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Selective epoxidation of soybean oil with performic acid catalyzed by acidic ionic exchange resins

Abstract: This work studied the epoxidation of soybean oil with aqueous hydrogen peroxide and formic acid, in the presence of acidic ionic exchange resins as catalysts. Amberlyst 16 was found to actively and highly selectively promote this reaction, and it also had good resistance to thermal and physical degradation. These properties also allow this resin to be used in continuous processes. A detailed study was carried out to determine the best operating conditions for the epoxidation of soybean oil in semibatch reactors, and preliminary epoxidation runs were performed in a continuous packed bed tubular reactor.

Keywords: acid resins; epoxidation; soybean oil.

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1 Introduction

The epoxidation of vegetable oil is an important reaction, because the epoxides obtained from these renewable resources have a wide range of applications as plasticizers and stabilizers of polyvinyl chloride (PVC) [1].

On the industrial scale, this reaction is currently carried out using a peracid, which is formed *in situ* by the reaction between a carboxylic acid and hydrogen peroxide [2], in the presence of soluble mineral acid catalysts such as sulfuric or phosphoric acid. Hydrogen peroxide reacts with a carboxylic acid (formic or acetic acid) when both are dissolved in the aqueous phase, yielding the peracid. The peracid then migrates from the aqueous to the oil phase and then quickly reacts with the double bonds of the oil molecules, giving rise to the oxirane products.

The carboxylic acid that is also produced in this reaction, then returns to the aqueous phase, restarting the catalytic cycle [3].

Mass and heat transfer limitations may impose several process constraints, because the epoxidation reaction occurs in a biphasic system and is highly exothermic [4].

One of the disadvantages of the process described above is related to the use of soluble mineral acids as catalysts, because they promote side reactions, such as oxirane ring opening, resulting in a dramatic decrease in selectivity. Moreover, the use of a homogenous acid catalyst requires neutralization with a base, such as NaOH, at the end of the reaction. However, an alkaline environment favors the hydrolysis of triglycerides, forming soaps that have a negative effect on the quality of the desired product.

The use of acidic ionic exchange resins (AIER) as heterogeneous catalysts was found to minimize the side reactions and improve the selectivity [5].

Acid resins are characterized by the presence of strong isolated acid sites located inside the pore structure, which are not easily accessible to the bulky oil molecules containing oxirane rings, and are therefore protected from reaction with protons. However, hydrogen peroxide and formic or acetic acids easily react with the acid sites, yielding the corresponding peracid. This product migrates from the aqueous to the oil phase, where it promptly reacts with double bonds, giving rise to epoxide rings. These epoxide rings are not easily opened by an acid attack, because the oil molecules do not enter the pores of the resin. For this reason, the reaction remains highly selective to epoxides.

Several polystyrene sulfonic resins with different amounts of divinylbenzene as a cross-linking agent were tested in the epoxidation of vegetable oils [6, 7]. The results showed that the resins with lower degrees of cross-linking were more porous, or swelled sufficiently to allow the oil to contact the sulfonic acid groups. Resins containing 2%–4% divinylbenzene yielded a higher amount of byproduct than the resins cross-linked with 8% or more divinylbenzene [6]. For this reason, the most commonly

used sulfonic acid resin is Amberlite IR-120 (8% divinyl-benzene content), which exhibits a high selectivity for oil epoxidation and has been extensively used in the literature [8].

Previous studies using acidic resins as catalysts, reported that peracetic acid was the preferred peracid, but performic acid is more frequently used in industrial scale epoxidation using homogenous mineral acid catalysts, because it is more active than peracetic acid and because its complete decomposition at the end of the process means that it does not have to be recovered [9]. Resin studies have chosen peracetic acid due to its selectivity compared with performic acid in the epoxidation of vegetable oil using acid resin catalysts [10].

The use of Amberlite IR-120 with peracetic acid involves some disadvantages, such as the very large amount of resin required (typically 22 wt% based on the amount of oil) [11], due to the low reaction rate. Moreover, it is difficult to use gel-type resins, such as Amberlite IR-120, in continuous packed bed reactors, because its osmotic swelling can cause significant mechanical stress, resulting in resin breakage and problems with pressure drops [11].

The drawback of reactor plugging can be solved using a catalyst such as a macroreticular sulfonic resin, which maintains its shape in the reaction environment [11]. Clearly, the problem of the low reaction rate observed with performic acid compared with peracetic acid must be solved by choosing the right resin and the right reaction conditions to obtain both high activity and selectivity.

The main objective of this work is to solve the problems discussed above and to demonstrate the possibility of using acidic resins in continuous packed bed reactors to improve the productivity of the soybean oil epoxidation process. This investigation suggests that Amberlyst 16 could be the optimal choice for this reaction, which had not been previously reported as a catalyst for this reaction. Amberlyst 16 is attractive, due to its strong mechanical resistance (no swelling phenomena were observed, avoiding the reactor plugging problem experienced by Amberlite IR-120) and to the high selectivity and high conversion (in contrast to the results for Amberlyst 15). These two important characteristics make Amberlyst 16 highly attractive for the development of a continuous epoxidation process.

Several acidic resins were tested in this work, and Amberlyst 16 was selected as the best catalyst. The effects of temperature, catalyst amount, and reagent ratio on the epoxidation reaction using Amberlyst 16 catalyst were studied in a semibatch reactor. Finally, the performance of Amberlyst 16 was verified in a continuous packed bed reactor.

2 Materials and methods

2.1 Materials

Amberlyst IR-120, Amberlyst 15, and Amberlyst 16 were purchased from Rohm and Haas (Rohm and Haas Italia S.R.L., Milano, Italy) (the main characteristics of the resins are reported in Table 1). Hydrogen peroxide (60 wt% in water) was kindly provided by Solvay Italia. Soybean oil with an iodine number of 128 (128 g_I consumed per 100 g_{sample}) was purchased in a local food store, and its fatty acid composition was determined by gas-chromatographic analysis as (%, w/w): palmitic=11, stearic=4, oleic=23, linoleic=56, linolenic=5, and others=1. Formic acid (96%, w/w), sulfuric acid (97%, w/w), and all other reagents were supplied by Sigma Aldrich (Milano, Italy) at the highest level of purity available (>99.9%) and were used as received without further purification.

2.2 Experimental setup

Soybean oil epoxidation reactions were carried out in a cylindrical jacketed glass reactor (500 ml) with three necks, equipped with a thermocouple and a reflux condenser. The oxidant was fed into the reactor by a syringe pump at a constant flow rate of 0.3 cm^3/min. The reaction mixture was mechanically stirred at 750 rpm. Temperature was controlled by re-circulating thermostated water inside the reactor jacket. The temperatures of the water entering and exiting the reactor jacket and of the reaction mixture were continuously monitored and recorded using a data acquisition module purchased from the National Instruments Co.

The tubular reactor consisted of a jacketed glass tubular reactor filled with a homogeneous blend of glass spheres and resin, with an interstitial volume of 4.84 cm^3.

Table 1 Resin properties.

Resin	Pore Diameter (Å)[a]	Specific area (m^2/g)[a]	Acidity meqH⁺g⁻¹[b]
Amberlite IR- 120	–	–	4.69
Amberlyst 15	300	53	4.52
Amberlyst 16	250	30	3.90

[a]Data furnished by Rohm and Haas Italia S.R.L.
[b]The number of Brønsted acid sites was determined by ion exchange with 1.0 M NaCl (10 ml/g catalyst) and titration of the residual solution with 0.01 M NaOH.

2.3 Experimental procedure

2.3.1 Semibatch epoxidation experiments

For each epoxidation reaction, a known amount of soybean oil was introduced into the reactor and a fixed amount of catalyst was added, with catalyst loading expressed as the weight percent in reference to the amount of oil, ranging from 2.5 wt% to 10 wt%. Then, the mixture was continuously stirred and heated until it reached the reaction temperature (range: 45°C to 65°C). A mixture of formic acid (carboxylic acid to double bond molar ratio ranging from 0.18 to 0.72) and hydrogen peroxide (1.1 per mole of double bonds) was then added in a continuous flow through a syringe pump at a rate of 0.3 cm^3/min. After the oxidant mixture addition was complete, the reaction was continued for the desired duration. The course of the reaction was followed by withdrawing samples at regular time intervals. The collected samples were quenched and centrifuged to separate the organic phase from the aqueous phase. Before the analysis, the samples were washed with water until they were acid free and analyzed for oxirane number and iodine number according to the analytical methods reported in the literature [12, 13] (see section 2.4).

All experimental runs performed in the semibatch reactor using these reaction conditions are reported in Table 2.

2.3.2 Continuous epoxidation experiments

For each experimental run performed in the continuous tubular reactor, a preheated stream of oil was fed to the reactor containing the catalyst, while a mixture of hydrogen peroxide and formic acid at room temperature was mixed with hot oil at the inlet of the continuous reactor. Periodically, samples were withdrawn from the reactor outlet, rapidly cooled, pretreated, and analyzed in the same way as described for the semibatch runs. Table 3 provides a list of the runs performed in the continuous reactor.

2.4 Analytical methods

Iodine number was determined using a Wijs solution according to the Wijs method [13]. The oxirane number was determined by potentiometric titration with perchloric acid in glacial acetic acid, using cetyl trimethylammonium bromide (CTAB, 0.1 м in acetic acid) as the reagent [14].

The soybean oil used in the epoxidation reaction was analyzed by gas chromatography to determine the fatty acid composition according to the EN 14103 method [15], using a GC (HP5890) with an EC-WAX column (30 m, 0.5 mm ID, 0.25 μm film thickness, with polyethylene glycol as the stationary phase). A methyl heptadecanoate solution was used as an internal standard. The iodine number found by gas-chromatographic analysis agrees with the number determined by titration, with a difference of <6%.

From the iodine number, the double bond conversion was determined as:

$$Conversion = \frac{[\text{Iodine number}]_{soybean\,oil} - [\text{Iodine number}]_{sample}}{[\text{Iodine number}]_{soybean\,oil}} \times 100$$

Table 2 List of experimental runs performed in the fed-batch reactor.

Run	Catalyst	T(°C)	Catalyst (wt%)	Molar ratios C=C/HCOOH/H$_2$O$_2$
1	–	55	–	1/0.36/1.10
2	Amberlite IR 120	55	5.00	1/0.36/1.10
3	Amberlyst 15	55	5.00	1/0.36/1.10
4	Amberlyst 16	55	5.00	1/0.36/1.10
5	Amberlyst 16	55	2.50	1/0.36/1.10
6	Amberlyst 16	55	1.25	1/0.36/1.10
7	Amberlyst 16	55	2.50	1/0.36/1.10
8	Amberlyst 16	45	2.50	1/0.36/1.10
9	Amberlyst 16	65	2.50	1/0.36/1.10
10	Amberlyst 16	55	2.50	1/0.18/1.10
11	Amberlyst 16	55	2.50	1/0.72/1.10

Table 3 List of experimental runs performed in the tubular packed bed continuous reactor. All experiments used an oxidant mixture consisting of 15.71 g H$_2$O$_2$ (60 wt%) and 4.20 g of formic acid.

Run	Catalyst loading (g)	Temperature (g)	Q$_{oil}$ (cm^3/min)	Q$_{oxidant}$ (cm^3/min)	Residence time (s)	Double bonds conversion (%)	Selectivity (%)
1	2.2	60	4	4	36	30.1	80.1
2	2.2	60	4	2	48	22.2	81.1
3	2.2	69	4	2	48	31.8	81.4

The selectivity to oxirane was determined as:

$$Selectivity = \frac{[\text{Oxirane number}]_{sample} \times 253.8}{([\text{Iodine number}]\text{soybean oil} - [\text{Iodine number}]_{sample}) \times 16} \times 100$$

The analytical errors of the iodine and oxirane numbers were determined by repeating the entire analysis under the same conditions and calculating the standard deviation σ and the coefficient of variation CV (% ratio of the standard deviation to the average value). The following results were obtained in this way: iodine number: σ=0.3, CV=0.8%; oxirane number: σ=0.04, CV=0.7%.

3 Results and discussion

Figure 1 compares the performances of two macroreticular resins (Amberlyst 15, run 3; Amberlyst 16, run 4) and a gel type resin (Amberlite IR-120, run 2) in soybean oil epoxidation. Figure 1 also reports the conversion and selectivity obtained in the absence of a catalyst for comparison. While performic acid has an intrinsic activity, the use of catalysts significantly improved the reaction rate.

All the resins tested here exhibited roughly the same activity, which is expected, because all three resins have similar numbers of acid sites (see Table 1). However, these results confirm that Amberlite IR-120 achieves the best selectivity at high conversion (>90%). The selectivity of Amberlyst 15 is comparable with that obtained with sulfuric acid [4], while Amberlyst 16 performs better, with a selectivity of more than 75% at a conversion of 98%.

These results can be explained by considering the different degrees of cross-linking of the resins studied here.

The results are in agreement with the data reported by Rios et al. [11], who found that when using peracetic acid as the oxidant and toluene as the solvent, the selectivity to epoxide increases when the degree of cross-linking is increased from 2% to 8%. Further increases in the degree of cross-linking lead to a decrease in sensitivity (20%, Amberlyst 15). This result was attributed to the fact that higher degrees of cross-linking reduce the pore size of the resins, reducing the possibility of contact between the epoxide and the acid sites. However, when the degree of cross-linking is increased, a macroreticular structure is formed (as in the case of Amberlyst 15), yielding a resin with a high external surface area on which epoxides can be protonated and opened with water to form glycols [11]. While Amberlyst 16 has a macroreticular structure, it achieves better selectivity than Amberlyst 15, because of its lower external surface area (see Table 1).

While Amberlite IR-120 is the best catalyst in terms of both activity and selectivity, it swells to a significant degree after contact with the reagents used in this reaction (see Figure 2A).

Consequently, it is difficult to recover this catalyst, and it is not suitable for continuous operation. In contrast, Amberlyst 15 and Amberlyst 16 maintain their granular shape during and after the reaction (see Figure 2B), and therefore can be easily recovered under semibatch conditions, or used in a packed bed continuous reactor without problems.

In conclusion, the screening analysis demonstrated that Amberlyst 16 was active, sufficiently selective, and dimensionally stable. For this reason, we have focused our attention on the study of Amberlyst 16 as a catalyst for the epoxidation of soybean oil, in particular on evaluating
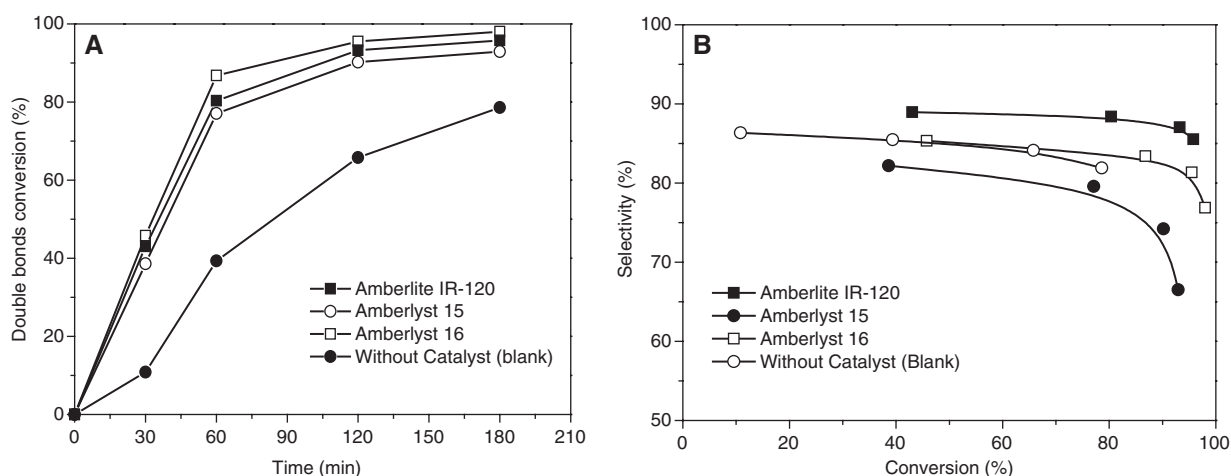

Figure 1 Performances of the various sulfonic acid resins (Amberlite IR-120: run2; Amberlyst 16: run 4; Amberlyst 15: run 3) in double bond conversion (A) and selectivity to oxirane (B). The blank run is reported for comparison (run 1). The reaction conditions are listed in Table 2.
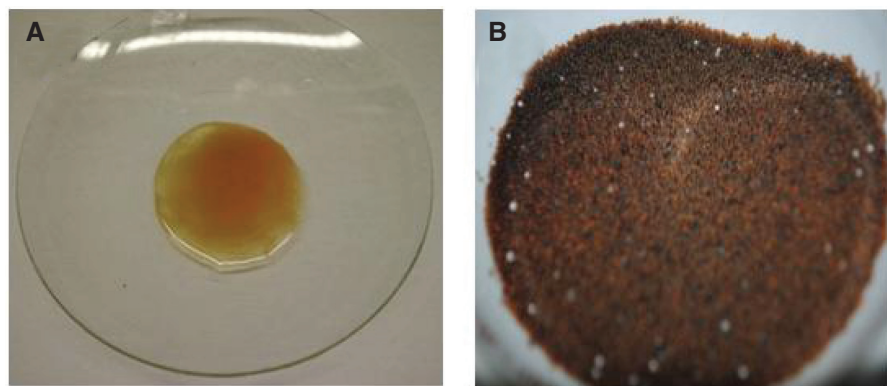
Figure 2 Images of the resins after the epoxidation run: (A) Amberlite IR-120; (B) Amberlyst 16.

the effects of various reaction parameters to optimize the operating conditions.

3.1 Effect of resin (Amberlyst 16) loading

The effect of the resin concentration on the epoxidation reaction performed in semibatch conditions was investigated by using 2.5 wt% (run 6), 5 wt% (run 5), and 10 wt% (run 4) of Amberlyst 16, while keeping all other reaction conditions constant (see Table 2). The increase in catalyst loading from 2.5 wt% to 5 wt% increases the initial epoxidation rate, while increasing the resin concentration from 5 wt% to 10 wt% did not affect the reaction rate (see Figure 3A). This behavior is probably due to the mass transfer limitation occurring at high resin concentrations. The reactive system under investigation is complex, including mass transfer between the two liquid phases and between the solid resin and the bulk liquid. Partitioning equilibria of various components are present, altering the composition of the two liquid phases. Moreover, the aqueous phase is preferentially adsorbed by the resin, which could strongly influence the reaction rate. Finally, external (liquid to solid) and internal diffusion should be taken into account to construct a complete and exhaustive interpretation of the reactive system. These phenomena can exert a different influence on the reaction system, depending on the amount of resin catalyst in the reactor. Due to this complexity, a more rigorous approach can be developed, as reported in our previous work [16].

However, the catalyst amount did not influence the selectivity (see Figure 3B). Thus, the optimal catalyst loading was found to be 5 wt% under the experimental conditions tested here.

3.2 Effect of temperature

Experiments were conducted at different temperatures (65°C, run 9; 55°C, run 7; 45°C, run 8) to investigate the
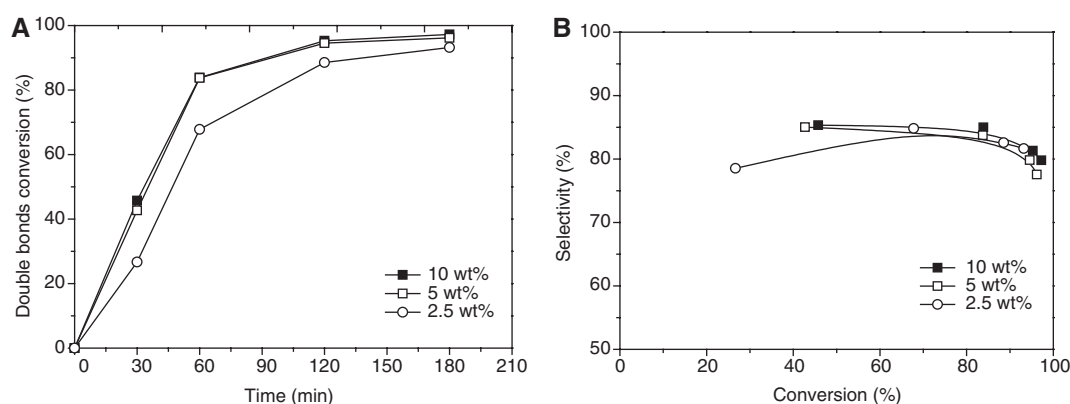

Figure 3 Effect of resin loading (2.5 wt%, run 6; 5 wt%, run 5; 10 wt%, run 4) on double bond conversion (A) and selectivity to oxirane (B). The other reaction conditions are disclosed in Table 2.

influence of this parameter on both activity and selectivity. The reaction rate increases with temperature (see Figure 4A). For the experiments at 65°C and 55°C, differences in the reaction rate can only be appreciated at high conversion. This behavior can again be explained in terms of the mass transfer limitation. Clearly, this limitation only operates at low conversions where the reaction rates are higher. In contrast, the selectivity slightly decreases as the temperature increases over the range examined here (see Figure 4B).

3.3 Effect of the formic acid to unsaturated fatty acid molar ratio

The influence of formic acid concentration was investigated by performing experiments at three different formic acid/initial double bond molar ratios: 0.18, run 10; 0.36, run 7; 0.72, run 11.

The reaction rate increased as the formic acid/initial double bond molar ratio was increased from 0.18 to 0.36, but a further increase to 0.72 did not further influence the intervention of the mass transfer limitation (see Figure 5A). The initial reaction rates for all the experiments that we considered to be affected by mass transfer limitations due to high temperature, high catalyst concentration, or high formic acid/initial double bond molar ratios (see Figures 3A, 4A, and 5A) are quite similar, yielding a conversion of approximately 42% in 30 min in all cases.

The increase in the formic acid concentration has a detrimental effect on the selectivity for the oxirane ring, as the acid promotes the hydrolysis of the epoxides, thereby decreasing its final yield (see Figure 5B).

As shown in Figure 5, the acid to unsaturated fatty acid molar ratio of 0.36 seems optimal, as it allows for a high epoxidation rate and a ring opening reaction rate comparable with the experiments at lower formic acid concentrations.
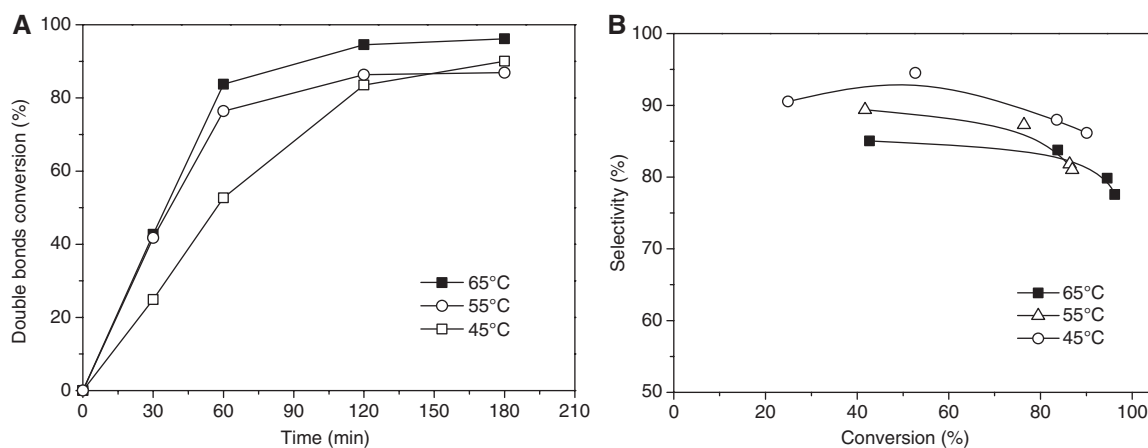

Figure 4 Effect of temperature (65°C, run 9; 55°C, run 7; 45°C, run 8) on double bond conversion (A) and selectivity to epoxides (B). The other reaction conditions are listed in Table 2.
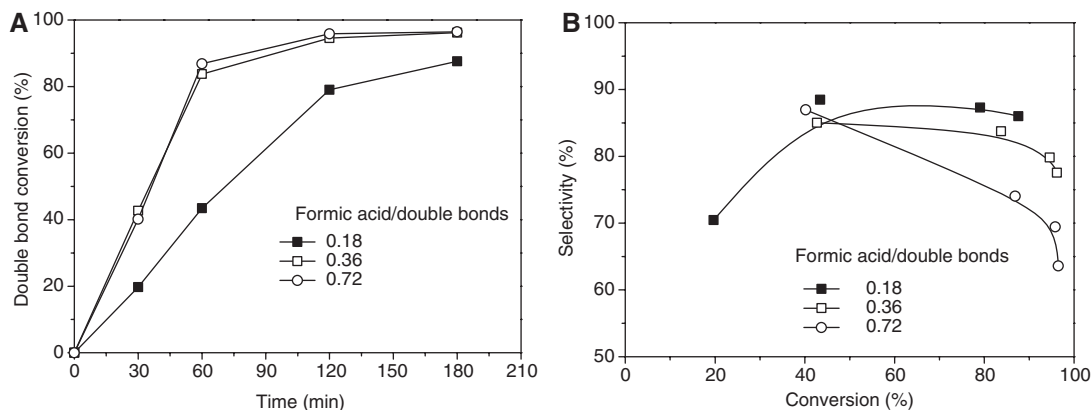

Figure 5 Conversion of double bonds and selectivity to epoxides as a function of formic acid concentration (formic acid/initial double bond molar ratio: 0.18, run 10; 0.36, run 7; 0.72, run 11). The other reaction conditions are reported in Table 2.
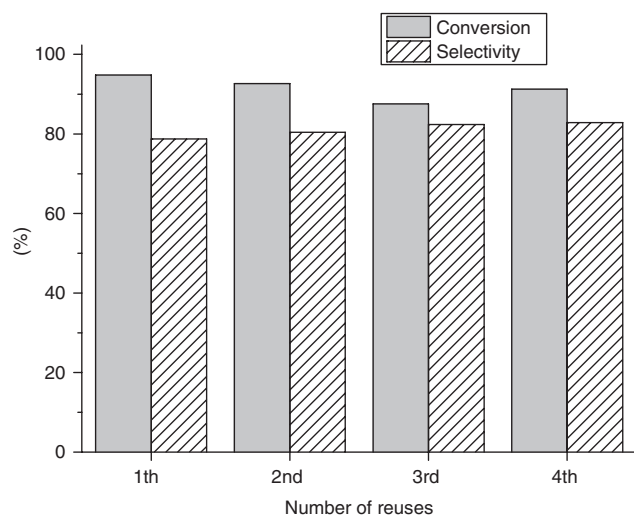
Figure 6 Double bond conversion and selectivity to epoxides as a function of the number of uses of Amberlyst 16. The reaction conditions are 5 wt% catalyst, 1/0.36/1.10 double bond/formic acid/ hydrogen peroxide molar ratios, T=55°C, reaction time=120 min.

3.4 Reuse of Amberlyst 16

The stability of the Amberlyst 16 resin was studied by repeating the epoxidation reaction several times using the same catalyst. The reaction was carried out as described above. At the end of the reaction, the catalyst was removed by filtration, air-dried, and reused. The reusability of the catalyst was evaluated by performing five sequential experiments with the same catalyst, with filtration occurring after each experiment.

The re-use tests for Amberlyst 16 (see Figure 6) indicate that this catalyst can be reused up to five times without significant losses in conversion or epoxide selectivity.

These results clearly indicate that Amberlyst 16 is a highly promising heterogeneous catalyst for oil epoxidation that can be recycled without any significant loss of activity. Moreover, the resin can also be used in a packed bed continuous reactor.

3.5 Preliminary continuous epoxidation runs

To increase the production of epoxidized soybean oil, satisfy market demand, and reduce the risk of explosion through enhanced control, it is imperative to shift from batch to continuous operation [17, 18].

In the case of the heterogeneous catalyst (Amberlite IR-120), the cascade process was reported to be the most promising catalyst for continuous operations [6]. Stirred reactors are placed in series in this procedure [6], all the reagents are fed to the first reactor, and the reaction mixture overflows into the other reactors over time. However, the continuous tubular reactor achieves better process economics. To evaluate the possibility of using Amberlyst 16 in continuous tubular reactors, some preliminary epoxidation reactions have been performed in jacketed glass tubular reactors described above.

Table 3 reports the results of the continuous reactor experiments, together with the operating conditions. The results are highly promising, considering the very high selectivity achieved (approximately 80%) and the good resistance of the resin. The conversion can be increased by scaling up the reactor.

4 Conclusions

The soybean oil epoxidation process with minimal oxirane cleavage was optimized using hydrogen peroxide, formic acid, and Amberlyst 16 catalyst. In a semibatch reactor, the reaction was optimal at a temperature of approximately 55°C, with a formic acid to unsaturated fatty acid molar ratio of 0.36 and a catalyst loading of 5 wt% with respect to the amount of oil. Under these conditions, 98% of double bond conversion was achieved, with selectivity to oxirane >80%, after only 3 h of reaction.

The macroreticular structure of Amberlyst 16 is resistant to physical degradation, enabling its use in a continuous process. Preliminary continuous runs were promising in terms of both activity and selectivity.

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