International Journal of Engineering & Technology, 7 (4.40) (2018) 152-155

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper

Selective Epoxidation of Crude Oleic Acid-Palm Oil with *in situ* Generated Performic Acid

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Abstract

The potential utility of epoxidized vegetables oil has begun to be realized in industrial application with increasing the concern of research to develop value added products from the available vegetables oil. Epoxidized oleic acid is often regarded as a high value oleochemical due to wide range of industrial applications including cosmetic, lubricants, painting and as chemical precursor. For safety reason epoxidation of oleic acid using peracid formed *in situ* by reacting a carboxylic acid with concentrated hydrogen peroxide (H_2O_2) was selected. The aim of this study is to optimize the epoxidation of oleic acid of palm oil. The method was evaluated on different parameters such as oxygen carrier, concentration of catalyst as well as different type of vegetables oil. The optimum relative conversion to oxirane (86%) was achieved for 20 minutes of reaction time. From the findings formic acid is a good oxygen carrier for *in situ* epoxidation. Epoxidation results were based on complete conversion oxirane, rate of epoxidation and stability of the oxirane. This study shown oleic acid was succefuly transformed into epoxide and oleic acid derived from palm oil potential raw material for production of sustainable and friendly epoxide.

***Keywords**: Epoxidation, oleic acid, vegetable oils, palm oil, oxirane content*

1. Introduction

In recent years, renewable material such as vegetable oil has attracted great interests due to the environmental pollution concerns and increasing cost of fossil fuels. The traits of vegetables oil, such as cost-effectiveness and eco-friendliness to environment makes them as an alternative for the production of epoxide. In Malaysia, the crude palm oil production for 2017, rose from 17.32 million to 19.92 million [1]. Studies in the area of reaction condition, optimization for improvement in yield and selectivity of epoxidized oleic acid are lacking. Apart from this unsaturated fatty acid from palm oil was selected to maximize the form of the epoxy group. Due to oleic acid characteristic which more thermally stable than polyunsaturated fats, they are enormously favored components in vegetables oils in producing epoxide.

The epoxidation uses vegetables oil because of high content of unsaturated fatty acids, and the process breaks the double bond by trans-forming into more reactive oxirane ring [2]. The double bond itself are converted to main product which is epoxide itself. Palm oil primarily based on crude oleic acid is contained a certain degree of unsaturation, accordingly offered the chemical reaction sites for further changes to provide diverse useful derivatives. Due to characteristic which more thermally stable than polyunsaturated fats, they are enormously favored components in vegetables oil which are suitable in producing epoxide.

The oils and fats containing long chain fatty acid (C18 and above) such as palm oil, soybean, rapeseed and sunflower as well as animal fats like tallow are used for application in the polymer, lubricant and cosmetics product [3]. Thus modification of basic oleochemical gives rise many advantages for oleochemical and numerous application in industry.

One of the primary markets for epoxidized vegetable oils is a plasticizer and hydrogen chloride acceptors for use in plastic materials mostly polyvinyl chloride (PVC). As PVC exposed to heat and light, HCI evolved which cause the development of undeniable color and rapid deterioration of the polymer. Plasticizers are additives integrated into rigid polymeric material to improve their flexibility, workability and dispensability thereby increasing the plastic utility in numerous application.

2. Material and Method

2.1 Materials

Palm oleic acid (87%), hydrogen peroxide (30%), formic acid, acetic acid, sulphuric acid and nitric acid employed were supplied by Qrec (Asia) Sdn. Bhd. and were used as received

2.2 Method

The epoxidation procedures were similar to those described in our previous work [4]. Initially, a mass of 100 g of palm oleic acid was mixed with a specific molar ratio of formic acid to oleic acid in a 500-mL three-neck round-bottom flask which was equipped with a magnetic stirrer, a thermometer, and a reflux condenser, and was immersed in a thermostatic oil bath.

The experimental oxirane oxygen content (OOC_{exp}) was determined using AOCS Tentative Method Cd 9-57. The equation used to calculate the experimental oxirane oxygen content (OOC_{exp}), in moles/100 g is shown in Equation 1

$$OOC_{\exp} = \frac{T \times N_{HBR} \times 1.6}{W}$$

where, T is the volume of hydrogen bromidein mL that is required to titrate the sample, N_{HBR} is the normality of the hydrogen bromide and W is the weight of the sample in grams. Equations 1, were used to calculate the relative percentage conversion to oxirane (RCO)

$$RCO = \frac{OOC_{\exp}}{OOC_{the}} \times 100\%$$

where OOC_{the} is the theoretically obtainable maximum oxirane oxygen and was determined to be 1.8213. the stock of epoxidized oleic acid was prepared early to further analyse with ring opening by hydrolysis.

3. Result and Discussion

3.1 Effect of oxygen carrier on the rate of reaction

Their influences on the epoxidation of oleic acid are shown in Fig. 1. It shall be noted that epoxidation can be carried out using either formic acid or acetic acid [5]. It is quite common for these peracids to be used in solvent or solvent free systems but conditions must be carefully controlled for the solvent free epoxidation method as it is typical for the epoxide to be ring opened without the solvent [3]. It can be seen from Fig.1 that the maximum yield of epoxide was achieved when formic acid was used as the oxygen carrier compared to acetic acid. It is likely that the high epoxide yield obtained was due to the immediate reaction between the performic acid formed with the C=C double bonds in the oleic acid chain as well as minimization of oxirane ring degradation [6]. Formic acid participates in the reaction in two capacities which is as a catalyst in the formation of oxirane ring and as a reactant in the hydrolysis of oxrane ring [7]. According to Jalil *et al.,*(2017) [8] formic acid has the ability to minimize oxirane ring-opening by preventing the deprotonation of performic acid. Nevertheless, should the *in situ* performic acid concentration becomes too high, it will contribute to a strong acidic condition which causes severe loss of epoxide by ring opening route. Selection of oxygen carrier does not only affect the rate of conversion to oxirane, but also the stability of oxirane produced [5]. Furthermore, it clearly shown that optimum reaction time to achieved highest Relative Conversion to Oxirane (RCO%) for formic acid was at 20 minutes while acetic acid at 25 minutes. Nevertheless, should the *in situ* performic acid concentration becomes too high, it will contribute to a strong acidic condition which causes severe loss of epoxide by ring opening route

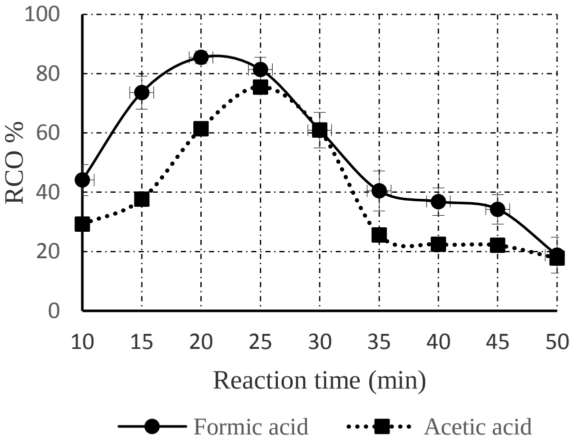

Fig.1: Effect of formic acid and acetic acid on epoxidation

3.2 Effect Catalyst Loading

In this study, the sulphuric acid concentration was varied from 0.25 to 1.0 g and the results are illustrated in Fig 2. Clearly, the rate of epoxidation reaction increases with an increase in sulfuric acid loading. It is also apparent that high RCO (~86%) was achieved at a shorter reaction time using 0.5g sulfuric acid. Increasing the catalyst loading to 1.0g resulted in higher epoxidation rate but lower RCO at around 70%. This result is noteworthy when compared to the findings of Campanella *et al.,* (2008) [9] who investigated the epoxidation of fatty acid methyl esters by *in situ* performic acid without the addition of catalyst. The results of Campanella *et al.,* (2008) [9]showed a conversion to oxirane of 83.5% at 40 °C was only achieved after a reaction time of 600 minutes. In contrast, the maximum conversion to oxirane was attained within 20 minutes at 75 °C in this study. This shows extra hydrogen ions from the external acid catalyst can affected to the increase in an oxirane ring formation.

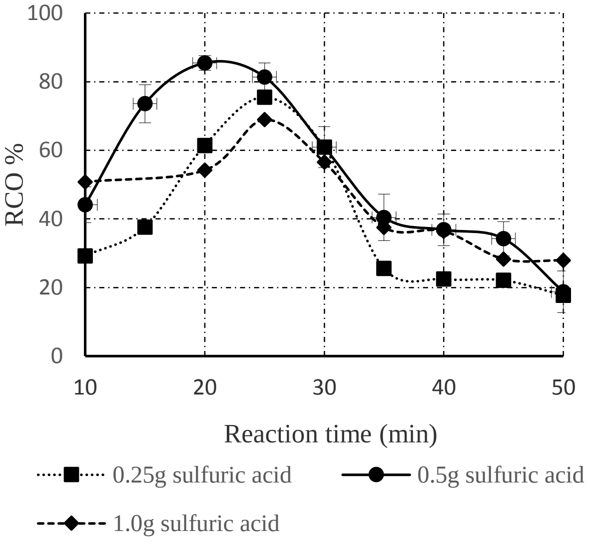

Fig.2: Effect of catalyst concentration on epoxidation

3.3 Comparison studies of epoxidation of Jatropha curcas oil and palm olein

Jatropha oil with containing 44.7% oleic acid and 32.4% linoleic acid was epoxidized in situ with optimum condition of epoxidation with presence of sulfuric acid as catalyst as stated from the previous researcher [10]. From the Fig 3. it's clearly shown that by using jatropha oil as raw material its take long time to achieve higher percentage of RCO. The result complied with work from

Valibhav (2010) et al [7] showed a conversion to oxirane of 78.5% at 30 °C was only achieved after a reaction time of 4 hours. It is believed that vegetables oil is more complicated than single fatty acid since epoxidized product more diverse. Thus epoxidized oleic acid increases reaction time and selectivity [11]. Palm olein is liquid fraction of palm oil consist of mainly mono-unsaturated triacylycerol (42.8%) and di-unsaturated triacylgyecerol (35.7%). Base on optimum reaction condition study by Darfizzi et al (2009) [12], a high yield of oxygen content value was obtained after 4 hour. It can be concluded that, the selection of vegetables oil is most significant factor for the production of epoxide based vegetables oil.

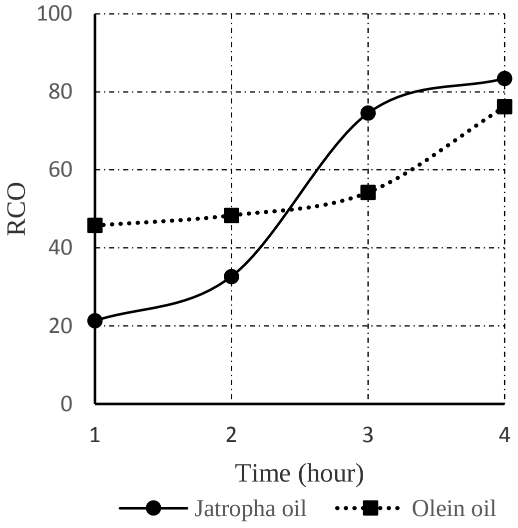

Fig.3: Various type of vegetables oil on epoxidation

3.4 Hydrolysis of Epoxidized Oleic Acid

By hydrolysis reaction of epoxidized palm oleic acid, a high-value hydroxyl fatty acid called dihydroxystearic acid (DHSA) is produced. DHSA ($C_{18}H_{36}O_4$) is also known as glycolic stearic acid that contains two alcohol groups a carboxylic group in a long hydrocarbon chain [13]. DHSA is derived from *in-situ* epoxidation of the unsaturated fat in the palm oil with peracetic acid in the presence of catalyst followed with hydrolysis of the epoxide with hydrogen donor such as water. DHSA has been used widely in industry nowadays, as primary and secondary emulsifiers, pigments coating agents and oil gelling agent in cosmetic formulation [14].

DHSA is produces by reacting the epoxidized palm olein with water in the presence of catalyst [13]. This reaction is called hydrolysis reaction where oxirane ring opening of the epoxidized palm olein is done to produce crystal-like solid DHSA. From the epoxidation process done earlier, the epoxidized oil with H_2SO_4 as catalyst and reaction temperature of 75^{o}C is suitable to be chosen to produce DHSA. Epoxidized palm oil is reacted with distilled water with presence of alumina as catalyst and heated at 60^{o}C. Figure 4.3 shows the RCO% of the hydrolysis reaction for 5 hours.

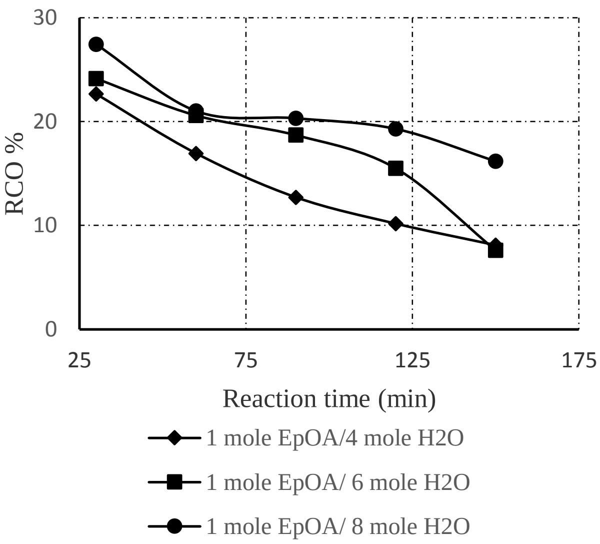

Fig. 4: RCO% of the Hydrolysis Reaction for Synthesis of DHSA

Based on Figure 4, the percentage of RCO is decreasing with time. After 5 hours, the RCO is decreasing to 16.10%. The progress of the hydrolysis reaction was followed by measuring the RCO and considered as complete when the RCO approaches zero but after 5 hours the RCO is not approaching zero yet [8]. For chemical characteristic, conversion of palm oil to DHSA resulted in lower iodine value (IV) because of conversion of unsaturated fat to saturated fat and higher hydroxyl value (OHV) because of formation of hydroxyl group [14]. It can be concluded that hydrolysis need to takes longer time to decreasing the RCO to zero. The finding also shown DHSA production is depend on the mole oh water used. This is indicated that the the mola ratio to epoxidized oleic acid need to consider for production of DHSA in term of time consuming or costing.

4. Conclusion

The potential utility of epoxidized oleic acid has begun to be realized in industrial application with increasing the concern of research to develop value added products from available vegetables oils. The studies revealed the importance of the technological parameters in manufacturing palm oil epoxides. A compilation of the variation ranges of parameters determining the highest values of conversions indicates the area of common parameters; type of oxygen carrier, type of vegetables oils and catalyst loading. In this study, oleic acid based palm oil was successfully produced with high oxirane contents.

Acknowledgement

The authors would like to thank the Ministry of Education Malaysia and IRES with registration number is 600-IRMI/PTB 5/3 (016/2017).

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