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Degradation of the oxirane ring of epoxidized vegetable oils in a liquid–liquid–solid heterogeneous reaction system

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Abstract

The main oxirane-ring opening reactions that occur during the manufacture of epoxidized vegetable oils using a strongly acidic, gel-type ion exchange resin (IER) (Amberlite IR-120, 8% crosslinking) were analyzed. By using a heterogeneous liquid–liquid–solid model, the reactivity on each phase was individually assessed, taking into account each transport step as well as the relevant partition equilibria.

The combined results on the attack onto the oxirane ring of epoxidized vegetable oils by either hydrogen peroxide (H_2O_2) or solvated acetic acid (AA) indicate that under 'regular' process conditions these attacks proceed in the kinetic regime; that is, they are not mass-transfer controlled. The study indicated that most of the degradation occurs on the catalyst and, also, confirmed that the *external* surface protons of the IER are the main responsibles of the deleterious degradation of the oxirane ring as, in both cases, the degradation rate was directly proportional to the available external area of the catalyst.

Keywords: Oxirane ring opening; Liquid–liquid–solid reacting systems; Ion exchange resins

1. Introduction

Epoxidized vegetable oils are well established among the available plasticizers for manufacturing low cost, PVC-derived industrial items and household plasticware. Nowadays, they have also been recognized as an excellent intermediate towards the synthesis of biodegradable lubricants. The epoxidation of vegetable oils and/or their fatty acid methyl esters (FAME) with percarboxylic acids is the preferred route in industrial scale. Peracetic acid, prepared in situ using hydrogen peroxide (H_2O_2) as the primary source of oxygen and aqueous acetic acid (AA) as the oxygen carrier between the aqueous and the oil phases, is – most generally – the reactant of choice [1–5]. The process usually requires an acidic catalyst and although traditionally low cost mineral acids have been employed, they often hinder the achievement of high yields, owing to oxirane ring opening caused by deleterious consecutive reactions. The use of a heterogeneous catalyst capable of preventing the access of the oxirane group to the active catalytic sites has been, then, a strategy largely pursued.

In this regard, we recently began to study and evaluate (using a pseudohomogeneous model as a first step), the relative importance of each of the consecutive degradation reactions that occur during the epoxidation of soybean oil (SBO) with peracetic acid, when a sulfonic (strongly acidic), gel-type ion exchange resin (IER), such as Amberlite IR-120, is used [6,7]. This functionalized resin is hydrophilic, allowing only water, acetic acid and hydrogen peroxide into the gel phase; peracetic acid is produced inside and at the surface of the resin by sulfonic acid groups. Unlike macroreticular resin beads, the gel structure of IR-120 does not let large molecules such as triglycerides or FAME into the polymer network. Hence, a low oxirane-ring opening is expected as, in principle (and unlike with conventional heterogeneous catalysts), the acid-catalyzed oxirane degradation reactions can only occur on the external surface of the catalyst.

Then, the liquid–liquid–polymer catalyst system is truly heterogeneous: for the epoxide groups (Ep) to be degraded by the catalyst, they must cross the liquid–liquid interface as well as the liquid–solid interface (see Fig. 1). The occurrence of further, homogeneous degradation reactions makes the complete

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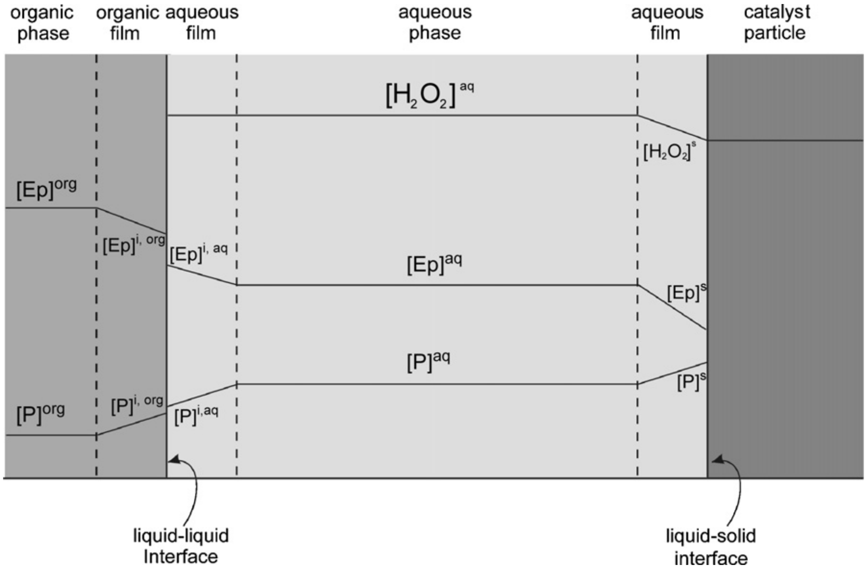

Fig. 1. Concentration profiles of the reactants and product in the liquid–liquid–solid reacting system under study, as exemplified by the degradation of the oxirane ring of epoxidized soybean oil by H_2O_2 (aq), using Amberlite IR 120 ion exchange resin (IER) as heterogeneous catalyst.

analyses somewhat more involved but, nevertheless, manageable. Thus, this work presents a detailed re-analysis on the case of two reactions occurring on these liquid–liquid–solid reacting system (the only truly relevant in the vegetable oil epoxidation process [8]): the opening of the oxirane ring with hydrogen peroxide and with solvated acetic acid, taking into account each of the transport and intrinsic kinetic steps in each phase. Separate series of experiments were conducted, using either aqueous H_2O_2 or solvated acetic acid.

2. Experimental

2.1. Materials

Crude soybean oil was refined (i.e., degummed, neutralized, bleached and deodorized) in the laboratory. Its fatty acid (FA) composition, as determined by GLC [9], was the following (wt.%): saturated FA (C16 + C18): 15.1, oleic acid: 21.5, linoleic acid: 55.7; linolenic acid: 7.7. The iodine value was 137.

Glacial acetic acid (acs, 99.8%), formic acid (acs, 99.8%), benzene (pa) and hydrogen peroxide (50 wt.%) were purchased from Fisher Scientific (Pittsburg, PA, USA). Heptadecanoic acid methyl ester (capillary CG, 99%) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Amberlite IR-120 (Rohm & Haas), a strongly acidic, gel-type ion exchange resin with a DVB-styrene matrix and 8% crosslinking, functionalized with sulfonic groups, $d_p(\text{dry}) = 215–775\ \mu\text{m}$ ($54.5\% < 530\ \mu\text{m}$; $75.3\% < 600\ \mu\text{m}$; $94.8\% < 670\ \mu\text{m}$), was used throughout the work.

2.2. Preparation of epoxidized soybean oil (ESBO) stocks

The refined soybean oil was epoxidized in depth at low temperature (293–313 K) with performic acid generated in situ, using benzene as diluent of the organic phase, to minimize ring opening [5]. This procedure demands about 22 h to achieve reaction completion, though. The molar ratio of hydrogen peroxide/formic acid/SBO unsaturation (double bonds) was 20/2/1 and 500 ml of benzene per mol of double bond were added as well. The SBO, benzene and formic acid were jointly placed into a well-stirred, round-bottom glass reactor kept at 293 K. Then, dilute (30 wt.%) hydrogen peroxide (also at 293 K) was added dropwise, after which the reactor temperature was slowly raised to 313 K, to complete the reaction.

Two different ESBO stocks were prepared. The final content of epoxy oxygen in the first stock, used for the study of the degradation of the oxirane ring with hydrogen peroxide was 5.9 wt.%, while in the second ESBO stock (which was used to study the attack by solvated acetic acid) it was 5.5 wt.%. These figures are equivalent to a content of 0.36 and 0.34 kmol of oxygen/100 kg of ESBO, respectively. The final iodine values of said stocks were 3.6 and 2.2, respectively, while their final hydroxyl values were 0.1 and 0.5.

2.3. Determination of distribution constants

The distribution constants, or – more appropriately – the equilibrium molar ratios of the refined soybean oil and the ESBO in pure water and in aqueous solutions of hydrogen peroxide, were determined at 333–358 K, with and without H_2SO_4 added to the aqueous phase (pH 1).

On each test, 5 g of the soybean oil, or ESBO, were placed together with 20 g of water, or H_2O_2 (aq), in an erlenmeyer. The mixtures were equilibrated to the desired temperature, under constant stirring, during 4 h. Then, they were left to stand for at least 1 h until complete separation of the phases was achieved. Afterwards, an aliquot of the aqueous phase was carefully taken, using a syringe and a 0.2 μm teflon pre-filter. The determination of the distribution constants was done by measuring the amount of total organic carbon (TOC) in the aqueous phase,