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Hydroxylation Kinetics of Epoxidized Tung Oil Using Methanol as Nucleophilic Agent

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Abstract. The synthesis of vegetable oil-based polyols has been carried out through the epoxidation-hydroxylation process. However, Tung oil has never been explored in the process, even though Tung oil has a high double bond. Epoxidized Tung Oil (ETO) with oxirane numbers of 3.92 to 4.04 mmol/g were hydroxylated with methanol and catalyzed by Sulfuric Acid (H_2SO_4). The objective of this study is to produce polyols from ETO and to evaluate the influence of temperature and catalyst concentration on the hydroxylation process. A second-order reaction kinetic study was also developed to represent the reaction. The ETO hydroxylation was carried out in a batch reactor for four hours. The reaction rate was determined based on the concentration of ETO (oxirane number) and Hydroxyl Value (OHV). The result shows that temperature and catalyst concentration have a directly proportional correlation to OHV and are inversely proportional to the concentration of ETO (epoxy). For temperatures above 40°C, the decreasing rate of the epoxy concentration at the beginning was relatively much faster than at the end of the reaction. In the temperature variation, the highest OHV obtained was 3.70 mmolKOH/g or 207.39 mgKOH/g at 80°C. The optimum catalyst concentration obtained in this study was 3%. The evaluated kinetics model gave great results for all reaction temperatures, with the highest total SSE for epoxy concentration and OHV data fitting of 0.156 and 0.045, respectively. The calculated activation energy (Ea) was 30.41 kJ/mol and the pre-exponential factor (A) was 255.00 $g.mmol^{-1}.min^{-1}$.

Keywords: Catalyst concentration; Epoxidized Tung Oil (ETO); Hydroxylation; Kinetics; Methanol

1. Introduction

Polyol is an organic compound that has more than one hydroxyl (-OH) group. Bio-polyols that are synthesized from vegetable oils are a great alternative to replace petrochemical polyols. Oleochemical polyols have several characteristics, such as flexible, mechanical and chemical resistant, hard, and hydrophobic (Borowicz, Paciorek-Sadowska, and Isbrandt, 2020; Purnomo, Setyarini, and Anggono, 2020; Lavrenyuk, Parhomenko, and Mykhalichko, 2019). They are required in the manufacturing industries such as flooring, coatings, and foaming in the polymer industry, polyols are compounds that contain hydroxyl function groups that can be used for other chemical reactions. The main use of polyols is to be used as a reactant to make polymers. Polyols can also be used for other purposes, such as intermediate chemicals, lubricant formulations, and stabilizers (Bresolin

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et al., 2018; Gasni *et al.*, 2017; Pavani, Pola-Rao, and Prasad, 2017; Kamalakar *et al.*, 2015). Polyols are widely used in the manufacture of polyurethane. The synthesized polyol can be processed from renewable (e.g., vegetable oils) and unrenewable materials (e.g., petroleum). The hydroxyl group can be made from vegetable oils with a high content of unsaturated fatty acids through epoxidation followed by the hydroxylation process (Borowicz, Paciorek-Sadowska, and Isbrandt, 2020). Some vegetable oils have high unsaturated fatty acid content and some of them naturally contain other functional groups which cause various processes in synthesizing vegetable oil-based polyols. The four methods used to produce polyols are a) epoxidation followed by the ring-opening of the oxirane to form secondary hydroxyl groups; b) the enzymatic reaction; c) transesterification; and d) hydroformylation and reduction of aldehyde oil (Dong-Feng *et al.*, 2019; Ionescu *et al.*, 2016).

Hydroxylation is the addition process of hydroxyl groups (-OH) to organic compounds. Theoretically, vegetable oils can be converted to hydroxy in several ways, such as catalytic hydrogenation, hydrochlorination or hydrobromination, and ring-opening reactions with the addition of alcohol, amino alcohol, or acid (Coman *et al.*, 2021; Borowicz, Paciorek-Sadowska, and Isbrandt, 2020; Guo, Javni, and Petrovic, 2000). Hydroxylation reactions can be performed in the absence of solvents with acidic catalysts. The catalysts used are mineral acids, metal, and metal carbonyl. The ratio of molar hydroxyl and epoxide groups ranges from 1:1 to 1:10 and the optimum temperature is around 50°C (Petrovic *et al.*, 2010). In recent years, the ring-opening method of epoxy has been widely investigated for the manufacturing process of vegetable oil-based polyol compounds. This method involves two steps, i.e., epoxidation of unsaturated fatty acids in vegetable oils and the ring-opening reaction of epoxy using nucleophilic reagents such as amines, carboxylic acids/ halogenated acids, or alcohol. The ring-opening reaction of epoxy with the addition of alcohol produces β-alkoxy alcohol (Gallo, Teixeira, and Schuchardt, 2006; Williams, D Bradley, and Lawton, 2005). This reaction can be carried out using both alkaline and acidic catalysts. Some of the catalysts that have been used in these reactions include Lewis acid (Firouzabadi *et al.*, 2006), Brønsted acid (Gallo, Teixeira, and Schuchardt, 2006), and porphyrin complexes (Zakavi, Karimipour, and Gharab, 2009).

Some researchers make polyols from several vegetable oils, such as castor oil, flaxseed oil, sunflower seed oil, soybean oil, peanut oil, and cotton seed oil through ozonolysis and hydrogenation processes (Tran, Graiver, and Narayan, 2005) as well as epoxidation and hydroxylation processes (Petrovic *et al.*, 2010). Vegetable oils generally do not contain hydroxyl groups but hold a relatively high content of unsaturated fatty acids (Helmiyati and Anggraini, 2019). The double bonding part of unsaturated fatty acids can be converted into an epoxy group at atmospheric pressure through epoxidation and further converted into a hydroxyl group with the hydroxylation process. Petrovic *et al.* (2010) patented epoxidized oil alcoholysis with different molecules such as water, monoalcohol (methanol, ethanol, propanol, and butanol), and their mixture using tetrafluoro boric acid as a catalyst (Petrovic *et al.*, 2010; 2002). Polyol can be synthesized from several epoxidized natural oils, such as epoxidized methyl oleate, epoxidized cocoa butter, epoxidized palm olein, and epoxidized soybean. Polyols were produced through a copolymerization reaction between the epoxidized oils and tetrahydrofuran with a Lewis acid catalyst (Hoong *et al.*, 2015). Mohammed *et al.* (2013) synthesized polyols by reacting palm oil and soybean oil with glycerol. The polyols were further processed in the manufacture of polyurethane (Mohammed *et al.*, 2013).

Tung oil is one of the types of non-edible vegetable oil with a high content of unsaturated fatty acids. The use of Tung oil as a raw material in the synthesis of polyols has several advantages, such as: being renewable, relatively biodegradable, sustainable, and not contradictory to food industry needs. Tung seeds kernel can result from crude oil of 45-50% yield with a high content of unsaturated fatty acids, i.e., oleic acids, linoleic acids, and α-oleo stearate acids. The percentage of fatty acid contained in Tung oil is about 66.17% of oleo stearic acid, 21.72% of palmitic acid, 0.27 % of linoleic acid, 9.58% of oleic acid, and 2.26% of other saturated fatty acids (Budiyati *et al.*, 2020). Synthesis of bio-polyols can be carried out by epoxidation of double bonds in unsaturated fatty acids and ring-opening of epoxides with nucleophilic reagents. The advantages of chemical flow, such as increased process safety and reliability, easy automation, and reproducibility are leveraged to increase productivity and product quality in the ring-opening epoxy. Pantone *et al.* (2017) investigated the methanolysis reaction of Soy Oil Oxidized (ESO) in a continuous flow system (Pantone *et al.*, 2017). Various chemical modifications to Epoxidized Soybean Oil (ESBO) are performed through the opening of epoxy rings. The ring-opening reaction with nucleophilic compounds is one of the most commonly used processes. Several previous studies examined the hydroxylation of epoxy rings with acids (acetic acid, formic acid, and phosphoric acid) (Campanella and Baltanás, 2007; Guo *et al.*, 2007). Alcoholysis using methanol, 1-decanol, 1-butanol, and 2-ethylhexanol was studied for the manufacture of lubricant formulation (Hwang, Adhvaryu, and Erhan, 2003; Hwang and Erhan, 2001). The alkoxylate synthesis of triacylglycerol from ESBO was developed using perchloric acid for the opening of epoxy rings (Adhvaryu, Liu, and Erhan, 2005).

Based on the literature review, the hydroxylation process with Tung oil as raw material has never been carried out. Evaluations of the hydroxylation kinetics and the process variables' effects (such as temperature and catalyst concentration) also have not been discussed specifically in the previous studies. Several previous studies evaluated the reaction rate constants of the hydroxylation (epoxy and alcohol) as a part of the side reaction in the epoxidation of vegetable oils (Kousaalya *et al.*, 2018; De Haro *et al.*, 2016; Dai *et al.*, 2009). Overall, this research has novelties in the type of vegetable oil (i.e., Tung oil) and the proposed reaction kinetics. Therefore, this study aims to evaluate the influence of temperature and concentration of catalyst, as well as the second-order reaction kinetics in the hydroxylation of ETO.

2. Methods

2.1. Materials

Epoxidized Tung Oil (ETO) was produced from the epoxidation process of Tung seed oil (*Reutealis trisperma* (Blanco) Airy Shaw) (Budiyati *et al.*, 2020). It has an initial concentration of epoxy and hydroxy of 3.92 to 4.04 mmol/g and 0.11 to 0.16 mmol/g, respectively. Pyridine, crystal violet indicator, hydrobromic acid (47 wt%), methanol, sulfuric acid 98 wt%, glacial acetic acid (AR Grade), and potassium hydroxide were purchased from CV. Zirconia Jaya, Yogyakarta, Indonesia. Acetic anhydride and potassium hydrogen phthalate were purchased from CV. Multikimia, Yogyakarta, Indonesia.

2.2. Hydroxylation Process

Epoxidized Tung Oil (ETO) was produced from Tung seed oil epoxidation. Peracetic acid was used as an oxidator (in-situ generated) and sulfuric acid as the catalyst. The epoxidation process was carried out for 4 hours at a temperature of 60°C and the stirring speed was maintained constant at 600 rpm (Budiyati *et al.*, 2021). ETO was hydroxylated with 6 g of methanol and 3% (of the total solution) sulfuric acid in an Erlenmeyer flask. As much as 75 g of epoxidized Tung oil and a mixture of methanol and sulfuric acid were fed into the reactor. The process was carried out isothermally (at a temperature of 40°, 50°, 60°, 70°, and 80°C) with a stirring velocity of 700 rpm. Then, the catalyst concentration was varied at 1%, 2%, 3%, and 5%. The Hydroxylation process ran for 4 hours with a sampling time interval of 30 minutes. The samples were purified in the separation funnel using warm distilled water. The obtained samples were analyzed to determine their oxirane number and hydroxyl value. A schematic illustration of this experiment is shown in Figure 1.

2.3 Determination of Concentration of ETO and Hydroxyl Value

The concentration of ETO was represented by the oxirane number. It was analyzed by hydrobromic acid solution with glacial acetic acid method (Budiyati *et al.*, 2020). The Hydroxylation Value (OHV) of polyols was determined according to the ASTM method D1957-86 with the mixture of pyridine and acetic anhydride as a hydroxyl number reagent. Potassium hydroxide was used as a titrant in the titration process.

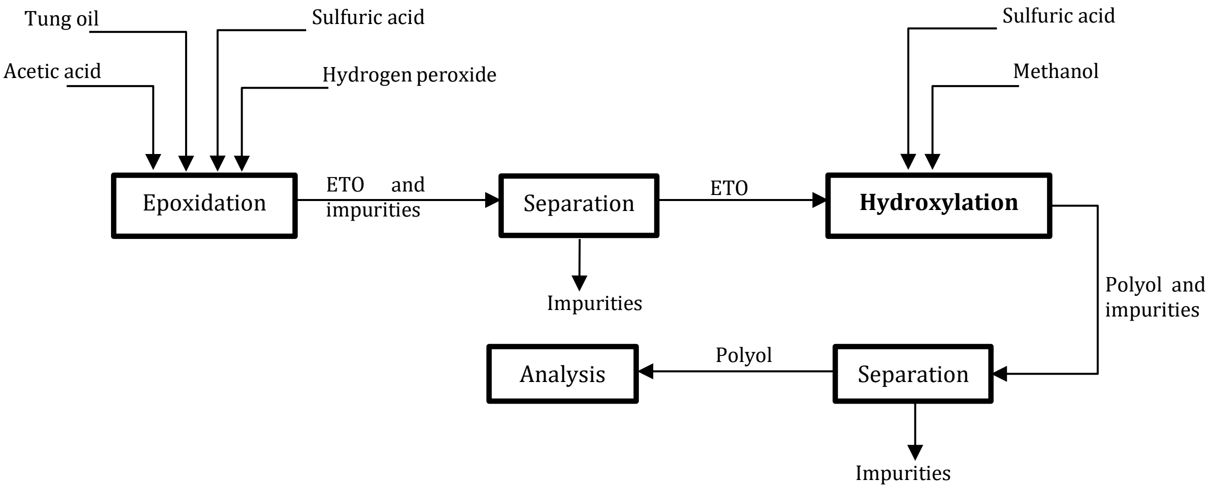


Figure 1 Schematic illustration of this experiment

3. Results and Discussion

3.1. Effect of Temperature on Hydroxylation

Temperature significantly affects chemical reactions, including ETO hydroxylation. In this study, the optimum temperature evaluation was conducted. ETO as a reactant or raw material is naturally highly reactive. Before the raw materials were used in experiments, they were stored in the freezer with limited storage time (maximum about 2 days) at a temperature of 4°C. After the freezing pre-treatment, the raw materials were ready to be fed into the reactor which has varied temperatures of 40°, 50°, 60°, 70°, and 80°C. Figure 2(a) presents a correlation between epoxy/ETO concentration and reaction time at various temperatures of hydroxylation. From Figure 2(a), it is seen that the concentration of ETO decreased with the increase in reaction time and this condition occurred at all observed reaction temperatures. It is obvious because the longer the reaction time, the more ETO moles (as reactants) reacted. As a consequence, there are more epoxy molecules converted in the process. The temperature has a similar effect as the reaction time to the hydroxylation of ETO. The rising temperature decreases the ETO concentration. This phenomenon happens because the increase in temperature enlarged the kinetic energy and reactiveness of the reactant molecules. The decreasing rate of epoxy concentration at the lowest temperature, 40°C, was relatively slow from the beginning to the end of the reaction. At higher temperatures, 50° to 80°C, the decreasing rate of the epoxy concentration at the beginning was relatively fast and began to stable after 120 minutes. As mentioned previously, at a higher temperature the molecular kinetics of the reactants will increase, thus increasing the collision factor and accelerating the reaction rate (Yang *et al.*, 2010).

Methanol was a primary alcohol that can be a powerful nucleophile in the hydroxylation of ETO. It is seen from the final conversions (of about 84%) with a reaction time of 4 hours. This result supports previous research which states that the hydroxylation conversion of epoxide compounds with primary alcohol was higher compared to secondary and tertiary alcohols (Mirza-Aghayan *et al.*, 2014). Mirza-Aghayan, *et al.* (2014) stated that a long reaction time is required for the opening of epoxide rings with secondary alcohol. However, the generated conversions in this study were lower than in previous studies. Hydroxylation of styrene epoxide with methanol-catalyzed Graphite Oxide (GO) resulted in a conversion of about 94%. This significant difference was due to the use of different raw materials and catalysts (Mirza-Aghayan *et al.*, 2014).

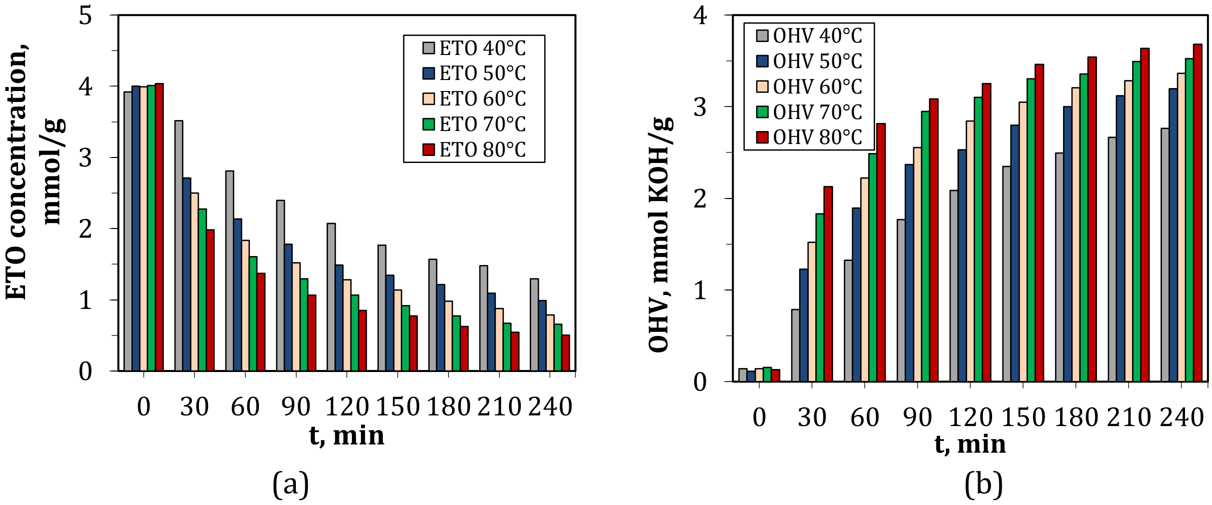


Figure 2 Effect of temperature and reaction time on (a) the Epoxidized Tung Oil (ETO) concentration, and (b) on the polyol concentration (OHV)

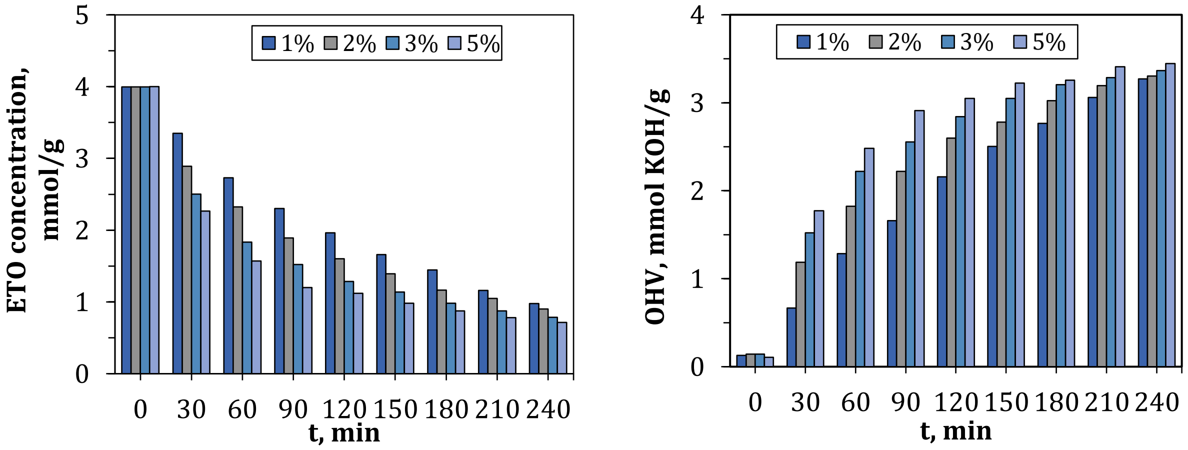
Figure 2(b) shows OHV at various reaction times and temperatures. The observed concentration of polyols or OHV increased with reaction time, for all temperatures. This phenomenon occurs because a longer reaction time increased particle contact. At the same reaction time, the samples treated with higher temperatures have more OHV produced. The molecular kinetics of the reactant molecules rose with the increase in temperature and this condition triggered the collision molecules. The highest OHV obtained in this study (from the optimum temperature variation) was approximately 3.70 mmol KOH/g or 207.39 mg KOH/g. This result was in accordance with the previous studies, which are 180.34 mg KOH/g (Dai *et al.*, 2009) and 191±15 mg KOH/g (Pantone *et al.*, 2017). Dai *et al.* (2009) also conducted similar research with different types of alcohol, namely 1,2-ethanediol, and 1,2-propanediol. The obtained OHV values are 253.33 mg KOH/g (for 1,2-ethanediol) and 289.31 mg KOH/g (1,2-propanediol). The vegetable oil used in the two aforementioned studies was soybean oil, while this research also used vegetable oil. Based on these results, it can be concluded that the type of vegetable oil and operating conditions are parameters that have a significant effect on the results of the hydroxylation reaction.

3.2. Effect of The Catalyst Concentration on Hydroxylation

The evaluation of the catalyst's influence on ETO hydroxylation was conducted at the temperature of 60°C and a constant stirring velocity of 600 rpm. The catalyst used in this study was sulfuric acid (H_2SO_4). The catalyst activated methanol as a nucleophilic agent, then activated methanol reacted with ETO. Catalyst concentration is an important parameter in reaction kinetics. Catalysts can accelerate reactions, but on the other hand, can produce burnt or dark brown polyols. In this study, the catalyst concentrations were varied at 1%, 2%, 3%, and 5% to obtain the optimum value.

Figure 3(a) describes the correlation between the concentration of epoxy/ETO against the time and catalyst concentration. As explained in the previous discussion, a longer reaction time resulted in a lower concentration of epoxy. Generally, the concentration of catalysts had an inverse correlation to the ETO concentration. Higher catalyst concentration promotes more epoxy molecules to react. Catalysts reduce the activation energy; therefore, reactions can run faster. However, the addition of a catalyst has its limit. The addition of catalyst concentrations from 1% to 3% had a significant effect on the reaction kinetics while the addition of catalysts from 3% to 5% produced a less significant effect.

The initial concentration of ETO was around 3.99 – 4.00 mmol/g. The initial concentration of ETO was not fixed at a single value due to the highly reactive properties of epoxy compounds. In practice, ETO was prepared in a time adjacent to its hydroxylation process. At the end of the reaction, the ETO converted were approximately 75.58%, 77.46%, 80.34%, and 81.00% for catalyst concentrations of 1%, 2%, 3%, and 5%, respectively. In addition, the use of an H_2SO_4 catalyst at relatively high concentrations (≥ 5%) caused the discoloration of polyols, i.e., dark brown. This can lead to denaturation of the product, resulting in decreased quality of polyols. From these data, a catalyst concentration of 3% can be recommended as the optimum value in this reaction. These results differ slightly from those reported by Yadav and Singh (2014), optimum catalyst concentration was 5% (Yadav and Singh, 2014). This was due to the different types of catalysts and epoxy used. The types of catalysts used in the previous study and this research are ferrocenium tetrafluoroborate and sulfuric acid, respectively. Then, the previous study used non-vegetable oil-based epoxies, such as 1,2-epoxydodecane and 1,2-epoxyhexane.



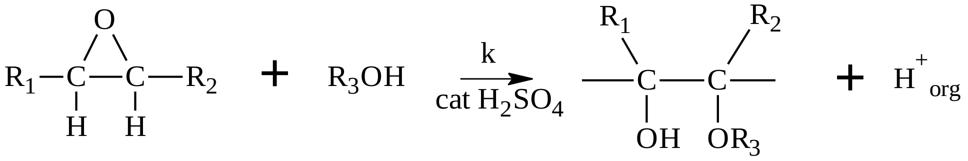
(a) (b)

Figure 3 Effect of catalyst concentration and reaction time on (a) the epoxidized Tung oil (ETO) concentration and (b) the polyols concentration (OHV)

The correlation between polyol concentration (OHV) and reaction time at various catalyst concentrations is presented in Figure 3(b). From the figure, it is clear that changes in catalyst concentration had a significant influence on the reaction time of fewer than 180 minutes. The role of catalysts as agents that can accelerate reactions by lowering activation energy was highly visible from the curve. The OHV obtained increased dramatically with the addition of catalyst concentrations. For example, at a reaction time of 90 minutes, the obtained OHV for catalyst concentrations of 1% and 5% were about 1.66 mmol KOH/g and 2.90 mmol KOH/g, respectively. The difference in the obtained OHV was significant which means the addition of catalyst concentration was effective. However, at reaction time ≥ 180 minutes, the increase in catalyst concentration is insignificant to the OHV obtained, especially for catalyst concentrations of 3% and 5%. At the end of the reaction (240 minutes), all catalyst concentrations had almost the same obtained OHV. This indicates that the addition of a catalyst was ineffective, due to the possibility of achieving an equilibrium condition. The obtained OHV for catalyst concentrations of 1% and 5% were 186.96 mg KOH/g and 190.08 mg KOH/g, respectively. The OHV value of around 3.34 mmol KOH/g was considered the optimum value for the hydroxylation processes at various catalyst concentrations in this study. Based on Figure 2(b), it is seen that the addition of catalyst concentration did not provide a significant change to OHV. This was because the equilibrium condition was almost reached. In addition, the results of GC-MS analysis of Tung seed oil obtained show that the highest content of unsaturated fatty acids is α-oleo stearic acid, which was 66.17%. In the ETO synthesis from Tung oil (with in-situ epoxidation), there was a side reaction, i.e., the opening reaction of the epoxy ring. It affected the yield of epoxidation and the resulting OHV value.

3.3. Hydroxylation Kinetics

The second-order reaction model was evaluated on the hydroxylation kinetics. Two assumptions were taken in this research: (1) the hydroxylation was a pseudo-homogeneous reaction and (2) there is no side reaction occurred. The reason for taking the assumption (1) is that methanol and ETO are organic compounds that can dissolve well with each other. Then, sulfuric acid is an inorganic compound that has limited solubility in these organic compounds. The amount of sulfuric acid is inconsiderable (i.e., 3%). So, overall, the reaction can be considered a pseudo-homogeneous. While, the reason for assumption (2) is that based on the experimental results, the concentration of the oxirane (which reacts) is proportional to the concentration of the formed polyol. The molar ratio of epoxy (ETO) to methanol was 1:1 (equimolar). The concentration of the H_2SO_4 catalyst was 3% of the total weight of the reactants. The used catalyst concentration was based on the discussion in the previous section (i.e., section 3.2.), which concluded that the optimum catalyst concentration was 3%. The process was carried out in a batch reactor for four hours. The reaction took place isothermally and at a constant stirring speed (700 rpm). The mechanism of the ETO hydroxylation is shown in Equation (1).



(1)

Epoxidized Tung Oil (ETO) Polyol (OHV)

The elementary reaction law states that the rate of a reaction is proportional to the concentration of each reactant.

Then, the rate of reaction can be represented by Equation (2).

$$\frac{d[OHV]}{dt} = k[R_3OH][ETO] \tag{2}$$

Because of equimolar ($[R_3OH]_0 = [ETO]_0$) and coefficient of R_3OH = coefficient of epoxy (ETO), so $[R_3OH] = [ETO]$. Then Equation (2) changed into Equation (3).

$$\frac{d[OHV]}{dt} = k[ETO]^2 \tag{3}$$

The reaction rate equation followed Equation (3), where the hydroxylation had a reaction order of 2 or could be called a second-order reaction.

The sum of the square of errors (SSE) of this kinetics model was determined by Equation (4).

$$SSE = \sum\{[OHV]_{data} - [OHV]_{calc}\}^2 + \sum\{[ETO]_{data} - [ETO]_{calc}\}^2 \qquad (4)$$

The experimental data used in this model were the ETO concentration and OHV for each temperature. The kinetic parameter (k) was obtained by minimizing the sum of the square of error (SSE) as the objective function. The algorithm for determining the reaction rate constant is shown in Figure 4.

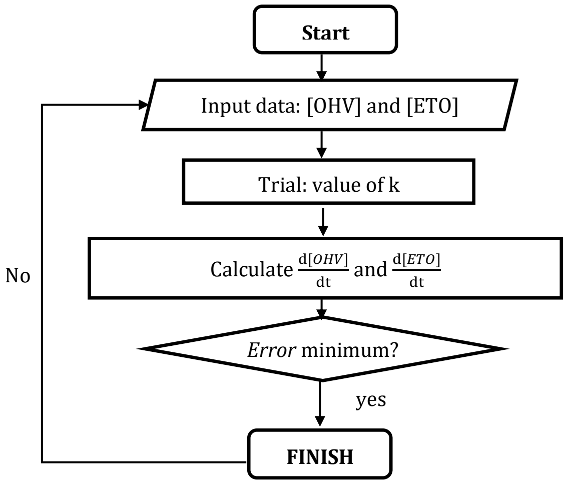


Figure 4 Algorithm for determining the reaction rate constant (k)

The experimental data and resulting model concentrations of ETO and OHV are shown in Figure 5. From Figure 5, it is clear that at all evaluated reaction temperatures, experimental data on epoxy and polyol concentrations were fit to the modeling results. This indicates that in the reaction system, there was no side reaction and the reaction rate has an order of 2 (two). At 40°C, the deviation between the experimental data and the model (especially for epoxy concentrations) was relatively greater than at higher temperatures. For example, at a reaction time of 30 minutes, the ETO concentrations were about 3.52 mmol/g (experiment) and 3.18 mmol/g (model). This was due to the high viscosity property of epoxidized Tung oil. At the beginning of the reaction, this high viscosity causes poor homogeneity in the reaction system and a low reaction rate. This high viscosity was not considered in the model, as there is no viscosity parameter from Equation (2) to (3). The deviation between the ETO concentration of experimental data and the model was getting smaller by the time $t > 30$ minutes because homogeneity was achieved.

The reaction rate constant and the Sum of the Square of Errors (SSE) for each temperature are shown in Table 1. The reaction rate constant had a reaction order of 10^{-3} g.mmol^{-1}.min^{-1}. This result is in agreement with the previous study (De Haro *et al.*, 2016). The reaction rate constant was directly proportional to the reaction temperature. The k values for the range temperatures of 40 – 80°C were 1.98 x10^{-3} to 7.83 x10^{-3} g.mmol^{-1}.min^{-1}. The smallest SSE for epoxy and polyol concentrations were obtained at 60°C and 70°C. In addition, the sample treated at 40°C resulted in the highest SSE, with an average SSE of 0.100. From Table 1, it is seen that in the temperature range of 40°C to 70°C, the average SSE value decreased with the increase in temperature. However, at a temperature of 80°C the SSE average rose again. It indicates that it was possible that the side reactions began to occur at such a temperature. The observed SSE for polyol concentrations/OHV was around

0.004 to 0.045 while the SSE of epoxy was 0.013 to 0.156. This suggests that experimental data from epoxy and polyol concentrations were fit to the results of the model. Overall, the evaluated kinetics model provided satisfactory results.

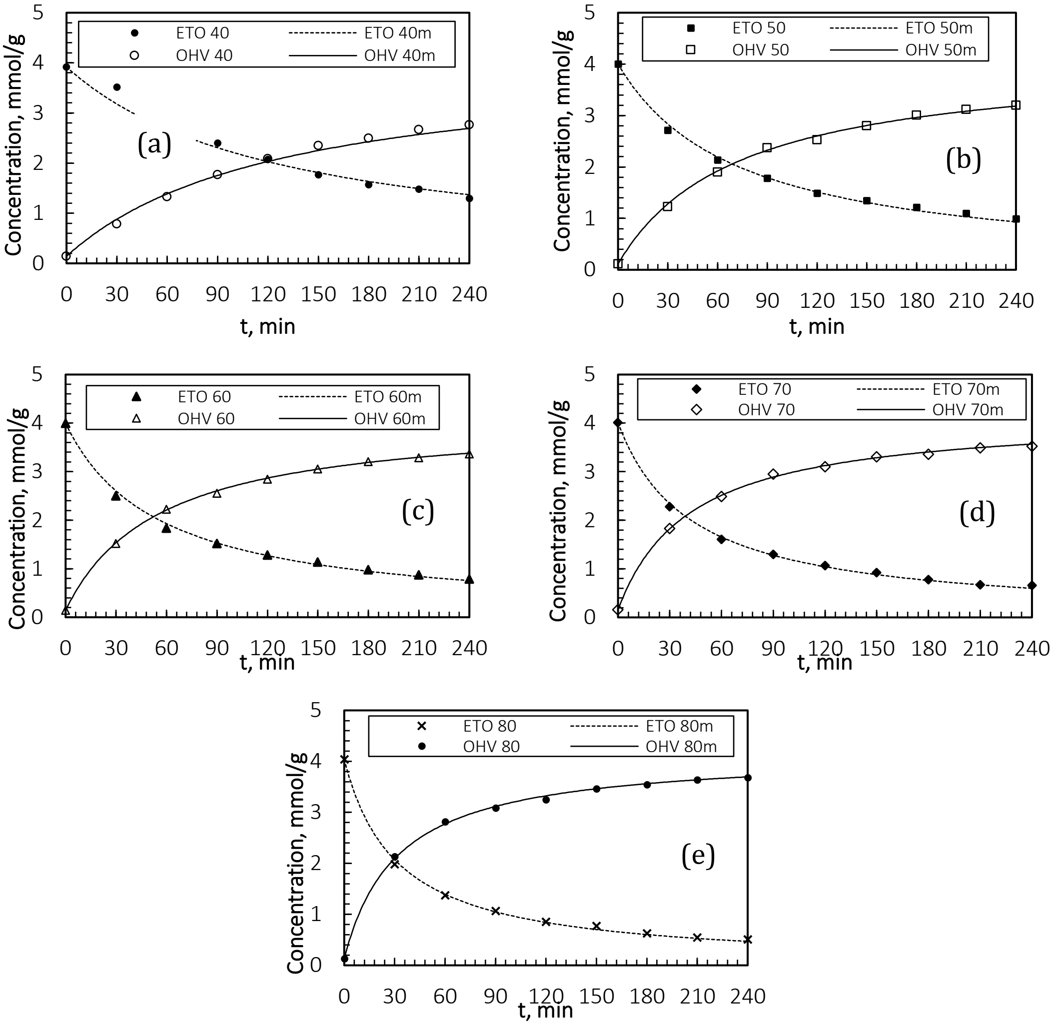


Figure 5 The experimental and model concentrations of ETO and polyol (OHV) as a function of reaction time at various temperatures: (a) 40°C, (b) 50°C, (c) 60°C, (d) 70°C, and (d) 80°C

Table 1 Reaction rate constant (k) and SSE values for hydroxylation kinetics model

T (°C)	T (K)	k x 10^3 ($g.mmol^{-1}.min^{-1}$)	SSE		
			Epoxy	Hydroxyl	Average
40	313.15	1.98	0.155	0.045	0.100
50	323.15	3.43	0.031	0.014	0.023
60	333.15	4.48	0.025	0.004	0.015
70	343.15	5.92	0.013	0.009	0.011
80	353.15	7.83	0.016	0.010	0.013

The reaction rate constants obtained from each temperature can be further used as the input data to determine the Activation Energy (Ea) and Pre-exponential Factor (A) using the Arrhenius equation. The relative error value of the curve was low and the r-square parameter shows a satisfactory value of 0.98. The curve slope is the value of (-Ea/R), where R is the ideal gas constant. Meanwhile, the intercept curve is the ln (A) value. The calculated energy (Ea) is 30.41 kJ/mol and the Pre-exponential Factor (A) is 255.00 $g.mmol^{-1}.min^{-1}$. The Ea values in this study were a bit different from the previous studies, which were 29.56

and 39.99 kJ/mol (Dai *et al.*, 2009) and 43.11 kJ/mol (Kousaalya *et al.*, 2018). The vegetable oils used in the previous study were soybean oil and Perilla oil, respectively. Overall, the type of vegetable oil directly affects the value of the resulting Ea of hydroxylation.

4. Conclusions

Polyols were successfully synthesized from epoxidized Tung oil through hydroxylation using methanol as a nucleophilic agent. Sulfuric acid (H_2SO_4) was added as a catalyst. From this study, it can be concluded that the resulting polyol concentrations (OHV) were directly proportional to the temperature, time of reaction, and catalyst concentration. On the other hand, the concentration of ETO is inversely proportional to the mentioned parameters. The highest OHV obtained from the temperature variation was 207.39 mg KOH/g at 80°C. A catalyst concentration of 3% can be recommended as the optimum condition in this reaction. A proposed second-order reaction kinetics model can represent hydroxylation kinetics. A good agreement between experimental data and calculated concentration was achieved. The k values for the range temperatures of 40°C – 80°C were about 1.98 x10^{-3} to 7.83 x10^{-3} g.mmol^{-1}.min^{-1}. Future research shall focus on the characterization and application of Tung oil-based polyol products.

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