RECENT ADVANCES IN EPOXIDATION OF VEGETABLE OILS

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Abstract— Vegetable oils are among the most promising renewable raw materials because of their ready availability, inherent biodegradability, and their many versatile applications. Vegetable oils are the fats and lipids containing triglyceride molecules. Due to the increase in environmental issues like waste disposal problems, non-biodegradable resources, greenhouse effect, etc. and the reduction of petroleum oil resources, renewable oils from vegetable origin have become an important issue. The lubricants from renewable resources are a successful reality in many parts of the world. Vegetable oils have many advantages such as high flash point, high viscosity index, high lubricity and low evaporative loss besides eco-compatible, renewability and non-toxicity. This paper reviews the methods that are recently been practiced for the epoxidation of vegetable oils.

Index Terms— Epoxidation, Vegetable oil, Oxirane Content, Peracids.

I. INTRODUCTION

Vegetables or plant oils represent a renewable resource that can be used as reliable starting material to access new products with a wide array of structural and functional variations. The ample availability and the relatively low cost make plant oils an industrially attractive raw material for the plastics industry. [2] Epoxides are well known commercially because of the many important reactions they undergo. [7] Fats and oils are renewable resources that can be treated chemically or enzymatically to produce materials which often act as a replacement for petroleum-derived materials. [4] Due to high reactivity of the oxirane ring, epoxides also act as a raw material for a variety of chemicals, such as alcohols, glycols, alkanol amines, carbonyl compounds, olefinic compounds and polymers like polyesters, polyurethanes, and epoxy resins. [7] Four technologies are used to produce epoxides from olefinic-type molecules: (i) epoxidation with percarboxylic acids , which is widely used in industry and can be catalyzed by acids or by enzymes; (ii) epoxidation with organic and inorganic peroxides, which includes alkaline and nitrile hydrogen peroxide epoxidation as well as transition metal-catalyzed epoxidation ; (iii) epoxidation with halohydrins, using hypohalous acids (HOX) and their salts as reagents for the epoxidation of olefins with electron-deficient double bonds ; and (iv) epoxidation with molecular oxygen [9]. Epoxidation of vegetable oils with molecular oxygen leads to the degradation of the oil to smaller compounds, such as aldehydes and ketones, as well as short-chain dicarboxylic acids. [4] It is, therefore, not an efficient method for the epoxidation of vegetable oils. [4] The largest sources of vegetable oils are annual plants such as soybean, corn, linseed, cottonseed or peanuts. However, other sources are oil-bearing perennials such as the palm, olive or coconut. [2] The main constituents of plant oils are triglycerides (see Figure 1(A)). 90% - 95% of the total weight of triglycerides accounts for fatty acids and their content is characteristic of each plant oil (Figure 1(A)). The structures of some frequently studied fatty acids are depicted in Figure 1(B). Fatty acid percentage composition of common plant oils is given in Table 1. [2]

Figure 1(A)[2]
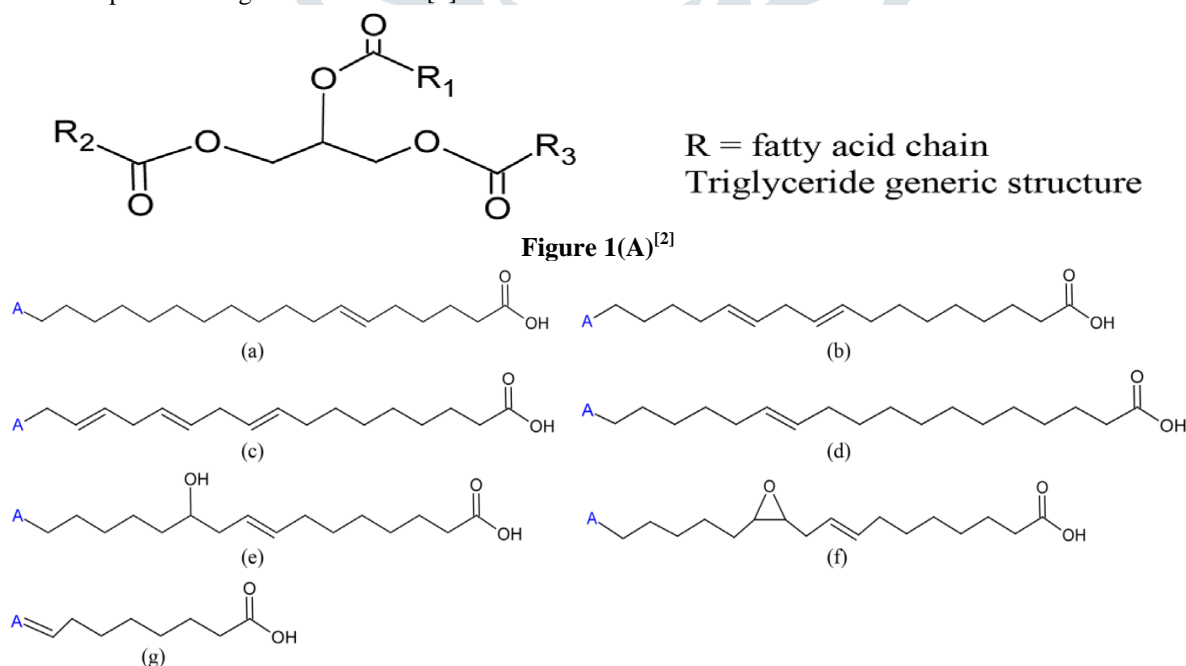

Figure 1(B) [2]

Figure 1. (A) General triglyceride structure; (B) Fatty acids commonly used in polymer chemistry: (a) oleic acid; (b) linoleic acid; (c) linolenic acid; (d) erucic acid; (e) ricinoleic acid; (f) vernolic acid; (g) 10-undecenoic acid. [2]

Table 1. Fatty acid percentage composition of common plant oils (x: y stands for chain carbon atoms: number of unsaturation) [2]

	14:0	14:1	16:0	16:1	17:0	17:1	18:0	18:1	18:2	18:3	20:0	20:1
Canola	0.1	0.0	4.1	0.3	0.1	0.0	1.8	60.9	21.0	8.8	0.7	1.0
Corn	0.1	0.0	10.9	0.2	0.1	0.0	2.0	25.4	59.6	1.2	0.4	0.0
Linseed	0.0	0.0	5.5	0.0	0.0	0.0	3.5	19.1	15.3	56.6	0.0	0.0
Olive	0.0	0.0	13.7	1.2	0.0	0.0	2.5	71.1	10.0	0.6	0.9	0.0
Palm	1.0	0.0	44.4	0.2	0.1	0.0	4.1	39.3	10.0	0.4	0.3	0.0
Soybean	0.1	0.0	11.0	0.1	0.0	0.0	4.0	23.4	53.2	7.8	0.3	0.0
Sunflower	0.0	0.0	6.1	0.0	0.0	0.0	3.9	42.6	46.4	1.0	0.0	0.0
High oleic	0.0	0.0	6.4	0.1	0.0	0.0	3.1	82.6	2.3	3.7	0.2	0.4

The world production of major vegetable oils has risen from 95 million tonnes in 2002/2003 to 154 million tonnes in 2012/2013 at an average rate just over 5 million tonnes a year. Majority of vegetable oils are produced for domestic purposes while a few minor vegetable oils like linseed oil and castor are used for industrial purposes. Research on development of vegetable oil based polymeric materials, including additives, bio-composites and nanocomposites, has attracted increasing attention in recent years.

II. EPOXIDATION

Epoxidized oil contains epoxide groups or oxirane rings. The term epoxide can be defined as cyclic ethers which consist of three elements in the epoxide ring. The general process for the synthesis of the epoxide groups is known as an epoxidation reaction wherein an alkene is reacted with an organic peroxy acid. [1]
Established methods of epoxidation are as follows:
- Epoxidation by Conventional Method
- Epoxidation using acid ion exchange resin (AIER)
- Epoxidation using enzymes
- Epoxidation using metal catalyst
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III. EPOXIDATION BY CONVENTIONAL METHOD

It is the most widely used process of epoxidation. In this process Peroxyacetic acid is used as an oxidizing agent wherein the peracid is formed *in situ* by the reaction of H_2O_2 with acetic acid. In this method, a mineral acid (H_2SO_4, HNO_3, H_3PO_4, HCl), alkane sulphonic acids or strongly acidic ion exchange resins are used as catalysts in the synthesis of peracids. [6] The disadvantages of peracid catalyzed epoxidation are poor selectivity and side reactions. **Goud et al. (2005)** [7] carried out an epoxidation reaction of mahua oil using hydrogen peroxide where they studied parameters like catalyst type, temperature, molar ratio of reactants and mixing speed on the reaction. They concluded that H_2SO_4 is the best inorganic catalyst for the system producing a high conversion of double bonds to oxirane groups when the epoxidation reaction was performed at the intermediate temperature of 55^0C to 65^0C to reduce the hydrolysis reaction. [1]

IV. EPOXIDATION USING ACID ION EXCHANGE RESIN(AIER)

Acidic Ion Exchange Resin (AIER) is an insoluble gel type catalyst in the form of small yellowish organic polymer beads. Peroxy acid is obtained by reaction of H2O2 with carboxylic acid ($HCOOH/CH_3COOH$). The peroxy acid interacts with the catalyst by way of entering the pores of the catalyst. [1] Thus, when AIER loaded into the reactor its pores get filled with peroxy acid. It leads to low oxirane degradation as triglyceride couldn't enter the gel type structure of AIER. [8]. It is investigated that the conversion of unsaturated fatty acids to oxirane ring using peroxy acid either peroxy-formic acid or peroxyacetic acid in the presence of AIER shows different conversion for different vegetable oil. [1] **Goud et al. (2006)** [9] worked on in-situ epoxidation of karanja oil with aqueous hydrogen peroxide and acetic acid in presence of Amberlite IR120 acidic ion exchange resin as catalyst. The parameters studied were catalyst loading, temperature, molar ratio of reactants and stirring speed. They reported that the intermediate temperature in the range of 55^0C to 65^0C gives maximum conversion of double bonds to oxirane groups and the reaction time was minimized. Further they added that molar ratio of acetic acid to karanja oil is 0.5 mol and a mole ratio of 1.5 for hydrogen peroxide to oil was the optimal concentration for the epoxidation reaction.

V. EPOXIDATION USING ENZYMES

To avoid side reactions and to make the process more environmental friendly, enzyme catalyst is preferred. Immobilized Candida Antarctica lipase was used as the catalyst. Enzymatic catalyst for epoxidation is a good alternative to chemical treatment. The epoxidation reaction can be improved by adding the lipase step wisely. [1] **Orellana-Coca et al. (2007)** [10] reported that the stepwise addition of the enzyme may prevent enzymatic inactivation by H_2O_2 which is the major problem for lipase-mediated epoxidation. The parameters affecting the lipase activity and operational lifetime during chemoenzymatic epoxidation of fatty acids were investigated. **Ankudey et al. (2006)** [11] reported that urea hydrogen peroxide (UHP) served as a better oxidant for the enzymatic epoxidation by lipase. However, **Tornvall et al. (2007)** [12] reported that use of aqueous H_2O_2 or UHP both deactivated the enzyme making no significant difference.

VI. EPOXIDATION USING METAL OXIDES

In search of some new methods or techniques to develop the current technology, Experts and Scholars are contributing in increasing the efficiency of the epoxidation reaction. One such method is the use of metal catalyst such as tungsten, titanium and molybdenum. The peracid oxidant is obtained in situ when a carboxylic acid (usually acetic acid) reacts with hydrogen peroxide in the presence of mineral acids that act as catalysts. [1] The peracid process has many drawbacks that should be improved. Hence researches are carried out to overcome these drawbacks. **Campanella et al. (2004)** [13] studied the epoxidation of soybean oil and soybean methyl esters with hydrogen peroxide in dilute solution (6 wt. %) using an amorphous heterogeneous Ti/SiO2 catalyst in the presence of tert-butyl alcohol. **Mohamed et al. (2007)**

[14] worked on the epoxidation kinetics of sunflower oil using tungsten as a catalyst. But in this case, they got less conversion as compared to peroxy acid system.

VII. EPOXIDATION REACTION MECHANISM [6]

In the epoxidation method by carboxylic peracids precede simultaneously two reactions the formation of peracid (1), which is consumed in the intrinsic epoxidation (2), during a contact with ethylenic unsaturation of oil (Fig. 1).
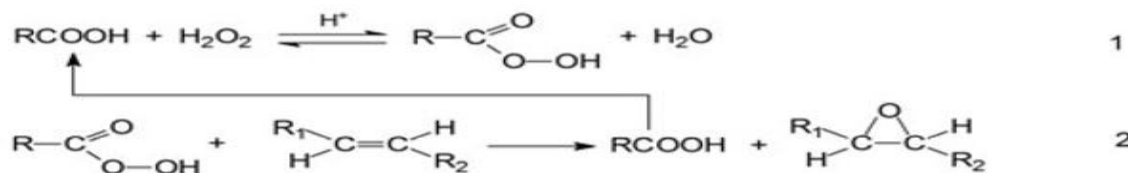

Figure 1. Scheme of vegetable oil epoxidation: peracid formation (a), epoxidation reaction (b)

The carboxylic acid, reproduced in the reaction (2) again undergoes reaction with hydrogen peroxide and new amounts of peracid are formed. The reaction (1) proceeds significantly slower in comparison with reaction (2), what limits the process. The rate of peracid formation, thereby, the process rate increases by introduction of mineral acid as a catalyst, most often sulphuric(VI) acid or strongly acidic ion exchange resins. The presence of such type catalyst is not necessary in the reaction 2. A strongly acidic catalyst accelerates the side reactions of oxirane ring opening.

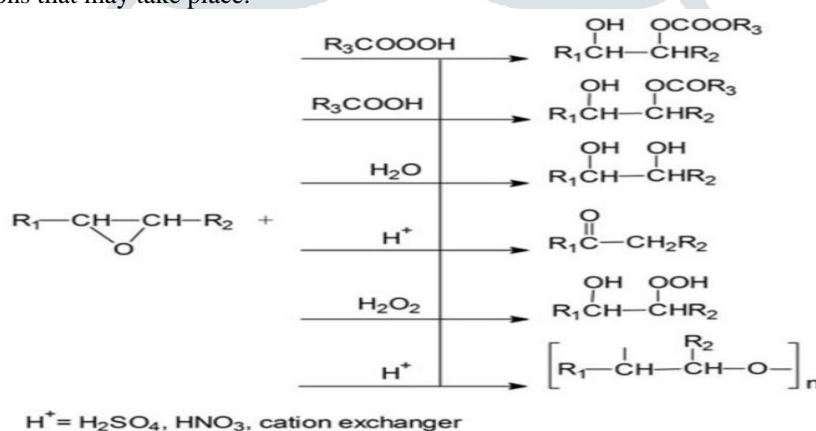The following are the side reactions that may take place.

Figure 2. Side reactions of epoxidation in the presence of acidic ion exchange resins [15]

VIII. NEW PROGRESS IN EPOXIDATION PROCESS

The epoxidation of vegetable oils is more complicated than the epoxidation of unsaturated fatty acid esters because the epoxidized products can be much more diverse (i.e., mono-, di- or tri-epoxides) depending on the seed oil origin. [3] Hence the selection of the right epoxidation method is crucial to produce the desired product. Apart from the conventional methods to study epoxidation, methods like epoxidation using a tungsten-based catalyst, Ti(IV)- grafted silica catalyst or Mo(VI) complex catalyst, epoxidation in conventional solvents and neoteric ionic liquids (ILs) are studied.

Epoxidation using a tungsten-based catalyst

The tungsten and Mo polyoxometalates (POMs) catalyst system was developed by the groups of **Venturello and Ishii** to epoxidize alkenes with the use of H_2O_2. [3] **Yadav and Satoskar (1997)** [16] carried out a comparative study between the kinetics of a traditional peracid epoxidation and an ion-exchange resin facilitated epoxidation where they found that the in situ peracid epoxidation resulted in the lowest conversion yield and lowest selectivity.
Poli et al. (2009) [17] reported that the solvent-free epoxidation of methyl oleate (MO) using the tungsten-containing catalyst "Tetrakis" with H_2O_2 and air (oxygen) as oxidizing agents could decrease MO dimerization and result in the complete conversion of MO into its epoxide.

Epoxidation using titanium-grafted mesoporous silica

The silica is prepared by impregnation, also known as grafting, the metal compounds onto the surface of the silica or by the sol–gel method. The silica-supported titanium catalyst serves as a promising heterogeneous epoxidation catalyst that is useful for continuous operation in a liquid phase, and this process has been used commercially for the epoxidation of propene. [18] In the limited number of studies that have attempted to apply titanium-containing heterogeneous catalysts for the epoxidation of mono-unsaturated fatty acid methyl esters (FAMEs), good conversion rates and high selectivity have been observed. In these studies, tert-butyl hydroperoxide (TBHP), instead of aqueous H_2O_2, was used as the oxidative agent because silica-supported titanium catalyst is more prone to be deactivated by strong coordinating ligands, especially water. The studies also demonstrated that the reaction specificity depends on the substrates. For example, in the epoxidation of the castor oil FAME, a 97% conversion rate and greater than 98% selectivity were obtained. However, for the epoxidation of the soybean oil FAME using the same catalyst, the conversion rate was only 90% with 56% selectivity. [3] Clearly, the mesoporous molecular sieve-supported titanium catalysts represent a promising class of heterogeneous catalysts for epoxidation that deserve further investigation. Unfortunately, all investigations to date have been limited to the epoxidation of FAMEs, while the epoxidation of glycerides (plant oils), which have more commercial value for plasticizer production, have not been studied. [3]

Epoxidation using molybdenum(VI) complex

The Mo(VI) complex is one of the best metallic catalysts that can promote epoxidation reactions in olefin. [3] **Farias et al.** [19] first reported the epoxidation of soybean oil with bis (acetyl-acetonato) dioxo-molybdenum(VI) [$MoO_2(acac)_2$] as the catalyst in the presence of TBHP as the oxidizing agent . The reaction was carried out in refluxing toluene with the Mo complex and TBHP to produce 54% of epoxides with 77% selectivity and a 70% conversion of the substrates within 2 h. In high oxidation states, transition-metal complexes facilitate the heterolysis of hydrogen peroxide to form alkyl hydroperoxides. The advantages of using alkyl hydroperoxides as epoxidation agents include relatively high yields, a high degree of selectivity, ease of accessibility and usability in a diluted form to reduce the element of risk during epoxidation. Notably, when compared to Ti-MCM-41, the Mo(VI) complex catalyst did not achieve a higher conversion rate or selectivity; however, the epoxidation of plant oil using the Mo(VI) complex catalyst has been reported. [19] Further improvements in the conversion rate and selectivity of the reaction may facilitate the commercial use of the Mo(VI) complex as a catalyst. [3]

Epoxidation using Ionic Liquids (ILs)

Ionic Liquids are receiving attention because of their special properties. ILs have been termed as neoteric "green" media because of their negligible vapor pressure, which is not discharged into the atmosphere like conventional volatile solvents. Therefore, the use of these methods can be "green" technology. [20] The thermodynamics and kinetics of reactions in ILs are different from conventional solvents. [3] A recent study demonstrated that the epoxidation of unsaturated fatty acids methyl esters in the presence of a SO_3H-functional acidic IL as a catalyst resulted in a faster conversion rate compared to the use of sulfuric acid. Additionally, this study demonstrated that the IL catalyst could be recycled up to 4 times. Enzymatic epoxidation using ILs remains a new system that has yet to be extensively implemented. Because ILs can be designed for specifically desired properties, the development of suitable IL systems for enzymatic epoxidation with high yields and selectivity should be achievable. [3]

Epoxidation using supercritical carbon dioxide (SC CO_2)

Supercritical carbon dioxide has been used for extractions and chemical reactions.CO_2 is cheap, non-inflammable and eco-friendly. Hence use of supercritical carbon dioxide has been considered as a green process. But the energy required for the compression of CO_2 gas into a liquid form makes the process expensive. **Gao et al. (2009)** [21] reported that SC CO_2 could be used for the asymmetric epoxidation of olefins with CO_2-soluble chiral salen-Mn(III) complexes as the catalyst. **Li and Wang (2008)** [22] investigated the epoxidation of soybean oil using hydrogen peroxide in supercritical carbon dioxide. Their results showed that the presence of $NaHCO_3$ or the phase transfer catalyst, sodium dodecyl benzene sulfonate (SDBS), greatly improved the conversion of soybean oil.

IX. APPLICATION

Epoxidized vegetable oils and fatty acid esters are receiving more attention because the components are renewable resources and low cost. The products obtained from the epoxidation reaction have various applications like

- high temperature lubricants
- polyurethane dispersions [5]
- polymeric materials
- paints, coatings and adhesives [2]
- nanocomposites
- surfactants [2]
- hydraulic oils
- bio-diesel
- Stabilizers [2]
- plasticizers. [2]

X. CONCLUSION

Epoxidized vegetable oil is receiving more attention in recent days because of its availability, cost and applications. Epoxidation is usually carried out using conventional methods like chemical treatment, Ion exchange resin etc. New methods are being practiced carrying out epoxidation which prove to be efficient and environment friendly. These methods are still new and need to be implemented extensively.

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