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Premilinary Results: Heterogeneous Reaction of Epoxidation Palm Kernal Oil

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Abstract

The epoxidized vegetables oils can be used a raw material for a broad range of products, from pharmaceutical and plastics to paint and adhesives. Epoxidation of oleic acid was carried out by using hydrogen peroxide as an oxygen donor and formic acid as an oxygen carrier in the presence of sulphuric acid act as catalyst. The crude oleic acid contained 75% oleic acid, 12.2% linoleic acid, 6.5% palmitic acid and 7.5% stearic acid, and had an iodine value of 98.99 g/100 g. The epoxidation of oleic acid with almost complete conversion of unsaturated carbon and negligible oxirane cleavage can be obtained by the *in situ* techniques. An analytical approach for the prediction of the partition coefficient for formic acid between oleic acid and water, dependent on temperature and composition, has been proposed.

Keywords: Oleic acid, epoxidation, partition coefficient, heterogeneous system

1.0 INTRODUCTION

Vegetable oil can be epoxidized, as they consist of unsaturated double bond of fatty acid [1]. Produces epoxides are valuables as intermediates for resin, as paint and coating components, as well as the plasticizers and stabilizers for poly(vinylchloride) [2]. The epoxidation is carried out by reacting the double bonds of the oils with peroxyacid (generally peroxyacetic or peroxyformic acid) generated in situ by reacting concentrated hydrogen peroxide with formic acid in the present of a mineral acid as catalyst [3]. A small amount of sulphuric acid is necessary to catalyze the oxidation of the formic acid to the corresponding performic acid. Four technologies are used to produce epoxides from vegetable oils: (i) epoxidation with molecular oxygen catalyzed by silver (ii) epoxidation with halohydrin using hypohalous acids (HOX) and their salts (iii) epoxidation with organic and inorganic peroxides catalyzed by transition metal catalyst (iv) epoxidation using percaboxylic acid, which is widely used in industry by acid or by enzymes [4].

Base on previous investigation, epoxidation with halohydrins are prepared by the addition of HOX to olefinic compounds and subsequent is not wise choice since this is a highly environmental-unfriendly reaction system [5]. This is due to classical stoichiometry synthesis that is characterized by an extensive use of reactant and the production of by-products such as dihalides, halogen, ether and salts [6]. Other than that, epoxidation with molecular oxygen catalyzed by silver is rendered as the cheapest and greenest route, since oxygen is cheap oxidant with no waste management problems [5]. However, this method limited to as small number of simple petrochemicals such as ethylene and butadiene, evidenced by low yield in the case of other alkenes [7]. Epoxidation with molecular oxygen that are catalyzed by compounds of elements belonging to group IV-B, V-B and VI-B show high selectivity but low activity. With elements from group I-B, VII-B and VIII-B the epoxidation are more active but less selective. Silver is a unique catalyst for heterogeneous epoxidation with molecular oxygen but unfortunately it is mostly restricted to a few substrates such as ethylene and butadiene.

Until now publish kinetic models of the system for epoxidation of oils, fatty acids and their ester can be classified into two groups; approximate and rigorous [8]. In the first group of models, in which the mixture of oil and water considered as a single phase (homogenous models), the overall concentration of components was used [9]. In the second group the local concentration of components in the oil and water phase were introduces in the modeling. The rigorous models contain more parameters such as rate constants, chemical equilibrium constant, and partition coefficient between phases, mass transfer and

interfacial areas. For this reason, the purpose of this paper is for studies on epoxidation of oleic acid with provided preliminary result for reaction kinetic of heterogeneous system of epoxidation.

2.0 METHODOLOGY

2.1 Material

Crude oleic acid was purchased from Chung Chemical Sdn. Bhd. Aqueous hydrogen peroxide (30%), formic acid, sulfuric acid, sodium hydroxide and phosphorus acid were all purchased from Merck Sdn. Bhd.

2.2 Methods

Oleic acid, formic acid and sulphuric acid was added into a reactor and temperature was raised until stabilized. The hydrogen peroxide was then added drop by drop at room temperature while stirring continues. After preselected time intervals, 5-ml samples were taken out of the reactor determine the reaction advance. The detailed methodology has been shown in a previous study [10]. Iodine value of the crude oleic acid sample was calculated based on Eq. 1 in accordance with AOCS Official Method C Id-92:

$$\text{IV (g } I_2\text{/100 g sample)} = \frac{(B-S)\text{x } N_{Na2s2o3} \text{ x } 12.69}{\text{mass of crude oleic acid,g}} \quad (1)$$

where B = volume of titrant for blank (mL), S = volume of titrant for sample (mL) and $N_{NA2S2O3}$ = normality of sodium thiosulphate solution.

Partition coefficients for formic acid between oil and water was measured by mixing different amounts of oil, water and formic acid in glass-stopper Erlenmeyer flask. The Erlenmeyer was placed in a shaker bath, which had temperature control. After 3h of mixing, the shaking was stopped and the aqueous and oil phases were allowed to separate at the desired temperature. Each sample was titrated with sodium hydroxide with used phenolphthalein as indicator.

3.0 RESULTS AND DISCUSSION

3.1 Iodine test

Analytical method was conducted with the objective to measure the iodine value (IV) of the raw material used in the reaction, crude oleic acid (Palmac 770). Iodine value determined the degree of unsaturation of fatty acid reacted with iodine compound [11]. It is measured in term of grams of iodine absorbed per 100g of sample (g I_2/100 g sample). The results are shown in Table 1. With high iodine value, it shown oleic acid sitbale use as raw meterials for production of epoxide.

Table 1. Iodine value of crude oleic acid (Palmac 770)

Run 1	B (mL)	S (mL)	$Na_2S_2O_3$	Oleic Acid	Iodine Value
1	3.7	1.95	0.980	0.224	97.150
2	3.7	1.9	0.980	0.210	106.60
3	3.7	2.05	0.980	0.220	93.320
Average Iodine Value					98.99

3.2 Partition Coefficients

An analytical approach for the prediction of the partition coefficient for formic acid between oleic acid and water dependent on the temperature and composition has been proposed. For those working system, the partition coefficients for formic acid increases with the increases the temperature as mentioned in previous work. During oil extraction from the formic acid compound are distributed between the oil and aqueous phases. It is important to determine the partition coefficients of these compounds on oil/water mixtures because their concentration has beneficial affect on the stability and properties of the oil. Then the process will be continue with polols production after epoxidation with aadding of hydroxyl group besouse the cost is unexpensive and have good effectiveness. The results are shown in Table 2.

Table 2. Partition coefficient values of formic acid determined experimentally

Temp. (C°)	Calculated coefficient formic acid Mixture			
		Reading 1	Reading 2	Mean
35	E1	0.55	0.56	0.555
	E2	0.62	0.59	0.603
	E3	0.65	0.62	0.635
55	E1	0.59	0.51	0.546
	E2	0.62	0.533	0.577
	E3	0.56	0.68	0.628

[a] E1, E2 and E3 mixtures of oleic acid, formic acid and water were of the following composition given in: 100.0, 13.8 and 107.1; 100.0, 20.6 and 107.1; and 100.0, 27.6 and 107.1, respectively

4.0 CONCLUSION

The result from this study shows that the epoxidation was carried out at moderate temperature (55 °C) with the minimum epoxide degradation. Iodine value are best parameters to identify tha pyscical characterization of epoxide based palm oil since most the epoxide useful for lubricant and cosmetic products. The kinetic parameters vary with temperature and useful for the scale-up production of epoxidized oleic acid using the *in situ* technique.

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