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Key role of temperature monitoring in interpretation of microwave effect on transesterification and esterification reactions for biodiesel production

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HIGHLIGHTS

- Temperature monitoring is more accurate using an optical fiber than an infrared sensor.
- Transesterification is not accelerated under microwave irradiation.
- Esterification with methanol is not accelerated under microwave irradiation.
- Main cause of "the microwave effect" is temperature underestimation.
- Temperature underestimation may be associated with superheating of methanol.

ARTICLE INFO

ABSTRACT

Microwave effects have been quantified, comparing activation energies and pre-exponential factors to those obtained in a conventionally-heated reactor for biodiesel production from waste cooking oils via transesterification and esterification reactions. Several publications report an enhancement of biodiesel production using microwaves, however recent reviews highlight poor temperature measurements in microwave reactors give misleading reaction performances. Operating conditions have therefore been carefully chosen to investigate non-thermal microwave effects alone. Temperature is monitored by an optical fiber sensor, which is more accurate than infrared sensors. For the transesterification reaction, the activation energy is 37.1 kJ/mol (20.1–54.2 kJ/mol) in the microwave-heated reactor compared with 31.6 kJ/mol (14.6–48.7 kJ/mol) in the conventionally-heated reactor. For the esterification reaction, the activation energy is 45.4 kJ/mol (31.8–58.9 kJ/mol) for the microwave-heated reactor compared with 56.1 kJ/mol (55.7–56.4 kJ/mol) for conventionally-heated reactor. The results confirm the absence of non-thermal microwave effects for homogenous-catalyzed reactions.

1. Introduction

1.1. Context

In recent years, bio-sourced raw material has been investigated as a substitute for fossil fuels or as solvents for renewable energy and green chemistry applications. Virgin and food-grade oils were initially studied to produce the first generation of biofuels, constituted of Fatty Acids Methyl Esters (FAME). Waste Cooking Oils (WCO) are of particular interest for biodiesel production for two reasons. Firstly, WCO are two to three times cheaper than virgin oils (Zhang et al., 2003). Secondly, by re-using and transforming of WCO, instead of discarding it into sewers, water treatment costs are significantly decreased (Banerjee and Chakraborty, 2009). This double effect propels WCO as a very good environment-friendly feedstock.

The use of waste cooking oil, however, brings additional challenges. During the cooking process oils are subjected to high temperatures, and in the presence of water (released by foods) fatty acids are formed by a hydrolysis reaction (Gui et al., 2008). Normally transesterification is base-catalyzed since the reaction is 4000 times faster than that with acid catalysis (Fukuda et al., 2001). However, with a basic catalyst the high acidity of the oil leads to undesired soap formation, which decreases the reaction yield and acts as a surfactant between the two final immiscible

products, making downstream separation more difficult. The limit of acceptable acidity is not clearly defined; the advised limit is 1 mg KOH/g_{oil} (fatty acid mass fraction of 0.5%) (Banerjee and Chakraborty, 2009), however reactions have been successfully performed at 3 mg KOH/g_{oil} (fatty acid mass fraction of 1.5%) (Banerjee and Chakraborty, 2009; Enweremadu and Mbarawa, 2009). The water content is limited to 0.05% vol/vol (ASTM D6751 standard) because it forms inactive alkaline soaps (Leung et al., 2010). Due to these undesirable outcomes, WCO needs to be pre-treated before reactions are performed.

1.2. FAME production from waste cooking oils

The first pre-treatment step required is to reduce the acidity of the oil. Both physical (such as drying, filtration, or distillation (Tur et al., 2012)) and chemical pre-treatment can be used. Chemical treatment is carried out with an acid-catalyzed esterification reaction. The fatty acids in the oil react with methanol producing methyl esters and water. This is an immiscible liquid–liquid reaction, which is mass-transfer limited (Santacesaria et al., 2007). After the esterification reaction the oil mainly contains tri, di and mono glycerides and the mass fraction of fatty acids is generally below 1.5%.

Following the esterification reaction and after a water removal step, the pretreated oil is then transformed using a base-catalyzed transesterification. Like the esterification reaction, the transesterification reaction is mass-transfer limited at the beginning due to the immiscibility of triglycerides and methanol, as well as at the end of the reaction because most of the catalyst is in the glycerol phase (Cintas et al., 2010).

A number of types of reactors can be used to carry out the esterification and transesterification of WCO transformations and these have been reviewed in our previous paper (Mazubert et al., 2013). In comparison to conventional batch reactors, a number of intensified equipment types (such as microstructured reactors, cavitational reactors, microwave reactors, oscillatory flow reactors, membrane reactors, as well as static mixers and reactive distillation) have shown to enhance FAME production. Microwave reactors show particularly promising results in terms of residence times, which are significantly reduced compared with other technologies. The next section presents the basic principle of microwave heating and some background on their use for biodiesel production.

1.3. Microwave background

1.3.1. Principle

The two major mechanisms involved in microwave technology are dipolar polarization and ionic conduction. Dipolar polarization occurs when dipoles are forced to align with the direction of the electric field that is imposed by the microwave. The electric field rapidly oscillates, as does the dipole, which tries to realign itself with the field as fast as possible by rotation. The frequency of the microwaves is sufficiently high to cause a phase difference between the field and the dipole orientation. The frictional and collision forces between the molecules thus generate heat. The second mechanism is ionic conduction. It occurs as the charged dissolved particles oscillate under the influence of the microwave field. When the direction of the electric field changes, the ions slow down and change direction, dissipating their kinetic energy as heat. This dissipation is caused by friction (Lidström et al., 2001; Mingos and Baghurst, 1991).

The absorption of microwaves by a dielectric compound can be characterized by the complex permittivity ε^*, which depends on the dielectric constant ε' that represents the ability of the compound to store energy, and the dielectric loss ε'' that represents

the ability of the compound to convert the absorbed energy into heat.

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \tag{1.1}$$

One limitation of the use of microwaves on a larger scale is the small penetration depth of the microwaves in the reactive media. This penetration depth, d_p, is a function of the dielectric properties and the frequency of the microwaves. A limited penetration depth will make uniform heating difficult at higher volumes.

As it is expressed in literature (Metaxas and Meredith, 1983), the general expression for the penetration depth approximates to:

$$d_p = \frac{\lambda_0 \sqrt{\varepsilon'}}{2\pi\varepsilon''} \text{ where the free space wavelength is} \qquad \lambda_0 = \frac{c_0}{f} \tag{1.2}$$

As an example, at 2.45 GHz the penetration depth of microwaves in methanol at 20 °C is 0.76 cm and at 60 °C, it is 1.4 cm (calculated from work of Grant and Halstead (1998)). This small penetration depth is the reason why mechanical stirring is required to homogenize temperature.

1.3.2. Microwave effects

It is generally believed that reaction enhancement and other observed effects in microwave-assisted processes are due to thermal phenomena caused by the microwave dielectric heating mechanisms. Amongst the different thermal effects caused by microwaves some examples are (Kappe et al., 2012):

- The superheating of solvents due to extremely fast heating to temperatures above the solvent boiling point; in such cases solvents boil at temperatures that are higher than the usual boiling point due to absence of nucleation points.
- The heating of selected phases or reagents of the reaction medium, e.g. microwave-absorbing solid catalysts.
- The generation of inverted temperature gradients between the wall and the bulk of the reactor, and the subsequent elimination of wall effects.

Despite some controversy, claims that non-thermal microwave effects on reactions still exist (Perreux et al., 2013). The reduction of reaction times exclusively due to microwave irradiation is referred to as non-thermal microwave effects when the comparison of reaction performance with and without microwave irradiation is made at the same temperatures and operating conditions (e.g. agitation intensity, mixing quality). It has been postulated that these effects are due to the interaction of the electromagnetic field with the molecules in the reaction medium. It is believed for some reactions that the electromagnetic field modifies the orientation of the molecules and could change the pre-exponential factor A in the Arrhenius equation:

$$K = A.e^{\left(-\frac{\Delta G}{RT}\right)} \tag{1.3}$$

where ΔG is the activation energy or entropy term. The pre-exponential factor, which describes the probability of molecular impacts, depends on the vibration frequency of the atoms at the reaction interface. It is thought that this vibration frequency could be affected under microwave irradiation and leads to an increase of the pre-exponential factor. The decrease in activation energy under microwaves is attributed to the increase of the entropy term.

1.3.3. Transesterification and esterification reactions under microwaves

The use of microwaves for enhancing chemical reactions has been a topic of significant interest in past years (Baig and Varma, 2012) and the investigations of transesterification and esterification

reactions under microwave irradiation has been numerous as identified by Mazubert et al. (2013). For these reactions in particular, microwave efficiency is increased by the high polarity and high dielectric loss of methanol. Indeed, the dielectric constant of methanol at 25 °C and 2.45 GHz is 32.7 (Albright and Gosting, 1946) compared with that of water at 78.5, which is high, and that of oil is only between 3 and 4. The dielectric loss for methanol at 25 °C is around 11.8, which is close to that of water, around 13.

In general, the literature studies show that for homogenous base-catalyzed transesterification reactions under microwave irradiation in batch conditions, high conversions or yields are attained at very short reaction times in comparison with conventionally heated systems. For example:

- A 98% conversion of triolein is obtained in 1 min at 50 °C using an initial power of 25 W in a 100 mL round-flask reactor (Leadbeater and Stencel, 2006).
- A 93.7% conversion of rapeseed oil is obtained in 1 min at 40 °C using a power of 1200 W (Azcan and Danisman, 2008).
- A yield greater than 96% is obtained in 6 min with a KOH catalyst, at 60 °C using a maximum power of 500 W in a 50 mL reactor (Zu et al., 2009).
- A 97.2% conversion of rice oil is obtained in 5 min at 60 °C, using a maximum power of 1600 W in a 270 mL reactor (Kanitkar et al., 2011).
- A 98.4% conversion of safflower oil is obtained in 6 min at 60 °C using a maximal power of 300 W in a 500 mL reactor (Duz et al., 2011).

Similar results have also been found in continuous reactors. For example, using a 9 mm diameter coiled tube in a household microwave and a flow rate of 19.8 L/h Lertsathapornsuk et al. (2008) obtained a 97% conversion in 30 s using ethanol, at an average outlet temperature of 78 °C with a maximal power of 800 W. In a 4 L non-agitated continuous tank with a flow rate of 432 L/h, a 98.9% conversion was obtained in 30 s at 50 °C using a maximum power of 1600 W in a large multimode microwave cavity (Barnard et al., 2007).

Few studies on the esterification of fatty acids with a homogenous catalyst have been carried out; indeed most investigations on esterification reactions with microwaves have used heterogeneous catalysts. The use of microwaves for decreasing the fatty acid content with a homogenous catalyst has only recently been shown: the acidity of Jatropha oil was decreased from 14% to 1% using a sulfuric acid catalyst at a power of 110 W in a 500 mL reactor in 35 min (Jaliliannosrati et al., 2013).

In summary, the literature results globally show that the use of microwaves for FAME reactions allows high yields or conversions to be attained in very short times compared with conventionally heated reactors. However, it should be pointed out that very few of these studies provide details on how the temperature in the microwave reactor is measured. This is an extremely important point, which has been highlighted recently by Kappe and co-workers (Herrero et al., 2008; Kappe, 2013; Kappe et al., 2013). These authors report that erroneous temperature measurements and poor mixing of the reaction mixture are often responsible for the observation of reaction enhancement due to non-thermal microwave effects. Infrared (IR) temperature sensors are typically used for temperature measurement in commercial microwave systems. However, it is known that the use of IR sensors that measure the temperature at the outer bottom surface of the reactor do not provide correct information on the internal reaction temperature. *In situ* fiber-optic temperature probes provide much more accurate temperature measurements and therefore are highly recommended. As a result, it is clearly understood that poor temperature measurements in microwave reactors give misleading results in terms of reaction performance. Indeed, in the current literature on the use of microwave heating for enhancing FAME reactions, infrared sensors are very often used and one may question the real gain in using this novel heating method compared with conventional techniques.

1.4. Present work

This work investigates the effects of microwaves on the performance of transesterification and esterification reactions using WCO as feedstock. To do this, the reactions performed in a conventionally heated reactor and a microwave reactor have been compared under the same operating conditions (temperature and stirring conditions). The microwave reactor operates in single mode and is equipped with a mechanical rotating impeller to ensure good mixing quality and homogenous temperature in the reactor. The temperatures are measured directly in the reaction medium by a fiber optic probe to ensure the accuracy of the temperature measurements. To quantify a potential enhancement of the reaction by the microwave irradiation, the influence of microwave irradiation on the Arrhenius equation is presented for both reactions.

2. Methods

2.1. Products

WCO was collected in restaurants and supplied by the company Coreva Technologies (Auch, France). Two different WCOs are studied: one with low fatty acid content (2.1%) and the other with a higher level of fatty acids (39%). Both oils contain no water or solid wastes. The profiles of the carbon chains are as follows:

- Oil with 2.1% of FFA: palmitic C16:0 (15.2%), palmitoleic C16:1 (3.5%), stearic C18:0 (4.6%), oleic C18:1 (36.5%), linoleic C18:2 (36.1%) and alpha-linoleic C18:3 (3.5%).
- Oil with 39% of FFA: palmitic C16:0 (13.1%), stearic C18:0 (3.7%), oleic C18:1 (54.3%), linoleic C18:2 (24.6%), arachidic C20:0 (4.3%).

Methanol (99% HPLC grade), sodium hydroxide pellets, sulfuric acid (96%), cyclohexane (analytical grade) and ethanol (absolute, 99.9%) were supplied by VWR, France. Phenolphthalein and KOH-ethanol solution (1 M or 0.1 M) were supplied by Sigma–Aldrich, France. Methyl imidazole (MI) was supplied by Alfa Aesar. N-méthyl-N-triméthylsilyl-heptafluorobutyramide (MSHFBA) was supplied by Marcherey-Nagel.

2.2. Experimental apparatus

The conventionally heated reactor, as shown in Fig. 1(a), consists of a 1L-jacketed vessel equipped with a 3-bladed paddle, a cooling system to avoid the vaporization of methanol and a mercury thermometer. The agitation speed is fixed at 300 rpm for both reactions. The transesterification is carried out at four temperatures (25 °C, 40 °C, 50 °C and 60 °C) using the 2.1% FFA oil. The methanol to oil molar ratio is 6:1 and the mass fraction of KOH catalyst (with respect to the mass of oil) is 1%. An initial mass of 600 g of oil is preheated in the reactor before adding the methanol and catalyst solution.

The esterification is also carried out at four temperatures (30 °C, 40 °C, 50 °C and 60 °C) using the 39% FFA oil in the conventionally heated reactor. The methanol to oil ratio is 36:1 and the mass fraction of the sulfuric acid catalyst (with respect to the mass of oil) is 7%. The methanol and sulfuric acid are preheated in the reactor,
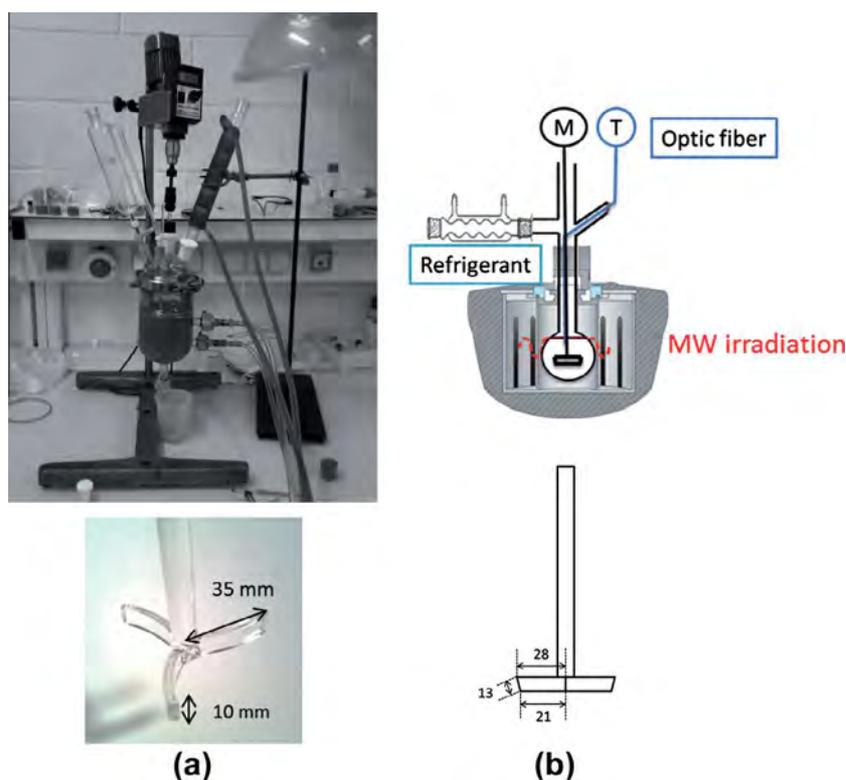
Fig. 1. Two experimental systems: (a) the conventionally heated reactor and its agitator and (b) the microwave heated reactor with its mechanical agitator (M) and temperature monitored by optical fiber (T). Dimensions are given in mm.

whilst the oil is preheated in a thermal bath. The total volume is fixed at 1 L.

The microwave reactor is a CEM® Discover SP ($f = 2.45$ GHz) operates at atmospheric pressure and is equipped with a 100 mL round-flask and a 2-bladed paddle impeller made of PTFE, as shown in Fig. 1(b). The maximum power is 300 W. The power is automatically adjusted to the measured temperature via an optical fiber. The agitation speed is fixed at 300 rpm. The 2-bladed paddle impeller has been used instead of the conventional magnetic stirrer in order to homogenize the temperatures in the microwave cavity and to ensure good mixing of the reactants. Indeed, the default magnetic stirrer provided in the microwave reactor was unable to rotate in the viscous oils and therefore provided insufficient mixing. The temperature homogeneity was also assisted by the use of a single mode microwave reactor, instead of a multi-mode reactor type that has often been used in previous studies (Barnard et al., 2007; Lertsathapornsuk et al., 2008). The total reaction volume is 80 mL. The transesterification and the esterification are carried out at the four different temperatures as in the conventionally heated reactor. As stirring and microwave irradiation start simultaneously, the initial time is set to when the agitation starts even if the desired temperature is not reached yet. The times required to reach each of the set temperatures are given in Table 1.

2.3. Characterization of reaction performance

The composition of FAME produced from the transesterification and esterification reactions was characterized by gas chromatography (GC) using a Perkin Elmer Instrument based on the EN-14103 method. The chromatograph is equipped with a flame ionization detector (FID). The column used was Restek (CP-Sil 8 Rtx-5: 5% diphenyl, 95% dimethylpolysiloxane) 15 m × 0.32 mm × 0.25 μm.

Table 1
Comparison of temperature measurements using an optical fiber probe (OF) and infrared sensor (IR) for the esterification reaction. The reactor volume is 80 mL and the stirring speed using an mechanical agitator is 300 rpm.

Experimental tests				
Setpoint T (°C)	30	40	50	60
Time needed by OF to reach setpoint T (s)	20	26	34	45
T (OF) (°C)	30	40	50	60
T (IR) (°C)	23	33	39	33

The injection is "on-column" because the di- and triglycerides are not vaporized in the injector and are injected as liquids in the column. One internal standard (heptadecane) and six reference materials (triolein, monoolein, diolein, triolein, oleic acid, methyl oleate) supplied by Sigma–Aldrich were used for the GC calibration. The samples are diluted in cyclohexane (Analytical grade) supplied by VWR, France. The operating conditions used for the oven were 55 °C for 30 s, 45 °C/min to 80 °C, 10 °C/min to 360 °C and hold for 11 min. The carrier gas was helium at a constant pressure at the top of the column of 15 psi. The hydrogen flow was kept at 45 mL/min and the air flow was kept at 450 mL/min. The hydroxyled compounds (fatty acids, mono, di- and triglycerides) are silyled by a mixture of N-methyl-N-trimethylsilyl-heptafluoro-butyramide (MSHFBA) and methylimidazole (MI). This reaction increases the volatility and the stability of injected hydroxyled compounds to enhance their detection.

The fatty acid level is determined by titration with a 0.1 N KOH-ethanol solution using a Mettler Toledo DL50 titrator based on the ISO 660 norm. The sample (about 1 mL) is diluted in ethanol (about 30 mL). The titrator gives the exact volume added at the equivalence point, which is determined by a pH sensor. Phenol-phthalein is used as the colored indicator to detect the equivalence point. The percentage of acidity Ac is given by the relationship:

Ac = ($V_{eq} \cdot M_{C18} \cdot C_{KOH}$)/mass of oil, where V_{eq} is the volume at the equivalence point, M_{C18} the molar mass of fatty acids and C_{KOH} the concentration of the KOH-ethanol solution. The percent conversion is given by the relationship: $X = (Ac_{initial} - Ac_{final})/Ac_{initial}$ where $Ac_{initial} = 39\%$.

2.4. Operating conditions requirements

2.4.1. Reproducibility

In order to ensure the reproducibility of results, the microwave-assisted transesterification reaction has been performed five times for a duration of 8 min. The standard deviation, the interval of confidence at 95% and the average values of the compounds present following the reaction are given in Table 2. The quantity of esters is 91.3% (±1%). The uncertainties of the other compounds are relatively larger in comparison to the small measured quantities. The control of the temperature and the reproducibility are therefore regarded as satisfactory considering the small changes in ester production for a fixed duration of reaction time.

2.4.2. Effect of hydrodynamics

As described above, the vessels used with conventional heating and with microwave heating have different sizes (1 L and 100 mL, respectively) and different agitators. To ensure that any potential enhancement of the reactions is not caused by differences in the mixing quality and hydrodynamics of the liquid–liquid reactive medium the reactions were also performed in the 100 mL vessel with conventional heating, using a thermal bath with a temperature of 60 °C. After 5 min, the concentration of esters in the 1 L conventionally heated reactor is 2.25 mol/L (2.23–2.28 mol/L) whereas for the 100 mL vessel heated with the thermal bath, the concentration of esters is 2.24 mol/L (2.26–2.21 mol/L). Theses concentrations obtained in both vessels are very close, thereby showing that the vessel size and the different agitators have no effect on the reaction performance. Consequently, it is supposed the difference of shape or size of the two different reactors has a small impact on reaction rates, and thereby makes it possible to directly compare the reaction performance in the reactor.

2.4.3. Importance of temperature monitoring

In order to quantify the difference in temperature measurements using different types of probes two experiments have been conducted. The first compares the temperature measured within the reaction medium during an esterification reaction using and optic fiber probe (OF) and the temperature measured by an infrared sensor (IR) at the bottom wall of the vessel. Table 1 shows that the temperatures measured by OF are equal to the set point temperature and are approximately 10–20 °C greater than those measured by IR. The second experiment aims at assessing the response time of the OF and IR probes when heating water in the microwave reactor; the results are given in Table 2. In the first step of this experiment, the power is fixed at 100 W for 90 s and the water temperature from 18 °C to 45 °C according to OF measurement and to 41 °C according to IR measurement; the difference in measurements is 4 °C. When the water is heated again for 30 s at a power of 300 W, the temperature increases from 37 °C to 64 °C

according to OF measurement but still reads as 37 °C with the IR sensor. At least half a minute is necessary for the IR sensor to detect the increase and temperature and the IR sensor finally measures 57 °C. After 30 more seconds of microwave irradiation, the temperature increases from 61 °C to 82 °C according to OF measurement but still reads as 60 °C with the IR sensor. The response time of the IR sensor is therefore somewhere between 30 and 60 s. Indeed, this time is incompatible with the very fast heating rates provided by microwaves (see Table 1). Finally, temperature measurements in the reactor using the optical fiber and the IR sensor are compared to the value given by a mercury thermometer inserted in the reactor without microwave irradiation. The results show that the IR always measures lower temperatures than OF and mercury thermometers. This confirms that the OF provides correct temperature measurements.

The reason for this difference is due to nature of the measurement. Indeed, the IR sensor measures the external surface temperature of the reaction vessel that is made of borosilicate glass, which has a low thermal conductivity ($1.2 \, W \, m^{-1} \, K^{-1}$). This thermal inertia has been already been described in the literature in a study on the influence of reactor material on the synthesis of ionic liquids using microwaves (Obermayer and Kappe, 2010). Other authors show that the temperatures measured with OF probes are higher than those measured with the IR sensor (Herrero et al., 2008). The difference between the two types of measurements is also recognized by the microwave reactor manufacturer CEM who recommends the use of OF probes.

In some recent works focused on transesterification and esterification reactions under microwave irradiation, the temperature is controlled with an infrared sensor (Azcan and Danisman, 2008; Leadbeater and Stencel, 2006; Zu et al., 2009) or at the outlet of the reactor with a mercury thermometer (Lertsathapornsuk et al., 2008); only one study has used an OF probe (Barnard et al., 2007). The rest of the cited studies do not however specify how the temperature was measured. As a result, it is highly probable that many of the temperatures indicated in these literature studies were lower than the real temperature in the reaction medium. A consequence of inaccurate temperature measurement is the non-detection of superheating of the reaction media, which is purely thermal phenomena, not a non-thermal microwave effect. In order to ensure the accuracy of temperature measurement and the absence of superheating in the current experiments, temperature is monitored with an OF probe.

3. Results and discussion

3.1. Transesterification: conventional versus microwave reactor

In a previous study, it was found that the kinetics of sunflower transesterification at low temperatures is governed by three regimes: a mass-transfer limited regime, an irreversible pseudo-homogenous regime and a reversible pseudo-homogenous regime (Stamenkovic et al., 2008). In the current study, the regime is assumed to be a reversible pseudo-homogenous regime since the temperatures are higher and the agitation is strong, and thereby takes into account the reaction in both directions.

Table 2

Repeatability study for transesterification reaction performed at $T = 60$ °C for 8 min: statistics of the mass fraction of methyl esters (EM), fatty acids (FA), monoglycerides (MG), diglycerides (DG) and triglycerides (TG).

						Standard deviation (%)	Interval of confidence (%)	Average (%)
%EM	91.8	91.8	90.1	90.9	92.1	0.84	1.0	91.3
%FA	2.1	2.4	3.4	2.3	2.6	0.50	0.6	2.6
%MG	2.4	2.4	2.4	2.7	2.3	0.17	0.2	2.4
%DG	2.1	1.9	1.9	2.1	1.5	0.25	0.3	1.9
%TG	1.6	1.6	2.3	2.0	1.5	0.31	0.4	1.8

The global equation is:

$$TG + 3A \underset{k_2}{\overset{k_1}{\rightleftarrows}} 3E + GL \tag{3.1}$$

During the reaction, the reaction rate is written as:

$$r = -\frac{d[TG]}{dt} = [TG]_0(1 - X) - k_2[TG]_0 3X \tag{3.2}$$

$$\frac{dX}{dt} = k_1(1 - X) - k_2(3X) \tag{3.3}$$

$$\frac{dX}{dt} + (k_1 + 3k_2)X - k_1 = 0 \tag{3.4}$$

The solution of this differential equation is:

$$X = Ke^{-(k_1 + 3k_2)t} + \frac{k_1}{k_1 + 3k_2} \tag{3.5}$$

At the initial time $t = 0$, X is equal to 0, therefore:

$$K = \left(-\frac{k_1}{k_1 + 3k_2}\right) \tag{3.6}$$

The expression of X is then:

$$X = \frac{k_1}{k_1 + 3k_2}(1 - e^{-(k_1 + 3k_2)t}) \tag{3.7}$$

Gas chromatography gives access to the molar fraction x of methyl esters in the media. The quantity of methyl esters in moles E is therefore assumed to be:

$$E = 3[TG]_0 x \tag{3.8}$$

The experimental data is fitted with the equation:

$$E = a(1 - e^{bt}) \tag{3.9}$$

The coefficients are determined by identification:

$$\begin{aligned} -k_1 &= \left(\frac{ab}{3[TG]_0}\right) \\ -k_2 &= \frac{b}{3} - \frac{ab}{9[TG]_0} \end{aligned} \tag{3.10}$$

The experimental data and the corresponding models are presented in Fig. 2. Model and experimental data show good agreement. Mass fractions of esters increase with higher temperatures.

The kinetic constants, the pre-exponential factor and the activation energy have been determined from the data and are presented in Table 3. The minimum and maximum values given for coefficients b and c have been estimated with the Curve Fitting Tool in Matlab (R2011b). This tool uses a nonlinear least-squares method (*lsqcurvefit* function) which consists in minimizing the square of the difference between $E = a(1 - e^{bt})$ and E obtained in experiments. Interval of confidence C is then calculated by *confint* function, given by:

$$C = b \pm t\sqrt{S} \tag{3.11}$$

where b contains the coefficients of the fit, t is the critical t value of the Student t-distribution with a confidence level of 95% at a degree of freedom equals to $n - p$ (where n is the number of experiments and p is the number of coefficients). S is a vector of diagonal elements of covariance matrix equal to $(X^TX)^{-1}s^2$, where X is the Jacobian of the fitted values and s^2 the mean squared error. The minimum and maximum values of kinetic constants ha then been deduced from these values respecting error propagation rules:

$$s(k_1)^2 = \left(\frac{1}{3[TG]_0}\right)^2 s(ab)^2 \tag{3.12}$$

$$s(ab)^2 = (ab)^2\left[\left(\frac{s(a)}{a}\right)^2 + \left(\frac{s(b)}{b}\right)^2 + 2\mathrm{cov}(a,b)\right] \tag{3.13}$$

Table 3
Difference of temperature measured by IR or OF for 80 g of water in the 100 mL vessel heated at fixed power for 90 and 30 s. Magnetic agitation speed is 600 rpm. Temperatures are measured simultaneously by IR, OF and by a mercury thermometer (T_{Hg}).

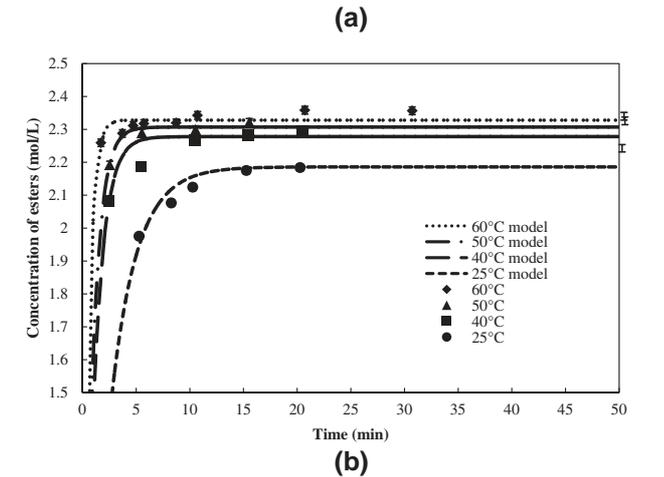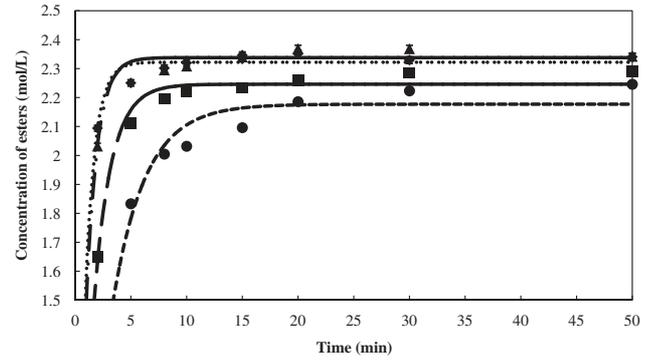| $P = 100$ W, $t = 90$ s, T_0 (°C) = 18 | | |
T_{IR} (°C)	T_{OF} (°C)	ΔT (°C)
41	45	4
$P = 300$ W, $t = 30$ s, T_0 (°C) = 37		
T_{IR} (°C)	T_{OF} (°C)	ΔT (°C)
37	64	10
After 30 s without irradiation		
T_{IR} (°C)	T_{OF} (°C)	ΔT (°C)
57	61	4
$P = 300$ W, $t = 30$ s, T_0 (°C) = 58		
T_{IR} (°C)	T_{OF} (°C)	ΔT (°C)
60	82	22
After cooling at the open air		
T_{IR} (°C)	T_{OF} (°C)	T_{Hg} (°C)
67	79	77
60	66	64
58	63	62
56	60	60
22	18	18

(a)

(b)

Fig. 2. Quantity of esters produced in the transesterification reaction as a function of time at different temperatures in the (a) conventionally heated and (b) microwave reactor.

$$\begin{aligned} s(k_2)^2 = {} & 2\left(-\frac{b}{9[TG]_0}\left(\frac{1}{3} - \frac{a}{9[TG]_0}\right)\right)^2 \mathrm{cov}(a,b) \\ & + \left(-\frac{b}{9[TG]_0}\right)^2 s(a)^2 + \left(\frac{1}{3} - \frac{a}{9[TG]_0}\right)^2 s(b)^2 \end{aligned} \tag{3.14}$$

The covariance cov(a,b) is the value of non-diagonal elements of the covariance matrix. The interval of confidence, I, of the kinetic constants is then given by the relation:

$$I = k \pm t \, s(k) \tag{3.15}$$

The method for the determination of interval of confidence of regression coefficients has been used for the calculation of activation energy with the relation ln $k = A - Ea/RT$), where A and Ea/R the coefficients of the fit between ln k and $1/T$ values, keeping the same method as for determination of intervals of confidence of the kinetic constants.

Models and experimental data are compared in Fig. 2. Corresponding parameters are given in Table 4. The differences in the kinetics obtained in the microwave reactor and the conventionally heated reactor are shown in Fig. 3. From these results, the following observations are made:

- Considering the intervals of confidence, the activation energies are close in both reactor types, with mean values of Ea_1 equal to 37.1 kJ/mol in microwave reactor compared with 31.6 kJ/mol in the conventionally heated reactor, and 17.9 kJ/mol in microwave reactor compared with 9.7 kJ/mol for Ea_2. The confidence level of 95% of Ea_2 gives negative values. To respect physical considerations by obtaining only positive values, t value has been reduced, corresponding to a confidence level between 80% and 90%.
- The pre-exponential factors are in the same range for both systems with values in the range 10^2–10^8 L/mol/min for A_1 and in the range 10^{-4}–10^2 L/mol/min for A_2.
- The average values of the kinetic constants are slightly higher in the microwave reactor, however the intervals of confidence of these constants shown in Fig. 3 suggest that there is little difference between the two reactor types.

These results can be compared with those found in the literature in conventionally heated reactors in the same temperatures conditions as present with a molar ratio of methanol to oil of 6 and a mass fraction of KOH of 1%. Darnoko and Cheryan (2000) calculated an activation energy of 61.4 kJ/mol with palm oil and a constant speed provided by a magnetic stirrer and Stamenkovic et al. (2008) found a value of 53.5 kJ/mol with sunflower oil at a constant speed of 200 rpm.

3.2. Esterification: conventional versus microwave reactor

The model used is a pseudo-homogeneous second-order model.

$$\frac{dE}{dt} = k \cdot FFA^2 \tag{3.16}$$

$$\frac{dE}{dt} = FFA_0 \cdot \frac{dX}{dt} = k \cdot (FFA_0 \cdot (1 - X)^2) \tag{3.17}$$

$$\frac{dX}{(1 - X)^2} = k \cdot FFA_0 \cdot dt \tag{3.18}$$

The integration between 0 and X and 0 and t gives:

$$\frac{1}{1 - X} = k \cdot FFA_0 \cdot t + 1 \tag{3.19}$$

The experimental data and the corresponding models are presented the Fig. 4. Model and experimental data show good agreements. Conversion increases with higher temperatures.

The kinetic constants, the pre-exponential factor and the activation energy have been determined and presented in Table 5. The intervals of confidence have been determined with a method

Table 4

Comparisons of model coefficients, kinetic constants, activation energies and pre-exponential factors obtained at different temperatures in the microwave and conventionally heated reactor for the transesterification reaction. These values are given in bold and are associated with an interval of confidence that is given in italics.

Microwave heating				
T (°C)	25	40	50	60
b (L/mol/min)	−0.422	−0.979	−1.183	−2.038
Min value/max value	−0.507/−0.337	−1.235/−0.724	−1.320/−1.046	−2.534/−1.542
a (mol/L)	2.186	2.278	2.307	2.328
Min value/max value	2.136/2.235	2.224/2.333	2.291/2.324	2.307/2.350
R^2	0.9983	0.9977	0.9998	0.9992
k_1 (L/mol/min)	**0.376**	**0.909**	**1.112**	**1.933**
Min value/max value	0.291/0.460	0.650/1.168	0.975/1.249	1.444/2.421
k_2 (L/mol/min)	**0.015**	**0.024**	**0.024**	**0.035**
Min value/max value	0.011/0.020	0.014/0.033	0.020/0.028	0.025/0.046
Conventional heating				
T (°C)	25	40	50	60
b (L/mol/min)	−0.3415	−0.646	−1.017	−1.149
Min value/max value	−0.416/−0.267	−0.713/−0.579	−1.134/−0.900	−1.312/−0.987
a (mol/L)	2.177	2.246	2.338	2.322
Min value/max value	2.107/2.247	2.213/2.278	2.310/2.365	2.295/2.349
R^2	0.9948	0.9982	0.999	0.9987
k_1 (L/mol/min)	**0.302**	**0.590**	**0.969**	**1.087**
Min value/max value	0.237/0.368	0.529/0.652	0.852/1.085	0.928/1.245
k_2 (L/mol/min)	**0.013**	**0.018**	**0.016**	**0.021**
Min value/max value	0.009/0.017	0.015/0.022	0.012/0.020	0.016/0.026

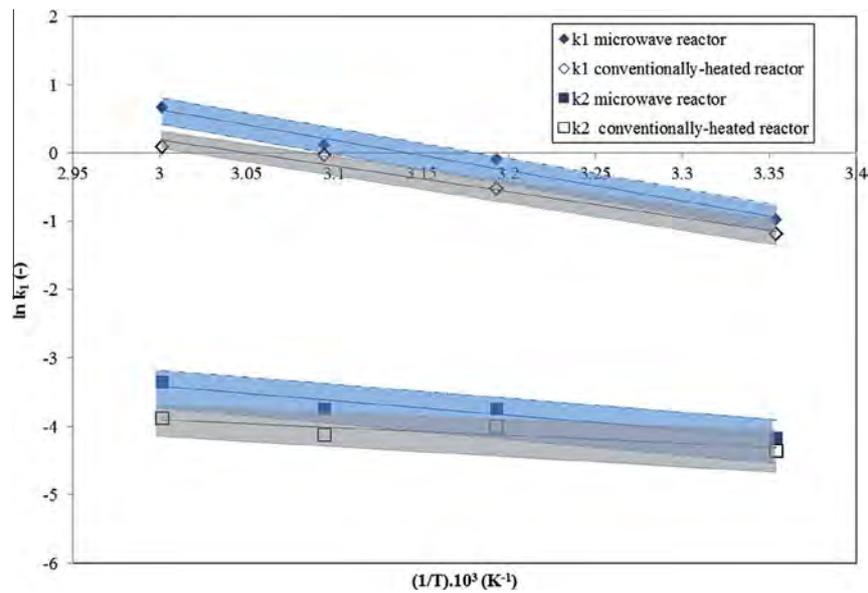|	Microwave heating		Conventional heating	
Ea_1 (kJ/mol)	**37.1**	R^2	**31.6**	R^2
Min value/max value	20.1/54.2	0.978	14.6/48.7	0.970
A_1 (L/mol/min)	**1.3×10^6**		**1.1×10^5**	
Min value/max value	1.9×10^3/8.2×10^8		1.7×10^2/7.2×10^7	
Ea_2 (kJ/mol)	**17.9**	0.886	**9.7**	0.748
Min value/max value	2.2/33.5		0/19.4	
A_2 (L/mol/min)	**2.1×10^1**		**6.7×10^{-1}**	
Min value/max value	5.5×10^{-2}/7.9×10^3		9.8×10^{-4}/4.6×10^2	

Fig. 3. Comparison of ln k as a function of the inverse of temperature in conventionally heated and microwave reactors for the transesterification reaction with the limits of intervals of confidence denoted by (- -) for the microwave reactor and (…) for the conventionally heated reactor. Corresponding zones are represented with a blue surface for results obtained in microwave, and in grey for results obtained in batch reactor. The intersection of the zones is darker. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
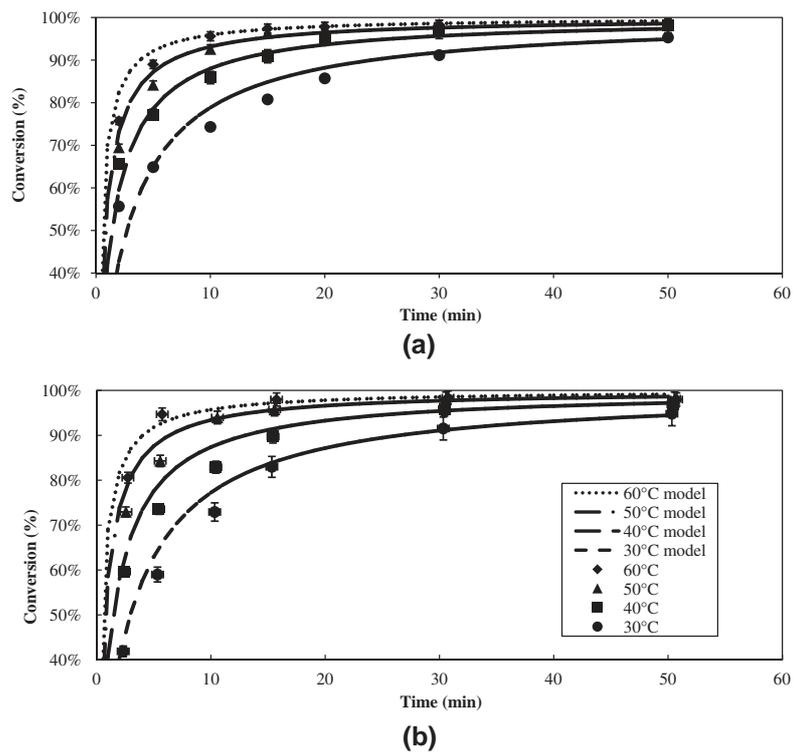

Fig. 4. Conversion as a function of time at different temperatures in the conventionally heated (a) and microwave reactor (b).

analogous to that used in the previous part, with the following regression function:

$$\frac{1}{1-X} = a \cdot t + 1 \quad \text{with } a = \text{k} \cdot \text{FFA}_0. \tag{3.20}$$

The differences in the kinetics between the microwave reactor and the conventionally heated reactor are shown in the Fig. 5.

The remarks pertaining to the results presented in Table 5 are very similar to those made for the transesterification reaction.

- The activation energies are approximately the same considering the intervals of confidence with an average value of 45.4 kJ/mol in the microwave reactor compared with 56.1 kJ/mol in the conventionally heated reactor.
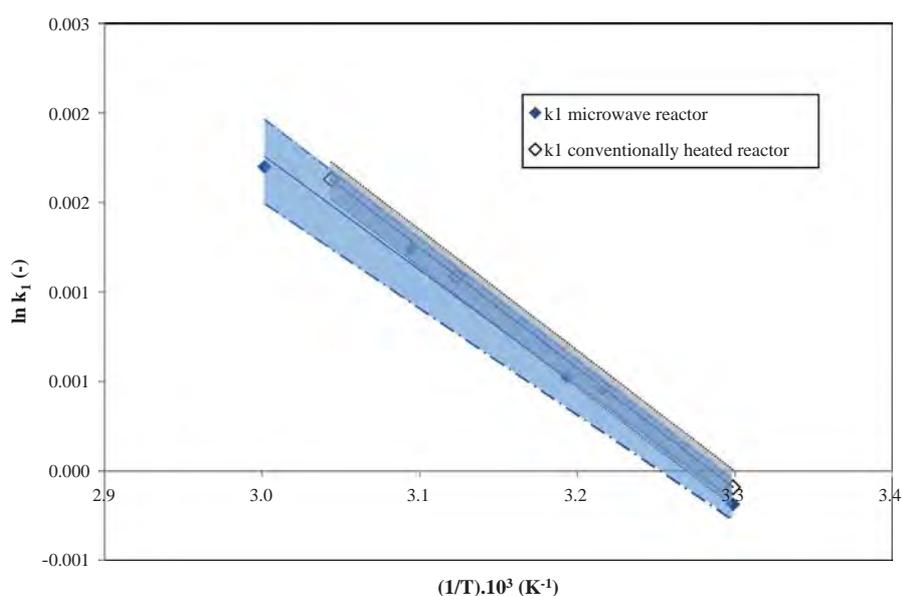
Fig. 5. Comparison of ln(k) as a function of the inverse of temperature in the conventionally heated and microwave reactors for the esterification reaction with the intervals of confidence denoted by (- -) for the microwave reactor and (…) for the conventionally heated reactor. Results relative to microwave are represented in blue. Corresponding zones are represented with a blue surface for results obtained in microwave, and in grey for results obtained in batch reactor. The intersection of the zones is darker. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 5
Comparisons of model coefficients, kinetic constants, activation energies and pre-exponential factors obtained at different temperatures in the microwave and conventionally heated reactor for the esterification reaction. These values are given in bold and are associated with an interval of confidence that is given in italics.

Microwave heating				
T (°C)	30	40	50	60
a (L/mol/min)	0.339	0.691	1.413	2.236
Min value/max value	*0.305/0.374*	*0.571/0.812*	*1.216/1.610*	*1.603/2.868*
R^2	0.985	0.960	0.978	0.914
k_1 **(L/mol/min)**	**0.830**	**1.691**	**3.457**	**5.471**
Min value/max value	*0.739/0.921*	*1.374/2.009*	*3.011/3.903*	*4.038/6.904*
Conventional heating				
T (°C)	30	37.8	47	55.4
a (L/mol/min)	0.373	0.654	1.212	1.872
Min value/max value	*0.332/0.414*	*0.5966/0.711*	*1.076/1.348*	*2.086/2.299*
R^2	0.972	0.990	0.992	0.975
k_1 **(L/mol/min)**	**0.913**	**1.600**	**2.966**	**5.104**
Min value/max value	*0.813/1.013*	*1.459/1.741*	*2.632/3.299*	*4.582/5.626*

	Microwave heating		Conventional heating	
Ea$_1$ (kJ/mol)	**45.4**	R^2	**56.1**	R^2
Min value/max value	*31.8/58.9*	0.991	*55.7/56.4*	1
A$_1$ (L/mol/min)	**7.0 × 10^7**		**4.2 × 10^9**	
Min value/max value	*4.1 × 10^5/1.2 × 10^{10}*		*3.7 × 10^9/4.8 × 10^9*	

- Considering the intervals of confidence, the pre-exponential factors are also approximately the same for both reactors, with a mean value of 7.0×10^7 L/mol/min in the microwave reactor compared with 4.2×10^9 L/mol/min in the conventionally heated reactor.

Fig. 5 shows that considering the intervals of confidence, the kinetic constants are more or less the same under microwave irradiation or in the conventionally heated reactor.

4. Conclusions

In similar operating conditions, with accurate temperature monitoring, kinetics of transesterification and esterification reactions have been compared with conventional or microwave-heating. Similar results support the belief that non-thermal microwave effects do not exist as claimed in previous reports. It also suggests the enhancement of transesterification and esterification reactions observed in previous studies may be an artifact of poor temperature measurements, underestimated using infrared sensors, and therefore results in higher reaction conversions since the real temperature is higher and possibly superior to boiling points due to the superheating of reactive media. Nevertheless, microwave thermal effects reduce heating and therefore process times .

References

Albright, P.S., Gosting, L.J., 1946. Dielectric constants of the methanol–water system from 5 to 55°. J. Am. Chem. Soc. 68, 1061–1063.

Azcan, N., Danisman, A., 2008. Microwave assisted transesterification of rapeseed oil. Fuel 87, 1781–1788.

Baig, R.B.N., Varma, R.S., 2012. Alternative energy input: mechanochemical, microwave and ultrasound-assisted organic synthesis. Chem. Soc. Rev. 41, 1559.

Banerjee, A., Chakraborty, R., 2009. Parametric sensitivity in transesterification of waste cooking oil for biodiesel production – a review. Resour. Conserv. Recycl. 53, 490–497.

Barnard, T.M., Leadbeater, N.E., Boucher, M.B., Stencel, L.M., Wilhite, B.A., 2007. Continuous-flow preparation of biodiesel using microwave heating. Energy Fuels 21, 1777–1781.

Cintas, P., Mantegna, S., Gaudino, E.C., Cravotto, G., 2010. A new pilot flow reactor for high-intensity ultrasound irradiation. Application to the synthesis of biodiesel. Ultrason. Sonochem. 17, 985–989.

Darnoko, D., Cheryan, M., 2000. Kinetics of palm oil transesterification in a batch reactor. J. Am. Oil Chem. Soc. 77, 1263–1267.

Duz, M.Z., Saydut, A., Ozturk, G., 2011. Alkali catalyzed transesterification of safflower seed oil assisted by microwave irradiation. Fuel Process. Technol. 92, 308–313.

Enweremadu, C.C., Mbarawa, M.M., 2009. Technical aspects of production and analysis of biodiesel from used cooking oil – a review. Renew. Sustainable Energy Rev. 13, 2205–2224.

Fukuda, H., Kondo, A., Noda, H., 2001. Biodiesel fuel production by transesterification of oils. J. Biosci. Bioeng. 92, 405–416.

Grant, E., Halstead, B.J., 1998. Dielectric parameters relevant to microwave dielectric heating. Chem. Soc. Rev. 27, 213–224.

Gui, M.M., Lee, K.T., Bhatia, S., 2008. Feasibility of edible oil vs. non-edible oil vs. waste edible oil as biodiesel feedstock. Energy 33, 1646–1653.

Herrero, M.A., Kremsner, J.M., Kappe, C.O., 2008. Nonthermal microwave effects revisited: on the importance of internal temperature monitoring and agitation in microwave chemistry. J. Org. Chem. 73, 36–47.

Jaliliannosrati, H., Amin, N.A.S., Talebian-Kiakalaieh, A., Noshadi, I., 2013. Microwave assisted biodiesel production from Jatropha curcas L. seed by two-step in situ process: optimization using response surface methodology. Bioresour. Technol. 136, 565–573.

Kanitkar, A., Balasubramanian, S., Lima, M., Boldor, D., 2011. A critical comparison of methyl and ethyl esters production from soybean and rice bran oil in the presence of microwaves. Bioresour. Technol. 102, 7896–7902.

Kappe, C.O., 2013. How to measure reaction temperature in microwave-heated transformations. Chem. Soc. Rev. 42, 4977.

Kappe, C.O., Pieber, B., Dallinger, D., 2013. Microwave effects in organic synthesis: myth or reality? Angew. Chem. Int. Ed. 52, 1088–1094.

Kappe, C.O., Stadler, A., Dallinger, D., 2012. Microwave theory. In: Microwaves in Organic and Medicinal Chemistry, third ed. Wiley-VCH, Weinheim, pp. 9–39.

Leadbeater, N.E., Stencel, L.M., 2006. Fast, easy preparation of biodiesel using microwave heating. Energy Fuels 20, 2281–2283.

Lertsathapornsuk, V., Pairintra, R., Aryusuk, K., Krisnangkura, K., 2008. Microwave assisted in continuous biodiesel production from waste frying palm oil and its performance in a 100 kW diesel generator. Fuel Process. Technol. 89, 1330–1336.

Leung, D.Y.C., Wu, X., Leung, M.K.H., 2010. A review on biodiesel production using catalyzed transesterification. Appl. Energy 87, 1083–1095.

Lidström, P., Tierney, J., Wathey, B., Westman, J., 2001. Microwave assisted organic synthesis – a review. Tetrahedron 57, 9225–9283.

Mazubert, A., Poux, M., Aubin, J., 2013. Intensified processes for FAME production from waste cooking oil: a technological review. Chem. Eng. J. 233, 201–223.

Metaxas, A.C., Meredith, R.J., 1983. Industrial Microwave Heating. IET.

Mingos, D.M.P., Baghurst, D.R., 1991. Tilden lecture. Applications of microwave dielectric heating effects to synthetic problems in chemistry. Chem. Soc. Rev. 20, 1.

Obermayer, D., Kappe, C.O., 2010. On the importance of simultaneous infrared/fiber-optic temperature monitoring in the microwave-assisted synthesis of ionic liquids. Org. Biomol. Chem. 8, 114.

Perreux, L., Loupy, A., Petit, A., 2013. Nonthermal effects of microwaves in organic synthesis. In: Microwaves in Organic Synthesis, third ed. Wiley-VCH, Weinheim, pp. 127–208.

Santacesaria, E., Tesser, R., Di Serio, M., Guida, M., Gaetano, D., Garcia Agreda, A., 2007. Kinetics and mass transfer of free fatty acids esterification with methanol in a tubular packed bed reactor: a key pretreatment in biodiesel production. Ind. Eng. Chem. Res. 46, 5113–5121.

Stamenkovic, O.S., Todorovic, Z.B., Lazic, M.L., Veljkovic, V.B., Skala, D.U., 2008. Kinetics of sunflower oil methanolysis at low temperatures. Bioresour. Technol. 99, 1131–1140.

Tur, E., Onal-Ulusoy, B., Akdogan, E., Mutlu, M., 2012. Surface modification of polyethersulfone membrane to improve its hydrophobic characteristics for waste frying oil filtration: radio frequency plasma treatment. J. Appl. Polym. Sci. 123, 3402–3411.

Zhang, Y., Dube, M.A., McLean, D.D., Kates, M., 2003. Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis. Bioresour. Technol. 90, 229–240.

Zu, Y., Zhang, S., Fu, Y., Liu, W., Liu, Z., Luo, M., Efferth, T., 2009. Rapid microwave-assisted transesterification for the preparation of fatty acid methyl esters from the oil of yellow horn (Xanthoceras sorbifolia Bunge). Eur. Food Res. Technol. 229, 43–49.