Abstract: Epoxidation of castor oil was carried out in benzene with in situ formed peroxoacetic acid in the presence of different catalysts: sulphuric acid and an ion exchange resin. The effects of reaction variables and the conditions for obtaining a maximum of epoxide yield were determined. The relative yield of epoxidized oil of 78.32% and selectivity of 0.85 were achieved at 50°C after 7h when 0.5 mol of acetic acid and 1.5 mol of 30% aqueous hydrogen peroxide per mol of unsaturation of oil dissolved in the equivalent quantity of benzene in the presence of 15%wt of Amberlite were used.

Key Words: In situ Epoxidation / Castor Oil / Reaction Variables

1. INTRODUCTION

Epoxidation of vegetable oils (triglycerides) is commercially important reaction since epoxides obtained from these renewable resources have wide application; they are used directly as plasticizers and polymer stabilizers, as paint and coating components, and lubricants, but also as intermediates for alcohols, glycols, alkanolamines, and polymers (such as polyurethanes, polyesters, and epoxy resins) production due to the high reactivity of the epoxy ring. On an industrial scale, the epoxidation of vegetable oils, i.e. their unsaturated triglycerides, is currently carried out with a peroxoacrylic acids, such as peroxoacetic and peroxoformic acid, usually obtained in situ through the acid catalyzed peroxidation of the respective organic acids with hydrogen peroxide. Soluble mineral acids, such as sulphuric acid, or acidic cation exchange resins of sulphonated polystyrene types, such as Amberlite, are commonly used as catalysts for this reaction [1,2].

Castor oil is, as many other vegetable oils, a very valuable renewable resource for the chemical industry. Like other vegetable oils, castor oil is triacylglycerol composed of various fatty acids and glycerol. The fatty acids consist of up to 90% ricinoleic acid (12-hydroxy-9-octadecenoic acid) and varying small amounts of different saturated and unsaturated fatty acids. Due to the high content of ricinoleic acid, castor oil is very valuable. The ester linkages, double bonds and hydroxyl groups in this acid provide reaction sites for the preparation of many useful derivatives, among which is epoxidized castor oil [2,3].

The objective of this work was to find the conditions for obtaining the maximum epoxy yield of epoxidation of castor oil with peroxoacetic acid formed in situ in the presence of the homogeneous (sulphuric acid) catalyst, in one case, and the heterogeneous (cationic ion exchange resin) catalyst, in another case. The effect of following reaction variables on the epoxidation was studied: molar ratio of the reactants (unsaturation of oil:acetic acid:hydrogen peroxide), temperature, the type of catalyst and catalyst concentration, as well as the possibility of reusing the ion exchange resin.

2. EXPERIMENTAL PROCEDURES

2.1. Materials

Castor oil with an iodine number of 81.5 was provided by Duga Co. Cationic ion exchange resin Amberlite IR-120 from Rohm&Hass Co. was used in its acid form. Sulfuric acid (96%), glacial acetic acid, 30% (w/w) solution of hydrogen peroxide, analytic grade benzene, sodium sulfate, diethyl ether, pyridine, and HCl were purchased from J.T.Backer.

2.2. Epoxidation of castor oil

The epoxidation method reported in our previous paper [4] was applied in the present work. The oil was epoxidized with in situ formed peroxoacetic acid.

When sulfuric acid was used as catalyst, castor oil was dissolved in benzene and glacial acetic acid before being introduced into a three-neck glass reactor equipped with magnetic stirrer, thermometer, reflux condenser and dropping funnel. Reactor was placed in water bath. Reaction mixture was heated up to 30°C. At that temperature sulphuric acid and H₂O₂ were added dropwise within 1 hour. Reaction mixture was then heated up to desired temperature which was held until epoxidation was done. The temperature was kept to within ±0.5°C and the stirring speed was constant (1000 rpm). The reaction was followed by withdrawing and analyzing 5 mL samples of the reaction mixture after
defined time intervals. After cooling the sample, oil and water phases were separated. An oil phase sample was used for further analysis. It was firstly dissolved in ether, then washed with water (30 °C) few times in order to remove acid, and dried by adding anhydrous Na2SO4. After filtration, ether, benzene and water were evaporated on 3-4 kPa and 60°C. Sample was then analyzed for iodine number and epoxy oxygen content.

Unlike sulfuric acid, activated ion exchange resin was added to the reactor before reactants. Apparatus and the epoxidation procedure, as well as oil phase sample preparation and analysis, were the same as it is described above.

Epoxidation was also catalyzed by regenerated ion exchange resin. Regeneration of used resin, previously separated from reaction mixture, washed with water and ether, and dried, was done by activation with HCl solution (7.5%). The solution was applied until effluent concentration was equated with the influent one. Then, the resin was washed with water. Disappearance of Cl- ions was detected by titration with 0.1 M AgNO3 in the presence of K2CrO4 as indicator. An extra amount of about 10% wt of fresh catalyst was added to regenerated catalyst to compensate regeneration losses.

2.3. Characterization of samples

The extent of epoxidation was measured by titration and Fourier Transform Infrared Spectroscopy (ATR-FT-IR). The Hanus method for the iodine number [5] and the standard HBr-acetic acid method [6] for the epoxy oxygen content were applied. A FT-IR Thermo Electron Corp. spectrophotometer, model Nicolet 5700, was used to follow the disappearance of double bonds and the formation of epoxy groups in oil. Spectra were performed in the 4000-400 cm−1 range, with 64 scans and a resolution of 4 cm−1.

3. RESULTS AND DISCUSSION

Variations of the iodine value (IN) and epoxy oxygen content (EO) with reaction time (t) for in situ epoxidation of castor oil (CO) with peroxyacetic acid are displayed via kinetic curves for each investigated parameter.

Besides titration methods, the characterization of oil phase samples was carried out by interpreting wave bands of FT-IR spectra. FT-IR spectrum of epoxidized castor oil (Figure 1) has bands attributable to hydroxyl group (3467 cm−1), as well as to ester group assigned to C=O (1737 cm−1) and to C-O-C (1163 cm−1). Typical asymmetric and symmetric vibrations of CH2 group were observed at 2927 and 2855 cm−1, respectively. Band at 3009 cm−1 was attributed to vibration of -CH=CH- group and its intensity decreases with extent of epoxidation. The absorptions that appeared as specific doublet at 843 cm−1 and 824 cm−1 indicate epoxy group. The doublet was chosen for measuring of epoxy oxygen content while band at 3009 cm−1 was used as measurement of unsaturation (iodine number).

Due to high viscosity caused by intermolecular hydrogen bonds formed between hydroxyl groups of ricinoleic acid, the epoxidation of castor oil is better to be performed in the presence of an inert solvent which, by reducing viscosity of the reaction mixture, enhances better phase contact. Solvent also diminishes negative influence of acid catalyst since it reduces side reactions of epoxy rings cleavage especially at higher temperatures [2]. In our work benzene was used as solvent with CO:benzene weight ration 1:1 for all synthesis.

3.1. Epoxidation in the presence of sulfuric acid

Epoxidation of castor oil in benzene catalyzed by mineral acid was firstly done with 0.5 mol of CH3COOH and 1.1 mol of H2O2 per mol of double bonds of castor oil and 2% wt (regarding acetic acid and hydrogen peroxide) H2SO4 (50%) at 50°C. Sulphuric acid was poured into the reaction mixture prior its pre-heating and addition of hydrogen peroxide. After one hour, reaction mixture completely polymerized. It probably happened under influence of mineral acid on specific structure of ricinoleic acid glyceride. In order to prevent polymerization, reaction parameters were changed.

When concentration of H2O2 was increased to 1.5 mol per mol of double bonds alongside decreasing of temperature to 40°C, polymerization occurred after 2 hours. Then, under the same conditions, sulfuric acid was differently introduced into the reaction mixture: instead of being added to reactor before, it was added dropwise simultaneously with hydrogen peroxide. Polymerization was not prevented, but time until it occurred was prolonged to 4 hours.

Maximum relative epoxy yield (REY) of 31.5% was, however, reached after 6 hours when 30% sulfuric acid was added dropwise simultaneously with hydrogen peroxide at 50°C. Selectivity (SE) of the reaction was 0.39. After 6 hours, yield of epoxide was decreasing and the reaction mixture completely polymerizes after 8 hours (Figure 2).

Because of a low epoxy yield reached in the presence of mineral acid as catalyst, in a second attempt in situ epoxidation of castor oil was catalyzed by an ion exchange resin.
In situ epoxidation of castor oil in benzene with 0.5 mol of CH₃COOH and 1.5 mol of H₂O₂ (30%) per mol of double bonds of oil in the presence of 2% wt sulfuric acid (30%) at 50°C

3.2. Epoxidation in the presence of ion exchange resin

Cationic ion exchange resin has the same effect as an inert solvent allowing high selectivity of in situ epoxidation of castor oil, and it offers some advantages over the homogenous acid catalyst with respect to corrosion, and product recovery [2]. Therefore, effects of reaction parameters on epoxidation were investigated in the presence of the Amberlite IR-120 as an ion exchange catalyst.

3.2.1 Effect of temperature

The effect of temperature on epoxidation was examined by carrying it out at 30, 50 and 75°C (Figure 3). Increment of temperature had a favorable effect on shortening of a reaction time for reaching the same epoxy yield. However, epoxy yield did not increase with increasing temperature. For example, maximum epoxy oxygen content (EOexp) at 75°C reached after 7 hours was 3.75%. Relative epoxy yield (REY) for epoxy oxygen content of 3.75% is 76.69%, since REY is ratio between measured epoxy oxygen content (EOexp) and theoretical maximum epoxy oxygen content (EOth) calculated on the basis of initial iodine number (IN₀) (Table 1).

Maximum epoxy oxygen content at 50ºC reached after 8 hours was 3.81%, meaning that relative epoxy yield is 77.91%. Epoxy yield was found to decrease with increasing temperature above 50ºC due to more intensive epoxy rings cleavage. Selectivity (SE), a measure of the extent of side reactions occurring during epoxidation, was 0.68 at 30°C, 0.85 at 50 and 0.84 at 75°C (Table 1). Results showed that yields of side reaction products after 8 hours for 75°C, 50°C and 30°C were 17%, 15% and 13%, respectively. In the Figure 3 is obvious that epoxidation rate increases with temperature, as well as epoxy yield, but to some extent. Since at 50°C was reached the maximum REY, this value of temperature is chosen for further investigations of epoxidation parameters.

Besides 1.5, the influence of 1.1 mol of H₂O₂ (30%) per mol of double bonds on in situ epoxidation of castor oil was studied (Figure 4). Maximum relative epoxide yields (REY) were reached for both concentrations after the same reaction time of 9 hours. Higher REY was obtained for 1.5 mol of H₂O₂ used per mol of double bonds of oil, exactly 73.82%, which is 4.16% higher than for applied lower quantity of H₂O₂. Selectivity for both H₂O₂ concentrations was the same: 0.86 (Table 1).

Maximum relative yield of epoxide (REY) for applied 10% wt of resin was 77.91%. That was 5.25% higher yield than those obtained when 5% wt of resin was used for epoxidation, and only 0.52% lower than yield reached with 15% wt of resin. For both resin concentrations, 10% and 15% wt, the selectivity (SE) was 0.85, but the time necessary to reach maximum epoxy yield was longer when 10% wt resin was used. From economic point of view 10% wt of Amberlite is recommendable concentration of catalyst for epoxidation.
3.2.4 Effect of recycling the catalyst

A deactivation of an ion exchange resin was examined in order to consider the possibility of its reusing. Reactions of epoxidation were done with molar ratio: unsaturation of oil:CH₃COOH:H₂O₂=1:0.5:1.5 in the presence of 10% wt Amberlite in benzene at 50°C.

Results for first, second and fourth run were shown in Figure 6 and Table 1. Maximum relative epoxy yield decreased with number of resin reuse, while time to gain it was prolonged due to decrease of epoxidation rate. For fourth use of regenerated catalyst the REY was 3.3% lower than those reached at first use. Selectivity also decreased with the number of resin reuse from 0.85 to 0.84 and 0.82 for first, second and fourth use, respectively. Since difference between these yields is lower than tolerance of 5%, it is possible to conclude that resin may be used at least four times when it is regenerated between syntheses. Unfortunately, a considerable catalyst loss occurred during regeneration due to conglomeration of the resin, even when huge amount of solvent was used.

Conversion of double bonds (X), relative epoxy yield (REY) and selectivity (SE) of conducted synthesis (IER) of epoxidized castor oil when molar ratio of the reactants (unsaturation of castor oil:acetic acid:hydrogen peroxide) was 1:0.5:1.1 (IER1) and 1:0.5:1.5 (IER2-IER8), are presented in Table 1.

<table>
<thead>
<tr>
<th>Synth. No.</th>
<th>Amberlite (wt. %)</th>
<th>T (°C)</th>
<th>t (h)</th>
<th>X (%)</th>
<th>REY (%)</th>
<th>SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>IER1</td>
<td>5</td>
<td>50</td>
<td>9</td>
<td>83.2</td>
<td>70.75</td>
<td>0.86</td>
</tr>
<tr>
<td>IER2</td>
<td>5</td>
<td>50</td>
<td>9</td>
<td>85.8</td>
<td>73.82</td>
<td>0.86</td>
</tr>
<tr>
<td>IER3</td>
<td>10</td>
<td>50</td>
<td>8</td>
<td>91.3</td>
<td>77.91</td>
<td>0.85</td>
</tr>
<tr>
<td>IER4</td>
<td>15</td>
<td>50</td>
<td>7</td>
<td>92.8</td>
<td>78.32</td>
<td>0.85</td>
</tr>
<tr>
<td>IER5</td>
<td>10</td>
<td>75</td>
<td>7</td>
<td>89.7</td>
<td>76.69</td>
<td>0.84</td>
</tr>
<tr>
<td>IER6</td>
<td>10</td>
<td>30</td>
<td>24</td>
<td>68.0</td>
<td>46.22</td>
<td>0.68</td>
</tr>
<tr>
<td>IER7</td>
<td>10</td>
<td>50</td>
<td>9</td>
<td>90.8</td>
<td>76.28</td>
<td>0.84</td>
</tr>
<tr>
<td>IER8</td>
<td>(2 times)</td>
<td>50</td>
<td>10</td>
<td>91.0</td>
<td>74.64</td>
<td>0.82</td>
</tr>
<tr>
<td>IER8-4</td>
<td>(4 times)</td>
<td>50</td>
<td>10</td>
<td>91.0</td>
<td>74.64</td>
<td>0.82</td>
</tr>
</tbody>
</table>

For IN₀=81.5 and EOₜₜₜₒ=4.89%, EOₜₜₒ is defined as the theoretical maximum content of epoxy oxygen in 100 g of oil, calculated as EOₜₜₒ=[(IN₀/2Aₒ)][100+(IN₀/2Aₒ) ×Aₜ]×Aₒ>100, where Aₒ=126.9 and Aₜ=16.0

\[ X = \frac{(IN₀-INO)}{IN₀} \times 100 \]

\[ REY = 100 \times \frac{EO_{exp.}}{EO_{thor.}} \]

\[ SE = \frac{EO_{exp.} \times IN₀}{EO_{thor.} (IN₀-IN)} \]

The highest conversion of double bonds of 92.8% and maximum relative yield of epoxidized castor oil of 78.32% were achieved at 50°C after 7 hours of epoxidation when 0.5 mol of glacial acetic acid and 1.5 mol of 30% aqueous hydrogen peroxide per mol of double bonds of castor oil dissolved in the equivalent weight of benzene as inert solvent were used. For this in situ epoxidation 15% wt (related to the sum of the weights of the acetic acid and hydrogen peroxide used) of an ion exchange resin Amberlite IR-120 as catalyst was applied. The selectivity of 0.85 was achieved.

4. ACKNOWLEDGMENTS

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5. REFERENCES


