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OPTIMIZATION OF EPOXIDIZED OLEIC ACID VIA PERACETIC ACID USING OFAT METHOD

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Abstract— Epoxidation of vegetable oil is one of the most interesting areas. Petroleum-derived items are not environmentally friendly because of their conventional attributes of broad environmental impact. Therefore, biobased alternatives are substitutes. Due to sustainability and global warming concerns, bio-based epoxide from renewable resources is important. Epoxidation reaction is highly unstable, and the active intermediate products can easily cause a ring opening. This study investigates the optimal parameters for epoxidized oleic acid to maximize relative conversion to oxirane (RCO) yield using a one-factor-at-a-time method (OFAT). Therefore, studies on the

effects of parameters such as stirring speed (150rpm, 300rpm, and 450rpm), temperature (40°C, 55°C, 70°C), molar ratios of hydrogen peroxide and acetic acid of (0.5, 1.0, and 1.5) were investigated to the ratio of oleic acid. The optimal epoxidation conditions were 55°C for 60 minutes, a ratio of 0.5:1 for acetic acid to oleic acid, 1.5:1 for hydrogen peroxide to oleic acid, and 300rpm for stirring speed. The maximum RCO value reached approximately 58.34% under these conditions.

I. Introduction

In recent years, epoxidation processes have been widely used in the development of material. Epoxidation is the process by which an oxirane group is created when peroxyl acids, also known as peracid, react with aromatic and olefinic double bonds. Epoxides undergo several reactions, which makes them incredibly important in the business sector [1]. Previously, epoxides were mostly made from petroleum-based sources. The epoxidation of petroleum-based products can have a range of effects, both positive and negative. It was discovered that the oxidative stability of biodiesel made from epoxidized waste used oil was enhanced.

Vegetable oil is a good substitute for epoxide manufacturing because of its favorable environmental qualities and affordability [2-4]. Due to their abundance from renewable sources plant oils are becoming increasingly popular in the chemical industry. Finding viable sustainable and renewable resources has drawn more attention as environmental issues like climate change and global warming become more prominent [5-7]. The epoxidation of plant-based oils, such as palm kernel oil, palm oleic acid, tung oil, and Karanja oil, has been explored as a

sustainable and environmentally friendly alternative to petroleum-based epoxidation [8]. Oleic acid has the largest lipid concentration among all fatty acids.

This study was conducted to discover and investigate the optimal parameter such as temperature, molar ratios of acetic acid to oleic acid, molar ratios of hydrogen peroxide to oleic acid, and stirring speed to the Relative conversion oxirane (RCO) percentage. This study employed a one-factor-at-a-time method to determine the optimal condition that would maximize both the yield and selectivity of the oleic acid epoxidation process.

II. Methodology

A. Material

Oleic Acid with a molecular weight of 282.46g/mol was purchased from R&M Chemical. Hydrogen peroxide (30%) with a molecular weight of 34.01g/mol was purchased from Chemiz. Sulfuric acid (95-97%) acts as a catalyst were purchased from Supelco. Hydrobromic acid 48% was purchased from QReC. A 60.05g/mol of acetic acid with molecular weight was purchased from R&M Chemical. Crystal violet as indicator was purchased from R&M Chemical.

B. Experimental Set-up (Epoxidation process)

In a 250ml beaker, the epoxidation experiment was carried out. The experimenter's hot plate served as the heating source. First, a 250ml beaker with thermometer and magnetic stirrer was added with 50gm of oleic acid. The stirrer speed was 300rpm, 2g of the sample was taken from mixture for each 10 minutes and mix with 10ml of acetic acid and two drops of crystal violet [8]. Titration with hydrogen bromide (HBr) acid solution to determine the oxirane oxygen content (OOC) and to calculate the RCO value. Experiment was repeated for different parameters such as stirring speed (150rpm, 300rpm, and 450rpm), temperature (40°C, 55°C, and 70°C) and molar ratios of hydrogen peroxide and acetic acid of (0.5:1, 1.0:1, and 1.5:1) in relation to the ratio of oleic acid.

C. Determination of Relative Oxirane (RCO)

To determine the relative conversion to oxirane (RCO) by calculating the oxirane oxygen content (OOC) as shown in Equation (1), (2) and (3).

$$OOC_{exp}\ (\%) = 1.6 \times N \times \left(\frac{V-B}{W}\right) \quad (1)$$

where:
N = represents HBr
V = HBr solution volume (mm)
B = titration volume (mm)
W = sample weight (gm)

To calculated theoretical oxirane oxygen content (OOC_{theo}) the Equation (2) is used.

$$OOC_{theo} = \frac{\left(\frac{IV_0}{2AI}\right)}{\left[100+\left(\frac{IV_0 A}{2AI}\right)A_0\right]} \times A_0 \times 100 \quad (2)$$

where:
A_0 = molar mass of oxygen
AI = molar mass of iodine
IV_0 = starting iodine value

Equation (3) is then used to get the proportion of relative conversion to oxirane (RCO). RCO showed that when the oxirane ring formed, unsaturated fatty acid had already changed into epoxidized fatty acid.

$$RCO = \left(\frac{OOC_{exp}}{OOC_{theo}}\right) \times 100\% \quad (3)$$

III. Results and Discussion

A. Effect of Different Temperature on RCO

The result of this experiment is Figure 1. Three different temperature ranges were used for this experiment: 40°C, 55°C, and 70°C. The highest RCO was achieved when the reaction was carried out at a temperature of 55°C for a time of 40 minutes. Additionally, the kinetic and thermodynamic factors of epoxidation suggest that raising the temperature can accelerate the formation of epoxides [2, 3].

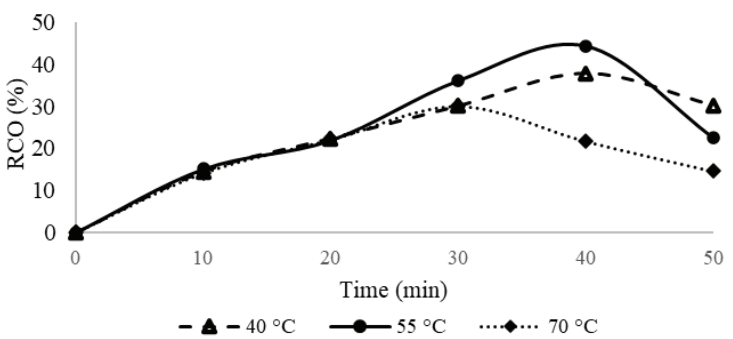

Figure 1: Effect of Different Temperatures on RCO Percentage

After 40 minutes, the RCO decreased due to the instability of epoxide (oxirane) due to the reaction taking place very fast [11]. The reaction reaches 44.4% RCO in only 40 minutes, demonstrating that a little more heat makes the reaction faster and more efficient. Temperature has an important effect on oleic acid epoxidation. Higher temperatures typically lead to faster reactions and higher yields due to epoxidation processes enhanced by higher temperatures [9]. Thus, it may be said that greater temperatures generally enhance oleic acid epoxidation. The response slows down at 70°C after reaching 30.1% RCO in 30 minutes despite starting off quickly. This implies that maintaining ideal circumstances becomes more difficult [6], whereas high temperatures can facilitate epoxidation, they can also negatively impact the characteristics of epoxy materials because increasing the reaction temperature can lead to a reversible chemical reaction of peracetic acid [10].

B. Effect of Stirring Speed on RCO

Figure 2 shows the highest RCO (44.68%) is at 300rpm, and the reaction time is 40 minutes. The second highest value of RCO was obtained at 150rpm, followed by 450rpm with RCO values of 35.7% and 28.4%, respectively.

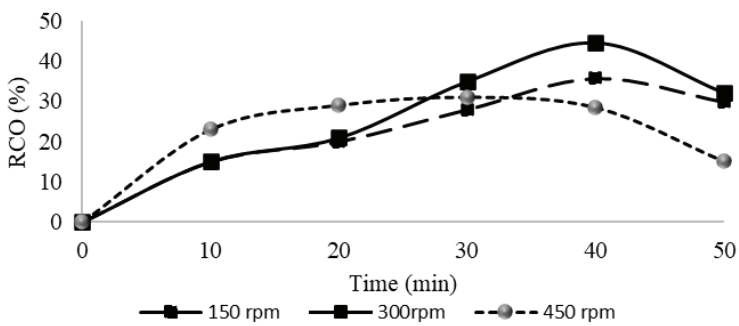

Figure 2: Effect of Stirring Speed on the RCO

The reason is that well-mixed solutions happen due to continuous stirring. However, overmixing may cause the oxirane rings to lose stability in the chemical structure [11]. The

outcomes closely match those of earlier research [9, 11]. From the previous study, it was discovered that moderate stirring speeds (200-350rpm) increased the oxirane production rate [8].

C. Effect of Molar Ratio Hydrogen Peroxide Concentration on RCO

As the molar ratio of hydrogen peroxide increased, there was a gradual increase in the rate at which oxirane production occurred as shown in Figure 3. From the previous study, it showed that higher concentrations of hydrogen peroxide resulted in slightly higher rates of ring opening [10, 11]. When compared with a 1.1 molar ratio, the stability of oxirane found for this ratio is similar. In contrast, the highest proportion change into oxirane was with a 1.5 molar ratio, as proved by experiments carried out under this condition. At the beginning of this experiment, the epoxidation reaction occurred at the same rate for each concentration, but after 10 minutes, the RCO value slowly changed for each concentration. After 30 minutes of reaction time, the hydrogen peroxide molar ratios were found to be like the saturation molar ratio at the highest RCO. The molar ratio of 1.5:1 produced the greatest RCO value (44.88%) and had a significant impact on the RCO percentage after 30 minutes. The lowest RCO was obtained in a molar ratio to the degree of unsaturated at 0.5:1.

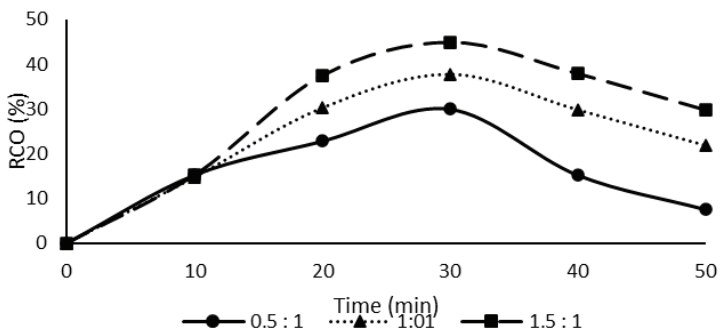

Figure 3: Effect of Hydrogen Peroxide to the RCO

D. Effect of the Molar Ratio Acetic Acid to the RCO

Figure 4 shows, the maximum epoxide yield (45.25%) was achieved when the reaction period was 30 minutes and the molar ratio of acetic acid to oleic acid was 0.5:1. This indicates that there is a full conversion to oxirane. The RCO value of 37.8% was observed when the molar ratio of acetic acid to oleic acid was 1:1, and the RCO value of 37.1% was observed when the molar ratio was 1.5:1. These values were obtained after a reaction period of 30 minutes. The RCO value gradually decreased as the molar ratio of acetic acid to oleic acid increased, indicating that the high concentration of formic acid is what is causing the oxirane ring to disintegrate [12, 14]. Peracetic acid serves as a good oxygen carrier whose optimum quantities are essential for the formation of sufficient amounts of epoxides at the water phase. The molar ratio can even impact the overall rate reaction and kinetics of the reaction [13].

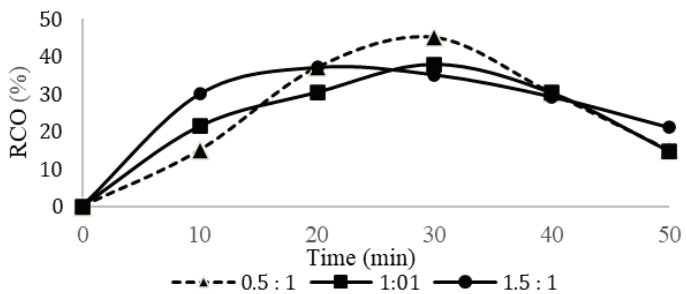

Figure 4: Effect of the Molar Ratio Acetic Acid to the RCO

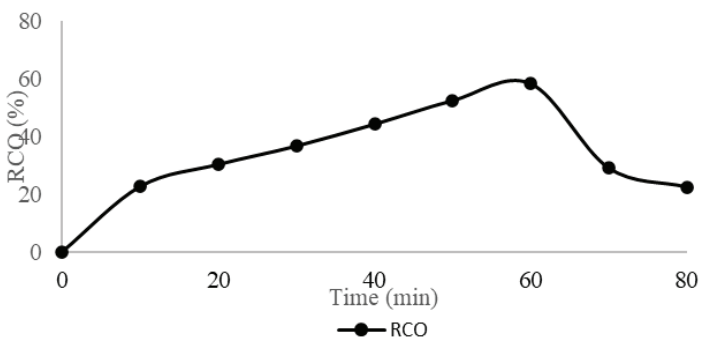

Figure 5: Optimization Epoxidation of Oleic Acid

E. Optimization Epoxidation of Oleic Acid

The parameter optimization for this study for temperature was 55°C, a speed of 300rpm, and a molar ratio of hydrogen peroxide to acetic acid to oleic acid of 1.5:0.5:1. From Figure 5, maximum RCO conversion aligned to the maximum epoxidation process, where the average time for this process is approximately 60 minutes. The highest RCO value is 58.34%. The epoxide yield was enhanced by elevated temperature, indicating how sensitive the reaction is to temperature. The study also highlighted the need to optimize this parameter by revealing the consequences of speed fluctuations. Varying molar ratios showed different.

IV. Conclusion

In the present study, epoxidizing of oleic acid was obtained by using in situ peracetic acid. It has been found that temperature, hydrogen peroxide ratio, stirring speed, acetic acid ratio effect are some of the factors that influence epoxidation oleic acid. The highest value of RCO obtained was about 58.34%, resulting from the optimization of these variables, the temperature of 55°C, a reaction time of 60 minutes, molar ratio of hydrogen peroxide to oleic acid was 1.5:1 and molar ratio of acetic acid 0.5:1 to oleic acid at a stirring speed of 300rpm.

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