

# Study on the Kinetics of Epoxidation Reaction of RBD Palm Olein

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**Study on the Kinetics of Epoxidation Reaction of RBD Palm Olein**

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**Abstract.** This research aimed at studying the effect of reaction time, temperature and the type of catalyst on oxirane number and determining reaction kinetics data. There were two types of catalysts used were bentonite and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). The epoxidation reaction was done in-situ using hydrogen peroxide, acetic acid and benzene with bentonite and H<sub>2</sub>SO<sub>4</sub> into the RBD palm olein to form epoxidized RBD palm olein. The main equipment used in this research was a 500 mL three-necked flask, equipped with a reflux condenser, thermometer, water bath and magnetic stirrer. The product was analysed of % of oxirane using a titration method. The results of this research showed that bentonite catalysts was optimally working at the temperature of 70°C for 4 hours with an oxirane level of 1.02%, while H<sub>2</sub>SO<sub>4</sub> was optimally working at the temperature of 60°C for 3 hours with oxirane level of 2.31%.

**Keywords:** RBD palm olein, catalyst, epoxidation, oxirane number, kinetics of reaction

## 1. Introduction

Unsaturated fatty acids of RBD palm olein are capable of epoxidation reaction. In this epoxidation reaction, the opening of double bonds into epoxide groups occurs. The epoxides of petroleum and vegetable fatty acids are commercial products primarily used as polyvinyl chloride (PVC) stabilizers and other polymers and as intermediates on the preparation of biolubricant, detergent and polyurethane [1,2]. Generally, epoxidation of triglycerides is using hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). The nature of H<sub>2</sub>O<sub>2</sub> as an oxidizing agent is not strong enough so it should be transformed into other form which is more active such as peroxy acid in in-situ process. Epoxidation method with percarboxylic acids is commonly developed to produce a clean and efficient process that can be accelerated using catalysts [3,4]

Epoxidation reaction is a catalytic reaction. The use of sulfuric acid catalyst in epoxidation reaction has been studied by several researchers because of its low cost and it is also quite effective to be catalyst [3,4]. The use of sulfuric acid as catalyst can facilitate the occurrence of oxirane ring degradation. In this study the catalysts used were bentonite and H<sub>2</sub>SO<sub>4</sub>. Benzene as solvent is used to prevent the degradation of the oxirane ring during the reaction process. This study aimed at studying the effect of both time and temperature of reaction and the type of catalyst on the percentage of oxirane and determining the reaction kinetics data. The catalysts used were bentonite and H<sub>2</sub>SO<sub>4</sub>. The results of this study were expected to provide information about kinetics data and conditions of epoxidation operation so that it can be used in the design of epoxidation reactors and control of such operations



**2. Experimental Method**

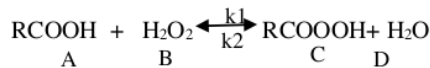
The main raw materials used were palm oil that had been through the process of RBD (Refine, Bleached and Deodorized). Other materials used were sulfuric acid, glacial acetic acid, bentonite, hydrogen peroxide, benzene, aquades and so on.

RBD palm olein was reacted with peroxy acetic acid consisting of glacial acetic acid, hydrogen peroxide, benzene and sulfuric acid / bentonite ascatalyst at 50-70°C and 0- to 4-hour reaction time. The reaction generated oil which was analyzed to determine the % of its oxirane.

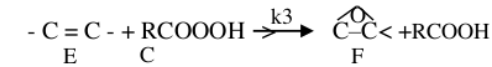
*2.1 Kinetics of Epoxidation Reaction*

Steps of epoxidation reaction [5]:

Step I: Formation of Peroxyacetic acid (fast reaction)



Step II: Epoxidation reaction (slow reaction)



Based on the reaction equations mentioned above, we can form equation of kinetics of the reaction as follows:

$$\frac{dC_A}{dt} = -k_1 C_A C_B + k_2 C_C C_D + k_3 C_C C_E \dots (1)$$

$$\frac{dC_B}{dt} = -k_1 C_A C_B + k_2 C_C C_D \dots \dots \dots (2)$$

$$\frac{dC_C}{dt} = k_1 C_A C_B - k_2 C_C C_D - k_3 C_C C_E \dots (3)$$

$$\frac{dC_D}{dt} = k_1 C_A C_B - k_2 C_C C_D \dots \dots \dots (4)$$

$$\frac{dC_E}{dt} = -k_3 C_C C_E \dots \dots \dots (5)$$

$$\frac{dC_F}{dt} = -k_3 C_C C_E \dots \dots \dots (6)$$

Equations (1)–(6) are solved simultaneously using Runge-Kutta method. Furthermore, the value of parameter  $k_3$  is determined by using SSE minimization

$$SSE = \sum_{n=0}^n ([F]_{data} - [F]_{count})^2 \dots (7)$$

To obtain the value of activation energy ( $E_A$ ) and frequency factor ( $A$ ), the following Arrhenius equation was used:

$$k = A e^{-E_a/RT} \dots \dots \dots (8)$$

$$\ln k = \ln A - \frac{E_a}{R} \frac{1}{T} \dots \dots \dots (9)$$

The value of  $E_a$  would be obtained from the graph of the relationship between  $\ln k$  as and  $1/T$

### 3. Results And Discussion

#### 3.1 Effect of Reaction Time on Epoxidation Results (% of Oxirane)

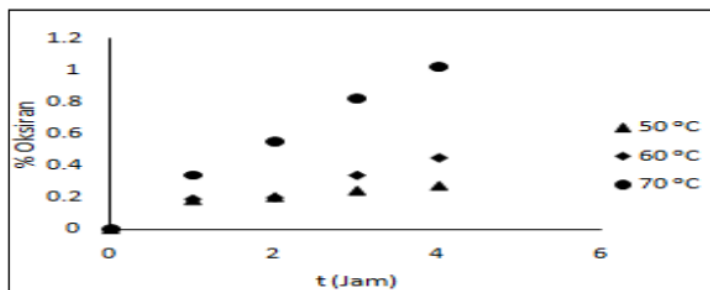


Figure 1. The effects of time and temperature on % of Bentonite as catalyst

Figure 1 shows that optimum content of oxirane of 1.02% was obtained at the temperature of 70°C and 4-hour reaction time. This was due to the lack of H<sup>+</sup> ion in bentonite so that the process of degradation inhibition by benzene could take place efficiently.

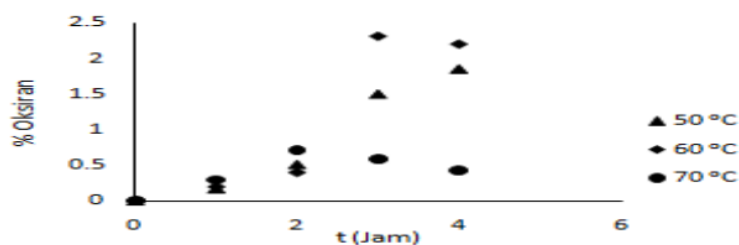


Figure 2. The effects of time and temperature on % of H<sub>2</sub>SO<sub>4</sub> as catalyst

Figure 2 shows that at 60°C, the % of oxirane obtained achieved the highest value at 3-hour reaction time, that is, of 2.31%. The longer the reaction time the more the chances of reaction molecules to collide with each other. The degradation of oxirane groups occurring during the epoxidation reaction was also due to the presence of acetic acid derived from the reaction of the formation of a reversible peroxy acetate acid. Acetic acid and H<sub>2</sub>SO<sub>4</sub> were able to perform side reactions i.e. ketone compounds [6]. The longer the reaction time the greater the degradation of oxirane. This was in line with previous researches [7,8]. The addition of benzene in the reaction would minimize oxirane degradation so that more oxirane would be formed.

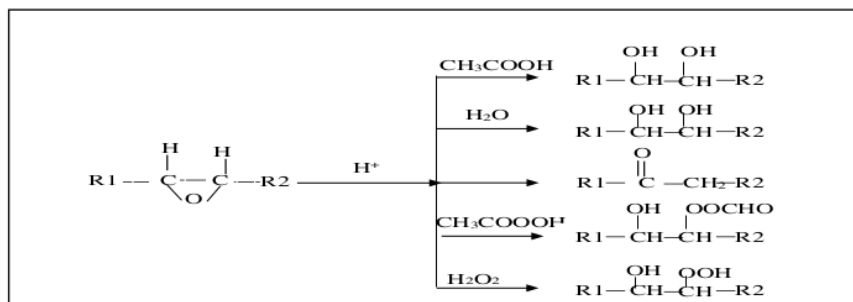


Figure 3. Reaction of Oxirane Ring Degradation by Acids [5].

From the data obtained it can be concluded that the value of oxiran number produced by using bentonit as catalyst was lower instead of using H<sub>2</sub>SO<sub>4</sub> (homogeneous catalyst). This was because H<sup>+</sup> ion of H<sub>2</sub>SO<sub>4</sub> could move freely so that it worked more optimum than bentonite catalyst. This results were similar to the results of a research conducted by [9] using a Ni catalyst in the epoxidation reaction of methyl oleate. The best reaction results were obtained at a catalyst concentration of 20%, (reaction temperature at 70°C, and 4-hour reaction time with a measured oxirane number of 1.24. An earlier study used Amberlit IR-120 with an oxirane number of 1.15% using Cell Suspension of *Methylosinus trichosporium* IMV 3011 with epoxythane 1.6% [10].

### 3.2 Determining Parameter of Kinetics of the Reaction

The kinetics of reaction is based on the velocity of the epoxy compound formation expressed in% of oxiran. The epoxidation reaction order at each temperature and type of catalyst is a pseudofirst order. This is in line with the research [11].

Added CH<sub>3</sub>COOH serves to oxidize the double bonds present in the sample added excessively so that the concentration of the peroxyacetic acid is constant during the course of the reaction. This illustrates that the reaction rate does not seem to depend on [C], so the reaction seems to be the order of 0 for [C], order 1 for [E] and order 1 for the whole orders.

Based on the result of calculation which have been done by using equation (1) to (6) we get the rate constants of k<sub>3</sub> at various temperature as presented in Table 1.

**Table 1.** Rate Constante Each Time and Temperature Change for each Catalyst

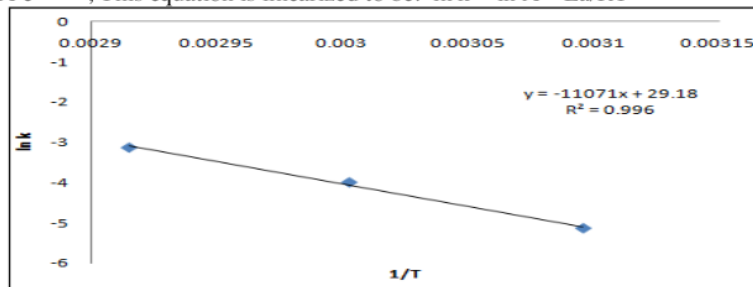
T (°C)	T (K)	k (h <sup>-1</sup> )	
		Bentonite	H <sub>2</sub> SO <sub>4</sub>
50	323	0.005934	0.351592
60	333	0.018487	0.388819
70	343	0.043688	3.443214

From Table 1 it can be seen that the value of k is produced from the epoxidation reaction using a catalyst, both catalysts tend to increase in accordance with the amount of % of oxirane obtained.

### 3.3 Calculating the Activation energy and frequency factor

From the data of reaction rate constants, the values of A and Ea can be calculated based on Arrhenius equation: as follows

$$k = A e^{-E_a/RT}, \text{ This equation is linearized to be: } \ln k = \ln A - E_a/RT$$



**Figure 4.** Relationship between 1 / T and ln k for bentonite catalyst

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