Kinetic study of epoxidation of Tung oil (*Reutealis trisperma* (Blanco) Airy Shaw) by peroxyacetic acid

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Abstract. The use of vegetable oils (VOs) to replace petroleum derivatives is very interesting. This is due to the advantages of VOs, which are relatively biodegradable and renewable. The VOs containing high unsaturated fatty acid, such as Tung oil, soybean oil, rubber oil are very potential materials for biopolymers, which can be reacted further into epoxy, polyols, and even polymers. The kinetic of epoxidation of Tung oil by peroxyacetic acid produced in-situ process was studied. In this study, the formation of peroxyacetic acid was considered as rate determining step, which controlled the overall reaction rate. The process was conducted in batch reaction at atmospheric pressure, constant mixing rate and constant ratio of raw material to acetic acid. The temperature was varied at 40, 50, 60, and 70°C. The reaction samples were taken at specific time during 2-4 hours of reaction. The result shows that the proposed simple kinetics model fits appropriately at lower reaction temperature, but does not agree at higher temperature (more than 60°C). The reaction rate constants is in the range of (3.307–9.634) x 10^-6 L.mol^-1.s^-1, in which its collision factor and activation energy are 286,768 gram.mol^-1.min^-1 and 30,900 Joule/mol, respectively.

1. Introduction

The fossil resource, which is not renewable, has been decreasing steadily, due to the extensive use in the petrochemical industry. On the other hand, relentless effort to find natural resources is undergoing, in order to replace these non-renewable fossil resources. Alternative resources should have multiple criteria: renewable, relatively inexpensive, easily accessible, manufactured in large and virtually unlimited [1,2]. The vegetable oils (VOs) are one alternative resource, because they fulfill such criteria. Furthermore, they can be obtained from various plants. VOs can be used to produce soap, in the food industry, and also as bio-lubricants [3]. VOs are converted into bio-diesel through transesterification and green-diesel. In 2018, the world vegetable oil production was 197.23 million tons / year [4]. Tung (*Reutealis trisperma* (Blanco) Airy Shaw) plant is a one of the vegetable oils producing plants in Southeast Asia. The productivity of Tung oil plants can reach 12 tons/hectare/year. This is higher than Jatropha curcas, which only reaches 10 tons/hectare/year [5].

Recently, the production of epoxy from vegetable oils has been developed. Epoxidation can be implemented for alkene, cycloalkene, unsaturated fatty acids, unsaturated esters, unsaturated alcohols, and unsaturated ketones [6]. VOs containing high unsaturated fatty acid, such as Tung oil, soybean oil, rubber oil has potential reactive sites; such as double bonds and carboxylic functional groups in fatty
acids, which can be converted further into epoxy, polyols, and even polymers. The epoxidation of VO$s$ is relatively more complex when compared to the epoxidation of unsaturated fatty acid esters. There are several methods that can be used for epoxidation of vegetable oils and fatty acid esters, namely the peracid $in-situ$ epoxidation [7-15], heterogeneous epoxidation (epoxidation method with solid catalyst) [16-21], enzymatic epoxidation [22-26], epoxidation using ionic liquids (ILs) [27,28], and the supercritical CO$_2$ epoxidation [29,30].

Some types of organic peroxycarids that can be used in the epoxidation of VO$s$, including peroxyacetic acid, peroxyformic acid, peroxyflouroacetic acid, peroxybenzoic acid, and others [31]. Among these peroxycarids, peroxyacetic acid is the most often used due to its easy availability, relatively low price, and reasonable stability at ordinary temperatures. In addition, peroxyacetic acid also has high efficiency, and can be produced in water, non-water, homogeneous and heterogeneous [16]. The use of peroxyacid to epoxide the VO$s$ was established in 1940’s. Generally, the method can be divided into two ways, with preformed peroxo acid and with $in-situ$ formed peroxo acid. For preformed peroxo acid, peroxyacetic acid is made first by reacting hydrogen peroxide with acetic acid. However, this method has a poor security level because explosive mixture can be formed, then when the second heating occurs the concentrated active oxygen of the material can explode. Whereas in the $in-situ$ process, peroxyacetic acid is made simultaneously with an epoxidation in the catalyst [31,32]. The $in-situ$ process is more often used on an industrial scale because the process is relatively safer and can save the acid and hydrogen peroxides usage [16].

The ability of some commercially inorganic acids (such as H$_2$SO$_4$, H$_3$PO$_4$, HNO$_3$, and HCl) as catalysts was investigated under the similar and controlled conditions. In the certain and short reaction time, the oxirane conversion obtained from the epoxidation by using HCl and HNO$_3$ catalysts was noticeably smaller than those gained with H$_2$SO$_4$ and H$_3$PO$_4$ as catalysts. Using H$_3$PO$_4$ as a catalyst, the oxirane value increased monotonically within the experimental time limit. It was discovered that the sequence of catalyst effectiveness for reaction based on mineral acids were H$_2$SO$_4$ > H$_3$PO$_4$ > HNO$_3$ > HCl [33].

Although some studies of process and kinetics of epoxidation of VO$s$ were carried out, there is lack information about epoxidation of Tung oil ($Reutealis trisperma$ (Blanco) Airy Shaw). The main purpose of this paper is to study the effect of reaction temperature on the epoxidation of Tung oil by peroxyacetic acid and sulphuric acid as catalyst. A further objective of this work is to propose a simple mathematical model for the reaction system and an estimation of the unknown kinetic parameters of the proposed model.

2. Material and method

2.1. Materials

Glacial acetic acid 99%, hydrogen peroxide 30 wt%, hydrobromic acid in acetic acid 47 wt%, potassium hydrogen phthalate, crystal violet, sulfuric acid 98 wt%, Wij$s$ solution, sodium thiosulfate, kalium iodide were obtained from Merck. Tung oil ($Reutealis trisperma$ (Blanco) Airy Shaw) was purchased from farmer in Majalengka and Sulawesi, Indonesia.

2.2. Epoxidation process

A mixture of fatty acid of Tung oil (50 grams), acetic acid and sulfuric acid catalyst (H$_2$SO$_4$) were poured into a three-neck flask (volume of 250 mL), which was equipped with a bath, thermometer, magnetic stirrer, and condenser. The mixture was heated and stirred at constant stirring speed (around 500 rpm). The reaction was conducted at temperature 40-70°C and atmospheric pressure. After the desired temperature was reached, hydrogen peroxide was discharged drop by drop into the flask. The process was carried out for 2-4 hours, where samples were taken during the reaction time at particular time. The sample was cooled to room temperature, then was decanted to separate epoxidized Tung oil from the water phase (the epoxy product was located in the upper layer). The epoxy product was then washed with distilled water to remove the impurities, and was analyzed to determine its oxirane number and iodine value.
2.3. The composition of reactant

The mol ratio of fatty acids: acetic acid was 2:1. Molecular weight of fatty acids was determined from the iodine value (IV). The mol of hydrogen peroxide was 1.2 times of the fatty acids mol. The amount of used catalyst was 1.5% of the total weight of acetic acid and hydrogen peroxide.

2.4. Analysis method

Iodine value was determined by Wijs method, and the oxirane number was determined by using hydrobromic acid solution in glacial acetic acid.

3. Result and discussion

In the previous study [5], the Tung seed oil fatty acids composition was determined, and the results was 50% of α-oleostearic, 21% of linoleic, 10-12% of oleic, 8.32-10% of palmitic, 4.7 – 9.0 % of behenic, 3.73% of stearic, 1.28 % of palmitoleic, and 0.01% of myristic (in %wt). In this research, the fatty acid produced by hydrolysis of Tung oil (from Majalengka and Sulawesi) has IV of 99.63 and its calculated molecular weight is around 254.94 g/mol.

3.1. Effect of reaction temperature

Effect of reaction temperature on the reaction rate of epoxidation was studied at reaction temperatures of 40, 50, 60, and 70°C. It is clear that increasing temperature causes the reaction rate rise. The experimental results are shown in Fig. 1 (oxirane number) and Fig. 2 (Iodine number IV). At low reaction temperature, 40° and 50°C, within the reaction time up to 240 minutes, the oxirane number increases slowly and steadily with reaction time, without any declination. On the other hand, at high reaction temperature (60°C and above), the oxirane number rises up to a maximum value at some time, then decreases during the remain reaction time. The decrease is quite strong at temperature of 70°C. The unsaturated bond C=C in fatty acids is expressed in the iodine value (IV). Fig. 2 shows that the IV continuously declines with reaction time for all temperature variation. However, at 70°C reaction time, the IV decline was relatively faster at the beginning compared to the end of the reaction. Based on the results shown in Fig. 1 and Fig. 2, reaction at lower temperatures results in a lower rate but gives a more stable oxirane ring. This suggests that the optimal epoxidation reaction can be acquired at shorter period of time at reaction temperature range of 50 – 60°C, where side reaction can be ignored.

![Graph 1: Oxirane number as a function of temperature (T) and reaction time (t)](image1)

![Graph 2: Iodine value (IV) as a function of temperature (T) and reaction time (t)](image2)

Epoxidation of Tung oil required a strong oxidator to break the double bond in the unsaturated fatty acids into the oxirane group. With some considerations, hydrogen peroxide (H₂O₂) is the most commonly used in the epoxidation. However, the nature of H₂O₂ is not the strong oxidator, so it should be transformed into another more active form such as peroxyacid. Acetic acid reacted with hydrogen peroxide by using sulphuric acid as a catalyst to form peroxyacetic acid. The reaction takes place in reversible and exothermic. Subsequently, peroxyacetic acid reacts with the unsaturated fatty acid (UFA) of Tung oil forming epoxy.
3.2. Epoxidation kinetics

The mechanism of epoxidation of Tung oil by peroxyacetic acid. It is assumed that the reaction is pseudo homogeneous (one phase), through two steps; 1) formation of peroxyacetic acid (PAA) by reacting acetic acid (AA) with hydrogen peroxide (HP) generated in-situ process and 2) reaction of double bond or unsaturated fatty acid (UFA) by peroxyacetic acid [32]. The first step is proposed as reversible reaction, and the second one is irreversible. Further assumption is that there is no side reaction and also the advanced reaction of oxirane ring cleavage.

\[
\begin{align*}
\text{CH}_3\text{COOH} + \text{H}_2\text{O}_2 & \underset{k_1}{\overset{}{\rightleftharpoons}} \text{CH}_3\text{COOOH} + \text{H}_2\text{O} \\
\text{PAA} & \quad \text{W} \\
\text{CH}_3\text{COOOH} + >\text{C}==\text{C}< & \rightarrow >\text{C}---\text{C}< + \text{CH}_3\text{COOH} \\
\text{PAA} & \quad \text{UFA} \\
\text{EP} & \quad \text{AA}
\end{align*}
\]

In this study, the first reaction was considered as rate determining step, which controlled the overall reaction rate. If the concentration of peroxyacetic acid was essentially constant during the reaction process, the rate of reaction can be written by following equations:

\[
\begin{align*}
\frac{d[\text{EP}]}{dt} &= k_1 ([\text{HP}]_0 - [\text{EP}]) [\text{AA}]_0 \\
\ln([\text{HP}]_0 - [\text{EP}]) &= k_1 [\text{AA}]_0 t - \ln[\text{HP}]_0
\end{align*}
\]

Where, subscript 0 signifies the initial concentrations. The reaction rate constant \( k_1 \) can be easily determined by plotting \( \ln([\text{HP}]_0 - [\text{EP}]) \) vs reaction time \( t \), which gives linear line with the slope \( k_1[\text{AA}]_0 \). Fig. 3 presents the plot of \( \ln([\text{HP}]_0 - [\text{EP}]) \) vs reaction time \( t \). Sample was taken in every 30 minutes during the epoxidation reaction. The duration of reaction at temperature 40, 50, 60, and 70°C was 240, 240, 180, and 120 minutes, respectively. After setting the linear trendline for each reaction temperature (as shown by Fig. 3), it is apparent that data at low temperature (40° and 50°C) fits well with linear line of Equation (2). However, data at higher temperature (60 and 70°C) generates the significant discrepancy with the linear line of Equation (2). This indicates that at high temperatures, side reactions, especially the oxirane ring opening reaction, probably takes place. Hence, the use of previous model in this system (pseudo homogeneous, no side reactions or advanced reactions) is less appropriate for high temperatures.

![Fig. 3. Ln([HP]₀ - [EP]) as a function of temperature and reaction time](image1)

![Fig. 4. Ln k₁ as a function of (1/T)](image2)
Table 1 presents the value of reaction rate constant of epoxidation and its deviation, evaluated with Equation (2) concept.

Table 1. Rate constant of epoxidation ($k_1$) and R-Squared values at various temperatures

| Temperature ($^\circ$C) | Rate constant of epoxidation ($k_1$ (gram. mol$^{-1}$.min$^{-1}$)) | $k_1 \times 10^6$ (L.mol$^{-1}$.s$^{-1}$) | R-Squared value |
|------------------------|---------------------------------------------------------------|---------------------------------|----------------|
| 40                     | 1.9895                                                        | 3.3073                          | 0.9986         |
| 50                     | 3.0275                                                        | 5.0328                          | 0.9606         |
| 60                     | 3.8925                                                        | 6.4708                          | 0.9583         |
| 70                     | 5.7956                                                        | 9.6342                          | 0.8768         |

The rate constants gained for the epoxidation are of the order of $10^{-6}$ L.mol$^{-1}$.s$^{-1}$ and are relative appropriate with the values reported for cottonseed, mahua, soybean, karanja, Jatropha, and MEPOL oil [33, 34,35, 36, 31, and 32]. Using Arrhenius equation to express the rate of reaction constant, as given by:

$$k_1 = Ae^{\frac{E_a}{RT}} \quad (3)$$

$$\ln k_1 = \ln A - \frac{E_a}{RT} \quad (4)$$

it is found that the value of A (collision factor) is 286,768 gram. mol$^{-1}$.min$^{-1}$ and the activation energy (Ea) is 30,900 Joule/mol. Fig. 4 illustrates the evaluation of Arrhenius constants A and Ea.

4. Conclusions

The epoxidation of Tung oil using in-situ produced peroxyacid with sulphuric acid as a catalyst could be conducted at temperature range of about 50 – 60°C. The proposed simple kinetics model is relatively appropriate at lower reaction temperature, but deviates significantly at higher temperature (more than 60°C). The kinetic parameters were determined in the temperature range of 40-70°C. The reaction rate constants were in the range of $(3.307–9.634) \times 10^{-6}$ L.mol$^{-1}$.s$^{-1}$. The activation energy and collision factor values for the epoxidation were found to be 286,768 gram. mol$^{-1}$.min$^{-1}$ and 30,900 Joule/mol, respectively.

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List of symbol

| Symbol | Description |
|--------|-------------|
| A      | collision factor (g. mol$^{-1}$.min$^{-1}$) |
| AA     | acetic acid |
| [AA]   | acetic acid concentration (mol/g) |
| [AA]$_0$ | initial acetic acid concentration (mol/g) |
| Ea     | activation energy (J.mol$^{-1}$) |
| EP     | epoxidized Tung oil |
| [EP]   | epoxidized Tung oil concentration (mol/g) |
| HP     | hydrogen peroxide |
| [HP]   | hydrogen peroxide concentration (mol/g) |
| [HP]$_0$ | initial hydrogen peroxide concentration (mol/g) |
| HP     | hydrogen peroxide |
| W      | water |
| IV     | iodine value (g I$_2$/100 g sample) |
| UFA    | unsaturated fatty acid |
| PAA    | peroxyacetic acid |
| [PAA]$_0$ | peroxyacetic acid concentration (mol/g) |
| R      | universal gas constant (J mol$^{-1}$.K$^{-1}$) |
| t      | reaction time (minute) |
| T      | temperature (K) |
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