Production of epoxy compounds from unsaturated fatty acids derived from crystallization of used cooking oil

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Abstract. Epoxy compound is a compound produced from an epoxidation of vegetable oil or a natural oil with an unsaturated bond. Epoxy compound can be applied as a stabilizer and plasticizers in polyvinyl chloride (PVC) and can be used as an antioxidant in natural rubber processing, as a surfactant, anti-corrosive additive agent in lubricants and pesticide raw materials. The purpose of this research was to utilize used cooking oil as raw material of making the epoxy compound. In this research, used cooking oil was separated into unsaturated and saturated acids. Unsaturated fatty acid was reacted with hexane, glacial acetic acid, H₂O₂, and sulphuric acid as catalysts with the variable of 1.5%, 2.1%, 2.5%, 3.1% and 3.5%. The reaction time was also varied for 60, 120, 180, 240 and 300 min. The results showed the highest oxirane oxygen number in the epoxy compound was 2.422. The conversion of oxirane oxygen reached 68.612% and the lowest iodine number was 0.560 g I₂/100 g raw material at the condition of 300 min reaction time and by using 2.5% catalyst.

Keywords: epoxy compounds, unsaturated fatty acids, cooking oil, crystallization

1. Introduction
The object of this study was to know the effect of reaction time and amount of H₂SO₄ catalyst to epoxidation by using palm fatty acid distillate as raw material to form epoxy compound. Epoxidation is a reaction between organic peroxy with compounds with double bond to form oxirane compound (epoxy) [1]. Epoxidation can convert vegetable oil into polymer epoxy resin [2]. The epoxy compound is a commercial product that can be applied as a stabilizer, plasticizers on polyvinyl chloride (PVC) to enhance the flexibility and elasticity of PVC, but it can also replace phthalates as plasticizers, since phthalates has been banned in many countries because they have bad effects to our health [3], as well as for antioxidants in natural rubber processing. The epoxy compound can also be used as a surfactant and an additive anti-corrosive agent in lubricating oils and pesticide raw materials [4]. Epoxy has a better corrosive resistance characteristic than polyester but it is not acid resistant. [5] The epoxy compound is a compound produced from an epoxidation reaction of vegetable oil or natural oil which has unsaturated bond. To make epoxy compound, the used oil is needed to be crystallized first. This crystallization is done to separate saturated fatty acid and unsaturated fatty acid. The usage of natural oil as a raw material is rarely done because of its limitness [6]. Used cooking oil contains 22.62% oleic acid; linoleic acid 52.68%; and 2.60% linolenic acid which is an unsaturated fatty acid [5]. Used cooking oil is a waste which disposal has caused major problems in almost all parts of the world. This environment-threatening problem can turn out to be both economically and environmentally sound with the proper utilization and waste management of used cooking oil [7]. Unsaturated palm fatty acid is a byproduct of biodiesel production [8]. Unsaturated fatty acid is fatty acid with one double bond in the
carbon chain [9]. Epoxidation using palm fatty acid distillate has been done before by Alamsyah, et al. (2013) [10] and Syawaluddin (2009) [11]. It was found that the epoxy form about 39-44%. It was found that the conversion of the reaction was 70.802%. Unsaturated palm fatty acid derived from waste cooking oil is one of the alternative sources because other oils is quite expensive. Used cooking oil also can be easily collected from industries and restaurant [12]. The continuous usage of used cooking oil can damage human health, cause cancer, and consequently can reduce the intelligence of the next generation. By considering the theory above, this research is needed to be done by using palm fatty acid distillate by crystallization using peroxyacids and \( \text{H}_2\text{SO}_4 \) catalyst and by varying amount of catalyst used to compare the oxirane oxygen number and iodine number obtained and to reduce the waste of used cooking oil.

2. Materials and Methods

2.1. Epoxidation Methods

The main raw materials used were unsaturated fatty acids obtained from Roti Ketawa Pelangi Store, Pematang Siantar. Hydrogen peroxide and methanol were obtained from Rudang Jaya Medan. The preparation procedure used is preparation by Haryati and Buana (1992). Separation of unsaturated and saturated fatty acids was carried out by crystallization of used cooking oil by using methanol as solvent at temperature of 5\(^\circ\)C for a certain time. Then, the crystallized unsaturated fatty acid was measured for 100 ml and was poured into a three-necked flask placed over a hot plate equipped with reflux condenser, thermometer and magnetic stirrer. 61.087 ml of hexane was added as solvent, then 15.3 ml glacial acetic acid was added to the mixture and sulphuric acid was added as catalyst and was varied then the mixture was heated. After the mixture temperature reached 50 \(^\circ\)C. 30 percent hydrogen peroxide was added as much as 56 ml slowly and the temperature was maintained at 50 \(^\circ\)C [13]. After the addition of hydrogen peroxide, the mixture was heated at 60 \(^\circ\)C for the specified time variation. After the reaction was stopped, the mixture was washed with hot water at 40-45 \(^\circ\)C to separate residual hydrogen peroxide (\( \text{H}_2\text{O}_2 \)) and sulfuric acid (\( \text{H}_2\text{SO}_4 \)), then the epoxy product which still contained n-hexane was separated by rotary evaporator at 80 \(^\circ\)C for 15 min.

2.2. Epoxy Compound Characterization

2.2.1. Fourier Transform Infrared Spectroscopy (FT-IR). Functional groups of epoxy compound was analyzed by using IR Prestige-21 Shimadzu. The analysis using FT-IR represented spectrum data in graphic and wave numbers of each data that provided functional groups of epoxy compound.

2.2.2. Iod Analysis. Iod number shows the amount of double bond (unsaturated) in oil and fat. Iod number is also the indicator of epoxidation. Iod number of epoxy compound was analyzed by using the standard of SNI-01-3555-1998.

2.2.3. Oxirane Oxygen Content Analysis. Oxirane oxygen content is the amount of oxirane (epoxy) formed. Oxirane Oxygen Content Water of epoxy compound was analyzed by using the standard of (AOCS Official Methods Cd 9-57 (1989)).

3. Results

3.1 Characteristic of Raw Materials

Main raw material used in this study was unsaturated fatty acid which was derived from the crystallization of used cooking oil (used cooking oil). Gas Chromatography (GC) was done to analyze the composition of the raw material before and after pretreatment. Fatty acid composition of raw materials can be seen in Table 1 below.
Table 1. Fatty acid composition of raw material

| Fatty Acid       | Component  | Composition (%) Before Pretreatment | Composition (%) After Pretreatment |
|------------------|------------|--------------------------------------|------------------------------------|
| Saturated Fatty Acid | Lauric Acid | 0.57                                 | 0.43                               |
|                   | Miristic Acid | 1.70                                 | 1.61                               |
|                   | Palmitic Acid | 32.05                                | 23.16                              |
|                   | Stearic Acid  | 8.04                                 | 5.62                               |
|                   | Arakidic Acid | 0.86                                 | 0.68                               |
| **Total**         |             | 43.22                                | 31.5                               |
| Saturated Fatty Acid | Palmitoleic Acid | 0.37                                 | 0.33                               |
|                   | Oleic Acid  | 41.20                                | 47.97                              |
|                   | Linoleic Acid | 14.49                                | 17.89                              |
|                   | Linolenic Acid | 0.41                                 | 2.04                               |
|                   | Eikosenioic Acid | 0.31                                | 0.27                               |
| **Total**         |             | 56.78                                | 68.5                               |

The result of gas chromatography analysis shows that the content of unsaturated fatty acids in the sample of used cooking oil before pretreatment is 56.78% and after pretreatment is 68.5%.

3.2 Effect of Reaction Time and Catalyst Concentration on Iodine Number and Oxirane Oxygen Content.

![Figure 1](image-url)  
**Figure 1.** Effect of reaction time and catalyst concentration on (a) iod number (b) oxirane oxygen content

The iodine number represents the number of double bonds in a sample qualitatively [13]. The iodine number decreased as the epoxidation rate (oxirane oxygen number) increased [14]. Figure 1 (a) shows the longer the reaction time resulted the iodine number decreased for each variation of catalyst used. As shown in the figure, at the concentration of 2.500% catalyst with 60 min reaction time, the iodine number was 24.250 and the iodine number gets lower when the reaction time was increased to 300 min. The iodine number become 0.56 g I$_2$/100 g for 300 minutes of reaction time. This can be caused by the epoxidation reaction of used cooking oil causes the termination of double bond by peroxyacids to form the oxygen group. Thus, during the epoxidation reaction, the iodine number will decrease. The iodine number of oil or fat indicates the number of double bonds (unsaturated bonds contained in the oil or fat) [4]. Figure 1 (b) shows that the longer the reaction time the oxirane oxygen number increased for each variable of catalyst concentration. The figure shows that at 2.500% catalyst concentration with 60 minutes reaction time gave the oxirane oxygen number of 0.449 and when the reaction time was increased to 300 minutes the oxirane oxygen number become 2.422. This is caused by the binding of oxygen derived from peroxide acids by the present of double bonds in the oil increases [4]. This increase
leads to the conversion of unsaturated compounds to epoxy compound increases so that the yield of the epoxy compound as measured by oxirane oxygen number also increases.

3.3 Fourier Transform Infrared Spectroscopy (FT-IR)

The result of the FTIR Spectrophotometry is shown in figure 2 below.

![Figure 2. FTIR Spectrophotometry of Epoxy Compound.](image)

From the Figure 2 above we can see that the functional groups of epoxy compound generated several peaks of wave numbers in each range of region. Peak at wave numbers 3327.667 cm\(^{-1}\) (O-H bond), indicates the absorption caused by the hydroxy. Peak at the wave numbers 2872.167 cm\(^{-1}\) indicates the absorption caused by the C-H bond and peak at the wave number 1746.837 cm\(^{-1}\) indicates the absorption of C=O bond (type of ester compound). Peak at wave number of 1246.900 cm\(^{-1}\) dan 846.796 cm\(^{-1}\) indicates the absorption caused by the C-O-C bond.

3.4 Correlation between Oxirane Oxygen Numbers and Iodine Numbers

The oxirane oxygen number is a number which indicates the amount of oxygen bond that comes from the peroxide acid and the double bond contained in the oil [4]. While iodine number is a number that shows the number of double bonds in a sample qualitatively [15]. Iodine number decreases as the epoxidation rate increases [14]. This is due to the binding of oxygen derived from peroxide acids by the present of double bonds in the oil increases [4]. This increase leads to the conversion of unsaturated compounds to epoxy compound increases so that the yield of the epoxy compound as measured by oxirane oxygen number also increases. The relationship between the iodine number and the oxirane oxygen number at the reaction temperature can be seen in Figure 3 below.

![Figure 3. Correlation of Iodine Number and Oxirane Oxygen Number](image)

Figure 3 above shows the relationship between the iodine number with oxirane oxygen number are inversely proportional. The decrease of iodine numbers did not cause the oxirane oxygen number
increases. It is caused by the epoxidation reaction produces a side reaction. Thus, a control or prevention is needed to avoid such side reactions. Some of the causes of side reactions in this study are the concentration of solvents, double bonds that have been oxidized, and temperature of reaction control [4]. In the epoxidation reaction, double bonds was broken by the peroxyacids to form the oxygen group. Thus during the epoxidation reaction happens, the iodine number will decrease. As the iodine number decreases, the epoxidation number (oxirane oxygen number) increases [15].

4. Conclusion
The oxygen group is formed by double bond oxidation in used cooking oil by using peroxyacids, glacial acetic acid as solvent and H\textsubscript{2}SO\textsubscript{4} as the catalyst. The result showed that the best oxirane oxygen number was 2.422, the lowest iodine number was 0.560 g I\textsubscript{2}/100 g with the conversion of 68.612% at the reaction condition of 60°C, 300 min reaction time and by using 2.5% H\textsubscript{2}SO\textsubscript{4} catalyst concentration.

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**Acknowledgments**

The authors gratefully acknowledge that the present research is supported by the universitas Sumatera Utara through Non-PNBP funds in accordance with talent research contract 2017.