International Journal of Trend in Research and Development, Volume 5(2), ISSN: 2394-9333
www.ijtrd.com

Review: Epoxidation of Vegetable oils

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Abstract: Vegetable oils are most versatile substitutes for other exhaustive hydrocarbon compounds for production of epoxides. Most vegetable oils have high content of unsaturated bond and can be converted into epoxidized fatty acids. These days, epoxidized vegetable oils are great concern as they are obtained from sustainable, renewable natural resources and are environmental friendly. Epoxidation of vegetable oils on an industrial scale is most frequently carried out with peroxyacetic and peroxyformic acids, the products being used as PVC plasticizers. Typical conversions of double bonds to epoxy groups are about 90%. The present paper is review work on various methods and literature survey of epoxidation of vegetable oil.

Keywords*: Sustainability, Vegetable oil, Epoxides, Ion Exchange Resin, FTIR*

I. INTRODUCTION

Renewable raw materials are environmentally friendly, biodegradable, low cost, and readily available. The possible use of these resources as a substitute for petrochemical derivatives has attracted the attention of many researchers. Plant oils and animal fat are members of this group of renew-able resources. Vegetable oils rich in oleic, linoleic, and linolenic acyl groups may be used to introduce functional groups such as epoxides.

Epoxidation of plant oils, commonly termed "vegetable oils," is a commercially important reaction because the epoxides obtained from these renewable raw materials and from methyl oleate, their transesterification product, have applications in such materials as plasticizers and polymer stabilizers .Owing to the high reactivity of the oxirane ring, epoxides also act as a raw material for a variety of chemicals, such as alcohols, glycols, alkanolamines, carbonyl compounds, olefinic compounds, and polymers, e.g., polyesters, polyurethanes, and epoxy resins. [1] Epoxides are well known commercially because of the many important reactions they undergo. [2] 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. [3] 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. [4] 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 [5]. 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. [6] It is, therefore, not an efficient method for the epoxidation of vegetable oils. [2] 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. [7] The main constituents of plant oils are triglycerides. 90% - 95% of the total weight of triglycerides accounts for fatty acids and their content is characteristic of each plant oil. An attempt was made to formulate that would permit the prediction of rise velocity, a variable that greatly affect the bubble column operation [47].

Epoxidation of long-chain olefins and unsaturated FA derivatives of vegetable oils such as soybean, linseed, rapeseed, olive, corn, safflower, melon seed, and cotton seed is carried out on an industrial scale. Today, one of the most important epoxidized vegetable oils is epoxidized soybean oil. Its world-wide production is about 200,000 t/yr. [8] within the past few years, researchers are striving to improve sustainability as a result of using less petroleum-based by-products. Petroleum-based by-products have resulted in negative consequences both economically and environmentally. Environmentally, using these products has a major effect of producing vast amounts of carbon dioxide emissions in the earth's atmosphere that contributes to extreme climate changes. As the need for petroleum continues to increase, eventually there will be a drastic depletion in crude oil that limits its use in a number of industries. Therefore, it is imperative to convert our everyday use of petroleum based products into completely bio-based products. [9]

Typically, the conversion to bio-based products uses vegetable oils as the primary source, particularly because they are sustainable, renewable, abundant, biodegradable, and has low toxicity. Of all the vegetable oils, soybean oil is one that is used extensively in research to produce bio-based products particularly for polymeric use. The wide use of soybean oil is due to its large production, low cost, and easy conversion of the double bonds to a three membered epoxide groups.[10] In soybean oil, the double bonds are provided primary from linolenic, linoleic, and oleic fatty acids containing three, two and one double bonds, respectively. It is the highly concentrated double bonds within the unsaturated fatty acids that make the fatty acids prone to oxidation by way of autoxidation of the molecular oxygen in the oil, which can lead to a decrease in properties over-time. However, oxidation can be reduced by functionalization of the oil at the location of double bonds to form epoxide groups via an epoxidation process. [11] Epoxidation can be carried out in a number of ways that include the conventional chemical treatment, using acid ion exchange resins (AIER), using enzymes, or using metal catalyst. Among all methods listed, the chemical conversion process is the most preferred one. This method uses formic acid or acetic acid to act as the oxygen carrier and hydrogen peroxide that acts as the oxygen donor. Reacting together, the formic or acetic acid and hydrogen peroxide form a performic or peracetic acid that reacts further with the double bonds in the oil to further produce epoxide groups. Thus, it is important to achieve a high number of epoxide groups (or high

oxirane content) that will result in increased crosslinking and consequently increased properties. However, due to different percentages of fatty acids in oils, the physical and physiological properties may vary. Thus, high oxirane content between 5.5 and 7% is recommended for the epoxidation of soybean oil. The ability to achieve desirable oxirane oxygen content requires precise optimization of the system to aid in a reduction of production time and cost. However, there are a number of factors that can affect the epoxidation reaction like reaction time, reaction temperature, amounts of formic or acetic acid, amount of hydrogen peroxide, and stirring speed. [12] Hence, in order to properly synthesize an epoxidized soybean oil system, this research focuses on the effect of varying the reaction time, reaction temperature, and molar ratios of hydrogen peroxide. The overall goal then is to understand how the percent oxirane oxygen changes as a result of these factors. [13]

There are four known technologies to produce epoxides from olefinic type of molecules:

- **Epoxidation with percarboxylic acids:** The most widely used in industry, can be catalyzed by acids or by enzymes
- **Epoxidation with organic and inorganic peroxides:** Which includes alkaline and nitrile hydrogen peroxide epoxidation as well as transition metal catalyzed epoxidation
- **Epoxidation with halohydrins:** Using hypohalous acids (HOX) and their salts as the reagents for the epoxidation of olefins with electron deficient double bonds
- **Epoxidation with molecular oxygen** [14]

The double bonds in the vegetable oils are used as reactive sites in coatings and they can also be functionalized by epoxidation. The utilization of epoxidized vegetable oil has become more common in the past few years. Moreover, plasticizers and additives for polymer PVC derived from vegetable oil based have been shown to have improved performance in terms of high resistance to heat and light. 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. [15]

1.1 Epoxidation of vegetable oil materials used here:

1. Epoxidized soyabean oil: Soybean oil containing 26% oleic acid, 7% Linolenic, 4% Stearic, 11% Palmitic and 52% linoleic acid, was epoxidized with hydrogen peroxide as oxygen donor, carrier in presence of catalytic amount of a formic acid. Today, one of the most important epoxidized vegetable oils is epoxidized soybean oil. Its world- wide production is about 200,000 t/yr. [2]

2. Epoxidized karanja oil: Epoxidation of karanja oil (KO), a nondrying vegetable oil, was carried out with peroxyacetic acid that was generated in-sit from aqueous hydrogen peroxide and glacial acetic acid. KO contained 61.65% oleic acid and 18.52% linoleic acid, respectively, and had an iodine value of 89 g/100 g. Unsaturated bonds in the oil were converted to oxirane by epoxidation. [16]

1.2 Established methods of epoxidation:

1. **Epoxidation by Conventional Method:** It is the most widely used process of epoxidation. For safety point of view these epoxidation are usually carried out using peracids formed in-situ, by reacting a carboxylic acid with concentrated hydrogen peroxide. This process performs industrially on large scale.
2. **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/CH3COOH). The peroxy acid interacts with the catalyst by way of entering the pores of the catalyst.
3. **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. The epoxidation reaction can be improved by adding the lipase step wisely.
4. **Epoxidation using metal catalyst:** Recently it has been shown that the incorporation of Ti on an amorphous silica support produces oxidation catalysts that are highly effective in epoxidation reactions with hydrogen peroxide. [17,18]

II. LITERATURE SURVEY

In 2012, Kouroosh Saremi et al; worked on the epoxidation of soybean oil. In this study, produce epoxidized soybean oil (ESO), the epoxidation was carried out by conventional chemistry at 50°C, speed of 550 RPM, and atmospheric pressure for about 10 hours. An excess amount of hydrogen peroxide was necessary in the reaction to achieve high reaction conversion. A possibly undesirable side reaction was reaction of the epoxy ring opening resulting in hydroxyl functional groups observed by Fourier Transform Infrared Spectroscopy (FTIR). The highest epoxy content of ESO produced had 6.1% (wt). [19]

In 2008, Dinda et al; worked on the epoxidation kinetics of cottonseed oil using a hydrogenperoxide catalyzed by liquid inorganic acids i.e. HCl (35%), H_2SO_4 (98%), HNO_3 (70%) and H_3PO_4 (85-87%). They used carboxylic acid i.e. CH_3COOH (99-100%) and HCOOH (85%). The Out of all the liquid inorganic acid catalysts studied, H_2SO_4 was found to be the most efficient and effective. Higher temperature and higher acid concentrations reduced the reaction time needed to reach the maximum conversion to oxirane value. The epoxidation of cottonseed oil using in situ generated peroxyacid could be carried out at moderate temperature of about 60 degrees. CH_3COOH was found to be more effective oxygen carrier than HCOOH. [20]

In 2011, Dinda et al; investigated the kinetics of epoxidation of cottonseed oil by peroxyacetic acid (PAA) generated in situ from hydrogen peroxide and glacial acetic acid (AA) in the presence of acidic ion exchange resin (AIER) catalysts, namely Amberlite IR-120. The effect of several variables including temperature, stirring speed, catalyst loading, and particle size, concentration of hydrogen peroxide and AA on oxirane conversion was studied. A satisfactory level of oxirane conversion (greater than 65%) with high selectivity (greater than 90%) could be obtained if the epoxidation was carried out at optimum conditions, using in situ generated PAA. The Langmuir–Hinshelwood–Hougen–Watson (L–H–H–W) kinetic model approach has been adopted for the development of overall reaction rate equations, and the proposed kinetic model includes the major side reactions for the estimation of kinetic parameters. Kinetic parameters were estimated by fitting experimental data using a nonlinear regression method. From the estimated kinetic constants, the activation energy for the

AIER catalysed epoxidation of cottonseed oil was found to be 10.1 kcal mol^{-1}. [21]

Tayde Saurabh et al. (2011), worked on the epoxidation of vegetable oils: a review. Study the potential utility of epoxidized vegetable oil has begun to be realized in industrial applications with increasing the concern of research in aspirants to develop value added products from the available plant oils. Vegetable oil could be epoxidized successfully by peroxy acid generated 'in-situ' by reacting formic or acetic acid with hydrogen peroxide at isothermal temperature condition. The epoxidation can be confirmed by iodine value, FTIR analysis and NMR analysis. In-situ epoxidation of vegetable oil is more convenient and economically viable method for large scale epoxidation which shows utility especially in plasticizer and stabilizer used in polymers. [22]

Meyer et al. (2008), worked on the epoxidation of the soybean oil and jatropha oil by conventional method. They carried out the epoxidation reaction at 50°C and atmospheric pressure for about 10 hours. The maximum reaction conversion was 83.3% for epoxidation of soybean oil as catalyst. [23] In 2015, M.S. Gaikwad et al; worked on Eco-friendly polyurethane coatings from cottonseed and karanja oil. The cottonseed (G. arboreum) and karanja (Pongamia) oils were successfully epoxidized using hydrogen peroxide and Amberlyst resin. A series of polyester polyols were also synthesized by the reaction of epoxidized cottonseed and karanja oils and characterized by the FTIR and NMR spectroscopy. The eco-friendly polyurethane coatings were prepared by the reaction of polyester polyols and different diisocyanates using dipentene, as an eco-friendly solvent. The polyurethane coating showed very good thermal stability and coating properties. [24]

Table 1: Chemical Structure of Common Fatty Acid [8]

Fatty Acid	Systematic Name	Structure	Formula
Lauric	Dodecanoic	12:0	$C_{12}H_{24}O_2$
Myristic	Tetradecanoic	14:0	$C_{14}H_{28}O_2$
Palmitic	Hexadecanoic	16:0	$C_{16}H_{32}O_2$
Stearic	Octadecanoic	18:0	$C_{18}H_{36}O_2$
Arachidic	Eicosanoic	20:0	$C_{20}H_{40}O_2$
Behenic	Docosanoic	22:0	$C_{22}H_{44}O_2$
Lignoceric	Teracosanoic	24:0	$C_{24}H_{48}O_2$
Oleic	*cis*-9-octadecanoic	18:1	$C_{18}H_{34}O_2$
Linoleic	*cis*-9, *cis*-12- octadecadienoic	18:2	$C_{18}H_{32}O_2$
Linolenic	*cis*-9, *cis*-12, *cis*-15-Octadecatrienoic	18:3	$C_{18}H_{30}O_2$
Erucic	*cis*-13-Docosenoic	22:1	$C_{22}H_{42}O_2$

Table 2: Chemical Composition of Vegetable Oils [8-9]

Vegetable Oil	Fatty Acid Composition, Wt %									
	14:0	16:0	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3
Corn	0	12	2	Tr	0	0	25	0	6	Tr
Cottonseed	0	28	1	0	0	0	13	0	58	0
Crambe	0	2	1	2	1	1	19	59	9	7
Linseed	0	5	2	0	0	0	20	0	18	55
Peanut	0	11	2	1	2	1	48	0	32	1
Rapseed	0	3	1	0	0	0	64	0	22	8
Safflower	0	9	2	0	0	0	12	0	78	0
H.O.Safflower	Tr	5	2	Tr	0	0	79	0	13	0
Sesame	0	13	4	0	0	0	53	0	30	0
Soybean	0	12	3	0	0	0	23	0	55	6
Sunflower	0	6	3	0	0	0	17	0	74	0

Table 3: Properties of Vegetable Oil [10-11]

Vegetable Oil	Kinematic Viscosity (at 38 °C mm^2 /s)	Density (kg/l)	Iodine Value Gms of I_2 /100 gms of oil
Corn	34.9	0.9095	127-133
Cottonseed	33.5	0.9148	98-118
Linseed	27.2	0.9236	170-204
Peanut	39.6	0.9026	86-107
Rapeseed	37.0	0.9115	97-108
Safflower	31.3	0.9144	141-147
Sesame	35.5	0.9133	104-120
Soybean	32.6	0.9138	120-141
Sunflower	33.9	0.9161	118-141
Palm	39.6	0.9180	50-55

According to Cai et al. (2008), worked on the kinetics of in-situ epoxidation of soybean oil, sunflower oil and corn oil by peroxyacetic acid catalysed H_2SO_4. The epoxidation of soybean oil by peroxyacetic acid generated in situ can be carried out at moderate temperatures with minimum epoxide degradation. In this work they found that soybean oil has greatest conversion rate and lowest activation energy for epoxidation using peroxyacetic acid. The activation energy of the reaction follows the sequence: soybean oil> corn oil > sunflower oil. [25]

Petrovic et al. (2002); It is investigated that the conversion of unsaturated fatty acids to oxirane ring using peroxy acid either peroxyformic acid or peroxyacetic acid in the presence of AIER shows different conversion for different vegetable oil. Worked on the epoxidation kinetics and side reactions of soybean oil in toluene with peroxyacetic acid and peroxy formic acid in the presence of AIER as a catalyst. They found that peroxyacetic acid is less efficient than peroxy formic acid. Acidic ion exchange resin can be used as catalyst to synthesize peroxy acids followed by in-situ epoxidation of vegetable oils. While studying the kinetics of in-situ epoxidation of soybean oil in bulk catalyzed by ion exchange resin, they find that AIER has prominentadvantages over conventional chemical method of epoxidation of vegetable oil is that by improving the selectivity and undesirable side reactions can be reduced to certain level. [26]

In 2016, Kornelia Malarczyk-Matusiak et al; worked on the vegetable oils epoxidation processes carried out in the presence of strongly acidic ion exchange resins are obtained similar results by using acetic or performic acid. Because of the easy recovery of acetic acid from the reaction solution, and safety, acetic acid is used instead of formic acid. So far the epoxidation results in batches were described. The most suitable epoxidationtemperature of frequently used vegetable oils using peracetic acid is 65–70°C, with the amount of strongly acidic ion exchanger 16 wt%. It is also important to determine the molar ratio of acetic acid to hydrogen peroxide and ethylenic unsaturation: $CH_3COOH/H_2O_2/C{=}C$ = 0.5:1.5:1. The 90% conversion of ethylene unsaturation was obtained at these technological parameters after 8 hours. [27]

In 2006, Vlcek and Petrovic et al; worked on the Optimization of chemoenzymatic epoxidation of soybean oil. In this work hey find that the rate of reaction is affected by the concentration of lipase biocatalyst. Along with the catalyst loading (not more than 4 wt% of catalyst loading) reaction temperature, molar ratio of hydrogen peroxide to ethylenic unsaturation, oleic acid concentration and solvent concentration. [28]

The ability of bis(acetyl-acetonato)dioxo-molybdenum (VI) [MoO2(acac)2] to catalyse the epoxidation ofsoybean oil in the presence of tert-butyl hydroperoxide as oxidizing agent has been investigated. Theinfluence of reaction time and temperature in the course of the epoxidation reaction was evaluated byquantitative 1H NMR. When epoxidation was carried out in refluxing toluene at 110 ◦C for 2 h, a 70.1%conversion of substrate was obtained, producing 54.1% epoxidation with a selectivity of 77.2%. The 1HNMR spectroscopic method selected for the purpose of this work allowed a simple and rapid evaluationof the mono- and diepoxides obtained following the epoxidation of soybean oil.[29]

In 2008, Sinadinovic-Fiser et al; worked on the kinetics of epoxidation of soybean oil in bulk by peracetic acid formed in situ, in the presence of an ion exchange resin as the catalyst. The catalytic reaction of the peracetic acid formation wascharacterized by adsorption of only acetic acid and peracetic acid on the active catalyst sites and irreversible surface reaction was the overall rate determining step. They investigated that increasing the catalyst concentration, reaction temperature and acetic acid to ethylenic unsaturation molar ratio increases the reaction rate and oxirane content. [30]

In 2011, Jia Liankun et al; worked on the synthesis of vegetable oil based polyether polyols via epoxidation followed by ring-opening reaction. In this study, epoxidation of cottonseed oil with epoxy oxygen content from 5.25 wt% to 6.15 wt% was first produced by peroxyformic acid generated in-situ from hydrogen peroxide and formic acid, they used HBF_4 (40 wt%) The presence of strong mineral inorganic acid such as H_2SO_4 as acid catalyst leads to many side reactions such as oxirane ring opening to diols, hydroxyl esters, estelloids and other dimer formation. [19]

Shangde Sun et al. (2011); worked on enzymatic epoxidation of Sapindus mukorossi seed oil. The Sapindus mukorossi seed oil (SMSO) was epoxidized using hydrogen peroxide as oxygen donar and Stearic acid as active oxygen carrier in the presence of immobilized Candida antartica lipase B. The effect of the amount of Stearic acid on the enzymatic epoxidation was investigated. The variables of the reaction temperature and enzyme load were the most significant in the process. They compared with reaction time and substrate ratio, reaction temperature and enzyme load had significant effects on the epoxidation and reaction temperature had a negative effect on the enzyme activity at higher temperatures. [31]

M. Klass, S. Warwel et al; worked on the complete and partial epoxidation of plant oils by lipase-catalysed perhydrolysis. They studied epoxidation of plant oils such as rapeseed, sunflower, soybean and linseed using immobilized lipase catalyst. Theyfind that the epoxidation using lipase biocatalyst was very selective and epoxidation conversion rate was exceeding 90%. [32]

In 2008, Mungroo et al; worked on the epoxidation of canola oil with H_2O_2 as oxygen donar, acetic acid as oxygen carrier and AIER (22 % loading) as catalyst. The heterogeneous catalyst, AIER, was found to be reusable and exhibited a negligible loss in activity. The formation of epoxy adduct of canola oil was confirmed by FTIR and H NMR spectral analysis. [33]

Goud et al. in 2006 worked on in-situ epoxidation of karanja oil with aqueous hydrogen peroxide and acetic acid in presence of Amberlite IR- 120 acidic ion exchange resin as catalyst. The variables studied were stirring speed, hydrogen peroxide to ethylenic unsaturation molar ratio, acetic acid to ethylenic unsaturation molar ratio, temperature and catalyst loading. The effects of this parameter on the conversion to epoxidized oil were studied at the optimum condition for the maximum oxirane content was established. They reported that the intermediate temperature in the range of 55ºC to 65ºC 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. [34]

In 1990, Bjorkling et al. published the first results related to chemo-enzymatic epoxidation. Later, progress was made towards reducing the limitations of industrial scale syntheses

by making the procedure a more environmentally acceptable alternative for vegetable oil transformations. [35]

While studying the new synthesis with oil and fats as a renewable raw material for the chemical industry, Ursula et al. had stated that the lipasecatalyst exhibited excellent stability and activity during the epoxidation process and can reuse many times. [36]

Rosana de Cassia et al. worked on the Chemo Enzymatic Epoxidation of Sunflower Oil Methyl Esters. They investigated the chemo-enzymatic epoxidation of the methyl esters of sunflower oil with lipase from Candida antarctica B and aqueous H_2O_2 in the presence and absence of an acyl donor. The biphasic system (CH_2Cl_2/H_2O) comprised Candida antarctica B lipase (CALB, 1000 u g^{-1}) and 30% (v/v) aqueous hydrogen peroxide. In some cases, the conversion was higher than 99%. The best results were obtained for the biphasic system after 16 h of reaction, at 30°C, using 10 mol of octanoic acid in relation to 1 g of the oil, 6 mL of dichlomethane and 5 mL of water. [37]

Campanella et al; worked on the epoxidation of soybean oil and soybean methyl esters with hydrogen peroxide in dilute solution (6 wt %) using an amorphous heterogeneous Ti/SiO_2 catalyst in the presence of tert-butyl alcohol. Under the experimental conditions employed in this work, no degradation of the oxirane ring was observed. Recently it has been shown that the incorporation of Ti on an amorphous silica support produces oxidation catalysts that are highly effective in epoxidation reactions with hydrogen peroxide. [38]

Mohamed et al; 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. [39]

An epoxidation reaction of mahua oil using hydrogen peroxide was done by Goud et al; (2005). In order to optimize the process, they studied various parameter and factors including catalyst type, temperature, reactants molar ratio and mixing speed on the epoxidation reaction. Also they statedthat the economic value of mahua oil could be increased by converting oil to epoxidized mahua oil. They used H_2O_2 as oxygen donar and glacial acetic acid as oxygen carrier in the presence of catalytic inorganic acid i.e.H_2SO_4 and HNO_3 but they concluded that sulphuric acid is the best inorganic catalyst for this system producing a high conversion of double bonds to oxirane groups when the epoxidation reaction performed at the intermediate temperature of 55ºC to 65ºC to reduce the hydrolysis reaction. [40]

It is,demonstrated that certain cobalt compounds which are autoxidation catalysts atlow concentrations become inhibitors at higher concentrations. In all these cases inhibitionimplies **a** lengthening of the induction period, but only in a few systems (N-alkylamide +cobaltous acetate) is the inhibitory effect observable beyond the induction period. In thecase of hydrocarbons and cobalt(I1) salicylaldimines the rate of oxygen uptake beyondthe substantially increased induction period is not reduced even at the highest catalystconcentrations. A reaction mechanism and a kinetic scheme, consistent with the novel experimentalobservations, are proposed.[41]

The ability of bis(acetyl-acetonato)dioxo-molybdenum (VI) [MoO2(acac)2] to catalyse the epoxidation of soybean oil in the presence of tert-butyl hydroperoxide as oxidizing agent has been investigated. The influence of reaction time and temperature in the course of the epoxidation reaction was evaluated by quantitative 1H NMR. When epoxidation was carried out in refluxing toluene at 110 ◦C for 2 h, a 70.1% conversion of substrate was obtained, producing 54.1% epoxidation with a selectivity of 77.2%.[30] The 1H NMR spectroscopic method selected for the purpose of this work allowed a simple and rapid evaluation of the mono- and diepoxides obtained following the epoxidation of soybean oil. Support, does not offer any additional advantage otherthan high surface area for the epoxidation of plant oils. The presence of pores is not necessary; the results suggest that the reaction occurs over a large external surface area. The epoxidation can also be carried out with a non-crystalline amorphous Ti–SiO2. The important issue here is to have the titanium center finely dispersed over a relatively high surface area.[42] The temperature should be below 70 ◦C tominimize ketone formation. The best solvent with this catalyst is one apolar and aprotic, like *n*-hexane. Ti–SiO2 catalyst was shown to be truly heterogeneous under the reaction conditions and was re-usable at least four times. The epoxidationsystem TBHP/Ti–SiO2 has not been reported so far in the literature for the epoxidation of vegetable oils and methyl oleate, the transesterification product, and, based on the results presented here, it could have a great potential for industrial use.[43]

III ANALYTICAL TECHNIQUES

Gas Chromatography (GC):

Gas Chromatography (GC) provides a quantitative analysis of volatile and semi-volatile organic compounds found in a variety of matrices (gases, liquids and solids) in foods, medical materials, plastics, environmental samples and occupational monitoring samples.[44]

Nuclear Magnetic Resonance (NMR):

Samples are typically dissolved in a deuterium-labelled solvent to form, a clear solution before being transferred to a thin, transparent glass NMR tube. The sample is then placed into a very strong magnetic field whereby the nuclei of the atoms absorb and then re-emit electromagnetic radiation at a particular resonance frequency. This information provides structural and electronic information which translates into an extremely powerful analytical technique.[45]

Fourier Transform Infrared Radiation Spectroscopy (FTIR):

FTIR provides detailed information on the bond structures within compounds. FTIR depends upon the absorption of infrared radiation arising from the vibrational and rotational characteristics of dipolar chemical compounds. The arrangement and strength of chemical bonds within a molecule have a direct effect on the characteristic modes of vibration and vibrational bond frequencies of a molecule, resulting in the formation of a series of characteristic mid-infrared absorption bands (4000-400 cm^{-1}) which can be used to characterise and quantify individual compounds.[46]

IV. ECONOMIC FEASIBILITY OF EPOXIDIZED VEGETABLE OIL

India used to grow and has rich forest resources with a wide range of plants and oilseeds. The economic feasibility of the epoxidized vegetable oil depends on the price of crude petroleum oil. It is very certain that the cost of crude petroleum is increasing day by day due to increase in its demand and limited supply. The cost of epoxidized vegetable oil can be considerably reduced if we consider non-edible oil, used frying oil and acid oils instead of edible oils. The non-edible oils such

as babassu, mahua, neem, karanja, jatropha etc. are easily available in manyparts of the world including India and are very cheap as compared to edible oil. In many countries including Australia,Netherland, U.S.A,Germany, Belgium, Austria and Japan the used frying oils are discarded that can be used for epoxidation purpose. [8]

CONCLUSION

The present work was on epoxidation of vegetable oil instead of using non-renewable hydrocarbons. Since there are vast applications of epoxides it becomes necessary to find advanced methods for manufacturing and also optimized work on new methods.

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