

# Formation of Dihydroxystearic Acid (DHSA) from Epoxidized Palm Oleic Acid by Peracid Mechanism and their Kinetic Study

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## ABSTRACT

*Dihydroxystearic acid (DHSA) is a product derived from a chemical modification of palm oleic acid. Application of these valuable fatty acids can be found in cosmetics, as a thickening agent and as a coating agent for pigments due to its unique structure. This study investigates the effect of a catalyst on epoxidation and the formation of DHSA by peracid mechanism. The epoxidation yield calculated by relative conversion to oxirane (RCO%) with a high yield of 95% achieved. Thereafter, the epoxidized oleic acid was hydrolyzed to produce DHSA. The formation of DHSA was verified by analysed the physicochemical properties using Fourier Transform Infra-red (FTIR). The kinetic model was being conducted to determine reaction rate using Particle Swarm (PS). The result showed that PS obtained a minimum error of 0.2005 and a correlation coefficient,  $r$  of 0.9999.*

**Keywords:** *epoxidation, DHSA, palm oils.*

## **Introduction**

In this progressive new era, the world is narrowed to utilize the potential of renewable sources in developing product synthesis. Alternative substances that can be treated chemically rather than petroleum is fats and oils [1]. One of its options is vegetable oil whereas, it generally have similar or greater properties than petroleum in terms of viscosity, toxicity, flash point, loss of evaporation, and biodegradation for the purpose as a base oil for lubricants [2]. Palm oil produces crude oleic acid which consisted of unsaturated fatty properties, thus assisting the chemical reaction sites for alteration into useful derivatives. Due to the more thermally stable properties than polyunsaturated fats, it is become attractive selections in vegetable oil for producing epoxide [3]. Among the chemical alterations of polyols, epoxidation is the most recommended way for introducing a new reactive group and useful properties. Epoxidized oils have a market demand and are well known in the oleo chemical industry for enhancing the end-product and as an intermediates in chemical reactions [4]. Due to the synthesis of the chemical reaction of epoxide, many inventions related to form new products for many other purposes. The interest was shown to the epoxidation of vegetable oil because of the high content of unsaturated fatty acids, and the process breaks off the double bond then turns it into a reactive oxirane ring. The conversion of the double bond to the main product already produces the epoxide [5]. Catalyst can accelerate the opening of the oxirane ring in the epoxidation process. One of the hydroxyl fatty acids is dihydroxystearic acid (DHSA), a product of the palm oil epoxidation reaction by using a peracid mechanism. Then, the epoxide is goes further to the hydrolysis reaction resulting in 9,10-DHSA [6]. The presence of hydroxyl and carboxyl groups in DHSA paves the way for the generation of any other derivatives [7]. Researchers have proven that the DHSA product can enhance the properties of pigment as well as a thickening agent for developing formulated cosmetic specimens and polymeric applicants [8].

In general, epoxy from petroleum is the most common application in the industry which is non-renewable resources. Nowadays, alternative advances focus on vegetable oils due to their fatty acid content. Moreover, previous investigations of the epoxidation process have not pointed out the kinetic study but particularly focused on epoxide to produce oxirane oxygen content. Hence, further research is needed for design consideration to set up the industry scale of an epoxide. It is necessary to determine the optimum kinetic reaction for epoxidized oleic acid for future researchers as a reference to expand the scope of the study and aspects of improvisation as well. Therefore, the objective of this study is to investigate DHSA formation by using different types of catalysts by determining the physicochemical properties of DHSA. In addition, to identify the best kinetic model of DHSA formation by using Genetic Algorithm or Particle Swarm (PS)

## Material and Method

### Materials

Oleic acid from palm oil (PO) was used as a raw material in this study. Formic acid (99%) and hydrogen peroxide (30%) was used as a reactant. Sulphuric acid was purchased from Sigma Aldrich also same goes for catalysts of alumina and zeolite.

### Methods

Epoxidation of oleic acid is a process reaction between oleic acid, formic acid, and hydrogen peroxide. The raw materials are mixed with molar ratio 1:1:1.5 of oleic acid, formic acid and hydrogen peroxide, respectively. Sulphuric acid is added dropwise into the mixture. Then, the mixture was heated at the optimum temperature of 55°C. This experiment was heated and stir simultaneously at a constant 400 rpm [9]. The sample is taken every 5 minutes after reached the optimum temperature and every 1 hour for DHSA production. The collected sample is then going through titration to calculate Oxygen Oxirane Content. Hydrogen bromide inserts in the burette and sample was mixed with acetic acid and violet blue as an indicator in the conical flask.

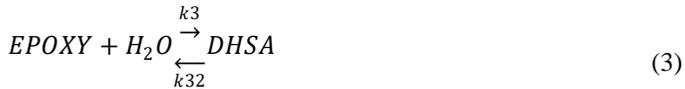
### Determination of physicochemical properties of DHSA

The formation of DHSA is predicted to form after the oxirane ring decreases until zero within 3 hours. A sample was taken to undergo a verification process by identifying their physical and morphological properties. The previous studies have shown a high interest in the habits and morphology of DHSA to introduce this product to consumers [10].

### Numerical modelling of epoxidation of palm oleic acid

*In-situ* epoxidation is characterized by two main reactions involving formation of performic acid and formation of epoxide as illustrated in Equation 1 and Equation 2. The degradation of epoxide thus, formation of DHSA is described in Equation 3.





where formic acid (FA), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), palm fatty acid (PFA), water (H<sub>2</sub>O), oleic acid (OA), and EPOXY are formic acid, hydrogen peroxide, water, oleic acid and epoxide vegetable oil respectively.

## Results and Discussion

### Epoxidation of oleic acid by using a zeolite catalyst

In this study, the catalyst was used to achieve the maximum yield potential for epoxidation reaction. The function of catalyst is to lower the activation energy and increase the reaction rate, which also achieves a high RCO % in a short period of time. The epoxidation experiment was carried out at a moderate temperature of 55 °C, low agitation speed at 400 rpm and different types of catalysts as parameter namely alumina and zeolite. The highest percentage of RCO usually indicated at 25 min of reaction time [11]. Epoxidation process without catalyst was achieved with approximately 88% RCO similar to Jumain [12]. Meanwhile, alumina as an example was the type catalyst that suitable in aqueous hydrogen peroxide to increase epoxide yield. 95% RCO conversion to epoxide is obtained by using alumina in the absence of homogenous acids. Therefore, it is the good alternative to acid catalysts and much cheaper [13]. Other similar features as alumina are zeolite, an organic catalyst to substitute acid catalysts with high conversion to oxirane. The experiment is done in Figure 1 using zeolite in the epoxidation of oleic acid which produced in 95% RCO in 20 minutes. Many pores in a zeolite's open structure are like millions of tiny test tubes in which atoms and molecules are trapped and chemical reactions are easily to occur. Since the pores in a particular zeolite are of a fixed size and shape, zeolite catalysts can work selectively on certain molecules, which is why they're sometimes referred to as shape-selective catalysts. After 35 minutes the graph showed an increase of RCO % until 68.5 then decrease to 38 due to the unreactive took place to the conversion of epoxy group [14]. The uncertain reaction is only up to 40 minutes after all epoxy groups have formed, and the degradation process occur until 60 minutes

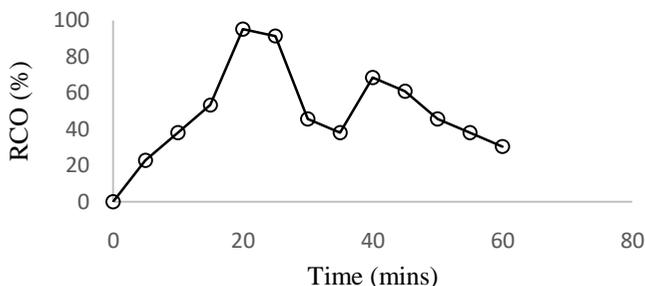


Figure 1: Epoxidation process using zeolite as a catalyst.

### DHSA production based on different catalyst

The epoxidation process conducted earlier was added by water with a 1:1 of molar ratio for hydrolysed product. This reaction is called a hydrolysis reaction where the oxirane ring-opening of the epoxidized oleic acid produces secondary hydroxyl compound O-H to form DHSA. The sample was retrieved every 1 hour of the process to measure the oxygen oxirane content (OOC) for RCO calculation. Figure 2 illustrates the results of RCO % overtime where alumina catalysts took 4 hours to approach zero. Alumina has been proof to be an effective catalyst for the oxirane ring-opening by oxygen-containing and nitrogen-containing nucleophiles which acts as a heterogeneous catalyst that can promote epoxide to undergo hydrolysis [15]. A shorter period to produce DHSA is preferred to reduce operating costs. The zeolite catalyst took 5 hours for the RCO to reach zero which is quite longer compared to alumina. The catalyst performance for selectivity inside the mesoporous order depends on the reactive site where the high polarity of particles reacts to form other functional group such as hydroxyl [16]. The efficiency of zeolite during the epoxidation process may attract unconverted epoxide into the substrate molecules and the hydrolysis reaction prolongs the time to react. A normal reaction without additional catalysts took 8 hours for the RCO to be zero. The reaction rate was slightly slower compared to alumina and zeolite with 22.8% RCO remaining at 3 hours. The cleavage of the oxirane ring initiated the conversion of epoxide to hydroxyl group to produce DHSA. DHSA produced visually appeared as a white and waxy substance.

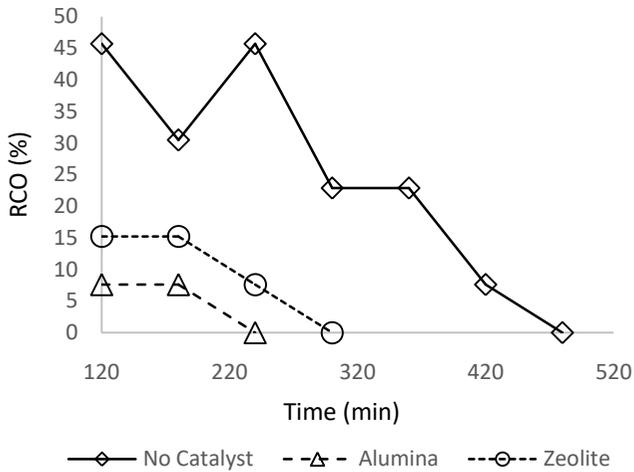


Figure 2: DHSA production from epoxidized oleic acid.

### The physicochemical properties of DHSA

The functional groups of DHSA were identified by the FTIR analysis suggested by previous studies. Figure 3 shown the absorption band at 1200-1500 refers to the carboxyl group. The peak transmission of the C-H bond occurred at 2800-3000 while the hydroxyl group can be observed at 3300-3400  $\text{cm}^{-1}$  of wavenumber. This can be confirmed by referring to other research done by Susetyo [19], Koay [17] and Jumain [15]. The difference between oleic acid and epoxide can be seen clearly at wavenumber 1200-1500  $\text{cm}^{-1}$  in which epoxy groups are formed. This is due to the breakdown of carbon double bond which can be pointed at wavenumber 3000  $\text{cm}^{-1}$ . Meanwhile, the hydroxyl group only can be identified after an absorption band of 1200-1500 epoxy groups is disappeared. DHSA in the hydroxyl group only can be proven when the O-H bond illustrated at 3300-3400  $\text{cm}^{-1}$ .

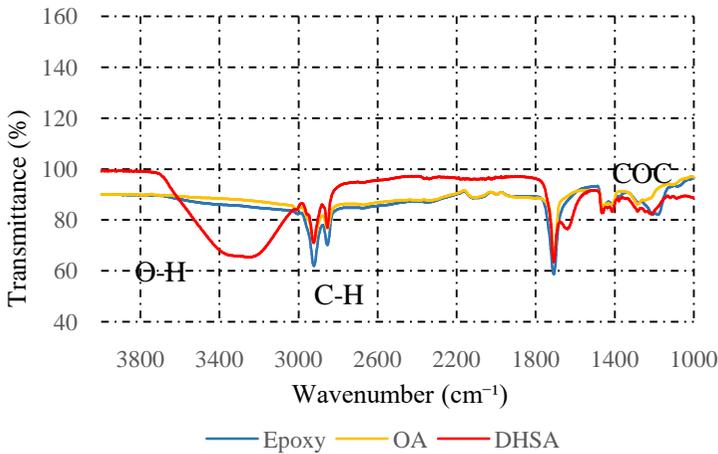


Figure 3: FTIR spectrum of three different samples.

### Optimization of kinetic study

In experiment data, epoxidation of palm oil (PO) fatty acid based on oleic acid was varied with three different temperatures to reach optimum yield. The process was slowly increasing to form an epoxide, due to different phases where the formic acid was partitioned between the oil whereas the hydrogen peroxide was not soluble in oil. According to Jumain [22], high epoxide yield obtained due to the immediate reaction between the double bond in oleic acid chain and performic acid. Moreover, the epoxidation of vegetable oils with performic acid is faster than the one with peracetic acid [16]. The epoxidized PO was also used to study the oxirane cleavage, where hydrogen peroxide, formic acid and water were used to degrade the epoxide itself. In this study, a kinetic model for catalytic epoxidation of palm oleic acid based on palm oil (PO) had been developed by using MATLAB Simulation. The kinetic data for the epoxidation and degradation of the PO corresponded to the initial concentration. Particle Swarm (PS) method was used to fit the experimental data and the Runge-Kutta Fourth Order method was applied using the ODE45 tool to solve the system of the differential equations. The experimental data had been obtained from the previous experiments and the simulation was based on that data. The initial concentration of formic acid (FA), hydrogen peroxide ( $H_2O_2$ ), and oleic acid (OA) from previous experimental data were being chosen as a reference to find the kinetic rate constant,  $k$ . On the other hand, by using the kinetic rate, it was used to determine the concentration of dihydroxy stearic acid (DHSA) in oxirane cleavage. This was occurring when the epoxide reacts with water.

It was corresponding to the objective of this study to find the best kinetic model for epoxidation of palm oleic acid.

Theoretically, the maximum epoxidation reaction takes place about 20 minutes for high RCO conversion. After that, the degradation of the oxirane ring that can observe until it reaches zero. The duration of the experiment was about 480 minutes for three different temperatures to produce the reaction rate and concentration of each reactant and product. Based on Figure 4, there was no difference between PS simulations at 35C to compare with experiment data. The predicted simulation tended to deviate from experimental data. There is an assumption made when to compare the simulated data with the experimental data. Using numerical simulation, it acts as an ideal behaviour. As the operation in MATLAB simulation does not consider the heat loss and heat transfer during the reaction. Besides, it is solely relying on the chemical equation, and the reaction takes place at the same time. Meanwhile, in experimental lab work, any of vaporizing gas cannot be determined.

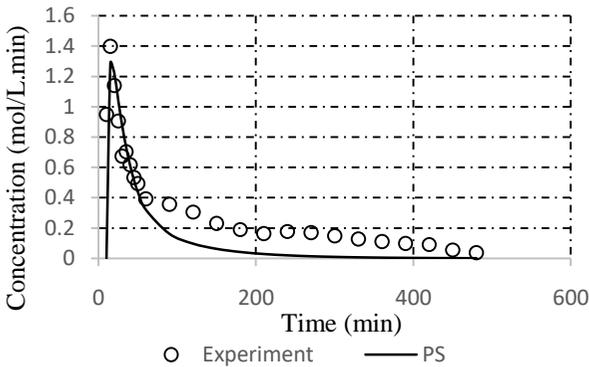


Figure 4: Comparison of epoxy concentration at 35°C.

## Conclusion

The epoxidation of oleic acid with the addition of organic catalysts such as zeolite results in the high conversion of 95% RCO. Conversions are similar to acid catalyst but alternative options using organic compounds are more preferable for industrial applications. Modification of epoxide by hydrolysis reaction leads to the production of DHSA after a long period of time. The estimation for DHSA produce is when the RCO reaches zero based on theoretical studies. The production period of DHSA is shortened with the assistance of organic catalysts such as alumina and zeolite. Comparison without added catalyst is 8 hours while organic catalyst only takes 5 hours to

reach zero. DHSAs validation is performed by analysing the physicochemical properties using, and FTIR. The functional group of each compound such a stearic group is classified using FTIR to distinguish with epoxide and oleic acid. Moreover, this study involved the selection of best kinetic models for epoxidation oleic acid. The method used was PS to solve the differential equations using the ODE 45 Runge Kurta method. This study found that PS resulted in a fittest solution between experiment and simulation with a minimum error of 0.2005. The correlation coefficient,  $r$  is 0.9999 which is suitable as a reference for further kinetic study.

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## **References**

- [1] E. Sharmin and F. Zafar, "Preparation of Epoxidized Palm Olein As Renewable Material By Using Peroxy Acids," *Polyurethane*, vol. 63, no. 3, pp 259–264, 2012.
- [2] E. Purwanto, "The Synthesis of Polyol From Rice Brand Oil (RBO) Through Epoxidation and Hydroxidation Reactions," *Thesis Master*, 2010.
- [3] M. E. Norhaizan, S. Hosseini, S. Gangadaran, S. T. Lee, F. R. Kapourchali, and M. H. Moghadasian, "Palm oil: Features and applications," *Lipid Technol.*, vol. 25, no. 2, pp 39–42, 2013.
- [4] B. Nagendran, U. R. Unnithan, Y. M. Choo, and K. Sundram, "Characteristics of red palm oil, a carotene- and vitamin E-rich refined oil for food uses," *Food Nutr. Bull.*, vol. 21, no. 2, pp 189–194, 2000.
- [5] M. J. Jalil, A. F. M. Yamin, I. S. Azmi, S. K. Jamaludin, and A. R. M. Daud, "Mechanism and Kinetics Study in Homogenous Epoxidation of Vegetable Oil," vol. 7, pp 124–126, 2018.
- [6] P. Czub and I. Franek, "Epoxy resins modified with palm oil derivatives - Preparation and properties," *Polimery/Polymers*, vol. 58, no. 2, pp 135–139, 2013.
- [7] R. Ismail, R. Awang, and A. H. Hazimah, "Palm dihydroxystearic acid (DHSAs): A multifunctional ingredient for various applications," *J. Oil Palm Res.*, vol. 27, no. 3, pp 195–211, 2015.
- [8] O. Of, "Chemical Modification of Epoxidized Palm Oil for Biolubricant Application," *Malaysian J. Anal. Sci.*, vol. 21, no. 6, pp 1423–1431, 2018.
- [9] M. J. Jalil, A. F. M. Yamin, S. H. Chang, I. S. Azmi, N. Morad, and A. Hadi, "Selective epoxidation of crude oleic acid-palm oil with in situ

- generated performic acid,” *Int. J. Eng. Technol.*, vol. 7, no. 4, pp 152–155, 2018.
- [10] G. F. L. Koay, T. Chuah, S. Zainal-abidin, S. Ahmad, and T. S. Y. Choong, “Development , Characterization and Commercial Application of Palm Based Dihydroxystearic Acid and Its Derivatives: an Overview,” vol. 265, no. 5, pp 237–265, 2011.
- [11] N. Mohamed, J. Jalil, S. K. Jamaludin, A. Rafizan, and M. Daud, “Epoxidation of Palm Oil-Based Oleic Acid at Low Agitation Speed.”
- [12] M. Jumain Jalil “Synthesis of Epoxidized Oleic Acid- Based Palm Oil by Peracid Mechanism,” *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 551, no. 1, 2019.
- [13] J. Sepulveda, S. Teixeira, and U. Schuchardt, “Alumina-catalyzed epoxidation of unsaturated fatty esters with hydrogen peroxide,” *Appl. Catal. A Gen.*, vol. 318, pp 213–217, 2007.
- [14] M. A. Kadi, N. Akkouche, S. Awad, K. Loubar, and M. Tazerout, “Kinetic study of transesterification using particle swarm optimization method,” *Heliyon*, vol. 5, no. 8, pp e02146, 2019.
- [15] A. Rafizan, M. Daud, N. Mohamed, J. Jalil, and S. K. Jamaludin, “Formation of Dihydroxystearic Acid from Hydrolysis of Palm Kernel Oil Based Epoxidized Oleic Acid,” *J. Appl. Sci. Agric. J. Appl. Sci. Agric.*, vol. 9, no. 911, pp 86–92, 2014.
- [16] B. M. Abdullah and J. Salimon, “Epoxidation of vegetable oils and fatty acids: Catalysts, methods and advantages,” *J. Appl. Sci.*, vol. 10, no. 15, pp 1545–1553, 2010.
- [17] G. F. L. Koay “Crystallization of dihydroxystearic acid (dhsa) produced from commercial grade palm oil based crude oleic acid employing isopropyl alcohol as solvent,” vol. 3, no. 1, pp 115–124, 2006.
- [18] G. F. L. Koay, C. T. Guan, S. Zainal-Abidin, S. Ahmad, and T. S. Y. Choong, “Habit and morphology study on the palm-based 9,10-dihydroxystearic acid (DHSA) crystals,” *Mater. Chem. Phys.*, vol. 114, no. 1, pp 14–17, 2009.
- [19] M. Ni, F. Fong, and J. Salimon, “Epoxidation of Palm Kernel Oil Fatty Acids” *Journal of Science and Technology*, vol. 4, pp 87–98, 2012.
- [20] O. Of, “Palm Oil-Based Precursors for Development of Polymeric Delivery System,” *Malaysian J. Anal. Sci.*, vol. 21, no. 2, pp 496–511, 2017.
- [21] Y. B. Tee, R. A. Talib, K. Abdan, N. L. Chin, R. K. Basha, and K. F. Md Yunos, “Comparative study of chemical, mechanical, thermal, and barrier properties of poly(lactic acid) plasticized with epoxidized soybean oil and epoxidized palm oil,” *BioResources*, vol. 11, no. 1, pp 1518–1540, 2016.
- [22] M. J. Jalil, N. Mohamed, S. K. Jamaludin, A. M. Som, and A. R. Mohamad Daud, “Epoxidation of Palm Kernel Oil-Based Crude Oleic Acid,” *Adv. Mater. Res.*, vol. 906, no. November, pp 125–130, 2014.