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Continuous flow-microwave reactor: Where are we?

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ABSTRACT

This article presents the different microwave continuous reactors existing, which are reported in literature to carry out chemical synthesis with a more efficient way. It shows how the methods and tools of chemical engineering can be useful and necessary to define, characterize and optimize the microwave reactors. This review scans continuous microwave reactors, by describing the different types of microwave technologies used (multimode, single-mode, coaxial or guided transmission ...). It then focuses on the various existing reactor geometries and on the control of the electromagnetic field homogeneity. The problem of temperature measurement and overall instrumentation is also addressed (input power, reflected power, continuous adaptation ...).

This review scans the most efficient microwave continuous flow reactors existing in the literature and highlights how the microwave technology is used as well as chemical engineering tools. It points out the reactors geometries, the control of the electromagnetic field and the measurement of the physical parameters (Temperature, microwave power, etc.).

Finally, the scale-up of continuous-flow microwave reactors is examined through the existing lab-scale and semi industrial pilot plants described in literature.

1. Introduction: towards continuous flow process

Since the application of microwaves to chemistry launched by Gedye [1] and Guiguere [2] in 1986, many researchers studied the effects of microwave heating on numerous chemical reactions in batch systems. The number of articles published is very impressive: more than 43,750 publications on MW-assisted reactions between 1986 and 2016! (Source Thomson Reuters, based on Scopus, keywords search on ‘microwave and reaction’). The enthusiasm of the scientists for the microwave systems remains always strong especially in organic synthesis, extraction, polymer, biomass area. (respectively, 19,700; 15,500; 10,800; 1050 publications).

The main benefits obtained in chemistry consist in an increase the reaction rate, the reduction of the side-products, the improvement of the product purity compared to conventional heating. Chemistry under microwave enables the reduction of the solvent quantity, the use of green solvents as water and sometimes synthesis under dry media conditions can be carried out. These advantages have been listed by many authors [3–5] and microwave processes are known now as environmentally friendly process and which enables energy saving.

The major limit of microwaves is the penetration depth which is only a few centimetres in usual solvents and chemical environments with favourable properties that excludes the use of high-volume reactors.

Coupling microwave heating and continuous flow technology eliminates the main drawbacks of microwaves and creates a very promising way to produce high value added chemicals or key pharmaceutical intermediates since unlike the batch, the continuous flow has been demonstrated to facilitate process intensification and contribute to a safe, efficient and sustainable production [1,4].

The first systems coupling microwave and continuous flow were studied in the 1980’s and concerned the polymer heating and the solid drying [6,7]. In chemical synthesis, about 780 papers on the continuous reactors have been published since 30 years, 286 are in the field of microwave flow chemistry and 220 deals with microwave continuous reactor which described systems with a large range of size from some millimetres or less to some centimetres. The continuous flow under microwaves appears in 1990’s at the same time than flow chemistry. The reactor consisted

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in a Teflon coil placed in a commercial microwave oven. It has been used for several organic syntheses, including preparative-scale samples, but the quantities remain small because of the limited volume of the reactor (10 mL°).

In most papers published, the emphasis is on the chemical reactions and the part dedicated to the reactor consists generally in a brief description of the systems. Among the 43,750 articles, only 430 are identified in the area of chemical engineering that represents less than 1% of the papers! The percentage falls dramatically to 0,2% when using the key-words microwave; chemical reaction and chemical engineering.

The main objective of this work is to present a state of the art in the area of the continuous microwave systems, to provide a critical analysis, to highlight the process parameters and to propose some tools of chemical engineering useful for the development of more efficient microwave processes.

2. About energy and heating

Light that interacts with matter can be reflected, absorbed or transmitted, wherever absorption occurs, heat energy is generated. As light, microwaves are electromagnetic radiations (EMR), which are synchronized oscillations of the electric and magnetic fields propagating at the speed of light through a vacuum. The oscillations of the two fields are perpendicular to each other and perpendicular to the direction of energy and wave propagation, forming a transverse wave.

The energy of the wave is stored in the electric and magnetic fields. In the quantum theory of electromagnetism, electromagnetic microwave radiations consist of photons, the elementary particles responsible for all electromagnetic interactions.

The quantum energy of microwave photons is in the range 0.000001 to 0.001 eV (300 MHz to 300 GHz) which is in the range of energies separating the quantum states of molecular rotation and torsion. Since the quantum energies are a million times lower than those of X-rays, they cannot produce ionization and the characteristic types of radiation damage associated with ionizing radiation. They also cannot play a role in chemical bonding where quantum energy is at least a thousand times bigger.

Microwave heating is based on the electromagnetic energy conversion which requires the existence of a direct interaction between the bulk and the microwaves and a sufficient penetration depth. For a given frequency, this interaction exists only if the dielectric properties of the bulk are suitable. The latter are very sensitive to any change in composition or in temperature. The energy conversion can be due to several mechanisms such as dipolar polarization, ionic conduction, Wagner effect . . . In the case of dielectric system heating, dipolar polarization and ionic conduction are the most frequently encountered phenomena. Even without chemical reaction, the specificity of microwave heating, results from the temperature dependence of dielectric properties (Fig. 1). In many cases, the complex dielectric permittivity depends on the temperature and the dynamic behaviour of microwave heating is then governed by this thermal change [8].

It is important to specify that for continuous flow applications, the dielectric and thermal properties, in the reaction volume are both spatially and temporally variable. For example, Fig. 2 shows the behaviour of dielectric properties during the reaction of decomposition in isothermal mode (89 °C) of AIBN [2,2′-Azobis(2-methylproprionitrile)] in TMSN [Tetramethylsuccinonitrile] (Scheme 1) [9].

On top of that variability of the properties is not the only key factor, for a good coupling of the electromagnetic field with the medium. The value itself of the dielectric properties is important, since the electric field propagation and amplitude depend respectively on the real and imaginary part of the dielectric

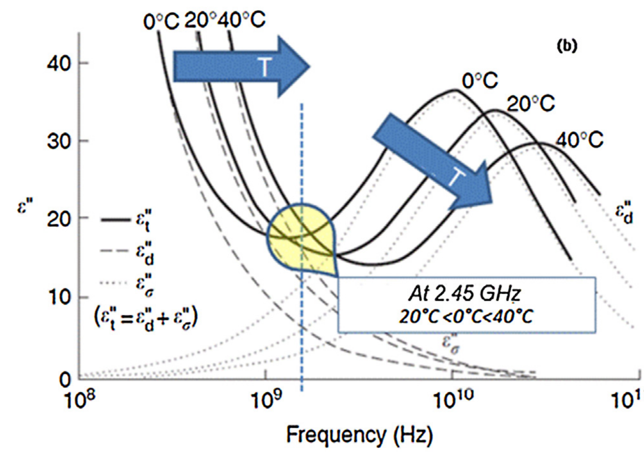

Fig. 1. Frequency and temperature dependence of dielectric properties of NaX zeolites [8].

permittivity. For example, the higher the real part of the dielectric permittivity is, the more important reflexions are. For liquid medium with a priori favourable properties, like water or ionic solvents, when the imaginary part is propitious for heating, important reflexions can dramatically decrease the electromagnetic field intensity and thereby the overall efficiency of the energy conversion. When dipolar polarization is the main phenomenon, dielectric heating involves unorganized movements at micro scale due to the inability of molecule clusters to move exactly with the electric field. This hysteresis phenomenon explains how the organised energy of electromagnetic field is transferred as Brownian movement into matter, many authors call this phenomenon **"**internal friction**"** [10]. The characteristic time scale of this conversion is some picoseconds [11], i.e. very fast compared to thermal diffusion which is around some seconds.

For those reasons, it is expected that a homogeneous electric field gives an isothermal medium, whereas for fast heating rates, classic thermal transfers need high thermal gradients at the system walls (Fig. 3). In fact, this absence of thermal boundary layer at the wall – sometimes called inversion of the thermal gradient compared with conventional heating (when the walls are colder than the bulk) – gives the ability to raise the heat source for fast homogeneous heating. At the opposite, inhomogeneous electromagnetic fields produce local high thermal gradients called **"**hot spots**"**.

Many surveys have shown that rapid heating and enhancements of chemical yields are achieved with microwaves [12–15]. In solid chemistry and in heterogeneous solid-liquid systems, many experiments led to significant differences in reaction rates obtained between conventional and microwave heating. If at least one of the components of a reaction mixture couples very strongly with microwaves, then it is possible to use that property to rapidly heat the reaction mixture and thereby obtain the final product more quickly and sometimes with a better yield. In the special case of heterogeneous reactions with solid phase or in general when dielectric properties increase with composition or temperature, the absorption rate of microwave energy also increases, hence thermal runaway can result; at the opposite when properties decrease the system is self-regulated. Consequently, controlling heating rate and electromagnetic field homogeneity are essential for both repeatability and industrial applications. Therefore, to achieve these objectives, one key step is the measurement of the dielectric properties and another is the modelling of the electromagnetic field.

For temperature and power control feedback, in a running process, one major problem results in the temperature