

OPTIMIZATION OF THE EPOXIDATION OF METHYL ESTER OF PALM FATTY ACID DISTILLATE

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ABSTRACT

Methyl ester of palm fatty acid distillate (PFAD-ME) can be used for producing epoxide compounds. PFAD-ME consists of 39.3% of oleic acid (C18:1) and has an iodine value of 49.2 g I₂/100 g. It can be converted to a low oxirane content epoxide which can be used for several applications, such as plasticizers, polyols or alkanolamines, with appropriate modification. Temperature, mole ratio of hydrogen peroxide to unsaturation, and mole ratio of formic acid to unsaturation were optimized in the epoxidation of PFAD-ME. The study showed that more than 98% conversion of unsaturation to the epoxide ring moiety can be achieved within 3 hr of reaction by using the optimum molar ratio of 1:1:4 (unsaturation: formic acid: hydrogen peroxide) and a temperature of 50°C.

Keywords: epoxidation, palm fatty acid distillate, hydrogen peroxide, epoxidized vegetable oil.

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INTRODUCTION

Vegetable oil-based products are well-known as being environment-friendly, biodegradable, low in cost and readily available. Their use as alternative substitutes for petroleum-based products has received increased attention due to the rising concerns for the environment and rising costs of petroleum products. Epoxidation is the key process to introduce the epoxy function into the unsaturation system present in the fatty acid molecules. Epoxide compounds can be used as plasticizers and stabilizers in polyvinyl chloride and ultra-violet coating, lubricant additives, reactive diluents for paints, surfactants and corrosion protection agents (Okieimen *et al.*, 2005; Orellane-Coca *et al.*, 2005; Vlček and Petrović, 2006). Moreover, epoxides are important precursors for a variety of chemicals such as alcohols, glycols, carbonyls,

alkanolamines, substituted olefins, polyesters, polyurethanes and epoxy resin (Yadav and Manjula, 2001; Vaibhav *et al.*, 2006).

There are several methods for producing epoxides from vegetable oils, fatty acids or methyl esters. These include epoxidation with percarboxylic acid generated *in situ* or preformed (Okieimen *et al.*, 2005; Vaibhav *et al.*, 2006), epoxidation with organic and inorganic oxidants such as potassium peroxomonosulfate, meta-chloroperoxybenzoic acid and ethylmethyl dioxirane (Carlson *et al.*, 1994; Marcel *et al.*, 1998; Sonnet and Foglia, 1996; Aerts and Jacobs, 2004), epoxidation with halohydrins, and epoxidation with molecular oxygen (Vaibhav *et al.*, 2006). However, epoxidation with percarboxylic generated *in situ* from carboxylic acid (*i.e.* formic acid or acetic acid) with hydrogen peroxide is widely used on an industrial scale (Piazza *et al.*, 2001; Campanella and Baltanás, 2004). This is for safety and efficiency reasons as the process prevents the production of substantial quantities of explosive percarboxylic acid.

Palm fatty acid distillate (PFAD) is a by-product from the deacidification-deodorization process in the refining of crude palm oil. It contains a significant amount of phytonutrients such as tocopherols, tocotrienols, squalene and phytosterols. Esterification with methanol followed by distillation removes the by-product palm fatty acid distillate

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methyl ester (PFAD-ME), leaving the valuable phytonutrients as residue. Utilization of PFAD-ME as a new intermediate for chemicals will benefit the palm oil industry. The fatty acid composition show that PFAD-ME consists of 39.3% of oleic acid (C18:1) and has an iodine value of 49.2 g I₂/100 g sample. This article focuses on the influence of various reaction parameters on the epoxidation process. The main objective of the study was to find the optimum conditions for maximum epoxy yield with regard to the highest conversion of double bonds to epoxy rings in shortest reaction time.

MATERIALS AND METHODS

Materials

Methyl ester of palm fatty acid distillate (PFAD-ME) was obtained from Sime Darby Sdn Bhd, Malaysia. Formic acid with a purity of 98%-100% (Merck, Germany) and hydrogen peroxide of ~50% concentration (R & M Chemicals, UK) were used without further purification. A 1% sodium chloride solution (Mallinckrodt, Mexico) and 4% sodium carbonate solution (Mallinckrodt, Mexico) were used for washing the reaction mixture. Anhydrous sodium sulphate (Merck, Germany) was used for drying the epoxidized PFAD-ME.

Characterization of Products

Oxirane oxygen content, iodine value, acid value and hydroxyl value were determined using AOCS Method Cd-9, AOCS Method Cd 1d-92, AOCS Method Te-2a and AOCS Method Tx-1a-66, respectively. The conversion of double bonds to epoxy rings was observed under FTIR spectra (Nicolet Magma IR 550 spectrometer series II, Japan). The samples were spread as a thin film on KBr plates and a total of 64 scans were taken for every sample. The disappearance of double bonds (3002 cm⁻¹) and the formation of epoxy groups (838 cm⁻¹) were used to determine the conversion of the epoxidation reaction. The IR spectra were recorded in the range of 4000 to 500 cm⁻¹. The ¹³C-NMR and ¹H-NMR (JEOL 400 MHz ¹H/ 100 MHz ¹³C, Japan) of PFAD-ME and the epoxidized derivatives were analysed for their structural confirmation using deuterated chloroform as the solvent in all the experiments.

Epoxidation of PFAD-ME

The epoxidation reaction of PFAD-ME was carried out in a solvent-free medium and without using any catalyst. Formic acid and acetic acid are generally used in the industrial production of percarboxylic acid. Hence, several trials had been carried out by using formic acid or acetic acid as an oxygen carrier. The results show that performic acid successfully converted double bonds of PFAD-ME into oxirane rings at a higher conversion rate and shorter reaction time compared to peracetic acid at the same molar ratio. Peracetic acid is only formed at a high concentration when a catalyst is added. However, this catalyst also catalyzes the epoxy ring-opening reaction (Scala and Wool, 2002; Du *et al.*, 2004). Thus, formic acid was used as the oxygen carrier for the following epoxidation reactions.

The reaction mechanism of epoxidation (Figure 1) and side reactions of the epoxy group (Figure 2) were proposed by Gan *et al.* (1992) and Petrović *et al.* (2002). In Figure 1, the formation of performic acid *in situ* is the rate determination step for epoxidation. The formic acid regenerated in the reaction will react with more hydrogen peroxide to perpetuate the reaction.

Nevertheless, an excess of hydrogen peroxide or formic acid will cause unwanted side reactions as illustrated in Figure 2. The excess reagents can react with the epoxy rings to produce various types of undesirable compounds. In order to obtain a high yield of epoxy rings, optimization of several reaction parameters was carried out using mole ratios of hydrogen peroxide to unsaturation, from 2.0 to 6.0; mole ratios of formic acid to unsaturation, *i.e.* between 0.5 to 1.5; and three different reaction temperatures, 50°C, 60°C and 70°C ± 5°C. The conversion rate was determined by the oxirane oxygen content analysis obtained by the titration method, and the rate was plotted against the reaction time.

The epoxidation of PFAD-ME was carried out using performic acid generated *in situ* from aqueous hydrogen peroxide and formic acid. The mole ratio of the reactants for the reaction was calculated based on the amount of unsaturated bonds in the PFAD-ME. The unsaturated bonds were converted into oxirane rings in the epoxidation process. The 150 g of PFAD-ME were pre-mixed with a predetermined amount of formic acid (13.9 g) in a 250-ml three-necked round bottom flask placed in a water bath.

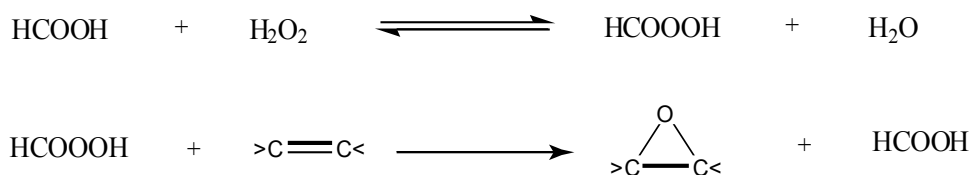


Figure 1. Reaction mechanism of epoxidation.

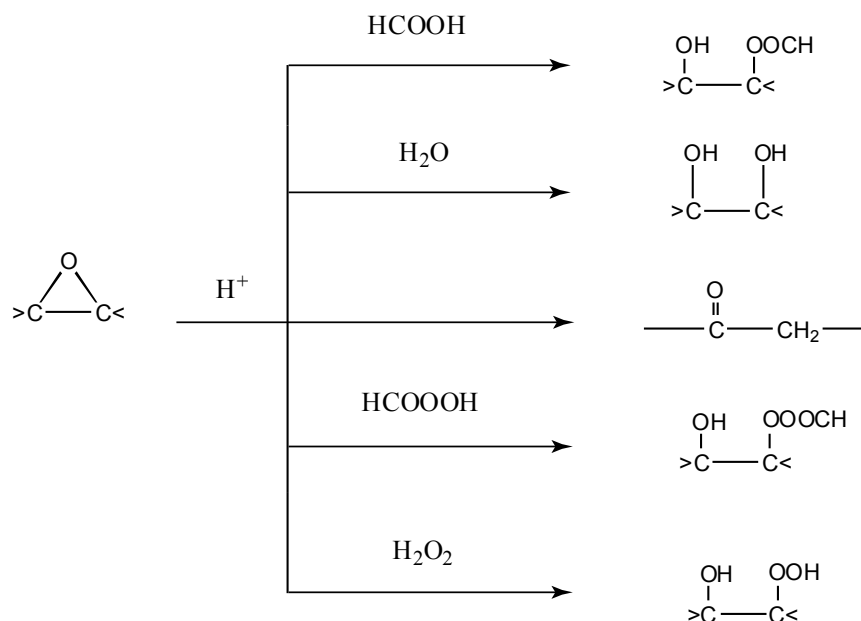


Figure 2. Side reactions of epoxy ring cleavage.

With agitation, 41.2 g of hydrogen peroxide were added drop-wise into the mixture at a temperature 5°C below 50°C. Thereafter, the temperature of the content in the flask would rise due to the exothermic nature of the reaction. The reaction was maintained at 50°C throughout with the help of ice cubes. The magnetic agitation was maintained at high speed to ensure that all the peroxide formed was quickly dispersed into the reaction mixture.

Oxirane oxygen content (OOC) and iodine value (IV) of the samples were determined every 30 min after the addition of hydrogen peroxide was finished. After the reaction was completed, the remaining formic acid and hydrogen peroxide were separated from the epoxidized PFAD-ME by washing with 1% sodium chloride solution to stop the ring-opening reaction of performic acid, which was still present in the mixture. The reaction mixture was further washed with 4% sodium carbonate solution to neutralize the remaining acid. The epoxide was washed a few times with 1% sodium chloride solution until neutral, before drying over anhydrous sodium sulphate. The theoretical OOC of PFAD-ME is 3.00%, calculated from the equation according to Vaibhav *et al.* (2006). Equation (1) was used to calculate the percentage conversion of the double bonds of the methyl esters to epoxy rings.

$$\text{Conversion, \%} = \frac{\text{OOC}_d}{\text{OOC}_t} \times 100 \quad (1)$$

where OOC_d is the experimentally determined oxirane content, and OOC_t is the calculated theoretical maximum oxirane content.

The experiment was repeated at different amounts of hydrogen peroxide, different concentrations of formic acid, and at temperatures 60°C and 70°C.

RESULTS AND DISCUSSION

The reaction mechanism (Figure 1) showed that performic acid formed instantly upon the addition of hydrogen peroxide. The generated intermediate compound, performic acid, was reactive and unstable. Therefore, hydrogen peroxide was added drop-wise to avoid an excessive vigorous reaction. Performic acid reacts with the double bonds present in the PFAD-ME to form oxirane rings. Excess hydrogen peroxide in relation to the amount of double bonds is needed to obtain the highest oxirane conversion in the shortest reaction time.

A series of reactions with different amounts of hydrogen peroxide was investigated (Table 1). Figure 3 shows that the conversion increased up to the mole ratio of 4, then decreased at the mole ratio of 6, with the conversion decreasing after 1 hr. This was due to the high amount of performic acid available for reacting with the double bonds. The OOC of the final product obtained from the system using 4.0 moles of hydrogen peroxide per mole of unsaturation was highest with 98.8% conversion. The conversion rate of double bonds to epoxide rings was lowest for 2.0 moles of hydrogen peroxide per mole of unsaturation, achieving only 84.5% conversion of the product to the epoxy system. This explained the reason why the IV of the final product was the highest among all (Table 1). The optimum mole ratio for the maximum yield of the desired products was

TABLE 1. CHARACTERISTICS OF EPOXIDIZED METHYL ESTER OF PALM FATTY ACID DISTILLATE (PFAD-ME) USING DIFFERENT MOLE RATIOS

Parameter	1: 1: 6 ^a	1: 1: 5 ^a	1: 1: 4 ^{a,b}	1: 1: 3 ^a	1: 1: 2 ^a	1: 1.5: 4 ^b	1: 0.5: 4 ^b
PFAD-ME: formic acid: H ₂ O ₂							
Conversion, %	98.1	95.8	98.8	95.4	84.5	95.8	89.2
Oxirane oxygen, %	2.95	2.88	2.97	2.87	2.54	2.88	2.68
Iodine value (g I ₂ /100 g sample)	0.80	0.41	0.37	0.59	4.25	0.06	6.82
Acid value (mg KOH g ⁻¹ sample)	0.17	0.14	0.14	0.14	0.11	0.20	0.12
Hydroxyl value (mg KOH g ⁻¹ sample)	7.43	8.67	8.58	NA	NA	16.68	7.39

Note: ^aOptimization on the amount of H₂O₂.

^bOptimization on the amount of formic acid.

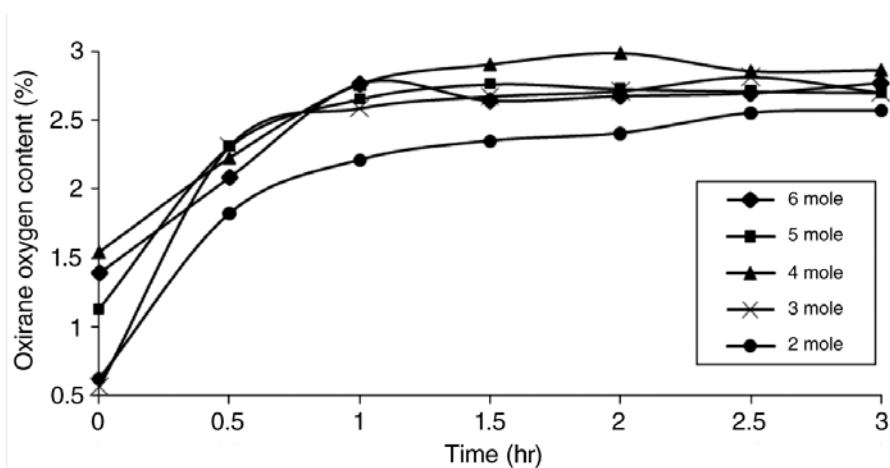


Figure 3. The effect of different moles of hydrogen peroxide per mole unsaturation. Condition: methyl ester of palm fatty acid distillate (PFAD-ME), 250 g; formic acid, 23.23 g; reaction temperature, 50°C.

found to be 4.0 moles of hydrogen peroxide per mole of unsaturation.

The study on different formic acid concentrations as an oxygen-carrier was optimized from 0.5, 1.0 and 1.5 moles per mole of unsaturation for the conversion rate with respect to 4.0 moles hydrogen peroxide (H₂O₂) per mole of unsaturation (Table 1). Despite being an oxygen carrier, formic acid also acts as a reactant in the hydrolysis of the oxirane ring (Figure 2). Hence, an optimal concentration of formic acid is required to accelerate the formation of oxirane rings with minimal oxirane ring cleavages. As illustrated in Figure 1, increasing the amount of formic acid leads to more production of performic acid. Figure 4 indicates that the conversion rate was increased as the mole ratio of the formic acid used was increased. The conversion of double bonds to epoxy rings achieved 95.8% within the first hour when 1.5 moles of formic acid was used. However, if 0.5 moles of formic acid per mole of unsaturation was used, only 89.2% conversion was obtained after 3 hr of reaction. On the other hand, the hydroxyl value (OHV) was

used to monitor the side reaction of epoxy ring opening. Increasing the mole ratio of formic acid from 0.5 moles to 1.5 moles resulted in an increase in OHV of the final products from 7.39 mg KOH g⁻¹ to 16.68 mg KOH g⁻¹ due to the side reactions (Table 1). A comparison between the mole ratios of 1:1.5:4 and 1:1:4 showed that the latter could give a higher conversion rate of 98.8% compared to 95.8% if the former ratio was used. Therefore, 1.0 mole of formic acid per mole of unsaturation was chosen because it balanced the effects of the oxirane ring formation and its destruction resulting in a stable maximum in oxirane content. Furthermore, using less formic acid also resulted in cost-savings.

The effect of the reaction temperature on the yield of the desired product was also evaluated (Table 2). Reactions at the same molar ratio of 1:1:4 (double bond: formic acid: 50% H₂O₂) were performed at three different temperatures of 50°C, 60°C and 70°C, respectively. The H₂O₂ was added into the mixture when the temperature was about 5°C below the reaction temperature. The temperature increased

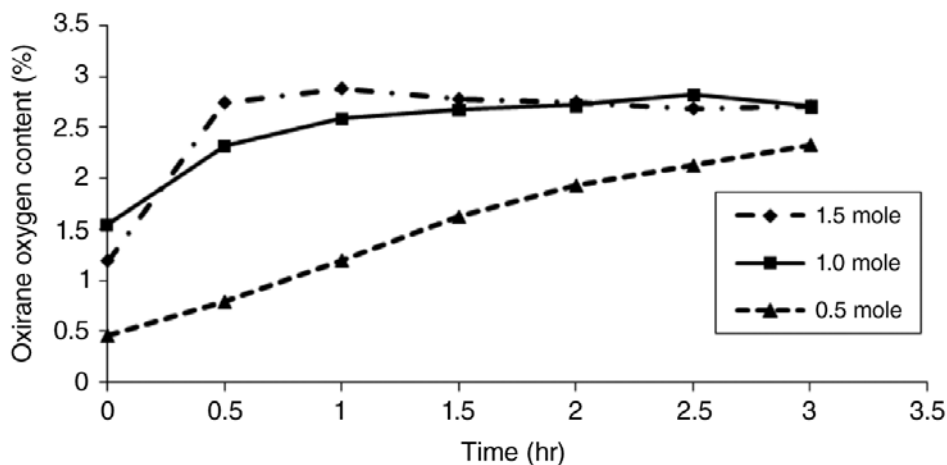


Figure 4. The effect of different moles of formic acid per mole unsaturation.

Condition: methyl ester of palm fatty acid distillate (PFAD-ME), 250 g; hydrogen peroxide, 68.65 g; reaction temperature, 50°C.

TABLE 2. CHARACTERISTICS OF METHYL ESTER OF PALM FATTY ACID DISTILLATE (PFAD-ME) PREPARED AT DIFFERENT REACTION TEMPERATURES

Parameter	50°C	60°C	70°C
Conversion, %	93.8	93.5	91.8
Oxirane oxygen (%)	2.82	2.81	2.76
Iodine value (g I ₂ /100 g sample)	0.59	0.42	0.42
Acid value (mg KOH g ⁻¹ sample)	0.09	0.13	0.18
Hydroxyl value (mg KOH g ⁻¹)	4.51	7.32	10.53

Note: Reactions were carried out using a molar ratio of double bonds: formic acid: 50% hydrogen peroxide of 1:1:4.

thereafter and was maintained at 50°C, 60°C or 70°C, respectively, until completion of the reaction. Increasing the reaction temperatures not only accelerated the formation of performic acid which resulted in a faster epoxidation rate, but also led to the opening of epoxy ring system (Vaibhav *et al.*, 2006). The results showed a faster initial reaction rate, and the maximum oxirane content was attained in a shorter time as the reaction temperature increased

(Figure 5). However, there was a non-significant difference in the final conversions of 93.8%, 93.5% and 91.8% for temperatures 50°C, 60°C and 70°C, respectively. Consequently, the OHV became higher, from 4.51 and 7.32 to 10.53 mg KOH g⁻¹ sample, as the reaction temperature increased (Table 2). This indicates that high temperatures not only accelerated the formation reaction but also tended to destroy the epoxy rings. Hence, a lower temperature is preferred

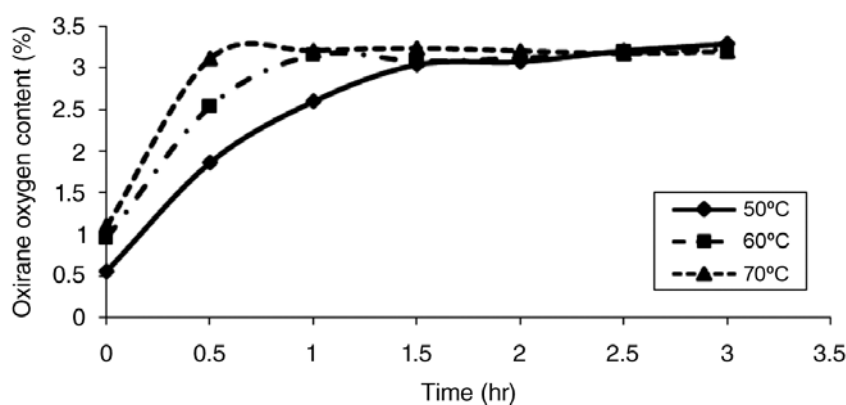


Figure 5. The effect of different reaction temperatures of 50°C, 60°C and 70°C.

Condition: methyl ester of palm fatty acid distillate (PFAD-ME), 250 g; formic acid, 23.23 g; hydrogen peroxide, 68.65 g.

in order to minimize the side reactions. Moreover, an explosion hazard is more likely to occur due to the explosive nature of the reaction at high temperature, especially on an industrial scale. For safety purposes, 50°C is preferred as the maximum epoxy yield was attained in an acceptable reaction time with minimal side reactions.

FT-IR and NMR were used not only to monitor the formation of the product, but also to monitor the possible side reactions (formation of -OH group). The FTIR spectra of PFAD-ME and epoxidized PFAD-ME are presented in *Figure 6*. The emergence of the epoxy peak at 838 cm⁻¹ provided evidence that epoxidation took place in the reaction using PFAD-ME. The absence of double bonds was reflected by the disappearance of the peak at 3002 cm⁻¹ which is assigned to the alkene C-H stretch. IR spectra showed no trace of the OH absorption peak at approximately 3300-3500 cm⁻¹, indicating ring opening did not occur during the reactions.

The comparison of ¹H NMR spectra between PFAD-ME and epoxidized PFAD-ME is shown in *Figure 7*. It clearly indicates the disappearance of olefin protons at 5.3 ppm (-CH=CH-) and allylic protons at 1.9 ppm and 2.0 ppm (-CH₂-CH=CH-CH₂-). This is subsequently confirmed by the presence of new signals of epoxy protons at 1.4 ppm and 1.5 ppm (-CH₂-CHOCH-CH₂-), and 2.89 ppm (-CHOCH-) in the epoxidized PFAD-ME, which were totally absent in PFAD-ME. This confirmed the conversion of the double bonds to oxirane rings via epoxidation. Furthermore, the proton signals of hydroxyl and

formate groups were not observed in both PFAD-ME and epoxidized PFAD-ME, indicating that no significant side reaction took place during the main reaction. *Figure 8* presenting the ¹³C NMR spectra of PFAD-ME and its epoxidized derivative indicates the apparent disappearance of chemical shifts for double-bond carbon atoms at 129.7 ppm and 129.9 ppm. By comparing the spectra, the chemical shifts of carbon atoms to epoxy were readily visible at 57.1 ppm and 57.2 ppm and the subsequent allylic carbons at 27.7 ppm and 27.8 ppm, respectively.

CONCLUSION

The results show that PFAD-ME can be used for synthesizing epoxide. More than 98% yield of epoxidized PFAD-ME was successfully produced by using the optimum molar ratio of 1:1:4 (double bonds: formic acid: hydrogen peroxide) and at the optimum temperature of 50°C. Utilization of by-products such as methyl ester of PFAD will lead not only to a value-added application, but also to a zero-waste strategy in the palm oil industry.

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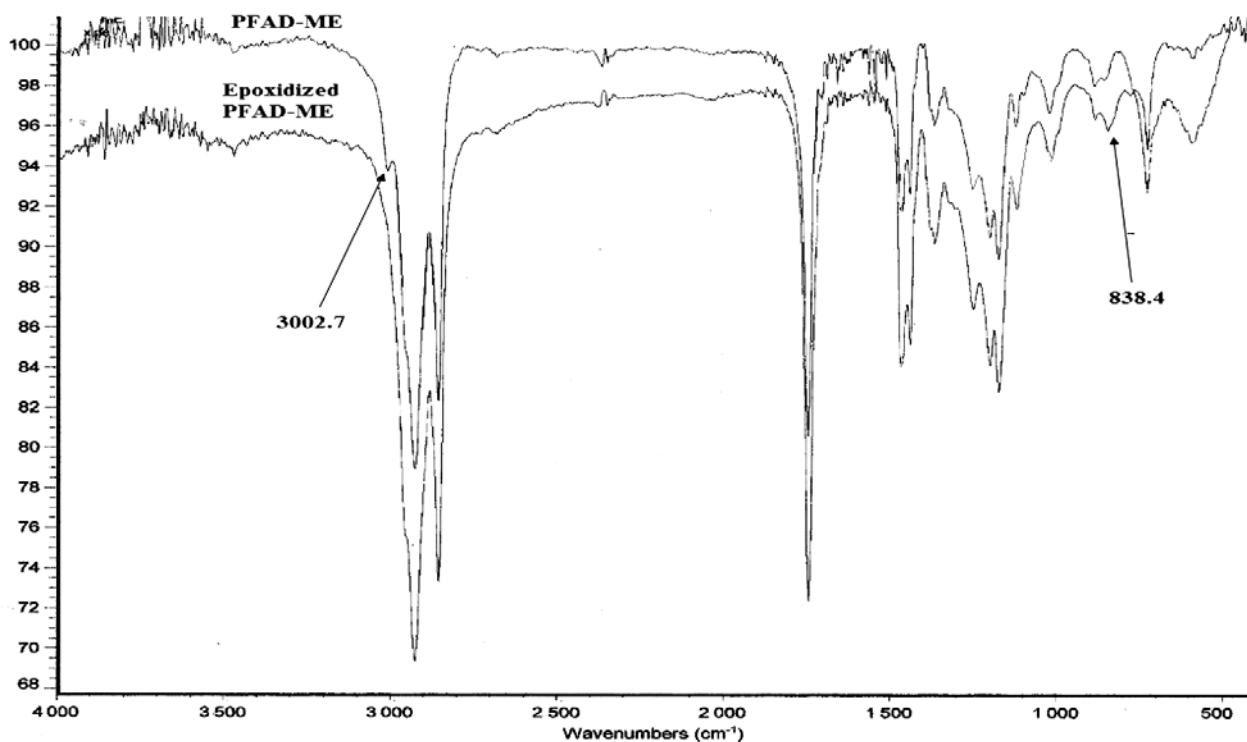


Figure 6. FTIR spectra of methyl ester of palm fatty acid distillate (PFAD-ME) and epoxidized PFAD-ME.

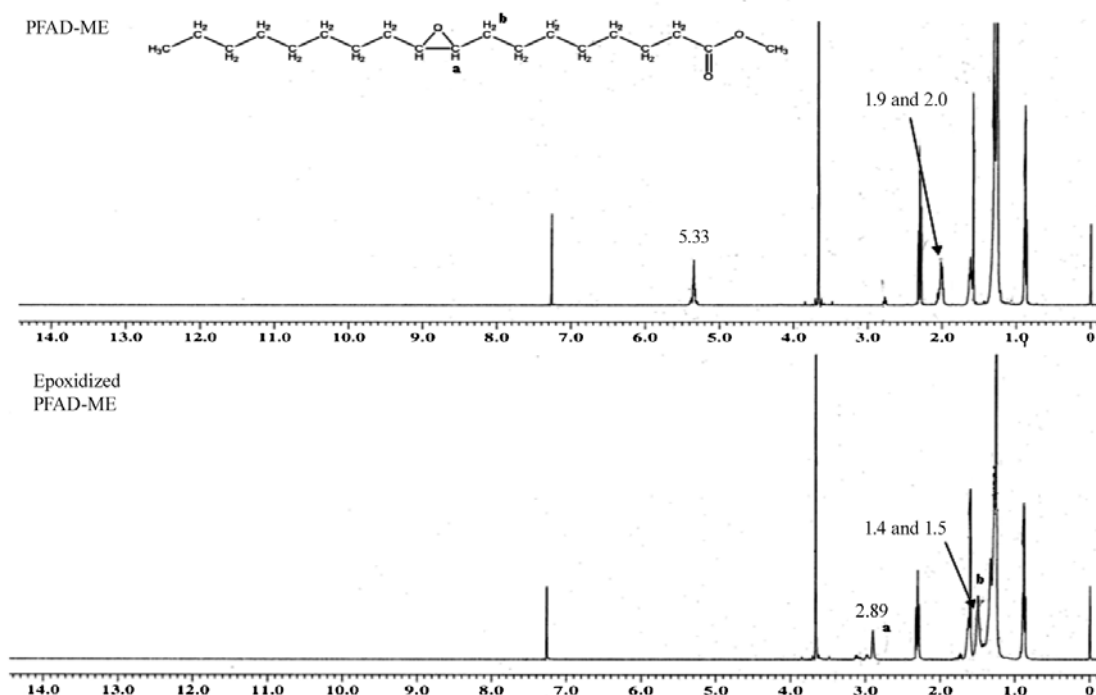


Figure 7. The ^1H NMR spectra of methyl ester of palm fatty acid distillate (PFAD-ME) and epoxidized PFAD-ME.

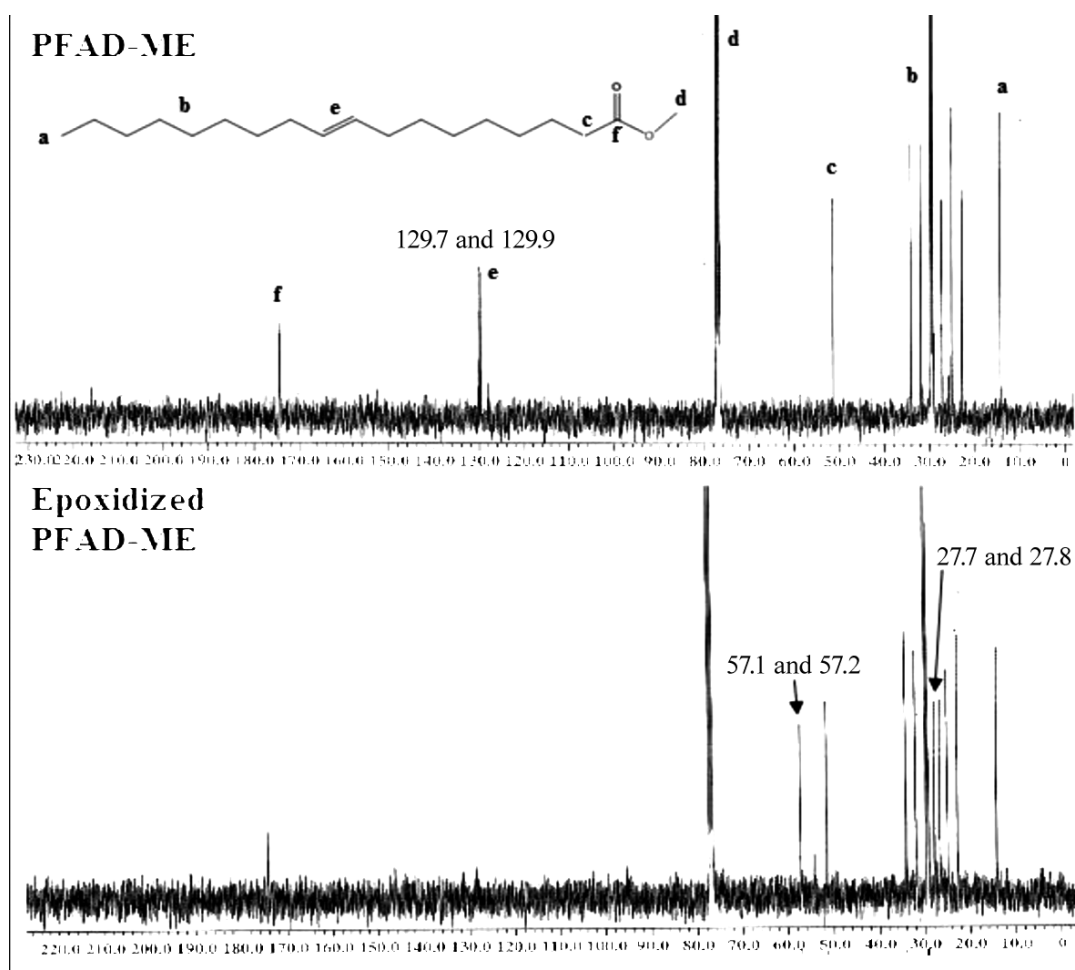


Figure 8. The ^{13}C NMR spectra of methyl ester of palm fatty acid distillate (PFAD-ME) and epoxidized PFAD-ME.

REFERENCES

- AERTS, H A J and JACOBS, P A (2004). Epoxide yield determination of oils and fatty acid methyl esters using ^1H NMR. *J. Amer. Oil Chem. Soc.*, 81(9): 841-846.
- CAMPANELLA, A and BALTANÁS, M A (2004). Degradation of the oxirane ring of epoxidized vegetable oils with solvated acetic acid using cation-exchange resins. *Eur. J. Lipid Sci. Technol.*, 106: 524-530.
- CARLSON, K D; KLEIMAN, R and BAGBY, M O (1994). Epoxidation of *Lesquerella* and *Limnanthes* (meadowfoam) oils. *J. Amer. Oil Chem. Soc.*, 71(2): 175-182.
- DU, G; TEKIN, A; HAMMOND, E G and WOO, L K (2004). Catalytic epoxidation of methyl linoleate. *J. Amer. Oil Chem. Soc.*, 81(4): 477-480.
- GAN, L H; GOH, S H and OOI, K S (1992). Kinetic studies of epoxidation and oxirane cleavage of palm olein methyl ester. *J. Amer. Oil Chem. Soc.*, 69(4): 347-351.
- PIAZZA, G J; FOGLIA, T A and NUÑEZ, A (2001). Optimizing reaction parameters for the enzymatic synthesis of epoxidized oleic acid with oat seed peroxygenase. *J. Amer. Oil Chem. Soc.*, 78(6): 589-592.
- MARCEL, S F; LIE, K J and MOHAMMED, K P (1998). Epoxidation reactions of unsaturated fatty esters with potassium peroxomonosulfate. *Lipids*, 33(6): 633-637.
- PETROVIĆ, Z S; ZLATANIĆ, A; LAVA, C C and SINADINOVIĆ-FIŠER, S (2002). Epoxidation of soybean oil in toluene with peroxyacetic and peroxyformic acids – kinetics and side reactions. *Eur. J. Lipid Sci. Technol.*, 104: 293-299.
- OKIEIMEN, F E; PAVITHRAN, C and BAKARE, I O (2005). Epoxidation and hydroxylation of rubber seed oil: one-pot multi-step reactions. *Eur. J. Lipid Sci. Technol.*, 107: 330-336.
- ORELLANE-COCA, C; CAMOCHO, S; ADLERCREUTZ, D; MATTIASSON, B and HATTIKAUL, R (2005). Chemo-enzymatic epoxidation of linoleic acid: parameters influencing the reaction. *Eur. J. Lipid Sci. Technol.*, 107: 864-870.
- SCALA, J L and WOOL, R P (2002). Effect of FA composition on epoxidation kinetic of TAG. *J. Amer. Oil Chem. Soc.*, 79(4): 373-378.
- SONNET, P E and FOGLIA, T A (1996). Epoxidation of natural triglycerides with ethylmethyldioxirane. *J. Amer. Oil Chem. Soc.*, 73(4): 461-464.
- VAIBHAV, V G; NARAYAN, C P and ANAND, V P (2006). Epoxidation of karanja (*Pongamia glabra*) oil by H_2O_2 . *J. Amer. Oil Chem. Soc.*, 83(7): 635-640.
- VLČEK, T and PETROVIĆ, Z S (2006). Optimization of the chemoenzymatic epoxidation of soybean oil. *J. Amer. Oil Chem. Soc.*, 83(3): 247-252.
- YADAV, G D and MANJULA, D K (2001). A kinetic for the enzyme-catalyzed self-epoxidation of oleic acid. *J. Amer. Oil Chem. Soc.*, 78(4): 347-351.