



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.

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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.

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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

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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, cavitation 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; Míngos 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.

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (1.1)$$

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:

$$d_p = \frac{\lambda_0 \sqrt{\epsilon'}}{2\pi\epsilon''} \quad \text{where the free space wavelength is} \quad \lambda_0 = \frac{c_0}{f} \quad (1.2)$$

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:

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

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

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