Production of tung oil epoxy resin using low frequency high power ultrasound

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A B S T R A C T

Epoxy resins made from vegetable oils are an alternative to synthesize epoxy resins from renewable sources. Tung oil is rich in α -eleostearic fatty acid, which contains three double bonds producing epoxy resins with up to three epoxy groups per fatty acid. This work studied the production of tung oil epoxy resin using hydrogen peroxide as an oxidizing agent and acetic and formic acid as percarboxylic acid precursors, applying low frequency high power ultrasound. This study evaluated the effects of ultrasound power density, hydrogen peroxide concentration, acetic acid concentration, and formic acid concentration on the yield into epoxy resin, selectivity, and by-products formation. Application of ultrasound was carried out using a 19 kHz probe ultrasound (horn ultrasound) with a 1.3 cm diameter titanium probe, 500 W nominal power, 2940 W L^{-1} maximum effective power density applied to the reaction mixture. Ultrasound technology yielded up to 85% of epoxy resin in 3 h of reaction. The use of formic acid resulted in a slightly lower oil conversion than acetic acid but with a much higher selectivity towards epoxidized tung oil. However, using acetic acid resulted in the production of high-value by-products, such as 2-heptenal and 2,4-nonadienal. The ultrasound-assisted epoxidation showed to be particularly efficient when applied to oils containing conjugated double-bonds.

1. Introduction

Vegetable oils are valuable renewable resources. They usually have a low cost, are biodegradable, and can be modified by several reaction routes to develop green-labeled products [1]. Vegetable oils can be chemically modified to obtain epoxides that can be used as an alternative to petroleum-based epoxides [2]. The epoxidation of tung oil increases its reactivity, making it an intermediate or monomer to produce a wide range of materials with applications in plasticizers, lubricants, surface coating formulations, and polymer stabilizers [3,4]. The increase in reactivity occurs by converting carbon–carbon double bonds to oxirane rings. Epoxidation of vegetable oils is usually carried out by reacting the vegetable oil with a percarboxylic acid, generated *in situ* by the reaction of a carboxylic acid and hydrogen peroxide [5–8]. An increase in the reaction rate can be attained by adding a strong mineral acid, such as sulfuric acid, to the mixture [9]. However, the addition of sulfuric acid leads to severe corrosion problems. In this study, we propose to increase the rate of reaction employing sonication.

Acetic acid and formic acid are the most common carboxylic acids used in epoxidation processes. Acetic acid is less reactive than formic

acid in converting lipid double bonds into epoxy rings but has the advantage of being much less corrosive and more environmentally friendly [6,8,10].

The epoxidation of tung oil is carried out with peroxycarboxylic acids and concentrated hydrogen peroxide (Fig. 1). The carboxylic acid reacts with hydrogen peroxide in the aqueous phase producing peroxycarboxylic acid and water. Hydrogen peroxide acts as an oxygen donor, and carboxylic acid acts as an oxygen carrier in the epoxidation reaction. The peroxycarboxylic acid then diffuses into the organic phase and reacts with the oil's double bonds producing epoxidized tung oil. The latter reaction regenerates the carboxylic acid, which is transferred back to the aqueous phase restarting the reaction cycle (Fig. 1) [6,9].

Ultrasound was reported as a promising technology for intensifying the epoxidation of vegetable oils [2,11,12]. Ultrasound generates turbulence and micro-jets that increase mass transfer, and localized hot spots with high temperatures and pressures due to cavitation can help intensify several chemical reactions. Ultrasound application in aqueous systems induces the formation of hydroxyl radicals and hydrogen peroxide, which can intensify epoxidation reactions [13].

Although ultrasound can intensify several chemical reactions, it has

been little applied to epoxidation reactions despite its potential. Chavan et al. [2] reported one of the few studies on ultrasound-assisted epoxidation. Their study successfully epoxidized soybean oil with tetra-n-butyl ammonium bromide achieving conversions as high as 83% in 4 h. Low-frequency ultrasound was also applied in the epoxidation of sunflower oil with acetic acid and Indion 225H catalyst, attaining yields up to 91% of oxirane oxygen [11]. More recently, Maia and Fernandes [13] reported on the application of low-frequency high-power ultrasonic reaction of soybean oil with formic and acetic acid using sulfuric acid as percarboxylic acid co-catalyst.

In this work, we advance in the knowledge of ultrasound-assisted epoxidation providing more information on the effects of ultrasound on epoxidation reactions. New data on tung oil epoxidation is presented. We also present a case where the use of acetic acid as percarboxylic precursor results in higher oil conversion and epoxy yield than the use of formic acid, and which valuable by-products can be produced. Summarizing, this work investigated the epoxidation of tung oil through sonochemistry. The effects of the carboxylic acid (formic and acetic acid), carboxylic acid concentration, the concentration of hydrogen peroxide, and ultrasound power density were investigated and discussed.

2. Materials and methods

2.1. Materials

Tung (*Vernicia fordii*) oil was purchased from Campestre (São Paulo, Brazil). Hydrogen peroxide (30%), acetic acid, and formic acid (85%) were bought from Synth (São Paulo, Brazil).

2.2. Production of tung oil epoxy resin

Tung oil was added with acetic or formic acid to a 250 mL jacketed glass reaction vessel and heated to 40 °C. The volume of hydrogen peroxide (30%) used in the reaction was divided into nine aliquots of the same volume. Each aliquot was added to the reactor every 20 min. Sonication was carried out for 5 min each time that an aliquot of hydrogen peroxide was added to the reactor. The reaction was carried out for 180 min. Aliquots of 2 mL were taken from the reaction mixture each 20 min and immediately cooled in ice to stop the reaction.

Table 1 presents the amounts of tung oil, acetic acid, formic acid, and hydrogen peroxide added to the reactor in each assay. The volume of tung oil was fixed at 130 mL (0.13 mol). The acetic acid to tung oil molar ratio and the formic acid to tung oil molar ratio varied from 0 to 0.8 mol/mol. This range was based on the molar ratios reported in the literature to produce soybean oil epoxy resin [14]. The hydrogen peroxide to tung oil molar ratio varied from 11.4 to 15.0. This range was also based on the molar ratios reported in the literature to produce soybean oil epoxy resin [14]; however, lower molar ratios were applied because ultrasound applied in aqueous or acid mixtures produces hydrogen peroxide [15].

Sonication was carried out using a probe ultrasound (Unique model DES500, Brazil) operating at 19 kHz, 500 W nominal power, 2940 W L^{-1} effective power density, and a 1.3 cm titanium probe. Sonication was carried out for 5 min each time due to equipment limitation caused by excessive heating of the piezoelectric component. The temperature of the reaction mixture was controlled using external water circulating bath (Tecnal model TE2005, Brazil) set at 30 °C to remove the heat of the reaction. The effective ultrasonic power density applied varied between 1620 and 2940 W L^{-1}, corresponding to nominal ultrasonic powers between 275 and 500 W (Table 1). The real ultrasonic power density was determined through the calorimetric method [16].

This operation mode was done because the temperature of the reaction mixture increased from 40 to 80 °C in 5 min when hydrogen peroxide was added to the reaction and sonication started. Cooling water at 30 °C passed continuously through the vessel jacket to cool down the reaction mixture. After each sonication cycle, the reaction mixture took about 15 min to cool down from 80 to 40 °C. The temperature was continuously monitored using a digital thermometer.

For reference purposes, control runs were carried out in a stirred batch reactor. The reaction was performed using a 400 mL stainless steel batch reactor provided with mechanical agitation and temperature control (Metalquim model R400). A volume of tung oil was fixed at 130 mL (0.13 mol). The acetic acid to tung oil molar ratio was set at 0.8 mol/mol and the hydrogen peroxide to tung oil molar ratio at 15.0 mol/mol. Three agitation speed were applied 0, 100, and 600 rpm, corresponding to autocatalysis, poor agitation, and perfect mixing, in this configuration of reactor. All reactions were carried out at the average temperature attained during the ultrasound-assisted reaction.

2.3. Chemical characterization

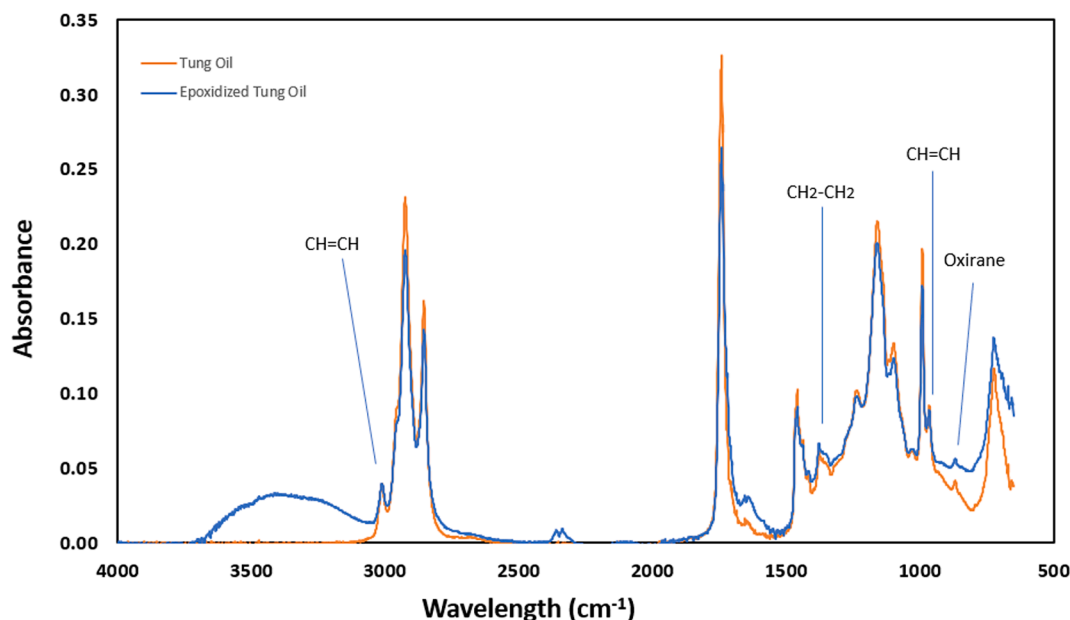The chemical characterization of the reaction products was carried

Fig. 1. FTIR spectrum of tung oil and epoxidized tung oil.

Table 1

Conversion of tung oil, yield into epoxy resin and selectivity. Results achieved using a 19 kHz probe ultrasound with a 1.3 cm diameter titanium probe, 500 W nominal power, 2940 W.L^{-1} maximum effective power density applied to the reaction mixture.

Run	Ultrasound power density (W.L^{-1})	Acetic acid to oil molar ratio	Formic acid to oil molar ratio	Hydrogen peroxide to oil molar ratio	Oil conversion (%)	Yield into epoxy resin (%)	Time of higher yield (min)	Productivity (g.L^{-1}.min^{-1})
Effect of the peroxidation acid								
1	1620	0.8	0	15	88.0 ± 7.0 [a]	66.1 ± 5.1 [bc]	180	1.9 ± 0.2 [c]
2	2060	0.8	0	15	89.4 ± 7.2 [a]	72.1 ± 5.6 [b]	140	2.9 ± 0.3 [b]
3	2450	0.8	0	15	85.9 ± 6.8 [a]	78.2 ± 6.1 [ab]	180	2.7 ± 0.3 [b]
4	2940	0.8	0	15	64.7 ± 5.2 [b]	54.2 ± 4.2 [d]	140	2.2 ± 0.2 [c]
5	1620	0	0.8	15	52.4 ± 2.7 [c]	52.4 ± 2.7 [d]	180	2.0 ± 0.2 [c]
6	2060	0	0.8	15	82.0 ± 6.4 [a]	82.0 ± 6.4 [a]	140	4.1 ± 0.3 [a]
7	2450	0	0.8	15	85.0 ± 6.6 [a]	85.0 ± 6.6 [a]	140	4.3 ± 0.3 [a]
8	2940	0	0.8	15	64.2 ± 2.0 [b]	64.2 ± 2.0 [c]	140	3.2 ± 0.3 [b]
Effect of the carboxylic acid to oil molar ratio								
9	2450	0	0	15	63.9 ± 9.9 [c]	63.9 ± 9.9 [b]	180	2.5 ± 0.2 [ab]
10	2450	0.66	0	15	96.4 ± 6.0 [a]	81.0 ± 6.0 [a]	180	2.6 ± 0.2 [ab]
11	2450	0.74	0	15	81.0 ± 6.5 [b]	70.4 ± 9.9 [ab]	180	2.3 ± 0.2 [b]
12	2450	0.82	0	15	85.9 ± 6.8 [ab]	78.2 ± 6.1 [a]	180	2.7 ± 0.2 [a]
Effect of the hydrogen peroxide to oil molar ratio								
13	2450	0.8	0	11.4	73.7 ± 2.8 [b]	66.3 ± 3.1 [b]	180	2.4 ± 0.2 [b]
14	2450	0.8	0	13.9	76.6 ± 2.8 [ab]	64.2 ± 3.1 [b]	180	2.1 ± 0.2 [b]
15	2450	0.8	0	15	85.9 ± 6.8 [a]	78.2 ± 6.1 [a]	180	2.7 ± 0.2 [a]
Control experiment in stirred batch reactor								
16	0 rpm	0.8	0	15	21.6 ± 1.0 [d]	12.3 ± 1.0 [e]	180	0.4 ± 0.1 [d]
17	100 rpm	0.8	0	15	37.3 ± 2.0 [d]	17.6 ± 2.0 [e]	180	0.6 ± 0.1 [d]
18	600 rpm	0.8	0	15	71.3 ± 3.0 [b]	69.1 ± 3.0 [b]	180	2.4 ± 0.2 [b]

out by Fourier-transform infrared spectroscopy (FTIR) and gas chromatography-mass spectrometry (GCMS) analysis.

The reaction yield was calculated based on the chemical changes measured by FTIR. Aliquots of 0.1 mL of the oil-epoxy mixture were analyzed by an FTIR spectrometer (Agilent model Cary 63), which collected the spectrum in a wavelength ranging from 400 to 4000 cm^{-1} and spectral resolution of 1.0 cm^{-1}. All analyses were carried out in triplicate. The analysis was based on the methods described by Tavassoli-Kafrani et al. [17], Meng et al. [18], Man et al. [19], and Xu et al. [20].

The reaction product characterization was determined by GCMS analysis. The samples (0.1 mL) were transesterified with methanol and sodium hydroxide (1 mol L^{-1}, 2 mL) for 24 h at 40 °C before analysis. The transesterified samples (50 μL) were transferred to a vial containing 1.5 mL of methanol. The chromatographic analysis was carried out in a GCMS (Thermos model ISQ). The separation of the compounds was carried out using a 30 m DB-1 capillary column with a 0.25 mm internal diameter. An aliquot of 1 μL was injected into the chromatograph. The injector and detector temperatures were set at 230 and 250 °C, respectively. The mass spectrometer was set at 70 eV. Oven programming started at 50 °C, maintaining this temperature for 1 min, raising to 250 °C at 5 °C min^{-1}, and maintaining the final temperature for 10 min. The identification of the chromatogram peaks was based on the National Institute of Standards and Technology (NIST) component mass-spectrum library.

2.4. Reaction yield and selectivity

The reaction yield was calculated based on the absorbance at 990 cm^{-1} corresponding to the carbon double bonds (Equation (1)). The selectivity of the reaction was based on the absorbance at 840 cm^{-1} that corresponds to the epoxy group (Equation (2)).

$$C(\%) = \Delta\frac{A_{C=C}}{A_{alk}} = 3\left(\frac{\left(\frac{A_{C=C}}{A_{alk}}\right)^{to} - \left(\frac{A_{C=C}}{A_{alk}}\right)^{sample}}{\left(\frac{A_{C=C}}{A_{alk}}\right)^{to}}\right)100 \quad (1)$$

$$Y(\%) = \Delta\frac{A_{ox}}{A_{alc}} = \left(\frac{\left(\frac{A_{ox}}{A_{alk}}\right)^{sample} - \left(\frac{A_{ox}}{A_{alk}}\right)^{to}}{\left(\frac{A_{ox}}{A_{alk}}\right)^{eto} - \left(\frac{A_{ox}}{A_{alk}}\right)^{to}}\right)100 \quad (2)$$

where A_{alk} is the absorbance at 1435 cm^{-1}, $A_{C=C}$ is the absorbance at 990 cm^{-1}, A_{ox} is the absorbance at 840 cm^{-1}, C is the conversion of tung oil into epoxy and other by-products (%), and Y is the yield of tung oil into epoxidized tung oil (%); the superscripts *eto* refer to epoxidized tung oil, *to* to tung oil, and *sample* to the samples taken during the reaction.

The productivity of epoxidized tung oil was calculated using Equation (3).

$$P = \frac{M_{eo}C_{to}}{t}\frac{Y}{100} \quad (3)$$

where M_{eo} is the molar mass of epoxidized tung oil (g mol^{-1}), C_{to} is the molar concentration of tung oil (mol L^{-1}), P is the productivity (g L^{-1}h^{-1}), and t is the processing time (min).

3. Results and discussions

3.1. Tung oil characterization

Tung oil was analyzed by gas chromatography with the mass spectrum. The composition of tung oil was determined as 80% of α -eleostearic acid, 15% of oleic acid, 4% palmitic acid, and 1% of stearic acid. Fig. 1 presents the FTIR spectrum of tung oil, characterized by peaks at 990 and 3010 cm^{-1} corresponding to the carbon double bonds, 1435 cm^{-1} to alkane chains, and 3400 cm^{-1} to hydroxyls.

3.2. Effect of the peroxidation acid on the production of tung oil epoxy

Table 1 (Runs 1 to 8) presents the oil conversion and epoxy resin yield for the sonochemical production of epoxidized tung oil using acetic or formic acid as peroxidation acid precursors. The epoxidation of tung oil, which contains α -eleostearic fatty acids and oleic fatty acids, occurs according to the scheme presented in Fig. 2. During the reaction, the
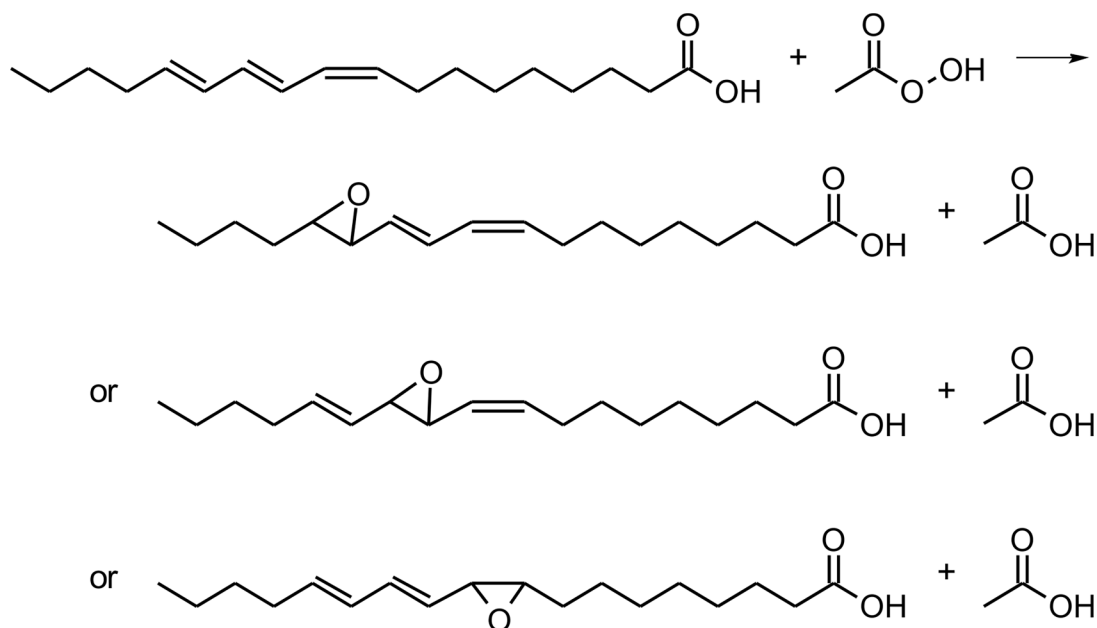
Fig. 2. Epoxidation of α -eleostearic acid (the major compound in tung oil).

number of carbon double bonds decreases while the number of oxirane groups increases. Fig. 1 shows the FTIR spectra of the tung oil epoxy resin, characterized by the same peaks that characterize tung oil plus the peak at 840 cm^{-1} corresponding to oxirane groups.

The reaction using acetic acid presented a higher conversion of oil into products (up to 89.4 ± 7.2 %) than the reaction carried out with formic acid (85.0 ± 6.6 %), but both conversions were statistically similar. The main difference between the use of acetic and formic was in the formation or not of by-products. The reaction applying formic acid resulted mainly in epoxidized tung oil. In contrast, the reaction applying acetic acid produced epoxidized tung oil and other by-products resulting from the cleavage of the epoxy molecule. By-product formation will be discussed later on.

The reaction using formic acid tended to yield more epoxidized tung oil than applying acetic acid. The highest yield (85.0 ± 6.6 %) was attained by applying 2450 W L^{-1} of ultrasonic power density using formic acid as a peroxidation acid precursor. However, no significant difference (78.2 ± 6.1 %) was observed when applying the same power density using acetic acid as a peroxidation acid precursor. The slight

difference is due to the formation rate of performic acid being higher than that of peracetic acid, leading to a faster reaction [21].

The yield obtained herein applying formic acid was slightly higher than for low-frequency ultrasonic epoxidation of soybean oil (71.5 % after 240 min) [2]. On the other hand, the yield was lower than low-frequency ultrasonic epoxidation of soybean oil using lipase as biocatalyst (91%) [12]. Table 2 presents a comparative table of several processes for the production of vegetable oil epoxy resins. The table shows that the ultrasound-assisted epoxidation presents good performance in comparison to other processes.

3.3. Effect of ultrasonic power on the production of tung oil epoxy

Table 1 (Runs 1 to 8) also presents the oil conversion, the yield into epoxy resin for tung oil epoxy subjected to ultrasound power densities between 1620 and 2940 W L^{-1}. The conversion of oil into epoxy and other by-products increased with increasing ultrasound power density up to 2060 W L^{-1} when using acetic acid (89.4 ± 7.2 %) and 2450 W L^{-1} when using formic acid (85.0 ± 6.6 %). Above this power density, its

Table 2
Comparison between several processes on epoxidation of vegetable oils.

Process	Vegetable Oil	Percarboxylic acid	Oil conversion (%)	Yield into epoxy resin(%)	Best condition	Reference
Ultrasound	Tung oil	Acetic acid	85.9	78.2	2450 W L^{-1} ultrasound power density0.8 acetic acid:oil (mol/mol)15.0 H$_2$O$_2$:oil (mol/mol)	This work
Ultrasound (pulsed)	Soybean oil	Acetic acid	83.0	69.0	120 W ultrasound nominal power10 s on, 10 s off60 °C0.5 acetic acid:unsaturation (mol/mol)1.5 H$_2$O$_2$:unsaturation (mol/mol)	[2]
Ultrasound (pulsed)	Sunflower oil	Acetic acid + Indion 225H	61.7	36.4	90 W ultrasound nominal power5 s on, 5 s off60 °C0.5 acetic acid: unsaturation (mol/mol)1.5 H$_2$O$_2$:unsaturation (mol/mol)	[11]
Microwave	Oleic acid	Acetic acid	100	N.I.	1950 W nominal power60 °C, 650 rpm2.0 acetic acid:oil (mol/mol)1.0 H$_2$O$_2$:oil (mol/mol)	[30]
Stirred Batch Reaction	Oleic acid	Acetic acid	50	N.I.	60 °C, 650 rpm2.0 acetic acid:oil (mol/mol)1.0 H$_2$O$_2$:oil (mol/mol)	[30]
Stirred Batch Reaction	Cotton seed oil	Formic acid	80	65	75 °C, 2400 rpm0.5 formic acid:unsaturation (mol/mol)1.0 H$_2$O$_2$: unsaturation (mol/mol)2% sulfuric acid	[9]
Stirred Batch Reaction	Castor oil	Acetic acid + Ion exchange resin	92.8	N.I.	50 °C0.5 acetic acid:unsaturation (mol/mol)1.5 H$_2$O$_2$: unsaturation (mol/mol)	[31]
Stirred Batch Reaction	Soybean oil		93.9	71.6	65 °C, 750 rpm0.1 formic acid:oil (w/w)0.4 H$_2$O$_2$:oil (w/w)0.008 H$_2$SO$_4$:oil (w/w)	[23]

N.I. – not informed. Standard deviation was not informed in most references.

increase resulted in a steep drop in conversion, most probably caused by the degradation of the percarboxylic acid by ultrasound. The highest yields into epoxidized tung oil were attained at 2450 W L^{-1} for both percarboxylic acids.

The percarboxylic acid is an oxygen doner in the reaction mechanism, and it is responsible for the formation of oxirane in the epoxy molecule. Without a percarboxylic acid, the reaction does not occur in conventional stirred batch reactors. In ultrasound-assisted reactions, hydroxyl radicals are formed and donate oxygen to form oxiranes. However, the addition of a percarboxylic acid in ultrasound-assisted reaction increases the rate of reaction and yield.

The degradation of percarboxylic acids by ultrasound has been addressed by Li et al. [22]. Their work showed that peracetic acid concentration decreased with temperature rise and ultrasound application above 50 °C, phenomena attributed to higher hydrolysis and decomposition of peracetic acid. In our work, higher ultrasound power densities resulted in higher temperature rises (section 3.6). Thus, at 2940 W L^{-1}, the ultrasound power density applied and temperature rise probably contributed to the degradation of peracetic and performic acids.

Fig. 3 presents the dynamic behavior of the reaction at different ultrasound power densities. Overall, higher ultrasound power densities induced high reaction rates in the first hour of reaction, but the reaction rates diminished after achieving approximately 60% of conversion. Lower ultrasound power densities presented lower initial reaction rates but reached higher conversions after 180 min of reaction. This behavior corroborates with a probable degradation of the percarboxylic acid by high ultrasound power densities.

Although high ultrasound power densities induced a higher overall conversion of tung oil, the conversion has only partially yielded
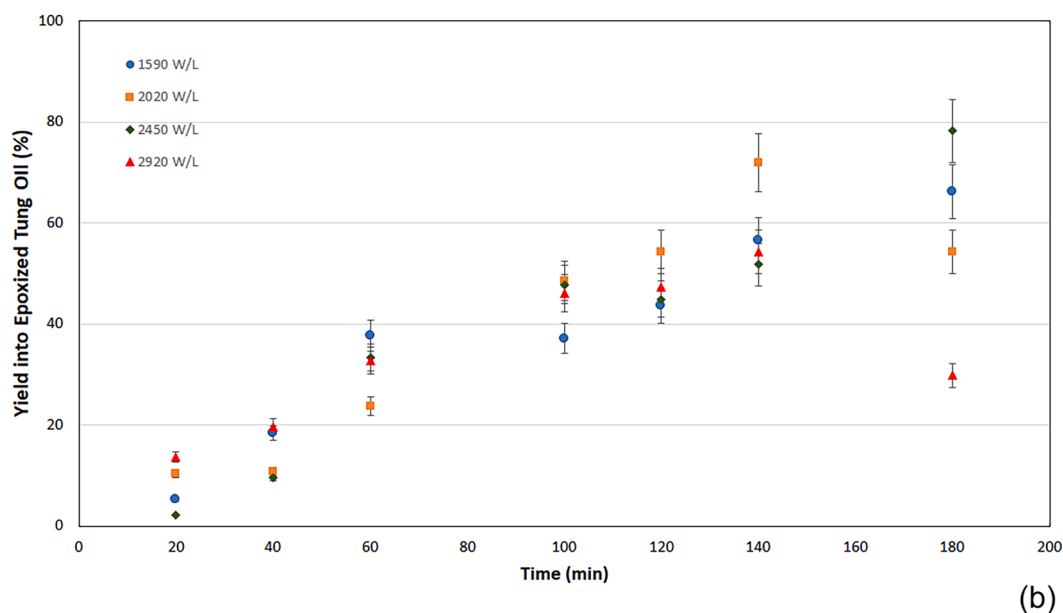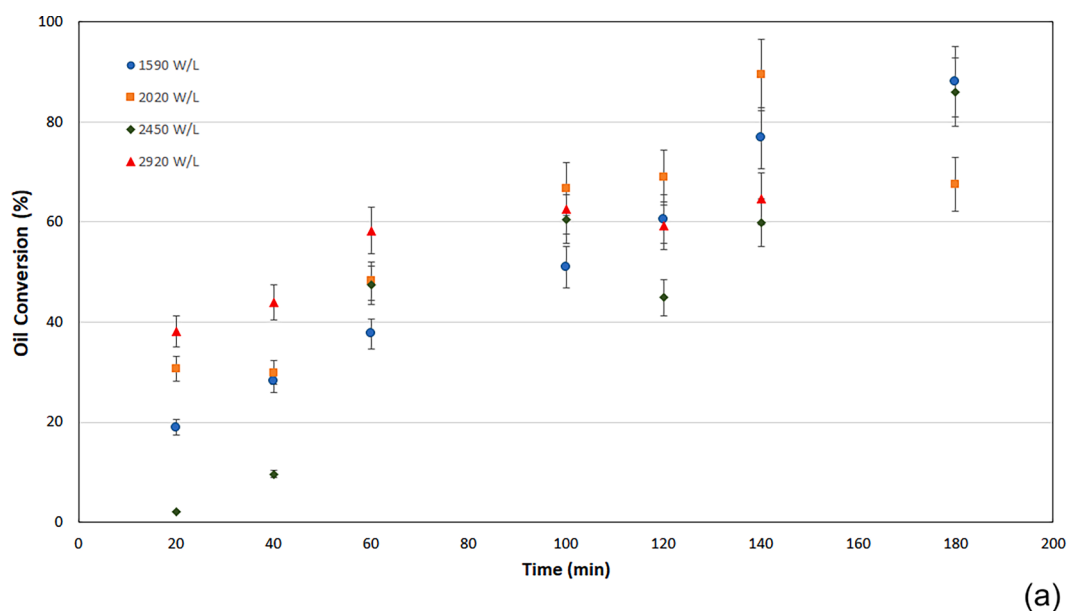

Fig. 3. Conversion of tung oil into products (a) and yield of epoxidized tung oil (b) as a function of the reaction time and ultrasound power densities for the epoxidation of tung oil using acetic acid as percarboxylic acid. Results achieved using a 19 kHz probe ultrasound with a 1.3 cm diameter titanium probe, 500 W nominal power, 2940 W L^{-1} maximum effective power density applied to the reaction mixture.

epoxidized tung oil, mainly when acetic acid was employed. The yield into epoxidized tung oil reduced steeply after 140 min of reaction when the highest ultrasound power density was applied (2920 W L^{-1}), indicating a continuous fragmentation of the epoxy into by-products. The cleavage of epoxy molecules occurred at lesser intensity when intermediate, and low ultrasound power densities were applied. Fragmentation of epoxidized tung oil generated 2-heptenal, 2,4-nonadienal, and traces of octanal, octanoic acid, nonanoic acid, 2,4-dodecadienal, 9-oxononanoic acid, and 2-ethyl-hexen-1-ol, as revealed by GCMS analysis (Fig. 4).

Fragmentation of epoxidized vegetable oils induced by ultrasound application has been previously reported by Chavan and Gogate [11] for sonicated sunflower oil in the presence of acetic acid. However, α -glycol was the main by-product form during ultrasonic-assisted epoxidation of sunflower oil.

Control runs were performed in stirred batch reactors to evaluate the epoxidation reaction carried out with and without sonication (Table 1, runs 16 to 18). The autocatalyzed reaction resulted in a very low oil conversion (21.6 ± 1.0 %). As agitation level increased, oil conversion and yield into epoxy resin increased as expected for this kind of reaction. At 600 rpm (perfect mixing for the reactor), an oil conversion of 71.3 ± 3.0% was obtained. This conversion was 17% lower than the conversion achieved using ultrasound-assisted reaction. Thus, sonication was not only responsible for mixing, but had a positive effect in catalyzing the reaction.

3.4. Effect of acetic acid ratio on the production of tung oil epoxy

The influence of the acetic acid molar ratio in the reaction was studied, varying the molar ratio of acetic acid to tung oil from 0.66 to 0.82 mol/mol. Table 1 (Runs 9 to 11) presents the oil conversion and the yield into epoxy resin for the epoxidation of tung oil using acetic acid as the percarboxylic acid precursor.

Ultrasound-assisted epoxidation carried out without the percarboxylic acid precursor achieved an oil conversion of 63.9 ± 9.9%. Sonication produces hydroxyl radicals from both water and hydrogen peroxide contributing to the epoxidation. However, oil conversion and yield into epoxidized tung oil were significantly lower than applying a percarboxylic acid precursor.

The best acetic acid to tung oil molar ratio that resulted in the highest oil conversion and yield into epoxidized tung oil was attained at 0.66

mol/mol. Under this condition, an oil conversion of 96.4 ± 6.0% and a yield into epoxidized tung oil of 81.0 ± 6.0% were observed. Increasing the acetic acid to tung oil molar ratio slightly decreased oil conversion and yield into epoxidized tung oil. The peracetic acid acts as an oxygen doner for the formation of oxirane rings in the vegetable oil. Higher concentration of acetic acid increases the formation of peracetic acid because this reaction is very fast. The increase in concentration of acetic acid, however, had only limited effect on the yield into epoxidized tung oil because the formation of oxirane is a slow reaction and therefore is the limiting reaction in the system. Above 0.66 mol/mol, the increase in concentration of acetic acid, and consequently the increase in concentration of peracetic acid were not enough to increase considerably the reaction rate for oxirane formation.

The application of acetic acid as the percarboxylic acid precursor was more successful in the production of epoxidized tung oil than in soybean oil. The yield into epoxidized soybean oil achieved only 22% in ultrasound-assisted epoxidation. Yields of 69% were attained when sulfuric acid was employed as a peroxidation catalyst but at a higher temperature (80 °C) [13]. The difference in performance may be related to the chemical composition of the oils. Soybean oil consists mainly of oleic and linoleic acids with double-bonds in cis configuration and no conjugated double-bonds. In contrast, tung oil consists primarily of α -eleostearic acid with double-bonds in trans and cis configurations and two conjugated double-bonds.

3.5. Effect of hydrogen peroxide ratio on the production of tung oil epoxy

The influence of the hydrogen peroxide concentration was studied, varying the molar ratio of hydrogen peroxide to tung oil from 11.4 to 15.0 mol/mol. Table 1 (Runs 13 to 15) presents the oil conversion and the yield into epoxy resin for the epoxidation of tung oil using acetic acid as the percarboxylic acid precursor at different hydrogen peroxide to tung oil molar ratio.

Increasing the hydrogen peroxide to tung oil molar ratio increased significantly (p > 0.05) oil conversion and yield into epoxidized tung oil. Although ultrasound can generate small amounts of hydroxyl radicals, it is not enough to reduce hydrogen peroxide addition. The increase in hydrogen peroxide concentration significantly influenced the production of epoxidized tung oil, increasing both selectivity and productivity. The best hydrogen peroxide to tung oil molar ratio that resulted in the highest oil conversion and yield into epoxidized tung oil was attained at
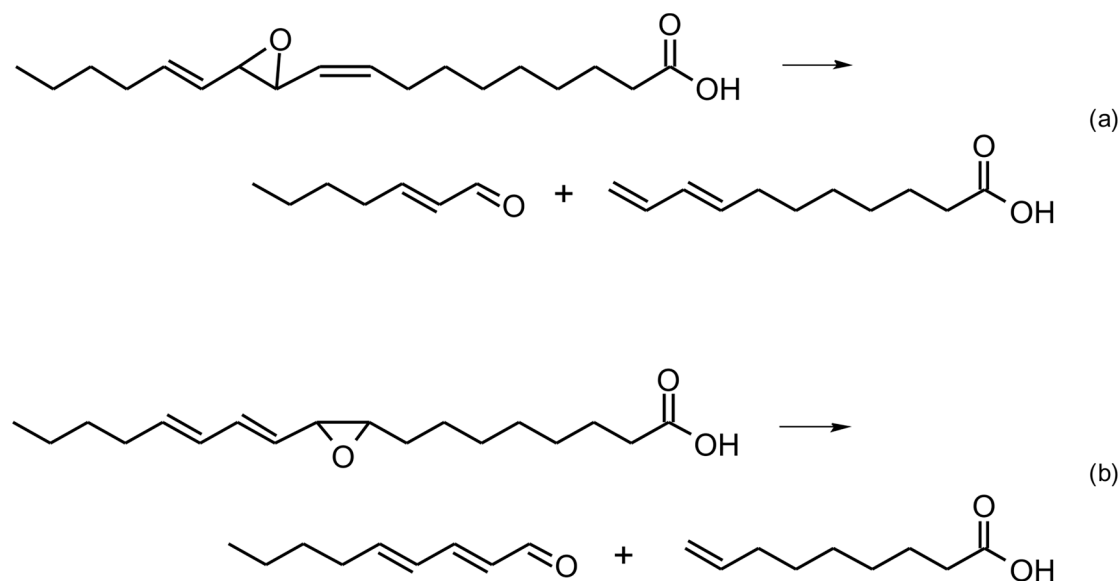

Fig. 4. Peroxycyclization-dioxetane fragmentation of epoxidized eleostearic acid producing (a) 2-heptenal and (b) 2,4-nonadienal. Results achieved using a 19 kHz probe ultrasound with a 1.3 cm diameter titanium probe, 500 W nominal power, 2940 W L^{-1} maximum effective power density applied to the reaction mixture.

15.0 mol/mol.

The increase in hydrogen peroxide concentration has a more significant effect on the formation of oxirane rings than the increase in acetic acid concentration. The reason may rely in the fact that hydrogen peroxide produces peracetic acid and hydroxyl radicals, both reacting with the oil molecule to produce oxirane rings. Thus, a net increase in oxirane forming reaction rates is observed. On a negative side, the increase in hydrogen peroxide has direct effect on reaction temperature rise, which could raise safety concerns if higher hydrogen peroxide concentrations were to be applied.
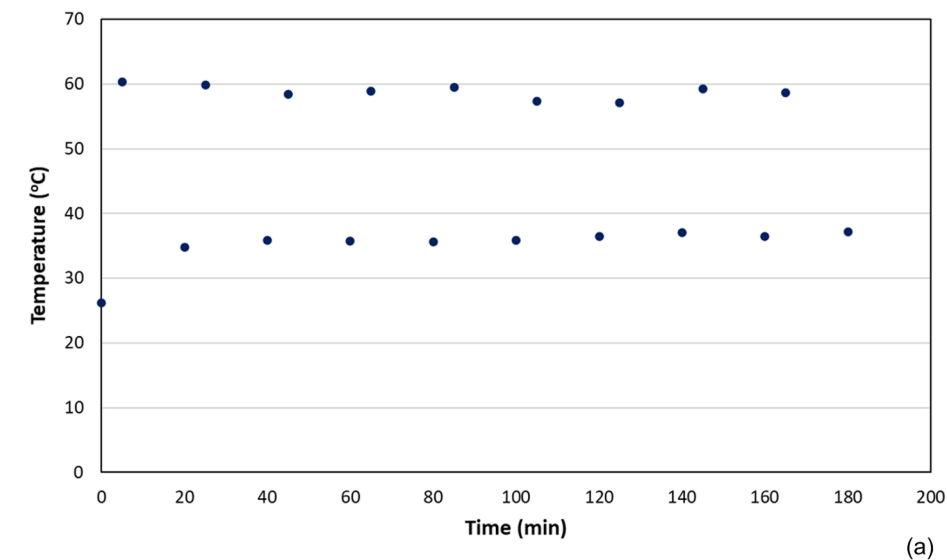
Fig. 5. Temperature profile during the production of epoxidized tung oil. Operating conditions: (a) 2450 W L^{-1} ultrasound power density, 15.0 hydrogen peroxide to tung oil molar ratio, 0.8 acetic acid to tung oil molar ratio, results achieved using a 19 kHz probe ultrasound with a 1.3 cm diameter titanium probe, 500 W nominal power, 2940 W L^{-1} maximum effective power density applied to the reaction mixture; (b) batch reaction at 100 rpm, 15.0 hydrogen peroxide to tung oil molar ratio, 0.8 acetic acid to tung oil molar ratio; (c) batch reaction at 600 rpm, 15.0 hydrogen peroxide to tung oil molar ratio, 0.8 acetic acid to tung oil molar ratio.
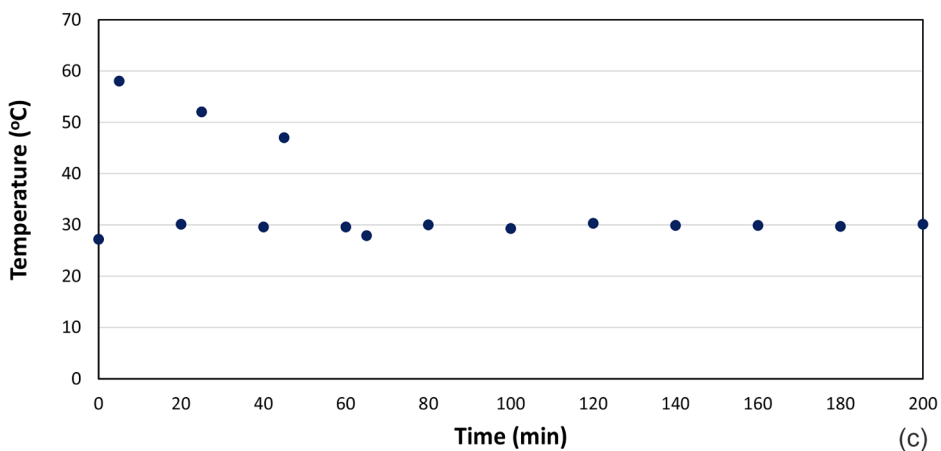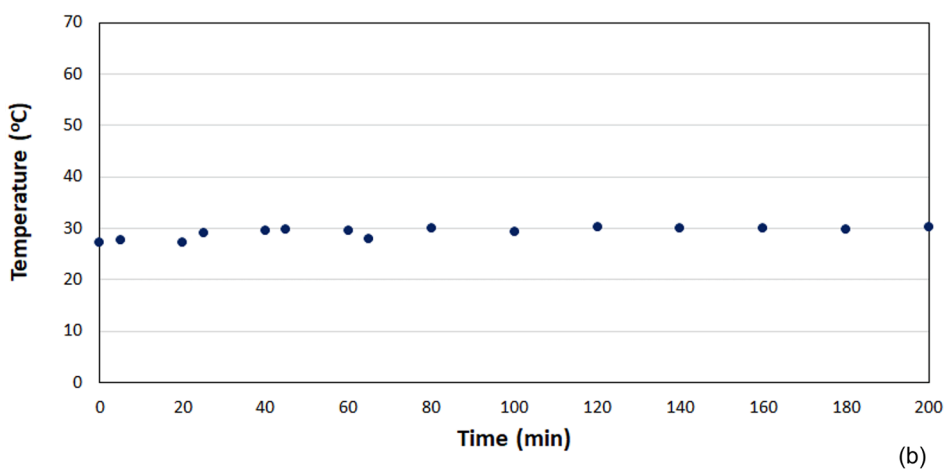
3.6. Temperature profile during ultrasound-assisted production of epoxidized tung oil

Fig. 5 presents a typical temperature profile obtained during the epoxidation of tung oil through sonication and the profile obtained for the reaction carried out without sonication. Temperature spikes were observed after the addition of hydrogen peroxide and the application of ultrasound, indicating a highly exothermic reaction. Santacesaria et al. [23] reported difficulty maintaining constant temperature because of the reaction's strong exothermicity. Other studies reported a similar temperature profile on the production of epoxidized soybean oil in conventional and sonochemical reactors [13,14].

The reaction carried out without ultrasound application did not present the temperature spikes observed in the ultrasound-assisted reaction (Fig. 5b). The temperature profile was basically flat, with the reaction temperature being only slightly above the bath temperature. The lower oil conversion and yield into epoxy resin were related to this lower average temperature. The comparison between the temperature profiles of the reaction with and without ultrasound application also evidences the contribution of ultrasound towards this reaction system.

The conventional batch reaction presented some spikes that were observed after the addition of hydrogen peroxide as a result of the highly exothermic reaction (Fig. 5c). The intensity of the spikes was less intense than the observed for the ultrasound-assisted reaction, and halted after 100 min of reaction.

3.7. Reaction by-products

The reaction carried out with formic acid produced mainly epoxidized tung oil and only traces of other by-products, which accounted for less than 1% (w/w). However, the reaction carried out with acetic acid produced up to 25% (w/w) of by-products. The analysis of the products formed during the sonochemical reaction of tung oil showed that the final product comprised of a mixture of unreacted tung oil, epoxidized tung oil, 2-heptenal, 2,4-nonadienal, 2,4-dodecadienal, and traces of octanal, octanoic acid, 2-none-1-ol, nonanoic acid, 9-oxo-nonanoic acid, and 2-ethyl-hexen-1-ol.

The presence of 2-heptenal, 2,4-nonadienal, 2,4-dodecadienal, and 9-oxo-nonanoic acid, as shown in Fig. 4, indicate that ultrasound processing induces peroxycyclization-dioxetane fragmentation of the fatty acids [24].

Although by-products are not usually welcome in the chemical industry, the by-products formed during the sonochemical reaction can be labeled high-value products. Both 2-heptenal and 2,4-nonadienal are used in the food industry and the cosmetic industry as flavoring compounds [25–27]. Both products have higher commercial value than epoxidized tung oil. As such, the production of these by-products can be interesting.

Table 3 presents mass fractions of the compounds produced during the epoxidation of tung oil. Chromatographical analysis showed that 2,4-nonadienal was the more abundant by-product, followed by 2-heptenal. Thus, ultrasound-induced fragmentation of epoxidized tung oil occurred preferentially in the oxirane positioned at the 9th carbon of the α-eleostearic fatty acid, formerly a double-bonds in the cis configuration. Fragmentation of the epoxidized tung oil at the 11th and 13th carbon of the fatty acid was less frequent. The oxiranes in these two positions of the fatty acid were formerly conjugated double-bonds in trans configuration. Thus, ultrasound-induced fragmentation favored the oxirane positioned in a former double-bond in the cis configuration.

The mass fraction of 2,4-nonadienal increased when operating at low ultrasound power density (1620 W L^{-1}), low acetic acid to tung oil molar ratio (0.66 mol/mol), or low hydrogen peroxide to tung oil molar ratio (13.9 mol/mol). A similar trend was observed for the increase in the generation of 2-heptenal.

The aldehyde 2,4-dodecadienal is generated from the fragmentation of epoxidized α-calendic acid, an isomer of α-eleostearic acid. Unlike 2,4-nonadienal, the contents of 2,4-dodecadienal increased with increasing carboxylic acid and hydrogen peroxide to tung oil molar ratio. The different behavior is probably related to the latter compound being generated by oxirane fragmentation positioned at the former double-bond in the trans configuration, which was less prone to fragmentation than the oxiranes positioned at former double-bond in the former cis configuration.

Industrial production of 2-heptenal and 2,4-nonadienal is carried out by lipoxygenase of oleic and linoleic acids. The enzymatic process is much longer, requiring at least 8 h for completion. The reaction products depend significantly on the type of enzyme and operation conditions applied. The process carried out with soybean type-I lipoxygenase produces mainly hexanal (>20%, more usually > 70%) and traces of several minor components, such as pentanol, hexanol, pentanal, heptanal, 2-octenal, 2-nonenal, 2,4-nonadienal, 2,4-decadienal, 2-heptanone, and 3-octen-2-one [28]. However, the process carried out with an enzyme mixture consisting of crude full-fat soy flour extract lipoxygenase and purified Lox-1 lipoxygenase induces the production of mainly hexanal, heptanal, nonanal, 2-nonenal, and traces of other aldehydes, including 2,4-nonadienal [29]. As a common feature, the enzymatic process produces high amounts of short-chain saturated aldehydes. In contrast, the sonochemical process studied herein is capable of producing higher

Table 3

Components produced during ultrasound-assisted epoxidation of tung oil and their respective mass fractions in the product. Results achieved using a 19 kHz probe ultrasound with a 1.3 cm diameter titanium probe, 500 W nominal power, 2940 W.L^{-1} maximum effective power density applied to the reaction mixture.

Run	Ultrasound power density (W.L^{-1})	Acetic acid to oil molar ratio	Formic acid to oil molar ratio	Hydrogen peroxide to oil molar ratio	Epoxidized tung oil (w/w)	2-Heptenal (w/w)	2,4-Nonadienal (w/w)	2,4-Dodecadienal (w/w)
Effect of the peroxidation acid								
1	1620	0.8	0	15	0.75	0.02	0.23	0
3	2450	0.8	0	15	0.91	0	0.06	0.03
5	1620	0	0.8	15	1	0	0	0
6	2060	0	0.8	15	1	0	0	0
7	2450	0	0.8	15	1	0	0	0
8	2940	0	0.8	15	1	0	0	0
Effect of the carboxylic acid to oil molar ratio								
9	2450	0	0	15	1	0	0	0
10	2450	0.66	0	15	0.84	0.03	0.12	0.01
11	2450	0.74	0	15	0.89	0.01	0.09	0
12	2450	0.82	0	15	0.91	0	0.06	0.03
Effect of the hydrogen peroxide to oil molar ratio								
13	2450	0.8	0	11.4	0.9	0.01	0.09	0
14	2450	0.8	0	13.9	0.84	0.01	0.14	0.01
15	2450	0.8	0	15	0.91	0	0.06	0.03

quantities of specific unsaturated aldehydes.

The explanation on why oil and epoxy fragmentation occurred only in the presence of acetic acid is still unclear and the phenomena should be further studied. The information presented in the literature regarding the peroxycyclization-dioxetane fragmentation still does not provide a strong basis to explain the real cause. The acidic strength difference between acetic and formic acid may be one explanation [11,30,2,9,31,23].

4. Conclusions

Application of ultrasound on epoxidation reaction was carried out using a 19 kHz probe ultrasound (horn ultrasound) with a 1.3 cm diameter titanium probe, 500 W nominal power, 2940 W L^{-1} maximum effective power density applied to the reaction mixture. The ultrasound-assisted reaction showed to be technically feasible, and resulted in high oil conversions (up to 96%) and high yields into epoxidized tung oil (up to 85%).

The higher performance of ultrasound-assisted epoxidation of tung oil than in others oils can be related to the chemical composition of tung oil. The analysis of the oil's chemical composition and the by-products produced during the reaction indicates that ultrasound favors the epoxidation of oils containing conjugated double-bonds.

The epoxidation process applying low frequency high power ultrasound can be routed into producing flavoring agents, used in the cosmetic and food industry by fragmentation of the epoxidized oil. This route could open new possibilities to easily produce specific flavoring agents from different vegetable oils or fatty acids.

Current limitations of the ultrasound technology, such as rapid heating of the ultrasonic horn and needing to work in pulsed mode, prevent better results for ultrasound-assisted epoxidation and reduction of processing time. Future developments in ultrasound equipment may change this scenario, reducing the processing time considerably.

CRediT authorship contribution statement

Raquel S. Silva: Investigation, Formal analysis, Writing – original draft. **Dayanne L.H. Maia:** Methodology, Writing – original draft. **Fabiano A. N. Fernandes:** Conceptualization, Funding acquisition, Formal analysis, Supervision, Writing - review & editing.

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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