

Recent Advances in the Catalytic Epoxidation of Oleic Acid for Bio-polyol Synthesis: Challenges and Opportunities

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Abstract

The catalytic epoxidation of oleic acid is a key process in bio-polyol synthesis, offering a renewable alternative to petroleum-based materials. This review explores recent advances in catalyst development, process optimisation, and kinetic modelling, with an emphasis on the transition from conventional homogeneous catalysts to more sustainable heterogeneous alternatives, such as zeolites and metal oxides. Key factors influencing reaction efficiency, including catalyst stability, oxirane retention, and by-product control, are critically analysed. The discussion also highlights industrial applications and potential improvements to enhance process scalability and economic feasibility. This review provides insights into overcoming current challenges and advancing sustainable bio-polyol production.

Keywords

Epoxidation, oxirane ring, catalyst, kinetic models, polyol

1 Introduction

Palm oil can be used as a feedstock to produce epoxides, which are compounds that can replace petroleum-based epoxides in various applications. Epoxides originating from palm oil exhibit similar properties and performance as those derived from petroleum.¹ Additionally, palm oil-based epoxides have the advantage of being a renewable resource, which makes them more sustainable than their petroleum-based counterparts.² The epoxidation process is employed to convert vegetable oils into intermediate molecules by converting their unsaturated fatty acids. In the case of palm oil, this procedure entails changing the fatty acid double bonds into epoxide groups, resulting in the creation of epoxidised palm oil. Various oxidising agents, including peracids and peroxides, can be utilised in this epoxidation process.^{3,4} Epoxidised vegetable oils serve as plasticisers, scavengers, lubricants, and polymer intermediates in conventional syntheses, all of which are essential to the manufacture of PVC.⁵

These oils are highly appealing for epoxy production due to their ability to serve as a sustainable alternative to petroleum-based ingredients used in a range of applications.⁶ Not only do they reduce reliance on fossil fuels, but they also offer additional environmental and health benefits.⁷ Unlike their petroleum-based counterparts, vegetable oils are non-toxic and biodegradable, posing no harm to the environment or human health.⁸ The use of non-toxic, biodegradable oils significantly reduces the potential for pollution and harmful emissions commonly associated with petroleum-derived chemicals.⁹ Furthermore, their sustain-

able nature helps in mitigating the negative environmental impacts commonly associated with traditional petrochemical processes.¹⁰ The use of non-toxic, biodegradable oils aligns with growing industry and consumer preferences for eco-friendly products, enhancing their appeal and adoption across various applications.¹¹

In order to produce polyols — which are widely used in the manufacture of polyurethanes, coatings, and adhesives — epoxides are frequently used in ring-opening reactions. Polyols derived from epoxidised vegetable oils react with various nucleophiles, such as water, alcohols, and amines through ring-opening processes.^{12,13} As potential substitutes for petroleum-based polyols, these bio-based polyols exhibit high reactivity, superior mechanical properties, and excellent thermal stability. Furthermore, owing to their biodegradability and origin from renewable resources, the use of epoxidised vegetable oils as precursors for polyols presents a sustainable and environmentally responsible alternative.¹⁴ The ring-opening reaction typically involves an alcohol, water, or other nucleophile attacking the electrophilic carbon in the epoxide ring, leading to ring cleavage and the formation of a hydroxyl group, thereby producing a polyol.¹⁵

This review provides an overview of recent advancements in the catalytic epoxidation of oleic acid as a key intermediate step in bio-polyol synthesis. As depicted in Fig. 1, particular attention is given to emerging strategies that enhance reaction efficiency, improve selectivity, and support sustainability objectives. Unlike conventional studies focused on homogeneous acid catalysts, this work highlights the potential of heterogeneous catalysts such as functionalised zeolites, metal oxides, and ion-exchange resins, which offer better reusability and a lower environmental

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impact. Additionally, it examines kinetic modelling and process optimisation strategies that deepen the mechanistic understanding of epoxidation. By addressing challenges like catalyst stability, oxirane ring retention, and waste minimisation, this review provides fresh insights into the development of scalable, eco-friendly bio-polyol production methods aligned with green chemistry principles.

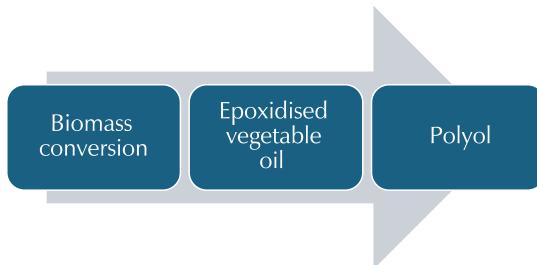


Fig. 1 – Schematic pathway for polyol production from biomass via epoxidation of vegetable oil

2 Materials and methods

2.1 Materials

The fatty acid composition of vegetable oil plays a crucial role in its suitability for epoxidation, as the process specifically targets carbon-carbon double bonds in unsaturated fatty acids.¹⁶ Oils with high concentrations of monounsaturated (e.g., oleic acid) and polyunsaturated fatty acids (e.g., linoleic and linolenic acids) offer greater potential for epoxide formation due to their multiple reactive sites. In contrast, saturated fatty acids such as palmitic and stearic acids lack double bonds, making them unreactive in epoxidation. The proportion of unsaturated to saturated fatty acids differs among vegetable oils, with soybean, linseed, and sunflower oils exhibiting higher degrees of unsaturation, making them more suitable for epoxide production.¹⁷ Modifying the fatty acid profile through oil blending or refining can further enhance epoxidation efficiency, improving the quality and performance of bio-based epoxides in industrial applications.

2.2 Epoxidation process using vegetable oil

Environmental pollution has largely resulted from the use of non-degradable materials that harm ecosystems and disrupt natural life cycles. In contrast, biodegradable materials offer a more sustainable alternative, as they can help reduce pollution and mitigate environmental impact. These materials can decompose into simpler organic compounds, such as carbon dioxide or methane, through microbial activity, and are thus considered environmentally friendly. Any organic material that may break down into simple organic molecules like carbon dioxide or methane with the help of microbes is considered biodegradable.¹⁸ Examples of such materials include wood, wool, cotton, animal waste, and so on. Such materials contribute to the development of renewable energy and biomass energy sys-

tem. Vegetable oils are derived from plant sources such as soybeans, corn, sunflower, palm, and others.¹⁹ These crops can be cultivated and harvested repeatedly, making vegetable oils a renewable resource. Utilising vegetable oils as raw material reduces dependence on finite fossil fuel resources and promotes a more sustainable and environmentally conscious approach.²⁰ Due to their biodegradability, non-toxicity, and versatility, vegetable oils have gained significant attention as renewable raw materials in various industries.

Because it is environmentally beneficial and derived from naturally occurring, renewable resources, epoxidised vegetable oil is in high demand in the modern world.²¹ Epoxidised vegetable oil (EVO), owing to the strong reactivity of the oxirane ring and its notable oxirane oxygen concentration, is an important starting material for the synthesis of several chemicals, including polyols,²² glycols,²³ carbonyl compounds,²⁴ lubricants,²⁵ and polymer plasticisers.²⁶ During epoxidation, an oxidising agent is used to add a single oxygen atom (C=C) to each unsaturated fatty acid chain, converting it into an epoxy group.²⁷ The epoxidation reaction mechanism is illustrated in Eqs. (1) and (2), where a carboxylic acid (R-COOH) reacts with hydrogen peroxide to form a peracid (R-COOOH) *in situ*. The generated peracid then acts as an electrophilic oxidising agent, attacking the alkene double bond to form a three-membered epoxide ring while regenerating the parent carboxylic acid. Vegetable oils contain unsaturated compounds that can undergo chemical modification through a complex process known as epoxidation. Since the oxirane ring is so reactive, epoxides can be used as building blocks for synthesising a variety of chemicals, including plasticisers, lubricants, olefinic compounds, polyols (alcohols), glycols, and stabilisers for polymers.²⁸ The rising demand for epoxides reflects the growing emphasis on sustainable alternatives that minimise environmental harm and support the circular economy.



Vegetable oils consist of a blend of triglycerides-glycerine triesters with fatty acids. The fatty acids constitute approximately 94–96 % of the total mass of triglyceride molecules, with chain lengths ranging from 14 to 22 carbon atoms (with C16 and C18 being the most common) and 0 to 3 double bonds per chain.²⁹ Vegetable oils contain double bonds that can be functionalised through epoxidation and act as reactive sites in coatings. Furthermore, vegetable oil-based plasticisers and additives have demonstrated enhanced heat and light resistance.³⁰ The cyclic ethers known as epoxide groups, or oxirane rings, are formed of three parts within the epoxide ring and are present in oxidised oil. Acid ion exchange resin (AIER) epoxidation, enzyme epoxidation, and traditional epoxidation are the three recognised epoxidation techniques.

2.3 Epoxidation using a traditional approach

The most widely used epoxidation technique is the traditional approach. To ensure safety, this process typically

uses *in situ*-formed peracids, produced by reacting concentrated hydrogen peroxide with a carboxylic acid. This procedure is commonly employed in the industrial sector. The study by Dinda et al.³¹ examined the kinetics of hydrogen peroxide-catalysed epoxidation of cottonseed oil, using liquid inorganic acids such HCl , H_2SO_4 , HNO_3 , and H_3PO_4 . They found that acetic acid (CH_3COOH) was more effective than formic acid (HCOOH) as an oxygen carrier during the epoxidation process involving carboxylic acids. Among the inorganic acids evaluated as catalysts, sulphuric acid (H_2SO_4) was identified as the most effective and productive catalyst. Dislich et al.³² used the conventional method to epoxidise soybean and jatropha oils. The reaction was conducted at 50 °C and atmospheric pressure for approximately 10 h. Under these conditions, the highest conversion rate for soybean oil was 83.3 %.

To improve the process, the researchers investigated several variables and elements that affected the epoxidation reaction, such as the type of catalyst, temperature, molar ratio of the reactants, and mixing speed. They also explored the economic potential of converting mahua oil into epoxidised mahua oil. The study used catalytic inorganic acids like H_2SO_4 and HNO_3 , coupled with H_2O_2 as an oxygen donor, and glacial acetic acid as an oxygen carrier. The findings confirmed that sulphuric acid was the most effective inorganic catalyst for this system, achieving a high double bond to oxirane group conversion. They found that conducting the epoxidation reaction at intermediate temperatures ranging from 55 to 65 °C mitigated hydrolysis reactions.³³

2.4 Epoxidation using acid ion exchange resin

Acidic ion exchange resin (AIER) is an insoluble gel-type catalyst in the form of a tiny organic polymer bead. H_2O_2 reacts with carboxylic acid ($\text{HCOOH}/\text{CH}_3\text{COOH}$) to generate peroxy acid. Through its pores, the peroxy acid reacts with the catalyst. Consequently, triglycerides cannot pass through the gel-like structure of AIER, which causes its pores to become saturated with peroxy acid upon loading into the reactor. This results in reduced oxirane degradation.³⁴ Studies have demonstrated that different vegetable oils react differently to peroxy acids in converting unsaturated fatty acids into oxirane rings.³⁵ In the presence of AIER, peroxy acid may be either peroxyformic acid or peroxyacetic acid. Vlček and Petrović et al.³⁶ investigated the epoxidation kinetics and side reactions of soybean oil in toluene using peroxyacetic and peroxyformic acids, catalysed by AIER. They concluded that peroxyformic acid was more effective than peroxyacetic acid. AIER can serve both as a catalyst for peroxy acid formation and as an initiator for the *in situ* epoxidation of vegetable oils.³⁷ It offers notable benefits over traditional chemical methods by enhancing selectivity and reducing undesired side reactions during the kinetics of *in situ* epoxidation of soybean oil in bulk catalysed by ion exchange resin.

Goud et al.³⁸ investigated the *in situ* epoxidation of karanja oil using aqueous hydrogen peroxide and acetic acid, catalysed by Amberlite IR-120 acidic ion exchange resin. Variables such as stirring speed, temperature, catalyst loading, and the ratios of acetic acid to hydrogen peroxide and

ethylenic unsaturation were investigated. Maximum conversion of double bonds to oxirane groups was achieved at an intermediate temperature of 55 to 65 °C with a shorter reaction time. They also found that the optimal concentrations for the epoxidation process were 0.5 mol for acetic acid to karanja oil, and 1.5 mol for hydrogen peroxide to oil. Mungroo et al.³⁹ investigated the epoxidation of canola oil using hydrogen peroxide as the oxygen donor, acetic acid as the oxygen carrier, and AIER (22 % loading) as the catalyst. They found that AIER, a heterogeneous catalyst, was reusable with minimal activity loss. The formation of epoxy adducts in canola oil was confirmed through FTIR and ^1H NMR spectral analysis. Janković et al.⁴⁰ examined the kinetics of soybean oil epoxidation in bulk using peracetic acid formed *in situ*, with an ion exchange resin as the catalyst. They determined that the catalytic reaction involved the adsorption of acetic acid and peracetic acid on active catalyst sites, with the overall rate-determining step being an irreversible surface reaction. They also observed that increasing the catalyst concentration, reaction temperature, and the molar ratio of acetic acid to ethylenic unsaturation improved the reaction rate and oxirane content.

Dinda et al.⁴¹ analysed the kinetics of cottonseed oil epoxidation using peroxyacetic acid (PAA) generated *in situ* from hydrogen peroxide and glacial acetic acid (AA) in the presence of acidic ion exchange resin (AIER) catalysts, specifically Amberlite IR-120. They examined the effects of various factors such as temperature, stirring speed, catalyst loading, particle size, hydrogen peroxide concentration, and acetic acid (AA) on the conversion of oxirane. Using *in situ* generated peroxyacetic acid (PAA), a high degree of oxirane conversion (over 65 %) and excellent selectivity (greater than 90 %) were achieved under optimal conditions. The overall reaction rate equations were developed using the Langmuir–Hinshelwood–Hougen–Watson (L–H–H–W) kinetic model. This kinetic model included the main side reactions to calculate the kinetic parameters. Kinetic parameters were determined via nonlinear regression technique to fit the experimental data, and the activation energy for the AIER-catalysed epoxidation of cottonseed oil was found to be 10.1 kcal mol⁻¹, as indicated by the estimated kinetic constants.

2.5 Homogeneous catalytic epoxidation

Homogeneous catalysts were frequently used in the peracid mechanism epoxidation procedure. A catalyst is said to be homogeneous if it is in the same phase as the reactant, which is often liquid. Homogeneous catalysis offers several advantages, including high oxirane yields, high purity and efficiency of epoxide production, low cost, intrinsic safety, low chemical and instrument requirements, and broader applicability.⁴² However, the homogeneous epoxidation process, which employs strong mineral acids (HCl , HNO_3 , H_2SO_4 , and H_3PO_4), has several drawbacks, such as low epoxide selectivity, severe reactor corrosion, challenges in isolating the end products from the acidic by-products, and unfavourable side reactions.⁴³ The use of performic acid produced *in situ* for the catalytic epoxidation of palm oleic acid has been explored in terms of optimisation and kinetic investigations.⁴⁴

The highest relative conversion of palm oleic acid to oxirane reached almost 85.6 %. Through epoxidation and the use of inorganic acids as homogeneous catalysts, *Silviana et al.*⁴⁵ investigated the use of waste cooking oil as a bio-plasticiser. Due to its high content of unsaturated triglycerides, waste cooking oil was a great resource for this investigation. To prepare the epoxidised waste oil, hydrochloric, nitric, and sulphuric acids were used. The concentration of double bonds in these triglycerides rendered them promising raw resources. The double bond component is a source for bio-plasticiser.

The study's objective was to determine which inorganic acid conversion was optimal for a given oxirane conversion and iodine value at different time intervals. The standard hydrogen peroxide-acetic acid procedure involved an epoxidation reaction. The outcome demonstrated that, compared to other acid catalysts, sulphuric acid achieved higher conversion. Using liquid inorganic acids such as hydrochloric acid, sulphuric acid, nitric acid, and phosphoric acid as catalysts, *Dinda et al.*⁴⁶ examined the kinetics of cottonseed oil epoxidation using aqueous H_2O_2 . Using H_2SO_4 or H_3PO_4 as a catalyst, cottonseed oil converted to oxirane to a higher degree than it did with HCl and HNO_3 , according to the findings. Using H_2SO_4 as a catalyst, as opposed to H_3PO_4 , allowed for the maximum oxirane conversion (70.4 %) to be reached in the shortest amount of time (after 6 h).

2.6 Heterogeneous catalytic epoxidation

Vegetable oils are catalytically epoxidised to produce a wide range of commodity compounds for commercial usage. This process also yields several intermediates, fine chemicals, and medicines. Heterogeneous catalysts are used in a specific type of catalytic epoxidation, typically involving metal-based materials such as alumina, zeolite, titanium, tungsten, molybdenum, or rhenium. Their use was intended to reduce reliance on strong acids, minimise side reactions, facilitate the separation and recycling of acids from epoxides, limit oxirane ring degradation, and improve the overall efficiency and environmental performance of the epoxidation process.⁴⁷ In the industrial sector, heterogeneous catalysis is commonly employed due to its facile separation, resulting in reduced operating expenses. *Yunus et al.*⁴⁸ investigated the *in situ* epoxidation of palm olein using TiO_2 and zeolite ZSM-5 catalysts. According to the study, heterogeneous catalysts like TiO_2 and zeolite ZSM-5 are frequently employed in many chemical reactions. In addition to being affordable and eco-friendly, they offer other benefits. Performic acid, generated *in situ*, was used to oxidise palm olein in a semi-batch reactor at 45 and 60 °C with an agitation speed of 400 rpm to produce epoxidised palm olein. The effects of the two catalysts were investigated to assess each catalyst's efficiency in catalysing the *in situ* epoxidation. Fourier transform infrared (FTIR) spectroscopy and relative conversion to oxirane (RCO %) were used for evaluation.

Brunauer-Emmett-Teller (BET) analysis showed that TiO_2 achieved a higher RCO % at 45 °C than zeolite ZSM-5, suggesting that it is a superior catalyst for the *in situ* epoxidation of palm olein. It indicates that the catalyst is the bet-

ter choice because the reaction needs to occur at a lower temperature to prevent the oxirane ring from opening. The ZSM-5 performs best at temperatures above 60 °C. The capacity of the catalyst to simultaneously yield higher conversion and improved epoxy ring stability in the epoxidation at lower temperature, however, is what really distinguishes the superior catalyst. Since TiO_2 offered the maximum percentage of RCO and epoxy ring stability over an extended period of time at low temperatures, it was determined to be the optimal catalyst. *Azmi et al.*⁴⁹ demonstrated that TiO_2 is a highly effective catalyst for oxirane ring opening with nucleophiles containing nitrogen and oxygen, leading to heterogeneous catalysis that encourages epoxide hydrolysis.

The reactive site, where high polarity particles react to generate additional functional groups, such as hydroxy, determines the catalyst performance for selectivity inside the mesoporous order. The effectiveness of the zeolite in the epoxidation process may cause unconverted epoxide to be drawn into the substrate molecules, causing the reaction time to increase. Acid zeolites were employed by *Turco et al.*⁵⁰ as a potential catalyst for the epoxidation of soybean oil using formic acid and hydrogen peroxide. An alternative to the soluble mineral acid that could be utilised to limit side reactions and improve selectivity is an acid heterogeneous catalyst. The minuscule intracrystalline pores of zeolite, which allow compounds in the aqueous phase access but prevent large triglyceride molecules from doing so, are thought to be the reason for the material's advantageous properties. The absence of mineral acid in the aqueous solution outside the pores reduces the negative effects of ring opening. As a result, using epoxidised soybean oil, the zeolite may produce nearly complete double bond conversion (96 %) with a respectable selectivity (82 %).

2.7 Polyol formation

Polyols are alcohols with multiple hydroxyl groups, derived from petrochemicals or renewable sources such as vegetable oils, used cooking oil, and rice bran oil. While petrochemical-based polyols dominate the market, they are costly, energy-intensive, and non-biodegradable. Polyols can be synthesised through various methods, including transesterification of fatty acids with glycerol or glycerine. However, the combination of high temperature and extended reaction times may cause premature degradation, which can be exacerbated by this approach.⁵¹ Another method is the hydroformylation process, which begins with vegetable oil that has an aldehyde function and hydrogenates it to alcohol. One limitation of this approach is that the yield percentage changes according to the type of catalyst used.⁵² Subsequently, the olefin is subjected to high molecular oxygen oxidation, followed by acetal hydrolysis and reduction to alcohol. To achieve a high yield, this intricate technique needs to run at high pressure. Furthermore, it can also be produced using the ozonolysis process. But this approach is costly and inefficient.⁵³ Finally, natural oil-based processes like epoxidation and hydroxylation of vegetable or animal oil can be used to create polyols.

The most cost-effective and eco-friendly method involves epoxidation and hydroxylation of vegetable oils using

readily available alcohols and water, with acid catalysts enabling fast, multi-step reactions without compromising product quality. Epoxidised palm oil (EPO) forms when peracids from hydrogen peroxide and formic acid react with oleic acid, followed by hydroxylation, which introduces hydroxyl groups via ring opening. Because sulphuric acid performs better than strong bases, which suggests a larger hydroxyl group content, it is a preferred catalyst in this process. The reason for this is that these catalyst types have the potential to produce the largest relative conversion of oxirane (RCO), which is approximately 88 %, according to Amri et al.⁵⁴ Researchers had worked on initiatives to replace petroleum-based polymers during the course of the year. The polyol derived from jatropha oil (JOL) in this study was created by oxirane ring opening and epoxidation, a two-step process. The oxirane oxygen content (OOC) of epoxidised jatropha oil (EJO) was influenced by temperature, reaction time, and the oil double bond-to-formic acid ratio. At 60 °C, a 1 : 0.6 molar ratio, and a 4-hour reaction time, OOC ranged from 26 to 4.30 %, achieving a 75 % conversion.

The oxirane ring opening of EJO was then followed by the effective synthesis of a series of JOLs with hydroxyl numbers between 138 to 217 mg KOH/g in a reaction time of 2.25 to 4.5 h. The resulting JOLs showed low viscosity values between 430 and 970 mPas and molecular weights between 1349 and 2129 g mol⁻¹, demonstrating Newtonian behaviour. The successful synthesis of polyurethane from JOL was verified by FTIR analysis. Good colloidal stability was indicated by the average tiny particle size of the polyurethane dispersion that was obtained. Ji et al.⁵⁵ investigated soybean oil hydroformylation for bio-polyol production. They investigated the catalyst's impact on the procedure and the characteristics of the final products. Ninety-five percent of the samples were converted using a costly rhodium catalyst, while only 67 % were converted with a cobalt catalyst. In the former instance, the polyol also showed increased functionality, molecular weight, and hydroxyl value. However, adopting rhodium catalysts would be economically feasible only if their full recovery from the process were to be achieved, which would require costly techniques.

2.8 Effect of process parameters on polyol formation from epoxidised vegetable oil

Hazmi et al.⁵⁶ conducted an in-depth investigation into the influence of various reaction parameters on the properties of the resulting polyols. Key variables such as temperature, pressure, catalyst loading, reactant molar ratios, and reaction time were examined. Temperature and reduced pressure were identified as critical factors influencing the rate of the initial esterification reaction. Moreover, catalyst concentration significantly influenced both the reaction rate and the colouration of the final product. The reactant molar ratios and reaction duration were also found to play crucial roles in determining the properties of the final product during the subsequent epoxidation step, in which temperature control remained essential. The amount of catalyst utilised in the final reaction step, alcoholysis, had a notable impact on the characteristics of the end product.⁵⁷

Furthermore, research by Jalil et al.⁵⁸ on optimising the epoxidation of palm-based oleic acid for polyol production yielded promising results. The model's relative oxirane content (%RCO) value of 85 % closely matched the experimental value of 81 %, indicating excellent model accuracy. The results indicated that temperature, as well as the molar ratios of formic acid-to-oleic acid and hydrogen peroxide-to-oleic acid, significantly influenced the epoxidation process ($p < 0.05$), with strong parameter interactions ($p < 0.0001$).

3 Conclusion

The catalytic epoxidation of oleic acid offers a sustainable and promising pathway for bio-polyol synthesis, providing a viable alternative to fossil-based feedstocks. The use of heterogeneous catalysts has improved reaction efficiency, selectivity, and catalyst reusability, aligning closely with green chemistry principles. Despite these advancements, several challenges persist, notably oxirane ring instability, catalyst deactivation, and the scalability of the process for industrial application. To overcome these limitations, future research should focus on process optimisation, robust kinetic modelling, and the development of innovative, stable catalyst systems. Particular emphasis should be placed on designing catalysts that are not only efficient but also environmentally benign and economically viable. Additionally, the incorporation of greener oxidants, solvent-free systems, and energy-efficient technologies will be essential in developing a truly sustainable epoxidation process. Overall, addressing these challenges through interdisciplinary approaches will be crucial for advancing the commercial viability of bio-polyols derived from oleic acid and expanding their application across various green polymer industries.

Availability of data and materials

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

Ethics approval and consent to participate

Not applicable.

Competing interests

The authors declare no competing interests.

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Author contribution

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References Literatura

1. F. Marriam, A. Irshad, I. Umer, M. Arslan, Vegetable oils as bio-based precursors for epoxies, *Sustain. Chem. Pharm.* **31** (2023) 100935. doi: <https://doi.org/10.1016/j.scp.2022.100935>.
2. D. Derawi, J. Salimon, W. A. Ahmed, Preparation of Epoxidized Palm Olein as Renewable Material by Using Peroxy Acids, *Malay. J. Anal. Sci.* **18** (2014) 584–591.
3. J. Thomas, R. Patil, Enabling green manufacture of polymer products via vegetable oil epoxides. *Ind. Eng. Chem. Res.* **62** (4) (2023) 1725–1735, doi: <https://doi.org/10.1021/acs.iecr.2c03867>.
4. N. M. Noor, T. N. M. T. Ismail, M. A. M. Noor, K. D. P. Palam, M. N. Sattar, N. 'Ain Hanzah, S. Adnan, Y. S. Kian, Physico-chemical Properties of Palm Olein-Based Polyols Prepared Using Homogeneous and Heterogeneous Catalysts, *J. Oil Palm Res.* **34** (2022) 167–176, doi: <https://doi.org/10.21894/jopr.2021.0034>.
5. V. N. Sahana, R. C. Kumar, Manufacturing of Pongamia Oil-based Bio-lubricant for Machining Application, *Int. Res. J. Eng. Technol.* **6** (2019) 1639–1645, url: <https://www.irjet.net/archives/V6/I7/IRJET-V6I7530.pdf>.
6. E. R. Gunawan, D. Suhendra, P. Arimanda, D. Asnawati, Murniati, Epoxidation of *Terminalia catappa* L. Seed oil: Optimization reaction, *S. Afr. J. Chem. Eng.* **43** (2023) 128–134. doi: <https://doi.org/10.1016/j.sajce.2022.10.011>.
7. A. González-Benjumea, G. Marques, O. M. Herold-Majumdar, J. Kiebist, K. Scheibner, J. C. del Río, A. T. Martínez, A. Gutiérrez, High Epoxidation Yields of Vegetable Oil Hydrolyzates and Methyl Esters by Selected Fungal Peroxygenases, *Front. Bioeng. Biotechnol.* **8** (2021) 605854, doi: <https://doi.org/10.3389/fbioe.2020.605854>.
8. A. Khoon Poh, L. Choy Sin, C. Sit Foon, C. Cheng Hock, Polyurethane wood adhesive from palm oil-based polyester polyol, *J. Adhes. Sci. Technol.* **28** (2014) 1020–1033, doi: <https://doi.org/10.1080/01694243.2014.883772>.
9. E. Vanags, M. Kirpluks, U. Cabulis, Z. Walterova, Highly Functional Polyol Synthesis from Epoxidized Tall Oil Fatty Acids, *J. Renew. Mater.* **6** (2018) 764–771, doi: <https://doi.org/10.7569/JRM.2018.634111>.
10. P. D. Jadhav, A. V. Patwardhan, R. D. Kulkarni, Kinetic study of in situ epoxidation of mustard oil, *Mol. Catal.* **511** (2021) 111748, doi: <https://doi.org/10.1016/j.mcat.2021.111748>.
11. T. Cogliano, R. Turco, M. Di Serio, T. Salmi, R. Tesser, V. Russo, Epoxidation of Vegetable Oils via the Prilezhaev Reaction Method: A Review of the Transition from Batch to Continuous Processes, *Ind. Eng. Chem. Res.* **63** (2024) 11231–11262, doi: <https://doi.org/10.1021/acs.iecr.3c04211>.
12. S. S. Narine, J. Yue, X. Kong, Production of polyols from canola oil and their chemical identification and physical properties, *J. Am. Oil. Chem. Soc.* **84** (2) (2007) 173–179, doi: <https://doi.org/10.1007/s11746-006-1021-5>.
13. M. Musik, M. Bartkowiak, E. Milchert, Advanced Methods for Hydroxylation of Vegetable Oils, Unsaturated Fatty Acids and Their Alkyl Esters, *Coatings* **12** (2022) 13, doi: <https://doi.org/10.3390/coatings12010013>.
14. K. Carvalho, R. M. B. Alves, L. Kulay, Environmental performance of alternative green polyol synthesis routes: A proposal for improvement, *Processes* **9** (2021) 1122, doi: <https://doi.org/10.3390/pr9071122>.
15. Y. Guo, J. H. Hardesty, V. M. Mannari, J. L. Massingill, Hydrolysis of epoxidized soybean oil in the presence of phosphoric acid, *J. Am. Oil Chem. Soc.* **84** (2007) 929–935, doi: <https://doi.org/10.1007/s11746-007-1126-5>.
16. K. P. Ang, C. S. Lee, S. F. Cheng, C. H. Chuah, Synthesis of palm oil-based polyester polyol for polyurethane adhesive production, *J. Appl. Polym. Sci.* **131** (2014) 39967, doi: <https://doi.org/10.1002/app.39967>.
17. N. Weber, K. Vosmann, E. Fehling, K. D. Mukherjee, D. Bergenthal, Analysis of hydroxylated fatty acids from plant oils, *J. Am. Oil Chem. Soc.* **72** (1995) 361–368, doi: <https://doi.org/10.1007/BF02541097>.
18. M. Kurańska, E. Malewska, Waste cooking oil as starting resource to produce bio-polyol – analysis of transesterification process using gel permeation chromatography, *Ind. Crops Prod.* **162** (2021) 113294, doi: <https://doi.org/10.1016/j.indcrop.2021.113294>.
19. E. Faujdar, R. K. Singh, Methyl oleate derived multifunctional additive for polyol based lubricants, *Wear* **466–467** (2021) 203550, doi: <https://doi.org/10.1016/j.wear.2020.203550>.
20. L. L. Monteavarro, E. O. Silva, A. P. O. Costa, D. Samios, A. E. Gerbase, C. L. Petzhold, Polyurethane Networks from Formiculated Soy Polyols: Synthesis and Mechanical Characterization, *J. Am. Oil Chem. Soc.* **82** (2005) 365–371, doi: <https://doi.org/10.1007/s11746-005-1079-0>.
21. S. O. Egbuna, U. J. Nwachukwu, C. M. Agu, C. O. Asadu, B. Okolo, Production of biolubricant samples from palm kernel oil using different chemical modification approaches, *Eng. Reports* **3** (2021) e12422, doi: <https://doi.org/10.1002/eng2.12422>.
22. B. Nim, P. Sreearunothai, A. Petcharasuk, P. Opaprakasit, Preparation of TiO_2 -loaded electrospun fibers of poly(lactide)/poly(vinylpyrrolidone) blends for use as catalysts in epoxidation of unsaturated oils, *J. Nanoparticle Res.* **20** (2018) 100, doi: <https://doi.org/10.1007/s11051-018-4199-1>.
23. E. Milchert, A. Smagowicz, G. Lewandowski, Optimization of the reaction parameters of epoxidation of rapeseed oil with peracetic acid, *J. Chem. Technol. Biotechnol.* **85** (2010) 1099–1107, doi: <https://doi.org/10.1002/jctb.2405>.
24. M. Bahadi, N. Salih, J. Salimon, Synthesis and characterization of green biodegradable palm oleic acid based polyester, *Biointerface Res. Appl. Chem.* **11** (2021) 14359–14371, doi: <https://doi.org/10.33263/BRIAC116.1435914371>.
25. Y. N. Lye, N. Salih, J. Salimon, Optimization of Partial Epoxidation on *Jatropha curcas* Oil Based Methyl Linoleate Using Urea-hydrogen Peroxide and Methyltrioxorhenium Catalyst, *Appl. Sci. Eng. Prog.* **14** (2021) 89–99, doi: <https://doi.org/10.14416/JASEP.2020.12.006>.
26. W. N. W. Tajulruddin, A. R. Rahmat, R. A. Majid, Synthesis of Bio-Based Hydrogel from Epoxidized Palm Oil Catalyzed by Fluoroantimonic Acid Hexahydrate, *Malaysian J. Anal. Sci.* **20** (2016) 1129–1137, doi: <https://doi.org/10.17576/mjas-2016-2005-19>.
27. D. N. A. Raofuddin, N. H. A. Rasnan, I. S. Azmi, S. M. A. Rahman, M. Z. Yeop, M. Z. A. Kadir, M. J. Jalil, Epoxidation of Unsaturated Oleic Acids via *in Situ* Catalytic Performic Acid, *Iran. J. Chem. Chem. Eng.* **42** (2023) 1491–1498, doi: <https://doi.org/10.30492/ijcce.2022.557155.5425>.
28. W. H. Chen, M. Carrera Uribe, E. E. Kwon, K. Y. A. Lin, Y. K. Park, L. Ding, L. H. Saw, A comprehensive review of thermoelectric generation optimization by statistical approach: Taguchi method, analysis of variance (ANOVA), and response surface methodology (RSM), *Renew. Sustain. Energy Rev.* **169** (2022) 112917, doi: <https://doi.org/10.1016/j.ener.2022.112917>.
29. A. Freites Aguilera, R. Hämäläinen, K. Eränen, P. Tolvanen, T. Salmi, Prilezhaev epoxidation of oleic acid in the presence and absence of ultrasound irradiation, *J. Chem. Technol. Biotechnol.* **96** (2021) 1874–1881, doi: <https://doi.org/10.1002/jctb.6706>.

30. I. S. Azmi, S. A. Adnan, A. N. Masri, S. D. Nurherdiana, S. N. Abdullah, M. J. Jalil, *In situ* epoxidation of oleic acid with applied natural zeolite as a catalyst, *Environ. Prog. Sustain. Energy* **43** (2024) 14421, doi: <https://doi.org/10.1002/ep.14421>.
31. S. Dinda, N. S. R. Veeram, R. B. Adusumalli, Production of bio-epoxide and bio-adhesive from non-edible oil, *Korean J. Chem. Eng.* **33** (2016) 2915-2922, doi: <https://doi.org/10.1007/s11814-016-0136-0>.
32. C. Dislich, A. C. Keyel, J. Salecker, Y. Kisel, K. M. Meyer, M. Auliya, A. D. Barnes, M. D. Corre, K. Darras, H. Faust, B. Hess, S. Klasen, A. Knohl, H. Kreft, A. Meijide, F. Nurdiansyah, F. Otten, G. Pe'er, S. Steinebach, S. Tarigan, M. H. Tölle, T. Tschartinke, K. Wiegand, A review of the ecosystem functions in oil palm plantations, using forests as a reference system, *Biol. Rev.* **92** (2017) 1539-1569, doi: <https://doi.org/10.1111/brv.12295>.
33. V. V. Goud, A. V. Patwardhan, N. C. Pradhan, Studies on the epoxidation of mahua oil (*Madhumica indica*) by hydrogen peroxide, *Biores. Technol.* **97** (12) (2006) 1365-1371, doi: <https://doi.org/10.1016/j.biortech.2005.07.004>.
34. N. D. Kasmin, I. S. Azmi, S. D. Nurherdiana, F. A. M. Yusof, M. J. Jalil, Chemical modification of linoleic acid via catalytic epoxidation of corn oil: A sustainable approach, *Environ. Prog. Sustain. Energy* **43** (2024) 14362, doi: <https://doi.org/10.1002/ep.14362>.
35. M. Kurańska, M. Niemiec, Cleaner production of epoxidized cooking oil using a heterogeneous catalyst, *Catalysts* **10** (2020) 1261, doi: <https://doi.org/10.3390/catal10111261>.
36. T. Vlček, Z. S. Petrović, Optimization of the chemoenzymatic epoxidation of soybean oil, *J. Am. Oil Chem. Soc.* **83** (2006) 247-252, <https://doi.org/10.1007/s11746-006-1200-4>.
37. V. B. Borugadda, V. V. Goud, Epoxidation of castor oil fatty acid methyl esters (COFAME) as a lubricant base stock using heterogeneous ion-exchange resin (IR-120) as a catalyst, *Energy Procedia* **54** (2014) 75-84, <https://doi.org/10.1016/j.egypro.2014.07.249>.
38. V. V. Goud, A. V. Patwardhan, S. Dinda, N. C. Pradhan, Epoxidation of karanja (*Pongamia glabra*) oil catalysed by acidic ion exchange resin, *Eur. J. Lipid Sci. Technol.* **109** (6) (2007) 575-584, doi: <https://doi.org/10.1002/ejlt.200600298>.
39. R. Mungroo, N. C. Pradhan, V. V. Goud, A. K. Dalai, Epoxidation of canola oil with hydrogen peroxide catalyzed by acidic ion exchange resin, *J. Am. Oil Chem. Soc.* **85** (2008) 887-896, doi: <https://doi.org/10.1007/s11746-008-1277-z>.
40. M. R. Janković, S. V. Sinadinović-Fišer, O. M. Govedarica, Kinetics of the Epoxidation of Castor Oil with Peracetic Acid Formed *In Situ* in the Presence of an Ion-Exchange Resin, *Ind. Eng. Chem. Res.* **53** (2014) 9357-9364, doi: <https://doi.org/10.1021/ie500876a>.
41. S. Dinda, V. V. Goud, A. V. Patwardhan, N. C. Pradhan, Selective epoxidation of natural triglycerides using acidic ion exchange resin as catalyst, *Asia-Pacific J. Chem. Eng.* **6** (6) (2011) 870-878, doi: <https://doi.org/10.1002/api.466>.
42. M. B. Mahadi, I. S. Azmi, M. A. A. H. M. Tajudin, E. A. Saputro, M. J. Jalil, Sustainable epoxidation of sunflower oil via heterogenous catalytic *in situ* peracids mechanism, *Biomass Convers. Biorefinery* **15** (4) (2024) 5719-5727, doi: <https://doi.org/10.1007/s13399-023-05258-7>.
43. F. M. de Souza, M. R. Sulaiman, R. K. Gupta, Materials and Chemistry of Polyurethanes, in R. K. Gupta (ed.), *Materials and Chemistry of Flame-Retardant Polyurethanes Volume 1: A Fundamental Approach*, ACS Symp. Ser., Vol. **1399**, American Chemical Society, Washington, DC, 2021, pp. 1-36, doi: <https://doi.org/10.1021/bk-2021-1399.ch001>.
44. M. J. Jalil, A. Hadi, I. S. Azmi, Catalytic epoxidation of palm oleic acid using *in situ* generated performic acid – Optimization and kinetic studies, *Mat. Chem. Phys.* **270** (2021) 124754, doi: <https://doi.org/10.1016/j.matchemphys.2021.124754>.
45. S. Silviana, D. D. Anggoro, A. C. Kumoro, Waste Cooking Oil Utilisation as Bio-plasticiser through Epoxidation using Inorganic Acids as Homogeneous Catalysts, *Chem. Eng. Trans.* **56** (2017) 1861-1866, doi: <https://doi.org/10.3303/CET1756311>.
46. S. Dinda, A. V. Patwardhan, V. V. Goud, N. C. Pradhan, Epoxidation of cottonseed oil by aqueous hydrogen peroxide catalysed by liquid inorganic acids, *Biores. Technol.* **99** (9) (2008) 3737-3744, doi: <https://doi.org/10.1016/j.biortech.2007.07.015>.
47. Y. Meng, F. Taddeo, A. F. Aguilera, X. Cai, V. Russo, P. Tolvanen, S. Leveneur, The Lord of the chemical rings: Catalytic synthesis of important industrial epoxide compounds, *Catalysts* **11** (7) (2021) 765, doi: <https://doi.org/10.3390/catal11070765>.
48. M. M. Yunus, S. K. Jamaludin, S. A. Karim, A. Abd Gani, A. Sauki, Catalytic efficiency of titanium dioxide (TiO_2) and zeolite ZSM-5 catalysts in the *in-situ* epoxidation of palm olein, In: IOP Conference Series: Materials Science and Engineering, IOP Publishing. **358** (1) (2018) 012070, doi: [10.1088/1757-899X/358/1/012070](https://doi.org/10.1088/1757-899X/358/1/012070).
49. I. S. Azmi, M. R. Mustafa, N. I. S. Mohd Zalman, M. D. Haqeeq Norazlan, N. Mahdir, M. S. Md Zaini, M. J. Jalil, Synthesis of bio-polyol from epoxidized palm oleic acid by homogeneous catalyst, *J. Elastomers Plast.* **55** (2) (2022) 1-13, doi: <https://doi.org/10.1177/00952443221147029>.
50. R. Turco, R. Tesser, R. Vitiello, V. Russo, S. Andini, M. Di Serio, Synthesis of Biolubricant Basestocks from Epoxidized Soybean Oil, *Catalysts* **7** (2017) 309, doi: <https://doi.org/10.3390/catal7100309>.
51. M. S. A. Rahman, M. J. Jalil, M. Muain, V. Gloria, I. S. Azmi, A. Hadi, A. F. M. Yamin, N. Morad, Epoxidation of waste cooking oil using catalytic *in situ* generated performic acid, IOP Conf. Ser. Earth Environ. Sci. **476** (1) (2020) 012143, doi: <https://doi.org/10.1088/1755-1315/476/1/012143>.
52. A. Sardari, A. A. S. Alvani, S. R. Ghaffarian, Synthesis and characterization of novel castor oil-based polyol for potential applications in coatings, *J. Renew. Mater.* **7** (2019) 31-40, doi: <https://doi.org/10.32604/jrm.2019.00045>.
53. M. Kurańska, A. Prociak, M. Kirpluks, U. Cabulis, Polyurethane-polyisocyanurate foams modified with hydroxyl derivatives of rapeseed oil, *Ind. Crops Prod.* **74** (2015) 849-857, doi: <https://doi.org/10.1016/j.indcrop.2015.06.006>.
54. M. R. Amri, S. S. O. Al-Edrus, C. T. Guan, F. M. Yasin, L. S. Hua, Jatropha Oil as a Substituent for Palm Oil in Biobased Polyurethane, *Int. J. Polym. Sci.* **2021** (1) (2021) 6655936, doi: <https://doi.org/10.1155/2021/6655936>.
55. D. Ji, Z. Fang, W. He, Z. Luo, X. Jiang, T. Wang, K. Guo, Polyurethane rigid foams formed from different soy-based polyols by the ring opening of epoxidised soybean oil with methanol, phenol, and cyclohexanol, *Ind. Crops Prod.* **74** (2015) 76-82, doi: <https://doi.org/10.1016/j.indcrop.2015.04.041>.
56. A. S. A. Hazmi, M. M. Aung, L. C. Abdullah, M. Z. Salleh, M. H. Mahmood, Producing *Jatropha* oil-based polyol via epoxidation and ring opening, *Ind. Crops Prod.* **50** (2013) 563-567, doi: <https://doi.org/10.1016/j.indcrop.2013.08.003>.
57. Y. Li, X. Luo, S. Hu, Bio-based Polyols and Polyurethanes, Springer Cham, Heidelberg, New York, Dordrecht, London, 2015, doi: <https://doi.org/10.1007/978-3-319-21539-6>.
58. M. J. Jalil, M. H. N. Ishak, I. M. Rasib, M. Z. A. Kadir, M. Noorafzida, I. S. Azmi, Epoxidation of Hybrid Oleic Acid-derived Palm Oil Using an *In Situ* Performic Acid Mechanism, *Kem. Ind.* **73** (2024) 477-481, doi: <https://doi.org/10.15255/KUI.2024.010>.

SAŽETAK

Nedavni napreci u katalitičkoj epoksidaciji oleinske kiseline za sintezu biopoliola: izazovi i mogućnosti

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Katalitička epoksidacija oleinske kiseline ključan je proces u sintezi biopoliola te predstavlja obnovljivu alternativu materijalima dobivenim iz nafte. Ovaj pregledni rad obuhvaća najnovije napretke u razvoju katalizatora, optimizaciji procesa i kinetičkom modeliranju, s naglaskom na prijelaz s konvencionalnih homogenih katalizatora na održivije heterogene sustave poput zeolita i metalnih oksida. Kritički se analiziraju ključni čimbenici koji utječu na učinkovitost reakcije, uključujući stabilnost katalizatora, očuvanje oksiranskog prstena i kontrolu nusprodukata. U radu se raspravlja i o industrijskim primjenama te potencijalnim poboljšanjima koja mogu unaprijediti skalabilnost procesa i njegovu ekonomsku isplativost. Ovaj pregled pruža uvid u načine prevladavanja postojećih izazova i daljnog razvoja održive proizvodnje biopoliola.

Ključne riječi

Epoksidacija, oksiranski prsten, katalizator, kinetički modeli, poliol

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