A SIMPLE MODEL OF MICROWAVE-INDUCED HEAT TRANSFER IN CYLINDRICAL REACTANTS WITH STRONG CONVECTION

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ABSTRACT. Microwave-assisted reactions have become very popular in preparative chemistry due to many advantages of internal "green" heating by microwave energy. In dedicated equipment, however, the microwave units operate as *black boxes* keeping the role of the thermal effects in microwave-assisted chemical processes somewhat obscure. To address this issue, in this paper, we propose a simple mathematical model for computing microwave-induced temperature in a three-media cylindrical structure representing a core element of a microwave reactor with the reactant assumed, in accordance with our earlier experimental observations, to be stirred by convection flows. The model determines the average temperature of the reactant for the known absorbed microwave power. The computed time-temperature characteristic of water heated in the resonator reactor *MiniFlow 200SS* is shown to be in excellent agreement with an experiment, while the CPU time of the computation is negligible.

INTRODUCTION

Microwave-assisted chemistry is a rapidly growing discipline utilizing microwaves as the means of enhancing and accelerating chemical reactions. Microwave heating is the phenomenon behind such advantages as accelerated reaction rate, higher chemical yield, lower energy use, and some other benefits observed in comparison with conventional heating methods [1, 2]. Currently, there exists a range of dedicated equipment for use in preparative chemistry; however, the development of new reaction routes remains difficult because of lack of data on the interaction between the reactants and corresponding microwave units [2, 3].

It appears that sufficiently adequate computer models could help clarify some issues of this interaction. Indeed, modeling of the underlying electromagnetic (EM) and thermal (T) processes has already found a well-defined niche in other technologies employing microwave energy, such as food and materials processing, as a useful and instructive tool determining the key characteristics and assisting in design of microwave applicators [4-7]. In [8], a modeling-based technique has been proposed to specifically design/scale up energy efficient microwave reactors [8].

In our previous work [3], we developed an advanced model capable of simulating EM and T phenomena in the *MiniFlow 200SS* reactor, a commercially available apparatus for microwave-assisted chemistry designed and produced by SAIREM SAS, Neyron, France. The same modeling concept can be used to build multiphysics models of the same capacity for other equipment. Experimental verification of computational results, however, has revealed that while the model is overall quite adequate, in liquid reactants the actual temperature fields are more uniform than they appear in the model's output due to convection flows acting as an

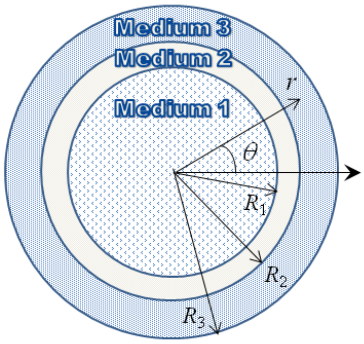

Figure 1. Cross-section of a three-media cylindrical element of a microwave reactor.

effective mechanism of averaging the reactant's temperature [3]. Understanding the impact made by convection on temperature characteristics of the microwave-induced reactions in low viscosity reactants therefore becomes a point of significant interest.

In this paper, we present a simple analytical model allowing for determining the average temperature of a liquid reactant exposed to microwave heating and well stirred due to the convection effect (or by manual/mechanical stirring). We consider a three-media concentric cylindrical structure (Figure 1): Medium 1 is the reactant (a liquid or low viscosity substance), Medium 2 is the material of a vessel (usually glass or Pyrex), and Medium 3 represents a container (made of Teflon or another low loss dielectric) holding the vessel. The whole structure is presumed to be inside a closed metal cavity (a waveguide or a resonator) and heated by microwaves. This scenario is natural for preparative microwave-assisted chemistry and can be found implemented in some dedicated commercial equipment (e.g., in *MiniFlow 200SS*).

The model is based on a number of physical assumptions which are expected to be held in practice when using microwave energy with liquid reactants. Input parameters of the model include physical data for Media 1 and 3 (mass m, specific heat c, density ρ and thermal conductivity k) and a time characteristic of the absorbed microwave power (usually available from the related experiments). The model is used to compute time evolution of the average temperature of water in a Pyrex vial inside a Teflon cup; geometrical parameters were taken as in the *MiniFlow 200SS* system. Modeling results are found to be in an excellent agreement with temperature values measured by a fiber optic sensor. The validated model is finally used for estimation of temperature evolution of two other substances (ethanol and methanol) heated in the same reactor.

MATHEMATICAL MODEL

The heat transfer problem is formulated for the concentric scenario in Figure 1 under the following assumptions suggested by physics of the considered heating process:

- Compared to Medium 1 (the reactant) and Medium 3 (e.g., Teflon), Medium 2 (e.g., Pyrex or glass) is usually a material of lower specific heat, smaller mass, and higher thermal conductivity.
- The specific heat and mass of Medium 3 are each comparable to or greater than those of Medium 1, and the thermal conductivity of Medium 3 is lower than that of Medium 1.
- In comparison with Media 2 and 3, Medium 1 has comparable or greater mass and a much high loss factor.

This suggests that Medium 1 may be assumed to be the only material in this scenario that is heated by microwaves, whereas Media 2 and 3 are heated conventionally, considering that the heat from Medium 1 and the heat absorbed by Medium 2 may be negligible.

As an element of a microwave reactor, the concentric structure in Figure 1 is confined inside of a metal cavity and surrounded by air. We therefore consider all outer surfaces of this structure (side walls, top, and bottom) to be thermally insulated.

A typical general model of the microwave heating process is based on solving an EM-T coupled problem (i.e., Maxwell's equations coupled with the heat transfer equation, assuming appropriate boundary and initial conditions) and requires the use of advanced numerical techniques and substantial computational resources [4, 5, 7]. In the EM part of the problem, the absorbed microwave power per unit volume is proportional to the squared magnitude of the electric field, which can vary significantly from point to point. However, here we consider substances with strong convention flows that, as seen in the related experiments [3], stir the reactants and homogenize temperature distributions. We thus deduce that the same effect could be produced, in the absence of convection, by a uniform electric field. Assuming perfect convection, we consider the electric field, as well as the power absorbed by the volume of Medium 1, to be uniform.

Relating the EM problem to the T one, we consider two heat transfer equations in polar coordinates with the origin in the center of the structure:

$$\text{Medium 1: } \frac{\partial u_1}{\partial t} = \alpha_1 \nabla^2 u_1 + q,$$

$$\text{Medium 3: } \frac{\partial u_3}{\partial t} = \alpha_3 \nabla^2 u_3, \tag{1}$$

where $u_{1,3} = u_{1,3}(r,t)$ denote temperatures and $\alpha_{1,3}$ are thermal diffusivities of Medium 1 and 3, respectively, and $q = P_a/c_1 m_1$ is the heat source term due to microwave absorption, where m_1 and c_1 are the mass and specific heat of Medium 1, and P_a is microwave power absorbed by Medium 1.

Aiming to determine the average temperature of the reactant, in the following derivation we reduce the problem to a 1-D scenario in which temperature changes only in the r-direction. By expanding in (1) the Laplacian in polar coordinates, we obtain the governing equations:

$$\text{Medium 1: } \frac{\partial u_1}{\partial t} = \alpha_1 \left[\frac{1}{r}\frac{\partial u_1}{\partial r} + \frac{\partial^2 u_1}{\partial r^2}\right] + q, \tag{2}$$

$$\text{Medium 3: } \frac{\partial u_3}{\partial t} = \alpha_3 \left[\frac{1}{r}\frac{\partial u_3}{\partial r} + \frac{\partial^2 u_3}{\partial r^2}\right]. \tag{3}$$

The thermal insulation on the outer surface of Medium 3 is given by the boundary condition:

$$\frac{\partial u_3(R_3,t)}{\partial r} = 0\,. \tag{4}$$

Also, because of symmetry of the system around $r = 0$, we assume a zero temperature gradient at the center of Medium 1, i.e.:

$$\frac{\partial u_1(0,t)}{\partial r} = 0\,. \tag{5}$$

To introduce average temperatures of Media 1 and 3, we integrate both sides of (2) over the portion of the domain occupied by Medium 1. Satisfying the boundary condition (5), we obtain:

$$A_1 \frac{\partial \bar{u}_1}{\partial t} = \alpha_1 \left\{\int_0^{R_1} \left[\frac{1}{r}\frac{\partial u_1}{\partial r} + \frac{\partial^2 u_1}{\partial r^2}\right] r\, dr \int_0^{2\pi} d\theta\right\} + A_1 q = 2\pi\alpha_1 R_1 \frac{\partial u_1}{\partial r}(R_1,t) + A_1 q, \tag{6}$$

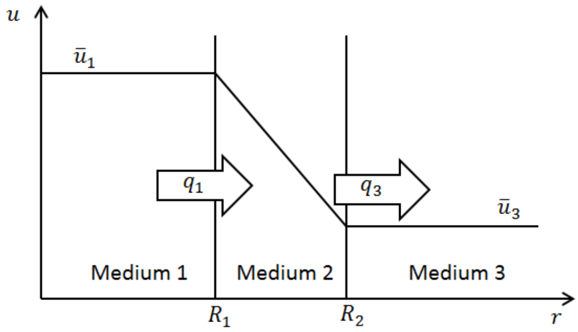

Figure 2. Heat flux at the boundaries of all three media.

where $A_1 = 2\pi R_1^2$, and $\bar{u}_1$ is the average temperature of Medium 1.We simplify (6) to

$$\frac{\partial \bar{u}_1}{\partial t} = D_1 \frac{\partial u_1}{\partial r}(R_1, t) + q \,, \tag{7}$$

where

$$D_1 = \frac{2\alpha_1}{R_1}. \tag{8}$$

Similarly, we integrate both sides of (3) over the domain and, assuming the boundary condition (4) is satisfied, obtain:

$$A_3 \frac{\partial \bar{u}_3}{\partial t} = \alpha_3 \left\{ \int_{R_2}^{R_3} \left[\frac{1}{r}\frac{\partial u_3}{\partial r} + \frac{\partial^2 u_3}{\partial r^2} \right] r\, dr \int_0^{2\pi} d\theta \right\} = 2\pi\alpha_3 [\, R_3 \frac{\partial u_3}{\partial r}(R_3, t) - R_2 \frac{\partial u_3}{\partial r}(R_2, t)] \tag{9}$$

where $A_3 = \pi(R_3^2 - R_2^2)$ is the area of the domain, and $\bar{u}_3$ is the average temperature of Medium 3. We also reduce equation (9) to

$$\frac{\partial \bar{u}_3}{\partial t} = -\, D_3 \frac{\partial u_3}{\partial r}(R_2, t), \tag{10}$$

where

$$D_3 = \frac{2\alpha_3 R_2}{2(R_3 - R_2)R_2 + (R_3 - R_2)^2} \;. \tag{11}$$

By Fourier's law of conduction, the heat flux (as shown in Figure 2) exiting Medium 1 is:

$$q_1 = k_1 \frac{\partial u_1}{\partial r}(R_1, t), \tag{12}$$

where k_1 is thermal conductivity of Medium 1. Similarly, the heat flux entering Medium 3 is:

$$q_3 = k_3 \frac{\partial u_3}{\partial r}(R_2, t) \,, \tag{13}$$

where k_3 is thermal conductivity of Medium 3. The heat flux through Medium 2 could be calculated similarly, but since the thickness of Medium 2 is small, the gradient through it is instead taken to be the difference of temperatures across Medium 2 divided by its thickness (as illustrated in Figure 2). The heat flux through Medium 2 is thus expressed as

$$q_2 = \frac{k_2[\bar{u}_1(R_1,t) - \bar{u}_3(R_2,t)]}{R_2 - R_1}, \tag{14}$$

where k_2 is the thermal conductivity of Medium 2. Because of energy conservation, the heat flux is conserved, i.e.:

Table 1. Geometrical Parameters and Masses of the *MiniFlow 200SS* Reactor

R_1 (mm)	R_2 (mm)	R_3 (mm)	Mass of Pyrex walls (g)	Mass of Teflon walls (g)
10	12	14.3	2	26.3

Table 2. Thermal Media Parameters Used in Simulation

	Density (g/m^3)	Specific heat (J/(gK))	Thermal conductivity (W/(mK))
Medium 1: water	1.00×10^6[9]	4.2 [9]	0.6 [9]
Medium 1: ethanol	7.89×10^5[9]	2.35 [10]	0.167 [9]
Medium 1: methanol	7.93×10^5[9]	2.53 [9]	0.202 [9]
Medium 2: Pyrex	–	0.75 [10]	1.0 [9]
Medium 3: Teflon	2.20×10^6[9]	1.45 [11]	0.25 [11]

$$q_1 = q_2 = q_3 \; . \tag{15}$$

Combining (12) through (15), we find the temperature gradients at R_1 and R_2 in relation to the average temperatures in Media 1 and 3 to be:

$$\frac{\partial u_1}{\partial r}(R_1, t) = \frac{\bar{u}_3 - \bar{u}_1}{R_2 - R_1}\frac{k_2}{k_1}, \tag{16}$$

$$\frac{\partial u_2}{\partial r}(R_2, t) = \frac{\bar{u}_3 - \bar{u}_1}{R_2 - R_1}\frac{k_2}{k_3}. \tag{17}$$

Substituting (7) and (10) into (16) and (17), we obtain the following system of differential equations, which can be solved for $\bar{u}_1$ and $\bar{u}_3$:

$$\frac{\partial \bar{u}_1}{\partial t} = -\frac{D_1 k_2}{(R_2 - R_1)k_1}\,\bar{u}_1 + \frac{D_1 k_2}{(R_2 - R_1)k_1}\,\bar{u}_3 + \frac{P_a}{c_1 m_1} \tag{18}$$

$$\frac{\partial \bar{u}_3}{\partial t} = \frac{D_3 k_2}{(R_2 - R_1)k_3}\,\bar{u}_1 - \frac{D_3 k_2}{(R_2 - R_1)k_3}\,\bar{u}_3 \; . \tag{19}$$

To summarize, the input data needed to solve (18) and (19) are: microwave power absorbed by Medium 1, material parameter of Media 1 and 3 (density, mass, specific heat, and thermal conductivity), and radii of all three cylinders. In the absence of data on thermal diffusivities for (8) and (11), the values of $D_{1,3}$ could be determined through the densities of the respective media as $\alpha_{1,3} = k_{1,3}/(\rho_{1,3}c_{1,3})$.

COMPUTATIONAL RESULTS AND EXPERIMENTAL VALIDATION

A computer code solving the system (18)-(19) has been implemented as a MATLAB script using the function `ode45`. Geometrical and material parameters were taken to replicate the resonator reactor of the *MiniFlow 200SS* system; these parameters are presented in Tables 1 and 2.

Similar to [3], experimental validation of the model was made with 15.7 g of water in a cylindrical, 30 mm high Pyrex vial. A series of six experiments, each heating this sample up to 80 C by 100 W of incident microwave power at 2.45 GHz was performed. The values of power and frequency were strictly maintained by the control system of a solid state generator

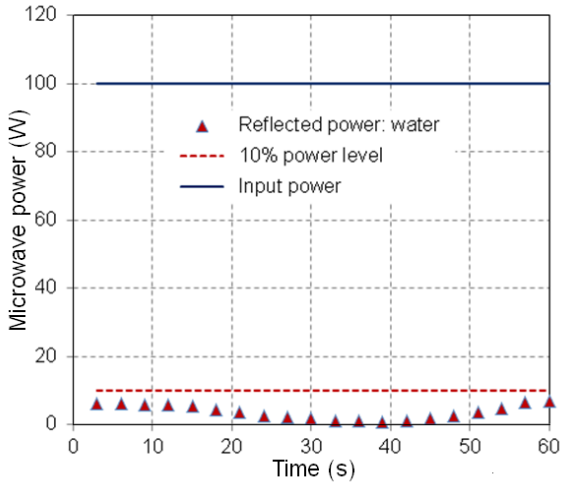

Figure 3. Average reflected power in six experiments of microwave heating of water (15.7 g) in *MiniFlow 200SS* by 100 W of incident power.

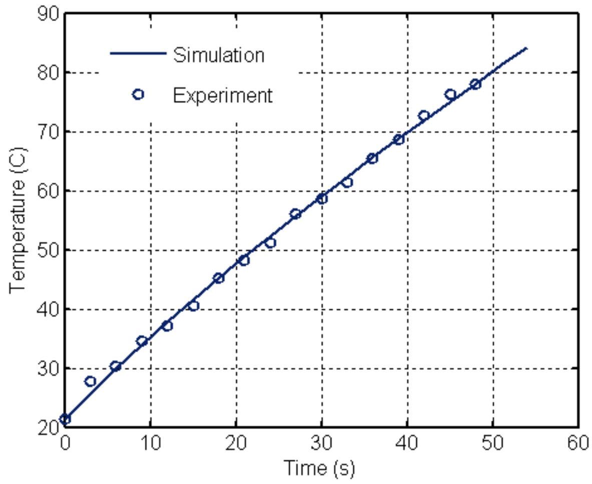

Figure 4. Average temperature of a 15.7 g sample of water as function of heating time – model (18)-(19) and measurement.

in the *MiniFlow 200SS* system. A fiber optic sensor held inside a glass capillary was used to measure temperature at six different points along the central axis of the vial. The absorbed power P_a, an input parameter of the model (18)-(19), was calculated from the reflected power recorded for each heating experiment every 3 seconds; the averaged time characteristic of the reflected power is shown in Figure 3.

Figure 4 shows the average temperature of Medium 1 (water) obtained from the simulations and measurements. Computational and experimental results are in excellent agreement. This confirms our hypothesis that the convection flows make a significant impact on the microwave-induced temperature fields in liquid reactants. The reported model is therefore directly applicable to any other low viscosity substances (whose mass, density, specific heat, and thermal conductivity are known) heated in other microwave systems featuring a similar cylindrical concentric element as in Figure 1. Figure 5 shows the results of application of the model to two other common chemical substances (ethanol and methanol, whose thermal properties are also collected in Table 2) in comparison with water. The dimensions of the scenario are again taken as in *MiniFlow 200SS* (Table 1).

DISCUSSION

When solving the heat transfer problem (2)-(5), we employ the approach of integrating heat equation over its domain rather than analytically solving for temperature distribution, because of our interest in the average temperatures rather than the temperature fields themselves.

In Figure 5, we present the upper and lower bounds of the time-temperature characteristics corresponding to zero- and 10% loss of microwave power. These curves were calculated for the particular levels P_a = 100 W and P_a = 90 W of absorbed (rather than incident) microwave power. As such, Figure 5 shows the difference in heating of the considered substances due to their thermal properties rather than their loss factors (which are higher and lower, respectively, for ethanol and methanol compared to that of water [12]), and this calculation is based on the prescribed level of P_a. However, if experimental data on the absorbed power (similar to the one in Figure 3) is available prior to calculation with (18)-(19), the model may be capable of generating a precise time-temperature characteristic of the process (similar to the curve in Figure 4).

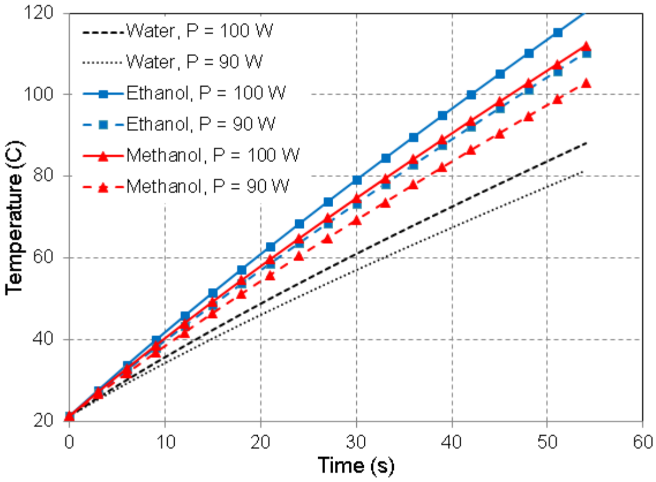

Figure 5. Computed time evolution of average temperatures of the 15.7 g ethanol and methanol samples in *MiniFlow 200SS*.

This consideration suggests that knowledge of reflected (and thus absorbed) power of the MW-assisted chemical reaction may make the proposed simple model an efficient and accurate computational tool determining average temperature of substances with strong convection. If corresponding equipment and the reactants are not accessible for experimentation, the required characteristics could be produced with the use of an appropriate general-purpose electromagnetic modeling software (like *QuickWave-3D* [13] used for modeling of *MiniFlow 200SS* in [3]).

CONCLUSION

In this paper, the coupled EM-T problem of microwave heating of liquid substances with convection has been considered in a three-media concentric cylindrical structure. In general, modeling convection flows in microwave-assisted chemistry is a problem that is both mathematically complicated and computationally expensive. To simplify the analysis, we have suggested using the average temperature to characterize a homogenization effect produced by convection flows, and excluding the coupled problem from consideration.

On the basis of a series of physics-based assumptions, the problem has been decoupled and the thermal portion reduced to a linear system of ordinary differential equations; time characteristics of the average temperature of the stirred liquid reactant have been computed from this system. If the microwave power absorbed by the reactant in the course of heating is known (from prior measurement or modeling), the proposed model, as confirmed by experiments with SAIREM's *MiniFlow 200SS* resonator reactor, can predict evolution of average temperature with a high level of accuracy.

The model is computationally very inexpensive and takes only a few seconds of CPU time. For comparison, a *QuickWave-3D* simulation of the coupled problem representing a one-minute microwave heating process in the *MiniFlow 200SS* system (without taking into account convection) takes about 3 hours of operation of an advanced GPU workstation.

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