

Advances in the Epoxidation of Non-Edible Oils: Prileschajew Reaction, Hydroxylation, and Hydrolysis for DHSA Production

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Abstract

Growing environmental pressures and uncertainties in fossil-based resources have intensified efforts to convert non-edible oils into value-added bio-based chemicals such as dihydroxystearic acid (DHSA). This review synthesises recent developments in the epoxidation of non-edible oils by outlining key reaction pathways, including Prileschajew oxidation, hydroxylation, and hydrolysis, and examining approaches to enhance oxirane formation while minimising undesirable ring-opening side reactions. Particular attention is given to sustainable catalytic systems and optimised reaction conditions that improve selectivity and overall process performance. By integrating these findings, the review highlights the progress made toward translating laboratory-scale epoxidation studies into viable industrial applications, especially in cosmetics, biopolymers, and other emerging bio-based sectors.

Keywords

Epoxidation, DHSA, oxirane content, hydrolysis

1 Introduction

Concerns over fossil fuel supply uncertainties, carbon emissions, and rising petroleum prices drive the search for alternatives.¹ Environmental regulations and societal demands further emphasise the need for sustainable options.² Vegetable oils stand out as a renewable and eco-friendly resource with lower emissions.³ Neem oil also known as *Azadirachta indica*, is extracted from the neem tree and is commonly found in India, but can also be found in other countries across Africa and Asia. There, it is widely used as a pesticide due to the presence of active compounds such as caryophyllene oxide, limonene, and organosulphur compounds.⁴ The alternative medicine sector in Ethiopia also uses neem oil to treat malaria and skin diseases.⁵ Epoxidation converts unsaturated fatty acids into reactive epoxides, which are used in various chemicals and polymers.⁶ This process replaces a carbon-carbon double bond with oxygen, typically using *in situ*-generated performic acid from formic acid and hydrogen peroxide.⁷

Under acidic conditions, epoxides undergo ring cleavage, leading to further modifications like dihydroxystearic acid (DHSA) via hydrolysis. The process involves two steps: (1) HCOOH reacts with H₂O₂ to form HCOOOH, and (2) HCOOOH donates oxygen to oleic acid, forming oxirane rings, which subsequently hydrolyse.⁸ The structure of DHSA is beneficial for various cosmetic applications because it can be used as a thickening and binding agent in

powders, a coating agent for lipsticks, and a binding agent in deodorants, making it widely used in this industry.⁹ Its good polarity enables DHSA to bind easily with other polar compounds.

Although significant progress has been made in the epoxidation of non-edible oils, challenges remain in maximising oxirane yield while minimising side reactions such as ring cleavage and hydrolysis, which reduce epoxide stability.¹⁰

This review provides a comprehensive analysis of key epoxidation pathways, including the hydroxylation and hydrolysis, with particular emphasis on the production of dihydroxystearic acid (DHSA) from non-edible oils. Its uniqueness lies in evaluating how catalyst selection, reaction conditions, and mechanistic factors influence oxirane stability and epoxide selectivity. Recent studies have shown that conventional acid-catalysed *in situ* peracid systems, although effective in generating high oxirane yields, are often limited by issues such as equipment corrosion, challenging product separation, and the promotion of ring-opening side reactions under strongly acidic environments. In contrast, base catalysts offer milder and potentially safer conditions, yet their role in peracid formation and their mechanistic behaviour remain less explored, creating a gap in comparative understanding between acidic and basic catalytic systems.

This review therefore examines the potential of environmentally benign catalysts as alternatives to traditional mineral acids, highlights critical parameters governing oxirane formation and stability, and identifies areas where mechanistic insight is still lacking. By addressing these issues,

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the review aims to support the development of more sustainable, selective, and industrially viable epoxidation processes for converting non-edible oils into DHSA and other high-value bio-based products.

2 Raw materials

The materials used in this study included vegetable oil as the primary feedstock; hydrogen peroxide (30–35 %) and formic acid (85 %) as the oxidising system; and sodium hydroxide pellets and hydrochloric acid (37 %) as the base and acid catalysts. Additional reagents consisted of glacial acetic acid, hydrogen bromide in acetic acid (48 %) for oxirane titration, crystal violet indicator, distilled water, and methanol. All experiments were carried out using standard laboratory glassware together with a hot plate equipped with magnetic stirring, a temperature-controlled water bath, an analytical balance, and a digital thermometer.

In developing countries such as Ethiopia, rural people use neem leaves as an alternative medicine to cure malaria and diabetes. Ayurvedic medicine, which originated from India 7,000 years ago, also uses neem oil to treat cardiovascular disease, ulcers, and skin conditions. However, the use of neem seed oil as an antimicrobial and food preservative raises concern as several reports have documented side effects associated with the synthetic oils.¹¹ The main component found in neem oil is azadirachtin, which is mainly found in the seeds. Other parts of the neem plant contain lower amounts. Its chemical structure is shown in Fig. 1.

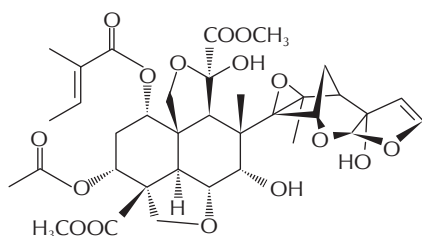


Fig. 1 – Chemical structure of azadirachtin

3 Epoxidation by peracid mechanism

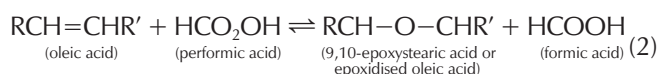
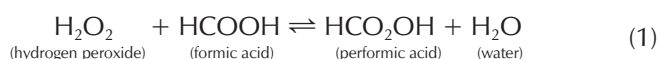
A peracid is a type of chemical species that contains a peroxide functional group (–OOH), and can act as a strong oxidising agent. The mechanism of a peracid reaction involves cleavage of the O–O bond to produce a highly reactive species, known as a peroxyacid anion.¹² This species then reacts with a substrate to generate an intermediate, which undergoes a series of rearrangements to finally produce the desired product. In the epoxidation of oleic acid, H₂O₂ and COOH are used as peracid, prior to the epoxidation process.¹³

In situ epoxidation converts unsaturated fatty acids in vegetable oil into epoxy fatty acids using an oxidising agent such as hydrogen peroxide or benzoyl peroxide, typically with a Lewis acid catalyst. The resulting epoxy fatty acids

can serve as plasticisers, stabilisers, and other additives in a variety of applications, including the production of PVC, rubber, and other polymer materials.¹⁴

In situ epoxidation of vegetable oil has several advantages over traditional methods of epoxidation, including a lower environmental impact, reduced cost, and improved efficiency. The reaction can be performed using a relatively small amount of oxidising agent, which reduces the amount of waste generated and the cost of the process. Additionally, the reaction can be performed at a lower temperature, which reduces energy consumption and increases the efficiency of the process.¹⁵

Epoxides are reactive three-member rings formed from oleic acid double bonds via epoxidation with peracids in a concerted mechanism.¹⁶ Highly electrophilic, they undergo nucleophilic ring opening, yielding various products. The process involves two steps: (1) HCOOH reacts with H₂O₂ to form HCOOOH, and (2) HCOOOH transfers oxygen to oleic acid, forming epoxidised oleic acid, which can hydrolyse into DHSA via oxirane ring opening.



Epoxidation of cottonseed oil can be achieved using the peracid mechanism, in which HCOOH and H₂O₂ are mixed before being introduced to the double bonds of the vegetable oil to produce epoxidised oil.¹⁷ In this process, HCOOH acts as the oxygen carrier and H₂O₂ as the oxygen donor, while the resulting epoxidised oil is analysed by FTIR to confirm the formation of the hydroxyl groups.¹⁸ A previous study was also conducted by Derawi¹⁹ on the epoxidation of palm olein using performic acid, where the optimum reaction temperature was identified. Their results showed that the epoxidation rate increases proportionally with reaction temperature, but gradually decreases over time due to degradation. The mechanism of epoxidation of vegetable oils involves a chemical reaction that occurs at the double bonds of the triglycerides.²⁰ Epoxidation is a crucial process for functionalising these double bonds. Epoxidised vegetable oils, also known as oxirane rings, are highly reactive and serve as valuable precursors for alcohols, polyols, glycol monoesters, glycol diesters, carbonyl compounds, and epoxy polymers.²¹ To date, several methods for epoxidation have been developed, including enzymatic approaches. However, the most commonly chosen method is the Prileschajew reaction, which involves *in situ* production of performic or peracid in the presence of a catalyst.²²

The *in situ* epoxidation method remains the most widely adopted by researchers. Differences among studies usually involve the type of vegetable oil used and the choice of catalyst, whether homogeneous or heterogeneous. The findings of various researchers are summarised in Table 1.

A homogeneous catalyst is a catalyst that exists in the same phase as the reactant throughout the reaction. This type of catalyst offers advantages such as regioselectivity, meaning the preferential formation or cleavage of a bond in one di-

Table 1 – Findings of other researchers on epoxidation

Author	Type of oil	Oxidising agent	Catalyst	Findings
<i>Turco et al.</i> ²⁶	Linseed and soybean	Performic acid	Phosphoric acid	Ring opening for epoxidised linseed oil is four times higher than for soybean oil due to reciprocal inductive effects exerted by the vicinal oxirane groups.
<i>N. M. Nor and J. Salimon</i> ²⁷	Palm oil	Performic acid	Formic acid	An 86 % epoxide yield was obtained. Oxidative stability, flash point, and viscosity index increased for epoxidised palm oil, making it suitable for use as an industrial fluid.
<i>Norhaizan et al.</i> ²⁸	Soapstock	Hydrogen peroxide	<i>C. regusa</i> lipase	RCO at 7.86 % shows that the free fatty acid content in soapstock has potential as a low-cost raw material for epoxides. However, hydrogen peroxide inhibition is a major limiting factor for higher epoxidation rates. Microchannel bioreactors can accelerate the reaction by increasing mass transport and reducing biocatalyst deactivation.
<i>Aguilera et al.</i> ²⁹	Oleic acid	Peracetic acid	Dowex 50x8	Catalyst effects are more dominant for the epoxidation rate compared to conventional or microwave heating, as the solid acid catalyst enhances the slow step of the process, which is the perhydrolysis of acetic acid.

reaction over all other possible reactions because all catalyst sites are accessible in their liquid form.² The main benefits for manufacturers are high product conversion rates and reduced waste generation, making homogeneous catalysts more reliable.²³ Homogeneous catalysts are not affected by the disadvantages such as separation after the reaction, because each catalytic site is directly associated with an active atom. Homogeneous catalysts are involved in the formation of peracids, which are further used to react with fatty acid oil to produce its epoxide.³⁰ In this process, the unsaturated carbon double bond in fatty acid oil is replaced by oxygen from the peracid, producing the epoxide of its oil. Hydrogen peroxide serves as the primary oxygen donor to the fatty acid oil. However, since it is insoluble in organic matter, an oxygen carrier such as formic or acetic acid is required. Sulphuric acid plays a critical role as the catalyst in peracid formation. As discussed by *Dera-wi et al.*,²⁴ variations in sulphuric acid loading significantly affected both the reaction rate and the thermal power generated. Their results showed that both increase proportionally with catalyst loading, demonstrating that sulphuric acid, with its strong catalytic activity, enhances the overall epoxidation process.

Further research by *Fridrihsone et al.*³¹ shows that the rate of double-bond conversion increases gradually with sulphuric acid catalyst loading, where 88.7 % of the double bonds in tall oil fatty acids were oxidised, with a relative conversion of 19.7 % to oxirane rings.

4 Oxirane ring opening

Oxirane, also known as an epoxide, is a three-membered ring structure containing a heteroatom (oxygen) as one of its ring atoms. Ring opening of oxirane can occur through various mechanisms, depending on the reaction conditions and the presence of catalysts or reactants. One common method for oxirane ring opening is reaction with an acid or base. In acidic conditions, the oxirane ring is attacked by a

hydronium ion, leading to ring opening and formation of a diol. Under basic conditions, the oxirane ring is attacked by a hydroxide ion, resulting in ring opening and the formation of a trans-dihydroxyether.³²

Another method involves nucleophilic attack by nucleophiles such as amines, alcohols, or water. This reaction occurs via formation of a new bond between the nucleophile and one of the carbon atoms in the oxirane ring, leading to ring opening and the formation of a new product. Ring opening of oxiranes is an important reaction in the synthesis of various chemical compounds and is widely used in the chemical, pharmaceutical, and polymer industries.³³

It is important to carefully control the conditions of the ring-opening reaction to ensure high yield and high stereoselectivity of the desired product. Several products that can result from oxirane ring opening are presented in Fig. 2.²⁸

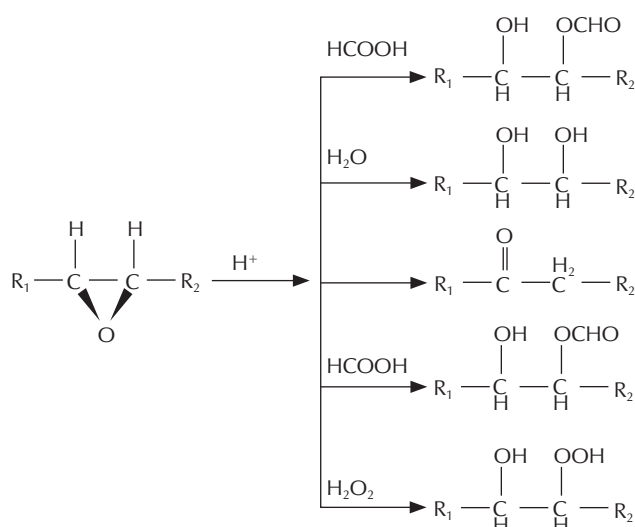


Fig. 2 – Possible side reactions during epoxide ring opening

Epoxides can undergo ring opening with nucleophiles under acidic conditions. Two steps are involved in this process.³⁴ Firstly, the oxygen of the epoxide is protonated, making it a better leaving group. Subsequently, the nucleophile tends to attack the more substituted carbon, resulting in cleavage of the weaker carbon-oxygen bond. The process is illustrated in Fig. 3.²⁹

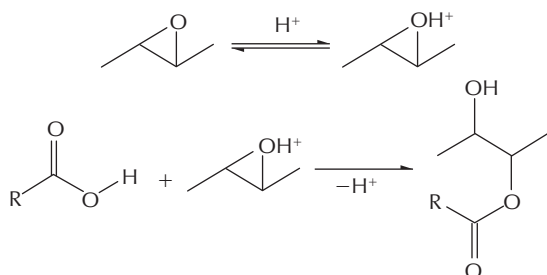


Fig. 3 – Nucleophilic addition to carboxyl group of epoxide²⁷

As reported by *Ifa et al.*³⁵, the epoxidation of palm olein was carried out using bentonite as a catalyst and benzene as a solvent. This approach was adopted because they found that the use of sulphuric acid as a catalyst and acetic acid as a solvent can promote side reactions leading to the formation of ketone compounds, compared to H^+ ions derived from H_2SO_4 that are highly mobile, which can facilitate oxirane ring opening. Epoxides, also known as oxiranes, are three-membered ring structures in which one of the vertices is an oxygen and the other two are carbon. The strain created by the three-membered ring causes epoxides to behave differently from other esters. Epoxides are considerably more reactive than most esters because the release of ring strain during nucleophilic attack drives ring-opening reactions, as shown in Fig. 4.¹⁵

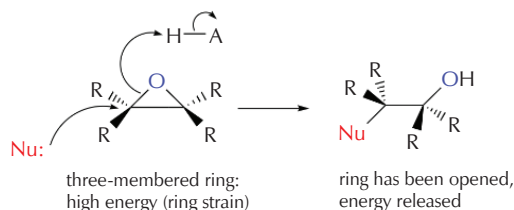


Fig. 4 – Nucleophilic attack on oxirane ring¹⁵

*Dworakowska et al.*³⁶ in their study on the synthesis of polyols from epoxidised rapeseed oil, implemented nucleophilic attack on the epoxide using a peracid mechanism during the epoxidation process. The presence of water, mineral and organic acids in the reaction mixture, arising from intermediate of peracid formation, further hydrolysed the oxirane ring in rapeseed oil, leading to the formation of polyols. However, the reaction was carried out using microwave irradiation as the heating method rather than conventional heating to reduce reaction time and improve energy efficiency. Ring opening, also known as the fusion process of epoxide, has been studied by various researchers across different areas. Variations in reactants, types of epoxidised substrates, and key findings from these studies are summarised in Table 2.

5 Dihydroxystearic acid (DHSA)

DHSA, a hydroxyl fatty acid derived from palm or palm kernel oil, is a white solid with a mild acid odour after purification. Its reactive carboxyl and hydroxyl groups offer multiple modification sites.³⁹ DHSA interacts strongly with pigments and fillers, enhancing colour, adhesion, and fin-

Table 2 – Findings of other researchers on ring opening

Author	Epoxide	Ring-opening reactant	Findings
<i>Dworakowska et al.</i> ³⁶	Rapeseed oil	Diethylene glycol (DEG)	Polyol with OH values between 114 to 196 mg KOH/g were obtained. Partial substitution of petroleum polyol with rapeseed polyol improved cellular structure and tensile strength for the formation of flexible polyurethane foams.
<i>Fang et al.</i> ³⁷	Palm oil	Bisphenol A (BPA)	The hydroxyl groups of BPA in palm oil epoxide initiate reactions involving free phenolic groups leading to macromolecular structures of modified oil, thereby increasing the potential for producing novel epoxy polyurethane materials.
<i>Nor and Salimon</i> ²⁷	Linoleic acid	Oleic acid with <i>p</i> -toluene sulfonic acid	Hydroxyl esters suitable for biolubricant production were obtained. Each oxirane ring in epoxidised linoleic acid generates one ester group and one hydroxyl group in the final product.
<i>Hazmi et al.</i> ³⁸	Biodiesel	2-ethyl hexanol with amberlyte as catalyst	Ring opening products exhibit improved viscosity, higher flash point, and excellent tribological properties compared to epoxidised biodiesel.

ishing properties.⁴⁰ Its hydrophobicity and polarity make it ideal for coloured cosmetics and pigment coatings. The chemical structure is shown in Fig. 5.

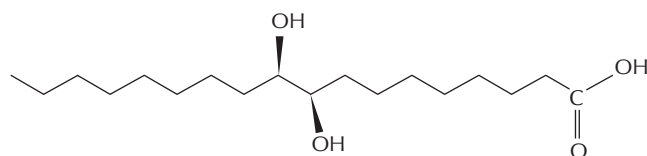


Fig. 5 – 9,10-Dihydroxystearic acid (DHSA)³⁶

DHSA formation involves two continuous steps: epoxidation of oleic acid followed by hydrolysis. *Hadi et al.*⁴¹ epoxidised palm kernel oil-based oleic acid using performic acid but conducted hydrolysis separately. In contrast, *Ismail et al.*⁴² performed *in-situ* epoxidation and hydrolysis, monitoring oxirane oxygen content every 5 min. *Ismail et al.*²⁵ compared peracetic and performic acid as oxidisers, finding that performic acid yielded 96 % DHSA at 30 % lower cost than peracetic acid (72.5 % yield).

6 Difference between crude and purified DHSA

DHSA formed after the hydrolysis of epoxidised oleic acid is referred to as crude DHSA. One of its major applications is in the cosmetics industry.⁴³ However, the presence of medium-chain acids, which are naturally found in palm oil-based oleic acid, such as octanoic and decanoic acids, renders crude DHSA potentially irritating to human skin.⁴⁴ Other impurities present in crude DHSA include lauric, palmitic, and stearic acids. Purified DHSA, typically in granular form, offers advantages in terms of ease of transportation and re-melting for formulation purposes compared to its crude, waxy form.⁴⁵ The main step involved in the purification of crude DHSA is crystallisation. In this process, the crude DHSA is mixed with isopropyl alcohol and water, followed by cooling to allow purified DHSA to crystallise and settle at the bottom of the mixture, after which separation is carried out. According to *Koay et al.*,⁴⁶ a higher solvent-to-crude DHSA ratio (1.5 : 1) produces higher purity of DHSA (92.5 %) compared to a 1 : 1 ratio (90.5%). This indicates that the solvent reduces the viscosity of crude DHSA, resulting in higher diffusivity and increased selectivity and phase separation. Similarly, *Ismail et al.*²⁵ demonstrated that purification can also be achieved using ethanol as a solvent at a ratio of 1.5 : 1, yielding 73.3 % to 91.3 % purified DHSA. In addition to acidity, which contributes to skin irritancy, comparisons of other properties of crude and purified DHSA are presented in Table 3.

Table 3 – Comparison of the properties of crude and purified DHSA³⁰

Specifications	Crude DHSA	Purified DHSA
DHSA purity / %	56.6–58.0	70.9–79.9
Water content / %	5.2	1.1–1.3
OHV / mgKOH g ⁻¹	220.7	291.5–357.6
Iodine value / g I ₂ /100 g	7.3–9.1	2.9–4.0
Acid value / mgKOH g ⁻¹	160.6	172.7
Melting point / °C	79.4–79.8	89.8–90.3
Irritancy	irritant	non-irritant
Form/particle size / μm	semi-solid	40–120

DHSA's unique polarity and long-chain structure make it a valuable hydroxyl fatty acid in cosmetics. It functions as a thickener, gelling agent, binder, mechanical enhancer, and pigment dispersant in decorative formulations. Its applications in personal care products are listed in Table 4.³⁴ *Aydoğmuş and Kamlıli*²¹ epoxidised palm kernel oil-based oleic acid using performic acid but conducted DHSA hydrolysis separately. In contrast, *Ramírez et al.*²² performed *in-situ* DHSA production, monitoring oxirane oxygen content every 5 min. *Derawi*²³ compared peracetic and performic acid, finding that performic acid yielded 96 % DHSA at 30 % lower cost than peracetic acid (72.5 % yield). DHSA is also used as an emulsifier in oil-phase gel candles and water-based cosmetic formulations.²⁴ Fig. 6 shows the structure of DHSA.²⁰

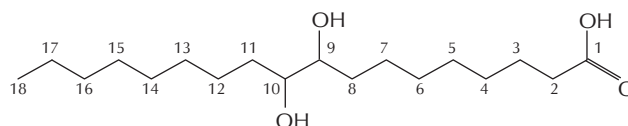


Fig. 6 – DHSA structure²⁰

Table 4 – Application of DSHA in personal care products

Personal care product	Application / DHSA functionalities
Lipsticks	Enhances its mechanical properties. Lipsticks containing DSHA exhibit higher breaking strength.
Liquid foundation	Improves colour development and facilitates easier spreading on the skin.
Mascaras	Increases eyelash volume, resulting in improved curling effects.
Compact powders	Acts as a binding agent, enhancing adhesion to the skin and enabling uniform distribution during application.
Metal soaps	Sodium soaps of DHSA exhibit better detergency than stearic soaps at room temperature and show improved biodegradability.

7 Conclusion

The literature indicates that successful epoxidation of non-edible oils depends strongly on optimising reaction parameters that govern oxirane formation and stability. High oxirane yields are typically achieved under controlled temperatures (50–70 °C), moderate hydrogen peroxide and peracid ratios, and carefully adjusted acid concentrations that promote peracid formation while minimising ring-opening. Among the catalytic systems reported, performic acid generated *in situ* using mineral acids remains highly effective, although recent studies demonstrate that solid acid catalysts, ion-exchange resins, and enzymatic systems can offer improved selectivity, reduced corrosion, and better process safety.

Strategies such as tuning catalyst loading, limiting excess water, selecting oils with higher oleic or linoleic content, and minimising prolonged exposure to strongly acidic environments have been consistently shown to enhance reaction efficiency and reduce unwanted side reactions. Overall, the collective findings indicate clear pathways toward more selective, sustainable, and industrially scalable production of DHSA and related derivatives from non-edible oils.

Availability of data and materials

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

Competing interests

The authors declare no competing interests.

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SAŽETAK

Napredak u epoksidaciji nejestivih ulja: Prileschajew reakcija, hidroksilacija i hidroliza u proizvodnji DHSA

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Rastući pritisci na okoliš i neizvjesnost u pogledu dostupnosti fosilnih sirovina potaknuli su intenzivnija istraživanja usmjerena na pretvorbu nejestivih ulja u visokovrijedne biobazirane kemikalije, poput 9,10-dihidroksistearinske kiseline (DHSA). U ovom preglednom radu sažeta su najnovija dostignuća u području epoksidacije nejestivih ulja s naglaskom na ključne reakcijske putove, uključujući Prileschajew oksidaciju, hidroksilaciju i hidrolizu. Posebna pozornost posvećena je strategijama za povećanje stvaranja oksiranskog prstena uz istodobno smanjenje neželjenih sporednih reakcija otvaranja prstena. Nadalje, razmatraju se održivi katalitički sustavi i optimirani reakcijski uvjeti koji doprinose povećanju selektivnosti reakcije i ukupne učinkovitosti procesa. Integracijom rezultata dosadašnjih istraživanja prikazan je napredak u prijenosu laboratorijskih postupaka epoksidacije prema industrijski primjenjivim procesima, osobito u području kozmetike, proizvodnje biopolimera i drugih rastućih sektora temeljenih na biobaziranim sirovinama.

Ključne riječi

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