

Research Paper

STUDIES ON SYNTHESIS OF BIOBASED EPOXIDE USING COTTONSEED OIL

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ABSTRACT

Epoxidized vegetable oils are promising candidates as a substitute for petroleum oil based plasticizer, lubricants and stabilizers. Chemical modification of fatty acid chain of triglyceride appears to be one route towards this objective of substitution of petroleum product. In this study cottonseed oil having an iodine value of 96 g I₂/100g oil was epoxidized in situ using 30% aqueous hydrogen peroxide as oxygen donor and glacial acetic acid as oxygen carrier in presence of sulphuric acid as a catalyst. The effect of various parameters such as temperature, hydrogen peroxide to ethylenic unsaturation mole ratio, acetic acid to ethylenic unsaturation mole ratio and stirring speed on epoxidation rate were studied. The product structure characterization was accomplished by employing FTIR analysis.

KEY WORDS: Epoxidized vegetable oil, in situ, oxygen donor, oxygen carrier.

1. INTRODUCTION

Vegetable oils are a sustainable and renewable raw material resource. The unsaturation present in vegetable oils can be chemically modified to a value added product by a reaction called 'epoxidation'. Due to the high reactivity of the oxirane ring, epoxides serve as a raw material for synthesis of variety of chemicals such as alcohols (polyols), glycols, olefinic compounds, lubricants, plasticizer and stabilizer for polymers. The demand of lubricants, plasticizers and stabilizer for polymers is increasing day by day. Vegetable oil represents one of the cheapest and most abundant biological feedstock available in large quantities. 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. High molecular weight products can be obtained by increasing the cross linking. The increasing level of awareness regarding environment is driving the development of sustainable green materials. Petrochemical based resins such as epoxy, polyester and vinyl ester find a number of engineering applications due to 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 need to develop novel biobased product from renewable feedstock. Hence a number of researchers have studied vegetable oils as alternative feedstock to substitute petroleum^[2-5]

2. EXPERIMENTAL

A) MATERIALS

For synthesis of epoxidized cottonseed oil, refined cottonseed oil was procured from super market, glacial acetic acid (99-100 wt %), aqueous hydrogen peroxide (30 wt %), sulphuric acid (98 wt %) were obtained from Merck Specialities Pvt Ltd. For analytical purpose hydrogen bromide, sodium hydroxide, Wij's solution, sodium thiosulphate,

potassium iodide were obtained from reputed company and were AR grade.

B) METHODS

The epoxidation reaction is carried out in a 1 lit three neck flask equipped with mechanical glass stirrer. The whole assembly was immersed in a water bath. 200ml of cottonseed oil was taken in the reactor and with respect to this calculated amount of CH₃COOH and was added to the reactor and the mixture was stirred for about 30 minutes. Then the required amount of 30 % aqueous H₂O₂ was added drop wise in such a way that the addition was completed in half an hour and the reaction was continued further for the required time duration.



Fig.1 Reaction Set-up

Samples were taken out intermittently, considering the completion of H₂O₂ addition as zero time. The collected samples were filtered and then extracted with diethyl ether in a separating funnel, after that washed with cold and slightly hot water successively to remove free acid. The final product pH was checked to have a value 7.0 and then analyzed for iodine value, oxirane content.



Fig.2 Layer Separation



Fig.3 Final Product After Separation

C) ANALYTICAL METHODS

The % oxirane oxygen was determined by the method of AOCS Cd9-57(1997) under which the oxygen is titrated directly with hydrogen bromide solution in acetic acid. Iodine Value was determined according to Wij's method [6]. The conversion of double bonds to oxirane rings were observed under FTIR spectra. From the oxirane content, the percentage relative conversion to oxirane was determined using the following formula [7]:

$$\text{Relative conversion to oxirane (RCO)} = \frac{[\text{OOex} / \text{OOth}] \times 100}{100}$$

Where OOex (g/100gm sample) is the experimentally obtained oxirane oxygen and OOth is the theoretically obtained maximum oxirane oxygen. The theoretical oxirane oxygen can be determined by the following formula:

$$\text{OOth} = \left\{ \frac{(\text{IVo} / 2\text{Ai})}{[100 + (\text{IVo} / 2\text{Ai}) \times \text{Ao}]} \right\} \times \text{Ao} \times 100$$

Where Ai and Ao are the atomic weights of iodine and oxygen respectively and IVo is the initial iodine value of the oil sample.

D) EPOXIDATION PARAMETERS AND REAGENT COMPOSITION

- Stirring Speed: 300-1200 rpm
- Temperature: 50-60 °C
- H₂O₂ to double bond mole ratio: 1.5-2.5:1
- CH₃COOH to double bond mole ratio: 0.3-0.5:1
- H₂SO₄ (catalyst) expressed as percentage of total weight of H₂O₂ and CH₃COOH added together: 2-3%

3. RESULTS AND DISCUSSION

a. Fatty Acid Composition of Cottonseed Oil on weight basis [8]:

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 cottonseed 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 cottonseed oil is in terms of double bonds thus the C=C acts as a reaction site for chemical modification in vegetable oil. The table 1 gives the fatty acid composition of cottonseed oil. Following table 1 gives the fatty acid composition of cottonseed oil.

Table 1

Fatty Acids	Compositi on (wt %)	Molecular Weight
Myristic Acid (C ₁₄ H ₂₈ O ₂)	0.8	228.37
Palmitic Acid (C ₁₆ H ₃₂ O ₂)	23.9	256.42

Palmitoleic Acid (C ₁₆ H ₃₀ O ₂)	0.7	254.4
Stearic Acid (C ₁₈ H ₃₆ O ₂)	2.35	284.48
Oleic Acid (C ₁₈ H ₃₄ O ₂)	17.4	282.46
Linoleic (C ₁₈ H ₃₂ O ₂)	53.4	280.45
Linolenic (C ₁₈ H ₃₀ O ₂)	0.37	278.4
Arachidic (C ₂₀ H ₄₀ O ₂)	0.1	312.53

b. Relative conversion to oxirane at different stirring speeds:

Stirring RPM is an important parameter because this factor substantially affects the conversion to oxirane. Epoxidation was performed at different speeds varying from 300-1000 rpm to study the effect of agitation rate on mass transfer resistance.

Table 2

Particulars	STIRRING SPEEDS, RPM			
	350 RPM		850 RPM	
Time(Hrs)	4	6	4	6
Iodine Value (g I ₂ /100 g Oil)	33.92	18.20	21.4	16.3
Conversion (Based on Iodine Value)	64.48	80.94	77.70	82.93
Oxirane Value	3.16	2.96	3.68	3.42
% Epoxidized double bond (Based on Oxirane Value)	55.14	51.65	64.22	59.68

Conditions: Mole H₂O₂ per mole double bond=2.0, mole CH₃COOH per mole unsaturation= 0.5, H₂SO₄ loading= 2%, Temperature= 60 °C

c. Effect of temperature on iodine value and oxirane oxygen conversion.

The effect of reaction temperature on the yield of oxirane content was investigated in the following table 3.

Table 3

Particulars	TEMPERATURE °C			
	50 °C		60 °C	
Time(Hrs)	4	6	4	6
Iodine Value (g I ₂ /100 g Oil)	34.40	18.36	33.92	18.20
Conversion (Based on Iodine Value)	63.97	80.77	64.48	80.94
Oxirane Value	3.06	2.92	3.16	2.96
% Epoxidized double bond (Based on Oxirane Value)	53.40	50.95	55.15	51.65

Conditions: Mole H₂O₂ per mole double bond=2.0, mole CH₃COOH per mole unsaturation= 0.5, H₂SO₄ loading= 2%, RPM= 350

d. Effect of catalyst loading

The catalyst help to increase the rate of epoxidation reaction because of active moieties present in it. In our experimentation H₂SO₄ (98 wt %) was used as catalyst and the effect of catalyst loading presented in following table 4. It was find that the oxirane oxygen value obtained is more at 2% loading of H₂SO₄ than 3% loading.

Table 4

Particulars	SULPHURIC ACID LOADING %			
	2%		3%	
Time(Hrs)	4	6	4	6
Iodine Value (g I ₂ /100 g Oil)	33.92	18.20	34.2	18.5
Conversion (Based on Iodine Value)	64.48	80.94	64.18	80.62
Oxirane Value	3.16	2.96	3.13	2.91
% Epoxidized double bond (Based on Oxirane Value)	55.14	51.65	54.62	50.78

Conditions: Mole H₂O₂ per mole double bond=2.0, mole CH₃COOH per mole unsaturation= 0.5, Temperature= 60 °C., RPM=350.

e. Effect of acetic acid to ethylenic unsaturation molar ration on iodine value conversion: Acetic acid acts as the oxygen carrier and gets regenerated once epoxidation reaction takes place. Increasing acetic acid concentration was found to increase the iodine value conversion but up to certain limit. It was found that the oxirane oxygen value was more at 0.5:1 molar ratio of glacial acetic acid to double bonds present in cottonseed oil. The results obtained were given in table 5.

Table 5

Particulars	Acetic Acid to Double Bond Molar Ratio			
	0.3		0.5	
Time(Hrs)	4	6	4	6
Iodine Value (g I ₂ /100 g Oil)	32.98	17.84	33.92	18.20
Conversion (Based on Iodine Value)	65.46	81.31	64.48	80.94
Oxirane Value	3.08	2.85	3.16	2.96
% Epoxidized double bond (Based on Oxirane Value)	53.75	49.73	55.14	51.65

Conditions: Mole H₂O₂ per mole double bond=2.0, H₂SO₄ loading=2%, Temperature=60 °C., RPM=350.

f. Effect of hydrogen peroxide to double bond molar ration on iodine value conversion

Hydrogen peroxide is used as oxygen donor for epoxidation reaction. It was found that the oxirane oxygen value obtained is more at 2:1 molar ratio of hydrogen peroxide to double bond present in the oil. The results obtained for the epoxidation reaction were given in table 6

Table 6

Particulars	Hydrogen Peroxide to Double Bond Molar Ratio			
	1.5		2.0	
Time(Hrs)	4	6	4	6
Iodine Value(g I ₂ /100 g Oil)	33.52	18.10	33.92	18.20
Conversion (Based on Iodine Value)	64.90	81.04	64.48	80.94
Oxirane Value	3.04	2.93	3.16	2.96
% Epoxidized double bond (Based on Oxirane Value)	53.05	51.13	55.14	51.65

Conditions: Mole CH₃COOH per mole of double bond=0.5, H₂SO₄ loading=2%, Temperature=60 °C., RPM=350.

4. CHARACTERIZATION OF COTTONSEED OIL & EPOXIDIZED COTTONSEED OIL:

a. Physical Properties

The experimental physical properties of cottonseed oil and epoxidized cottonseed oil obtained were given in table 7.

Table 7

Characteristics	Experimentally Obtained (Cottonseed Oil)	Experimentally Obtained (Epoxidized Cottonseed Oil)
Specific Gravity at 30 °C	0.917	0.973
Iodine value (g I ₂ /100 g Oil)	96	21.40
Acid Value(mg KOH/g Oil)	0.55	-
Oxirane value	-	3.68

b. Fourier transforms infrared (FTIR) spectroscopy analysis

The FTIR spectra of cottonseed oil and epoxidized cottonseed oil are shown in following figure. From the figure it is clear that the peak related to carbon-

carbon double bonds from cottonseed oil at 3010 cm⁻¹ disappeared on epoxidation and the epoxy groups were found in epoxidized cottonseed oil (doublet at 823 cm⁻¹ and 843 cm⁻¹) indicating that all of the carbon-carbon double bonds were turn into epoxy groups. Vleck and Petrovic^[9] reported the presence of epoxy groups at 822–833 cm⁻¹, which agrees well with this study. Following Fig.2 and Fig.3 shows the FTIR spectra of cottonseed oil & epoxidized cottonseed oil respectively.

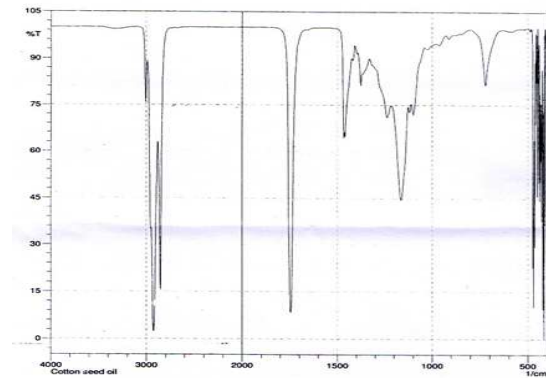


Fig.2 FTIR spectra of cottonseed oil

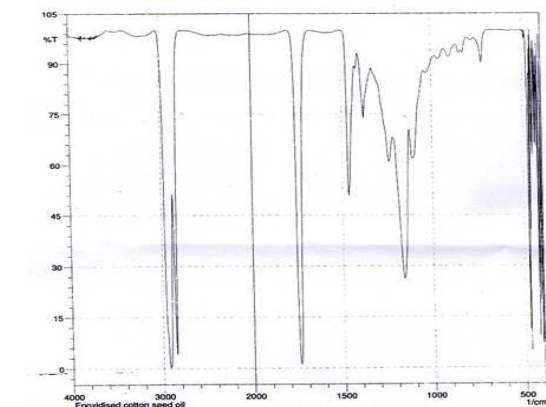


Fig.3 FTIR spectra of epoxidized cottonseed oil

5. REACTION MECHANISM

The cis-olefin gives rise to a cis epoxide. Therefore, a cis olefin gives rise to a cis epoxide and a trans olefin to a trans epoxide. This can be proceeds by the following mechanism (fig.4) giving cis-stereo specific addition^[10]

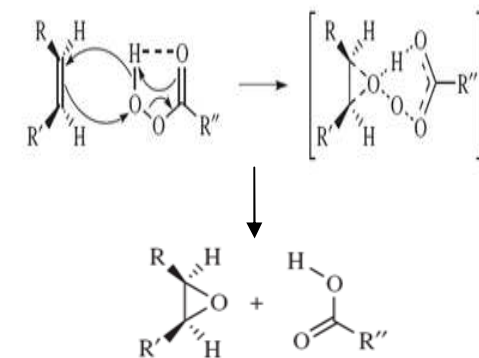
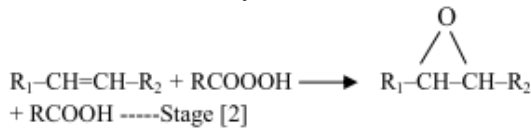


Fig.4 Epoxidation mechanism proposed by Bartlett.

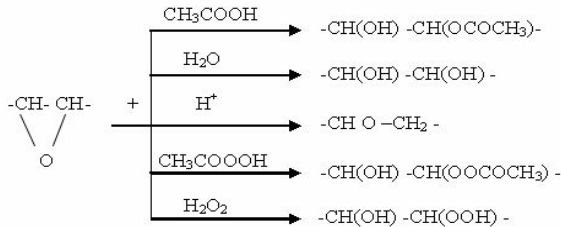
In situ epoxidation of vegetable oil with carboxylic acid in the presence of suitable catalyst in which peracetic acid formation is an acid-catalyzed reaction^[4,11].



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



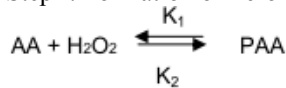
The followings are the possible side reactions of the epoxy ring cleavage that may take place are acid-catalyzed [12]. (Fig.5)



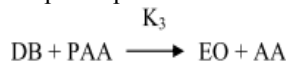
6. EPOXIDATION REACTION KINETICS:

During the first stage, peroxyacetic acid is formed from the reaction of acetic acid and hydrogen peroxide while in second stage epoxidized oil is produced from the reaction between peracetic acid and double bond in the oil. Precisely it can be represented as [13]:

Step I: Formation of Peroxyacetic acid



Step II: Epoxidation Reaction



Where, AA represents Acetic Acid, PAA represents Peroxyacetic Acid, DB represents Double Bonds, EO represents Epoxidized Oil and K_1, K_2, K_3 are reaction rate constants.

The 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. [Ref] 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:

$$r = \frac{-d[\text{DB}]}{dt} = k_3 [\text{DB}]^{n_1} [\text{PAA}]^{n_2}$$

Where, r is the rate of disappearance of carbon-carbon double bonds, $[\text{DB}]$ is the molar concentration of double bond; $[\text{PAA}]$ is the molar concentration of peroxyacetic acid, k_3 is the reaction rate constant, n_1 is the reaction order with respect to double bonds concentration and n_2 is the reaction order with respect to peroxyacetic acid concentration. If it is assumed that the reaction is pseudo first order with respect to double bonds, the rate equation for the pseudo first order can be expressed as:

$$\frac{-d[\text{DB}]}{dt} = k [\text{DB}]^{n_1}$$

$$k = k_3 [\text{PAA}]^{n_2}$$

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

$$[\text{DB}] = [\text{DB}]_0 (1-X)$$

The equation above can be simplified as

$$\frac{-d[\text{DB}]}{dt} = k [\text{DB}]$$

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

$$[\text{DB}]_0 \frac{dX}{dt} = k [\text{DB}]_0 (1-X)$$

$$\frac{dX}{dt} = k(1-X)$$

$$\frac{dX}{(1-X)} = k dt$$

Integration at $t=0 \rightarrow X=0$ and $t=t \rightarrow X=X$

$$\int_0^t \frac{dX}{(1-X)} = k \int_0^t dt$$

$$\ln \frac{1}{1-X} = k.t$$

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).

a. Determination of k at 50 °C

Following table 8 gives the conversion obtained based on iodine value.

Table 8 Determination of reaction kinetics at 50°C

t(hr)	X	1/(1-X)	ln [1/(1-X)]
0	0	0	0
1	0.1258	1.1439	0.1344
2	0.2894	1.4072	0.3416
3	0.4688	1.8825	0.6326
4	0.6397	2.7754	1.0207
5	0.7190	3.5587	1.2693
6	0.7812	4.570	1.5195

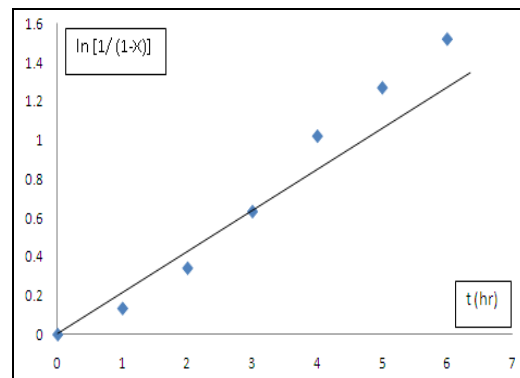


Fig.6 gives plot of t (h) vs. $\ln [1/(1-X)]$ at 50 °C

From the above plot, Slope = 0.1947

$$\therefore k = 0.1947 \text{ hr}^{-1}$$

b. Determination of k at 60 °C

Following table 9 gives the conversion obtained based on iodine value.

Table 9 Determination of reaction kinetics at 60°C

t(hr)	X	1/(1-X)	ln [1/(1-X)]
0	0	0	0
1	0.1397	1.1629	0.1509
2	0.3091	1.4473	0.3696
3	0.4861	1.9459	0.6657
4	0.6448	2.8153	1.035
5	0.7012	3.3467	1.2079
6	0.8094	5.2465	1.6575

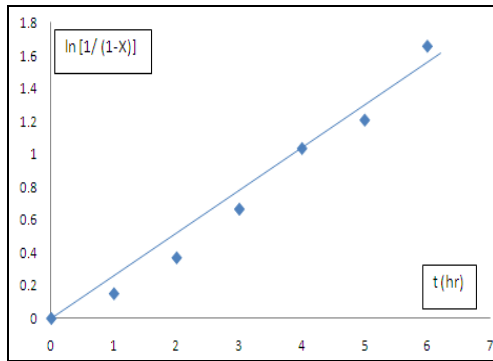


Fig.7 gives plot of reaction time vs $\ln [1/ (1-X)]$ at 60°C

From the above plot, slope= 0.2668

$$\therefore k = 0.2668 \text{ hr}^{-1}$$

7. DETERMINATION OF ACTIVATION ENERGY:

The activation energy for epoxidation reaction is determined from the rate constants at different temperature using Arrhenius equation^[14].

$$k = k_0 e^{-E/RT}$$

$$k = k_0 e^{-E/RT}$$

$$\ln k = \ln k_0 - E/RT$$

Therefore the activation energy can be calculated from the plot of $\ln K$ vs $1/T$.

T(k)	1/T	K(hr ⁻¹)	lnK
323	0.003095	0.17	-1.770
333	0.003003	0.2326	-1.458

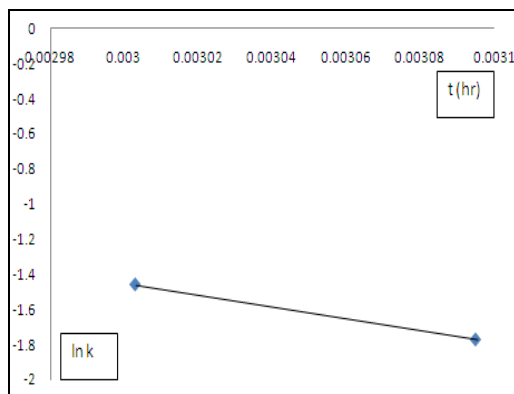


Fig.8 gives the plot of $\ln k$ vs $1/T$

From the plot of $\ln k$ vs $(1/T)$,
slope = $-(E/R) = -3391.3043$

$$\therefore E = 3391.3043 \times 8.314$$

$$= 28195.3039 \text{ J/mol.K}$$

$$= 28.1953 \text{ kJ/mol.K}$$

8. THERMODYNAMIC PROPERTIES OF THE EPOXIDIZED COTTONSEED OIL

The enthalpy of activation can be calculated using following equation^[15]

$$\Delta H = E_a - RT$$

Where,

E_a = Activation Energy J/mol, T= Temperature K, R= Universal Gas Constant J/mol

The entropy of activation (ΔS) and free energy of activation (ΔG) were calculated^[15]

$$k = (RT/Nh)e^{\Delta S/R} e^{-\Delta H/RT}$$

$$\Delta G = \Delta H - T \Delta S$$

Where,

k = Rate Constant, N = Avogadro Constant, h = Plank's constant, ΔS = Entropy of activation, J/ (mol.K), ΔG = Free energy of activation, J/mole.

Table 5

Temperature, k	ΔH , J/ (mol.k)	ΔS , J/(mol.k)	ΔG , J/mole
323	25509.8819	-180.20	83714.16
333	25426.7419	-180.45	85517.00

a. Significance of thermodynamic properties for epoxidation reaction

The present reaction was found to be endothermic in nature as the value of as the value of enthalpy of activation was positive. The positive value of free energy of activation indicates that the present reaction is non-spontaneous and the non-spontaneity of the reaction should increase since ΔG will be more positive and hence, at any particular time instant, the yield of oxirane will increase.

Process flow diagram

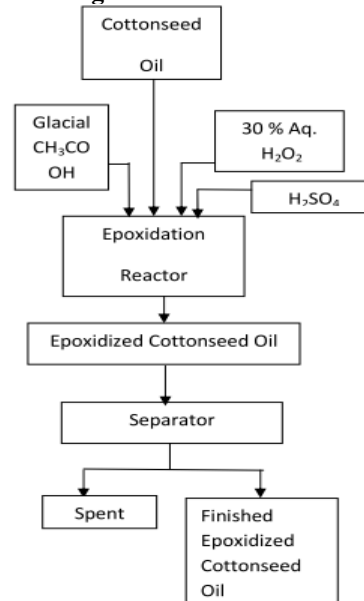


Fig.3 Process flow diagram for epoxidation of cottonseed oil

RECOMMENDATIONS FOR FUTURE RESEARCH

- To attain higher oxirane oxygen value in epoxidation step acid ion exchange resin or metal catalyst can be used.
- To determine other factors influencing epoxidation reaction such as stirring speed, catalyst concentration, mole ratio of hydrogen peroxide to oil and mole ratio of glacial acetic acid to oil and reaction temperature.
- To evaluate economic analysis to know the cost of optimized process for epoxidized cottonseed oil.

CONCLUSIONS

The epoxidized cottonseed oil is yet to be commercialized. The study on optimization of synthesis of epoxidized cottonseed oil has to be conducted before it can be commercialized. The results obtained from FTIR analysis show that the cottonseed oil can be successfully epoxidized by employing peracetic acid generated in *in-situ*. The optimum conditions obtained from the present study include temperature of 60°C , hydrogen peroxide to ethylenic unsaturation ratio of 2:1, acetic acid to ethylenic unsaturation ratio of 0.5:1 and the sulphuric acid loading was 2% by weight of the total weight of

hydrogen peroxide and acetic acid at stirring speed of 850 rpm.

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