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Study on the key problems of interaction between microwave and chemical reaction

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Abstract Microwave has been found as an efficient heating method in chemical industry. However, in present days the interaction between microwave and chemical reactions has not been deeply understood, which restricts a wider application of high power microwave in chemical industry. In this paper, the key problems of interaction between microwave and chemical reaction are investigated, such as complex effective permittivity of chemical reaction, simulation of microwave heating on chemical reaction and non-thermal effect of microwave, which will enhance further knowledge of the mechanism of interaction between microwave and chemical reaction. Moreover, such an analysis is beneficial for handling with difficulties in application of microwave chemical industry.

Keywords microwave, chemical reaction, interaction, complex effective permittivity, numerical simulation, non-thermal effect

1 Introduction

Early in 1967, Williams had reported the research results that microwave heating could accelerate some chemical reactions. However, at that time people were not aware that it was forecasting a revolution in the chemistry. Till 1986, Gedye et al. found that 4-cyanatophenyl ions and SN_2 of cyanobenzyl nucleophilic substitution reaction rate could be enhanced by 1 240 times with yield enhancement to a certain degree under microwave radiation [1], thus chemical reactions accelerated and controlled by microwave were taken into account. Presently, microwave has been widely applied in various chemical domains from inorganic reaction to organic

reaction, from medicine chemical industry to food chemical industry and from simple molecules to complex life process. With wide application of microwave in various chemical branches, conceptions established in conventional microwave heating and microwave chemistry by using commercial microwave oven have been severely challenged. First, it is found that microwave can accelerate chemical reaction and meanwhile inhibits reaction under certain conditions. Besides, microwave can also change reaction process. It is indicated by researches in recent years that the effect of microwave on chemical reaction may include “non-thermal effect” and thermal effect [2]. Moreover, it is important that chemical reaction is a non-equilibrium system that old substances are continuously consumed while new substances are continuously generated and various phase interfaces may cause random variation. All these reasons lead to nonlinear response of reaction system to microwave. It is necessary to make clear the interaction between microwave and chemical reaction in order to design effective and reasonable microwave chemical reactors.

1.1 Effects of microwave on chemical reaction

Due to the unique microwave selective heating and sensitivity of chemical reaction rate to temperature, it is naturally associated to make use of microwave in chemical reaction to enhance the reaction rate. In recent years, many experiments have proved that microwave can greatly enhance the reaction rate of some chemical reactions, which are hard to react under conventional conditions [3,4]. For example, some organic and inorganic reactions in 560 W microwave oven can react faster to certain extent than those under conventional heating conditions [5,6], and the use of microwave can save energy as well [7]. However, these data have not provided the temperature of reactants under the microwave radiation, and they were visually deemed by predecessors that enhancement of reaction rate should be all attributed to the thermal effect of microwave. However, it is found by researches in recent years that the effect of microwave on chemical reaction is very complex. For example, under microwave radiation, some

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Arrhenius type reactions do not satisfy Arrhenius relation any more [7]. Pagnotta et al. reported that specific phenomena occurred during the conversion from α -D glucose to β -D glucose [5]. Moreover, it was found that pulse-modulated microwave radiating reactants could achieve better effects. Thuillier and Jullien found in experiment that sclerous reaction rate of diglycidyl ether of bis phenol A (DGEBA) and diaminodiphenylsulfone (DDS) mixture did not depend on reaction temperature directly [5]. Beldjoudi et al. found that microwave pulses at repeat frequencies of 23.8, 200 and 1 000 Hz could achieve the best effect on cross-linking [5]. So far it has not been clear of mechanism of this phenomenon yet.

1.2 Nonlinear response in microwave chemical system

As to incidental microwave, chemical reaction is a non-equilibrium system. Some unexpected results may occur during the interaction between microwave and the non-equilibrium system. A typical microwave chemical reaction unit adopts cylinder cell operating in TE₁₁₁ model and coaxial bidirectional coupler is used to monitor input power and reflected power, the system is shown in Fig. 1.

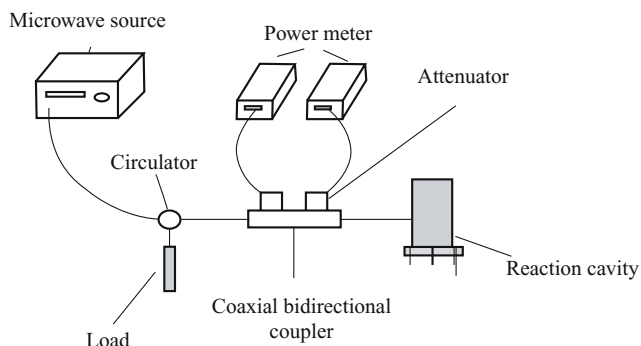


Fig. 1 Terminal type microwave chemical reaction system

Under the condition of constant 45 W input power, during peak heating process, temperature in the center of the cell and reflected power varying with time can be seen in Fig. 2 [8]. It can be seen from Fig. 2 that reflected power descends rapidly right after the reaction starting and then gradually rises. When reaction is conducted for 12–14 min, there is an endothermic process in the reaction as well as an odd peak in the reflected power curve. This sudden variation of microwave reflection is dangerous for high power microwave system. Meanwhile, if the rapid rise of temperature is not controlled, organic substances in the reaction cell can be burned out. These nonlinear responses should be sufficiently taken into account.

1.3 Effective permittivity of non-equilibrium system

Strictly speaking, permittivity that conventionally describes macroscopic electromagnetic behaviors of substances cannot

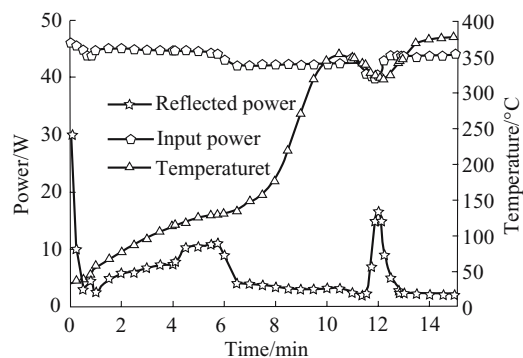


Fig. 2 Temperature in the center of cell and reflected power varying with time

be used to describe electromagnetic behaviors in chemical reaction system, because chemical reaction system is a non-equilibrium dynamic system without deterministic “relaxation constant” and dipole orientation probability distribution does not satisfy Boltzmann distribution any more. Currently, it can only be presumed that this non-equilibrium system consists of series of equilibrium systems, i.e. local equilibrium in time and space. Each equilibrium system can still use effective permittivity to describe its electromagnetic behaviors. Even this, it is difficult to calculate the effective permittivity of chemical reaction mixture because it is function of time, temperature and coordinates in space. So far, there is no good theory used to calculate effective permittivity of chemical reaction mixtures. A feasible method is to measure effective permittivity of chemical reaction mixtures by experiment and then calculate electromagnetic wave propagation and absorption law in chemical reactions if understanding interaction between microwave and chemical reactions. During the experiment, it is impossible to measure the effective permittivity of reactants varying simultaneously with time and temperature. Because chemical reaction is a dynamic process and reactant-to-reactant ratio varies all the time before reaction ending, effective permittivity of this mixture also changes. Moreover, chemical reaction is always accompanied with heat absorption and release and thus the temperature of the mixture varies all the time in the reaction. Under microwave radiation, the non-uniform effect of microwave on chemical reactions changes temperature and chemical reaction rate of mixtures, resulting in non-uniform temperature distribution in the mixtures, which also leads to effective permittivity being a function of space. Thus, it is impossible to measure effective permittivity at each point of the mixtures. In order to solve the problems above, reactant mixture in the experiment can be considered to be homogeneous under persistent stirring during the reaction and special approaches are used to control temperature, thus effective permittivity of chemical reaction mixture varying with time can be measured. Effective permittivity of chemical reactant mixture varying with time and temperature can be obtained with theoretic and experimental approaches as follows.

2 Calculation of effective permittivity in chemical reactions

2.1 Empirical formula for calculating the complex effective permittivity of aqueous electrolyte solution at microwave frequency

The dielectric property of an aqueous electrolyte solution is interesting to many researchers in geophysics, remote sensing and environment measurement. Therefore, it is not surprising that the topic has been the subject of numerous studies. Many liquid-phase reactions can be easily controlled and stirred [9]. Thus, it is necessary to understand permittivity of an aqueous electrolyte solution under microwave frequencies firstly. Meanwhile, water molecules structure and dynamics variation in an aqueous electrolyte solution can be further researched and microwave absorption and reflection by different electrolyte solutions can be understood. According to Ref. [10] and experimental verification, the following experimental equation can be employed to calculate complex effective permittivity of electrolyte solution [11]

$$\varepsilon_{\text{eff}} = \varepsilon_{\text{H}_2\text{O}} - \sum_i (\alpha_i \mu_i + \nu_i \beta_i) C(x_i) \quad (1)$$

where ε_{eff} means complex effective permittivity of electrolyte solution, $\varepsilon_{\text{H}_2\text{O}}$ means complex permittivity of water, α_i and β_i are the absolute value of ionic and anionic valences respectively, μ_i and ν_i are the complex influence factors of ion and anion in the i th electrolyte to complex permittivity of water. $C(x_i)$ means concentration function of the i th electrolyte. The complex effective permittivities of different aqueous electrolyte solutions have been obtained and compared with the measured results at 915 and 2 450 MHz. A good agreement can be observed [11].

2.2 Calculation of effective permittivity in chemical reactions

2.2.1 Semi-empirical equation for reactant permittivity varying with temperatures

According to Onsager's theory [12] and the like, temperature coefficient of permittivity is a complex function $f(1/T)$

$$\frac{1}{\varepsilon_{\text{eff}}} \frac{d\varepsilon_{\text{eff}}}{dT} = f\left(\frac{1}{T}\right) \quad (2)$$

where $f(1/T)$ means continuous function, T means absolute temperature, ε_{eff} means effective permittivity. Expand $f(1/T)$ and neglect the high-order integral, and then the following equation can be obtained

$$\ln\left(\frac{\varepsilon_{\text{eff}}}{\varepsilon_{\text{eff}}^0}\right) = \ln\left(\frac{T}{T_0}\right)^{-\alpha} - \beta(T - T_0) \quad (3)$$

where α and β are constants $\varepsilon_{\text{eff}}^0$ is the effective permittivity of the substance under the temperature of T_0 . Substances with different composition have different α and β . It is assumed that chemical reaction rate constant is K_1 under temperature T_1 and K_2 under temperature T_2 . Then, the following equation can be obtained.

$$K_1 t_1 = K_2 t_2 \quad (4)$$

When t_1 and t_2 satisfy Eq. (4) under different temperature T_1 and T_2 , the reactants have the same composition. Complex effective permittivity measured under different constant temperatures T_1 , T_2 and T_3 can be utilized to obtain the value of various constants in Eq. (3). Then, according to Eq. (3) and effective permittivity $\varepsilon_{\text{eff}}^0$ of reactants varying with time measured under temperature T_0 , effective permittivity ε_{eff} of reactants varying with time measured under temperature T can be obtained.

2.2.2 Experimental verification

In order to verify correctness of the theory, an iodine reaction of acetone was carried out under four temperatures (30°C, 37°C, 44°C and 52°C). Then, complex effective permittivity of the corresponding mixing solution can be obtained through inversion of genetic algorithm in terms of the measured reflection coefficients. Figure 3 [13] is a comparison of the measured and calculated complex permittivity of the mixing solution at 2 450 MHz.

3 Kinetic model for the interaction between microwave and chemical reaction

Calculating electromagnetic field distribution and temperature distribution is always an important problem waiting to be solved in the microwave chemical engineering as well as an important basis for designing reasonable microwave chemical reactor. Generally speaking, it is necessary to obtain the solution of the problem with simultaneous equations of electromagnetic field, heat conduction and chemical reaction.

For example, when microwave is used to heat ethyl acetate saponification, it can be solved according to the following three equations:

Maxwell equations

$$\begin{aligned} \nabla \times \mathbf{E} &= -\frac{\partial \mathbf{B}}{\partial t} \\ \nabla \times \mathbf{H} &= \frac{\partial \mathbf{D}}{\partial t} + \sigma(t)\mathbf{E} \end{aligned} \quad (5)$$

Heat conduction equation

$$\begin{aligned} \rho_m C_m \frac{\partial T(x, y, z, t)}{\partial t} &= k_i \nabla^2 T(x, y, z, t) - V_s [T(x, y, z, t) - T_a] \\ &+ P_d(x, y, z, t) \end{aligned} \quad (6)$$

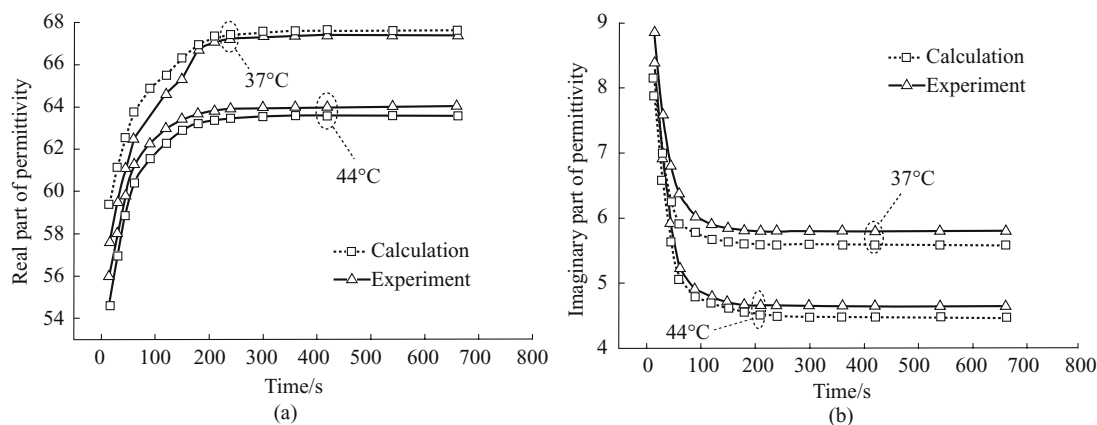


Fig. 3 Comparison of the calculated and measured effective permittivity at 2.45 MHz
(a) Real part; (b) imaginary part

Chemical reaction equation



Due to the exothermic reaction of ethyl acetate saponification, the effect of reaction heat released on the temperature of the solution should be taken into account when numerical simulation calculation is conducted. The chemical reaction is set to be carried out in the dilute aqueous solution. According to experimental results, the real part of relative permittivity of the solution is quite close to that of water while conductivity varies significantly with time and can be obtained through chemical reaction equation. At the same time, considering the effect of temperature rising on permittivity and conductivity, numerical method should be employed to solve by simultaneous Eqs. (6)–(8). The finite-difference time-domain (FDTD) method is verified to be an effective numerical method [14]. The microwave effect [15] is applied by transverse electromagnetic cell (TEM) cell instead of waveguide to carry out Ethyl Acetate Saponification. The experimental system is as follows.

It will take a very long time to stimulate the whole chemical reaction. Therefore, a dual leapfrog technology is employed to work out this problem well [16]. Herein, temperature rising and temperature distribution results are as follows [17].

It can be seen from the numerical stimulation results that temperature calculated from stimulation agrees well with the temperature measured by experiment, which provides references for application of microwave in chemical industry.

4 Non-thermal effects of interaction between microwave and chemical reaction

The non-thermal effect means the system response, which cannot be attributed to temperature variation after the system absorbs electromagnetic energy [18]. Some literatures name the non-thermal effect as the specific effect. However, the specific effect is different from the non-thermal effect. The so-called specific effect means the effect specifically caused by microwave radiation. Generally speaking, the non-thermal effect should belong to the specific effect while the specific effect does not belong to non-thermal effect. The difference lies in that the specific effect does not exclude the correlation with temperature. For example, phenomena such as different thermal gradient and local overheating caused by microwave heating, which is different from conventional heating, can be called as the specific effect other than non-thermal effect. In recent years, the non-thermal effect problem caused by microwave is attracting more attention [19]. Moreover,

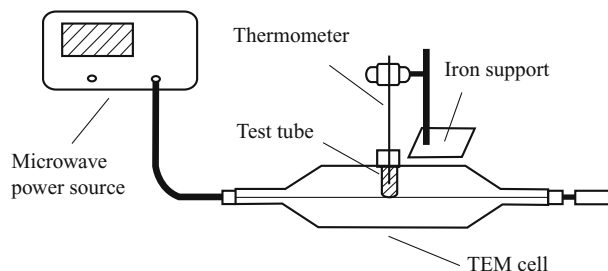


Fig. 4 Experimental system of ethyl acetate saponification heated by microwave

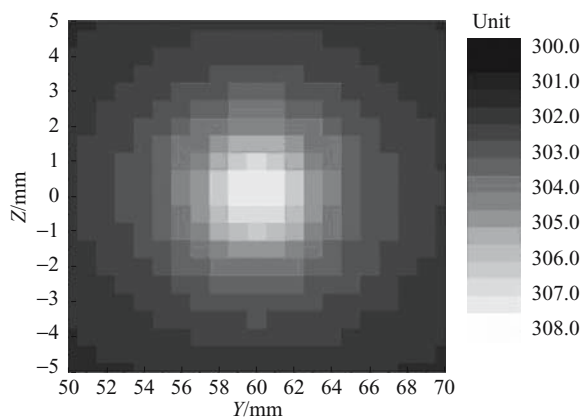


Fig. 5 Temperature simulation distribution TEM cell on the cross section of the TEM cell

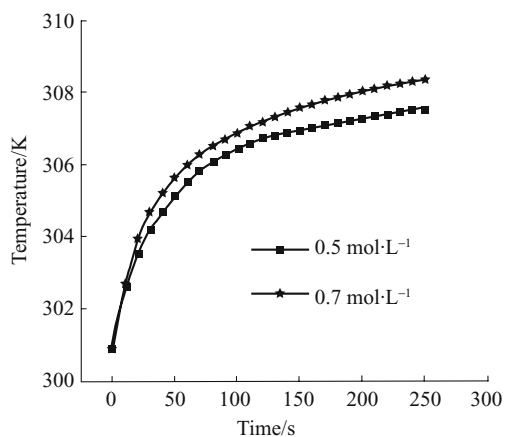


Fig. 6 Comparison of calculated values with the initial concentrations of 0.5 and 0.7 mol·L⁻¹ respectively

microwave non-thermal effects observed are mainly from some non-equilibrium systems: life system and chemical reaction system [20–23]. Non-thermal effects always occur in systems far from the equilibrium state and their characteristics are directly related to the non-equilibrium state itself.

Is there indeed existing a non-thermal effect? There has been no final conclusion yet. Some scientists represented by A. Loupy believed in the existence of the non-thermal effect [24]. Their theories all derive from the interaction between microwave and chemical reactions to prove the existence of the non-thermal effect through non-equilibrium dissipation theory. However, these theories are still in the exploratory stage and cannot provide believable answers. Presently, most of verification work of the non-thermal effect is still based on the experiments, mainly four types as follows.

1) Microwave heating and conventional heating were employed to heat the research subjects up to the same temperature and obtain different effects, thus considering the existence of the non-thermal effect. In 1998, Bednarz and Bogdal observed that in the organic synthetic experiments,

reaction rate under microwave heating was different from that under conventional heating [25]. In 1990, Bose and Manlas placed reactants in a beaker containing ice/water mixture to ensure constant temperature. Under this condition, they obtained different results from those under conventional heating [26]. Many scientists, such as Gedye and Mingos, found that there were obvious differences between microwave heating and conventional heating in many chemosynthesis when heated to the same temperature [27–30]. All these experiments were based on the idea above to prove the existence of the non-thermal effect [31–33].

2) Weak microwave or single electromagnetic pulse was employed to affect the system, considering that such a weak microwave or single electromagnetic pulse signal would not cause the macroscopic temperature rising of the system and the different action effects obtained under this condition were considered to be with no relationship to temperature and could be called as the non-thermal effect. In 1994, Azanza and del Moral reported that under weak microwave radiation, the biochemical reaction of pericellular membranes were affected [34]. In 1999, Elizabeth et al. reported the effect of weak electromagnetic pulse on cell protein [35]. Meanwhile, plenty of related literatures reported the non-thermal effects obtained on the basis of this experimental idea [36–39]. However, there are few literatures on the interaction between weak electromagnetic wave and chemical reactions. Actually, this method is also incredible, because under the single electromagnetic pulse or weak microwave, though it cannot cause the macroscopic temperature rising of the system, microwave can selectively heat the system, and thus it is impossible to exclude the possibility of local temperature rising. Moreover, this temperature rising is difficult to be measured. How to exclude this difficult measured macroscopic temperature rising? That is a large problem to overcome when adopting this method so as to ensure the correctness of the results.

3) Effects can be obtained under microwave heating but cannot be obtained under conventional heating, thus non-thermal effects are considered to exist. In 1998, Maoz et al. found changes, which could not be obtained under conventional heating during the process by fixing a self-assembled bi-layer on the inert silicone resin [40]. In 1999, Haswell and Howarth observed phenomena during the solid phase separation under microwave radiation, which could not be observed under conventional heating [41]. However, these experiments cannot indicate the existence of the non-thermal effect, either. That is because that microwave heating can obtain high temperature or temperature distribution that cannot be obtained under conventional heating, such as boiling points of various chemical dissolvent (including water) rising under microwave heating [42–44], as well as homogeneous heating or thermal gradient. Therefore, the difference caused by different temperature state of course cannot be attributed to the non-thermal effect. In this sense, the special effect related to temperature must be excluded so as to ensure the correctness of this method.

4) Effects obtained from microwave effect satisfy the characteristics of the non-thermal effect: window property, coherency, coordination and nonlinearity. Senise and Jermolovicious from IMT found that there were power windows when synthesizing emulsified unsaturated polymer resins [4]. Many other literatures reported the non-thermal effect in the related experiments [45–49]. Actually, non-thermal properties are not the necessary and sufficient condition for the non-thermal effect, because during the process of microwave heating, if high power of microwave, the intensity of polarization of substances cannot satisfy the linear relationship any more under high-field and permittivity itself can be affected by electric field and in relation to electric field and the rate of electric field change. Thus, system response to microwave is highly possible to possess non-thermal properties. However, in this case, it is very difficult to separate the non-thermal effect from the thermal effect. In addition, in case that the power is not high, Maxwell equations are linear equations, but heat conduction equation is a nonlinear one. During the heating process, nonlinear properties are introduced into microwave heating problems via the heat conduction equation. In such a process, it is possible to observe some properties of nonlinear systems. Besides, for the typical chemical reaction system, its effect permittivity variation possesses the typical nonlinear and nonequilibrium characteristics, and thus it is possible to generate characteristics of the non-thermal effect.

It can be seen from the analysis above that the existing experiments proving the non-thermal effect all have the following problems:

- 1) unreasonable experiment design, lack of genuinely and logically refined and persuasive experiment methods;
- 2) individual difference among experimental subjects and poor repeatability of the experimental data;
- 3) despite the repeatability of experimental data, due to that radiation strength is not so low, it may lead to local temperature rising which is usually difficult to be measured.

In addition, scientists such as Stuerger and Gaillard [50, 51] thought that microwave light quantum is insufficient to destroy any chemical bonds. Actually, even though microwave light quantum is very low, its action subject is not a completely generated chemical bond but a process of old chemical bond breakdown and new chemical bond generation. During this process, some chemical bonds are significantly weakened and can be easily broken down with vibration, thus microwave photon is possible to influence them. Scientists such as Stuerger and Gaillard calculated and obtained in terms of the second Wien's effect that only electric field of about 10^7 V/m could change the chemical reaction equilibrium. Actually, this estimation is inaccurate. First, it is also based on the theory of equilibrium state. With the continuous increase of electric field, variation of intensity of polarization before and after the reaction is not in a linear relationship to the field strength any more. Second, the so-called weak microwave means low power but does not

mean that it is impossible of high-field. For example, if there are fine conductive media existing in the action system, extremely high field can be generated near these media. Therefore, it is a one-sided view to consider that low power is impossible to cause the moving of chemical equilibrium.

Based on the calculating results of Langevin function that at the room temperature, obvious molecular orientation can be caused only under a high field of about 10^5 V/m, scientists such as Stuerger thought that weak microwave was impossible to cause self-organization behavior of substances. However, they neglected that Langevin function was on the basis of Maxwell-Boltzmann distribution of equilibrium theory, which is doubtful to be used in the corresponding calculation of nonequilibrium theory. Besides, lots of literatures have reported the fact that in the chemical reaction there are molecules with one or more unpaired electrons whose rotation direction can be affected by electromagnetic field [52], for example, the microwave effect is possible to cause molecular orientation.

In summary, the non-thermal effect is a complex problem related to non-equilibrium state and it is incorrect of any simple affirmation and denial. To truly work out this problem entails further development of the interaction mechanism of microwave and chemical reaction as well as the non-equilibrium-state theory.

5 Conclusion

Microwave chemistry is a new interdisciplinary science. Researches within this domain have the very important practical significance and profound theoretical significance to develop the classic electromagnetic theory and make it suitable for the non-equilibrium system. These researches are focused on the non-linearity and non-equilibrium processes of microwave heating, which contributes to radically work out the two stringent problems currently in the application of microwave chemical industry: nonlinear response prediction of the reaction system to microwave and the design of high-efficient and homogeneous-heating reactors. Moreover, it can provide theoretical guides for other microwave chemical engineering application problems so that it can be more possible to recognize the interaction mechanism between microwave and chemical reaction. Currently, there are immature in many aspects of the domain, especially in the description of the electromagnetic properties of the reaction system and kinetic system stimulation that requires further researches.

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