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Short Communication

Temperature cycle measurement for effective permittivity of biodiesel reaction

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A B S T R A C T

The aim of this communication is firstly to describe the effective permittivity of the biodiesel reaction for multiphysics calculation of microwave heating. An innovatively method was proposed to get the effective permittivity of the biodiesel reaction solution through one measurement, which can be directly applied for the thermal analysis of microwave heating on biodiesel reaction based on the multiphysics calculation. The effective permittivity of biodiesel reaction at any temperature and concentration obtained in this paper. The maximum relative error of real part is 4.10%, and 5.65% for imaginary part. The calculated results also show good agreement with the measured results at constant temperature.

1. Introduction

As a new technique on chemical engineering, microwave heating has been developed rapidly in recent years, for the advantages of using microwave processing applications in chemical engineering lie in energy saving, improved quality, reduced wastage, instantaneous control and unique characteristics induced by "volumetric" heating (Jin et al., 1999; Gedye et al., 1986; Hasna, 2011). Microwave also presents a good prospect in the biodiesel production (Muthukumar, 2008; Ruan et al., 2011; Leadbeater et al., 2006). Unfortunately, inhomogeneous heating and thermal runaway prevent high-power microwaves from being widely adopted in chemical engineering industry (Chen et al., 1993; Sontos et al., 2011; Horikoshi et al., 2011). To industrialize the microwave-assisted biodiesel production, it is essential to accomplish the simulation of microwave-assisted biodiesel reactions with multiphysics calculation at first. Besides, the measurement and description of the effective permittivity of the biodiesel reaction is preliminary and necessary for multiphysics calculation. For liquid chemical reaction, the effective permittivity can be determined by the reacting solution's component and temperature. In the previous paper, a method was proposed to calculate the effective permittivity of the reacting mixture solution, by using three measured curves of effective permittivity with time at three constant temperatures (Zhu et al., 2012). However, the reaction must be carried out three times and the derived formula of effective permittivity is a function of reaction time, which makes it be inconvenient to be used directly.

In this communication, the method in Zhu et al. (2012) is improved. Firstly, the effective permittivity of the reacting mixture solution was described by a bivariate function with the concentration of one reactant and temperature. Then, the bivariate function was expanded into the power series of the concentration and the exponential function of temperature. Finally, measurement was innovatively carried out in a temperature cycle way to obtain the coefficients in the expansion. The effective permittivity of the reacting mixture solution with the concentration of one reactant and temperature can be obtained by a measurement and simple calculation.

The synthesis of biodiesel is carried out to validate the method. The effective permittivity of both reactions is measured at 2450 MHz which is the widely used ISM band in the world. The calculated results show good agreement with the corresponding measured results, and the maximum errors are 5.31%.

2. The description of effective permittivity

For a liquid chemical reaction, the effective permittivity of the reacting mixture solution can be determined by the component and temperature of reacting solution. The reacting solution's component can be described with the concentration of one reactant; consequently, the effective permittivity should be described by a bivariate function of temperature and the concentration of one reactant. According to Debye's equation (Debye, 1929), the permittivity of most substances exponentially changes with temperature varia-

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tion. On the other hand, nonlinear model, for example, Gaussian function, has potential to better fit nonlinear data with a small number of coefficients (Green et al., 2006). Therefore, the effective permittivity of reacting mixture solution was expanded into the power series of the concentration and exponential function of temperature. The formula can be expressed as follows:

$$\varepsilon'_{eff} = \varepsilon_0\varepsilon'_r = \varepsilon_0\left[\sum_{i=0}^{N} a_i C^i + d_0 \exp\left(-\left(\frac{T-d_1}{2d_2}\right)^2\right)\right] \tag{1.a}$$

$$\varepsilon''_{eff} = \varepsilon_0\varepsilon''_r = \varepsilon_0\left[\sum_{i=0}^{N} b_i C^i + g_0 \exp\left(-\left(\frac{T-g_1}{2g_2}\right)^2\right)\right] \tag{1.b}$$

where, ε'_{eff} and ε''_{eff} are the real part and imaginary part of effective permittivity, respectively. T stands for the temperature of the reacting mixture solution. C refers to the concentration of one reactant in the reacting solution. a_i, b_i, d_i and g_i are unknown coefficients. Usually, $N = 2$ is enough to fit the change of the effective permittivity with the concentration of one reactant. In this case, there are 6 coefficients which should be determined in Eq. (1). a_0, a_1, a_2, d_0, d_1 and d_2 are used to calculate the real part of effective permittivity. b_0, b_1, b_2, g_0, g_1 and g_2 are for the imaginary part. Here, the measurement was innovatively implemented in a temperature cycle way and measurement of the effective permittivity in a wide temperature range. The curve of effective permittivity with time and temperatures can be obtained via one measurement. By using reaction rate equation, the measured result can be transferred into a new curve with the concentration of one reactant and temperature. Then, the data in Eq. (1) was substituted and calculate the coefficients a_i, b_i, d_i and g_i via the least square fitting, this step operated by MATLAB.

3. Experimental

3.1. Experimental system

Agilent E8362B microwave vector network analyzer is used to measure the reflection coefficients from a special designed coaxial probe (Huang et al., 2003) in the measurement system, which is merged in the reacting solution and the probe's location must be in the same as mathematic model when we calculate the Artificial Neural Network samples by FDTD method. The measurement is performed at 2450 MHz which is the worldwide used ISM band. A well-designed 3-necked florence flask whose volume 500 ml is utilized. At the same time, UMI-8 optical fiber thermometer is employed to measure the temperature of the mixture solution. The 85-2 magnetic stirrer's rotation speed in the experiment is 2000 rpm. A customized water bath trough is used to control the temperature of the reacting solution in the flask by exquisitely controlling the temperature and the speed of influent water. In this way, a temperature curve can be obtained as expected; meanwhile, the scattering coefficients of the reaction system are measured online by the coaxial probe.

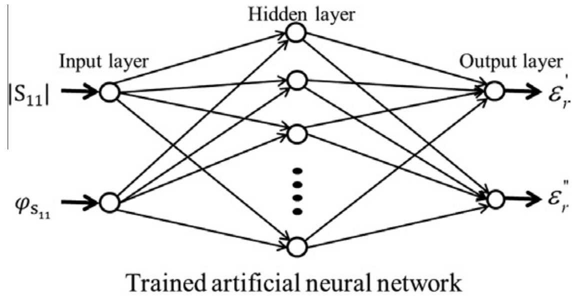

Fig. 1. The inversion of effective permittivity by trained network.

3.2. Inversion of effective permittivity

The Artificial Neural Network computational module has been widely used in microwave technology recently. Here, ANN model based on BP training algorithm was employed to inverse the effective permittivity. Firstly, a measurement system is designed and the scattering parameter at 2450 MHz is calculated by the frequency dependent finite difference time domain (FDTD) method. Secondly, a BP nerve network and enough simulated samples were combined to train the networks. Then, the trained BP neural network was employed to reconstruct the effective permittivity by the measured scattering parameter, and the inverse process shown in Fig. 1.

3.3. Chemical reaction

Biodiesel is produced by esterification of fatty acids and methanol. As a typical fatty acid, oleic acid is employed to produce biodiesel with methanol. Catalyst in the reaction is concentrated sulfuric acid. Following is the reaction equation:

$$RCOOH + CH_3OH \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} RCOOCH_3 + H_2O \tag{2}$$

As for the synthesis of biodiesel, the molar ratio of methanol to oleic acid was 6:1, and the mass fraction of concentrated sulfuric acid to the whole reaction solution was 1%. The reaction rate equation can be written as follows:

$$-\frac{d\left(C^0_{RCOOH} - C_{H_2O}\right)}{dt} = k_1\left(C^0_{RCOOH} - C_{H_2O}\right)\left(C^0_{CH_3OH} - C_{H_2O}\right) - k_{-1}C^2_{H_2O} \tag{3}$$

where C^0_{RCOOH} and $C^0_{CH_3OH}$ are the initial concentrations of oleic acid and methanol respectively, C_{H_2O} stands for the concentration of water, k_1 is the rate constant for the forward reaction and k_{-1} is the rate constant for the reverse reaction, the rate constant satisfy Arrhenius equation:

$$k_1 = A_1 \exp\left(-\frac{E_a^+}{RT}\right) \tag{4.a}$$

$$k_{-1} = A_{-1} \exp\left(-\frac{E_a^-}{RT}\right) \tag{4.b}$$

where E_a^+ and E_a^- are the activation energy of the forward and reverse reaction, the values are 33.8 and 13.9 kJ/mol, respectively. And the pre-exponential factor A_1, A_{-1} are respectively 743.6 and 0.606 (Peng, 2009). R is universal gas constant.

Therefore, the concentration of water in the reaction can be calculated. Then, the measurement results as a function of time can be transferred to be a function of resultant's concentration.

4. Results and discussion

Due to the boiling point of methanol is 64.8 °C under standard atmospheric pressure. And the bubbles will affect the scattering parameter of the solution. Therefore, the reaction was carried out in a temperature range from 20 °C to 60 °C. The measurement temperature and measured effective permittivity with time are shown in Fig. 2. The effective permittivity at different resultant's concentrations and temperatures can be obtained by Eq. (3). Then, combine with Eq. (1), the coefficients in the equation can be obtained via the least square fitting. Finally, the effective permittivity at any temperature and concentration can be obtained.

As the effective permittivity of reaction solution is a bivariate function of reaction's component and temperature. Here describe it as a 3D plot, which the change trend with the concentration of