Estimation of Outlet Temperature of a Flow Reactor Heated by Microwave Irradiation

doi: 10.1002/tcr.201800102

Estimation of outlet temperature of a flow reactor heated by microwave irradiation

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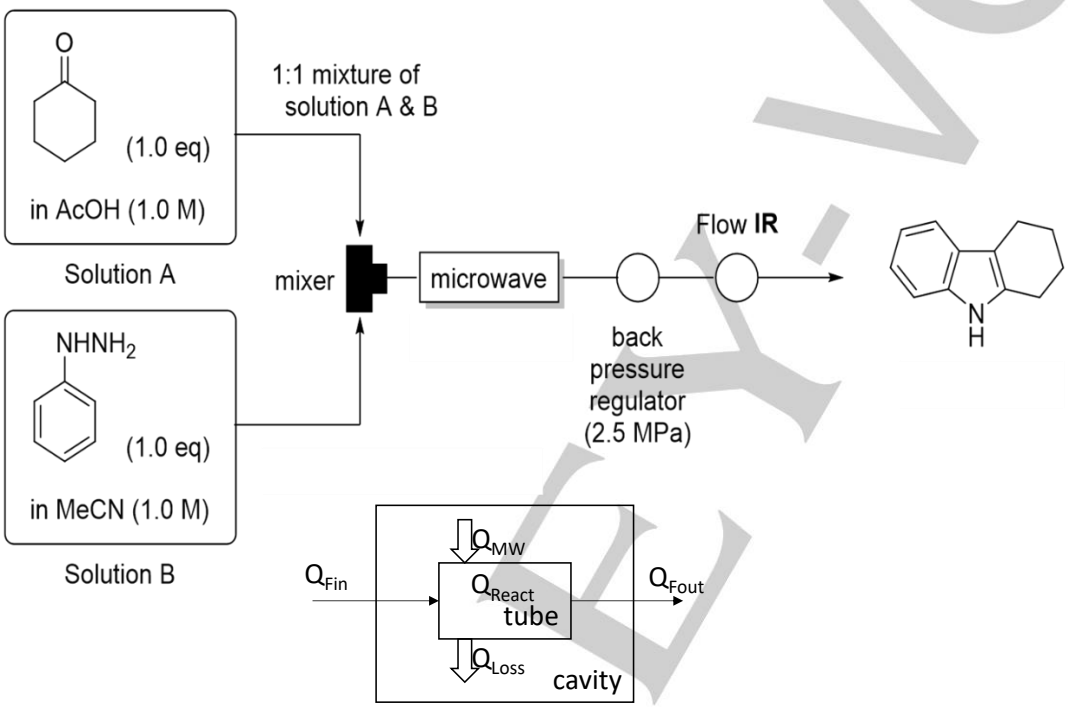

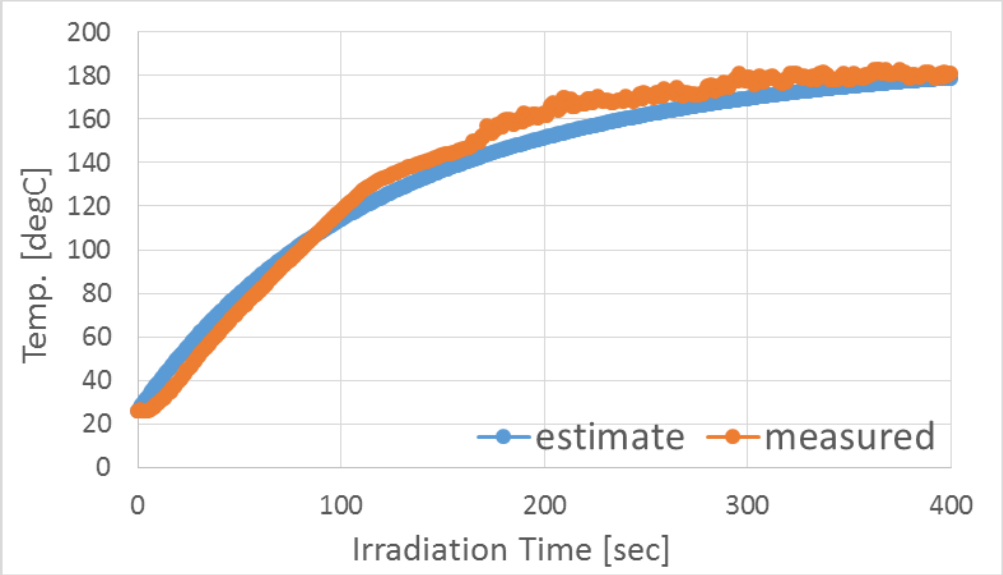

Abstract: Flow reactors heated by microwave irradiation attract attention. The reactors are suitable for difficult synthesis processes due to rapid heating and cooling, and easy pressurization. In order to predict the quality of the product, it is appropriate to estimate the outlet conditions of the reactor. In this paper, the outlet temperature of the flow direction is estimated by using the flow condition and dynamic thermal energy balance of the reactor.

1. Introduction

An Organic synthesis heated by microwave irradiation [1] has many merits, such as faster reaction rate, higher purity, less byproducts, less amount of solvents than conventional heating. Therefore, a microwave irradiated process is hoped to be environmental friendly and saving energy. The one of the defect of the process is that the shallow penetration depth prevent large scale reactor. When energy is efficiently transferred from the microwave to the solvent, the microwave attenuates quickly and does not penetrate deeply. Toward this, a thin flow reactor can overcome the defect because the reactor is enough thin to receive the microwave power [2]. A flow reactor system heated by microwave irradiation is illustrated in Figure 1.

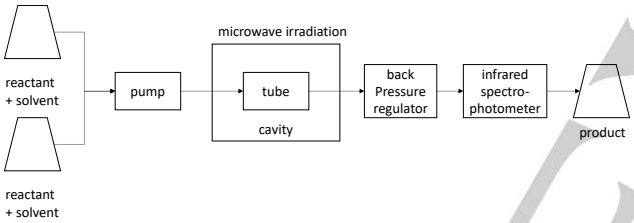

Figure 1 Schematic of a flow reactor heated by microwave irradiation.

In the reactor system, reactants are mixed in the thin tube, compressed by back pressure regulator, heated by microwave irradiation, and cooled and depressurized as products. The reactor can produce some tons of products per year, because the diameter of a thin tube is not a micrometer size but a millimeter size. High pressure, high temperature, and high concentration can achieve high space time yield even difficult synthesis. The temperature can be rapidly and correctly controlled with heating by microwave irradiation. Furthermore, using real-time infrared spectrophotometer, the output compositions can be measured online. Therefore, the system can be more safely, reliably, efficiently, and sustainably produce than a batch reaction system [3]. Shanga et al. [4] proposed the flow reactor heated by microwave irradiation can achieve higher yield with properly conditions than a batch reactor, and higher yield by multi-step reactor system.

For assurance of quality, flowrate, pressure, reactant concentration, temperature and so on should be controlled. Yokozawa et al. [5] used design of experiments method for finding an optimal condition of the flow reactor heated by microwave irradiation. Flowrate, pressure, and reactant concentration can be easily measured and controlled. While the output temperature can be easily measured, it is difficult to measure the temperature distribution profile in the reactor. Because the profile can be easily measured for a micro reactor without using microwave irradiation, the profile is investigated [6]. Although, for the flow reactor heated by microwave irradiation, a thermocouple cannot be inserted into the cavity of the reactor because the metal disturbs the electromagnetic field, optical fiber sensor cannot be inserted into the reactor because the fiber disturb the flow, and infrared sensor can only measure the fluid surface temperature not the internal temperature. Estimating the outlet temperature can help to estimate the temperature distribution by dividing the reactor in axial direction. Therefore, estimating the quality of the products, the dynamic temperature of the outlet of the reactor should be estimated. Then, this paper proposes an estimation method of the outlet temperature of the reactor based on the dynamic energy balance equation.

2. Theory

For estimating outlet temperature, conversion distribution in radial direction in a reactor is derived. Using the distribution, the outlet temperature is derived.

2.1. Conversion Distribution in Reactor

In case of a plug flow reactor, residence time of the reactor τ is given by Equation (1)

$$\tau = \frac{V}{F} \tag{1}$$

where V [m^3] is volume of the reactor and F [$m^3\ s^{-1}$] is flowrate. In an actual system, the flow is not a plug flow but a laminar flow with the low Reynolds number representing a flow state of a dimensionless number. According to the Hagen-Poiseulle's law, the flow velocity of a laminar flow at distance r from center of a circular tube is given by the Equation (2)

$$\frac{u_r}{u_{max}} = 1 - \left(\frac{r}{R}\right)^2 \tag{2}$$

where u_r [$m\ s^{-1}$] is flow velocity at distance r from tube center, u_{max} [$m\ s^{-1}$] is maximum flow velocity at center, and R [m] is radius of the tube. The residence time at distance r from tube center is given by Equation (3)

$$\tau_r = \frac{L}{u_r} \tag{3}$$

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where τ_r [s] is residence time at distance r from tube center and L [m] is length of the reactor. Using Equation (4), reaction rate gives the outlet concentration of the reactor

$$\int_{C_{Ar_{in}}}^{C_{Ar_{out}}} \frac{dC_A}{r_A} = \tau_r \tag{4}$$

where C_{Arin} [mol m^{-3}] is the inlet concentration of the reactor, C_{Arout} [mol m^{-3}] is the outlet concentration of the reactor, and r_A [mol m^{-3} s^{-1}] is reaction rate. For example, if a reaction is first order of the reactant, then the outlet concentration is given by Equation (5)

$$\mathrm{C_{Ar_{out}}} = \mathrm{C_{Ar_{in}}} \exp(-\mathrm{k}\tau_r) \tag{5}$$

where k is reaction rate constant. Therefore, the outlet yield y_r [-] at distance r from tube center of the reactor is given by Equation (6)

$$y_r = \frac{C_{A_{in}} - C_{Ar_{out}}}{C_{A_{in}}} \tag{6}$$

The outlet yield distribution is given by calculation of Equation (6) from r =0 to r = R.

2.2. Temperature Profile of Reactor by Dynamic Energy Balance

The dynamic energy balance equation of the reactor is formulated. Heat energy is accumulated by balance of along with inlet stream Q_{Fin} [J s^{-1}], along with outlet stream Q_{Fout} J s^{-1}], heated by microwave irradiation Q_M [J s^{-1}], dissipation from surface of the reactor Q_L [J s^{-1}], and heat of reaction Q_R [J s^{-1}] as shown in Figure 2. The time series of dynamic temperature of the reactor is given by solving the initial value problem of an ordinary differential equation as shown in Equation (7).

$$C_{PA} \cdot V \cdot \frac{dT}{dt} = Q_{F_{in}} - Q_{F_{out}} + Q_M - Q_L + Q_R \tag{7}$$

where C_{PA} [J kg^{-1} K^{-1}] is heat capacity of whole reactor, and V [kg] is mass of the reactor.

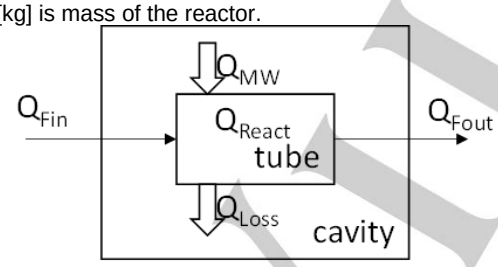

Figure 2 Heat energy flow around a reactor.

The heat energy input and output along with fluid is given by Equation (8)

$$Q_{F_{in}} - Q_{F_{out}} = \sum_{component\ \ i} F_{in,i} \cdot C_{P,i}\left(T_{in} - T_{ref}\right) - \sum_{component\ \ i} F_{out,i} \cdot C_{P,i}\left(T_{out} - T_{ref}\right) = \sum_{component\ \ i} F_{in,i} \cdot C_{P,i}(T_{in} - T_{out}) \tag{8}$$

Where $F_{in,i}$ [kg s^{-1}] is inlet flowrate of component i, $F_{out,i}$ [kg s^{-1}] is outlet flowrate of component i, T_{in} [K] is inlet temperature, T_{out} [K] is outlet temperature, T_{ref} [K] is reference temperature, and $C_{p,i}$ [J kg K^{-1}] is heat capacity of component i. Q_M may be estimated by microwave power and microwave absorption rate of fluid and the tube. Although, the absorption rate is characteristic value for each component and vary with temperature. Furthermore, the composition of the mixture may be varied by reaction in reactor and the absorption rate of mixture may not be followed the mixing law. The absorption rate and mixing law considering above is not given. Therefore, relationship between Q_M and microwave power are approximated as Equation (9)

$$Q_M = a \cdot P_M \tag{9}$$

Where P_M [W] is microwave power and a [s^{-2}] is experimental parameter of overall absorption rate of fluid and the tube. The tube in the cavity is not insulated to heat by microwave irradiation. Therefore, dissipation from surface of the tube is not negligible. Q_L is given by Equation (10)

$$Q_L = b \cdot \Delta T \tag{10}$$

Where ΔT [K] is temperature difference between surface of the tube and ambient and b is parameter of dissipation. The parameter corresponds to the product of the tube surface area and the sum of the film heat transfer coefficient between the fluid and the tube, the heat transfer coefficients of the tube, and the film heat transfer coefficient between the tube and the ambient. The film heat transfer coefficient between the fluid and the tube is varied with reaction. Therefore, parameter of dissipation b may be determined by experiments. Q_R is given by Equation (11)

$$Q_R = \left(\sum_{component\ \ i} H_{P,i} - \sum_{component\ \ i} H_{R.i}\right) \cdot n \tag{11}$$

where n [mol s^{-1}] is amount of products, $H_{p,i}$ [J mol^{-1}] is specific enthalpy of product i, and $H_{R,i}$ [J mol^{-1}] is specific enthalpy of reactant i. n follows yield in Equation (6) because products are generated by reaction. From the above, dynamic temperature profile is given by Equation (7).

3. Experiments

3.1. Object Reaction

Object reaction system is shown in Figure 3. Reactants of object reaction were cyclohexanone and phenyl-hydrazine. Cyclohexanone was solved in acetic acid at 1.0 M and phenyl-

hydrazine was solved in acetonitrile at 1.0 M. These solutions were mixed on 1:1 through the mixer. The flowrates were 1.0 or 2.0 mL/min. The mixture was heated by microwave irradiation. The powers of microwave irradiation were 10, 20, or 30 W. The dielectric constants of solvents, reactants, and product were shown in Table 1. The dielectric properties of the mixture cannot be estimated using the dielectric constants, because the constants of the product were unknown, and the mixture were heated by conductive loss of acetate and dielectric loss of the mixture. The helical tubular borosilicate glass reactor was pressurized at 2.5 MPa. The reactor was enveloped in the TM110 type rectangular resonant cavity. The product yield was measured by the flow IR. Ambient temperature was 298 K.

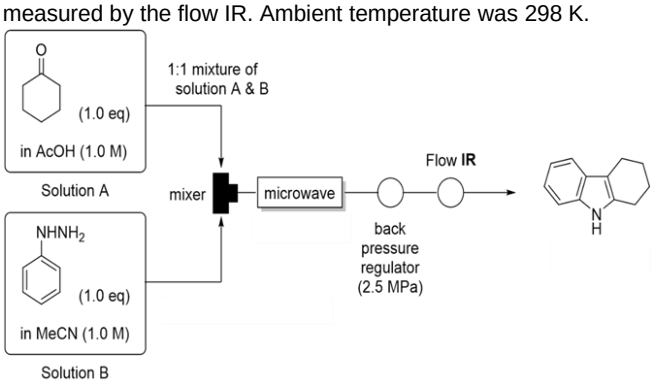

Figure 3 Object reaction system.

Table 1. Dielectric Constants of Solvents, Reactants, and Product.

	Dielectric constants [-]
Acetic acid	6.2 @ 298.15 K
Acetonitrile	36.1 @ 298 K, 0.1 MPa
Cyclohexanone	15.421@ 303.2 K, 0.1 MPa
Phenyl-hydrazine	7.2 @ 298 K
n-phenyl-benzenamine	-

3.2. Flow Condition

In object reaction system, density, viscosity, and heat capacity of reactants and products were negligible because solvents were much enough than reactants and products. Density, viscosity, and heat capacity of the mixture in the reactor were determined by mixing law as shown in Table 2. The radius of the reaction tube was 1.2 mm. The flow was laminar because Reynolds number of the flow was 2228.

Table 2. Physical Properties of Solvents.

	Density [g/cm3]	Viscosity [cp]	Heat capacity [J/(kg K)]
Acetic acid	1.05	1.1	1272
Acetonitrile	0.786	0.35	2152
Mixture	0.899	0.725	1712

3.3. Outlet Concentration of Product

Order of object reaction was 0.79. The outlet concentration of product at distance r from the tube center is given in Equation (12)

$$C_{Ar_{out}} = \sqrt[0.21]{C_{Ar_{in}}{}^{0.21} - 0.21k\tau_r} \quad (12)$$

Standard enthalpies of formation of reactants and product as shown in Table 3 were estimated using PM6 method, which was a semi-empirical method in Gaussian 16. Then, heat of reaction was 245.8 kJ/mol. Remaining parameters were determined by solving simultaneous energy balance equations.

Table 3. Estimated Standard Enthalpies of Formation of Reactants and Product.

	Standard enthalpies of formation [kJ/mol]
Cyclohexanone	29.1
Phenyl-hydrazine	201.7
n-phenyl-benzenamine	225.1

It was assumed that irradiated microwaves were not absorbed by the reactants and product but were absorbed by the solvents, because the solvents were sufficiently large compared to the reactants. When solvents flow without reactants through the reactor at steady state, then left side of Equation (7) was zero and $Q_{Rqloeact} = 0$. Therefore, Equation (7) became

$$0 = Q_{F_{in}} - Q_{F_{out}} + Q_M - Q_L \quad (7)'$$

Solving Equation (7)' for two different flowrates simultaneously, parameters *a* and *b* could be obtained. Table 4 shows the experimental conditions. Figures 4 shows the experimental temperature for time series. From these results, we obtained *a*=0.83 and *b*=0.07 J/(s K). Then, C_{PA} can be obtained as 7.77 J/(kg K) by substituting *a* and *b* to Equation (7).

Table 4. Experimental Conditions to Identify Parameters.

Case	Flowrate [mL/min]	Microwave irradiation power [W]
1	1	10
2	2	10

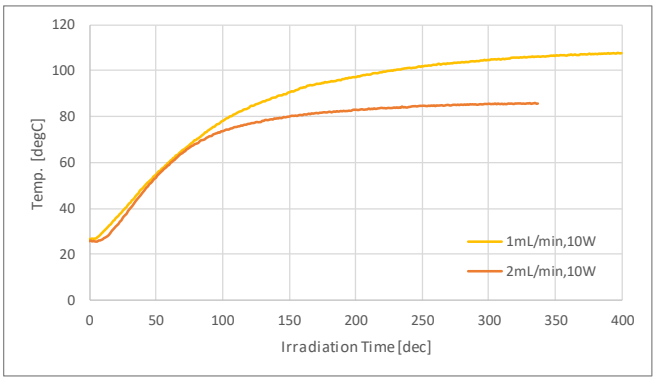

Figure 4 Temperature trend for microwave irradiation.

4. Results and Discussions

4.1. Estimation of Outlet Temperature in Case of Uniform State of Reactor

First, outlet temperature was estimated as uniform state of the reactor. The flowrates were 1.0 mL/min or 2.0 mL/min. The powers of microwave irradiation were 10 W, 20 W, and 30 W. The experimental and estimated outlet temperature are shown in Figures.5.

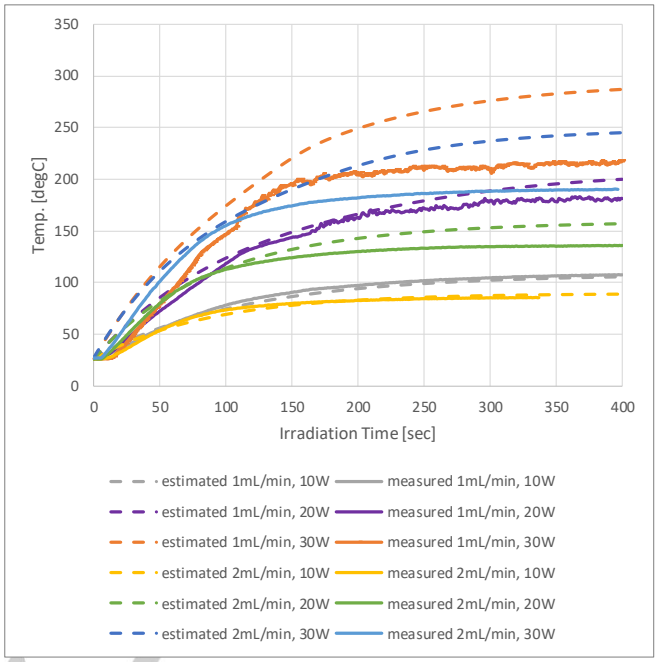

Figure 5 Measured and estimated temperature profile for microwave irradiation.

When the power of microwave irradiation was 10 W, the estimations of the outlet temperature were good agreement for any flowrate. The higher the power of microwave irradiation, the larger the error between the experimental value and the estimated value. Therefore, microwave absorption parameter *a* was adjusted to minimize the error. The optimized *a* was 0.75 for 20 W and 0.66 for 30 W. The estimated outlet temperature using the adjusted *a* are shown in Figures 6. As a results, although the adjusted *a* became smaller corresponding to the reduction of the microwave power, the absorption parameter *a* is considered to be related with the solvents temperature regardless of the microwave power.

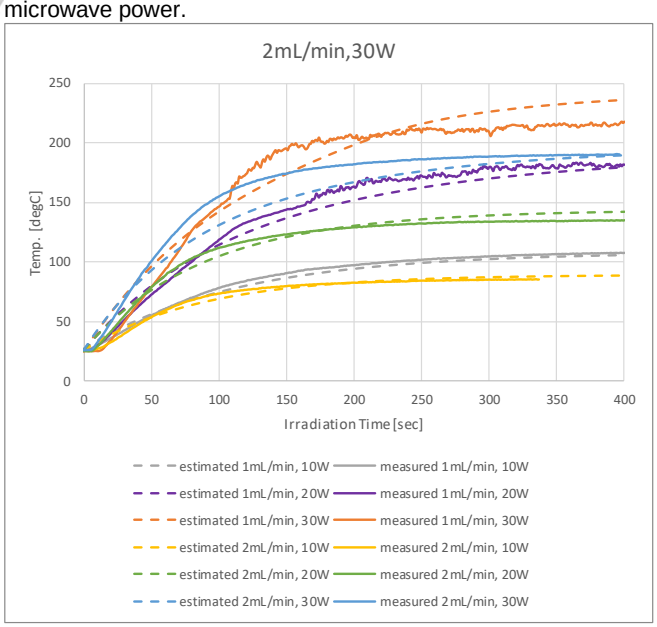

Figure 6 Measured and estimated temperature profile using optimized parameter a for microwave irradiation.

5. Conclusions

This work estimated the dynamic temperature profile of the outlet of the reactor. The estimation of the outlet temperature of the reactor were good agreement to the measured value at 10 W. Although, the higher the power of microwave irradiation, the larger the estimation error. Then, adjusting the absorption parameter *a*, the error became smaller. For future research, by improving the reaction system so that the temperature distribution profile will be measured.

Acknowledgements

The authors are grateful to Saida FDS Inc. for providing the flow microwave reactor and technical support.

Keywords: microwave irradiation, flow reactor, estimation, dynamic heat energy balance

[1] O. Kappe, C., and A. Stadler, *Microwaves in organic and medical chemistry*, **2005**, 1-409.
[2] Lionel E., M. Poux, N. Benamara, I. Polaert, *Chemical Engineering and Processing*, **2017**, 113, 56-64.
[3] L. J. Martin, A. L. Marzinzik, S. V. Ley, and I. R. Baxendale, *Organic Letters*, **2011**, 13, 320-323.
[4] M. Shanga, T. Noëla, Q. Wanga, Y. Sua, K. Miyabayashi, V. Hessela, S. Hasebe, *Chemical Engineering Journal*, **2015**, 260, 454-462.
[5] S. Yokozawa, N. Ohneda, T. Okamoto, H. Odajima, *RSC Advances*, **2015**, 5, 10204–10210.
[6] P. C. Pontes, C. P. N.-Cotta, J. N.N. Quaresma, *International Journal of Thermal Sciences*, **2017**, 118, 104-122.

Kazuhiro Takeda was born in 1967 in Takamatsu, Japan. He received his Ph.D. degree from Kyushu University under the supervision of professor Matsuyama Hisayoshi in 1995. He began his academic career as an assistant professor at Kyushu University in the same year. He is now an associate professor of applied chemistry and biochemical engineering at the graduate school of engineering, Shizuoka University since 2005. His current research interests are as follows. 1) Design optimization and automated operation of microwave flow reactor, 2) Business process model for safety operation, 3) Kinetic analysis of conjugal transfer of plasmid.

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Entry for the Table of Contents (Please choose one layout)

Layout 2:

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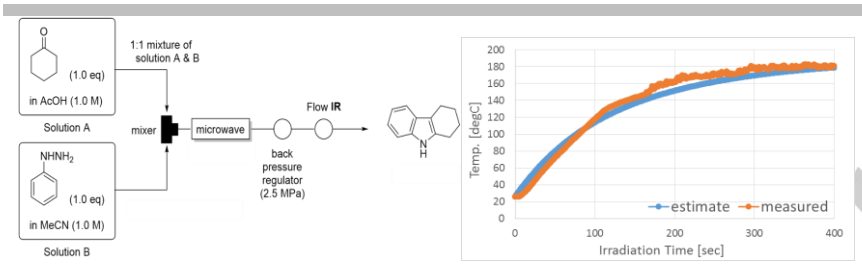

The outlet temperature of the flow direction is estimated by using the flow condition and dynamic thermal energy balance of a flow reactor heated by microwave irradiation. The temperature estimation can contribute to estimate the quality of the product.

Kazuhiro Takeda, Nana Yanagi, Keisuke Nonaka and Nobuyuki Mase*

Page No. – Page No.
Estimation of outlet temperature of a flow reactor heated by microwave irradiation