

# Recent Advances in Greener and Energy Efficient Alkene Epoxidation Processes

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**Abstract:** Chemical industry is considered to be one of the largest consumers of energy in the manufacturing sector. As the cost of energy is rising rapidly, coupled with the increasingly stringent standards for the release of harmful chemicals and gases into the environment, more attention is now focused on developing energy efficient chemical processes that could significantly reduce both operational costs and greenhouse gases emission. Alkene epoxidation is an important chemical process as the resultant epoxides are highly reactive compounds that are used as platform chemicals for the production of commercially important products for flavours, fragrances, paints and pharmaceuticals. A number of epoxidation methods have been developed over the past decade with the ultimate aim of minimising waste generation and energy consumption. In this review paper, some of the recent advances in epoxides synthesis using energy efficient processes have been discussed. The epoxidation methods could provide sustainability in terms of environmental impact and energy consumption.

**Keywords:** Alkene epoxidation; epoxides; continuous reactors; energy efficient process; catalytic process.

## 1. Introduction

The rate of energy consumption either for electricity, steam or heating purposes has been increasing rapidly during the past decades due to rapid developments being experienced globally in the transportation, industrial, agricultural, residential, commercial and other related sectors [1]. Fossil fuels including coal, oil, and natural gas are currently the largest sources of energy worldwide. However, the use of carbon based fossil fuels has contributed significantly to an increase in the concentration of CO<sub>2</sub> and related greenhouse gases in the atmosphere with negative impact on the environment [2–4]. Consequently, highly industrialized nations popularly known as the G8 have been promulgating measures aimed at cutting greenhouse gases emissions associated with energy exploration and utilisation to prevent further deterioration of the environment [5,6]. In this respect, miniaturisation of chemical processes through intensification and integration of multiple operations play a significant role by providing means of reducing energy consumption and waste generation [7–10].

Epoxides, also known as oxiranes, are mainly products of alkene epoxidation. They are key raw materials or intermediates in organic synthesis, particularly for the functionalisation of substrates and production of a wide variety of chemicals such as pharmaceuticals, plastics, paints and adhesives [11–15]. The highest consumption of ethylene oxide (C<sub>2</sub>H<sub>4</sub>O) worldwide is in the production of ethylene glycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>), which is a building block in the production of pharmaceuticals, textiles, automobiles and detergents [16]. Similarly, propylene oxide (C<sub>3</sub>H<sub>6</sub>O) has found applications in the production of cosmet-

ics, drugs, plasticisers as well as in the manufacture of unsaturated polyester resins used in the textile and construction industries [17]. Furthermore, epichlorohydrin ( $C_3H_5ClO$ ) is an important epoxide that is widely employed in the manufacture of epoxy resins, glycerols, plastics and elastomers [18]. Epoxidation of limonene and  $\alpha$ -pinene yields the corresponding 1,2-limonene oxide and  $\alpha$ -pinene oxide, which are both vital intermediates for the production of fragrances, perfumes, food additives and pharmaceuticals [19].

The conventional epoxidation methods in the fine chemicals industries employ *in situ* generated peracids such as peracetic ( $C_2H_4O_3$ ) or performic acid ( $CH_2O_3$ ) as oxidising reagent in liquid phase batch reactions in the presence of a mineral acid as a catalyst [20,21]. However, the employment of peracid for alkene epoxidation is not an environmentally benign method as equivalent amount of acid waste is produced. In addition, there are safety issues associated with handling and storage of peracid [21]. Molecular oxygen is probably the most suitable oxidant for alkene epoxidation from environmental and economic considerations due to its high oxygen content and its ability to produce water as the only by-product. However, one of the major limitations of epoxidation with molecular oxygen is low product selectivity [22]. Similarly, hydrogen peroxide ( $H_2O_2$ ) is another eco-friendly reagent for epoxidation since it also gives water as the only waste product [23]. As in the case with molecular oxygen, epoxidation with  $H_2O_2$  could result in poor product selectivity [24]; although researchers in recent years have developed catalytic systems that could activate the oxidant to give up to 98% epoxide selectivity [25]. On the other hand, there are limited applications of hypochlorites as oxygen sources for epoxidation due to their serious health and environmental hazards that include the release of toxic gases such as chlorine when acidified or heated, and their reaction with ammonia or with substances that generate ammonia to yield chloramines which are also toxic and have explosive potential [26,27]. Alkyl hydroperoxides including *tert*-butyl hydroperoxide ( $C_4H_{10}O_2$ ) (TBHP), cumene hydroperoxide ( $C_9H_{12}O_2$ ) and ethylbenzyl hydroperoxide ( $C_9H_{12}O_2$ ) are commonly used as oxygen sources in epoxidation reaction since the reagents are readily available and inexpensive [28–30]. However, *tert*-butyl hydroperoxide (TBHP) has received considerable attention in recent times as an oxidant of choice for the reaction due to its numerous advantages including high thermal conductivity, good solubility in polar solvents and neutral pH [31–33]. In addition, the oxidant is atom efficient since it yields *tert*-butanol, a major industrial feedstock as a by-product [34–36].

There are numerous examples of epoxidation reactions carried out with broad range of heterogeneous catalysts based on either transition metals or main group elements. Some of the catalysts tend to be more active on certain alkene substrates than others and the selectivity of a particular catalyst for epoxidation depends on the properties of the active component, a combination of ligands and the oxidant used. For instance, a number of heterogeneous catalysts have been developed for epoxidation reaction by immobilisation of catalytically active metal species on organic or inorganic materials such as alumina [37,38], silica [39,40], zeolites [41,42], polymers [43], ion-exchange resins [44,45] and metal organic frameworks [46]. However, polymers have gained more attention as a suitable support for transition metal catalysts as they are inert, non-toxic, insoluble and often recyclable [11–13,31,34,47].

The main purpose of this review paper is to highlight some of the techniques being developed to achieve intensification of alkene epoxidation process by reducing the volume of hazardous material and replacing large, energy-intensive equipment and stages with the ones that are smaller, less expensive and energy efficient.

## 2. Important Reactions of Epoxides

Epoxides are highly reactive cyclic ethers having a three-membered ring structure with an oxygen atom connected to two neighbouring carbon atoms by single bonds. The high reactivity of epoxides is due to their polarity and strain of the three-membered ring, which weakens the carbon-oxygen (C-O) bond [48]. As shown in Scheme 1, epoxides can readily undergo ring-opening reactions and form a variety of products that could serve

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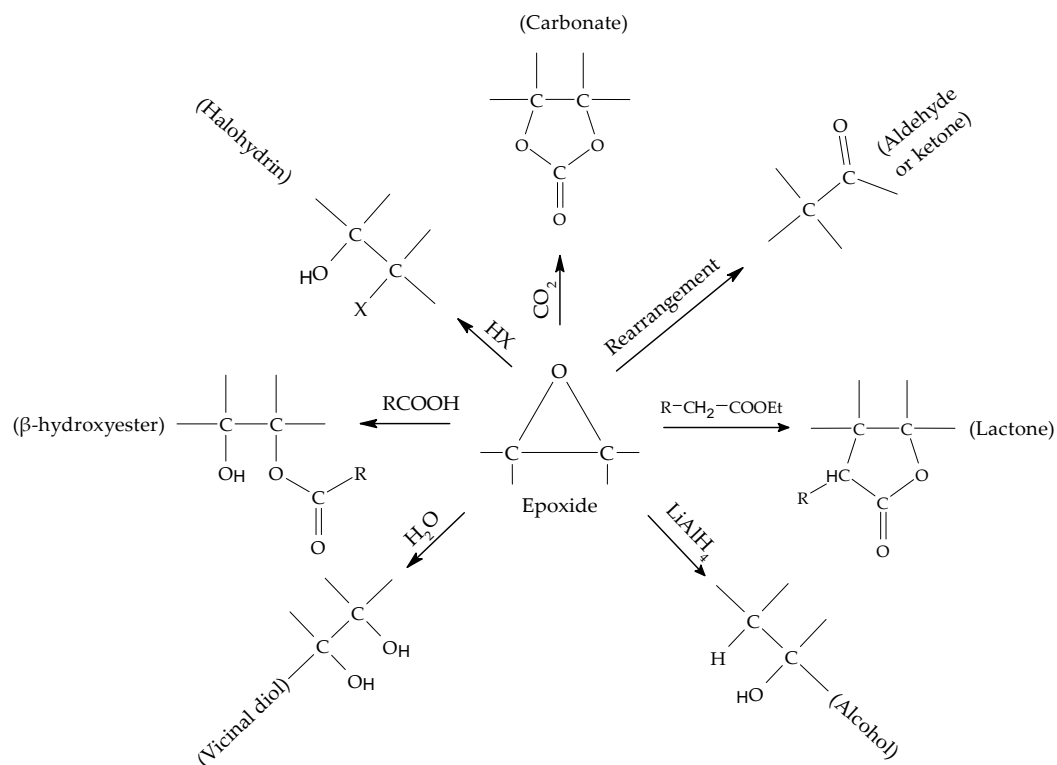
as starting material or intermediate in the production of commercially important products for flavours, adhesives, fragrances, paints and pharmaceuticals [14,48,49]. The reactions involving epoxides are usually catalyzed by many acidic and basic substances, as well as by acceptor-donor compounds [50,51].

The reaction of epoxides and CO<sub>2</sub> yields carbonates and polycarbonates as two major valuable products [52]. However, the selectivity toward either of the products depends on the reaction conditions and the type of catalysts used [53,54]. A number of transition metal-based catalysts have shown good activity in the solvent-free synthesis of propylene carbonate by cycloaddition reaction of propylene oxide and CO<sub>2</sub> under mild reaction conditions [55,56].

Epoxides could be cleaved on hydrolysis by either aqueous base (NaOH/H<sub>2</sub>O) or acid (H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O) to form vicinal diol in SN<sub>2</sub> or SN<sub>1</sub> mechanism [57,58]. In the presence of an aqueous base, the nucleophile (H<sub>2</sub>O) attack the least substituted carbon atom based on an SN<sub>2</sub> like reaction leading to ring-opening of the epoxide, while in the aqueous acid solution, the more substituted carbon is the site of nucleophilic attack according to the SN<sub>1</sub> displacement mechanism [59]. Similarly, epoxides undergo cleavage of the ether bond in the presence of anhydrous acids including HCl, HI, HBr to form halohydrin in the SN<sub>1</sub> or SN<sub>2</sub> like reactions depending on whether the carbon attacked by the halogen anion is a primary, secondary or tertiary carbon [60,61].

Epoxides are capable of undergoing intramolecular rearrangement often initiated by Lewis or Brønsted acids to form aldehydes or ketones [62–64]. Ring-opening of epoxide with Ketene Silyl Acetals is regarded as the best choice approach for the preparation of an important class of extensive biologically active compounds,  $\gamma$ -lactones [65–68]. Furthermore, the reduction of epoxide by lithium aluminum hydride (LiAlH<sub>4</sub>) occurs at the least sterically hindered side of the epoxide to give the corresponding alcohol [69,70]. The nucleophilic addition reaction of epoxides with carboxylic acids such as pivalic acid (C<sub>5</sub>H<sub>10</sub>O<sub>2</sub>) results in acidolysis ring-opening to form hydroxyalkyl esters [71]. However, when epichlorohydrin (C<sub>3</sub>H<sub>5</sub>ClO) is used as the epoxy compound, the hydroxyalkyl ester formed can further undergo the ring-closure reaction with alkali by dehydrochlorination to yield vital intermediates for the coating and polymer industries such as glycidyl methacrylate [72,73] and glycidyl neodecanoate [74,75]. The reaction schemes of the notable reactions of epoxides and their products are presented in Scheme 1.

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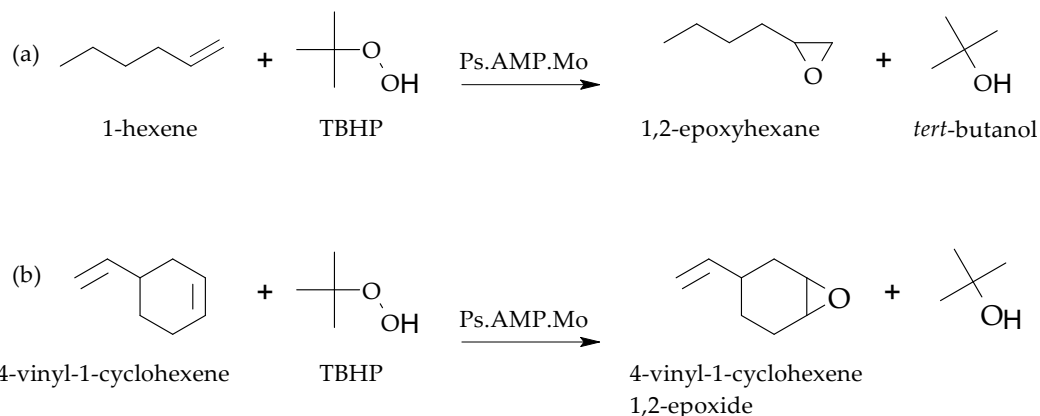
**Scheme 1.** Schemes of some important reactions of epoxide

### 3. Energy Efficient Alkene Epoxidation Processes

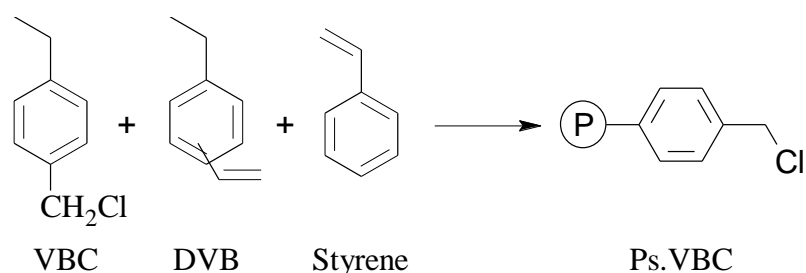
The search for an energy efficient method for the preparation of epoxide has been an active research area in recent years due to the significance of the compound not only as a synthetic end product but as a versatile intermediate in organic synthesis. To date, several methods of epoxide synthesis have been developed and most of these methods employ alkene as a starting material, which is subsequently oxidised by a suitable reagent to give the desired product. However, some alternative methods that utilise aldehydes and imines for the production of epoxides have also been reported.

#### 3.1. Continuous Flow Epoxidation Process

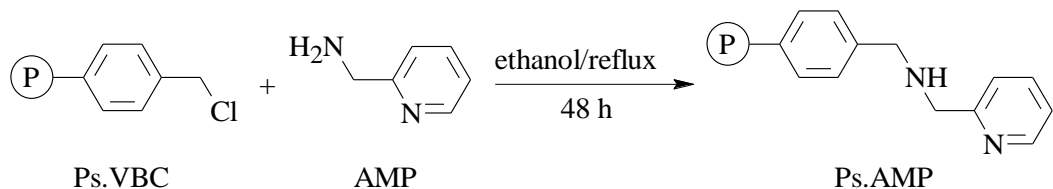
The development of a continuous flow approach to synthetic organic chemistry has received considerable interests over the last few decades [76–78]. The inherently closed nature of continuous flow reactors enhanced the reaction safety due to proper containment of harmful or toxic reagents and allows rapid optimization of reaction conditions from a small quantity of reactants under different reaction conditions with minimal energy consumption. FlowSyn reactor (supplied by Uniqsis Ltd) is one of the energy efficient continuous flow reactors currently employed for laboratory-scale synthesis of various organic products [79]. We had earlier employed the Flowsyn reactor for continuous epoxidation of 1-hexene ( $C_6H_{12}$ ) and 4-vinyl-1-cyclohexene ( $C_8H_{12}$ ) using *tert*-butyl hydroperoxide (TBHP) and a polystyrene 2-(aminomethyl)pyridine supported molybdenum(VI) complex (Ps.AMP.Mo) as a catalyst (Scheme 2) [12,31]. The catalyst was prepared by immobilizing the molybdenum metal species derived from molybdenyl acetylacetonate ( $MoO_2(acac)_2$ ) on an already synthesized cross-linked polystyrene-based resin code-named as polystyrene 2-aminomethyl(pyridine) (Ps.AMP) as shown in Schemes (3–5).



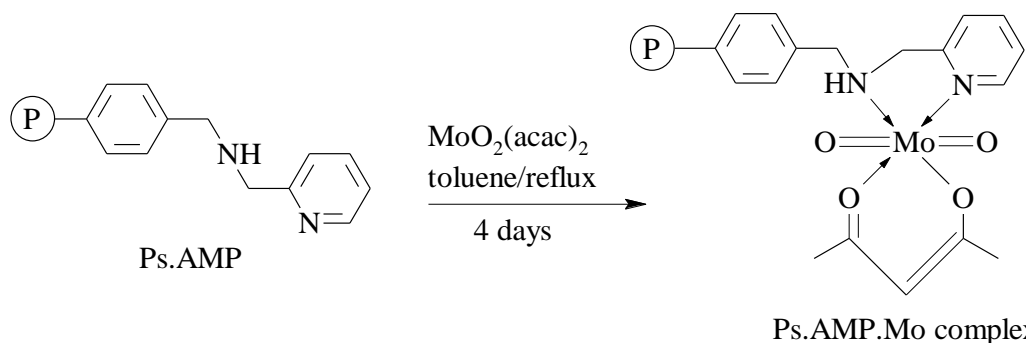
**Scheme 2.** Reaction schemes for epoxidation of (a) 1-hexene; (b) 4-vinyl-1-cyclohexene with TBHP catalysed by Ps.AMP.Mo complex



**Scheme 3.** Synthesis of poly (divinylbenzene-co-vinylbenzyl chloride-co-styrene) (Ps.VBC) resin.



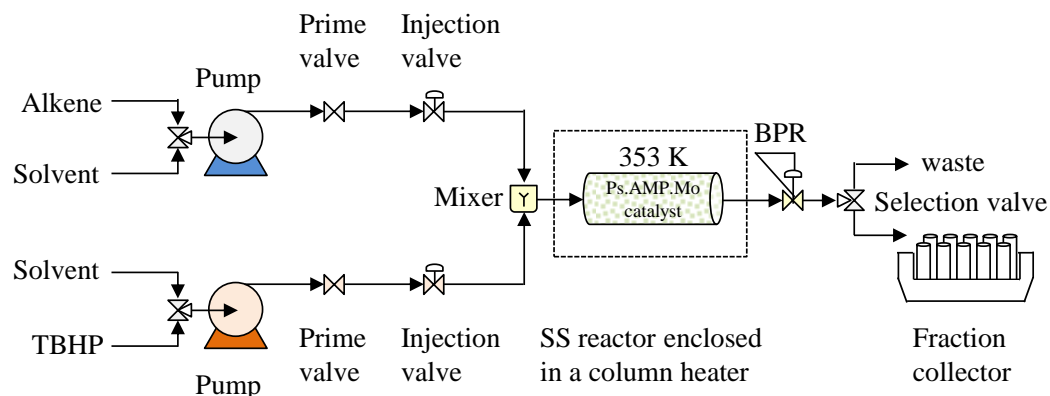
**Scheme 4.** Synthesis of polystyrene 2-(aminomethyl)pyridine (Ps.AMP) beads.



**Scheme 5.** Loading of Mo(VI) into polystyrene 2-(aminomethyl)pyridine (Ps.AMP) beads to produce polystyrene 2-(aminomethyl)pyridine supported Mo(VI) (Ps.AMP.Mo) complex.

The continuous flow epoxidation has enabled rapid evaluation of the catalytic performance of Ps.AMP.Mo from a small quantity of reactants under different reaction conditions. For instance, the catalyst has demonstrated high catalytic performance in the continuous epoxidation of 4-vinyl-1-cyclohexene ( $\text{C}_8\text{H}_{12}$ ) as compared to 1-hexene ( $\text{C}_6\text{H}_{12}$ ).

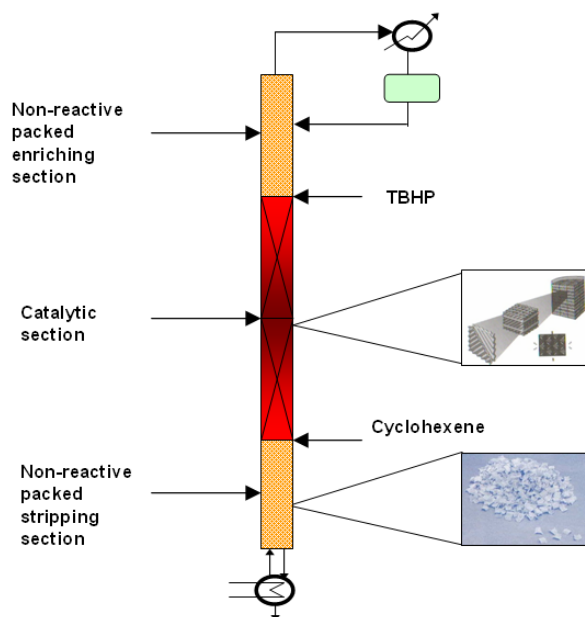
Experiment carried out at a feed molar ratio of 4-vinyl-1-cyclohexene ( $C_8H_{12}$ ) to TBHP of 5:1, reaction temperature of 353 K and feed flow rate of 0.1 mL/min resulted in ~95% conversion of TBHP and ~82% yield of 4-vinyl-1-cyclohexane 1,2-epoxide ( $C_8H_{12}O$ ) at steady state. However, continuous epoxidation of 1-hexene ( $C_6H_{12}$ ) at similar conditions gave ~79% conversion of TBHP and ~64% yield of 1,2-epoxyhexane. The continuous epoxidation in a FlowSyn reactor has shown considerable time savings, high reproducibility and selectivity along with remarkable improvements in catalyst stability compared with the reactions carried out in a batch reactor [13,80]. The schematic of the experimental set-up for the continuous epoxidation process in the FlowSyn reactor is shown in Figure 1.



**Figure 1.** Schematic representation of continuous epoxidation of 4-vinyl-1-cyclohexene with TBHP using a FlowSyn reactor.

### 3.2. Epoxidation in a Reactive Distillation Column (RDC)

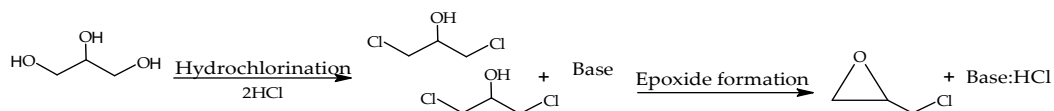
Reactive distillation (RD) is a unit operation that combines chemical reaction and distillation in the same vessel in a single step. By conducting chemical reaction and product separation simultaneously, equilibrium could be shifted to achieve almost complete conversion of the feedstock [81–87]. Thus RD technology has many key advantages such as reduced investment and operating costs and significant energy savings, as it can simplify complex separation and purification processes [88]. Saha and co-workers [81–87] have designed an RDC for the continuous epoxidation process using molybdenum-based complexes as catalysts for the epoxidation of alkenes/terpenes using *tert*-butyl hydroperoxide (TBHP) as an oxidant. The RDC consists of three distinct parts: a catalytic section containing the catalyst, packed in a well-structured “rolled belt” type catalyst packing. The catalytic section is enclosed in between a non-reactive enriching section and a non-reactive stripping section, both packed with ceramic raschig rings as shown in Figure 2.



**Figure 2.** Schematic of an RDC set-up

The epoxidation process developed by Saha and co-workers [81–87] could be termed as atom efficient since it forms *tert*-butanol, which is a valuable industrial feedstock as a co-product of the reaction. In addition, the process achieved nearly 100% conversion of cyclohexene [81–87] and 4-vinyl-1-cyclohexene (C<sub>8</sub>H<sub>12</sub>) [31] to cyclohexene oxide (C<sub>6</sub>H<sub>10</sub>O) and 4-vinyl-1-cyclohexane, 1-2-epoxide (C<sub>8</sub>H<sub>12</sub>O) respectively, under mild reaction conditions. .

The conventional method for the production of epichlorohydrin (C<sub>3</sub>H<sub>5</sub>ClO) uses energy-intensive multistep processes involving the addition of chlorine to propene (C<sub>3</sub>H<sub>6</sub>) at high temperatures to give allyl chloride (C<sub>3</sub>H<sub>5</sub>Cl) and subsequently, reacting the product with hypochlorous acid (HOCl) to form two dichlorohydrins isomers. Finally, dichlorohydrins are reacted with sodium hydroxide (NaOH) to yield epichlorohydrin (C<sub>3</sub>H<sub>5</sub>ClO) [89,90]. In addition to the high energy requirements, this method has major drawbacks including, the application of hazardous chlorine, low atom efficiency of the chlorine as well as a large number of by-products for disposal [91]. However, a more energy efficient and sustainable process for the production of epichlorohydrin (C<sub>3</sub>H<sub>5</sub>ClO) could be achieved by utilizing glycerol (C<sub>3</sub>H<sub>8</sub>O<sub>3</sub>) based on two reaction steps; catalytic chlorination of liquid glycerol (C<sub>3</sub>H<sub>8</sub>O<sub>3</sub>) with gaseous hydrochloric acid (HCl), and then, reacting the dichlorinated compounds formed with an inorganic base in an RDC to form the product (Scheme 6) [92,93]. Although the stoichiometric bases used in the second step of the reaction could be soluble in the reaction mixture, thus, increasing the difficulty in product isolation and purification, this problem could be surmounted when a heterogeneous catalyst is applied in the first step, it can be recovered from the reaction easily by filtration [94].



**Scheme 6.** Reaction scheme for the conversion of glycerol into epichlorohydrin [93]

### 3.3. Microwave-assisted epoxidation

Microwave offers energy efficient heating by the interaction of the generated electromagnetic radiations with the molecules (polar) thereby generating heat for the reaction without direct contact with the reaction mixture. The microwave provides substantial energy savings due to rapid and uniform heating during the chemical reaction in contrast

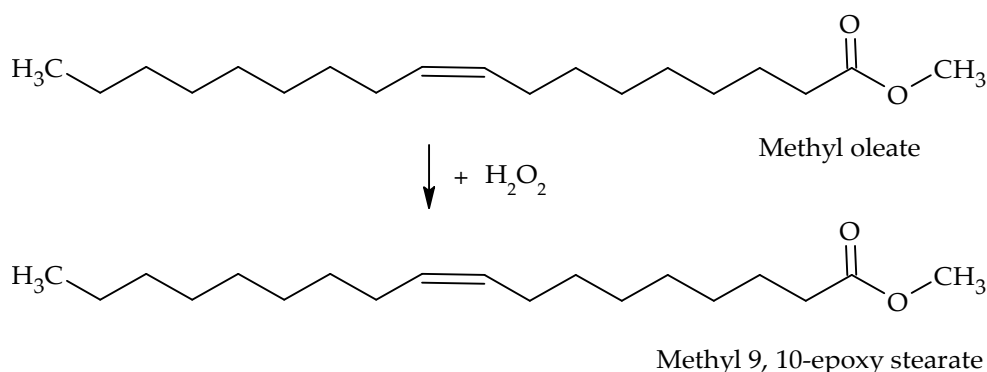




### 3.4. Epoxidation in Microreactors

Microreactors are chemical reactors of extremely small dimensions made from silicon, polymers, glass, metal and other materials, employing a variety of fabrication techniques often requiring special equipment and skills to fit the intended reaction [103,104]. The small channel sizes provide a high surface area to volume ratio, which results in uniform heating across the reaction site as well as efficient heat and mass transfer characteristics [105,106]. Microreactors have helped to minimize reagent and energy consumption in chemical synthesis due to their small dimensions and allow safe handling of hazardous or highly exothermic reactions [107,108].

A microreactor coated with a catalytic  $\text{TiO}_2$  layer has achieved higher oxirane selectivity (92%) in the epoxidation of methyl oleate ( $\text{C}_{19}\text{H}_{36}\text{O}_2$ ) with  $\text{H}_2\text{O}_2$  as oxidant and recorded a higher reaction rate of epoxide production (23 times) compared with the reaction carried out in a conventional batch reactor with an average yield of 75% (Scheme 9) [109]. The higher epoxide selectivity obtained in the microreactor was attributed to the efficient mixing of reactants, high surface to volume ratio and accurate control of the substrate to oxidant ratio [109]. Moreover, a microfluidic device that generates dielectric barrier discharge (DBD) plasma at the gas-liquid interface has efficiently diffused the reactive oxygen species (ROS) to the liquid phase via microbubbles in trans-stilbene ( $\text{C}_{14}\text{H}_{12}$ ) epoxidation to a trans-stilbene epoxide ( $\text{C}_{14}\text{H}_{12}\text{O}$ ) [106]. The highest epoxide yield of ~94% was obtained at the optimum operating conditions of short bubble-liquid contact times (~2 s) with frequent exposure to freshly generated microbubbles containing reactive oxygen species by continuous liquid recirculation [106].



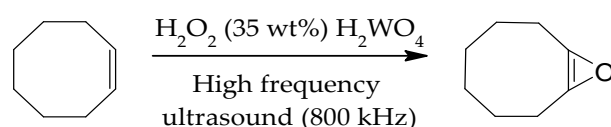
**Scheme 9.** Epoxidation of methyl oleate with  $\text{H}_2\text{O}_2$

Monolithic microreactors are continuous unitary structures consisting of parallel channels, with catalyst either incorporated into a thin layer of a porous oxide deposited on the channel wall (acting as support for the catalyst) or into the wall of the reactor itself [110,111]. Catalytic monolith reactor offers high catalytic efficiency in the chemical reaction due to high concentrations of active sites per unit volume, and provides better heat and mass transfer, and very low pressure drop along the channels [112–114]. A flow reactor used for the continuous epoxidation of styrene ( $\text{C}_8\text{H}_8$ ) with TBHP as an oxidant in the presence of a monolith catalyst gave a good conversion (55%) and excellent selectivity (74%) towards styrene oxide ( $\text{C}_8\text{H}_8\text{O}$ ) within 50 min residence time and allowed easy separation of the catalyst and recyclability of more than 7 cycles without a significant loss in catalytic activity [115]. A comparison of a monolith reactor and a Confined Taylor Flow (CTF) reactor in the heterogeneous catalytic epoxidation of propene ( $\text{C}_3\text{H}_6$ ) to propene oxide ( $\text{C}_3\text{H}_6\text{O}$ ) with hydrogen peroxide revealed that the production rate of propene oxide ( $\text{C}_3\text{H}_6\text{O}$ ) was higher in the monolith reactor in the entire range of operating pressures due to its larger catalyst coating area, larger mass-transfer surface area and more frequent recycling of liquid flow [116].

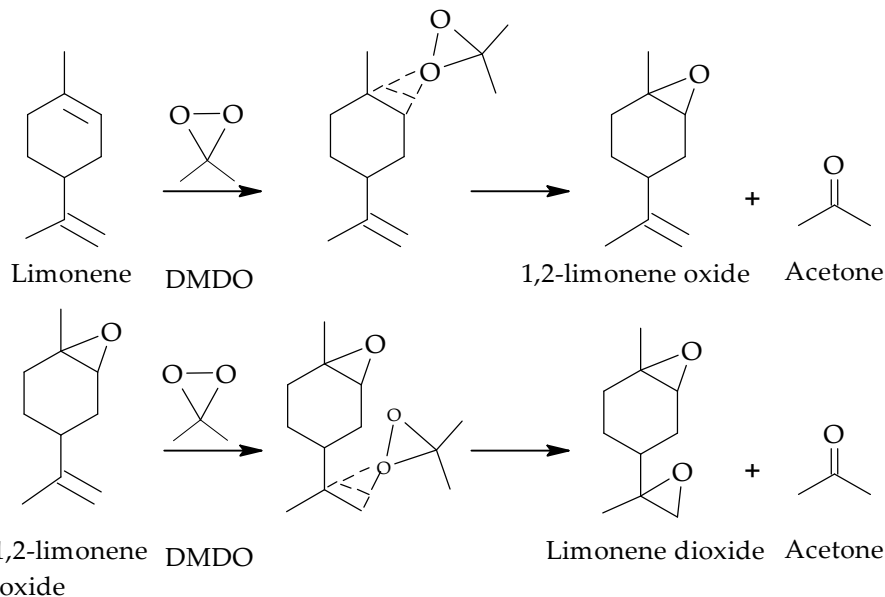
### 3.5. Sonochemical Synthesis of Epoxides

Sonochemical synthesis (sonochemistry) involves chemical reactions between molecules due the application of powerful ultrasound radiation usually in the range of 20 kHz–10 MHz [117]. The chemical reaction is derived from a physical phenomenon referred to as acoustic cavitation, which is responsible for the formation, growth, and collapse of tiny acoustic bubbles inside a liquid, thereby inducing high temperatures (up to 5000 K) and very high pressures (up to 1000 atm) inside such cavities as well as a shock wave at the interface and bulk liquids leading to enhanced heat and mass transfer, reduced reaction times and lower energy consumption [118–121].

A catalytic system consisting of a combination of mild mixing brought by high-frequency ultrasonic irradiation (800 kHz) with precise temperature regulation of the double jacketed sonochemical reactor has achieved a higher yield of cyclooctene oxide (C<sub>8</sub>H<sub>14</sub>O) (96%) and selectivity (98%) within 30 min in the epoxidation of 1-octene mediated by H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>WO<sub>4</sub> compared with silent conditions (Scheme 10) [122]. Similarly, ultrasonic-assisted limonene epoxidation using in-situ generated dimethyl dioxirane, C<sub>3</sub>H<sub>6</sub>O<sub>2</sub> (DMDO) as the oxidizing agent achieved 100% yield of the limonene dioxide product within 4.5 min as compared to 97% yield obtained in the reaction conducted using conventional agitation with magnetic stirrer after 1.5 h [123]. A proposed two steps mechanism for the reaction is presented in Scheme 11. Furthermore, epoxidation of α-pinene (C<sub>10</sub>H<sub>16</sub>) to α-pinene oxide (C<sub>10</sub>H<sub>16</sub>O) under ultrasound conditions by DMDO gave 100% after 4 min, and takes 60 min to achieve similar yield with the traditional method [123].



**Scheme 10.** Epoxidation of 1-octene with H<sub>2</sub>O<sub>2</sub>



**Scheme 11.** Epoxidation mechanism of limonene to limonene dioxide by dimethyl dioxirane (DMDO) [123]

Chavan and co-workers [124] observed a substantial reduction in the reaction time for soybean oil epoxidation using the ultrasonic horn in the presence of tetra-n-butyl ammonium bromide as a phase transfer catalyst for similar levels of conversion compared with the conventional stirring approach. It was found that the relative percentage conversion to epoxide using the conventional method was about 87% in 10 h while the reaction carried out in ultrasound horn under optimised conditions (20 kHz with pulse of 5 s ON and 5 s OFF ) achieved almost 83% in 4 h of reaction time.

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#### 4. Conclusions

It can be deduced from the foregoing that the technologies used for the synthesis of epoxides are continuously being improved with a view to reducing the environmental impact, energy consumption and overall costs. The recent advances in this respect are geared towards the process intensification approaches, by utilizing equipment and processes that are smaller, safer, less expensive and more energy efficient. Thus, industrial application of the energy efficient epoxidation techniques could significantly reduce the cost associated with energy consumption, waste generation and product purification in epoxide production. For instance, the continuous flow epoxidation we had carried out in a FlowSyn reactor shows substantial benefits that include fast heat and mass transfer, short setup and reaction times, the flexibility of scaling-up reactions, complete non attended operation and remarkable catalyst stability compared with the experiments carried out in a classical batch reactor at similar reaction conditions.

Although epoxidation processes described in this review have been successfully carried out at the laboratory scale, the development of scaled-up processes is recommended first of all to move the chemistry on from small-scale laboratory reactions to large-scale industrial production. The energy efficient epoxidation techniques including continuous flow chemistry, reactive distillation as well as microwave, microreactor and sonochemical syntheses could significantly reduce the cost associated with energy consumption, waste generation and product purification in epoxide production.

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#### Abbreviations

AMP	2-aminomethyl pyridine
CTF	Confined Taylor Flow
DBD	Dielectric Barrier Discharge
DMDO	Dimethyl dioxirane
DVB	divinylbenzene
MoO <sub>2</sub> (acac) <sub>2</sub>	Molybdenyl acetylacetonate
Ps.AMP	Polystyrene 2-(aminomethyl) pyridine
Ps.AMP.Mo	Polystyrene 2-(aminomethyl) pyridine supported Mo(VI) complex
RDC	Reactive Distillation Column
ROS	Reactive Oxygen Species
TBHP	<i>tert</i> -butyl hydroperoxide
VBC	Vinylbenzyl chloride

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