Effect of Reaction Time and Catalyst Concentration on Making of Epoxy Compounds Using Sulphuric Acid Catalyst Based on Crystallized Palm Fatty Acid Distillate

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Abstract. Epoxy is produced from an epoxidation reaction of vegetable oils such as linseed oil, corn oil, palm oil or natural oils that have unsaturated bonds. The aim of this research is to produce epoxy compound based on Crystallized Palm Fatty Acid Distillate. First, the gas chromatography analysis was done to the palm fatty acid distillate. Then, before the epoxidation reaction began, crystallization process was done based on solubility of saturated and unsaturated fatty acid in organic solvent (methanol). In this research, the Crystallized Palm Fatty Acid Distillate that has reacted with acetic acid glacial and hydrogen peroxide, toluene as solvent, sulfuric acid as a catalyst in a three-neck flask fitted with condenser reflux at 70°C and stirred at 500 rpm. The catalyst concentration varied from 1.5%, 2.0%, 2.5%, 3.0% and 3.5% and epoxidation reaction time varied from 60 minutes, 120 minutes, 180 minutes, 240 minutes and 300 minutes. The results showed that the highest epoxy conversion was achieved at reaction time of 120 minutes with 2.5% sulfuric acid catalyst concentration against the amount of hydrogen peroxide and acetic acid used. The result of this analysis shows that oxirane oxygen content is 0.96%, iodine number is 17.16g iod / 100 g oil and conversion equal to 81.61%.

1. Introduction
Epoxy compound is commercial product that can be applied as a stabilizer, plasticizers on polyvinyl chloride (PVC) to enhance PVC flexibility, in addition it can also replace phthalates as plasticizers, because phthalates have been banned in many countries because they have negative health effects [9], and as well as an antioxidant in natural rubber processing [12]. The epoxy compound is produced from an epoxidation reaction of vegetable oil or a natural that has unsaturated bond. The use of natural oil as a raw material is rarely used with the limitations of natural oil raw materials [11]. The epoxy compound can be synthesized from vegetable oils such as linseed oil, corn oil [5] and palm oil [11]. The need of palm oil about 90% is used for foodstuffs such as cooking oil, margarine, shortening, cocoa butter substitutes and for industries needs such as industry of bakery, chocolate, ice cream, biscuits and snacks. Besides of production of main products as cooking oil, also produce by products of palm fatty acid distillate (PFAD) [1]. Palm oil contains saturated fatty acids and contains high levels of unsaturated fatty acids, that palmitic acid (saturated fat) and oleic (unsaturated fat) are the major acid component [13].

Indonesia is the largest producer and exporter of palm oil in the world. The crude of palm oil (CPO) in Indonesia has increased drastically from 21.39 million tons in 2009 to 30.95 million tons in 2015. Potential markets that produce palm oil or palm kernel oil are the fractionation/refining industry (specialty cooking oil), specialty fats, margarine, oleochemicals, and bath soap [3]. In the cooking oil
industry there is refining stage that aims to improve the quality of oil produced. At this stage, in addition to the main products produced in the form of cooking oil, also produced byproducts of palm fatty acid distillate (PFAD) [4]. Palm fatty acid distillate (PFAD) has been used in the soap making industry, as feed ingredient and as raw material for the oleochemical industry [17]. Palm fatty acid distillate (PFAD) contains 46.1% oleic acid, linoleic acid 8.6% and 0.3% linolenic acid and 0.4% arachidic acid which is included in unsaturated fats which can be used as raw material for the manufacture of epoxy compounds [10]. The raw material in the manufacture of this epoxy compound should also have low production cost and can be used on a large production scale. Considering these matters, it is necessary to study the manufacture of epoxy compound using fatty acid distillate by using H2SO4 catalyst so it is expected to increase the added value of distillation of palm fatty acid and also obtain high oxirane oxygen number.

2. Material and Method

2.1 Material and Tools
Raw materials used in this research were palm oil fatty acid distillate, toluene, glacial acetic acid, 30% hydrogen peroxide and sulfuric acid as catalysts. The equipments used in this research were three-neck flask as the site of the reaction, which is equipped with thermometer, hot pale with magnetic stirrer used as a heating medium, reflux, separating funnel, rotary evaporator and digital scales. The experiments were performed with percent of catalyst variations of 1.5%, 2.0%, 2.5%, 3.0% and 3.5% and variations of time 60 minutes, 120 minutes, 180 minutes, 240 minutes and 300 minutes at round speed 500 rpm. The raw material of palm oil fatty acid distillate will be analyzed by Gas Chromatography type Shimadzu QP 2010 Brands and Analysis of epoxy group produced from Fourier Transform Infra Red (FTIR).

2.2 Crystallization Process
This crystallization method is based on solubility differences of saturated and unsaturated fatty acids in organic solvent (methanol) at certain temperature [19]. Fatty acid solubility is higher than the glyceride component. The fatty acids are soluble in both polar and non-polar organic solvents. Polar fatty acids tend to dissolve in polar solvents and non-polar soluble acids in non-polar solvents. The longer the carbon chain the solubility of oil / fat is lower. Unsaturated fatty acids are more soluble than unsaturated fatty acids with the same chain length, thus fatty acids with a higher degree of unsaturation are more easily soluble [20].

2.3 Epoxidation Reaction
Epoxidation reaction began by weighing the distillation of the distillation of 20 grams of distillation, then inserted into three-neck flask placed over a hot plate equipped with a condenser reflux, thermometer and magnetic stirrer. Furthermore, 9 to 9 ml of toluene was added as solvent, 100% glacial acetic acid added by 9.23 grams and addition of sulfuric acid as the catalyst was varied in number and then heated. After the mixture temperature reached 50°C, then 30% hydrogen peroxide was added as much as 16.87 grams and gradually maintained at 50 °C for the addition of hydrogen peroxide [11]. After completion of the addition of hydrogen peroxide, the mixture was heated according to the temperature and time determined by the experimental treatment. After the reaction was stopped, the mixture was washed with 40-45°C hot water to separate residual hydrogen peroxide (H2O2) and sulfuric acid, then the epoxy product mixed with toluene was separated by a rotary evaporator at 80 °C for 15 minutes after separation, the epoxy compound was then analyzed. Analysis analyzed was iodine number (Method AOCS 1- and oxygen oxyren oxidation analysis (Method Adapted From Siggia (1963)).

3. Results and Analysis
The raw material of fatty acid distillate was analyzed by gas chromatography (GC) to know the composition of fatty acids contained therein. The fatty acid composition of used cooking oil can be seen in table 1.
### Table 1. Fatty Acid Composition of Distillate Palm Fatty Acids

| Name           | Amount of C | Composition (%) |
|----------------|-------------|-----------------|
| Lauric Acid    | C-12-0      | 0.2070          |
| Mirror Acid    | C-14-0      | 1.0278          |
| Palmitic Acid  | C-16-0      | 46.3740         |
| Palmitolemic Acid | C-16-1  | 0.1636          |
| Stearic Acid   | C-18-0      | 4.1780          |
| Oleic Acid     | C-18-1      | 37.9485         |
| Linolenic Acid | C-18-2      | 0.3182          |
| Gadoleic Acid  | C-20-1      | 0.1123          |
| Arachidic Acid | C-20-0      | 0.3055          |
| Linoleic Acid  | C-18-3      | 9.3650          |

Based on the results of GC analysis, fatty acid composition of used cooking oil can be seen from the table above. The result of gas chromatography analyzes is content of unsaturated fatty acid about 48%.

#### 3.1 Effect of Time Variation of Reaction and Catalyst Concentration on Iodized Number

The relation between effect of reaction time variation and Catalyst Concentration on iodine number at 70 °C reaction temperature and 500 rpm stirring rate can be seen in the figure.

![Figure 1. Relation between reaction time and catalyst concentration to iodine numbers.](image)

It can be seen in Fig. 1 that the longer reaction time, the resulting iodine number decreases on the five variations of the concentration of sulfuric acid catalysts being tried, i.e. 1.5%, 2.0%, 2.5%, 3.0% and 3.5%. Decrease in iodine number can be seen in the graph above at 60 minutes to 300 minutes can be seen the number of iodine decreased.

This is due to the fact that the iodine number in the epoxidation reaction with time addition tends to decrease due to the breaking of the double bond into the form of the epoxy ring [2].

It can be seen in the figure that the increasing of catalyst concentration hence the number of iodine produced tends to decrease at the five variation of reaction time which is tested. The decrease of iodine number at catalyst concentration by using sulfuric acid catalyst 1.5% to 3.5% can be seen decreasing iodine number.

This is due to the fact that the iodine number in the epoxidation reaction with the addition of catalyst concentration tends to decrease due to the breaking of the double bond into the form of the epoxy ring [2].

#### 3.2 Effect of Time Variation of Reaction and Catalyst Concentration on Oxygen Numbers

The relation between reaction time variation and catalyst concentration to oxirane oxygen number at reaction temperature 70°C and 500 rpm stirring rate can be seen in the figure.
In Figure 2 it can be seen that the longer reaction time (60 minutes to 180 minutes) of oxirane/oxygen increases and at reaction time (240-300 minutes) the oxirane oxygen value decreases.

The results of this study have been in accordance with the research reported by Redjeki (2015) [2] that with increasing reaction time (60-180 minutes) increases the oxirane number. Furthermore, at the time of reaction (240-300 minutes) the oxirane oxygen value decreases this is due to the sulfuric acid catalyst requiring a shorter / faster time so that the longer use of reaction time will not increase the oxirane oxygen value but degrade the oxirane oxygen epoxide) resulting in a decrease in the oxygen value of the oxygen and converting it to glycol [15]. Thus, the optimum oxirane oxygen value is achieved after a 3 hour reaction time.

Based on the Figure, it can be seen that the increasing concentration of catalyst (1.5%, 2.0%, 2.5%, and 3.0%) oxygen oxygen tends to increase and at catalyst concentration using sulfuric acid catalyst (3.5%) oxirane oxygen values decreased. However, at 120 minutes and 300 minutes there was decreasing in the oxirane number at a catalyst concentration of 2.5% to 3.0%.

The results of this study have been in accordance with research that has been reported by Ariatmi (2008) that the concentration of catalyst will increase oxygen value of oxirane and then will decrease. At a catalyst concentration of 3.5% the oxirane oxygen decreased after addition of the sulfuric acid catalyst. This is due to the presence of H⁺ ions released by sulfuric acid catalyst which on one side accelerate the epoxidation reaction, but on the other hand, as more H⁺ ions are released, the opening of the epoxy ring [8] is caused by the oxyfraction group having high reactivity and the oxygen ring is easily open both in acidic or alkaline conditions [6]. Thus, the optimum oxygen oxygen value is achieved at a concentration of 3.0%.

3.3 Effect of Reaction Time and Catalyst Concentration on Conversion of Oxirane Oxygen

The relation between reaction time variation and catalyst concentration to conversion at 70 °C reaction temperature and 500 rpm stirring rate can be seen in Figure 3.
Figure 3. Relation between reaction time and catalyst concentration to oxirane oxygen conversion.

Based on Figure 3, it can be seen that the longer reaction time (60, 120, 180 minutes) the oxygen-oxide conversion produced will be higher in the catalyst concentration variations (1.5%, 2.0%, 2.5% and 3.0%). But at reaction time (240 and 300 minutes) there is a decrease of conversion.

Based on the figure that the longer reaction time (60 minutes to 180 minutes) for catalyst concentration variations (1.5%, 2.0%, 2.5%, 3% and 3.5%) conversion increases, this is due to the catalyst sulfuric acid takes a shorter time compared to other catalysts [15]. While at reaction time (240-300 minutes) oxirane oxygen value decreased. According to Syawaluddin [16] this occurs because under 180 minutes, it is possible to react between the catalyst and fatty acid distillate which is accompanied by the addition of hydrogen peroxide so that there is a restriction by the substrate on the epoxidation reaction while the time is above 3 hours or when the optimum time point reaches, double begins to decline which means the compound is nearing saturation. It can be said that epoxidation reaction will run slowly resulting in the content of the resulting epoxy compound decreases so that the addition of time will not increase the conversion but degrade oxirane oxygen resulting in decreased conversion. This is due to the insignificant addition of oxygen to the oxygen value thereby decreasing the conversion [2].

Based on Figure 3, it shows the catalyst concentration increases (1.5%, 2.0%, 2.5%, and 3.0%) conversion tends to increase and at catalyst concentration (3.5%) oxirane oxygen value decreases. However, at 120 minutes and 300 minutes, there was a decrease in conversion at 2.5% to 3.0% catalyst concentration. For catalyst concentration using sulfuric acid catalyst (1.5%, 2.0%, 2.5%, 3.0%) can be seen the conversion increases. This is in accordance with the theory that in general the increase in catalyst concentration will result in an increase in the oxirane number so that it will increase the conversion [15].

However, at 120 minutes and 300 minutes there was a decrease in conversion at 2.5% to 3.0% catalyst concentration. This was caused by the unstable temperature during epoxidation reaction. At temperatures that exceed the optimum temperature the formation of epoxy has a significant decrease because at high temperatures it can trigger the oxygen ring which has formed open and form a polyol [15]. While on the concentration of sulfuric acid catalyst, 3.5% of the oxygen conversion of the oxirane decreases. This is due to the presence of H⁺ ions released by sulfuric acid catalyst which on one side speed up the epoxidation reaction, but on the other hand, as more H⁺ ions are released, the opening of the epoxy ring [6] occurs. Concentrated sulfuric acid in addition to having the ability as a catalyst also has the ability to degrade the oxygen group is quite high [15]. This is also due to the oxyfaction group having a high reactivity rate and an easily open oxirane ring in both acidic or alkaline conditions [7]. Thus, the optimum conversion was achieved when the catalyst concentration of 3.0% and reaction time was 180 minutes, ie 69.88%.

4. Conclusion
The epoxidation reaction is the reaction of the formation of the oxygen group by means of double bond oxidation using the peroxy of glacial acetic acid and sulfuric acid as the catalyst. The result showed that the best oxygen oxygen content was 0.96, iodine 17,16 g I₂/100 g Oil with conversion of 81,61 at reaction condition 70oC, reaction time 120 minutes and concentration of 2.5% H2SO4 catalyst.

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