Progress In Electromagnetics Research, PIER 49, 273–289, 2004

NUMERICAL SIMULATION OF MICROWAVE HEATING ON CHEMICAL REACTION IN DILUTE SOLUTION

K.-M. Huang, Z. Lin, and X.-Q. Yang

College of Electronics and Information Engineering
Sichuan University
Chengdu 610064, Sichuan, China

Abstract—currently, microwaves are widely used in chemical industry to accelerate chemical reactions. Some research results have shown that microwave heating can significantly accelerate the reaction. However, there is a need to develop efficient methods to improve the design of microwave applicator in chemistry. In this paper, a numerical model was presented to study the microwave heating on saponification reaction in test tube, where the reactant was considered as a mixture of dilute solution. The coupled electromagnetic field equations, reaction equation (RE) and heat transport equation (HTE) were solved by using finite difference time domain (FDTD) method. To overcome the difficulty of long time calculation with FDTD, two types of techniques were employed. To verify the methods, the temperature rising in the test tube and transmitted power through the transversal electromagnetic (TEM) cell were measured and compared with the computational results. Good agreement can be seen between the measured and calculated results.

1. INTRODUCTION

In the early 1980's, microwaves were proposed to be used for accelerating chemical reactions by their efficient heating of the reactants. Many recent reports indicated that microwave could evidently accelerate reactions, and the rate enhancement factor could reach over one thousand. Currently, microwaves have been widely used in chemistry [1]. However, some difficulties arose in the application of high-power microwaves in chemistry, which limited the transfer of laboratory experiment system to industrial applications. Two of the major problems are the follows: (1) The reflection and absorption of microwave by the reactants change nonlinearly with time during the reaction [2]. When high-power microwaves are applied, the rapidly increment of reflection and absorption may destroy the microwave generator and may burn the organic reactants, which is a similar phenomenon as the dielectric breakdown that may happen in the application of microwaves in dielectric heating [3]; (2) It is difficult to get a uniform microwave heating in the reactants. The industry application demands well-designed and efficient reactors. To overcome these difficulties, the interaction between microwaves and the chemical reaction needs to be further studied. Recently, a number of efficient numerical approaches have been used to study the microwave heating. The coupled electromagnetic and thermal equations were used to study the microwave heating on foods in a domestic microwave oven [4]; Three major types of microwave heating applicators were analyzed by using of FDTD [5]; A technique for simulation of conductive and radiant heat transfer was presented in [6]; The microwave-heated, packed-bed and fluidized-bed catalytic chemical reactors were discussed in [7]. However, for the chemical reactions in solution, the dielectric properties of the solution change with not only temperatures but also the reaction time. This means that we have to combine the electromagnetic field equations, reaction equation and heat transport equation to study the microwave heating on chemical reactions.

In this paper, we present a method to simulate the interaction between microwaves and chemical reactions. Here, the model includes a typical saponification reaction in test tube placed in transversal electromagnetic cell. Since the saponification reaction is carried out in dilute solution, reaction system is considered as mixtures of solution. According to the preliminary measurement, the real part of effective permittivity of the solution is approximately the real part of permittivity of H_2O; but the conductivity, which changes with time, could be derived from reaction equation. The change of permittivity and the conductivity with temperature rising in test tube are considered as well. Then, the heating process, which is described by Maxwell's equations, reaction equation and heat transport equation, is analyzed by FDTD method. In order to get the enough accurate results, the time step in FDTD is set as the order of 10^{-12} second. Nevertheless, the reaction usually takes several minutes or hours; hence, the calculation will be enormously time-consuming. In this paper, two special techniques of scaling factor and dual-stage leapfrog are employed to solve this problem.

In order to verify the calculated results, a special designed experimental system is established and the temperature rising in test tube and transmitted power through the transversal electromagnetic cell are measured. These measured results are compared with the computed results. Good agreement can be seen between the both of results.

2. SAPONIFICATION REACTION AND EXPERIMENTAL SYSTEM

2.1. Saponification Reaction

Saponification reaction, which has important applications in industry, has been studied carefully for many years. Our model includes a typical saponification reaction with $CH_3COOC_2H_5$ and NaOH.

The reaction equation is as follows:

$$\mathrm{CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH}$$

$$\begin{array}{lllll} \text{reaction time} = 0 & C_0 & C_0 & 0 & 0 \\ \text{reaction time} = t & C_0 - x & C_0 - x & x & x \\ \text{reaction time } t \rightarrow \infty & 0 & 0 & C_0 & C_0 \end{array} \quad (1)$$

In the above reaction, the initial concentration of the reactants is set as C_0 (mol/l) and the concentration of product is set as x (mol/l) at the reaction time t.

The rate equation can be written as [8]:

$$\frac{dx}{dt} = k(t) \cdot (C_0 - x) \cdot (C_0 - x) \quad (2)$$

Where $k(t)$ is the rate constant $k(t) = Ae^{-\frac{E_a}{RT}}$, A is the pre-exponential factor, E_a is the activation energy, R is the gas constant, and T is the absolute temperature. In our experiment, the initial concentrations are $C_0 = 0.5\,\mathrm{mol/l}$ and $C_0 = 0.7\,\mathrm{mol/l}$ respectively, the activation energy, and pre-exponential factor are given by [8]:

$$E_a = 61KJ, \qquad A = 4.1 \times 10^9$$

By integrating the both side of Equation (2), we can get the concentration of product with respect to time,

$$x(t) = C_0 - \frac{1}{\left[1/C_0 + \int\limits_0^t k(t)dt\right]} \tag{3}$$

It is well known the conductivity at very low frequency is mainly determined by the concentration of OH^- [8]. According to the above rate equation, the conductivity of the reaction system reducing with time can be described as

$$\sigma(t) = \sigma_0 + [x(t)/C_0] \cdot (\sigma_\infty - \sigma_0) \tag{4}$$

Where σ_0 is the initial conductivity of the solution, and σ_∞ is the terminal conductivity of the solution. When C_0 equals $0.5\,\mathrm{mol/l}$, σ_0 and σ_∞ are $0.8\,\mathrm{s/m}$ and $0.38\,\mathrm{s/m}$ respectively. When C_0 equals $0.7\,\mathrm{mol/l}$, σ_0 and σ_∞ are $0.94\,\mathrm{s/m}$ and $0.43\,\mathrm{s/m}$ respectively.

It should be noted the reaction is exothermic reaction. One mol $CH_3COOC_2H_5$ and one mol NaOH will produce the thermal energy of 76.09 KJ. This will be included in the heat transport equation.

Because the reaction is carried out in dilute solution, according to the preliminary experimental results, the real part of permittivity of the solution is approximately the real part of permittivity of H_2O, but the conductivity, which changes with time, is given by Equation (4).

2.2. Experimental System

The experimental system is shown in Fig. 1.

A special designed TEM cell is used to establish uniform electromagnetic fields [9]. Here we use TEM cell to replace the waveguide in the experiment because the experimental system can be established to test microwave effect in a wide frequency band. TEM cell is a kind of rectangular coaxial transmission line. Fig. 2(a) shows the dimension of TEM cell, where part I denotes the main section, part II denotes the taper, and the part III denotes the coaxial line.

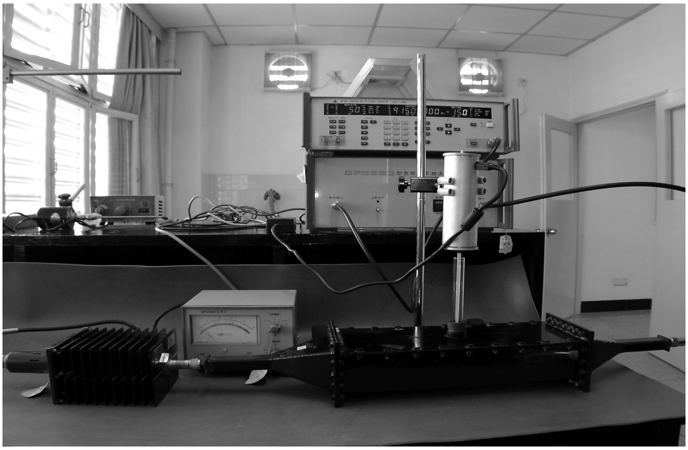

Figure 1. Experimental system.

The length of the three part is $L_1 = 270\,\mathrm{mm}$, $L_2 = 100\,\mathrm{mm}$ and $L_3 = 100\,\mathrm{mm}$ respectively. In the experiment, a hole with diameter of $d = 20\,\mathrm{mm}$ was made on the top of TEM cell and connected with a cut-off circular waveguide with height of $h_1 = 30\,\mathrm{mm}$ to avoid the emission of microwave. The test tube with reactants is inserted into the TEM cell through the hole. The thickness of the test tube is 2.0 mm. Fig. 2(b) shows the cross section of TEM cell, where the width of outer and inner conductor is $w_1 = 120\,\mathrm{mm}$ and $w_2 = 90\,\mathrm{mm}$ respectively, the height of TEM cell is $h_2 = 60\,\mathrm{mm}$.

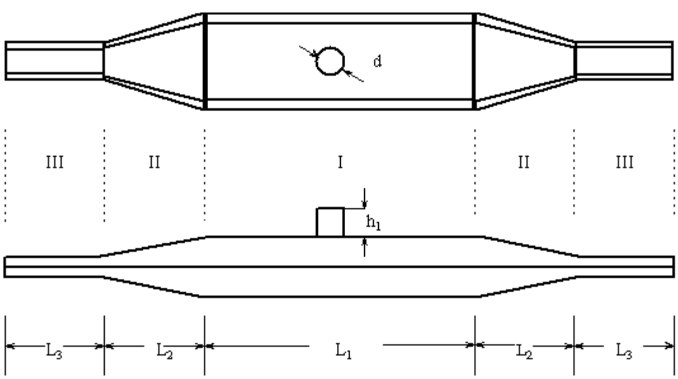

Figure 2a. The geometry of TEM cell.

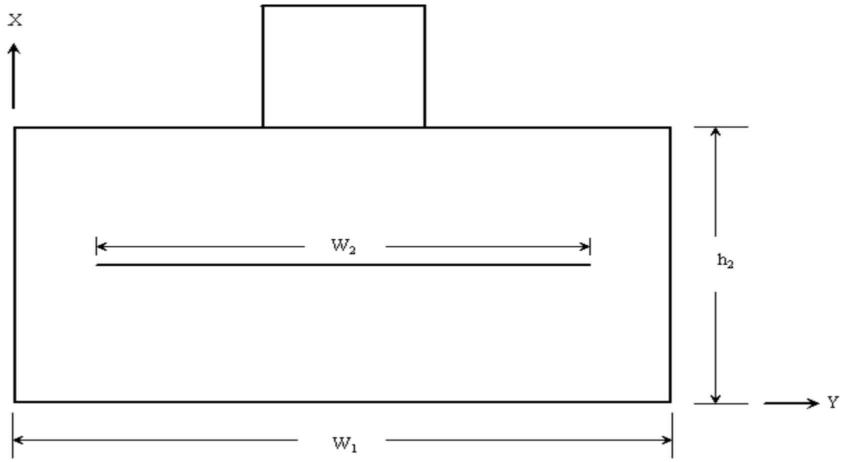

Figure 2b. Cross section of TEM cell.

QF1481 microwave source and QF3860 power amplifier are used to generate 5 W power; the frequency range is from 10 MHz to 2.4 GHz. In the experiment, the frequency is fixed at 915 MHz. GH2461 power meter is used to measure the output power. Since the solution is corrosive and irradiated by microwave, HIKO-1 optical fiber thermometer with diameter of 1 mm is employed to measure the temperature inside the test tube in vivo.

3. THE COUPLED EQUATIONS

The model used to study the interaction between microwaves and chemical reactions can be described by Maxwell's equations [4], heat transport equation, and reaction equation.

The heat transport equation is given by [10]:

$$\rho_m C_m \frac{\partial T(\vec{r},t)}{\partial t} = k_t \nabla^2 T(\vec{r},t) + P_d(\vec{r},t) + P_e(\vec{r},t) \tag{5}$$

$$P_e(\vec{r},t) = C_q \cdot A e^{-\frac{E_a}{RT}} (C_0 - x)^2 \tag{6}$$

$$\vec{P}_d = \frac{1}{2}\left(\vec{E} \cdot \frac{\partial \vec{D}}{\partial t} - \vec{D} \cdot \frac{\partial \vec{E}}{\partial t}\right) + \vec{J} \cdot \vec{E} \tag{7}$$

$$\vec{J} = \sigma(t) \vec{E} \tag{8}$$

Where $P_e(\vec{r},t)$ is the releasing power per unit volume produced by the reaction $(W \cdot m^{-3})$, $P_d(\vec{r},t)$ is the electromagnetic power dissipated per unit volume ($W \cdot m^{-3}$), ρ_m is the medium density ($kg \cdot m^{-3}$), C_m is the specific heat of the medium ($J \cdot K^{-1} \cdot kg^{-1}$), k_t is thermal conductivity of the medium ($W \cdot m^{-1} \cdot K^{-1}$) and C_q is the thermal energy produced by 1 mol reactant ($J \cdot mol^{-1}$).

The permittivity of H_2O with the temperature can be described by the first-order Debye's equation [11]:

$$\varepsilon(\omega) = \varepsilon_1 - j\varepsilon_2 = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega\tau} \tag{9}$$

$$\varepsilon_s(T) = \frac{3\varepsilon_\infty T + A_1(\varepsilon_\infty + 2)^2}{12T} + \frac{\sqrt{\left(3\varepsilon_\infty T + A_1(\varepsilon_\infty + 2)^2\right)^2 + 72\varepsilon_\infty^2 T^2}}{12T} \tag{10}$$

$$\tau(T) = \tau_0 e^{\frac{W_a}{kT}} \tag{11}$$

Where ε_s, is the static permittivity, ε_∞ is the infinite frequency permittivity, τ is the relaxation time, w_a is the activation energy, and τ_0 is a constant of medium. The values of these parameters can be found in [11].

The conductivity of the solution with respect to the time is determined by Equation (4). The above equations are used to calculate the temperature distribution and rising with time in the test tube.

4. CALCULATION

Generally, it is difficult to obtain an analytical result for these differential equations. Some numerical methods, such as FDTD, could be employed to solve these equations [12]. The first step in FDTD is to determine the calculation domain. The calculation domain is shown in Fig. 3. In this model, we suppose microwave propagates along z direction, I-D MUR absorbing boundary condition (ABC) is used at $z = \pm 135$ mm, and $x = 90$ mm respectively. The incident plane is located at $z = -120$ mm, and the incident field solved previously for infinite rectangular coaxial transmission line is TEM wave.

In order to simulate the distribution of electromagnetic field precisely, the time step for the discrete Maxwell's equations should be set to be the order of 10^{-12} second at 915 MHz; but usually, the saponification reaction takes several minutes. This means the calculation will be enormously large. Here two special techniques characterized as dual-stage leapfrog and scaling factor are used to solve this problem.

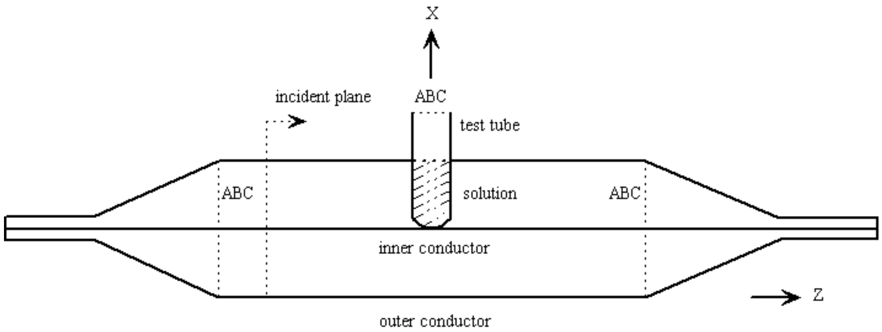

Figure 3. The calculation domain.

4.1. Dual-Stage Leapfrog Scheme

In fact, the change of temperature and reaction is much slower than that of electromagnetic field. It hints that the time step for the discrete reaction equation and heat transport equation is not required to be small as the order of 10^{-12} second. Therefore, in our calculation two types of time step are used. One is Δt_{field} for the "leapfrog" calculation of discrete Maxwell's equations as explained in [12] and another is $\Delta t_{\text{temperature}}$ for the "leapfrog" calculation of discrete reaction equation and heat transport equation. In our calculation, Δt_{field} is set to be the order of 10^{-12} second, and $\Delta t_{\text{temperature}}$ is set to be 1 second. Temperature and permittivity of the solution maintain constant within $\Delta t_{\text{temperature}}$. In the calculation of FDTD, the distribution of electromagnetic field can achieve stable after 10000 steps of Δt_{field} or ten periods of microwave, and then, this distribution maintains constant and is not necessary to be calculated in the remaining time of $\Delta t_{\text{temperature}}$. Consequently, the releasing power $P_e(\vec{r}, t)$, dissipated power $P_d(\vec{r}, t)$ and temperature can be calculated by substituting the electromagnetic field into Equations (5)–(8). Therefore, the calculation time of microwave heating can be significantly reduced by the dual-stage leapfrog scheme.

4.2. Scaling Factor

Another simple way to reduce the calculation time is multiplying Equation (5) by a constant α [11]. This leads to a new form of Equation (5) as follows:

$$\alpha \frac{\partial T}{\partial t} = \frac{\alpha k_t}{\rho_m C_m} \nabla^2 T(\vec{r}, t) + \frac{\alpha P_d(\vec{r}, t)}{\rho_m C_m} + \frac{\alpha P_e(\vec{r}, t)}{\rho_m C_m} \tag{12}$$

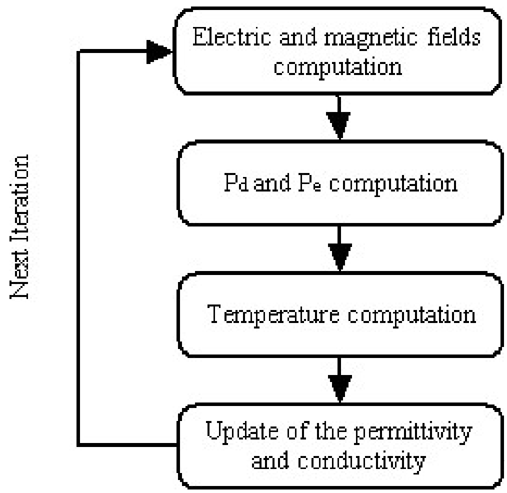

Figure 4. Calculating proceeding of combined electromagnetic, chemical, and thermal equations.

From the above equation, we can see if the releasing power $P_e(\vec{r},t)$, dissipated power $P_d(\vec{r},t)$, and the thermal conductivity k_t, are multiplied by α, the temperature change $\frac{\partial T}{\partial t}$ is α times quicker, while the spatial evolution remains the same. Therefore, this method scales the heating time down to the duration of electromagnetic field computation. Where the scaling factor α is defined as

$$\alpha = \Delta T_{\text{temperature}}/\Delta T_{\text{field}} \tag{13}$$

It must be chosen correctly. Too large value of α will cause large error in the beginning of chemical reaction. In our calculation, α is 0.5×10^{12}.

The whole calculating proceeding for both techniques is shown in Fig. 4.

The CPU time normally is about 250 minutes for "dual-stage leapfrog" calculation and 40 minutes for another on a PC with CPU of AMD Athlon XP 1700^{+}.

The thermal properties of the medium in the model are shown in the Table 1 [10].

The spatial steps in our FDTD calculation are $\Delta x = \Delta y = \Delta z = 1\,\text{mm}$.

Table 1. The thermal properties of the medium in the calculation.

	$C_m(J * kg^{-1} * K^{-1}$	$\rho_m(kg * m^{-3})$	$K_t(W * m^{-1} * K^{-1})$
water	4180	1000	0.55
Air	3505.9	1.293	0.0261
Glass	837.4	2707.04	0.76164
Copper	385	8939	20

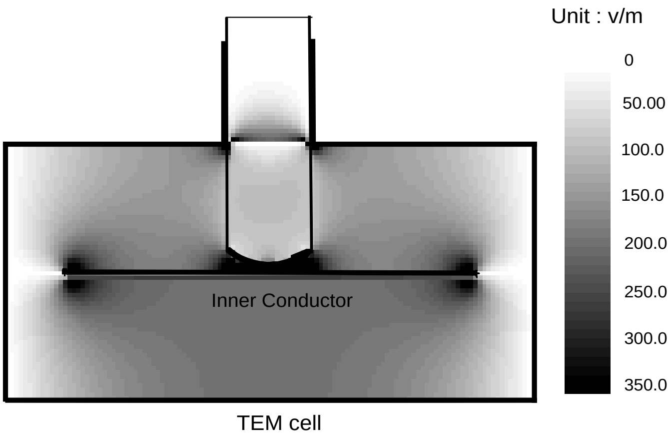

Figure 5. The distribution of electric field on the cross section of TEM cell.

5. COMPARISON OF MEASURED AND CALCULATED RESULTS

In our experiment, a maximal microwave power of 5 W is inputted into TEM cell. The initial electric field distribution on the cross section of TEM cell is drawn in Fig. 5 for $C_0 = 0.5\,\text{mol/l}$.

From Fig. 5 we can see the distribution of fields in the test tube is acceptable uniform; the emission of microwave from the cut-off circular waveguide can be disregarded. Meanwhile, the calculated and measured transmitted power under 5 W input power are compared in Fig. 6.

It can be seen that the error between measured and calculated results are less than 0.1 W.

The temperatures with respect to time at two points along the axis of the test tube are measured and compared with the calculated

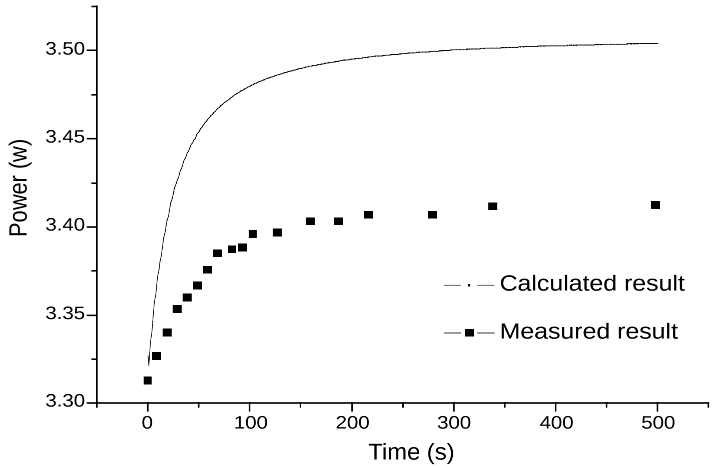

Figure 6. Measured and calculated transmitted power.

results. The two points are located at P_1 ($x = 45$ mm, $y = 60$ mm, $z = 0$ mm) and P_2 ($x = 60$ mm, $y = 60$ mm, $z = 0$ mm) respectively.

From the above figures, good agreement can be seen between the measured and both calculated results in the later temperature rising. In the earlier temperature rising, the measured results are less than the calculated results; the difference is due to the fast change of reaction, which causes that the equilibrium condition for the effective permittivity expression of solution is not strictly satisfied. The difference in Fig. 8 is larger than that in Fig. 7 because the loss of the solution is higher and the temperature rising is quicker while $C_0 = 0.7$ m/l. It also can be seen that the calculated results by leapfrog are better than that by scaling factor. Nevertheless, the leapfrog calculation takes about 6 times longer than the scaling factor calculation.

From Fig. 9 we can see that the temperature rising in test tube is quite different while the initial concentrations are different.

The temperature distribution on the cross section of test tube at $t = 250$ s is also calculated; the result is shown in Fig. 10. It can be seen that the temperature distribution is not uniform even in the small test tube. The temperature reduces along the radius due to the heat convection on the surface. The temperature declines along the propagation direction of microwave. From these results, it is not difficult to understand that getting a uniform temperature distribution in the reactor is not very easy.

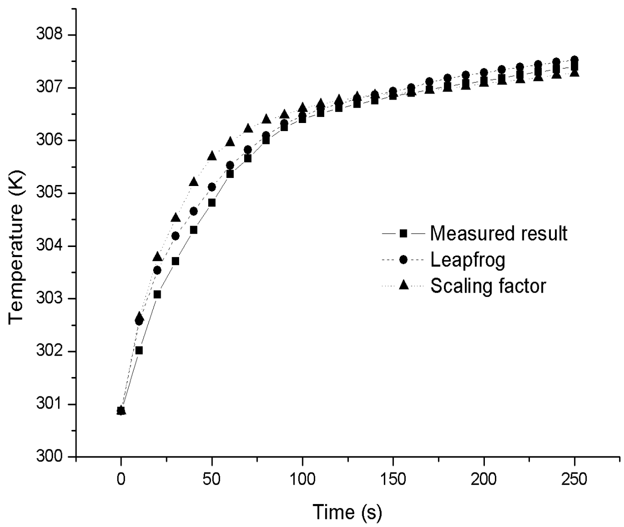

Figure 7a. Measured and calculated results at P_1.

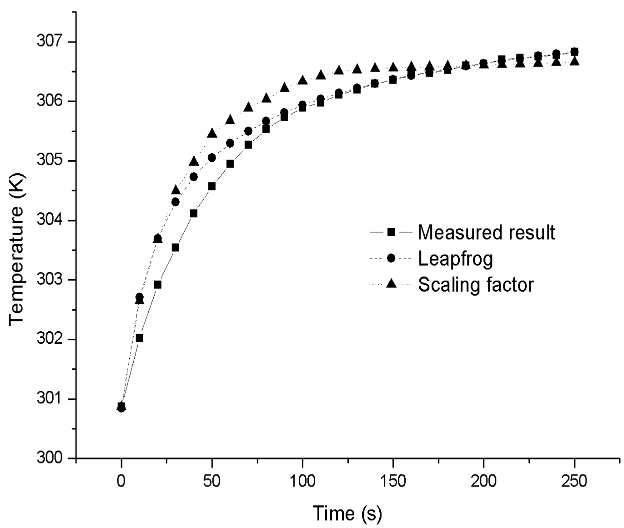

Figure 7b. Measured and calculated results at P_2 while $C_0 = 0.5\,\text{mol/l}$.

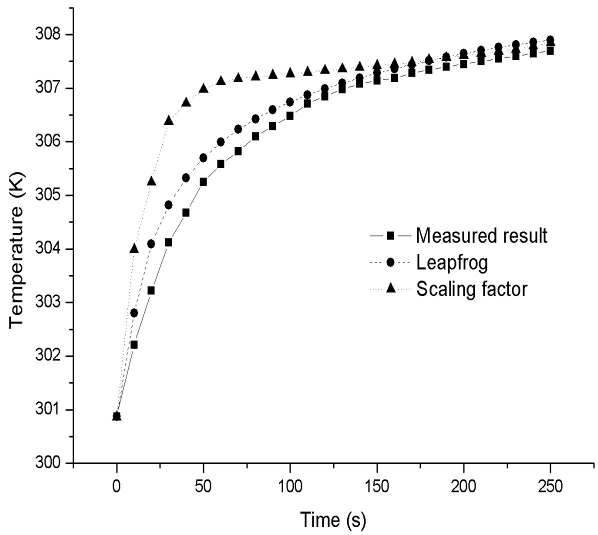

Figure 8a. Measured and calculated results at P_1.

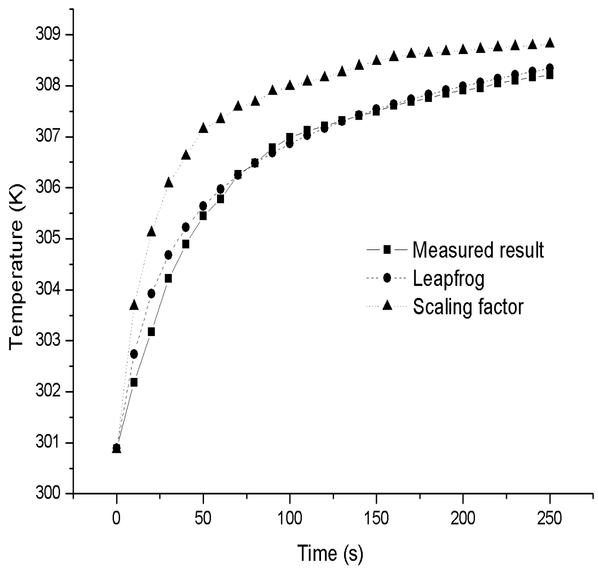

Figure 8b. Measured and calculated results at P_2 while $C_0 = 0.7\,\text{mol/l}$.

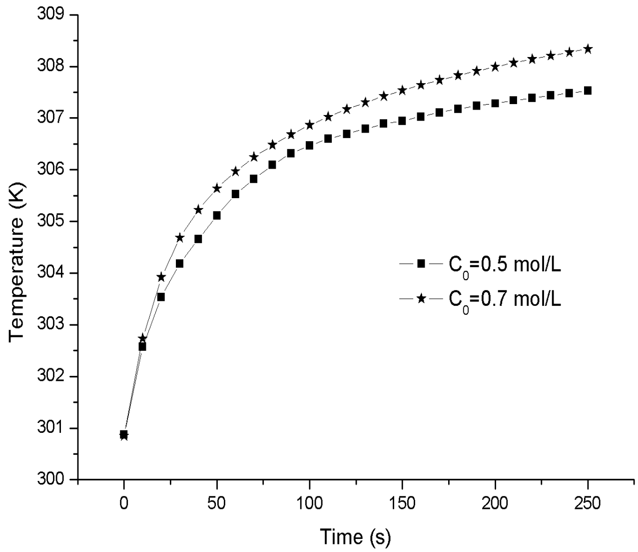

Figure 9. Temperature rising at P_1 with different C_0.

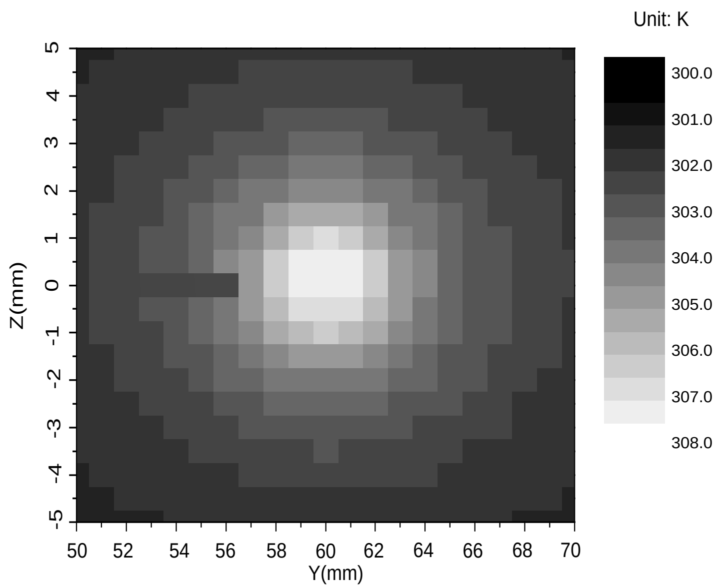

Figure 10. Temperature distribution on the cross section of test tube.

6. CONCLUSIONS

The application of microwave in chemistry demands the analysis of interaction between microwaves and chemical reaction. In this paper, we present a method to study the microwave heating on chemical reaction in dilute solution. The temperature distribution and change with time in the solution are obtained by solving coupled Maxwell's equations, heat transport equation, and reaction equation. The numerical method of FDTD is employed to solve these differential equations. Two types of technique are used to reduce the computation time. In order to verify the feasibility of the numerical method, a special designed experimental system is used, and the temperature risings with time inside the test tube and transmitted power through the transversal electromagnetic cell are measured. Good agreement between measured and calculated results has been obtained.

ACKNOWLEDGMENT

This project was supported by National Science Fund of China for Distinguished Young Scholars.

REFERENCES

1. Jin, Q., S. Dai, and K. M. Huang, *Microwave Chemistry,* Sciences Press, Beijing, 1999.
2. Chen, M., J. W. Hellgeth, E. J. Siochi, T. C. Ward, and J. E. Mcgrath, "The microwave processability of semicrystalline polymers," *Polymer Engineering and Science,* Vol. 33, No. 17, 1122, 1993.
3. Baker-Jarvis, J. and R. Inguva, "Dielectric heating of oilshales by monopoles and modified coaxial applicators," *Journal of Microwave Power and Electromagnetic Energy,* Vol. 23, 160–170, 1984.
4. Zhang, H. and A. K. Datta, "Coupled electromagnetic and thermal modeling of microwave oven heating of foods," *Journal of Microwave Power & Electromagnetic Energy,* Vol. 35, No. 2, 71–86, 2000.
5. Harms, P. H., Y. Chen, R. Mittra, and Y. Shimony, "Numerical modeling of microwave heating systems," *Journal of Microwave Power & Electromagnetic Energy,* Vol. 31, No. 2, 114–122, 1996.
6. Haala, J. and W. Wiesbeck, "Simulation of microwave, conventional and hybrid ovens using a new thermal modeling

technique," *Journal of Microwave Power & Electromagnetic Energy,* Vol. 35, No. 1, 34–44, 2000.

7. Thomas Jr., J. R. and F. Faucher, "Thermal modeling of microwave heated and fluidized bed catalytic reactors," *Journal of Microwave Power & Electromagnetic Energy,* Vol. 35, No. 3, 165–175, 2000.
8. Daniels, F., R. A. Alberty, J. W. Williams, C. D. Cornwell, P. Bender, and J. E. Harriman, *Experimental Physical Chemistry,* McGraw-Hill, Inc., New York, 1975.
9. Ma, Y., K. M. Huang, K. Wang, and N. Liu, "Calculation of electric field distribution in TEM cell with EUT," *Chinese Journal of Radio Science,* Vol. 15, No. 1, 75–79, 2000.
10. Rohsenow, W. M. et al. (eds.), *Handbook of Heat Transfer Fundamentals,* Second edition, McGraw-Hill, 1985.
11. Torres, F. and B. Jecko, "Complete FDTD analysis of microwave heating processes in frequency-dependent and temperature-dependent media," *IEEE Trans. on Microwave Theory Tech.,* Vol. 45, 108–116, 1997.
12. Allen T., *Advances in Computational Electrodynamics,* Artech House, Inc., 1998.

Kama Huang received the M.S. in 1988 and Ph.D. in 1991 in microwave theory and technology both from the University of Electronic Science and Technology, China. He has been a professor of the Department of Radio and Electronics of Sichuan University, China, from 1994, and the director of the Department since 1997. In 1996, 1997, 1999, and 2001, he was a visiting scientist at the Scientific Research Center "Vidhuk" in Ukraine, Institute of Biophysics CNR in Italy, Technical University Vienna in Austria, and Clemson University in USA, respectively. At these institutions, he cooperated with the scientists to study the interaction between electromagnetic fields and complex media in biological structure and reaction systems. He has published over one hundred papers and received several research awards from Chinese government. His research interests are in the areas of microwave chemistry and electromagnetic theory.

Zhen Lin received the B.S. in the Department of Radio and Electronics from Sichuan University, Chengdu, China in 2001. Currently, he is a Ph.D. student and studies in the Institute of Applied Electromagnetics. Sichuan University. His research mainly considers the interaction between chemical reactions and microwave.

Xiaoqing Yang received M.S. in biomedical materials form Sichuan University, Chengdu, Chin, in 2003. He is studying for the Radio and Electronics doctorate at present in the Institute of Applied Electromagnetics Sichuan University. His research interests are in the areas of microwave chemistry.