

Hybrid Oxygen Carrier System of Formic and Acetic Acids for Soybean Oil Epoxidation

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ABSTRACT

Green chemistry's commitment to sustainable and eco-friendly materials is exemplified by the epoxidation of soybean oil, which transforms a common crop into epoxidized soybean oil (ESBO), a versatile chemical asset. ESBO, a bio-based resource, serves as a plasticizer, stabilizer, and reactive diluent in industries like plastics and cosmetics. The study focused on the peracid method and hybrid oxygen carriers like formic and acetic acid to create ESBO, a valuable chemical feedstock. This study examined the effect of reaction temperature on the epoxidation process found that the relative conversion to oxirane (RCO) value for the experiment at 65°C (40.68%) is higher compared to those at 75°C and 85°C, indicating that 65°C is the ideal temperature for the epoxidation process of soybean oil. The research highlights the importance of temperature in the kinetics of chemical reactions and the benefits of using a hybrid system for a more sustainable and eco-friendly approach to producing ESBO.

Keywords: Epoxidation; Epoxidized Soybean Oil; Peracid Mechanism; Plasticizer; Relative Conversion To Oxirane



INTRODUCTION

The pursuit of sustainable and eco-friendly materials is a cornerstone of green chemistry, a field dedicated to designing products and processes that minimize the use and generation of hazardous substances. The epoxidation of soybean oil is a prime example of such innovation, where a widely cultivated agricultural product is converted into epoxidized soybean oil (ESBO), a valuable chemical feedstock. ESBO is a bio-based resource that acts as a plasticizer, stabilizer, and reactive diluent, with applications across various industries, including plastics manufacturing and cosmetic [1].

One key application of canola oil is its role as a precursor in epoxidation reactions. The successful execution of these reactions relies heavily on the unsaturated fatty acid content within canola oil's chemical composition. It is essential to discuss the advantages of using canola oil as a feedstock for epoxidation reactions, followed by a detailed analysis of its unsaturated fatty acid composition and the properties that make successful epoxidation possible. The composition table presents a detailed breakdown of the various fatty acids found in canola oil. Fatty acids are fundamental components of fats and oils, and canola oil comprises a mixture of saturated, monounsaturated, and polyunsaturated fatty acids. Table 1 lists these fatty acids, along with their respective amounts or percentages.

Table 1: Composition of the fatty acids from canola oil [2]

Fatty Acid	Percentage (%)
Linoleic acid	53.2
Oleic acid	24.0
Palmitic acid	11.0
Alpha-linolenic acid	7.8
Stearic acid	4.0
Eicosenoic acid	1.0
Behenic acid	0.5
Arachidic acid	0.3
Myristic acid	0.1
Palmitoleic acid	0.1
Margaric acid	0.1

The epoxidation process is a crucial chemical reaction used to convert alkenes into epoxides, valuable intermediates in synthesizing various organic compounds [3]. Several methods exist for achieving epoxidation, each with its own advantages and applications. Among these, the peracid mechanism is particularly notable. Mahadi *et al.* [4] claim that this traditional method involves the reaction of alkenes with peracids and is favored for its high cost-efficiency, simplicity, and safety. It typically requires less expensive materials and chemicals, yielding around 75% and producing epoxides with good selectivity under mild conditions. Compared to other methods, such as the use of acidic ion exchange resins (AIER) [5], chemo-enzymatic approaches [6], and metal-catalyzed processes [7], the peracid mechanism avoids the need for recyclable resins [5], costly enzymes [8], or potentially toxic metal catalysts [3]. Its alignment with green chemistry principles by producing water as a byproduct and operating under benign conditions [4], which further supports its suitability for large-scale industrial applications, making it the method of choice for this study [9].

The epoxidation process involves the conversion of the carbon-carbon double bonds present in the unsaturated fatty acids of soybean oil into oxirane rings [10]. This reaction is traditionally carried out using peracids, which are potent oxidizing agents capable of transferring an oxygen atom to the olefinic substrates [11]. However, this method poses several challenges, including the handling of corrosive reagents, the generation of hazardous by-products, and the need for stringent reaction conditions [12]. To address these challenges hybrid oxygen carriers, such as formic acid and acetic acid were introduced to offer a milder and more environmentally benign alternative. Figure 1 shows the epoxidation process to form ESBO from linoleic acid derived from soybean oil. These organic acids serve a dual purpose: they act as solvents, providing a medium for the reaction, and as reactants, generating peracids in situ through their reaction with hydrogen peroxide (HP).

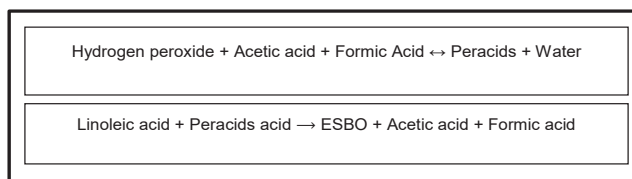


Figure 1: Epoxidation Process Follow by Peracid to Form ESBO

The resulting peracids are then available to epoxidize the soybean oil, all within the same reaction vessel [13]. The advantages of using a hybrid system are manifold. Firstly, it allows for the controlled generation of peracids, reducing the risk of over-oxidation and by-product formation. Secondly, the reaction can be conducted at lower temperatures and pressures, making it safer and more energy-efficient. Thirdly, the use of acetic and formic acids, which are relatively benign and readily available, minimizes the environmental footprint of the process [13]. Considering the significant advantages of using hybrid oxygen carriers like formic acid and acetic acid, this study sets out to explore how different temperatures affect the epoxidation process. Therefore, the objectives of this study is to study the effect of the reaction temperature on the epoxidation process using hybrid oxygen carrier.

The focus on temperature as a variable stems from its critical role in the kinetics of chemical reactions, affecting both the rate and selectivity of epoxidation. The procedure will be sustained for one hour for each experimental trial, with subsequent repetitions conducted at elevated temperatures of 75 °C and 85 °C. This research will not cover on lower temperature of epoxidation process. This is due to the epoxidation of soybean oil requires overcoming a certain activation energy threshold. At low temperatures, the molecular kinetic energy is insufficient to surpass this threshold, leading to a markedly slower reaction rate. The Arrhenius equation, which describes the temperature dependence of reaction rates, underscores this phenomenon, showing that lower temperatures exponentially decrease the reaction rate [14]. Consequently, the low kinetic energy at reduced temperatures hampers the necessary molecular collisions and alignments, making the process inefficient. Besides, if is catalysts used for soybean oil epoxidation, these catalysts exhibit temperature-dependent activity profiles. At low temperatures, the activity of these catalysts significantly diminishes. For instance, the optimal temperature range for enzymatic catalysts is usually above ambient temperatures, where the enzyme's active site can facilitate substrate binding and turnover effectively. In acidic catalysis, the formation of the active peracid species and its subsequent interaction with the double bonds in soybean oil are also less efficient at lower temperatures [15]. Therefore, maintaining an appropriate temperature is crucial to ensure the optimal performance and the overall efficiency of the epoxidation process.

METHODOLOGY

Material

Soybean oil was purchased from local supermarket. Formic acid (2 M, concentration: 85%), hydrogen peroxide (3.5 M, concentration: 30, 35, and 40%), and sulphuric acid were purchased from BT Science Sdn. Bhd. Hydrogen bromide (3.0 M, concentration: 48%) and glacial acetic acid (1 M, concentration: 100%) were acquired from BT Science Sdn. Bhd. and Merck Sdn. Bhd., respectively, for the titration procedure.

Experimental Procedure

A 500-mL beaker was filled with 100 g of soybean oil and placed in a water bath to maintain a constant reaction temperature. Specific amounts of formic acid and acetic acid were then added to the beaker. HP, calculated in the required amount, was added dropwise to the mixture of soybean oil and acids. The solution was stirred at 350 rpm until it reached 65°C. The titration process began, with all chemicals mixed every 10 minutes. Afterward, a 0.5 g sample was taken from the beaker, placed in a vial, and mixed with two drops of crystal violet and 10 mL of glacial acetic acid. The mixed sample was titrated by measuring the difference between the initial and final hydrogen bromide concentrations. The procedure was sustained for one hour for each experimental trial, with subsequent repetitions conducted at elevated temperatures of 75 °C and 85 °C.

Analytical techniques

To evaluate the effectiveness of the epoxidation process, studies measured the relative conversion to oxirane (RCO) by both theoretical predictions and experimental measurements of the oxirane oxygen content (OOC). The OOC, which reflects the oxygen amount in the oxirane rings [16], was experimentally quantified using a titration method with hydrobromic acid (HBr) to gauge the unsaturation level in palm oil. This method aligns with the established American Oil Chemists Society's Official Method Cd 9–57. The experimentally derived OOC is a reliable measure to confirm the completion of the reaction [17]. The RCO (Eq. (1)) was then computed using the OOC values obtained from both theoretical (Eq. (2))

and experimental (Eq. (3)) approaches.

$$RCO = \frac{OOC_{experimental}}{OOC_{theoretical}} \times 100 \tag{1}$$

$$OOC_{theoretical} = \left\{ \left(\frac{X_0}{A_i} \right) / \left[100 + \left(\frac{X_0}{2A_i} \right) (A_o) \right] \right\} \times A_o \times 100 \tag{2}$$

$$OOC_{experimental} = 1.6 \times N \times \frac{(V-B)}{W} \tag{3}$$

Here, N is the HBr normalcy, V is the volume of the HBr solution used as a blank in millilitres (mL), V is the volume of the HBr solution used for titration, and W is the sample weight. X_0 indicates the initial iodine value. A_i and A_o are the molar masses of iodine and oxygen, respectively.

RESULTS AND DISCUSSION

Figure 2 indicates that the RCO value for the experiment conducted at 65°C (40.68%) is higher than those conducted at 75°C and 85°C, suggesting that 65°C is the optimal temperature for the epoxidation process of soybean oil.

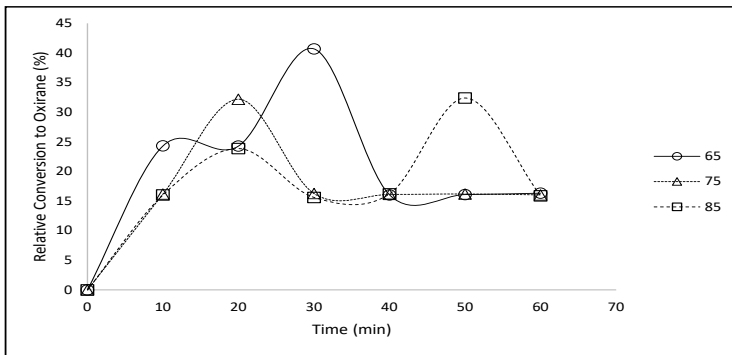


Figure 2: Effect of Reaction Temperature on the RCO

This observation highlights the critical role temperature plays in balancing the reaction kinetics and stability of the reactants and products in the epoxidation process. The epoxidation of soybean oil involves the conversion of double bonds in unsaturated fatty acids to epoxide rings using HP as an oxidizing agent. The reaction mechanism benefits from an increase in temperature due to enhanced kinetic energy, which accelerates molecular collisions and, consequently, the reaction rate. However, this

benefit is limited to a certain optimal temperature threshold, beyond which the reaction dynamics become counterproductive. At 65°C, the kinetic energy is sufficient to facilitate the formation of the desired epoxide rings without inducing significant thermal degradation or unwanted side reactions. The elevated temperature ensures efficient mixing and interaction between the HP and the unsaturated fatty acids, promoting a higher conversion rate. This optimal temperature strikes a balance between maximizing the reaction rate and maintaining the stability of the epoxide rings, leading to a higher RCO value.

In contrast, as the temperature increases beyond 65°C, the reaction becomes increasingly exothermic. This excess heat poses several challenges. Firstly, higher temperatures accelerate the decomposition of HP [18]. HP is a critical source of active oxygen atoms required for the epoxidation process. As temperature rises, the decomposition rate of HP increases significantly, reducing the availability of active oxygen. This reaction not only depletes the HP but also releases oxygen gas, which does not contribute to the epoxidation reaction. The loss of HP leads to a decline in the overall efficiency of the process, as less active oxygen is available to react with the double bonds in the soybean oil. Moreover, the stability of the ESBO is compromised at higher temperatures. The epoxide rings, which confer the desired chemical properties to the final product, are thermally labile and prone to decomposition at elevated temperatures. The decomposition of epoxide rings can result in the formation of smaller, less desirable molecules such as aldehydes and ketones. These by-products not only reduce the yield of the epoxidized product but also degrade its quality. The presence of aldehydes and ketones can impart unwanted properties to the ESBO, making it less suitable for its intended applications [19].

Supporting this observation, Mungroo *et al.* [20] found that the optimal temperature for their epoxidation study was also 65°C. Their research indicated that higher temperatures led to increased formation of unwanted by-products. For instance, at 75°C, the epoxide rings in the ESBO were more prone to opening, resulting in the formation of glycol, an undesirable by-product. The opening of oxirane rings is a significant issue, as it not only reduces the epoxide content but also leads to the formation of compounds that can negatively impact the physical and chemical properties of the final product. Additionally, the decomposition rate of HP is highly temperature-

dependent. Research indicates that within the temperature range of 20°C to 100°C, the decomposition rate of HP approximately doubles with every 10°C increase [21]. This rapid decomposition at higher temperatures poses several risks. The accelerated breakdown of HP reduces the amount of active oxidizing agent available for the epoxidation reaction, thereby lowering the efficiency of the process. Moreover, the rapid release of oxygen gas during the decomposition of HP can lead to increased pressure within the reaction vessel. This pressure buildup poses potential safety hazards, including the risk of explosions, which necessitates careful temperature control and monitoring during the reaction.

The optimal temperature of 65°C thus ensures that the reaction proceeds efficiently without excessive decomposition of HP or thermal degradation of the epoxide rings. This temperature allows sufficient kinetic energy to drive the reaction while maintaining the integrity of the reactants and products. The balance achieved at this temperature results in a higher RCO value, indicating a more efficient and productive epoxidation process. Furthermore, the thermal stability of the epoxidized product is crucial for its practical applications. ESBO is used in various industries, including as plasticizers, stabilizers, and intermediates in polymer synthesis. The quality and performance of ESBO are highly dependent on the preservation of the epoxide rings, which impart unique chemical properties to the material. At higher temperatures, the risk of epoxide ring opening and subsequent formation of by-products can compromise the material's performance. Therefore, maintaining an optimal temperature during the epoxidation process is essential to ensure the production of high-quality ESBO with desirable properties.

CONCLUSION

Green chemistry's commitment to sustainable and eco-friendly materials is exemplified by the epoxidation of soybean oil, which transforms a common crop into ESBO, a versatile chemical asset. ESBO, a bio-based resource, serves as a plasticizer, stabilizer, and reactive diluent in industries like plastics and cosmetics. The epoxidation reaction, pivotal for creating epoxides from alkenes, employs various methods, including the cost-effective peracid mechanism. This traditional approach uses peracids to

convert unsaturated fatty acids' double bonds into oxirane rings, offering a safe and simple process that aligns with green chemistry by producing water as a byproduct under mild conditions. Despite its advantages, the peracid method has drawbacks, such as handling corrosive reagents and generating hazardous by-products. To overcome these, hybrid oxygen carriers like formic and acetic acid were introduced, providing a gentler, eco-friendlier alternative. These acids act as solvents and reactants, creating peracids in situ from HP, which then epoxidize the soybean oil. The hybrid system's benefits include controlled peracid generation, reducing over-oxidation and by-product risks, and allowing reactions at lower temperatures and pressures, enhancing safety and energy efficiency. This study investigates how varying temperatures impact the epoxidation process using hybrid oxygen carriers. Temperature significantly influences reaction kinetics, affecting the rate and selectivity of epoxidation. Therefore, it is essential to maintain the epoxidation process at temperatures below 70°C. Operating at or around 65°C ensures that the reaction proceeds efficiently, preserving the epoxy rings and preventing the decomposition of reactive agents. This temperature balance helps to maximize the yield and stability of the ESBO while minimizing the formation of unwanted by-products and ensuring safe operational conditions. Maintaining a lower temperature also aligns with green chemistry principles by reducing energy consumption and mitigating the risk of hazardous conditions, making the process more sustainable and environmentally friendly.

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