The Ozonation Process for Increasing Value Added Tallow of Cow as A Polyol

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***Abstract*— The purpose of this research is to produce polyol, through the ozonation process and to find the best catalysts and solvents for the formation of hydroxyl group. The hydroxyl group is indicator of the formation polyol. The process of making polyols is unsaturated fatty acids of the cow through the process of ozonation, using the solvents of sorbitol and glycerol, as well as catalysts of sulfuric acid and sodium hydroxide. The reaction temperature is run at 50^{o}C and ozone levels are 4.33, 4.795, 5.021, 5.480 grams. The best results used a glycerol solvent, a sodium sulfate catalyst, and a 5.48 gram ozon content.**

Keywords—Component; Tallow, Polyol, Glycerol, Sodium sulfate, Ozon

I. Introduction

One cow weighing 400 kg will get a carcass (a part of the animal's body that has been slaughtered, whole, or cleaved along the spine, only the head, legs, skin, internal organs (viscera), and tail separated) in the form of fat (tallow) around 96-100 kg [1]. From this number, tallow will be able to produce about 25% of one cow with ideal weight. Meanwhile according to Lusiana Mustinda [2], in 100 grams of beef contains 14 grams of tallow. Tallow is a by-product from slaughtering cows. Tallow is still considered as cutting waste because its utilization has not been maximized. Currently, the use of tallow as food has begun to be abandoned due to the consideration of high saturated fat content. Food with high saturated fat content is considered a trigger for the narrowing of blood vessels. Besides, fat which relatively contains many unsaturated double bonds, will experience oxidation and form an unpleasant rancid odor so that its existence is often disputed [3]. This potential situation is the reason for the need for technology in the use of tallow to be used as raw material with more value.

Tallow has been widely used as a raw material for making soap because of the high stearic acid content in tallow can act as a soap hardener. Whereas in addition to being used as a raw material for making soap, tallow has the potential as a raw material for making polyols. Polyols are organic compounds that have more than one hydroxyl group, and in the material, the industry is widely used as intermediate and additive materials [4]. The amount of FFA (Free Fatty Acid) from tallow is between 0.75 - 0.7%. The titer point of tallow is generally above 40^{o}C. The main content of tallow is unsaturated fatty acids 43-49% (oleic acid 40-45%, and linoleic acid 3-4%) and saturated fatty acids 40.2-64% (palmitic acid 24-37%, stearic acid 14 –19%, myristic acid 2-8%, and lauric acid 0.2%) [5]. Because it has a large enough unsaturated fatty acid content in Tallow, Tallow can be used as a raw material for polyols through the ozonation process with the help of sorbitol or glycerol solvents. The use of polyols in the cosmetics world is as a substitute for non-natural moisturizers for skin cell tissue.

Application of ozonation technology in polyol synthesis using tallow with process conditions at 50^{o}C, ozonation time 54 hours, ozone content 4.32 gram, and fat ratio with solvent 0.75:1. The optimum process conditions at the hydroxyl number of 68.08 mg KOH/gram polyols are obtained so that they meet the minimum standard polyols that can be used in the manufacture of cosmetics [6]. In addition to ozonation technology, epoxidation methods can also be used for polyol synthesis. In 2014 Murniati et al [7] synthesized polyols from walnut seed oil and obtained the highest conversion percentage in the use of bentonite catalysts because in the epoxidation reaction the bentonite catalyst was able to degrade the group of oxygen quite high. Therefore this research aims is to produce polyols through the ozonation process and to find the best catalyst and solvent for the formation of hydroxyl groups.

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II. Research Methodology

The study was conducted using a series of ozonation devices presented in Figure 1 and the material used presented in Table 1.

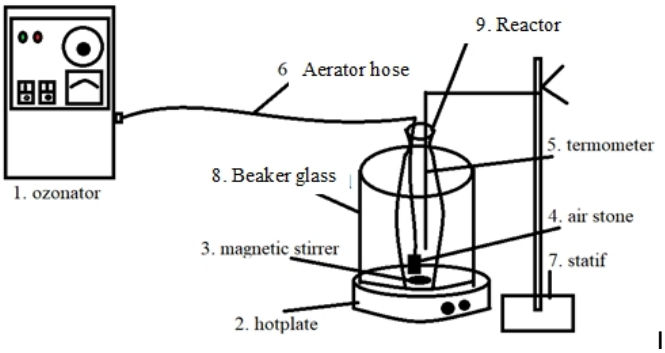

Figure 1. Series of ozonation tools

Table 1. Research material

Material	Spesification
Tallow	Solids
Sorbitol	Liquid (70%)
Glycerol Sulfuric acid	Liquid Liquid (98%)
Sodium Hydroxide	Solid (technical grade)
Sodium Carbonate	Solid (technical grade)
Silica Gel	Solid (technical grade)
Kalium Iodida	Solid
Sodium Thiosulfate	Solid
Potassium Hydroxide	Solid
Acetic acid	Solid
Pyridin	Solid
Acetic Acid	Liquid

The study was conducted by varying ozone levels (4.33; 4.795; 5.021; 5.480 grams), catalysts (H_2SO_4 and NaOH), solvents (sorbitol and glycerol) by setting the operating temperature (50^{o}C), catalyst volume (1%), and reactor volume (250 ml). Research parameters observed were hydroxyl numbers (BOH), acid numbers, and iodic numbers by testing through FTIR and NMR analysis. The research scheme refers to Figure 2.

The steps to do the research scheme began with the preparation of raw materials (liquefaction), followed by determining the best solvents (sorbitol and glycerol). The best results were followed by the selection of the best catalyst with the appropriate variable ozonation dose. The ozonation results were then measured parameters and analyzed using FTIR and NMR (Figure 3).

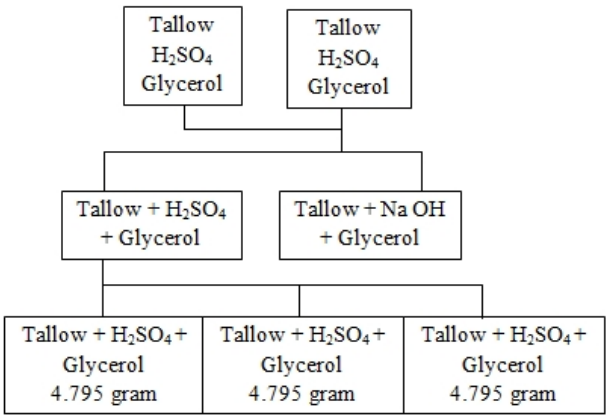

Figure 2. Research sceme

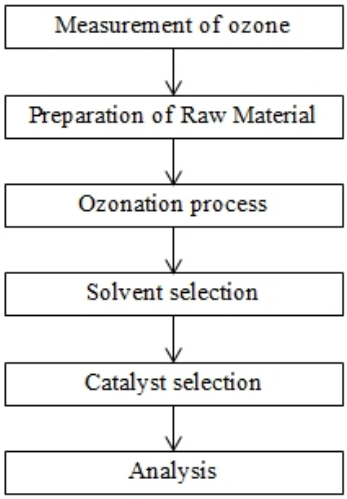

Figure 3. Flow chart

III. Results and Discussion

A. *Effect of Solvent on Polyols*

The solvent used is glycerol while the sorbitol solvent refers to the research of Adha & Gibson [6].

Table 2. Effect of Solvent on BOH number

Solvent	Temperature (^{o}C)	Ozone content (gram)	BOH mg.KOH/gram polyol
Sorbitol	50	4.33	68.08
Glycerol	50	4.33	72.56

The hydroxyl value produced by the glycerol solvent is higher than the sorbitol at the same temperature and ozone levels. This shows that the use of glycerol solvents is better used in the manufacture of polyol because glycerol is a major component of all fats and oils, in the form of esters called glycerides. The hydroxyl number produced by glycerol is higher in the manufacture of

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polyol from vegetable fat at 200ºC with an epoxidation time of 2.5 hours produced by BOH of 93.82 mg KOH/gram polyol [8]. A triglyceride molecule consists of one glycerol molecule combined with three fatty acid molecules. Triglycerides are the largest ingredient in oils or fats, which are components that are highly desirable to be reacted with glycerol. The reaction of triglyceride formation from glycerol with fatty acids is shown in Figure 4. The double bond found in the polyol is broken and the glycerol reacts to the polyol ester so that the number of polyol esters formed is directly proportional to the hydroxyl number.

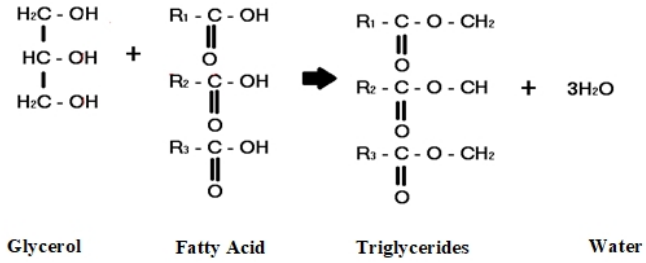

Figure 4. Reaction of Triglyceride Formation from Glycerol with Fatty Acid

If the fatty acids are reacted with sorbitol, the reaction will be imperfect because the amount of carbon in sorbitol is 6 while the fatty acid itself only has 3 carbon. So when reacted using sorbitol as if reacting with 2 glycerol (Figure 5).

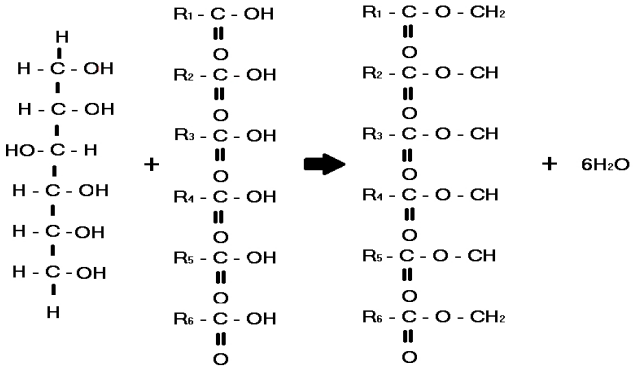

Figure 5. Reaction of Triglyceride Formation from Glycerol with Fatty Acid

B. *Effects of Catalysts on Polyol*

A chemical reaction can take place because of reactant molecules at a certain time experience an active state that is if the energy of the molecule is in an activation energy state. In this way, the chemical bonds in the molecule can break so that the product is formed. The function of the catalyst is to accelerate chemical reactions by reducing its activation energy [8].

Table 3. Effect of Catalyst on BOH Produced

Catalyst	Temperature (°C)	Ozone content (gr)	BOH mgKOH/gram poliol
H_2SO_4	50	4.33	72.56
NaOH	50	4.33	-

H_2SO_4 catalysts under the same temperature and ozone levels in mg KOH/gram polyol can be used in the process of bio polyol synthesis from beef tallow through the ozonation process. This condition is due to ozone having a stable ability under acidic conditions so that ozone is easier to break double bonds. This is reinforced in the research conducted by [6] catalysts used to obtain the best results in the initial study of bio polyol synthesis from beef fat, H_2SO_4 catalysts with a hydroxyl number of 68.08 mgKOH/gram polyol. Research conducted by Galuh & Hanafi (2008) [9] esterification of lauric acid with glycerol was reversible when catalyzed by acid because acid catalysts cause carboxylic acids to become conjugated. Esterification reaction with 1% H_2SO_4 catalyst can optimize the production of methyl esters due to the presence of proton (H^+) which is owned by H_2SO_4, and it is easier to release protons because it is fully ionized (α=1). The advantage of using an acid catalyst compared to an alkaline catalyst is that it remains effective as long as the reaction takes place in oil which still contains free fatty acids, but has a disadvantage when separating the reaction product. The more H_2SO_4 is added, the faster the epoxidation reaction takes place, but the oxygen obtained is getting lower. This is caused by the addition of concentrated H_2SO_4 which can increasingly accelerate the degradation of the oxidant group. Concentrated sulfuric acid which is still present in the aqueous phase can be a catalyst for the degradation of the oxidant group through side reactions in the form of hydroxylation reactions and the formation of ketone compounds and can be seen in Figure 6.

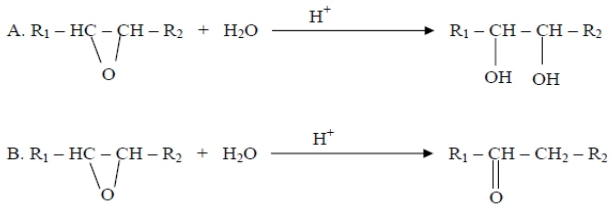

Figure 6. The Hydroxylation Reaction (A) and the Reaction of The Ketone Compound (B) in the Epoxidation using H_2SO_4

NaOH catalyst cannot produce hydroxyl numbers, because the desired product becomes soap. This is because the saponification reaction occurs,

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saponification is a hydrolysis reaction between an alkaline base and fatty acids that will produce glycerol and salt called fatty acid soap used, which is unsaturated fatty acids because it has at least one double bond between the constituent carbon atoms and is less stable so it is easy to react with other elements. Soap is an alkaline salt of high tribal fatty acids so that it will be partially hydrolyzed by water. Therefore the soap solution in water is alkaline. Triglyceride mixture is processed into soap through the saponification process with sodium hydroxide solution liberating glycerol. Saponification reaction using alkali is triglyceride reaction with alkali (NaOH or KOH) which produces soap and glycerin. In a study conducted by Wara & Rosidah (2012) [10] was used 1% NaOH catalyst in the manufacture of biodiesel from a mixture of beef tallow (Beef Tallow) and palm oil with a mole ratio of oil and methanol 1:6 then produces methyl esters which are transesterified oils.

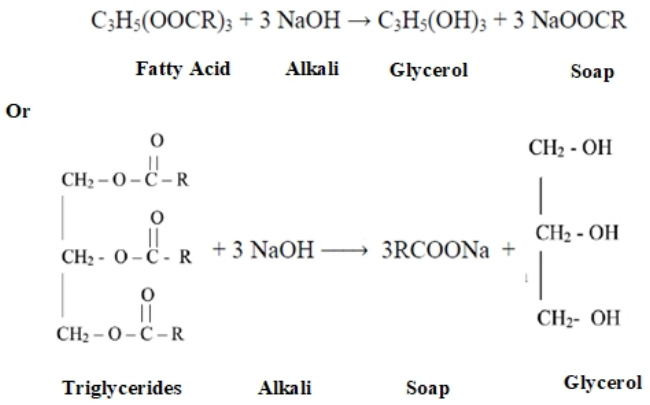

Figure 7. Saponification Reaction using NaOH

C. *Effect of Ozone on Formed Polyol*

Table 4. Effect of Ozone on Formed Polyol

Ozon content (gram)	Iod number (iod/100 gram sample)	Acid number (mgKOH/gram sample)	BOH (mgKOH/ gram poliol)
4.33	49.068	0.321	72.559
4.795	43.146	-	81.154
5.021	38.239	-	84.520
5.480	29.779	-	86.764

The table shows that the more ozone levels reacted in the polyol. the more bonds are broken and glycerol reacts to polyol esters. The more polyol esters formed. the higher the number of hydroxyls produced. This is made clear by Haifan (2017) [11] through the mechanism of ozonation reactions in fats to produce polyol where at low ozonation temperatures and high ozone levels are used to maintain the solubility of ozone in these fats or oils so that the hydroxyl number will increase. The higher the hydroxyl number of the polyol shows the quality of the polyol. the better the quality of the polyol. The higher the hydroxyl number. the greater the OH group which will make the molecular weight bigger [8,12]. The increase in hydroxyl number of the amount of ozone contained in polyols is inversely proportional to the number of acids produced. Acid numbers indicate the amount of free fatty acids present in the oil [12]. Large acid numbers indicate large free fatty acids derived from oil hydrolysis or due to poor processing. The higher the acid value the lower the quality.

The increase in ozone levels used for the ozonation process results in a decrease in acid numbers. Even the ozone level is more than 4.33 gram. there are no free fatty acids in polyols. In a study conducted by Murniati et al (2014) [7]. the acid number on the H_2SO_4 catalyst increased from the original walnut seed oil before epoxidation of 7.21 mg KOH/oil with H_2SO_4 catalyst to 23.07 mg KOH/gram oil with other catalysts decreased. at catalyst HCl the acid number is 1.12 mgKOH/gram oil and the Bentonite catalyst is 0.90 mgKOH/gram oil.

The effect of ozone levels on iod numbers produced also decreased with increasing levels of ozone given. The decrease in the iodic number is due to the termination of the double bond with increasing time of ozonation. A high iodine number indicates the unsaturation of a high oil or fat. The amount of iodine absorbed indicates the number of double bonds or unsaturated bonds. In a study conducted by Sri Seno Murniati et al (2014) [7] a decrease in iod number occurred. the iodine seed oil iod number was 111.50 iod /100 gram after oil became polyol through the epoxidation process with different catalysts. the iodic number decreased with a catalyst H_2SO_4 iod number of 84.22 iod /100 gram oil. HCl catalyst at 66.92 iod/gram oil and Bentonite at 30.82 iod/100 gram oil.

D. *FTIR analysis*

The formed polyols were characterized using Fourier Transform Infra-Red (FTIR). This characterization aims to determine the location of OH groups formed from the results of conversion into polyol. The ozonation reaction that occurs in the alkene groups in bovine fat will decrease with the increase of OH groups in the product. with the increase in OH groups indicating an increase in the number of polyol.

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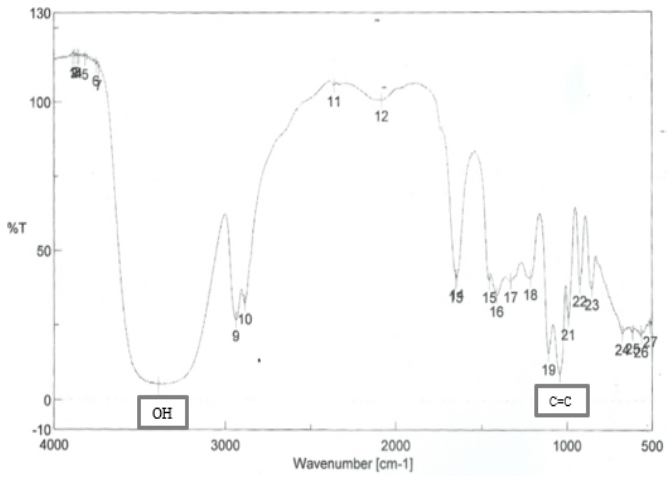

Figure 7. Wave number vs %T poliol

From the peak of absorption produced it can be seen that the formation of O-H functional groups and alkene groups (C=C) in polyol products. The O-H function group formed can be seen at wave number 3389.76 cm^{-1} with absorbance 1.2941. The peak absorption results were also seen in the alkene group (C=C) formed at wave number 1043.3 cm^{-1} with an absorbance of 1.0655. From these data. it can be seen that the absorbance value of the alkene group is smaller than the hydroxyl group. This shows that the decreasing alkene bond forms an increased hydroxyl (OH) group based on the FTIR test. Polyol synthesis was successful because of the absorbance of the alkene absorbance and the increase in the absorbance of the hydroxyl group.

E. NMR analysis

NMR spectrometry is used to find out more about functional groups that change in the formed polyol product. One parameter that can help interpret NMR spectra is the chemical shift. ^{1}H-NMR spectrophotometer aims to determine the number of hydrogen atoms in the polyol formed. Measurement with this spectrophotometer is done with methanol solvent. The 1H-NMR spectrum is shown in Figure 8.

Chemical shifts for the synthesis of polyols from bovine fat at 3.696 ppm indicate the presence of ^{1}H atoms in the OH group. Whereas based on the literature obtained by polyol compounds in general. the 1H atom in the OH group is at 3.65 ppm. These results indicate the number of hydrogen atoms in the synthesis compared with the number of hydrogen atoms from the literature is not much different.

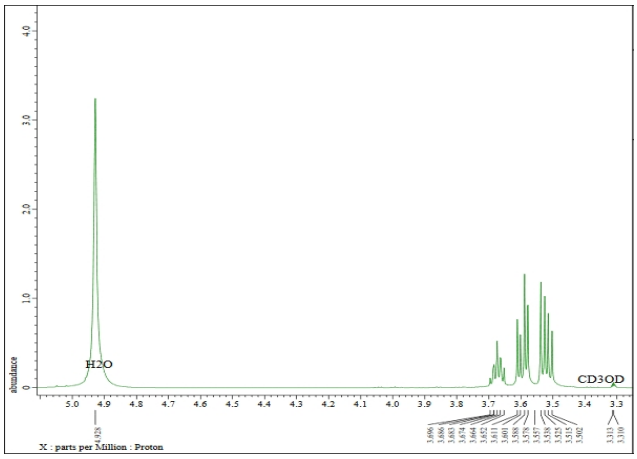

Figure 8. ^{1}H-NMR spectrum of syntesis of polyol

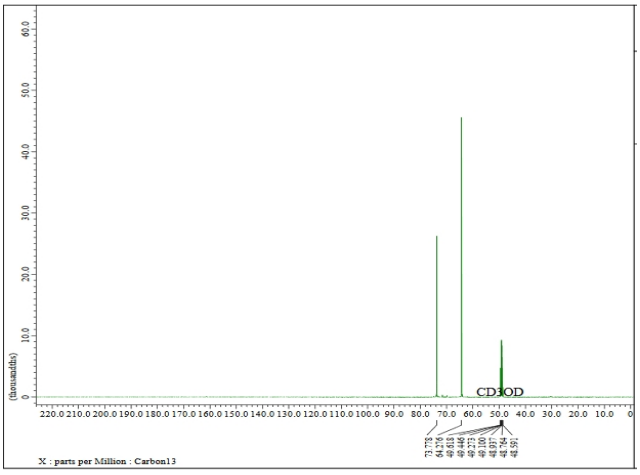

Figure 9. ^{13}C-NMR spectrum syntesis of poliol

The ^{13}C-NMR spectrum is shown in Figure 9. ^{13}C-NMR aims to find out the number of carbon atoms in the synthesis of cow fat polyols that are formed. Measurement with this spectrophotometer is done with methanol solvent.

C-H bonds at 64.276 ppm which indicate that the C-H bond signal is still forming. Whereas in the polyol literature in general the C-H bond signal is formed at 69.0 ppm. There is not a significant difference between the C-H bond signal in the synthesis results with the literature.

IV. Conclusion

The choice of catalyst and solvent influences the synthesis of polyols through the ozonation process. The best solvents are glycerol with H2SO4 catalyst and ozone levels of 5.480 grams.

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