Alejandrina Campanella
Miguel A. Baltanás

INTEC, Santa Fé, Argentina

Degradation of the oxirane ring of epoxidized vegetable oils with solvated acetic acid using cation-exchange resins

Vegetable oil epoxides (oxiranes) are customarily manufactured using acetic acid (AA) as oxygen carrier and reactant source, in aqueous/organic media. Further attack of the oxirane ring by AA proceeds in this acid-catalyzed process, lowering yield. We report a study of the degradation of the ring by water-solvated AA, using Amberlite IR-120 as heterogeneous catalyst. The ring opening with solvated AA was found to be first order with respect to the concentration of epoxide groups and second order with respect to the carboxylic acid, with an activation energy of 58.7 ± 0.42 kJ mol^{-1}. This value is within the range found in liquid-liquid systems (51.3–66.3 kJ mol^{-1}). Yet, using IR-120, the degradation increases identically either by adding more mass of catalyst 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) on the outer surface of the ion exchange resin beads. These free protons, in turn, become available to catalyze 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.

Keywords: Epoxidized vegetable oils, ion exchange resin, solvated acetic acid, oxirane ring opening.

1 Introduction

In recent decades much emphasis has been placed on the utilization of renewable resources as an alternative to fossil raw materials [1]. Thanks to the advancement of oleochemical technology, a wide range of plasticizers and stabilizers of PVC and related resins, lubricant additives, components of thermosetting plastics, *etc*., obtained from epoxidized vegetable oils (VO) or their derivatives (*e.g.*, fatty acid methyl esters – FAME) are now available [2]. In process terms, it is most desirable to seek the highest possible concentration of the reactive oxirane group in the molecules of these oleochemical intermediates (*i.e.*, the highest 'oxirane index') in their manufacture, and therefore, medium or highly unsaturated VO (from, *e.g.,* soybean or linseed) are frequently chosen.

Correspondence: *Miguel A. Baltanás*, Instituto de Desarrollo Tecnológico para la Industria Química (INTEC), Universidad Nacional del Litoral and Consejo Nacional de Investigaciones Científicas y Técnicas, Güemes 3450, S3000GLN Santa Fé, Argentina. Phone: +54-342-455-9175, Fax: +54-342-455-0944, e-mail: tderliq@ceride.gov.ar

The epoxidation of VO or FAME with percarboxylic acids, commonly prepared *in situ,* is the preferred route in industrial scale, where peracetic acid is, most generally, the reactant of choice [3–8]. The process usually requires an acidic catalyst, and although low-cost mineral acids have been employed traditionally, they often hinder the achievement of high yields, owing to oxirane ring opening caused by deleterious consecutive reactions. Then, the use of a heterogeneous catalyst capable of preventing the access of the oxirane group to the active catalytic sites has been a strategy largely pursued.

Acidic ion exchange resins (IER) allow, in principle, the isolation of strong acid sites from the liquid mixture, together with their easy separation. In these *in situ* processes, three phases are simultaneously present in the reacting system: (1) an aqueous phase, immiscible with (2) the organic phase and (3) the solid catalyst (which is hydrophilic). Hydrogen peroxide – an oxidant – is made to react with acetic acid (AA) – an oxygen carrier – in the aqueous phase, to give peracetic acid (PAA), inside the resin beads. Peracetic acid attacks the double bonds of the unsaturated VO in the organic phase to form the oxi-

rane ring, giving acetic acid as the co-product, which returns to the aqueous phase to close the sequence. A succint diagram, without taking into consideration the undesired consecutive reactions due to the attack (ring opening) by AA, PAA, H_2O and H_2O_2, is given in Fig. 1.
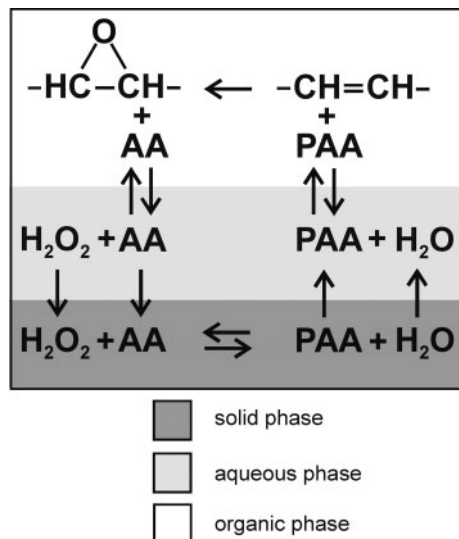

Fig 1. (■ give legend please ■)

Until recently, the only oxirane ring-opening reaction studies related to middle- or long-chain epoxides obtained from VO and/or FAME addressed the impact of carboxylic acids (formic, acetic or heptanoic), pure or in organic phase exclusively [8–11]. Under realistic process conditions, though, the reactants and intermediate products are solvated. Recently, we began a systematic study of all the consecutive degradation reactions acting on the oxirane ring of epoxidized soybean oil (ESBO) in the two-phase aqueous/organic liquid reacting media, using sulfuric acid as homogeneous catalyst. Among these, the opening of the oxirane ring with water-solvated acetic acid emerged as the most relevant [12]. Besides, in this process, this oxygen carrier was always present in high concentration in the system, resembling a phase-transfer catalyst in this respect.

A standard, sulfonic (strongly acidic) gel-type ion exchange resin, Amberlite IR-120, was chosen for this work, which was aimed at studying the specific impact of the attack of solvated AA on the epoxide ring already formed. IR-120 is readily available in the market, and it is known to yield epoxidized oils with good oxirane values. The functionalized resin is hydrophilic, allowing only water, AA and H_2O_2 into the gel phase; peracetic acid is produced inside the resin, by the sulfonic groups. Unlike macroreticular resin beads, the gel structure of IR-120 does not let large molecules such as triglycerides or

FAME move into the polymer network, and thus, a low oxirane ring opening is expected. Furthermore, Amberlite IR-120 allows an almost complete elimination of VO unsaturation at a relatively low reaction temperature and with a moderate reaction time. Also, the cross-linking and the absence of metal impurities favor the efficiency and conversion of the PAA. From an industrial point of view, although an ion exchange resin can be moderately costly, its use is economically sound, as the resin can be reused in successive epoxidation batches, aside from the obvious advantage represented by its separation from the process stream.

2 Materials and methods

2.1 Materials

Crude soybean oil (SBO), kindly provided by *Oleaginosa Humboldt* (Santa Fé, Argentina), was refined (*i.e.,* degummed, neutralized, bleached, and deodorized) in the laboratory. Its fatty acid (FA) composition was determined by gas liquid chromatography (GLC) after derivatizing the triglycerides 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 and glacial acetic acids (acs, 99.8%), benzene (pa) and hydrogen peroxide (50 wt-%) were purchased from *Fisher Scientific* (Pittsburg, PA, USA). A strongly acidic, gel-type ion exchange resin (*Rohm & Haas* Co., Philadelphia, PA, USA), Amberlite IR-120, with a DVB-styrene matrix, 8% cross-linking, 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 °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 dropwise (also at 20 °C), after which the reactor temperature was slowly raised to 40 °C to complete the reaction. This procedure, which does not require adding any catalyst, takes about 20 h to achieve reaction completion. The (experimentally determined) concentration of oxirane groups in this epoxidized soybean oil was 5.50 wt-%, which is equivalent to a content of 0.34 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 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/H_2O) until complete elimination of the residual salinity. Lastly, glacial acetic acid was used to substitute the water inside the resin.

The exchange capacity of IR-120, as determined by titration using conventional volumetric techniques, was $[H^+]° = 4.507$ meq g^{-1} (dry basis). The dry polymer density, as measured by picometry using *n*-heptane, was 1.437 kg m^{-3} [15]. A portion of the dry resin was crushed and sieved; successive washing and decantation in distilled demineralized water allowed the removal of fines adhered to the crushed particles. Three sieved fractions, with nominal diameters of 50, 200 and 500 μm, were used to evaluate the possible impact of mass transfer resistances or proton 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 the solvated AA (which is partitioned between the aqueous and the organic phase), in the presence of the strongly acidic, heterogeneous cata-

lyst Amberlite IR-120. For each run, aliquots of the preconditioned IER were mixed with the appropriate amount of an aqueous solution of AA 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. 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 derivatization and chemical analysis.

A molar excess of AA (aq.) with respect to the epoxide groups was always used (*e.g.,* a molar ratio AA/oxirane = 20 was employed in runs 1–4 and 8–10; Tab. 1). The experimental program included several levels of stirring (1000–1500 rpm), temperature (60–80 °C), acetic acid concentration in the reacting system (4–14 M), 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 Tab. 1.

2.5 Analyses 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 GLC, using a Shimadzu GC-

Tab. 1. Reaction conditions and final weight percent of epoxide groups in the organic phase (conversion) in the acid-catalyzed opening of the oxirane ring of epoxidized soybean oil (ESBO) by water-solvated acetic acid (AA), using Amberlite IR-120 ion exchange resin as heterogeneous catalyst.

Run	Stirring [rpm]	T [°C]	$C_{AA}°$ [M]	Amount of IER [% wt/wt][†]	IER particle diameter [μm]	Total duration [min]	Final amount of epoxide groups [wt-%][‡]	Final % conversion[#]
1	1000	70	12	2.83	500	180	2.35	57.30
2	1500	70	12	2.83	500	180	2.35	57.21
3	1500	60	12	2.83	500	180	3.44	37.51
4	1500	80	12	2.83	500	180	1.13	79.40
5	1500	70	14	2.83	500	180	1.26	77.01
6	1500	70	8	2.83	500	180	3.05	44.57
7	1500	70	4	2.83	500	180	4.65	15.38
8	1500	70	12	8.49	500	180	0.42	92.42
9	1500	70	12	2.83	200	180	0.73	86.73
10	1500	70	12	2.83	50	60	0.48	91.28

[†] Weight percent of the ion exchange resin (IER) with respect to the mass of ESBO introduced into the reactor, dry basis.
[‡] Final weight percent of epoxide groups of oil in the organic phase (% Ep$_{final}$).
[#] Percent conversion of epoxide groups, calculated as: $[(\% \, Ep_{initial} - \% \, Ep_{final})/\% \, Ep_{initial}] \times 100$, where % Ep$_{initial}$ stands for the initial weight percent of epoxide groups (the % Ep$_{initial}$ was 5.50).

17ATF unit furnished with a PE-5 (*Perkin-Elmer*, Norwalk, CT, USA) capillary column: 30 m × 0.53 mm i.d. × 1.5 μm film. Analytical conditions were as follows: Split/splitless injector, injector port at 250 °C, FID detector at 270 °C, H_2 carrier gas (90 psig, 20 mL min^{-1}), and isothermal oven at 200 °C. The response factors were obtained using capillary CG, 99% grade, heptadecanoic acid methyl ester (*Sigma-Aldrich*, St. Louis, MO, USA) as internal standard. Prior to injection, the dry samples were derivatized to FAME with sodium methoxide. This GLC 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 Tab. 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, on purpose, included conditions known to cause extensive ring opening (Tab. 1), following the strategy we also applied employing sulfuric acid as homogeneous catalyst in a liquid-liquid reacting system [12]. 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. On these grounds, a constant volumetric ratio equal to 72/15 (mL aqueous phase/mL ESBO) was used throughout this work.

The inspection of the time course of the epoxide ring degradation in runs 1 and 2 in Tab. 1, where only the stirring rate was changed while keeping the rest of the process variables constant, shows that 1000 and 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 1000 rpm. Nevertheless, mostly for reasons of mechanical stability, but also to be able to 'absorb' possible changes in viscosity or surface tension at high conversion, stirring at 1500 rpm was chosen to perform the study.

A pseudohomogeneous kinetic rate expression suitable for describing the attack of acetic acid on the oxirane ring is given by:

$$v = kC_{AA}^{\alpha}C_{ep}^{\beta} \tag{1}$$

where

$$k_{obs} = (C_{AA}^{o})^{\alpha} \tag{2}$$

when an excess of AA is used. Under the latter conditions, the reaction was indeed found to be first order with respect to the epoxide groups (Figs. 1A, 2A).
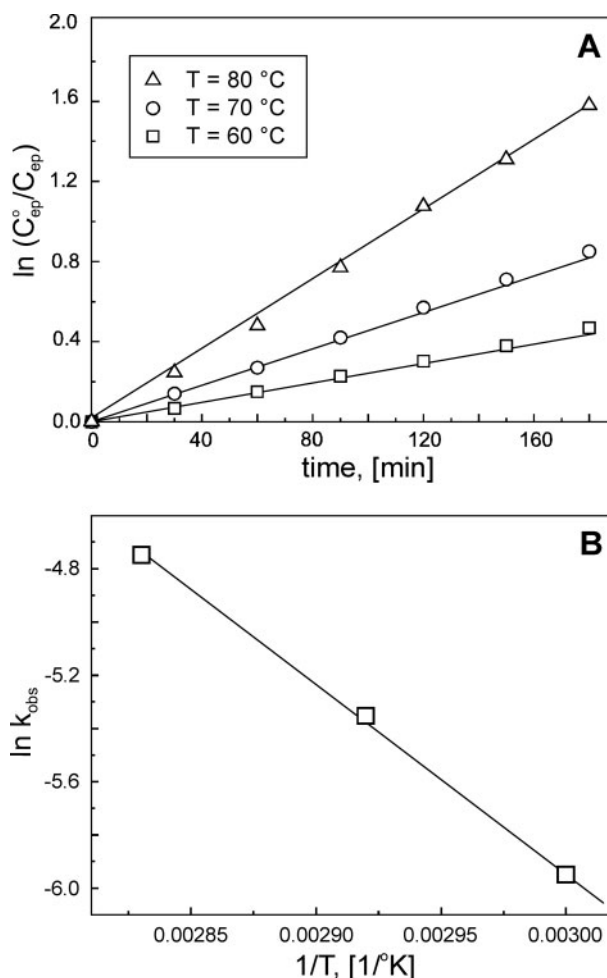

Fig. 2. (**A**) Effect of reaction temperature and (**B**) ln k_{obs} *vs.* 1/T on the ring-opening reaction of the oxirane group of ESBO with solvated acetic acid, AA, using Amberlite IR-120 (d_p = 500 μm), 2.83 wt-% – dry basis – with respect to the mass of ESBO (process conditions: 1500 rpm, initial concentration of AA in the reacting system, C_{AA}^{o} = 12 M).

The effect of the reaction temperature was studied between 60 and 80 °C (runs 2–4 in Tab. 1), avoiding IER softening, higher thermal exposure. For these experimental conditions, the calculated reaction rate constant at 70 °C, using Eqs. (1) and (2), was k = 3.28 ± 0.065 × 10^{-5} L^2 mol^{-2} min^{-1}, with an activation energy E_a = 58.68 ± 0.42 kJ mol^{-1}. The oxirane ring-opening reactions are irreversible, and so they are always favored by temperature rises. The value of E_a is within the range of the activation energy found in liquid-liquid systems by *Zaher* et al. (66.30 kJ mol^{-1} – using glacial AA) [9] and

the calculated one by us in our study of the opening of the oxirane ring with solvated acetic acid employing sulfuric acid as homogeneous catalyst, 51.32 kJ mol^{-1} [12].

This side reaction is known to be highly dependent on the concentration of the carboxylic acid in the system. To predict the order of reaction with respect to AA, a set of values of k_{obs} were obtained at 70 °C, using a wide range of concentrations of acetic acid: 4, 8, 12 and 14 M (runs 2, 5–7 in Tab. 1, and Fig. 3A). Linearizing Eq. (2):

$$\ln k_{obs} = \ln k + \alpha \ln C_{AA}^o \qquad (3)$$

the reaction was found to be second order with respect to the acid (Fig. 3B), just like it was reported in homogeneous systems, using both neat or solvated AA [9, 12].
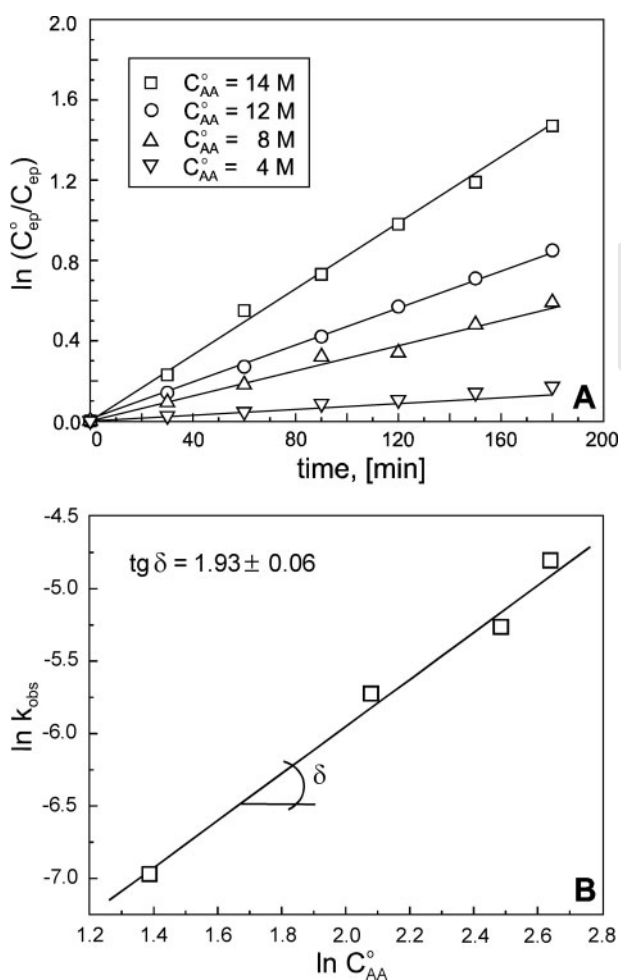

Fig. 3. Effect of the initial concentration of acetic acid in the reacting system, $C_{AA}°$, on the degradation of the oxirane ring of ESBO with solvated AA, using Amberlite IR-120 ($d_p = 500$ μm), 2.83 wt-% – dry basis – with respect to the mass of ESBO (process conditions: 1500 rpm, 70 °C). (**A**) Order of reaction with respect to the epoxide groups; (**B**) order of reaction with respect to $C_{AA}°$ (see text).

To specifically assess whether this side reaction is homogeneous or not, the impact of employing the same amount of the acidic resin, but with different particle sizes, was tested. The dry IER was crushed and sieved, and three fractions (nominal diameters = 500, 200 and 50 μm) were pretreated and conditioned as described in Sect. 2, prior to their use in comparison tests, using 2.83 wt-% of resin and $C_{AA}° = 12$ M, at 70 °C (reactions 2, 9 and 10 in Tab. 1). The calculated values of the reaction rate constants, k_{obs}, were $47.5 \pm 0.94 \times 10^{-4}$, $111 \pm 5.42 \times 10^{-4}$ and $404 \pm 1.26 \times 10^{-4}$ min^{-1}, respectively, indicating that the use of the catalyst in a finely divided form quite significantly favors the opening of the ring, *via* attack with acetic acid. 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 resulting active centers (*i.e.*, free protons associated to the sulfonic group) on the external surface of the IER. 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 [3].

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, $a = 6/d_p$ (cm^2 cm^{-3}). Thus, realizing that:

$$k_{obs} = k_s a = k_s \cdot 6/d_p, \qquad (4)$$

it is then sufficient to compare the products of k_{obs} and d_p. Using the nominal diameters of each sieved fraction, 500, 200 and 50 μm, these products were, respectively, 3.96×10^{-5}, 3.70×10^{-5} and 3.36×10^{-5} cm min^{-1} (*i.e.*, about equal within the experimental error), which confirms that indeed surface protons (*viz.*, a heterogeneously catalyzed reaction) are responsible for the undesired attack on the ring by AA. Along this line of thought, the impact of the amount of catalyst introduced in the reactor was considered as well, by triplicating the mass of catalyst (runs 2 and 8, Tab. 1). The ratio between the calculated values of the reaction rate constants, k_{obs} (8.49 wt-%) *vs*. k_{obs} (2.83 wt-%), was 2.92, close enough to the theoretical value of 3.

Fig. 4 shows the time course of the degradation reaction of the epoxide groups by solvated acetic acid upon using 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, H$_2$SO$_4$ (aq.), under similar operating conditions (1500 rpm; 70 °C; $C_{AA}° = 12$ M), but for moderate pH values. Certainly, the total amount of protons brought into the system by the IER is higher than that resulting from the addition of
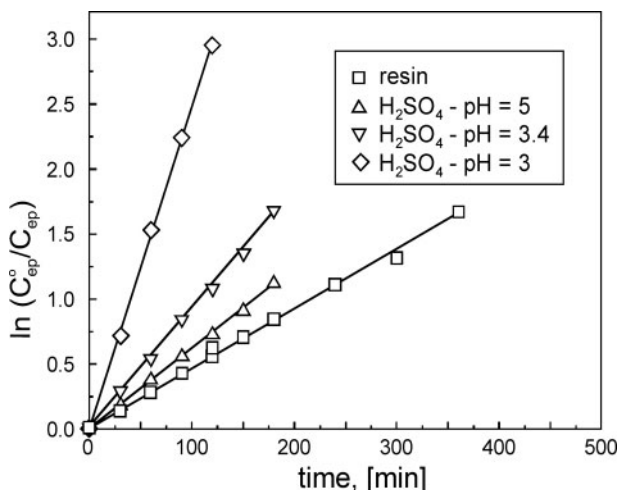
Fig. 4. Comparative degradation of the oxirane ring of ESBO with solvated acetic acid, using Amberlite IR-120 (d_p = 500 μm), 2.83 wt-% – dry basis – with respect to the mass of ESBO *vs.* a homogeneous mineral acid catalyst, H_2SO_4 [12]. (Process conditions: 1500 rpm, 70 °C, $C_{AA}°$ = 12 M).

H_2SO_4 to give pH = 1 in the aqueous phase, but nevertheless, the ensuing ring opening becomes far more restricted. 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.

The analysis of these experimental results indicates that in this three-phase liquid/liquid/solid reacting system, the catalytic chemistry is identical to the one observed in two-phase liquid/liquid media using mineral acids. Even though it is not possible to completely suppress the degradation of the oxirane ring as a consequence of the presence of free protons on the catalyst surface, such degradation is reduced by several orders of magnitude. Nevertheless, if packed beds of IER were used to have a high concentration of resin in the reacting media and, therefore, high per-pass conversion (with or without recycling of reactants), one would also inevitably have 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 would become unavoidable.

A final consideration is noteworthy. As it was mentioned in the introduction section, our group has studied the relative impact of each of the degradation reactions of the oxirane ring of epoxidized vegetable oils under conditions found in industrial practice (*i.e.*, in solvated media), using a homogenous catalyst [12] and, in particular, the consecutive reaction owing to the presence of the main reac-

tant, PAA. The kinetic rate constant of the latter reaction was found to be about twenty-fold larger than that of acetic acid, but fortunately, PAA is always present in very low amounts in the reacting system [8, 19]. Conversely, under process conditions, acetic acid is constantly regenerated in the reacting system, so that its concentration is kept about equal over time. Hence, one can safely conclude that the most important degradation reaction of the epoxide ring – under practical conditions – is the opening with acetic acid.

Acknowledgements

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