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Synthesis of carbonated vegetable oils: investigation of microwave effect in a pressurized continuous-flow recycle batch reactor

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Abstract:

With the depletion of fossil resources, it is essential for the chemical industry to find alternative raw materials for polymers. Polyurethanes can be synthesized from vegetable oils and CO₂ via an environmentally friendly, non-isocyanate pathway. Carbonation of epoxidized vegetable oil is a key step allowing the feasibility of this method. Because it requires a high temperature, high pressure and long reaction time to achieve complete conversion, microwave technology (MW) is an interesting approach for the intensification of the carbonation process. However, MW-irradiated batch reactor has multiple issues regarding scale-up. A microwave irradiated continuous-flow recycle batch reactor which can operate at high temperature (130°C) and moderate pressure (8 bar) was used in the present work. The effect of microwave irradiation on the kinetics of carbonation reaction was studied. A kinetic model was developed to compare quantitatively the performance under microwave and conventional heating (CH). It was found that the activation energy

of the carbonation reaction was slightly lower with the use of MW irradiation, where the values for CH and MW are respectively $0.385\text{E}+04$ J/mol and $0.376\text{E}+04$ J/mol.

Keywords: Vegetable oil; Process intensification; Microwave; Carbonation; Recycle batch reactor

1. Introduction

One of the major problems that humanity is facing is the depletion of petroleum-based resources, which affects not only the global energy supply, but also the availability of raw materials for the chemical industry. The search for alternatives for petroleum-derivates receives increasing attention, and vegetable oils (VOs) are excellent candidates for the production of chemicals and biofuels (Ma and Hanna, 1999; Rosillo-Calle et al., 2009).

The utilization of vegetable oils possesses numerous advantages, because they are nontoxic, readily available, potentially bio-degradable and can be easily functionalized (Petrovic, 2008; Wagner et al., 2001). Transesterified vegetable oils are used as biofuels, and modified VOs, such as epoxidized soybean oil, has found application as PVC additives, biolubricants, etc. (Adhvaryu and Erhan, 2002; Baltacioğlu and Balköse, 1999; Schuchardt et al., 1998). The industrial consumption of VO represents approximately 22% of the total consumption in 2015 (United States Department of Agriculture, 2016).

Synthesis of polymers from VOs has always been an interesting topic. Oils containing large amounts of double bounds such as linseed oil can be hardened under oxygen by crosslinking, and therefore, they have been used as ingredients of paints for hundreds of years. Various polymers from VOs have been developed in recent years, such as polyester (PE), polyurethane (PU), polyolefin (PO), etc. (Kolanthai et al., 2015; Miao et al., 2014; Petrovic, 2008; Tallman et al., 2004). Currently, the usage of highly toxic isocyanates has been essential in the production of PUs. In 2004, it was shown by Tamami et al. (Tamami

et al., 2004), that polyurethanes can be synthesized using vegetable oils and CO₂ as raw materials via a non-isocyanate route (NIPUs). Combining chemicals from renewable sources, this synthetic pathway would allow a lucrative fixation of CO₂, the main greenhouse gas, to a solid form.

CO₂ can be used as a raw material for the construction of more complex molecules, potentially replacing their petrochemical counterparts (Das Neves Gomes et al., 2012). The global usage of CO₂ in the chemical industry mainly consists of the production of urea via the Bosch-Meiser process (Bosch and Meiser, 1922), the production of various inorganic carbonates, methanol, etc.. Compared with geological sequestration, the valorization of CO₂ adds value to the gas, and is much more mature in terms of volume (200 Mt/y for usage compared with 4-5 Mt/y for storage) (Aresta et al., 2013). With the development of CO₂ capture and utilization technology (CCU), it is preferable to develop products with a longer lifespan, such as polymers (Cuéllar-Franca and Azapagic, 2015).

The pathway proposed for the synthesis of NIPUs generally consists of four steps: epoxidation of vegetable oils, carbonation, synthesis of monomers and polymerization. The epoxydation reaction has been studied extensively, whereas the carbonation step is less studied, especially with large molecules such as vegetable oils. Tetra-butylammonium bromide (TBAB) has been used as catalyst in most studies, and high temperature and high CO₂ pressure was required to obtain a complete conversion in a reasonable amount of time (Miloslavskiy et al., 2014). The thermal stability of epoxidized and carbonated vegetable oils has been demonstrated to be safe (Ait Aissa et al., 2016).

Several investigations have been devoted to improve the reaction both in terms of catalysis by using various co-catalysts or by using heterogeneous catalysts (Alves et al., 2015; Bähr and Mülhaupt, 2012; Jalilian et al., 2010; Li et al., 2008; Parzuchowski et al.,

2006; Wang et al., 2012). In terms of process intensification, the effect of supercritical CO₂ and microwave heating has been investigated and shown promising results (Doll and Erhan, 2005; Foltran et al., 2012, p. 2; Mazo and Rios, 2012). It has been observed that compared to conventional heating (CH), microwave heating (MW) has a significant impact on reaction the kinetics of the carbonation. The time to reach 95% conversion was shortened from 70h to 25h using an ETHOS MW digester (Mazo and Rios, 2012). Indeed, it has been shown that the use of MW heating could be beneficial in the valorization of vegetable oils, for example, epoxidation of VOs (Aguilera et al., 2016), (Leveneur et al., 2014) and production of biodiesel via transesterification (Liao and Chung, 2011). On the other hand, MW could also lead to improvements in the synthesis of short-chain five-membered organic carbonates (Dharman et al., 2010; Ono et al., 2007; Tharun et al., 2013).

However, batch MW reactor setups cannot be easily scaled up for industrial production due to the limitation in the microwave penetration depth and electromagnetic field homogeneity issues. A solution proposed is to use continuous-flow or stop-flow reactors, where the MW irradiation is applied over a small cylinder as the products flow pass (Glasnov and Kappe, 2007; Saillard et al., 1995).

In this work, a microwave-assisted continuous-flow recycle reactor was designed for the carbonation of epoxidized vegetable oil (i.e. at elevated temperature and under pressure), with single mode resonance system which ensures a high-intensity MW irradiation. The effect of microwave over the carbonation reaction was investigated with controlled temperature, pressure and MW power. The oil was transformed into its methyl ester form to take advantage of its low viscosity, thus keeping a high flowrate to prevent overheating.

The general reaction pathway is illustrated in Fig. 1.

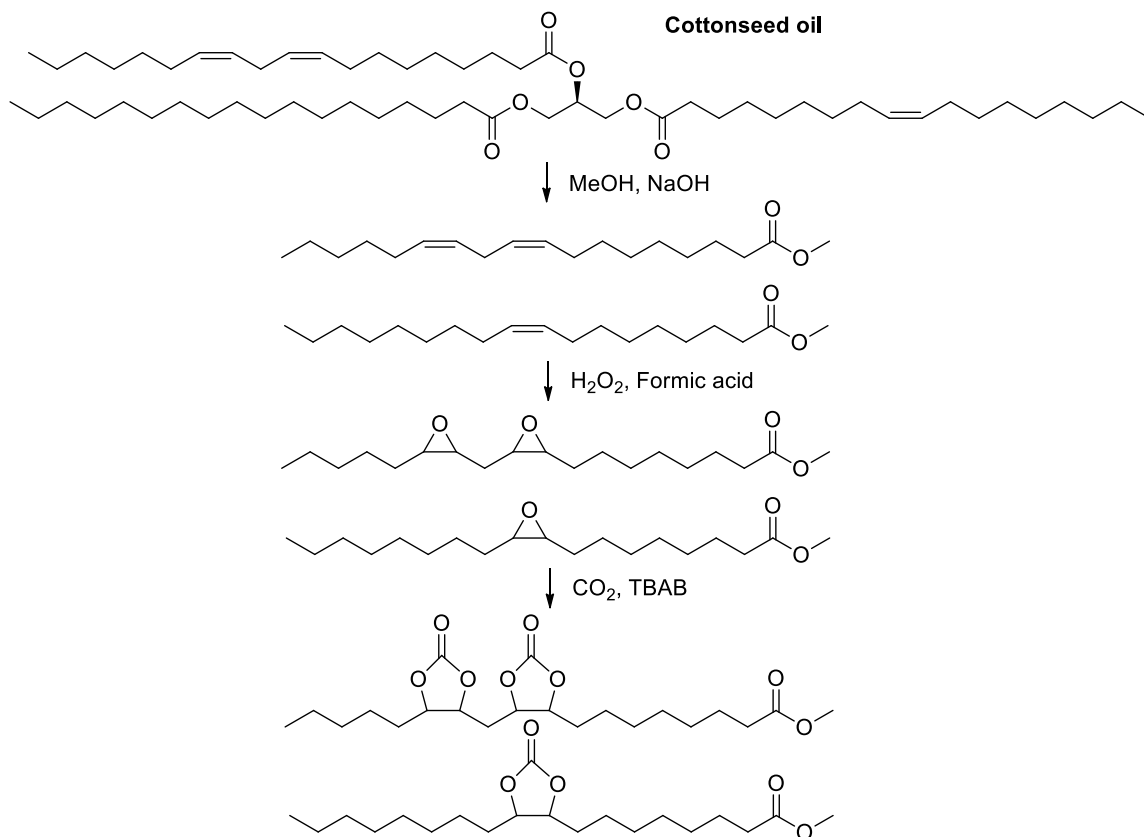


Fig. 1. Synthesis of carbonated cottonseed oil methyl ester

2. Experimental section

2.1. Materials

Cottonseed oil, formic acid (>95 %), methanol (99.8 %), sodium hydroxide (98%), Amberlite® IR120 hydrogen form, perchloric acid 0.1 M in glacial acetic acid, chloroform (>99 %), tetrabutylammonium bromide (>99%) were purchased from Sigma-Aldrich Co. Hydrogen peroxide (30 wt% in water) was purchased from Merck Co.. All chemicals were used directly without further modification.

2.2. Apparatus and experimental procedures

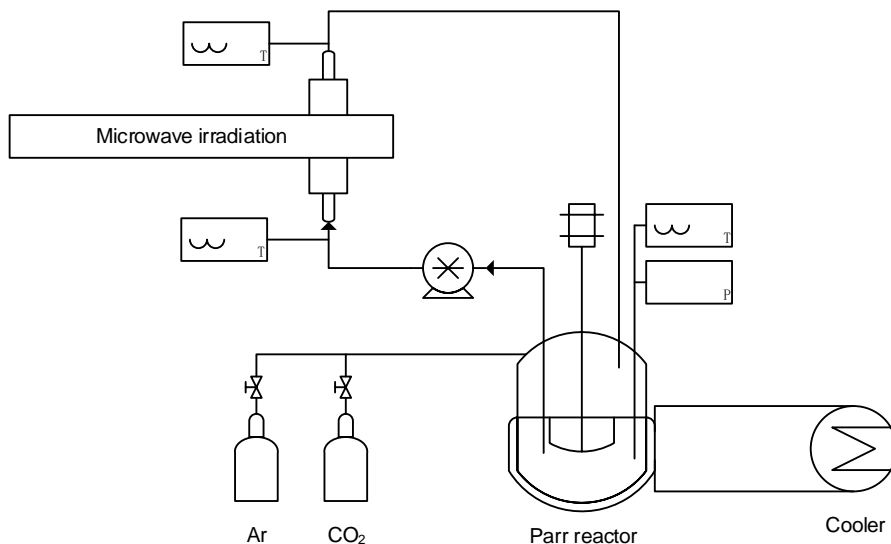


Fig. 2. Reactor setup

The carbonation reaction was carried out in a continuous-flow recycle microwave-assisted reactor similar to the one used previously by our group (Aguilera et al., 2016). A MW-generator with magnetron operating at 2450 ± 25 MHz has been used and the power output was 0 – 1950 W, with a WR 340 motorized waveguide. An automatic impedance turner was used to ensure impedance matching.

The experimental setup is shown on Fig. 2. A 300-mL stainless steel Parr reactor was used to hold the reaction mixture, where it could be heated or cooled by installing external devices. For heating purposes, a resistance heater was used; for cooling purposes, a copper coil with a water / glycerol mixture circulating at -10°C was wrapped around the Parr reactor.

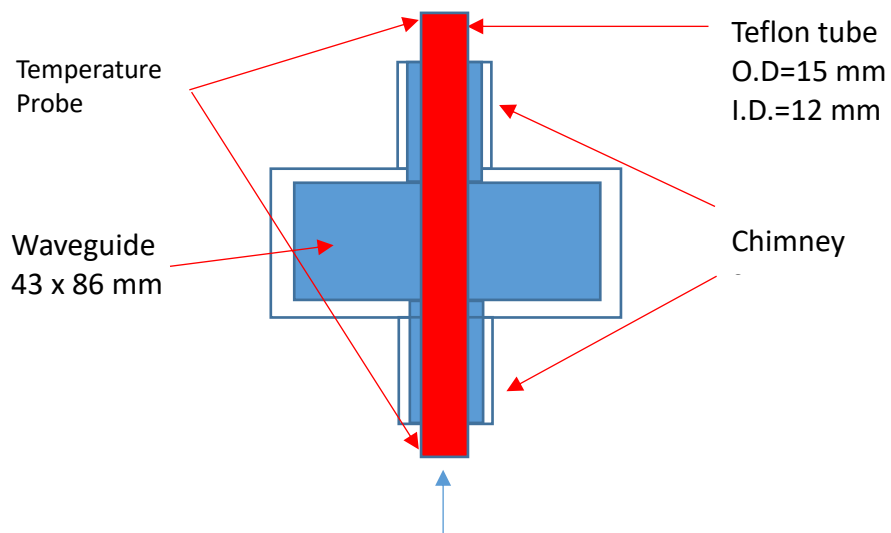


Fig. 3. The microwave chimneys

The reaction mixture was pumped through a Teflon tube with the help of a gear pump, where microwave irradiation was applied. The Teflon tube had an outer diameter of 15 mm and an inner diameter of 12 mm and the overall length of the tube was 295 mm. It is only through the Teflon tube the MW could pass. The Teflon tube was inserted through the waveguide which cross section is of rectangular shape of 43 mm x 86 mm (Fig. 3). The Teflon tube was connected by stainless steel tubes with the pump and the reactor to ensure air tightness.

The temperature in the Parr reactor, before the point of MW irradiation and as well as immediately after MW irradiation was monitored. The pressure in the system was controlled using the pressure regulator connected to the gas bottle. The temperature in the reactor was controlled by adjusting the power of the microwave source. A gas entrainment impeller (diameter 2.5 cm) with a hollow shaft was used and a baffle were installed in the Parr reactor to increase gas-liquid mass transfer efficiency.

2.2.1 Carbonation reaction

Approximately 150g of epoxidized cottonseed oil methyl ester (ECSO ME) and desired amount of catalyst were introduced into the autoclave, and the system was purged with argon to evacuate air. The reaction mixture was heated by microwave while adjusting the MW power until the temperature in the Parr reactor was stabilized at the desired value. Continuous stirring was applied and a pumping rate of 8 mL/s was maintained. Stirring was then stopped and the system was purged with CO₂. The reaction was assumed to begin when the agitation was restored. Samples were withdrawn at different time intervals during the course of reaction and the epoxide concentration was analyzed by titration using Jay's method (Maerker, 1965). Comparative experiments with conventional heating was performed within the Parr reactor alone (without recycle flow) using the resistance heater.

Table 1 shows the experimental matrix.

Table 1. Experimental matrix

Run	Microwave	Temperature (°C)	Temperature in the MW cavity (°C)	Pressure (bar)	wt% TBAB	Stirring speed (rpm)	Net absorbed MW power (W)	Conversion after 7h (%)
1	no	120	--	6	4	950	--	49
2	yes	120		6	4	950	80	52
3	yes	120		6	4	950	120	51
4	yes	120		6	4	950	300	46
5	no	120	--	6	5.5	950	--	62
6	yes	120		6	5.5	950	250	63
7	no	120	--	6	8	950	--	73
8	yes	120		6	8	950	230	73
9	no	120	--	6	5.5	1200	--	62
10	yes	120		6	5.5	1200	300	64
11	no	120	--	6	5.5	500	--	61
12	yes	120		6	5.5	500	260	63
13	no	120	--	2.5	4	950	--	31
14	yes	120		2.5	4	950	230	30
15	no	100	--	6	5.5	500	--	34
16	yes	100		6	5.5	500	180	37

2.2.2 Synthesis of cottonseed oil methyl ester

For the transesterification of cottonseed oil, the method described by Campanella et al. (Campanella et al., 2008) was followed. 700 mL of cottonseed oil and 270 mL of methanol were stabilized at 70°C under agitation in a 1L glass jacketed reactor equipped with a reflux condenser. Around 8.2g of sodium hydroxide was added and the reaction was carried out for 1 hour. The agitation was stopped, allowing the two phases to separate. The heavier fraction was discarded, and the lighter fraction was firstly washed once with 100 mL of 0.015M phosphoric acid solution, then 3 times with 300 mL of water. Residual water in the organic phase was removed using a rotary evaporator.

2.2.3 Epoxidation of cottonseed oil methyl ester

Around 180g of CSO FAME, 200g of 30 wt.% hydrogen peroxide solution and 20g of Amberlite 120 was stabilized at 55°C under agitation in a 1L glass jacketed reactor. Formic acid was added via a peristaltic pump at the rate of 2.2 mL/min for 25 minutes. After the end of addition, the reaction was carried out for another 65 minutes and the stirring was stopped to allow the two phases to separate. The aqueous phase and the catalyst were removed, and the organic phase was washed four times with 300 mL of water. The product was dried using a rotary evaporator and stored under argon. The final product had a conversion exceeding 95% and selectivity 85% toward epoxide groups.

3. Result and discussions

3.1 Investigation of microwave effect

The effect of microwave heating was investigated under different MW powers, and at different stirring velocities, temperature, pressure and catalyst loading, with respect to conventional heating under similar conditions.

Fig. 4 has shown the temperature profile measured experiment N°4. The reactional mixture was cooled down by about 5 °C before entering the MW chimney, and heated up about 15 °C by microwave.

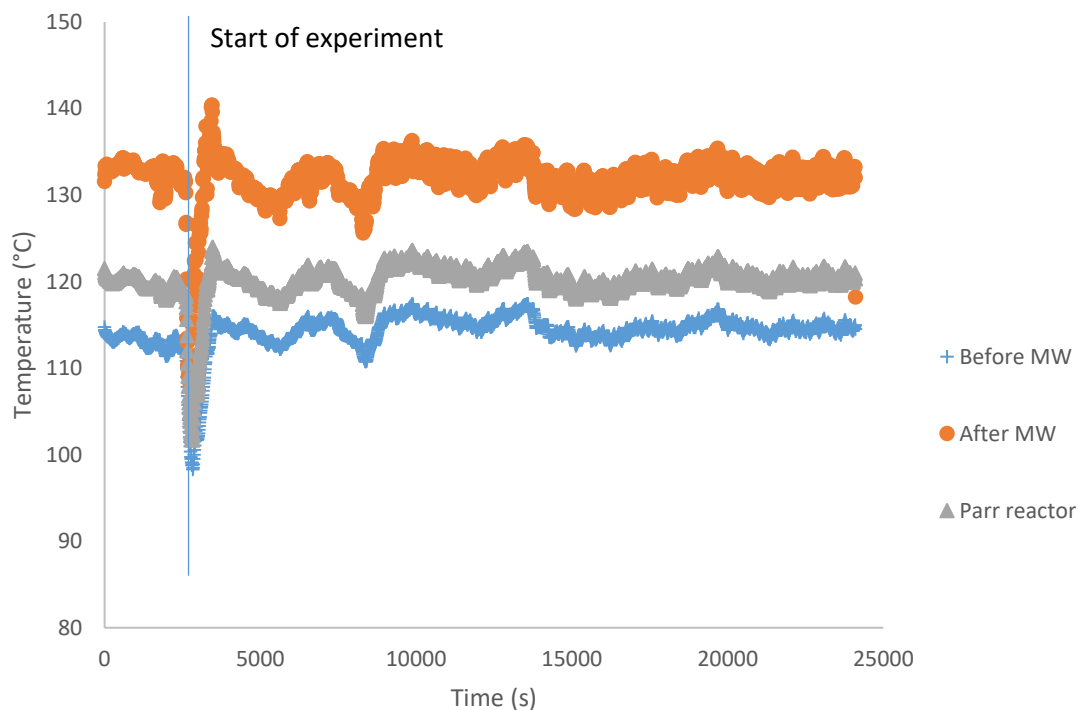


Fig. 4. Temperature profile for run N°4.

In the Teflon tube, a cylindric part with a diameter of 12 mm and length of 43 mm was directly irradiated by microwave at the cross section with the waveguide. However, it is

difficult to determine the exact irradiated volume, since that MW could pass into the chimney. For the sake simplicity, we have considered that the cavity inside the Teflon tube starting from the lower point of cross section with the waveguide, to the top where the Teflon tube was connected to steel tube, to be overheated by MW with temperature measured by the thermocouple (Fig. 5). The measured temperature was 5-10 °C higher than the Parr reactor depending on the condition, and the corresponding volume was 19.1 mL. The temperature within the connecting steel tubes was not considered due to their low volume. The measured process temperature was used in the modeling step, which is discussed below.

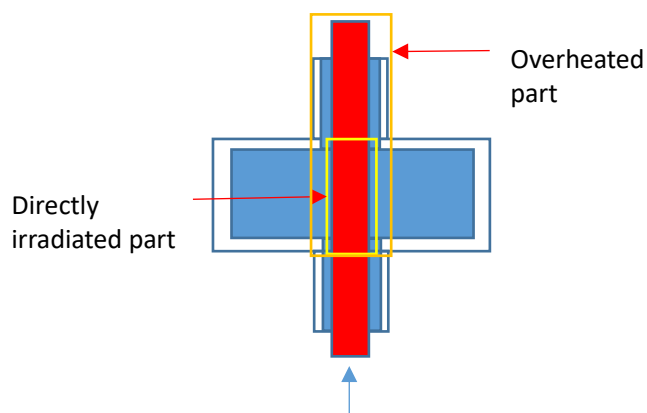


Fig. 5. The directly irradiated volume and the volume which is overheated by MW.

First of all, the influence of stirring speed was investigated for both CH and MW reactions in order to determine the mass transfer limitation for the system.

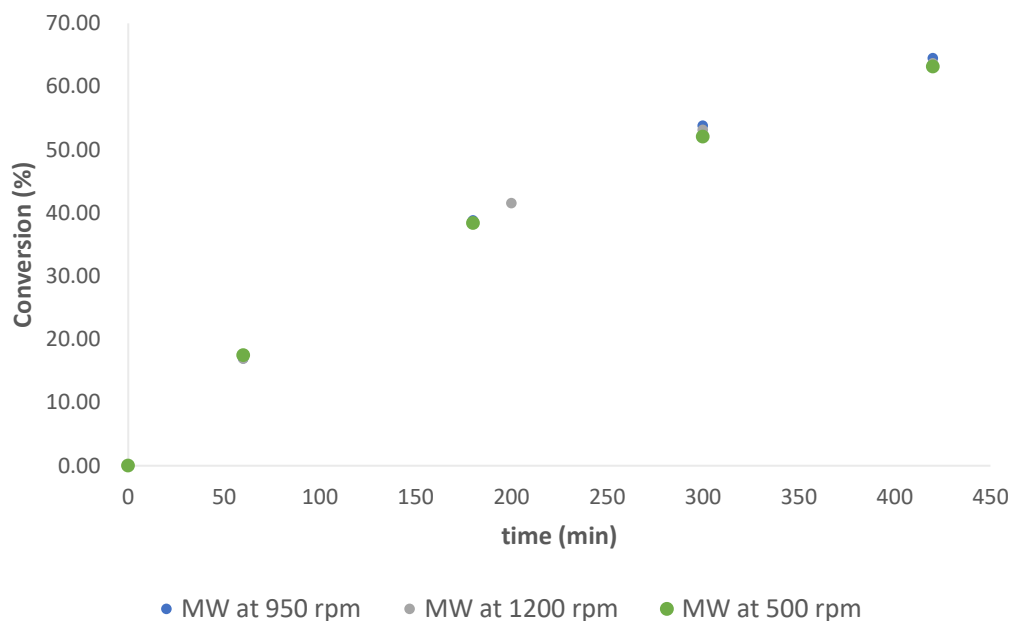


Fig. 6. Comparison of epoxide conversion rate under different stirring speed with microwave heating. Conditions: 120°C, 6 bars, 5.4 wt% TBAB.

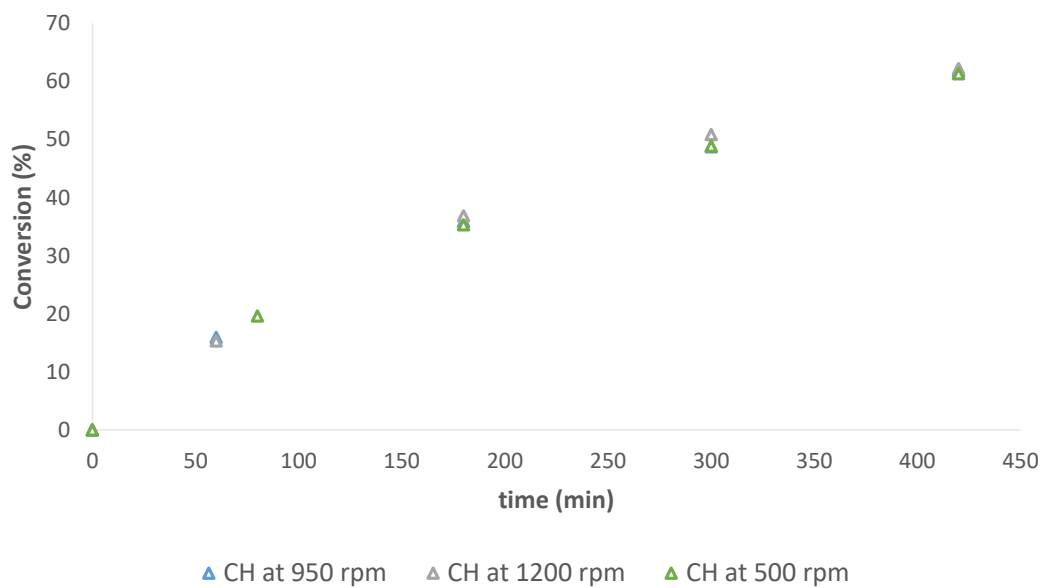


Fig. 7. Comparison of epoxide conversion rate under different stirring speed with conventional heating. Conditions: 120°C, 6 bars, 5.4 wt% TBAB.

No major difference was observed in the reaction kinetics in the range of 500 – 1200 rpm as shown in Fig. 6 and 7, which lead to the conclusion that the gas-liquid mass transfer is not a limiting factor. Indeed, with the usage of a gas entrainment impeller combined with a baffle, the mass transfer is greatly improved.

By changing the power of the MW irradiation while keeping the temperature constant, it has been reported that one could possibly observe a difference in the reaction rate (Hosseini et al., 2007). This assumption was tested in the work by adjusting the cooling power on the Parr reactor. When the power of MW irradiation was fixed at 80W, an external heat source was applied to maintain the temperature. For a power of MW irradiation of 120W, the reactor was cooled by air. At a power of MW irradiation of 300W the reactor was wrapped by cooling coils with glycerol/water mixture as a cooling fluid operating at -10°C.

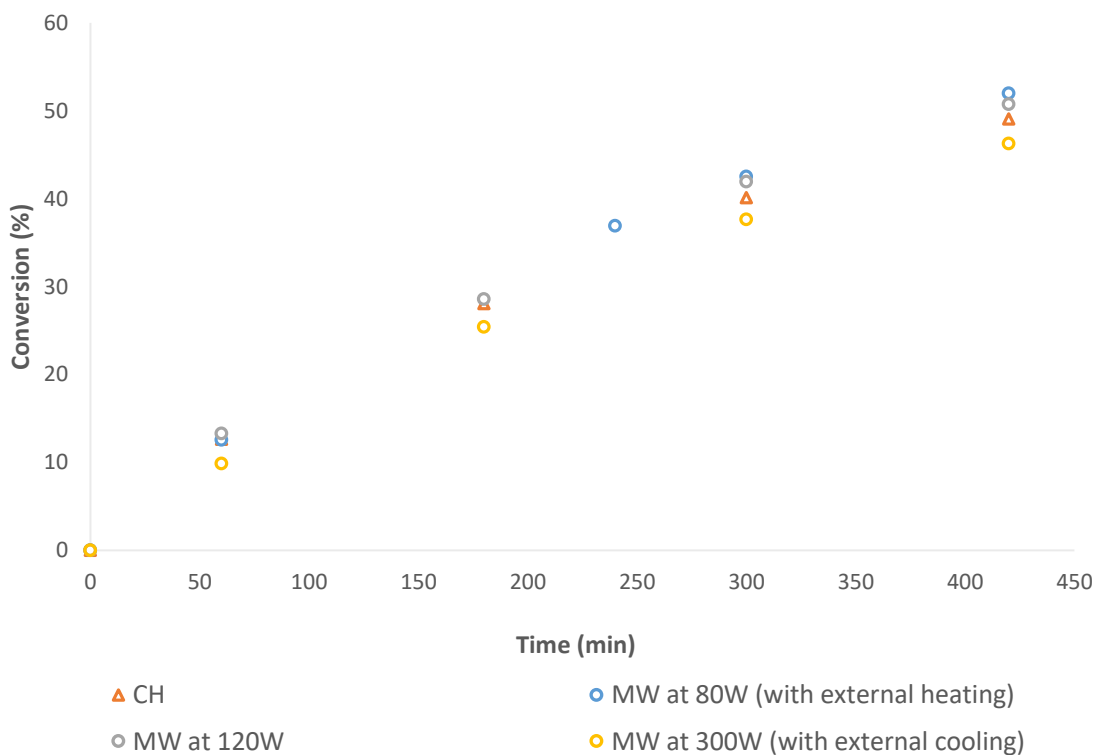


Fig. 8. Comparison of epoxide conversion rate under different microwave power.

Operating conditions: 120°C, 4 wt% TBAB, 950 rpm, 6 bars

According to Fig. 8, the increase of the MW power does not lead to a direct increase in reaction rate, while the conversion rate for all the MW experiments were slightly faster than the one with conventional heating.

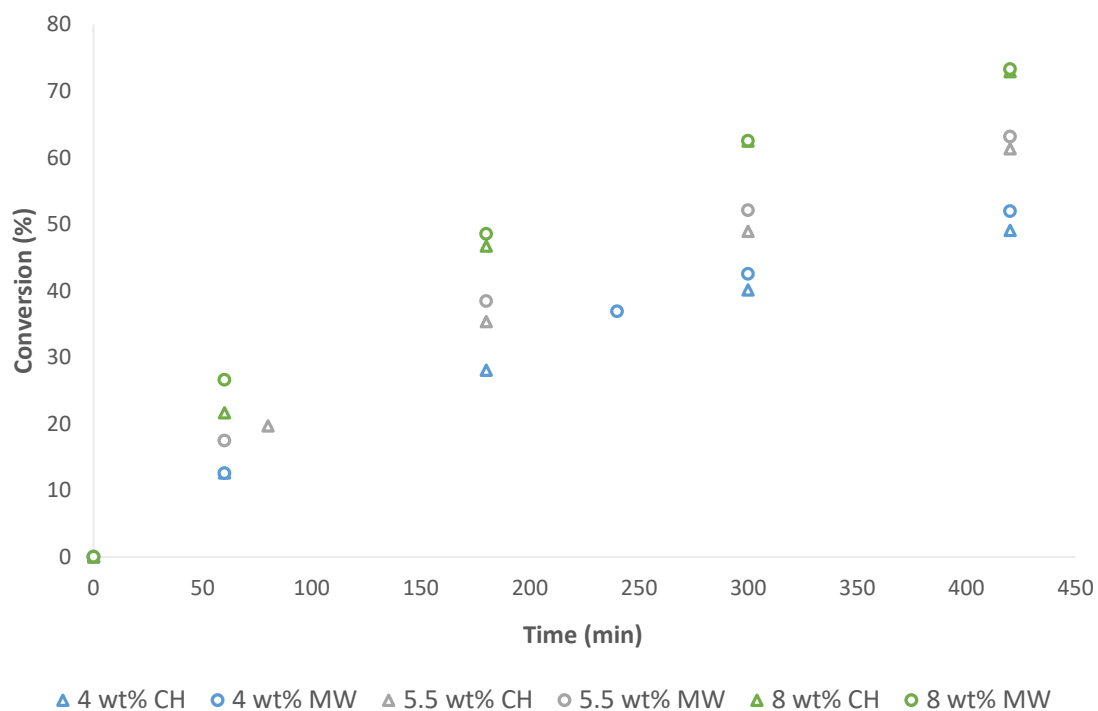


Fig. 9. Comparison of epoxide conversion rate with different catalyst loading with microwave and conventional heating. Operating conditions: 120°C, 6 bars, 950 rpm

From Fig. 9, a slight MW effect was observed with 4 wt% and 5.5 wt% of TBAB, and also in the first three hours of reaction with 8 wt% TBAB.

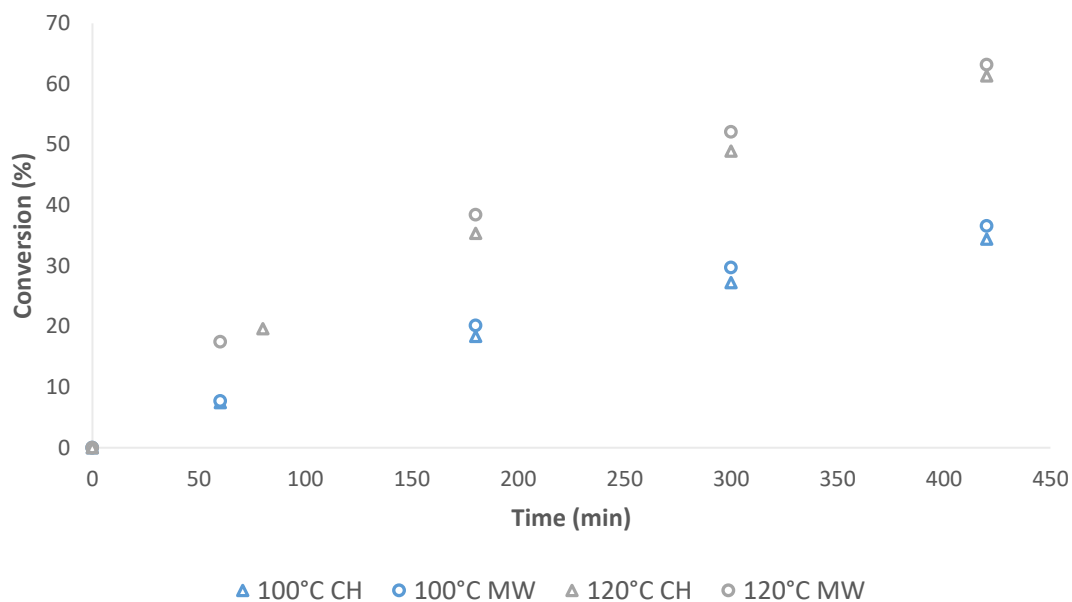


Fig. 10. Comparison of epoxide conversion rate under different temperature with microwave and conventional heating. Operating conditions: 6 bars, 5.5 wt% TBAB 950 rpm

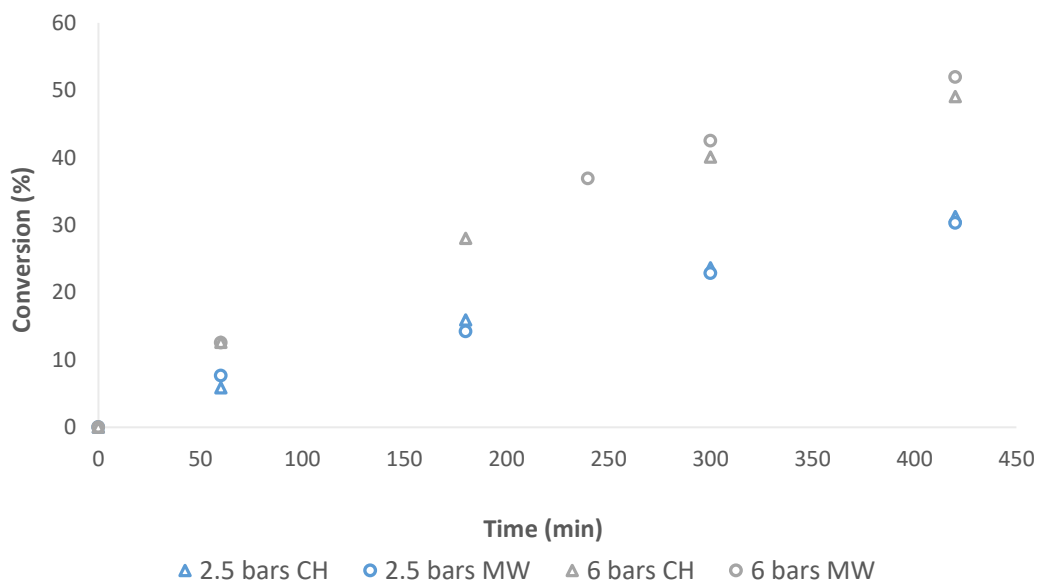


Fig. 11. Comparison of epoxide conversion rate under different pressure with microwave and conventional heating. Conditions: 120°C, 4 wt% TBAB, 950 rpm

Figs. 10 and 11 show the reaction kinetics at different temperatures and pressures. In most cases, the reaction rate under microwave heating was slightly higher than under conventional heating, except the experiment carried out at 2.5 bar, in which the MW reaction was slower.

3.2 Study of MW absorption rate of the reactional mixture

We observed that during MW experiments, the MW absorption rate of the reaction mixture increases with time and can be correlated with the conversion of the epoxy groups. As a consequence, the input MW power needs to be adjusted during the entire experiment to prevent overheating. The MW absorption rate was calculated as:

$$P_{abs} \% = \frac{P_{input} - P_{reflected}}{P_{input}} \times 100\%$$

Fig. 12 shows the linear correlation of experiments carried out under different conditions.

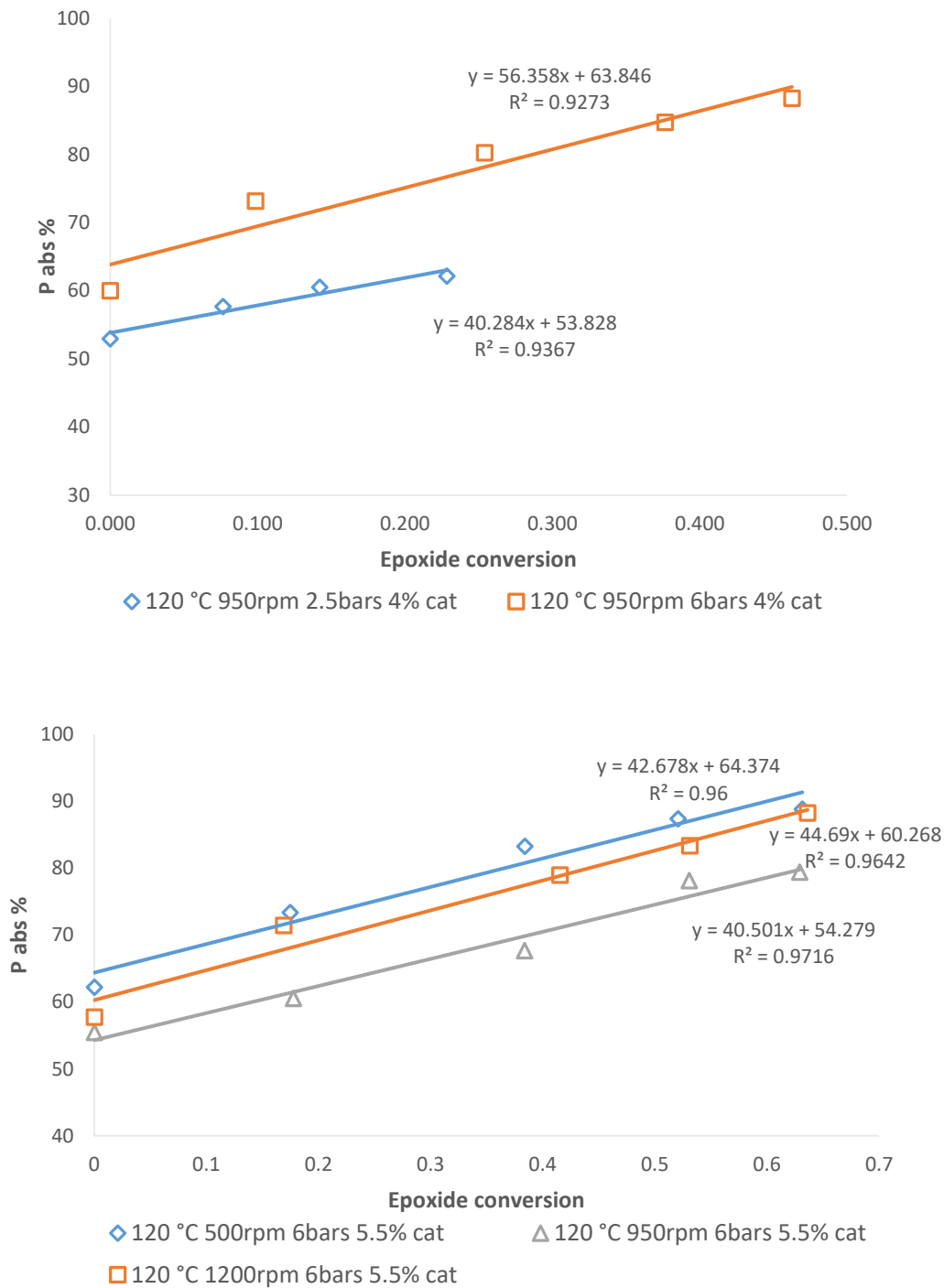


Fig. 12. Linear correlation of MW absorption rate vs epoxide conversion

The MW absorption rate depends on the polarity of the molecule, and a five-membered carbonate group is more polar than an epoxy group. In the range studied, one can assume

that the MW absorption rate depends linearly on the conversion of the epoxy groups, and the following equation can be written:

$$P_{abs} \% = a \cdot Y + b \quad (1)$$

where a and b are two constants and Y the conversion of the reaction. The linear correlation of experimental data gives:

$$a = 45 \pm 6$$

$$b = 59 \pm 4$$

where b represents the initial MW absorption rate, and $a + b$ the final absorption rate when the reaction is complete. Due to such increase in MW absorption rate, it is imperative to have proper temperature regulation systems to prevent thermal runaway.

3.3 Kinetic modeling

To have a quantitative measure of the effect of MW, the tool of modeling was introduced to have a comparison of the reaction rates under CH and MW. A semi-empirical kinetic model has been developed adopting the result from our previous works with a few simplifications (Cai et al., 2017).

The reaction rate of carbonation is expressed by eq. (2),

$$r_{Carb} = \frac{k_{Carb} \cdot [CO2]_{liq} \cdot [TBAB]^n \cdot ([EP] + \gamma [Carb])}{\alpha + \beta [CO2]_{liq}} \quad (2)$$

where n , α , β , γ are parameters describing the kinetics of the three-step reaction of vegetable oil carbonation (Cai et al., 2017). By using the values ($n=0.58$, $\alpha=0.33$, $\beta=1$,

$\gamma=0.07$) obtained from the previous work of our group, a good fitting can be obtained.

We have verified that the mass transfer efficiency is not a limiting factor in this system, thus the following simplification can be adopted to express the concentration of CO₂ in the liquid phase:

$$[CO_2]_{liq} = H_e \cdot P \quad (3)$$

where H_e is the Henry's constant of CO₂ with the reaction mixture and P is the CO₂ pressure, it was then merged with k_{carb} to simplify the equation. Eq. (2) becomes:

$$r_{Carb} = \frac{k'_{Carb} \cdot P \cdot [TBAB]^{0.58} \cdot ([EP] + 0.07 \cdot [Carb])}{0.32} \quad (4)$$

A modified Arrhenius equation was used to explain the temperature dependency:

$$k'_{Carbonation} = k'_0 e^{-E_a/R(\frac{1}{T} - \frac{1}{T_{ref}})} \quad (5)$$

where T_{ref} is the reference temperature, k'_0 is the rate constant at the reference temperature and E_a the activation energy and R is the gas constant.

Two different kinetic models have been used for CH and MW experiments. For the model with CH heating, the mass balance of the system was written as:

$$\left(\frac{d[Ep]}{dt}\right)_{CH} = -r_{Carb,CH} \quad (6)$$

$$\left(\frac{d[Carb]}{dt}\right)_{CH} = r_{Carb,CH} \quad (7)$$

For the modeling of MW experiments, due to the effect of overheating in the MW chimney, we have divided the system into two parts: the MW chimney and the Parr reactor.

$$\left(\frac{d[Ep]}{dt}\right)_{MW} = -\frac{V_{MW}\cdot r_{Carb,T1}+V_r\cdot r_{Carb,T2}}{V_{MW}+V_r} \quad (8)$$

$$\left(\frac{d[Carb]}{dt}\right)_{MW} = \frac{V_{MW}\cdot r_{Carb,T1}+V_r\cdot r_{Carb,T2}}{V_{MW}+V_r} \quad (9)$$

V_{MW} is the overheated volume in the MW chimney shown in Fig. 5 and V_r the remaining volume which is not irradiated by MW (in the Parr reactor), with the total volume of the introduced reagent $Vt = V_{MW} + V_r$. $r_{Carb, MW, T1}$ and $r_{Carb, MW, T2}$ are respectively reaction rates within the MW chimney and the Parr reactor, with $T1$ and $T2$ the temperature measured after the MW chimney and in the Parr reactor (Fig. 4). The concentration of epoxide groups was used as an observable in the parameter estimation.

The software ModEst was used to estimate k'_0 and Ea . The objective function Eq. (10) was minimized by simplex, then by Levenberg–Marquardt algorithms so that the estimation was commenced with the simplex algorithm and switched to the Levenberg–Marquardt algorithm as the minimum of the objective function was approached.

$$\omega = \sum_i \sum_t (y_{i,t} - \hat{y}_{i,t})^2 \quad (10)$$

The modeling runs were performed for MW and conventional heating, Figs. 13 and 14 show a few examples of the fitting results, and the estimated values are listed in Table 2.

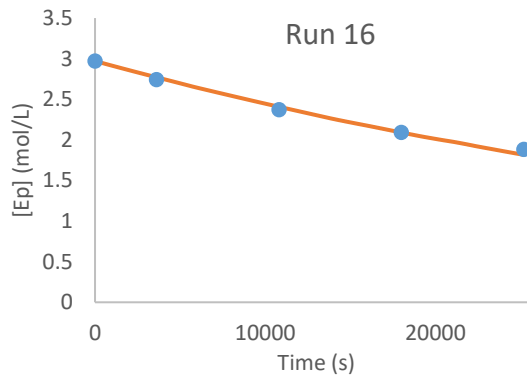
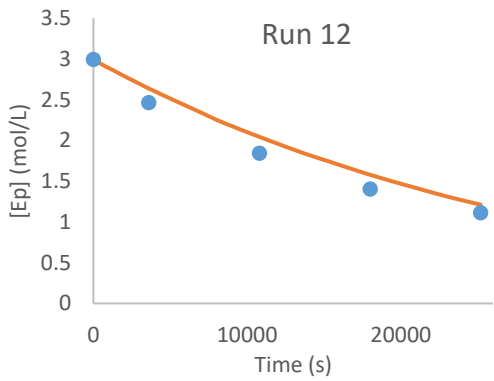
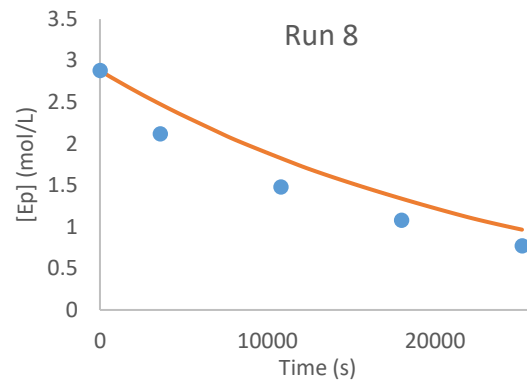
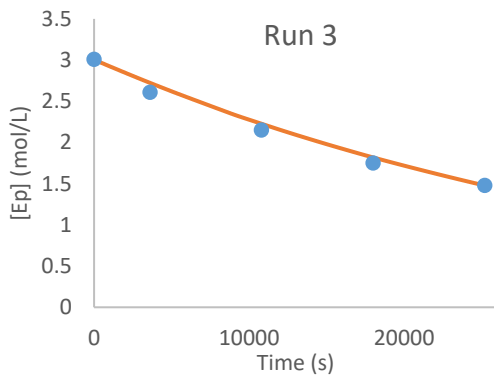
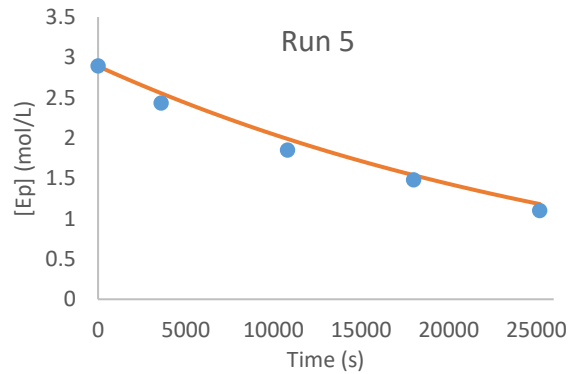
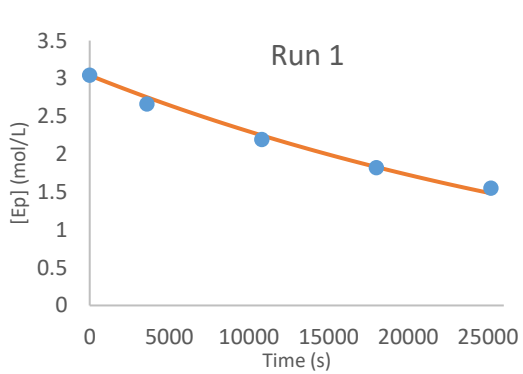


Fig. 13. Fitting result from MW experiments. Point represents experimental results, line represents model predicted values.



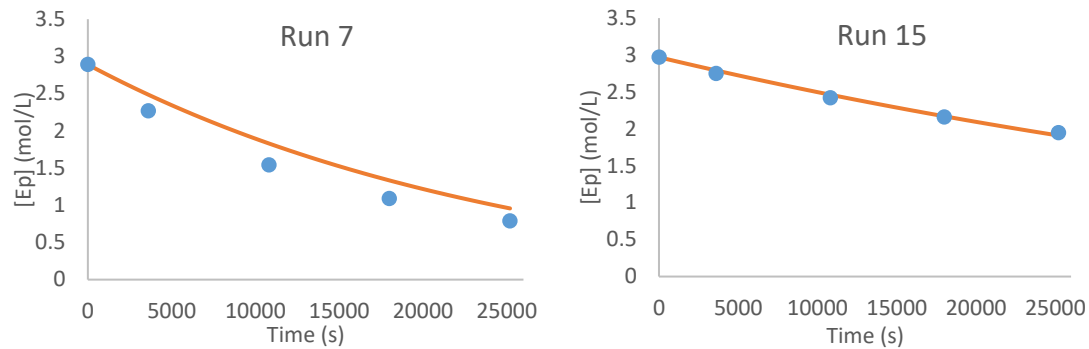


Fig. 14. Fitting result from CH experiments. Point represents experimental results, line represents model predicted values.

Table 2. Estimated value with $T_{\text{ref}} = 403 \text{ K}$

	Estimated value	Standard error	Standard error (%)
$k'_{0,\text{CH}}$ (L/mol.s)	0.141E-03	0.115E-04	8.1
$E_{a,\text{CH}}$ (J/mol)	0.417E+05	0.385E+04	9.2
$k'_{0,\text{MW}}$ (L/mol.s)	0.125E-03	0.506E-06	0.4
$E_{a,\text{MW}}$ (J/mol)	0.338E+05	0.432E+03	1.3

From the modeling results, one can notice that the activation energy for MW reactions is slightly lower than for conventional heating. Because this difference was smaller than the standard error, the result could be translated into a slight MW effect over the carbonation reaction. It should also be noticed that the E_a values were similar to the ones obtained in our previous work by using ECSO.

4. Conclusions

In this work, we have presented a continuous-flow recycle microwave reactor, which can operate under high temperature (110-130°C) and mid pressure (6 bars). The kinetics of the carbonation of epoxidized cottonseed oil methyl ester was studied under microwave heating, in the temperature range of 100 – 120°C and the pressure range of 2.5 – 6 bars, with 80 to 300 W of absorbed MW power. A linear increase in the MW absorption rate has been observed with the conversion of epoxy groups, which could lead to thermal runaway without proper control.

For a better comparison, a kinetic modeling was performed based on the previous work of our team, and the kinetic parameters were estimated for the chemical reaction under microwave and conventional heating. The modeling result showed that carbonation performed under microwave irradiation have a minor decrease in activation energy. One reason of this decrease can be the presence of a slight temperature gradient. The difference between these kinetic results and the ones obtained by Mazo et al. (Mazo and Rios, 2012) might be linked to the irradiated volume. Indeed, in the work of Mazo et al., the reaction volume was fully irradiated.

As of future, it would be interesting to discuss about its influence over the reaction kinetics, which could be beneficial for better understanding of reaction mechanism under MW, as well as process scale up.

Acknowledgments

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Nomenclature

a	Microwave absorption rate of epoxy groups
b	Microwave absorption rate of carbonate groups
c	Microwave power absorbed by ester groups and fatty acid chain
w_{ep}	Molar percentage of epoxy groups
w_{carb}	Molar percentage of carbonate groups
Y	Reaction conversion
E_a	Activation energy [kJ/mol]
k	Rate constant
k_0	Reference rate constant
H_e	Henry's constant of CO_2
ω	Objective function during estimation
$\hat{y}_{i,t}$	Model predicted value for parameter i
$y_{i,t}$	Experimental data for parameter i

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