

Epoxidation of Palm Kernel Oil Fatty Acids

Michelle Ni Fong Fong¹, Jumat Salimon^{*,1}

¹School of Chemistry & Food Technology, Faculty of Science and Technology
Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia.

**Corresponding email: jumat@ukm.my*

Abstract

Epoxidation of palm kernel oil fatty acids using formic acid and hydrogen peroxide was carried out effectively using a homogeneous reaction. It was found that epoxidation reaction occurred optimally at a temperature of 40°C and reaction time of 120 minits. The oxirane conversion was the highest at 1.46mol and 0.85mol of hydrogen peroxide and formic acid respectively. It was found that a maximum of 99% relative conversion of ethylenic oxirane was obtained, similar to the conversion of iodine value. The formation of epoxide adduct of palm kernel oil fatty acids (FAPKO) was confirmed by ¹H NMR and ¹³C NMR spectral analysis showed the disappearance of double bonds and replaced by epoxy group in the EFAPKO.

Keywords: palm kernel oil; epoxidation, hydrogen peroxide; formic acid

1. INTRODUCTION

Vegetable oils in general have excellent properties such as high viscosity index, high lubricity, high flash point, low evaporative loss, high bio-degradability and low toxicity with regard to their use as base oils for lubricants. On the negative side they are known to possess low thermal, oxidative and hydrolytic stabilities and poor low-temperature characteristics [1,2,3]. The properties of vegetable oils are determined by their fatty acid composition. A high content of linoleic/linolenic acid decreases thermal oxidative stability. Whereas, a higher proportion of long chain saturated fatty acid leads to inferior cold flow behavior. Palm kernel oil belongs to unique group of vegetable oils called lauric oils; similar to coconut oil. The most abundant fatty acid in this group is lauric acid [4].

Fats and oils are renewable resources that can chemically or enzymatically treated to produce materials that can often act as a replacement for materials derived from petroleum. One of the important reactions that can be used to improve these fats and oils' performance is epoxidation. Epoxidation processes are becoming popular due to its role as a starting material to many other reactions. An epoxide is cyclic ether with three ring atoms. This ring approximately defines an equilateral triangle, which makes it highly strained. The strained ring makes epoxides more reactive than other ethers. Fatty epoxides are used directly as plasticizers that are compatible with polyvinyl chloride (PVC) and as stabilizers for PVC resins to improve flexibility, elasticity, and toughness and to impart stability of polymer towards heat and UV radiation. The high reactivity of oxirane ring enables epoxides to act as raw material for a variety of chemicals, such as alcohols, glycols, alkanolamines, carbonyl compounds, olefinic compounds and polymers like polyesters, polyurethanes, and epoxy resin [5,6,7,8].

In recent years, epoxidation process had been carried out using vegetable oils such as soybean oil, canola oil, jatropha oil, castor oil and cottonseed oil. Carbon double bonds of unsaturated fatty acids were epoxidized via acid catalysis producing epoxy functional groups. Parameter used to optimized the epoxidation of vegetable oil were reaction temperature, the concentration of oxygen donor such as hydrogen peroxide, concentration of oxygen carrier and also as catalyst such as formic acid and acetic acid as reported by Dinda et al. [5], Goud et al. [8] and Mungroo et al. [9]. From the oxirane content values, the relative fractional conversion to oxirane reported by Goud et.al [9] was calculated from the following expression:

$$\text{Relative conversion to oxirane (RCO)} = \frac{OOc}{OOt}$$

Where,

OOc = experimental oxygen oxirane

OOt = theoretical maximum oxirane oxygen from the expression:

$$OOt = \left(\frac{IVo/2Ai}{100 + (IVo/2Ai)Ao} \right) Ao \times 100$$

Where,

Ai (126.9) and Ao (16.0) are the atomic weights of iodine and oxygen respectively and IVo is the initial iodine value of sample.

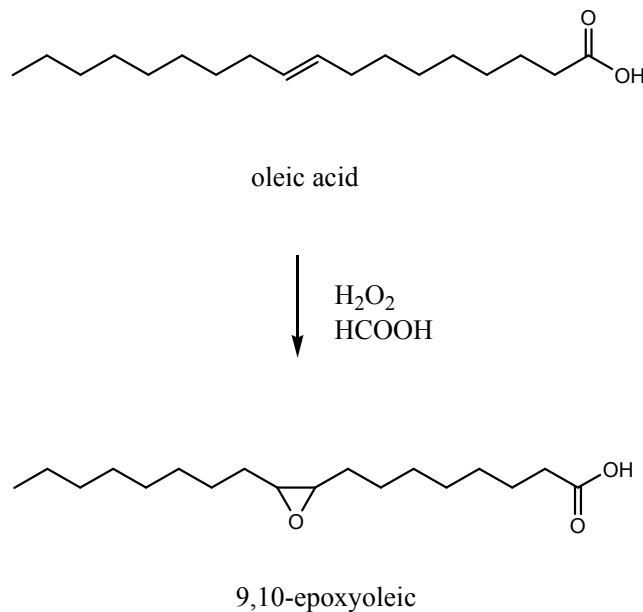


Figure 1: A schematic diagram of epoxidation reaction

In this paper, the main purpose was to develop value-added products from locally available renewable resources in Malaysia. Palm kernel oil is the oil produced from the kernel of an oil palm seeds, *Elaeis guineensis*. Palm kernel oil has been evaluated for its lubricating properties by Musa [4]. Palm kernel oil were compared with heavy duty oil (SAE 40) and light duty oil (SAE 30). The result showed that palm kernel oil's flash/fire point, pour point, specific density and viscosity met the required SAE specifications. Thus, palm kernel oil was a promising base oil for production of value-added lubricating products. Therefore, epoxidation of double bond in palm kernel fatty acid with hydrogen peroxide and performic acid generated *in-situ* was monitored and optimized to produced value-added palm kernel fatty acid epoxides. A further objective of this work was to open the oxirane ring in FAPKO with its major saturated acids to produce improved value biolubricant base stock.

2. MATERIALS AND METHODS

2.1 Materials

RBD palm kernel oil which was used as raw material for free fatty acid production was purchased from Jomalina Sdn Bhd. Aqueous hydrogen peroxide 30%, formic acid 98%, hexane 99% and ethanol were all chemicals from System[®].

2.2 Preparation of FAPKO

Free fatty acid was produced manually in batches by hydrolysis process before epoxidation of the double bonds takes place. 50g of RBD palm kernel oil was filled in a two-necked round bottom flask and was added with ethanolic potassium hydroxide. The solution was mixed together before underwent hydrolysis process at 60°C for 2 hours. Samples were extracted using hexane and wash with water before drying using anhydrous sodium sulphate. Final product was dried using vacuum rotary evaporator.

2.3 Epoxidation of FAPKO

The reaction was studied in a mechanically stirred three-necked round bottom flask (500ml) attached with thermometer on a hot plate. A reflux condenser completed the set-up. Performic acid used in the experiment was prepared in-situ. About 0.85 mol of formic acid per moles of double bonds in FAPKO were added into the reactor and heated to reaction temperature, under vigorous agitation (1200rpm). Then, about 1.46 mol of H₂O₂ solution were added, drop by drop and the reaction mixture was held at constant temperature and under stirring for several hours. After reaction completed, the mixture was washed with a solution of sodium bicarbonate (5 wt%), next with water until complete elimination of acidity in organic phase and finally with sodium chloride (5 wt%). The final product was cooled to solidified organic phase and dried in a refrigerator for 24 hours. Epoxides in FAPKO (EFAPKO) was dried using Whatman no.4.

2.4 Analysis and Data Processing

The stocks of FAPKO were analyzed to check its acidity value that was used in identifying the percentage of free fatty acid present in the sample. Method used was referred from AOCS methods. Iodine value and saponification value were evaluated using PORIM recommended practices. Sample also analyzed by GC, using Agilent Tech 6809 N unit furnished with column BPX-70. The characterization results are shown in Table 1. The evaluation of epoxidation reactions was followed by measuring the oxirane oxygen (%OOc) according to AOCS recommended practices and iodine value (IV). Epoxides formed in FAPKO are analyzed by ¹H-NMR and

^{12}C -NMR spectra on a JEOL JNM-ECP 400 spectrometer using chloroform as solvent in all experiments.

3. RESULTS AND DISCUSSION

Synthesis: Following the formula above, the maximum percentage of theoretical oxirane is 1.16%. The effects of the following reaction parameter were considered: the moles of hydrogen peroxide and formic acid with respect to the moles of oleic acid in FAPKO, reaction time and temperature. Table 1 showed the characteristic of FAPKO.

Table 1: Some of FAPKO physical chemical properties

Acidity ^a	99.92% (max)
Iodine Value ^a	18.7 mgI ₂ /g (average)
C8:0 (capric) ^b	2.79%
C10:0(caprylic) ^b	3.04%
C12:0(lauric) ^b	47.34%
C14:0(miristic) ^b	17.10%
C16:0(palmitic) ^b	8.96%
C18:0(stearic) ^b	2.38%
C18:1(oleic) ^b	16.43%
C18:2(linoleic) ^b	1.97%

^a Following AOCS method & PORIM Recommended Test Method

^b By GC analysis

Epoxide produced in this study was in liquid form in room temperature, deviates from expected solid form that were produced by other vegetable oils with higher unsaturation value. This is due to the abundance of saturated fatty acids such as lauric acid presence in the epoxide mixture. Though palm kernel oil is a drying oil, the abundance of medium chain fatty acids has lower tendency to undergo uniform staking process forming macro crystalline structure than long chain fatty acids of other non-drying product such as soybean oil and cottonseed oil in room temperature [10]. However, in low temperature the epoxide of FAPKO (EFAPKO) will still solidify into solids. The abundance of lauric acids will be used as reactants for ring opening and capping in base oils in further experiments.

Effect of Hydrogen Peroxide to Ethylenic Unsaturation: Figure 2 shows the effects of moles of hydrogen peroxide. As the moles of hydrogen peroxide increase, the oxirane conversion rate increase followed by decreasing of iodine value. The maximum relative conversion obtained is at 1.46 mol of hydrogen peroxide (75%). For higher concentration of hydrogen peroxide at the same conditions; temperature and reaction time, the reaction rate becomes constant. An increase in hydrogen peroxide concentration will increase the oxirane conversion rate. However, the stability of oxirane ring produced in a very high concentration of H_2O_2 is very poor, thus increasing the production of diol and α -glycol as side products [5,9].

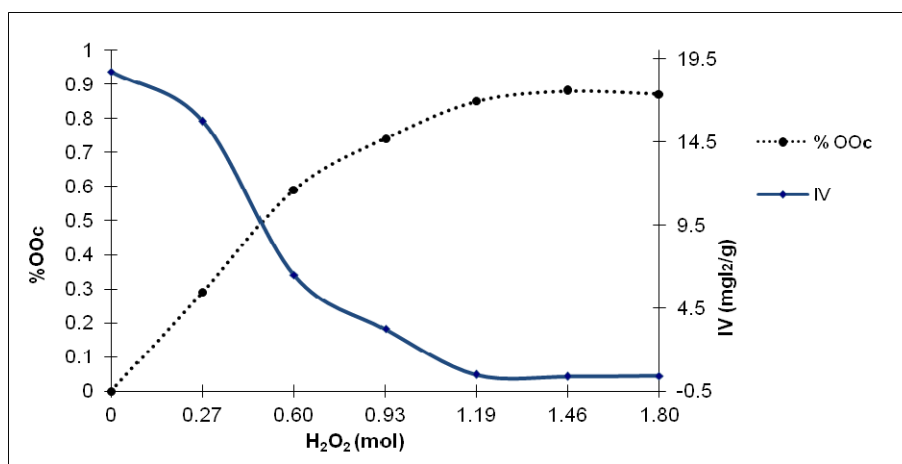


Figure 2: Graph of moles of hydrogen peroxide with oxirane conversion rate and iodine value

Effect of Formic Acid to Ethylenic Unsaturation: Figure 3 expressed the effect of moles of formic acid towards the yield of epoxide. As the concentration of formic acid increase to 0.87mol, the oxirane conversion rate increase to its highest (72%). However, when the formic acid concentration is further increased, %OOC and the iodine value decrease significantly. This showed that the oxirane ring has been degraded from high concentration of formic acid. Formic acid is a good oxygen carrier and indeed crucial for producing enough epoxides in the aqueous phase. Unfortunately, it also is the main culprit that is responsible for the hidrolisis of oxirane rings [11]. The amount of formic acid used per mole of unsaturation recommended by Niederhauser & Koroly 1949 is 1 mole and less. This ratio used not only for economical reasons but also to reduce by-products such as dihydroxy and dihydroxyformoxy derivatives that can reduce the oxirane production [11].

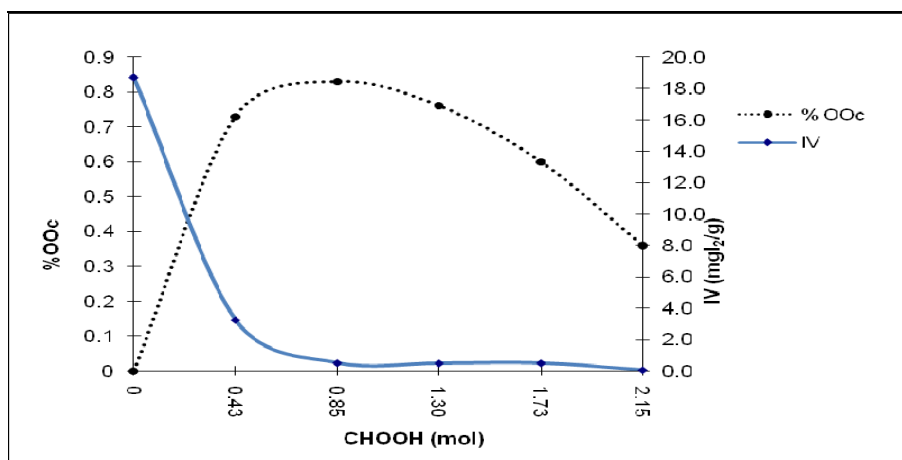


Figure 3: Graph of moles of formic acid with oxirane conversion rate and iodine value

Effect of Time and Temperature: Figure 4 expressed the effect of reaction time toward the yield of epoxides. The maximum %OOC value and percentage conversion of oxirane (99%) obtained within 120 minutes of reaction time. Nonetheless, the almost similarity of %OOC at other reaction time shows that effect of reaction time towards epoxidation of FAPKO is not very obvious. Moreover, oxirane rings produced in the reaction were not considered stable in the presence of acidity. Figure 5 shows the effect of temperature towards the epoxidation reaction. The optimum temperature for epoxidation process that produces maximum %OOC is at 40°C with relative conversion reaching 87%. At lower temperature, FAPKO tends to solidify and lower the chance of interfacial interactions of the reactants. Thus, the epoxide yield decreased. At higher temperature, the yield of epoxide not only decreased, there were evidents of oxirane decomposition shown by the iodine value. This phenomenon was similar in [5,9,11].

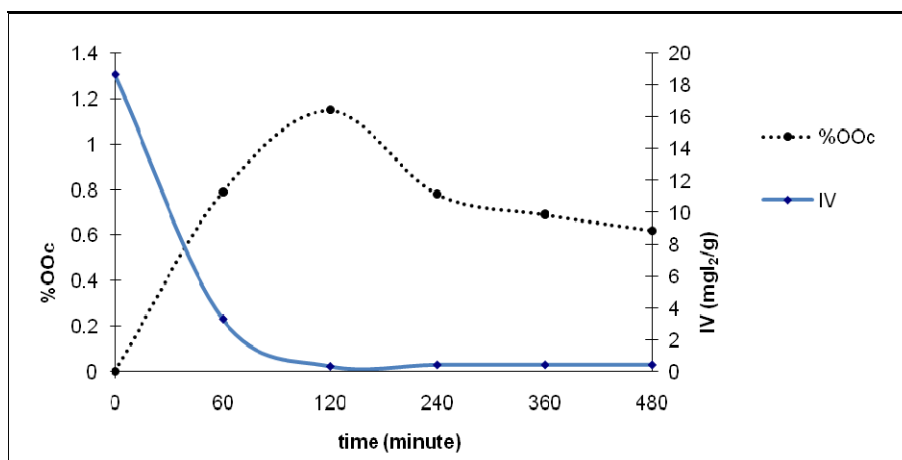


Figure 4: Graph of reaction time with the yield of epoxides

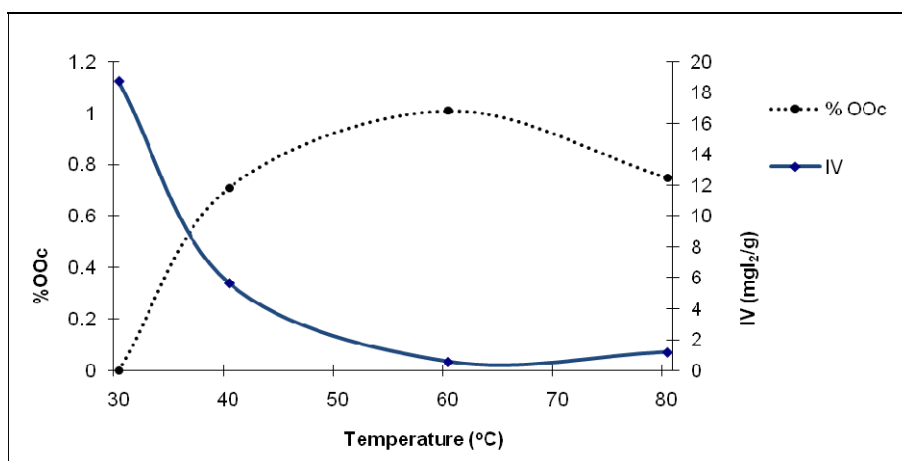


Figure 5: Graph of temperature with the epoxidation reaction

NMR Spectral Analysis: The formation of the epoxide adduct in FAPKO was confirmed by the difference of PKO, FAPKO and EFAPKO chemical shifts in ^1H NMR and ^{13}C NMR spectrum as shown in Table 1 and 2. ^1H NMR for EFAPKO showed the presence of epoxy group in the region of 2.7 ppm and disappearance of double bonds at the region of 1.6-5.2 ppm. However, both ^1H NMR of FAPKO and EFAPKO showed the presence of carboxylic group in the 11-12 ppm region. This showed that there were an abundance of saturated fatty acids in the epoxidized FAPKO. These saturated fatty acids would be use to produced branching molecule in the furthered ring opening reaction. ^{13}C NMR of FAPKO the disappearance of the double bond peaks 120-140 ppm and replaced by chemical shifts at 56-59 ppm region in EFAPKO. Thus, it is found that from NMR spectrum the double bonds in FAPKO have completely undergone epoxidation process to form EFAPKO.

Table 1: The difference of PKO, FAPKO and EFAPKO chemical shifts in ^1H NMR spectrum

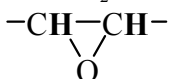
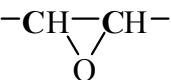
Types of proton	Reference, δ (ppm)	PKO, δ (ppm)	FAPKO, δ (ppm)	EFAPKO, δ (ppm)
α -CH ₂ -COOR	2.1-2.5	2.1-2.2	2.2-2.3	2.0-2.1
R-COO-CH-	3.5-4.8	3.9-4.1	-	-
R-COOH	11.0-12.0	-	11.6	11.0
C=C-H	4.5-6.5	5.1-5.2	5.2	-
C=C-C-H	1.6-2.6	1.4	1.6-1.8	-
R-CH ₃	0.7-1.3	0.7-1.1	0.8	0.7-1.2
R-CH ₂ -R	1.2-1.4	1.1	1.2	1.3
	2.5-3.5	-	-	2.7

Table 2: The difference of PKO, FAPKO and EFAPKO chemical shifts in ^{13}C NMR spectrum

Types of carbon	Reference, δ (ppm)	PKO, δ (ppm)	FAPKO, δ (ppm)	EFAPKO, δ (ppm)
R ₂ -CH ₂ -	15-55	22-31	22-32	28-33
R-CH ₃	8-30	13	14	17
	40-80	-	-	56-59
C=C	100-150	129	128-129	-
R-COOR	155-185	172	-	-
R-COOH	155-185	-	180	179

Reference: Pavia et al. 2001

4. CONCLUSIONS

The epoxidation of palm kernel fatty acids using hydrogen peroxide and performic acid generated *in-situ* was carried out and produced about 80% of epoxidized FAPKO yield. Although the maximum yield of oxirane ring produced from FAPKO were considered very low (1.15%) compare to other industrial vegetable oil due to its saturated nature, but the amount of oxirane conversions are optimum (99%) in the oil itself. From the relative conversion data obtained, it can be concluded that it is possible to develop value-added products, such as epoxide from palm kernel fatty acids.

Acknowledgments

The authors would like to thank the School of Chemical Sciences and Food Technology, Faculty of Science and Technology and Universiti Kebangsaan Malaysia for the financial support via research grant (UKM-GUP-NBT-08-27-113 and UKM-OUP-NBT-29-150/2011).

REFERENCES

- [1] Hwang, H.S. & Erhan, S.Z. 2005. Synthetic lubricant base stocks from Epoxidized soybean oil and Guerbert alcohols. *Industrial Crops and Products* 23: 311-317.
- [2] Lathi, S.P. & Mattiason, B. 2006. Green approach for the preparation of biodegradable lubricant base stock from epoxidized vegetable oil. *Journal of Applied Catalysis B: Environmental* 69: 207-212.
- [3] Sharma, B.K., Adhvaryu, A., Liu, Z. & Erhan Z.S. 2006. Chemical Modification of Vegetable Oils for Lubricant Applications. *JAOCs* 83: 129-136.
- [4] Musa, J.J. 2009. Evaluation of the lubricating properties of palm kernel oil. *Leonardo Electronic Journal of Practice and Technologies* 14: 107-114.
- [5] Dinda, S. Patwardhan, A.V., Goud, V.V. & Pradhan, N.C. 2008. Epoxidation of cottonseed oil by aqueous hydrogen peroxide catalyzed by liquid inorganic acids. *Bioresource Technology* 99: 3737-3744
- [6] Gerbase, A.E., Gregório J.R., Martinelli, M., Brasil M.C. & Mendes, N.F. 2002. Epoxidation of soybean oil by methyltrioxorhenium- $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}_2$ catalytic biphasic system. *JAOCs* 79: 179-181.
- [7] Goud, V.V., Patwardhan, A.V. & Pradhan, N.C. 2005. Studies on the epoxidation of mahua oil (*Madhumica indica*) by hydrogen peroxide. *Bioresource Technology* 97: 1365-1371.
- [8] Goud, V.V., Pradhan, N.C. & Patwardhan, A.V. 2006. Epoxidation of Karanja. (*Pongamia glabra*) oil by H_2O_2 . *JAOCs* 7 (83): 635-640.
- [9] Gryglewicz, S., Piechocki, W. & Gryglewicz, G. 2003. Preparation of Polyol Esters Based on Vegetable and Animal Fats. *Bioresource Technology* 87: 35-39.

- [10] Kleinová, A., Fodran, P., Brnčalová, L. & Cvengroš, J. 2008. Substituted Esters of Stearic Acid as Potential Lubricants. *Biomass and Bioenergy* 32: 366-371.
- [11] Campanella, A., Fontanini C. & Baltanás M.A. 2008. High Yield Epoxidation Of Fatty Acid Methyl Esters With Performic Acid Generated *In-Situ*. *Chemical Engineering Journal*.

