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Oxidation of 1,2,3 –Propanatriol with Molecular Oxygen Using Pd/Γ-Al2o3 Catalyst in Water Solvent

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ABSTRACT

1,2,3-Propanetriol has been oxidized with molecular oxygen and catalysed by heterogeneous catalyst Pd/γ-Al2O3 in water solvent to produce glyceric acid (32.62%w). Glyceric acid was formed then reacted with sodium hydroxide in methanol to produce sodium glycerate (27). Product of reaction were characterized by FT-IR and 1H-NMR spectroscopy.

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1. INTRODUCTION

Indonesia is rich in natural vegetable resources such as palm oil, coconut, jatropha, soybeans and others. Along with the depletion of diesel fuel derived from petroleum, it is now being developed to manufacture biodiesel from plants such as jatropha and others as an alternative to diesel fuel.

Glycerol is a by-product of transesterification between triglycerides and methanol to produce biodiesel (methyl ester).[1]. With the increase in biodiesel production, it is certain that there will be an increase in glycerol production[2]. This caused the price of glycerol in the market to fall by more than 50% from the price in previous years[3].

Furthermore, glycerol can be a starting point for use in the synthesis of a large number of intermediates and other chemical products, such as their oxidation products which have high potential in organic synthesis.[4].

The glycerol molecule contains primary alcohol groups and secondary alcohols that can undergo oxidation reactions[5]. In general, secondary alcohol groups are more difficult to oxidize than primary alcohol groups, so that when glycerol is oxidized,[5]At first, an aldehyde will be formed and on further oxidation it will form a carboxylic acid: glyceric acid or tartronic acid.

Several previous researchers have also carried out glycerol oxidation using different catalysts, namely: oxidation of glycerol using an Au/graphite catalyst in NaOH solution to produce sodium glycerate product with a catalyst weight of 1% yielding up to 100% yield, oxidation of glycerol with

hydrogen peroxide using a bonded silicate in metals (Ti, V, Fe) and aluminophosphates with metals (Cr, V, Mn, Co) to give formic acid and a monoformate ester and a mixture of acetals as products, glycerol oxidation using a bimetallic Au-Pd catalyst on activated carbon with different ratio in liquid phase[6], yielding glyceric acid and glycolic acid as products.

The use of homogeneous catalysts in chemical reactions has been widely used, but the drawbacks of this catalyst are:[7]The resulting product will be difficult to separate from the catalyst. Meanwhile, with the use of heterogeneous catalysts, the product can be separated from the catalyst easily[8].

The Pd/γ-Al2O3 catalyst was used by Fatimah (2006) in the Inorganic Chemistry laboratory of USU's FMIPA to oxidize glucose in a mixed solvent of acetone and water to produce a mixture of open gluconic acid, gluconic acid in the form of lactone, and unoxidized glucose.[9], was used by Siahaan (2006) to oxidize sorbitol in aqueous solvents to produce glucaric acid, and was used by Lubis (2007) to oxidize fructose in sodium hydroxide solution to produce the sodium 2-keto gluconate salt.

Based on the brief review above, the researchers are interested in oxidizing the two primary alcohol groups of glycerol using oxygen and activated by a heterogeneous catalyst, namely Pd/γ-Al2O3 in water solvent to produce dicarboxylic acid.

This study aims to examine the function of heterogeneous catalyst Pd/γ-Al2O3 on the primary alcohol group oxidation reaction of glycerol using oxygen as an oxidizing agent. The results of the research are aimed at developing the utilization of a heterogeneous Pd/γ-Al2O3 catalyst system in oxidation reactions using molecular oxygen which will add information to chemistry, especially transition organometallic chemistry and to increase the usability of glycerol.

2. RESEARCH METHOD

2.1 Research procedure

2.1.1 1,2,3-Propanatriol . Oxidation

A total of 5 mL of 1,2,3-Propanatriol (79.89 mmol) was put into an autoclave tube equipped with a magnetic stirrer. Put into it as much as 25 mL of distilled water[10]. 0.0735 g of Pd/γAl2O3 catalyst was added. The autoclave tube was tightly closed, then oxygen gas flowed to a pressure of 150 psi and heated at a temperature of 600C[11]. Reaction time is stopped when oxygen is no longer absorbed[12]. Furthermore, the reaction results are filtered, then the filtrate is evaporated by the solvent and then vacuumed[13]. The products obtained were characterized by FT-IR and 1H-NMR . spectroscopy[14].

2.1.2 Making Salt from Glycerol Oxidation Results

Into a two neck flask equipped with a magnetic stirrer 0.3 g of the oxidation product was added and NaOH solution was added (0.5 g NaOH in 15 mL of methanol).[15]. The reaction mixture was refluxed at 600C for 5 hours[16]. The precipitate formed was then filtered and rinsed with methanol[17]. The precipitate was vacuumed to dry and then analyzed by spectroscopy[18]FT-IR and 1H-NMR.

2.2 Research Chart

2.2.1 1,2,3-Propanatriol . Oxidation

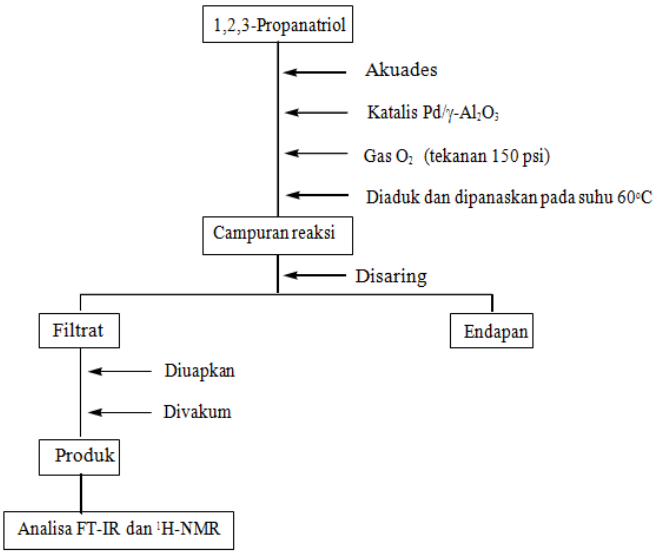

Figure 1. Oxidation of 1,2,3-Propanatriol

2.2.2 Making of Oxidized Salt

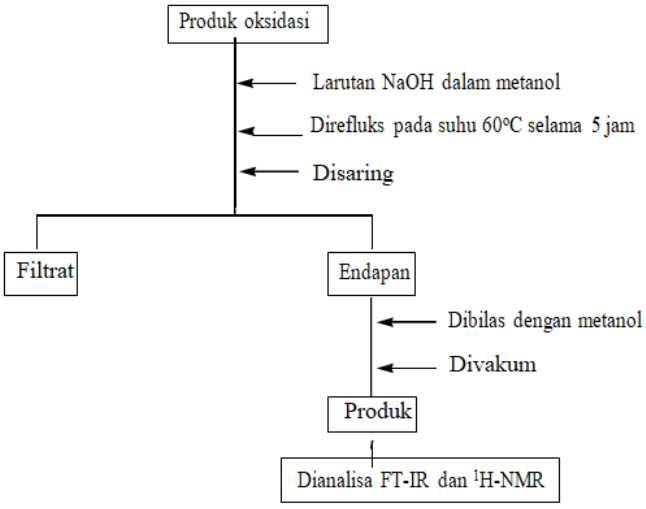

Figure 2.Making of Oxidized Salt

3. RESULT AND DISCUSSION

3.1 Results

3.1.1 1,2,3-Propanatriol . Oxidation

From the oxidation reaction of 1,2,3-Propanatriol (5 mL, 79.89 mmol) with molecular oxygen using a heterogeneous catalyst Pd/γ-Al2O3 in water solvent which took place at a temperature of 600C and

oxygen pressure of 150 psi resulted in an acidic solution (pH= 3) black in color. The mixture is filtered to separate the black solid[19]. The filtrate was then evaporated and then vacuumed to obtain a clear solution of 2.055 g (32.62%). The FT-IR spectrum (Figure 4.1) shows the absorption band in the wave number region 3367.78 cm-1, 2939.88 cm-1, , 1732, 02 cm-1, 1654.22 cm-1, 1420.01 cm-1 , 1227.57 cm-1, 1039.82 cm-1, 993.31 cm-1, 923.71 cm-1. Meanwhile, from the 1H-NMR spectrum (Figure 4.2), the chemical shifts were found in the 3.4-3.8 ppm and 4.2-4.8 ppm regions.

3.1.2 Making Salt from Oxidation Hasil

The reaction between the oxidation product with NaOH in methanol solvent produces 27% sodium glycerate salt. The FT-IR spectrum (Figure 4.3) shows absorption bands in the wave number region of 3416.70 cm-1, 1653.36 cm-1, 1443.29 cm-1, 1044.96 cm-1. And the 1H-NMR spectrum (Figure 4.4) showed a chemical shift at 2.6 ppm and 3.2-3.6 ppm and 8 ppm.

3.2 Discussion

3.1.2 1,2,3-Propanatriol . Oxidation

The oxidation reaction of 1,2,3-Propanatriol with molecular oxygen using a Pd/γ-Al2O3 catalyst in aqueous solvent produces glyceric acid. Glycerol has a primary alcohol group and a secondary alcohol group[20]. Because the oxidizing agent used in this oxidation is molecular oxygen which is a mild oxidizing agent, the primary alcohol group being oxidized is the primary alcohol group.

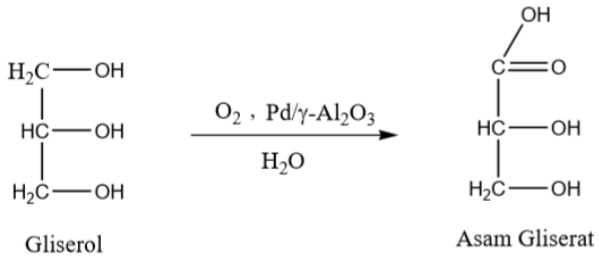

Figure 3. Oxidation of 1,2,3-Propanatriol

The FT-IR spectrum of the oxidation product (Figure 4.1) shows a wide absorption band in the wave number region of 3367.78 cm-1, due to the presence of OH groups from OH alcohols and acids. The presence of the alcohol OH group is supported by the C-OH absorption band of the primary alcohol which appears at a wave number of 1039.82 cm-1.

The appearance of absorption at wave number 2939.88 cm-1 was caused by CH absorption while in the 2850s it was caused by CH2 stretching. According to Silverstein (1986), the CH absorption is located in the 3000-2840 cm-1 region while the CH2 stretch is located near 2853 cm-1. Wave numbers 1732.02 cm-1 and 1654.22 cm-1 indicate that the C=O group of carboxylic acid has been formed. This can be compared with the wave numbers of glyceric acid obtained from SDBS (Spectra Data Base System) (Appendix 1), where the C=O group is found at wave numbers 1734 cm-1 and 1636 cm-1. According to Pavia, the C=O group in carboxylic acids is at a wavelength of 1730-1700 cm-1, and according to Biemann, the C=O group in carboxylic acids is at a wavelength of 1800-1650 cm-1.

Meanwhile, the CO stretching band for carboxylic acids appears wide at 1227.57 cm-1, and the out-of-plane bending of OH is at a wavelength of 923 cm-1. According to Silverstein and Pavia, out-of-plane bending is present at a wavelength of about 930 cm-1. So from the above information it is obtained that there is only 1 primary C atom that is oxidized.

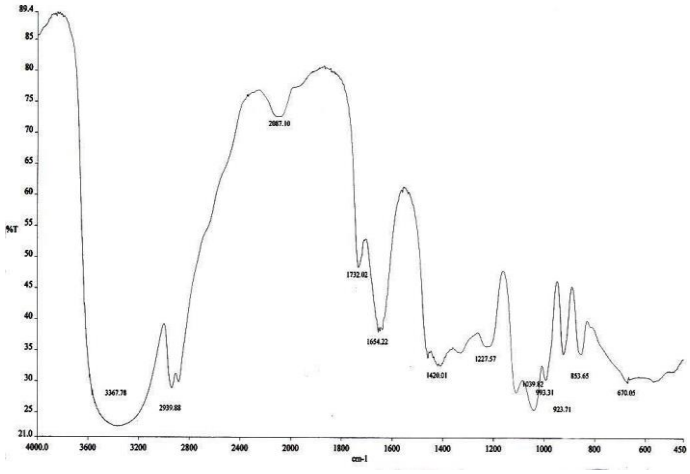

Figure 4. FT-IR Spectrum of Oxidation Results (KBr)

While the 1H-NMR spectrum of the oxidation product (Figure 4.2) in DMSO solvent showed a chemical shift in the 3.4-3.8 ppm and 4.2-4.8 ppm regions. The chemical shift at 3.4-3.8 ppm is caused by the H protons bonded to the C2 and C3 atoms. While the shift at 4.2-4.8 ppm was caused by protons in the hydroxyl group. The hydroxyl chemical shift area varies widely, ie 2.0-4.0 ppm; 3.5-5.5 ppm, and 6.1 ppm. This arises because the position of the OH signal depends on conditions such as the solvent used, the concentration and purity of the alcohol and the presence or absence of water in the solvent or sample. In this case, 1H-NMR is only run between 0-10 ppm, so that the acid proton peak which is expected to appear at 11-13 ppm is not visible.

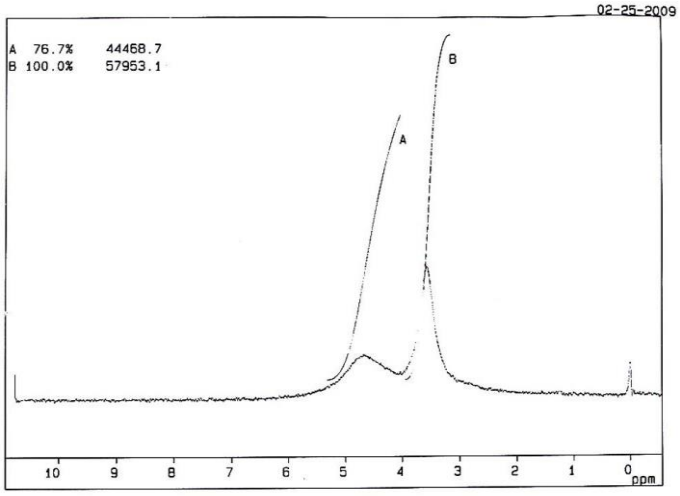

Figure 4. Spectrum of 1H-NMR Oxidation Results (DMSO)

3.2.2 Making Salt from Oxidation Hasil

Reaction Among results oxidation with NaOH in solvent methanol yields the sodium glycerate salt.

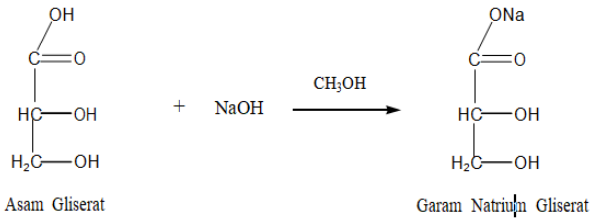

Figure 5. Making Salt from Oxidation Results

The salted FT-IR spectrum (Figure 4.3) shows an absorption at a wave number of 2800-3500 cm -1 which is the strain of OH alcohol supported by C-OH absorption of primary alcohol at 1044.96 cm-1. The presence of C-OH absorption in this primary alcohol indicates that there is a primary alcohol that is not oxidized. The formation of carboxylate salts can be seen by the asymmetrical strain at wave number 1653.36 cm-1 caused by the COO- strain which is supported by an absorption band in the 1590 cm-1 absorption band and the symmetrical strain is even weaker at 1443.29 cm-1.

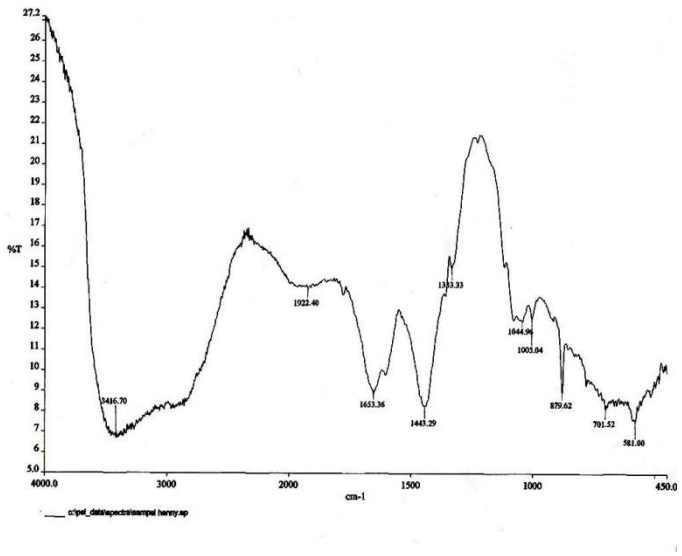

Figure 6. FT-IR Spectrum of Oxidized Salt (KBr)

The salted 1H-NMR spectrum (Figure 4.4) in DMSO solvent showed a chemical shift at 2.6 ppm and 3.2-3.6 ppm and 8 ppm. The chemical shift at 3.2-3.6 ppm is due to the H protons bonded to the C2 and C3 atoms. The shift at 8 ppm is probably due to the presence of impurities. While the shift at 2.6 ppm was caused by protons in the hydroxyl group. The hydroxyl chemical shift area varies widely, ie 2.0-4.0 ppm; 3.5-5.5 ppm, and 6.1 ppm . This arises because the position of the OH signal depends on conditions such as the solvent used, the concentration and purity of the alcohol and the presence or absence of water in the solvent or sample.

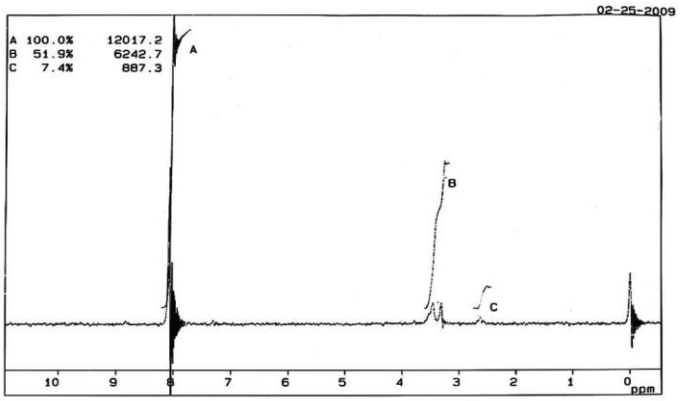

Figure 7. 1H-NMR Spectrum of Oxidized Salt (DMSO)

The mechanism of the reaction catalyzed by heterogeneous catalysts proposed by Morrell (2003) are:

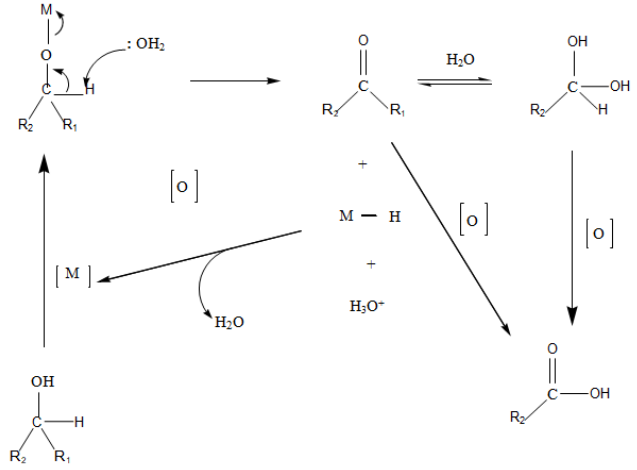

Figure 8. Mechanism of Catalytic Reaction

The alcohol is adsorbed on the metal surface and rapidly dehydrogenates to form a metal-hydride and release a carbonyl. The metal-hydride then reacts with oxygen to produce water and regenerates the metal surface to react again with the alcohol to continue the catalytic cycle. If the product is a ketone then there is no further reaction and the ketone is the only product. If the product is an aldehyde (R1 is H) then it reacts rapidly with water to give an aldehyde hydrate which can rapidly react with oxygen to produce a carboxylic acid. In an aqueous system, the reaction between the aldehyde hydrate and oxygen is very rapid to produce a carboxylic acid.

3. CONCLUSION

The conclusions drawn from the research are: (1) From the oxidation of 1,2,3-Propanatriol using molecular oxygen with a Pd/γ-Al2O3 catalyst in water solvent, the oxidation result of glyceric acid is 32.62%. (2) The results of the oxidation are carried out by reacting it in a solution of NaOH in methanol, yielding 27% sodium glycerate salt. Suggestions in this research is to use heterogeneous Pd/γ-Al2O3 catalysts, it is necessary to think about the right reaction conditions so that they can be used to catalyze oxidation reactions selectively.

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