

Epoxidation of Hybrid Oleic Acid-derived Palm Oil Using an *In Situ* Performic Acid Mechanism

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Abstract

The purpose of this study was to determine the effects of different types of catalysts – sulphuric acid titanium dioxide, and Amberlite – and to investigate the effect of catalyst loading (0.1 g, 0.5 g, 1.0 g) on the relative conversion to oxirane (RCO %). This study examines the influence of these different catalyst types and their loadings on the epoxidation of palm oil to identify the optimum conditions for the process. The epoxidised palm oil was analysed using RCO % and Fourier transform infrared spectroscopy (FTIR). The results showed that 0.5 g sulphuric acid as a catalyst with a loading of 0.5 g achieved the highest RCO % at 76.16 %. FTIR spectra revealed the presence of an epoxy group at 833.10 cm^{-1} . In conclusion, using 0.5 g of sulphuric acid as the catalyst provides the optimum conditions for the epoxidation process.

Keywords

Epoxidation, palm oil, biomass conversion, kinetic model

1 Introduction

Finding new and sustainable alternatives to replace petroleum-based resources has become increasingly important as the need to move away from fossil fuels grows by the day. One promising method is the epoxidation process, which offers a window into a future where ecologically friendly, reliable, and sustainable energy sources are essential for meeting our growing energy needs.¹ Epoxidation is a chemical reaction that forms an epoxide, also known as an oxirane.² An epoxide is a three-membered cyclic ether with one oxygen atom and two adjacent carbon atoms. This reaction involves adding an oxygen atom to a double bond, creating a cyclic structure.³

The chemical process of epoxidation adds an oxygen atom to a carbon-carbon double bond to create an epoxide, or oxirane ring.⁴ One of the main benefits of epoxidation is its applicability to a wide range of substrates, including various alkenes and unsaturated compounds. This versatility makes it a valuable method for synthesising diverse organic compounds, producing polyols from vegetable oil,⁵ plastic materials⁶, and polymers.⁷ The formation of epoxides, or oxirane rings, through this reaction provides unique three-membered ring structures that offer diverse opportunities for further functionalisation.⁸ Several methods exist for performing this reaction, and the method used is determined by the substrate and reaction conditions.⁹ In the general mechanism of peroxyacid epoxidation, the peroxyacid attacks the carbon-carbon double bond, resulting in the formation of an epoxide. The specific peroxyacid used can influence the details of the peroxyacid epoxidation mechanism.¹⁰ Previous work has presented a catalytic protocol for the efficient epoxidation of vegetable oils, combining a manganese catalyst, sulphuric acid cata-

lyst, and acetic acid as an additive.¹¹ Vegetable oils, which contain unsaturated fatty acids, have limited reactivity and are susceptible to oxidative degradation. Oxidation is a chemical reaction that occurs when oxygen is added to unsaturated fats due to the presence of double bonds in those fats.¹² Epoxidation can make vegetable oils more reactive and useful. However, certain peroxides are hazardous and potentially harmful to the environment. The use of strong acid compounds, such as concentrated sulphuric acid, is highly corrosive and requires careful consideration and precautionary measures by researchers.¹³ To fully utilise epoxidised vegetable oils in the production of green chemicals, biodegradable polymers, and other value-added products, these challenges must be overcome. To address the concerns regarding conversion efficiency, selectivity, and environmental impact, it is imperative that the epoxidation process for vegetable oils be improved and optimised. Overcoming these challenges can facilitate the development of more environmentally friendly and sustainable substitutes in the chemical and materials industries, paving the way for the broader use of epoxidised vegetable oils in commercial applications. To date, there have been few studies on the effect of catalyst type and catalyst loading on the epoxidation of palm oil. Therefore, this research investigates the effect of different types of catalysts (homogeneous and heterogeneous).

2 Materials and methods

2.1 Materials

Palm oil (Knife brand) was used as the raw material. The following chemicals were obtained from Qrec Sdn. Bhd.: formic acid (conc. 85 %), hydrogen peroxide (conc. 50 %), hydrobromic acid (conc. 45 %), acetic acid (conc. 50 %),

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Amberlite, titanium dioxide, and sulphuric acid (conc. 99 %) as catalysts, and crystal violet as indicator.

2.2 Synthesis method

The reaction began with 100 g of palm oil, 24.08 g of hydrogen peroxide, and 8.14 g of formic acid, measured and mixed in a 500-ml beaker. The solution was heated in a pot filled with water using the water bath concept. The heating process acts as an insulator to maintain constant temperature. A magnetic stirrer was used to stir the solution at 350 rpm to ensure uniform mixing. Once the temperature reached 70 °C, 0.5 g sulphuric acid (99 %) was added to the solution. The timer was started and time lag was done every 5 min to take samples of approximately 2.0 g for titration. Before titrating, 10 ml acetic acid (conc. 50 %) was added to a small 50-ml beaker containing the 2.0-g sample, and two drops of crystal violet. The sample was titrated until the solution colour changed from dark blue to yellowish-green.¹⁴

2.3 Analytical procedure

Samples were retrieved every 5 min to determine the oxirane oxygen content (OOC), which was used to calculate the relative conversion to oxirane (RCO %). RCO % was calculated according to Eq. (1), based on the experimental oxirane oxygen content (OOC_{exp}) (Eq. (2)), determined through the titration process, and the theoretical oxirane oxygen content (OOC_{theo}) (Eq. (3)). Here, X_o is the preliminary iodine value, A_i is the iodine molar mass, A_o is the oxygen molar mass, N is the normality of the HBr solution, B is the volume of the HBr solution used for the blank in millilitres, V is the volume of the HBr solution used for titration in millilitres, and W is the weight of the sample.

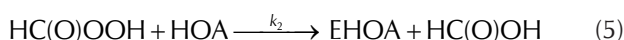
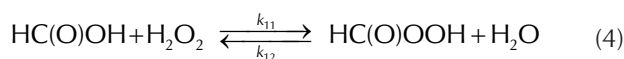
$$RCO \% = \frac{OOC_{exp}}{OOC_{theor}} \cdot 100 \quad (1)$$

$$OOC_{exp} (\%) = 1.6 \cdot N \cdot \frac{V - B}{W} \quad (2)$$

$$OOC_{theo} (\%) = \frac{\frac{X_o}{A_i}}{100 + \frac{X_o}{2A_i} A_o} \cdot A_o \cdot 100 \quad (3)$$

2.4 Kinetic modelling of epoxidation of palm oil

The epoxidation process is characterized by two primary reactions, as indicated in Eqs. (4) and (5), which involve the *in-situ* formation of performic acid (HC(O)OOH) and the reaction with hybrid oleic acid (HOA), resulting in the formation of epoxidised oleic acid (EHOA).



The kinetic modelling method for the epoxidation process was developed using the following rate constants: k_{11} , k_{12} , k_2 , as shown in Eqs. (6)–(10).

$$\frac{dc(HC(O)OH)}{dt} = -k_{11}c(HC(O)OH)c(H_2O_2) + k_{12}c(HC(O)OOH)c(H_2O) + k_2c(HC(O)OOH)c(HOA) \quad (6)$$

$$\frac{dc(H_2O_2)}{dt} = -k_{11}c(HC(O)OH)c(H_2O_2) + k_{12}c(HC(O)OOH)c(H_2O) \quad (7)$$

$$\frac{dc(HC(O)OOH)}{dt} = k_{11}c(HC(O)OH)c(H_2O_2) - k_{12}c(HC(O)OOH)c(H_2O) - k_2c(HC(O)OOH)c(HOA) \quad (8)$$

$$\frac{dc(H_2O)}{dt} = k_{11}c(HC(O)OH)c(H_2O_2) - k_{12}c(HC(O)OOH)c(H_2O) - k_2c(HC(O)OOH)c(HOA) - k_3c(EHOA)c(H_2O) \quad (9)$$

$$\frac{dc(HOA)}{dt} = -k_2c(HC(O)OOH)c(HOA) \quad (10)$$

3 Results and discussion

3.1 Effect of catalyst type

The epoxidation reaction was conducted using two types of catalysts: sulphuric acid as a homogeneous catalyst, and titanium dioxide and Amberlite as a heterogeneous catalysts, at a temperature of 70 °C and stirring speed of 350 rpm. As shown in Fig. 1, using 0.5 g sulphuric acid as the catalyst resulted in a 76.19 % yield of epoxide, achieving the highest RCO % at 20 min. This was followed by titanium dioxide, with a yield of 71.06 % conversion, and Amberlite with a yield of 67.32 %. Consequently, within a brief reaction time (3 h), 98 % of double bond conversion and more than 80 % selectivity were achieved with only 5 % of the catalyst. The oxirane ring did not degrade under the experimental conditions used in this study. Recent studies have demonstrated that titanium dioxide can be incorporated onto an amorphous silica support to create highly effective oxidation catalysts for hydrogen peroxide epoxidation reactions. Among the liquid inorganic acids investigated, sulphuric acid was found to be the most efficient and effective catalyst. *Meyer and Huynh* researched the conventional method of epoxidation of soybean and jatropha oil in the same year.¹⁵ They conducted the epoxidation reaction at 500 °C and atmospheric pressure for roughly ten hours, achieving a maximum reaction conversion of 83.3 % with soybean oil as the catalyst. Similarly, *Cai et al.* studied the kinetics of sulphuric acid-catalysed *in-situ* epoxidation of soybean, sunflower, and maize oils.¹⁶ Their work found that soybean oil had the highest conversion rate and the lowest activation energy when epoxidised with peroxyacetic acid, while jatropha oil had the lowest activation energy at 87.4 %.¹⁷

Different types of catalysts can lead to different yields or conversions in chemical reactions due to their unique characteristics and interactions with reactants. Catalysts are added to reactions to speed up the reaction without affecting the equilibrium constant of the reaction. They accelerate both forward and reverse reactions by providing a new route to forming intermediate products with a lower energy barrier.¹⁸ Thus, sulphuric acid offers more surface area and selectivity compared to titanium dioxide and Amberlite.

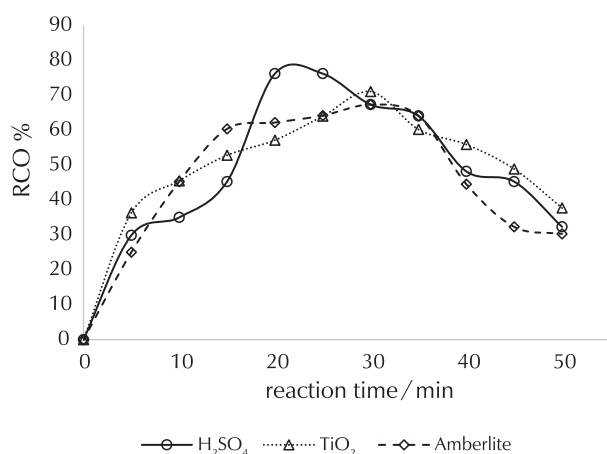


Fig. 1 – Relative conversion to oxirane (RCO %) vs. reaction time for catalyst types

3.2 Effect of catalyst loading

Fig. 2 shows that using 0.5 g sulphuric acid as a catalyst resulted in the highest RCO %, reaching 76.16 %. The second highest RCO % was observed with 1.0 g sulphuric acid as catalyst, followed by 0.1 g sulphuric acid as catalyst with values of 72.57 % and 75.32 %, respectively. Catalyst loading, or the amount of catalyst used in a chemical reaction, can significantly impact the reaction results, which can lead to more active sites, improving reaction kinetics, increasing selectivity, and enhancing substrate accessibility.¹⁹

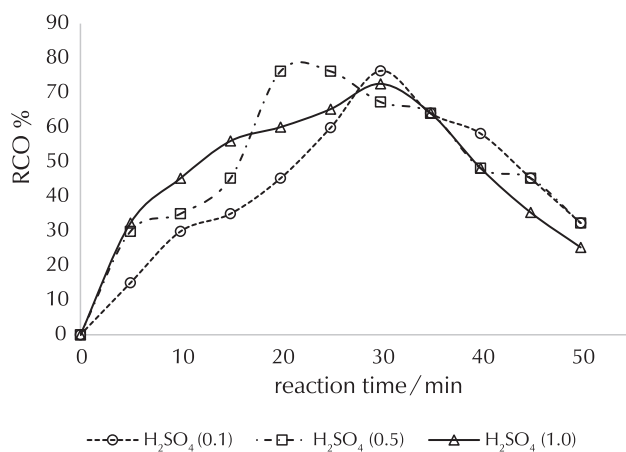


Fig. 2 – Relative conversion to oxirane (RCO %) vs. reaction time for various catalyst loading (g)

3.3 Fourier transform infrared spectroscopy analysis

In this study, the functional groups of the samples were identified using a FTIR spectrometer (Spectrum One, PerkinElmer, USA). The FTIR spectra were recorded within a wavenumber range of 400–4000 cm^{-1} , which is the mid-infrared region corresponding to the fundamental vibration modes of the molecules. Fig. 3 shows the FTIR graph, which identifies the presence of the oxirane group in epoxidised palm oil and the disappearance of the double bond in palm oil. The FTIR spectra of the epoxides were attributed to the vibrations of the epoxy ring and aldehyde compounds, respectively, which differ from the palm oil FTIR by bands at 917 and 1678 cm^{-1} . The disappearance of the double bond group peak at 3000 cm^{-1} demonstrates the conversion of the double bond in linoleic acid to the epoxy group.¹

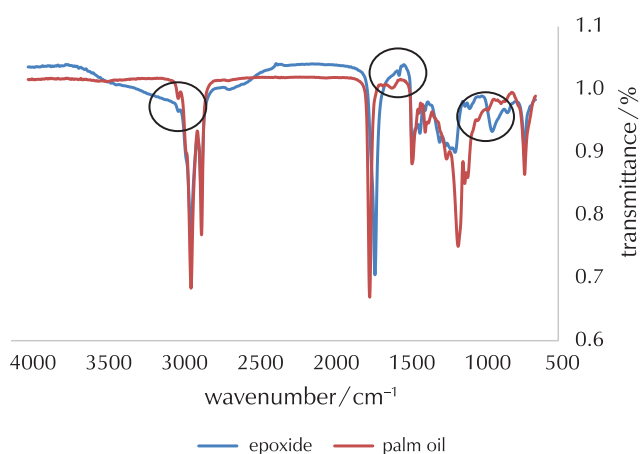


Fig. 3 – FTIR spectra of palm oil and epoxidised palm oil

3.4 Numerical kinetic modelling

The ideal reaction conditions for the epoxidation process were determined using kinetic modelling with MATLAB software. The reaction rate values, k , are listed in Table 1. For each chemical, the k values derived from the experimental data match the initial concentrations. The reaction rate k_{11} was found to be slower than k_{12} . This was because the reaction only consists of the formation of performic acid and its byproduct, which was water.

Table 1 – Rate constants for epoxidation and ring opening of epoxide

Reaction rate	Value/ $\text{mol l}^{-1} \text{min}^{-1}$
k_{11}	0.0163
k_{12}	14.91
k_2	0.128

Fig. 4 shows a noticeable difference between the simulation and experimental results for OOC. The simulation graph exhibited quite low values, with the highest point reaching just below 0.6 OOC. In contrast, the experimental graph showed higher OOC values, peaking at almost 0.8, but significantly decreasing after the twentieth minute. This could be due to the purity of the solutions used or the efficiency of the epoxidation reaction.

There was a notable difference in the time taken to reach the maximum concentration of epoxidised oleic acid; the experimental results peaked between 20 and 30 min, whereas simulations indicated otherwise. The challenge in pinpointing the maximum point on the experimental curve arose from the complexity of the reactions involved, leading to this disparity. Unlike the experimental setup, the simulated reaction is governed strictly by the chemical reaction equations, where multiple sub-reactions (such as epoxide formation and oxirane ring degradation) occur simultaneously.

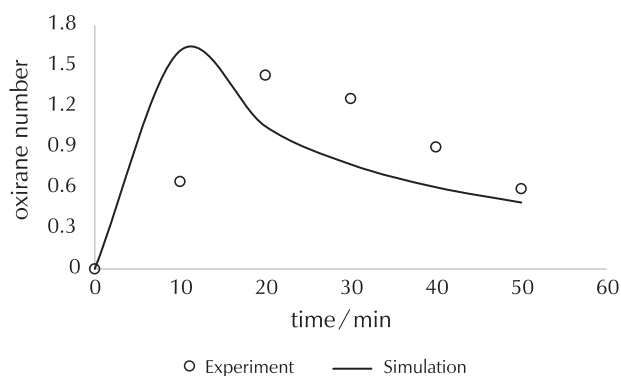


Fig. 4 – Comparison of the oxirane content between experimental and simulation results

4 Conclusion

In this study, both objectives were successfully achieved: determining the effect of catalyst type (sulphuric acid, titanium dioxide and Amberlite), and catalyst loading (0.1 g, 0.5 g, 1.0 g) on RCO % in the epoxidation of palm oil. The epoxidation process was effectively performed using titanium dioxide, sulphuric acid, and Amberlite as catalysts. The different catalysts were evaluated to determine their effect on the RCO %, and the results were tested by FTIR. Using sulphuric acid as a catalyst, an RCO % value of 76.16 % was achieved. The study also found that varying the catalyst loading (e.g., 0.1 g, 0.5 g, 1.0 g) did not significantly increase the amount of product but did increase the reaction time. The formation of epoxide from palm oil was confirmed by FTIR analysis, which showed the functional groups of the epoxide ring within the range of 917 to 1678 cm^{-1} , and the disappearance of the double bond group peak at 3000 cm^{-1} .

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SAŽETAK

Epoksidacija hibridne oleinske kiseline (iz palmolina ulja) primjenom *in situ* mehanizma permravlje kiseline

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Cilj ovog istraživanja bio je ispitati utjecaj različitih katalizatora: sumporne kiseline, titanijeva dioksida i Amberlita, na epoksidaciju palmolina ulja. Ispitan je utjecaj dodane mase katalizatora (0,1 g, 0,5 g, 1,0 g) na relativnu konverziju u oksiran (RCO %). Analiza procesa temeljila se na RCO % podacima i FTIR analizi. Rezultati su pokazali je optimalna epoksidacija ostvarena primjenom 0,5 g sumporne kiseline dajući RCO % vrijednost od 76,16 %. FTIR analiza ukazala je na prisutnost epoksi skupine (pri 833,10 cm^{-1}).

Ključne riječi

Epoksidacija, palmolina ulja, konverzija biomase, kinetički model

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