ABSTRACT
Vegetable oils are the fats and lipids containing triglyceride molecules. Most of the vegetable oils have high contents of unsaturated fatty acid and can be converted into epoxy fatty acid by conventional epoxidation, catalytic acidic ion exchange resin, metal catalyst epoxidation or using chemoenzymatic epoxidation. Nowadays epoxidized vegetable oil is having great concern as they obtain from sustainable, renewable natural resource and are environmental friendly. Epoxidized vegetable oil (EVO) can act as a raw material for synthesis of variety of chemicals including polyols, glycol, carbonyl compound, lubricants, plasticizers for polymer etc. because of their respectable oxirane oxygen content and high reactivity of oxirane ring. This paper presents an overview of epoxidation of different vegetable oils.

KEY WORDS Epoxidation, EVO, Oxirane Oxygen Content

INTRODUCTION
This review focused on the finding of the potential utility of epoxidized vegetable oil and developing newer means for its widespread applications. Vegetable oil finds sustainable and renewable source of raw material. The unsaturation present in vegetable oils can be chemically modified to a value added product by a complicated reaction called ‘epoxidation’. Due to the high reactivity of the oxirane ring epoxides can also act as a raw material for synthesis of variety of chemicals such as alcohols (polyols), glycols, olefinic compounds, lubricants, plasticizer and stabilizer for polymers and their demand is increasing day by day. Vegetable oil represents one of the cheapest and most abundant biological feedstock available in large quantities and its use as starting material offers numerous advantages such as low toxicity and inherent biodegradability[1]. Thus the economic value of the vegetable oil could be increased by converting the vegetable oil into epoxidized vegetable oil. The double bonds in the vegetable oil are used as reactive sites in the coatings and they can also be functionalized by epoxidation. Thus the high molecular weight products can be obtained by increasing the cross linking. Now due to the increasing levels of awareness regarding environment is driving the development of sustainable green materials. Petrochemical based resin such as epoxy, polyester and vinyl ester find more engineering application because of their advantageous material properties such as high stiffness and strength. However these resins have serious drawbacks in terms of biodegradability, initial processing cost, energy consumption and health hazards. Consequently there is a requirement to develop novel biobased product from renewable feedstock. Therefore a number of researchers have been studied vegetable oils as alternative feedstock to substitute for petroleum[2-5]. Hence it needs to be explored for the various applications in chemical industry

VEGETABLE OILS: STRUCTURE, COMPOSITION, PROPERTIES AND EXTRACTION
Vegetable oils are predominantly the triglyceride molecules. Triglycerides are also known by the name triacylglycerol (TAG). In vegetable oil glycerol molecule is attached to the three fatty acid chains of unsaturated and saturated fatty acids. The unsaturated fatty acids present in vegetable oil are oleic acid, linoleic acid and linolenic acid containing one, two and three double bonds between two carbon atoms respectively. The functionality present in vegetable oil is in terms of double bonds in vegetable oil is as reaction site for chemical modification in vegetable oil[7].

1) COMPOSITION AND PROPERTIES
Many naturally occurring fats are containing fatty acids with variation in chain length between 14-22 carbon atoms and single to triple bonds between two carbon atoms. The unsaturated fatty acids present in vegetable oil are oleic acid, linoleic acid and linolenic acid containing one, two and three double bonds between two carbon atoms respectively. The functionality present in vegetable oil in terms of double bonds thus the C=C acts as a reaction site for chemical modification in vegetable oil[7].
Table 1. Chemical Structure of Common Fatty Acid[8]

<table>
<thead>
<tr>
<th>Fatty Acid Systematic Name</th>
<th>Structure</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric</td>
<td>12:0</td>
<td>C_{12}H_{25}O</td>
</tr>
<tr>
<td>Myristic</td>
<td>14:0</td>
<td>C_{14}H_{27}O</td>
</tr>
<tr>
<td>Palmitic</td>
<td>16:0</td>
<td>C_{16}H_{31}O</td>
</tr>
<tr>
<td>Stearic</td>
<td>18:0</td>
<td>C_{18}H_{35}O</td>
</tr>
<tr>
<td>Arachidic</td>
<td>20:0</td>
<td>C_{20}H_{41}O</td>
</tr>
<tr>
<td>Behenic</td>
<td>22:0</td>
<td>C_{22}H_{45}O</td>
</tr>
<tr>
<td>Lignoceric</td>
<td>24:0</td>
<td>C_{24}H_{49}O</td>
</tr>
<tr>
<td>Oleic</td>
<td>cis-9-Octadecanoic</td>
<td>18:1</td>
</tr>
<tr>
<td>Linoleic</td>
<td>cis-9, cis-12-Octadecadienoic</td>
<td>18:2</td>
</tr>
<tr>
<td>Linolenic</td>
<td>cis-9, cis-12, cis-15-Octadecatrienoic</td>
<td>18:3</td>
</tr>
<tr>
<td>Erucic</td>
<td>cis-13-Docosanoic</td>
<td>22:1</td>
</tr>
</tbody>
</table>

Table 2. Chemical Composition of Vegetable Oil[8-9]

<table>
<thead>
<tr>
<th>Vegetable Oil</th>
<th>Fatty Acid Composition, Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>14:0</td>
</tr>
<tr>
<td>Corn</td>
<td>0.0</td>
</tr>
<tr>
<td>Cottonseed</td>
<td>0.0</td>
</tr>
<tr>
<td>Crambe</td>
<td>0.0</td>
</tr>
<tr>
<td>Linseed</td>
<td>0.0</td>
</tr>
<tr>
<td>Peanut</td>
<td>9.0</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>0.0</td>
</tr>
<tr>
<td>Safflower</td>
<td>0.0</td>
</tr>
<tr>
<td>H.O.Safflower</td>
<td>Tr</td>
</tr>
<tr>
<td>Sesame</td>
<td>0.0</td>
</tr>
<tr>
<td>Soybean</td>
<td>0.0</td>
</tr>
<tr>
<td>Sunflower</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 3. Chemical Composition of Vegetable Oil[8-9]

<table>
<thead>
<tr>
<th>Vegetable Oil</th>
<th>Fatty Acid Composition, Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>14:0</td>
</tr>
<tr>
<td>Rice‐Bran</td>
<td>0.4-0.6</td>
</tr>
<tr>
<td>Sal</td>
<td>4.5-5.6</td>
</tr>
<tr>
<td>Mahua</td>
<td>16.0-28.2</td>
</tr>
<tr>
<td>Neem</td>
<td>0.2-0.26</td>
</tr>
<tr>
<td>Karanja</td>
<td>3.7-7.9</td>
</tr>
</tbody>
</table>

Table 4. Properties of Vegetable Oil[10-11]

<table>
<thead>
<tr>
<th>Vegetable Oil</th>
<th>Kinematic Viscosity (at 38 °C mm²/s)</th>
<th>Density (g/cm³)</th>
<th>Iodine Value (% of I₂/100 gms of oil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn</td>
<td>34.9</td>
<td>0.9995</td>
<td>127-133</td>
</tr>
<tr>
<td>Cottonseed</td>
<td>33.5</td>
<td>0.9148</td>
<td>98-118</td>
</tr>
<tr>
<td>Linseed</td>
<td>27.7</td>
<td>0.9736</td>
<td>170-234</td>
</tr>
<tr>
<td>Peanut</td>
<td>39.6</td>
<td>0.9026</td>
<td>86-107</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>37.0</td>
<td>0.9133</td>
<td>97-108</td>
</tr>
<tr>
<td>Safflower</td>
<td>31.3</td>
<td>0.9144</td>
<td>141-147</td>
</tr>
<tr>
<td>Sesame</td>
<td>35.5</td>
<td>0.9133</td>
<td>104-129</td>
</tr>
<tr>
<td>Soybean</td>
<td>32.6</td>
<td>0.9138</td>
<td>126-141</td>
</tr>
<tr>
<td>Sunflower</td>
<td>33.9</td>
<td>0.9161</td>
<td>118-141</td>
</tr>
<tr>
<td>Palm</td>
<td>39.6</td>
<td>0.9189</td>
<td>50-55</td>
</tr>
</tbody>
</table>

2) EXTRACTION OF OIL FROM OILSEEDS

Oilseeds usually have the oil encased in minute “cells” that are deeply embedded in fibrous structures. Most oilseeds, therefore, require grinding or flaking to rupture the cells and heat treatment, sometimes cooking and drying, to help release the oil. Vegetable oilseed could either be processed by traditional crude method of crushing seed without delinting in undecorticated from or by scientific process which involves removal of linter, decortications, separation of hull, expelling, solvent extraction and refining of oil. The chief disadvantages of solvent extraction are the high initial cost of the equipment and the fact that some oil seeds disintegrate under the influence of the solvent and consequently are difficult to handle. However, extraction with solvents constitutes the most efficient method for the recovery of oil from any oil-bearing material. The minimum oil content to which oil cake can be reduced by mechanical expression is approximately the same for all oil seeds, ie. about 2-3%. Consequently, the oil unrecoverable by mechanical expression, in terms of percentage of the total oil, increases progressively as the oil content of the seed decreases Substitution of solvent extraction for pressing methods increases the yield of oil [12].

PROCESS OF EPOXIDATION

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[13]. 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 peroxo acid. 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
- Other Systems

I) CONVENTIONAL CHEMICAL TREATMENT

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.

In 2008, Dinda et al; worked on the epoxidation kinetics of cottonseed oil using a hydrogen peroxide catalysed by liquid inorganic acids i.e. HCl, H$_2$SO$_4$, HNO$_3$ and H$_3$PO$_4$. They used carboxylic acid i.e. CH$_2$COOH and HCOOH as oxygen carrier but they found that acetic acid is more effective oxygen carrier than formic acid. Out of all liquid inorganic acid studied as catalyst, H$_2$SO$_4$ was found to be most efficient and effective [14].

In the same year 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 $^\circ$C and atmospheric pressure for about 10 hours. The maximum reaction conversion was 83.3% for epoxidation of soybean oil as catalyst[17].

Similarly 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$_2$SO$_4$. In this work they found that soybean oil has greatest conversion rate and lowest activation energy for epoxidation using peroxyacetic acid [18]. and 87.4% for epoxidation of jatropha oil[15]. 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 stated that the economic value of mahua oil could be increased by converting oil to epoxidized mahua oil. They used H$_2$O$_2$ as oxygen donor and glacial acetic acid as oxygen carrier in the presence of catalytic inorganic acid i.e.H$_2$SO$_4$ 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 55 $^\circ$C to 65 $^\circ$C to reduce the hydrolysis reaction[16].

In 2010, 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$_2$SO$_4$ as acid catalyst leads to many side reactions such as oxirane ring opening to diols, hydroxyl esters, esteloids and other dimer formation[19]. The presence of this side reaction in commercial preparation of fatty epoxide diminishes their attractiveness as a starting material for further elaboration, as producers may require expensive purification[20].

II) ACID ION EXCHANGE RESIN (AIER) METHOD

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 H$_2$O$_2$ with carboxylic acid (HCOOH/CH$_3$COOH). The peroxy acid interacts with the catalyst by way of entering the pores of the catalyst. 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 into the gel type structure of AIER[21].

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. Petrovic et al. 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 prominent advantages 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[22]. 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 \(55^\circ C\) to \(65^\circ C\) 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 hydrogen peroxide to oil was the optimal concentration for the epoxidation reaction[23].

Mungroo et al. worked on the epoxidation of canola oil with \(H_2O_2\) as oxygen donor, 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 \(^1H\) NMR spectral analysis[24].

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 was characterized 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[25].

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\(^{-1}\)[26].

**III) ENZYMATIC METHOD**

To avoid side reactions and to make the process more environmentally friendly, enzyme catalyst are preferred. Immobilized Candida Antarctica lipase was used as the catalyst. The epoxidation reaction can be improved by adding the lipase step wisely. Enzymatic catalyst for epoxidation is a good alternative to chemical treatment. The main limitation however is the low stability of the lipase under the reaction conditions. The parameters affecting the lipase activity and operational lifetime during chemoenzymatic epoxidation of fatty acids were investigated [27].

It is found that in biocatalyzed reactions, enzymatic activity may also be lost due to elevated concentrations of hydrogen peroxide or to temperature effects. However, some recent papers have shown that Candida antarctica B lipase remained stable above 50 °C, although this was not favorable, mainly due to the decomposition of hydrogen peroxide. Furthermore, at higher temperatures, the enzyme acquires a more open conformation, possibly increasing the accessibility to sensitive amino acids in the inner regions of the enzyme, and thus decreasing its catalytic activity [28].

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 [29]. 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 lipase catalyst exhibited excellent stability and activity during the epoxidation process and can reuse many times[30].

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 donor and Stearic acid as active oxygen carrier in the presence of immobilized Candida antarctica 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].

Klass. M. Warwel, S 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. They find that the epoxidation using lipase biocatalyst was very selective and epoxidation conversion rate was exceeding 90%[32].

Vlcek and Petrovic worked on the Optimization of chemoenzymatic epoxidation of soybean oil. In this work they 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[33].
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\textsubscript{2}O\textsubscript{2} in the presence and absence of an acyl donor. The biphasic system (CH\textsubscript{3}Cl/H\textsubscript{2}O) comprised Candida antarctica B lipase (CALB, 1000 u g\textsuperscript{-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[34].

IV) METAL CATALYST METHOD
Researchers and scientist are always in search of some new methods and techniques to improve the existing technology. In the same line many workers and co-workers have given their contribution to increase the oxirane content and improve the efficiency of epoxidation reaction. Various metal catalysts such as titanium, molybdenum, tungsten. 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. Several drawbacks must be improved in the peracid process, including: (i) the selectivity to epoxidized products is relatively low due to acid catalyzed oxirane ring-opening; (ii) the separation of acidic byproducts, whose presence may be detrimental for further applications, is not easy; (iii) the handling of highly concentrated hydrogen peroxide and strong acids is dangerous and causes corrosion problems. Thus, in recent years several papers have dealt with the setting up of catalytic processes aimed at overcoming such disadvantages, using more sustainable compounds and technologies. 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\textsubscript{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 [35]. 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[36].

REACTION MECHANISM
In situ epoxidation of vegetable oil with carboxylic acid in the presence of suitable catalyst in which peracetic acid formation is an acid-catalyzed reaction.

\[
\text{RCOOH} + \text{H}_2\text{O}_2 \rightleftharpoons \text{RCOOOH} + \text{H}_2\text{O} \quad [1]
\]

Whereas the main reaction involving the epoxy group formation is an uncatalyzed reaction:

\[
\text{R}_{1}\text{CH} = \text{CH} - \text{R}_2 + \text{RCOOOH} \rightarrow \text{R}_{1}\text{CH} = \text{CH} - \text{R}_2 + \text{RCOOH} \quad [2]
\]

Precisely it can be represented as[37].

The followings are the possible side reactions of the epoxy ring cleavage that may take place are acid-catalyzed [38].

![Fig.2. Epoxidation Side Reactions](image)

KINETICS OF EPOXIDATION
There are two major reactions involved in the epoxidation reaction as mentioned above. During the first stage, peroxy acid is formed from the reaction of formic or acetic acid and hydrogen peroxide while in second stage epoxidized oil is produced from the reaction between peracid and double bond in the oil[39]. Considering hydrogen peroxide as oxygen donar and acetic acid as oxygen carrier, we can write following steps[40>:</p>

**Step I: Formation of Peroxyacetic acid**

\[\text{AA} + \text{H}_2\text{O}_2 \rightleftharpoons \text{PAA} \]

**Step II: Epoxidation Reaction**

\[\text{DB} + \text{PAA} \rightarrow \text{EO} + \text{AA} \]

Where,

- AA = Acetic Acid
- PAA = Peroacetic Acid
- DB = Double Bonds
- EO = Epoxidized Oil

\begin{align*}
K_1, K_2, K_3 = \text{Reaction Rate Constant} \\
\text{The reaction was found to be overall second order and a one step mechanism (Step 2) has been proposed[41]. Kinetic studies of epoxidation of soybean oil with peroxyacetic acid and peroxyformic acid have been reported and found to be pseudo-first order with respect to both double bonds as well as peroxy acid. If the first step is considered rate determining and the concentration of peroxy acetic acid is assumed constant throughout the reaction then following rate laws can be applied:}
\end{align*}

\[
\frac{d[DB]}{dt} = K_3 [DB]_1^n [PAA]_2^n
\]
With respect to double bonds, the rate equation for the pseudo-first order with respect to double bonds, the rate equation for the pseudo-first order can be expressed as:

\[ -\frac{d[DB]}{dt} = K_1[DB]_0 \]

\[ K = K_2[PAAC]_0 \]

Then the rate equation data for the epoxidation reaction using peroxyacetic acid is fitted with the equation above. If X is expressed as the conversion of double bonds in the oil, after integration the equation above and defines

\[ [DB] = [DB]_0(1-X) \]

the equation above can be simplified as

\[ -\frac{d[DB]}{dt} = K[DB] \]

\[ -\frac{d[DB]_0 (1-X)}{dt} = K_1[DB]_0(1-X) \]

\[ [DB]_0 \frac{dx}{dt} = K(1-X) \]

\[ \frac{dx}{1-X} = K dt \]

Integration at \( t=0 \rightarrow X=0 \) and \( t=t \rightarrow X=X \)

\[ \int_{0}^{1} \frac{dt}{1-X} = K \int_{0}^{t} dt \]

\[ \ln \frac{1}{1-X} = Kt \]

The rate constant (K) value for each temperature can be determined as slope of plot of \( \ln \frac{1}{1-X} \) Vs. reaction time (t).

**THERMODYNAMIC PROPERTIES OF THE EPOXIDIZED VEGETABLE OIL**

The enthalpy of activation can be calculated using following equation

\[ \Delta H = E_a - RT \]

Where, \( E_a \) = Activation Energy

\( T \) = Temperature

\( R \) = Universal Gas Constant

The entropy of activation (\( \Delta S \)) and free energy of activation (\( \Delta F \)) were calculated at the same temperature using following equation

\[ \Delta F = \Delta H - T \Delta S \]

Where, \( k = \) Rate Constant

\( N = \) Avogadro Constant

\( h = \) Planck’s constant

\( \Delta S = \) Entropy of activation, Cal/ (mol.K).

\( \Delta F = \) Free energy of activation, Cal/mole.

Goud et al. worked on epoxidation of mahua oil, they determined the thermodynamic parameters such as enthalpy, entropy, and free energy of activation and were found to be \( \Delta H = 13.8 \) kcal /mol, \( \Delta S = -51.1 \) cal/ (mol K) and \( \Delta F = 30.6 \) kcal/mol. Similarly Dinda et al. worked on epoxidation of cottonseed oil. While doing this, the thermodynamic parameters such as enthalpy, entropy, and free energy of activation were determined to be of 11.0 kcal /mol, -51.4 cal/(mol.K) and 28.1 kcal/mol, respectively. The thermodynamic properties show that, the present reaction is endothermic in nature because the enthalpy of activation is positive and hence an increase in the reaction temperature may lead to an increase in the conversion to oxirane oxygen. As the free energy of activation is positive, the reaction is non spontaneous under the present experimental conditions. With an increase of temperature, the nonspontaneity of the reaction should increase since \( \Delta F \) will be more positive and hence, at any particular time instant, the yield of oxirane will increase. However, the net conversion to oxirane will maximize if the in situ epoxidation occurs at optimum temperature, which depends on the type of catalyst used in such process.

**INDUSTRIAL MANUFACTURING PROCESSES**

There are many processes available for the manufacturing of epoxidized vegetable oil. The most widely used method of epoxidation of unsaturated vegetable oil is pre or in-situ epoxidation. Although the epoxidation of unsaturated oils using continuous epoxidation process is limited.

1) **IN-SITU EPOXIDATION**

*In-situ* epoxidation using hydrogen peroxide as oxygen donor and acetic or formic acid as the peroxygen carrier has achieved commercial importance. With hydrogen peroxide and acetic acid, however, acid catalysts, such as sulfuric acid or strong cation exchange resins, are needed to speed up peracid formation, whereas performic acid formation requires no strong acid. The reaction is always carried out under isothermal condition. The schematic flow diagram for the in-situ epoxidation can be given in following manner.

![Fig. 3 Schematic Flow Diagram of In-Situ Epoxidation.](image-url)
2) CONTINUOUS EPOXIDATION FLOW PROCESS

This process includes three or four stirred-tank epoxidation reactors with the same volume, a continuous feed and sampling outlet, and temperature and stirring controllers. Unsaturated oil, formic acid, and hydrogen peroxide were continuously introduced into the first reactor, then the reaction mixture was continuously fed to the next reactor, and finally the crude product from the last reactor was placed in a separator. The aqueous layer was drawn off, and the ester layer was washed in successive steps until acid-free. The final product was analyzed for the iodine and oxirane values according to standard methods [45]. As compared with a batch process, a continuous process has three advantages: (i) stable product quality; (ii) convenience, because of use of automatic control; and (iii) lower production costs. Also, the continuous process is useful for controlling by product formation and improving reaction selectivity and yield by changing material contacting time and reaction temperature.

Fig 2. Continuous Flow Stirred Tank Cascade

EPOXIDATION PROCESS

Epoxidized vegetable oil has unlimited and bright future prospects as it is found to be potential and renewable biobased material. Increasing the concern about environmental issues and limiting supply of petroleum and fossil fuel again adds the importance to epoxidized vegetable oil. Epoxidized vegetable oil possesses epoxy ring in their backbone chain and produces flexibility and elasticity when it is treated with thermoplastic or thermosetting polymer along with suitable curing agent. Because of this special kind of application EVO can easily replace the phthalates which are petroleum based. Looking forward this it is expected that EVO oil has a great future.

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 many parts 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.

CONCLUSION

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 peroxo 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.

REFERENCES


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