Effect of Oxygen Carrier and Reaction Temperature in Enhancing the Epoxy Ring Stability in the Epoxidation of Palm Kernel Oil

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Abstract. Palm kernel oil (PKO) naturally composed of lauric, myristic and oleic acid. Oleic acid is one of the unsaturated fatty acids that has double bond in its chain. This double bond can be altered into epoxide acid by epoxidation reaction. This study investigated the effect of oxygen carriers and reaction temperature in epoxidation of palm kernel oil. The result showed that formic acid is the best oxygen carrier with the maximum conversion to oxirane (RCO) of 60.59% under optimum temperature of 55°C. The formation of epoxide from palm kernel oil was confirmed by FTIR analysis which shows the functional groups of epoxide ring at 2922.12 cm⁻¹, 1742.74 cm⁻¹ and 650.4 cm⁻¹.

1. Introduction
Oil palm which is also known as Elaeis guineensis produces two different types of oil which are palm oil and palm kernel oil [1]. The palm fruits appeared such a plum where the outer flesh mesocarp contributes the oil palm and the kernel which is inside a hard shell contributes the palm kernel oil. These two kinds of oils from the same fruit are totally different in the composition of fatty acid and properties [2]. Light yellowish fatty oil is obtained from the palm kernel oil specifically from crushed nuts of palm. It is composed of fatty acids, esterifies with glycerol. The oil produced from the kernel by extraction process is commonly colourless or pale yellow.

Epoxidation is the reaction in which an oxygen atom is inserted into a compound containing a double bond of unsaturated fatty acids to form a three-membered ring [3]. Thus, there are two carbon atoms and one oxygen atom present in the ring or known as cyclic ether. The product produced from this reaction is known as epoxide. This ring forms in an equilateral triangle, which makes it strain, and therefore very reactive compared to other ethers. Generally, low molecular weight epoxides are colourless, nonpolar and usually volatile. Epoxy ring, which is known as epoxide or oxirane is favorable in plasticizers and polymer stabilizers industries [4,9].

An alepoxidation is commonly carried out by reacting the double bond of fatty acids hydrocarbon chain with peracids, which can be either preformed or formed in situ [5,10]. The reaction of carboxylic acid and hydrogen peroxide formed the peracid. In the epoxidation, carboxylic acid acts as the oxygen carrier while hydrogen peroxide acts as the oxygen donor. The oxygen carrier is responsible in
carrying oxygen from hydrogen peroxide to react with double bond in unsaturated fatty acid carbon chain in order to form epoxide rings. Figure 1 shows the reaction occurred in the epoxidation process.

In this work, the in-situ epoxidation of palm kernel oil was investigated. The effect of different oxygen carrier (formic acid, propionic acid and stearic acid) and reaction temperature (40 ºC, 55 ºC and 60 ºC) on the relative conversion to oxirane (RCO) were discussed.

![Reaction in the Epoxidation Process](image)

**Figure 1.** Reaction in the Epoxidation Process [6].

2. Experimental

2.1. Materials and Chemicals

Crude palm kernel oil was chosen as raw material and was supplied by Chung Chemical Sdn. Bhd. Meanwhile, aqueous hydrogen peroxide (30wt%), formic acid (99%), propionic acid (99%) and stearic acid (99%) were purchased from Merck Sdn. Bhd. In order to find the best oxygen carrier, a constant temperature needs to be set (50ºC). For the Oxirane Oxygen Content (OOC) analysis, titration process has been done according to AOCS Tentative Method CD-57 developed by American Oil Chemist’s Society (1963) by using glacial acetic acid, crystal violet indicator and hydrogen bromide solution that has been purchased from the Merck Sdn. Bhd.

2.2. Epoxidation Process

250 gram of crude palm kernel oil and predetermined amount of of formic acid were weighed and transferred into the 500 mL beaker. Then the beaker was immersed in the water bath that act as insulation to keep the reaction temperature constant. The solution was stir at 300 rpm using motored impeller. The thermometer was placed into the beaker to measure the temperature. Then, 1 mole of hydrogen peroxide was weighed and filled into a burette. The burette is attached to the beaker by clipping on the retort stand. Once the desired temperature (55ºC) was obtained, the hydrogen peroxide was added drop by drop to the solution. Then, the time for the OOC analysis was started and the samples were taken out from the beaker every 5 minutes by using disposable syringe. The solution was put into a small conical flask for titration process. A small amount of sodium sulphate and 10 mL of acetic acid were added into the conical flask to quench the reaction. Then, the mixture was shaken for a few seconds to homogenise them before adding five drops of crystal violet solution. The solution was titrated with hydrogen bromide until the bluish green colour appeared as the end point. The process was waited for about 30 seconds before the reading was recorded. The conversion to oxirane percentage (RCO%) was then calculated by the following equation [7]:

\[
\text{RCO} (%) = \left( \frac{\text{OOC}_{\text{experiment}}}{\text{OOC}_{\text{theoretical}}} \right) \times 100%
\]

where the OOC_{experiment} is calculated by:

\[
\text{OOC}_{\text{experiment}} = \left( T \times N_{\text{HBr}} \times 1.6 \right) / \text{weight sample}
\]

where \( T \) is the volume of titrant used and \( N_{\text{HBr}} = 0.1 \). The OOC_{theoretical} was found to be 0.4768.

2.3. FTIR Analysis

The PKO and epoxidized palm kernel oil (EPO) was characterized by FTIR analysis to observe their functional group. The TGA/SDTA 851 of FTIR machine was used to obtain an infrared spectrum of absorbed emissions. Each sample was scanned from 500 to 4000 cm\(^{-1}\) with resolution of 200 cm\(^{-1}\).
3. Results and Discussions

3.1. Effect of Different Types of Oxygen Carrier
To investigate the most effective oxygen carriers on the epoxidation process, three weak acids with the best capability to ionize were tested. The result is presented in figure 2. The results indicated that the formic acid achieved the highest RCO% of 60.59% within 25 min reaction time. In epoxidation, effective oxygen carrier could be regarded as the one that able to achieve high percentage of RCO within short reaction times.

Propionic acid and stearic acid achieved the highest percentage of RCO of 37.71% and 30.22% at reaction time of 40 min and 30 min, respectively. Lower percentage of RCO was obtained for stearic acid as compared to formic acid was probably due to the stearic acid act as a catalyst by itself to enhance the epoxidation reaction. Performic acid is formed from the reaction of the formic acid with hydrogen peroxide. The performic acid then reacts with the double bonds of the PKO by donating an oxygen atom to form epoxide group. Formic acid has the shortest hydrocarbon chain compared to propionic acid and stearic acid. The longer hydrocarbon chain, the more inductive effect, thus stearic acid will have the least positive charge and formic acid will have the largest positive charge. Because of the inductive effect, least hydrocarbon chain will push fewer electrons towards the carboxylic group, releasing the proton (H+) easier and enhanced the formation of epoxide. Hence, the formic acid appears to be the best oxygen carrier in the epoxidation of palm kernel oil.

![Figure 2](image)

**Figure 2.** Effect of oxygen carrier on the relative conversion to oxirane (RCO%). Reaction conditions: [H₂O₂] = 1 mol, reaction temperature = 55 °C.

3.2. Effect of Reaction Temperature
The effect of reaction temperature on the epoxidation of PKO was investigated by varying the reaction temperature from 45 to 65 °C. The result, as illustrated in figure 3, indicates that as reaction temperature increased from 45 to 55 °C, the maximum RCO increased from 46.18% to 60.59% and decreased to 60.07% as the reaction temperature reached 65°C. The highest RCO of 60.59% was obtained at temperature 55°C. This result is in agreement with the results obtained [4] in the in-situ epoxidation of PKO using sulfuric acid as catalyst. They reported that highest RCO was obtained at 55°C instead of 75°C due to the reversible reaction of performic acid, and hence, shifting the equilibrium to the left in accordance to Le Chateleir Principle. Lower RCO for temperature 60°C could be attributed by the partially hydrolyzed oxirane cleavage, resulting to lower epoxy content. For epoxy ring stability, temperature 65°C was observed to be the most stable since it exhibits the longest
duration (35 min) of peak conversion maintained before degradation of epoxy ring occur. The stability duration for the formation of maximum epoxide ring for temperature 45 °C and 55 °C were 25 and 30 min, respectively.

Figure 3. Effect of reaction temperature on the relative conversion to oxirane (RCO%) Reaction conditions: [H₂O₂] = 1 mol, oxygen carrier = formic acid.

3.3. FTIR Analysis

Figure 4 shows the FTIR spectra of epoxidized palm kernel oil (EPO). The presence of epoxy group can be observed at 2922.12 cm⁻¹ (C-H saturated bond), 1742.74 cm⁻¹ (C=O) and 650.4 cm⁻¹ (epoxy bond). The presence of the epoxide peak confirms the formation of oxirane ring in the EPO.

Figure 4. FTIR spectra of epoxidized palm kernel oil.
4. Conclusions
The best oxygen carrier is the formic acid with the maximum conversion to oxirane (RCO) of 60.59% under optimum temperature of 55 °C. In terms of stability duration of epoxide ring, temperature 65 °C was observed to be most stable since it showed the longest duration (35 min) of peak conversion maintained before degradation of epoxy ring occur. The formation of epoxide from palm kernel oil was confirmed by FTIR analysis which shows the functional groups of epoxide ring at 2922.12 cm⁻¹, 1742.74 cm⁻¹ and 650.4 cm⁻¹.

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