OPTIMATION OF GLYCEROL CARBONATE FROM REACTING GLYCEROL AND UREA USING LIMESTONE AS CATALYST SOURCE

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Abstrak. Penelitian tentang sintesis dan optimasi gliserol karbonat dari gliserol dan urea menggunakan batu kapur alam sebagai sumber katalis telah dilakukan. penelitian itu bertujuan untuk menghasilkan gliserol karbonat dengan menggunakan katalis $CaCO_3$ dan CaO dari batu kapur alam yang tersebar luas di Sulawesi Tenggara. Katalis ini dibuat melalui proses kalsinasi batu kapur pada suhu 750^oC selama 3 jam kemudian dikarakterisasi menggunakan X-Ray Flourescence (XRF). Katalis yang telah diperoleh ditambahkan dalam gliserol dan urea (substrat) untuk menguji sifat katalisnya melalui reaksi karbamoilasi dengan rasio mol substrat 1:1 dengan konsentrasi katalis 5 % massa terhadap gliserol. Optimasi reaksi dilakukan dengan mengubah beberapa parameter reaksi yaitu temperatur, waktu reaksi dan rasio katalis terhadap reaktan. Identifikasi produk dilakukan menggunakan Fourier Tansform Infrared Spectroscopy (FTIR) dan didukung oleh data Gas Chromatography (GC). Optimasi suhu,waktu dan konsentrasi katalis pada reaksi katalisis diperoleh pada temperatur 140oC selama 4 jam dan menggunakan rasio mol katalis terhadap substrat 5%

Kata kunci: Gliserol karbonat, Katalis, Batu Kapur alam

Abstract. Synthesis of glycerol carbonate from glycerol and urea using natural limestone as a catalyst source has been conducted. The research aims to produce glycerol carbonate using $CaCO_3$ and CaO As catalysts from limestone which is widespread in Southeast Sulawesi.This catalyst was made from calsined limestone at a 750^oC for 3 hours and then characterized using X-Ray Fluorescence (XRF). The catalyst obtained was added to glycerol and urea (substrate) to test the catalyst properties with a 1: 1 mole substrate ratio with a catalyst concentration of 5% mass to glycerol. Reaction optimization was cunducted by changing reaction parameters namely temperature, reaction time and the ratio of catalyst to reactant. Characterization Product using Fourier Tansform Infrared Spectroscopy (FTIR) and Gas Chromatography (GC) . Optimization of temperature, time and catalyst concentration in the catalysis reaction was obtained at 140^oC for 4 hours and using a catalyst mole ratio to 5% substrate

Keywords: Glycerol Carbonate, Catalyst, Limestone

INTRODUCTION

Glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one) is the one of a glycerol derivative that has several uses such as elastomer, surfactant, adhesive, ink, paint, lubricant, electrolyte, and as important intermediate from polycarbonate, polyester, polyurethane, and polyamide. Glycerol have a dual function in which there is a cyclic carbonate group and a nucleophilic hydroxy group, this dual function compound that allows these

compounds to be used as a protective polar solvent, and safe for the environment. this compound can be applied to various organic and inorganic compounds as solvent, for example in the fields of cosmetics, paints, accumulators, and others (Damayanti *et al*., 2012).

The synthesis of glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one) from glycerol and urea is a new method to increase the use value of glycerol as a by-product of the biodiesel industry. This topic has taken a lot of attention from chemists, because it has many advantages, for example reducing CO_2 emissions because it is used in the synthesis reaction of glycerol carbonate (Zhou et al., 2008) and can replace the route of synthesis of glycerol carbonate from toxic substances such as phosgene and CO (Jerome *et al*., 2008).

The synthesis route and type of catalyst used to produce glycerol carbonate have been reported based on literature studies such as the reaction of glycerol and dimethyl carbonate (Ochoa-Gomez et al., 2009). However, this reaction route produces ethylene glycol (a by-product) that is difficult to separate from the product (Turney et el., 2013). The catalysts that have been used in this reaction are ZnSO4 (Zhang et al., 2003), MgSO4 (Okutsu, 2007). Both are quite effective homogeneous catalysts. Other catalysts that have been studied are Al / MgOx, Al / LiOx metal oxide mixture (Zhou et al., 2008), zirconium phosphate (Zhou et al., 2008), Co3O4 / ZnO (Rubio-Marcos et al., 2010), La2O3 (Wang et al., 2011), Au nanoparticles (Hammond et al., 2011), and zinc monoglycerate (Turney et al., 2013). Some catalysts have produced a high conversion reaching 70% with selectivity <100% at temperatures of 135oC. In addition 83% conversion was obtained at 140oC using zinc monoglycerate as a catalyst (Turney et al., 2013). Another route being developed at this time is the reaction of glycerol and urea through the carbamoylation-carbonation reaction used a Lewis acid catalyst. In this method, glycerol and urea are reacted with the same equivalent mole ratio under conditions of temperature 130-150oC in vacuum conditions followed by the separation of ammonia gas to maintain the equilibrium reaction. Some catalysts used in this reaction are Ni-based metal catalysts (Damayanti et al, 2012), ZnSO4 (Jimmy et al., 2015). Although several catalysts have been developed for the production of glycerol carbonate with quite good efficiency, however the reaction mechanism and the synthesis methods are still a topic that need to be developed to produce catalysts with high performance in normal conditions.

Limestone is a one of natural rock type that is widely available in Indonesia especially in Southeast Sulawesi. it is a type of sedimentary rock containing carbonate compounds. in general, the limestone are containing calcium carbonate ($CaCO_3$) crystal form calcite. This rock has white yellowish white, gray to black color surfaces. this rock is formed from the remains of shellfish as well as from the process of chemical precipitation with Density ranges 2.6 to 2.8 g/cm3 in a pure state with the crystalline form of calcite ($CaCO_3$) (Lukman *et al*., 2012).

The other calcium carbonate crystal form in limestone is aragonite ($CaCO_3$) which is a unstable mineral because at certain times it can change to calcite ($CaCO_3$) (Sucipto *et al*., 2007).The latest industrial products from limestone are ground calcium carbonate flour (GCC) and Precipitate Calcium carbonate (PCC) as a substitute for kaolin in paper industry (Aziz, 2010). Calcite mineral (CaCO3) is

the most stable phase and is widely used in the paint, paper, magnetic recording, textile, detergent, plastic, and cosmetics industries (Lailiyah *et al*., 2012). The calcium carbonate mineral can be converted to calcium oxide (CaO) through calcination to obtain pure calcium (Ca) which is used as a catalyst. therefore, limestone can be used as a catalyst source.

In this paper, the researcher developed a method of synthesizing glycerol carbonate by designing a catalyst derived from limestone and applying it to produce glycerol carbonate. This catalyst is expected to be a catalyst that has good catalytic properties. Therefore, this research is expected to be able to provide information about the continued use of local limestone of Kolaka which has been used as building material and has potential in the field of research and technology that can be developed

MATERIAL AND METHOD

Instrumentation

Oven, Furnace, Fourier Tansform Infrared Spectroscopy (FTIR) Alpha Bruker, Gas Chromatography Techcomp D-7900E, X-Ray Flourescence (XRF) ED Epsilon 3.

Materials

Limenstone, glycerol ($C_3H_5(OH)_3$), urea ($CO(NH_3)_2$), aquadest, methanol (CH_3OH) p.a

METHODS

1. Preparation of catalyst

Limestone is obtained from home industries in Pomala subdistrict, Kolaka, Southeast Sulawesi. The limestone is cleaned using aquadest and dried on the oven for 1 hour at 100oC. then, the limestone is crushed using mortar and pastel until to be lime powder (CaCO3) and filtered using a 200 mesh sieve. 30 gram CaCO3 is calcined at 750 oC for 3 hours and then characterized using X- Ray Flourescence (XRF)

2. Synthesis Glyserol Carbonates (Catalyst Test)

Glycerol 50 mmol (4.6 g) is reacted with 50 mmol urea (3.0 g), catalyst (CaCO3 and CaO) as much as 5 mol% against glycerol. This reaction is stirred at a constant rate of 640 rpm while being heated at the temperature as tested. Then 1 mL methanol is added. Catalyst separated using the filtration method.

3. Product Identification

Glycerol carbonate analysis using FTIR to see vibration of C=O Esters (-COester 1735-1820 cm-1) and Gas Chromatography (GC) at retention time (t) 17.5 minutes. Fifth, optimization of the catalyst reaction. is carried out as in the third stage with temperature variations namely 110, 120, 130, 140, 150, 160, 170^oC. Time variations are 1, 2, 3, 4, and 5 hours, and variations of catalysts concentration ; 1:20, 1:40, 1: 100, 1: 1000 to the glycerol substrate (4.6 g, 50 mmol) and urea (3 g, 50 mmol).

RESULTS AND DISCUSSION

1. Preparation of catalyst

The stages of limestone preparation starts from heating at 100^oC to remove the water content in the rock. then proceed with calcination at 750^oC for 3 hours to remove organic compounds that composed in limestone and to decompose $CaCO_3$ into CaO which can be used as a catalyst source. XRF analysis (X Ray Fluorescence) was carried out to determine the chemical composition of the limestone shown in table 1.

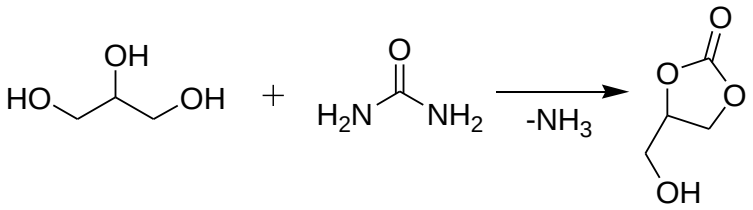
Table 1. Composition of limestone from XRF analysis (*X- Ray Flourescence*)

Sample	Weight (gr)	CaO	$CaCO_3$	Al_2O_3	Cr_2O_3	Fe_2O_3	K_2O	MgO	MnO	Na_2O	P_2O_5	SiO_2	SO_3	TiO_2	ZnO
		%	%	%	%	%	%	%	%	%	%	%	%	%	%
Calcined limestone (750 °C)	10,00	**52,22**	**28,16**	7,85	0,021	<0,01	<0,01	5,822	0,1	0,66	<0,01	5,32	<0,01	<0,01	<0,01
limestone	10,00	**47,53**	**32,8**	8,69	<0,01	<0,01	<0,01	7,945	0,1	0,73	<0,01	3,09	<0,01	<0,01	<0,01

The results of analysis show that the composition of limestone has CaO and $CaCO_3$ content at 47.53% and 32.8%, respectively. While natural limestone calcined at a temperature of 750^{o}C has CaO and $CaCO_3$ at 52.22% and 28.16%, respectively.

2. Catalytic Test and Product Characterization

The catalyst test in glycerol carbonate formation reaction is carried out by reacting glycerol and urea and calcined limestone (CaO) as catalyst at 750^{o}C and limestone without calcination ($CaCO_3$) with substrate mole ratio at 1:1 with a catalyst concentration of 5% mass against glycerol. Furthermore, gas nitrogen (N_2) is flowed to separate the ammonia formed as a byproduct. Urea is a source of carbonyl group and the source of ammonia gas formation in the reaction of glycerol carbonate formation.Synthesis reactions of Glycerol carbonate showed in figure 1. this Synthesis reaction namely carbamoylation/ carbonation. this method was carried out in schlenk flask without solvents and at ambient pressure at (1 atm).



Glycerol Urea Glycerol carbonate

Figure 1. Reaction of glycerol and urea to producing glicerol carbonate

The formation of glycerol carbonate species will be characterized by changes in vibration of the carbonyl group (CO amine) to the carbonyl group (CO ester) cyclic. From the results of the catalysis test validated by FT-IR, it was seen that the carbonyl group (CO ester) was formed in the reaction catalyzed by the calcined limestone at 750^{o}C as in Figure 2.

Identification of glycerol carbonate species was characterized by changes in vibration of the carbonyl group of CO amine to the CO cyclic ester. The results of the catalysis test validated by FT-IR, it was confirmed that the carbonyl group (CO ester) was formed in the reaction catalyzed by the calcined limestone at 750^{o}C as in Figure 2.

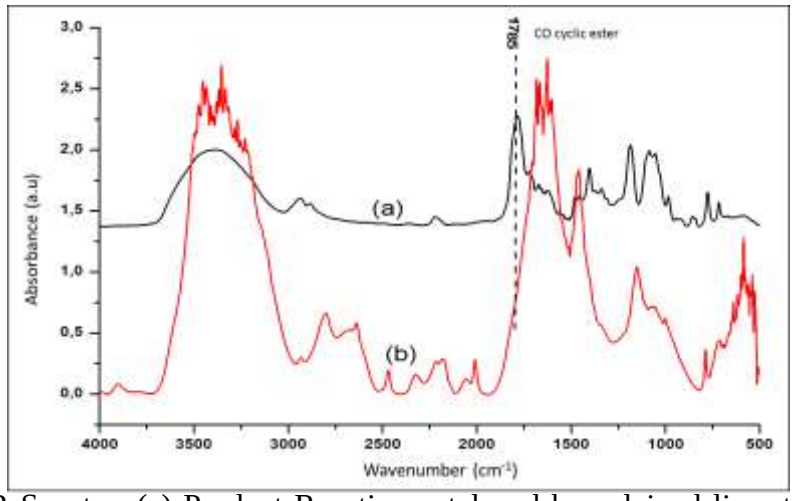


Figure 2. FTIR Spectra, (a) Product Reaction catalyzed by calcined limestone at 750^{o}C and (b) product reaction catalyzed by uncalcined limestone

Based on the results of identification using FTIR (Figure 2), the vibration of the carbonyl group (C=O) ester at wave number 1785 cm^{-1} was indicated as a typical vibration of glycerol carbonate. This guess is reinforced by the results of stacking between the product and the starting material used in the reaction as shown in Figure 3. The condition showing a change in vibration of the urea carbonyl (CO) amine group at wave number 1643 cm-1 becomes a vibration of the carbonyl group (CO ester) at wave number 1786 cm^{-1} was indicated that glycerol carbonate has been formed.

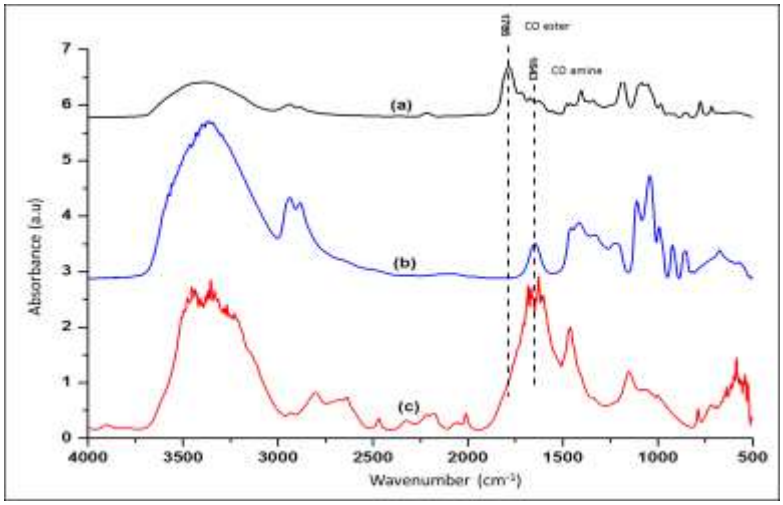


Figure 3. Glycerol Carbonate Spectra ; (a) calcined limestone catalyst at T 750^{o}C, (b) urea, and (c) glycerol

Identification using gas chromatography instruments (Gas Chromatography) was confirmed that the product (glycerol carbonate) have been formed and detected at a retention time of 17.5 minutes. This GC data reinforces FTIR data which shows that the synthesis of glycerol carbonate reaction

from glycerol and urea using limestone was successfully carried out.

Based on the data from the research conducted starting from limestone preparation, catalytic reaction testing of glycerol and urea, and characterization of product, this has given us information that the local limestone of Kolaka has the potential to be further developed in the catalyst sector.

3. Optimization of Catalytic Reaction

Optimization of time is done at a time variation of 1; 2; 3; 4 and 5 hours at the reaction time of 1 hour produced 35% of the product and increasingly stopped at the reaction time of 4 hours with a conversion amount of 71%. the conversion decreased when the reaction exceeded 4 hours to 54% (Table 2). FTIR analysis results show that there are other species formed besides glyserol carbonate, which are 5-(hydroxymethyl) oxzolidin-2-on at 5 hours (Turney et al., 2013) which are characterized by the formation of CO carbamate vibrations at 1736 cm-1.

Table 2. Effect of time on the conversion product

Number	Time (hour)	convertion (%)
1	1	35
2	2	39
3	3	46
4	4	71
5	5	54

Temperature optimization of the glycerol carbonate formation reaction was carried out in the range of 120–160^{o}C (table 3). The table shows that at a temperature of 140^{o}C gives the best increase in conversion to 58%, while at a temperature of 150–160^{o}C the conversion decreases to 13%. This decrease in conversion is caused by the formation of a side product species namely 5- (hydroxymethyl) oxozolidin-2-one at wave number 1736 cm−1 (Turney *et al*., 2013). This species is formed at temperatures above 150^{o}C.

Table 3 . Effect of temperature on the conversion of product

Number	Temperature (^{o}C)	Convertion (%)
1	120	34
2	130	46
3	140	58
4	150	21
5	160	13

Exp: reaction conditions: 5% cao mass to glycerol, glycerol-urea mole ratio = 1: 1, reaction temperature 140^{o}c, reaction time 4 hours. glycerol carbonate conversion is calculated based on the results of analyzes using gas chromatography.conclusion

Optimization of the amount of catalyst to the conversion is also done, the reaction is carried out by varying the catalyst concentration ie 0%, 1%, 2%, 2.5% and 5% mass of the substrate. Based on Table 4 the CaO catalyst has a good activity of a concentration of 1% to glycerol, whereas without the addition of the catalyst the reaction of glycerol with urea runs very slowly and results in very low conversion. The best conversion of the amount of catalyst is 2.5% and 5% with conversions reaching 51% and 71%.

Tabel 4. Effect of catalyst concentration in conversion

Number	Catalyst concentration (%)	Convertion (%)
1	0	6
2	1	9
3	2	11
4	2,5	51
5	5	71

Exp: Reaction conditions: 5% cao mass to glycerol, glycerol-urea mole ratio = 1: 1, reaction temperature 140^{o}c, reaction time 4 hours. Glycerol carbonate conversion is calculated based on the results of analyzes using gas chromatography.conclusion

CONCLUSION

The test of catalytic activity of CaCO3 and CaO from limestone for the synthesis of glycerol carbonate was successfully carried out. synthesis of glycerol carbonate from technical glycerol and urea was carried out with optimum reaction conditions at a temperature of 140oC for 4 hours, using mole ratio of 5% catalyst to substrate

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