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UTILIZATION OF UNSATURATED FATTY ACID FROM PAPAYA SEED OIL WASTE (*Carica papaya L*) AS RAW MATERIALS IN THE MAKING OF EPOXY COMPOUNDS

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ABSTRACT

Epoxy compounds are commercial products that can be used as stabilizers, plasticizers in PVC (polyvinyl chloride) and can be used as antioxidants in natural rubber processing, a s surfactants, anti-corrosive additives in lubricating oils and pesticide raw materials. Epoxy compounds produced by the reaction between unsaturated fatty acids and peroxy acid. The raw material in this research is papaya seed oil. The purpose of this research is to study the combination of catalyst concentration, the amount of H_2O_2 (mL) and stirring speed (rpm) on the characteristics of the epoxy compounds. In this study, the fatty acids contained in the raw material were reacted with hexane, glacial acetic acid, H_2O_2 with variations of 40 mL, 50 mL, 60 mL, and 70 mL, sulfuric acid as a catalyst with variations of 1.5%, 2%, 2.5%, stirring speed with variations of 400 rpm, 500 rpm, and 600 rpm for 180 minutes. The results showed that the best epoxy compounds results were obtained at a catalyst concentration of 2.5%, 70 mL H_2O_2, and a stirring speed of 600 rpm, which obtained an oxirane oxygen number of 3.52, an iodine number of 10.4058 and an oxirane oxygen conversion of 73 .76471 %.

Keywords: epoxy, epoxidation, papaya seed, oxirane oxygen.

INTRODUCTION

Papaya (Carica papaya L.) is an annual living plant in Indonesia. According to the Central Statistics Agency, in 2017 papaya production is 875.112 tons. The most widely used part of the plant is the fruit. Papaya seeds are only used as waste even though they contain oil that can be utilized as vegetable oils. Papaya seed oil contains oleic (C18: 1, 72.60%), palmitic (C16: 0, 18.00%), linoleic acid (C18: 2, 5.80%), stearic (C18: 0, 3.60 %), and other fatty acids such as myristic acid (C14: 0), palmitolet acid (C 16: 1), linoleanate (C18: 3), arachidic acid C (20: 0) which is less than 0.5% [1]. The content of fatty acids contained in papaya seed oil is potential to be used as a raw material in the making of epoxy compounds.

Epoxy compounds are the results obtained from the epoxidation process. The epoxidation reaction is defined as the process of oxidation of a double bond between two carbon atoms by an oxygen atom to form an epoxy/ oxirane ring [2]. Epoxidation reactions are influenced by several factors such as catalyst concentration, reactant concentration, stirring, reaction temperature, and reaction time. Epoxy compounds can be used directly as adhesives, appropriate flexors for polyvinyl chloride (PVC), and as a stabilizer for PVC resins to increase flexibility, elasticity, the strength and to maintain polymer stability against heat transfer and UV radiation. High oxirane ring reactivity causes epoxy can also be used as a raw material for several chemicals, such as alcohol, glycol, alkanolamin, carbonyl compounds, olefin compounds, and polymers such as polyester and resins. The characterization of epoxy compounds can be classified or named based on their oxirane content [3]. The content of fatty acids in papaya seeds makes papaya seed oil potential if used as a raw material in the making of epoxy compounds. Reports on the making of epoxy compounds with papaya seed oil as raw material have never been done before, it is necessary to examine the potential of papaya seed oil for the epoxy compounds produced.

EPOXIDATION

Epoxidation can be defined as an oxirane group reaction by oxidation of double bonds using oxidation of peroxy acetic acid and catalysts. Oxidation aims to convert double bonds in oil to epoxide by reacting oil with a mixture of formic acid and hydrogen peroxide [4].

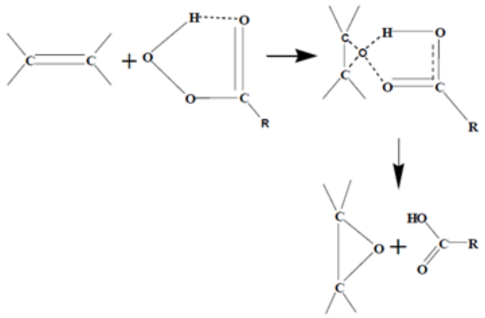

Figure-1. Reactions from the epoxidation process [6].

The characteristic of epoxy compounds is the presence of oxirane content. The higher the oxirane content, the better the epoxy compound produced. The number of double bonds contained in oil is determined by measuring the iodic number. The greater the iodic number, the greater the number of double bonds, the lower the melting point, and the higher the epoxy level. Fats that have low iodine numbers are more resistant to damage due

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to oxidation processes [5]. The reaction of the epoxidation process can be seen in Figure-1.

RESEARCH METHODOLOGY

Materials and Equipments

The raw materials used in this study are papaya seed oil, hexane pro-analyst (C_6H_{14} 40%), glacial acetic acid pro-analyst (CH_3COOH 100%), hydrogen peroxide (H_2O_2 30%), sulfuric acid (H_2SO_4 96%) as a catalyst, potassium iodine for analysis (KI), carbon tetrachlorine for analysis, KGaA brand reagents, Germany, Sodium Thiosulfate ($Na_2S_2O_3$), Hydrogen bromide for analysis (HBr). The equipment used in this study was a 500 mL three neck flask as a place for the reaction to take place, which was equipped with a thermometer, a hot plate with magnetic stirrer used as a heating medium, reflux, separating funnel, rotary evaporator and digital scales. The study was conducted with a variation of percent catalyst and variations in the amount of reactants (H_2O_2) with a rotation speed of 500 rpm. Papaya seed oil raw material will be analyzed by means of Gas Chromatography (GC) and the results of epoxy compounds will be analyzed by Fourier Transform Infra Red (FTIR) type Alpa FTIR Spectrometers.

PROCEDURES

The epoxidation reaction begins by mixing papaya seed oil with hexane, glacial acetic acid and sulfuric acid as a catalyst, then heated. After the mixture temperature reaches 50ºC, 30 percent hydrogen peroxide is added according to the variation, the temperature is slowly maintained at 60ºC during the addition of hydrogen peroxide. After finishing the addition of hydrogen peroxide. Then the mixture is heated according to the temperature and time determined based on the experimental treatment. Then the mixture is washed and evaporated to remove hexane. The analysis carried out is the analysis of iodine numbers using the method of WIJS (SNI-01-3555-1998) and analysis of oxygen (AOCS Official Methods CD 9-57 (1989)).

RESULTS AND DISCUSSIONS

The raw material used in this research is papaya seed oil which contains unsaturated fatty acids. Papaya seed oil is obtained from the extraction of papaya seeds that have been collected from salad vendors in the environment of the University of North Sumatra (USU) and then dried, mashed and extracted.

Papaya seed oil extraction yield obtained by 25% ± 5 (bk). Papaya seed oil that has been extracted first analyzed using Gas Chromatography (GC) to determine the components of fatty acids contained therein. After analyzing using GC, the content of unsaturated fatty acids was 51%. So it can be concluded that the raw material is potential to be processed into epoxy compounds because epoxy compounds are produced from the reaction between the double bonds contained in unsaturated fatty acids with active oxygen, which will convert the double bonds into oxirane rings so that epoxy compounds are formed [7].

Fourier Transform Infra Red (FT-IR) Analysis

Fourier Transform Infra Red (FT-IR) analysis of raw materials is carried out to identify functional groups contained in raw materials and epoxy compounds.

In Figure-2 (raw material) used there are several absorption peaks that appear, namely 2922, 47 cm-1, 1742, 58 cm-1, 1452, 55 cm-1, and 1159 cm-1. While in Figure-3 (epoxy compound), the absorption peaks that appear are 2923, 23 cm-1, 1741, 34 cm-1, 1452, 66 cm-1, 1452, 66 cm-1, 1159, 11 cm-1, and 841, 39 cm-1. The large absorption peaks at wave number 2922, 47 cm-1 contained in Figure-2 (raw material) and 2823, 23 cm-1 contained in Figure-3 (epoxy compound) indicate the presence of C-H groups. This C-H group indicates the presence of unsaturated fatty acids [8].

The absorption peaks at wave number 1742, 58 cm-1 contained in Figure-2 (raw material) and 1741, 35 cm-1 contained in Figure-3 (epoxy compound) indicate the presence of C=O groups. The carbonyl group seen in the results of the FT-IR analysis showed the presence of esters in papaya seed oil [9].

The absorption peaks at wave number 1452, 55 cm-1 contained in Figure-2 (raw material) and 1452, 66 cm-1 in Figure-3 (epoxy compound) indicate the presence of OH groups derived from fatty acid content [10]. The absorption peak at wave number 1159 cm-1 in papaya seed oil and 1159, 11 cm-1 in epoxy compounds indicates the presence of C-O ester groups. This group was obtained because of the addition of carboxylic acids which open the epoxide ring [11].

The absorption peak at wave number 841, 39 cm-1 in the epoxy compound indicates the presence of an oxirane group. The presence of these oxygenation oxirane groups is caused by the oxidation reaction of oil double bonds by active oxygen. Peroxy acid is obtained from the reaction between carboxylic acid and hydrogen peroxide [4]. The formation of oxirane groups is also affected by the presence of a catalyst, namely sulfuric acid (H_2SO_4) which will open the double bonds in papaya seed oil so that hydrogen peroxide can react and form oxidant groups. The mechanism of reaction of formation of oxirane groups can be seen in the following figure [6].

The Effect of H_2O_2 Volume and Catalyst Concentration on Oxygen Oxirane

The effect of the catalyst on the epoxidation reaction is directly proportional to the concentration of the catalyst used. The more catalysts used, the more double bonds are converted into epoxy so that the greater the amount of oxygen produced [12]. As the catalyst concentration increases, the amount of catalyst used will increase, so that the breaking of the double bond becomes more effective. This is shown in Figure-4 which shows the relationship of H_2O_2 volume and catalyst concentration at a constant stirring speed to the oxygen oxirane number.

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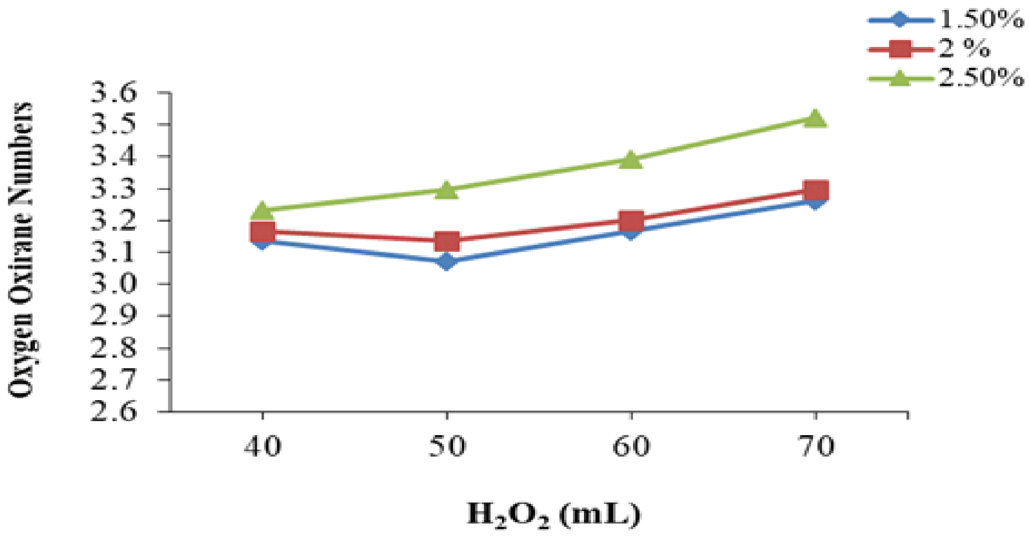

Figure-2. Relationship between H_2O_2 Volume and catalyst concentration at a stirring speed of 600 rpm for oxygen oxirane at a reaction temperature of 60ºC and reaction time of 180 minutes

The epoxidation reaction is also affected by the concentration of reactants, in this case hydrogen peroxide acts as a reactant. The greater the concentration of reactants will accelerate collisions between molecules so that the oxirane formed will be even greater [12].

Hydrogen peroxide will react with carboxylic acids and produce peracetic acid. Peracetic acid will react with a double bond to the unsaturated fatty acids.

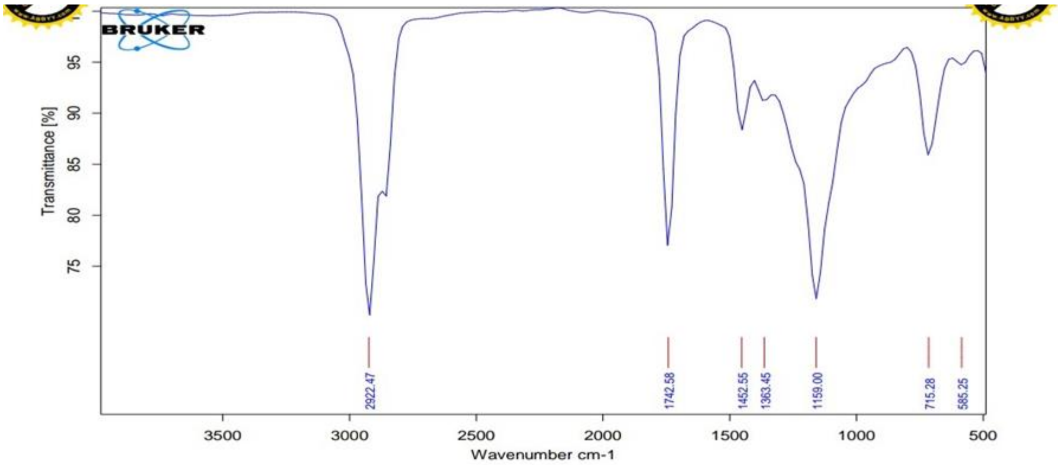

Figure-3. Results of Fourier Transform Infra Red (FT-IR) analysis of papaya seed oil as a raw material.

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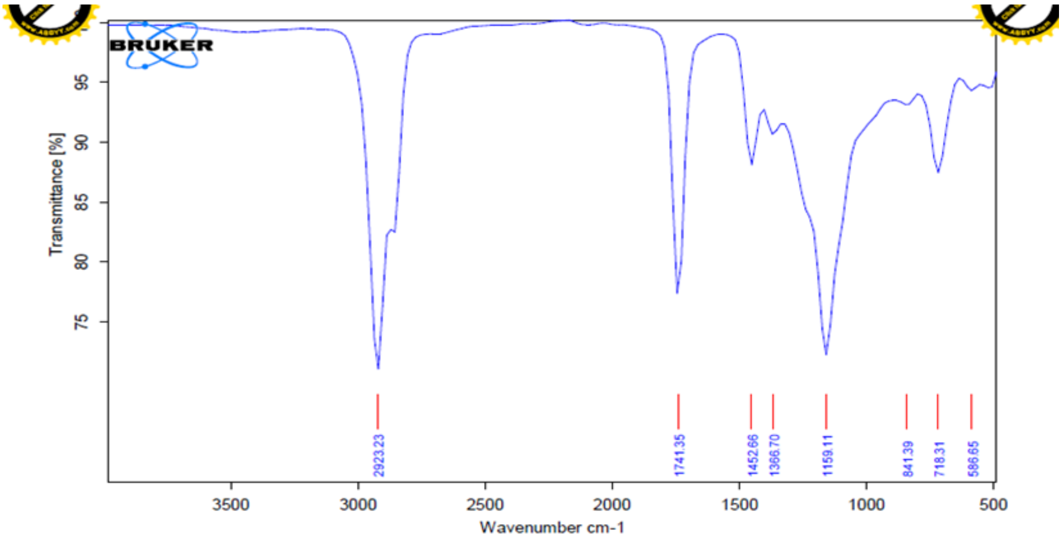

Figure-4. Results of FT-IR analysis of epoxy compounds.

In which it will react to the unsaturated fatty acids that have been broken by the catalyst and form an oxirane group. The more H_2O_2, the more peracetic acid is formed and the more oxygen groups are produced. With the number of oxirane groups produced, the iodine number will decrease, this is caused by the breakdown of the double bond so that the unsaturation of oil acids also decreases.

In Figure-4 you can see that the oxirane number increases with the addition of the amount of hydrogen peroxide used. However, at some point there is a decrease, this can be caused by the decomposition that occurs together with the oxidation reaction resulting in incomplete oxidation of the double bonds and reducing the oxygen bonds formed and also this reaction is reversible and exothermic so that there will be acetic acid and hydrogen peroxide return and temperature that is not fixed will result in the formation of peracetic acid is reduced. The reduction of peracetic acid that is formed will affect the oxidation of the double bonds and result in the formation of oxygen [13].

The highest value of oxygen oxirane is found in the making of epoxy compounds with the use of 70 mL H_2O_2, catalyst concentration of 2.5%, and the stirring speed of 600 rpm which is 3.52. The presence of this oxidation group is proven by the presence of epoxy groups that appear in the results of the FT-IR analysis in Figure-3. The results obtained are better than the results of the research obtained by Tambubolon [14] and Sinaga [15]. The oxygen oxirane number is one of the characterizations that become the standard in the use of epoxy compounds as plasticizers. The minimum limit value so that the epoxy compound can be applied as a plasticizer is 3.5 and the maximum value is 9 [16]. Then the best result of oxygen oxirane number in this study is 3.52 which has fulfilled the oxygen oxirane number criteria that can be applied as plasticizer.

Effect of H_2O_2 Volume and Catalyst Concentration on Fixed Speed on Iodine Numbers

Epoxy compounds are compounds that contain oxygen oxirane groups. Epoxy compounds are compounds produced from vegetable oil reactions that contain unsaturated bonds [13]. The level of unsaturation in oils or fatty acids can be expressed by iodine numbers. The iodine number indicates the magnitude of unsaturation of the fatty acids that make up the oil or fat. The higher the iodine number of oil or fatty acid, the higher the level of unsaturation of the oil or fat [17].

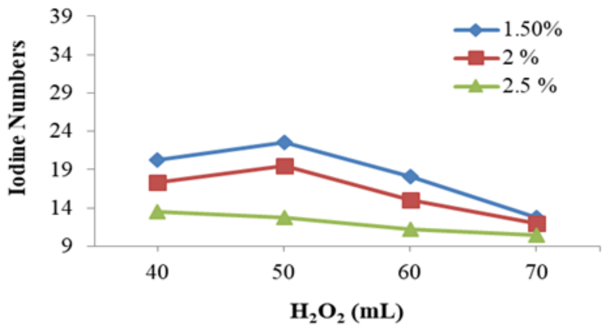

Figure-5. Relationship between H_2O_2 volume and catalyst concentration at 600 rpm stirring speed with iodine at reaction temperature of 60°C and reaction time of 180 minutes.

In this experiment, the lowest iodine number was found in the experiment with a catalyst concentration of 2.5%, 70 mL H_2O_2, and a stirring speed of 600 rpm, which is 10, 4058. The decrease in iodine number was caused by the occurrence of a double bond termination reaction in the fatty acids found in raw material by catalyst. The more double bonds that are broken off, the greater the chance of forming an oxirane group. The broken double bond will react with peracetic acid which acts as a reactant and forms an oxidant group. The reactants will help speed up the course of the reaction. The more reactants used, the

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more effective a reaction takes place in this case the formation of an oxirane group. In order to accelerate collisions between the ingredients used, stirring is carried out [18].

The decrease in iodine number will be proportional to the increase in oxygen oxirane number because the more double bonds are broken, the more likely it is to convert to an oxirane group. This is shown in the lowest iodine number, the oxygen oxirane number obtained, which is 3.52, which is the highest oxygen oxirane number in this experiment.

However, the results obtained in this experiment were no better than Tampubolon [14] which obtained the lowest iodine value of 0.44. This can be caused by the oxirane group having a high reactivity so that it is easy to open either in an alkaline or acidic state so that it is possible to form a by-product in the form of water.

Effect of H_2O_2 Volume and Catalyst Concentration on Fixed Speed on Oxygen Oxirane Conversion

In this experiment, the highest conversion was 73.76%. The conversion obtained will be proportional to the increase in the oxirane number. The increase in oxygen oxirane levels is influenced by the concentration of the catalyst, the higher the concentration of the catalyst used, the more double bonds in the fatty acids are broken. Then the broken double bond will react with the reactant, namely peracetic acid (formed from the reaction of H_2O_2 with acetic acid) and will convert the double bond to an oxirane group. Then, the more reactants used, the higher the conversion. In this reaction stirring is carried out which will help speed up collisions between material particles so that it can make the reaction more effective and result in higher conversions.

It is proven at the highest conversion, the highest oxygen oxirane number is obtained 3.52. The biggest conversion in this experiment was obtained with a variation of 70 mL H_2O_2, catalyst concentration of 2.5%, and the stirring speed of 600 rpm that is equal to 73.76%. The results obtained are better than the results reported by Tampubolon [14], which is 68.61%.

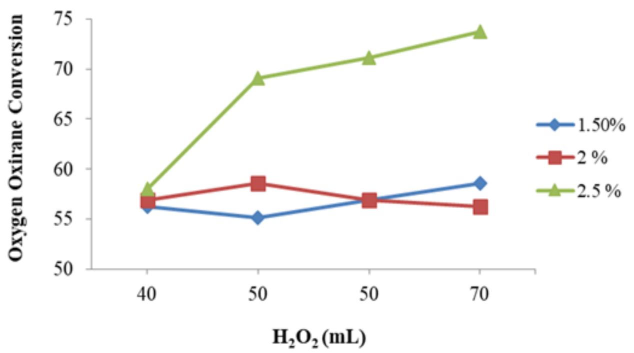

Figure-6. Relationship between H_2O_2 volume and catalyst concentration at a stirring speed of 600 rpm for oxygen oxirane conversion at a reaction temperature of 60°C and a reaction time of 180 minutes.

Correlation between Iodine Numbers and Oxygen Oxirane Numbers

In a compound iodine number states the unsaturation of the compound while the oxygen oxirane number is a number that shows the amount of oxygen bound from peroxide acid and the double bonds contained in oil [14].

The correlation of oxygen oxirane numbers and iodine numbers can be expressed by using this equation below.

Iodine Number = (-10,949 x oxygen oxirane number) + 48,733

Decreasing iodine number will be inversely proportional to the oxygen oxirane number. This is shown in Figure-7, which shows that an increase in oxygen oxirane will be accompanied by a decrease in iodine numbers. An increase in oxygen oxirane shows an oxirane group formed at the same time as the breaking of the double bond results in a decrease in unsaturation of fatty acids so that a decrease in iodine number occurs.

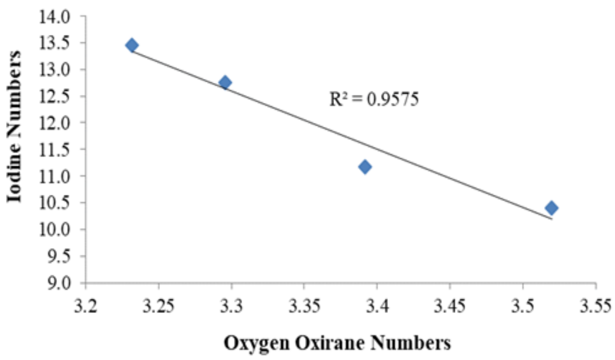

Figure-7. Relationship between iodine numbers and oxygen oxirane numbers.

CONCLUSIONS

Papaya seed oil can be used as a raw material in the making of epoxy compounds. The best oxygen oxirane number in this study is 3.52 so that it can be applied as a plasticizer because it meets the oxygen oxirane standard of the epoxy compound which can be applied as a plasticizer. The optimum conditions for obtaining the maximum oxygen oxirane in this study were at a catalyst concentration of 2.5%, 70 mL H_2O_2, and a stirring speed of 600 rpm.

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