

Degradation of the oxirane ring of epoxidized vegetable oils with hydrogen peroxide using an ion exchange resin

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Abstract

The influence of different process variables (stirring, temperature, hydrogen peroxide concentration, particle diameter and amount of catalyst added) on the oxirane ring-opening reaction caused by hydrogen peroxide (H_2O_2) during the manufacture of epoxides obtained from triglycerides using a gel-type strong acid ion exchange resin, Amberlite IR-120, is analyzed. The degradation reaction with H_2O_2 is first-order with respect to the epoxide [$k_{\text{obs}}(70\text{ }^\circ\text{C}) = 3.37 \pm 0.606 \times 10^{-4} \text{ min}^{-1}$; $E_a = 99.2 \pm 1.3 \text{ kJ mol}^{-1}$] and second-order with respect to H_2O_2 , as expected, but only if moderate concentrations of peroxide are used. Highly concentrated H_2O_2 attacks the structure of the polymer and exposes free protons from the resin network. Ring opening increases either by adding a higher amount of catalyst to the system or by decreasing the particle size of the catalyst since, in both cases, the external area of the catalyst (i.e., available surface protons) becomes larger. © 2005 Elsevier B.V. All rights reserved.

Keywords: Amberlite IR-120; Epoxidized vegetable oils; Hydrogen peroxide; Oxirane

1. Introduction

Long-chain epoxides, or oxiranes, which can be readily obtained from both triglycerides (TG) and fatty acid methyl esters (FAME) of vegetable oils (VO), are extensively used by industry, especially in PVC manufacturing. They are also used to improve the properties of a large variety of polymers, as lubricants and detergents, in the production of ceramic coatings and paints and, more recently, in cosmetics and pharmaceuticals formulations [1–4]. In process terms, it is most desirable to seek their highest possible concentration (i.e., the highest ‘oxirane index’) in their manufacture.

Epoxidations are carried out using a peracid, either preformed or formed in situ, by reacting a carboxylic acid (usually acetic acid) with concentrated hydrogen peroxide [5–8]. Homogeneous (e.g., sulfuric acid) or heterogeneous strong acid catalysts (e.g., ion exchange resins) can be used since, in both cases, free solvated protons are the actual catalyst. In some cases, formic acid (AF) is preferred to

acetic acid (AA) because, owing to its high reactivity, no catalyst is required in the formation of performic acid [9]; but the production costs increase because AF price is frequently higher than AA’s. Nevertheless, besides the main reaction (the formation of the oxirane ring by reaction of unsaturated double bonds of the hydrocarbon chain of the VO with the peracid) several other, deleterious consecutive reactions occur. They all imply process losses via oxirane ring opening and must be minimized (Fig. 1).

Heterogeneous catalysts, which are generally preferred owing to their easy separation from the reacting mixture, also bring an opportunity to allow for an ‘isolation’ of protons from the reacting mass and, then, to minimize ring-opening losses. Nevertheless, it is not straightforward nor obvious to be able to predict, a priori, the relative impact of this heterogeneization strategy on the different consecutive reactions listed in Fig. 1.

A standard, sulfonic (strongly acidic) gel-type ion exchange resin, Amberlite IR-120 was chosen for this work, as it is readily available in the market and it is known to yield epoxidized oils with good oxirane values. The resin is hydrophilic, allowing only water, AA and H_2O_2 into the

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a	total external area of the IER catalyst, cm^2
a_p	external surface area of a catalyst bead, cm^2
d_p	diameter of a catalyst bead, cm
E_a	activation energy, kJ mol^{-1}
Ep	epoxide group
k	pseudohomogeneous reaction rate constant, $\text{l}^2 \text{mol}^{-2} \text{min}^{-1}$
k_{obs}	observable reaction rate constant, min^{-1}
k_s	reaction rate constant based in the external IER surface, cm min^{-1}
S	external surface area per unit mass of the IER beads, $\text{cm}^2 \text{g}^{-1}$
T	temperature, $^\circ\text{C}$
V	total volume of the IER beads, cm^3
v	pseudohomogeneous reaction rate, $\text{mol l}^{-1} \text{min}^{-1}$
V_p	volume of a catalyst bead, cm^3
w	total mass of the IER beads (dry basis), g
$[j]$	concentration of j , mol l^{-1}
<i>Greek symbols</i>	
α	order of reaction with respect to hydrogen peroxide
β	order of reaction with respect to epoxide group
ρ	density, g cm^{-3}
<i>Superscripts</i>	
o	initial value

gel phase; peracetic acid is produced inside the resin, near the sulphonic groups. The gel structure, unlike macroreticular resin beads, does not let large molecules such as TG or FAME into the polymer network and, thus, a low oxirane ring opening is expected. Besides this, Amberlite IR-120 allows an almost complete elimination of unsaturation of the VO at a relatively low reaction temperature and with a moderate

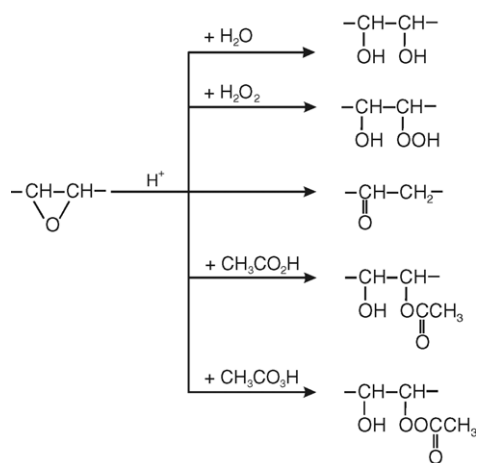


Fig. 1. Oxirane ring-opening reactions of epoxidized vegetable oils in the conventional acetic acid-hydrogen peroxide process.

reaction time. The crosslinking and the absence of metal impurities favor, also, the efficiency and conversion of the peracetic acid. From an industrial point of view, although an ion exchange resin (IER) can be moderately costly, its use is economically sound, as the resin can be reused in successive epoxidation batches, besides the obvious advantage that its separation from the process stream represents.

The kinetics and the reaction mechanism of VO and/or FAME epoxidation, without considering all the deleterious reactions (Fig. 1), are well known [6–9]. This paper reports part of our work, currently in progress at INTEC, in regard to a systematic program aimed at evaluating the relative impact of the degradation reactions of the oxirane ring on the yield of the epoxidation process. So far, each of the ring-opening reactions of epoxides of VO using a homogeneous catalyst (sulfuric acid) were analyzed [10,11]. Our strategy is to build up a knowledge basis on the consecutive oxirane ring-opening reactions once the ring has been formed, which in principle can be minimized when IER are used, as we observed in the degradation of the epoxide group with solvated acetic acid [12]. In particular, we report here on the degradation of epoxidized soybean oil (ESBO) with hydrogen peroxide, the essential reagent used to form the peracid.

2. Experimental

2.1. Materials

Crude soybean oil (SBO), kindly provided by Oleaginosa Humboldt (Santa Fe, Arg.), was refined (i.e., degummed, neutralized, bleached and deodorized) in the laboratory and used as a model VO feedstock. Its fatty acid (FA) composition was determined by gas chromatography (GC) after derivatizing the TG into FAME, following a standard procedure [13], and was the following (wt.%): saturated FA, 6.8; oleic acid, 23.5; linoleic acid, 61.2; linolenic acid, 8.5. The iodine value was 137 [14]. Formic acid (acs, 99.8%), benzene (pa) and hydrogen peroxide (50 wt.%) were purchased from Fisher Scientific (Pittsburg, PA). A strongly acidic, gel-type ion exchange resin, Rohm & Haas Co. (Philadelphia, PA, USA) Amberlite IR-120, with a DVB-styrene matrix, 8% crosslinking, d_p (dry) = 215–775 μm (54.5%: <530 μm ; 75.3%: <600 μm ; 94.8%: <670 μm), functionalized with sulfonic groups, was used throughout the work.

2.2. Preparation of the stock of ESBO

The refined soybean oil was epoxidized in depth at low temperature (20–40 $^\circ\text{C}$), with performic acid generated in situ, using benzene as diluent of the organic phase, to minimize ring opening [8]. The molar ratio of hydrogen peroxide/formic acid/SBO unsaturation (double bonds) was 20/2/1. Soybean oil, benzene and formic acid were jointly placed into a well-stirred, round-bottom glass reactor kept at

20 °C. Then, dilute (30 wt.%) hydrogen peroxide was added (also at 20 °C), dropwise, after which the reactor temperature was slowly raised to 40 °C, to complete the reaction. This procedure, which does not require adding any catalyst, demands about 20 h to achieve reaction completion, though. The (experimentally determined) maximal concentration of oxirane groups in this epoxidized soybean oil was 5.9 wt.%, which is equivalent to a content of 0.37 mol of oxirane-oxygen/100 g of ESBO.

2.3. Activation and conditioning of the ion exchange resin

As the IER is commercially available in its sodic form, hydrochloric acid (10 wt.%) was used to activate it, in successive ion-exchange steps (seven in total), with further washing using distilled demineralized water (1:10 wt./wt. IER-to-H₂O) until complete elimination of the residual salinity. Lastly, glacial acetic acid (purity: >99.7 wt.%) was used to substitute water inside the resin.

The exchange capacity of IR-120, as determined by titration using conventional volumetric techniques, was: $[H^+]^0 = 4.507 \text{ meq g}^{-1}$ (dry basis). The dry polymer density, as measured by picnometry using *n*-heptane [15], was 1.437 kg m^{-3} . A portion of the dry resin was crushed and sieved; successive washing and decantation in distilled demineralized water allowed the removal of the undesired fines, adhered to the crushed particles. Three sieved fractions, with nominal diameters 50, 200 and 500 μm , were used to evaluate the possible impact of mass-transfer resistances or protons availability (see below) on the process rate.

2.4. Oxirane ring-opening studies

The stock of ESBO was used to study the opening of the oxirane ring caused by hydrogen peroxide in the presence of

the strongly acidic, heterogeneous catalyst Amberlite IR-120. The preconditioned resin was washed with triple distilled demineralized water until complete elimination of acetic acid and then dried. For each run, aliquots of the IER were mixed with the appropriate amount of an aqueous solution of H₂O₂ and placed into a 3-bore thermostated round-bottom flask, furnished with a reflux condenser and a mechanical stirrer. The mixture was left to stand for 24 h and then the system was heated to working temperature. Next, a suitable volume of ESBO, previously thermostated at the same temperature, was added to the reactor. The reactor temperature was kept to within ± 1 °C. Periodically, samples were taken, and the IER was separated from the liquid phase, which was then thoroughly washed to eliminate acidity and dried using a rotary evaporator, prior to their derivatization and chemical analysis.

A molar excess of hydrogen peroxide with respect to the epoxide groups was always used (e.g., a molar ratio H₂O₂/oxirane = 20 was used in runs 1–5 and 10–12, Table 1). The experimental program included several levels of stirring (1000–1500 rpm), temperature (60–85 °C), hydrogen peroxide concentration (15–45 wt.%), IER amount (2.83–8.49 wt.%, dry basis with respect to the mass of ESBO introduced in the reactor) and resin particle diameter (50–500 μm), as detailed in Table 1.

2.5. Analysis and data processing

Iodine, oxirane and hydroxyl values of the stock of epoxidized soybean oil were analyzed using AOCS recommended practices [14,16,17]. The oxirane ring-opening reaction was followed by GC, using a Shimadzu GC-17ATF unit furnished with a PE-5 (Perkin-Elmer, Norwalk, CT) capillary column: 30 m \times 0.53 mm i.d. \times 1.5 μm film. Analytical conditions were as follows: Split/splitless injector, injector port at 250 °C, FID detector at 270 °C,

Table 1

Reaction conditions and final weight percent of epoxide groups in the organic phase (conversion) in the acid-catalyzed degradation of the oxirane ring of epoxidized soybean oil (ESBO) by H₂O₂ (aq.), using Amberlite IR-120 ion exchange resin as heterogeneous catalyst

Run	Stirring (rpm)	<i>T</i> (°C)	[H ₂ O ₂] ⁰ (wt.%)	Amount of IER (% wt./wt.) ^a	IER particle diameter (μm)	Total duration (min)	Final amount of epoxide groups (wt.%) ^b	Final conversion ^c (%)
1	1000	70	30	2.83	500	360	5.71	3.19
2	1300	70	30	2.83	500	360	5.29	10.28
3	1500	70	30	2.83	500	390	5.09	13.71
4	1500	60	30	2.83	500	1530	4.89	17.12
5	1500	85	30	2.83	500	450	3.67	37.79
6	1500	70	40	2.83	500	330	3.98	32.61
7	1500	70	45	2.83	500	450	2.84	51.93
8	1500	85	20	2.83	500	400	4.07	31.08
9	1500	85	15	2.83	500	400	3.71	37.16
10	1500	70	30	2.83	200	330	3.16	46.48
11	1500	70	30	2.83	50	240	4.52	23.35
12	1500	70	30	8.49	500	660	5.23	11.40

^a Weight percent of the ion exchange resin (IER) with respect to the mass of ESBO introduced in the reactor, dry basis.

^b Final weight percent of epoxide groups oil in the organic phase (%Ep_{final}).

^c Percent conversion of epoxide groups, calculated as: $(\%Ep_{\text{initial}} - \%Ep_{\text{final}}) / \%Ep_{\text{initial}} \times 100$, where %Ep_{initial} stands for the initial weight percent of epoxide groups (%Ep_{initial} was 5.90).

H₂ carrier gas (90 psig, 20 ml/min), and isothermal oven at 200 °C. The response factors were obtained using capillary GC, 99% grade, heptadecanoic acid methyl ester (Sigma–Aldrich, St. Louis, MO) as internal standard. Prior to injection, the dry samples were derivatized to FAME with sodium methoxide. This GC analysis is able to simultaneously discriminate among the fatty acid methyl esters of the saturated and unsaturated carbon chains, as well as their epoxides and glycols [18]. The results shown in Table 1 are the means of three replicates; the coefficients of variation were always less than 6%. Standard deviations in the regression analyses are given for a 95% confidence interval.

3. Results and discussion

To fully take into account the impact of the main process variables on the degradation of the epoxide ring, the experimental program purposely included conditions known to cause extensive ring-opening (Table 1), following the strategy we also applied employing sulfuric acid as homogeneous catalyst in a liquid–liquid reacting system [10]. During said study, a high ratio of the polar (aqueous) to the nonpolar (ESBO) phase, which causes the latter to be dispersed into tiny droplets, was always used. No significant differences were observed whenever the volume ratio was made 1/1 or higher, which implies that under the same operating conditions the dispersity of the organic phase (i.e., the available interfacial area) was such that process was not controlled by liquid–liquid mass transfer. On these grounds, a constant volumetric ratio equal to 25/15 (ml aqueous phase/ml ESBO) was used throughout this work.

The inspection of the time course of the epoxide ring degradation in runs 1–3 in Table 1, where only the stirring rate was changed while keeping the rest of the process variables constant, shows that either 1300 or 1500 rpm gave identical results. In other words, with our experimental set up the reaction rate was no longer controlled by the external mass transfer above 1300 rpm. Nevertheless, mostly for mechanical stability reasons but also to be able to ‘absorb’ possible changes in viscosity or surface tension at high conversions, stirring at 1500 rpm was chosen to perform the study.

Under conventional process conditions the attack of H₂O₂ on the oxirane ring is fairly mild. So, within a sizable portion of the experimental grid, it was statistically undistinguishable (using the integral method of reaction data analysis) the zero-order versus the first-order with respect to the molarity of epoxide, except for high temperature (85 °C), extremely high concentration of H₂O₂ (45 wt.%) or finely divided catalyst (50 μm), where first-order kinetics was frankly observed. Therefore, for kinetic rate constant evaluation first-order kinetics with respect to the epoxide groups was always considered.

The aqueous solution contains water and hydrogen peroxide. Yet, for identical process conditions (viz., pH,

temperature and degree of mixing), the comparative impact of the hydrolysis on the oxirane ring opening is minimal [10]. A (pseudohomogeneous) kinetic rate expression suitable for describing the oxirane ring opening is given by:

$$v = k[\text{H}_2\text{O}_2]^\alpha [\text{Ep}]^\beta, \quad (1)$$

where

$$k_{\text{obs}} = k([\text{H}_2\text{O}_2]^0)^\alpha \quad (2)$$

when an excess of hydrogen peroxide is used.

The effect of process temperature on the reaction rate was evaluated at three different levels, using 30 wt.% H₂O₂. As shown in Fig. 2 (runs 3–5 in Table 1), moderate increases in temperature may lead to severe degradation. After 360 min, the mass percent of remaining epoxide groups was 5.26 (conversion = 4.3%) at 60 °C, decreasing to 4.88 (conversion = 11.24%) at 70 °C and, further, to just 3.72 (conversion = 37.8%) at 85 °C. The calculated value of the reaction rate constant (pseudohomogeneous, normalized by total organic phase volume only) was $k_{\text{obs}}(70\text{ °C}) = 3.37 \pm 0.606 \times 10^{-4} \text{ min}^{-1}$, with an activation energy, E_a , of $99.2 \pm 1.3 \text{ kJ mol}^{-1}$. Using sulfuric acid as homogeneous catalyst the experimental value of E_a was 68 kJ mol^{-1} [10].

As in this three-phase liquid/liquid/solid reacting system the ring-opening catalytic chemistry is *identical* to the one found in two-phase liquid/liquid media using mineral acids; the difference in these experimentally determined E_a are most likely due to the progressive swelling and expansion of the IER at higher temperatures so that, then, more active centers (protons) become available (vide infra).

The impact of the concentration of hydrogen peroxide on the ring-opening reaction was first investigated in the high-range region of the concentration space (runs 3, 6 and 7, Table 1), at 70 °C. The degradation of the oxirane value was greatly accelerated upon using 30 or more wt.% of H₂O₂ (aq.) in the reacting media. As indicated above, a high molar

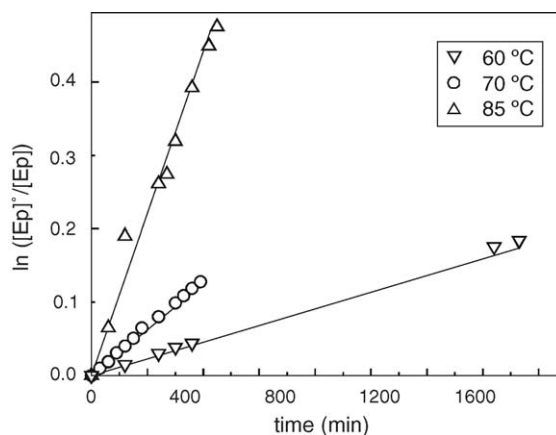


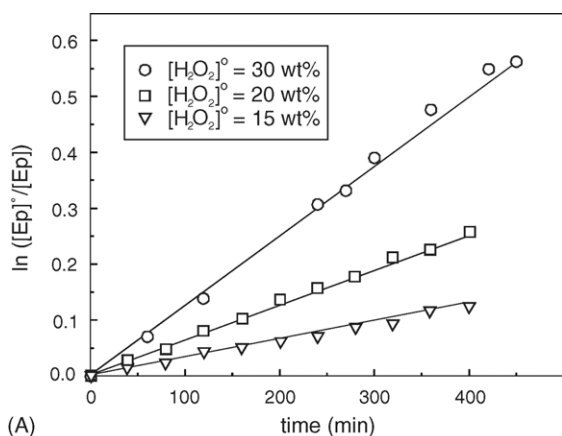
Fig. 2. Effect of reaction temperature in the ring-opening reaction of the oxirane group of epoxidized soybean oil (ESBO) with aqueous hydrogen peroxide using Amberlite IR-120 ($d_p = 500 \mu\text{m}$), 2.83 wt.%, dry basis, with respect to the mass of ESBO (process conditions: 1500 rpm, H₂O₂ (aq.)/ESBO volume ratio = 25/15, [H₂O₂]⁰ = 30 wt.%).

ratio of H_2O_2 to epoxide groups was used in every case, so that the observable (pseudohomogeneous) reaction rate constants, k_{obs} , can straightforwardly account for such effect. Linearizing Eq. (2):

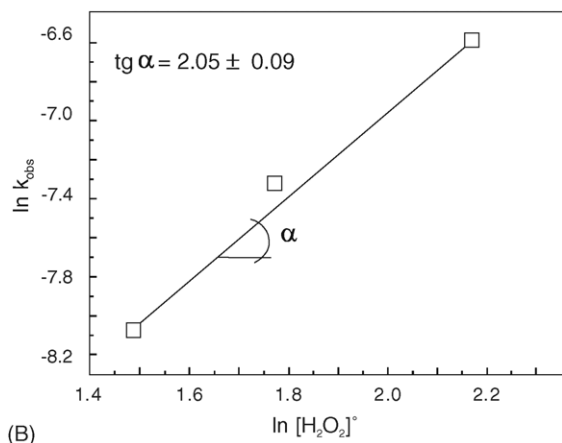
$$\ln k_{\text{obs}} = \ln k + \alpha \ln([\text{H}_2\text{O}_2]^0) \quad (3)$$

The graphical representation of $\ln k_{\text{obs}}$ versus $\ln[\text{H}_2\text{O}_2]^0$ (Eq. (3)) gave, nevertheless, an order of reaction near to 4 (actually, 4.35 ± 0.11) with respect to H_2O_2 , which certainly does not agree with any foreseeable reaction kinetics and indicated, instead, that concentrated hydrogen peroxide was attacking the structure of the resin and, so, exposing an increasing amount of protons from the IER network. This finding is in agreement with literature reports regarding older ion exchange resins [19,20].

A new set of data was obtained under conditions such that the hydrogen peroxide was no longer attacking the physical structure of the polymer (viz., $[\text{H}_2\text{O}_2]^0 < 30$ wt.%), using a somewhat higher reaction temperature (85°C) to keep the total reaction times within reasonable limits (runs 5, 8 and 9 in Table 1, and Fig. 3). Under these conditions, the order of



(A)



(B)

Fig. 3. (A) Effect of the concentration of H_2O_2 (aq.) (moderate concentration range) in the degradation of the oxirane group of ESBO with aqueous hydrogen peroxide using Amberlite IR-120 ($d_p = 500 \mu\text{m}$), 2.83 wt.%, dry basis, with respect to the mass of ESBO (process conditions: 1500 rpm, 85°C , H_2O_2 (aq.)/ESBO volume ratio = 25/15). (B) Order of reaction with respect to the initial concentration of H_2O_2 (aq.) for same process conditions.

reaction obtained from the regression of the data (Eq. (3)) was close to 2 – the expected value – (Fig. 3(B)), as it was also found in the two-phase, liquid–liquid reacting system, using a strong acid as homogenous catalyst [10]. In homogenous systems, this order of reaction is explained by a concerted attack of two molecules of the ring-opening reagent on the epoxide group, as exemplified by Pocker et al. for the oxirane ring opening via hydrolysis [21].

The impact of employing the same amount of the acidic resin, but with different particle sizes, was tested as well. The dry IER was crushed and sieved and three fractions (nominal diameters = 50, 200 and $500 \mu\text{m}$), were pretreated and conditioned as described in the Experimental section, prior to their use in the comparison tests (reactions 3, 10 and 11 in Table 1). Fig. 4 shows that the use of the catalyst in a finely divided form favors the opening of the ring, by attack with hydrogen peroxide, quite significantly. This is because the lower the particle diameter, the higher the surface-to-volume ratio of the solid is and, thus, the higher the amount of active centers (i.e., free protons associated to the sulphonic group) in the external surface of the IER becomes. These free protons, in turn, become available to catalyze the attack on the oxirane groups of the long chain fatty acids of the ESBO, which cannot enter (diffuse) into the gel phase of the resin [5].

Because k is intrinsically volumetric, a more appropriate yardstick parameter must then be used, to explicitly take into account the external surface area of the IER per unit volume of resin beads. Thus, realizing that

$$\begin{aligned} k_{\text{obs}} &= k_s S \rho = k_s \left(\frac{a}{w} \right) \left(\frac{w}{V} \right) = k_s \frac{a_p}{V_p} = k_s (\pi d_p^2) \left(\pi \frac{d_p^3}{6} \right)^{-1} \\ &= k_s \left(\frac{6}{d_p} \right) \end{aligned} \quad (4)$$

it is then sufficient to compare the products of k_{obs} and d_p . Using the nominal diameters of each sieved fraction, 500,

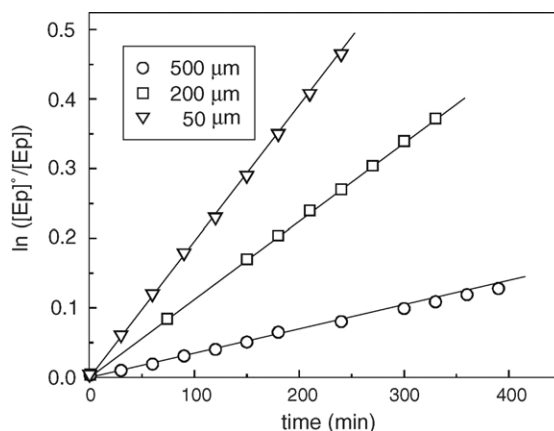


Fig. 4. Effect of particle diameter of Amberlite IR-120 on the oxirane ring-opening observable rate (process conditions: 1500 rpm, 70°C , $[\text{H}_2\text{O}_2]^0 = 30$ wt.%, H_2O_2 (aq.)/ESBO volume ratio = 25/15, 2.83 wt.%, dry basis, of IER with respect to the mass of ESBO).

200 and 50 μm , these products were, respectively, 2.81×10^{-6} , 2.57×10^{-6} and $2.33 \times 10^{-6} \text{ cm min}^{-1}$ (i.e., about equal within the experimental error) which confirms that indeed surface protons (viz., a heterogeneously catalysed reaction) are responsible for the undesired attack on the ring by H_2O_2 .

Finally, the amount of catalyst introduced in the system was tripled (see paired runs 3 and 12, Table 1). The reactivity ratio between this two runs was $k_s(8.49 \text{ wt.}\%)/k_s(2.83 \text{ wt.}\%) = 2.82$, close enough to the theoretical value of three. This experimental result (as those found above when the particle diameter of the resin was changed while keeping the mass constant) can be, again, assigned to the increase in the total amount of external, active surface sites.

A comparison between the observable, pseudohomogeneous reaction rate constants corresponding to the degradation of the epoxide groups by hydrogen peroxide using standard Amberlite IR-120 beads (500 μm , 2.83 wt.%, dry basis, with respect to the amount of ESBO) versus the one resulting from the use of a homogeneous catalyst [10], H_2SO_4 (aq.), upon introducing an equivalent amount of free protons in the reacting systems and for similar process conditions (1500 rpm, 70 °C, H_2O_2 30 wt.%) is most revealing: At pH = 1, $k_{\text{obs}}(\text{H}_2\text{SO}_4)/k_{\text{obs}}(\text{IR-120}) = 5.7 \times 10^3$ (Fig. 5). Truly, the total amount of protons brought into the system by the IER is higher than that resulting from the addition of H_2SO_4 to give pH = 1 in the aqueous phase. This huge difference (and improved performance of the IER with respect to mineral acids) is entirely due to the gel-like nature of Amberlite IR-120, as it was already discussed.

When commercial beads of a strong acid ion exchange resin, such as Amberlite IR-120, are used under typical process conditions (e.g.: $T = 70 \text{ }^\circ\text{C}$, $[\text{H}_2\text{O}_2]^0 = 30 \text{ wt.}\%$) for manufacturing epoxidized vegetable oils in the conventional peracetic acid process, the degradation (opening) of the oxirane ring caused by hydrogen peroxide is minimal. This

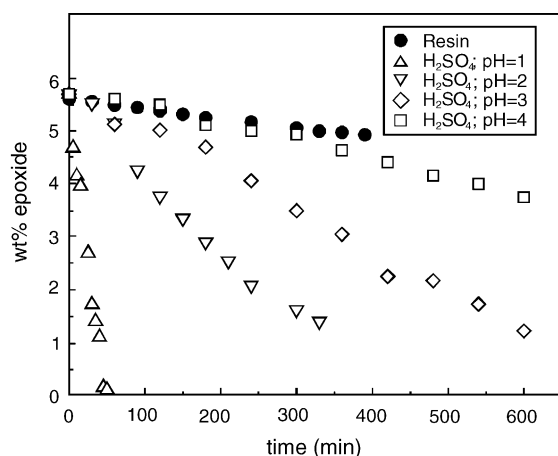


Fig. 5. Comparative degradation of the oxirane ring of ESBO with H_2O_2 (aq.) using Amberlite IR-120 ($d_p = 500 \mu\text{m}$), 2.83 wt.%, dry basis, with respect to the mass of ESBO vs. a homogeneous mineral acid catalyst, H_2SO_4 [10] (process conditions: 1500 rpm, 70 °C, $[\text{H}_2\text{O}_2]^0 = 30 \text{ wt.}\%$).

is the more so since usually the molar excess of hydrogen peroxide is around 10% (i.e., the molar ratio $\text{H}_2\text{O}_2/\text{double bonds}$ is 1.1/1) [5–7], instead of the high molar ratios employed in this work. Nevertheless, in processes in which packed beds are used to have a high concentration of resin in the reacting media and, so, high per-pass conversion (with or without recycling of reactants), one has also (inevitably) a high external surface area of catalyst per unit volume of reactor, even if coarser particles were used to minimize pressure drop. In these cases, higher degradation of the oxirane ring becomes unavoidable.

4. Conclusions

The ring opening with hydrogen peroxide was found to be first-order with respect to the molar concentration of epoxide groups [$k_{\text{obs}}(70 \text{ }^\circ\text{C}) = 3.37 \pm 0.606 \times 10^{-4} \text{ min}^{-1}$; $E_a = 99.2 \pm 1.3 \text{ kJ mol}^{-1}$] and second-order with respect to H_2O_2 . Using IR-120 the degradation increases either by adding more mass of catalyst and/or by reducing its particle diameter while keeping the total mass constant, as both situations lead to higher external (exposed) area of the acidic catalyst (i.e., free protons associated to the sulfonic group) in the outer surface of the ion exchange resins beads. These free protons, in turn, become available to catalyse the attack on the oxirane groups of the long chain fatty acids, which cannot enter (diffuse) into the gel phase of the resin. Despite the unavoidable presence of surface-exposed protons, the degradation can be reduced by several orders of magnitude – for similar process conditions – by using this type of heterogeneous catalysts instead of mineral acids.

Even though the use of this type of ion exchange resins does not completely eliminate the attack on the oxirane group by H_2O_2 during the epoxidation process, this deleterious reaction only seems to be important under extreme process conditions (viz., high temperature, excessive concentration of H_2O_2 and/or high $\text{H}_2\text{O}_2/\text{double bonds}$ molar ratios), which are not commonly found in industrial practice.

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