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Epoxidation of Wild Safflower (*Carthamus oxyacantha)* Oil with Peroxy acid in presence of strongly Acidic Cation Exchange Resin IR-122 as Catalyst

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Abstract: Epoxidation brings out the transformations at the unsaturated part of oil molecule to introduce reactive oxirane ring. These plant oil-based epoxides are sustainable, renewable and biodegradable that can replace petroleum-derived materials in numerous industrial applications, such as plasticizer, lubricant and in coatings formulations. In present work wild safflower oil (WSO) with an iodine value of 155(g I_2/100g), and containing 13% oleic acid ($C_{18:1}$) and 72% linoleic acid ($C_{18:2}$), was epoxidised using a peroxy acid generated *in situ* by the reaction of aqueous hydrogen peroxide and carboxylic acid in presence of strongly acidic cation exchange resin, Amberlite® IR-122. Acetic acid was found to be a better oxygen carrier than formic acid and the use of catalyst improved the epoxide yield. The influence of various reaction parameters such as temperature, stirring intensity, catalyst loading, and molar reactant ratio exerted on the epoxidation reaction was examined to optimize the condition for achieving maximum epoxy group formation. The formation of the epoxide adduct was confirmed by FTIR spectral analysis.

The rate of epoxidation was not substantially affected with stirring speed beyond 2000 rpm under the given conditions. A high temperature of above 60°C is detrimental since at continued reaction it accelerated the rapid destruction of oxirane rings. Higher concentrations of acetic acid and hydrogen peroxide (above 0.5 & 1.5 mol/mol of ethylenic unsaturation respectively) are also unfavorable as they lead to epoxy ring opening. The study shows that a relative conversion to epoxide ring moiety of 85% can be achieved by using the optimum molar ratio 1:0.5:1.5 (ethylenic unsaturation: acetic acid: hydrogen peroxide) at temperature 60°C and 2000rpm.

Key words: Epoxidation, wild safflower oil, acidic cation exchange resin, reaction parameters.

INTRODUCTION

Vegetable oils and fats, the important renewable resources, are biodegradable, low in cost and readily available. A number of methods such as chemical and enzymatic modification of oils have been suggested for improving their properties. The modified oils serve as feedstock that can replace petroleum-derived materials in many applications [1]. Thus, there is an immediate need of attention towards effective utilization of these biobased products taking into the consideration of current environmental harm and steadily rising price of petroleum. Moreover, this trend will reduce the dependence on imported petroleum and will promote the sustainable agricultural initiative.

The unsaturation present in fatty acid molecule of the vegetable oil can be used to introduce various functional groups by carrying out chemical reactions. Among them, epoxidization is one of the most widely used reaction. Epoxidation introduces the high strain energy three-membered oxirane ring into the unsaturated part of the oil molecule, thereby increasing its complexity and chemical reactivity with a variety of compounds such as amines and carboxylic acids [2, 3] and serves as a chemical intermediate for the preparation of derivatives that would be difficult to obtain directly from the unsaturated bonds of fatty acids [4]. This leads to a wide spectrum of commercial uses for epoxides. There are several methods for producing epoxides from vegetable oils, fatty acids and methyl esters. These includes epoxidation with percoarboxylic acid generated *in situ* in the presence of acids or enzymes as catalysts [5,6] , epoxidation with organic and inorganic oxidants such as potassium peroxomonosulphate, meta-chloroperoxybenzoic acid and ethyl methydioxirane [7,8,9,10], epoxidation with halohydrins for the epoxidation of olefins with electron-deficient double bonds and epoxidation with molecular oxygen[6] . From process, environmental safety and efficiency point of view epoxidation of vegetable oils in one step, i.e., with peroxy acid generated *in situ* from carboxylic acid (formic/acetic acid) with hydrogen peroxide in the presence of acid catalyst is widely used on an industrial scale. However, the use mineral acid as catalyst in epoxidation is inefficient because of problems associated with separation of the catalyst from the reaction product. The process can be made competitive with the use of ion-exchange catalyst instead of traditional homogeneous one in epoxidation of unsaturated compounds [11]. Epoxidized vegetable oils are widely used in polymer chemistry because of their excellent plasticizing action for poly (vinyl chloride) and as effective component for stabilizing polymer formulations [12,13]. Epoxides find industrial application as diluents [14], lubricants [15] and coatings [16].

Industrially epoxides have been prepared from castor, linseed, rapeseed, soybean and sunflower oils containing high to moderate unsaturation. The progress on the utilization of other seed oils of semidrying nature like flax, canola, karanja, jatropha, rubber seed, cottonseed, olive, corn etc. for epoxide synthesis at laboratory level is very encouraging towards development of an efficient and safe epoxidation process. Safflower is an important oil seed crop of the tropical countries, which belongs to the family Compositae or Asteraceae and genus *Carthamus*. *C. tinctorius* is the only cultivated species of this genus which is used primarily for edible oil and the other sister species are wild and weed. Taking into account of higher proportion of unsaturation in fatty acid composition of the safflower oil, it is characterized as semidrying and finds its use in paints, textile and leather industries [17, 18]. India is the largest producer of safflower in the world with an area of 3.63 $\times 10^6$ hectares, production of 2.29 $\times 10^6$ tonnes and productivity of 631 kg/ha [19]. However, being almost completely utilized as edible oil in India, there is an increased attention of researchers to search the low cost renewable resource as alternate to the cultivated safflower oil. Among the wild & weed species, *C. oxyacantha* and *C. palaestinus* were reported to be progenitor of *C. tinctorius,* being closely related to cultivated species with similarity coefficient more than 0.95 [20] . The wild species *C. oxyacantha* is widespread in Turkey, subtropical regions of western Iraq, Iran, North-west India, throughout kazakistan, Turkmenistan and Uzbekistan [21]. In India wild safflower grows in the arid regions of North India particularly in Punjab and Uttar Pradesh. It is winter growing anuual plant with distribution in the wheat fields near Bhognipur, Bhigapur, Pokhrayan, Ghatampur and adjoining areas of Kanpur district. The fatty acid composition of raw and refined oil extracted from the seeds of *C. oxyacantha* is reported by *Banerji et.al.* [22]. The exploitation of wild safflower seed oil (WSO) in preparation of epoxides is still the area not discussed. This paper investigates the wild safflower seed oil epoxide (EWSO) synthesis methodology with the use of strongly acidic cation exchange resin (Amberlite® IR-122) as catalyst. Both formic acid and acetic acid were used as carboxylic acids and a screening of four acid–catalyst combinations were done to find out the most efficient one. The influence of various reaction parameters such as temperature, stirring speed, catalyst loading, acetic acid-to-ethylenic unsaturation molar ratio, hydrogen peroxide-to-ethylenic unsaturation molar ratio on epoxidation reaction is focused with intention to optimize the condition for maximum epoxy yield with highest conversion of double bonds to oxirane rings.

MATERIALS AND METHODS

Materials

About 20 Kg seeds of *C. oxyacantha* were collected from the adjoining regions of Punjab district and extracted in lab-scale immersion-percolation type batch extractor (**Fig.1**) with Rankosolv SG (distillation range 63.0-70.0°C; water content, as determined by KF method, 0.1%) solvent obtained from Rankem RFCL, New Delhi. The five number of extraction stages (20 min for each stage) were evaluated, below the boiling point of solvent with miscella recycle flow rate of 9mL/sec, for oil yield . The seeds yielded 26% of pale yellow oil, which after due analytical study was used for epoxidation as such without any refinement. The chemicals glacial acetic acid, 98% and formic acid, 90% were obtained from Qualigens India Ltd., Mumbai. AR grade hydrogen peroxide (30 wt.%), Iodine monochloride and Wij's solution were procured from S.D. Fine Chemicals Ltd., Mumbai.

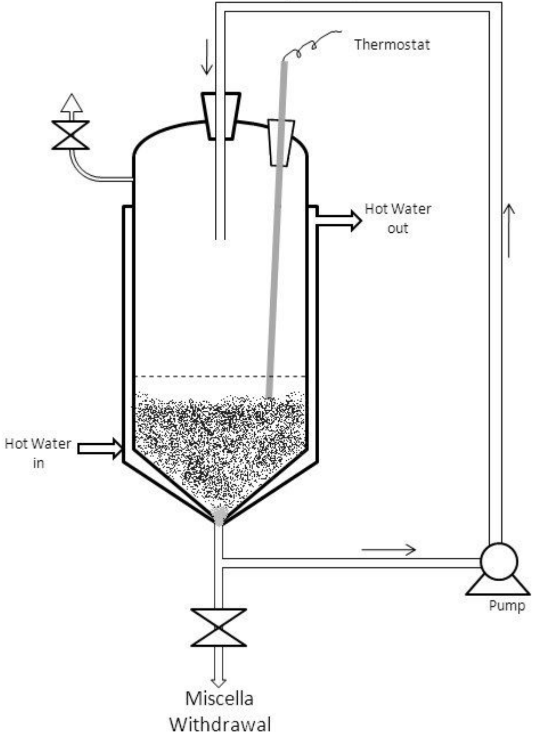


Figure 1: Lab-scale immersion-percolation type batch extractor

HBr in acetic acid (33 wt.%) was obtained from Fischer Scientific, Mumbai and then diluted with glacial acetic acid to make 0.1N HBr. Strongly acidic cation exchange resin (Amberlite® IR-122, sulfonic acid functionality) with total cation exchange capacity of 2.1meq/mL was procured from Sigma–Aldrich (USA).

Epoxidation experiments

The epoxidation of WSO was carried out in batch mode in a glass reactor consisting of a four-necked round bottom flask of 500ml capacity. A motor driven speed regulator stirrer was inserted in the reactor through the central neck while other neck was used for thermo-electrode. A condenser was fitted to the reactor through third neck and the fourth neck is used for dropping the raw materials into the reactor. The reactor was heated by an electric heating mantle having special arrangement for smooth and accurate control of the temperature within ±1°C of the desired temperatures.

The epoxidation method reported by *Dalai et.al.* [23] was used, and the same procedure was employed for all of the experimental runs dealing with different parameters. The epoxidation reactions were first carried out with both formic acid and acetic acid as carboxylic acids and with & without catalyst (IR-122) combinations. These initial epoxidation experiments were conducted to select the most active carboxylic acid-catalyst combination. Further epoxidation runs were carried out with the best reagent–catalyst combination using the following range of parameters: stirring speeds, 1000-2500 rpm; temperature, 40-80°C; hydrogen peroxide-to-ethylenic unsaturation molar ratio, 0.5-2.0 and acetic acid-to-ethylenic unsaturation molar ratio, 0.3-1.0; catalyst loading (expressed as the weight percentage of WSO used), 5-20%.

A calculated amount of WSO (35 g) was introduced in the reactor and heated with agitation to a temperature of 40°C for 15 min. The requisite amount of acetic/formic acid (carboxylic acid to ethylenic unsaturation molar ratio, 0.5:1) and catalyst (20 wt.%) were added, and the mixture was continuously stirred at 2000 rpm for 30 min. Then, 33.76 g of 30% aqueous hydrogen peroxide (1.5 mole of hydrogen peroxide per mole of ethylenic unsaturation) was added dropwise to the reaction mixture at a rate such that the hydrogen peroxide addition was completed over a period of 30 min with gradual increase in temperature to 60°C. After complete addition of hydrogen peroxide, the reaction was continued for 8 hours, considering the completion of addition of hydrogen peroxide to be the zero time, at controlled temperature 60±1°C with continuous stirring to ensure fine dispersion of oil. The course of the reaction was followed by withdrawing samples at regular intervals, the first being taken after one hour since zero time. The collected samples were washed with warm water successively to make them acid free and extracted with diethyl ether in a separating funnel to enhance the separation of the oil product from water phase and dried using a rotary evaporator. The progress of epoxidation was monitored by determination of oxirane content and iodine value of the washed aliquots of the reaction mixture. Two replication of each experiment were performed alongside to determine the percentage deviation between two experimental results and the deviation was found to be less than 5%.

Analytical methods

Acid value, Saponification value, Iodine value and Specific gravity of the raw WSO were determined according to AOCS Method Cd 3d-63, AOCS Method Cd 3-25, AOCS Method Cd 1b-87 and MS 817:1989 respectively. The percentage of oxirane oxygen content was determined using AOCS Official Method Cd 9-57 (1997) under which the oxygen is titrated directly with hydrogen bromide solution in acetic acid. The conversion of double bonds to oxirane rings were observed under FTIR spectra, measured on Shimazdu FTIR-8400spectrometer equipped with DLATGS detector and a KBr beam splitter into the range of 4000 to 400 cm^{-1}. The absorbance spectra for each analysis were averaged over 32 scans with a nominal 4 cm^{-1} resolution.
From the oxirane content, the percentage relative conversion to oxirane was determined using the following formula [3]:

Relative conversion to oxirane (RCO)
$$= [OO_{ex} / OO_{th}] \times 100 \quad \text{----------------------------(1)}$$

where OO_{ex} is the experimentally determined content of oxirane oxygen and OO_{th} is the theoretical maximum oxirane oxygen content in 100 g of oil, which was calculated to be 8.90% using the following expression [24] :

$$OO_{th} = \{(IV_o / 2A_i) / [100 + (IV_o / 2A_i) \times A_o]\} \times A_o \times 100 \quad \text{----------------------------(2)}$$

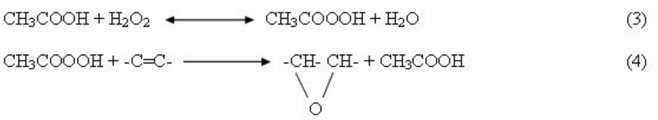
where A_i (126.9) and A_o (16.0) are the atomic weights of iodine and oxygen respectively and IV_o is the initial iodine value of the oil sample.

RESULTS AND DISCUSSION

The properties of WSO, with fatty acid composition, were analyzed as follows: specific gravity = 0.922 (at 25°C); acid value (mg KOH/g) = 2.2; iodine value (g I_2/100 g) = 155; saponification value (mg KOH/g) = 194; oleic acid, $C_{18:1}$ = 13%; linoleic acid, $C_{18:2}$ = 73%.

Effect of carboxylic acid

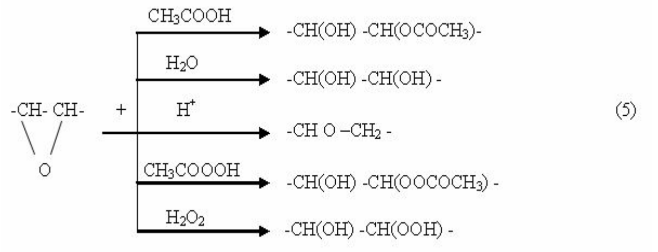
In situ epoxidation reactions were carried out with both formic acid and acetic acid as carboxylic acids; with and without catalyst reagent with 1:0.5:1.5 molar ratio of ethylenic unsaturation: carboxylic acid: hydrogen peroxide at a temperature 60°C. The variations of iodine values with reaction time for epoxidation of WSO with acidic ion exchange resin IR-122 as catalyst is shown in **Fig.2.** The mechanism of double bond conversion to epoxy ring in epoxidation reaction as proposed by *Gan et.al.* [25] is as follows:



$$CH_3COOH + H_2O_2 \longleftrightarrow CH_3COOOH + H_2O \quad (3)$$

$$CH_3COOOH + \text{-C=C-} \longrightarrow \underset{O}{\text{-CH- CH-}} + CH_3COOH \quad (4)$$

The excess reagents can react with the epoxy rings to cause unwanted side reactions as depicted below [1]:



From Fig.2 it can be shown that the relative conversion of ethylenic unsaturation is faster in presence of acetic acid than formic acid and addition of catalyst improves the rate of reduction of iodine value (IV). With formic acid/IR-122 combination, a slightly elevated reduction in IV is achieved as compared with the use of acetic acid with no resin. **Fig.3** shows the relative percentage conversion to oxirane as function of time, from which it is inferred that formic acid/IR-122 combination is less effective than acetic acid and acetic acid/IR-122 combination towards ethylenic unsaturation conversion to oxirane. The 65.4% conversion to oxirane was obtained for formic acid/IR-122 after 8 hours while with acetic acid the conversion was 72%. Acetic acid/IR-122 combination resulted into 85% conversion to oxirane with corresponding iodine conversion of 87.2% was considered a better combination for epoxidation of WSO with aqueous hydrogen peroxide. Further experiments were, therefore, carried out with acetic acid/ IR-122 to study the effect of various parameters on conversions to oxirane oxygen and the conversion of iodine value.

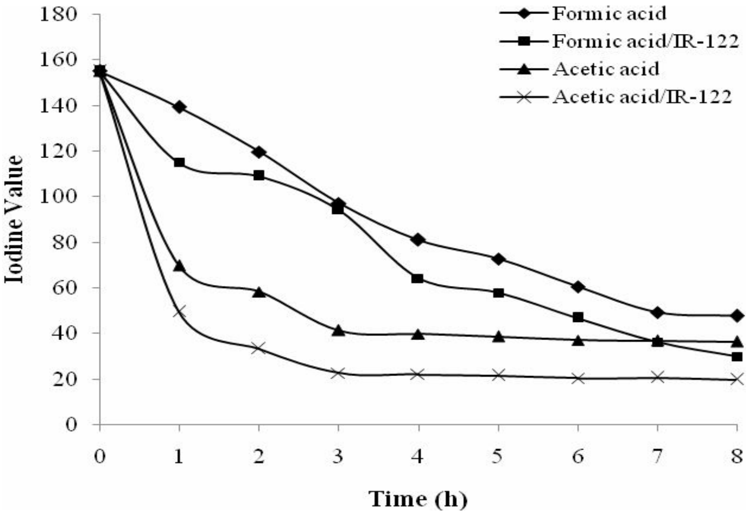


Figure 2: Variation of iodine value with time during epoxidation of WSO with acidic ion exchange resin IR-122 as catalyst.

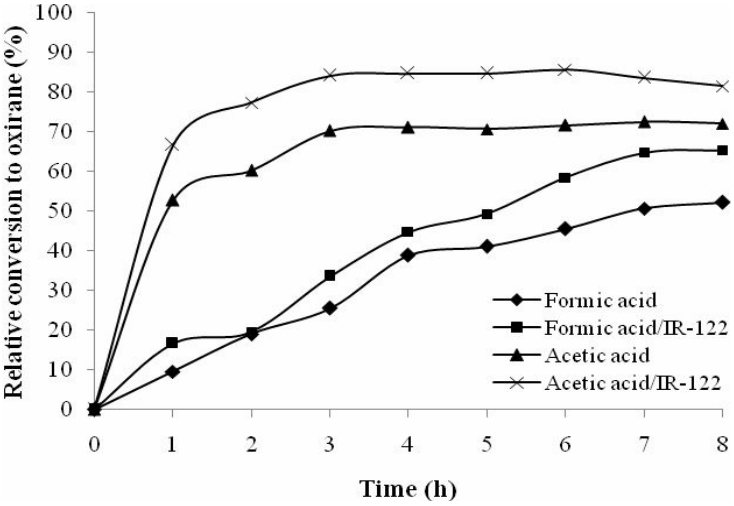


Figure 3: Activities of carboxylic acids in the epoxidation of WSO with acidic ion exchange resin IR-122 as catalyst. *Conditions:* Temperature, 60°C; carboxylic acid-to-ethylenic unsaturation molar ratio, 0.5:1; hydrogen peroxide-to-ethylenic unsaturation molar ratio, 1.5:1; catalyst loading, 20 wt.% of oil; stirring speed, 2000 rpm

Effect of stirring speeds

Agitation rate is an important parameter because this factor substantially affects the conversion to oxirane. Epoxidation was performed at different speeds varying from 1000-2500 rpm to study the effect of agitation rate on mass transfer resistance. In reaction, 35 g of WSO was treated with 13.76 g of hydrogen peroxide, 5.95g of acetic acid and 7g resin, as catalyst at 60°C. The % IV reductions and relative percentage conversions to oxirane at different speeds are shown inTable-1 and Fig.4 respectively. The oxirane formation rate improved with agitation rate upto 2000 rpm but beyond that no significant control was observed under the given conditions. Thus, all experiments were performed at 2000 rpm assuming that the reaction is free from mass transfer resistance beyond 2000 rpm.

Table 1: Relative conversion to oxirane at different stirring speeds

	Stirring Speeds, rpm							
	1000		1500		2000		2500	
Time (h)	4	8	4	8	4	8	4	8
Oxirane oxygen[a] (%)	6.42	6.87	7.00	7.23	7.53	7.70	7.62	7.40
Iodine value[b,c] (g I_2/100g)	41.2	32.9	21.2	19.0	22.6	19.8	24.5	20.6
% Iodine value conversion[d] (A)	73.4	78.8	86.3	87.7	85.4	87.2	84.2	86.7

[a] Experimentally determined oxirane oxygen content; [b] IV_0,Initial iodine value=155;

[c] IV Experimentally determined iodine value;

[d] Conversion of ethylenic unsaturated bonds as related to IV_0 calculated as $A=\{(IV_0-IV)\times 100/IV_0\}$

Table 2: Effect of temperature on iodine value conversion

	Temperature (°C)							
	40		50		65		80	
Time (h)	4	8	4	8	4	8	4	8
Oxirane oxygen[a] (%)	3.42	5.01	5.63	6.06	7.76	6.44	8.22	6.29
Iodine Value[b,c] (g I_2/100g)	93.6	66.0	55.4	48.0	18.9	16.9	15.2	12.2
% Iodine conversion[d] (A)	39.6	57.5	64.3	69.1	87.8	89.1	90.19	92.13

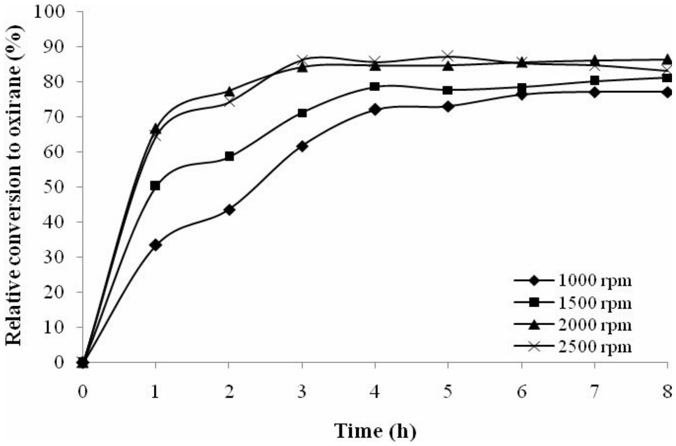


Figure 4: Effect of stirring speeds on the relative conversion to oxirane. *Conditions:* Temperature, 60°C; acetic acid to ethylenic unsaturation molar ratio, 0.5:1; hydrogen peroxide to ethylenic unsaturation molar ratio, 1.5:1; catalyst loading, 20 wt.% of oil

Effect of temperature

The effect of reaction temperature on the yield of oxirane content was investigated (Table-2). Reactions at the molar ratio of 1:0.5:1.5 (ethylenic unsaturation: acetic acid: H_2O_2) were performed at five different temperatures, namely 40, 50, 60, 65 and 80°C. Being exothermic in nature the epoxidation reaction may cause an excessive temperature rise and pose serious reaction control related issues like potential explosion hazards. In order to have better control over the reaction, the H_2O_2 was added to the mixture when the temperature was about 10°C below the desired reaction temperature. The temperature increased thereafter to actual reaction temperature, and was maintained there until the completion of reaction. From Fig.5, it is evident that increase in the temperature favored epoxidation reaction and a maximum of 92.3% conversion of iodine value was obtained at 80°C after a reaction time of 4 hours. The relative conversion to oxirane was found to increase with increase in temperature but the epoxy functionality was retained more at lower reaction temperature. The oxirane content of the EWSO, synthesized at 60°C reached a maximum of 85.6 % after 6 hours of reaction and oxirane cleavage was very mild when the reaction continued further. At 65°C, although the epoxidation rate not improved much, but a sharp epoxy ring breaking was observed after 4 hours of continuation of reaction. A similar trend appeared at higher reaction temperature and longer reaction durations. Therefore, a temperature of 60°C was considered optimal for the epoxidation reaction under investigation.

Table 3: Effect of catalyst loading on iodine value conversion

	AIER, IR122 loading (%)							
	5%		10%		15%		20%	
Time (h)	1	4	1	4	1	4	1	4
Oxirane oxygen[a] (%)	4.17	5.74	4.46	6.51	5.17	6.75	5.93	7.53
Iodine Value [b,c] (g I_2/100g)	76.8	51.2	72.1	40.8	62.3	32.5	49.5	22.6
% Iodine value conversion [d] (A)	50.4	66.9	53.4	73.6	59.8	78.9	68.1	85.4

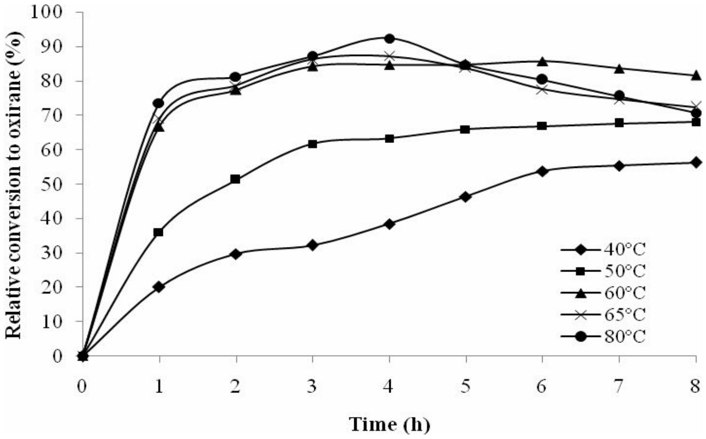


Figure 5: Effect of temperature on the relative conversion to oxirane. ***Conditions:*** **acetic acid to ethylenic unsaturation molar ratio, 0.5:1; hydrogen peroxide to ethylenic unsaturation molar ratio, 1.5:1; catalyst loading, 20 wt.% of oil; stirring speed, 2000 rpm**

Effect of catalyst loading

In general, increasing the solid catalyst loading leads to increase in both the total active matter and the total surface area of the catalyst. The active moieties present in catalyst increases the rate of epoxidation with increase in the catalyst concentration in the reaction system. In our experimentation, IR-122 resin (16-50 wet mesh size, macroreticular form) was used as catalyst and the effect of catalyst loading on the relative conversion to oxirane is presented in Fig.6. This figure shows that the conversion of ethylenic unsaturation to oxirane increases rapidly with catalyst dosage in the beginning and very slowly towards the end of the reaction. The relative conversion to oxirane increased from 64 to 75% with increasing dosage of resin from 5 to 15% after 4 hours of reaction. With use of 10% resin a slight oxirane cleavage is observed after 3 hours of reaction and maximum conversion is 72.9%, only 2 units less than that obtained with 15% catalyst loading. However, the maximum conversion of 84% was obtained with 20% catalyst loading under identical conditions and the product has stable oxirane ring. Therefore, 20% catalyst loading was considered to be optimum for the epoxidation reaction.

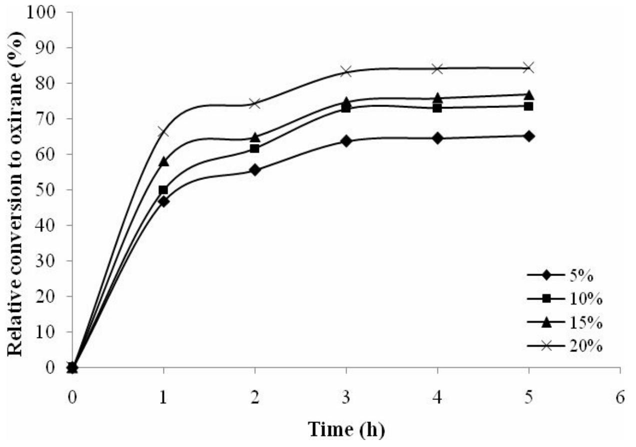


Figure 6: Effect of catalyst loading on the relative conversion to oxirane. ***Conditions:*** **Temperature, 60°C; acetic acid to ethylenic unsaturation molar ratio, 0.5:1; hydrogen peroxide to ethylenic unsaturation molar ratio, 1.5:1; stirring speed, 2000 rpm**

Table 4: Effect of acetic acid-to-ethylenic unsaturation molar ratio on iodine value conversion

	Acetic acid to ethylenic unsaturation molar ratio							
	0.3		0.5		0.8		1.0	
Time (h)	4	8	4	8	4	8	4	8
Oxirane oxygen[a] (%)	5.38	6.48	7.53	7.70	7.45	6.69	7.85	7.34
Iodine Value[b,c] (g I_2/100g)	57.5	32.8	22.6	19.8	21.3	15.1	18.6	14.3
% Iodine conversion[d] (A)	62.9	78.8	85.4	87.2	86.2	90.3	88.0	90.8

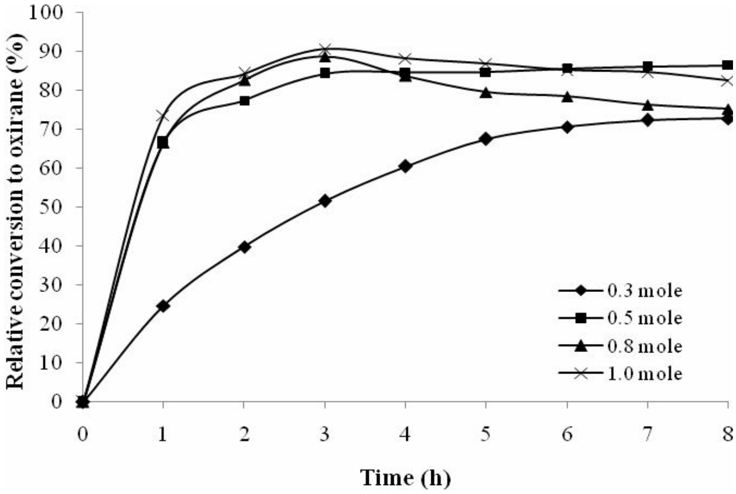


Figure 7: Effect of acetic acid to ethylenic unsaturation molar ratio on the relative conversion to oxirane. *Conditions:* Temperature, 60°C; hydrogen peroxide to ethylenic unsaturation molar ratio, 1.5:1; catalyst loading, 20 wt. % of oil; stirring speed, 2000 rpm

Effect of acetic acid to ethylenic unsaturation molar ratio

Optimization of acetic acid concentration was investigated at 0.3, 0.5, 0.8 and 1.0 mole per mole of ethylenic unsaturation for rate conversion to oxirane with respect to 1.5 mole of H_2O_2 per mole of unsaturation. Acetic acid acts as the oxygen carrier and gets regenerated once epoxidation reaction takes place. However, it can also act as reactant in hydrolysis of the oxirane ring formed. Therefore, an optimum level of acetic acid is desired to speed up the conversion to oxirane ring with minimal epoxy ring breaking. The influence of acetic acid concentration on the relative conversion to oxirane is shown in Fig.7. Increasing acid concentration was found to increase the iodine value conversion (Table-4) and leads to more production of peracetic acid. The higher conversion rate of the double bond to epoxide was observed with increased mole ratio of acetic acid used. The reaction conversion of 73.7% was achieved within first hour when 1.0 mole acetic acid was used while the same conversion was obtained after 8 hour of reaction for 0.3 mole. However, considering the stability of epoxy rings, the use of higher acid concentrations is of no significance as the excess acid promotes the hydrolysis of the epoxide. From Fig.7 it can be seen that an acid-to-ethylenic unsaturation molar ratio of 0.5 is optimum with a moderately high rate of epoxidation reaction and negligible ring-opening reaction.

Table 5: Effect of hydrogen peroxide-to-ethylenic unsaturation molar ratio on iodine value conversion

	Hydrogen peroxide to ethylenic unsaturation molar ratio							
	0.5		1.0		1.5		2.0	
Time (h)	4	8	4	8	4	8	4	8
Oxirane oxygen[a] (%)	3.89	4.19	5.07	6.16	7.53	7.70	8.03	6.61
Iodine Value[b,c] (g I_2/100g)	85.6	78.6	64.8	45.6	22.6	19.8	16.4	13.6
% Iodine conversion[d] (A)	44.8	49.3	58.2	70.6	85.4	87.2	89.4	91.2

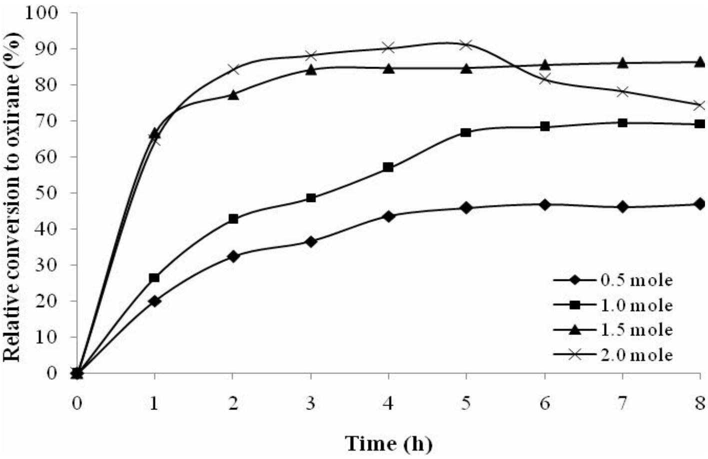


Figure 8: Effect of the hydrogen peroxide to ethylenic unsaturation molar ratio on the relative conversion to oxirane. *Conditions:* Temperature, 60°C; acetic acid to ethylenic unsaturation molar ratio, 0.5:1; catalyst loading, 20 wt. % of oil; stirring speed, 2000 rpm

Effect of hydrogen peroxide to ethylenic unsaturation molar ratio

The effect of different mole ratios of H_2O_2-to-ethylenic unsaturation on rate of oxirane formation and iodine conversion was studied by carrying out a series of reactions (**Table-5**). As seen in Fig.8 the reaction rate increased with an increase in concentration of H_2O_2 in the reaction. However; although the maximum conversion (91.2 %) of double bonds to epoxide rings was achieved with 2.0 mole of H_2O_2 concentration after 5 hours, it also tend to destroy the epoxy rings when reaction was continued further. For a lower H_2O_2 dosing of 0.5 and 1.0 mole, the maximum oxirane level and initial epoxidation rates were significantly lower as compared to that obtained with use of 1.5 mole H_2O_2. Moreover, the epoxy rings formed for 1.5:1 mole ratio of H_2O_2 -to-ethylenic unsaturation shows excellent stability. Therefore, the optimal hydrogen peroxide-to-ethylenic unsaturation molar ratio was found to be 1.5 mol/mol, with a relative conversion to oxirane of 86.5% and iodine value conversion of 87.2% after 8 hours of reaction.

Fourier transform infrared (FTIR) spectroscopy analysis

Shimazdu FTIR-8400 spectrometer was used for monitoring the disappearance of double bonds and formation of epoxy groups during the reaction by qualitative identification of main signals. Only two spectra are analyzed: the raw oil, WSO and epoxide adduct, EWSO (**Fig.9A & 9B,** respectively), to show the changes in their functional groups. For WSO the characteristic peaks at 3008 cm^{-1}, 1650 cm^{-1} and 721cm^{-1} are attributed to the stretching vibration of the double bonds: =C-H, C=C, *cis*-CH=CH, respectively. *S. Hernandez-Lopez et.al.* [26] reported the diminution of peak, C=C-H stretching at 3020 cm^{-1} after epoxidation reaction, which supports our study where the almost complete disappearance of double bonds band at 3008 cm^{-1} at 60^0C after 8 h was observed. This confirms that almost all the C=C-H had taken part in the epoxidation reaction. Also, there is decrease in the intensity of the other important unsaturated bond signals in comparison with the unreacted oil, giving reliable support of its chemical transformation to an oxirane ring. The presence of new peaks in the FTIR spectrum of WSFO at 831 cm^{-1}, attributed to the epoxy group, confirmed the success of the epoxidation reaction of WSO. *Vleck and Petrovic* [27] reported the presence of epoxy groups at 822–833 cm^{-1}, which agrees well with this study. The other new peak at the 3470 cm^{-1} was attributed to the hydroxyl functional group, derived from the epoxy functional group via partial epoxy ring opening reaction. The intensity of the 3470 cm^{-1} band indicated the extent of hydrolysis of EWSO. The epoxy ring opening reaction could occur either by acid catalysis in the presence of water associated with aqueous solution of H_2O_2 used [28]. The hydrolysis of the ester groups during epoxidation reaction in oils is the main side reaction. The band corresponding to carboxylic acid group is located at 1650 cm^{-1} and is usually very intense even at low carboxylic group concentration [29, 30]. In case of hydrolysis, a carboxylic acid functional group is formed and this carbonyl group will appear near but differentiable of the ester carbonyl stretching C=O in the glyceride moiety at 1744 cm^{-1}. However; in the course of the epoxidation reaction carried out in our study, no evidence of the carbonyl from carboxylic acid group signal was observed.

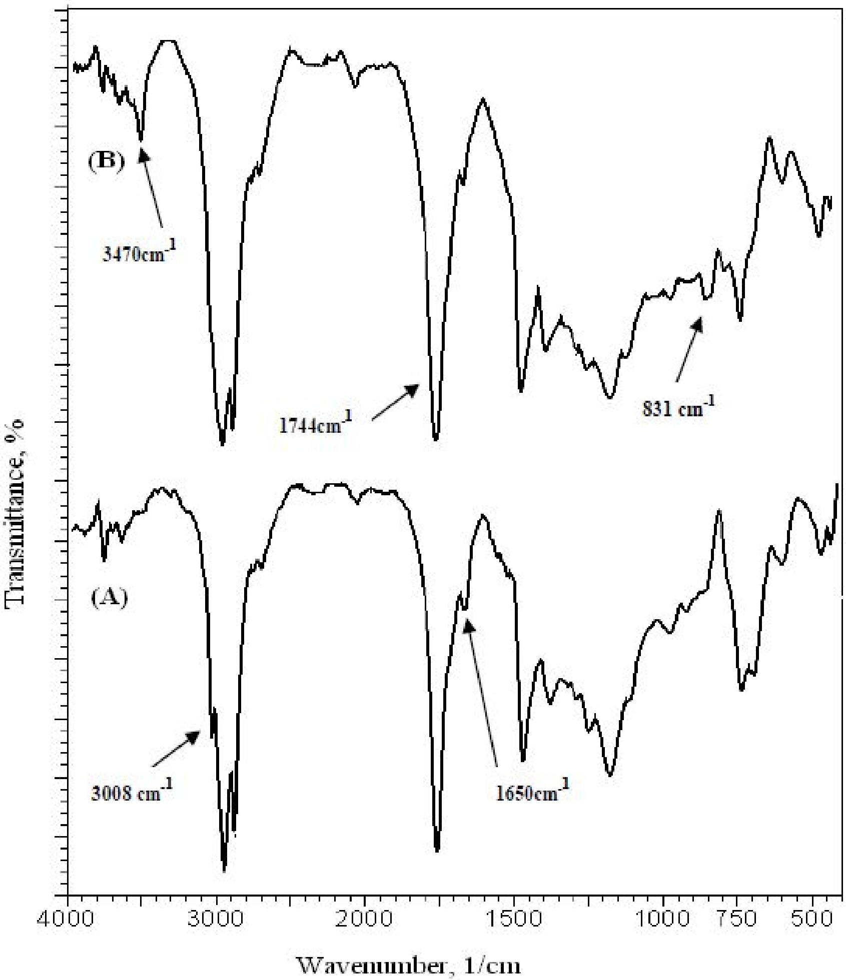


Figure 9: FTIR spectra of (A) wild safflower oil and (B) and epoxidised wild safflower oil. Epoxidation Conditions: Temperature, 60°C, carboxylic acid (acetic acid)-to-ethylenic unsaturation molar ratio, 0.5 : 1;hydrogen peroxide-to-ethylenic unsaturation molar ratio, 1.5 : 1; catalyst loading, 20 wt. % of oil; reaction time, 8 h; stirring speed, 2000 rpm

CONCLUSION

The results of the present investigation shows that WSO can be successfully utilized for epoxidation using peroxy acid generated *in situ*. Acetic acid–IR-122 combination was found to be most effective for higher epoxide yield at shorter reaction time. The optimized parameters to get higher degree of epoxidation with minimum epoxy ring breaking were noted as temperature of 60°C, stirring speed 2000 rpm ensuring kinetically control of reaction, an acetic acid to ethylenic unsaturation molar ratio of 0.5:1, a hydrogen peroxide to ethylenic unsaturation molar ratio of 1.5:1, and a catalyst (IR-122) loading of 20 wt% of WSO. The completion of reaction was supported by FTIR spectral analysis. The epoxy signals were well identified and intensity of the signals due to the double bonds vibrations was evidenced by the spectroscopic techniques used. Under these optimum conditions, 7.87% oxirane oxygen content in synthesized ESWO was obtained. The synthesized epoxide WSO is an attractive intermediate for the preparation of various derivatives of industrial importance.

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