Pseudo-homogeneous Kinetic Evaluation for in-situ Epoxidation of Oleic Acid

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Abstract. Epoxidation of unsaturated fatty materials is useful route to synthesize valuable material especially bio-based polymers. Oleic acid (OA, iodine value of 90 gram I₂/100 gram) is the most common unsaturated fatty material that can be found in vegetable oils or animal fats. Epoxidation of oleic acid with peracetic acid generated in-situ has been performed in batch system. Kinetic evaluation was conducted by varying the reaction temperature from 40 to 70 °C under constant value of stirring speed, H₂O₂:OA molar ratio, acetic acid:OA molar ratio, and catalyst concentration. Double bond conversion, oxirane yield, and selectivity of oxirane has been evaluated. The result shows that the degree of side reaction (ie: ring opening) is high in temperature of 60 and 70 °C. Pseudo-homogeneous kinetic model is well fitted in 40 and 50 °C but it gives significant deviation in 60 and 70 °C. The activation energy of oleic acid epoxidation has been found to be 62.2 kJ/mol.

1. Introduction
Epoxidation is process for producing epoxides from olefinic materials. Epoxides have cyclic carbon-oxygen bonds that has been known to be highly reactive and make them suitable to be used as valuable intermediate products. For example, ethylene oxide, as the simplest form of epoxides, can undergo several reactions to produce ethylene glycol, glycol ether, and polymers [1]. Epoxides derived from long chain olefins such as unsaturated fatty materials, provide greener alternatives than shorter chain olefins that usually are petroleum based. Unsaturated fatty materials can be varied from vegetable oil triglyceride, fatty acids, or fatty esters. Among the various number of epoxidized fatty materials, epoxidized soy bean oil has been commercialized as plasticiser and stabiliser for poly(vinyl) chloride (PVC) [2]. Due to inherent reactivity of epoxides group, several types of bio-based polymers, such as polyurethane, polyol, polyether, and polyester, have been synthesized from epoxidized fatty materials [3-6].

Oleic acid is a monounsaturated fatty acid and the most abundant unsaturated fatty materials found in nature. Epoxidation of oleic acid and other unsaturated fatty materials was first investigated in 1945 using preformed peracetic acid [7]. Eleven years later, in 1956, Greenspan and Gall patented their invention on oleic acid epoxidation using in-situ method where the performic acid was generated simultaneously with the epoxidation reaction in the same reaction system [8]. Instead of peroxides,
The kinetic model of epoxidation reaction in general depends on the epoxidation methods and reaction mechanism. Although many methods have been developed, in-situ epoxidation is believed to be the most efficient way to produce epoxides from unsaturated fatty materials [14]. In the typical in-situ epoxidation, the double bonds of fatty materials are reacted with peracetic acid (PAA) or performic acid (PFA). PAA or PFA is generated by reacting $\text{H}_2\text{O}_2$ with acetic acid or formic acid, with or without catalyst [15]. Therefore, the reaction system is in liquid-liquid phase or in liquid-liquid-solid phase if solid catalyst is used. These systems can be approached by pseudo-homogeneous or heterogeneous kinetic model. Pseudo-homogeneous approach is the simplest form and was developed by Gan et al., [16] on the epoxidation of palm olein methyl esters. The main assumption used in this model is that the oil phase is well disperse due to controllable mixing. More advanced kinetic model on the similar approach was also developed by de Haro et al. on the epoxidation of grape seed oil [17]. Meanwhile, the heterogeneous kinetic model was gained attention and can be categorized into two schemes: (a) heterogeneous liquid-liquid kinetic model [18], and (b) heterogeneous liquid-solid kinetic model [19]. The specific kinetic study of oleic acid epoxidation was early published in 1970 using acetic acid as oxygen carrier [20]. More complicated kinetic model that taken into account the thermal and kinetic parameters was proposed by Leveneur et al. [21]. The latest work on the development of kinetic model of oleic acid epoxidation was proposed by Aguilera et al. which also adopt the heterogeneous approach to compare the conventional and microwave heating quantitatively [22]. The aim of this paper is to evaluate pseudo-homogeneous kinetic model as the simplest model to be applied in the in-situ epoxidation of oleic acid.

2. Materials and Methods

2.1. Materials

Oleic acid technical grade (90 wt%) was purchased from Sigma-Aldrich. Iodine value of oleic acid was found to be 90 gram I$_2$ / 100 gram (Wijs method). Glacial acetic acid (99 wt%), hydrogen peroxide (30 wt%), and sulfuric acid (98 wt%) were purchased from Merck. Reagents for analysis such as sodium thiosulfate, Wijs solution, potassium iodide, hydrogen bromide, soluble starch, crystal violet indicator, etc., were also purchased from Merck and use directly without further purification.

2.2. Epoxidation reaction

The reaction was conducted in three neck flat bottomed flask equipped with magnetic stirrer, reflux system, sampling system, and thermometer. The flask was immersed in water bath under constant temperature (± 1 °C). Oleic acid was poured into the flask, followed by certain amount of glacial acetic acid and sulfuric acid. The reaction mixture was heated at fixed reaction temperature. Simultaneously with the heating process, hydrogen peroxide at certain amount was slowly added over 20 minutes. The molar ratio of oleic acid (OA):acetic acid (AA):hydrogen peroxide (HP) was 1:0.5:1.2 and sulfuric acid acid concentration was 1.5% based on total weight of AA and HP. Reaction time was assumed to be zero when the addition of hydrogen peroxide was finished. As the reaction proceed, small amount of sample was taken periodically and was then washed with water until acid free. The trace of water was completely removed with centrifugation.
2.3. Analytical procedure
The purified sample was analysed for iodine and oxirane number. Iodine value was determined using Wijs Methods and oxirane number was determined using direct titration by hydrogen bromide in acetic acid solutions [23].

3. Results and Discussion
3.1. Effect of temperatures
Oleic acid has a single cis carbon-carbon double bond between C9 and C10. This double bond was reacted with PAA and resulting epoxidized oleic acid. PAA was generated in-situ from the reaction between H₂O₂ dan acetic acid catalysed by sulfuric acid. In order to evaluate the kinetic model, the effect of temperature on the reaction progress was conducted at four different temperature of 40, 50, 60, and 70 °C. Typical temperature range for epoxidation of fatty materials is usually between 20-85 °C. Based on the previous investigation, at the temperature range 20-30 °C, the reaction rate was very low, and at the temperature above 75 °C, the selectivity was poor. Therefore, the temperature range of 40-70 was chosen to be studied. The reaction progress is represented by the increase of oxirane number and the decrease of iodine number for given time interval. Iodine number not only gives the exact quantity of double bond in the sample but also indicate how much oleic acid has been reacted with peracetic acid. However, quantitative data of iodine number is insufficient without the information of oxirane number at the same data point. Oxirane number shows the exact value of desired product i.e. epoxides. The correlation between iodine number and oxirane number does not always have the same trend as can be seen in Figure 1(a) and Figure 1(b).

![Figure 1](image)

**Figure 1.** Effect of temperature on iodine number (a) and oxirane number (b) for in-situ epoxidation of oleic acid.

Figure 1(a) shows that the rate of disappearance of double bonds at 40 °C is observed to be the slowest rate and final iodine number of 69 gram I₂/100 gram was achieved. This rate is constantly increase with temperature. The lowest iodine number was obtained in the end of reaction at temperature of 70 °C with the final iodine number of 7 gram I₂/100 gram, in other word, iodine value conversion was found to be 92%. The rate of formation of epoxide, however, shows the similar trend only at the reaction temperature of 40 and 50 °C as can be found in Figure 1(b). There is a decrease of oxirane number in the final point at temperature of 60 °C. This tendency was likely to be worsen at 70 °C for which the oxirane number was decrease significantly and nearly reach zero in the last two points. This is probably caused by series of side reactions i.e. oxirane cleavage or ring opening of epoxide, that are favourable at high reaction temperature. There are several possibilities of side reactions, but dominantly, epoxides were first protonated and then reacted with H₂O and acetic acid to form glycolic compounds [2]. As the reaction proceed, double bond was always consumed (iodine number was constantly decrease) and
produced epoxides. However, when side reactions occur, epoxide was then reacted with another species to form side products. These not only reduced the epoxides present in the sample, but also resulted in lower yield and selectivity. The calculated value of final selectivity at the temperature of 40, 50, 60, and 70 °C were 89, 79, 57, and 1%, respectively. It indicated that side reaction was also occur at low temperature but proceed slowly so that the value of oxirane number was still increase with reaction time. From these results, the optimum reaction temperature was considered to be 50-60 °C.

3.2. Kinetic evaluation

In-situ epoxidation is a consecutive reaction. The first step is formation of peracetic acid as a result from the reaction between acetic acid and H₂O₂ catalysed by H₂SO₄. The second step is reaction between peracetic acid and double bond in oleic acid to form epoxided oleic acid. The first step occurs in the aqueous phase, while the second step in organic phase. In order to be reacted with oleic acid, peracetic acid is transferred from aqueous to organic phase. Due to rapid mixing, mass transfer or peracetic acid is assumed to be very fast so that mass transfer limitation can be minimized and the system can be treated as pseudo homogeneous. The reaction mechanism can be written as follows:

\[
\text{CH}_3\text{COOH} + \text{H}_2\text{O}_2 \rightleftharpoons \text{CH}_3\text{COOOH}
\]

\[
\text{CH}_3\text{COOOH} + -\text{C}=\text{C} \rightarrow -\text{C}^\cdot\text{C}^\cdot + \text{CH}_3\text{COOH}
\]

When the first step is assumed to be the rate limiting step and peracetic acid concentration remain constant during the reaction, rate equation can be expressed as follows [16]:
\[
\frac{d[\text{EP}]}{dt} = k_1 ([\text{H}_2\text{O}_2]_0 - [\text{EP}]) ([\text{CH}_3\text{COOH}]_0
\]

Equation (1) can be integrated and yields the following equation:
\[
\ln ([\text{H}_2\text{O}_2]_0 - [\text{EP}]) = k_1 ([\text{CH}_3\text{COOH}]_0 t + \ln [\text{H}_2\text{O}_2]_0
\]

These equations were derived with assumption that all double bond will be convert to epoxide without the occurrence of side reactions. When this assumption is fulfilled, plot of \(\ln ([\text{H}_2\text{O}_2]_0 - [\text{EP}])\) vs time (t) resulted from Equation (2) should yields a straight line with \(-k_1[\text{CH}_3\text{COOH}]_0\) as the slope and \(\ln [\text{H}_2\text{O}_2]_0\) as the intercept. Any deviation from linearity suggest that there is a significant extent of ring opening. The plot between \(\ln ([\text{H}_2\text{O}_2]_0 - [\text{EP}])\) vs time (t) at different reaction temperature for in-situ epoxidation of oleic acid can be seen in Figure 2(a). The pseudo homogeneous kinetic model is observed to be well fitted at 40 °C, slightly deviate at 50 °C, and considerably high deviation is observed at 60 and 70 °C. In the case of high deviation, initial slope was used. The calculated reaction rate constants were \(9.78 \times 10^6\), \(3.21 \times 10^5\), \(6.12 \times 10^5\), and \(9.17 \times 10^5\) kg mol\(^{-1}\)s\(^{-1}\) for reaction temperature of 40, 50, 60, and 70 °C, respectively. The values of reaction rate constant were expressed in the unit of kg mol\(^{-1}\)s\(^{-1}\) instead of L mol\(^{-1}\)s\(^{-1}\) because mass is remains in the same value throughout the reaction, not depends on the reaction temperature.

Activation energy (Eₐ) for epoxidation of oleic acid was obtained from the slope of Arrhenius plot (Figure 2(b)) and found to be 62.2 kJ/mol (14.9 kcal/mol). This value is comparable with the previous investigation using the same kinetic model and the same type of peracid i.e. peracetic acid but different raw materials. The values obtained from literature are tabulated in Table 1. Most of raw material used in previous investigation are triglyceride oil, except palm olein methyl esters. Activation energy obtained from this work is similar with the activation energy obtained by Gan and co-workers [16] probably because the similarity of raw material (fatty acid vs fatty esters). However, value of activation energy from various oils are considered to be independent from its initial iodine value.
Figure 2. (a) Plot of $\ln ([H_2O_2]_0 - [EP])$ vs time at different reaction temperature; (b) Arrhenius plot of $\ln k_1$ vs $1/T$ for in-situ epoxidation of oleic acid

Table 1. Comparison of activation energy

| Raw material                  | IV$_0$ (g I$_2$/100 g) | T ($^\circ$C) | Ea (kcal/mol) | Ref. |
|-------------------------------|-------------------------|---------------|---------------|------|
| Palm olein methyl ester       | 60                      | 20-60         | 14.8          | [16] |
| Rubber seed oil              | 156                     | 30-70         | 15.7          | [24] |
| Mahua oil                    | 88                      | 30-85         | 14.5          | [25] |
| Cottonseed oil               | 105                     | 30-75         | 11.7          | [26] |
| Jatropha oil                 | 104                     | 30-85         | 14.1          | [27] |
| Nahor oil                    | 91                      | 30-70         | 12.4          | [2]  |

4. Conclusions
Epoxidized oleic acid was obtain from oleic acid through in-situ epoxidation and kinetic evaluation was performed. The effect of reaction temperature on reaction progress was monitored from iodine number and oxirane number of samples. Iodine number decreased linearly with temperature, but oxirane number increase in the same trend only at low temperature. At temperature of 60 and 70 $^\circ$C, there was a peak observed in oxirane number at certain reaction time, and after that, oxirane number start to decrease. Pseudo homogeneous kinetic model was used to evaluate the data. The results show good linearity at 40 $^\circ$C and deviation from linearity was observed to be increase with temperature. The reaction rate constants were observed in the range of 9.78-9.17×10$^{-5}$ kg mol$^{-1}$ s$^{-1}$ and activation energy was found to be 62.2 kJ/mol (14.9 kcal/mol). These values are comparable with the previous investigation on the same kinetic model.

Nomenclature
- $[EP]$ : epoxide concentration, mol kg$^{-1}$
- $[H_2O_2]_0$ : initial molar concentration of $H_2O_2$, mol kg$^{-1}$
- $[CH3COOH]_0$ : initial molar concentration of acetic acid, mol kg$^{-1}$
- $Ea$ : activation energy, kcal/mol
- $k_1$ : reaction rate constant, kg mol$^{-1}$s$^{-1}$
- $T$ : temperature, K
- $t$ : time, s
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