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Synthesis of Bio Epoxide from Sunflower Oil by In Situ Epoxidation

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ABSTRACT

Depletion of non-renewable resources throughout the years remains the hot topic on the table. One of the solutions available is vegetable oils whereas, in general have similar properties or better than petroleum in terms of viscosity, toxicity, flash point, evaporative loss and biodegradable sources.

1. Introduction

The global dependent on non-renewable resources especially in manufacturing and domestics application could jeopardize the sustainability of environment. Moreover, the spike of prices during the pandemics and political war between oil producer countries affected the industry worldwide [1]. As the world growing old, urbanization growing to the other side. Information beyond the fingertips for society become increasingly aware of declining fossil fuel as raw materials beside the limited reserves [2]. Health-related issues, stringent environmental protection policies and the quest for renewability, sustainability, and high-performance materials for technical applications have led to perfervid research in the production of renewable high applicable polymers from plant seed oils and shift in focus from the petrochemical based polymers [3][4].

The petroleum-based products basically applicable in almost of our essential living items from household until industrial purpose. For instance, petroleum-based plasticizers contained butylbenzylphthalate (BBP), di-(2-ethylhexyl) phthalate (DEHP) and di-n-butylphthalate (DBP), which were mainly used as softener and plasticizer in toys, packaging materials, cosmetics and PVC industry contained high toxicity which impacts health and environment of living organisms [5]. Hence, the risk can be avoided by using vegetable oils as alternatives such as rubber seed oils, neem oil, mahua oil,

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olive oil, corn oil, castor oil, soybean oil and palm oil [6][7][8]. The substitute materials for plasticizers are lower toxicity [9], good lubricity [10], lower volatility, low cost, renewable and biodegradability [11]. Modification of chemical derivatives using vegetable oils found it ways to have similar properties as petroleum based. The use of epoxidized derivatives of soybean oil, sunflower, castor oil and palm oil offer interesting feature as they simultaneously provide an intrinsic thermal stabilization effect due to presence of oxirane ring [12].

Chemical reaction to convert alkenes to epoxide (oxirane ring) using peracids as oxidizing agents also known as Prilezhaev method [13]. This method had been commercially practiced by industry due to straightforward and mild condition for the reactions. Other method used for epoxidation of vegetable oils include the use of dioxiranes. There have been reports on the use of the methyltrioxorhenium (MTO)-H_2O_2 system for converting double bond of alkenes to epoxide. MTO combined with hydrogen peroxide is a very active and selective catalytic precursor for the epoxidation of normal olefins, functionalized or not, and high molecular weight poly(butadiene) . It can be used in homogeneous or biphasic systems. The advantages of using biphasic systems are the easy control of epoxidation degree and protection of the sensitive epoxides that remain in the organic phase, where they are not in constant contact with the aqueous acidic phase. However, by-products emerge after the reaction and high selective amount of catalyst to fatty acid become the disadvantages of this method [14]. Thus, the objective of this study is to investigate effect for molar ratio of hydrogen peroxide toward rate of epoxidation.

2. Methodology

2.1 Materials and Method

Sunflower oil was used as raw material in this study. Formic acid (99%) and hydrogen peroxide (50%) were use as reactant.

2.2 Epoxidation Procedure

Epoxidation of sunflower oil is a process reaction between oleic acid, formic acid and hydrogen peroxide. The raw materials are mix with molar ratio 1:1.5 of oleic acid, and hydrogen peroxide respectively. Then, the mixture is heat at optimum temperature of 75˚C. This experiment is simultaneously heat and stir at 300 rpm. Sample is taken every 10 minutes to collected sample is then going through titration to calculate oxygen oxirane content hydrogen bromide insert in burette and sample mix with acetic acid and violet blue as indicator in conical flask. Chemical equation for epoxidation via peracid reaction illustrated on Figure 1.

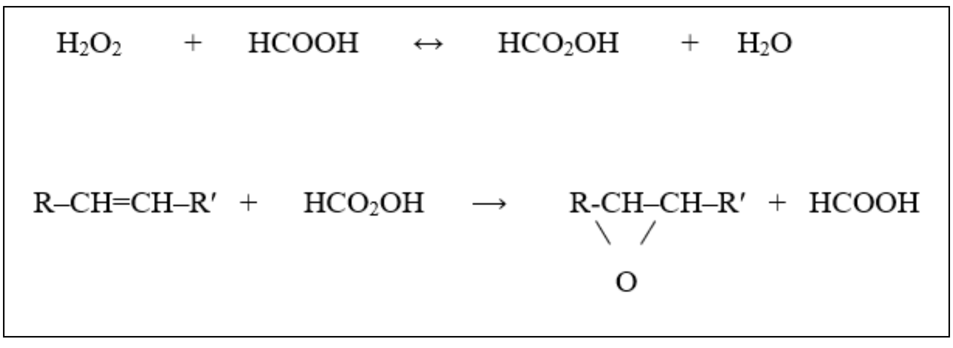

Fig. 1. Schematic of Epoxidation Via *in Situ* Peracids

The experiment conducted to determine the RCO value by calculation of oxirane oxygen content (OOC) theoretically and using direct titration of hydrobromic (HBr) acid solution method to indicate the degree of unsaturation in palm oil to calculate OOC experimentally. As the equation of RCO (1) include both of OOC value theoretically (2) and experimentally (3) [85].

$$RCO= \frac{OOC_{expiment}}{OOC_{theoretical}} \text{ x } 100 \quad (1)$$

$$OOC_{the}=\left\{\left(\frac{X_0}{A_i}\right)/\left[100+\left(\frac{X_0}{2A_i}\right)(A_o)\right]\right\} \text{x } A_o \text{ x}100 \quad (2)$$

$$OOC_{Exp}=1.6 \text{ x N x} \frac{(V\text{-}B)}{W} \quad (3)$$

Where X_o indicates the initial iodine value, A_i is molar mass of iodine, A_o is molar mass of oxygen, N is normality of HBr, V is volume of HBr solution used for blank in ml, V is volume of HBr solution used for titration and W is weight of sample.

3. Results and Discussion

3.1 Effect of molar ratio of hydrogen peroxide

Hydrogen peroxide used as an oxidizing agent in epoxidation reactions, particularly for the synthesis of epoxides from alkenes. Epoxides are three-membered cyclic ethers with a characteristic ring structure, and they are important intermediates in organic synthesis. The most common reaction mechanism for epoxidation using hydrogen peroxide involves the use of a catalyst. From Figure 2, it clearly shows generally higher molar ratio of hydrogen peroxide can causes the rate of epoxidation of sunflower. This is due to the higher molar ratio of hydrogen peroxide can lead to a faster reaction rate, as there are more oxygen atoms available to react with the unsaturated bonds in the sunflower oil [15]. Additional hydrogen peroxide can increase the concentration of active oxygen species, which are essential for the epoxidation process.

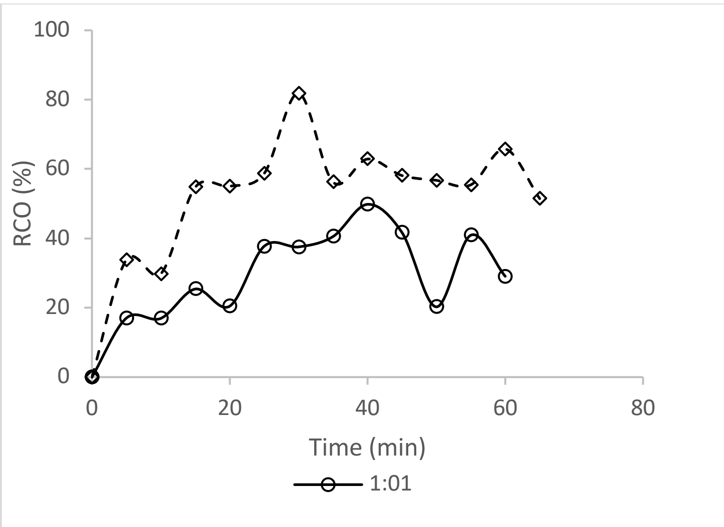

Fig. 2. Effect of hydrogen peroxide on epoxidation

3.1 Reaction rate determination

Kinetic study is involved in the degradation of epoxidation of palm oil. Moreover, the information based on the kinetic study can be simulated using MATLAB software to determine the value of kinetic rate equation, which involves the derivatives or differentials of the dependent variable [16]. It is important to understand the kinetics of a reaction to provide sufficient residence time for the reaction to achieve the desired degree of conversion. Knowledge on the reaction kinetics will facilitate the prediction of the conversion rate for certain reaction conditions. The crucial aspects of reaction kinetics are the rate and selectivity of the reaction as well as the dependency of these parameters on the process where the rate value were, k_{11}= 8.424, k_{12}= 0.885, and k_2= 0.040.

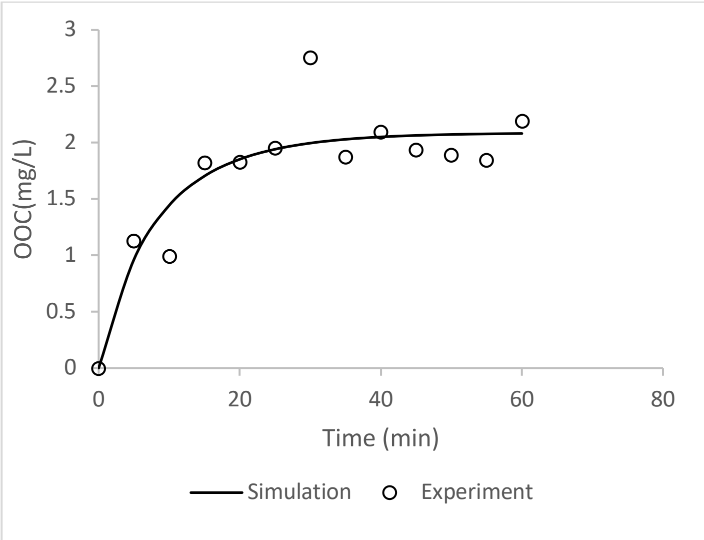

Fig. 3. Experiment vs simulation

4. Conclusions

The potential future of sunflower oil as renewable resources is huge, not only for food consumption but also for industrial applications. Epoxidized sunflower oil is one of chemical alterations that has similar properties as petroleum-based product. The available method for epoxidation of oleic acid only focuses on heterogeneous catalyst presence such sulphuric acid which need extendable process for purification of epoxides. Hence, this study confirms the epoxidation of oleic acid and its optimum process condition. The kinetics study also been observed to find the rate of reaction with minimum error between experiment and simulations.

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