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► **To cite this version:**

Sébastien Leveneur, Alain Ledoux, Lionel Estel, Bechara Taouk, Tapio Salmi. Epoxidation of vegetable oils under microwave irradiation. *Chemical Engineering Research and Design*, 2014, 92 (8), pp.1495-1502. 10.1016/j.cherd.2014.04.010 . hal-02328198

HAL Id: hal-02328198

<https://hal.science/hal-02328198>

Submitted on 19 Jan 2022

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Epoxidation of vegetable oils under microwave irradiation

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ABSTRACT

This paper presents a study of the epoxidation of vegetable oil in an isothermal batch reactor system equipped with microwave or conventional heating. The epoxidation reaction was performed by peroxyacetic acid formed in situ from acetic acid and hydrogen peroxide. It was demonstrated that microwave irradiation can accelerate the epoxidation velocity when the continuous phase is aqueous, which is not transparent to microwave. This tendency was observed for peroxyacetic and peroxypropionic acids.

Keywords: Process intensification, Microwave, Epoxidation, Biolubricant

1. INTRODUCTION

Energy saving, use of biomass resources and non-toxic chemicals are the main challenges and perspectives for the chemical industry. The majority of chemical processes are still using conventional heating, losing energy to heat the vessel walls of the reactor, the inserts, the solvent and the catalyst. Microwave technology could provide an alternative to optimize the energy consumption. Indeed, there is no direct contact between the energy source and the reaction mixture, vanishing thermal convection. Furthermore, according to the dielectric permittivity of the matter, a rapid heating rate and selective heating can be achieved. The use of microwave in the field of organic synthesis is extensively described in literature, e.g., roughly 6000 articles have been published since 1998. The debate between the existence or non-existence of a non-thermal microwave effect is still going on. One should mention the work of Prof. Kappe on the use of microwave irradiation on organic synthesis [1].

This study is focused on illustrating the selective heating of microwave during a liquid-liquid reaction, namely epoxidation of vegetable oils by peroxy-carboxylic acids.

The ability to convert electromagnetic energy into thermal energy depends on the dielectric properties of each material and it can be described by using the complex permittivity (ϵ). The real part (ϵ') characterizes a material ability to store charge, and the imaginary part (ϵ'') defines effectiveness of a material to convert

electromagnetic energy into heat. The dielectric properties are dependent on composition, temperature and frequency.

Thus, some materials can be transparent or absorbent to microwave, which could be an advantage in a multiphase reaction system [1-5], such as epoxidation of vegetable oils.

Epoxidized vegetable oils are used for various purposes, such as lubricants [6], as intermediates for polymer synthesis, as plasticizers and as scavengers in the synthesis of PVC. Indeed, the world consumption of lubricants is estimated to be 40 million tons per year used in different applications, from car engines to office chairs. As in fuel industry, the majority of lubricants used are petroleum-derived. Depletion of oil will increase the price of petroleum raw material and several studies have shown that 30-40% of lubricants escape into the environment through such routes as spills, leaks and evaporation [7]. For these reasons, researchers have focused on inexpensive, non-toxic and renewable sources of lubricants, i.e., bio-based lubricants. At present, the cost of bio-based lubricants is higher than petro-based lubricants, but compared to the maintenance and energy costs, it is a minor factor [7].

Prileshajev oxidation is the most used method to epoxidize vegetable oils. The method is based on the use of peroxy-carboxylic acids formed *in situ*. This method is greener than using halohydrin, safer than molecular oxygen and more efficient than the use of inorganic peroxides. Epoxidation of vegetable oils by conventional heating has been studied by several research groups [8-27].

According to a literature review, epoxidation under microwave irradiation is rare [28-29]. Saifuddin *et al.* [28] have mostly focused their research on developing a finite element model to predict the temperature profile and Pillai *et al.* [29] have studied the epoxidation of olefin over different hydrotalcite catalysts under microwave irradiation. However, these articles did not propose a comparison between conventional and microwave heating, which is an important issue.

Epoxidation of vegetable oil is an exothermic multiphase reaction system. Most carboxylic acids used are formic and acetic acids. Experiments carried out with formic acid are more exothermic than the ones carried out with acetic acid. Thus, in case of temperature control lost, thermal runaway could occur. Could microwave irradiation improve mass transfer? Thus, it would be possible to run experiments at lower temperature or to use less reactive peroxide species.

The goal of this article is to propose a comparison between conventional and microwave heating by studying different carboxylic acids and organic-to-aqueous phase ratios. For this purpose, experiments were carried out in an isothermal batch reactor under microwave and conventional heating. To follow the epoxidation reaction, a monosaturated fatty acid, i.e., oleic acid was selected as a test molecule. For the sake of simplicity, the reaction temperature was fixed to 60°C.

2. EXPERIMENTAL SECTION

2.1. Apparatus and experimental procedures

Experiments were carried out in a glass batch reactor equipped with a glass agitator, fiber optic as a temperature probe and a reflux condenser. Figure 1 shows a schematic view of the microwave reactor system. To minimize any deviation of electromagnetic waves, a transparent material, e.g., glass, must be used.

Fig. 1. Schematic view of the microwave heating and reactor system.

As shown in Fig. 1, the microwave heating system consists of a magnetron working at 2.45 GHz with a variable input power in the range 0-1950 W. Microwaves are carried in a WR 340 waveguide applicator for a resonant single mode TE₁₀₃ propagation which ensures a high intensity of electric field for the sample. Cylindrical samples are introduced through a metallic chimney to prevent microwave leakage. A short-circuit is used to optimize microwave power in the sample by keeping the reflected power to a minimum. The circulator protects the magnetron by diverting the reflected power into a water load. This system is also equipped with probes to measure the reflected and the incident powers.

To have a rigorous comparison between conventional and microwave heating, the same reactor system was used in both cases. To prevent contamination induced by alkaline and metal components, which could initiate catalytic decomposition of peroxy-carboxylic acid and hydrogen peroxide, all parts of the reactor system being in contact with the reaction solution were washed with hydrochloric acid, followed by another washing, with a phosphate-free detergent solution.

The addition procedure was the same for all the experiments. Firstly, carboxylic acid, water and oleic acid were added into the reactor, and when the desired temperature was reached, the preheated hydrogen peroxide solution was added. Table 1 introduces the experimental matrix.

Table 1. Experimental matrix.

2.2. Analytical methods

Samples were withdrawn from the reaction mixture by a plastic syringe (to avoid contamination of the solution by trace of metals). The concentration of hydrogen peroxide was determined by titration using a standard solution of ammonium cerium sulphate (0.1 N). The concentrations of oxirane and unsaturated groups, e.g., double bonds, were measured by FTIR (absorption band at 844 and 3006 cm^{-1} , respectively).

3. RESULTS AND DISCUSSION

3.1 Mechanism and kinetics

As mentioned previously, it is a liquid-liquid reaction system, where mass transfer plays an important role and different reactions occur in the aqueous and organic phases. The epoxidation of vegetable oil is done by peroxy-carboxylic acid, which acts as an oxygen carrier because the solubility of hydrogen peroxide in the organic phase is low or negligible [14-26]. This peroxy-carboxylic acid is formed *in situ* in the aqueous phase by carboxylic acid perhydrolysis, and then transferred to the organic phase. The peroxy-carboxylic acid epoxidizes the unsaturated group to form an oxirane group. Dissociation of carboxylic acid leads to production of hydroxonium ions leading to the activation of the oxirane group. The activated oxirane group can undergo ring-opening reaction by different nucleophilic agents such as water, hydrogen peroxide and carboxylic acid. Depending on the reaction conditions and nature of the carboxylic acid, peroxy-carboxylic acid can undergo decomposition reaction in the aqueous phase. Fig. 2 proposes a schematic view of the mechanism. Fig. 3 shows the different ways of ring-opening reactions.

Fig. 2. Simplified reaction scheme.

Fig. 3. Ring-opening reactions.

The goal of this paper is not to propose a kinetic model. However, for the sake of comprehensibility, kinetics and mass balance equation should be presented.

Kinetics

The rate expression for each reaction can be described as follows [26]:

Perhydrolysis of carboxylic acid,

$$r_{\text{perh}} = k_{\text{perh}} \cdot \left([\text{RCO}_2\text{H}]_{\text{aq}} [\text{H}_2\text{O}_2]_{\text{aq}} - \frac{1}{K^{\text{C}}} [\text{RCO}_3\text{H}]_{\text{aq}} [\text{H}_2\text{O}]_{\text{aq}} \right) \quad (1)$$

Decomposition of peroxy-carboxylic acid,

$$r_{\text{decomp}} = k_{\text{decomp}} \cdot [\text{RCO}_3\text{H}]_{\text{aq}} \quad (2)$$

Kinetic of peroxy-carboxylic acid decomposition decreases with the increase of carbon chain [29]

Epoxidation of oleic acid,

$$r_{\text{ep}} = k_{\text{ep}} \cdot [\text{RCO}_3\text{H}]_{\text{org}} \cdot [\text{oleic acid}]_{\text{org}} \quad (3)$$

Ring opening,

$$r_{\text{R.O}} = k_{\text{R.O}} \cdot [\text{Epoxide}]_{\text{org}} \cdot [\text{H}_3\text{O}^+]_{\text{aq}} \quad (4)$$

where $[\text{H}_3\text{O}^+]$ is mainly due to the dissociation of carboxylic acid. This reaction occurs with strong carboxylic acid, e.g., formic acid. Based on the work of Santacesaria [14-15], ring-opening reaction occurs at the liquid-liquid interface.

The first step is the activation of oxirane group.

Mass balance

Fig. 4 shows the different mass transfer phenomena based on the film theory. Aqueous species such as peroxy-carboxylic acid, carboxylic acid and water diffuse from aqueous to organic phase. Based on the observation of several authors [16-25], hydrogen peroxide solubility in vegetable oil is low, thus direct epoxidation by hydrogen peroxide is not possible. Solubility of organic species such as oleic acid, epoxidized oleic acid and ring opening products can be assumed negligible in the aqueous phase.

Fig. 4. Concentration profiles for aqueous species.

Mass balance on the species present in the aqueous phase gives:

$$\begin{aligned}
 \frac{d[CA]_{aq}}{dt} &= -r_{perh} - k_{aq-FA} \cdot \frac{V_{tot}}{V_{aq}} \cdot a_0 \cdot ([CA]_{aq} - [CA]_{aq}^*) \\
 \frac{d[HP]_{aq}}{dt} &= -r_{perh} \\
 \frac{d[W]_{aq}}{dt} &= -r_{perh} - k_{aq-W} \cdot \frac{V_{tot}}{V_{aq}} \cdot a_0 \cdot ([W]_{aq} - [W]_{aq}^*) \\
 \frac{d[PCA]_{aq}}{dt} &= r_{perh} - r_{decomp} - k_{aq-PCA} \cdot \frac{V_{tot}}{V_{aq}} \cdot a_0 \cdot ([PCA]_{aq} - [PCA]_{aq}^*)
 \end{aligned}
 \tag{5}$$

$[i]_{aq}^*$ represents the concentration at the interface liquid liquid.

Mass balance in the organic phase can be derived as:

$$\begin{aligned}
 \frac{d[\text{CA}]_{\text{org}}}{dt} &= k_{\text{org-CA}} \cdot \frac{V_{\text{tot}}}{V_{\text{org}}} \cdot a_0 \cdot ([\text{CA}]_{\text{org}}^* - [\text{CA}]_{\text{org}}) + r_{\text{Ep}} \\
 \frac{d[\text{PCA}]_{\text{org}}}{dt} &= k_{\text{org-PCA}} \cdot \frac{V_{\text{tot}}}{V_{\text{org}}} \cdot a_0 \cdot ([\text{PCA}]_{\text{org}}^* - [\text{PCA}]_{\text{org}}) - r_{\text{Ep}} \\
 \frac{d[\text{W}]_{\text{org}}}{dt} &= k_{\text{org-W}} \cdot \frac{V_{\text{tot}}}{V_{\text{org}}} \cdot a_0 \cdot ([\text{W}]_{\text{org}}^* - [\text{W}]_{\text{org}}) \\
 \frac{d[\text{OA}]_{\text{org}}}{dt} &= -k_{\text{org-OA}} \cdot \frac{V_{\text{tot}}}{V_{\text{org}}} \cdot a_0 \cdot ([\text{OA}]_{\text{org}} - [\text{OA}]_{\text{org}}^*) - r_{\text{Ep}} \\
 \frac{d[\text{Deg}]_{\text{org}}}{dt} &= -k_{\text{org-Deg}} \cdot \frac{V_{\text{tot}}}{V_{\text{org}}} \cdot a_0 \cdot ([\text{Deg}]_{\text{org}} - [\text{Deg}]_{\text{org}}^*) + r_{\text{R.O}} \\
 \frac{d[\text{EOA}]_{\text{org}}}{dt} &= -k_{\text{org-EOA}} \cdot \frac{V_{\text{tot}}}{V_{\text{org}}} \cdot a_0 \cdot ([\text{EOA}]_{\text{org}} - [\text{EOA}]_{\text{org}}^*) + (r_{\text{Ep}} - r_{\text{R.O}})
 \end{aligned} \tag{6}$$

where CA, PCA, OA, EOA, HP, W, Deg, represent respectively carboxylic acid, peroxy-carboxylic acid, oleic acid, epoxydized oleic acid, hydrogen peroxide, water and ring opening products. $[i]_{\text{org}}^*$ denotes concentration of organic species at the interface.

Mass transfer coefficient in the continuous aqueous phase

Relation of Calderbank and Moo-Young can be used to estimate the value of the mass transfer coefficient in the continuous aqueous phase:

$$k_{\text{c-i}} = 1.3 \times 10^{-3} \left[\frac{P \mu_{\text{c}}}{V_{\text{c}} \rho_{\text{c}}} \right]^{\frac{1}{4}} \left[\frac{\mu_{\text{c}}}{D_{\text{m-i}} \rho_{\text{c}}} \right]^{\frac{-2}{3}} \tag{7}$$

where, μ_c ($\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$), V_c (m^3) and ρ_c ($\text{kg}\cdot\text{m}^{-3}$) are viscosity, volume and density of the continuous aqueous phase, respectively. Parameter P ($\text{kg}\cdot\text{m}^2\cdot\text{s}^{-3}$) is the power dissipated by the agitator and D_{m-i} ($\text{m}^2\cdot\text{s}^{-1}$) is the diffusion coefficient in the multicomponent liquid mixture [30].

$$\text{The factor } P \text{ is equal to } P = \psi \rho_m n_a^3 D_a^5 \quad (8)$$

where ψ is the agitator power consumption number, ρ_m ($\text{kg}\cdot\text{m}^{-3}$) is the density of the mixture, n_a is the stirring velocity and D_a the stirrer diameter.

In the sake of clarity, the diffusion coefficient D_{m-i} in the multicomponent liquid mixture can be estimated by the equation of Perkins-Geankoplis [30]. Different type of diffusion coefficient could be used [30]. All of them have the same structure:

$$D_{A/B}^0 = \text{Constant} \cdot \frac{T}{\mu_B^\alpha} \quad (9)$$

Mass transfer coefficient in the dispersed organic phase

Organic droplet can be assumed to be rigid, thus Treybal correlation can be used to estimate the mass transfer coefficient.

$$k_{d-i} = \frac{2\pi^2 D_{m-i}}{3 d_{32}} \quad (10)$$

where d_{32} is the Sauter number (m) equal to $\frac{\sum n_i d_i^3}{\sum n_i d_i^2}$ where n_i represents the

number of drops with diameter d_i . The Sauter number d_{32} can be calculated as:

$$\frac{d_{32}}{D_a} = \frac{A f(\Phi_d)}{We^{0.6}} \quad (11)$$

where D_a is the stirrer diameter, A is a parameter varying between 0.04 and 0.4.

The Weber number (We) is expressed as:

$$We = \frac{\rho_c n_a^2 D_a^3}{\sigma} \quad (12)$$

where ρ_c is the density of the continuous phase, n_a is the stirring velocity and σ is the surface tension ($N.m^{-1}$) of the system.

The function $f(\Phi_d)$ is equal to

$$f(\Phi_d) = \left[\frac{1 + n_1 + C_2 \Phi_d}{1 + n_2 C} \right]^{-3} \quad (13)$$

where C_2 is equal to 0.011 and $C_3 \rightarrow 1$ in case of $\phi_d > 0.3$.

The purpose of this paragraph is to show that microwave irradiation could have an influence on kinetic and mass transfer parameters. Even though, all experiments were carried out under isothermal condition, one should remind that measured temperature is a global signal and local gradient temperature could occur. This local gradient temperature could have an influence on diffusion coefficients and interfacial surface tension. Binner *et al.* [31] confirmed that microwave irradiation has a selective heat effect on aqueous organic phases.

In such liquid-liquid reaction system, rotating speed plays an important role on mass transfer. To evaluate the influence of turbulence, the adimensional Reynolds number was used. To evaluate this number, one should calculate viscosity of the system. Viscosity has an influence on mass transfer coefficient and Sauter number. Viscosity of organic phase increases with conversion of oleic acid to ring opening products. Based on the work of Campanella *et al.* [25], at 50°C high oleic sunflower oil is 0.02 Pa.s, epoxidized high oleic sunflower oil is

0.1 Pa.s and acetylated high oleic sunflower is 1 Pa.s. Density of organic phase is quite constant.

In the same way, interfacial tension should change with the conversion of oleic acid. However, this parameter is difficult to measure.

However, only the initial and final Reynolds number can be calculated due to the change of viscosity.

$$R_e = \frac{\rho_m \cdot n_a \cdot D_a^2}{\mu_m} \quad (14)$$

Table 1 presents the value of Reynolds number at different rotating speed, organic-to-aqueous phase ratio, initial and final time, i.e, complete conversion to ring opening products. For the sake of simplicity, the results are presented in Table 1. μ_m and ρ_m are respectively viscosity and density of reaction mixture. Viscosity and density of water were used for the aqueous phase, and can be assumed to be constant along the reaction time. For the organic phase, viscosity of oleic acid was used for initial Reynolds number and viscosity of ring opening products was used for final Reynolds number.

Density and viscosity of oleic acid are respectively 860 kg/m^3 and 0.01 Pa.s at 60°C according to Aspen plus software. Based on the work of Campanella et al.[25], viscosity of ring opening products can be assumed to be 1 Pa.s .

Table 1. Evolution of the Reynolds number at 60°C .

One can notice a drastic evolution of Reynolds number between the beginning and the final experimental time. This shows that there is a decrease of turbulence in the reaction mixture.

3.2 Influence of the input power

In case of microwave heating, temperature effects result from the interaction between the electromagnetic radiation and the matter. Thus, to control the temperature, one should tune the input power and control the absorbed and reflected power during the reaction. Figs 5 and 6 show the absorbed power from the reaction mixture during an experiment carried out with a 30 wt.% and 70 wt.% of the organic phase, respectively. Time zero corresponds to the addition of the carboxylic acid into the reaction mixture.

Fig. 5. Evolution of the temperature towards the absorbed and reflected power for a 30 wt.% of organic phase mixture at 400 and 650 rpm.

From Fig. 5, the first ten minutes correspond to an induction period corresponding to the tuning period. The average absorbed power was 10 W.

Fig. 6. Evolution of the temperature towards the absorbed and reflected power for a 70 wt.% of organic phase mixture at 400 and 650 rpm.

In case of experiments carried out with a reaction mixture containing 70 wt. % of the organic mixture, the power absorbed was around 10 W.

The absorbed power in both cases was of the same order of magnitude.

3.3 Influence of the rotating speed

The rotation speed is a parameter which governs the value of the mass transfer coefficient of the aqueous and organic phase [32-34]. Based on preliminary experiments, it was found that a minimum of 300 rpm was needed to obtain a stable emulsion. In this section, the results concerning the conventional and microwave heating will be presented (Fig. 7).

Fig. 7. Effect of the stirring speed on the oleic acid conversion at 60°C in the presence of acetic acid.

Fig. 7 shows that the influence of the rotation speed is negligible in the range of 400-650 rpm under conventional heating. Thus, one can conclude that the size of the drop does not interfere with the kinetics in this rotation range. The initial Sauter numbers, measuring the average droplet diameter, can be estimated from Eq. (11) (Table 2). Based on Eq. (11), one can notice that Sauter number depends on continuous phase density, impeller diameter and interfacial surface tension.

The kinetics of the epoxide formation for experiments carried out at 400 rpm was the same under conventional and microwave heating. However, the experiment carried out under microwave irradiation and at 650 rpm presents a clearly accelerated conversion.

Table 2. Sauter number at different rotating speed.

Under conventional heating, rotating speed does not have any influence in the range 400-650 rpm, this mean that the exchange surface area is optimal. This leads to the conclusion that microwave irradiation does not interfere on this parameter.

By increasing the rotating speeds (cf. Eq. (8)), impeller power consumption increases. Under microwave irradiation, energy delivered to reaction mixture could be more efficient than under conventional heating. For that reason, kinetic increased at 650 rpm compared to 400 rpm. This explains why the epoxidation kinetics is faster at 650 rpm under microwave irradiation than at 400 rpm. A better energy dissipation would improve aqueous mass transfer coefficient k_{aqueous} due to a better homogenization of power delivered to reaction mixture. To have a better investigation of this phenomenon, change in aqueous to organic phase ratio was studied.

3.4 Influence of organic-to-aqueous phase ratio

As mentioned earlier, microwave irradiations are transparent to oil, i.e., $\epsilon' = 2.8$ and $\epsilon'' = 0.15$ for soybean oil [35]. Thus, one could expect different kinetic results according to the nature of the continuous phase. Experiments were carried out with 70 and 30 wt.% of the organic phase, using the stirring speed of 650 rpm to have an optimal exchange surface area.

Fig. 8. Influence of the heating source and nature of the continuous phase on the oleic acid conversion in the presence of acetic acid at 650 rpm and 60°C.

Fig. 9. Influence of the heating source and nature of the continuous phase on the mole fraction of epoxide in the presence of acetic acid at 650 rpm and 60°C.

From Fig. 8, one can notice that in case of experiments carried out with 70 wt.% of the organic phase, the influence of microwave irradiation on the conversion rate was less pronounced than with experiment carried out with 30 wt.%. Binner *et al.* [31] have demonstrated that there is a temperature gradient leading to a decrease of interfacial surface tension and a coalescence of the aqueous droplets. This coalescence diminishes the exchange surface area and thus limits mass transfer.

Fig. 9. presents the evolution of mole fraction of epoxide. Fig. 9 confirms that mass transfer phenomenon is improved under microwave irradiation than under conventional heating. Under microwave irradiation, energy dissipation is higher than under conventional heating, this increase the value of aqueous mass transfer coefficient at the interface leading to a better diffusion of hydroxonium ions and water to the organic phase. At both organic-to-aqueous phase ratios, the ring opening reaction increases. In order to confirm this hypothesis of mass transfer due to a better energy distribution, propionic acid will be tested. Propionic acid will produce peroxypropionic acid which is less reactive than peroxyacetic acid [29].

3.5 Influence of the carboxylic acids

Experiments without carboxylic acids were performed but there was no conversion of oleic acid. It can be noticed that the same tendency was observed for experiments carried out with propionic acid (Fig. 10), i.e., microwave irradiation increases the epoxidation velocity. However, this increase is slower than with acetic acid.

Fig. 10. Conversion of oleic acids under conventional and microwave heating using different carboxylic acid at 650 rpm and 60°C.

Fig. 11. Influence of the heating source and nature of the continuous phase on the mole fraction of epoxide at 650 rpm and 60°C.

Conversion of oleic acid is slightly improved by microwave irradiation due to faster mass transfer. In case of propionic acid (Fig. 10) ring opening reaction is faster under microwave irradiation than under conventional heating. As said earlier, peroxypropionic acid is less reactive than peroxyacetic acid but mass transfer of water from aqueous to organic phase occurs at similar velocity as with acetic acid.

By calculating the initial reaction rates, for which the ring opening reaction can be assumed to be negligible, the kinetics of epoxide formation is 2.5 times higher under microwave irradiation than under conventional heating.

Table 4. Initial rate of epoxide formation.

4. CONCLUSIONS

The epoxidation kinetics of vegetable oil under microwave and conventional heating was compared. Experiments were carried out in an isothermal batch reactor at different rotation speeds and different organic-to-aqueous phase ratios. It was shown that microwave irradiation does not have an influence on the experiments carried out with 70 wt.% of organic phase. However, it was revealed that microwave exposure increases the reaction rate when the continuous phase is the aqueous one for the rotation speed of 650 rpm. This observation was explained by a higher energy dissipation under microwave irradiation.

This tendency was confirmed by using peroxypropionic and peroxyacetic acids, and it was shown that the epoxidation kinetics is increased by a factor of 2.5 under microwave irradiation. The modification of the energy repartition at the interface was confirmed by the increase of the ring opening reaction rate under microwave irradiation.

ACKNOWLEDGMENT

The financial support from the Academy of Finland is gratefully acknowledged.

The authors express their gratitude to Bruno Daronat for his technical assistance.

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FIGURES

Fig. 1. Schematic view of the microwave heating and reactor system.

Fig. 2. Simplified reaction scheme.

Fig. 3. Ring-opening reactions.

Fig. 4. Concentration profiles for aqueous species.

Fig. 5. Evolution of the temperature towards the absorbed and reflected power for a 30 wt.% of organic phase mixture at 400 and 650 rpm.

Fig. 6. Evolution of the temperature towards the absorbed and reflected power for a 70 wt.% of organic phase mixture at 400 and 650 rpm.

Fig. 7. Effect of the stirring speed on the oleic acid conversion at 60°C in the presence of acetic acid.

Fig. 8. Influence of the heating source and nature of the continuous phase on the oleic acid conversion in the presence of acetic acid at 650 rpm and 60°C.

Fig. 9. Influence of the heating source and nature of the continuous phase on the mole fraction of epoxide in the presence of acetic acid at 650 rpm and 60°C.

Fig. 10. Conversion of oleic acids under conventional and microwave heating using different carboxylic acid at 650 rpm and 60°C.

Fig. 11. Influence of the heating source and nature of the continuous phase on the mole fraction of epoxide at 650 rpm and 60°C.

TABLES

Table 1. Experimental matrix.

Table 2. Sauter number at different rotating speed.

Table 3. Initial rate of epoxide formation.

Table 4. Initial rate of epoxidized oleic acid formation.

Figure

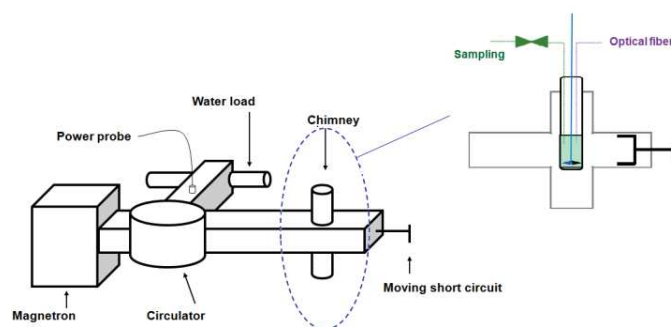


Fig. 1. Schematic view of the microwave heating and reactor system.

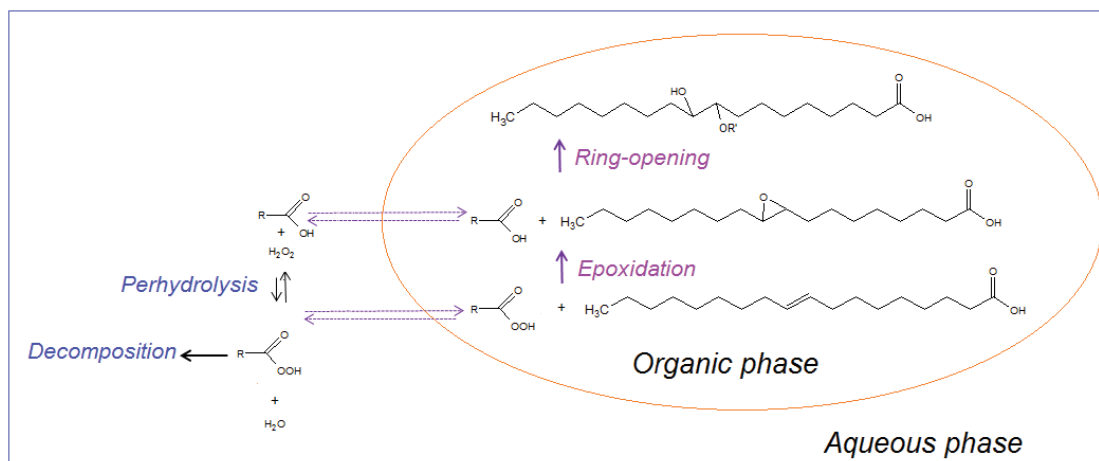


Fig. 2. Simplified reaction scheme.

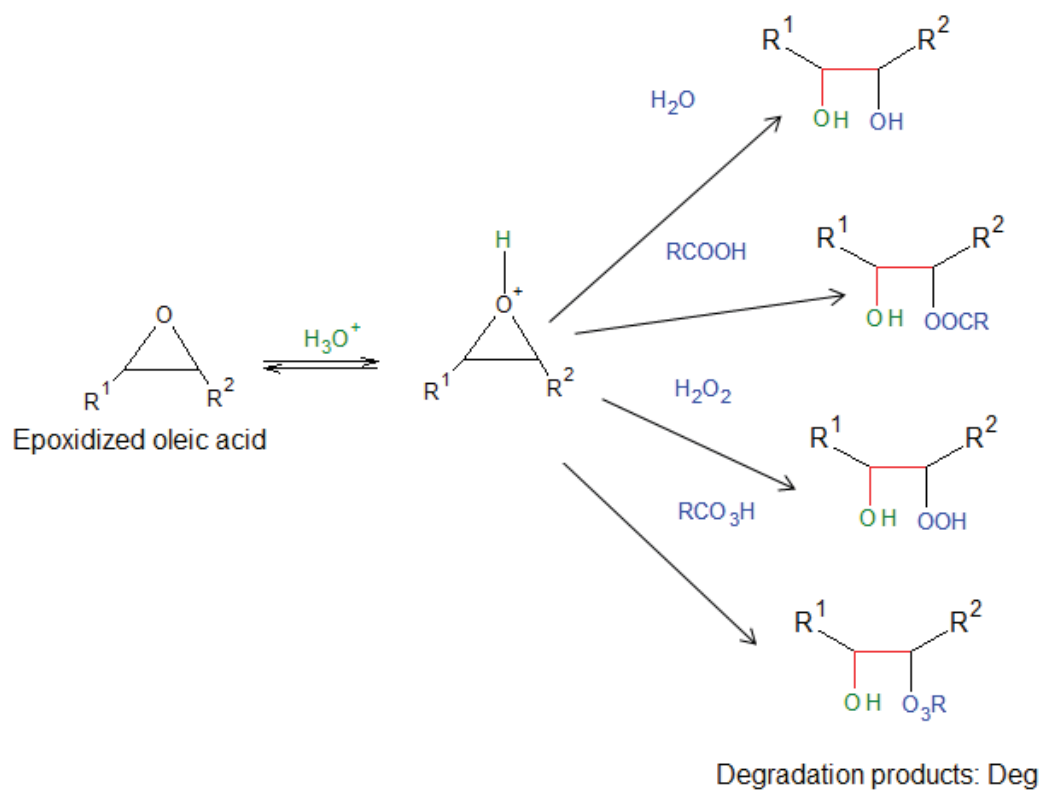


Fig. 3. Ring-opening reactions.

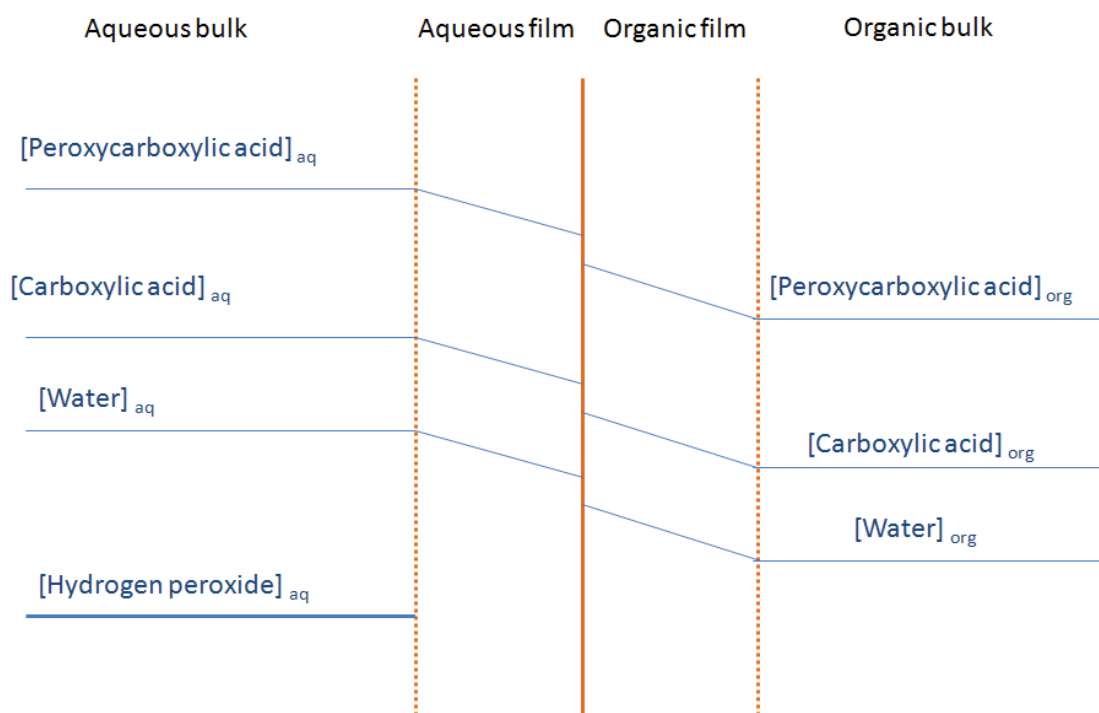


Fig. 4. Concentration profiles for aqueous species.

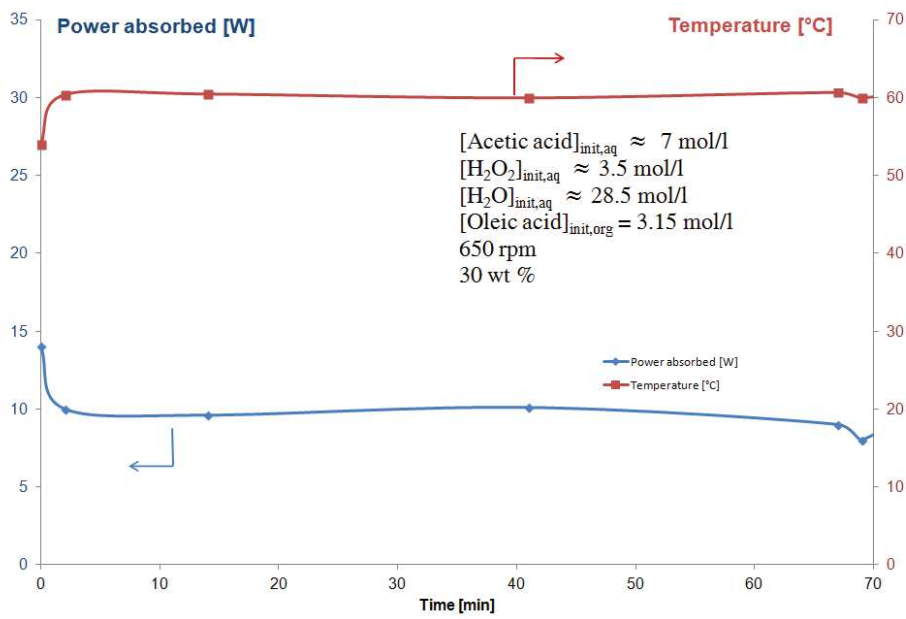
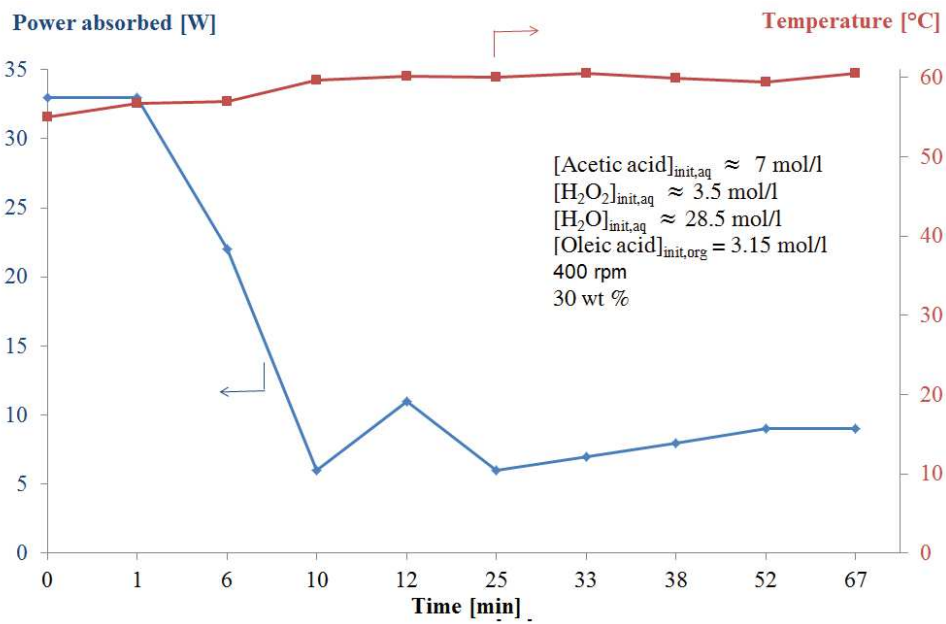


Fig. 5. Evolution of the temperature towards the absorbed and reflected power for a 30 wt.% of organic phase mixture at 400 and 650 rpm.

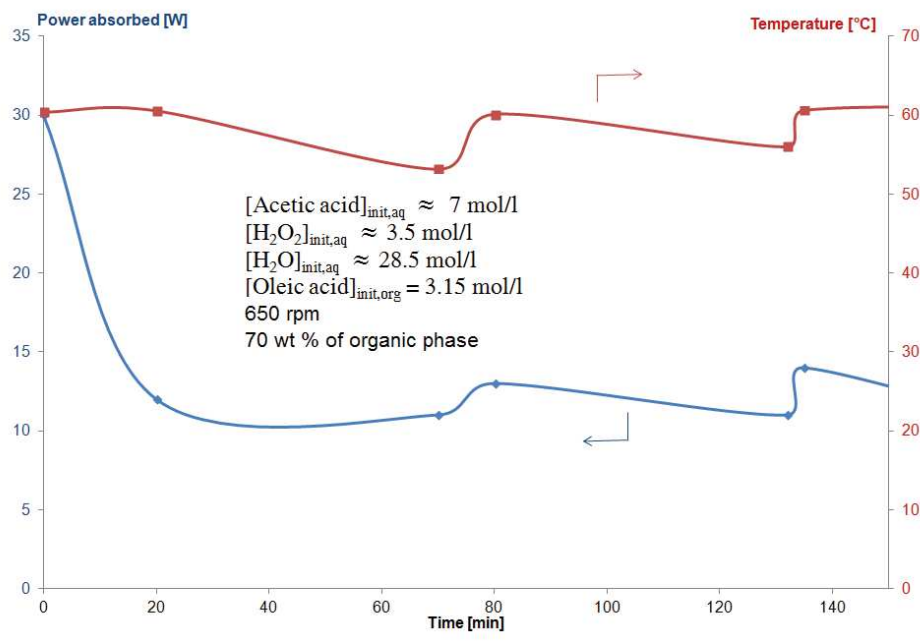
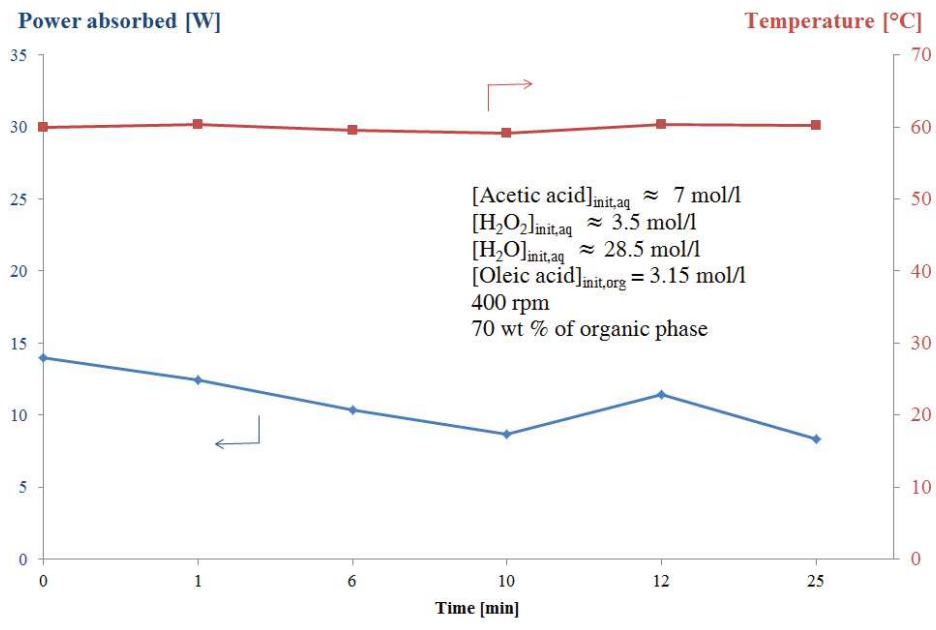


Fig. 6. Evolution of the temperature towards the absorbed and reflected power for a 70 wt.% of organic phase mixture at 400 and 650 rpm.

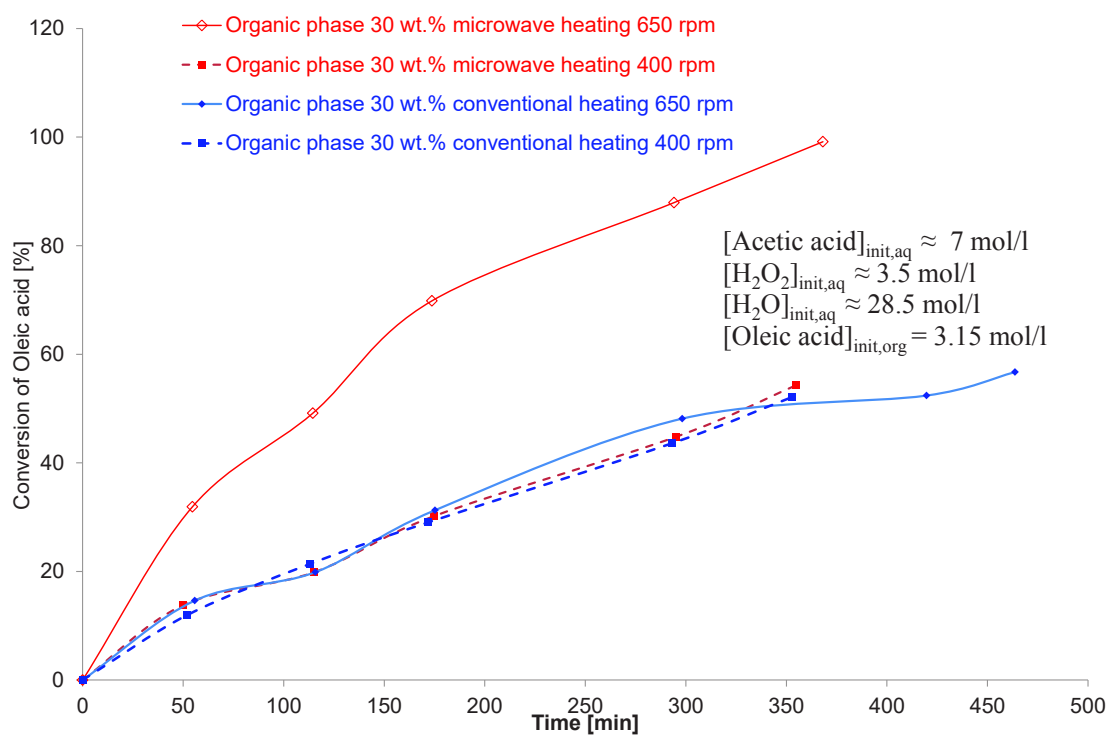


Fig. 7. Effect of the stirring speed on the oleic acid conversion at 60°C in the presence of acetic acid.

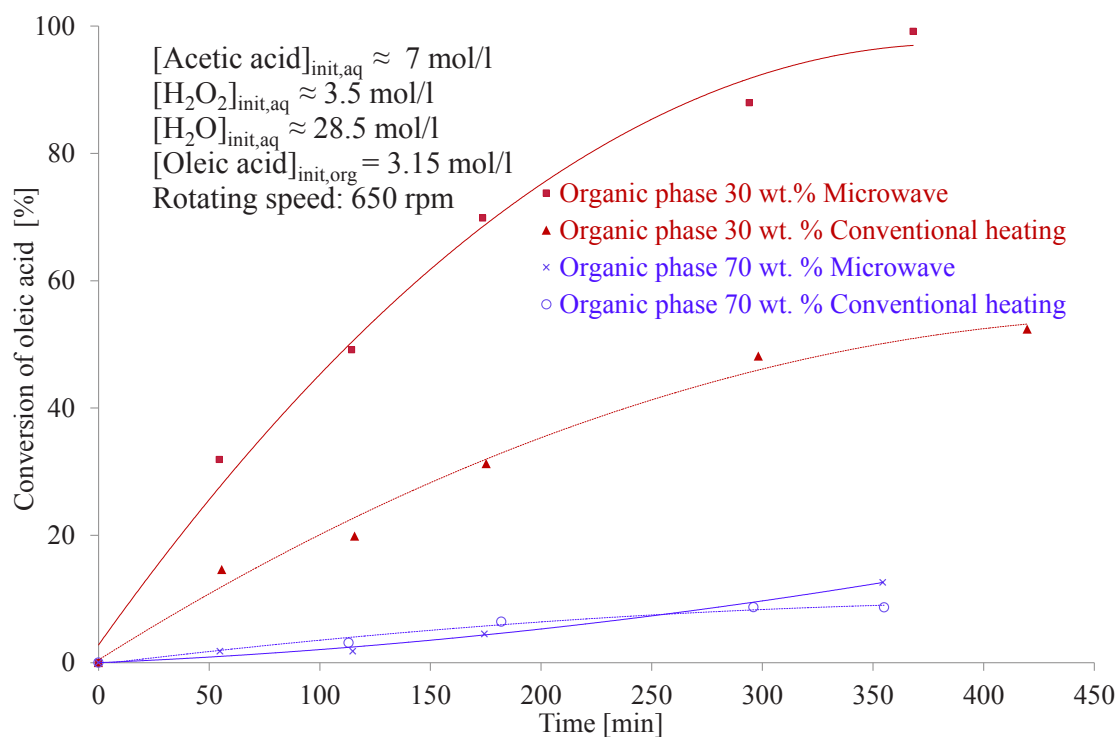


Fig. 8. Influence of the heating source and nature of the continuous phase on the oleic acid conversion in the presence of acetic acid at 650 rpm and 60°C.

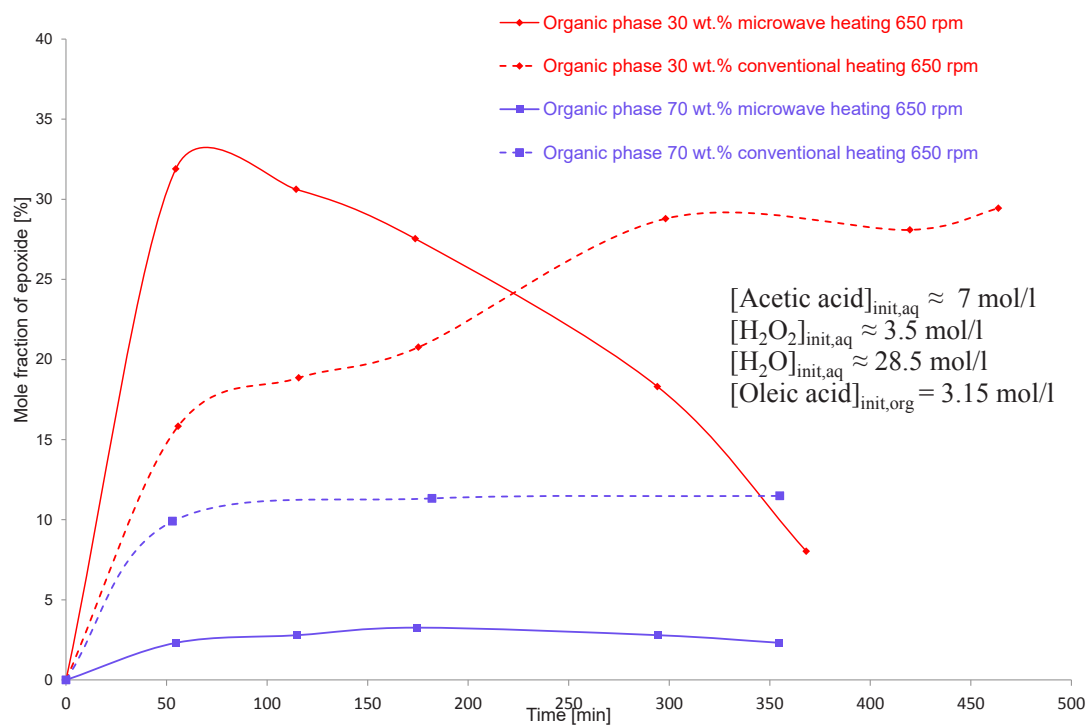


Fig. 9. Influence of the heating source and nature of the continuous phase on the mole fraction of epoxide in the presence of acetic acid at 650 rpm and 60°C.

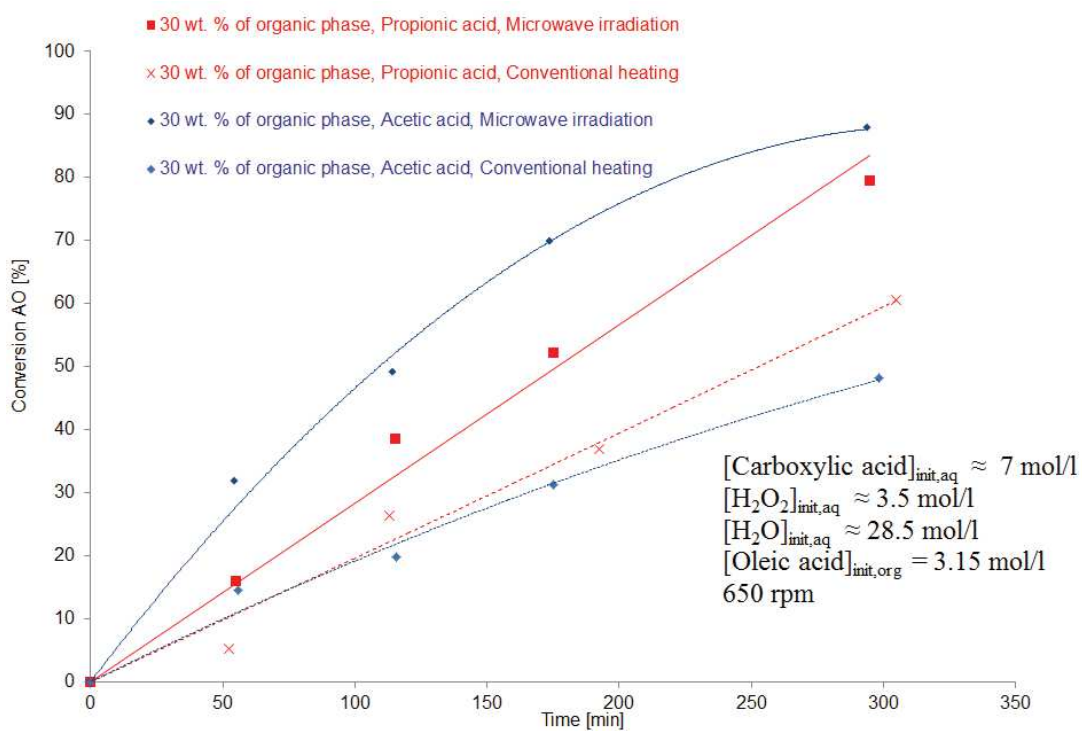


Fig. 10. Conversion of oleic acids under conventional and microwave heating using different carboxylic acid at 650 rpm and 60°C.

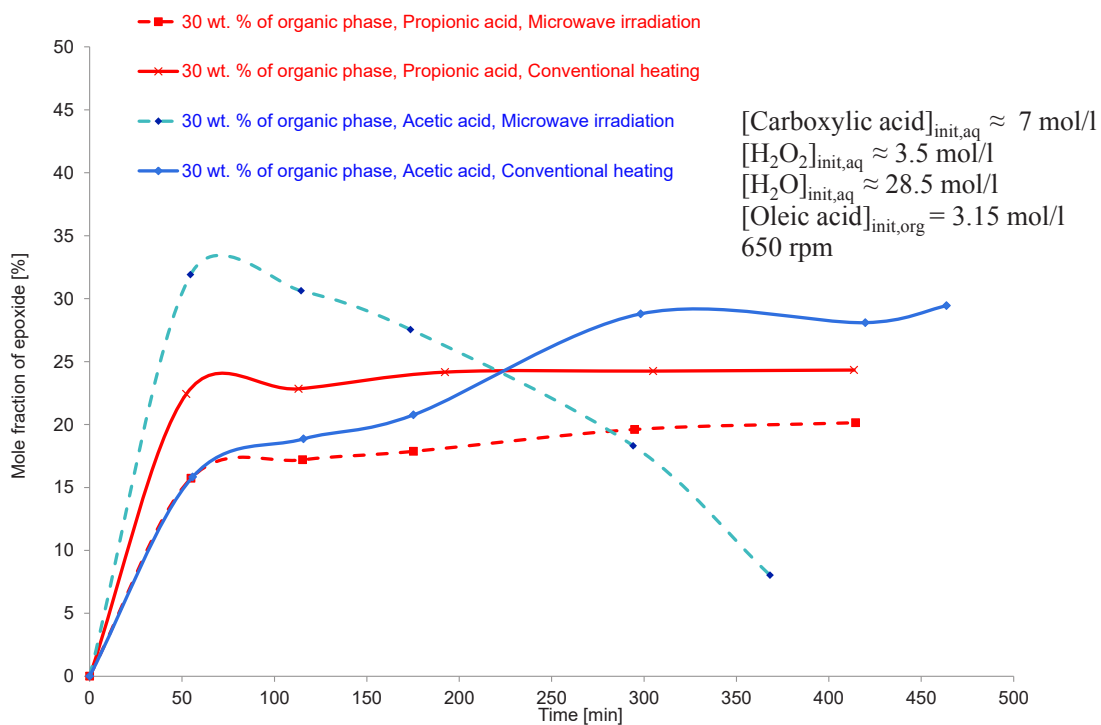


Fig. 11. Influence of the heating source and nature of the continuous phase on the mole fraction of epoxide at 650 rpm and 60°C.

Table

Table 1. Evolution of the Reynolds number at 60°C.

Rotation speed	30% organic phase		70% organic phase	
	Re (initial)	Re (final)	Re (initial)	Re (final)
400 rpm	2997	34	2846	14
650 rpm	4870	54	4624	22

Table 2. Experimental matrix.

Reaction temperature	60°C	
Rotation speed	300-650 rpm	
Initial amount of oleic acid	30-70 wt. %	0.05-0.11 mol
Initial amount of carboxylic acid	0-30 wt. %	0.00-0.22 mol
Initial H ₂ O ₂ amount	3-10 wt. %	0.05-0.11 mol
Initial H ₂ O amount	16-65 wt. %	0.20-1.5 mol
Reaction volume	50 ml	

Table 3. Sauter number at different rotating speed.

Rotation speed	Organic phase 30 wt. %	Organic phase 70 wt. %
400 rpm	$d_{32} = 582 \mu\text{m}$	$d_{32} = 831 \mu\text{m}$
650 rpm	$d_{32} = 268 \mu\text{m}$	$d_{32} = 382 \mu\text{m}$

Table 4. Initial rate of epoxide formation.

	$\left(\frac{dC_{\text{epoxide}}}{dt}\right)_{t=0} [\text{mol.l}^{-1}.\text{min}^{-1}]$
30 wt. % of organic phase, Acetic acid, Microwave irradiation	$2.76 \cdot 10^{-2}$
30 wt. % of organic phase, Propionic acid, Microwave irradiation	$4.36 \cdot 10^{-3}$
30 wt. % of organic phase, Acetic acid, Conventional heating	$1.21 \cdot 10^{-2}$
30 wt. % of organic phase, Propionic acid, Conventional heating	$1.54 \cdot 10^{-3}$