

# PROCESS CONTROL FOR EPOXIDATION OF RBD PALM OLEIN

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## ABSTRACT

An epoxidation reaction of different types of feedstock, depending on the iodine values, through percarbonic acid route generally generated different amount of heat. Thus, the heating and cooling temperature of the system and reaction need to be regulated to accommodate production of epoxidised products with oxirane oxygen content (OOC) value nearest to the targeted OOC. Four in situ epoxidation reactions, namely Entry 1-4, utilising formic acid and concentrated hydrogen peroxide, were conducted with continuous control of heating and cooling with real time temperature monitoring. All the reactions gave OOC values of between 3.17%-3.37% determined at the 240<sup>th</sup> min of the epoxidation process. These values were consistent with the theoretical OOC of 3.41% of refined, bleached and deodorised (RBD) palm olein. The neutralisation, washing and drying processes did not alter the OOC values of all the epoxidised products (EPO) giving final dry EPO of OOC between 3.19%-3.32%. The study revealed that epoxidation reaction of RBD palm olein has to be conducted at temperatures within 30°C to 60°C by suppressing the heat generated from the reaction through efficient heating and cooling system.

**Keywords:** epoxidised palm olein, exothermic, oxirane oxygen content.

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## INTRODUCTION

Epoxidation process of any unsaturated hydrocarbon feedstock through percarbonic acid route is known to be highly exothermic. Hence, by carrying out the reaction without a strategic control of the heat generated from the reaction mass, will result in the decomposition of the reactive three-membered epoxy ring and subsequently produce epoxidised material of low oxygen oxirane content (OOC). Excessive heat generation from uncontrolled on-going reaction may also result in a runaway reaction. The epoxidation reaction of vegetable oils and stabilising the content of their epoxy ring was

a breakthrough finding by Findley *et al.* (1945). It is a reaction that displaces active oxygen on a carbon-carbon double bond to give a three-membered epoxy or oxirane ring (Figure 1). The epoxidised vegetable oil, generally prepared using percarbonic acid serves as an important precursor in producing value-added oleochemical derivatives via further reactions at the reactive three-membered ring structure.

Epoxidation process involves two consecutive reactions which are dependent on hydrogen peroxide

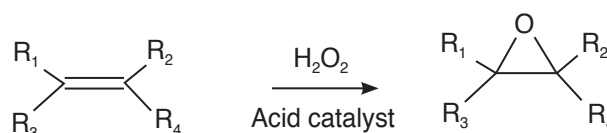


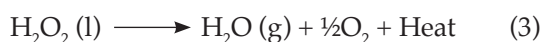
Figure 1. A general reaction showing the transformation of the carbon-carbon double bond via epoxidation to produce an epoxy group.

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( $\text{H}_2\text{O}_2$ ) concentration as illustrated in Equation (1). The formic acid (FA) reacts with  $\text{H}_2\text{O}_2$  to form performic acid (PFA) and water ( $\text{H}_2\text{O}$ ). In Equation (2), the PFA immediately reacts with the olefinic double bond (DB), to produce the epoxy group (EO). The FA is regenerated upon consumption of PFA during the epoxidation process.



The decomposition of  $\text{H}_2\text{O}_2$  and PFA are thermodynamically favourable and highly exothermic with the former, depending on the concentration which rapidly decomposes beyond  $60^\circ\text{C}$  (Shanley and Greenspan, 1947) and therefore, epoxidation using PFA was reported to be more favourable at low reaction temperature (Petrovic *et al.*, 2002; Goud *et al.*, 2007; Gan *et al.*, 1992). Generally, high reaction temperature shortens the reaction duration. However, extremely high temperature also expedites ring opening reactions and thus, resulted in lower OOC value of the expected epoxidised feedstock. Furthermore, in the absence of sufficient cooling capacity, a rapid temperature increment will ultimately intensify the decomposition rate of PFA and hence reduce the formation rate of an EO. According to Shanley and Greenspan (1947), exposing  $\text{H}_2\text{O}_2$  to high temperature has been proven to present safety hazard to the processing equipment and personnel due to sudden release of very large volume of gases and high energy content [Equation (3)].



Furthermore, high temperature stimulates the ring-opening of the epoxides and produces unwanted side products. These also explain the main cause of lower OOC value than the theoretical value. One practical approach, suggested by Derawi and Salimon, (2010), is to minimise the amount of acid catalyst and ensure the  $\text{H}_2\text{O}_2$  concentration used does not exceed 30% of the amount required.

EO is very reactive and hence, stabilising the epoxy ring formation throughout the reaction is important and has become the main interest in establishing process parameter for epoxidation reactions through percarbonic acid, for example, by applying inert solvent, regulating mole ratio and reaction temperature (Findley *et al.*, 1945; Petrovic *et al.*, 2002; Goud *et al.*, 2007; Salmiah *et al.*, 1987; Cai *et al.*, 2008; Derawi and Salimon, 2010; Hazmi *et al.*, 2013). Recently, Mohd Zan Arniza *et al.* (2015) showed the importance of an epoxidation process used as an intermediate route to obtain palm-based

polyols with hydroxyl values of between 300-330 mg KOH  $\text{g}^{-1}$  sample. In this article, the heating and cooling temperatures were regulated in order to control the heat released from the epoxidation reaction and at the same time, optimising the OOC values of the epoxidised feedstock.

## MATERIALS AND METHODS

### Materials

The refined, bleached, deodorised (RBD) palm olein with iodine value of 56 g  $\text{I}_2$  / 100 g, acid value of 0.2 mg KOH  $\text{g}^{-1}$ , viscosity of 76.4 cSt at  $25^\circ\text{C}$ , supplied by Southern Edible Oil Sdn Bhd, Malaysia was used without further pre-treatment. FA of 94% purity was purchased from Sigma-Aldrich while  $\text{H}_2\text{O}_2$  at 50 % solution was obtained from Columbus Chemical Industry. Sodium chloride and sodium carbonate were purchased from Kong Long Huat Chemicals Sdn Bhd, Malaysia.

### Epoxidation of Palm Olein using PFA

The *in situ* epoxidation of RBD palm olein was conducted according to a patented technology by the Malaysian Palm Oil Board (Hazimah *et al.*, 2011). The reactions were conducted in a 1 litre-3-necked jacketed glass vessel, equipped with a magnetic stirrer, thermometer, and graduated dropper funnel. The reaction temperature was regulated by a circulating waterbath for heating and cooling ( $5^\circ\text{C}$ - $90^\circ\text{C}$ ). About 350 g of RBD palm olein was charged into the reaction vessel under medium stirring and heated just to melt the reaction feedstock and to reduce the viscosity of the feedstock. A required amount of FA and  $\text{H}_2\text{O}_2$ , calculated for 1:2.5 mole ratios, was pre-mixed, and charged into the dropping funnel to allow formation of PFA. Under continuous stirring, the PFA was added drop wise at a flow rate of 2 ml  $\text{min}^{-1}$  within the first 75 min. The total reaction duration was fixed at 4 hr. Determination of OOC value was carried out to monitor the reaction progress. At the 240<sup>th</sup> min of reaction, the mixture was transferred to a separating funnel and the organic layer was thoroughly washed with distilled water, 2% sodium carbonate and 3% sodium chloride solutions in order to neutralise the residual acid and remove the resulting salt from the reaction mixture. The final product was then dried at  $70^\circ\text{C}$  under reduced pressure of 20 mbar. Four reactions were conducted, namely Entry 1-4, in order to establish the optimal parameter to obtain epoxidised palm olein with OOC value nearest to the theoretical value and to ensure the stability of the OOC ring is maintained on the triglyceride backbone.

### Analytical Methods

Determination of OOC value was done according to AOCS (Cd 9-57). Measurement of iodine and acid value were carried out as outlined in AOCS (Cd 1d-92) and AOCS (Cd 3d-63), respectively. Moisture level determination was done according to AOCS Ca 2e-84 (Karl Fisher Instrument) while specific gravity at 25°C was determined using the AOCS Cc 10a-25. Refractive index at 25°C was based on AOCS Ja 10-87 and viscosity measurement was carried out at 21°C using Brookfield model RV DV-II+Pro viscometer according to AOCS Tp 1a-64.

### RESULTS AND DISCUSSION

The theoretical conversion of carbon-carbon double bonding of a triglyceride to EO serves as the benchmark to achieve the maximum yield in the epoxidation process using PFA as the oxidising agent. The theoretical OOC in 100 g of palm olein at complete conversion was calculated to be 3.41% from Equation (4), where the atomic weight of iodine,  $A_i = 126.9$ , the atomic weight of oxygen,  $A_o = 16.0$ , and the initial iodine value (IV) of the RBD palm olein,  $IV_o = 56$ .

$$OO_{th} = \left\{ \frac{(IV_o/2A_i)}{[100 + (IV_o/2A_i)A_o]} \right\} \times A_o \times 100 \quad (4)$$

Therefore, the experimental OOC can then be calculated for 100 g of oil using the formula as in Equation (5).

$$OOC = 1.6 N (V-B)/W \quad (5)$$

where; N is the normality of hydrogen bromide (HBr) in acetic acid;  
 V is the volume (ml) of HBr consumed for sample;  
 W is the weight (g) of sample; and  
 B is the volume (ml) of HBr for blank.

For reaction conducted according to Entry 1, the heat generated from the epoxidation reaction was controlled by adjusting the cooling temperature so that the reaction temperature did not exceed 70°C as depicted in *Figure 1*. The first sample withdrawn at the 75<sup>th</sup> min of the reaction time, just when all the PFA had been added, and the reaction temperature was at 35°C, gave OOC value of 2%. Further addition of PFA was carefully regulated so as to maintain a steady increment of temperature due to the heat released from the epoxidation reaction from 33°C to 45°C. After the addition of PFA was completed, the cooling duty was turned off and the reaction mixture was heated up to a temperature just enough to activate the reaction towards a complete formation of epoxy ring. However, there was a large amount of heat dissipated from the process causing the temperature to accidentally overshoot to 70°C within 15 min. Even with the cooling duty returned online, it took more than 30 min to bring down the reaction temperature to 33°C. While allowing the reaction to occur, sample was withdrawn at the 150<sup>th</sup> min and subsequently at 195<sup>th</sup> min. The OOC values of the withdrawn samples were 3.15% and 3.17%, respectively.

For the reaction conducted according to Entry 2 (*Figure 2*), the heat generated from the epoxidation reaction was carefully controlled by the cooling duty throughout the 4 hr reaction duration between 30°C to 50°C. It was also observed that heat generated from the reaction was efficiently controlled between 33°C to 42°C by a prudent control of the addition rate of PFA at the 75<sup>th</sup> min of reaction. At the 90<sup>th</sup> min of reaction onwards, the reaction temperature was maintained at 50°C throughout the reaction. Samples were withdrawn at 120<sup>th</sup> min, 180<sup>th</sup> min and finally at 240<sup>th</sup> which then gave OOC values of 2.66%, 3.11% and 3.37%, respectively.

For the reaction conducted according to Entry 3, as illustrated in *Figure 3*, the rate of addition of PFA was controlled in such a way that process

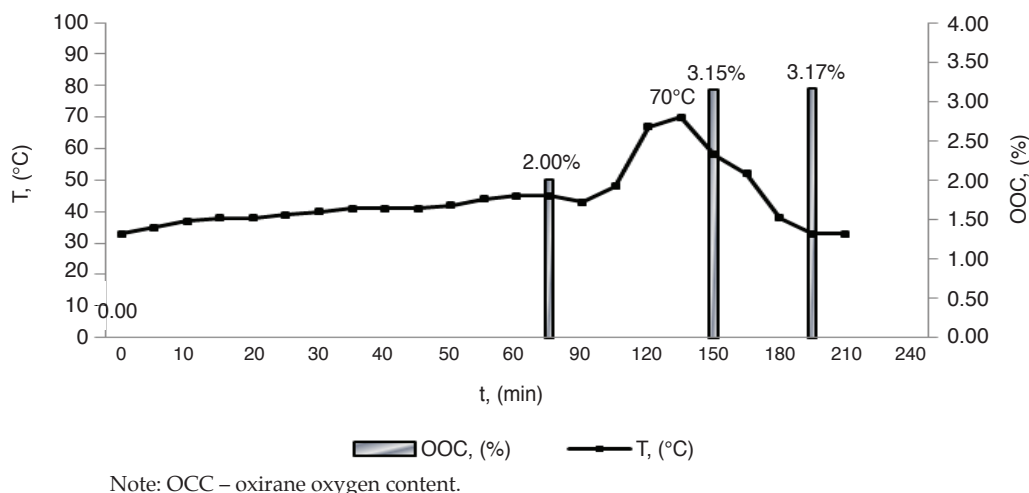
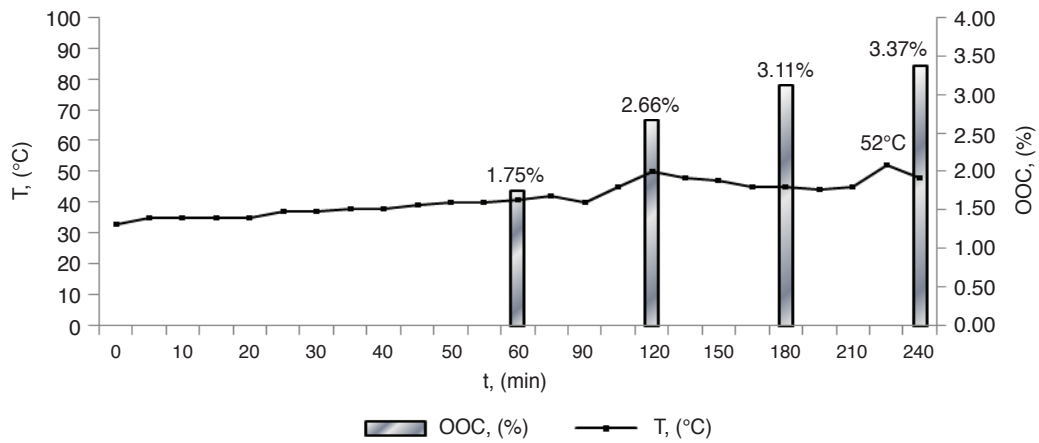
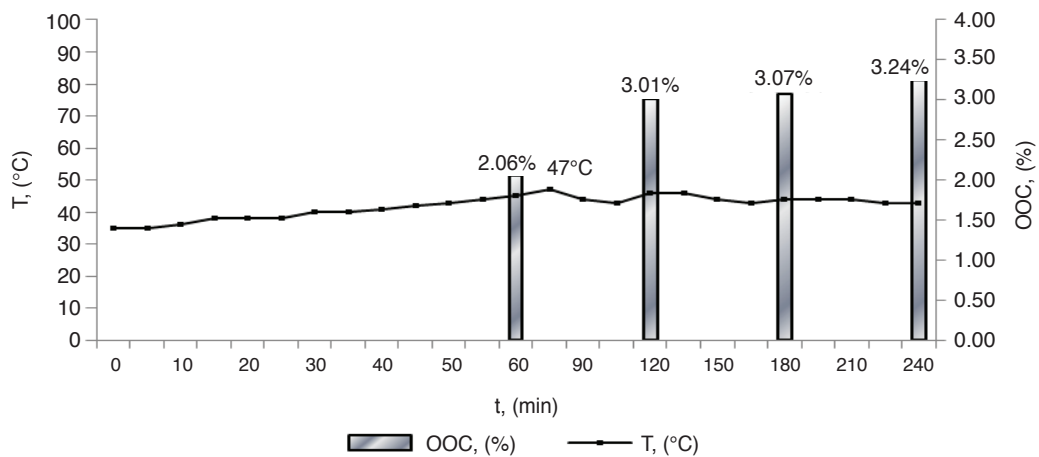


Figure 1. Epoxidation reaction between palm olein and performic acid at 1:2.5 ratio conducted between 30°C - 70°C, Entry 1.



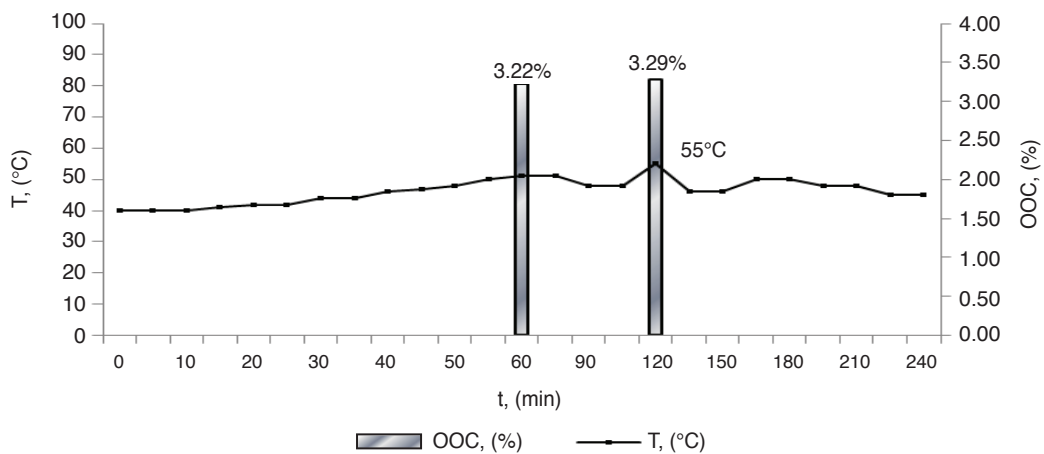
Note: OCC – oxirane oxygen content.

Figure 2. Epoxidation reaction between palm olein and performic acid at 1:2.5 ratio conducted between 30°C- 50°C, Entry 2.



Note: OCC – oxirane oxygen content.

Figure 3. Epoxidation reaction between palm olein and performic acid at 1:2.5 ratio conducted between 30°C - 45°C, Entry 3.



Note: OCC – oxirane oxygen content.

Figure 4. Epoxidation reaction between palm olein and performic acid at 1:2.5 ratio conducted between 30°C - 55°C, Entry 4.

temperature was maintained within 30°C and 45°C. Samples were withdrawn at the 60<sup>th</sup> min, 120<sup>th</sup> min, 180<sup>th</sup> min and finally at 240<sup>th</sup> min. With less temperature fluctuation, the OOC values were at the maximum of 3.24%.

For the reaction carried out based on Entry 4, the addition of PFA was initiated when the temperature of the reaction mixture reached 40°C. The high starting temperature resulted in a faster rate of epoxidation where maximum OOC value of 3.29% was obtained at the 120<sup>th</sup> min as shown in *Figure 4*. Despite being the most popular way to conduct epoxidation of vegetable oil, the conventional method is subjected to side reactions. This phenomenon is more favourable at elevated reaction temperature. Studies by Derawi and Salimon (2010) and by Hazmi *et al.* (2013) showed that an excessive loading of H<sub>2</sub>O<sub>2</sub> and acid catalyst resulted in shorter duration of epoxidation reaction. However, an acid-catalysed ring-opening reaction also occurred as a side reaction which then formed internal hydroxyl groups. The drawback has been successfully rectified by using a weaker acid.

It is paramount to neutralise the residual acid, preferably to acid value of less than 0.1 mg KOH g<sup>-1</sup> sample, so as to avoid inhibition or poisoning of downstream products such as polyurethane formation (Wirpsza, 1993).

The properties of the epoxidised palm olein (EPO) produced according to Entry 1-4 are tabulated in *Table 1*. It is assumed that all the four processes lead to a complete formation of epoxy group at the unsaturated sites of the triglyceride backbone. The increase in OOC values is directly proportional with the rate of disappearance of IV. The OOC values for EPO produced through Entry 1 and 2 were 3.19% and 3.12%, respectively. These entries exhibit incomplete epoxidation reaction because the applied reaction parameters were not sufficient enough to fully oxidise the olefinic carbons on the triglycerides of

RBD palm olein. This is revealed by the IV of 0.4 and 1.63 mg I<sub>2</sub>/100 g sample, respectively. These values also affect the efficiency of drying the resultant EPO as reflected by the moisture content of EPO obtained in Entry 1 and 2.

The viscosity exhibits typical increment upon transformation of double bond and was similar for all the EPO obtained according to Entry 1-4. This is lower than reported where higher viscosity of epoxidised vegetable oil usually indicates the presence of side reactions such as ring-opening and followed by internal polymerisation (Derawi and Salimon, 2010; Hazmi *et al.*, 2013). Specific gravity and refractive index of the final EPO were maintained.

## CONCLUSION

Production of EPO was efficiently carried out at low reaction temperature of between 30°C-60°C giving consistent OOC values with the calculated (theoretical) OOC value of epoxidised RBD palm olein which is 3.41%. The main factor in determining the quality of EPO is to control the heat generated from reaction mixture by regulating the heating and cooling duty of the reaction vessel and mixture. This finding will provide significant input on the design of a scale up reactor for the epoxidation of unsaturated feedstocks.

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TABLE 1. THE PHYSICO-CHEMICAL PROPERTIES OF EPOXIDISED PALM OLEIN (EPO) PRODUCED ACCORDING TO ENTRY 1-4

	Entry 1	Entry 2	Entry 3	Entry 4
OOO (%)	3.17(3.19)*	3.37(3.12)*	3.24(3.32)*	3.29(3.30)*
Moisture (%)	0.032	0.021	0.001	0.001
Acid value (mg KOH g <sup>-1</sup> sample)	0.68	0.07	0.55	0.111
Iodine value (mg I <sub>2</sub> 100 g sample)	0.4	1.63	-	-
Viscosity at 21°C (cP)	100	100	100	100
Specific gravity at 25°C	0.9413	0.9487	0.9431	0.9394
Refractive index at 25°C	1.465	1.466	1.465	1.465
Colour	-	Pale yellow	-	-
Odour	-	Typical	-	-

Note: \*Values for final/dried epoxidised product. OCC – oxygen oxirane content.

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