Jurnal Pijar MIPA
https://jurnalfkip.unram.ac.id/index.php/JPM

ISSN 1907-1744 (Print)
ISSN 2460-1500 (Online)

Effect of Acid Catalyst on Epoxydation Reaction of Nyamplung Seed Oil

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Received: December 20, 2024. Accepted: January 29, 2025. Published: January 30, 2025

Abstract: Epoxy is a cyclic ether compound that contains an oxirane group and has been widely applied as a stabilizer, plasticizer in polyvinyl chloride (PVC), surfactant, pesticide raw material, and as a polymer resin coating. The raw materials in epoxy synthesis come from petroleum derivatives, which are non-renewable natural resources. Therefore, there is a need for alternative raw materials that can be renewed, such as vegetable oil. In this study, nyamplung seed oil was used. Epoxy synthesis is usually carried out using carboxylic acid epoxidation with the help of an acid catalyst. This research aims to determine the effect of the type of acid catalyst and its concentration on the epoxidation reaction of nyamplung seed oil and the characterization of the epoxy produced. The research results show that using an acid catalyst can increase the formation of oxirane groups at a certain concentration, where the highest oxirane number value was obtained when using the H_2SO_4 catalyst, namely 3.15%. The resulting epoxy is pale yellow, has a typical absorption area (COC) at a wave number of 825 cm^{-1}, an iodine value of 13.96 g iod/100 g, a viscosity of 20.80 cP, and a relative per cent conversion to oxirane of 73.4%.

Keywords: Epoxy; Epoxidation; Acid Catalyst; Nyamplung Seed Oil.

Introduction

Epoxy compounds are cyclic ether compounds containing oxirane groups formed through epoxidation reactions [1]. Epoxidation reactions form oxirane groups from double bonds [2]. Epoxy compounds have been widely applied in the industrial sector as stabilizers, plasticizers in polyvinyl chloride (PVC), antioxidants in natural rubber processing, surfactants, anti-corrosive agents as additives in lubricating oils, raw materials for pesticides [3], raw materials for polyol synthesis [4], as well as as a polymer resin coating [5].

The raw materials used to synthesize epoxy compounds come from non-renewable petroleum derivatives. The use of petroleum continues to increase from year to year, causing its availability to become increasingly scarce, so there is a need for alternative raw materials that can be renewed, one of which is vegetable oil [6]. Vegetable oils that are good for use in the synthesis of epoxy compounds contain relatively high levels of unsaturated fatty acids, for example, soybean oil [1], palm oil [7], and corn oil [4]. According to Suhendra et al. [8], using vegetable oils that can be consumed will create competition with their needs as food ingredients. Therefore, other vegetable oils that cannot be consumed are needed as raw materials in synthesizing epoxy compounds, such as oil from the nyamplung plant *(Calophylum inophyllum*).

Nyamplung plants have quite high oil levels in the seeds [9]. Nyamplung seed oil content ranges from 40-73% [10]. The oil content is higher than other plants, such as castor oil, 40-60 %, and palm oil, 46-54% [11]. The fatty acid composition of nyamplung seed oil is palmitic acid 14.7%, palmitoleic acid 0.3%, stearic acid 13.2%, oleic acid 46.1%, linoleic acid 24.7%, linolenic acid 0.2%, and 0.8% arachidic acid [12]. These data show that the largest composition of nyamplung seed oil is unsaturated fatty acids, including oleic acid and linoleic acid. This causes nyamplung seed oil to have great potential to be used as a raw material in epoxy synthesis.

The synthesis of epoxy compounds uses varying methods depending on the nature of the reactants and catalyst used. The technique often used on a laboratory and industrial scale is epoxidation with per carboxylic acid formed in situ using an acid catalyst [13]. Enzymes as catalysts are less effective because enzyme activity tends to decrease due to increased concentration of hydrogen peroxide, formic acid, and temperature [14, 15]. Epoxidation using an enzyme catalyst is only stable at a temperature of 20 ^{o} C, and when the temperature is higher, there is a decrease in enzyme activity. Gradually [16]. Metal catalysts are also less effective because it is difficult to separate or purify the products from these catalysts [17].

According to Kuranska et al. [18], The type of catalyst and its concentration can affect the results of epoxy synthesis. This can be seen from the value of the oxirane number or the conversion value to the oxirane. Previous research conducted by Goud et al. [19] regarding epoxidation of mahua oil with a 2% H_2SO_4 catalyst and HNO_3 3.12 % obtained relative per cent conversion to oxirane of 60% and 36%, respectively. Research by Dinda et al. [20], namely, epoxidation of kapok seed oil, when using the 2% H_2SO_4 catalyst, the relative per cent conversion to oxirane was 70.4%, using the 1.5% H_3PO_4 catalyst was 67.5% and using the HNO_3 catalyst 1.5% obtained 43% and in research by Gunawan et al.[21] namely, epoxidation of Ketapang oil with a 5 % H_2SO_4 catalyst, the relative per cent conversion to oxirane was obtained at 70.4%. Each catalyst and concentration

How to Cite:
D. A. Saputri, D. Suhendra, E. R. Gunawan, and M. Murniati, "Effect of Acid Catalyst on Epoxydation Reaction of Nyamplung Seed Oil", *J. Pijar.MIPA*, vol. 20, no. 1, pp. 135–140, Jan. 2025. https://doi.org/10.29303/jpm.v20i1.6338

produces a different number of oxiranes and a relative percentage of conversion to oxiranes for each type of vegetable oil. Therefore, this research examines the effect of varying acid catalysts and their concentrations on synthesizing epoxy from nyamplung seed oil.

Research Methods

Epoxy synthesis was done using the in-situ method [13] with modifications and adjustments. Oil (8.72 g) was put into a three-neck flask with a thermometer and condenser. The oil is added with formic acid and hydrogen peroxide drop by drop; then, an acid catalyst is added and stirred using a mechanical stirrer. In the next stage, the mixture was transferred into a separating funnel, and 5% $NaHCO_3$, distilled water, and 5% NaCl were added. The mixture is then extracted liquid-liquid, and the organic phase product is analyzed qualitatively and quantitatively.

Three acid catalysts are used, namely H_2SO_4, H_3PO_4, and HNO_3, with a concentration of 0, 1.5, 3, and 4.5 %. The reaction conditions were constant with a mole ratio of oil, formic acid, and hydrogen peroxide, namely 1:3:6, a temperature of 45℃, and a reaction time of 6 hours.

Epoxy was characterized qualitatively and quantitatively. Qualitative characterization was carried out by observing the FTIR spectrum of the epoxidized oil obtained, and quantitative analysis was carried out by determining the oxirane number, iodine number, viscosity, and relative value of conversion to oxirane.

The value of the iodine number which can be calculated using the formula:

$$\frac{\text{(Vo-Vs) x N x } Na_2S_2O_3 \text{ x 12,691}}{\text{gram sampel}}$$

In. Note:

$$12{,}691 = \frac{\text{Atomic mass Iodium}}{10}$$

The iodine number is used to calculate *the theoretical oxirane content* (OOC_{th}) with the formula:

$$\left[\frac{(IV_0/2Ai)}{100 + (IV_0/2Ai) \times A_0}\right] A_0 \times 100$$

A_i is the atomic mass of iodine (126.9045), A_0 is the atomic mass of oxygen (16), and IV_0 is the iodine number of the sample (base material).

Experimental oxirane number analysis (*oxygen oxygen content*, OOC_{ex}) used the method from *the Association of Official Analytical Chemists* (AOCS Cd 9-57, 1997) with the formula:

$$\frac{\text{V HBr} \times 1{,}6 \times \text{N HBr}}{\text{w}}$$

V is the volume of HBr titrant for the sample, N is the concentration of HBr used (0.1 N), and w is the weight of the sample. The oxirane number is used to calculate the relative per cent conversion to oxirane (OOC) with the formula:

$$\frac{OOC_{ex}}{OOC_{th}} \times 100\%$$

Epoxy viscosity is measured using an Ostwald viscometer, which measures the time required to flow in the capillary tube from the upper to the lower boundary. The viscosity value is calculated using equation 3.10

$$\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2}$$

Results and Discussion

Epoxy compounds are synthesized through epoxidation reactions, namely, the oxidation reaction of oil double bonds by active oxygen. (Figure 1)[22]. The oxidizer used in this research was hydrogen peroxide, but because it was not strong enough, it had to be changed to a more reactive form, namely peroxy acid (performic acid). The performic acid formed will react directly with the double bonds in the oil, producing a pale yellow and thick epoxidized oil.

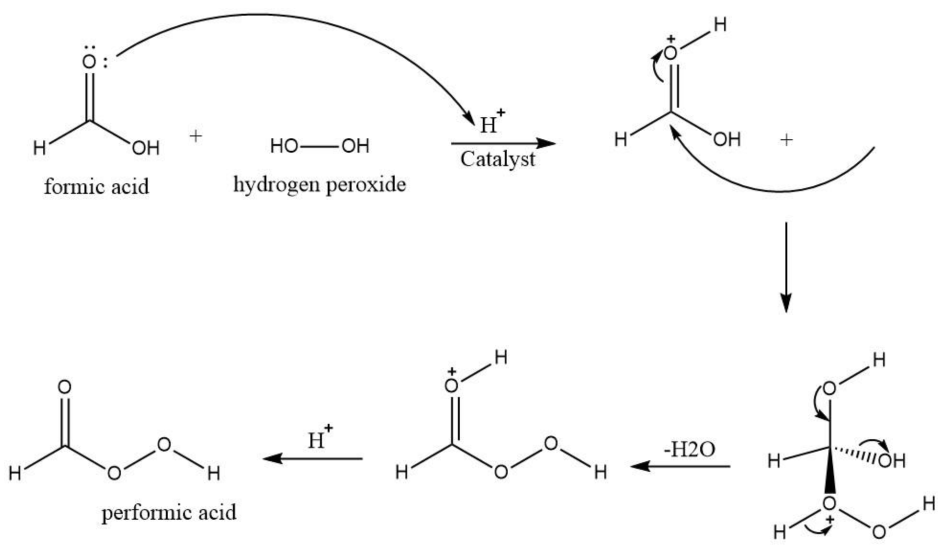

Figure 1. Reaction for the formation of performic acid

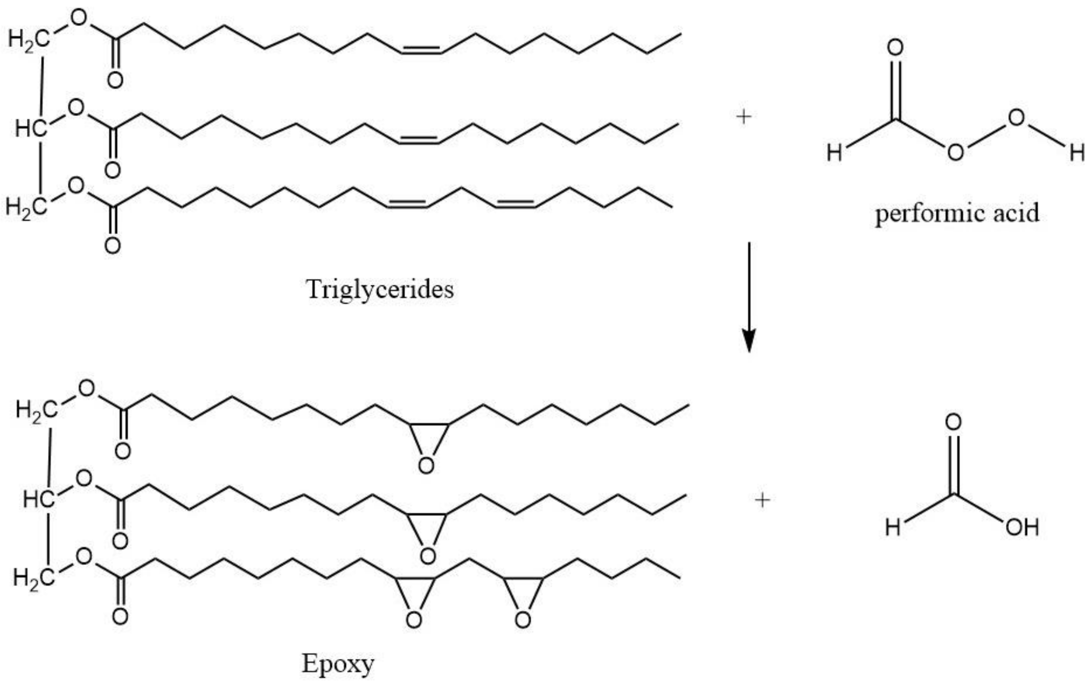

Figure 2. Epoxidation reaction of Triglycerides

The oxirane number value shows the results of epoxy synthesis. The higher the value of the oxidant number obtained, the better the quality of the epoxy produced. This is because the oxirane number shows the number of oxirane or epoxy groups formed through the epoxidation reaction. The higher the value of the oxirane number produced, the more epoxy is formed. One of the things that influences the epoxidation reaction is a catalyst. A high catalyst concentration causes more double bonds to be converted into oxirane groups, meaning that the value of the oxirane number obtained is high. Based on the research, an oxirane value of 2.41% was obtained to synthesize epoxy without a catalyst. As for the experiment with the addition of an acid catalyst, higher values of the oxirane number were obtained, including when using the HNO_3 catalyst, the value of the oxirane number increased up to a concentration of 4.5% with an oxirane number value of 2.83%. It decreased when the concentration was 6%, with a value of 2.83%. Oxirane 2.57%. The next catalyst used is H_2SO_4; the oxirane number increases to a concentration of 3% with an oxirane number value of 3.15% and decreases when the concentration is 4.5% to 2.53%. Using another catalyst, namely the H_3PO_4 catalyst, the oxirane number value increased to a concentration of 3% with an oxirane number value of 2.76% and decreased when the concentration was 4.5% to 2.52%.

Adding a catalyst to the epoxidation reaction will increase the oxirane number quickly. Still, besides that, the use of a concentration that is too high can accelerate the degradation or opening of the oxirane group so that the oxirane number value will decrease [15]. Based on data from the three acid catalysts, the 3% H_2SO_4 catalyst produces the highest oxirane value.

FTIR analysis compared the spectrum between nyamplung seed oil and epoxy synthesized with 3 % H_2SO_4. This aims to determine changes in functional groups in the oil before and after epoxidation.

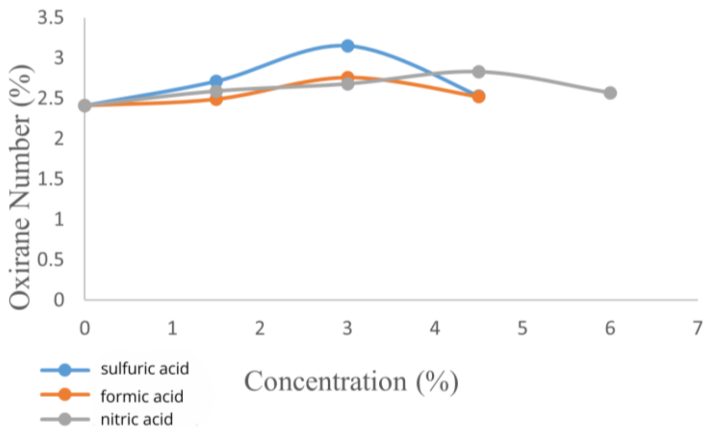

Figure 3. Effect of variations in type and concentration of acid catalyst on oxirane number

These changes can be seen from shifts. Based on Table 2, the epoxy absorption spectrum for the double bond at wave number 3003 cm $^{-1}$ is not readable; this shows the double bond disappearance or emergence of absorption areas.

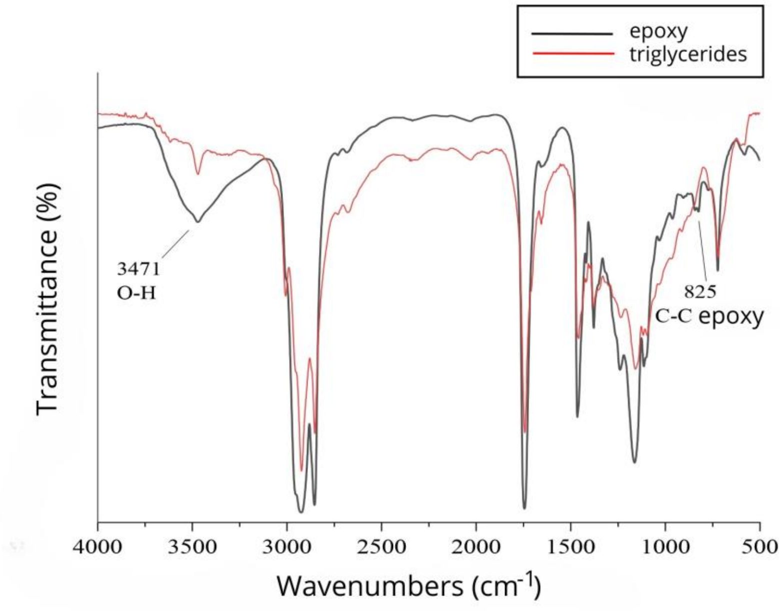

Figure 4. Comparison of the FTIR spectrum of nyamplung seed oil and epoxy

Table 1. Comparison of bond absorption areas in nyamplung seed oil and epoxy

Bond Type	Wave Number (cm $^{-1}$)	
	Nyamplung Seed Oil	Epoxy
C-C	719	722.93
Epoxy C-O-C	-	825
C-O ester	1162	1162.77
C=C	1653	1663
C=O ester	1747	1744.92
CH	2917-2856	2924.28-2854.32
	1457	1465.25
=CH	3003	-
OH	-	3471

Nyamplung seed oil has been converted into an oxirane group. This is indicated by the appearance of an absorption of 825 cm $^{-1}$ in the epoxy spectrum, which suggests the presence of an oxirane group. The presence of a wave number of 3471.9 cm $^{-1}$ indicates an OH group likely formed from a side reaction during the epoxidation process, for example, the opening of the oxirane ring by water or acid. This result is the same as that obtained by Kuranska et al. [18], that the OH group in the FTIR spectrum indicates a ring-opening reaction. According to Wibowo et al. [23], acid catalysts have disadvantages, such as easily degrading or opening oxirane groups. Apart from that, the appearance of C=C bonds at an absorption wave number of 1663 cm $^{-1}$ shows that there are still double bonds that have not been converted into oxirane groups; this is also demonstrated by the iodine number value of the epoxy that has been synthesized.

The iodine number is an indicator of the level of epoxidation, where the iodine number will decrease as epoxidation increases. Based on calculations, the iodine number from oil was 71.7 g iod/100 g, and from epoxy, it was 13.96 g iod/100 g. There is a decrease in the iodine number from oil to epoxy because the double bonds of the oil in the epoxy synthesis process are converted into oxirane rings.

The viscosity value at 28°C was obtained for nyamplung seed oil, namely, 11.52 cP; for epoxy, it was 20.80 cP. Based on these measurements, epoxy's viscosity value is higher than nyamplung seed oil's. This is because epoxidized oil has a larger molecular weight and a more polar structure, which means it has strong intermolecular interactions.

The next characterization, which indicates the success of epoxy synthesis, is the relative per cent conversion to oxirane, which is determined by comparing the oxirane number value based on experiments with the oxirane number value based on theory [24]. In this study, the value of the oxirane number based on theory was 4.29%, so the relative value of conversion to oxirane was 73.4%. The percentage conversion to oxirane in this study is higher than the research conducted by Dinda et al. (2008), which used 2% H_2SO_4 catalyst in the epoxy synthesis from kapok seed oil, achieving a conversion percentage of 70.4%. Similarly, in the study by Goud et al. (2006), which synthesized epoxy from mahua oil using the same rate and type of catalyst, a conversion of 60% was obtained. However, the percentage conversion in this study is lower than that obtained by Derawi et al. (2014) in the epoxy synthesis from palm oil using a 3% H_2SO_4 catalyst, which reached 95.5%. This difference is due to variations in reaction conditions and the type of oil sample used.

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Conclusion

The synthesis of epoxy from nyamplung seed oil is influenced by the type of acid catalyst and its concentration, where an acid catalyst with a certain concentration can increase the oxirane value. The most optimum acid catalyst used is H_2SO_4 3% with the characteristics of the resulting epoxy, including the presence of C-O-C bonds at an absorption wave number of 825 cm^{-1}, an iodine number of 13.96 g iod/100 g, a viscosity of 20.80 cP, and a conversion oxirane 73.4%. The results of this study can be used as a reference for the type and concentration of optimal and effective acid catalysts in synthesizing epoxy compounds from nyamplung seed oil.

Author's Contribution

Dita Ayu Saputri: contributed as the first author and participated in all experiments. Erin Ryantin Gunawan: contributed as a corresponding author and editor and coordinated data analysis. Dedy Suhendra: contributed as second author and designed the research plan. Murniati contributed as a third author, assisted in data analysis, and participated in some experiments.

Acknowledgement

This research is part of the Basic Research scheme of the Ministry of Education, Culture, Research, and Technology of the Republic of Indonesia in 2023 with contract number 2352/UN.Ll/P.P./2023.

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