

KINETICS OF GRAPE SEED OIL EPOXIDATION IN SUPERCRITICAL CO₂

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Abstract

The epoxidation of grape seed oil in supercritical CO₂ have been only superficially described in the literature. In this work, a deep study of the performance of the supercritical epoxidation of grape seed oil is performed in a wide range of conditions, and the kinetic parameters of the supercritical epoxidation of vegetable oils are reported for the first time in literature. The experimental work has covered a 40-60°C temperature range at 150 bar, sampling during a period of 48 h.

The nature and extent of the side reactions and secondary products obtained have been evaluated, being the hydrolysis products and their oligomerization derivatives the major by-products that appear with time.

Reaction rate constants (10^{-2} h^{-1} order) and activation energy parameter were finally calculated from the experimental conversion and epoxy yield data to establish the effect of temperature on the kinetic of the process.

Keywords

Supercritical, epoxidation, grape seed oil, carbon dioxide, CO₂, peroxy-carbonic, kinetics.

Abbreviations

scCO₂: Supercritical Carbon Dioxide

PTC: Phase Transfer Catalyst

HDTMAB: Hexadecyltrimethyl-ammonium Bromide

PCA: Peroxy-carbonic Acid

GSO: Grape seed oil

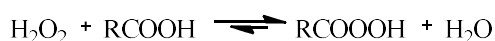
1. Introduction

The great importance of the use of epoxidized vegetable oils is due to their suitability as an alternative biobased precursor for many industrially relevant products. Thus, they can be used for the synthesis of lubricants, plasticizers, adhesives, thermosets, polyols or non-isocyanate polyurethanes. [1]

The most widespread way of carrying out the epoxidation of the double bonds present in vegetable oils involves the use of percarboxylic acids, that come from organic acids.

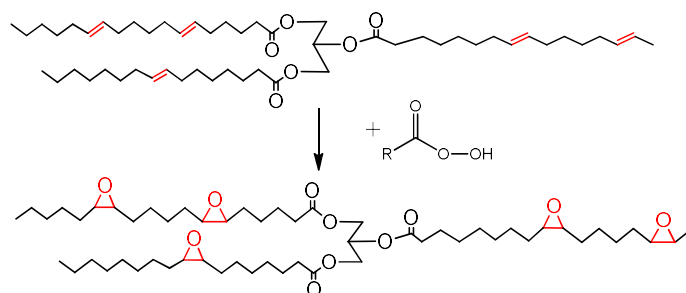
This procedure is carried out by what is known as the Prileschajew reaction, which firstly consists on the formation *in situ* of these peroxyacids from the reaction of acids such as acetic and formic with hydrogen peroxide (H₂O₂) molecules [2].

The peracid formation follows the reaction mechanism shown in Scheme 1.



Scheme 1. Peracid formation reaction.

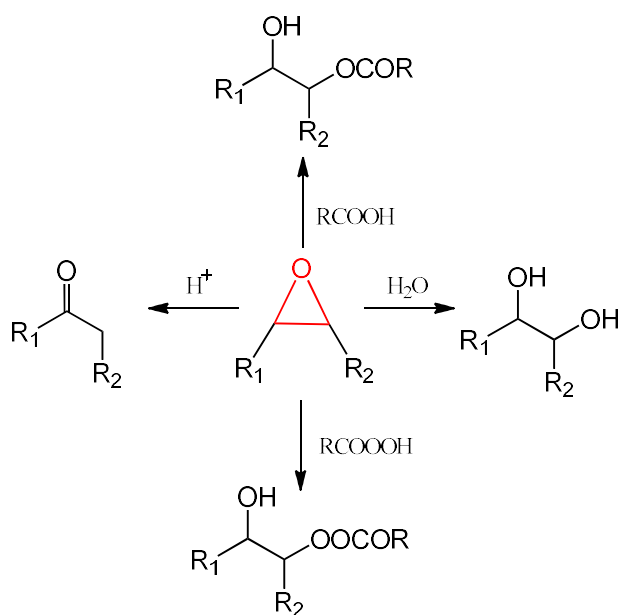
Furthermore, the peracid produced within the aqueous phase formed by the concentrated hydrogen peroxide is capable to migrate into the oil. There, acting as an oxygen carrier, generates oxirane rings in the active sites which are, in this case, unsaturations (Scheme 2), and releases the original carboxylic acid which allows the reaction cycle to be restarted [3,4]. This process also requires the use of acid type catalysts, such as sulfuric acid.



Scheme 2. Vegetable oil epoxidation reaction mechanism.

The product obtained requires a purification process consisting of the settling of the liquid phases, followed of a series of washing steps and neutralization of the oil phase and its final drying. This whole process is necessary in order to neutralize the acidity of the epoxidized oil to obtain an isolated product. Remaining of acidity and water traces can lead to further parallel oxirane ring cleavage and undesired side products [5]. The side

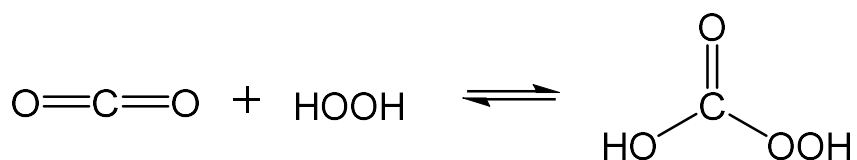
products generation reactions are the main issue in conducting the selectivity of the process to the formation of epoxides ^[4] and can be as diverse as those exemplified in the Scheme 3.



Scheme 3. Side product formation reactions ^[4].

Therefore, environmental concerns related to the use of mineral acids and organic solvents, in addition to the need to simplify and improve the purification processes of the products, leads to a growing interest in the outlining of an alternative route to the traditional epoxidation process.

In this context, arises the possibility of obtaining the oxygen transfer agent from an unconventional source, such as carbon dioxide, which acts as a substitute for conventional carboxylic organic acids and is able to react with hydrogen peroxide in a analogous way (Scheme 4) and to form its corresponding peracid, peroxy-carbonic acid (PCA) ^[6].



Scheme 4. Peroxycarbonic acid formation reaction ^[6].

CO₂ can be not only one of the reagents for epoxidation, but also the reaction media when CO₂ in supercritical conditions (scCO₂) is used as the reaction solvent. In addition, scCO₂ is neither explosive, nor toxic, can be removed after the process has been completed

simply by means of controlled depressurization and allows obtaining an epoxidized vegetable oil completely solvent-free.

In a previous work of our research group confirmed the feasibility of this reaction as well as the positive effect on the overall process performance of various enhancer compounds [7]. Firstly, sodium bicarbonate, which according to Nolen et al. (2002) ionizes peroxy-carbonic acid by increasing its effective concentration [5]; and secondly, the so-called phase transfer agents or PTCs, which improve the mass transfer between phases, which is one of the limiting factors when carrying out the transformation of the oil and obtaining optimum performance, especially as it is a multiphase system. In particular, hexadecyltrimethylammonium bromide (HDTMAB) was selected as the PTC agent that showed the best performance under the operating conditions studied.

So far, the background obtained by the group in supercritical epoxidation of vegetable oil has been obtained considering mild operating conditions and optimized the molar ratios of the reagents and enhancer compounds.

That is why, although the epoxidation kinetics according to Prileschajew's reaction has been widely studied with no CO₂ pressure, it seems compelling to extend this study to supercritical media, of which, to the best of our knowledge, there is no records in literature.

This study would allow an in-depth understanding of the mechanism involved in this conditions, how the use of peroxy-carbonic acid affects the occurrence of the abovementioned oxirane ring opening phenomena and the subsequent formation of side products, as well as the evolution of the whole system over time while the epoxides are formed, and its overall behavior when it is carried-out at different temperatures [8].

Therefore, the analysis and comprehension of the kinetics of the process is vital for the selection of optimal operating conditions that allow obtaining a yield of the epoxidized product close to that theoretically achievable according to the reaction thermodynamic.

2. Material and Methods

2.1. Materials

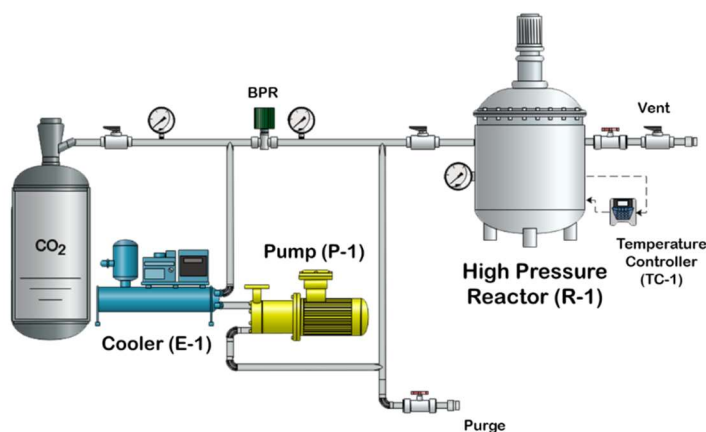
Grapeseed oil (GSO) was kindly provided by Alvinesa S.A. (Daimiel, Ciudad Real, Spain). Hexadecyltrimethyl-ammonium bromide (HDTMAB) (<98%), hydrogen peroxide solution (30% wt.), sodium bicarbonate (99.5-100.5%), oleic acid (analytical

standard) and 1,3-Dinonadecanoïn (standard) were supplied by Sigma-Aldrich, Inc. (Spanish division, Madrid, Spain).

Extended information about the oil composition is described as follows: C16:0 palmitic (6.9% wt.), C18:0 stearic (4% wt.), C18:1 oleic (19% wt.) and C18:2 linoleic (69.1% wt.) acids. Iodine value (IV) and average molecular weight (MW) were 137.05 g I₂/100 g sample and 877.29 g/mol respectively, determined in previous publications [7,9].

2.2 Experimental Setup

The experiments were carried out in a high-pressure setup operated as a closed system (**Figure 1**). The high-pressure reactor is a Berghof BR-300 model (300°C and 200 bar max.) and it is equipped with the following components: electrical heating jacket, mechanical stirring system, and a Berghof BTC-3000 temperature controller (Berghof Products + Instruments GmbH, Germany). It also counts with an outside steel vessel and an inner one made out of TFMTM-PTFE (390 ml and 310 ml respectively). Auxiliary equipment is depicted as a Milton-Roy Miniroyal Series (MD140G4M500/Z) dosing pump (Milton Roy Company, France) and a “Frigiterm-TFT-10 SELECTA” refrigeration bath (JP SELECTA, Spain).



36

Figure 1. Experimental high-pressure setup

2.3 Experimental procedure

Except for CO₂, all reactants are charged into the vessel before it is closed. Following that, CO₂ is cooled before being pumped into the reactor until it reaches operational pressure. Meanwhile, the heating system maintains the vessel's temperature at the desired process value. The stirring is then activated and maintained throughout the reaction time. Finally, the CO₂ is released through the vent valves, and the product is obtained from

within the vessel. The epoxidation product is then separated from the non-fatty byproducts using a 1760 g centrifuge.

2.4 Operating conditions

The operating conditions and reagent ratios were also set based on the results obtained formerly [7]. Pressure and temperature were established as 150 bar and 40°C. Reagents molar ratios used for the epoxidation experiments were the following: 1(Oil): 6(H₂O₂): 0.3(NaHCO₃): 0.075 (HDTMAB).

The aim of this study was to study the epoxidized oil product through a broad time range (0-48h), sampling every 3 hours during the first 24 h, with the final product at 48 h as final sample and reaction result. Agitation speed used for every experiment was 500 rpm.

2.5 Characterization Methods

2.5.1 Determination of the iodine value

The iodine value was determined by standard UNE-EN14111 procedure [10]. This determination was carried out in a Titrino 728 Stirrer automatic titrator.

2.5.2 Determination of oxirane oxygen

The determination of the amount of oxirane oxygen was calculated from the Epoxy Equivalent obtained from UNE-EN ISO 3001 Official Method [11].

$$EO = \frac{1}{EE} * MW_O \quad [1]$$

EO: Oxirane Oxygen (g oxygen/g sample)

EE: Epoxy Equivalent (g sample/ mol epoxide)

MW_O: Atomic weight of oxygen (g/mol)

2.5.3 Conversion and yield calculations

Conversion is calculated based on the double bonds disappearance, by means of the difference on its concentration, given by iodine value (IV).

$$x (\%) = \left(1 - \frac{IV}{IV_0}\right) \cdot 100 \quad [2]$$

Yield (η) is defined by the product of the conversion (x) of the double bonds involved in the reaction and the selectivity (s) to the transformation into oxirane rings.

$$\eta = x \cdot S \quad [3]$$

$$S (\%) = \frac{EO}{EO_{\max X}} \cdot 100 \quad [4]$$

$$EO_{\max X} = \frac{(IV_0 - IV) \cdot MW_O \left(\frac{g}{mol}\right)}{MW_{I_2} \left(\frac{g}{mol}\right) \cdot 100} \quad [5]$$

IV: Iodine value of the sample

*IV*₀: Iodine value of the unreacted reagent

*MW*_{I₂}: Atomic weight of molecular iodine (g/mol)

*MW*_O: Atomic weight of oxygen (g/mol)

EO: Oxirane oxygen content of the sample.

*EO*_{max X}: Maximum theoretical oxirane oxygen content, assuming 100% selectivity towards epoxides, considering conversion reached.

2.5.4 Infrared Spectrometry

Infrared spectra were carried out on a Spectrum Two spectrometer (Perkin Elmer, Inc) with a universal attenuated total reflectance (UATR) accessory. The samples were scanned from 4000 to 450 cm⁻¹ at a resolution of 16 cm⁻¹. All measurements were performed at room temperature.

2.5.5 Gel permeation chromatography (GPC)

The equipment used was a Shimadzu chromatograph (Izasa Scientific, Madrid, Spain) which incorporates two Waters HR-2 columns (pore size 500Å) and HR-0.5 (pore size 50Å) and detector of refractive index and viscosity (Waters España, Madrid, Spain), which allows the detection of molecular weights between 100 and 20000 g/mol. The analysis conditions were a flow rate of 1 ml/min and a sample concentration of 10 mg/ml using tetrahydrofuran (THF) as mobile phase. Polyethylenglycol was used as a standard for the calibration. Oleic acid and 1,3-Dinonadecanoin were used as standards for the identification of free fatty acids and diglycerides, respectively.

3. Results and Discussion

A qualitative approach to the grape seed oil epoxidation kinetic based on the FTIR spectra of GSO at different reaction time is shown in Figure 2.

A period of time as long as 48 h was selected as appropriate to be sure of having a complete view of the main product and the by-product formed by the evolution of the epoxy compound to oligomers or oxidation products until its complete conversion.

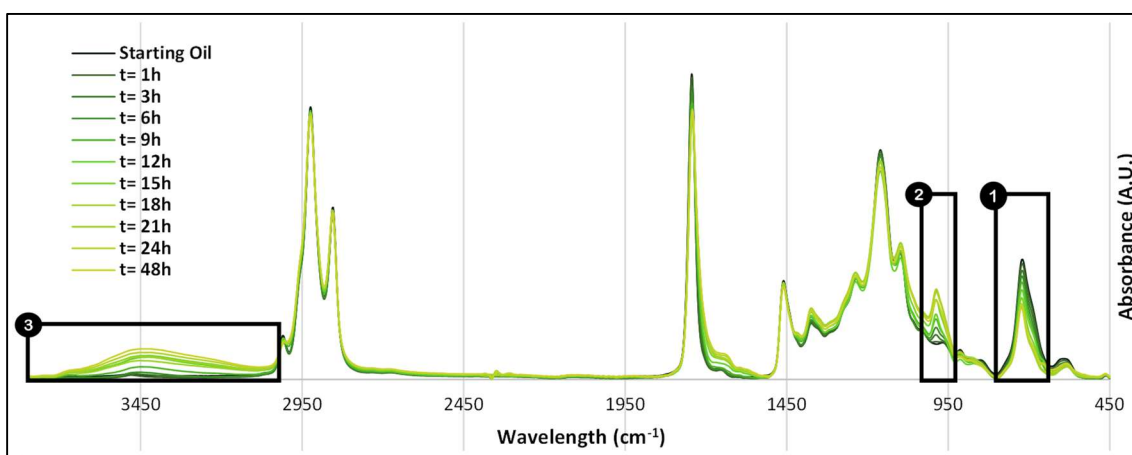


Figure 2. FT-IR spectra of the epoxidized products through time

The analysis of the different peaks allows to see the advancement of the reaction and the different phenomena that occur as the reaction time moves on. It is observed that at longer times there is a decrease in the intensity of the peaks related to the alkene groups (~ 720 cm^{-1} , ~ 3015 cm^{-1}), confirming the conversion of the double bonds present in the initial triglycerides. In the same way, there is a peak that was not found in the initial oil, which evolves gradually and is attributed to the formation of the oxirane group (~ 980 cm^{-1}), as well as the growth in intensity of the peak of the hydroxyl groups (~ 3450 cm^{-1}) which could indicate the presence of secondary products from hydrolysis and/or the opening of the epoxy rings previously formed.

In order to explore in detail the above-mentioned appearance of undesired secondary reaction products, a GPC analysis was carried out. Figure 3 shows the GPC chromatogram obtained, in which three clearly differentiated regions can be observed, in terms of molecular weights.

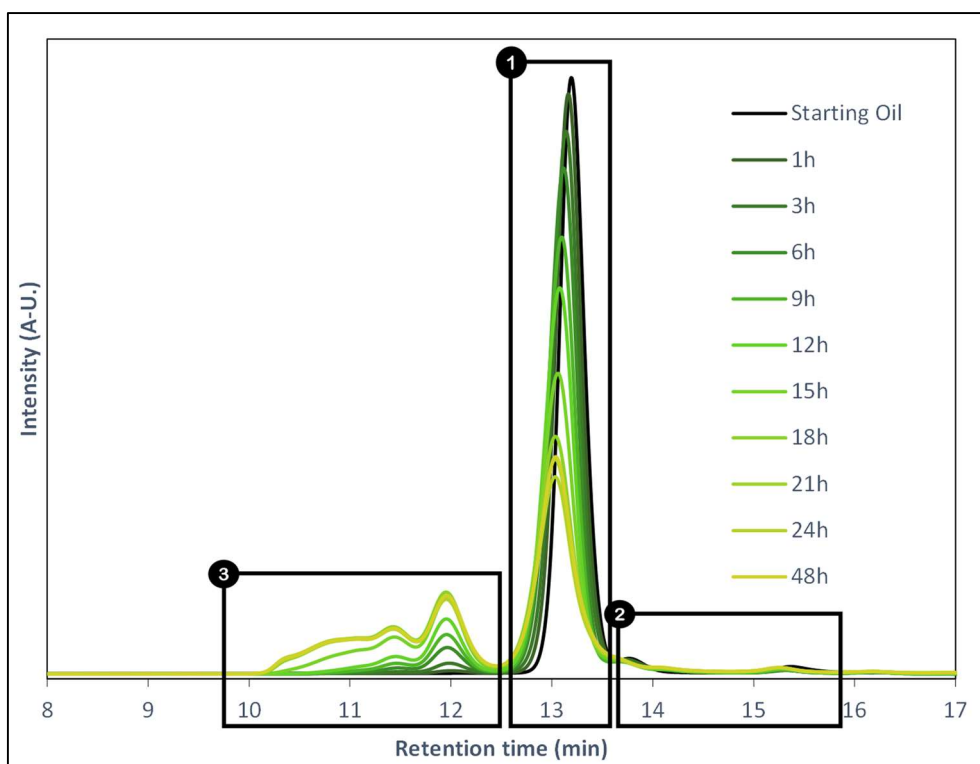


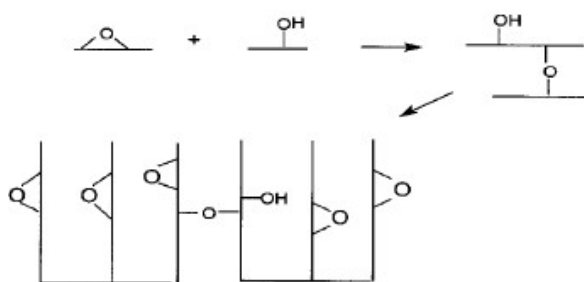
Figure 3. GPC chromatograms of the epoxidized products through time. 3 depicted regions (1: Triglycerides, 2: Low molecular weight products, 3: High molecular weight products)

Region n° 1 correspond to the main signal where the peak corresponding to the triglycerides appears (877 g/mol). A slight shift to the left is highlighted as the reaction time increases, which is directly attributed to the slight increase in molecular weight caused by the introduction of an oxygen atom to every double bond to form the oxirane ring. This shift is also consistent with the reaction advancement since it is proportional to the reaction time elapsed, and therefore, to the expected yield achieved. Another outstanding aspect is the decrease in the relative size of the area under this peak due to the transformation of triglycerides into compounds with a significant difference in molecular weight, which already suggests the formation of polymerization products.

Region n° 2 includes the peaks corresponding to low molecular weight products, i.e., mainly diglycerides and free fatty acids (confirmed by 1,3-dinonadecanoin and oleic acid standards). The most important aspect is that there is no significant generation of any of these products depending on the reaction time, remaining very similar to those already found in the starting oil. This behavior confirms that the relative decrease in the amount of triglycerides has not been oriented to the breakage of the ester links of the fatty acids

with the glycerol, and therefore, that the hydroxyl presence observed in the infrared spectrum is due to the opening of oxirane rings and not to the breaking of triglyceride chains.

In the case of Region n° 3, the appearance of a region of new products is observed, which did not exist in the raw material and correspond to molecular weights higher than the main region formed by triglycerides. The formation of these products is attributed to the development of post-oxirane cleavage polymerization, which occurs following the reactions that are alike as the exemplified in Scheme 5.



Scheme 5. Polymerization mechanism derived from an epoxidized and a hydrolyzed product

The different areas that are observed correspond to dimers (~1900-2000 g/mol), trimers or even high molecular weight oligomers (>3000 g/mol), all of which are the result of the polymerization reactions of the secondary products formed during epoxidation. ^[12]

In addition, in Figure 4 it can be seen a representation of the evolution of the relative amounts corresponding to each region as a function of time is carried out by calculating the enclosed areas under those curves.

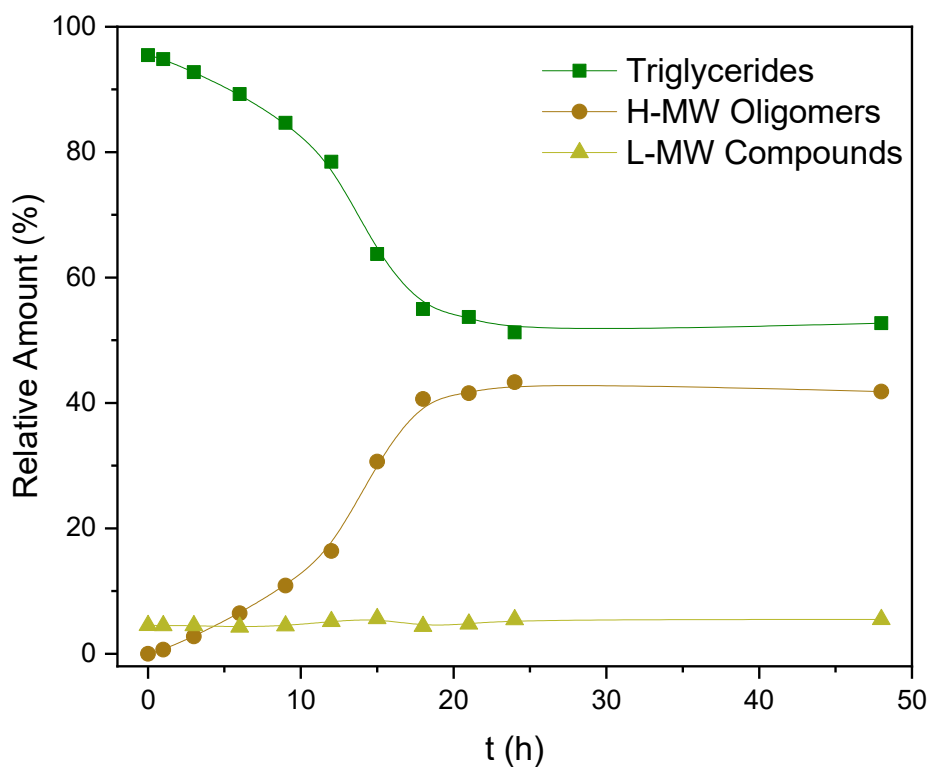


Figure 4. Molecular Weight distribution vs reaction time. T=40°C. L-MW: Low Molecular Weight, H-MW: High Molecular Weight.

It can be seen in Figure 4 that the relative concentration of low-molecular-weight compounds remains practically constant at considerably low values and yet the concentration of high-molecular-weight products increases in direct proportion to the way in which the triglycerides decrease.

Once primary characterization of the epoxidation products is concluded, the influence of temperature on the reaction kinetics was studied over the range 40 to 60°C. The values of conversion and epoxide yield is presented in Figure 5.

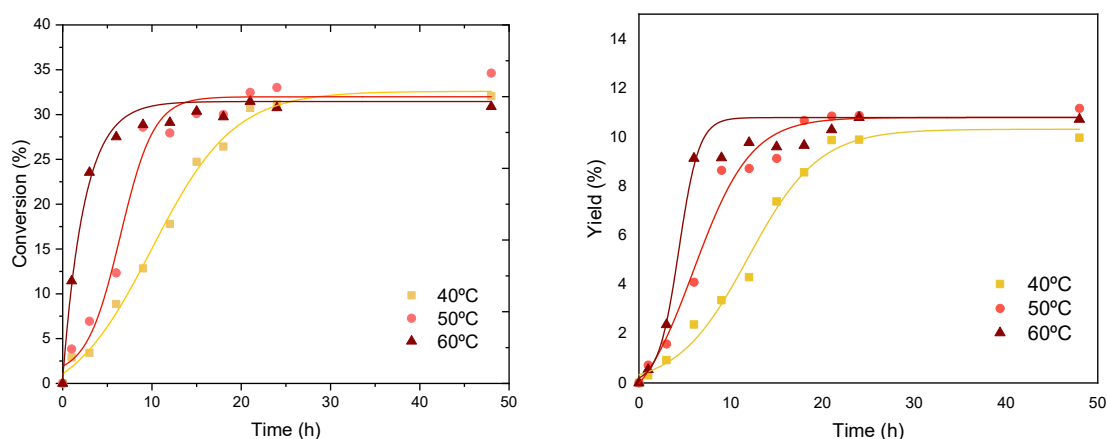
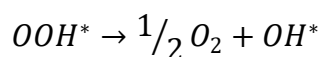
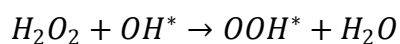


Figure 5. Conversion and yield values vs time for the supercritical epoxidation of grape seed oil. P=150 bar, T=40°C, 50°C, 60°C

As expected, the reaction kinetic is strongly affected by the temperature increase. While the final epoxy content is almost achieved in 9 h at 60°C, more than twice that time is needed at 40°C. However, the value of the maximum conversion of unsaturations into epoxy achieved is basically independent of temperature in the range studied, which suggest that still certain limitations to get greater levels of epoxidation in scCO₂ are not fully overcome.

As mentioned in section 1 and highlighted by different authors ^[13–15], the *in situ* formation of percarboxylic acids is the first and the controlling one of the two reaction steps that comprise the epoxidation mechanism, and is, therefore, essential for the completion cleavage of the double bonds of the oil. When the epoxidation is carried out in supercritical CO₂, seems to be clear that there is not sufficient peroxy-carbonic acid concentration to achieve the full conversion of the reactant and that may be due to different factors. The proposed hypothesis is that although mass transfer, key to put peroxy-carbonic acid precursors in contact, is enhanced by the use of PTCs, is not enough to counter the negative effect of H₂O₂ decomposition (**¡Error! No se encuentra el origen de la referencia.**), involving the reduction of the epoxidizing precursor concentration that competes with PCA formation ^[16] and releases oxirane ring cleaving species like the ones shown in Scheme 3. This fact is added to the low reactivity of CO₂ when compared to traditional organic acids, and the absence of mineral catalyst.



Scheme 6. Hydrogen peroxide decomposition ^[17]

Another fact that should be highlighted is that the profiles for the conversion and yield do not strictly coincide. Although both follow very similar trends, there is an offset between the conversion values and the total epoxy yield. The yield values are lower than the conversion one for the same reaction times. This observation confirms that it is not possible by these means to completely avoid the formation of ring-opening products, which occur from the beginning and in parallel with the *in situ* epoxidation and post-oxirane cleavage procedures ^[8], and they represent precisely the difference between the two parameters.

The initial hypothesis is that conversion of double bonds by peroxycarbonic acid is expected to behave similarly when compared with the kinetics of the epoxidation of vegetable oils with conventional solvents, that, when organic acids are used, according to the Prileschajew reaction, follows a pseudo-first-order kinetics ^[18].

In order to check that assumption, the kinetic equation that would define this process is taken as starting point:

$$-d[DB]/dt = k \cdot [DB]^{n1} [PCA]^{n2} \quad [6]$$

Where [DB] and [PCA] are molar concentrations of double bonds and peroxycarbonic acid, respectively, k is a kinetic constant, and n1, n2 are the reaction orders with respect to each one of the reagents.

Assuming that the reaction is of pseudo first order for both double bonds and peroxycarbonic acid, the rate equation would be expressed as follows:

$$-d[DB]/dt = k[DB] \quad [7]$$

Now the kinetic constant k is defined as $k = k'[PCA]$, and the equation 2 should be integrated, obtaining the final expression:

$$\ln([DB]_0/[DB]) = kt \quad [8]$$

Eq. 8 is plotted in Figure 6 taking into consideration that the measured parameter for the concentration of double bounds in this work is the iodine value, and assuming that it is directly proportional to it, and so $\ln([\text{DB}]_0/[\text{DB}]) = \ln(\text{IV}_0/\text{IV})$.

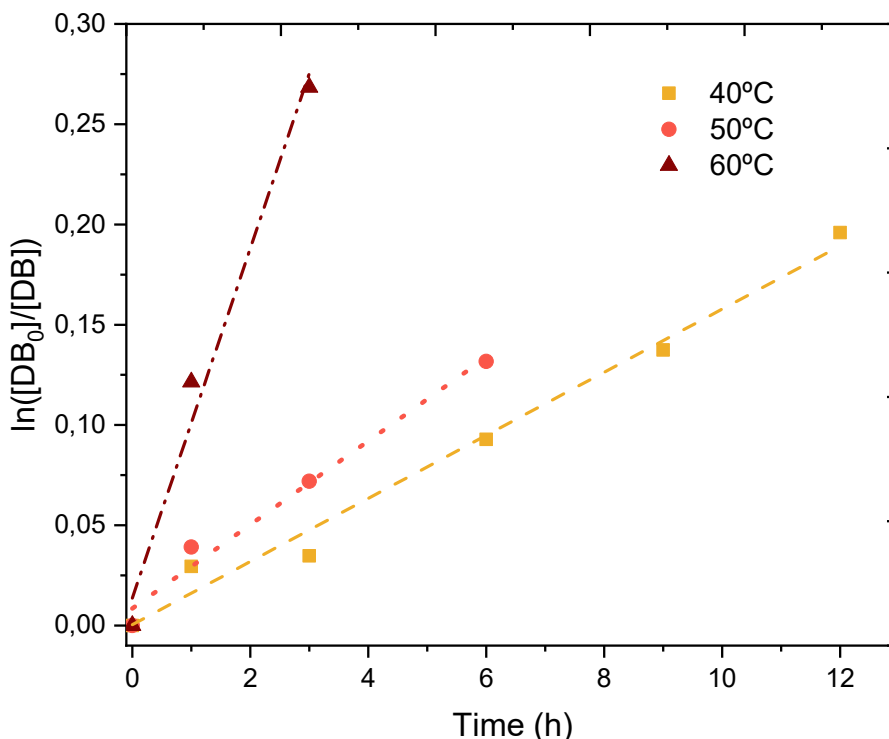


Figure 6. Reaction rate equation fitting of experimental data at 40, 50 and 60°C.

Coefficients of determination (R^2) and reaction rate constants (k) obtained from the slopes of the linearly fitted data in Figure 6 are shown in Table 1.

Table 1. Coefficients extracted from linear adjustment of the conversion experimental data at 40, 50 and 60°C

	40°C	50°C	60°C
R^2	0.9851	0.9814	0.9818
k (h^{-1})	0.0157	0.0209	0.0872

High R^2 values for the three temperatures series imply a really good fitting to a linear adjustment of the experimental data and confirms that the reaction follows pseudo-first order kinetics in the initial stages, when the rate of reaction control is the controlling step of the process.

Rate constants (k) values (Table 1) cover a range in the order of 10^{-2} h^{-1} , one order slower than catalyzed organic acid epoxidation like peracetic or performic acids [18]. Those values can be fitted to Arrhenius Equation (Eq. 9) in its linear form (Eq. 10), to calculate the

dependence of reaction rate with temperature ^[19] and to obtain activation energy (E_a) term as illustrated in **Figure 7**. Arrhenius fitting of rate constants

$$k(T) = Ae^{-\frac{E_a}{RT}} \quad [9]$$

$$\ln(k) = \ln(A) - \frac{E_a}{R} \left(\frac{1}{T}\right) \quad [10]$$

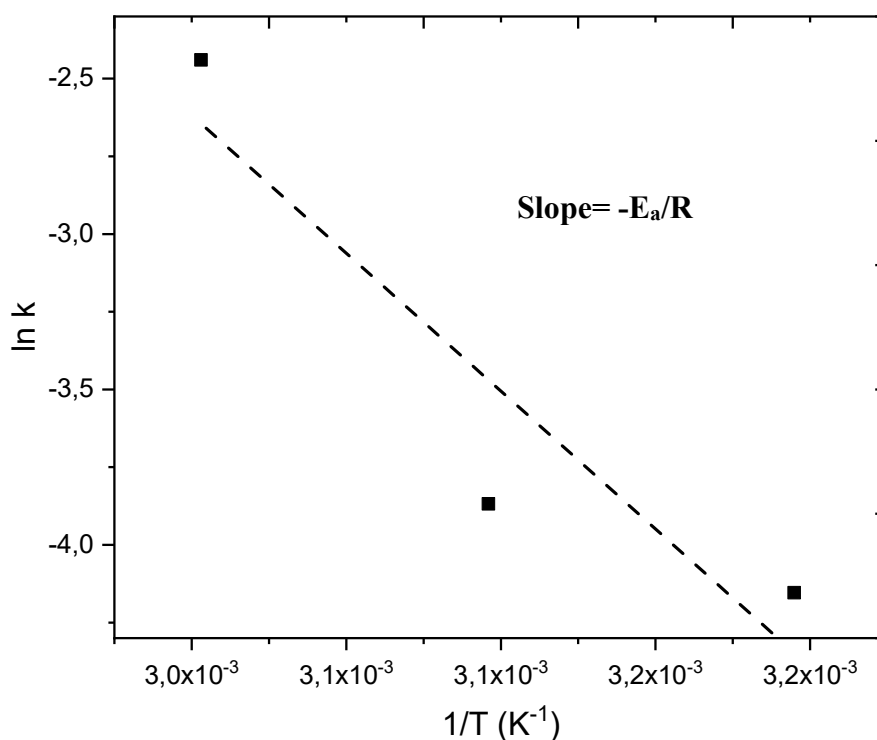


Figure 7. Arrhenius fitting of rate constants

The activation energy value calculated is 73.7 kJ/mol, a bit greater to those obtained in traditional epoxidation that used to be around ~55 kJ/mol.

4. Conclusions

A study of grape seed oil epoxidation reaction kinetics in supercritical media has been carried out at 40, 50 and 60°C.

The development of the overall reaction evolves rapidly and is clearly and positively influenced by the increase in temperature, reaching maximum conversion at around 9 h in the most favorable case.

Limited mass transfer between phases, undesired hydrolysis products, oligomer formation and rapid depletion of H₂O₂ were the main limitations to get greater values of epoxy yield.

The values obtained for reaction rate constants (k) were 0.0157 h^{-1} for 40°C , 0.0209 h^{-1} for 50°C and 0.0872 h^{-1} for 60°C . Activation energy calculated with the Arrhenius equation, was 73.7 kJ/kmol .

These facts highlight the needs to optimize the epoxidation process of vegetal oils in scCO_2 , under an environmental approach, and find a proper non-hazardous catalyst than could enhance the reaction rate and the selectivity the epoxidation in supercritical conditions.

5. Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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