Utilization of fatty acid from papaya seed waste oil (*carica papaya L.*) as a raw material in the making of epoxy compound

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Abstract. Epoxy is a compound that is produced from the reaction between double bond inside the fatty acid and active oxygen. This compound could be applied as a stabilizer, plasticizer on PVC (Polyvinyl Chloride) and could be used as an antioxidant in processing natural rubber, surfactant, anti-corrosive-additive agent on lubricant, and as raw material for pesticide. The raw material in this study was papaya seed oil. The aim of this research to get the effect of catalyst concentration, amount of H$_2$O$_2$ (ml) and stirring rate (rpm) on the characteristics of epoxy compounds. In this study, fatty acid, which was contained in raw material, was reacted to hexane, glacial acetic acid, H$_2$O$_2$ with the variation of 40ml, 50ml, 60ml, and 70ml, sulfuric acid as a catalyst with variation, stirring velocity with variation of 400 rpm, 500 rpm and 600 rpm for 180 minutes. The result of this study showed that the best epoxy compound result was acquired at 2.5% of catalyst concentration, 70ml H$_2$O$_2$ and 600 rpm of stirring speed, where the oxirane oxygen value was reached 3.52, iodine number was 10,4058 and oxygen conversion was 73.76471%.

1. Introduction

Papaya (*Carica Papaya L.*) is one of the plants that grows up in Indonesia. According to Indonesian Statistics Institution in 2017, papaya production was 857.112 tons. The most-utilized part is the flesh. Papaya seeds are only used as waste, even though papaya seeds contain oil that can be used as vegetable oil [1]. The fatty acid content contained in papaya seed oil has the potential to be used as a raw material for the manufacture of epoxy compounds. Epoxidation reaction is defined as a double bond oxidation process between two carbon atoms by an oxygen atom to form an epoxy / oxirane ring [2]. 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, 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, alkanolamine, carbonyl compounds, olefin compounds, and polymers such as polyester and resins [3]. Characterizing epoxy compounds could be classified or named based on oxirane value [4]. The fatty acid value in papaya seed makes papaya seed oil becomes potential if it is used as a raw material in the making of the epoxy compound. The report about epoxy making process by using papaya seed oil as a raw material has never been implemented before, it is necessary to examine the potential of papaya seed oil for the epoxy compounds produced.
2. Theory

Papaya (Carica Papaya L.) is one of horticulture plant which is highly cultivated in Indonesia. The seed value in papaya is approximately 14.3% of the whole fruit [5]. These seeds are generally discarded after the fruit is consumed. To make the roots have more economic value, the study on the utilization of papaya seed as a vegetable oil source needs to be done. The process of taking out the oil from the basis would be beneficial because it contains active compounds such as alkaloids, steroids, tannins, and essential oil. Yellow-colored papaya seed oil is known to have 71.60% of oleic acid, 15.13% of palmitate acid, 7.68% linoleic acid, 3.60% stearate acid, and other fatty acids in a little relative amount or limited [6, 7]. So, papaya seed oil could be used as a raw material to make the epoxy compound because its unsaturated fatty acid content is not high. Epoxy is produced from the reaction of vegetable oil epoxidation or natural oil, which has an unsaturated bond [8]. Epoxy could be applied as a stabilizer and plasticizer in Polyvinyl Chloride (PVC) it could be used as an anti-oxidant in processing natural rubber, as a surfactant, anti-corrosive-additive in lubricant and pesticide [9]. Epoxidase could also be defined as the establishment reaction of the oxirane cluster by oxidating double bond using peroxyacetic acid and catalyst. Epoxidation aims to change the double bond in oil become epoxide by reacting the oil with to the blend of formic acid and hydrogen peroxide [10,11].

![Figure 1. Reactions from the epoxidation process](image)

There are some methods that can be used in establishing an epoxy compound. In this study, the *in-situ* method is chosen. It is done by reacting carboxylic acids, in this case, acetic acid as an oxygen bearer with hydrogen peroxide as oxygen provider. In this case, sulfuric acid as a strong acid catalyst [13]. The mechanism of acetic acid and hydrogen peroxide establishment reaction which produces peracetic acid could be seen in this equation as followed:

\[
\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOOH} + \text{H}_2\text{O}
\]

The reaction process is affected by several things such as catalyst, reactant, and stirring speed.

3. Research methodology

This study was done in Chemical Process Laboratory, Department of Chemical Engineering Universitas Sumatera Utara, Medan. The research sequence is begun from the extraction of papaya seed raw material, then the process of epoxy compound making an epoxy compound identification. The materials which used in this research are pure water (H\textsubscript{2}O), Acetic Acid (CH\textsubscript{3}COOH), papaya seed fatty acid, Sulfuric Acid (H\textsubscript{2}SO\textsubscript{4}), 30% of Hydrogen Peroxide (H\textsubscript{2}O\textsubscript{2}), Methanol (CH\textsubscript{3}OH), and n- Hexane (C\textsubscript{6}H\textsubscript{14}) [14]. The making of the epoxide compound is implemented by modifying Gall and Greenspan’s performance.

Papaya seeds are dried-off in the oven for 6 hours with 80℃. Furthermore, they are refined and filtered by the 70 mesh-sized sieve. Extraction is done with the solvent ratio toward raw material as 15:1 mL/g. The extraction will last for 180 minutes with 65℃. Epoxy making process started by measuring 100 grams of raw material, then 40 grams of n-hexane solvent is added, followed by 15 grams of glacial acetic, and H\textsubscript{2}SO\textsubscript{4} catalyst. After reaching 50℃, hydrogen peroxide is added for 30%, and the temperature of the reaction is increased to 60℃ with reaction time for 180 minutes. After the response stopped, the blend is washed with 40-45℃ of hot water, and then the epoxy compound is separated by using a rotary evaporator with 80℃ for 15 minutes [15].
4. Results

Papaya seed oil is obtained from the extraction of papaya seeds that have been collected from salad vendors in the environment of the Universitas Sumatera (USU). The extraction yield of papaya seed oil was acquired as 25% ± 5.

| Fatty Acid Type(s) | Compiler Component (s) | Composition % (b/b) |
|-------------------|------------------------|---------------------|
| Saturated Fatty Acid | Myristic Acid (C14:0) | 0.9 |
|                    | Palmitic Acid (C16:0)  | 43.2 |
|                    | Stearic Acid (C18:0)   | 4.1 |
|                    | Arachidic Acid (C20:0) | 0.4 |
| **Total**          |                        | **48.6**            |
| Unsaturated Fatty Acid | Palmitoleic Acid (C16:1) | 0.5 |
|                    | Oleic Acid (C18:1)     | 43.9 |
|                    | Linoleic Acid (C18:2)  | 6.8 |
|                    | Eicosanoid Acid (C20:1)| 0.2 |
| **Total**          |                        | **51.4**            |

It could be seen that the raw material totally contained more than 50% of unsaturated fatty acids. Then it could be concluded that the raw material was potentially be processed to become epoxy compound.

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

Figure 2. Results of Fourier transform infra-red (FT-IR) analysis of papaya seed oil

It could be seen that there was no oxidant clusters exist yet on papaya seed oil raw material. Meanwhile, FT-IR result after the epoxidation process could be seen as followed:
Figure 3. Results of FT-IR analysis of epoxy compounds

The figure above showed the FT-IR analysis results on the epoxy compounds from papaya seed oil raw material. The absorption peak at phase number 841.39 cm\(^{-1}\) on epoxy compound indicated the existence of oxidant cluster. Its existence was caused by the oxidation reaction of double oil bond by active oxygen. The reaction process was influenced by several things such as the catalyst, reactant, and mixing speed. The effect from catalyst, reactant and stirring speed toward resulting oxygen oxirane number had been shown in the following figure.

Figure 1 is the relationship between \(\text{H}_2\text{O}_2\) volume and catalyst concentration on stirring speed at (a) 400rpm, (b) 500rpm, and (c) 600rpm toward oxirane oxygen number at 60°C and 180 minutes reaction time.

The catalyst effect on epoxidation reaction was proportionally straight with utilized catalyst concentration. The more the catalyst was utilized, the more the double bond was transformed to become epoxy, so the oxirane number resulted more. As the catalyst concentration increased, the amount of utilized catalyst will get bigger, so double bond discontinuance became more effective. It was shown in Figure 4, where the resulting oxidant number increase as the catalyst concentration did. However, there were deviations in some points, such as Figure 4 depicted, where oxidant number at 2% catalyst concentration was 3.168 higher than the 2.5% catalyst that was 3.136.

The oxidation reaction was also affected by reactant concentration. In this case, hydrogen peroxide acted as a reactant. The reactant concentration will accelerate collisions among molecules so that the forming oxidant will get bigger [16, 17]. Hydrogen peroxide will react with a double bond on unsaturated fatty acid, which had been discontinued by catalyst and shape oxidant cluster. The more \(\text{H}_2\text{O}_2\), the more peracetic acid was formed, and the more oxidant cluster which could be created. As the oxidant cluster increase more, then the iodine number will decrease, this was caused by the discontinuance of double bond, so the unsaturation of oil acid will decrease as well. In Figure 4, it was seen that oxidant number got increase as the addition of utilized hydrogen peroxide amount.
Figure 4. Relationship between $\text{H}_2\text{O}_2$ volume and catalyst concentration on stirring speed at (a) 400 rpm, (b) 500 rpm, and (c) 600 rpm

However, in several points, reductions happened. This was because the existence of decomposition that happened together with oxidation reaction, so it caused imperfect double bond oxidation and reducing forming oxidant bond and this reaction was also reversible and exothermic that there will be acetic acid and hydrogen peroxide which came back and unstable temperature will cause the forming of peracetic acid got diminished. The diminished of peracetic acid formed furthermore will influence double bond oxidation and affect oxidation formed [18].

Stirring speed was also one of the factors that affected the epoxidation reaction. The moving process could increase particle movement, which existed in utilized materials. As the activity grew, so the collision and contact among particles will be more often than made the chemical reaction will last faster. In this epoxy compound forming response, by the existence of stirring, so the dismantling of the double bond to become oxidant will get faster and more effective. The quicker the stirring, the faster the chemical reaction occurs, so the oxygen oxirane numeral value which was produced will increase as
well. This was shown in oxygen oxirane numeral value at 600rpm of stirring VELOCITY tends to be better. The highest oxidant oxygen number that was 3.52, found in the making of the epoxy compound with the usage of 70 ml of H2O2, 2.5% of catalyst concentration, and 600rpm of stirring speed. Oxygen oxirane number that was 3.52 had fulfilled the criteria of applicable oxygen oxirane number as plasticizer.

5. Conclusion
Papaya seed oil could be utilized as a raw material in the making of the epoxy compounds. The best oxidant oxygen number in this study was 3.52, so it could be applied as plasticizer because it fulfilled the standard of applicable epoxy oxygen oxirane number as plasticizer. The optimum condition to acquire the maximum oxygen oxirane number in this study was at 2.5% of catalyst concentration, 70ml of H2O2, and 600rpm of stirring speed.

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