The effect of amount of hydrogen peroxide on utilization of unsaturated fatty acids from avocado seeds waste into sourcing of raw materials in the making of epoxy compounds

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Abstract. Epoxy compounds are compounds that contain oxygen groups that are formed by an epoxidation reaction between peroxide acid with aromatic unsaturated compounds. Epoxy compounds can be applied as stabilizers, plasticizers in PVC (polyvinyl chloride) and can be used as antioxidants in natural rubber processing, as surfactants, anti-corrosive additives in lubricating oils and pesticide raw materials. The raw material in this research is avocado seed oil. The purpose of this study was to determine the effect of catalyst concentration, sulfuric acid, the amount of \( \text{H}_2\text{O}_2 \) (ml) and stirring speed (rpm) on the characteristics of epoxy compounds. In this study, the fatty acids contained in the raw material were reacted with hexane, glacial acetic acid, \( \text{H}_2\text{O}_2 \) with variations of 40, 50, 60 and 70 ml, sulfuric acid as a catalyst with a variations of 1.5; 2.0; and 2.5%, stirring speed with a variation of 400, 500, and 600 rpm, a reaction time of 180 minutes. The results showed that the best epoxy compound results were obtained at a catalyst concentration of 2.5%, 70 ml \( \text{H}_2\text{O}_2 \), reaction time of 180 minutes, and a stirring speed of 600 rpm, which obtained an oxirane oxygen content of 3.552, an iodine number of 1.269 and an oxirane oxygen conversion of 72.489%.

1. Introduction
Avocado production in Indonesia continues to increase every year, it can be proven with avocado production data in Indonesia in 2017 from the Statistics of Annual Fruit and Vegetable Plants in Indonesia, 2017 which reached 363,157 tons per year, along with the increase in avocado production, the avocado seed waste produced also increases. Therefore, it is necessary to handle avocado seed waste by doing a research on avocado seeds. Avocado (Persea Americana Mill) is an original plant from Central America that has a tropical climate and has spread to almost all sub-tropical and tropical countries including Indonesia. Avocados consist of 65% fruit flesh (mesocarp), 20% seeds (endocarp), and 15% fruit skin (pericarp). According to Risyad, et al., 2016 in his research on extraction, avocado seeds contain 34% oil, the results of the research Prasetyowati, et al., 2010 also stated that avocado seeds contain 16.62–25.15% oil and according to Pramudono, et al., 2016 produce avocado seed oil 18.69%. Avocado seed oil can be obtained by the extraction method and the pressing method. The extraction method causes less oil loss in the process, so that more oil is produced [1].

Epoxy compounds are chemical compounds obtained through the epoxidation process. Epoxy compounds as commercial products can be applied as solvents (plasticizers), stabilizers, coatings on polymer resins, and are antioxidants in natural rubber processing. Epoxy compounds can also be used as surfactants and anti-corrosive agents, additives in lubricating oils and raw materials for pesticides.

The content of unsaturated fatty acids found in avocado seeds is the main source for producing epoxy compounds, therefore researchers are interested in conducting this experiment and there are opportunities for researchers to obtain avocado seeds. In this study avocado seeds were obtained from juice sellers around campus. To get unsaturated fatty acids in avocado seeds, extraction methods are used. The result obtained is used as a raw material in the making epoxy compounds by avocado seed fatty acids reacted with hexane, glacial acetic acid, \( \text{H}_2\text{O}_2 \) and sulfuric acid as a catalyst.
2. Theory

Epoxidation aims to convert the double bonds in oil to epoxide by reacting the oil with a mixture of formic acid and hydrogen peroxide. Epoxidation can also be defined as an oxirane group reaction by oxidation of a double bond using oxidation of peroxy acetic acid and catalysts [3]. Epoxidation of the C = C bond produces a reactive cyclic ether, known as an epoxide. On an industrial scale, peroxy carboxylic acid is produced in-situ from hydrogen peroxide and carboxylic acid, as the presence of strong acid catalysts such as sulfuric acid and phosphoric acid.

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 iodic numbers are more resistant to damage due to oxidation processes [5]. The oxirane oxygen number is a typical parameter for determining the quality of epoxy compound products. Iodic numbers are used to calculate theoretical oxirane numbers [6].

Polyunsaturated fatty acid (PUFA) is a fatty acid that contains more than one double bond in its hydrocarbon chain. The dominant unsaturated fatty acids are linoleic acid (C18: 2), linolenic acid (C18: 3), arachidonic (C20: 4), EPA (C20: 5) and DHA (C22: 6) [4].

According to Risyad, et al., 2016 in his research on the extraction of oil from avocado seeds, the avocado seed oil produced has a predominant fatty acid which is plural unsaturated fatty acids namely linoleic acid (C18: 2) of 47.3531% (w / w).

3. Methodology and Research

3.1 Raw Material Preparation

Avocado seeds are obtained from juice sellers around campus, avocado seeds are peeled, crushed, dried, and extracted.

3.2 Avocado Seed Oil Extraction

This extraction method follows the method of Risyad, et al., 2016 with the research title “Oil Extraction from Avocado Seeds (Persea Americana Mill) Using N-Heptane Solvent” the operating conditions at extraction are selected from the best yield (%). Avocado seeds are extracted with three neck flasks, condenser reflux, Soxhlet, thermometer and hot plate. Avocado seeds that have been crushed, mashed, dried and sifted are fed into the extractor then followed by the addition of n-heptane solvent at T = 98ºC, t = 150 minutes, W = 20 gr and V = 250 ml. Avocado seed oil extraction is obtained [1]. After the avocado seed oil extraction is obtained, a separation is carried out using a rotary evaporator to purify the oil from the solvent. After being separated, the oil is analyzed using GC to determine the fatty acids contained in avocado seed oil, and avocado seed oil is used as raw material in the epoxidation process.

3.3 Epoxidation Reaction

The epoxidation reaction begins by weighing the raw material as much as 100 grams then put into a three neck flask that has been strung together with the condenser reflux, thermometer, magnetic stirrer, and hot plate. Then add 40 grams of hexane solvent, then 15 grams of glacial acetic acid, and sulfuric acid catalyst as much (1.5% ; 2.0% and 2.5%) after the temperature reaches 50ºC, hydrogen peroxide 30% as much (40 ml, 50 ml, 60 ml and 70 ml) slowly and the temperature is kept constant. After the addition of hydrogen peroxide is finished, the reaction temperature is raised to 60ºC, the stirring speed is (400 rpm, 500 rpm and 600 rpm) and with a reaction time of 180 minutes. After the reaction is achieved, the mixture is washed with hot water (40-45ºC) to separate it from impurities. Then the epoxy compound was separated using a rotary evaporator at 80ºC for 15 minutes [7].
Parameter Analysis of Epoxy Compounds

Identifying functional groups using FT-IR, iodine numbers using the standard Wijs method namely SNI-01 3555-1998 and oxirane oxygen numbers using standard methods (AOCS Official Methods Cd 9-57 (1989)).

4. Result and Discussion

4.1. Avocado Seed Oil Characterization

Avocado seed oil is used as a raw material in the making of epoxy compounds. Avocado seed oil is obtained by using the extraction method. Avocado seed oil that has been extracted is first analyzed using GC (Gas Chromatography) to determine the composition of fatty acids contained therein.

![Figure 1. Analysis results of avocado seed oil fatty acid composition](image)

From Figure 1, the fatty acid composition data is presented again in Table 1. The composition that has the largest percentage of avocado seed oil can be seen in Table 1. The composition of unsaturated fatty acid composition that has the largest percentage of avocado seed oil from this research is found in oleic acids of 76.4% (w / w).
Table 1. Composition of avocado seed oil fatty acids

| Fatty Acids          | Composition % (w/w) |
|----------------------|----------------------|
| Myristic Acid (C\textsubscript{14}:0) | 0.2                  |
| Palmitic Acid (C\textsubscript{16}:0) | 14.8                 |
| Stearic Acid (C\textsubscript{18}:0)  | 4.4                  |
| Arachidic Acid (C\textsubscript{20}:0) | 0.3                  |
| Oleic Acid (C\textsubscript{18}:1)   | 76.4                 |
| Linoleic Acid (C\textsubscript{18}:2) | 3.6                  |
| Eicosanoid Acid (C\textsubscript{20}:1) | 0.3                 |
| Total                | 100.0                |

According to Marlina and Dian, 2018 stated that avocado seed oil which has the highest content of fatty acids is oleic acid / 71.715% oleic acid [8]. Avocado seed oil is potential to be processed into epoxy compounds, because epoxy compounds are compounds that contain oxirane oxygen groups that are formed through an epoxidation reaction between peroxide acid and unsaturated aromatic compounds. Aromatic compounds can be vegetable oils or natural oils that have unsaturated bonds [9].

4.2 Fourier Transform Infra Red (FT-IR) Analysis

FT-IR analysis to identify functional groups found in raw materials and also in epoxy compounds.

![FT-IR Analysis](image)

Figure 2. Results of FT-IR analysis of raw materials (avocado seed oil)

Figure 2. Shows the characteristics of avocado seed oil raw materials. The absorption area of avocado seed oil function groups can be seen in table 2 [10].
Table 2. Functional groups absorption area of avocado seed oil

| Type of bond            | Wave Number Frequency (cm\(^{-1}\)) | Avocado Seed Oil Frequency (cm\(^{-1}\)) |
|-------------------------|--------------------------------------|-----------------------------------------|
| Group C-H stretching    | 3000-2840                            | 2922.27                                 |
| Group C=O stretching    | 1870-1540                            | 1743.56                                 |
| Group O-H bending       | 1420-1300                            | 1452.77                                 |
| Group C-O stretching    | 1150-1085                            | 1157.79                                 |
| Group C-H bending       | 900-675                              | 715.86                                  |

In this study, avocado seed oil is used as a raw material in the making of epoxy compounds. There is a C-H group from Table 2.

![FT-IR analysis results of epoxy compounds with stirring speed of 600 rpm, 2.5% catalyst and 70 ml H\(_2\)O\(_2\).](image)

Figure 3. The FTIR analysis results of the best epoxy compounds with variations of 600 rpm, 70 ml H\(_2\)O\(_2\), and 2.5% catalyst. The groups in Figure 3. Can be seen in Table 3.

Table 3. Functional groups absorption areas of epoxy compounds.

| Type of bond            | Wave Number Frequency (cm\(^{-1}\)) | Epoxy Compound Frequency (cm\(^{-1}\)) |
|-------------------------|--------------------------------------|----------------------------------------|
| Group C-H stretching    | 3000-2840                            | 2923.02                                 |
| Group C=O stretching    | 1870-1540                            | 1742.71                                 |
| Group O-H bending       | 1420-1300                            | 1453.36                                 |
| Group C-O stretching    | 1150-1085                            | 1158.03                                 |
| Epoxy Group             | 950-810                              | 840.07                                  |

The absorption peaks at wave number 1743.56 cm\(^{-1}\) contained in Figure 2. Raw materials (avocado seed oil) and 1742.71 cm\(^{-1}\) contained in figure 3. (epoxy compound), indicate the presence of C = O groups. The carbonyl group contained in the FTIR analysis results showed the presence of esters in avocado seed oil [15]. The absorption peaks at wave number 2922.27 cm\(^{-1}\) contained in Figure 2. (avocado seed oil raw material) and 2923.02 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 [11].

The absorption peaks at wave number 1452.77 cm\(^{-1}\) contained in figure 2. (avocado seed oil raw material) and 1384.90 cm\(^{-1}\) contained in figure 3. (epoxy compound) indicate the presence of OH groups derived from the womb fatty acids [12]. The absorption peaks at wave number 1157.79 cm\(^{-1}\) contained in figure 2. (avocado seed oil raw material) and 1158.03 cm\(^{-1}\) contained in figure 3. (epoxy compound) in the epoxy compound indicate the presence of C-Oester groups. The C-O group is
obtained because of the addition of carboxylic acids which open the epoxide ring [13]. The absorption peak at the wave number 840.07 cm\(^{-1}\) in the epoxy compound indicates the presence of an oxirane group. The presence of this oxirane group is caused by the oxidation reaction of oil double bonds by active oxygen. Peroxide acid is obtained from the reaction between carboxylic acid and hydrograph peroxide [6]. The formation of an oxirane group is also influenced by the presence of a catalyst, namely sulfuric acid which will open the double bonds in avocado seed oil so that hydrogen peroxide can react and form an oxirane group [14].

4.3 Effect of \(\text{H}_2\text{O}_2\) Amount and Catalyst Concentration on Fixed Speed on Oxirane Oxygen Numbers

![Oxirane Oxygen Numbers](image1)

**Figure 4.** Relationship between the amount of \(\text{H}_2\text{O}_2\) and the catalyst concentration

In Figure 4. It appears that the oxirane number increases with the increase in the amount of hydrogen peroxide used. But at some point there is a decrease, this is due to the decomposition that occurs together with the oxidation reaction resulting in oxidation of incomplete double bonds and reduce the oxidation bonds formed and the reaction is reversible and exothermic so that there will be acetic acid and hydrogen peroxide which again results in the formation of acids peracetate is reduced. The reduction of peracetic acid that is formed affects the oxidation of the double bonds and results in the formation of oxygen [16].

4.4 Effect of \(\text{H}_2\text{O}_2\) Amount and Catalyst Concentration on Fixed Speed on Iodine Numbers

![Iodine Numbers](image2)

**Figure 5.** Relationship between the amount of \(\text{H}_2\text{O}_2\) and the catalyst concentration
Decreased iodine number is caused by the reaction of the termination of the double bonds in fatty acids found in avocado seed oil by the catalyst. The more double bonds that are broken 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 oxirane group. The reactants will help the reaction. The more reactants, the more effective a reaction, in this case is the formation of an oxirane group. To accelerate the collision between particles the ingredients used are stirred [10]. In figure 5. Shown at the lowest iodine number that is 1.2690 obtained an oxirane oxygen number of 3.552 which is the highest oxirane oxygen number and the lowest iodine number in this study. The results of this study are better than Listiana (2017) which states in the study that the lowest iodine number is 0.96 obtained oxirane oxygen number of 1.8874. It can be concluded that the higher the level of epoxidation, the more iodine number will decrease [17].

4.5 Effect of $H_2O_2$ Amount and Catalyst Concentration on Fixed Speed on Oxirane Oxygen Conversion

![Figure 6](image.png)

**Figure 6.** Relationship between the amount of $H_2O_2$ and the catalyst concentration

In Figure 6. The lowest conversion is shown at 61.38776% while the highest conversion is 72.44880%. This research is better than Listiana (2017) which states that the lowest conversion is 4.850% and the highest conversion is 62.259% [18]. The conversion obtained will be proportional to an increase in the number of oxirane and a decrease in iodine numbers.

5. Conclusion

Avocado seed oil is potential to be an epoxy compound. The resulting epoxy compounds meet the requirements to be applied plasticizers that have an oxirane oxygen value of 3.552%. The best results from this study were on oxygen conversion of 72.4898% with a stirring speed condition of 600 rpm, 70 ml $H_2O_2$ and 2.5% catalyst at a reaction temperature of 60ºC and reaction time of 180 minutes.

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