processes

MDPI

Article

Temperature-Dependent Catalytic Performance and Selectivity in the Phase-Transfer Epoxidation of Grapeseed and Sunflower Oils

Marlena Musik * and Michał Szurgociński

Department of Organic Chemical Technology and Polymer Materials, Faculty of Chemical Technology and Engineering, West Pomeranian University of Technology in Szczecin, 70-322 Szczecin, Poland
* Correspondence: marlena.musik@zut.edu.pl

Abstract

Recently, there has been an increased interest in more eco-friendly epoxidation using vegetable oils to produce environmentally friendly intermediates. The aim of this study was to determine the optimum epoxidation temperature for grapeseed oil and sunflower oil using phase transfer catalysis (PTC). The reaction was carried out in a system: a quaternary phosphonium salt coupled to a heteropolyacid via a 30% hydrogen peroxide solution under solvent-free conditions. Fourier transform infrared (FTIR) spectra of epoxidized grapeseed and sunflower oils showed oxirane peaks at 823 cm^{-1}. ^{1}H NMR confirmed the presence of an epoxide group at 2.00–3.15 ppm, while epoxide ^{13}C NMR signals were present at 52–60 ppm. The elemental contents, i.e., hydrogen, carbon and oxygen, of the crude grapeseed and sunflower oils and the products after epoxidation clearly showed that oxygen was incorporated. The results demonstrated that the optimum temperature depended on both the vegetable oil and the process criterion considered. For grapeseed oil, the highest epoxide number (0.305 mol/100 g) was obtained at 50 °C, whereas the highest apparent conversion of iodine-reactive unsaturation (88.0%) was observed at 40 °C. For sunflower oil, the highest epoxide number (0.271 mol/100 g) and apparent conversion of iodine-reactive unsaturation (92.6%) were obtained at 55 °C. These results demonstrate that temperature optimization in phase-transfer epoxidation should consider not only the conversion of iodine-reactive unsaturation but also the accumulation of oxirane functionality.

Keywords: epoxidation; heteropolyacid; phosphonium salt; sunflower oil; grapeseed oil; phase-transfer catalysis

1. Introduction

Vegetable oils are renewable feedstocks for the production of oxygenated intermediates and functional materials because their fatty-acid chains contain reactive carbon–carbon double bonds [1,2]. Epoxidation converts these unsaturated sites into oxirane groups, providing products that can be further transformed into polymers, plasticizers, thermosets, polyurethanes and other value-added materials [3–12]. The properties and reactivity of epoxidized vegetable oils depend not only on the initial degree of unsaturation of the feedstock but also on the extent to which the formed oxirane groups are retained during the reaction. Consequently, the simultaneous evaluation of unsaturation conversion and epoxide formation is important for the rational design of epoxidation processes.

Catalytic epoxidation of vegetable oils has been investigated using peracids generated in situ, ion-exchange resins, polyoxometalates, transition-metal catalysts and enzymatic systems [11]. Hydrogen peroxide is an attractive oxidant because water is the main stoichio-

Check for updates

Academic Editor: Massimo Iorizzo

Received: 14 September 2026
Revised: 9 October 2026
Accepted: 23 October 2026
Published: 29 October 2026

Copyright: © 2026 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license.

metric reduction product. Polyoxometalates, particularly tungsten-containing heteropolyacids, can form reactive peroxo species in the presence of H_2O_2 and are consequently useful catalysts for oxidation reactions [13–18]. In biphasic aqueous/organic systems, however, limited mutual solubility of the phases can restrict the effective contact between the oxidizing species and the organic substrate. Phase-transfer catalysis can overcome this limitation by facilitating transport of catalytically active species toward the organic phase. Quaternary phosphonium salts are therefore relevant phase-transfer components for H_2O_2-based oxidation systems.

Of particular relevance to the present work, Musik et al. investigated the epoxidation of rapeseed oil fatty acid methyl esters using aqueous H_2O_2 and $H_3PW_{12}O_{40}$ combined with different quaternary phosphonium salts [19]. The study showed that both the phosphonium salt and temperature affected the epoxy number, iodine number and glycol content, and the proposed kinetic model considered epoxidation together with competing epoxy-ring-opening reactions [19]. More recently, the same catalytic family was investigated with respect to the H_2O_2:C=C molar ratio, showing that oxidant stoichiometry and the nature of the phosphonium component influence the resulting epoxy number and iodine number [20]. These studies establish the relevance of the $H_3PW_{12}O_{40}$/phosphonium system, but they were performed with fatty acid methyl esters rather than intact vegetable oils.

The phase-transfer concept remains an active area in vegetable oil epoxidation. Hegelmann et al. recently reported a biphasic system using surface-active ionic liquids and H_2O_2 for vegetable oil epoxidation and emphasized the heterogeneous liquid–liquid nature of the process, including the importance of phase transfer and substrate uptake [21]. Such studies indicate that catalytic performance in multiphase epoxidation depends not only on intrinsic catalyst activity but also on interactions between the aqueous oxidant phase and the hydrophobic oil phase.

Temperature is a key process variable because it affects reaction kinetics, peroxide activation, interfacial transport and the rates of both desired and secondary reactions. Increasing temperature can accelerate the conversion of carbon–carbon double bonds, but it does not necessarily result in a proportional increase in the final concentration of stable oxirane groups. Previous studies have directly demonstrated that hydrogen peroxide can participate in oxirane-ring-opening reactions during the manufacture of epoxidized vegetable oils and that the extent of degradation depends on process conditions, including temperature and peroxide concentration [22,23]. A distinction between disappearance of iodine-reactive unsaturation and accumulation of stable oxirane functionality is therefore essential when optimizing an epoxidation process.

This issue is also evident for individual vegetable oil feedstocks. In grape seed oil epoxidation with peracetic acid generated in situ, temperature strongly affected the reaction rate, while hydrolysis and oligomerization were identified as relevant secondary reactions [24]. More recently, kinetic studies of sunflower-oil epoxidation showed that temperature, reaction time and oxidant ratio significantly affected both iodine and oxirane conversion; excessive heating promoted side reactions and reduced efficiency [25]. These findings support the view that the temperature giving the highest conversion of iodine-reactive unsaturation is not necessarily the temperature giving the highest accumulation of oxirane functionality.

The distinction between iodine value conversion and epoxide formation is therefore important for quantitative assessment of vegetable oil epoxidation. Iodine value reflects the amount of iodine-reactive unsaturation remaining in the sample, whereas epoxide-number or oxirane-oxygen measurements quantify the desired functionality. These quantities may not change proportionally because unsaturation consumption can occur together with secondary reactions involving the newly formed epoxide groups. For this reason, previous

studies have combined iodine value measurements with epoxide/oxirane measurements and spectroscopic characterization to obtain a more complete description of epoxidation performance [15]. FTIR and $^{1}H/^{13}C$ NMR are particularly useful for confirming the disappearance of olefinic functionalities and the formation of oxirane-containing structures.

Although previous studies have examined $H_3PW_{12}O_{40}$/phosphonium systems for the epoxidation of fatty acid methyl esters and other catalytic approaches for vegetable oils, the temperature-dependent behavior of intact grapeseed and sunflower oils under matched phase-transfer conditions has not been the focus of the studies discussed above. A direct comparison of these oils, which have comparable initial iodine values but non-identical fatty-acid compositions, can therefore provide additional insight into the relationship between feedstock composition, unsaturation conversion and epoxide accumulation. Grapeseed and sunflower oils both contain high proportions of linoleic acid and have very similar initial iodine values in the present study, but their detailed fatty-acid compositions are not identical. Comparing the two oils using the same catalyst and oxidant charges and the same temperature–time matrix makes it possible to examine whether similar initial levels of unsaturation necessarily lead to similar temperature-dependent epoxidation behavior.

Therefore, the aim of this study was to determine how temperature affects the epoxidation of grapeseed and sunflower oils in a heteropolyacid–phosphonium phase-transfer system using aqueous H_2O_2. The specific objectives were: (i) to determine the temperature giving the highest epoxide number, (ii) to quantify the apparent conversion of iodine-reactive unsaturation, selectivity and epoxidation efficiency, and (iii) to relate the titrimetric results to FTIR, ^{1}H NMR, ^{13}C NMR and elemental-analysis evidence. Particular attention was paid to the relationship between the decrease in iodine value and the increase in epoxide number, because these parameters do not necessarily change proportionally at advanced stages of the reaction.

The novelty of the present study lies in the systematic comparison of grapeseed and sunflower oils under identical $H_3PW_{12}O_{40}$–phosphonium phase-transfer conditions, despite their comparable initial iodine values. Rather than evaluating epoxidation performance solely in terms of iodine value-derived apparent conversion, the study simultaneously considers epoxide number, apparent conversion, selectivity and epoxidation efficiency over a defined temperature–time range. This approach makes it possible to distinguish conditions favoring high conversion of iodine-reactive unsaturation from those favoring the accumulation of measured oxirane functionality. From a process-engineering perspective, the results provide experimentally based information for selecting the operating temperature during the production of epoxidized vegetable oils. The different temperature responses observed for the two feedstocks indicate that operating conditions should be selected according to the desired product specification rather than transferred directly between vegetable oil feedstocks. The present study was conducted at the laboratory scale; therefore, scale-up effects, long-term reactor operation, heat- and mass-transfer limitations, catalyst recovery and economic performance were not investigated and require separate validation. Formulation or application testing of the resulting epoxidized oils was also outside the scope of this study.

2. Materials and Methods

2.1. Materials

Grapeseed oil BOUTON D'OR (GROUPE AVRIL, Asnières-sur-Seine, France) and sunflower oil WIELKOPOLSKI (EOL Polska Sp. z o.o., Szamotuły, Poland) were purchased from a local store. Hydrogen peroxide (30 wt.%) was supplied by STANLAB (Lublin, Poland)—CAS 7722-84-1. Phosphotungstic acid hydrate ($H_3PW_{12}O_{40}\cdot xH_2O$; LACHNER, Neratovice, Czech Republic)—CAS 12501-23-4 and trihexyltetradecylphosphonium tetraflu-

oroborate ($[P_{6\cdot6\cdot6\cdot14}][BF_4]$; FLUKA, Oakville, ON, Canada)—CAS 374683-55-3 were used as the catalytic system. Reagents used for titrimetric analyses included sodium thiosulfate, potassium iodide, tetraethylammonium bromide, starch, Hanus solution, chloroform, acetic acid, methanol, hexane, BF_3 in methanol, sodium chloride and sodium hydroxide. The experiments were conducted without an added organic solvent.

2.2. Epoxidation Procedure

The reactor was a 25 cm^3 three-necked round-bottom flask equipped with a mechanical stirrer, thermometer and reflux condenser and immersed in a thermostated water bath. For each individual experiment, 6.0000 g of sunflower oil or grapeseed oil, 3.4676 g of 30 wt.% aqueous H_2O_2, 0.2200 g of $H_3PW_{12}O_{40}$ and 0.1307 g of $[P_{6\cdot6\cdot6\cdot14}][BF_4]$ were used (Figure 1). The initial C=C content of each oil was calculated from its fatty acid composition determined by GC-FID and the corresponding average molecular weight of the triglyceride fraction. For sunflower oil, 6.0000 g of oil corresponded to 6.80735 mmol of triglycerides and 28.4014 mmol of C=C bonds, whereas for grapeseed oil the corresponding values were 6.87728 mmol and 29.8239 mmol, respectively. Based on 3.4676 g of 30 wt.% aqueous H_2O_2 (30.5833 mmol H_2O_2), the resulting H_2O_2/C=C molar ratios were 1.0768:1 and 1.0255:1 for sunflower and grapeseed oils, respectively, corresponding to an approximately equimolar H_2O_2/C=C ratio.

$H_3PW_{12}O_{40}$ was introduced first, followed by 30 wt.% aqueous H_2O_2, trihexyltetradecylphosphonium tetrafluoroborate and finally the vegetable oil. For both oils, 0.2200 g of $H_3PW_{12}O_{40}$ (0.076388 mmol) and 0.1307 g of $[P_{6\cdot6\cdot6\cdot14}][BF_4]$ (0.229029 mmol) were used, corresponding to a phosphonium salt/$H_3PW_{12}O_{40}$ molar ratio of 2.998:1 (approximately 3:1). The $H_3PW_{12}O_{40}$ loading relative to the initial iodine-reactive unsaturation was 0.269 mol% for sunflower oil and 0.256 mol% for grapeseed oil.

The reaction was conducted without an added organic solvent at 1100 rpm. Reaction temperatures were 35, 40, 45, 50 and 55 °C. The reaction-time range of 5–30 min was selected to characterize the initial and intermediate stages of the epoxidation process under the investigated phase-transfer conditions. Separate reaction mixtures were prepared for each reaction time (5, 10, 15, 20 and 30 min); therefore, no sequential sampling from a single reaction mixture was performed. The time at which the vegetable oil was added was defined as $t = 0$. At the specified reaction time, the reaction mixture was collected and immediately centrifuged at 7000 rpm for 10 min. The organic phase was subsequently used for analytical measurements.

Under the investigated phase-transfer conditions, peroxoheteropolyanion species are formed in situ from $H_3PW_{12}O_{40}$ and H_2O_2. The phosphonium cation is expected to facilitate transfer of catalytically active peroxo species toward the organic phase, where epoxidation of unsaturated fatty-acid chains can occur. This description is used as a mechanistic interpretation rather than as direct proof of the identity or location of the active species.

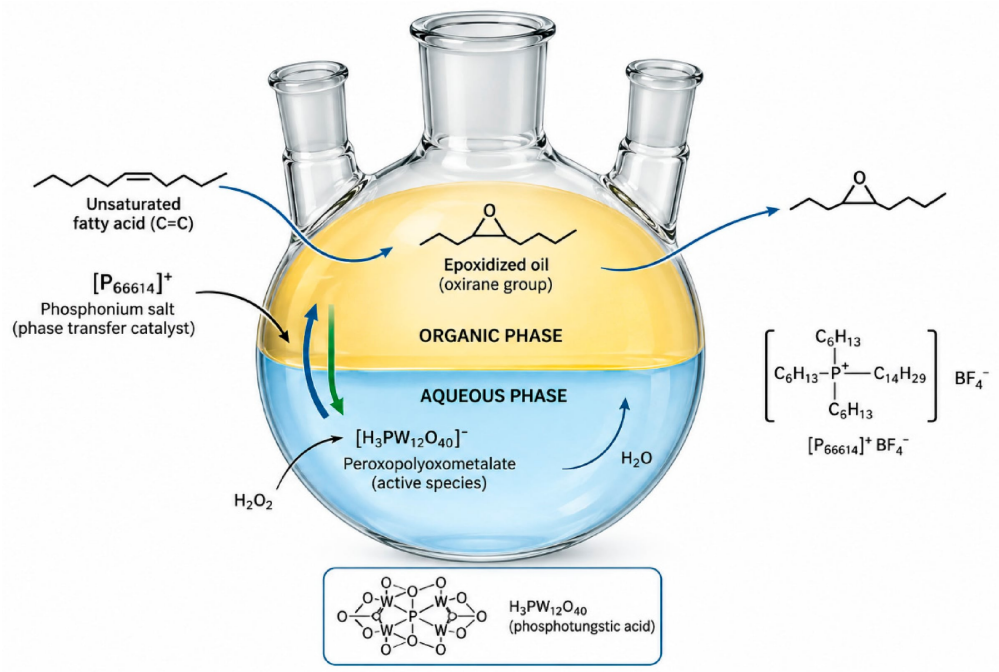


Figure 1. Scheme of the epoxidation process of sunflower and grapeseed oils.

2.3. Analytical Methods

2.3.1. Fatty-Acid Composition

The fatty-acid profile of the vegetable oils was determined using a Thermo Electron FOCUS, Rodano, Italy gas chromatograph equipped with a flame-ionization detector and a Trace^{TM} TR-FAME column (30 m × 0.25 mm × 0.25 µm). Helium was used as the carrier gas at 0.7 mL/min. The injector and detector temperatures were 200 and 250 °C, respectively. The oven was held at 60 °C for 7 min and then heated at 15 °C/min to 240 °C. The injection volume was 0.1 µL.

2.3.2. Iodine Value

The iodine value (IV) was used as a measure of iodine-reactive unsaturation. In the present study, the iodine value was experimentally determined using the Hanus titration procedure according to USP 40–NF 35, General Chapter <401>, Fats and Fixed Oils, Method I (Hanus Method) [26]. The general determination of iodine value in fats and oils is covered by ISO 3961:2024 [27] and was not used to define the specific experimental procedure applied in this study. The initial iodine values were 143.4 g I_2/100 g for grapeseed oil and 141.8 g I_2/100 g for sunflower oil. For conversion and selectivity calculations, these values were expressed as molar equivalents of iodine-reactive unsaturation per 100 g using the molar mass of I_2 (253.81 g/mol), giving 0.565 and 0.559 mol/100 g, respectively. All analytical determinations were performed in triplicate, and the reported values represent the arithmetic mean of three measurements.

$$\mathbf{IV} = \frac{[(B-V)\times N\times 12.69]}{W}$$

where

IV is to iodine number of sample (g I_2/100 g);
B is to the volume of $Na_2S_2O_3$ required for titration of blank solution (mL);
V is to the volume of $Na_2S_2O_3$ required for titration of sample (mL);
N is to normality of $Na_2S_2O_3$ solution (0.1 N);
W is to mass of sample used (g) for titration.

2.3.3. Epoxide Number

The epoxide number (EN) was determined according to EN ISO 3001 [28]. The method is based on the reaction of hydrogen bromide with epoxide groups; HBr is generated from tetraethylammonium bromide and standardized perchloric acid. EN is expressed as mol of oxirane groups per 100 g of sample. The calculation was performed according to the titrimetric relationship used in the experimental procedure. All analytical determinations were performed in triplicate, and the reported values represent the arithmetic mean of three measurements:

$$\mathbf{EN}=\frac{[(\mathrm{A}-\mathrm{C})\times 0.1\times 100]}{\mathrm{W}\times 1000}$$

where

EN is to epoxy number of the sample (mol/100 g);

A is to the volume of $HClO_4$ required for titration of sample (mL);

C is to the volume of $HClO_4$ required for titration of blank solution (mL).

2.3.4. NMR Analysis

The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a DPX-400 Avance III HD spectrometer (Bruker, Bremen, Germany) operating at 400.13 MHz for ^{1}H and 100.62 MHz for ^{13}C. TMS was used as an internal standard.

2.3.5. FTIR Analysis

FTIR spectra of the vegetable oils before and after epoxidation were recorded using a Thermo Fisher Scientific Nicolet 380 FTIR spectrometer. Samples were deposited directly on a diamond ATR element. Spectra were collected from 4000 to 400 cm^{-1} using 128 scans at a resolution of 1 cm^{-1}. Background spectra were recorded before measurements.

2.3.6. Elemental Analysis

The elemental contents, i.e., hydrogen, carbon and oxygen, of the oil samples before and after modification were determined by CH/O elemental analysis. Elemental analysis was performed using a ThermoScientific™FLASH 2000 CHNS/O Elemental Analyzer (Waltham, MA, USA).

2.3.7. Determination of Physicochemical Properties of the Starting Oils

The acid value of the starting sunflower and grapeseed oils was determined according to PN-EN ISO 660:2021-03 [29]. The saponification value was determined according to PN-EN ISO 3657:2024-01 [30]. The fatty acid composition of the starting oils was determined by GC-FID. The average molecular mass of the triglyceride fraction was calculated from the relative mass contribution of individual fatty acid components and the molecular mass of the corresponding triglycerides, taking into account their degree of unsaturation (number of C=C bonds):

$$\overline{M}_{TG} = \sum_{i=1}^{n} \frac{x_i}{100} M_{TG,i}$$

where $\overline{M}_{TG}$ is the calculated average molecular mass of the triglyceride fraction (g/mol), x_i is the percentage contribution of FAME component i determined by GC-FID, and $M_{TG,i}$ is the molecular mass assigned to the corresponding triglyceride component (g/mol).

The calculated average molecular masses were 881.4 g/mol for sunflower oil and 872.4 g/mol for grapeseed oil. The acid value and saponification value were determined in triplicate, and the values reported in Table 1 represent the arithmetic mean of three determinations. The average molecular mass was calculated from the GC-FID fatty-acid composition as described above.

Table 1. Fatty acid composition and selected physicochemical properties of the investigated oils.

Fatty Acid	Vegetable Oils (wt.%)	
	Sunflower Oil	**Grapeseed Oil**
Palmitic (16:0)	11.19	11.88
Oleic (18:1 n-9)	10.23	11.80
Linoleic (18:2 n-6)	64.09	65.90
Stearic (18:0)	8.70	8.91
Arachidic (20:0)	0.68	0.96
Gadoleic (20:1)	0.95	0.55
Behenic (22:0)	3.23	-
Lignocerate (24:0)	0.93	-
Properties	**Value**	
Iodine value, g I_2/100 g	141.8	143.4
Saponification value, mg KOH/g	190.5	192.3
Acid value, mg KOH/g	<0.5	<0.5
Calculated molecular mass, g/mol	881.4	872.4

Acid value and Saponification value are arithmetic means of three determinations. Molecular mass was calculated from the GC-FID fatty-acid composition using the weighted molecular mass of the corresponding triglyceride components.

3. Results and Discussion

The fatty-acid composition and selected physicochemical properties of the starting oils are presented in Table 1. Both oils contained the same major fatty-acid classes, and linoleic acid (C18:2) was the predominant unsaturated component: 65.90 wt.% in grapeseed oil and 64.09 wt.% in sunflower oil. The initial iodine values were also similar, 143.4 and 141.8 g I_2/100 g, respectively. Thus, the two substrates provide a useful comparison in which differences in epoxidation behavior cannot be attributed simply to a large difference in the overall degree of unsaturation.

The effects of reaction temperature (35–55 °C) and time (5–30 min) on epoxidation were evaluated under identical catalyst and oxidant ratios. The initial iodine values corresponded to approximately 0.565 and 0.559 mol of iodine-reactive unsaturation equivalents per 100 g for grapeseed and sunflower oils, respectively.

The small difference between the initial iodine values is important when interpreting the results. If the two oils behaved identically, similar temperature dependence might be expected. Instead, the experimental data show distinct temperature optima and different relationships between iodine value conversion and epoxide accumulation.

The epoxide number increased with reaction time at all investigated temperatures, but the magnitude of the increase depended strongly on temperature and oil type. For grapeseed oil, EN increased from 0.093 mol/100 g at 35 °C to 0.305 mol/100 g at 50 °C after 30 min. At 55 °C, EN reached 0.294 mol/100 g, slightly below the value at 50 °C. Thus, 50 °C gave the highest measured EN for grapeseed oil. For sunflower oil, EN increased more gradually at 35–40 °C, whereas a stronger increase was observed at 45–55 °C. The maximum EN of 0.271 mol/100 g was obtained at 55 °C after 30 min. At 30 min, sunflower oil showed a non-monotonic response between 45 and 55 °C: EN was 0.242 mol/100 g at 45 °C, decreased to 0.209 mol/100 g at 50 °C, and increased to 0.271 mol/100 g at 55 °C. This confirms that temperature optimization cannot be reduced to a simple linear temperature–EN relationship (Figure 2).

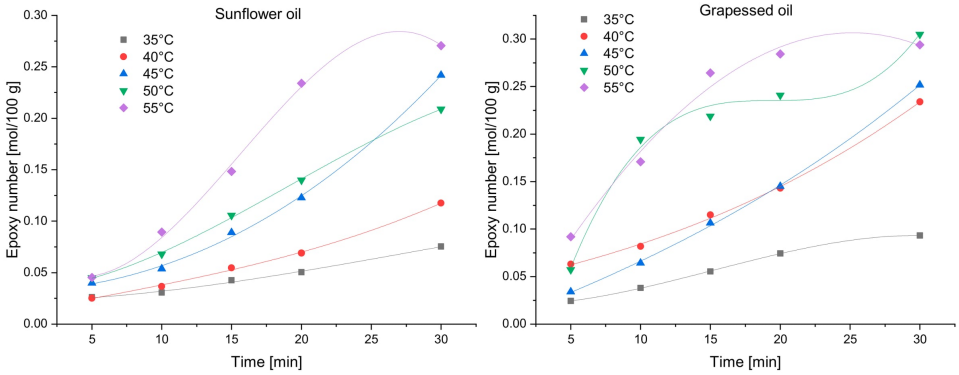


Figure 2. Effect of temperature and reaction time on the epoxide number of epoxidized sunflower and grapeseed oils.

The iodine value decreased as the reaction progressed, consistent with the consumption of iodine-reactive unsaturation. For grapeseed oil, the 30 min iodine values were 0.430, 0.068, 0.101, 0.117 and 0.100 mol/100 g at 35, 40, 45, 50 and 55 °C, respectively. For sunflower oil, the corresponding values were 0.439, 0.346, 0.275, 0.242 and 0.0416 mol/100 g. These values correspond to substantial decreases from the initial iodine equivalents of 0.565 and 0.559 mol/100 g, respectively (Figure 3).

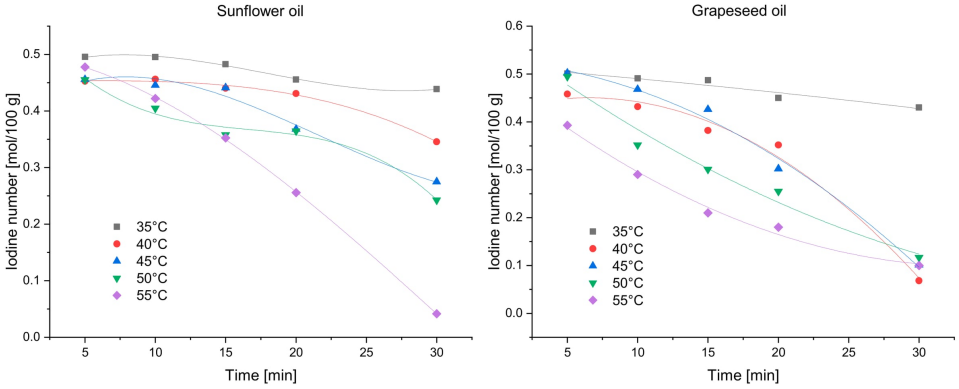


Figure 3. Effect of temperature and reaction time on the iodine value of epoxidized sunflower and grapeseed oils.

Conversion (C), selectivity (S) and efficiency (E) were calculated from the iodine and epoxide numbers using the relationships reported previously [31]. Conversion represents the apparent fraction of initial iodine-reactive unsaturation consumed, whereas selectivity describes the fraction of consumed unsaturation represented by the measured epoxide groups. Efficiency is defined as the ratio of the experimental EN to the maximum EN corresponding to complete conversion of the initial unsaturation. These parameters therefore describe different aspects of process performance:

$$E = \frac{EN}{EN_{max}} \cdot 100\%$$

EN—the epoxy number of the epoxidized oil after the epoxidation (mol/100 g);

EN_{max}—the theoretical maximum epoxide number calculated from the initial iodine-reactive unsaturation expressed as molar equivalents per 100 g.

$$C = \frac{IV_0 - IV}{IV_0} \cdot 100\%$$

IV_0—initial iodine value expressed as molar equivalents of iodine-reactive unsaturation per 100 g.

IV—iodine value at reaction time *t* expressed as molar equivalents per 100 g.

$$S = \frac{EN}{IV_0 - IV} \cdot 100\%$$

For grapeseed oil, the maximum apparent conversion of iodine-reactive unsaturation was 88.0% at 40 °C after 30 min (Figure 4). However, the maximum EN was obtained at 50 °C, where conversion was lower (79.3%) but EN reached 0.305 mol/100 g. At 45 and 55 °C, the 30 min conversion values were 82.1% and 82.3%, respectively. The separation between maximum conversion and maximum EN is one of the key findings of the study: maximizing the apparent consumption of iodine-reactive unsaturation does not necessarily maximize the accumulation of measured oxirane groups.

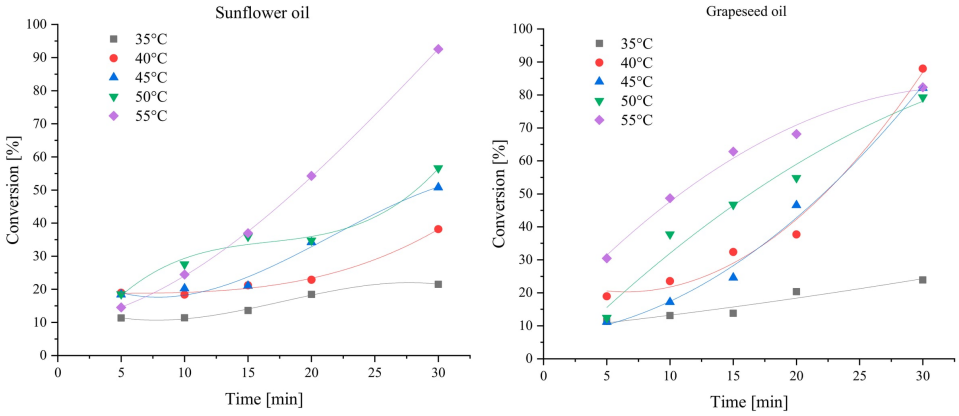


Figure 4. Apparent conversion of iodine-reactive unsaturation during epoxidation of sunflower and grapeseed oils at different temperatures.

Figure 5 presents the selectivity of conversion to epoxide groups. For sunflower oil, the highest selectivity at 30 min was observed at 45 °C (85.2%), whereas selectivity at 50 °C was 66.0% and at 55 °C decreased to 52.3%. At 55 °C, selectivity increased during the first 20 min and then decreased markedly at 30 min. A similar late-stage decrease was observed for grapeseed oil at 55 °C: selectivity increased from 53.4% after 5 min to 73.9% after 20 min and then decreased to 63.2% after 30 min. The simultaneous continued decrease in iodine value and decrease in selectivity at the longest reaction time suggest that secondary transformations may compete with the formation and/or preservation of oxirane groups. The present data do not establish a unique degradation pathway, so this behavior is interpreted conservatively rather than being assigned exclusively to oxirane-ring opening.

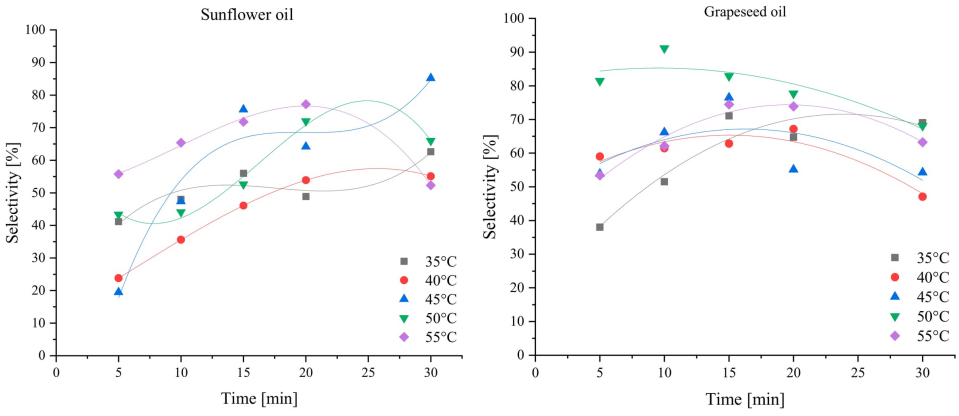


Figure 5. Selectivity of epoxidation of sunflower and grapeseed oils at different temperatures.

Figure 6 summarizes the efficiency of the epoxidation process. At 30 min, the calculated efficiency for grapeseed oil was 16.5, 41.4, 44.6, 54.0 and 52.0% at 35, 40, 45, 50 and 55 °C, respectively. For sunflower oil, the corresponding values were 13.5, 21.0, 43.3, 37.4 and 48.4%. For grapeseed oil, the maximum efficiency and maximum EN occurred at 50 °C, whereas for sunflower oil both maximum efficiency and maximum EN occurred at 55 °C. These results further demonstrate why conversion, selectivity and epoxide number should be considered together.

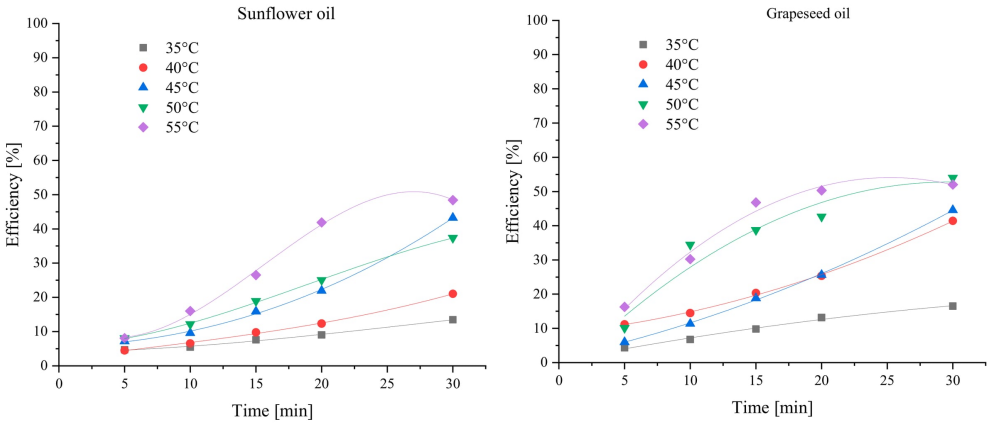


Figure 6. Efficiency of epoxidation of sunflower and grapeseed oils at different temperatures.

Table 2 highlights the distinction between conversion and epoxide accumulation after 30 min. For grapeseed oil, the highest apparent conversion of iodine-reactive unsaturation (88.0%) was obtained at 40 °C, whereas the highest EN (0.305 mol/100 g) and efficiency (54.0%) were obtained at 50 °C. For sunflower oil, 55 °C gave both the highest apparent conversion of iodine-reactive unsaturation (92.6%), EN (0.271 mol/100 g) and efficiency (48.4%). The different optima under otherwise identical reaction conditions indicate that disappearance of C=C bonds and accumulation of stable oxirane groups should be evaluated separately.

Table 2. Epoxidation parameters after 30 min calculated from the experimental iodine and epoxide numbers; Conversion represents the apparent conversion of iodine-reactive unsaturation.

Oil	T, °C	EN, mol/100 g	IV, mol/100 g	Conversion, %	Selectivity, %	Efficiency, %
Grapeseed	35	0.093	0.4300	23.9	69.0	16.5
	40	0.234	0.0680	88.0	47.1	41.4
	45	0.252	0.1010	82.1	54.3	44.6
	50	0.305	0.1170	79.3	68.1	54.0
	55	0.294	0.1000	82.3	63.2	52.0
Sunflower	35	0.075	0.4387	21.5	62.6	13.5
	40	0.118	0.3456	38.2	55.1	21.0
	45	0.242	0.2751	50.8	85.2	43.3
	50	0.209	0.2425	56.6	66.0	37.4
	55	0.271	0.0416	92.6	52.3	48.4

FTIR was used as an independent spectroscopic confirmation of chemical changes associated with epoxidation. For grapeseed oil, the starting material showed bands associated with unsaturation at approximately 3009 and 1650 cm^{-1}, which disappeared or strongly decreased after epoxidation (Figure 7 and Table 3). A new band at 823 cm^{-1} was observed in the epoxidized sample and is consistent with the C–O–C vibration of an oxirane ring. The ester carbonyl band near 1743 cm^{-1} remained essentially unchanged. The FTIR changes are

therefore consistent with the principal modification occurring at unsaturated sites rather than at the ester carbonyl functionality.

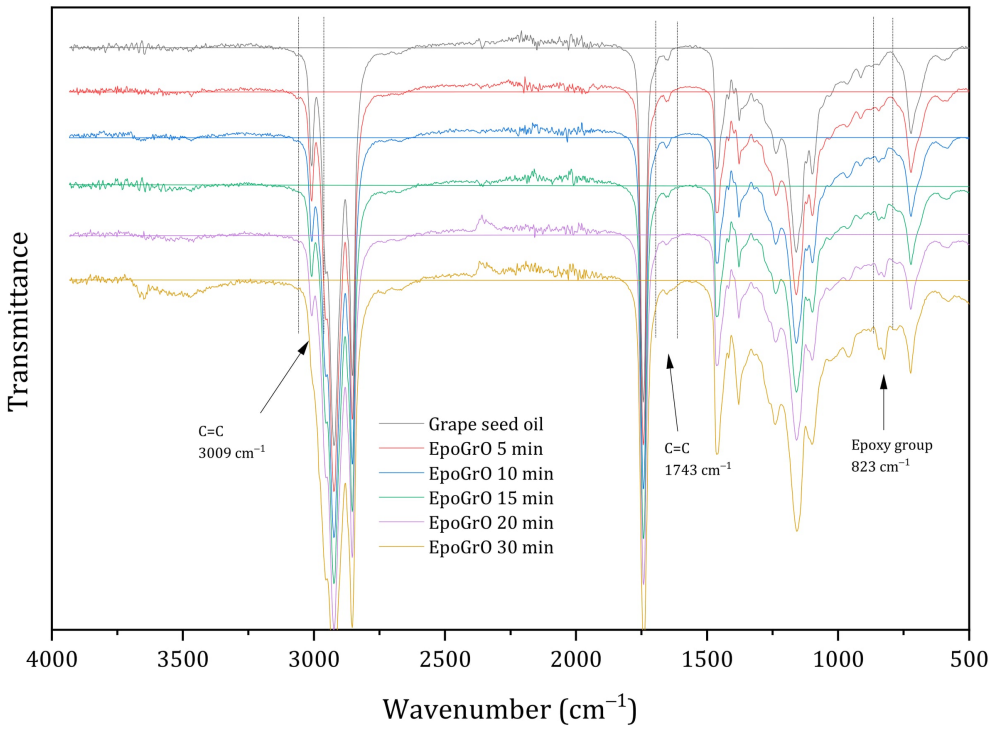


Figure 7. FTIR spectra of grapeseed oil before and after epoxidation at 50 °C.

Table 3. FTIR wavenumbers of grapeseed oil before and after epoxidation and band assignments.

Grapeseed Oil Wavenumber, cm^{-1}	Epoxidized Grapeseed Oil Wavenumber, cm^{-1}	Band Assignment
3009	-	C=CH stretching
2922 and 2853	2923 and 2854	–CH(CH_3) stretching asymmetric
1743	1742	–C=O (ester) stretching
1650	-	–C=C– (cis) stretching
1464	1463	–C–H (CH_2) bending (scissoring)
1377	1379	–C–H (CH_3) bending symmetric
1237 and 1160	1240 and 1157	C–O (ester) stretching
1098	1099	C–O stretching
965	963	trans –CH=CH– bending out of plane
913	-	trans –CH=CH– bending out of plane
-	823	C–O–C oxirane ring
722	723	C–H group vibration (aliphatic)

The sunflower-oil spectra showed the same qualitative changes. The characteristic unsaturation bands near 3008 and 1653 cm^{-1} decreased after epoxidation, while the oxirane-associated band at 823 cm^{-1} appeared. The bands near 2923 and 2853 cm^{-1} and the ester carbonyl band near 1743 cm^{-1} remained characteristic of the fatty-acid ester structure (Figure 8). Together with the titrimetric results, the FTIR spectra provide consistent evidence for the formation of oxirane-containing products from unsaturated groups [32].

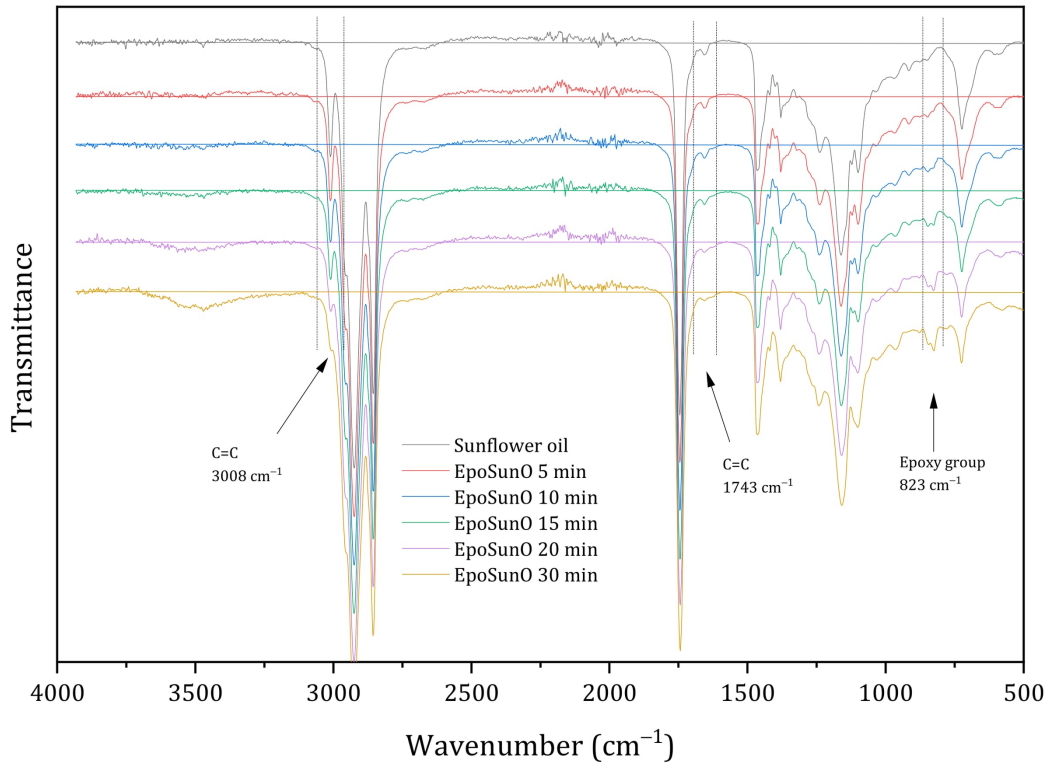


Figure 8. FTIR spectra of sunflower oil before and after epoxidation at 55 °C.

Elemental analysis (Table 4) provides complementary evidence of changes in bulk oxygen content. Oxygen increased from 10.9% in the starting sunflower oil to 16.0% in the 30 min epoxidized sample, while for grapeseed oil it increased from 10.9% to 14.4%. This trend is consistent with the formation of additional oxygen-containing functionalities. Because elemental analysis is a bulk compositional measurement, it is supporting rather than structure-specific evidence for oxirane formation.

Table 4. Elemental composition of raw and epoxidized oils determined by CH/O analysis.

Product	Elemental Composition, %		
	Carbon	Hydrogen	Oxygen
Sunflower oil	77.4	11.7	10.9
EpoSunO 5 min.	76.9	11.7	11.4
EpoSunO 15 min.	75.5	11.5	13.0
EpoSunO 30 min.	73.0	11.0	16.0
Grapeseed oil	77.5	11.6	10.9
EpoGrO 5 min.	76.9	11.5	11.6
EpoGrO 15 min.	75.6	11.4	13.0
EpoGrO 30 min.	74.4	11.2	14.4

The ^{1}H NMR spectra provide molecular-level evidence of the transformation (Figure 9). The olefinic proton signal around 5.34 ppm decreased after epoxidation, consistent with a decrease in olefinic environments, while new resonances appeared in the 2.80–3.15 ppm region, consistent with protons associated with oxirane carbons [33,34]. For sunflower oil, additional signals around 1.50, 1.74 and 2.20 ppm were observed and are attributable to methylene environments affected by epoxide formation. The decrease in the olefinic signal

and appearance of oxirane-region resonances are consistent with the decrease in iodine value and increase in EN.

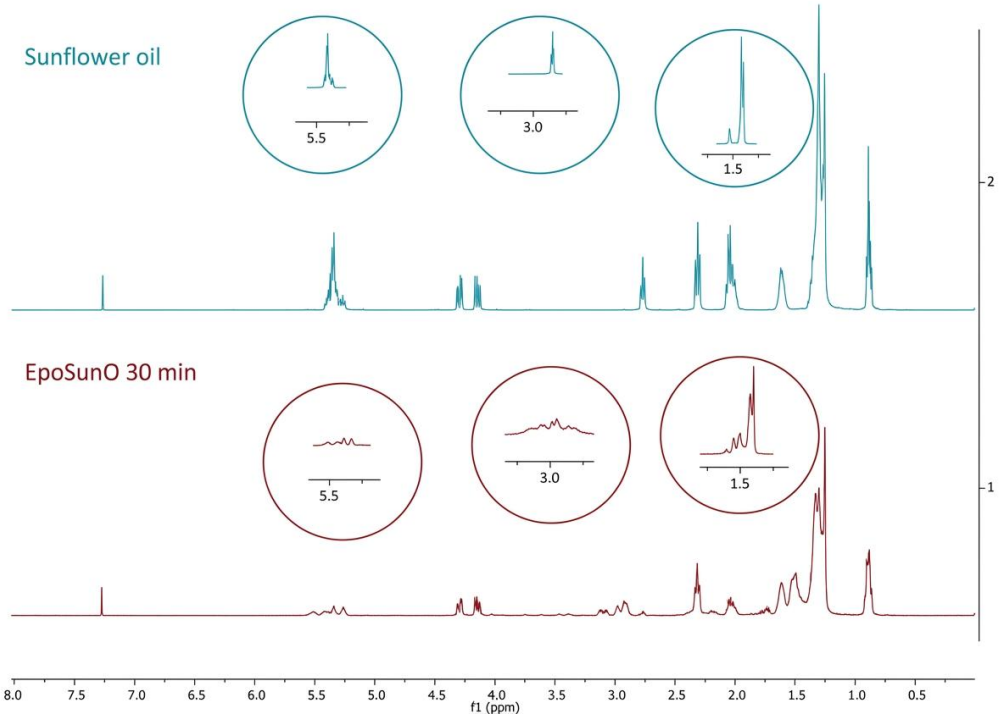


Figure 9. ^{1}H NMR spectra of sunflower oil and epoxidized sunflower oil.

In the ^{13}C NMR spectra of sunflower oil, signals in the 127.9–130.1 ppm region associated with unsaturated carbons decreased after epoxidation (Figure 10). At the same time, new signals at approximately 54.2–57.2 ppm appeared and were assigned to carbons in oxirane rings. Thus, the ^{13}C NMR data independently support the transformation of unsaturated carbon environments into epoxide-containing structures.

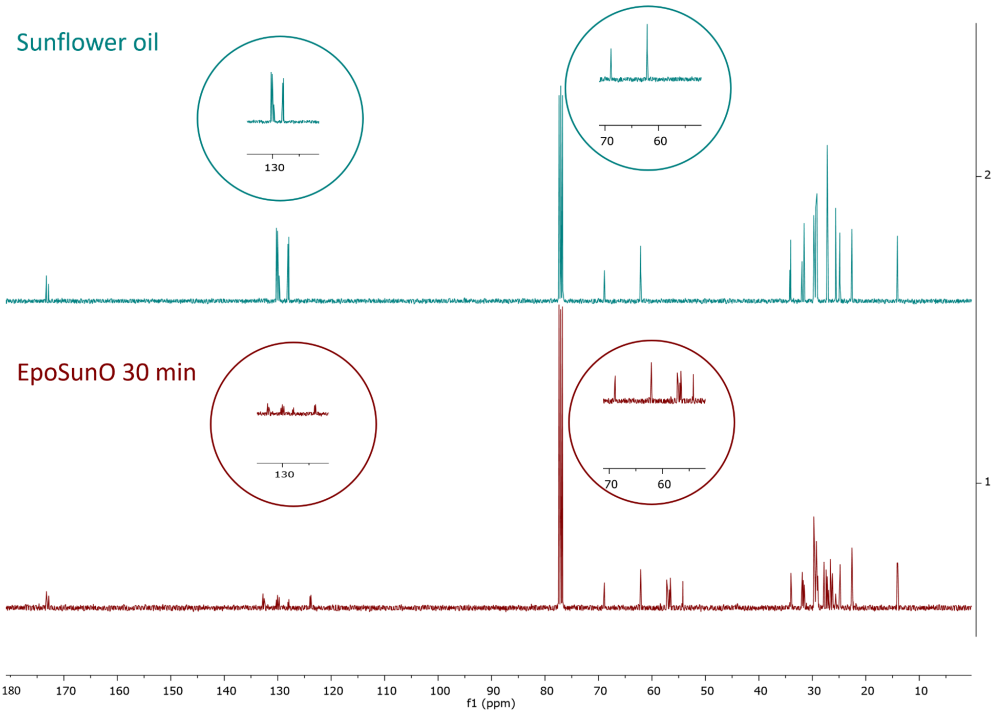
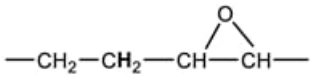
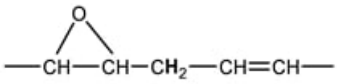
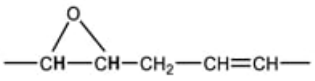
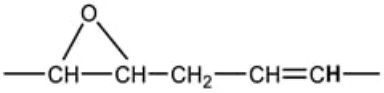


Figure 10. ^{13}C NMR spectra of sunflower oil and epoxidized sunflower oil.

For epoxidized grapeseed oil, characteristic groups of signals associated with epoxide-containing environments were observed (Table 5).

Table 5. Selected ^{1}H NMR chemical shifts in grapeseed oil before and after epoxidation.

Sample	Chemical Shift, ppm	Protons	Functional Groups
Grapeseed oil	0.88	CH_3–CH_2–CH_2–	methyl group
	1.62	–CH_2–CH_2–CO–O–	methylene group beta to acyl group
	2.03	–CH_2–CH_2–CH=CH–	allylic methylene group
	2.31	–CH_2–CH_2–CO–O–	methylene group alpha to acyl group
	2.77	–CH=CH–CH_2–CH=CH–	diallylic methylene group
	5.33	–CH=CH–	olefinic group
Epoxidized grapeseed oil (EpoGrO 30 min)	1.53		methylene group alpha to epoxy group
	2.18		methylene groups between an epoxy group and an olefinic group
	2.92–3.10		epoxy group beta to olefinic group
	5.34		olefinic group beta to epoxy group

In particular, resonances at 2.92–3.10 ppm are consistent with protons in oxirane-containing structures, while the olefinic signal near 5.34 ppm decreased after epoxidation (Figure 11).

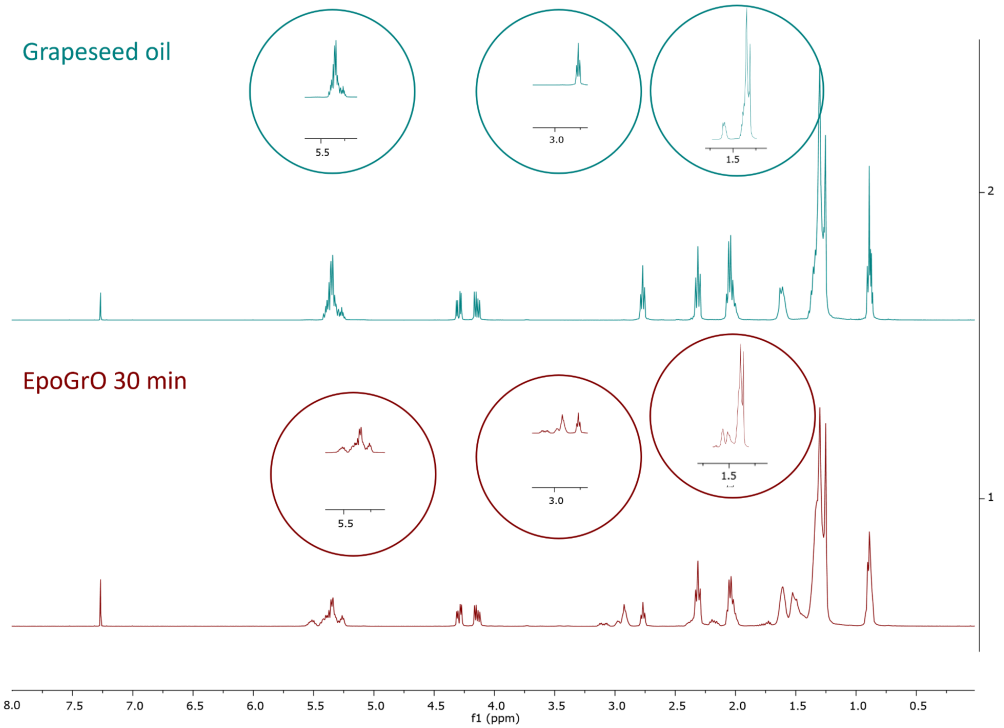


Figure 11. ^{1}H NMR spectra of grapeseed oil and epoxidized grapeseed oil.

In the ^{13}C NMR spectrum of epoxidized grapeseed oil, new signals in the 52–60 ppm region were observed and are consistent with carbons of oxirane rings (Figure 12). The agreement between the NMR observations, the appearance of the 823 cm^{-1} FTIR band, the decrease in iodine value and the increase in EN provides convergent evidence that epoxidation occurred.

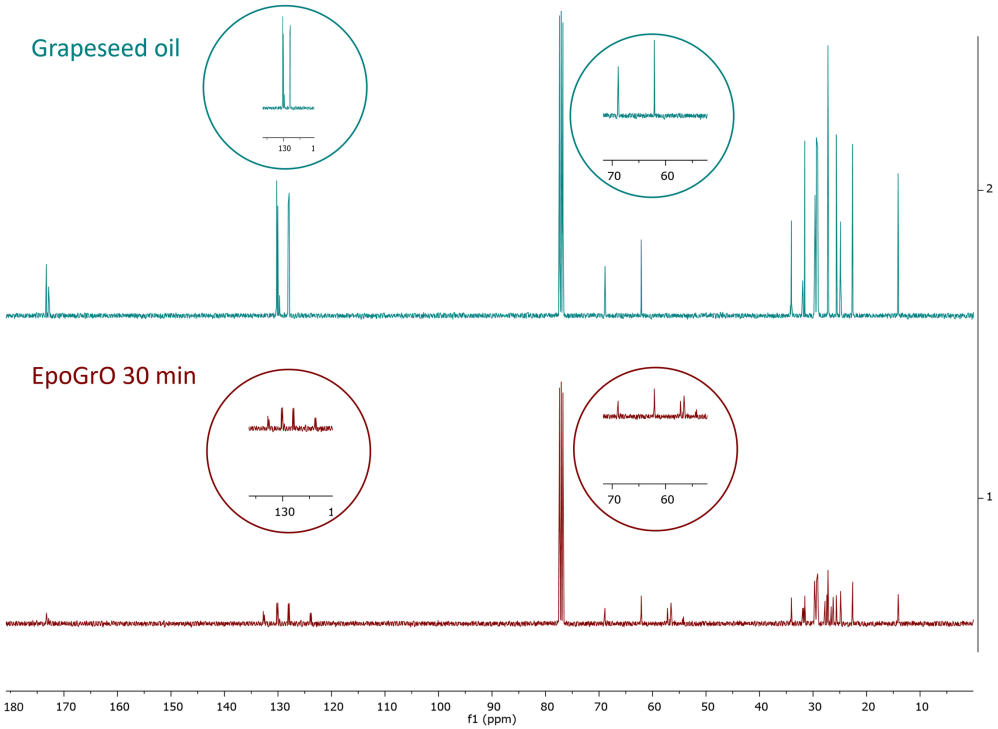


Figure 12. ^{13}C NMR spectra of grapeseed oil and epoxidized grapeseed oil.

4. Conclusions

The present study demonstrates that grapeseed and sunflower oils with very similar initial fatty-acid composition and iodine values can exhibit distinctly different temperature-dependent epoxidation behavior in the same heteropolyacid–phosphonium phase-transfer system. For grapeseed oil, the highest EN (0.305 mol/100 g) was obtained at 50 °C after 30 min, whereas the highest apparent conversion of iodine-reactive unsaturation (88.0%) occurred at 40 °C. For sunflower oil, both the highest EN (0.271 mol/100 g) and the highest apparent conversion of iodine-reactive unsaturation (92.6%) were obtained at 55 °C after 30 min. The comparison demonstrates that iodine value-derived apparent conversion of iodine-reactive unsaturation and the epoxide number (EN) describe different aspects of process performance and should not be treated as interchangeable measures of epoxidation. At advanced reaction stages, particularly at 55 °C, iodine value continued to decrease while selectivity decreased after 20 min, suggesting that secondary transformations may compete with the formation and/or preservation of oxirane groups. Under the investigated conditions, 50 °C gave the highest measured EN for grapeseed oil, whereas 55 °C gave the highest measured EN and apparent conversion for sunflower oil. FTIR, ^{1}H NMR and ^{13}C NMR supported the formation of oxirane-containing structures, while elemental analysis provided complementary evidence of increased oxygen content. The study was performed at the laboratory scale and within a reaction-time window of up to 30 min. Therefore, further work is required to assess long-term reaction behavior, scale-up effects, catalyst recovery, heat- and mass-transfer limitations and economic performance.

Author Contributions: Conceptualization, M.M. and M.S.; methodology, M.M.; formal analysis, M.M.; investigation, M.M. and M.S.; writing—original draft preparation, M.M.; writing—review and editing, M.M.; visualization, M.S.; supervision, M.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

Acknowledgments: The authors would like to acknowledge the members of the student scientific club for their assistance in the experimental work and for their involvement in scientific activities related to this study.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

C	Conversion
E	Epoxidation efficiency
EN	Epoxide number
FAME	Fatty acid methyl esters
FTIR	Fourier-transform infrared spectroscopy
GC-FID	Gas chromatography with flame ionization detection
HPA	Heteropolyacid
IV	Iodine value
NMR	Nuclear magnetic resonance
S	Selectivity

References

1. Kerenkan, A.E.; Béland, F.; Do, T.-O. Catalytic transformation of vegetable oils into high-value products. *Catal. Sci. Technol.* **2016**, *6*, 971–987. [CrossRef]
2. Biermann, U.; Bornscheuer, U.; Meier, M.A.R.; Metzger, J.O.; Schäfer, H. Oils and fats as renewable raw materials in chemistry. *Angew. Chem. Int. Ed.* **2011**, *50*, 3854–3871. [CrossRef] [PubMed]
3. Thomas, J.; Patil, R. Enabling Green Manufacture of Polymer Products via Vegetable Oil Epoxides. *Ind. Eng. Chem. Res.* **2023**, *62*, 1725–1735. [CrossRef]
4. Cecilia, J.A.; Plata, D.B.; Saboya, R.M.A.; Luna, F.M.T.; Cavalcante, C.L.; Rodríguez-Castellón, E. An overview of the epoxidation of vegetable oils and fatty acids. *Processes* **2020**, *8*, 257. [CrossRef]
5. Tsujimoto, T.; Takayama, T.; Uyama, H. Biodegradable Shape Memory Polymeric Material from Epoxidized Soybean Oil and Polycaprolactone. *Polymers* **2015**, *7*, 2165–2174. [CrossRef]
6. Mustata, F.; Rosu, D.; Varganici, C.-D.; Rosu, L.; Rosca, I.; Tudorachi, N. Assessing the thermal and fungal behavior of eco-friendly epoxy thermosets derived from vegetable oils for wood protective coatings. *Prog. Org. Coat.* **2022**, *163*, 106612. [CrossRef]
7. Bouti, M.; Irinislimane, R.; Belhaneche-Bensemra, N. Properties Investigation of Epoxidized Sunflower Oil as Bioplasticizer for Poly (Lactic Acid). *J. Polym. Environ.* **2022**, *30*, 232–245. [CrossRef]
8. Sun, S.; Ke, X.; Cui, L.; Yang, G.; Bi, Y.; Song, F.; Hu, X. Enzymatic epoxidation of Sapindus mukorossi seed oil by perstearic acid optimized using response surface methodology. *Ind. Crops Prod.* **2011**, *33*, 676–682. [CrossRef]
9. Yang, X.; Wang, S.; Liu, X.; Huang, Z.; Huang, X.; Xu, X.; Liu, H.; Wang, D.; Shang, S. Preparation of non-isocyanate polyurethanes from epoxy soybean oil: Dual dynamic networks to realize self-healing and reprocessing under mild conditions. *Green Chem.* **2021**, *23*, 6349–6355. [CrossRef]
10. Siahkali, M.J.M.; Guigo, N.; Vincent, L.; Sbirrazzuoli, N. Catalytic Effect of Eutectic Hardeners to Polymerize Epoxidized Vegetable Oil for the Synthesis of Fully Biobased Thermosets at Low Temperatures. *Macromolecules* **2025**, *58*, 601–615. [CrossRef]
11. Cogliano, T.; Turco, R.; Di Serio, M.; Salmi, T.; Tesser, R.; Russo, V. Epoxidation of Vegetable Oils via the Prilezhaev Reaction Method: A Review of the Transition from Batch to Continuous Processes. *Ind. Eng. Chem. Res.* **2024**, *63*, 11231–11262. [CrossRef]
12. Zhang, Y.; Huang, X.; Li, Y.; Zhang, H.; Chen, Y.; Lu, J.; Li, J.; Yin, Y. Epoxidized soybean oil-based waterborne polyurethane coatings modified by PEG and gemini quaternary ammonium salt for antifouling applications. *Ind. Crops Prod.* **2025**, *235*, 121747. [CrossRef]

13. Chen, W.; Tan, C.-H.; Wang, H.; Ye, X. Molybdenum/Tungsten-Based Heteropoly Salts in Oxidations. *Chem. Asian J.* **2021**, *16*, 2753–2772. [CrossRef] [PubMed]
14. Starks, C.M.; Liotta, C.L.; Halpern, M.E. *Phase-Transfer Catalysis: Fundamentals, Applications and Industrial Perspectives*; Chapman & Hall: New York, NY, USA, 1994.
15. Wai, P.T.; Jiang, P.; Shen, Y.; Zhang, P.; Gu, Q.; Leng, Y. Catalytic developments in the epoxidation of vegetable oils and the analysis methods of epoxidized products. *RSC Adv.* **2019**, *9*, 38119–38136. [CrossRef] [PubMed]
16. Maiti, S.K.; Snavely, W.K.; Venkitasubramanian, P.; Hagberg, E.C.; Busch, D.H.; Subramaniam, B. Reaction Engineering Studies of the Epoxidation of Fatty Acid Methyl Esters with Venturello Complex. *Ind. Eng. Chem. Res.* **2019**, *58*, 2514–2523. [CrossRef]
17. Yahya, R.; Craven, M.; Kozhevnikova, E.F.; Steiner, A.; Samunual, P.; Kozhevnikov, I.V.; Bergbreiter, D.E. Polyisobutylene oligomer-bound polyoxometalates as efficient and recyclable catalysts for biphasic oxidations with hydrogen peroxide. *Catal. Sci. Technol.* **2015**, *5*, 818–821. [CrossRef]
18. Pai, Z.P.; Khlebnikova, T.B.; Mattsat, Y.V.; Parmon, V.N. Catalytic oxidation of fatty acids. I. Epoxidation of unsaturated fatty acids. *React. Kinet. Catal. Lett.* **2009**, *98*, 1–8. [CrossRef]
19. Musik, M.; Janus, E.; Pełech, R.; Sałaciński, Ł. Effective Epoxidation of Fatty Acid Methyl Esters with Hydrogen Peroxide by the Catalytic System $H_3PW_{12}O_{40}$/Quaternary Phosphonium Salts. *Catalysts* **2021**, *11*, 1058. [CrossRef]
20. Musik, M.; Janus, E.; Pełech, R. A Study of the Catalytic System $H_3PW_{12}O_{40}$/Quaternary Phosphonium Salts for the Epoxidation of Fatty Acid Methyl Esters—The Effect of the Molar Ratio of Hydrogen Peroxide to the Double Bond. *Molecules* **2025**, *30*, 1109. [CrossRef] [PubMed]
21. Hegelmann, M.; Bohórquez, W.F.; Luibl, J.; Jess, A.; Orjuela, A.; Cokoja, M. Biphasic phase-transfer catalysis: Epoxidation of vegetable oils by surface active ionic liquids in water. *React. Chem. Eng.* **2024**, *9*, 2710–2717. [CrossRef]
22. Campanella, A.; Baltanás, M.A. Degradation of the oxirane ring of epoxidized vegetable oils with hydrogen peroxide using an ion exchange resin. *Catal. Today* **2005**, *107–108*, 208–214. [CrossRef]
23. Campanella, A.; Baltanás, M.A. Degradation of the oxirane ring of epoxidized vegetable oils in a liquid–liquid–solid heterogeneous reaction system. *Chem. Eng. Process. Process Intensif.* **2007**, *46*, 210–221. [CrossRef]
24. de Haro, J.C.; Izarra, I.; Rodríguez, J.F.; Pérez, Á.; Carmona, M. Modelling the epoxidation reaction of grape seed oil by peracetic acid. *J. Clean. Prod.* **2016**, *138*, 70–76. [CrossRef]
25. Purwanto, E.; Budianto, J.S.; Indrawanto, M.M.; Widianto, A.Y.; Setyopratomo, P. The kinetics of the epoxidation reaction of sunflower oil utilizing peroxyformic acid generated in situ. *Case Stud. Chem. Environ. Eng.* **2025**, *11*, 101175. [CrossRef]
26. General Chapter <401>, Fats and Fixed Oils, Method I (Hanus Method). In *USP 40–NF 35*; United States Pharmacopeial Convention: Rockville, MD, USA, 2017.
27. *ISO 3961:2024*; Animal and Vegetable Fats and Oils—Determination of Iodine Value. ISO: Geneva, Switzerland, 2024.
28. *EN ISO 3001*; Plastics. Epoxy Compounds. Determination of Epoxy Equivalent. CEN: Brussels, Belgium, 1999.
29. *PN-EN ISO 660:2021-03*; Animal and Vegetable Fats and Oils. Determination of Acid Value and Acidity. PKN: Warszawa, Poland, 2021.
30. *PN-EN ISO 3657:2024-01*; Animal and Vegetable Fats and Oils. Determination of Saponification Value. CEN: Brussels, Belgium, 2024.
31. Kurańska, M.; Niemiec, M. Cleaner Production of Epoxidized Cooking Oil Using A Heterogeneous Catalyst. *Catalysts* **2020**, *10*, 1261. [CrossRef]
32. Riyanta, A.B.; Riyanto, S.; Lukitaningsih, E.; Rohman, A. The employment of Fourier Transform Infrared Spectroscopy (FTIR) and chemometrics for analysis of candlenut oil in binary mixture with grape seed oil. *Food Res.* **2020**, *4*, 184–190. [CrossRef] [PubMed]
33. Abdullah, B.M.; Salih, N.; Salimon, J. Optimization of the chemoenzymatic mono-epoxidation of linoleic acid using D-optimal design. *J. Saudi Chem. Soc.* **2014**, *18*, 276–287. [CrossRef]
34. Xia, W.; Budge, S.M.; Lumsden, M.D. ^{1}H-NMR Characterization of Epoxides Derived from Polyunsaturated Fatty Acids. *J. Am. Oil Chem. Soc.* **2016**, *93*, 467–478. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.