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ORIGINAL PAPER

Epoxidation of Canola Oil with Hydrogen Peroxide Catalyzed by Acidic Ion Exchange Resin

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Abstract Canola oil with an iodine value of 112/100 g, and containing 60% oleic acid and 20% linoleic acid, was epoxidised using a peroxyacid generated in situ from hydrogen peroxide and a carboxylic acid (acetic or formic acid) in the presence of an acidic ion exchange resin (AIER), Amberlite IR 120H. Acetic acid was found to be a better oxygen carrier than formic acid, as it produced about 10% more conversion of ethylenic unsaturation to oxirane than that produced by formic acid under otherwise identical conditions. A detailed process developmental study was then performed with the acetic acid/AIER combination. The parameters optimised were temperature (65 °C), acetic acid to ethylenic unsaturation molar ratio (0.5), hydrogen peroxide to ethylenic unsaturation molar ratio (1.5), and AIER loading (22%). An iodine conversion of 88.4% and a relative conversion to oxirane of 90% were obtained at the optimum reaction conditions. The heterogeneous catalyst, AIER, was found to be reusable and exhibited a negligible loss in activity.

Keywords Canola oil · Epoxidation · Peroxyacetic acid · Ion exchange resin · Lubricant

Introduction

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. The unsaturation of the vegetable oils, which are rich in oleic, linoleic and linolenic acyl groups, can be used to introduce functional groups like epoxides. Plant oils containing epoxy groups, formed from the epoxidation of the double bonds in vegetable oils, are important oleochemicals. Epoxides have a wide spectrum of commercial uses because of their richly varied chemical reactivity, which arises due to the high strain energy of the three-membered oxirane ring. Fatty epoxides can be used directly as plasticizers to improve the flexibility, elasticity and stability of polymers towards heat and UV radiation [1, 2]. Because of the high reactivity of the oxirane ring, epoxides act as raw materials for products such as alcohols, glycols, alkanolamines and carbonyl olefinic compound polymers [3]. Epoxides can also be used as high-temperature lubricants, and the products obtained from ring opening can be employed as low-temperature lubricants [4]. Epoxides with higher oxirane values and lower iodine values are considered high-quality plasticizers [3, 5]. Because of their commercial importance, the epoxidation of long-chain olefins and unsaturated fatty acid derivatives, such as those from soybean and other plant oils, are carried out on an industrial scale [6]. Previous research has been done on many plant oils, including one of the most important epoxidised vegetable oils, soybean oil, the global production of which is around 200,000 t/year [7]. Laboratory-scale epoxidations of mahua oil [8], karanja oil [9, 10], cottonseed oil [11] and jatropha oil [12] have been reported.

Canada is the second-largest producer and the largest exporter of canola oil in the world. Saskatchewan province produces 38% of the total canola oil production in western Canada [13]. Other than biodiesel, no chemical derivatives are made from canola oil. So far, no

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detail reports have appeared in the literature on the kinetics of the epoxidation of canola oil. While Piazza and Foglia [1] reported the preparation of fatty amide polyols via the epoxidation of canola oil, epoxidised canola oil (ECO) was an intermediate product in their study. Canola oil, with its unique composition of approximately 60% oleic acid, is a perfect candidate for epoxidation [14]. Epoxidised canola oil (ECO) could be a promising source of biolubricating oil and a feedstock for the chemical industry. The objective of this research was to study the kinetics of the epoxidation of canola oil to produce ECO.

Generally, four technologies are employed for the production of epoxides from olefinic molecules: (1) the use of percaboxylic acid in the presence of acids or enzymes as catalysts—a well-known industrial method of epoxidation [15–17]; (2) with organic and inorganic peroxides [18]; (3) with halohydrins for the epoxidation of olefins with electron-deficient double bonds [19]—a process which is, however, is environmentally unfriendly; and (4) with molecular oxygen [19], which is the cheaper and greener method but one that is only effective for simple molecules. For example, epoxidation with molecular oxygen is mostly restricted to ethylene, with silver used as the only catalyst for the reaction [20]. 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 [11]. It is, therefore, not an efficient method for the epoxidation of vegetable oils.

It is evident from the above discussion that for the clean and efficient epoxidation of vegetable oils, percarboxylic acids and organic and inorganic peroxides could be used as reagents. Moreover, the processes can be made cleaner by using heterogeneous catalysts instead of traditional homogeneous ones [21].

The basic objective of this study was to explore the effects of two different carboxylic acids (i.e., formic and acetic acid) on the epoxidation of canola oil in the presence of a heterogeneous catalyst—an acidic ion exchange resin (AIER). Various reaction parameters were optimized with respect to the conversion of the double bond to oxirane and the iodine conversion using the best-performing carboxylic acids.

Experimental

Materials

Canola oil was obtained from Loblaws Inc. (Montreal, Canada). Glacial acetic acid (100%) from EMD Chemicals Inc. (Darmstadt, Germany), formic acid (88%) from Sigma-Aldrich (St. Louis, MO, USA), GR grade hydrogen peroxide (30wt%) from EMD Chemicals Inc., and Amberlite IR-120H ion exchange resin (Rohm & Haas Co., Philadelphia, PA, USA) were used in the study. Iodine monochloride and Wijs' solution were procured from VWR (San Diego, CA, USA). 33% HBr in acetic acid was obtained from EMD Chemicals Inc. and then diluted with glacial acetic acid to make 0.1 N HBr.

Experimental Setup and Procedure

Epoxidation reactions were carried out in a three-necked round-bottom flask (250 mL capacity), equipped with a magnetic stirrer and placed in a water bath, the temperature of which could be controlled to within ±1 °C of the desired temperatures. The central neck of the flask was connected to a reflux condenser, and a thermometer was introduced through one of the sidenecks in order to record the temperature of the reaction mixture.

The epoxidation method reported by Goud et al. (10) was used, and the same procedure was used for all of the experimental runs dealing with different parameters. A calculated amount of canola oil (22.6 g) was placed in the flask, the necessary amount of acetic/formic acid (carboxylic acid to ethylenic unsaturation molar ratio, 0.5:1) and catalyst (catalyst loading expressed as weight percentage of canola oil 22%) were added, and the mixture was continuously stirred for 30 min. Then, 17 g of 30% aqueous hydrogen peroxide (1.5 moles 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 within half an hour. After the complete addition of hydrogen peroxide, the reaction was continued for the desired time with rapid stirring. The rapid stirring was maintained throughout the experiments so that a fine dispersion of oil was achieved. The course of the reaction was followed by withdrawing samples at regular intervals, considering the completion of addition of hydrogen peroxide to be the zero time. The collected samples were then immediately extracted with diethyl ether in a separating funnel, washed with cold and slightly hot water successively to remove free acid, and then analysed for oxirane content, iodine value and glycol content.

Analytical Techniques

The oxirane oxygen content of each sample was determined using the direct method with hydrobromic acid solution in acetic acid, and the iodine value was determined using Wijs solution [22]. The glycol content was found using the method reported by May [23], based on the oxidation of glycol with benzyltrimethylammonium periodate in nonaqueous medium. The excess periodate and iodic acid formed was reduced with potassium iodide, and the liberated iodine was titrated with sodium thiosulfate. Fourier transform infrared (FTIR) spectroscopy experiments were performed on canola oil and ECO using a PerkinElmer (Wellesley, MA, USA) Spectrum GX instrument equipped with DTGS detector and a KBr beam splitter. The spectra for each analysis were averaged over 64 scans with a nominal 4 cm^{-1} resolution. ^{1}NMR and ^{13}C NMR spectra were recorded using a Bruker (Ettlingen, Germany) AMX-500 FT spectrometer.

From the oxirane content, the percentage relative conversion to oxirane was determined using the following formula:

$$\text{Relative conversion to oxirane (RCO)} = (\text{OO}_{\text{ex}}/\text{OO}_{\text{th}}) \times 100$$

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, determined using the following expression [24]:

$$\text{OO}_{\text{th}} = \{(\text{IV}_{\text{o}}/2A_{\text{i}})/[100 + (\text{IV}_{\text{o}}/2A_{\text{i}})A_{\text{o}}]\} \times A_{\text{o}} \times 100$$

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.

Some of the experimental runs were repeated under identical conditions to determine the percentage deviation between the two experimental results, and the deviation was found to be 1.5–4.5%.

Results and Discussion

The properties of canola oil, along with its fatty acid composition, were as follows: specific gravity = 0.915 (at 30 °C); acid value (mg KOH/g) = 1.0; iodine value (g iodine/100 g) = 112; saponification value (mg KOH/g) = 185; oleic acid (18:1) = 60%; linoleic acid (18:2) = 20%. Vegetable oils currently used for the production of epoxy esters have similar properties [25–27]. Canola oil is, therefore, considered a potential candidate for the epoxidation of its unsaturated fatty esters to give ECOs that have greater commercial value than the oil itself.

Epoxidation reactions were first carried out with both formic acid and acetic acid as carboxylic acids and Amberlite IR-120 H, an AIER, used as catalyst. Epoxidation experiments were thus carried out with two different carboxylic acid-catalyst combinations in order to find out the best one. Further experiments were conducted with the best reagent–catalyst combination using the following range of variables: temperature, 40–75 °C; hydrogen peroxide to ethylenic unsaturation ratio (mole per mole), 0.5–2.0; acetic acid to ethylenic unsaturation ratio (mole per mole), 0.3–1.0; catalyst loading (expressed as the weight percentage of canola oil used), 6–22%, with continuous and complete stirring performed in order to ensure that the system was free from mass transfer resistance.

Effect of Carboxylic Acid

Epoxidation experiments were carried out with formic acid/AIER and acetic acid/AIER at a temperature of 55 °C. Figure 1 shows the relative percentage conversion to oxirane as a function of time obtained with the above two carboxylic acid/AIER combinations. It is evident from this figure that the acetic acid/AIER combination was more active than the formic acid/AIER combination, with a conversion to oxirane of 83% after 7 h, compared to 73% obtained with the latter. The acetic acid/AIER combination also produced an 8% higher conversion of iodine than that obtained with formic acid/AIER, and the glycol content of the final product obtained with acetic acid/AIER was less than that obtained with formic acid/AIER, as shown in Table 1. However, the experiment was performed on the formic acid system with no resin under otherwise identical reaction conditions. Although the conversion to oxirane was closer to that obtained in the presence of resin, a slightly higher glycol content (i.e. 0.16 mol/100 g) was observed in the absence of resin (Table 1). Glycol is considered as an impurity in the epoxidised oil and, is therefore, undesired. Its formation also indicates the

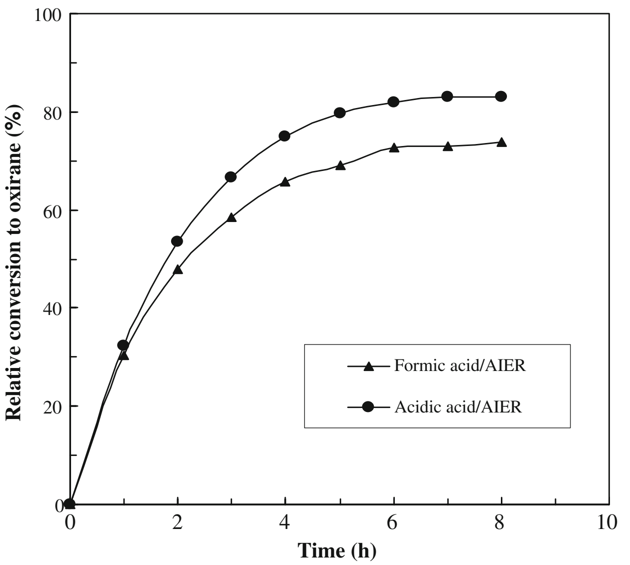

Fig. 1 Activities of carboxylic acids in the epoxidation of canola oil with acidic ion exchange resin used as catalyst. Conditions: Temperature, 55 °C; carboxylic acid to ethylenic unsaturation molar ratio, 0.5:1; hydrogen peroxide to ethylenic unsaturation molar ratio, 1.5:1; catalyst loading, 22 wt% of oil

Table 1 Comparison of the activities of formic acid and acetic acid in the epoxidation of canola oil

Parameter	Carboxylic acid		
	[a]Formic acid	[b]Formic acid with no resin	[a]Acetic acid
Iodine value (g/100 g)	26	29	16
Iodine conversion (%)	76.8	74.0	85.7
Glycol content (mol/100 g)	0.12	0.16	0.08

[a] Temperature, 55 °C; carboxylic acid to ethylenic unsaturation molar ratio, 0.5:1; hydrogen peroxide to ethylenic unsaturation molar ratio, 1.5:1; catalyst loading, 22 wt% of oil; reaction time, 7 h

[b] Temperature, 55 °C; formic acid to ethylenic unsaturation molar ratio, 0.5:1; hydrogen peroxide to ethylenic unsaturation molar ratio, 1.5:1; reaction time, 7 h

instability of the epoxide ring and the epoxide yield decreases with the formation of glycol through the hydrolysis of the oxirane ring. It is evident from the the above discussion that acetic acid/AIER is a better combination for the epoxidation of canola oil with aqueous hydrogen peroxide, and the product obtained is of a superior quality compared to that obtained with formic acid/AIER. Further experiments were therefore carried out with acetic acid/AIER to study the effects of various parameters on the conversion to oxirane oxygen and the conversion of iodine values.

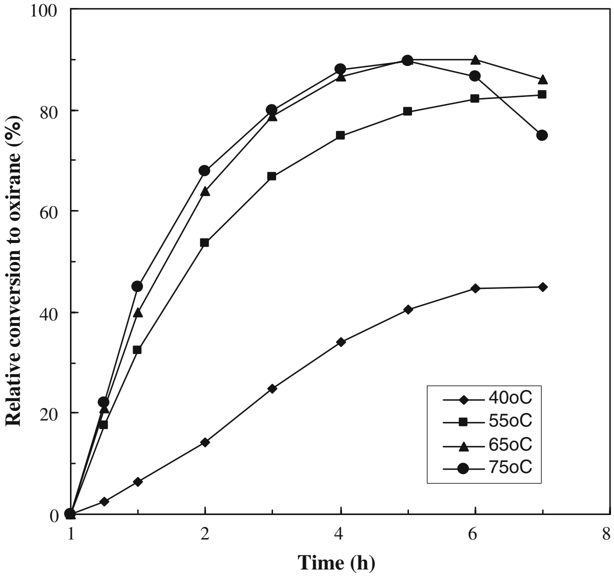

Fig. 2 Effect of temperature on the relative conversion to oxirane. Conditions: acetic acid to ethylenic unsaturation molar ratio, 0.5:1; hydrogen peroxide to ethylenic unsaturation molar ratio, 1.5:1; catalyst loading, 22 wt% of oil

Effect of Temperature

The effect of temperature on the course of epoxidation of canola oil was investigated at four different temperatures, namely 40, 55, 65 and 75 °C. In order to achieve better control over the exothermic reaction, the addition of H_2O_2 was performed at temperatures that were 10 °C below the actual reaction temperatures mentioned above. For example, for the reaction at 55 °C, H_2O_2 was added slowly at 45 °C for half an hour; thereafter, the temperature was raised to 55 °C and maintained there until the end of the reaction. Similar procedures have been used by other researchers [8, 28]. In all of these experiments, 50 mol% excess hydrogen peroxide relative to the ethylenic unsaturation as well as acetic acid at half of the ethylenic unsaturation were used to minimize the formation of glycol by-product through ring-opening reactions. The changes in the iodine value with the reaction time at four different temperatures are presented in Table 2. As expected, higher temperatures favoured the epoxidation reaction, and a maximum ~91% conversion of iodine value was obtained at 75 °C after a reaction time of 5 h. However, a similar conversion was obtained after 7 h of the reaction carried out at 65 °C. The variation in the relative conversion to oxirane with temperature is presented in Fig. 2. The relative conversion to oxirane was found to increase with increasing temperature. As can be seen from Fig. 2, performing the reaction at lower temperatures yielded lower

Table 2 Effect of temperature on the conversion of iodine

	Temperature (°C)							
	40		55		65		75	
Time (h)	5	7	5	7	5	7	5	7
Iodine value (g/100 g)	56.3	49.8	18.4	16.0	13.0	10.2	10.4	10.0
Iodine conversion (%)	49.7	55.5	83.6	85.7	88.4	90.8	90.7	91.1
Glycol content (mol/100 g)	0.02	0.04	0.04	0.06	0.05	0.08	0.09	0.13

Conditions: acetic acid to ethylenic unsaturation molar ratio, 0.5:1; hydrogen peroxide to ethylenic unsaturation molar ratio, 1.5:1; catalyst loading, 22 wt% of oil; initial iodine value, 112 g/100 g rates but produced a more stable oxirane ring compared to that obtained at higher temperatures. A reaction temperature of 65 °C gave 90% conversion to oxirane after a reaction time of 5 h. Almost the same conversion was obtained at 75 °C, and the conversion decreased when the reaction was continued further. Since no noticeable decrease in conversion was observed at 65 °C, it can be concluded that a temperature of more than 65 °C is detrimental to the oxirane ring when it is opened to form glycol, an unwanted by-product. A temperature of 65 °C was, therefore, considered optimal for the epoxidation reaction under investigation. Higher operating temperatures are also not preferred because the addition of hydrogen peroxide is an exothermic reaction, and higher temperatures can result in an excessive rise in temperature, leading to an explosion [8, 28].

Effect of the Acetic Acid to Ethylenic Unsaturation Molar Ratio

Acetic acid acts as the oxygen carrier and gets regenerated once the epoxidation reaction takes place. Hence, acetic acid also acts as a catalyst in the epoxidation reaction. However, acetic acid can hydrolyse the oxirane ring formed. The level of acetic acid should be such that both effects are balanced. The influence of the acetic acid to ethylenic unsaturation molar ratio was investigated at four different ratios: 0.3:1, 0.5:1, 0.8:1 and 1.0:1. Table 3 shows the effect of acetic acid concentration on the iodine value of the epoxidised oil. Increasing the acid concentration was found to increase the iodine conversion, and a faster reaction rate was observed.

Figure 3 shows the effect of the acetic acid concentration on the relative conversion to oxirane. The rate of reaction increases with increasing acid concentration, leading to higher conversion of the double bond to epoxide, as shown in Fig. 3. However, the increased acid concentration has a detrimental effect on the oxirane ring, as the acid promotes the hydrolysis of the epoxide, thereby decreasing its final yield. As can be seen from Fig. 3, an acid to ethylenic unsaturation molar ratio of 0.5 is optimum, since it gives a moderately high rate of epoxidation and a negligible rate of ring opening.

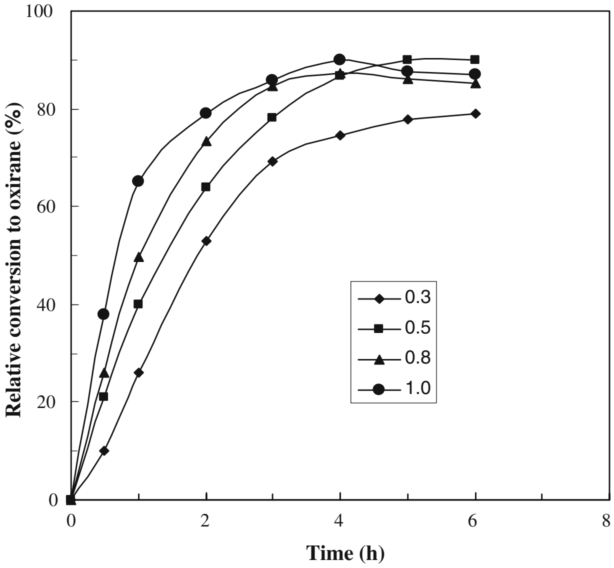

Fig. 3 Effect of acetic acid to ethylenic unsaturation molar ratio on the relative conversion to oxirane. Conditions: temperature, 65 °C; hydrogen peroxide to ethylenic unsaturation molar ratio, 1.5:1; catalyst loading, 22 wt% of oil

Effect of Hydrogen Peroxide to Ethylenic Unsaturation Molar Ratio

The molar ratio of hydrogen peroxide to ethylenic unsaturation was varied in the range 0.5–2.0, as shown in Fig. 4. With an increase in the hydrogen peroxide to ethylenic unsaturation molar ratio from 0.5 to 1.5, there was a progressive increase in the rate of oxirane formation along with a corresponding decrease in iodine value. However, as can be seen from Table 4 and Fig. 4, when the molar ratio was increased further to 2.0, a small difference in the final iodine value and final oxirane value was observed. However, the iodine value was lower for higher acid contents,

Table 3 Effect of acetic acid to ethylenic unsaturation molar ratio on the conversion of iodine

	Acetic acid to ethylenic unsaturation molar ratio							
	0.3		0.5		0.8		1.0	
Time (h)	1	5	1	5	1	5	1	5
Iodine value (g/100 g)	75.3	20.0	66.0	13.0	50.3	11.4	35.6	10.5
Iodine conversion (%)	32.7	82.1	41.1	88.4	55.1	89.8	68.2	90.6
Glycol content (mol/100 g)	0.01	0.03	0.01	0.05	0.02	0.07	0.02	0.1

Conditions: temperature, 65 °C; hydrogen peroxide to ethylenic unsaturation molar ratio, 1.5:1; catalyst loading, 22 wt% of oil; initial iodine value, 112 g/100 g

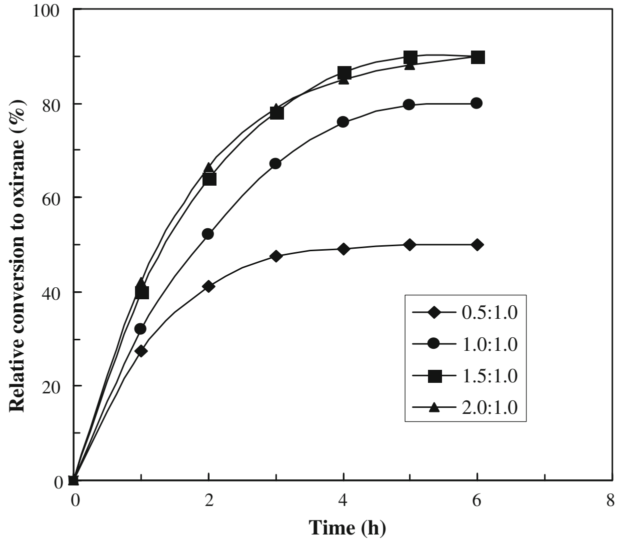

Fig. 4 Effect of the hydrogen peroxide to ethylenic unsaturation molar ratio on the relative conversion to oxirane. Conditions: temperature, 65 °C; acetic acid to ethylenic unsaturation molar ratio, 0.5:1; catalyst loading, 22 wt% of oil

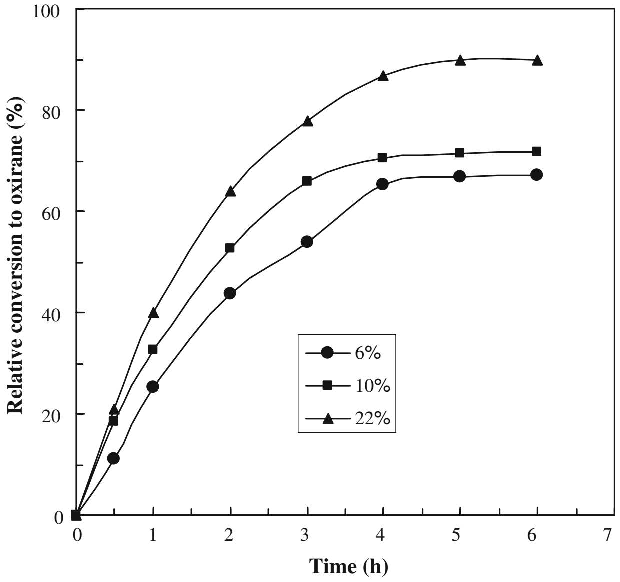

Fig. 5 Effect of catalyst loading on the relative conversion to oxirane. Conditions: temperature, 65 °C; acetic acid to ethylenic unsaturation molar ratio, 0.5:1; hydrogen peroxide to ethylenic unsaturation molar ratio, 1.5:1

indicating a higher conversion to alcohol. Initially the epoxidation reaction rate was higher at a higher molar ratio, but the maximum oxirane level was almost the same for both 1.5 and 2.0. For lower hydrogen peroxide to ethylenic unsaturation ratios, the maximum oxirane level and the initial epoxidation reaction rates were lower, as shown in Fig. 4. The optimal hydrogen peroxide to ethylenic unsaturation molar ratio was therefore found to be 1.5 mole/mole, because no significant change in the conversion was observed with further increases in the molar ratio.

Effect of Catalyst Loading

The effect of the catalyst (Amberlite IR–120H) loading was investigated in the range of 6–22 wt% of canola oil. Figure 5 shows the results obtained for the catalyst loading in that range.

An increase in the loading of solid catalyst (at a fixed particle size) leads to an increase in both the total active volume and the total surface area of the catalyst. The active species present enhance the epoxidation with increasing catalyst concentration. From Fig. 5, it is observed that an increase in catalyst loading not only increases the initial rate of epoxidation reaction but also brings about an increase in the maximum oxirane level obtained. At loadings of 6 and 10%, the maximum oxirane levels were relatively low compared to the one obtained at 22%. Hence, the optimal catalyst loading was considered to be 22% under the experimental conditions studied (Table 5).

Reusability of the Solid Catalyst

The reusability of the solid catalyst (Amberlite IR-120H) was assessed by repeating the reaction with the same catalyst four times. The reaction was carried out as described in the “Experimental” section under optimum conditions.

Table 4 Effect of the hydrogen peroxide to ethylenic unsaturation molar ratio on the conversion of iodine

	Hydrogen peroxide to ethylenic unsaturation molar ratio							
	0.5		1.0		1.5		2.0	
Time (h)	1	5	1	5	1	5	1	5
Iodine value (g/100 g)	76.0	52.0	70.5	20.4	66.0	13.0	61.5	12.0
Iodine conversion (%)	32.1	53.6	37.0	81.8	41.1	88.4	45.0	89.3
Glycol content (mol/100 g)	0.0	0.01	0.01	0.03	0.01	0.05	0.02	0.08

Conditions: temperature, 65 °C; acetic acid to ethylenic unsaturation molar ratio, 0.5:1; catalyst loading, 22 wt% of oil; initial iodine value, 112 g/100 g

Table 5 Effect of AIER loading on the conversion of iodine

	AIER loading (%)					
	6%		10%		22%	
Time (h)	1	5	1	5	1	5
Iodine value (g/100 g)	78	33	79	28	70	13
Iodine conversion (%)	30	70	29	75	37	88.4
Glycol content (mol/100 g)	0.0	0.02	0.01	0.03	0.01	0.05

Conditions: temperature, 65 °C; acetic acid to ethylenic unsaturation molar ratio, 0.5:1; hydrogen peroxide to ethylenic unsaturation molar ratio, 1.5:1

At the end of the reaction, the catalyst was removed by filtration and washed with water and diethyl ether. The washed catalyst sample was air-dried and reused. The catalyst reusability was studied with a smaller amount of catalyst (i.e. 6% loading), and it was observed that after the catalyst had been used four consecutive times, the relative conversion to oxirane and the iodine conversion were 61 and 65%, as compared to 66 and 70% obtained with the fresh catalyst. However, similar result were obtained when a catalyst loading of 22% was used. The activities of the reused catalysts (with catalyst loadings of 6 and 22%) are presented in Table 6 in terms of the iodine conversion and the relative conversion to oxirane. After the catalyst had been used four consecutive times, the relative conversion to oxirane and the iodine conversion were 83 and 85%, as compared to 90 and 88.4%, respectively, obtained with the fresh catalyst. This clearly indicates that the heterogeneous catalyst, Amberlite IR-120H, can be recycled with little loss of activity.

Table 6 Reusability of the ion exchange resin catalyst for two different loading conditions

Run no.	Catalyst loading (22%)			
	1	2	3	4
Iodine value (g/100 g)	13.0	14.0	15.2	16.8
Iodine conversion (%)	88.4	87.5	86.4	85.0
Relative conversion to oxirane (%)	90.0	88.5	86.0	83.0
Run no.	Catalyst loading (6%)			
	1	2	3	4
Iodine value (g/100 g)	33.6	36.4	37.6	39.2
Iodine conversion (%)	70.0	67.5	66.2	65.0
Relative conversion to oxirane (%)	66.0	64.0	62.0	61.0

Conditions: temperature, 65 °C; acetic acid to ethylenic unsaturation molar ratio, 0.5:1; hydrogen peroxide to ethylenic unsaturation molar ratio, 1.5:1; initial iodine value, 112 g/100 g; reaction time, 5 h

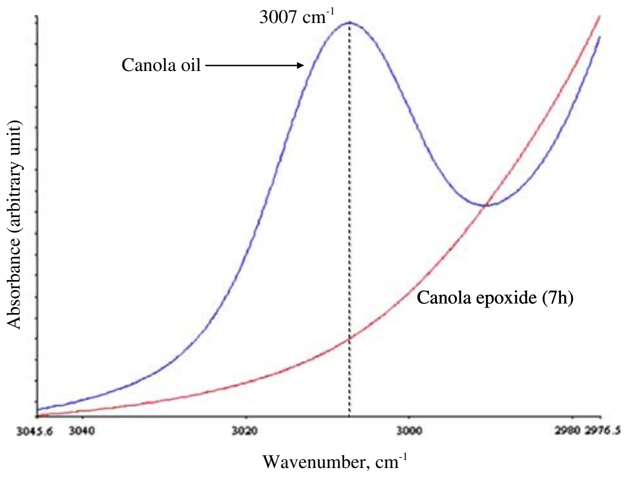

Fig. 6 FTIR spectra of canola oil. The presence of unsaturation in the canola oil was indicated by the appearance of a peak at 3,007 cm^{-1}, while the peak at 3,007 cm^{-1} had disappeared after 7 h of ECO formation

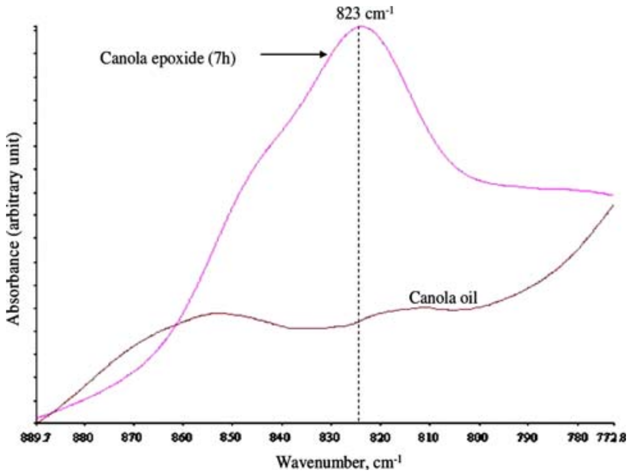

Fig. 7 FTIR spectra for epoxy formation at 823 cm^{-1}. The presence of the epoxide group in ECO was indicated by the peak at 823 cm^{-1}, while the canola oil shows no initial content of epoxide since the peak at 823 cm^{-1} is missing. Conditions: temperature, 65 °C; carboxylic acid (acetic acid) toethylenic unsaturation molar ratio, 0.5:1; hydrogen peroxide to ethylenic unsaturation molar ratio, 1.5:1; catalyst loading, 22 wt% of oil; reaction time, 7 h

Fourier Transform Infrared (FTIR) Spectroscopy Analysis

The disappearance of double bonds and the formation of epoxy groups were monitored during the synthesis using an FTIR spectrometer (a PerkinElmer Spectrum GX instrument). The peak due to the presence of double bonds in the canola oil appeared at 3,007 cm^{-1} (Fig. 6), while the formation of the epoxy group (peak at 823 cm^{-1}) at the

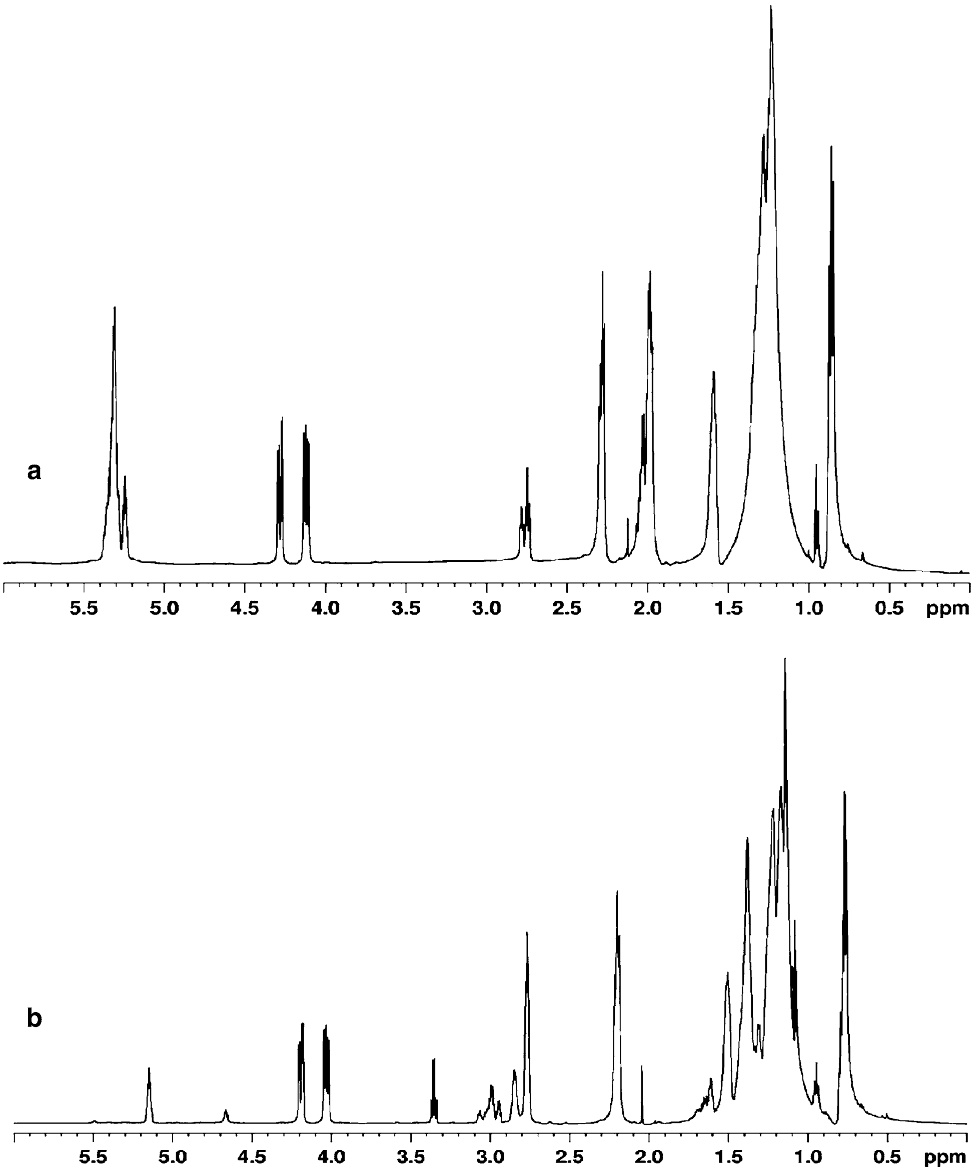

Fig. 8a–b The ^{1}H-NMR spectra of canola oil (**a**) and epoxidised canola oil (**b**). Conditions: temperature, 65 °C; carboxylic acid (acetic acid) to ethylenic unsaturation molar ratio, 0.5:1; hydrogen peroxide to ethylenic unsaturation molar ratio, 1.5:1; catalyst loading, 22 wt% of oil; reaction time, 7 h

specified reaction time is shown in Fig. 7. Vleck and Petrovic [29] reported the presence of epoxy groups at 822–833 cm^{-1}, which agrees well with this study, where the epoxy group was detected at 823 cm^{-1}.

NMR Spectral Analysis

The formation of the epoxide adduct of canola oil was confirmed by ^{1}H NMR and ^{13}C-NMR spectra, as shown in Figs. 8 and 9. ^{1}H NMR measurements for epoxidised canola oil indicate that the epoxy group is present in the ∂ 2.98–3.1 ppm region. The peaks at ∂ 2.98–3.1 represent the CH protons attached to the oxygen atoms of both the epoxy groups.

Conclusions

The epoxidation of canola oil using peroxycarboxylic acid generated in situ was carried out most effectively using the acetic acid–acidic ion exchange resin combination. The epoxidation process with minimum oxirane cleavage was, therefore, optimized using acetic acid and the Amberlite IR-120H (AIER) catalyst system. It was found that the epoxidation reaction occurred optimally at a temperature of 65 °C, 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 (AIER) loading of 22 wt% of total canola oil used. Under these optimum conditions, 90% conversion of ethylenic unsaturation to oxirane was

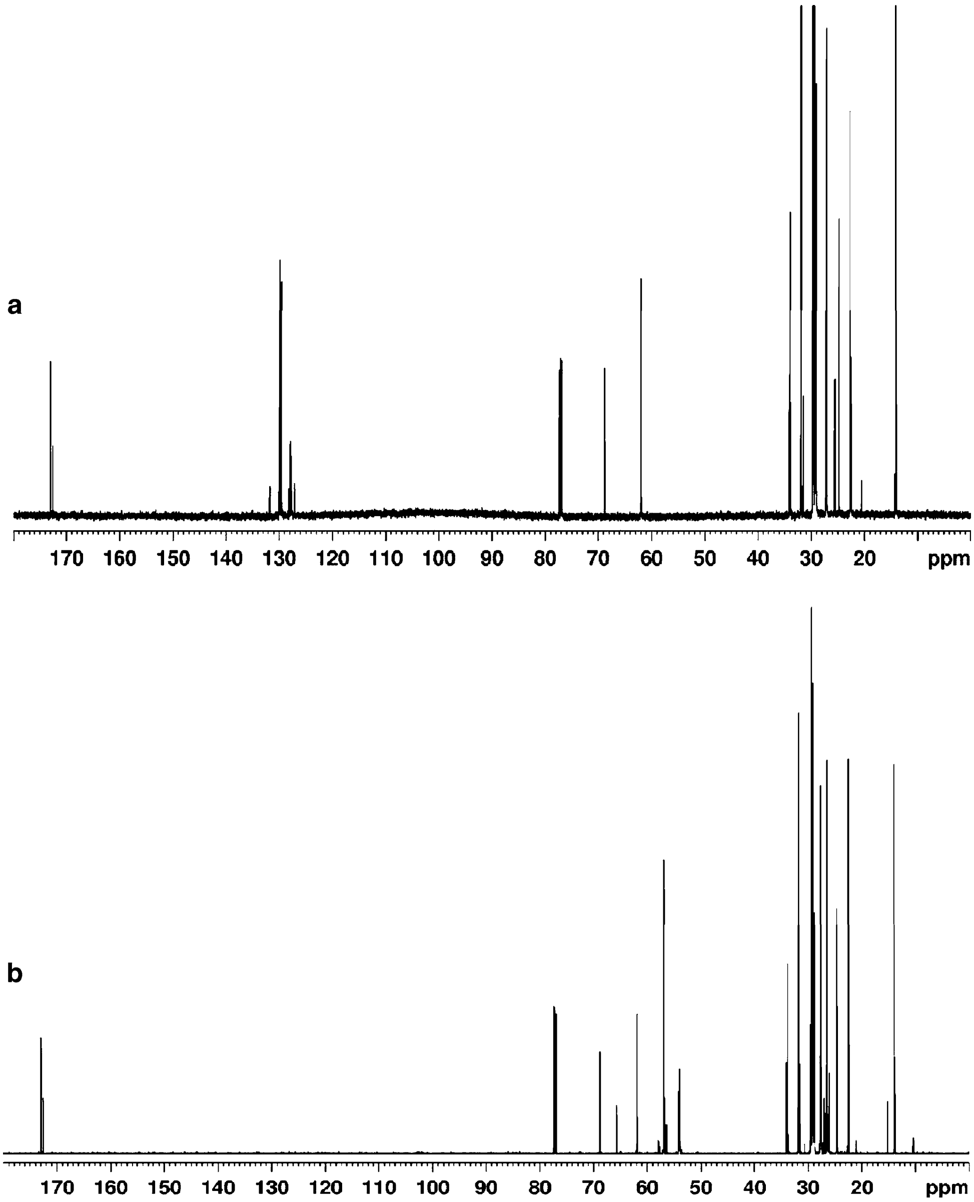

Fig. 9a–b The ^{13}C-NMR spectra of canola oil (**a**) and epoxidised canola oil (**b**). Conditions: temperature, 65 °C; carboxylic acid (acetic acid) to ethylenic unsaturation molar ratio, 0.5:1; hydrogen peroxide to ethylenic unsaturation molar ratio, 1.5:1; catalyst loading, 22 wt% of oil; reaction time, 7 h

obtained, with a similar conversion of iodine. The AIER catalyst was found to be reusable. The formation of the epoxide adduct of canola oil was confirmed by FTIR and ^{1}H NMR spectral analysis. From the relative conversion data obtained, it can be concluded that it is possible to develop value-added products, such as epoxide, from canola oil.

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