



Synthesis of Epoxidized Palm Oil-Based Trimethylolpropane Ester by *In Situ* Epoxidation Method

Ferra Naidir¹, Robiah Yunus^{1,3*}, Tinia Idaty Mohd. Ghazi¹ and Irmawati Ramli²

¹Department of Chemical and Environmental Engineering, Faculty of Engineering, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

²Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

³Institute of Advanced Technology, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

ABSTRACT

Palm oil-based Trimethylolpropane ester (TMP ester), with an iodine value of 66.4 g/100g, was epoxidized to produce epoxidized TMP esters. *In situ* epoxidation method was used with peracetic acid to eliminate fatty acid double bonds in palm oil-based TMP ester and change it into oxirane ring. This was done to improve the oxidative stability of trimethylolpropane ester which is a key concern limiting the useful service life in lubricants. The epoxidation was performed by reacting acetic acid as active oxygen carrier with concentrated hydrogen peroxide as oxygen donor and a small amount of homogeneous catalyst (sulphuric acid). The effects of various parameters on the rate of epoxidation (such as the ratio of mole acetic acid to ethylenic unsaturation, hydrogen peroxide to ethylenic unsaturation and acetic acid mole ratio, and amount of catalyst) were studied. The rate of oxidation was investigated by the percentage of oxirane oxygen analysis and iodine value.

Keywords: *In situ* epoxidation, peracetic acid, percentage of oxirane oxygen, sulphuric acid

INTRODUCTION

Vegetable oil based lubricant has superior tribological properties and is rapidly

biodegradable, and these make it suitable to be used as a base fluid in environmental acceptable lubricants (EAL). Vegetable oils contain fatty acids esters with unsaturated fractions such as oleic acid (C18:1), linoleic acid (C18:2) and linolenic acid (C18:3), as well as saturated fractions, namely palmitic acid (C16:0) and stearic acid (C18:0). The structures of the fatty acids, i.e. the chain length and degree of unsaturation, directly affect the operational stabilities and lubricating properties of the oil. The oxidative stability of

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Email addresses:

robiah@eng.upm.edu.my (Robiah Yunus),

tinia@eng.upm.edu.my (Tinia Idaty Mohd. Ghazi),

irmawati@science.upm.edu.my (Irmawati Ramli)

*Corresponding Author

vegetable oils increases with the decrease in the amount of polyunsaturated acids (Schneider, 2006). Oxidation is a major concern that limits the use of vegetable oil as lubricating fluid. Oxidation leads to polymerization and degradation whereby polymerization will increase viscosity and reduce lubrication functionality. Meanwhile, degradation leads to break down to products that are volatile, corrosive and diminish the structure and properties of the lubricants (Kodali, 2002). It is important to note that oxidative stability can be improved by either genetic or chemical modification of unsaturated acids. The unsaturated fatty acid structure of trimethylolpropane esters was modified through epoxidation reaction to produce epoxidized trimethylolpropane esters. Epoxidation is a reaction in which the double bond in unsaturated fraction is directly converted into oxirane (epoxide) groups by reaction with organic peracids, either preformed or generated *in situ*. The *in situ* synthesis takes place by reacting carboxylic acid with concentrated hydrogen peroxide to make percarboxylic acid. An oxygen atom from hydrogen peroxide through percarboxylic acid attaches itself to the double bonds of the fatty acid carbon chain of the oil, as shown in Fig.1 (Campanella & Baltanas, 2005).

Epoxidation reaction involves the opening of the double bond, followed by the formation of the oxirane ring on the opened bond. Peracetic acid was used as the epoxidizing agent and was prepared *in situ* using hydrogen peroxide (H_2O_2) as the primary source of oxygen and aqueous acetic acid (CH_3COOH) and as the oxygen carrier between the aqueous and the oil phases. A small amount of homogeneous catalyst (H_2SO_4) was applied and heptane was employed as an inert solvent to minimize the formation side product, such as the opening of the epoxy ring on oxirane, especially at higher temperatures (Gan *et al.*, 1992). This paper focuses on the effects of the ratio of mole acetic acid and hydrogen peroxide on the epoxidation reaction of palm oil based synthetic lubricant (TMPester) to reduce the double bond and to change it into oxirane ring. The effect of catalyst was also studied, where the progress of reaction was assessed based on the presence of double bond by measuring the IV value of the sample and the presence of oxirane oxygen.

MATERIALS AND METHODS

Materials

The palm oil based synthetic lubricant used in the experiment was trimethylolpropane ester (TMPester) derived from palm oil. TMPester was synthesized in our laboratory using palm oil methyl ester (POME) and trimethylolpropane as starting materials and sodium methoxide solution in methanol (30 w/w%) as a catalyst. The chemicals used in the epoxidation reaction were glacial acetic acid 99.7% (Rankem, India), heptane (Merck, Germany), sulphuric acid 96.5% (Rdh, Germany) and hydrogen peroxide 35% (Merck, Germany).

Experimental Procedure of Epoxidized TMP Ester

TMP ester was used as a starting material in the epoxidation reaction and the reaction was carried out based on the procedures described in the Encyclopedia of Chemical Technology (Kirk & Othmer, 1994). The required amount of TMPester and heptane as a solvent was added into the three-necked reaction flask connected to a reflux condenser. Peracetic acid, which

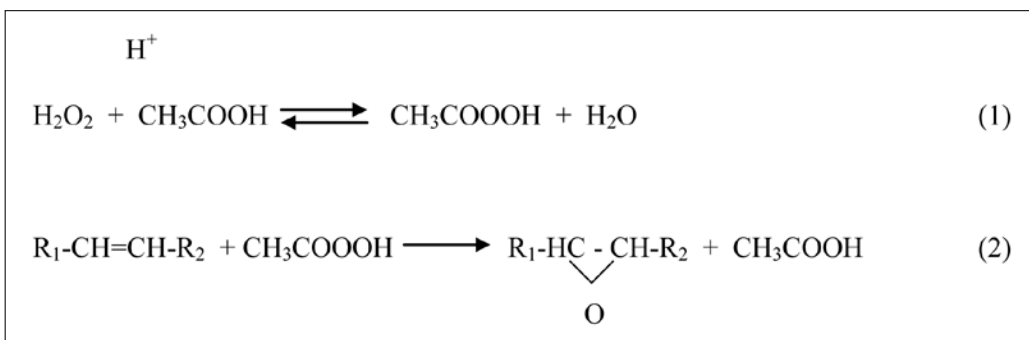


Fig.1: The Epoxidation of the Double Bonds of Vegetable Oils (Unsaturated Triacylglycerides) in the Conventional Acetic Acid-Hydrogen Peroxide Process

had been prepared *in situ* by reacting various mixtures of acetic acid and hydrogen peroxide in the presence of small amounts of concentrated sulphuric acid, was poured into a mixture of TMPester and heptane. Then, the mixture was heated to a desired temperature by using a hotplate with a magnetic stirrer and a thermometer. After the reaction was completed, the mixture was poured into a separatory funnel and the aqueous layer was drawn off. The oil layer was washed with successive portions of warm water ($\pm 40^\circ\text{C}$) and sodium hydroxide was added into the oil phase to neutralize the sulphuric acid, before it then was stripped off under a low vacuum pressure at 80°C . The mixture was cooled down and the epoxidized TMPester product was filtered. The product was analyzed for the iodine value based on the Porim Test Method (1985), and the percentage of oxirane oxygen was determined using the direct method as obtained in method Cd 9-57 by *American Oil Chemists' Society* (AOCS) (1984).

RESULTS AND DISCUSSION

The Effect of the Ratio of Mole Acetic Acid on Ethylenic Unsaturation

In the epoxidation reaction, acetic acid functions as an oxygen carrier for hydrogen peroxide to form peracetic acid, which then reacts with ethylenic unsaturation group in TMP ester to form oxirane groups. The reactions were performed at the ratios of 0.5, 0.8, 1 and 1.5 moles of acetic acid per mole of ethylenic unsaturation of TMP esters. The effect of acetic acid and the time of reaction on the epoxidation reaction of TMP esters are shown in Fig.2. The effect was determined based on the formation of oxirane ring oxygen. The yield of oxirane oxygen (%OO) is almost independent of acetic acid concentration. However, the figure shows that for a 20-hour reaction, the percentage of oxirane oxygen (%OO) increases with the concentration of acetic acid until it reaches the optimum value of 0.8 moles of acetic acid per mole of ethylenic unsaturation of TMP esters at which the %OO is 3.84%.

Meanwhile, Fig.3 shows that the lowest iodine value is 0.94 at mole ratio of glacial acetic acid 1.5 at 13 hours of reaction time. To achieve the minimum iodine value and the maximum percentage of oxirane oxygen, the optimum level of the acetic acid should be applied where both effects are balanced. The lower iodine value means a lower level of unsaturation in the epoxidized TMPesters. The opening of the double bonds allows for the formation of oxirane

in the epoxidized TMPEster. Acetic acid takes part in the overall reaction as a catalyst in the formation of oxirane ring and as a reactant in the hydrolysis of the oxirane ring (Goud *et al.*, 2006). In this study, the optimum mole ratio of glacial acetic acid to ethylenic unsaturation is 0.8 mole/mole, where the percentage oxirane is 3.84% and the iodine value is 1.3.

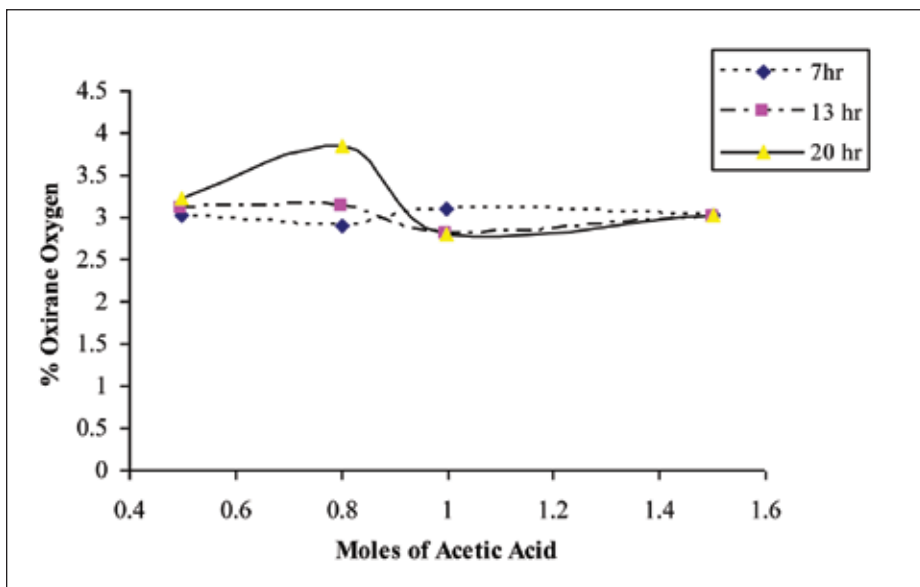


Fig.2: The Effect of Glacial Acetic Acid on the Percentage Oxirane Oxygen Forming an Epoxidized TMPEster

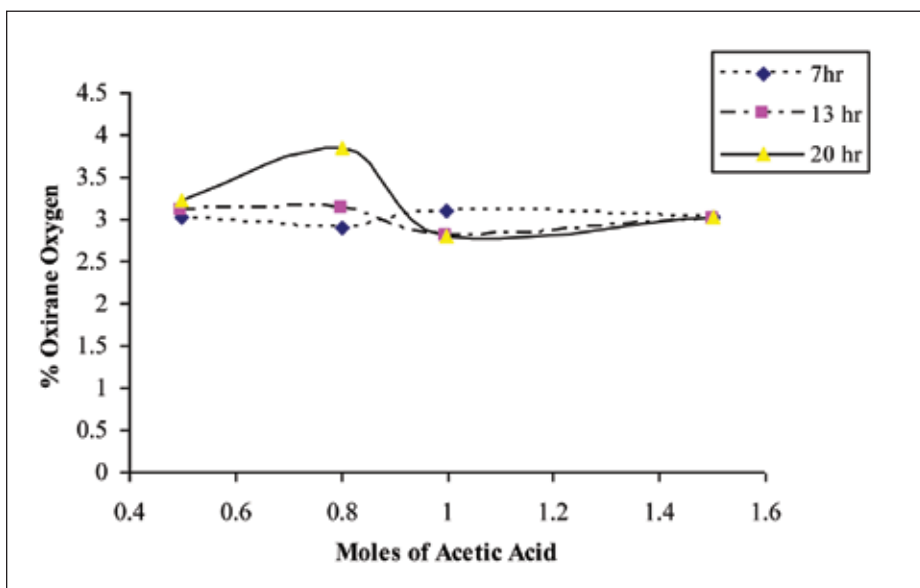


Fig.3: The Effect of Glacial Acetic Acid on the Iodine Value of Epoxidized TMP Esters

The Effect of Hydrogen Peroxide on the Ethylenic Unsaturation and Acetic Acid Mole Ratio

Hydrogen peroxide is the most important source of active oxygen in *in situ* epoxidation and in preformed peracid acid oxidations (Swern, 1971). As a source of oxygen, hydrogen peroxide should be in the stoichiometric quantity based on the number of ethylenic linkage that is present in the product to be epoxidized. In general, a slight excessive amount of hydrogen peroxide is employed (Niederhauser & Koroly, 1949). In this study, the reactions were applied with 3.5, 5, and 7.5 moles of hydrogen peroxide per mole of ethylenic unsaturation, with the aim of investigating the effect of hydrogen peroxide on the conversion of ethylenic unsaturation to oxirane ring. Fig.4 shows that the maximum percentages of oxirane oxygen are at 3.90%, 3.75%, 3.68% and 3.02% which have been obtained using 7.5:1 mole of hydrogen peroxide per mole of ethylenic unsaturation 0.5, 0.8, 1, and 1.5 mole of acetic acid, respectively. However, the minimum iodine value is at 1.75, 1.26, 1.26, and 0.94, which was obtained using 5:1 mole of hydrogen peroxide per mole ethylenic unsaturation to 0.5, 0.8, 1, and 1.5 mole of acetic acid (*see* Fig.5). These experiments show that both the percentages of oxirane oxygen and iodine value are affected by the amount of hydrogen peroxide used in the epoxidation of TMPester.

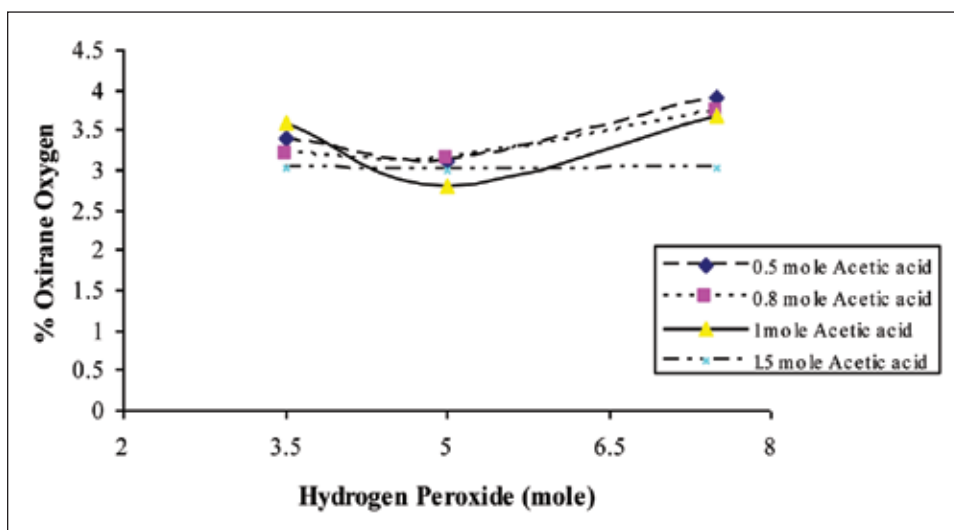


Fig.4: The Effect of Hydrogen Peroxide on the Percentage of Oxirane Oxygen

The Effect of Catalyst

The presence of catalyst in the reaction media is very important to obtain a high conversion of the ethylenic unsaturation in TMP esters to oxirane oxygen. In this study, sulphuric acid was used as a catalyst and the amount was based on the combined weight of acetic acid and aqueous hydrogen peroxide. The effect of catalyst concentration on ethylenic unsaturation TMP ester was studied at various catalyst concentrations of 1%, 2%, 3%, 4%, and 5%. Fig.6 illustrates the effect of sulphuric acid concentration in the epoxidation process to convert ethylenic unsaturation in the TMP esters to oxirane ring.

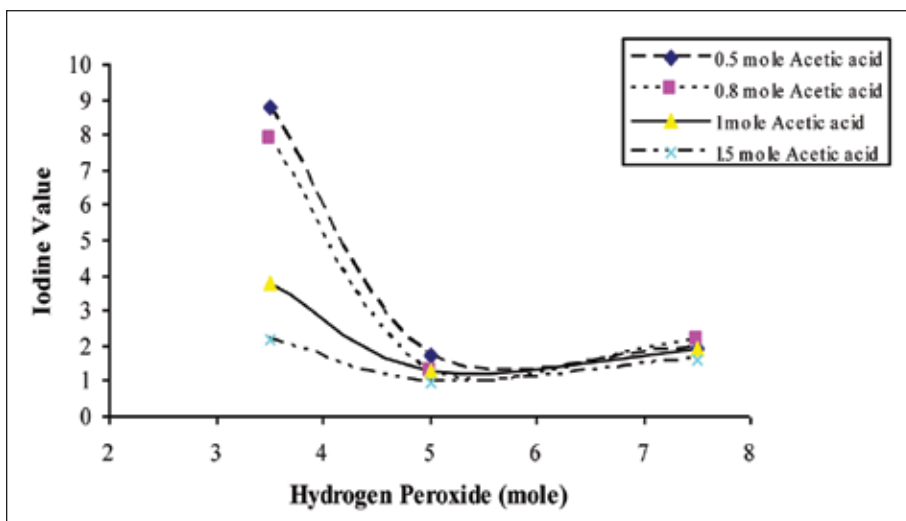


Fig.5: The Effect of Hydrogen Peroxide on Iodine Value

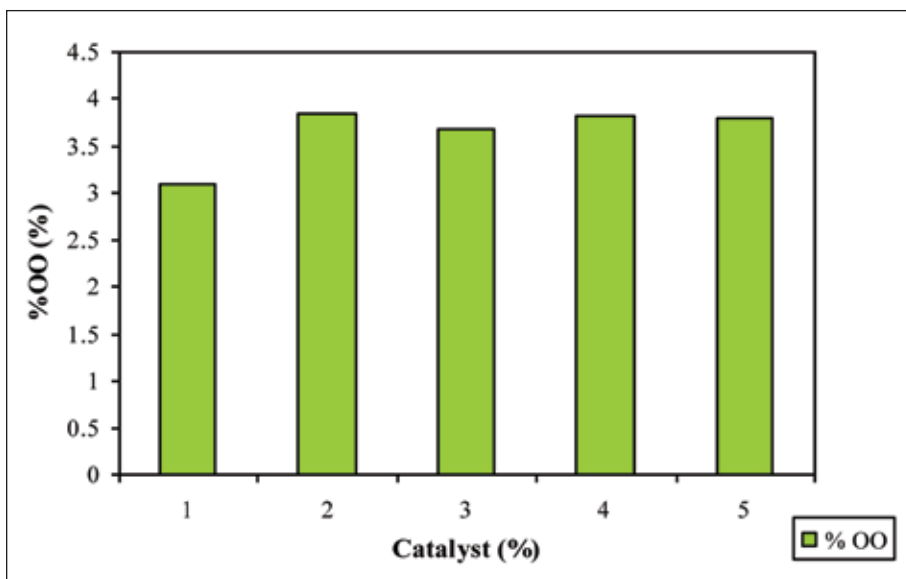


Fig.6: The Effect of Catalyst on Epoxidation Trimrthylolpropane Esters, T= 50°C, 8 Hours, 0.5/ 8/ 1 Ratio of Acetic Acid/ Hydrogen Peroxide/ Ethylenic Unsaturation

The experiment was carried out at 50°C, 8 hours of reaction, and 20% of solvent with 0.5/ 8/ 1 mole ratio of acetic acid/ hydrogen peroxide/ ethylenic unsaturation TMP ester. The optimum oxirane product was achieved at 2% of the catalyst at which the percentage of oxirane oxygen was 3.85%. The maximum percentage of oxirane oxygen that can be obtained from the experiment is 4.02% if 100% ethylenic unsaturated in TMP esters is converted into oxirane oxygen.

CONCLUSIONS

Based on the results gathered from the experiments on the epoxidized TMP esters, a suitable operation condition for the TMP esters epoxidation reaction was determined. The results show that the maximum yield of percentage oxirane oxygen is 3.9 % with the corresponding iodine value of 1.9, at which as much as 96% of the ethylenic unsaturation converted into oxirane ring. The optimum operation conditions for the epoxidation of TMP esters were 0.5 mole of acetic acid, 7.5 mole of hydrogen peroxide, 2% catalyst, 20% solvent, a temperature of 50°C, and 13 hours of reaction time.

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