

Synthesis of epoxy oil from Waste Cooking Oil (WCO) using acetic acid and amberlite resin IR-120 as catalyst

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Abstract

Several reports showed that the high unsaturated fatty acids present in waste cooking oil (WCO) held significant potential as a valuable raw material for the production of epoxy oil. Therefore, this study aimed to develop a method for effectively utilizing WCO in the synthesis of epoxy oil with acetic acid and amberlite resin IR-20 as catalyst. The synthesis process involved the use of a reflux method at 60°C with various epoxidation times (4, 6, and 8 hours) on a batch scale. The materials used included hydrogen peroxide, glacial acetic acid (homogeneous catalyst), and amberlite resin IR-120 (heterogeneous catalyst) with different mass ratio of WCO to amberlite resin IR-120 (100:0; 100:1.58; 100:3.15; and 100:6.3). The functional group analysis results using the Fourier transform infrared (FTIR) spectrophotometer showed the presence of stretching vibrations of the epoxy group (C–O–C) at 850–830 cm⁻¹ and 1240 cm⁻¹. Increasing the ratio of WCO to amberlite resin IR-120 from 100:0 to 100:3.15 led to a decrease in iodine number and an increase in oxirane number. A further increase in the ratio to 100:6.3 provided an increase in the iodine number and a decrease in the oxirane number. Furthermore, the highest oxirane number was achieved with a 100:3.15 ratio of WCO to amberlite resin IR-120. Based on the results, an increment in the epoxidation time from 4 hours to 8 hours led to a decrease in the iodine number and an increase in the oxirane number. The highest oxirane number of 2.4159% was achieved with a 100:3.15 ratio of WCO to amberlite resin IR-120 for 8 hours.

Keywords: Acetic acid, Amberlite resin IR-120, Epoxy oil, Waste cooking oil

1. Introduction

Waste cooking oil (WCO) is readily available in canteens, food industries, restaurants, and household kitchens, leading to the generation of a significant amount [1]. The underutilization of WCO has been reported to pose serious disposal challenges that can disrupt environmental equilibrium. The waste can contaminate groundwater resources, hinder degradation in water by preventing oxygen transfer, and cause clogging of collection pipes, potentially leading to sewer overflows [2]. To address this problem, several studies explored the potential of WCO as a raw material for the production of soap, lubricant, and biodiesel [1, 3-5]. However, further investigation is required to explore additional avenues for effective utilization, such as its conversion into epoxy oil.

Epoxy compounds can be produced from either crude or processed vegetable oil [6], with palm oil being one of the most popular. Palm oil is extensively used in industries and households for cooking purposes, but becomes WCO when discarded. WCO typically contains 20 wt% fatty acids [7], including unsaturated (45.15% oleic acid, 39.74% linoleic acid, 0.20% linolenic acid) and saturated (8.80% palmitic acid, 4.20% stearic acid) types [5]. The presence of high levels of unsaturated fatty acids presents an excellent opportunity for epoxy oil production. Epoxy oil is commonly used as a compound plasticizer in the rubber industry. Plasticizers play a crucial role in reducing the viscosity of rubber, rendering it softer and more pliable. They also facilitate the uniform distribution of additives, thereby enhancing the overall performance of the product.

At present, the majority of plasticizers in use are derived from non-renewable sources, such as paraffinic, naphthenic, phthalate, and aromatic oil. However, these non-renewable are currently experiencing diminishing availability [3] and concerns have been raised regarding their environmental impact, irritation, corrosiveness, and carcinogenicity [8-10]. These challenges had led to the development of various studies aimed at synthesizing bioplasticizer from renewable sources, such as peanut oil, soybean oil, tung oil, castor oil, palm oil, and other vegetable oils [11]. This current study is focused on developing alternative bioplasticizers from WCO.

The synthesis of epoxy from WCO has been previously reported, utilizing hexane as a solvent and employing catalyst, such as hydrogen peroxide, glacial acetic acid, and sulfuric acid [12]. The findings obtained from previous studies revealed that the optimum epoxidation time was 300 minutes with a 1.5% catalyst concentration [12]. Furthermore, several investigations have been carried out on the epoxidation of WCO using homogeneous (H₂SO₄ and H₃PO₄) and heterogenous (amberlite resin IR-120) catalysts [13]. Compared to previous reports, this current study employed glacial acetic acid as a homogeneous catalyst and amberlite resin IR-120

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as the heterogeneous variant. These materials have previously been used for the epoxidation of hazelnut oil [14] and rubber seed oil [15]. Amberlite resin IR-120 possesses a cyclic structure capable of binding oxygen and its heterogeneous nature facilitates easy removal from the final product. This catalyst is also cost-effective and readily available in the stock market. In comparison, acetic acid as a homogeneous catalyst, is more environmentally friendly and economical compared to strong acids, such as H_2SO_4 and H_3PO_4 . Therefore, this study aims to determine the effect of epoxidation time and the ratio of WCO to amberlite resin IR-120 on the quality of epoxy oil.

2. Methodology

2.1 Tools and materials

The materials used to synthesize epoxy oil included WCO, amberlite resin IR-120, 99.8% glacial acetic acid (Merck), 30% hydrogen peroxide (Merck), and distilled water. Furthermore, iodine number analysis of the sample was carried out using 99.5% cyclohexane (Merck), Wijs solution, 99.995% potassium iodide (Merck), 98.5% sodium thiosulfate (Merck), and amylum indicator. Oxirane number analysis of epoxy oil was carried out using various materials, including 47-49% hydrogen bromide (Loba Chemie), 99.8% glacial acetic acid (Merck), and crystal violet indicator.

The tools used in this study consisted of reflux column equipped with a cooling device, three-neck flask, thermometer, magnetic stirrer, heater, analytical balance, separatory funnel or centrifuge, glass beaker, Erlenmeyer, micro burette, bulpet, volume pipette, ladle, and PerkinElmer FTIR spectrophotometer. The epoxidation tool assembly is illustrated in Figure 1.

2.2 Synthesis of epoxy oil

The study scheme was outlined in the flow chart as presented in Figure 2. WCO was placed into a three-neck flask, followed by the addition of glacial acetic acid, and amberlite resin IR-120, as shown in Table 1. Subsequently, the mixture was heated to $50^\circ C$, and hydrogen peroxide was added, with the solution being regulated at $50^\circ C$. The molar ratio of double bonds, hydrogen peroxide, and acetic acid was 1:1.5:0.5. The solution obtained was then refluxed for 4, 6, and 8 hours at $60^\circ C$.

To purify the epoxy oil from its impurities, amberlite resin IR-120 was filtered off, and the filtrate was poured into a separatory funnel. The solution was then washed repeatedly using warm water until the pH of the filtrate was neutral. The remaining water in the epoxy oil solution was separated using a centrifuge at 400 rpm for 10 minutes.

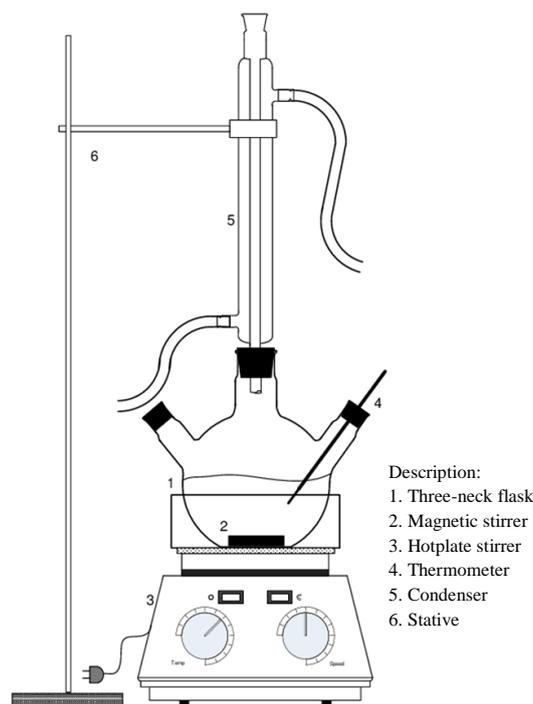


Figure 1 The epoxidation tool assembly

Table 1 Ratio of WCO to amberlite resin IR-120

No.	WCO (g)	Amberlite Resin IR-120 (g)
1	100	0
2	100	1.58
3	100	3.15
5	100	6.30

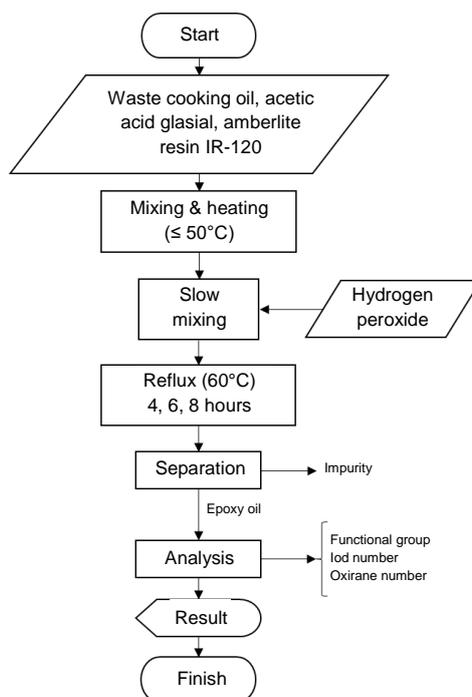


Figure 2 The epoxidation tool assembly

2.3 Characterization of epoxy oil

The formation of oxirane and the decrease of double bonds in WCO and epoxy oil were analyzed qualitatively using a PerkinElmer FTIR spectrophotometer at a wavelength range of 4000-650 cm^{-1} . The iodine number indicated the double bonds in the oil molecular chain, both in WCO and epoxy oil. Furthermore, the iodine number (g $\text{I}_2/100$ g oil) was determined with the Hanus method using Equation (1) with B is the volume of sodium thiosulfate used in the blank titration (mL). In Equation (1), S is the volume of sodium thiosulfate used in the sample titration (mL), N is the sodium thiosulfate normality after standardization, and G is the sample weight (g).

$$\text{The iodine number} = \frac{(B-S)}{G} \times N \times 12.69 \quad (1)$$

The iodine number analysis was performed by adding 0.5 g of epoxy oil, 10 ml cyclohexane, and 25 ml Wijs solution into an Erlenmeyer, which was later capped. The solution was stored in a cabinet for up to 30 minutes, followed by the addition of 10 ml potassium iodide and 50 ml distilled water. Subsequently, standardization was carried out with thio sulfate until the color turned yellow. The starch indicator was added to the solution and titrated until the color fades. The same procedure was performed for the blank.

Double bond conversion (X_{Iod}) was calculated using Equation (2), where IV_0 is the initial iodine number of WCO, and IV is the iodine number of epoxy oil [16].

$$X_{Iod} (\%) = \left(\frac{IV_0 - IV}{IV_0} \right) \times 100 \quad (2)$$

The oxirane number indicated the epoxy group on the molecular chain of the epoxy oil. Furthermore, the iodine number of WCO was used to calculate the theoretical oxirane number (OOC_t) using Equation (3), where A_I is the atomic weight of iodine (126.9045 g/mol), A_O is the atomic weight of oxygen (16 g/mol), IV_0 is the initial iodine number of WCO.

$$OOC_t (\%) = \left[\frac{(IV_0/2A_I)}{100 + (IV_0/2A_I)A_O} \right] A_O \times 100 \quad (3)$$

The experimental oxirane number (OOC) analysis was determined using direct titration and calculated using Equation 4, where V is the volume of hydrogen bromide used in the titration (mL), K is the hydrogen bromide normality, and G is the sample weight (g).

$$OOC (\%) = \frac{V \times K}{G} \times 1.60 \quad (4)$$

Oxirane number analysis was performed by adding 0.49 g of epoxy oil, 10 mL of glacial acetic acid, and 3 drops of crystal violet indicator into an Erlenmeyer. The solution was titrated with 0.1 N hydrogen bromide until the color changed from purple to blue and then to blue-green (persist for 30 seconds). During titration, the top of the micro burette was sealed with aluminum foil.

The relative percent conversion to oxirane (X_{OOC}) was calculated using Equation (5).

$$X_{OOC} (\%) = \frac{OOC_e}{OOC_t} \times 100 \quad (5)$$

3. Results and discussion

3.1 Characterization of epoxy oil functional groups

The conversion of unsaturated fatty acids in WCO to oxiranes (epoxy groups) and other functional groups was characterized using an FTIR spectrophotometer. The epoxy oil spectra synthesized from epoxidation for 6 hours using various ratios of WCO to amberlite resin IR-120 are presented in Figure 3. Meanwhile, the spectra of the epoxy oil produced from various epoxidation times are shown in Figure 4. The FTIR spectra in both Figures 3 and 4 were normalized.

Figure 3 showed that the epoxy oil produced from a 100:3.15 ratio of WCO to amberlite resin IR-120 had a higher peak absorption intensity compared to others. Figure 4 revealed that epoxidation for 8 hours gave the product with the highest peak absorption intensity.

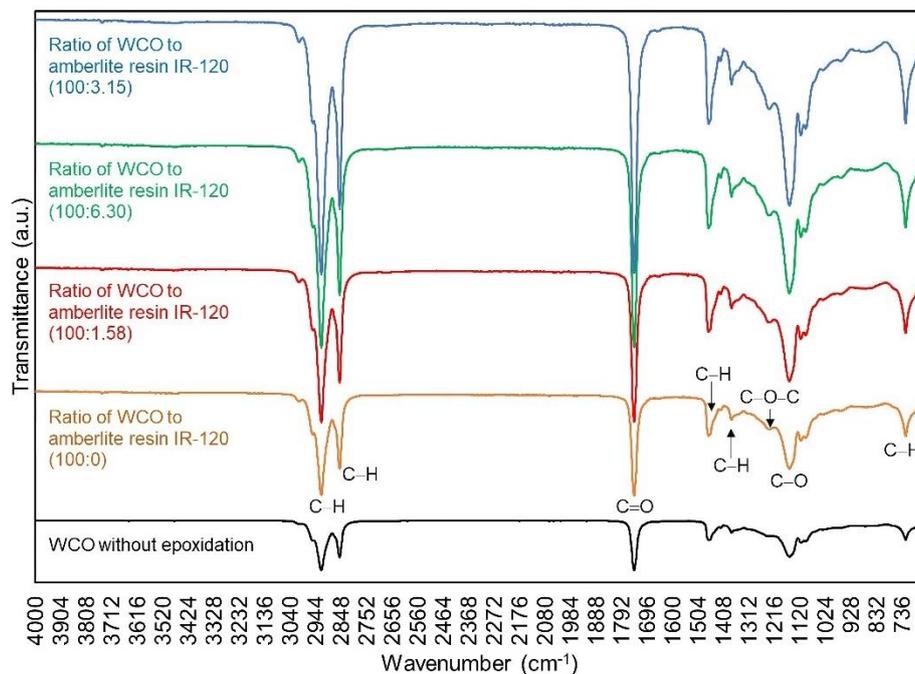


Figure 3 FTIR spectra of epoxy oil at various ratio of WCO to amberlite resin IR-120 for 6 hours epoxidation

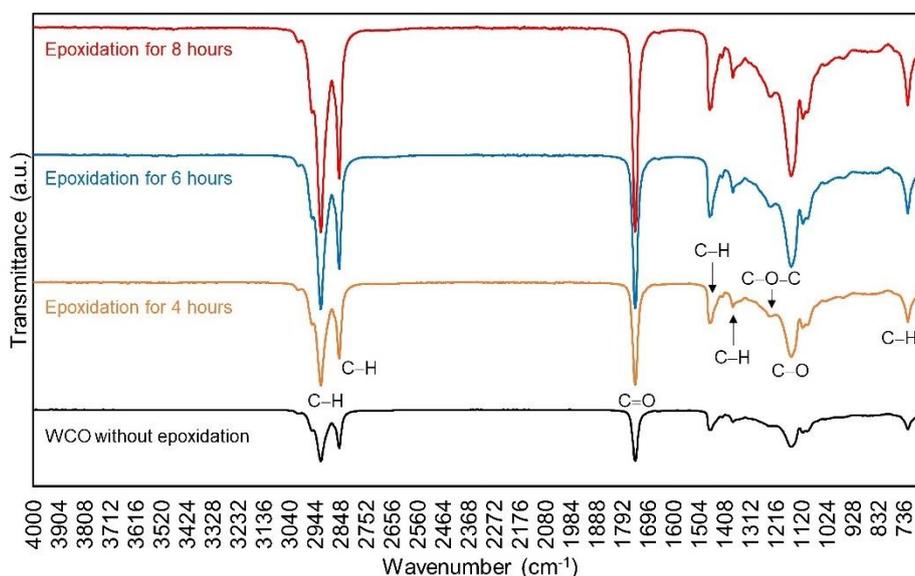


Figure 4 FTIR spectra of epoxy oil at various epoxidation times using ratio of WCO to amberlite resin IR-120 100:3.15

Figures 3 and 4 showed the strong C–H stretching band of the methyl group (CH_3) at 2922 cm^{-1} . Furthermore, C–H stretching bands of the methylene moieties (CH_2) were apparent at 2853 cm^{-1} and 1464 cm^{-1} . The deformation band of C–H was observed at 1377 cm^{-1} . The C–H group of epoxy oil produced in this study was in line with those synthesized in previous studies [17], which were present at 2922 cm^{-1} , 2853 cm^{-1} , 1464 cm^{-1} , and 1377 cm^{-1} . The spectra also showed C–H groups at 721 cm^{-1} as reported in another study by Borugadda and Goud [4]. The C=O ester group at 1744 cm^{-1} also appeared in the spectra of epoxy oil. This group was derived from the fatty acid triester of glycerol, and its presence was also shown in several reports [4, 18, 19].

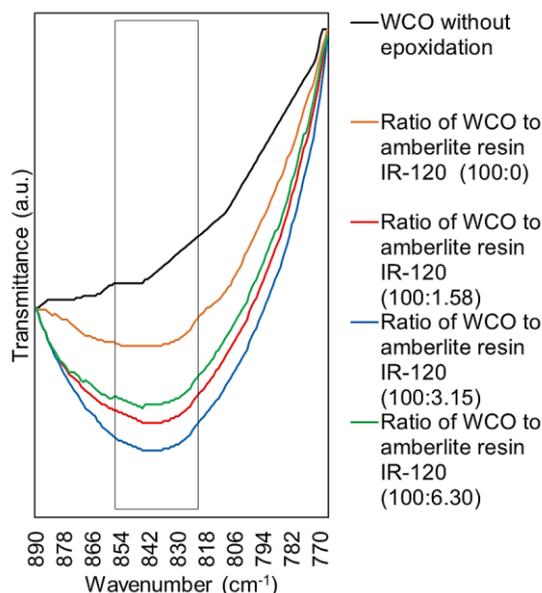


Figure 5 FTIR spectra of epoxy oil at various ratio of WCO to amberlite resin IR-120 for 6 hours epoxidation

Based on Figures 3 and 4, the stretching vibration of the epoxy group (C–O–C) appeared at 1240 cm⁻¹. Another stretching vibration was found in the bands between 850-830 cm⁻¹, as shown in the magnified FTIR spectra (Figure 5). The epoxy group vibration (C–O–C) at 850-830 cm⁻¹ and 1240 cm⁻¹ had also been identified by previous studies [17, 20]. Meanwhile, the epoxy group (C–O–C) of WCO without the epoxidation was not found at 1240 cm⁻¹ in the FTIR spectrum. This indicated that the epoxidation process had been successfully performed. The highest C–O–C absorption intensity was observed in the epoxy oil produced using WCO/AR of 100/3.15, as shown in Figures 3 and 5. The epoxidation time also showed an increasing trend of C–O–C absorption intensity as it increased from 4 hours to 8 hours (Figure 4). Based on the spectra analysis of epoxy oil, the synthesis of epoxy from WCO was successfully carried out.

Vibrations of the C-O-C ether and ester group were observed in the spectra of epoxy oil at 1160 cm⁻¹ and 1116 cm⁻¹, which could be associated with side reactions, such as oligomerization [13]. Since the vibrations were also found in the spectra of WCO without epoxidation at 1160 cm⁻¹ and 1116 cm⁻¹, it could be concluded that the oligomerization reaction did not take place during epoxidation.

3.2 Effect of WCO/AR Ratio

The analysis results of the iodine number and oxirane number of epoxy oil at various ratios of WCO to amberlite resin IR-120 were presented in Figures 6 and 7. The WCO in this study had an iodine number of approximately 46.4528 g I₂/100 g with an *OOC_i* of 2.8450%. After the epoxidation process for 6 hours, epoxy oil had a lower iodine number compared to WCO. This indicated that the epoxidation of WCO had occurred, causing the unsaturated bonds or double bonds (C=C) in the molecular chain to be cleaved and converted into single bonds in the form of epoxy compounds (C–O–C). The formation of epoxy groups was also indicated by the spectra analysis results in Figures 3, 4 and 5.

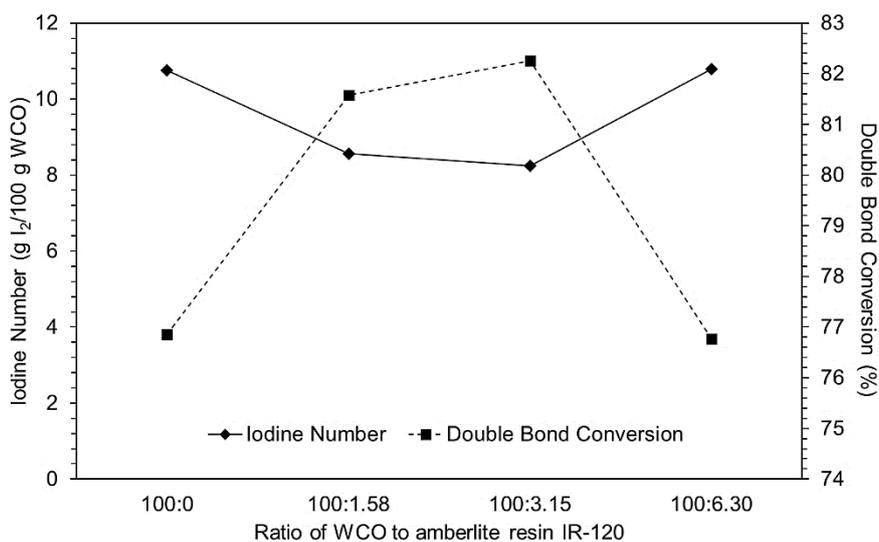


Figure 6 Effect of WCO to amberlite resin IR-120 ratio to iodine numbers and double bond conversion

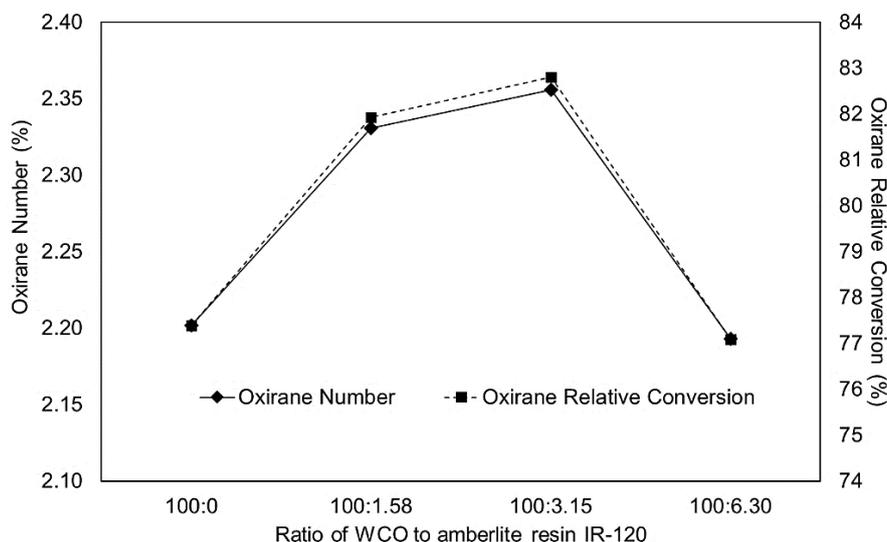


Figure 7 Effect of WCO to amberlite resin IR-120 ratio to oxirane number and oxirane relative conversion

In the formation of the oxirane ring, the resin acted as a catalyst and as a reactant in the hydrolysis [16]. To achieve the best oxirane number, the optimum amount of resin must be applied. The analytical results in Figures 6 and 7 also showed that the ratio of WCO to amberlite resin IR-120 affected the iodine and oxirane number. As the ratio of WCO to amberlite resin IR-120 increased from 100:0 to 100:3.15, there was a decreasing trend in iodine number, as well as an increasing trend in X_{Iod} , OOC , and X_{OOC} .

The resin used in the epoxidation process served as a carrier (channel) of active oxygen from the reactant (hydrogen peroxide) to the double bonds in WCO. Furthermore, its concentration indirectly determined the direction of the reaction. Increasing the catalyst concentration to a certain value could facilitate the transfer of active oxygen, leading to increased oxiranes production levels. Figures 6 and 7 showed that the greater the resin concentration (from ratio of WCO to amberlite resin IR-120 100:0 to 100:3.15), the greater the frequency of collisions between the reacting molecules. Increased frequency of collision could lead to a shift of reaction to the right (product), thereby increasing the number of double bonds in WCO being converted to epoxy. Similar results were also obtained by previous studies [21], stating that the greater the catalyst concentration, the more the double bonds were converted into epoxy.

Based on Figure 6, the highest X_{Iod} , OOC , and X_{OOC} were achieved with a 100:3.15 ratio of WCO to amberlite resin IR-120. Furthermore, increasing the ratio from 100:3.15 to 100:6.3 led to an increase in iodine number and a decrease in X_{Iod} , OOC , and X_{OOC} . This was probably due to epoxy ring cleavage caused by excess reagents, such as resin as stated by previous studies [22]. Excess reagents reacted with epoxy rings to form various undesired products, as shown in Figure 8.

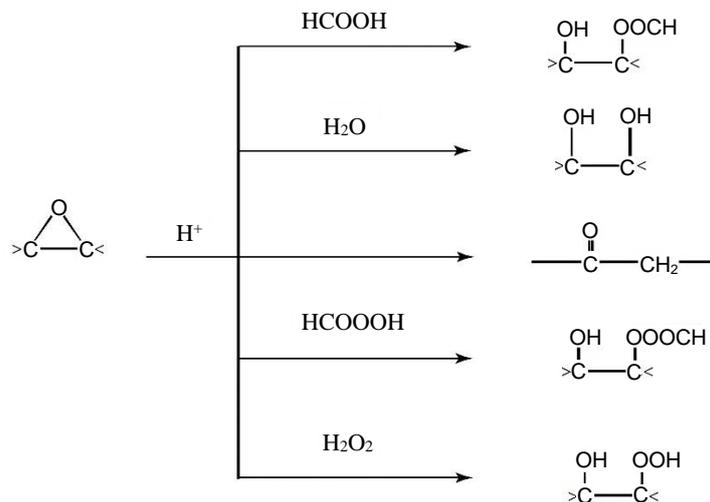


Figure 8 Schemes of epoxy ring cleavage reaction [23]

The highest oxirane relative conversion of 82.81% was achieved in this study with a 100:3.15 ratio of WCO to amberlite resin IR-120, which was higher compared to previous studies [13].

3.3 Effect of epoxidation time

The measurement results of the iodine number and oxirane number of epoxy oil at various epoxidation times are presented in Figures 9 and 10. Furthermore, the results showed that epoxidation time affected the iodine and oxirane numbers.

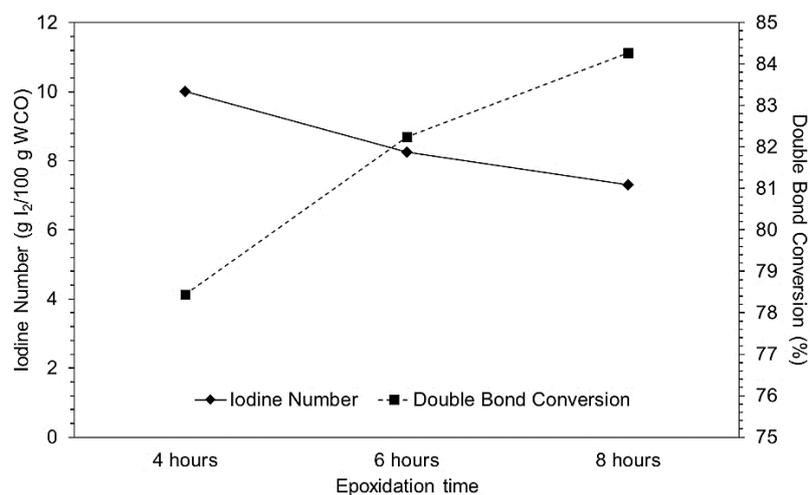


Figure 9 Effect of epoxidation time to iodine numbers and double bond conversion

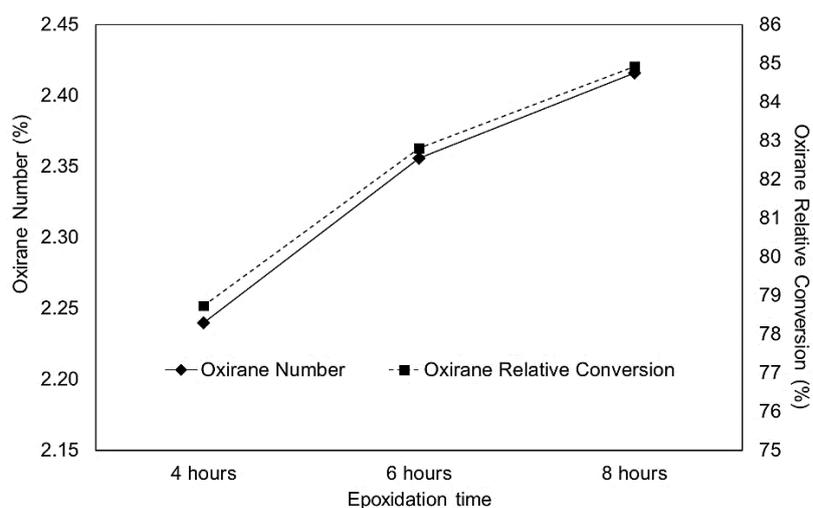


Figure 10 Effect of epoxidation time to oxirane number and oxirane relative conversion

Increasing the epoxidation time from 4 hours to 8 hours led to a decreasing trend of iodine number and simultaneously caused an increasing trend of X_{Iod} , OOC, and X_{OOC} . Furthermore, increasing the reaction time to a certain level led to a greater opportunity for the reactant molecules to collide with each other, as reported by previous studies [12, 24, 25]. This collision process led to the conversion of unsaturated compounds into epoxy compounds.

The highest X_{Iod} , OOC, and X_{OOC} were achieved when epoxidation was performed using a 100:3.15 ratio of WCO to amberlite resin IR-120 for 8 hours. Since the epoxidation reaction was alternating, an increment in time did not necessarily increase the oxirane oxygen number in the epoxy oil. Furthermore, an increase in the time could potentially lead to a decrease in the oxirane number and simultaneously increase the undesired products through the schemes, as shown in Figure 8.

The highest oxirane relative conversion of 84.92% was achieved in this study using a 100:3.15 ratio of WCO to amberlite resin IR-120 for 8 hours of epoxidation and this value higher compared to previous studies [13].

4. Conclusions

In conclusion, the results showed that increasing the ratio of WCO to amberlite resin IR-120 had a significant impact on the iodine number and oxirane number. Specifically, increasing the ratio from 100:0 to 100:3.15 resulted in a decrease in the iodine number and an increase in the oxirane number. Furthermore, further incrementing the ratio to 100:6.3 led to an increase in the iodine number and a decrease in the oxirane number. Notably, the highest oxirane number of 2.4159% was achieved with a 100:3.15 ratio of WCO to amberlite resin IR-120 after 8 hours of epoxidation time. These results highlight the importance of considering the ratio and epoxidation time in controlling the chemical properties of the mixture.

5. References

- [1] Sahar, Sadaf S, Iqbal J, Ullah I, Bhatti HN, Nouren S, et al. Biodiesel production from waste cooking oil: an efficient technique to convert waste into biodiesel. *Sustain Cities Soc.* 2018;41:220-6.
- [2] Moazeni F, Chen YC, Zhang G. Enzymatic transesterification for biodiesel production from used cooking oil, a review. *J Clean Prod.* 2019;216:117-28.
- [3] Panchal TM, Patel A, Chauhan DD, Thomas M, Patel JV. A methodological review on bio-lubricants from vegetable oil based resources. *Renew Sustain Energy Rev.* 2017;70:65-70.

- [4] Borugadda VB, Goud VV. Synthesis of waste cooking oil epoxide as a bio-lubricant base stock: characterization and optimization study. *J Bioprocess Eng Biorefinery*. 2014;3(1):57-72.
- [5] Bautista LF, Vicente G, Rodríguez R, Pacheco M. Optimisation of FAME production from waste cooking oil for biodiesel use. *Biomass Bioenergy*. 2009;33(5):862-72.
- [6] Murniati M, Gunawan ER, Suhendra D, Asnawati D, Qurba P. Synthesis of epoxy compounds from nyamplung oil fatty acids (*Calophyllum inophyllum* L.). *J Ris Kim*. 2022;13(1):89-99. (In Indonesia)
- [7] Kusdiana D, Saka S. Effects of water on biodiesel fuel production by supercritical methanol treatment. *Bioresour Technol*. 2004;91(3):289-95.
- [8] Pan S, Hou D, Chang J, Xu Z, Wang S, Yan S, et al. A potentially general approach to aliphatic ester-derived PVC plasticizers with suppressed migration as sustainable alternatives to DEHP. *Green Chem*. 2019;21(23):6430-40.
- [9] Khan AD, Alam MN. Cosmetics and their associated adverse effects: a review. *J Appl Pharm Sci Res*. 2019;2(1):1-6.
- [10] Bui TT, Giovanoulis G, Cousins AP, Magnér J, Cousins IT, de Wit CA. Human exposure, hazard and risk of alternative plasticizers to phthalate esters. *Sci Total Environ*. 2016;541:451-67.
- [11] Zhang Z, Jiang P, Liu D, Feng S, Zhang P, Wang Y, et al. Research progress of novel bio-based plasticizers and their applications in poly(vinyl chloride). *J Mater Sci*. 2021;56(17):10155-82.
- [12] Listiana Y, Tampubolon HR, Sinaga MS. Effect of catalyst concentration and reaction time to epoxy production from waste cooking oil. *J Tek Kim USU*. 2017;6(3):28-33. (In Indonesia)
- [13] Kurańska M, Beneš H, Prociak A, Trhlíková O, Walterová Z, Stochlínska W. Investigation of epoxidation of used cooking oils with homogeneous and heterogeneous catalysts. *J Clean Prod*. 2019;236:117615.
- [14] Rahmaniar, Priyanto G, Hamzah B. Rubber compounding with epoxy gandlenut oil addition. *Din Penelit BIPA*. 2009;20(35):59-68. (In Indonesia)
- [15] Rahmaniar, Prasetya HA. Epoxy rubber seed oil as a softener agent for radiator seal production epoxidized rubber seeds oil as a softener agent for radiator seals. *J Ris Ind*. 2011;V(1):71-8. (In Indonesia)
- [16] Campanella A, Fontanini C, Baltanás MA. High yield epoxidation of fatty acid methyl esters with performic acid generated in situ. *Chem Eng J*. 2008;144(3):466-75.
- [17] Salih A, Ahmad M, Ibrahim N, Dahlan K, Tajau R, Mahmood M, et al. Synthesis of radiation curable palm oil-based epoxy acrylate: nmr and ftir spectroscopic investigations. *Molecules*. 2015;20(8):14191-211.
- [18] Saha P, Kim BS. Preparation, characterization, and antioxidant activity of β -carotene impregnated polyurethane based on epoxidized soybean oil and malic acid. *J Polym Environ*. 2019;27(9):2001-16.
- [19] Zhang C, Ding R, Kessler MR. Reduction of epoxidized vegetable oils: a novel method to prepare bio-based polyols for polyurethanes. *Macromol Rapid Commun*. 2014;35(11):1068-74.
- [20] Sienkiewicz AM, Czub P. The unique activity of catalyst in the epoxidation of soybean oil and following reaction of epoxidized product with bisphenol A. *Ind Crops Prod*. 2016;83:755-73.
- [21] Cooney MT. Epoxidised resins from natural renewable resources [Dissertation]. Australia: University of Southern Queensland; 2009.
- [22] Lee PL, Wan Yunus WMZ, Yeong SK, Abdullah DK, Lim WH. Optimization of the epoxidation of methyl ester of palm fatty acid distillate. *J Oil Palm Res*. 2009;21:675-82.
- [23] Petrović ZS, Zlatanić A, Lava CC, Sinadinović-Fišer S. Epoxidation of soybean oil in toluene with peroxyacetic and peroxyformic acids-kinetics and side reactions. *Eur J Lipid Sci Technol*. 2002;104(5):293-9.
- [24] Saurabh T, Patnaik M, Bhagat SL, Renge VC. Epoxidation of vegetable oils: a review. *Int J Adv Eng Technol*. 2011;II(IV):491-501.
- [25] Sinaga MS. Effect of H₂SO₄ catalyst on the epoxidation reaction of PFAD methyl ester. *J Teknol Proses*. 2007;6(1):70-4. (In Indonesia)