Microwaves and microreactors: Design challenges and remedies

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HIGHLIGHTS

- Microwave application to microsystems is explored from an electromagnetic viewpoint.
- Key electromagnetics concepts are introduced by means of simple demonstrations.
- Familiar, commonly applied microwave equipment cannot be applied satisfactorily.
- A novel, radically different reactor concept is proposed.
- Its numerical optimization is demonstrated.

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ABSTRACT

Although microwave enhanced chemistry has become an established research topic, a significant knowledge gap exists with respect to the electromagnetic interactions. This paper aims to address this gap, in particular regarding to small and microstructured processing systems. By means of relatively simple demonstrations, key electromagnetics aspects are highlighted, pointing out the restricted control over operating conditions in familiar microwave systems. In response to these limitations, a radically different approach is presented in the shape of the coaxial traveling microwave multichannel reactor concept. Numerical simulations show that this concept enables controlled and optimized microwave processing.

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1. Introduction

1.1. Microwaves and microreactors—A promising concept

A promising concept in the framework of process intensification is the combination of micro- or millistructured reactors with microwave fields. Small-structured reactors offer many advantages when compared to traditional systems [1–9]; they enable high heat and mass transfer rates and allow for a tight control on operating conditions. Furthermore, smaller volumes form an inherently safer processing environment for production of toxic or explosive chemicals because they reduce inventory and thereby hazard risks. Finally, smaller systems enable flexible, on-demand and decentralized processing.

On the chemistry side, chemical activation by microwave fields has been a widely researched topic for several decades [10–33], as there are a number of notable aspects to this unconventional form of energy. There are two undisputed inherent advantages to

microwave fields. First, electromagnetic energy is transmitted at the speed of light, which is effectively instantaneous on the time scales of chemical processing. This may improve process control due to the absence of thermal inertia and alleviate heat transfer limitations. Second, electromagnetic energy can be dissipated selectively, heating processes or activating reactions at locations only where this is desired, as opposed to thermal activation, which heats non-selectively; e.g. activation by microwave fields may permit a desired reaction on a hot electromagnetically dissipating catalytic site, while maintaining cooler bulk conditions to prevent unwanted side reactions.

Furthermore, there are some interesting but also controversial additional aspects to microwave activation of chemical reactions. Ever since the first investigations on the subject [34,35] unexpectedly high reactant conversions have been reported [14,36–40]; some studies even report acceleration factors in the order of several hundred times the conventionally activated case. Speculations have risen regarding the possibility of direct interactions of the microwave field with the reaction mechanism, i.e. not due to thermal activation caused by the generation of heat through electromagnetic dissipation, but alternative explanations have also

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been proposed. A number of studies point out that heat generation occurs non-uniformly in a microwave field [41–43]; it is argued that it is possible that temperature is monitored by a sensor that is placed in a relatively cold zone, so that the dominant temperature development, which drives the reaction, remains hidden from observation. Indeed, there are studies [44–46] that describe cases in which apparent microwave effects disappear under vigorous stirring. Another alternative explanation that is proposed implicates the heterogeneity of reactant mixtures and the interaction of the microwave field over an interface between aggregation states; studies by Dressen et al. [47,48] relate for a number of cases an apparent microwave effect to the heterogeneity of the reactant mixture. In particular, they report that the addition of a co-solvent coincides with the disappearance of microwave specific conversion rates.

Despite these efforts however, it has proven very hard to draw any definite conclusions on the interactions between microwaves and chemical reactions. The reason is that the exact processing conditions generally are unknown. As explained above, temperature may develop non-uniformly under microwave conditions, causing uncertainty with respect to this particular parameter. Although stirring in some cases can alleviate this, in other processes stirring is impossible, ineffective or undesired. Some examples in this respect are: packed beds [41,42], highly viscous polymerization systems [49], or continuous flow (milli)reactors. The set of relevant processing conditions is not limited to temperature though. Far more fundamental to the behavior of microwave enhanced processing systems are the actual electromagnetic interactions of the microwave field, since it is this field that supplies the energy to drive the process. More specifically, it is the electric field component of the microwave field that exerts forces on the electric charges in the molecules, thereby inducing movement of these molecules. For one thing, this movement is rapidly thermalized by Brownian interactions, which amounts to heat generation by electromagnetic dissipation. In addition to this though, it is the interaction of the microwave field with the molecules – whether through the exerted electric forces or through specific molecular movements – that is suspected of influencing chemical reaction rates via a yet unknown mechanism. It is therefore essential to know what the electromagnetic conditions are. As a matter of course, make and model of microwave equipment as well as the method of operation – either power or temperature control – are carefully and dutifully reported in relevant literature, but this does not translate into anything quantifiable on the field as it is acting on the process fluids. *Indeed the actual physical properties of the electromagnetic field in terms of field strength, field vector direction and polarization are never reported. Additionally, frequencies outside the 2.45 GHz ISM [50] band are hardly ever considered for lack of available equipment.*

This brings us to a final potentially important aspect of combining process activation by microwave fields with micro- and millistructured processing systems; the high degree of control over the process conditions in small scale processing systems would enable detailed investigation of the microwave-chemistry interactions. In order to reach this objective, it is necessary to integrate the microwave field applicator – the structure that supports and contains the field – into the processing system. This poses an interesting challenge, as it requires bridging a fundamental knowledge gap between the fields of chemical engineering and electromagnetics engineering. Although many chemistry experiments have been conducted in microwave equipment, the theory of electromagnetics and electromagnetic wave propagation is largely absent from publications in the research field of microwave-assisted chemistry.

The scope of this paper is twofold: (1) to begin to fill in the aforementioned knowledge gap and (2) to introduce a radically new approach of applying microwaves to micro- or millireactors.

In this context, the next three Sections 2–4 introduce a number of key concepts regarding wave propagation and electromagnetic fields. Our aim of this brief review on these topics is not to present the theory in detail, as many publications already exist on them, rather we would like to raise awareness of a number of important concepts pertaining to electromagnetism within the chemical engineering community. Section 5 introduces the new concept of Coaxial Traveling Microwave Reactor (TMR) and describes its advantages through numerical simulations.

2. Characteristics of electromagnetic interactions

Because of their relative novelty to process engineering, this section will illustrate some relevant properties of microwave fields as they are applied in heating applications. Microwave fields are electromagnetic waves; as such, they obey Maxwell's electromagnetic field equations,

$$-\nabla \times \mathbf{H} + \partial_t \varepsilon \mathbf{E} + \sigma \mathbf{E} = \mathbf{0}$$
$$\nabla \times \mathbf{E} + \partial_t \mu \mathbf{H} = \mathbf{0} \tag{1}$$

These equations describe the relation between the time-dependent electric field **E** and the time-dependent magnetic field **H**. The term $\sigma \mathbf{E}$ denotes the electric current density – conductivity multiplied by the electric field, which plays a role in conductive media such as metal walls, but is absent in vacuum or electrically insulating media. The properties of the medium that the electromagnetic wave propagates through are the electric permittivity ε and the magnetic permeability μ; in the context of microwave assisted chemistry, usually only the value of the former medium parameter is relevant, because typically only non-magnetic media are considered. Therefore, the parameter μ is fixed to the permeability of vacuum μ_0. The coupling between the electric and magnetic constituent fields results in a wave pattern interaction that transmits energy through space.

In many applications – including the context of this paper – the electromagnetic field under consideration is time-harmonic, i.e. its constituent fields have sinusoidal time dependence. As such, the fields are conveniently expressed as a space-dependent complex parameter multiplied by $e^{i2\pi ft}$; by using the exponential function in this manner, with complex argument, it expresses a function that is harmonic over time with frequency f. The electric and magnetic fields thus become $\mathbf{E}(x,y,z,t) = \mathbf{E}(x,y,z)e^{i2\pi ft}$ and $\mathbf{H}(x,y,z,t) = \mathbf{H}(x,y,z)e^{i2\pi ft}$. Substitution into Eq. (1) yields,

$$-\nabla \times \mathbf{H} + i2\pi f \varepsilon \mathbf{E} = \mathbf{0}$$
$$\nabla \times \mathbf{E} + i2\pi f \mu \mathbf{H} = \mathbf{0} \tag{2}$$

In this time-harmonic representation of Maxwell's electromagnetic field equations, the medium parameters ε and μ are complex valued parameters. In case the respective imaginary parts are non-zero these relate to dissipative medium properties. As commonly only non-magnetic materials are considered in microwave chemistry, the relevant medium property is the dielectric permittivity, which in the time-harmonic representation is denoted as $\varepsilon = \varepsilon_0(\varepsilon' - i\varepsilon'')$. In literature, often only the bracketed terms are reported as the dielectric medium properties. Since they express the dielectric permittivity of a medium relative to the vacuum permittivity, ε_0, the combined parameters, $\varepsilon' - i\varepsilon''$, are called *relative permittivity*. These relative permittivity parameters in general may depend on frequency and temperature, but in the context of chemical engineering dependence on the composition of solutions or of mixed media and progressing reaction coordinates need also be taken in consideration. Finally, regarding these parameters, it is remarked here that they, and in particular their spatial