

Enhanced Advances in Epoxidation of Vegetable Oils

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ABSTRACT

Vegetable oils are among the most encouraging sustainable raw materials due to their prepared accessibility, intrinsic biodegradability, and their numerous flexible operations. In light of the expansion in natural issues like waste exchange issues, non-biodegradable resources, greenhouse effect, and so on and the diminishment of petroleum oil resources, reasonable oils from vegetable inception have transformed into a basic issue. The ointments from inexhaustible resources are a fruitful reality in numerous parts of the world. Vegetable oils have numerous favorable circumstances, for example, high blaze point, high thickness record, high lubricity and low evaporative misfortune other than eco-perfect, inexhaustibility and non-danger. This paper audits the strategies that are as of late been honed for the epoxidation of vegetable oils.

Keywords: Peracids, Vegetable oil, Epoxidation, Oxirane Content.

I. INTRODUCTION

Vegetables or plant oils speak to a sustainable asset that can be utilized as dependable beginning material to get to new items with a wide cluster of auxiliary and utilitarian varieties. The sufficient accessibility and the moderately minimal effort make plant oils a mechanically alluring raw material for the plastics business. [2] Epoxides are notable monetarily in view of the numerous critical responses they experience. [7] Fats and oils are inexhaustible resources that can be dealt with artificially or enzymatically to create materials which frequently go about as a substitution for petroleum-inferred materials. [7] Four advancements are utilized to create epoxides from olefinic-type molecules: (I) epoxidation with percarboxylic acids, which is generally utilized as a part of industry and can be catalyzed by acids or by proteins; (ii) epoxidation with natural and inorganic peroxides, which incorporates alkaline and nitrile hydrogen peroxide epoxidation. (iii) epoxidation with halohydrins using hypohalous acids (HOX) and its

salts as reagents for the epoxidation of olefins with electron-deficient twofold securities; and (iv) epoxidation with atomic oxygen [9]. Epoxidation of vegetable oils with sub-atomic oxygen prompts the debasement of the oil to littler compounds, for example, aldehydes and ketones, and also short-chain dicarboxylic acids. [4] It is, thusly, not an efficient strategy for the epoxidation of vegetable oils. The fundamental plant oils constituents are triglycerides (see Fig 1(A)). 90% - 95% of the aggregate weight of triglycerides represents unsaturated fats and their content is normal for each plant oil (Figure 1(A)). The structures of some as often as possible concentrated unsaturated fats are portrayed in Fig 1(B). Unsaturated fat rate arrangement of regular plant oils is given in Table 1.[2]

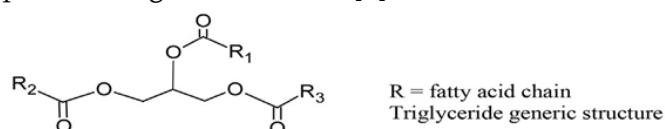


Figure 1(A)^[2]

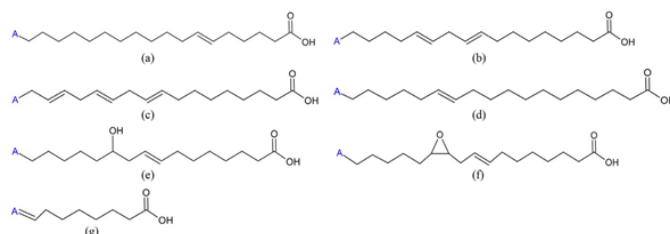


Figure 1(B) [2]

Figure 1. (A) Structure General triglyceride (B) Usage of Fatty acids in polymer chemistry

Table 1. Common plant oils Fatty acid percentage composition[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 creation of significant vegetable oils has ascended from 95 million tons in 2002/2003 to 154 million tons in 2012/2013 at a normal rate a little more than 5 million tons per year. Lion's share of vegetable oils are created for household purposes while a couple of minor vegetable oils like linseed oil and castor are utilized for modern purposes.

II. EPOXIDATION

Epoxidized oil incorporates epoxide gatherings or oxirane rings. The term epoxide can be characterized as cyclic ethers which comprise of three components in the epoxide ring. The general procedure for the blend of the epoxide bunches is known as an epoxidation reaction wherein an alkene is responded with a organic peroxy corrosive. [1]

Epoxidation Methods are:

Epoxidation By Conventional Method

It is the most broadly utilized procedure of epoxidation. In this procedure Peroxyacetic acid is utilized as an oxidizing specialist wherein the peracid is shaped in situ by the reaction of H_2O_2 with acidic acid. In this technique, a mineral acid (H_2SO_4 , HNO_3 , H_3PO_4 , HCl), alkane sulphonic acids or unequivocally acidic ion trade gums are utilized as impetuses in the combination of peracids. Goud et al. (2005) [7] completed an epoxidation reaction of mahua oil utilizing hydrogen peroxide where they considered parameters like impetus write, temperature, molar proportion of reactants and blending speed on the reaction. They reasoned that H_2SO_4 is the best inorganic impetus for the framework creating a high conversion of twofold bonds to oxirane bunches when the epoxidation reaction was performed at the middle temperature of $55^\circ C$ to $65^\circ C$ to decrease the hydrolysis reaction. [1]

Epoxidation By Using Aier(Acid Ion Exchange Resin)

Acidic Ion Exchange Resin (AIER) is an insoluble gel with impetus as little yellowish organic polymer beads. Peroxy acid is acquired by reaction of H₂O₂ by carboxylic acid (CH₃COOH /HCOOH). The peroxy acid communicates with the impetus by method for entering the pores of the impetus. The parameters contemplated were impetus stacking, temperature, molar proportion of reactants and stirring pace. They detailed that the transitional temperature in the scope of 550C to 650C gives greatest conversion of twofold bonds to oxirane gatherings and the reaction time was limited. Advance they included that molar proportion of acidic acid to karanja oil is 0.5 mol and a mole proportion of 1.5 for hydrogen peroxide to oil was the ideal concentration for the epoxidation reaction.

Epoxidation By Using Enzymes

To maintain a strategic distance from side reactions and to make the procedure more ecological cordial, enzyme impetus is favored. Immobilized *Candida Antarctica* lipase was utilized as the impetus. Enzymatic impetus for epoxidation is a decent other option to chemical treatment. The epoxidation reaction can be enhanced by including the lipase step carefully. [1] Orellana-Coca et al. (2007) [10] detailed that the stepwise addition of the enzyme may anticipate enzymatic inactivation by H₂O₂ which is the significant issue for lipase-mediated epoxidation. The parameters influencing the lipase action and operational lifetime during chemoenzymatic epoxidation of fatty acids were examined. Nonetheless, Tornvall et al. (2007) [12] revealed that utilization of fluid H₂O₂ or UHP both deactivated the enzyme having no huge effect.

Epoxidation By Using Metal Oxides

Looking for some new strategies or systems to build up the present innovation, Experts and Scholars are contributing in expanding the productivity of the epoxidation reaction. One such strategy is the utilization of metal catalyst, for example, tungsten,

titanium and molybdenum. The peracid oxidant is gotten in situ when a carboxylic acid (normally acidic acid) responds with hydrogen peroxide within the sight of mineral acids that go about as catalysts. [1] The peracid procedure has numerous drawbacks that ought to be moved forward. Henceforth inquires about are completed to beat these drawbacks. Campanella et al. (2004) [13] examined the epoxidation of soybean oil and soybean methyl esters with hydrogen peroxide in weak solution (6 wt. %) using a formless heterogeneous Ti/SiO₂ catalyst. [14] chipped away at the epoxidation energy of sunflower oil using tungsten as a catalyst. In any case, for this situation, they got less conversion when contrasted with peroxy acid system.

Epoxidation Reaction Mechanism [6]

In the epoxidation strategy via carboxylic peracids go before at the same time two reactions the formation of peracid (1), which is expended in intrinsic epoxidation (2), meanwhile a contact with ethylenic unsaturation of oil (Figure 1).

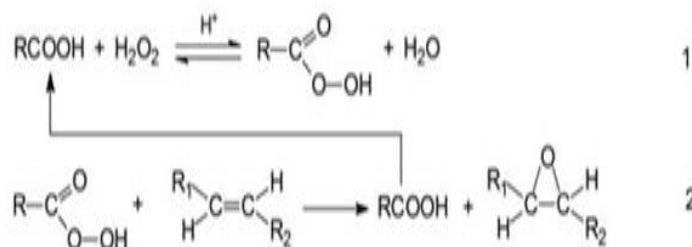


Figure 1. Scheme of vegetable oil epoxidation: peracid formation (a), epoxidation reaction (b)

The carboxylic acid, recreated in the reaction (2) again experiences reaction with hydrogen peroxide and new measures of peracid are shaped. The reaction (1) continues significantly slower in examination with reaction (2), what confines the procedure. The procedure rate increments by introduction of mineral acid as a catalyst, frequently sulphuric(VI) acid or firmly acidic ion exchange resins. The nearness of such sort catalyst isn't essential in the reaction 2.

The accompanying are the side reactions that may occur.

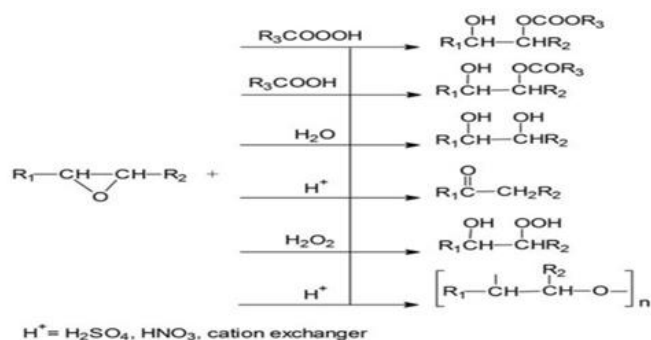


Figure 2. Epoxidation Side reactions towards the presence of AIER

III. NEW PROGRESS IN EPOXIDATION PROCESS

The epoxidation of vegetable oils is more confounded than the epoxidation of unsaturated fatty acid esters on the grounds that the epoxidized items can be significantly more various (i.e., mono-, di- or tri-epoxides) contingent upon the seed oil birthplace. [3] Hence the selection of the correct epoxidation technique is significant to create the coveted item. Aside from the conventional strategies to think about epoxidation, techniques like epoxidation using a tungsten-based catalyst, Ti(IV)- joined silica catalyst or Mo(VI) complex catalyst, epoxidation in conventional solvents and neoteric ionic fluids (ILs) are considered.

Epoxidation using titanium-grafted mesoporous silica

The silica is set up by impregnation, otherwise called grafting, the metal compounds onto the surface of the silica or by the sol-gel strategy. The silica-upheld titanium catalyst fills in as a promising heterogeneous epoxidation catalyst that is valuable for constant operation in a fluid stage, and this procedure has been utilized economically for the epoxidation of propene. In the predetermined number of concentrates that have endeavored to apply titanium-containing heterogeneous catalysts for the epoxidation of mono-unsaturated fatty acid methyl esters (FAMEs), great

conversion rates and high selectivity have been watched. In these investigations, tert-butyl hydroperoxide (TBHP), rather than watery H₂O₂, was utilized as the oxidative operator since silica-bolstered titanium catalyst is more inclined to be deactivated by solid organizing ligands, particularly water. The examinations additionally showed that the reaction specificity relies upon the substrates. For instance, in the epoxidation of the castor oil FAME, a 97% conversion rate and more prominent than 98% selectivity were gotten. Be that as it may, for the epoxidation of the soybean oil FAME using a similar catalyst, the conversion rate was just 90% with 56% selectivity. [3] Clearly, the mesoporous atomic strainer upheld titanium catalysts speak to a promising class of heterogeneous catalysts for epoxidation that merit advance investigation. Shockingly, all investigations to date have been restricted to the epoxidation of FAMEs, while the epoxidation of glycerides (plant oils), which have more business esteem for plasticizer production, have not been contemplated.

Epoxidation using molybdenum complex

The Mo(VI) complex is outstanding amongst other metallic catalysts that can advance epoxidation reactions in olefin. [3] first detailed the epoxidation of soybean oil with bis (acetyl-acetonato) dioxo-molybdenum(VI) [MoO₂(acac)₂] as the catalyst within the sight of TBHP as the oxidizing specialist. The reaction was completed in refluxing toluene with the Mo complex and TBHP to deliver 54% of epoxides with 77% selectivity and a 70% conversion of the substrates inside 2 h. In high oxidation states, transition-metal buildings encourage the heterolysis of hydrogen peroxide to shape alkyl hydroperoxides. The benefits of using alkyl hydroperoxides as epoxidation operators incorporate generally significant returns, a high level of selectivity, simplicity of availability and ease of use in a weakened frame to diminish the component of hazard during epoxidation. [11] Further changes in the conversion rate and selectivity of the reaction may encourage the

business utilization of the Mo(VI) intricate as a catalyst. [3]

Epoxidation using Ionic Liquids (ILs)

Ionic Liquids are accepting attention in view of their uncommon properties. ILs have been named as neoteric —green media in light of their unimportant vapor weight, which isn't released into the air like conventional unpredictable solvents. In this way, the utilization of these techniques can be green innovation. The thermodynamics and energy of reactions in ILs are unique in relation to conventional solvents. [3] A current report showed that the epoxidation of unsaturated fatty acids methyl esters within the sight of a SO₃H-functional acidic IL as a catalyst brought about a speedier conversion rate contrasted with the utilization of sulfuric acid. Additionally, this examination showed that the IL catalyst could be reused up to 4 times. Enzymatic epoxidation using ILs remains another framework that presently can't seem to be widely actualized. Since ILs can be intended for particularly wanted properties, the improvement of appropriate IL frameworks for enzymatic epoxidation with exceptional returns and selectivity ought to be achievable. [3]

Epoxidation using supercritical carbon dioxide (SC CO₂)

Supercritical carbon dioxide has been utilized for extractions and chemical reactions. CO₂ is modest, non-inflammable and eco-accommodating. Thus utilization of supercritical carbon dioxide has been considered as a green procedure. Yet, the vitality required for the compression of CO₂ gas into a fluid shape makes the procedure costly. Gao revealed that SC CO₂ could be utilized for the hilter kilter epoxidation of olefins with CO₂-solvent chiral salen-Mn(III) buildings as the catalyst. Li and Wang (2008) examined the epoxidation of soybean oil using hydrogen peroxide in supercritical carbon dioxide. Their outcomes demonstrated that the nearness of NaHCO₃ or the stage exchange catalyst, sodium

dodecyl benzene sulfonate (SDBS), incredibly enhanced the conversion of soybean oil.

IV. APPLICATION

Epoxidized vegetable oils and fatty acid esters are accepting more attention in light of the fact that the segments are inexhaustible resources and ease. The items got from the epoxidation reaction have different 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]

V. CONCLUSION

Epoxidized vegetable oil is accepting more attention as of late in light of its accessibility, cost and applications. Epoxidation is generally done using conventional techniques like chemical treatment, Ion exchange resin and so on. New techniques are being worked on doing epoxidation which end up being effective and condition benevolent. These techniques are still new and should be actualized broadly.

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