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Microreactor x millireactor: Experimental performance in the epoxidation of soybean oil

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ABSTRACT

In the Chemical Reaction Engineering (CRE) field, the concept of Process Intensification (PI) can be applied using microreactors and millireactors, i.e., tubular reaction devices with reduced dimensions, compared with typical reactors used industrially. This concept was explored in the present study by the conduction of the reaction system for the epoxidation of soybean oil without catalysts and droplet stabilizers. The biphasic reaction system generates the epoxidized soybean oil (ESO), a promising compound in the plasticizers field that follows Green Chemistry principles. Besides the effect of the equipment itself (microreactor or millireactor), the effects of the temperature and the mean residence time were also explored in this study. The results confirmed the intensification of the epoxidation process, particularly in the microreactor, due to the strong dependence of the reactions on mass and heat transfer effects. This led to significantly lower reaction times, in the order of minutes, comparatively to the typical reaction times of hours employed in industrial batch and fed-batch reactors, with the achievement of the most promising results of 19.77 g I_2/100 g for the iodine index and 5.67 g O/100 g for the oxirane index, values corresponding to 84.2% of double bond conversion and 74.9% of epoxy yield.

1. Introduction

Currently, there is a tendency in the chemical industry to search for alternatives to use materials from renewable sources, following one of the Green Chemistry principles. The chemical processing of vegetable oils fits this tendency, especially when generating products with low toxicity and biodegradability. Soybean oil shows a particular interest in undergoing an epoxidation reaction since the epoxidized soybean oil (ESO), the product of the reaction, presents the main application in plasticizers to polyvinyl chloride (PVC). The usage of ESO in this application offers an alternative to replace phthalates, which have carcinogenic potential [1–4]. The ESO can also be functionalized to generate monomers for polymerization reactions, for example [5,6].

Muobom et al. [7] present a global tendency of growth in the use of bioplasticizers: in 2016, the production was 887.3 kt, with a perspective of increasing to 1900 kt in 2025. In the same period, the market of bioplasticizers is expected to rise from USD 1124.3 million to USD 2683.7 million.

The production of ESO is typically performed in batch or fed-batch reactors. Still, the study of the development of a continuous operation shows great interest because of the expected increase in demand for this substance to replace phthalates. The main advantages of the continuous process are: benefiting from the quality control of the product, facility in process control and stability of the system, and reduction in operation costs by unit of product [8].

Process Intensification (PI) can be understood as new equipment or techniques that lead to a significant improvement in chemical or biochemical processes, with an impact on the reduction of equipment dimensions, cost minimization, increase in process security, development of sustainable technology, and increase in productivity of processes. Amongst the several examples of PI, there are chemical reactors with reduced dimensions, i.e., microreactors and millireactors, with the following advantages: intensification of heat and mass transfer, and facility of production increasing by numbering-up, comparatively to scale-up in traditional reactors with larger dimensions. However, corrosive effects, incrustation, and pressure drop also tend to be more significant in micro- and millireactors [9–11].

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Notation

II	Iodine index [g I_2/100 g]
M	Molar mass [g/mol]
n_H	Number of hydrogen atoms in a molecule group [-]
OI	Oxirane index [g O/100 g]
T	Temperature [°C]
X	Double bond conversion [%]
Y	Epoxy yield [%]

Greek letters

δ	Chemical shift [ppm]
τ	Mean residence time [s]

Subscripts

b	Value referent to the water bath
I_2	Value referent to the iodine molecule
j	Index for a molecule group
max	Maximum value
O	Value referent to the oxygen atom
SO	Value referent to the soybean oil

Typically, the epoxidation reaction is performed in a liquid-liquid system, involving an aqueous and an organic phase, strongly dependent on heat and mass transfer effects. To summarize, the following steps are verified in the reaction system: (1) in the aqueous phase, a carboxylic acid (formic or acetic acid) reacts with hydrogen peroxide, to obtain the correspondent peracid (performic or peracetic acid); (2) part of the peracid tends to migrate to the organic phase; (3) in the organic phase, the peracid reacts with the double bonds of the oil, generating an epoxy group, that characterizes the epoxidized oil, and the carboxylic acid; (4) part of the carboxylic acid returns to the aqueous phase; (5) undesired reactions may also occur, concerning the decomposition of hydrogen peroxide and the peracid, and the interfacial ring-opening reactions of the epoxy ring [12–21]. The rate-determining step of the reaction system is the peracid generation due to its reversibility and because the major part of the peracid tends to remain in the aqueous phase in the phase equilibrium [14]. Considering the carboxylic acids typically employed: acetic acid is less reactive, which disfavors the ring-opening reactions, but, for step (1) to occur efficiently, it requires the addition of catalysts (for example, sulfuric or phosphoric acid) that, for instance, intensify the ring-opening reactions; the formic acid is more reactive for both generation of performic acid and ring-opening reactions but with no need to add catalysts [16]. The carboxylic acid is intended to act similarly to a catalyst in this reaction system, with its consumption in the peracid generation, but with the regeneration of the carboxylic acid after the epoxidation reaction. Fig. 1 presents a scheme of the reaction system for the epoxidation of soybean oil, using formic acid as the carboxylic acid.

Several factors need to be considered for the epoxidation reaction system to occur efficiently. Since the epoxidation reaction and the decomposition of the peracid are very exothermic, extreme caution is required for heat transfer effects [2]. Also, since the reaction is biphasic, variables such as agitation/shear rate, interfacial area, and viscosity substantially affect the mass transfer, as well as can favor undesired ring-opening reactions. A detailed kinetic model was previously developed for this system, considering these factors [22].

Two main properties are typically adopted to characterize the advance in the epoxidation reaction: the iodine index and the oxirane index. The iodine index represents the amount of iodine (I_2), in grams, that can be added to the remaining double bonds present in 100 g of the oil, therefore, being associated with the conversion of double bonds. The oxirane index can be defined as the weight, in grams, of oxygen atoms of epoxy groups produced in a sample of 100 g of epoxidized oil. The oxirane index may be related to a yield [22].

The following studies analyzed the possibility of conducting the epoxidation reaction of vegetable oils in micro- or millireactors: Santacesaria et al. [23] studied the reaction in 1 cm diameter reactors, with the inclusion of homogeneous catalysts; He et al. [24] performed the reaction in a 37 mL reactor, including a homogeneous catalyst and a stabilizer; He et al. [25] used a sandwich microreactor to combine a transesterification and the epoxidation reaction catalyzed and with stabilizers; Cai et al. [26] analyzed the reaction system in a 10 mm diameter packed bed reactor with orifice plates. Vanoye et al. [27] made the reaction in a 3.5 mL reactor, but using a different mechanism to produce the epoxidized product, according to the Mukaiyama reaction; Phimsen et al. [28] used a stabilizer and a heterogeneous catalyst in a 0.13 mL reactor; Mashhadi et al. [29] employed a 0.5 mL reactor to perform the reaction with enzymatic catalysis; Cortese et al. [30] simulated the behavior of the system in microreactors to conduct the reaction in temperatures much higher than usual. The main common point resulting from these studies is the considerably reduced reaction time (order of minutes) compared to the typical adopted in the industry (8 to 12 hours). In a parallel study [31], we also performed computational simulations of the reaction media in a millireactor, without catalysts, in which the mass and heat transfer effects were considerably intensified, leading to promising results for a 2-hour residence time.

The objective of the present study was the analysis of the behavior of the reaction system for epoxidation of soybean oil in a millireactor and a microreactor, comparing the behavior observed in both equipment (i.e., the effects of the reactor size) and evaluating the effects of temperature

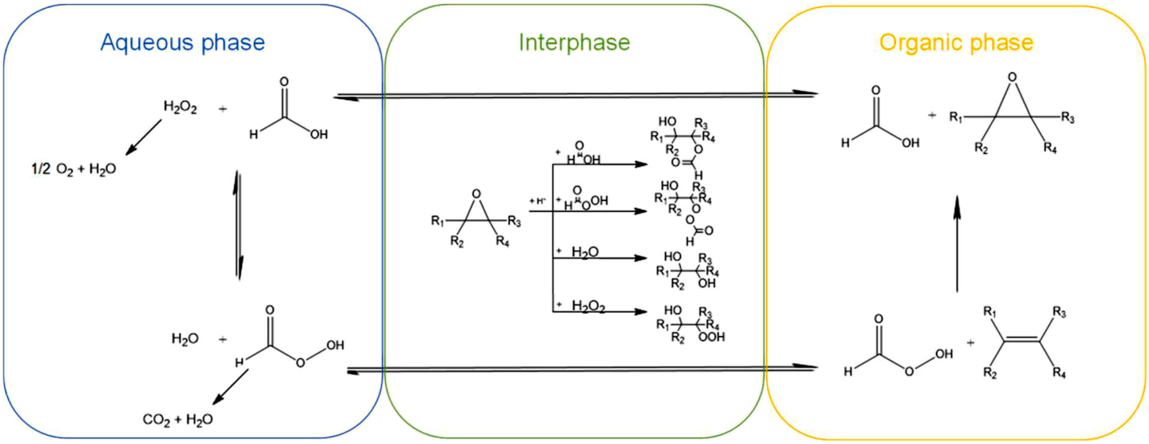

Fig. 1. Reactions occurring in the system for the epoxidation of soybean oil.

and mean residence time. The reaction system was performed without catalysts and droplet stabilizers as an alternative for application on larger scale to analyze the system's behavior with the minimum reactants required and avoid posterior separation problems due to the stabilizers. The products were characterized by spectroscopy of nuclear magnetic resonance of hydrogen (^{1}H-NMR) as a continuation of the study proposed by Cogliano et al. [32].

2. Materials and Methods

Soybean oil (Liza, iodine index = 125 g I_2/100 g), formic acid solution (LabSynth, 85 wt%), and hydrogen peroxide solution (LabSynth, 50 wt%) were used without further purification.

A transesterification reaction of soybean oil with sodium methoxide was performed to obtain the fatty acid methyl esters and analyze the oil composition by Gas Chromatography (GC). The Gas Chromatographer GC-2010 Plus (Shimadzu), the GC capillary column HT5 (SGE Analytical Science – 25 m × 0.32 mm × 0.1 μm), and a flame ionization detector (FID) were used in this analysis. The conditions were: *n*-hexane as a solvent, sample concentration of 2 mg/mL, sample volume of 1 mL, injection temperature of 280 °C, FID temperature of 360 °C, carrier gas (helium) flow rate of 7.59 mL/min, makeup gas (helium) flow rate of 30 mL/min, purge flow rate of 3 mL/min, split ratio of 1:10. The temperature ramp was: initial temperature of 60 °C (hold 1 min), 25 °C/min until 180 °C (hold 1 min), 5 °C/min until 250 °C (hold 2 min), 20 °C/min until 300 °C (hold 2 min), 30 °C/min until 360 °C (hold 7 min). The composition of soybean oil was expressed in terms of weight percentual of the corresponding fatty acids (number of carbons:number of double bonds): linoleic (18:2) – 52.4%; oleic (18:1) – 31.4%; palmitic (16:0) – 10.7%; stearic (18:0) – 3.8%; others – 1.7%.

The experiments in the millireactor were performed in a silicone tube with 2 mm of internal diameter and 1 m length (reaction volume ca. 3.1 mL) immersed in silicone oil in a glass vessel over a heating plate with magnetic stirring (Quimis, model Q261M23). The temperature of the silicone oil bath was controlled by a thermocouple attached to the heating plate equipment, which led to an isoperibolic reaction system. A peristaltic pump Minipuls 3 (Gilson) was used to flow an emulsion containing soybean oil and formic acid, mechanically stirred at 300 rpm. A syringe pump (manufactured in our department) was adopted for the flow of hydrogen peroxide. The streams were connected in the silicone tube through a needle, in which the generation of droplets of the aqueous phase was observed in a continuous stream of the organic phase. Fig. 2 presents a scheme of the reaction system employed for the experiments in a millireactor. Further details about the syringe pump can be checked in the Supplementary Material file.

In the millireactor experiments, the effects of the mean residence time (τ) and bath temperature (T_b) were analyzed, according to Table 1. All experiments were based on feed streams with 71.2% of the organic phase (in volume basis) and 13.0% of formic acid solution in the aqueous phase (in weight basis). These proportions were chosen based on one of the conditions of our previous study, in which there is an excess of hydrogen peroxide in relation to the formic acid and in relation to the double bonds of the oil [22].

The equipment Asia Flow Chemistry System (Syrris) was employed for the experiments in the microreactor. The reactor consisted of a glass chip with a reactive volume of 250 μL, a cross-section with dimensions varying from 250 and 400 μm, and a length of 2.509 m. The chip was coupled with a system to adjust the flow pressure and the temperature to the set point (heater), leading to an isothermal conduction of the reaction system. Two syringe pumps were used to flow the reagents to the reactor: one stream contained only soybean oil (organic phase), while the other contained a mixture of aqueous phase reactants (formic acid

Table 1
Experimental plan for the millireactor experiments.

Experiment	T_b / °C	τ / s
ML01	40	720
ML02	60	720
ML03	80	720
ML04	40	2400
ML05	60	2400
ML06	80	2400
ML07	40	7200
ML08	60	7200
ML09	80	7200

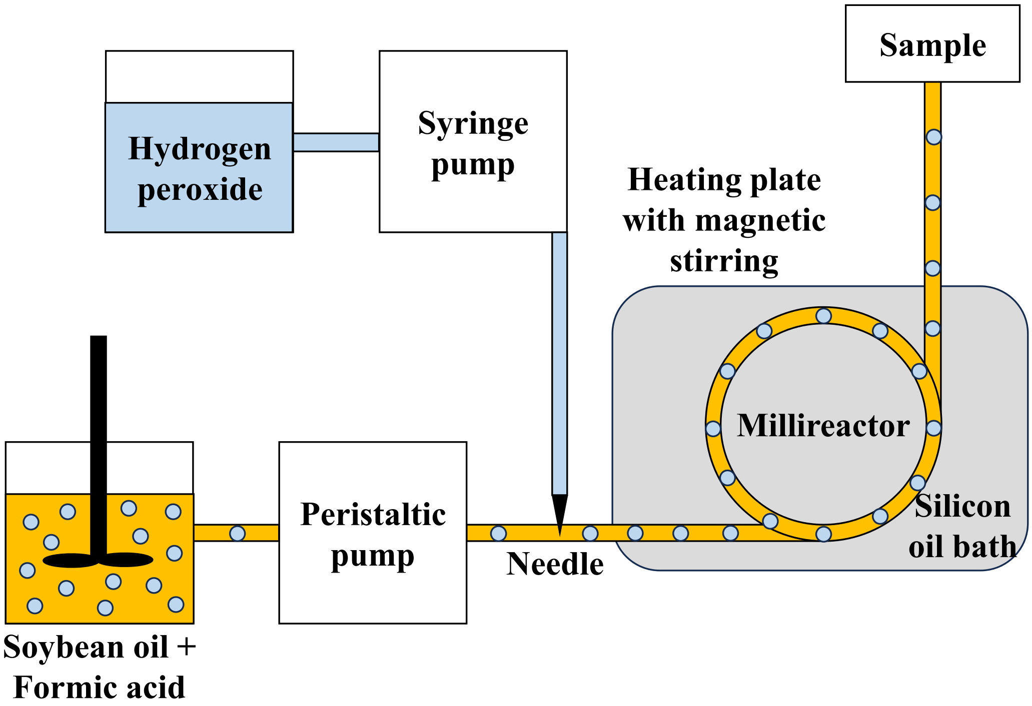

Fig. 2. Scheme of the reaction system for experiments in the millireactor.

solution and hydrogen peroxide solution). The encounter of streams occurred inside the chip, in a T-mixing junction, with the generation of the aqueous phase droplets in a continuous organic phase. Fig. 3 shows a scheme of the reaction system employed for the experiments in a microreactor.

In the microreactor experiments, the mean residence time (τ) and temperature (T) effects were analyzed, according to Table 2. Similarly to the millireactor, the experiments performed in the microreactor were also based on feed streams with 71.2% of the organic phase (in volume basis) and 13.0% of formic acid solution in the aqueous phase (in weight basis).

The output streams from both equipment were collected in amber vials and stored in a refrigerator. After phase separation, 60 μL aliquots of the organic phase were diluted in 600 μL of deuterated chloroform and characterized by the spectroscopy of nuclear magnetic resonance of hydrogen (^{1}H-NMR). The spectrometer Avance III (Bruker), with 500 MHz frequency, was employed in the analysis. The resulting spectra were processed using MestReNova (v. 14.3.0).

The chemical shifts (δ) related to the ^{1}H-NMR spectra for vegetable oils and epoxidized vegetable oils were studied by Goicoechea and Guillen [33], and the values were replicated in Table 3, coupled with the molecular groups to which they refer. The table does not include the peaks of 0 ppm, referent to tetramethylsilane (TMS – reference substance), and 7.26 ppm, related to residual chloroform in the solvent.

In order to estimate the iodine and oxirane indexes, firstly, the hydrogen atom of the molecule with a chemical shift of 5.23-5.32 ppm was taken as a reference. Within this, the signal integration was performed, i.e., the quantification of the actual number of hydrogen atoms associated with the number of each group in the molecule.

The average molar mass (M) of the products was estimated by equation (1) based on the integration of each signal, the molar mass of each group, and the number of hydrogen atoms in each group (n_{H}).

$$M = \sum_{j=1}^{n_{\mathrm{groups}}} \frac{\mathrm{Integration}_j}{n_{\mathrm{H},j}} M_j \tag{1}$$

The iodine index (II) was estimated by equation (2):

$$II = \frac{100 M_{\mathrm{I}_2} \left(\mathrm{Integration}_{-\mathrm{C}\underline{\mathrm{H}}=\mathrm{C}\underline{\mathrm{H}}-} \big/ 2 \right)}{M} \tag{2}$$

Table 2
Experimental plan for the microreactor experiments.

Experiment	T / °C	τ / s
MC01	40	480
MC02	60	480
MC03	70	480
MC04	80	480
MC05	60	720
MC06	70	720
MC07	80	720
MC08	40	960
MC09	60	960
MC10	70	960
MC11	80	960
MC12	40	1200
MC13	60	1200
MC14	80	1200

Table 3
Chemical shifts of the ^{1}H-NMR spectra and respective molecular groups[a].

δ / ppm	Molecular group
5.36-5.65	$-C\underline{H}=C\underline{H}-$
5.23-5.31	$>C\underline{H}OCOR$
4.11-4.33	$-C\underline{H}_2OCOR$
3.36-3.43	$-C\underline{H}(OH)-C\underline{H}(OH)-$
2.85-3.22	$-C\underline{H}-(O)-C\underline{H}-$
2.75-2.85	$=CH-C\underline{H}_2-CH-$
2.38-2.47	$-CH-(O)-CH-C\underline{H}_2-CH=CH-$
2.24-2.38	$-OCO-C\underline{H}_2-$
1.98-2.20	$-C\underline{H}_2-CH=CH-$
1.68-1.87	$-CH-(O)-CH-C\underline{H}_2-\ CH-(O)-CH-$
1.57-1.68	$-OCOCH_2-C\underline{H}_2-$
1.40-1.58	$-C\underline{H}_2-CH-(O)-CH-\ C\underline{H}_2-$
1.20-1.42	$-(C\underline{H}_2)_n-$
0.82-1.11	$-C\underline{H}_3$

[a] Goicoechea e Guillen [33].

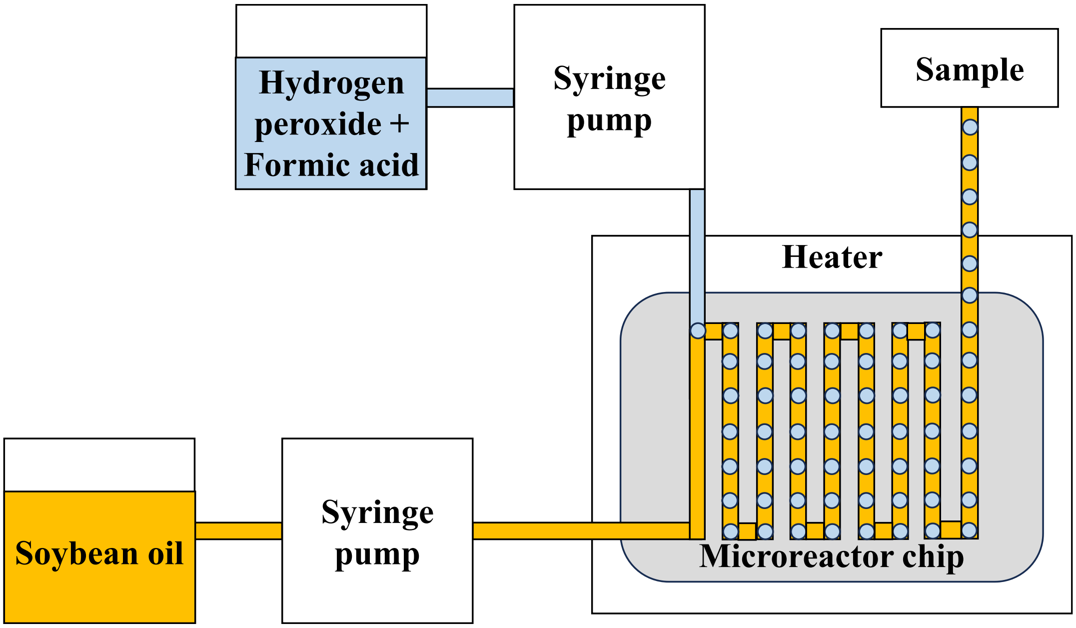

Fig. 3. Scheme of the reaction system for experiments in the microreactor.

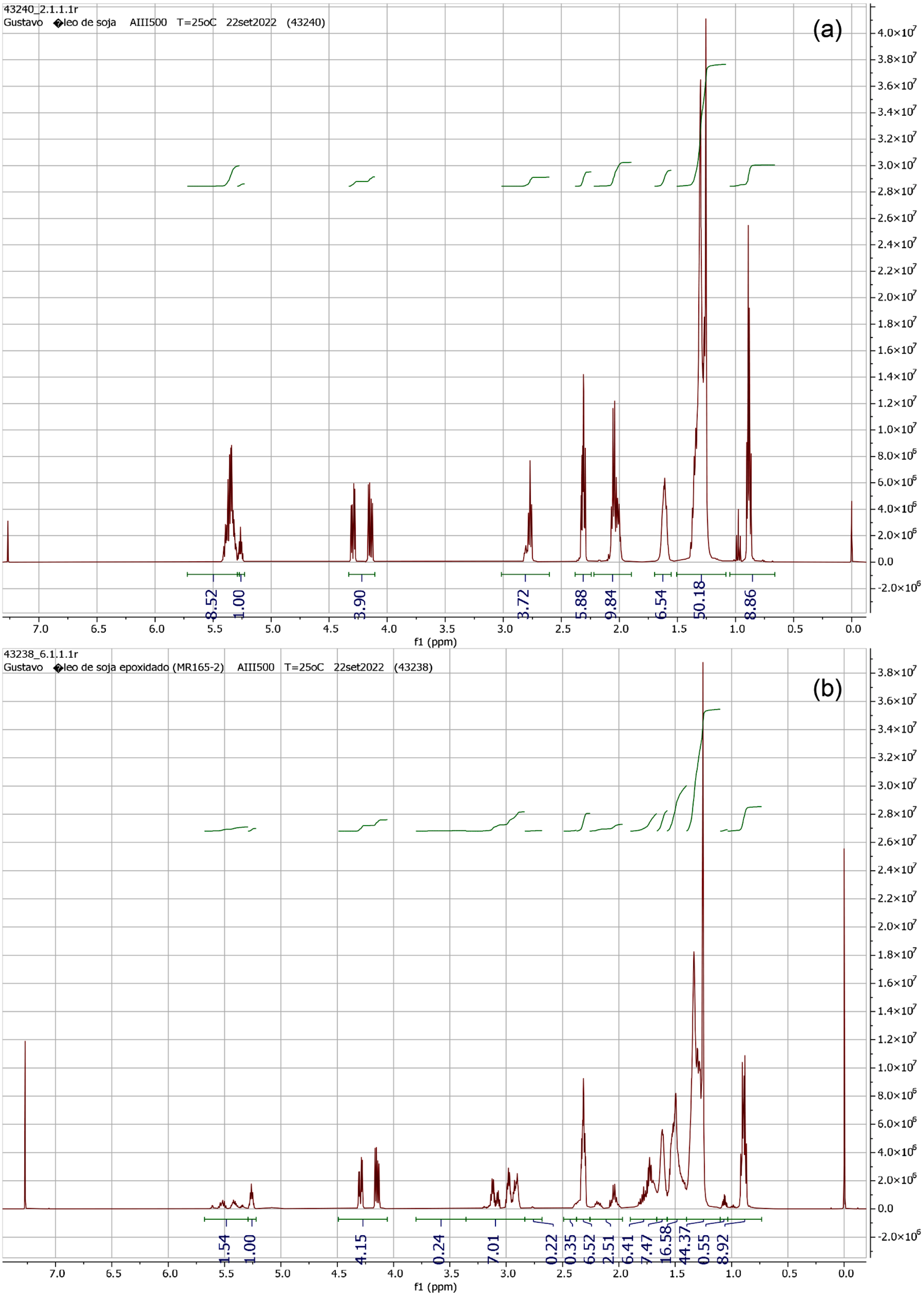

Fig. 4. ^{1}H-NMR spectra for: (a) soybean oil; (b) epoxidized soybean oil for experiment MC06.

And the oxirane index (*OI*) was estimated by equation (3):

$$OI = \frac{100M_{\mathrm{O}}\left(\mathrm{Integration}_{-\mathrm{C}\underline{\mathrm{H}}-(\mathrm{O})-\mathrm{C}\underline{\mathrm{H}}-}\Big/2\right)}{M} \tag{3}$$

The double bond conversion (*X*) was determined by the *II* values, according to equation (4), in which II_{SO} is the initial value of iodine index, corresponding to pure soybean oil:

$$X = 100\left(\frac{II_{\mathrm{SO}} - II}{II_{\mathrm{SO}}}\right) \tag{4}$$

The epoxy yield (*Y*) was determined by comparing the *OI* values with the theoretical maximum oxirane index ($OI_{\max}$), estimated as 7.33 g O/100 g by considering that all double bonds of the soybean oil are converted only into epoxy groups [22]:

$$Y = 100\frac{OI}{OI_{\max}} \tag{5}$$

3. Results and discussion

Fig. 4 presents the ^{1}H-NMR spectra for the soybean oil used and one of the ESO produced to exemplify, according to experiment MC07, performed in the microreactor.

The ^{1}H-NMR spectra were generated for all experiments specified in the Methodology section. After signal integration, the iodine and oxirane indexes were estimated and summarized in Table 4.

For the millireactor experiments, the results of the iodine index, oxirane index, double bond conversion, and epoxy yield were summarized in Fig. 5 as a function of the bath temperature, considering different mean residence times.

Amongst the analyzed conditions in the millireactor, the most satisfactory results were obtained in the temperature of 60 °C and mean residence time of 2400 s (40 min): iodine index equals to 58.64 g I_2/100 g and oxirane index of 3.73 g O/100 g. The minimum iodine index obtained in this condition represents the highest consumption of double bonds of soybean oil, i.e., the maximum conversions achieved. The maximum oxirane index is associated with the highest generation of oxirane groups, leading to the maximum yield achieved.

These results may differ from our parallel computational study [31], in which an iodine index of 9.16 g I_2/100 g and an oxirane index of 6.62 g O/100 g were estimated for a 2-hour residence time. However, the computational study did not include some effects observed experimentally, such as droplet coalescence and intense bubble generation that will be deeply discussed below.

Table 4
Results of iodine index (*II*), oxirane index (*OI*), double bond conversion (*X*), and epoxy yield (*Y*) for the millireactor and microreactor experiments for different temperatures (T_b) and mean residence times (τ).

Experiment	T_b / °C	τ / s	*II* / (g I_2/100 g)	*OI* / (g O/100 g)	*X* / %	*Y* / %
ML01	40	720	119.26	0.09	4.9	1.3
ML02	60	720	120.54	0.10	3.9	1.4
ML03	80	720	120.29	0.11	4.1	1.5
ML04	40	2400	59.67	3.66	52.4	50.0
ML05	60	2400	58.64	3.73	53.2	50.9
ML06	80	2400	79.11	2.48	36.9	33.8
ML07	40	7200	116.72	0.28	6.9	3.8
ML08	60	7200	117.60	0.22	6.2	3.0
ML09	80	7200	119.49	0.13	4.7	1.8
MC01	40	480	72.86	2.74	41.9	37.4
MC02	60	480	56.00	3.82	55.3	52.1
MC03	70	480	47.58	4.28	62.1	58.4
MC04	80	480	54.86	3.86	56.3	52.7
MC05	60	720	63.43	3.44	49.4	46.9
MC06	70	720	19.77	5.67	84.2	77.4
MC07	80	720	39.20	4.73	68.7	64.6
MC08	40	960	38.02	4.79	69.7	65.3
MC09	60	960	33.87	5.01	73.0	68.4
MC10	70	960	64.24	3.46	48.8	47.3
MC11	80	960	44.76	4.47	64.3	61.0
MC12	40	1200	68.97	3.07	45.0	42.0
MC13	60	1200	59.04	3.70	52.9	50.4
MC14	80	1200	65.57	3.29	47.7	44.9

At lower temperatures (40 °C), less consumption of double bonds would be expected, compared to higher temperatures (60 °C, for example), since the increase in temperature tends to make reactions faster. This should be evidenced by a higher iodine index when the experiment is conducted at 40 °C than at 60 °C. Nevertheless, a significant difference in these values for both temperatures cannot be observed. A possible reason derives from the absence of droplet stabilizers, i.e., substances that tend to stabilize the aqueous phase droplets. Despite their generation, the droplets tended to coalesce in all experiments.

Although the literature provides studies on the droplet coalescence topic, several variables could impact the performance of a liquid-liquid reaction system affected by droplet coalescence. Despite a deeper study can still be performed for the epoxidation of soybean oil, an interesting example in the literature is the sulfonation of naphthalene [34].

The tendency of droplet coalescence can be checked by the capillary number, a dimensionless number that relates viscous forces and surface tension forces. According to Shayunusov et al. [35], capillary numbers below 0.5 may lead to the tendency of droplet coalescence. Considering the flow rates employed here jointly with viscosity and surface tension data previously described [22,36–38], the capillary number for the experiments here remained below 0.03.

Several reasons can affect droplet coalescence, such as the viscosity of the continuous phase and the flow velocity. Meng et al. [39] verified that high viscosities of the continuous phase tend to hinder the coalescence of dispersed phase droplets; therefore, the reduction in the continuous phase viscosity tends to favor the droplet coalescence. In the present study, the organic phase viscosity decreases with the increase in temperature [38], which could facilitate the droplet coalescence and hence, reduce the interfacial area, limiting the reaction by mass transfer effects and hindering the growth in consumption of double bonds. The study of Mohammadi et al. [40] also corroborates this, showing that higher viscosities of the continuous phase increase the time for the droplets to coalesce.

The low oxirane indexes and high iodine indexes related to the mean residence time of 720 s may be explained by the following: a relatively small mean residence time may imply in low consumption of reactants, i.e., the reaction system does not stay in the reactor enough time to achieve high conversions. Conversely, by this logic, the mean residence time of 7200 s should have led to higher consumption of double bonds (lower iodine indexes), but the results were very similar to the ones achieved at 720 s. Once more, a possible explanation derives from the droplet coalescence observed experimentally. Although higher flow velocities (lower mean residence times) tend to decrease the time for droplets to coalesce [40], the coalesced droplets tend to remain more time in the reactor for lower flow velocities (higher flow residence times), contributing to the decrease in the double bond conversion [34].

Still, another greater phenomenon should explain why almost zero conversion (and, consequently, nearly zero yield) was achieved at 80 °C. At this temperature, there was the additional observation of bubbles inside the millireactor. The presence of bubbles could be associated with the decomposition of unstable reactants, such as hydrogen peroxide and performic acid, into gases. However, the hydrogen peroxide decomposition should not be expected intensively under the proposed reaction conditions [41]. Conversely, the performic acid decomposition is expected to be considerably intensified with the increase in the temperature once this reaction presents a high activation energy [22,42]. However, independently of the reaction that generated the gases, it involves reactants that affect the reaction system. Therefore, the epoxidation may have been disadvantaged since this intermediate was probably consumed by an undesired route at higher temperatures.

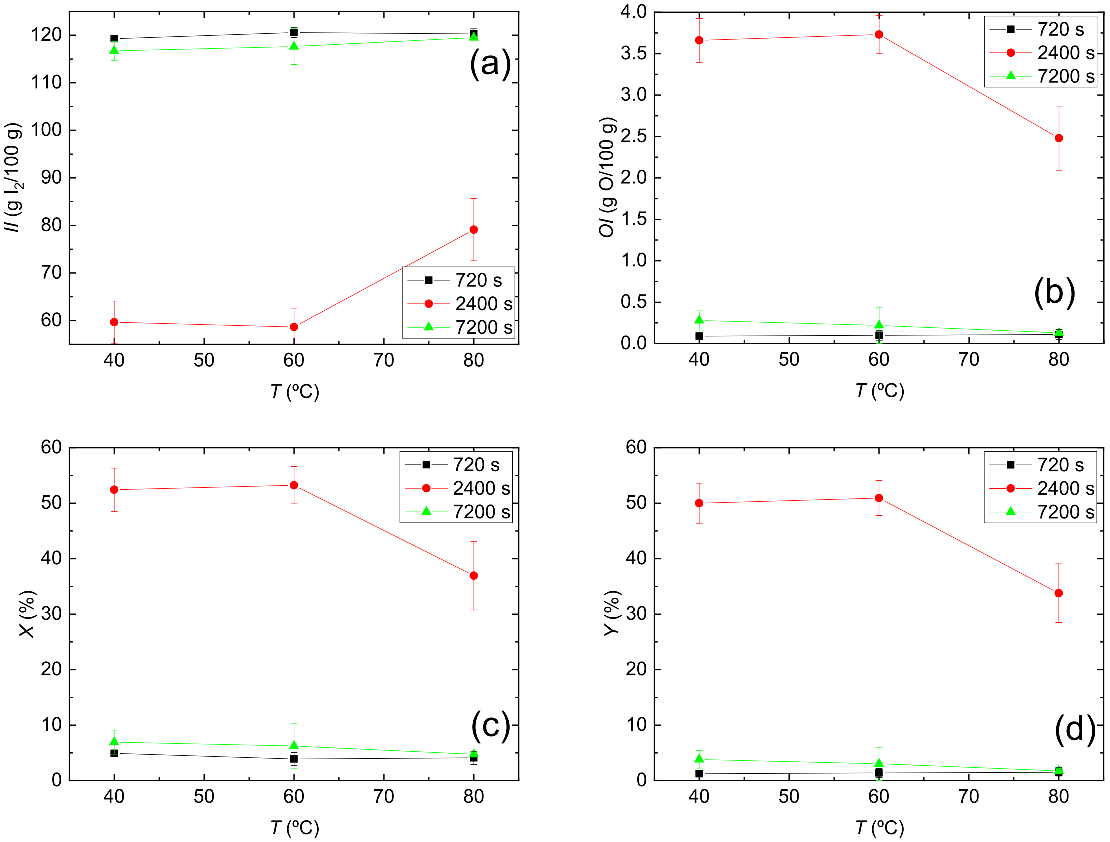

Fig. 5. Results for the millireactor experiments, as a function of the bath temperature (T_b) and for different mean residence times (τ): (a) iodine index (*II*); (b) oxirane index (*OI*); (c) double bond conversion (*X*); (d) epoxy yield (*Y*).

Moreover, the gas generation implied that part of the reactor was not fulfilled with the liquid reaction media, decreasing the mean residence time. This led to a higher iodine index and a lower oxirane index.

Differences in the double bond conversion and epoxy yield are also expected since the undesired ring-opening reactions of the oxirane group inherently tend to occur. Although using formic acid in this reaction system could favor these reactions, the absence of catalysts reduces this effect [43].

The results of the microreactor experiments were also expressed graphically: Fig. 6 presents the results of iodine index, oxirane index, double bond conversion, and epoxy yield as a function of the bath temperature, considering different mean residence times.

The microreactor experiments resulted in more promising values for the indexes that characterize ESO than the millireactor. Despite observing irregularities and droplet coalescence in the microreactor, the relatively high oxirane index values and low iodine index values corroborate the idea that very reduced dimensions for the reactor significantly intensify the reactions. This also stresses how the reaction system strongly depends on mass transfer effects, whose limitation reduces when employing ways to increase the interfacial area. The raised points may be exemplified by comparing the results of the system in the same conditions in the millireactor (ML02 and ML03) and in the microreactor (MC05 and MC07): the lower iodine indexes and higher oxirane indexes achieved in the microreactor evidence the reaction occurs much more intensively in this equipment.

The highest value for the oxirane index (5.67 g O/100 g) and the lowest iodine index value (19.77 g I_2/100 g) were achieved at MC06, i.e., temperature of 70 °C and mean residence time of 720 s (12 min). This represents a much inferior reaction time compared with the typical 8 to 12 hours employed industrially.

Moreover, there was a similar tendency of the microreactor results with the millireactor: in the absence of a droplet stabilizer in the reaction system, an optimum operation point was observed for the indexes as a function of both temperature and mean residence time. To summarize the discussion initiated in the millireactor results, in the case of the temperature, there is a “balance” between the following conflicting phenomena concerning the beneficiation of the reaction: the increase in temperature elevates the main reactions rates, but may also intensify the decomposition of performic acid and may favor the droplet coalescence. For mean residence time, the following “balance” was inferred: the increase in mean residence time tended to intensify the consumption of the reactants but also diminished the flow velocity and tended to favor the droplet coalescence.

However, there could remain a question of why the epoxidation reaction was much disfavored in the millireactor compared to the microreactor. In the present study, the epoxidation reaction and the performic acid decomposition are very exothermic, which was a concern in previous studies to avoid thermal runaway in other reactors [2,22,36,44]. The study of Russo et al. [45] compared, amongst other values, the effect of the pipe radius in micro-scale reactors for the ethoxylation of 1-dodecanol. In their study, the conversion gradient is flatter when the reactor radius decreases, and one factor that could contribute to that is the heat transfer. When the reactor radius is smaller, the heat transfer is expected to be more efficient. Considering these scenarios, it is possible that the heat transfer was more efficient in the microreactor than in the millireactor. This may have intensified the presence of hot spots at higher temperatures in the millireactor, favoring the performic acid decomposition. These effects were probably minimized in the microreactor due to the smaller radius.

Despite that, it is important to emphasize the inherent security of adopting micro- and millireactors, not only to enhance mass transfer effects but also to intensify the heat transfer effects [11]. This tends to reduce the probability of thermal runaway problems, frequent in higher dimension reactors with inefficient heat exchange [2,22,36].

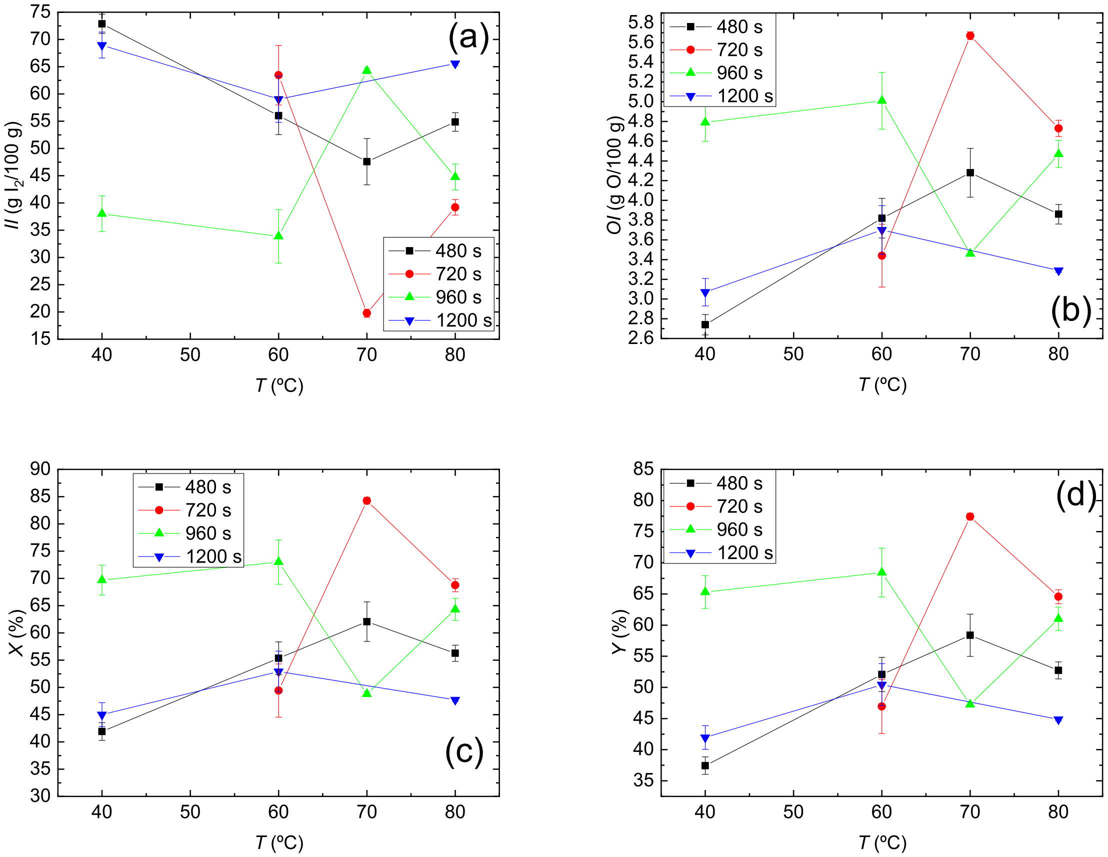

Fig. 6. Results for the microreactor experiments, as a function of the temperature (*T*) and for different mean residence times (τ): (a) iodine index (*II*); (b) oxirane index (*OI*); (c) double bond conversion (*X*); (d) epoxy yield (*Y*).

4. Conclusion

The present study evaluated the conduction of the biphasic reaction system for the epoxidation of soybean oil, considering two equipment: a millireactor and a microreactor. The temperature and mean residence time effects were analyzed for both reactors. The generated epoxidized soybean oil (ESO) was analyzed by spectroscopy of nuclear magnetic resonance of hydrogen (^{1}H-NMR). In both equipment, the droplet coalescence of the disperse phase was observed, reducing the interfacial area and limiting the mass transfer effects in the reaction system. Although explanations were proposed for the droplet coalescence related to temperature and flow velocity effects, based on the literature, a deeper investigation is suggested to optimize the conditions to enhance the process. In addition, the performic acid decomposition may have been favored at higher temperatures due to the experimental observation of bubbles, especially in the millireactor. These factors led to minimum and maximum points in the respective curves of iodine and oxirane indexes for the ESO as a function of the temperature. The millireactor's lowest iodine index of 58.64 g I_2/100 g and the highest oxirane index of 3.73 g O/100 g were achieved at 60 °C and a mean residence time of 2400 s. The microreactor led to more promising results: at the temperature of 70 °C and mean residence time of 720 s, the iodine index was 19.77 g I_2/100 g, and the oxirane index was 5.67 g O/100 g. The results emphasize the advantages of opting for reactors with reduced dimensions, leading to significantly lower reaction times than the applied industrially, with the intensification of heat transfer effects.

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.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cep.2023.109562.

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