

ANALYSIS AND OPTIMIZATION OF GRAPE SEED OIL EPOXIDATION IN SUPERCRITICAL CO₂

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ABSTRACT

In this work, it is proposed to check the viability of the epoxidation process of grape seed oil under supercritical conditions, select and optimize the ratios of the different reagents and/or additives that take part in it.

Different experiments were performed involving oil, hydrogen peroxide, CO₂ (as the supercritical fluid), sodium bicarbonate and different phase transfer catalysts (PTC) as enhancers for the performance. Operating conditions were set in 150 bar, 40°C and 15 h. Subsequently, a statistical study of the influence of each of the reagents on the yield was carried out. Finally, it was possible to reach 8.31% yield by means of the selection of an optimal PTC.

This is the first approach reported to the epoxidation of vegetable oils through the utilization of scCO₂ not only as a solvent but also as a reactant, using several PTCs and analyzing its effect and that of epoxy agents and enhancers.

KEYWORDS

Supercritical, epoxidation, grape seed oil, vegetable oil, CO₂, phase transfer catalyst.

Abbreviations

scCO₂: Supercritical Carbon Dioxide

PTC: Phase Transfer Catalyst

TBAB: Tetrabutylammonium Bromide

TPAB: Tetrapropylammonium Bromide

HDTMAB: Hexadecyltrimethylammonium Bromide

1. INTRODUCTION

Vegetable oils are obtained from different seeds, fruits or roots, as a chemically heterogeneous mixture of different compounds, including triglycerides, which account for 80-99% of the total components. These are esters formed by the union of glycerin and three fatty acids (with 8-24 carbons and 0-7 saturations each). [1]

These oils are presented as an alternative bio-renewable raw material for the production of different consumer or industrial goods, mainly as precursors in different polymerization processes, the effect of greenhouse gas emissions and in general the escalating environmental awareness that is associated with several strict regulations.

As a result, there has been a more than considerable increase in recent years in the use of vegetable oils in industries such as cosmetics [2], biofuels [3] and various traditionally petrochemical derivatives [4,5].

Castilla-La Mancha, a region located in central Spain, embraces one of the largest vineyard area and powerful winery industry in the world. As a result of its activity, approximately 100,000 tonnes of grape seeds are produced per year, with a content of oil near to 20 wt.% [6].

Its availability, affordable price in origin (as a consequence of being basically a by-product), high content in functionalizable unsaturated bonds and the fact of being a sustainable resource make grapeseed oil an attractive choice as the backbone for new chemical manufacturing.

The reactivity of vegetable oils is caused, in large part, by the availability of the double C=C bonds in their triglycerides molecules. This electron-rich double bond type π allows electrophilic or nucleophilic addition reactions such as hydrogenation, hydroxylation, epoxidation, etc. All these mechanisms lead to the obtaining of different products that can be used as final products with high added value or as intermediates that will serve for a further chemical synthesis of more elaborate compounds.

Epoxidation is one of the most versatile and used methods of those previously mentioned, and can generate a multitude of useful compounds in different applications such as epoxy resins [7], coatings [8], painting [9], plasticizers [10], or thermosets [11,12].

The processes that have been used to prepare epoxides are usually carried out by one of the following procedures: epoxidation with organic peracids using acid catalysts,

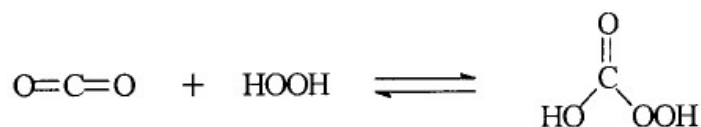
epoxidation with organic/inorganic peroxides and transition metal catalysts, epoxidation with halohydrins using hypohalous acids and their salts or epoxidation with molecular oxygen [13].

However, epoxidized vegetable oils are mostly obtained via the Prileschajew reaction, included in the first category abovementioned, which consists on the substitution of an unsaturation by an oxirane ring caused by a percarboxylic acid (peracetic or performic acids are the most common) that is formed *in situ* by the reaction of corresponding acid with hydrogen peroxide. The electrophilic addition of peracid oxygen to the alkene double bond generates an electronic rearrangement in the peracid; an epoxide and a carboxylic acid are formed as products [14–16]. Soluble mineral acids, commonly sulfuric acid, are used as catalysts for this reaction. Therefore, environmental concerns related to the handling of salts formed during the neutralization of the catalyst and technical and economic problems associated with corrosion and separation operations due to the use of both peracids and mineral acids, push-up the search for a substitute for this technology [17].

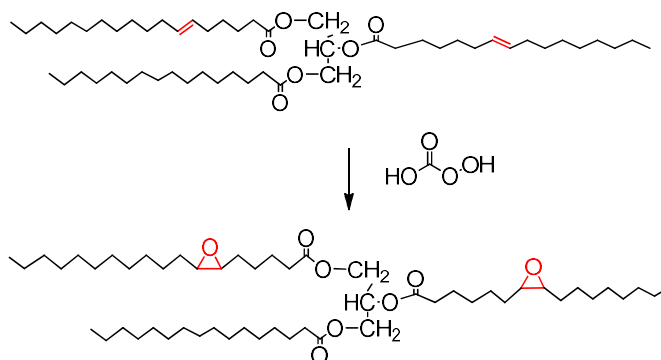
Carbon dioxide (CO_2) can react with H_2O to form carbonic acid, and by analogy, when finds hydrogen peroxide (H_2O_2) is expected to form the corresponding peracid, named by some authors as peroxy-carbonic acid [18]. This acid could replace traditional peracids as a cleaner reactive and easier to handle alternative for the epoxidation of olefins in general and vegetable oils in particular.

Hence, not only CO_2 , but supercritical CO_2 (scCO_2) could be a great substitute for the common carboxylic acids used in Prileschajew reaction. Such claim is based on the properties of the supercritical fluids, with a density high enough to grant them a considering solvating power, also a lower viscosity and a molecular diffusivity significantly higher than the corresponding to the liquid phase, both of them related to the improvement of mass transfer. All these properties in addition to the mild conditions needed to reach the supercritical point and that scCO_2 is affirmed to be GRAS (generally recognized as safe) make it a really attractive carrier in the epoxidation reaction process [19]. Finally, the use of the supercritical technology implies a great advantage since a nearly pure epoxidized product can be obtained after reaction through a simple depressurization, without the need of a neutralization step as pH of the epoxidized mixture results close to 7, due to the ease and complete separation of the scCO_2 [20].

Therefore, based on the results of previous grape seed oil epoxidation studies [18], the following alternative reaction scheme is proposed. The usage of the abovementioned peroxydicarboxylic acid as a main enabler intermediate. It is expected in the aqueous phase by the reaction of CO₂ with the H₂O₂ solved on it (Scheme 1), and its subsequent migration to the oily phase to complete the epoxidation mechanism (Scheme 2)



Scheme 1. Peroxydicarboxylic acid formation [18]



Scheme 2. Peroxydicarboxylic acid catalyzed triglyceride epoxidation

Actually, epoxidation of vegetable oils in supercritical carbon dioxide is a topic about which only a short communication of Li et al. (2008) [20] has been published, to our knowledge. Taking into account all these considerations, the aim of this work is the study and optimization of the epoxidation reaction of grape seed oil in supercritical CO₂ media, For this purpose, the use of sodium bicarbonate is also proposed in order to improve the performance of peroxydicarboxylic acid as an oxidizer, increasing its oxidizing power.

Additionally, in the light of the convoluted phase distribution and mass-transfer limitations between them it is considered appropriate to use the aid of what is known as a phase transfer catalyst or PTC.

To achieve the planned objective through this novel approach, therefore, it is proposed to check the viability of the epoxidation process, optimize the quantities of all the reagents

and/or additives that take part in it and select the PTC that presents the best performance among different ammonium salts.

2. MATERIAL AND METHODS

2.1. Materials

Grapeseed oil was kindly provided by Alvinesa S.A. (Daimiel, Ciudad Real, Spain). The tetrabutylammonium bromide (TBAB) (>98%), hexadecyltrimethyl-ammonium bromide (HDTMAB) (<98%), hydrogen peroxide solution (30% wt), and sodium bicarbonate (99.5-100.5%) were supplied by Sigma-Aldrich, Inc. (Spanish division, Madrid, Spain). The tetrapropylammonium bromide (>98 %) was supplied by Fluka (Spanish division, Madrid, Spain).

The grape seed oil fatty acid profile was already determined in a previous research work of our group [21], being the main composition formed by C16:0 palmitic acid (6.9% wt.), C18:0 stearic acid (4% wt.), C18:1 oleic acid (19% wt.) and C18:2 linoleic acid (69.1% wt.).

The iodine value (IV) and average molecular weight (MW) of the selected oil were 137.05 g I₂/100 g sample and 877.29 g/mol respectively, as determined in this study.

2.2 Experimental Setup

The experiments were carried out in a high-pressure set-up, shown in Figure 1. It was constructed and operated as a batch system. The high-pressure reactor is a Berghof BR-300 model (300°C and 200 bar max. operating conditions) with an electrical heating jacket, incorporated mechanical stirring system, and a Berghof BTC-3000 temperature controller. The reactor vessel has a volume of 390 ml and a TFMTM-PTFE Insert integrated of 310 ml volume (62.5 mm inner diameter and 98 mm inner height). Main auxiliary equipment used in the set up are a Milton-Roy Miniroyal Series (MD140G4M500/Z) dosing pump and a “Frigiterm-TFT-10 SELECTA” refrigeration bath.

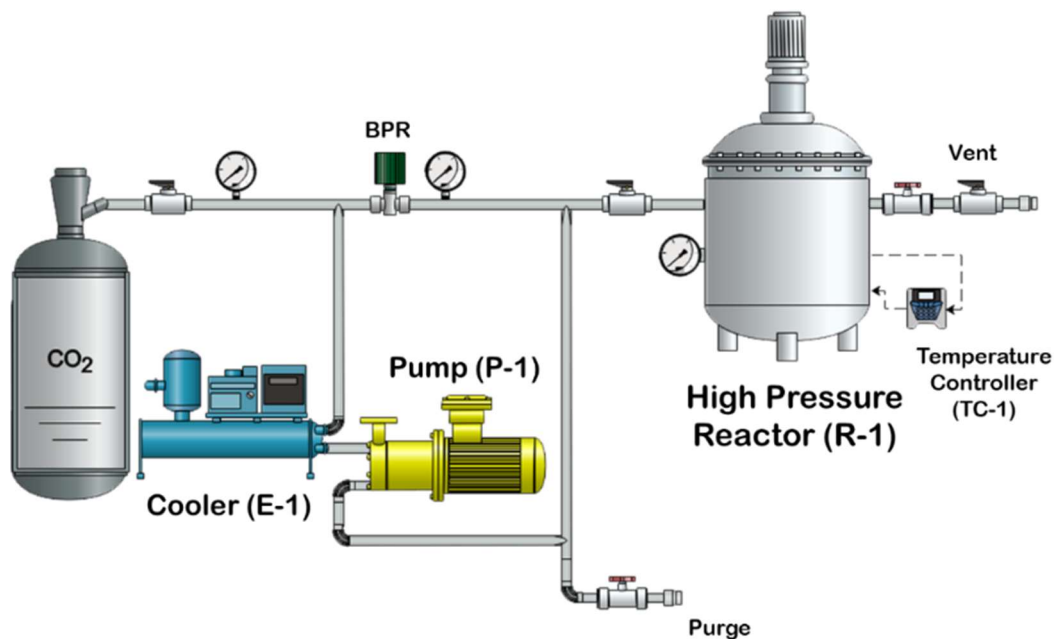


Figure 1. Experimental High-Pressure Set-up

Firstly, every reactant apart from CO₂ is charged into the vessel and then it's closed. Subsequently CO₂ is first cooled down and then pumped into the reactor until reaching the operational pressure. Meanwhile the heating system keeps the vessel at the desired process temperature. After that, the vessel is hermetically closed, and the stirring is maintained during the reaction time. Finally, the vent valves are used to release the CO₂ and the product is obtained from inside the vessel. The operating conditions were set on 40°C ,150 bar and 15 h based on previous studies on the solubility of grape seed oil from Duba et al. [22] and on the use of these PTC for a similar case from Li et al. [20] with the idea of working in the mildest possible conditions. Agitation speed used for every experiment was 500 rpm. This epoxidation product is lately separated from the by-products through a centrifuge at 4000 rpm.

2.3 Characterization Methods

Determination of the iodine value

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

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.

$$EO = \frac{1}{EE} * MW_O \quad \text{Eq. 1}$$

EO: Oxirane Oxygen (g oxygen/g sample)

EE: Epoxy Equivalent (g sample/ mol epoxide)

MW_O: Atomic weight of oxygen (g/mol)

Yield, selectivity and conversion calculations

In order to quantify the results obtained, the concept of yield (η) is detailed giving us an idea of the overall performance of the reaction and is defined by the product of the conversion (x) of the double bounds involved in the reaction and the selectivity (s) to the transformation into oxirane rings.

$$\eta = x \cdot s \quad \text{Eq. 2}$$

Being so, the conversion can be calculated as the difference in the number of double bonds at the beginning and at the end of the epoxidation process, which is given by the iodine value.

$$x = 1 - \frac{IV_0}{IV} \quad \text{Eq. 3}$$

Analogously, selectivity can be calculated as the relationship between the amount of epoxy groups contained in the sample and the maximum amount possible considering that all double bonds would have been specifically converted into oxirane rings.

$$S = \frac{EO(\%)}{EO_{max}(\%)} \quad \text{Eq. 4}$$

$$EO_{max}(\%) = \frac{(IV_0 - I) \cdot MW_O \left(\frac{g}{mol}\right)}{MW_{I_2} \left(\frac{g}{mol}\right) \cdot 100} \quad \text{Eq. 5}$$

IV: Iodine value of the sample

IV₀: Iodine value of the raw material

MW_O: Atomic weight of oxygen (g/mol)

EO: Oxirane oxygen content of the sample.

EO_{max}: Maximum theoretical oxirane oxygen content, assuming 100% selectivity towards epoxides.

Experiments have been replicated to ensure reproducibility and every one of them over 2% error has been discarded.

Infrared Spectrometry Equipment

This technique, based on the fact that chemical bonds of substances have specific vibration frequencies corresponding to molecular energy levels, was used to characterize the different bonds present in a sample.

The infrared spectra were obtained with a Varian 640-IR FT-IR spectrophotometer in the range of 4000 to 400 cm⁻¹, resolution 2 cm⁻¹ and 32 sweeps per sample.

Gel permeation chromatography (GPC)

Using this analytical technique, the molecular weight distribution of the different samples was determined. The equipment used was a Shimadzu chromatograph which incorporates two columns Waters HR-2 (pore size 500Å) and HR-0.5 (pore size 50Å) and detector of refractive index and viscosity, 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.

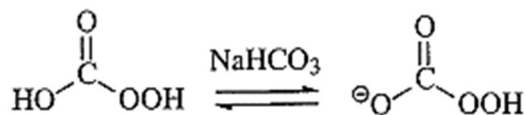
3. RESULTS AND DISCUSSION

3.1. Analysis of the influence of the additives/enhancers molar ratio

The research developed in this study focuses in the obtention of the epoxidized product from the grapeseed oil. Different epoxidations that have been already successfully carried out used vegetable oils such as soybean oil or castor oil, which have a really similar unsaturated fatty acids content, and therefore, iodine number [23,24].

The first step was to confirm that the additives proposed were the proper ones to carry out the epoxidation reaction in scCO₂.

Sodium bicarbonate (NaHCO_3) is one of the reagents chosen which is expected to increase the effective concentration of Peroxycarboxylic acid by the conversion to its ionized form [18] as it is showed in Scheme 3.



Scheme 3. Peroxycarboxylic acid ionization [18]

Quaternary ammonium salts are considered organophilic enough to transport the anion formed from peroxycarboxylic acid to the oily phase, but also with sufficient vapor pressure to have some solubility in supercritical CO_2 [25]. For that reason, the PTC selected initially for this study was tetrabutylammonium bromide.

For this reason, experiments following a experimental design with the H_2O_2 , NaHCO_3 and TBAB molar ratio with respect to oil as independent variables were carried out. Table 1 shows the experiment design for this first study.

Table 1. Interval for the variables studied for the feasibility study. P=150 bar T=40°C

Run	Molar ratio (with respect to oil)			
	Oil	H_2O_2	NaHCO_3	TBAB
H_2O_2	1	2		
$\text{H}_2\text{O}_2 + \text{NaHCO}_3$	1	2	0.1	
$\text{H}_2\text{O}_2 + \text{NaHCO}_3 + \text{TBAB}$	1	2	0.1	0.025

To confirm that the reaction has taken place, in Figure 2, infrared spectrometric analyses are shown, which allow confirmation of the presence of absorption signals around the range corresponding to the disubstituted epoxide group ($\sim 825\text{-}960\text{ cm}^{-1}$) [26].

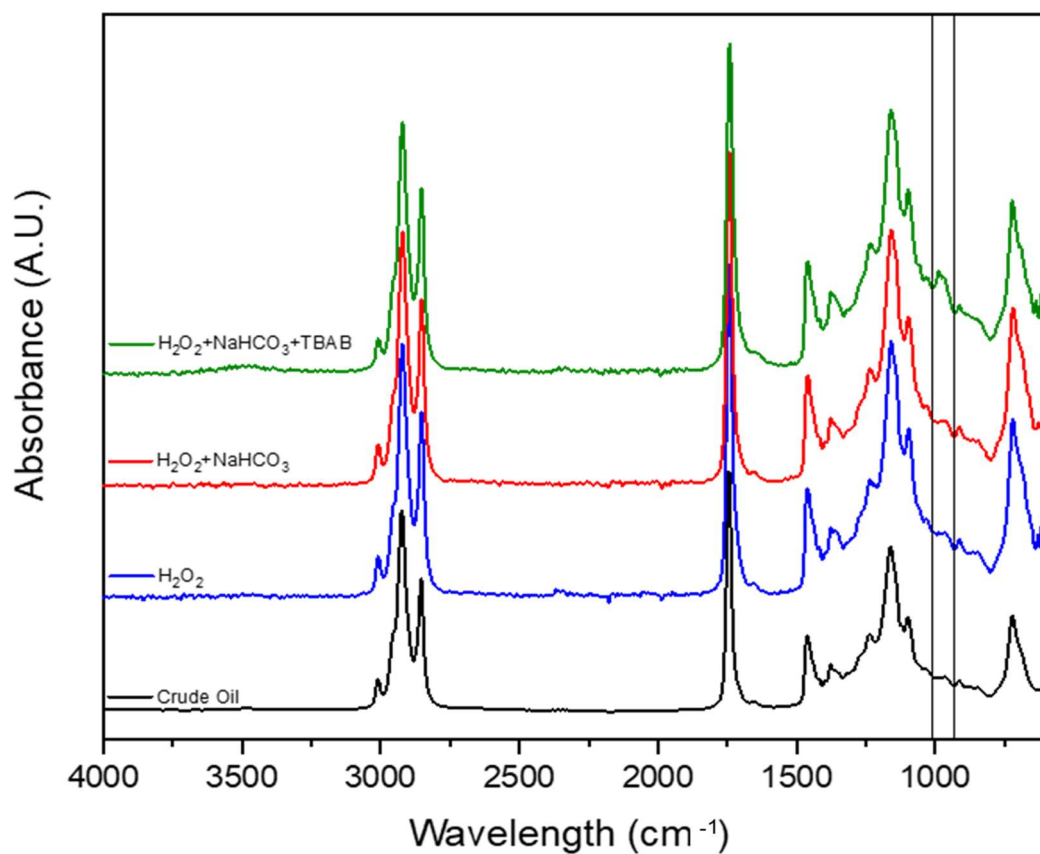


Figure 2. FTIR spectra of the feasibility study products.

Oil samples were characterized after reaction in order to calculate conversion, selectivity and yield as explained in point 2.2. In Figure 3, conversion, selectivity and yield of the initial experiments are shown.

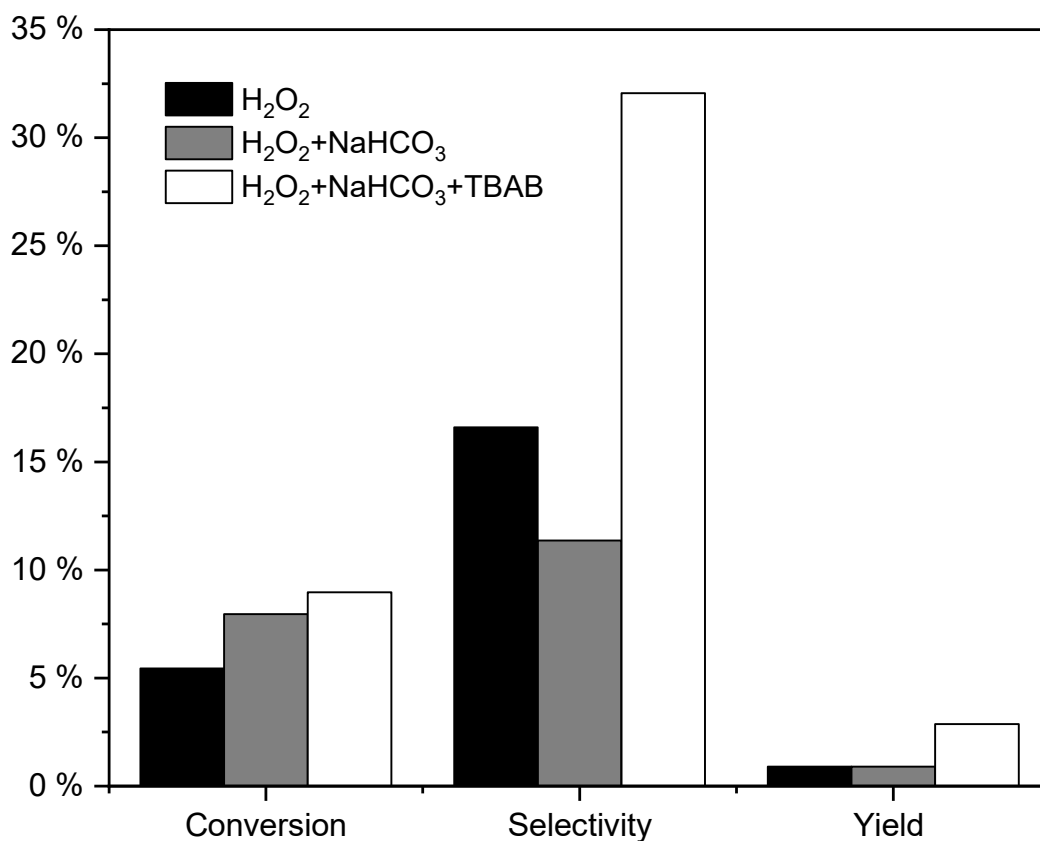


Figure 3. Feasibility study results

It can be observed that in all the experiments some epoxide has been generated in appreciable magnitude and so it can be claimed that the reaction has been carried out successfully.

Both enhancers show a positive influence mainly on the conversion, that raises to almost double the previous value in concordance to the ionization and mass transfer enhancement expected effects. PTC effect is much more pronounced in terms of epoxide yield, suggesting that mass transfer is a key limitation in this type of systems.

Once the viability of the process has been demonstrated, the issue of the low yield obtained in this first run of experiments is considered. In order to improve it, an increase in the relative quantities of the additives is proposed (as shown in Table 2), in such a way that the amount of hydrogen peroxide and NaHCO₃ becomes significantly different, maintaining the idea of increasing the effective concentration of peroxycarbonic acid, as well as PTC, which is directly involved in bringing into contact all the phases necessary for the reaction. It has been chosen to triple the ratios of these reagents in order to ensure a significant change in the results to be appreciated.

Table 2. Second series of experiments. T=40°C, P=150bar

Run	Molar ratio (with respect to oil)			
	Oil	H ₂ O ₂	NaHCO ₃	TBAB
H ₂ O ₂	1	6		
H ₂ O ₂ + NaHCO ₃	1	6	0.3	
H ₂ O ₂ + NaHCO ₃ + TBAB	1	6	0.3	0.075

As can be seen in Figure 4, there is a growing trend, mainly in terms of conversion. The ‘H₂O₂+ NaHCO₃+TBAB’ conversion value is actually the highest found so far for the epoxidation of oil in supercritical media in the literature to the best of our knowledge, where the maximum conversion previously reported was found in the work by Li et al. (2008) with the use of sodium bicarbonate and Sodium dodecylbenzenesulfonate (SDBS) as catalyst in the supercritical epoxidation of soybean oil, obtaining a value of 12% [20].

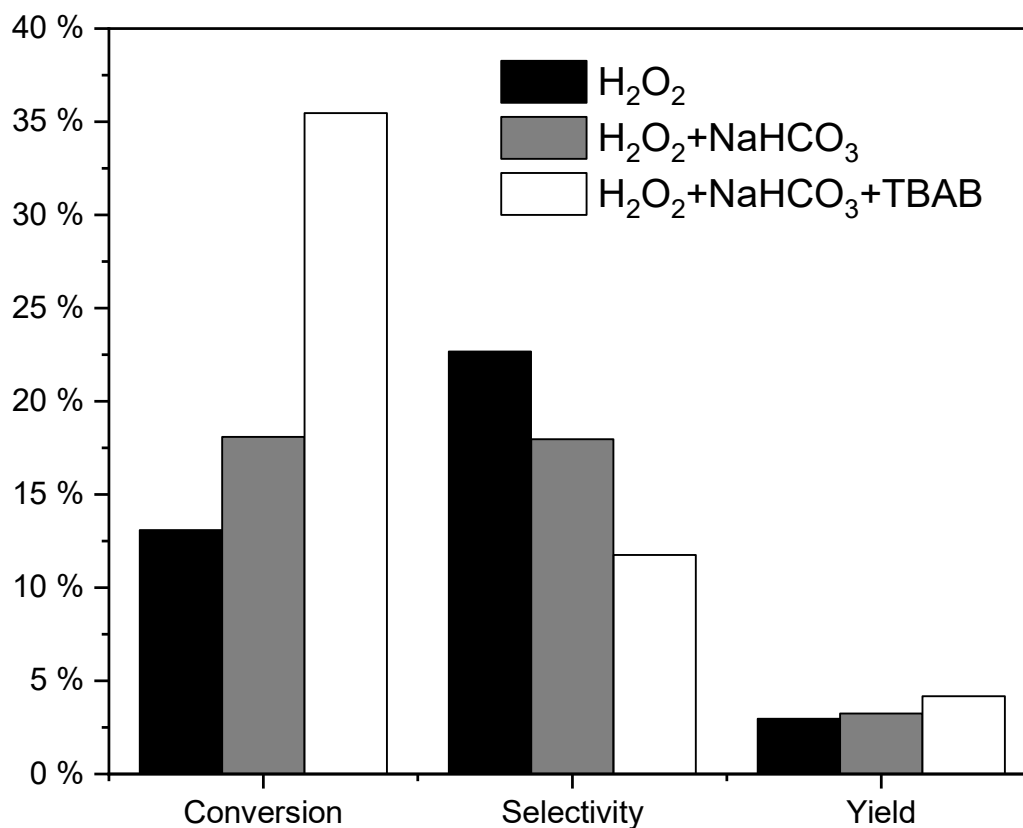


Figure 4. Characterization results from the second series of experiments

However, such a large increase in conversion leads to a downturn in the selectivity. While the epoxide concentration in the media is enhanced, some other types of secondary reactions, parallel and/or consecutive are promoted, such as oxirane ring opening which may result in a more heterogeneous and less suitable product for future chemical transformations. To verify this, an analysis of the products obtained by gel permeation chromatography was performed, the chromatograms of which are shown in Figure 5.

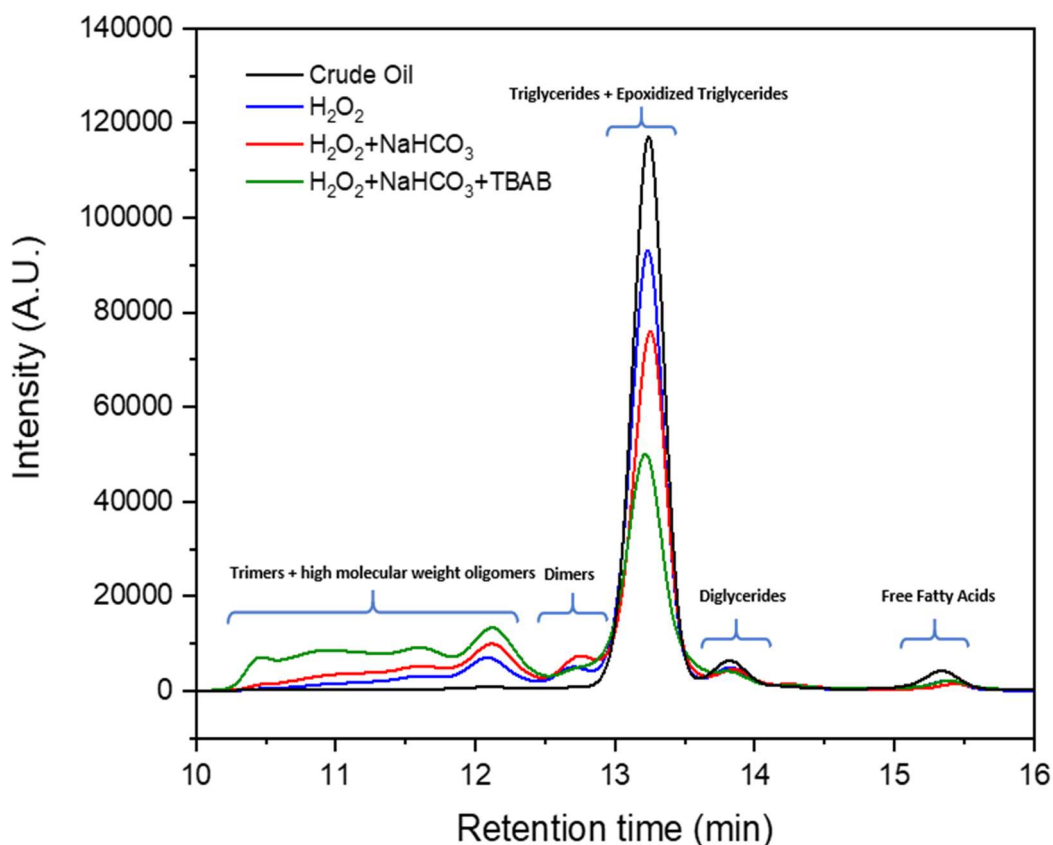
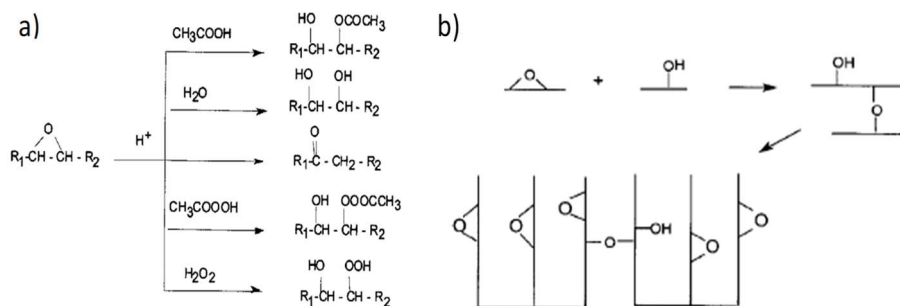
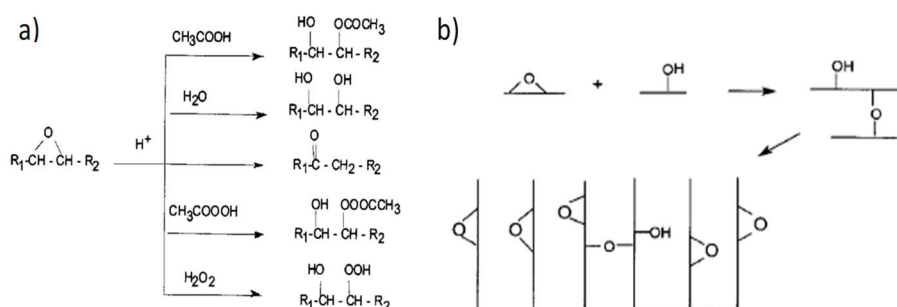


Figure 5. GPC chromatograms of the products from the second series of experiments

Figure 5 shows a slight displacement to the left in the retention time at the main peak of the reaction products, which represents an increase in the molecular weight, related to the addition of oxygen, due to the conversion of double bonds, present in the crude oil, into epoxides. Additionally, the presence of diglycerides and free fatty acids is deferred (when compared to the GPC analysis of a sample of pure oleic acid not shown in the picture), which in their great majority have not been formed in the reactions but were already found in the starting oil. Moreover, a multitude of secondary products appear that may have been formed during the course of the reaction.



Scheme 4 a) shows a series of possible secondary reactions, proposed by Petrović et al (2002) [27] that can occur once the epoxy has already been formed.



Scheme 4. Possible consecutive oxirane ring opening reactions for the formation of by-products a) Primary by-products b) Oligomerization products [27]

The main secondary reaction is the formation of oligomers by further polymerization between each functionalized triglyceride molecule. An example of a formation scheme for these compounds is shown in Scheme 4 b) where the attack of a proton on an epoxy group results in the formation of a hydroxyl and acetyl or formyl group. If the reaction stops here a polyol is obtained, but if it continues reacting with another epoxy group it results in the formation of oligomeric ethers.

Finally, from the GPC chromatograms, a semi-quantitative analysis is carried out integrating the areas corresponding to each signal, which allows to compare the proportion of each of the secondary products with respect to the total sample. The results are shown in Table 3, confirming that oligomeric products are the majority in these reactions, and in the case of $\text{H}_2\text{O}_2 + \text{NaHCO}_3 + \text{TBAB}$, as it was expected, because of its highest conversion and the lowest selectivity, it is where the secondary products are most abundant.

Table 3. Relative distribution of the presence of secondary products according to GPC analysis

Run	H ₂ O ₂	H ₂ O ₂ + NaHCO ₃	H ₂ O ₂ + NaHCO ₃ + TBAB
Triglycerides	73.14%	61.21%	43.56%
High-MW Oligomers	14.31%	24.73%	44.74%
Dimers	4.68%	6.62%	3.91%
OLIGOMERS	18.99%	31.35%	48.65%
Diglycerides	5.47%	5.47%	5.00%
Free Fatty Acids	2.40%	1.97%	2.79%
LOW-MW PRODUCTS	7.88%	7.44%	7.79%
TOTAL BY-PRODUCTS	26.86%	38.79%	56.44%

In order to conclude with this part of the study a more exhaustive design consisting on 18 experiments was performed (Table 4) based on the variation of the 3 reactants as influence factors and 2 or 3 levels for the molar ratio values for each one of them, towards the obtention of a more detailed vision of how each one of the enhancers affects to the formation of by-products and to the overall yield.

Table 4. Interval for the independent variables for the optimization of the supercritical epoxidation process

Molar ratios with respect to oil			
Oil	1		
H ₂ O ₂	2	6	
NaHCO ₃	0	0.1	0.3
TBAB	0	0.025	0.075

The yield obtained (Table 5) in the different experiments is the response variable for the statistical analysis that was performed.

Table 5. Experimental design and results from the optimization study. T=40°C, P=150bar

Run	Molar Ratio			Conversion (%)	Selectivity (%)	Yield (%)
	H ₂ O ₂	NaHCO ₃	PTC			
1	6	0.1	0.075	21.77	17.71	3.85
2	6	0.3	0.075	35.47	11.75	4.17
3	2	0.1	0	7.96	11.36	0.90
4	6	0.1	0	11.77	13.22	1.56
5	6	0	0	13.09	22.67	2.97
6	2	0	0.025	14.80	14.96	2.22
7	2	0.1	0.025	8.96	20.58	1.84
8	2	0.3	0.075	13.50	19.31	2.61
9	2	0.1	0.075	20.33	11.01	2.24
10	6	0	0.075	13.36	24.45	3.27
11	2	0.3	0	6.33	9.61	0.61
12	6	0.3	0.025	16.85	8.74	1.47
13	2	0	0	5.44	16.59	0.90
14	2	0	0.075	16.83	10.90	1.83
15	2	0.3	0.025	6.33	28.97	1.83
16	6	0	0.025	8.07	22.13	1.78
17	6	0.1	0.025	14.05	18.68	2.62
18	6	0.3	0	18.08	17.97	3.25

The first and most relevant conclusion from this experimental design is the maximum yield value of 4.17% obtained for the reaction (H₂O₂:NaHCO₃:TBAB, 6:0.3:0.075), with the maximum enhancer concentrations, which, therefore, will be the reference point for future experiments. It is the reaction with the highest conversion, therefore, the one with the highest EO_{max} . Theoretically if it were possible to lead the selectivity of the reaction,

without compromising the conversion values previously obtained, towards the formation of only epoxidized oil, a much higher overall yield could be achieved.

Subsequently, a fairly extensive statistical analysis is carried out thanks to STATGRAPHICS® software, setting equivalences between the selected levels for the factor molar ratios and the codes used within the tool provided by the software as follows in Table 6.

Table 6. Equivalence between molar ratio and code for analysis in STATGRAPHICS

Factor	Molar Ratio	Code
A: H ₂ O ₂	2	-1
	6	1
B: NaHCO ₃	0	-1
	0.1	0
	0.3	1
C: PTC (TBAB)	0	-1
	0.025	0
	0.075	1

Firstly, the estimated effects for each of the response variables are shown in Table 7.

Table 7. Estimated effects

Factor	Estimated Effect		
	Conversion	Selectivity	Yield
A: H ₂ O ₂	0.0578	0.0177	1.1067
B: NaHCO ₃	0.0416	-0.02238	0.1617
C: PTC (TBAB)	0.0976	0.0030	1.2967
AB	0.0780	-0.0803	0.1283
AC	-0.0054	-0.0028	-0.1267
BC	0.0322	0.0233	0.4225

The criteria to consider an effect as “statistically significant” has been that its p-value should be less than 0.05 which is the significance limit for the predetermined confidence level.

Firstly, it is observed that the interaction between two of the factors (H₂O₂ and NaHCO₃) results in a statistically significant effect both with almost same magnitude for the

conversion and for the selectivity, but of opposite sign, resulting in the neutralization of these effects when analyzed jointly in the yield.

However, there are still two clearly relevant and positively influencing effects in the conversion analysis that remain the same when studying the overall reaction yield, namely the amount of hydrogen peroxide and TBAB.

This fact reinforces two clear lines of reasoning: on the one hand, that hydrogen peroxide is key to increase the yield of the reaction, as it is the main precursor of the epoxidation agent; and on the other hand, that contact between phases is one of the most relevant aspects in this process, and that it certainly improves with the use of a PTC (in this case tetrabutyl-ammonium bromide).

Furthermore, a predictive model can be obtained that gives out the estimation of the trend and values of the epoxidation yield for the whole range among the conditions studied (using the code values presented before).

$$\text{Yield (\%)} = 2,2178 + 0.5533 * H_2O_2 + 0.0808 * NaHCO_3 + 0.6483 * PTC + 0.0642 * H_2O_2 * NaHCO_3 - 0.0633 * H_2O_2 * PTC + 0.2113 * NaHCO_3 * PTC \text{ Eq. 6}$$

H₂O₂: Equivalent code number (-1,1) for H₂O₂ molar ratio

NaHCO₃: Equivalent code number (-1,1) for NaHCO₃ molar ratio

PTC: Equivalent code number (-1,1) for PTC molar ratio

This model can be represented graphically, as different estimated response surface diagram. Figure 6 shows as an example three of these diagrams in which the value for each of the NaHCO₃ levels has been set, as this is a factor with no consistent effect, in order to crosscheck the other two relevant factors effect, and already using real molar ratio terms instead of code, as it may be more representative.

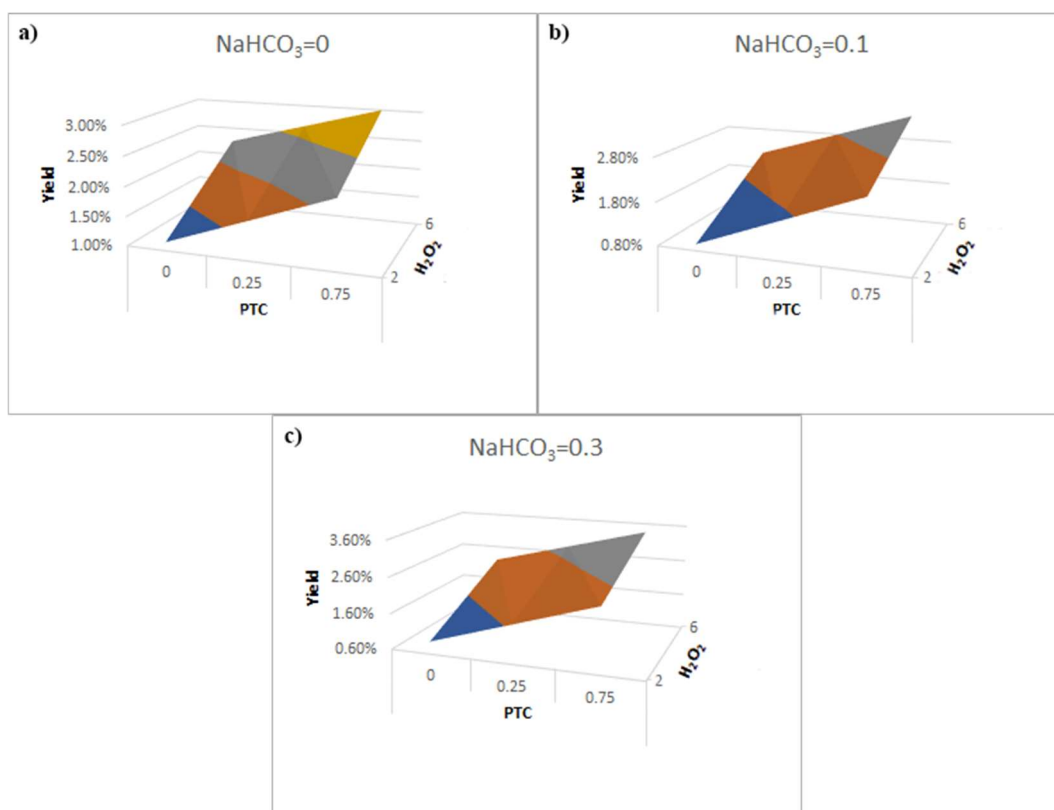


Figure 6. Response surface diagrams for the Yield predictive model representation. $NaHCO_3$ set value: a) 0, b) 0.1, c) 0.3

These graphs confirm the positive effect on the conversion of both factors due to the two effects commented in this same section, and it is observed that hydrogen peroxide is the one that even between these two, influences in a more forceful way, as it participates directly as a reagent in the global mechanism of the epoxidation reaction, and not only as an enhancer of the process.

Finally, this fact opens also the possibility to set the value for the variable related to the addition of sodium bicarbonate at 0.3, where the yield values are higher; and to initiate a future study to obtain a model applicable in a much wider range of conditions than the one analyzed so far, as it is necessary to study only two factors instead of three.

3.2. Phase Transfer Catalyst (PTC) Selection

The next step in the way to improve the performance of the epoxidation reaction of vegetable oil was to analyze how different molecules employed as PTC influence the yield of the process. For this purpose, three different quaternary ammonium salts were analyzed: Tetrabutylammonium bromide (TBAB), Tetrapropylammonium bromide (TPAB) and Hexadecyltrimethyl ammonium bromide (HDTMAB).

A new run of experiments is proposed maintaining the molar ratio for each one of the phase transfer catalysts as shown in Table 8.

Table 8. PTC selection experiments P=150 bar T=40°C

Run	Molar ratio with respect to oil					
	Oil	H ₂ O ₂	NaHCO ₃	TBAB	TPAB	HDTMAB
TBAB	1	6	0.3	0.075		
TPAB	1	6	0.3		0.075	
HDTMAB	1	6	0.3			0.075

Catalytic results for these experiments are displayed in **¡Error! No se encuentra el origen de la referencia.**Figure 7.

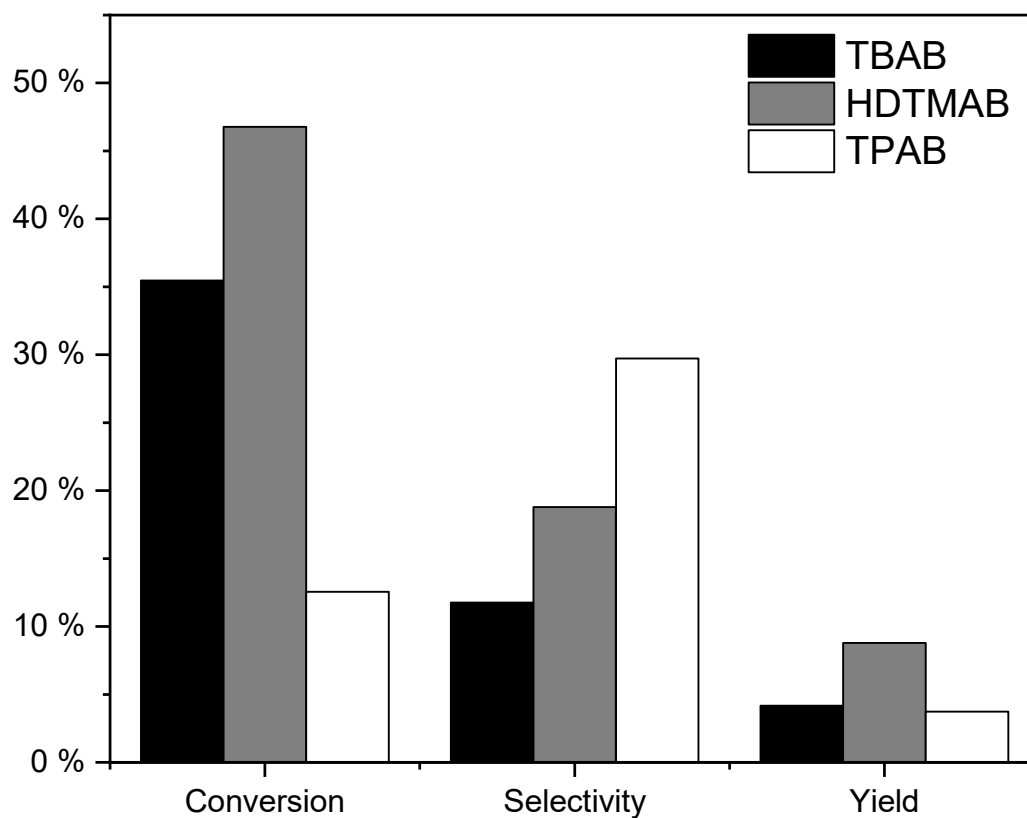
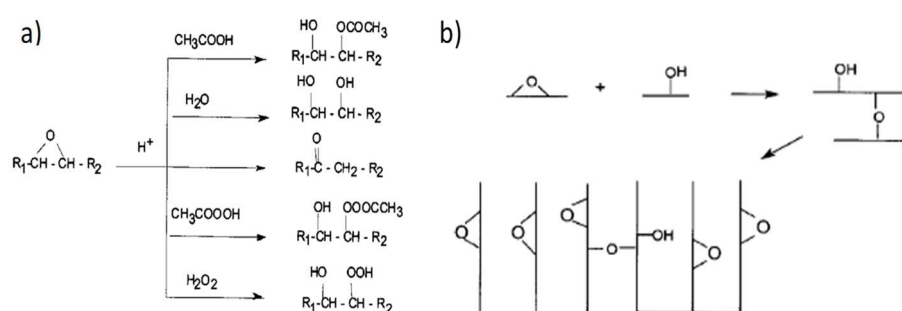


Figure 7. Catalytic results for the PTC selection experiments.

This comparison clearly shows that the PTC that presents the greatest performance is the HDTMAB, both in terms of conversion of unsaturation and the overall yield of the epoxidation reaction.

It is remarkable, however, that despite being this the reaction that globally provides a higher quantity of product, the reaction involving the use of TPAB shows a higher selectivity but a much lower conversion. This result points out one of the main problems when working with this reaction: when the conversion of the reaction reaches relatively high values the selectivity is compromised, probably because increasing the relative concentration of epoxies in the medium facilitates the contact of these with reactive species coming from mainly the aqueous phase (H_2O, H_2O_2, H^+), what leads to the formation of products of high molecular weight, as a result of oligomerization mechanisms (



Scheme 4).

Again, the GPC chromatograms of the reaction products are shown in Figure 8.

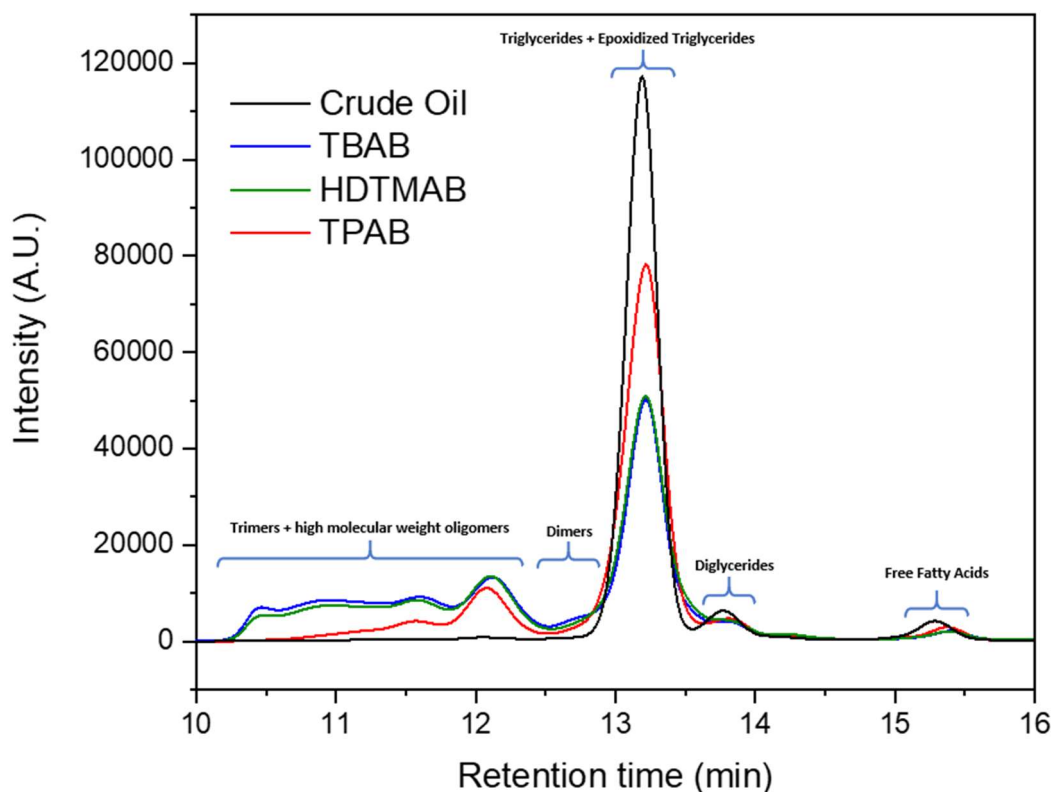


Figure 8. GPC chromatograms of the PTC Selection experiments products.

In view of the chromatograms shown, as well as the relative values of by-product formation (Table 9), the appearance of this phenomenon is confirmed, and so is the direct relationship between high quantity of oligomers formed and high conversion values accompanied by low selectivity.

Table 9. Relative distribution of the presence of secondary products according to GPC analysis

Run	TBAB	HDTMAB	TPAB
Triglycerides	44.82%	70.34%	49.81%
High-MW Oligomers	44.57%	18.89%	40.85%
Dimers	3.28%	2.07%	1.98%
Oligomers	47.84%	20.96%	42.84%
Diglycerides	4.44%	5.38%	4.71%
Free Fatty Acids	2.90%	3.32%	2.65%

Low-MW Products	7.34%	8.70%	7.35%
TOTAL By-products	55.18%	29.66%	50.19%

In all the previous experiments the reaction time was fixed in 15 h. It seems clear that the selectivity values can be improved stopping the reaction at the time in which the concentration of the epoxidized mono-oil is maximum. This is not an easy task because in a scCO₂ reactor is difficult the extraction of samples without affecting the reaction conditions, so the kinetic of the process will be the subject of the follow-on study.

4. CONCLUSIONS

The feasibility of grapeseed oil epoxidation in supercritical media and mild temperature conditions has been demonstrated.

The statistical analysis of the experimental design shown that the influence on the reaction performance of H₂O₂/oil and PTC/oil molar ratio is relevant, while the molar ratio NaHCO₃/oil has no statistically significant influence. Likewise, a mathematical expression has been obtained that allows predicting the overall yield as a function of the 3 variables studied.

Finally, it has been proved the great importance of the molecule added as phase transfer catalyst, obtaining the best results both in conversion and in yield with HDTMAB, reaching a value of 8.31% for the latter.

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