Degradation of catalytic epoxidation of oleic acid palm oil by in situ performic acid

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Abstract. Utilizing renewable resource such as palm oleic acid and convert into epoxide has attracted the interest of many researchers around the world. This paper aimed to study the effects of hydrogen peroxide, formic acid and water on the ring opening of epoxide groups using in situ generated performic acid. The results showed that the cleavage of oxirane rings was the most affected by hydrogen peroxide, followed by formic acid which led to the formation of diol and a-glycol as side products. The FTIR results indicated that the absorption band of hydroxyl group (O-H) was observed at 3100–3600 cm⁻¹ in placement of the epoxy ring group (C-O-C) at 1210 – 1250 cm⁻¹. It is imperative to minimize process losses via ring-opening in order to achieve good yields and high peroxide values of the epoxidized vegetable oil.

1. Introduction
Even though vegetable oils are mostly used for food production, these oils are attractive feedstock for synthesis of materials because they are renewable, biodegradable, non-toxic, and can be easily modified by various chemical reactions [1]. Because these oils can be mass produced, they have the potential to replace certain petrochemical products. The production of vegetable oils has been increasing steadily over the past several years, culminating in 2016, where ~179 million metric tonnes of oil were produced [2]. Soybean, canola, and palm oils account for ~80% of the vegetable oils produced and therefore, these oils are typically used to create renewable materials [3]. The epoxidation using vegetable oil due to the high content of unsaturated fatty acids, that attainable to functionalize its double bonds by transforming them into more reactive oxirane rings [4]. Plus, the cleavage of one of the carbon-oxygen bonds makes the ring opening reaction happened. By using both nucleophiles or electrophiles, the catalyzed through either acids or bases, the reaction can happen. Then, the protonation using solid acid catalyst can be promoted which it happened during the addition of nucleophilic of a carboxyl group to the center of epoxide. In addition, the rate of the oxirane ring opening from the epoxidized fatty acids emphatically depends on the nature and structure of carboxylic acid [5]. This is due to acid catalyst contributes in epoxide ring-opening by providing a better leaving group (an alcohol) at the carbon for undergoing the nucleophilic attack.
This is often happened once the oxirane ring cleavage was occurred in some critical condition to produce side product [6]. The epoxidation of vegetable oils have been used as a compounds of chemical intermediates, it is far possible to synthesize environmental-friendly lubricants but also plasticizers and stabilizers for polymers [1]. At the same time, degradation can occur during the epoxidation process [7]. Generally, epoxide is very reactive. Due to its molecular compound, which are composed of three-atom ring, and approximates an equilateral triangle, makes it strained and hence very reactive. Therefore, when the epoxide is reactive, it can undergo to degradation process. Ring opening or named as degradation of oxiranes, happened through the cleavage of one of the carbon and oxygen bonds [8]. Thus, this finding provided additional insight into developing the possible degradation of epoxidized oleic acid for future references.

2. Materials and Methods

2.1 Materials

Oleic acid-based palm oil in this study was obtained from Quality Reagent Chemical (QReC)-Rech in its raw material. Formic acid (85%), hydrogen peroxide (30-32%) and sulphuric acid (2 M) were also obtained from QReC.

2.2 Analytical Procedures

Crude oleic acid was epoxidized until it reached the highest conversion to epoxide. Without delaying, the FA was settled, the aqueous phase was discarded and the oil phases washed with distilled water to remove any excess formic acid and performic acid. Consequently, water and hydrogen peroxide were removed using rotary evaporator. Every 5 minutes, the sample was retrieved to determine the oxirane oxygen content according to AOCS Tentative Method Cd 9-57 [9], as in equation (1):

\[ \text{OOC}_{\text{exp}}(\%) = 1.6 \times \frac{(V-B)}{W} \]  

where \( V-B \) is denoted as the volume of hydrogen bromide in mL that is needed to titrate the sample, \( N_{\text{HBR}} \) is the molarity of the hydrogen bromide which is 3.56 and \( W \) is the weight of the sample which is 5 grams. Equations 2 and 3 are used to calculate the relative percentage conversion to oxirane (RCO).

\[ \text{RCO} = \frac{\text{OOC}_{\text{exp}}}{\text{OOC}_{\text{the}}} \times 100\% \]  

\[ \text{OOC}_{\text{the}} = \left( \frac{\text{IV} / 2 A_{o}}{100 + \left( \frac{\text{IV} / 2 A_{i}}{A_{o}} \right)} \right) A_{o} \times 100 \]  

where \( \text{OOC}_{\text{the}} \) is the theoretical maximum oxirane oxygen and was determined to be 1.8213. Meanwhile, IV\(_{0}\) is the initial iodine value of WCO sample which is 74.69, \( A_{o} \) (16.0) and \( A_{i} \) (126.9) are the atomic masses of oxygen and iodine, respectively. The effect of reaction time and molar ratio of formic acid and hydrogen peroxide were studied toward relative conversion to oxirane (RCO%).

3. Result and Discussion

3.1 Degradation of epoxide by formic acid

This ring opening reaction has been investigated extensively and various studies have reported on the kinetics of ring opening reaction [10]. The ring opening reaction is associated with the presence of hydrogen peroxide and formic acid at certain reaction temperature [11]. To overcome this hindrance which is side reaction of epoxide with formic acid and hydrogen peroxide, some researchers have tried organic solvents such as benzene and toluene [12]. The effect of reaction time on ratio on conversion of double bond to oxirane ring was investigated by conducting three
different ratios (60:40, 70:30, 80:20). High concentration of formic acid caused the epoxy group to be unstable and hence easier to be degraded. As shown in Figure 1 the Relative Conversion to Oxirane (RCO) percentage keeps decreasing after 25 minutes.

| Ratio (EpOA: FA) | Oxirane value | Relative conversion to oxirane (RCO%) after 45 minutes |
|------------------|---------------|------------------------------------------------------|
| 1) 60 : 40       | 0.4583        | 24.52                                                |
| 2) 70 : 30       | 0.3987        | 21.33                                                |
| 3) 80 : 20       | 0.4557        | 24.38                                                |

Table 1. RCO% after 45 minutes

Epoxy ring opening with formic acid was used as comparison reagents because it is one of the most co-product during epoxidation processes. For this study, three mole ratio of epoxidized oleic acid and formic acid were selected to examine the effect of formic acid to epoxy ring opening as tabulated in Table 1. From Figure 1, it is clearly shown that at the beginning, reaction rate significantly decreased before reaching 45 minutes where similar pattern of reaction rate and RCO percentage are achieved. This is because formic acid started to deactivate and completely reacted with epoxidized oleic acid to form diol and a-glycol [8]. This is consistent with the work by Cai et al. [13] that found that the kinetics study of ring opening of cottonseed oil production was due to the effect of acetic acid concentration. Meanwhile, the increased of formic acid concentration leads to increase performic acid production, that can open the epoxide group, the catalytic effect of formic acid on the hydrolysis and ring opening and nucleophile activity of formic acid toward ring opening reaction was several factors in rate enhancement with the formic acid.

Figure 1. Formic acid influence on degradation of epoxidized oleic acid (EpOA:FA)

FTIR spectra of the epoxidized oleic acid and ring opening by formic acid are presented in Figure 2. In comparison with the spectrum of epoxidized palm oil (EpOA), the disappearance of epoxy group at 1210 – 1250 epoxy show that the ring opening of epoxy ring has occurred as shown in Equation 4z. Meanwhile, the appearance of the broad OH band and 3500 cm⁻¹ is slightly occurring. Other than that, the formation peak of OCHO also was observed 1350-1400 cm⁻¹. It can be concluded that, reaction of formic acid less reactive due to small changer of peak between EpOA and formic acid (FA).
Degradation of epoxide by hydrogen peroxide

Epoxidation has been one of the most commonly used methods for the functionalization of carbon double bonds [14].

| Ratio (EpOA : H2O2) | Oxirane value | Relative conversion to oxirane (RCO%) after 45 minute |
|---------------------|---------------|-----------------------------------------------------|
| 60 : 40             | 0.2741        | 14.66                                               |
| 70 : 30             | 0.2278        | 12.19                                               |
| 80 : 20             | 0.3581        | 19.15                                               |

Contradictory to that of formic acid, ring opening by hydrogen peroxide (H2O2) is less stable and did not show the constant value RCO percentage at 45 minutes as shown in Table 2. However, average RCO percentage value was also 5% less as compared to epoxidized oleic acid attack by formic acid. This is due to hydrogen peroxide being very active and can cause high tendency to react. Other than that, formic acid also acts as a catalyst rather than as oxygen carrier. As shown in this Figure 3, the rate of hydrogen peroxide concentration with the ring opening slightly increased. Hydrogen peroxide could dissociate to produce proton as shown in Equation 5.

\[
H_2O_2 \leftrightarrow H^+ + H_2O
\]  

thus the enchainment of reaction rate with hydrogen peroxide cannot be linked to the acidity of hydrogen peroxide but maybe on its nucleophile activity instead.

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Figure 2. FTIR spectrum degradation by FA

Figure 3. Hydrogen peroxide influence on degradation of epoxidized oleic acid (EpOA:H2O2)
Epoxy ring-opening also known as epoxide cleavage or epoxide ring degradation occurs in the epoxidation of vegetable oils. It is imperative to minimize process losses via ring-opening in order to achieve good yields and high peroxide values of the epoxidized vegetable oil. The oxirane rings are highly reactive and susceptible to opening, especially in the presence of acidic conditions due to the fact that the epoxides act as intermediates for synthesis of other chemicals. The cleavage of oxirane rings is most pronounced in the presence of sulphuric acid, followed by formic acid, acetic acid and propionic acid. Acidic conditions promote ring-opening by protonation of the epoxide’s oxygen atoms, which consequently react with different types of nucleophilic reagents via back side attack in order to give anti-orientation type products [15]. Since the epoxidized oil is in cis configuration, its ring-opening products are in trans configuration.

\[
R-\text{CH-CH-R} + \text{H}_2\text{O}_2 \rightarrow R-\text{CH-CH-R} \quad \text{(6)}
\]

The formation of ring opening by hydrogen peroxide was confirmed by FTIR spectrum and illustrated in Figure 4. The band at epoxy group (C-O-C) clear disappeared at 1210 – 1250 cm\(^{-1}\) and formed new functional group OOH at wavenumber 1700 –1750 cm\(^{-1}\). In addition, a new band at 3100-3700 cm\(^{-1}\) was attributed to OH bond after hydrogen was added into EpOA. It suggested that hydrogen peroxide totally reacted with EpOA and side product was produced.

3.3 Hydrolysis of epoxidized oleic acid

By hydrolysis reaction of epoxidized palm olein, a high-value hydroxyl fatty acid called dihydroxystearic acid (DHSA) is produced. DHSA (C\(_{18}\)H\(_{36}\)O\(_4\)) is also known as glycolic stearic acid that contains two alcohol groups and is a carboxylic group in a long hydrocarbon chain [16]. DHSA is derived from in situ epoxidation of the unsaturated fat in the palm oil with peracetic acid in the presence of catalyst followed with hydrolysis of the epoxide with hydrogen donor such as water. DHSA has been used widely in industry nowadays - as primary and secondary emulsifiers, pigments coating agents, and oil gelling agent in cosmetic formulation [17]. DHSA is produced by reacting the epoxidized palm olein with water in the presence of catalyst. This reaction is called hydrolysis reaction where oxirane ring opening of the epoxidized palm olein is done to produce crystal-like solid DHSA. The reaction equation for synthesis of DHSA is as shown in Equation 7.

[Figure 4. FTIR Spectrum degradation by H\(_2\)O\(_2\)]
Figure 5. FTIR Spectrum degradation by H₂O

Figure 5 depicts the FTIR spectrum of the DHSA produce from palm oil oleic acid. After hydrolysis, the absorption band region of 1210 – 1250 cm⁻¹ corresponding to the C=O-C stretching. This indicates that the epoxy ring epoxidized oleic acid compound was cleaved by water to produce secondary hydroxyl compound O-H to from DHSA. The hydroxyl group confirmed the formation of DHSA was observed at the region of 3600-3200 cm⁻¹. The abroad and clear peak show that dwi-hydroxyl group are present after hydrolysis. Besides, plate 1 showed the various changes of epoxidized oleic acid after reacted with all the possible agents/reactants. Clearly show that epoxidized appear as white and waxy materials after ring opening with slurry semi sold form by H₂O₂ and H₂O, meanwhile ring opening of epoxy from FA quit similar with epoxy itself. This is can be concluded that the reaction of epoxy more reactive with H₂O₂ and H₂O that can be valid by FTIR result.

Plate 1. a) Ring opening of epoxy attack by FA  b) Ring opening of epoxy attack by H₂O₂  c) Ring opening of epoxy attack by H₂O

4. Conclusions
The traits of vegetable oil, such as cost-effectiveness and eco-friendly to environment, makes them as an alternative for the production of epoxide. The present formic acid and hydrogen peroxide can cause ring opening of epoxide. From the study, the effect of formic acid toward degradation less active compare to hydrogen peroxide since formic acid less reactive. Furthermore, deeper study is
required to obtain more on oxirane ring degradation reactions, to obtain the correct predictions to fit with the experimental data.

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