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Research paper

Numerical Modeling of Epoxidation Palm Kernel Oil Based Oleic Acid

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Abstract

The epoxidized of vegetable oil is one of the important chemical processes to produce commercial goods such as plastics, lubricants, and paints. A good kinetic model is necessary to predict the process outcome, especially for the big scale productions in which very helpful in predicting the actual production. In this study, the kinetic model of the epoxidation process of palm kernel oil was investigated. The kinetic model was developed based on the laboratory works done by Jumain [1]. The mathematical model was established and implements into the MATLAB by integrating numerically using a fourth order Runge-Kutta method. The reaction rates parameters denote as k_{11}, k_{12}, k_{13}, and k_{22} were then estimated using the Hooke-Jeeves algorithm until the convergence values obtained. After 100 increments, the reaction rates parameters are k_{11} = 0.1875 mol/L.min, k_{12} = 0.9997 mol/L.min, k_{21} = 0.0625 mol/L.min and k_{22} = 0.0000 mol/L with an absolute error of 0.0857. Good agreement was found between experiment and simulation. Based on the converged kinetic values, the evolution of the concentration for all the species was simulated. After the end of the simulations, the computed concentration of the epoxide is approximately 1.5169 mol/L.

Keywords: *Matlab, Epoxidation, Kinetic, Vegetable Oil, Reaction Rate*

1. Introduction

The unsaturation chain in vegetable oils can be modified into a very useful product by a series of a chemical process known as epoxidation. In this process, the oil will react to an oxygen donor substance to produce an epoxide. Due to the presence of the oxirane ring in the epoxide, it becomes one of the useful raw material in the synthesis of chemicals products such as pharmaceutical, paints, and adhesives.

Nowadays, the epoxidized of a vegetable oil having a great concern in the industry since it is renewable sources and easy to obtain through the plantation. Additionally, the vegetable oil can be considered as biodegradable compare with the petroleum oil since it is less toxicity. In Malaysia, the palm oil is quite abundant since the palm tree is a major plantation in Malaysia. Malaysia is also renowned as palm oil producer in the world. Since the resource is unlimited, it is a good opportunity to utilize this source as an epoxide substitution.

Noorfazlida [2] had conducted a synthesis of dihydroxystearic acid (DHSA) by reacting the epoxide-based palm-kernel oil with water. This epoxidation process is prepared at room temperature with generated *in situ* performic acid (*PFA*). Results from this study have shown a great potential of epoxide-based OA to replace the conventional epoxidation process in producing the end product.

There are numerous epoxidation methods to produce epoxidized fatty acid and among them is a catalytic epoxidation process using *in situ*-generated peracid. In this process, three phases involved which are 1) the formation of performic acid (PFA) in the solution; 2) the reaction of PFA in the oil phase to produce formic acid (FA) and epoxide; 3) the degradation of the epoxide ring in the oil phase. But, in this study, the degradation process of the oxirane ring is not considered. Jumain [1] had several experimental and kinetics studies of the epoxidation process of palm-kernel oil. Using the design of experiment (DOE) methodology, Jumain [1] founds the optimum process condition to produce higher epoxide formation.

Rangarajan [3] investigated the kinetic parameters of the epoxidation process using soybean. The reaction rate is found by fitting the experimental data, and the value obtained is 20.2 L/mol/min. In other studies, the kinetic epoxidation process of soybean was determined by employing the Nelder–Mead algorithm in MATLAB software [4]. Based on the parameters found, the evolution of epoxide concentration was simulated and compared. Good agreement between both simulation and experimental work. Rosa [5] done the epoxidation mechanism of soybean by implementing the second order kinetic rate. Using the Runge-Kutta and isqnonlin built-in function in MATLAB, the model parameters were then estimated. However, the models are only valid for primary reactions and reasonable temperatures. Outside these limits, the conjecture of irreversible reactions useful in the models is no extensive valid.

Most of the previous researcher focuses on laboratory works especially in the formation of epoxide in a certain condition such as initial concentration, type of catalyst and type oxygen carrier [6-7]. However, it is quite rare to see the extensive research about the kinetics reaction simulation during the epoxidation process, especially in palm-kernel oil. Thus, a further study needed to develop an overall kinetic model. The proposed model can become an essential design consideration of the chemical plant to produce an epoxide. By developing a set of differential equations, the reaction rates parameters can be found by integrating numerically using the numerical technique. Unfortunately, most of the kinetic rates parameters were determined through curve fittings by assuming a single reaction rate process. But, to assume in such extends, it is quite difficult, since it involved with one or more phases [8]. For example, the oxirane ring is a very reactive material, which easily to react with any substances to form saturated material. Thus, ignoring this effect resulting errors in parameters determination.

The aim of this work is to develop a kinetic model of the epoxidation process by solving a set of differential equations using the Runge-Kutta method. The process condition obtained from Jumain [1] was used to demonstrate the reliability of the model. The model proposed must be able to predict the epoxide formation with a relatively minimal error. The estimated values of the kinetic model were obtained by integrating two software, MATLAB, and I-SIGHT. The evolution of concentration for every species was then plotted and the detailed of the results were then further discussed.

2. Kinetic Modeling of the Epoxidation Process

The development model in the kinetic study of the epoxidation process is based on the assumptions that: 1) The epoxidation process takes in a single phase to avoids distribution constant for the qualification of different species in aqueous and oil phases; 2) Each phase's volume remains constant throughout the process; 3) All reactions involved were homogeneous process; 4) The reactions are away from the interface; 4) Any heat transfer involved were neglected; 5) No degradation process occurs in epoxide. The *In-situ* epoxidation is characterized by two main reactions involving the formation of performic acid and formation of epoxide as illustrated in Equation 1 and Equation 2.

$$FA + H_2O_2 \underset{k_{12}}{\overset{k_{11}}{\rightleftharpoons}} PFA + H_2O \quad (1)$$

$$PFA + OA \underset{k_{22}}{\overset{k_{21}}{\rightleftharpoons}} EPOXIDE + FA \quad (2)$$

where *FA*, H_2O_2, *PFA*, H_2O, *OA*, and *EPOXIDE* are formic acid, hydrogen peroxide, performic acid, water, oleic acid, and epoxide vegetable oil respectively. k_{11}, k_{12}, k_{21}, and k_{22} are the kinetics constant with respect to Equation 1 and Equation 2. From the given epoxidation process, the differential equations that described for each species are further derived as follow:

$$\frac{d[FA]}{dt} = \begin{matrix} -k_{11}[FA][H_2O_2] + k_{12}[PFA][H_2O] \\ +k_{21}[PFA][OA] - k_{22}[EPOXIDE][FA] \end{matrix} \quad (3)$$

$$\frac{d[H_2O_2]}{dt} = -k_{11}[FA][H_2O_2] + k_{12}[PFA][H_2O] \quad (4)$$

$$\frac{d[PFA]}{dt} = \begin{matrix} +k_{11}[FA][H_2O_2] - k_{12}[PFA][H_2O] \\ -k_{21}[PFA][OA] + k_{22}[EPOXIDE][FA] \end{matrix} \quad (5)$$

$$\frac{d[H_2O]}{dt} = +k_{11}[FA][H_2O_2] - k_{12}[PFA][H_2O] \quad (6)$$

$$\frac{d[OA]}{dt} = -k_{21}[PFA][OA] + k_{22}[EPOXIDE][FA] \quad (7)$$

$$\frac{d[EPOXIDE]}{dt} = +k_{21}[PFA][OA] - k_{22}[EPOXIDE][FA] \quad (8)$$

where $\frac{d[FA]}{dt}$, $\frac{d[H_2O_2]}{dt}$, $\frac{d[PFA]}{dt}$, $\frac{d[H_2O]}{dt}$, $\frac{d[OA]}{dt}$ and $\frac{d[EPOXIDE]}{dt}$ are the rate of changes in concentration of formic acid, hydrogen peroxide, performic acid, water, oleic acid and epoxide respectively.

The parametric studies were conducted to determine the rate coefficients numerically. There is two computing process involved which are solving a set of differential equations (Equation 3 – Equation 8) numerically and computing the errors between experimental and simulation. The ODE45 function from MATLAB was used to solve the differential equation by integrating numerically using the fourth-order Runge-Kutta method. The parameters values were predicted using the built-in Hooke-Jeeves algorithm in I-SIGHT software. The reliability of the parameters is verified by minimizing the error, *e* between the experiment and the simulation. By specifying the error, *e* as a minimum in I-SIGHT software, both software run simultaneously and continuously until the optimized values were found. Detail of the error function, *e* can be found in Equation 9.

$$e = \sum_{i=1}^{n} \frac{|[EPOXIDE]^{sim}{}_i - [EPOXIDE]^{exp}{}_i|}{n} \quad (9)$$

where $[EPOXIDE]^{exp}{}_i$ and $[EPOXIDE]^{sim}{}_i$ are the experimental and estimated concentration of epoxide in respected data points, *i* and *n* is the number of data points in experiment and simulation. Closer error, *e* value to zero indicate a good correspondence between computed and experimental data.

To demonstrate the following methodology, the experiment study done by Jumain [1] was used to determine the reaction rates parameters. Detail of the process condition is depicted in Table 1.

Table 1: Process condition done by Jumain [1]

Temperature (°C)	Pressure (atm)	Stirred Speed (rpm)
25	1	300
Initial Concentration (mol/L)		
Formic Acid	Hydrogen Peroxide	Oleic Acid
2.9428	2.9428	2.9428

The simulation time for determining the kinetic parameters is limited to 25 minutes. From the experimental data [1], it is observed that the concentration of the epoxide reaching a maximum value at 25 minutes and reduces significantly for subsequent minutes. Since the model is not considered in the degradation process of the epoxide, this model is valid as illustrated in Equation 1 and Equation 2.

3. Results and Discussion

3.1. Reaction Rate Parameters of Palm-Kernel Oil

As described in the previous section, numerical computation was done to determine the reaction rates parameters by integrating both software (MATLAB and I-SIGHT). After 100 increments using Hooke-Jeeves algorithmic, the converged values of the reaction rates are summarized in Table 2. Notice that the k_{12} coefficient value is much higher than the values of k_{11}. This trend is similar to the study reported by Juan [9]. These values indicate that the performic formation is unfavorable at higher temperatures

and mainly reversible at low temperature. Since the experiment was done at room temperature, these computed parameters are reasonable. It is worth to mentioned that the small rate coefficients of k_{21} indicating that the amount to produce epoxide is much slower. The order of magnitude of k_{21} value is in the same order found by Scala [10] and Campanella [4]. Thus, the k_{21} value obtained in the simulation is in the acceptable range.

Table 2: Estimated reaction rates parameters from simulation

Reaction Rates	Values (mol/L.min)
k_{11}	0.1875
k_{12}	0.9997
k_{21}	0.0625
k_{22}	0.0000

A good comparison of epoxide concentration between laboratory work [1] and simulation based on the kinetics values obtained in Table 2 is illustrated in Fig. 1. Excellent fits attained between both graphs with an error approximately 0.0857. A significant difference between times to reach the maximum concentration for experiment and computed concentration. That may be explained by the difficulty in locating the maximum point on the laboratory curve due to the combined reactions by producing and degrading the epoxide. As a result, it can be said that the kinetic model gives acceptable prediction with the experimental result.

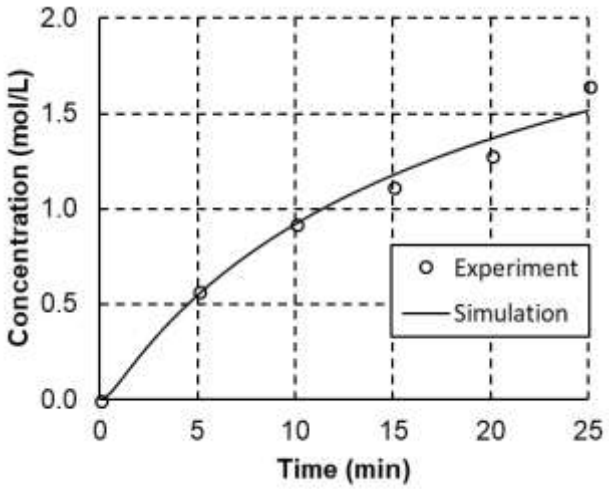

Fig. 1: Comparison of epoxide concentration between experiment [8] and numerical simulation

3.2. Simulation of Palm-Kernel Oil Epoxidation Process

Using the parameters in Table 2, the concentration for each species in the epoxidation of palm-kernel oil were simulated. Fig. 2 illustrates the concentration evolution of formic acid (FA), hydrogen peroxide (H_2O_2), performic fatty acid (PFA), water (H_2O), oleic acid (OA) and epoxide (EPOXIDE) in 25 minutes time durations. Initially, the concentration of FA, OA, and H_2O_2 are 2.9428 mol/L while others are zero. It is worth noting that the concentration of FA decreases rapidly until approximately 2 minutes. Then, it is increased slowly until the end of the simulation. Since FA is related to two process reactions (Equation 1 and Equation 2), thus it can act as an oxygen donor in Equation 1 and side product in Equation 2.

While for H_2O_2 and OA concentrations, the concentrations decreasing steadily from its initial concentration. At 25 minutes, the concentration of H_2O_2 and OA are 1.1280 mol/L and 1.4258 mol/L, respectively. Opposite with the PFA concentration, the concentration increases rapidly from 0 to 1.5 minutes to reach the maximum value of 0.76052 mol/L. Then, it reduces progressively to 0.29786 mol/L at 25 minutes.

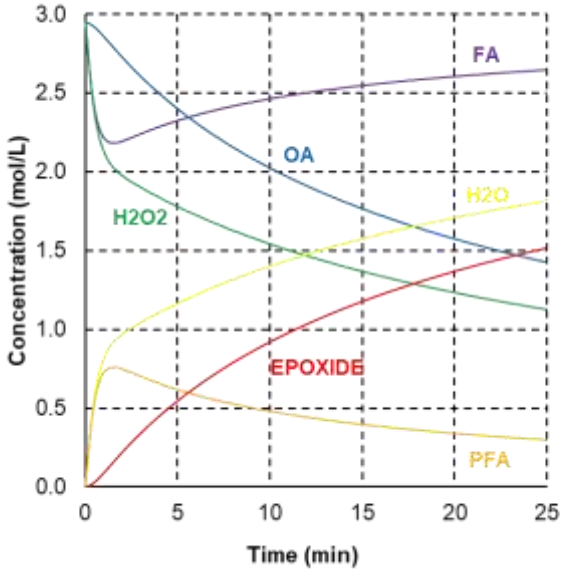

Fig. 2: Evolution of formic acid (*FA*), hydrogen peroxide (H_2O_2), performic fatty acid (*PFA*), water (H_2O), oleic acid (*OA*) and epoxide (*EPOXIDE*) concentration

Rapid progression of H_2O concentration at the beginning of the simulation even though the reverse reaction of k_{12} is higher than the forward reaction of k_{11}. After 1.5 minutes, the concentration of H_2O is slowly increased to 1.8148 mol/L. This is slightly due to the increased PFA concentration resulting in reducing the formation rate of H_2O. It also can be observed from the Fig. 2 that the epoxide is increased slowly from 0 to 1.5169 mol/L after simulation end. Since there is no degradation process of epoxide included in the kinetic model, the concentration of the epoxide will keep increasing until reach a saturation value for subsequent minutes.

4. Conclusions

Epoxidize palm kernel oil has gained great importance in the recent year since it is derived from renewable and sustainable resources. The epoxidation of oleic acid by the performic acid form in situ was used as an example. By developing the kinetic model of palm kernel oil, it was found that the kinetic parameters are k_{11} = 0.1875 mol/L.min, k_{12} = 0.9997 mol/L.min, k_{21} = 0.0625 mol/L.min and k_{22} = 0.0000 mol/L.min. A good agreement was found between the calculated and experimental study of epoxide formation. After 25 minutes, the computed concentration of the epoxide is 1.5169 mol/L.

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