

Effective and Fast Epoxidation Reaction of Linseed Oil Using 50 wt% Hydrogen Peroxyde

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Abstract Epoxidation of linseed oil was performed with peracetic acid formed *in situ* by the reaction of hydrogen peroxide and acetic acid in the presence of Amberlite 120H as catalyst, and toluene as solvent. Some variables were evaluated as temperature and the molar ratio and solution of aqueous hydrogen peroxide (30 and 50 wt%) for obtaining a maximum of yield and conversion of epoxidized oil. The characterization of conversion of double bonds (DB) to epoxy ring, the relative percentage of epoxidation and selectivity, were performed by ¹H-NMR and FTIR-HART. The conditions rendered a maximum epoxidation of 93.4%, a conversion of double bonds of 97% and a selectivity of 96.3% were obtained at 80°C, employing a molar ratio 1:1.5 of double bonds (DB) to H₂O₂ (50 wt%), 1:0.5 of DB to acetic acid, and 25 wt% of catalyst, in only 50 min and with a good reproducibility (±1.1%).

Keywords Epoxidation, Linseed oil, Acidic ion exchange resin

1. Introduction

Epoxides obtained from renewable sources [1-7] have application in a wide number of industrial and research processes: to obtain commercial products, and as reagents and intermediates used in the manufacture of polymers, resins, coatings, detergents, etc., generating a broad market and volume of consumption in the order of millions of tons per year. In this context, epoxidized vegetable oils (EVOs) [8-13] have been found viable due to their availability, low cost sustainability and non-toxicity; highlighting linseed oil, rapeseed oil and soybean oil for its higher production. The EVOs are commonly used as polyvinyl chloride (PVC) stabilizers, plasticizers [14], lubricants [15, 16], and starting materials to produce polyols [17-19], prepolymers [1, 20-24] and to synthesize polyurethane foams [25-29]. In addition, they are auxiliary agents used to improve the efficiency of linoleum production and the modification of other thermoset polymers [30-34].

The EVOs are usually produced at industrial scale with peroxycarboxylic acids formed *in situ* by reacting an organic acid as acetic acid, hydrogen peroxide and sulfuric acid [9, 35-41] (or any other soluble mineral acid) as the catalyst [42]. The search for optimize the epoxy yield conditions has been

widely investigated [9, 42-50]: temperature, stirring speed, concentration of H₂O₂, type (homogeneous and heterogeneous) and amount of catalyst, acid precursor of the peroxyacid (formic, acetic, oleic), formation *in situ* of peroxyacid or addition of a preformed peroxycarboxylic acid, use or not of solvent, etc. Of particular interest is the epoxidation reaction using a heterogeneous catalyst as Lipase B [51-55], Alumina [56], Amorphous Ti/SiO₂ [57-61], and Amberlite 120H. This last is an acidic ion exchange resin [62-71], which has been widely evaluated in many epoxidation reactions and has presented a better selectivity, less side reactions, it is easily recoverable and reusable, in comparison with the use of sulfuric acid as catalyst which are also more polluting and complex to separate, in addition to generating higher probability of secondary reactions, thereby reducing the epoxidation selectivity. The main results that gave the better conversion of DB to oxirane rings from the studies of epoxidation of several oils with Amberlite are [65] in the next ranges: temperatures oscillate between 60-75°C, amount of catalyst range from 15 to 25%, high speed stirring (above 1500 rpm), a molar ration 1:0.5 of DB to acetic acid, a molar ratio 1:1.0-1:1.5 of DB to H₂O₂ (30%), with or without solvent (usually toluene or benzene) and a reaction time between 3 and 7 h. All those conditions also depending on the kind of oil, and the best parameter of the epoxidation reaction should be determined individually for each oil. Related with hydrogen hydroperoxide, there are a few researches that used H₂O₂ (50 wt%) mainly for safety hazard to the personnel and reactor equipment due the instability of the concentrate peroxides and peroxyacids [41, 44, 65].

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Usually high temperatures are avoided when concentrate peracid is used. However, Haro [36] recently reported the epoxidation of grape seed oil at 90°C employing H₂O₂ (50 wt%), H₂SO₄ and acetic acid, rendered a conversion to epoxide of 90% in 60 min. At longer reaction times or higher temperatures than 90°C, aperture of epoxy groups and some oligomerization reactions usually have been detected [65]. In this work we evaluate the effect of the initial solution of hydrogen hydroperoxide, 30 and 50 wt% and the temperature at 65, 70 and 80°C, for epoxidation of linseed oil. Linseed oil is one of the most unsaturated triglycerides (6-6.4 DB) of particular interest for polymer synthesis. It would be very convenient to reach a conversion to epoxide up to 90% for this oil. As our better results, it was evidenced that using hydrogen peroxide at 50 wt% the conversion rate was fast reaching the maximal epoxidation (93.4%) in only 50 min at 80°C.

2. Methodology and Experimental

2.1. Reactants

The solvents Toluene, Ethyl Acetate and Acetone; chromatographic-grade α -Alumina, the catalyst Amberlite IR-120H (AIR-120H) and the reactive-grade Linseed Oil (LO) were supplied by Sigma-Aldrich, Co. LO consists of a clear yellow oil with a molecular weight of 865 g/mol, with a number of Iodine of 179.1 and 6.2 double bonds (DB) or ethylenic unsaturation, all determined by ¹H-NMR according to [72-74]. Acetic Acid and the H₂O₂ (30 and 50 wt%) were purchased from Fermont. With exception of the LO, the other reagents were used as they were received. LO was passed through a packed column of α -Alumina previous to use it, to eliminate the stabilizer.

2.2. Characterization

FT-IR spectroscopic measurements were performed on a FT-IR Prestige 21, Shimadzu spectrometer, equipped with a horizontal attenuated total reflectance (HART) modus, with a crystal made of diamond. For quantitative analysis [17, 73], spectra were performed in Absorbance mode, a resolution of 4 cm⁻¹, 64 scans in the range of 560 – 4000 cm⁻¹. Spectra were normalized with respect to the area under the curve of the signal at 1745 cm⁻¹ which corresponds to carbonyl vibration from ester groups of the triglyceride. The monitored signal by measure the area under the curve was the pair of bands centered at 821 and 798 cm⁻¹ corresponding to the epoxy ring vibration.

¹H-NMR spectra were recorder using a Bruker Avance III a 300 MHz spectrometer, using CDCl₃ as solvent and TMS as an internal standard. Quantification of conversion of DB, percentage of epoxidation and selectivity was calculated as described in [53, 72, 74].

2.3. Epoxidation Reaction Set up

The evaluated variables were three temperatures: 65, 70

and 80°C; the molar ratio of unsaturation respect to hydrogen peroxide (1:1 and 1:1.5) for the two aqueous solutions of hydrogen peroxide, 30 and 50%. Other values were fixed as the molar ratio of DB to acetic acid (1:0.5), a solvent quantity of 44 wt% and 25 wt% catalyst, both respect to the linseed oil weight. The times reactions were from 50 to 200 min and each reaction was made by triplicate.

A general procedure consists in: place into a two-neck reactor equipped with a magnetic stirrer, thermometer and reflux condenser, 10 g of Linseed Oil (LO) equivalent to 72 mmol of DB, 2.1 g of Acetic Acid (AA), 4.4 g of Toluene (Tol) and 2.5 g of Amberlite IR-120H (AIR-120H). Reactor was placed in a water bath at 50°C for 15 min. The addition of 1:1 or 1:1.5 of H₂O₂ (30 or 50 wt%) started dropwise under vigorous stirring. Due the exothermic process, temperature is controlled to not to exceed the 50°C to avoid the decomposition of H₂O₂ [44, 67]. Once the addition of H₂O₂ was complete, the reaction mixture was heated up at the established temperature (65, 70 or 80°C). The reaction was monitored by FT-IR spectroscopy each 10-20 min (considering the initial time the completion of H₂O₂ addition), and when epoxidation was stopped to the determined time, the mixture was cooled to room temperature. It was filtered to recover the catalyst, which was washed with ethyl acetate to remove the excess oil and then with isopropyl ether and allowed to dry for reuse. The organic phase was washed several times with a saturated sodium bicarbonate solution until neutralization; the organic phase obtained was dried with anhydrous magnesium sulfate. After filtration the organic solvents (ethyl acetate and toluene) were evaporated using a rotary evaporator under reduced pressure. The product (ELO) was placed for 48 hours in a vacuum desiccator to eliminate traces of solvents for finally do the corresponding characterization by FT-IR-HART and ¹H-NMR.

3. Results and Discussion

Characterization of the epoxidized products was performed employing ¹H-NMR and HART-FTIR spectroscopies. Usually the evaluation of the epoxidation reaction is employing analytical procedures; however, these processes involve time, chemical reactants, and they generate residues. High resolution NMR is an effective tool for determining iodine value of vegetable oils as determined by Miyaki, *et al.* [73]. He determined a correlation coefficient between traditional Wijs method and ¹H NMR being it $r^2 = 0.9994$ and within an error of ± 1 . Also, it is possible to calculate Iodine number and the molecular weight of the oil according to Natham and Díaz [72] and it has been a reliable technique for determine values of conversion, epoxidation and selectivity for an epoxidation reaction of oils [75].

FTIR spectroscopy is also an excellent tool for quantitative analysis. Using the relationship between the absorbance values and normalize the band of epoxide ring

include the bands at 820 and 795 cm^{-1} it is possible to cancel out background, instrument noise, sample thickness, etc. Using an equation (1), it is possible monitoring the epoxidation of oils:

$$\%E = \left[1 - \frac{(A_{\text{epx}}/A_{\text{ref}})_t}{(A_{\text{epx}}/A_{\text{ref}})_0} \right] \times 100 \quad (1)$$

Where A_{epx} is the area under the curve of the signal includes the bands at 820 and 795 cm^{-1} (that correspond to the vibration of the epoxy ring (864-764 cm^{-1}). A_{ref} is the area under the curve of the reference band that should be one that remain unchanged throughout the epoxidation reaction as the 1376 cm^{-1} [75] or carbonyl at 1743 cm^{-1} [17]. Núñez *et al.* [74] determined a correlation coefficient of 0.995 (and a maxima variation of ± 1.2) obtained by chemical analysis vs oxirane content determined by FTIR-ATR spectroscopy. We recently determined (resulted not published) an epoxide content correlation obtained by FTIR-HART and $^1\text{H-NMR}$ spectroscopies of 0.99515 with a variation of ± 1.2 .

3.1. Characterization of LO

FTIR-HART: Double bonds: 3009 cm^{-1} ($=\text{CH}_{(\text{v})}$), 1653.5 cm^{-1} ($\text{C}=\text{C}_{(\text{v})}$) and 719.5 cm^{-1} ($\text{C}=\text{C}_{(\text{cis-}\delta)}$). Methyl and methylene: 2956 cm^{-1} (terminal $\text{CH}_3_{(\text{asym-v shoulder})}$), 2922.4 and 2853 cm^{-1} ($-\text{CH}_2_{(\text{asym and sym-v})}$), 1460 cm^{-1} ($\text{CH}_2_{(\text{asym-}\delta)}$) and 1376.4 cm^{-1} ($\text{CH}_3_{(\text{sym-}\delta)}$). Ester carbonyl: 1743 cm^{-1} ($\text{C}=\text{O}_{(\text{v})}$); 1159.2 cm^{-1} ($\text{C}-\text{O}_{(\text{v})}$) and 719.5 cm^{-1} ($(\text{CH}_2)_{n(\delta)}$; being $n \geq 4$).

$^1\text{H NMR}$ (300 MHz, CDCl_3); δ in ppm (Integral, multiplicity, Hydrogen type): *0.88 (1.12, m, CH_3 - terminal groups); *0.97 (1.29, t, CH_3 - terminal group of linolenic acid); *1.31 (10.13, d, $-\text{CH}_2-$); *1.61 (1.55, s, $-\text{CH}_2-\text{C}=\text{O}$); *2.05 (2.70, m, $-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}$); *2.31 (1.51, t $-\text{CH}_2-\text{C}=\text{O}$); *2.80 (1.82, m, $-\text{CH}_2-\text{CH}=\text{CH}$); *4.15 – 4.3 (1, dd, CH_2-O of glyceride); *5.35 (3.37, m, $-\text{CH}=\text{CH}-$ and $\text{CH}-\text{O}$ of glyceride).

3.2. Following of the Epoxidation Reaction

In Figure. 1a, could be appreciated how the FTIR-normalized signals of LO corresponding to double bonds vibrations in 3009 cm^{-1} ($=\text{CH}_{\text{str}}$) and 1653.5 cm^{-1} ($\text{C}=\text{C}_{(\text{v})}$) vanished in the spectrum of the epoxidized product (insets from Figure. 1a), whereas the band at 719.5 cm^{-1} ($\text{C}=\text{CH}_{(\delta)}$ plus $(\text{CH}_2)_{n(\delta)}$; being $n \geq 4$) only diminishes in intensity as the reaction performed at 80°C, a molar ratio 1:1 LO to H_2O_2 (30 wt%) proceeds (run 9, Table 1). However, the two bands of the epoxy ring vibration (inset from Figure. 1b) centered between 820 and 795 cm^{-1} were observed in the first minutes of reactions and they increase as the reaction take place. This signal is the one is quantified with the course of the reaction until the established reaction time [17]. Both spectra (LO and ELO) have signals that match (do not change) with the course of the reaction. This bands corresponding to methyl and methylene groups at 2956, 2922.4, 2853, 1460 and 1376.4 cm^{-1} as well as the vibration corresponding to the ester carbonyl at 1743.6 and 1159.2 cm^{-1} .

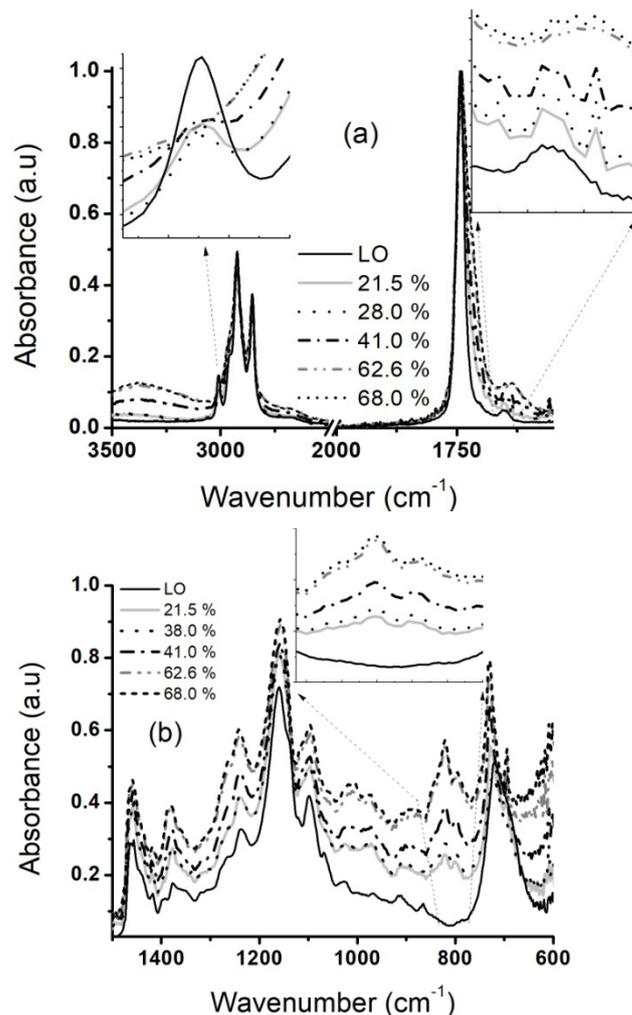


Figure 1. Normalized FTIR spectra monitoring the epoxidation reaction for run 5 (Table 1 and Figure 3): Temperature of 80°C, DB to acetic acid molar ratio, 1:0.5; DB to H_2O_2 (30 wt%), 1:1 molar ratio, and 25 wt% of AIR-120H

From $^1\text{H NMR}$ spectra it was possible to calculate the conversion of DB respect to the original DB in LO (6.2, 100%). At the start of the reaction, the same amount of reacted DB gave the same amount of epoxy rings however as the reaction continues, side reactions as aperture of epoxy ring start to take place. It is because the epoxy percent at the end of the reaction use to be minor to the calculated by the DB conversion. With this two conversions (DB and epoxy) it is possible to calculate the selectivity % as (epoxidation%)/(DB conversion %) [75]. Figure. 2 shows how the peak at 5.35 ppm in LO (0% of epoxidation) splits in two signals, one shifts a lower field (5.6 ppm) and their integration decrease from 3.37 to almost 0 as the epoxide conversion increases from 0 to 93.4%. This signal corresponds to vinyl hydrogens from DB. The other signal centered in 5.3 ppm corresponds to central Hydrogen of the glyceride moiety. Also the signal at 2.80 ppm corresponding to allyl hydrogen between double bonds, decreases their integration for the ELO spectrum. The appearance of signals at 3.1 ppm, 2.9 ppm and 1.5 ppm correspond to methylene

hydrogens between two epoxy rings, hydrogens of the carbons of epoxy rings and methylene hydrogens adjacent to epoxy rings, respectively [17].

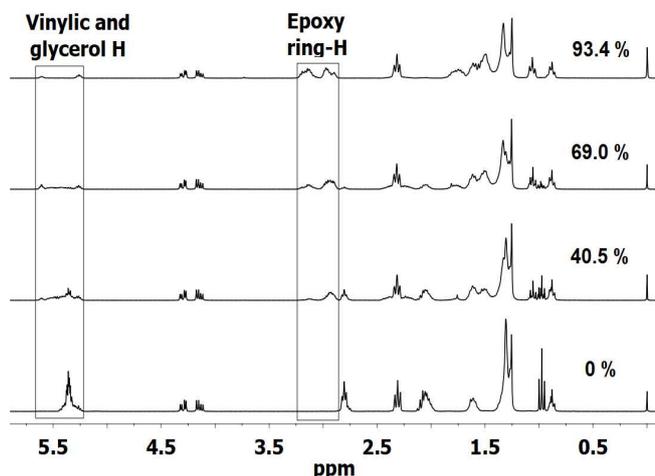


Figure 2. ^1H NMR spectra for different conversion of epoxide: 0% for LO, 40.5% (run 2, Table 1), 69.0% (run 3, Table 1) and 93.4% (run 3, Table 2)

3.3. Effect of the Concentration of the Solution of Hydrogen Peroxide: 30 and 50 wt%, and Temperature

Epoxidation of Linseed oil with peracetic acid formed *in situ* in the presence of an ion-exchange resin in a heterogeneous catalytic process. Peracetic acid diffuses through the water to the oil phase for reacting with the unsaturation of the oil to forming an epoxy group [42, 65]. This is the description of an ideal reaction however, has been well studied that excess of some reactants and/or changes on parameters as temperature, usually render side undesired reactions [42, 65, 67].

Figure 3 shows the sharp increase of the epoxidation conversion when H_2O_2 (50 wt%) is employed in comparison with H_2O_2 (30 wt%) at 80°C . The curve for H_2O_2 (30 wt%) was built with the data obtained from Figure 1. For reaction using H_2O_2 (50 wt%) the maximal conversion (93%) was achieved in 75 min, after this time the amount of epoxy groups started to diminish due side aperture reactions; whereas for reaction ran with H_2O_2 (30%) at the same time (75 min) it was only reached a 40% of conversion. This tangible difference between using H_2O_2 at 30 or 50 wt% is due to the higher concentration of active oxygen in H_2O_2 (50 wt%) that increases the rate of *in situ* formation of peracetic acid, and as consequence the rate of epoxidation of the DB in LO. Analyzing the runs 1 and 6 in Table 1, which were performed at 65°C but using H_2O_2 at 30 and 50 wt% respectively, it is notice an increase of 23% in the epoxidation percent at 180 min. For runs 2 and 7 carried out at 70°C , there was an increment on the conversion to epoxide of 37% in 50 min, while for reactions performed at 80°C (runs 4 and 9) there was only an increment of 15% in 50 min; however at this time the epoxidation conversion has reached 70%.

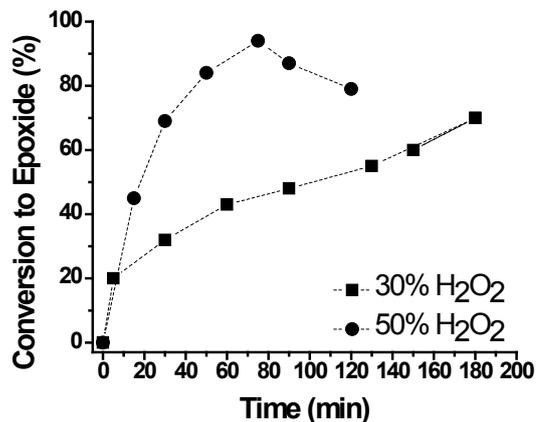


Figure 3. Epoxy conversion determined by monitoring the reaction by FTIR. Effect of the concentration of the H_2O_2 (30 and 50%). Other conditions: Temperature of 80°C , DB to acetic acid molar ratio, 1:0.5; DB to H_2O_2 , 1:1 molar ratio, and 25 wt% of AIR-120H

Three temperatures were evaluated on the course of epoxidation of LO: 65, 70 and 80°C . An increase in temperature not only increases the epoxidation conversion, but also decreases the reaction time required. In Table 1 are shown the results at the same time (50min and/or 180min) to compare them. For reaction carried out using 30% of H_2O_2 and at 65°C (run 1) and 75°C (run 3), are very slow; the epoxidation percent at 180 min is only 60 and 66%, respectively, meaning an uncompleted reaction. For temperatures of 60– 65°C , it is reported [68] times of around 7 h for reaching the maxima epoxidation (around 90%) reaction and around 5 h when reaction is carried out at 70 – 75°C .

Table 1. Results of epoxidation parameter at different temperatures and H_2O_2 (30 or 50 wt%)

Run No.	Temp ($^\circ\text{C}$)	$[\text{H}_2\text{O}_2]$ wt%	Time (min)	% Conv. of DB	%Epoxy.	% Select.
1	65	30	180	61.0	60.2	98.7
2	70	30	50	40.7	40.5	99.5
3	70	30	180	67.5	66.0	97.8
4	80	30	50	59.0	58.9	99.8
5	80	30	180	96.0	68.0	70.8
6	65	50	180	80.3	78.2	97.7
7	70	50	50	47.7	47.0	98.5
8	70	50	180	89.0	87.2	98.0
9	80	50	50	70.5	69.0	98.0
10	80	50	180	99.8	79.6	79.7

Conditions: DB to acetic acid molar ratio, 1:0.5; DB to H_2O_2 molar ratio, 1:1, and a catalyst load of 25 wt%.

At 80°C (run 4) stopped at 50 min had similar results as those obtained at 65°C for 180min. At 180 min for run 5 there is a high consumption of DB but the epoxidation percent is only 68% and at selectivity of 70.8. This is due to at high temperatures and prolonged time, the undesirable acid-catalyzed epoxy ring cleavage reactions take place [67, 69] and the number oxirane rings is diminished in relation to

the DB consumption. It becomes important to establish the time at which the maxima epoxidation reaction takes place before the epoxy rings suffer aperture. For 80°C the time reaction is minor to 180 min. But our interest is to optimize the reaction at 80°C but using a solution of 50% of H₂O₂. At least for 70 and 80°C is evident that reactions reached their maximal epoxidation conversion (around 93-94%) at 150 min and 75 min, respectively. That means the double of time.

3.4. Effect of the Molar Ratio of DB to H₂O₂ (50 wt%) and Temperature

It was demonstrated first the effect on increasing the molar ratio of DB to H₂O₂ (50 wt%) from 1.0:1.0 to 1.0:1.5 at 80°C.

Figure 4 shows that the molar ratio 1:1.5 of DB to H₂O₂ (50 wt%) was the most advantageous for epoxidation of linseed oil; there was a noticeable increasing on the rate of epoxidation at 80°C. The maximal conversion for both molar ratios is practically the same (93-94) however it takes 75 min when a molar ratio 1.0:1.0 is employed and only 50 min when a molar ratio 1.0:1.5 is added. After those times, the conversion started to diminish in both cases. The use of H₂O₂ (50%) and a high molar ratio as well 80°C of temperature; the reaction started to take place very fast and favorable in the first 30 min. At this time almost 80% of epoxides has been formed whereas only 60% of them are quantified when a molar ratio 1.0:1.0 has been employed.

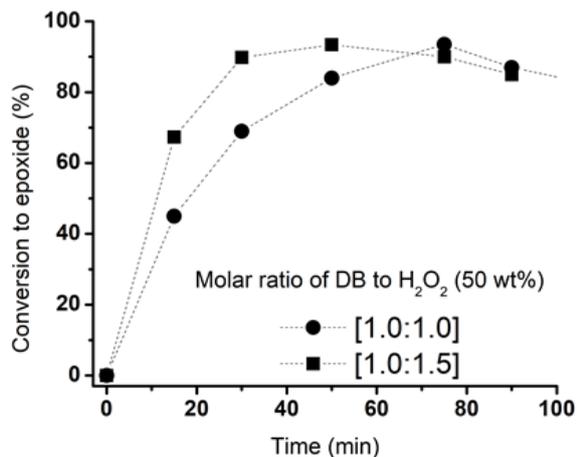


Figure 4. Effect of increasing the molar ratio of DB to H₂O₂ (50 wt%) on the conversion to epoxide. Other conditions: DB to acetic acid molar ratio, 1:0.5; and 25 wt% of catalyst, 80°C

To be sure of the effect of the temperature on the conversion to epoxide, the reaction was also carried out at 65 and 70°C. In Figure 5 is evidenced the effectiveness of the temperature on the epoxidation conversion.

We have two good results to highlight: at 70°C was reached the maximal conversion to epoxide (around 94%) in 135 min, whereas at 80°C it was reached practically the same epoxide conversion (93%) in only 50 min. In both cases the selectivity (Table 2) was very similar and acceptable (96.3%). From the original 6.2 DB, 6.0 reacted and 5.8 epoxides survived to the reaction conditions.

Table 2. Effect of the temperature on the epoxidation parameters

Run No.	Temp. (°C)	% Conversion of DB	% Epoxi.	% Select.
1	65	86.5	84.3	97.5
2	70	98.0	94.0	96.0
3	80	97.0	93.4	96.3

Conditions: DB to acetic acid molar ratio, 1:0.5; DB to H₂O₂ (50 wt%) molar ratio, 1:1.5, and a catalyst load of 25 wt%.

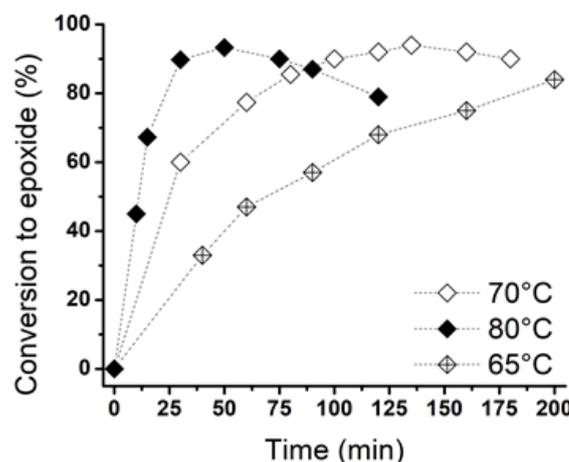


Figure 5. Effect of the temperature on the conversion to epoxide. Other conditions: DB to acetic acid molar ratio, 1:0.5; DB to H₂O₂ (50%), 1:1 molar ratio, and 25 wt% of catalyst

An explanation of why “extreme” conditions are necessary for epoxidation of linseed oil, is due to the high number of double bonds, most of half them are on a fat acid chain of linolenic acid (three double bonds). The feasibility of react (only by steric effects) of the central double bonds is minor than the one or two double bonds. Surely the conditions of high concentration of active oxygen and a relatively high temperature favors noticeably the rate of epoxidation (into the first 30 min) but also provides and ensure the continuous formation of peracetic acid, which is the most important intermediary due it spontaneously reacts with the double bonds forming the epoxy ring. Usually the concentration of peracetic acid in the system use to be low because the continuous consumption during epoxidation reaction. Under our established conditions this effect could be negligible or not enough as the less reactive DB could react. It is well supported by our results in which other conditions were used.

4. Conclusions

The results of the present investigation show that Linseed Oil could be efficiently epoxidized in a short time. The combination of parameters that render the better results of the epoxidation reaction of LO are: a molar relation of 1:0.5:1.5 of DB to acetic acid and H₂O₂ (50 wt%), 25 wt% of catalyst, 80°C and 50 min. As well the conditions: a molar relation rate of 1:0.5:1.5 of DB to acetic acid and H₂O₂ (50 wt%), 25 wt% of catalyst, 70°C and 135 min, rendered

practically the same results: conversion of DB, 97-98%; conversion to epoxide, 93% ($\pm 1\%$) and a selectivity of 96%. The monitoring and characterization of the reaction was performed by FTIR-HART and ^1H NMR spectroscopies. The double bonds and epoxy signals were well identified and quantified employing both spectroscopies, evidenced the good reliability of them for characterize the epoxidized oils.

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