Temperature Modeling for Reaction Development in Microwave-Assisted Chemistry

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Abstract — This paper addresses the problem of efficient control over microwave-assisted chemical reactions from a microwave engineering perspective. We report a precise reproduction of a lab-scale resonator-type reactor in a 3D model capable of monitoring electromagnetic and thermal processes. The reactant is represented by temperature-dependent complex permittivity, density, specific heat and thermal conductivity. Time-temperature histories of microwave heating of water are simulated and determined experimentally; the results are shown to be in a good agreement. A simple empirical model (also verified by measurements) is proposed to verify the effect of convection observed in the reactor. The developed principles can be used in the models of other reactors to help with key developments in microwave-assisted chemistry.

Index Terms — Convection, FDTD modeling, material parameters, microwave chemistry, temperature field.

I. Introduction

Microwave-assisted chemistry has recently emerged as a rapidly growing field benefiting from shorter reaction times, higher product yields, enhanced selectivity and other effects [1, 2]. Microwave heating is known to be a driving force behind these advantages, and numerous attempts have been made to evaluate and classify the effects of microwave irradiation. While it is commonly acknowledged that these effects are caused by heating *per se*, microwave heating occurs somewhat differently and is associated with heating rates conditioned by the loss factor of the processed ingredients, inverted temperature gradients, selective heating and some other effects [2].

Currently, the related lab studies are almost exclusively carried out on dedicated commercially available equipment, taking special care of convenience and safety of exposure of the reactants to the electromagnetic (EM) field. The microwave parts of those systems are, however, operational as "black boxes", keeping the details of interaction between the reactants and microwaves somewhat obscure, and the role played by the EM and thermal phenomena in microwave-assisted chemical processes not fully understood. Yet, in many situations, knowledge of temperature distribution and evolution in the reactant is vitally important: this information may help explain particular effects observed in microwave-assisted chemistry, which in turn may aid the design of new/modified reactions that improve the quality of the resulting product. This has led to a trend in which techniques to control the reactions are explored via trial-and-error experiments aiming to catch some correlation between the input parameters of the reactors and the output chemical characteristics of the products [2-4]. Such works may be laborious and effectively slow some principal developments in the field.

In other applications of microwave energy, such as materials processing and food technologies, one can observe an expanding use of multiphysics simulations helping to illuminate EM and thermal characteristics of the applicators and assist in designing efficient microwave systems [5-7]. However, the development and exploitation of adequate macroscopic models for the physics of microwave-assisted chemistry have not gained yet popularity: the related works are limited to either oversimplified/semi-empirical models [8], or one-way coupled procedures not accounting for temperature variation of material parameters [9], [10], or computational studies of fictional systems and randomly chosen reactants [4]. Yet, the development of new controllable and reproducible reaction routes could be significantly supported if the underlying EM and thermal processes in the systems are clarified and specified through sufficiently adequate computer simulation.

In this paper, we present an advanced two-way coupled 3D model capable of mimicking EM and thermal behavior of a resonator-type reactor designed for laboratory experiments with a small amount of the reactant. The latter is represented in the model by temperature-dependent electromagnetic and thermal materials parameters – dielectric constant ε', loss factor ε'', density ρ, specific heat c, and thermal conductivity k. Capabilities of the model are exhibited through computation of time evolution of 3D temperature fields; examples of simulation are shown for water in a cylindrical vial made of Pyrex glass. The modeling results are shown to be in good agreement with experimental data obtained by a fiber optic sensor at a series of points on the central axis of the vial. The analysis reveals the effect of convection on temperature patterns in a liquid reactant and suggests a framework of applicability of the EM-thermal models for process control in microwave-assisted chemistry.

II. Microwave System

A computer model has been developed for a reactor for laboratory-scale microwave-assisted processes in organic/inorganic chemistry, biochemistry, and other related disciplines. The system shown in Fig. 1 is designed, manufactured, and put on the market (under the name of *MiniFlow 200SS*) by

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(a) (b)

Fig. 1. General view of *MiniFlow 200SS* (a); internal view of the cavity with a metallic excitation structure and a Teflon cup for holding a vial (b).

SAIREM SAS, Neyron, France. The reactor consists of a cylindrical cavity (internal diameter 63 mm, height 46 mm) containing a concentrically positioned cylindrical Teflon cup (internal diameter 23 mm, height 67 mm) intended for holding the reactant in a cylindrical Pyrex vial (internal diameter 20 mm, height 75 mm). The resonator is fed via a coaxial cable (whose internal conductor is connected with a metal T-shaped structure inside the cavity) by a solid-state generator providing a robust control over the frequency of excitation (from 2.43 to 2.47 GHz with the step of 0.1 MHz) and the level of microwave power (from 0 to 200 W with the step of 1 W).

The reactant in the vial is put into the system through a cylindrical hole in the cavity's upper lid. Due to the large thickness of the lid (53 mm), this hole serves as a cutoff waveguide preventing leakage from the resonator. The opening on the top of the system is used for visual monitoring and as an entrance for a sensor measuring temperature of the reactant.

III. Model

The *MiniFlow 200SS* reactor has been precisely reproduced in a 3D parameterized model developed for the full-wave conformal FDTD simulator *QuickWave-3D* v. 2012 [11]. The layout of the components of the microwave system is shown in Fig. 2.

Computation of the temperature field in the reactant has been performed by an EM-thermal two-way coupled simulation designed in accordance with the iterative procedure [6, 7] based on the same FDTD mesh. Operations start from the EM portion whose solution is then used to solve the thermal part of the problem, i.e., to obtain the temperature field induced in the reactant after heating it for time $\Delta\tau_1$. At the next step, data on ε', ε'', k, ρ and c of the reactant are upgraded in each element of the spatial discretization in accordance with new values of temperature in these elements. Then the next iteration starts by solving the EM problem with new spatially evolved media parameters and $\Delta\tau_2$ as the heating time in the thermal solver.

The described procedure of multiphysics simulation was implemented using the core EM solver of the *QuickWave-3D* package and a dedicated unit for solving the heat transfer problem – the *QW Basic Heating Module*.

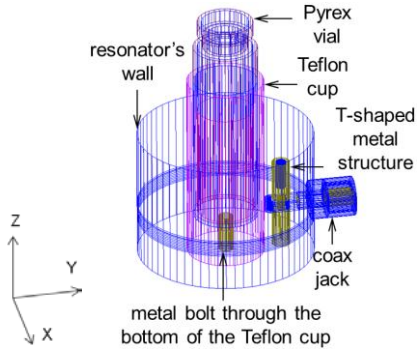

Fig. 2. 3D view of the *Mini Flow 200SS* reactor in the model.

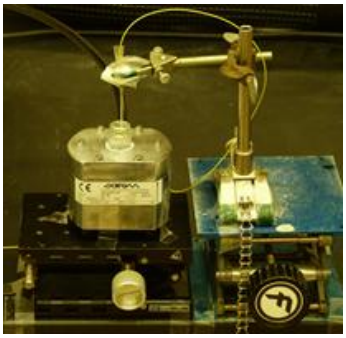

Fig. 3. Experimental setup: *MiniFlow 200SS* with a fiber optic sensor inside a glass capillary vertically inserted into the Pyrex vial.

Simulations were run on a Dell T-4700 workstation (64-bit Windows XP) with 16 GB RAM and two quad-core Intel Xeon 3.20 GHz processors.

To ensure high accuracy of the solution of the EM problem, the scenario was discretized with a non-uniform mesh (with max cell sizes of 1.2 mm in air and 0.4 mm in the reactant) making 1.4 to 1.7 million cells depending on the height of reactant. The simulations reach steady state after ~40,000 time steps, so a single EM computation takes 33 to 40 min. In the coupled problem, the heating time step was set at 3 s; each temperature computation took 24 to 30 min of CPU time.

IV. Simulation and Experiment

The process of microwave heating of water in *MiniFlow 200SS* was monitored experimentally (Fig. 3): a fiber optic cable (outer diameter 1.1 mm) was held (except its tip) inside a glass capillary (internal diameter 1.5 mm) and was able to move along the central axis of the vial to measure temperature dynamically at particular points inside the reactant.

While two examples comparing measured and simulated time-temperature characteristics (Fig. 4) generally confirm the adequacy of the developed model, the experiments reveal more homogeneous temperature fields than the ones determined via modeling (e.g., in Fig. 5) – they tend to be more spread towards the vial's walls. Since in the course of heating the measured temperatures never exceed the computed maxima, more uniform patterns can be explained by convection flows (not accounted for in the model) acting as an effective mechanism of averaging the reactant's temperature.

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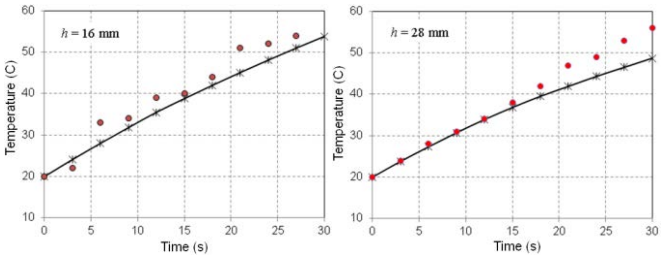

Fig. 4. Evolution of temperature in 15 ml sample of water (50 mm height) at different distances h from the bottom of the vial: values measured every 3 s (points) and computed characteristics (solid curve); microwave power 100 W, frequency 2.45 GHz.

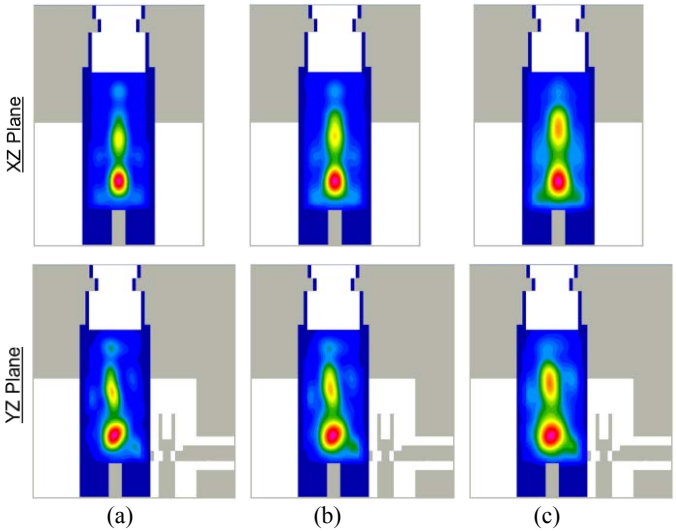

Fig. 5. Simulated relative temperature distributions in the vertical planes through the center of the reactor for 100 W and 50 mm height of water: T_{max} = 41.3°C after 6 s (a), T_{max} = 60.9°C after 15 s (b), and T_{max} = 80.2°C after 30 s (c).

To verify this hypothesis, we assume that convection is perfect (and thus the microwave-induced temperature field is uniform), the reactant is thermally insulated, and kinetic energy of the reactant can be ignored. Then, by conservation of energy, the increase of average temperature ΔT_a for the time interval Δt can be found from the formula:

$$\Delta T_a = \frac{P - P_r}{cm} \Delta t \qquad (1)$$

where m is the mass of the reactant, P is the incident power and P_r is the reflected power. Making one time-temperature characteristic by averaging data from 6 measurements (at h = 16 to 46 mm) and calculating the same characteristic from (1) using corresponding averaged experimental values for P_r, we compare the results graphically in Fig. 6.

The output of the empirical model turns out to be very close to the experimental data. The calculated characteristic predicts a faster increase in temperature because formula (1) ignores the heat conduction from water to the surrounding materials. Overall, the results in Fig. 6 confirm the hypothesis on an impact of convection flows on the distribution of microwave-induced temperature field in water; it is likely that the same homogenizing effect will be observed with other liquid reactants heated in the *MiniFlow 200SS* reactor.

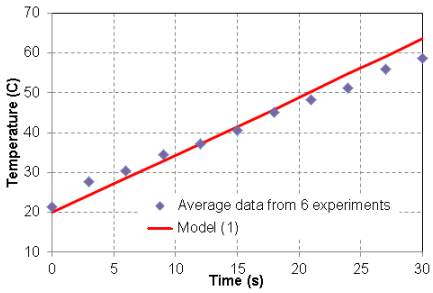

Fig. 6. Time-temperature characteristics obtained by the empirical model imitating the effect of convention (solid curve) and experimental data (points).

V. Conclusion

The presented model can be used for computational tests imitating microwave heating in the *MiniFlow 200SS* reactor. The only precondition for this "virtual experimentation" is availability of temperature-dependent EM and thermal material parameters of the reactant. While the developed coupled model may be unable to precisely capture the resulting temperature pattern disturbed by convection, it can be used to accurately compute upper temperature bounds. Following the presented principles, similar models can be built for other reactors, and may significantly facilitate the development of new controllable and reproducible reactions in many studies in microwave-assisted chemistry.

Acknowledgments

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