The effect of mixing speed on the increase of glycerol conversion can be seen in Figure 3. Conversions of glycerol at various times for the three variations of stirring rate looked almost the same. During 2 hours reaction time, the difference was quite noticeable. But after that, the value of glycerol conversions were almost the same. In other words, the speed of stirring did not affect the conversion of glycerol. This result was similar with the outcome of research conducted by Yadav & Chandan (2014) on the synthesis of glycerol carbonate by using hydrotalcite catalyst. The effect of stirring speed was studied in the range of 600-1,000 rpm. Yadav & Chandan's results showed no significant change in reaction rate and glycerol conversion. This indicated that the external mass transfer resistance of the reactant to the outer surface of the catalyst might be negligible.

Effect of Concentration of Catalyst

Catalyst provides an active surface for the reaction. The addition of the number of catalyst means that the increase in the number of active surfaces that will cause an increase in the frequency of reactant collisions. The effect of the catalyst concentration on the increase of glycerol

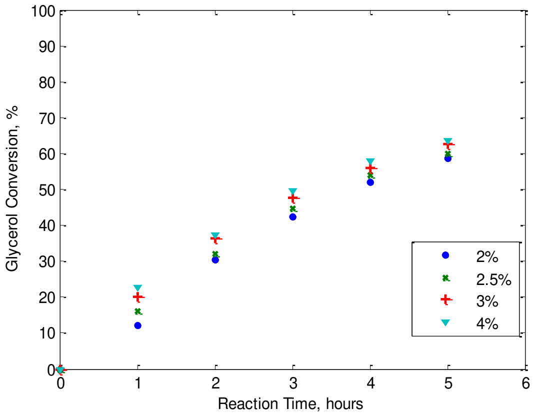

Figure 4. Effect of Catalyst Concentration on Glycerol Conversion.

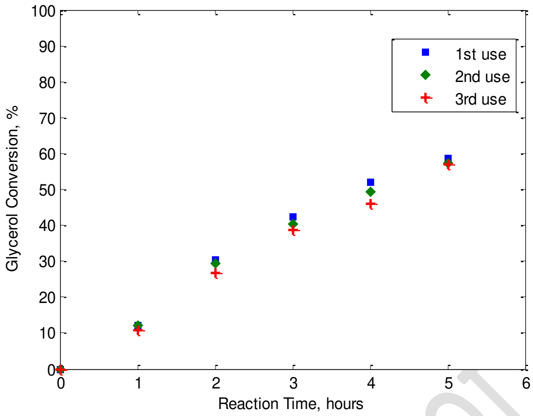

Figure 5. Effect of Amberlyst15 Reuse on Glycerol Conversion.

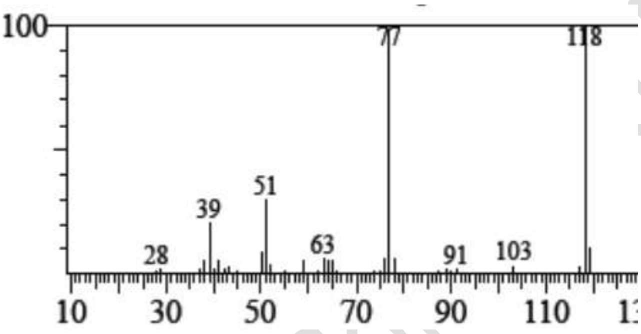

Figure 6. GC-MS Spectrogram

conversion can be seen in Figure 4. The experimental result showed that the increase of glycerol conversion from catalyst concentration 3% to 4% was very small compared to the increase of glycerol conversion from 2.5% to 3% concentration. Thus, it can be concluded that the concentration of Amberlyst15 3% was the optimum catalyst concentration because above that concentration, the increase of glycerol conversion was not significant.

Reusability Amberlyst15

The catalyst capability will decrease over time. This may result from overly high operating temperature or the presence of certain substances (reactants or reaction products) which may decrease the activity of the catalyst (Smith, 1981). The maximum operating temperature for Amberlyst15 is 120°C. To achieve a temperature of about 120°C, the heater regulator was set to about 150°C. In experiments, however, the reaction temperature often exceeded 120°C. The highest reaction temperature in the experiment was 127°C.

Figure 5 shows glycerol conversion at 3 times usage of Amberlyst15. The experimental result shows that there was no significant change in glycerol conversion. According to Teo & Saha (2004), partial desulphonation began to occur in Amberlyst15 when the reaction temperature was raised to 140 ° C. The highest reaction temperature in the experiments was still below 140°C so that it can be said that the stability of Amberlyst15 was quite good.

Analysis of Glycerol Carbonate

Glycerol carbonate or the desired product was analyzed using GC-MS (Gas Chromatography-Mass Spectrometry) to determine its presence in the mixture of reaction product. The GC-MS analysis yielded several peaks, one of which has a spectrum as shown in Figure 6. In Figure 6, it can be seen that there was a presence of a compound with molecular weight of 118, corresponding to the molecular weight of glycerol carbonate. This indicated that glycerol carbonate was formed in the reaction.

CONCLUSION

Based on the results and discussion, it can be concluded that the reaction of glycerol carbonate synthesis was influenced not only by the molar ratio of the reactant but also the concentration of the catalyst. Other variable such as stirring or mixing speed did not affect the conversion of glycerol. The optimum glycerol conversion of 62.76% was obtained under the operating conditions of constant reaction temperature of 120 o C, the stoichiometric reactant molar ratio, and the catalyst concentration of 3%. Amberlyst15 as catalyst could be reused at least for 3 times.

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