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by Didi Dwi Anggoro

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Waste Cooking Oil Utilisation as Bio-plasticiser through Epoxidation using Inorganic Acids as Homogeneous Catalysts

Silviana*, Didi Dwi Anggoro, Andri Cahyo Kumoro

Department of Chemical Engineering, Faculty of Engineering, Diponegoro University, Semarang 50275, Indonesia
silviana@undip.ac.id

This paper exposed the preparation of epoxidised waste cooking oil with sulfuric acid, nitric acid, and hydrochloric acid in order to utilise waste cooking oil economically efficient due to highly unsaturated triglycerides. These triglycerides act as potential raw material due to double bond content. The double bond content can be converted as bio-plasticiser. The paper aimed to investigate optimum conversion with different inorganic acids based on oxirane conversion and iodine value at different time. Epoxidation reaction was carried out in the conventional acetic acid-hydrogen peroxide process.

The result showed that sulfuric acid can obtain higher conversion than that of other acid catalysts. It resulted with 20 % of oxirane conversion for 5 h.

1. Introduction

Currently, it is encouraged to transform waste into new product to reduce environmental contamination. Considerable amount of waste cooking oil (WCO) as potential bio-plasticiser source is a promising alternative way. The amount of WCO released depends on the use of vegetable oil. It is predicted that today world annual amount of WCO is approximately 29 Mt (Lisboa et al., 2014). It has been well-investigated that vegetable oil is used as such biodiesel feedstock (Knothe et al., 2009), fatty acids and lipid production (Chen et al., 2015), bio-lubricant feedstock (Borugadda et al., 2015), substrate for carotene production (Nanou et al., 2016). There was investigation of epoxidised WCO by using formic acid as oxygen source together with zeolite as heterogeneous catalyst (Qinghong et al., 2013). Other report related epoxidation of vegetable oil-based plasticiser (Chua et al., 2012), palm oil olein (Derawi et al., 2014), rubber seed oil, Madhuca oil, and Neem oil (Gamage et al., 2009), cotton seed oil (Saurabh et al., 2012), palm kernel oil (Fong and Salimon, 2011), Jatropha curcas oil (Hong et al., 2015), soybean oil (Sinadinović-Fišer et al., 2001), cotton seed oil (Guenther et al., 2003), and mahua oil (Goud et al., 2006). Epoxidation of olefinic type can be carried out in the following available methods, i.e. epoxidation with percarboxylic acid (Wallace, 1978) with acid and enzyme catalyst (Biermann et al., 2000), epoxidation with organic and inorganic peroxides with transition metal catalyst (Rios et al., 2005), epoxidation with halohydrines and epoxidation with molecular oxygen (Wallace 1978). Clean and efficient epoxidation method for vegetable oils is obviously denoted with percarboxylic acid and epoxidation with organic and inorganic peroxides (Sharpless et al., 1983). Epoxidation using vegetable oil such as soybean oil has already established at plant scale (Saremi et al., 2013).

However, it is observed the cost effectiveness and easy availability of raw materials in order to obtain the optimum route generating product.

In this research, it was examined the epoxidation method by using inexpensive raw material (WCO) with homogeneous catalyst, i.e. several inorganic acids. The objective of this paper is to observe optimum conversion with different inorganic acids based on oxirane conversion and iodine value at different time. The oxygen source during epoxidation reaction used glacial acetic acid.

2. Experimental details

2.1 Materials

Waste cooking oil was collected from household frying in Semarang. Waste cooking oil was filtered from solid waste through pre-treatment. Hydrogen peroxide (H₂O₂ 50 %) and ethanol (96 %) were supplied from PT. Brataco. Glacial acetic acid for analysis (CH₃COOH 100 %), sodium hydroxide pro analysis (NaOH 99 %), kalium iodide for analysis (KI), cyclohexane (for analysis), nitric acid (HNO₃ 65 %), Wijs solution were obtained from Merck KGaA, Germany. Hydrochloric acid (HCl 37 %), sulfuric acid (H₂SO₄ 96 %) and diethyl ether (99.6 %) were obtained from Mallinckrodt. Sodium thiosulfate (Na₂S₂O₃ > 99.5 %) was supplied from Sigma Aldrich. All chemicals were directly used without any purification.

2.2 Experimental setup

The epoxidation reactions were carried out in magnetic stirrer of three neck flask (capacity of 500 mL). The flask was immersed in an oil bath controlled by thermocouple and equipped with water cooling.

2.3 Epoxidation procedure

The epoxidation was adapted from Goud (2007) and Dinda (2008). Temperature reaction was firstly considered at temperature of 60 °C in order to investigate the effect of several acid catalysts. The iodine value was determined by using the Wijs method (Siggia and Hanna, 1979). The oxirane oxygen was determined by using method from Siggia and Hanna (1979).

In the beginning determination of double bonding of WCO was analysed by GCMS-MS type Quadrupole. GCMS analysis used injection mode of split at temperature of 250 °C, dual rhenium coil type for filament, and column flow of 1.2 mL/min. The typical fatty acids composition profile of WCO can be seen in the following table.

Table 1: Fatty acids composition of WCO

Fatty Acid	wt%	Fatty Acid	wt%
Lauric acid	0.08	Stearic acid	5.44
Myristic acid	0.7	Dipalmitic acid	0.06
Pentadecanoic acid	0.03	Heptadecenoic acid	0.22
Palmitic acid	0.31	Arahidic acid	0.44
Hexadecanoic acid	29.74	Eucosapentanoic acid	0.04
Heptadecanoic acid	0.08	9-oktadecenoic	0.11
Linoleic acid	11.89	Lignoceric acid	0.09
Oleic acid	50.79		

Parameters used in this research were mole ratio of acetic acid to double bond (0.5 : 1), mole ratio of hydrogen peroxide to double bond (2 : 1), and mass of sulfuric acid (2 %). 250 mL of WCO was taken into the flask. Around 14.68 mL of glacial acetic acid and 0.57 mL of inorganic acid catalyst were poured into the flask. Temperature was adjusted at 60 °C then the mixture was started for about half an hour under stirring speed of 1,200 rpm. The calculated H₂O₂ was added drop-wise during the mixing. The reaction was further continued for a certain time (1 - 10 h). The samples were taken in each hour for 5 h then left until 10 h the end of sampling. The collected samples were extracted with diethyl ether in separating funnel. The samples were then washed with cold and hot water to remove free fatty acids. Afterwards, analysis of iodine value and oxirane content were done to describe conversion of epoxy in the double bonding of WCO. Structure analysis of WCO and epoxidised WCO used FTIR ATR Quest Diamont (SPECAC) in the wave number region of 450 – 4,000 cm⁻¹ with 1 cm⁻¹ for 24 scans.

2.4 Analytical procedure

Determination of iodine value was referred by using Eq(1).

$$\text{Iodine value } (IV_0) = ((B-S) \times M \times 12.69) / W \quad (1)$$

Conversion of iodine value can be expressed in Eq(2).

$$\text{Conversion } (\%X) = (IV_0 - IV) / IV_0 \times 100 \% \quad (2)$$

where IV₀ = initial iodine value and IV = iodine value at certain time.

Determination oxirane oxygen content was indicated by percentage of oxirane oxygen using Eq(3) (Siggia and Hanna, 1979).

$$\text{Oxygen content } (OO_{\text{exp}}) = \frac{(B-S) \times M \times 16 \times 100}{W \times 1,000} \quad (3)$$

where S = volume of NaOH solution required for the sample; B = volume of NaOH solution required for the blank; W = weight of sample used; M = molarity of the NaOH solution.

Relative percentage conversion to oxirane can be formulated as Eq(4).

$$\% \text{ Oxirane} = \left(\frac{OO_{\text{exp}}}{OO_{\text{the}}} \right) \times 100 \quad (4)$$

where OO_{exp} = oxirane oxygen content at certain time and OO_{the} = theoretical oxirane oxygen content, which was determined from Eq(5) (Sharpless et al., 1983).

$$OO_{\text{the}} = \left[\frac{(IV_0/2A_i)}{(100 + (IV_0/2A_i))} \right] A_0 \times 100 \% \quad (5)$$

where A_0 and A_i are the atomic weights of oxygen and iodine.

3. Results and discussion

Both parameters, iodine value and oxirane oxygen, are prominent properties to represent the epoxidation of vegetable oils (WCO). The iodine value denotes the prevailing unsaturation post reaction, while the oxirane oxygen denotes existence of epoxy group in the product. It was expected in the epoxidised vegetable oil with a lower iodine values and higher oxirane oxygen values. However, they did not entirely indicate conversion to epoxy group while there are degradation process during reaction generating side product. It can be seen mechanism of epoxidation and potential side reactions of epoxides in Figure 1.

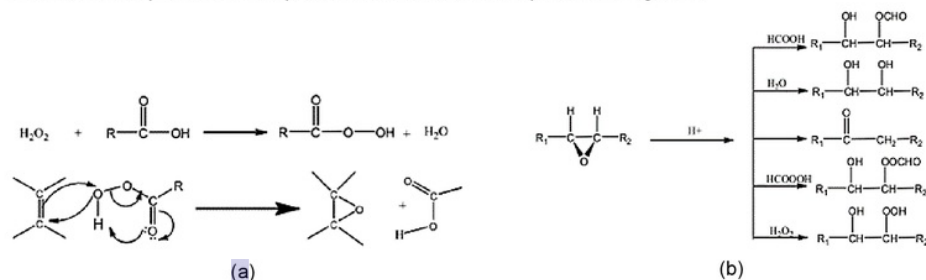


Figure 1: (a) Mechanism of epoxidation; (b) Potential side reactions of epoxides

Figure 2(a) describes yield of epoxide from WCO epoxidation catalyzed sulfuric acid reached at maximum content of 3.1 % within temperature of 60 °C for 5 h. Commonly epoxidation of vegetable oil can be obtained the oxirane oxygen content about 6 - 7 %. Figure 2 represents the effect of reaction time at temperature of 60 °C on conversion of iodine values and relative percentage conversions to oxirane oxygen values observing the optimum condition with different inorganic acids (HNO_3 , HCl , and H_2SO_4). Temperature condition has been conducted upon previous research of the epoxidation reaction such on cotton seed (Dinda et al., 2008), plum seed oil (Shagal, 2013), castor oil (Fuwanto et al., 2006), while epoxidation of soybean oil was succeeded at temperature of 50 °C. The results of relative percentage conversion to oxirane oxygen in the presence of three acid catalysts are shown in Figure 2(b). It shows that the oxirane conversion with H_2SO_4 was slightly higher than that of HCl and HNO_3 as catalysts at in the beginning reaction time and obviously at 5 h. However, first the oxirane conversion increased from 2 h to 5 h, beyond which gradually depletion in oxirane oxygen value conversion was noticed and attained at maximum reaction time of 5 h about 26%. The decrease was resulted from ring opening of epoxide due to side reactions. This epoxidation of WCO by peroxyacetic acid generated in situ hydrogen peroxide and glacial acetic acid in the presence inorganic acids as catalysts were not more efficient to convert double bonding of WCO become epoxidised WCO than it was compared to the epoxidation of cottonseed oil generated 70.4 % of oxirane conversion with 2 % of H_2SO_4 . However, it is evidenced that HCl and HNO_3 were not very effective for the epoxidation of cottonseed oil (Sharpless et al., 1983). It was conformed from literature that in the acid-catalysed epoxidation of cotton seed oil, there were the order of effectiveness of acid catalysts, i.e. sulfuric acid > phosphoric acid > nitric acid > hydrochloric acid (Karak, 2012). It was resulted from acceleration of equilibrium rate by adding a strong acid catalyst. Moreover, peracetic acid synthesis can be carried out by hydrolysis of acetic acid and hydrogen peroxide. In this system, H^+ mainly comes from dissociation of sulfuric acid and acetic acid. It is obviously that the H^+ in the system can

be thought being only from complete dissociation of sulfuric acid when the charge of sulfuric acid is large enough (Zhao et al., 2007).

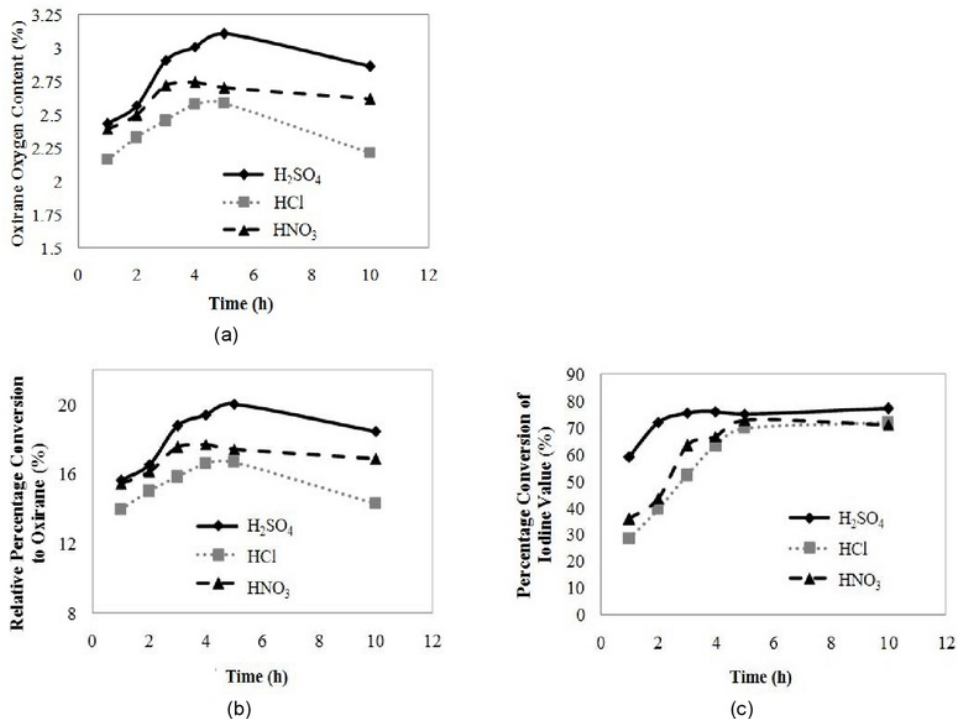


Figure 2: (a) Effect of inorganic acid catalysts on oxirane oxygen content; (b) on relative percentage conversions to oxirane; (c) on relative percentage conversions to iodine value

The effect of reaction time on iodine value is shown in Figure 2(c). The result shows that the conversion of iodine values increased steeply during 4 h with more than 90%. All of catalyst used have slight same trending to decrease to reaction time of 10 h. Unsaturated double bonds denoted in the WCO were converted to oxirane ring through epoxidation reaction. Therefore, the reaction conversion increased with reaction time. This result can be seen in Figure 2(a) which the reaction conversion attained maximum of 3.1% with H₂SO₄ as catalyst. A feasible clarification for this investigation might be that the higher reaction time, a high rate of oxygen ring opening producing epoxidised oil with lower oxirane.

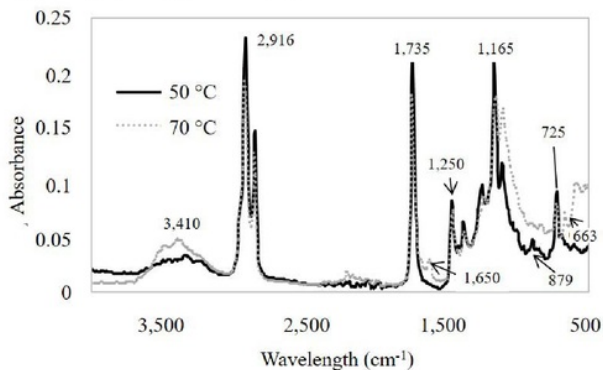


Figure 3: FTIR spectra of epoxidised WCO at temperature of 50 °C and 70 °C

Figure 3 shows the FTIR spectra of epoxidised WCO at temperature of 70 °C and 50 °C, 2 % of H₂SO₄ and stirring speed of 1,200 rpm in order to ensure at higher temperature. FTIR spectra at both temperature showed the epoxidised WCO still remained the C=O ester peak of triglyceride at 1,735 cm⁻¹, while spectra at 1,650 cm⁻¹ and 663 cm⁻¹ denoted unsaturated peak at temperature of 70 °C. The presence of unepoxidised WCO in the product was proven by FTIR result. In addition, there was epoxide ring opening at spectra as peak of C=O for ester of 3,410 cm⁻¹, while epoxide spectra can be presented at spectra of 725 cm⁻¹ and 879 cm⁻¹ as monosubstituted epoxide and ring vibrated trans epoxide, respectively (Socrates, 2001). Oxirane compound can be theoretically absorbs at wavelength of 750 - 880 cm⁻¹ and 815 - 950 cm⁻¹ (Derawi et al., 2014). Epoxides absorbs near 1,250 cm⁻¹ due to C-O stretching vibration and near 370 cm⁻¹ due to their ring deformation (Socrates 2001).

4 Conclusion

The epoxidation of WCO using in situ generated peroxyacetic acid by using hydrogen peroxide and glacial acetic acid with H₂SO₄ of 2 % and temperature of 60 °C. Furthermore, this reaction reached at relative percentage conversion to oxirane of 20 %, oxirane oxygen content at 3.1 %, and percentage conversion of iodine value at 74.9 % for 5 h. It was lesser than that of some vegetable oils epoxidation. Higher temperature could increase the rate constant but reduce conversion to oxirane. It might increase the epoxide ring opening reducing epoxidised WCO. The FTIR spectras of the epoxidised WCO denoted this evidences.

Acknowledgments

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Reference

- Biermann U., Friedt W., Lang S., Luhs W., Machmuller G., Metzger J.O., Klaas, M.R. Schafer, H.J. Schneider, M.P., 2000, New syntheses with oils and fats as renewable raw materials for the chemical industry. *Angewandte Chemie (International ed. in English)* 39, 2206–2224.
- Borugadda V.B., Goud V.V., 2015, Response surface methodology for optimisation of bio-lubricant basestock synthesis from high free fatty acids castor oil, *Energy Science & Engineering* 3 (4), 371–383.
- Chen J., Liu X., Wei D., Chen G., 2015, High yields of fatty acid and neutral lipid production from Cassava Bagasse Hydrolysate (CBH) by heterotrophic *Chlorella Protothecoides*, *Bioresource Technology* 191, 281–290.
- Chua S.C., Xu X.B., Guo Z., 2012, Emerging sustainable technology for epoxidation directed toward plant oil-based plasticisers, *Process Biochemistry* 47 (10), 1439–1451.
- Derawi D., Salimon J., Ahmed W.A., 2014, Preparation of epoxidised palm olein as renewable material by using peroxy acids, *The Malaysian Journal of Analytical Science* 18 (3), 584–591.
- Dinda S., Patwardhan A.V., Goud V.V., Pradhan N.C., 2008, Epoxidation of cottonseed oil by aqueous hydrogen peroxide catalysed by liquid inorganic acids, *Bioresource Technology* 99 (9), 3737–3744.
- Fong M.N.F., Salimon J., 2011, Epoxidation of palm kernel oil fatty acids, *Journal of Science and Technology* 4 (2), 87–98.
- Gamage P.K., O'Brien M., Karunanayake L., 2009, Epoxidation of some vegetable oils and their hydrolysed products with peroxyformic acid - optimised to industrial scale, *Journal of the National Science Foundation of Sri Lanka* 37 (4), 229–240.
- Goud V.V., Patwardhan A.V., Pradhan N.C., 2006, Studies on the epoxidation of mahua oil (*Madhumica Indica*) by hydrogen peroxide, *Bioresource Technology* 97, 1365–1371.
- Goud V.V., Patwardhan A.V., Pradhan N.C., 2007, Kinetics of in situ epoxidation of natural unsaturated triglycerides catalysed by acidic ion exchange resin, *Industrial and Engineering Chemistry Research* 46 (10), 3078–3085.
- Guenter S., Rieth R., Rowbottom K.T., 2003, *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed., Vol. 12, John Wiley and Sons, New Jersey, United States.
- Hong L.K., Yusop R.M., Salih N., Salimon J., 2015, Optimisation of the in situ epoxidation of linoleic acid of *Jatropha Curcas* oil with performic acid, *The Malaysian Journal of Analytical Sciences* 19 (1), 144–154.
- Karak N., 2012, *Vegetable oil-based polymers: properties, processing and applications*, Woodhead Publishing, Cambridge, UK.
- Knothe G., Steidley K.R., 2009, A comparison of used cooking oils: A very heterogeneous feedstock for biodiesel, *Bioresource Technology* 100 (23), 5796–5801.

- Lisboa P., Rodrigues A.R., Martin J.L., Simoes P., Barreiros S., Paiva A., 2014, Economic analysis of a plant for biodiesel production from waste cooking oil via enzymatic transesterification using supercritical carbon dioxide, *Journal of Supercritical Fluid* 85, 31–40.
- Nanou K., Roukas T., 2016, Waste cooking oil: A new substrate for carotene production by *Blakeslea Trispora* in submerged fermentation, *Bioresource Technology* 203, 198–203.
- Purwanto E., Fatmawati A., Setyoprato P., Junedi, Rosmiati M., 2006, Influence of epoxidation reaction period and temperature on the quality of polyol synthesised from soybean oil, in *Proceedings of the 13th Regional Symposium on Chemical Engineering Advanced in Chemical Engineering and Biomolecular Engineering*, Nanyang Technological University, Singapore, 277-279.
- Qinghong F., Xin J., Rui Z., Jing Q., 2013, Epoxidation treatment method of waste cooking oil, Patent China CN 103436367 A.
- Rios L.A., Weckes P., Schuster H., Hoelderich W.F., 2005, Mesoporous and amorphous Ti-silicas on the epoxidation of vegetable oils, *Journal of Catalysis*. 232, 19–26.
- Saremi K., Tabarsa T., Shakeri A., Babanalbandi A., 2012, Epoxidation of soybean oil, *annals of biological research* 3 (9), 4254-4258.
- Saurabh T., Patnaik M., Bhagat S.L., Renge V.C., 2012, Studies on synthesis of biobased epoxide using cottonseed, *Journal of Advance Engineering Research and Studies* 1 (2), 279-284.
- Shagal M.H., Barminas J.T., Aliyu B.A., Osemeahon S.A., 2013, Epoxidation of *Ximenia Americana* seed oil, *Journal of Petroleum Technology and Alternative Fuels* 4 (4), 72–77.
- Sharpless K.B., Woodard S.S., Finn M.G., 1983, On the mechanism of titanium tartrate catalysed asymmetric epoxidation, *Pure and Applied Chemistry*. 55, 1823–1836.
- Siggia S., Hanna J.G., 1979, *Quantitative organic analysis via functional groups*, Wiley Interscience, New York, US, 394–398.
- Sinadinović-Fišer S., Janković M., Petrović Z.S., 2001, Kinetics of in situ epoxidation of soybean oil in bulk catalysed by ion exchange resin, *Journal of the American Oil Chemists' Society*, 78, 7, 725–731.
- Socrates G., 2004, *Infrared and raman characteristic group frequencies., Tables and Chart*, 3rd, John Wiley & Sons, England.
- Wallace J.C., 1978, *Encyclopedia of Chemical Technology*, 3rd ed., Vol. 9, John Wiley and Sons, New York, US.
- Zhao X., Zhang T., Zhou Y., Liu D., 2007, Preparation of peracetic acid from hydrogen peroxide Part I: Kinetics for peracetic acid synthesis and hydrolysis, *Journal of Molecular Catalysis A: Chemical* 271, 246-252.

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