

# THERMAL PULSE-RESPONSE OF REVERSIBLE LIQUID REACTION IN A TUBULAR REACTOR(I)

## — Investigation of Possibility for the Parameter Estimation by Thermal Pulse-Response Technique —

Heung Joe Jung, Chang-Bock Chung and Chan Young Park\*

College of Engineering, Chonnam National University, Kwangju 500-757, Korea

(Received 28 June 1991 • accepted 5 December 1991)

**Abstract**—The transient action of a tubular reactor, in which the liquid mixtures react reversibly, in response to the pulse input establishing a set of nonlinear partial differential equations has been analysed. Using collocation with B-spline basis piecewise polynomial approximation, the solution protocols of the system has been formulated in order to estimate parameters, such as transport, kinetic and thermodynamic parameters, from stochastic temperature responses, instead of compositions, in the reactor. The thermal pulse-response technique has proved to be one of the efficient and plausible candidates for the fields of estimations with the exception of the activation energy of the reaction.

## INTRODUCTION

Mass and heat transfer during flow through a tubular reactor has numerous applications in process industries. Actual reactors are nonisothermal in nature since not a few reactions accompanied are exothermic or endothermic to some extent. Analysis of the nonisothermal reactor for diagnosis of malfunctioning without any composition measurements pose considerable difficulties caused from the fact that the transient reactor behavior should be described by a set of partial differential equations which are inherently nonlinear. Assuring the functioning of the reactor properly may be enhanced by utilization of various measuring tools for composition, temperature and pressure, etc. For the enhancement inquires cost-up, especially together with the circumstance of lack of on-line detectors and/or the hostile environment around sensor locations, the excessive measurement gives rise to much inappropriateness in practice. Consequently only a certain subset of these variables need to be measured for the determination of the residual process variables in industries.

Therefore an attempt is to be made in the present work to deal only with a measurement of temperature at one position, in which a thermal pulse or stress is arising, in the estimation of the parameters needed

in the diagnosis of a reactor, via a thermal pulse-response technique using the solution of the mathematical analysis for the reactor, in particular, in a case when a reversible liquid phase reaction proceeds. Thermal pulse-response technique is called this because it uses a heat pulse of adequate intensity so as not to thrust a causative interference into the reactor performance as a source of stress. A thermal detector at a point beyond measures the dispersed response of the stress, that is the temperature deviations from the normal steady state. Since the concentration and/or temperature profile in the reactor in relation to the mass and energy balance of which, in common, comprises partial differential equation, transport parameters besides the reaction parameters and thermodynamic parameters may or not be evaluated from the analysis of the predictions through the stochastic thermal deviations measured experimentally. In consequence, the present work provides a sound basis, foundations and limitations of the thermal pulse-response technique, so as to implement the method in the estimation of the parameters above. This work is comprised of the following:

(1) Transient action of the reactor in response to the pulse input establishing a set of partial differential equations. In the case of the reversible liquid reaction with only one reaction yields two simultaneous nonlinear equations, one for reactant concentration and the other for temperature.

\*To whom all correspondence should be addressed.

(2) Solution of the model equations by collocation using B-spline basis function [1], the most favorable of the solutions to which much effort has been devoted.

(3) Parameter estimation for the assessment of the process qualities, i.e., transport parameters such as dispersion coefficient and thermal conductivity of the reaction mixture in the reactor, kinetic parameters such as rate constant and activation energy of the reaction, and thermodynamic quantities such as heat of reaction and equilibrium constant. If there are any malefice in the reactor, one of the above mentioned parameters will, to some extent, be far from reasonable.

## MATHEMATICAL FORMULATION

### 1. Modeling of the Transient Action of Reactor; Thermal Pulse-response

Consider a single reaction

$$\sum_{j=1}^M v_j A_j = 0 \quad (1)$$

occurring in a nonisothermal tubular reactor of circular cross-section. Here  $A_j$  stands for chemical species and  $v_j$  for the corresponding stoichiometric coefficient with the usual notation that  $v_j > 0$  for products and  $v_j < 0$  for reactants. Assuming an axial dispersion model for the flow of the reaction mixture, the transient equations governing the reactor, being the previous one [2] modified with implication of pulse, yields

$$\frac{\partial C_j}{\partial t} = D_j \frac{\partial^2 C_j}{\partial x^2} - V \frac{\partial C_j}{\partial x} - f_j \quad (2)$$

0 < x < 1    t > 0    j = 1, 2, ..., M

$$\rho C_p \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} - V \rho C_p \frac{\partial T}{\partial x} + \left[ \frac{-\Delta H_r}{v_j} \right] f_j + \frac{UP}{A} (T_o - T) + Q(t, x) \quad (3)$$

0 < x < 1    t > 0

where  $C_j$  denotes concentration of species  $j$ ,  $f_j$ 's are the rate of reaction in moles of species  $j$  formed per unit volume per unit time,  $\Delta H_r$  is the heat of reaction, and  $Q(t, x)$  is the thermal pulse, heat per unit volume, which occurs at specific time and location during a definite period. The pulse is given in dimensionless function in Eq. (13). Boundary and initial conditions appropriate for the tubular reactor are:

$$\left. \begin{aligned} -D_j \frac{\partial C_j}{\partial x} &= V(C_{j0} - C_j) \\ -k \frac{\partial T}{\partial x} &= V \rho C_p (T_o - T) \end{aligned} \right\} \begin{aligned} x &= 0 & t &> 0 & j &= 1, 2, \dots, M \end{aligned} \quad (4)$$

$$\left. \begin{aligned} \frac{\partial C_j}{\partial x} &= 0 \\ \frac{\partial T}{\partial x} &= 0 \end{aligned} \right\} \begin{aligned} x &= 1 & t &> 0 & j &= 1, 2, \dots, M \end{aligned} \quad (5)$$

$$\left. \begin{aligned} C_j &= C_{j,ini}(x) \\ T &= T_{ini}(x) \end{aligned} \right\} \begin{aligned} 0 < x < 1 & t = 0 & j &= 1, 2, \dots, M \end{aligned} \quad (6)$$

With a key species' concentration and its stoichiometric coefficient, if the reaction was elementary, the concentrations of each reactants and products can be represented as

$$C_j = C_{j0} - \frac{v_k}{v_j} (C_{k0} - C_k) \quad (7)$$

here subscript 0 designates an initial state. Convenient are the dimensionless equations corresponding to the Eq. (2) and (3) for a key species  $k$ ,

$$\frac{\partial v}{\partial \tau} = \frac{1}{Pe_m} \frac{\partial^2 v}{\partial \xi^2} - \frac{\partial v}{\partial \xi} - Da(-r_k) \quad (8)$$

0 < \xi < 1    \tau > 0

$$\frac{\partial u}{\partial \tau} = \frac{1}{Pe_k} \frac{\partial^2 u}{\partial \xi^2} - \frac{\partial u}{\partial \xi} + \beta Da(-r_k) + \delta(u_w - u) + \mu(\tau, \xi) \quad (9)$$

0 < \xi < 1    \tau > 0

incorporated with the boundary and initial conditions equivalent to Eq. (4) to (6),

$$\left. \begin{aligned} \frac{\partial v}{\partial \xi} &= Pe_m(v-1) \\ \frac{\partial u}{\partial \xi} &= Pe_k(u-1) \end{aligned} \right\} \begin{aligned} \xi &= 0 & \tau &> 0 \end{aligned} \quad (10)$$

$$\left. \begin{aligned} \frac{\partial v}{\partial \xi} &= 0 \\ \frac{\partial u}{\partial \xi} &= 0 \end{aligned} \right\} \begin{aligned} \xi &= 1 & \tau &> 0 \end{aligned} \quad (11)$$

$$\left. \begin{aligned} v(\xi, 0) &= v_{ini}(\xi) \\ u(\xi, 0) &= u_{ini}(\xi) \end{aligned} \right\} \begin{aligned} 0 < \xi < 1 & \tau = 0 \end{aligned} \quad (12)$$

where the dimensionless quantities are defined as follows:

$$\begin{aligned} v &= \frac{C_k}{C_{k0}} & u &= \frac{T}{T_o} & \xi &= \frac{x}{1} & \tau &= \frac{t V}{1} \\ Pe_m &= \frac{V 1}{D_k} & Pe_k &= \frac{V \rho C_p 1}{k} & Da &= \frac{1 f_{k0}}{V C_{k0}} & \beta &= \frac{(-\Delta H_r) C_{k0}}{\rho C_p T_o} \\ \delta &= \frac{U P 1}{\rho C_p V A} & P &= \frac{R}{2} & r_k &= \frac{f_k}{f_{k0}} & u_w &= \frac{T_w}{T_o} \end{aligned}$$

The total  $M$  differential equations of Eq. (2) are reduced to a single one, Eq. (8) with algebraic remainders of Eq. (7) if elementary. The thermal pulse was de-

defined in dimensionless form as

$$\mu(\xi, \tau) = \begin{cases} \mu_{pulse} & \text{at } \xi_{start} \leq \xi \leq \xi_{end} \text{ and } \tau_{start} \leq \tau \leq \tau_{end} \\ 0 & \text{otherwise} \end{cases} \quad (13)$$

An equivalent form of Eq. (1) of the Diels-Alder type of reaction where 2-methyl furan reacts with maleic anhydride in 1,4-dioxane [3] is



With equilibrium constant  $K_{eq}$  defined by the ratio of the forward to the reverse rate constant obeying van't Hoff's isochore, and with the Arrhenius rate constant expression,  $f_A$  in Eq. (2) yields as follow [4],

$$-f_A = k_{1o} \exp\left[\frac{E}{R T_o} \left(1 - \frac{T_o}{T}\right)\right] - \frac{C_A C_B}{K_{eq,o} \exp\left[\frac{\Delta H_r}{R T_o} \left(1 - \frac{T_o}{T}\right)\right]} \quad (15)$$

$r_A$  in Eq. (8) is in subsequent

$$-r_A = \exp\left[\gamma\left(1 - \frac{1}{v}\right)\right] \left[ \frac{v(M_{AB} - 1 + v) - \exp\left[\Theta\left(\frac{1}{u} - 1\right)\right] \left[ \frac{M_{AC} + 1 - v}{K_{eq,o} C_{Ao}} \right]}{M_{AB} - M_{AC}/K_{eq,o}/C_{Ao}} \right] \quad (16)$$

In Eq. (16) new dimensionless parameters such as

$$\gamma = \frac{E}{R T_o}, \quad \Theta = \frac{\Delta H_r}{R T_o}, \quad M_{AB} = \frac{C_{Bo}}{C_{Ao}}, \quad M_{AC} = \frac{C_{Co}}{C_{Ao}}$$

are introduced.

## 2. Numerical Solution of the Model

The concentration and the temperature profiles, which is transient in the reactor in response to the impulse thermal input, needed for the estimation of parameters, shove finite element method into the approximate solution of both Eq. (8) and Eq. (9), for which produce solutions that, in contrast to those produced by finite difference method, are continuous over the subintervals partitioned along the dimensionless reactor length. The collocation method employed in this work implements the linear function space, B-spline basis [5]. According to the method of spline collocation at Gaussian points with the mesh

$$0 = x(1) < x(2) < \dots < x(l+1) = 1$$

the number of subintervals,  $l$ , into which the spatial domain  $[0, 1]$  is to be divided are chosen appropriately. meanwhile the  $l+1$  distinct breakpoints of the domain should be set into the array of  $x$  in strictly increasing order. The method is to find a set of  $\alpha$ 's

in Eq. (17) and Eq. (18), as the piecewise polynomial approximate solutions of Eq. (8) and Eq. (9),

$$v(\xi, \tau) = \sum_{j=1}^m \alpha_{j,1}(\tau) B_j(\xi) \quad (17)$$

$$u(\xi, \tau) = \sum_{j=1}^m \alpha_{j,2}(\tau) B_j(\xi) \quad (18)$$

Since the two approximates with the degree  $k$  of the approximating space must satisfy the Eq. (8) and Eq. (9), with the order  $M$  of the differential equations, exactly at  $m$  points, where  $m = (k-M) \times l + 1$ , the two equations Eq. (17) and Eq. (18) are incorporated into the Eq. (8) and Eq. (9) to correspond the followings

$$\sum_{j=1}^m B_j(\xi) \frac{d\alpha_{j,1}}{d\tau} = \frac{1}{Pe_m} \sum_{j=1}^m B''_j(\xi) \alpha_{j,1} - \sum_{j=1}^m B'_j(\xi) \alpha_{j,1} + Da r_A \left[ \sum_{j=1}^m B_j(\xi) \alpha_{j,1}, \sum_{j=1}^m B_j(\xi) \alpha_{j,2} \right] \quad (19)$$

$$i = 2, 3, 4, \dots, m-1.$$

$$\sum_{j=1}^m B_j(\xi) \frac{d\alpha_{j,2}}{d\tau} = \frac{1}{Pe_h} \sum_{j=1}^m B''_j(\xi) \alpha_{j,2} - \sum_{j=1}^m B'_j(\xi) \alpha_{j,2} - \beta Da r_A \left[ \sum_{j=1}^m B_j(\xi) \alpha_{j,1}, \sum_{j=1}^m B_j(\xi) \alpha_{j,2} \right] - \delta \left[ \sum_{j=1}^m B_j(\xi) \alpha_{j,2} - u_w \right] + \mu(\xi, \tau) \quad (20)$$

$$i = 2, 3, 4, \dots, m-1.$$

The Eq. (19) and (20) are comprised of the B-splines of degree  $k$  in subinterval  $[x(i), x(i+1)]$   $i = 1, 2, \dots, l$ . Addition of the next four equations, which are to be obtained by differentiating the boundary conditions Eq. (10) and Eq. (11) as

$$[-Pe_m B_1(\xi_1) + B_1'(\xi_1)] \frac{d\alpha_{1,1}}{d\tau} + B_2'(\xi_1) \frac{d\alpha_{2,1}}{d\tau} = 0 \quad (21a)$$

$$[-Pe_h B_1(\xi_1) + B_1'(\xi_1)] \frac{d\alpha_{1,2}}{d\tau} + B_2'(\xi_1) \frac{d\alpha_{2,2}}{d\tau} = 0 \quad (21b)$$

$$B_{N-1}(\xi_N) \frac{d\alpha_{N-1,1}}{d\tau} + B_N(\xi_N) \frac{d\alpha_{N,1}}{d\tau} = 0 \quad (21c)$$

$$B_{N-1}(\xi_N) \frac{d\alpha_{N-1,2}}{d\tau} + B_N(\xi_N) \frac{d\alpha_{N,2}}{d\tau} = 0 \quad (21d)$$

to the  $2(m-2)$  equations of the Eq. (19) and (20) of  $2m$  unknown coefficients of  $\alpha$ 's, complete the system of  $2m$  ordinary differential equations of the form

$$A \frac{d\alpha}{d\tau} = g(\tau, \alpha) \quad (22)$$

with initial conditions

$$\begin{cases} \alpha_{j,1}(0) = \omega_{j,1}(\xi) \\ \alpha_{j,2}(0) = \omega_{j,2}(\xi) \end{cases} \quad (22a)$$

**Table 1. Parameter lists for the thermal pulse-response technique**

| Transport parameters     |  |
|--------------------------|--|
| D                        | : dispersion coefficient                   |
| k                        | : thermal conductivity                     |
| Kinetic parameters       |  |
| E                        | : activation energy                        |
| $k_{10}$                 | : frequency factor of the forward reaction |
| Thermodynamic parameters |  |
| $K_{eq}$                 | : equilibrium constant                     |
| $\Delta H_r$             | : heat of reaction                         |

The initial condition Eq. (22a) is the steady state solution profiles of Eq. (23) obtained by setting the left side with zero of the Eq. (22) without pulse.

$$\frac{1}{Pe_m} \sum_{j=1}^m B''_j(\xi) a_{j,1} - \sum_{j=1}^m B'_j(\xi) a_{j,1} + Da \cdot r_A \left[ \sum_{j=1}^m B_j(\xi) a_{j,1} - \sum_{j=1}^m B_j(\xi) a_{j,2} \right] = 0 \quad (23a)$$

$$\frac{1}{Pe_h} \sum_{j=1}^m B''_j(\xi) a_{j,2} - \sum_{j=1}^m B'_j(\xi) a_{j,2} - \beta Da \cdot r_A \left[ \sum_{j=1}^m B_j(\xi) a_{j,1} - \sum_{j=1}^m B_j(\xi) a_{j,2} \right] - \delta \left[ \sum_{j=1}^m B_j(\xi) a_{j,2} - u_w \right] = 0 \quad (23b)$$

The integration of the initial value problem Eq. (22) with the steady state profiles implements the transient responses for the thermal pulse input. The nonlinear algebraic equations Eq. (23a, b) can be iterated from a set of approximated  $a_j$ 's by Newtonian method. The transient responses, the solution of Eq. (22), are straightforward. Integration step size strategy for accuracy improvement with implicit-explicit pair of Euler method can be used [5].

### 3. Estimation of the Model Parameters

Provided that we measure the temperature response of the thermal pulse at position  $\xi$  for a definite time period, minimization of the following sum of squares of Eq. (24) formulates an objective function satisfactory for the estimation of the parameters listed in Table 1.

$$J_{ls}(\mathbf{p}) = \sum_{j=1}^N \{ \mathbf{u}^{alc}(\xi, \tau_j; \mathbf{p}) - \mathbf{u}_j^{obs} \}^2 \quad (24)$$

Where  $\mathbf{u}^{alc}(\xi, \tau; \mathbf{p})$ 's are the temperatures calculated from solution of Eq. (22) with the  $k$ -th predefined set of parameters  $\mathbf{p}^{(k)}$ . The next  $(k+1)$ -th set of parameter  $\mathbf{p}^{(k+1)}$  are then adjusted so as to reduce the function by various method described in reference [6]. In Eq. (24)  $\mathbf{u}^{obs}$ 's are set of  $N$  pseudo-data. The pseudo-data are artificial ones made by adding a random number, of which order are  $1 \times 10^{-4}$  and  $1 \times 10^{-5}$ , to that from

**Table 2. Physical and kinetic data for simulation**

|          |                       |                    |              |                       |                        |
|----------|-----------------------|--------------------|--------------|-----------------------|------------------------|
| $C_{A0}$ | $5.00 \times 10^3$    | mol/m <sup>3</sup> | D            | $1.67 \times 10^{-8}$ | m <sup>2</sup> /s      |
| $C_{B0}$ | $5.00 \times 10^3$    | mol/m <sup>3</sup> | k            | 6.97                  | J/sec m K              |
| $C_{C0}$ | 0.0                   | mol/m <sup>3</sup> | U            | $5.77 \times 10^{-3}$ | J/sec m <sup>2</sup> K |
| $T_0$    | 318                   | K                  | $k_{10}$     | $1.33 \times 10^{-3}$ | m <sup>3</sup> /mol s  |
| $T_w$    | 298                   | K                  | E            | $2.64 \times 10^4$    | J/mol                  |
| P        | 0.025                 | m                  | $\Delta H_r$ | $6.00 \times 10^4$    | J/mol                  |
| I        | 1.00                  | m                  | $K_{eq,0}$   | $6.14 \times 10^{-4}$ | m <sup>3</sup> /mol    |
| V        | $3.30 \times 10^{-3}$ | m/s                | $\rho$       | $8.70 \times 10^3$    | mol/m <sup>3</sup>     |
| R        | 8.314                 | J/mol K            | $C_p$        | $5.77 \times 10^2$    | J/mol K                |

the solution of section II-2 in order to assess the thermal pulse-response technique.

Levenberg-Marquart algorithm employed in this work, which had already been developed by Garbow et al.[7], can minimize the objective function quite well with a relative efficiency. Outlines of the minimizing algorithms comprise of the following steps:

- (1) Guess the  $\mathbf{p}$  initial values  $p_1^{(0)}, p_2^{(0)}, \dots$
- (2) Generate  $\mathbf{u}^{alc}(\xi, \tau; \mathbf{p})$ 's by integrating Eq. (22) and evaluate the objective function.
- (3) Repeat step (2) with a little difference from the  $p_i$ 's one another and determine  $\Delta p_i$  to which direction the objective reduce.
- (4) Continue step (3) until no less reduction occur. Details of the algorithm are described elsewhere e.g. reference [8].

## RESULTS AND DISCUSSION

Data needed for both the numerical solution and the estimation of parameters in previous section, such as the reaction conditions, physical properties and kinetic and transport parameters, are listed in Table 2. The data are compiled ones from that of several experimental studies for Diels-Alder reactions of references 3, 9, 10 and 11. With the initial temperature and concentration profiles obtained from the steady-state solution of Eq. (23a, b) shown in Fig. 1, the results of the solutions of Eq. (22) with  $k=4$ ,  $v=2$  and  $l=50$  are depicted in Fig. 2 and Fig. 3 in three dimensional diagram. The thermal pulse conditions of the figures are summarized in Table 3. The mountain-shaped temperature curves of Fig. 2 stressed by the pulse, in contrast to the valley-shaped concentration curves depicted in Fig. 3, moves to the exit of the reactor along with time progress, so that its peak or the minimum reaches to the exit around  $\tau=0.6$ .

Hundred-times higher flow rate than that in Table 2 will sharpen the temperature and concentration curves. In that case the wrinkling of the profiles depicted

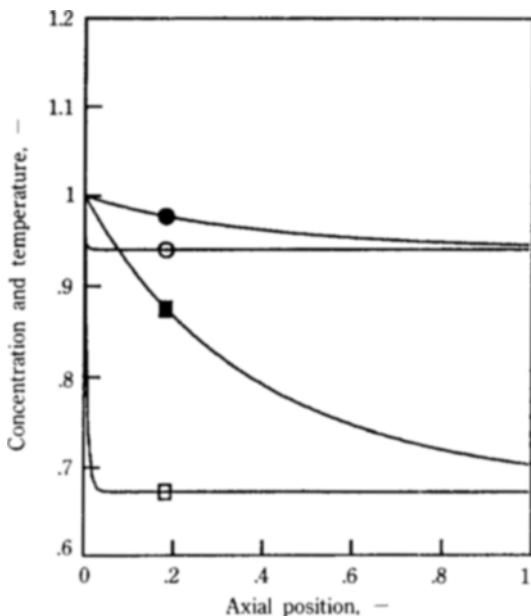


Fig. 1. Steady state solution calculated with the condition shown in Table 2 (□: concentration and ○: temperature) and that with the condition changed only one-hundred times higher flow rate than that in the table (■: concentration and ●: temperature).

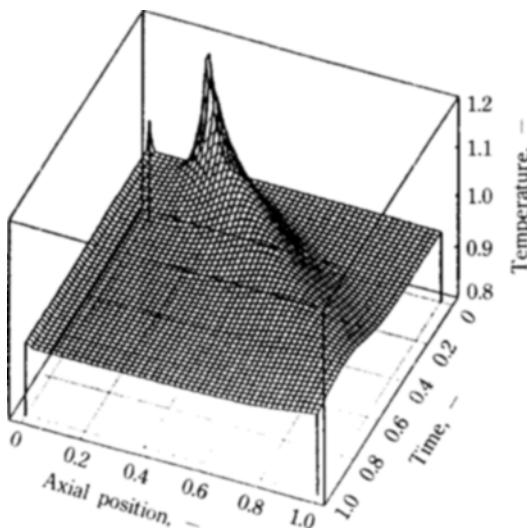


Fig. 2. Three dimensional plot of temperature variations along with time and position responding to a thermal pulse; calculated with the condition shown in Table 2.

respectively in Fig. 4 for the temperature and in Fig. 5 for the concentration means that the number of elements partitioned in this calculation is less than that

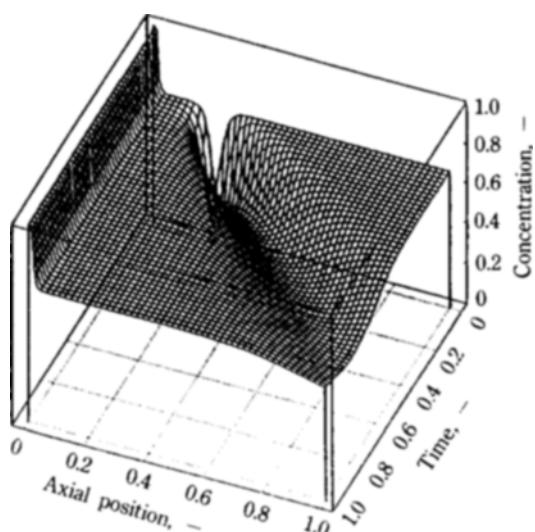


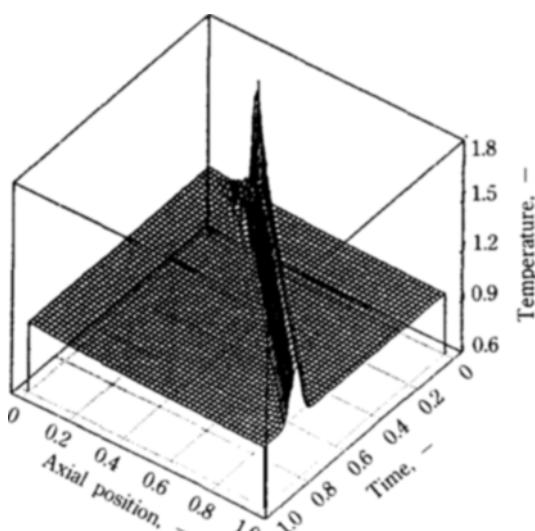
Fig. 3. Three dimensional plot of concentration variations along with time and position responding to a thermal pulse; calculated with the condition shown in Table 2.

Table 3. Thermal pulse condition

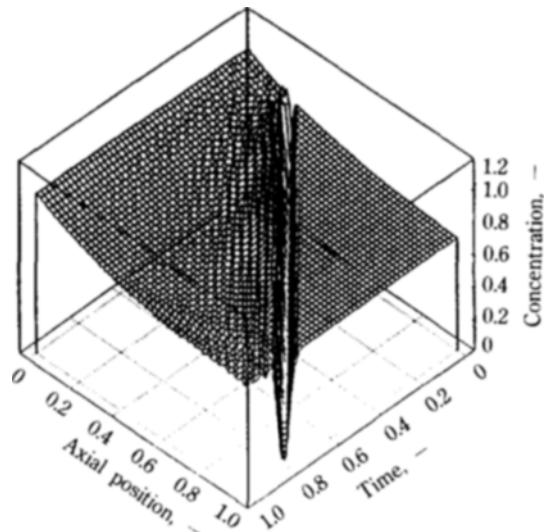
|             |                    |                    |
|-------------|--------------------|--------------------|
| Q           | $6.58 \times 10^5$ | J/m <sup>3</sup> s |
| $t_{start}$ | 0.00               | s                  |
| $t_{end}$   | 15.2               | s                  |
| $x_{start}$ | 0.19               | m                  |
| $x_{end}$   | 0.20               | m                  |

of satisfaction for the stable one. Or else it implies that the partial differential equations, Eq. (8) and Eq. (9), have confronted at a steep condition that the pulse should be reduced. This wrinkling, however, thrusts little interference, as would be shown later, if the velocity were no more than that of about hundred times, into the evaluation of the parameters by thermal pulse-response technique where the stochastic temperature detections are supposed to be made.

The cornerstone for the estimation was made for the response of Fig. 2. The pseudo-data sampled from the measurement at  $\xi=0.6$ , which is compared to true value and shown in Table 4, are redrawn in Fig. 6 with predefined dimensionless sampling times. With this figure the capability of the estimation of parameter could be drawn as shown in Fig. 7. The figure shows the trace of the single parameter D along with every estimation steps with its objective function values. Fig. 7 states that the objective function has minimum at D of  $1.67 \times 10^{-8}$ , the same as the parameter that were used in the calculation, conforming that the



**Fig. 4. Three dimensional plot of temperature variations along with time and position responding to a thermal pulse; calculated with the condition shown in Table 2 except one-hundred times higher flow rate than that in the table.**



**Fig. 5. Three dimensional plot of concentration variations along with time and position responding to a thermal pulse; calculated with the condition shown in Table 2 except one-hundred times higher flow rate than that in the table.**

estimation is a success if the initial guess were  $1.97 \times 10^{-8}$  starting from right side and/or  $1.07 \times 10^{-8}$  from left side. The number of steps needed for reaching the reasonable value can be seen from Fig. 8. The figure was redrawn from the results that made the course from the right in Fig. 7. A total of nine steps is sufficient to estimate the true value. Even if the trial value departs from the true one the estimation is successful, as can be seen in Fig. 9. Both the minimum initial value tried of  $7.0 \times 10^{-10}$  and the maximum of  $1.17 \times 10^{-5}$  could find the true value in the figure. Even though the hundred times higher velocity was attained in the reactor, as mentioned in the above paragraph, the pseudo-data measured at the same position as that in Fig. 6 proved itself to reflect little provision in the smoothness so that the search traces to the true  $D$ , since the corresponding stochastic temperature curve showed negligible fluctuations.

Similar effects for thermal conductivities can be seen in Fig. 10 in search by this estimation technique. When the order of random variable is  $1.0 \times 10^{-4}$ , the order of magnitude of the objective function is about  $-9$  compared with that of numerical solution,  $-18$ . However, the order of magnitude of the objective function is about  $-9$  when the order of random variable is  $1.0 \times 10^{-5}$ .

All the other parameters such as kinetic and thermodynamic parameters with single parameter estima-

tion succeeded in their search. Extreme care should be provided in the estimation of the activation energy of the reaction. The parameter so contributes in exponential order that the response of the pulse is very sensitive. The activation energy, however in general, is measured in batch reaction experiments. Park et al., provided the estimation algorithm for the activation energy in isothermal calorimeter [10]. In spite of the capability of the estimation technique in the present work, even if the stable region is narrow, we would like to recommend that it is not feasible to try to get the information about the activation energy with the thermal pulse-response technique because of its instability, if it were started from a relative departure.

Estimation of a couple of parameters by the thermal pulse-response technique contributed with fairly good satisfaction. Fig. 11 summarizes the gatherings of three different approaches originated from each point it had started, together in two dimensional diagram for the evaluation of the transport parameters such as thermal conductivity and dispersion coefficient, in simultaneous fashion. As mentioned previously the stable bounds for the thermal conductivity should be kept. In spite of our recommendation above, the kinetic parameters such as frequency factor and activation energy can be estimated fairly well as described in Fig. 12. Fifteenth iteration provides a good estimation of both parameters. Course of the tracing with the

**Table 4. The comparison of pseudo temperature data in the variance of the order of random variable along with time at dimensionless position  $\xi=0.6$** 

| Time          | Order of random variable | True value       | $1 \times 10^4$  | $1 \times 10^{-5}$ |
|---------------|--------------------------|------------------|------------------|--------------------|
| 0.00150000000 |                          | 0.93934059399056 | 0.93929080151009 | 0.93934059394086   |
| 0.00300000000 |                          | 0.93934029548081 | 0.93930906684311 | 0.93934029544479   |
| 0.00800000000 |                          | 0.93933939462204 | 0.93934486032028 | 0.93933939461816   |
| 0.01000000000 |                          | 0.93933907573976 | 0.93935742901124 | 0.93933907571903   |
| 0.02000000000 |                          | 0.93933779769903 | 0.93929811874395 | 0.93933779774265   |
| 0.03000000000 |                          | 0.93933697445708 | 0.93933082516509 | 0.93933697445878   |
| 0.04000000000 |                          | 0.93933645918918 | 0.93929747298313 | 0.93933645923568   |
| 0.05000000000 |                          | 0.93933609930807 | 0.93930422674948 | 0.93933609929580   |
| 0.06000000000 |                          | 0.93933584454676 | 0.93937123883387 | 0.93933584453566   |
| 0.07000000000 |                          | 0.93933568801589 | 0.93931024551100 | 0.93933568802158   |
| 0.08000000000 |                          | 0.93933557670651 | 0.93929937675533 | 0.93933557666624   |
| 0.09000000000 |                          | 0.93933546184756 | 0.93937242778995 | 0.93933546188574   |
| 0.10000000000 |                          | 0.93933536382529 | 0.93929691167686 | 0.93933536379491   |
| 0.11000000000 |                          | 0.93933531404307 | 0.93934063020518 | 0.93933531400284   |
| 0.12000000000 |                          | 0.93933529121364 | 0.93935749275173 | 0.93933529124537   |
| 0.15000000000 |                          | 0.93933525674125 | 0.93931004922172 | 0.93933525669225   |
| 0.18000000000 |                          | 0.93933524595470 | 0.93934912229747 | 0.93933524590515   |
| 0.20000000000 |                          | 0.93933527420683 | 0.93937155350371 | 0.93933527424918   |
| 0.22000000000 |                          | 0.93933612740604 | 0.93934555428593 | 0.93933612736576   |
| 0.24000000000 |                          | 0.93934916526439 | 0.93939008933666 | 0.93934916525144   |
| 0.26000000000 |                          | 0.93946116770742 | 0.93948871592519 | 0.93946116774850   |
| 0.28000000000 |                          | 0.94009239706841 | 0.94006491598931 | 0.94009239706613   |
| 0.30000000000 |                          | 0.94263406626259 | 0.94266254831825 | 0.94263406630347   |
| 0.32000000000 |                          | 0.95030537140974 | 0.95032709382185 | 0.95030537142412   |
| 0.34000000000 |                          | 0.96801178519221 | 0.96801919486018 | 0.96801178520070   |
| 0.36000000000 |                          | 0.99904751940265 | 0.99900529528156 | 0.99904751936417   |
| 0.38000000000 |                          | 1.03881691448443 | 1.03884030925981 | 1.03881691449319   |
| 0.40000000000 |                          | 1.07340918596244 | 1.07341854265183 | 1.07340918592436   |
| 0.42000000000 |                          | 1.08905997645729 | 1.08901412074434 | 1.08905997648585   |
| 0.44000000000 |                          | 1.08123004062812 | 1.08123843906565 | 1.08123004059647   |
| 0.46000000000 |                          | 1.05512229216821 | 1.05516217864280 | 1.05512229219050   |
| 0.48000000000 |                          | 1.02155671935790 | 1.02158905578375 | 1.02155671937082   |
| 0.50000000000 |                          | 0.99098405113300 | 0.99101924400410 | 0.99098405115082   |
| 0.53000000000 |                          | 0.96074346051231 | 0.96075658001915 | 0.96074346053183   |
| 0.56000000000 |                          | 0.94685628075099 | 0.94684484581446 | 0.94685628072652   |
| 0.60000000000 |                          | 0.94088832163732 | 0.94086675486486 | 0.94088832167938   |
| 0.65000000000 |                          | 0.93952367408580 | 0.93950219276256 | 0.93952367412078   |
| 0.70000000000 |                          | 0.93931894472560 | 0.93928321474513 | 0.93931894476563   |
| 0.75000000000 |                          | 0.93929077006557 | 0.93930454875209 | 0.93929077010511   |
| 0.80000000000 |                          | 0.93931565156973 | 0.93931623140371 | 0.93931565161824   |

number of iteration designated in the figure is conformed in Fig. 13 for the case of failure because the trial activation energy was too high, as expected in our recommendation. Thermodynamic parameters could be estimated easily with little restriction.

The results of the estimation for the three kinds

of parameters of doublet are summarized in Table 5. What is implied by the table indicates that the thermal pulse-response technique for the estimation of parameters of various kinds can be transmitted into the assessment of the reactor functioning. Suppose, as an example, a reactor is malfunctioning because of the

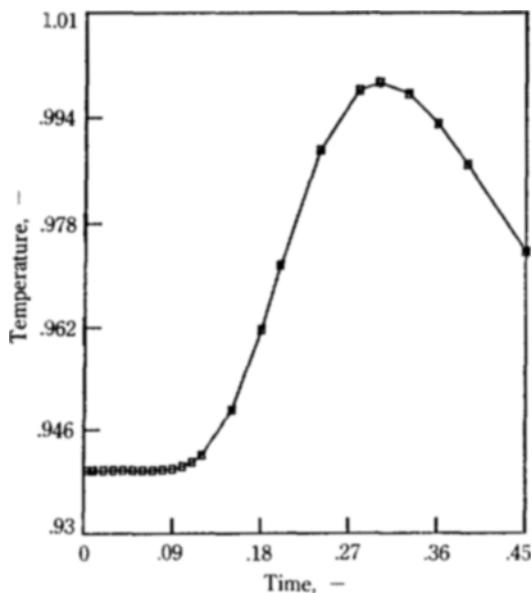


Fig. 6. Plot of pseudo temperatures along with time at dimensionless position  $\xi=0.6$  (the order of random variable:  $1 \times 10^{-4}$ ).

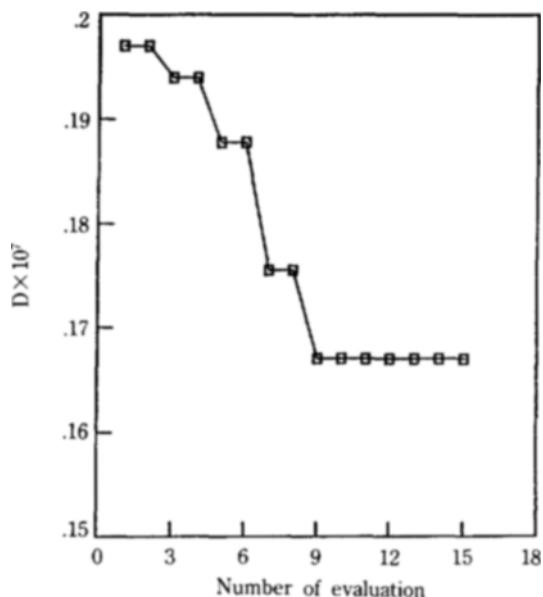


Fig. 8. An alternative view of the right-side trace of Fig. 6 exhibiting each step of modification.

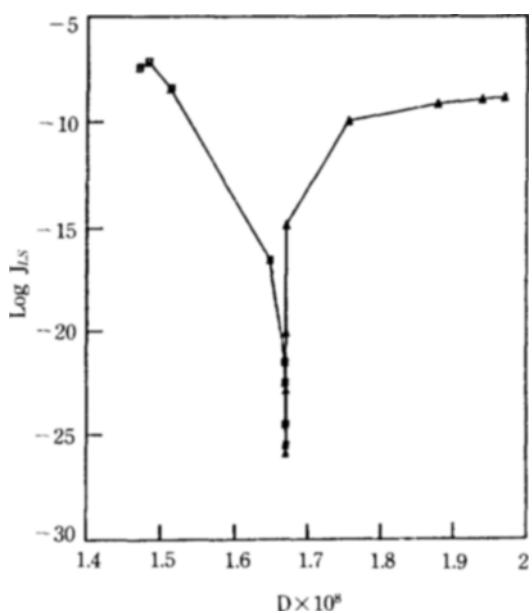


Fig. 7. Diagrammatic view of searching correct dispersion coefficient. Objective function shrinks dramatically from significant difference to reality as dispersion coefficient is being corrected. The final function value is  $-27$  order of magnitude at the dispersion coefficient of  $1.67 \times 10^{-8}$  (Initial guess  $\square$ :  $1.57 \times 10^{-8}$ ,  $\triangle$ :  $1.97 \times 10^{-8}$ ).

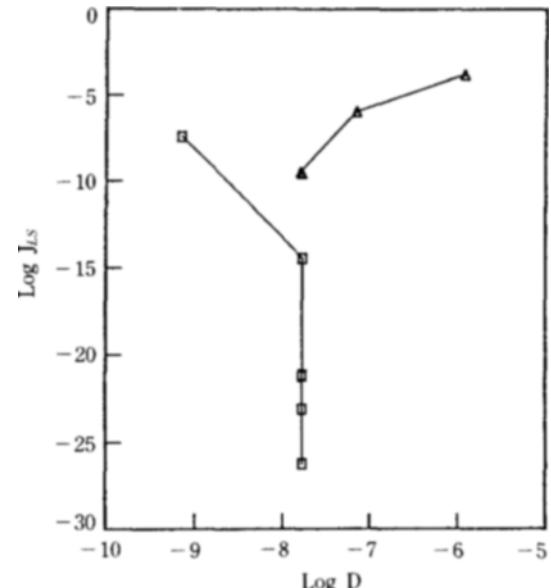


Fig. 9. Estimation of dispersion coefficient, Objective junction vs. dispersion coefficient  $1.67 \times 10^{-8}$  (Initial guess  $\triangle$ :  $1.17 \times 10^{-6}$ ,  $\square$ :  $7.0 \times 10^{-10}$ ; the order of random variable:  $1 \times 10^{-4}$ ).

short circuit by the catalyst agglomeration. If the thermal pulse-response of the reactor were to analyse by the present technique the dispersion coefficient should have been investigated since the target of the

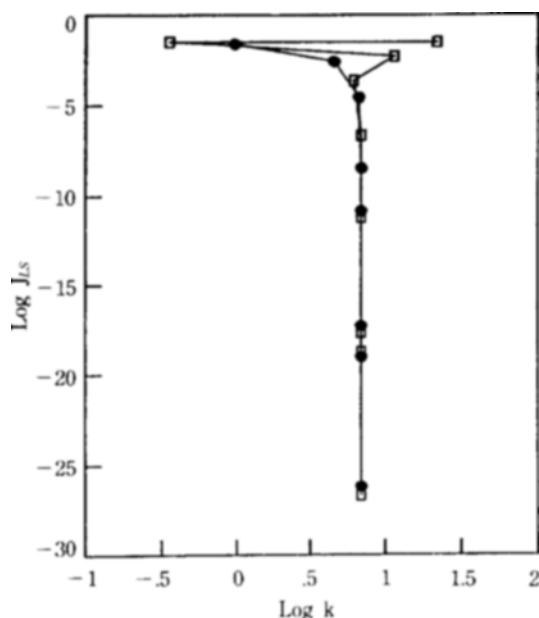


Fig. 10. Estimation of thermal conductivity, Objective function vs. thermal conductivity 6.97 (Initial guess ●: 0.97, □:  $2.19 \times 10^{-1}$ ; the order of random variable:  $1 \times 10^{-5}$ ).

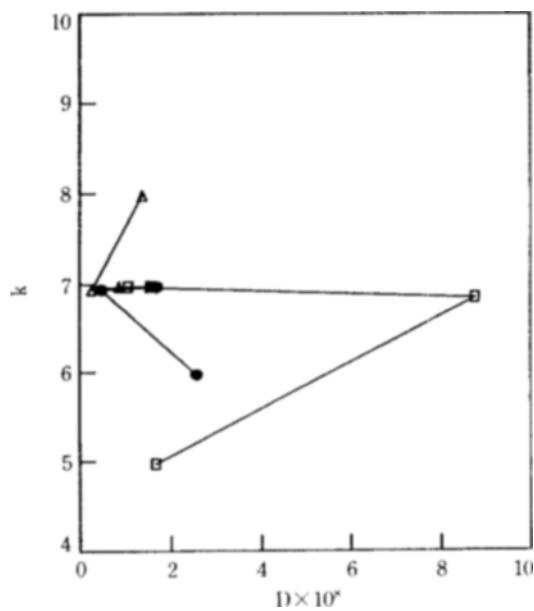


Fig. 11. Simultaneous estimation of thermal conductivity and dispersion coefficient from various pairs of initial guess (Initial guess 1:  $D = 1.67 \times 10^{-8}$  and  $k = 4.97$ ; 2: ●:  $D = 2.57 \times 10^{-8}$  and  $k = 5.97$ ; 3: ▲:  $D = 1.37 \times 10^{-8}$  and  $k = 7.97$ ; True value:  $D = 1.67 \times 10^{-8}$  and  $k = 6.97$ ).

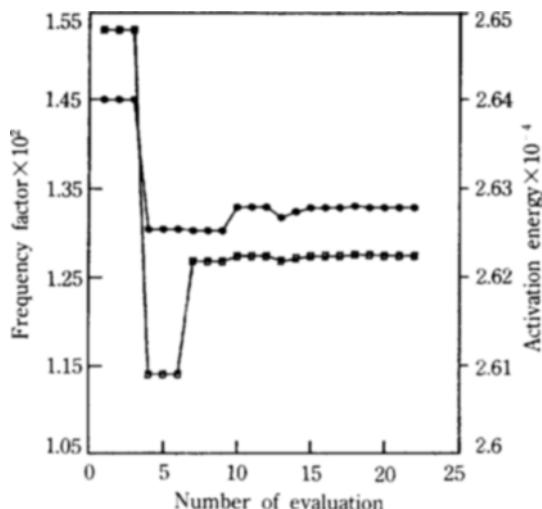


Fig. 12. Variations of frequency factor and activation energy with each evaluation step (Initial guess  $k_{10} = 1.53 \times 10^{-2}$  and  $E = 2.64 \times 10^4$ ; True value  $k_{10} = 1.33 \times 10^{-2}$  and  $E = 2.623 \times 10^4$ ).

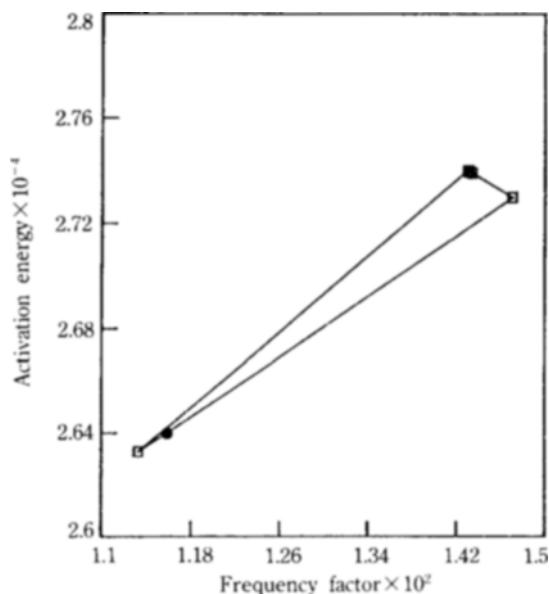


Fig. 13. Failure case of cycling in search for both of activation energy and frequency factor (Initial guess ●:  $k_{10} = 1.43 \times 10^{-2}$  and  $E = 2.73 \times 10^4$ ; True value ●:  $k_{10} = 1.16 \times 10^{-2}$  and  $E = 2.64 \times 10^4$ ).

analysis was the flow pattern in the reactor. The evaluated coefficient may not be the real one, of course, but the result can conform whether the reactor is partly plugged or not. Sometimes its temperature is mon-

**Table 5. The results of the simultaneous estimation of parameter pairs**

| Parameter group         | True value            | Initial guess         | Estimation            | Norm                   | Remark  |
|-------------------------|-----------------------|-----------------------|-----------------------|------------------------|---------|
| <b>Transport I</b>      |                       |                       |                       |                        |         |
| D                       | $1.67 \times 10^{-8}$ | $8.70 \times 10^{-9}$ | $1.55 \times 10^{-8}$ | $1.64 \times 10^{-5}$  | Success |
| k                       | 6.97                  | 4.97                  | 6.97                  |                        |         |
| <b>Transport II</b>     |                       |                       |                       |                        |         |
| D                       | $1.67 \times 10^{-8}$ | $2.57 \times 10^{-8}$ | $1.67 \times 10^{-8}$ | $2.15 \times 10^{-13}$ | Success |
| k                       | 6.97                  | 5.97                  | 6.97                  |                        |         |
| <b>Kinetic I</b>        |                       |                       |                       |                        |         |
| E                       | $2.64 \times 10^4$    | $3.14 \times 10^4$    | $2.56 \times 10^4$    | $2.53 \times 10^{-3}$  | Fail    |
| $k_{10}$                | $1.33 \times 10^{-2}$ | $8.30 \times 10^{-3}$ | $9.92 \times 10^{-3}$ |                        |         |
| <b>Kinetic II</b>       |                       |                       |                       |                        |         |
| E                       | $2.64 \times 10^4$    | $1.64 \times 10^4$    | $1.64 \times 10^4$    | $1.23 \times 10^{-1}$  | Fail    |
| $k_{10}$                | $1.33 \times 10^{-2}$ | $2.33 \times 10^{-2}$ | $2.33 \times 10^{-2}$ |                        |         |
| <b>Thermodynamic I</b>  |                       |                       |                       |                        |         |
| $K_{eq}$                | $6.14 \times 10^{-4}$ | $5.14 \times 10^{-4}$ | $6.14 \times 10^{-4}$ | $3.52 \times 10^{-12}$ | Success |
| $\Delta H_r$            | $6.00 \times 10^4$    | $7.00 \times 10^4$    | $6.00 \times 10^4$    |                        |         |
| <b>Thermodynamic II</b> |                       |                       |                       |                        |         |
| $K_{eq}$                | $6.14 \times 10^{-4}$ | $3.14 \times 10^{-4}$ | $6.15 \times 10^{-4}$ | $3.73 \times 10^{-6}$  | Success |
| $\Delta H_r$            | $6.00 \times 10^4$    | $8.00 \times 10^4$    | $6.00 \times 10^4$    |                        |         |

itored consistently of the purpose of the inspection of the reactor functions. In this case the odd behavior with respect to the normal temperature suggests that there is a problem to some extent. If there were unknown causatives which the thermal pulse-response technique cannot justify the cause exactly, this technique is required to attempt another appropriateness for a routinely intelligent working essentials to deal with. The essentials still may require a substantial number of treatment sophistications to deal with the actual experimental observations, strategy which will be given elsewhere [12].

## CONCLUSION

The thermal pulse-response technique presented in this work employs a thermal pulse as a stress and uses the thermal response, the temperature, only in the estimation of the transport, kinetic and thermodynamic parameters in a tubular reactor. The present work has contributed to the formulation of the model equations, the solution of the equations by the collocation using B-spline basis, and finally the stable estimation protocols of the parameters with the pseudo-data in order to assure the capability of using the technique in the future experimental observations in preparation by the authors. In conclusion, except for the activation energy, almost all the parameters could be estimated with the technique in a fairly good precision. The diagnostic sophistication still would be required to enhance the application of the technique to unexpected

reactor malfunctions.

## ACKNOWLEDGEMENT

The authors are grateful to Korean Science and Engineering Foundation for financial support (Contract No. 881-1002-002-1).

## NOMENCLATURE

|                 |  |
|-----------------|--|
| A               | : cross-sectional area of tubular reactor [ $m^2$ ]                    |
| A               | : reactant, chemical species in Diels-Alder reaction, 2-methyl furan   |
| A <sub>j</sub>  | : chemical species j   |
| B               | : reactant, chemical species in Diels-Alder reaction, maleic anhydride |
| B <sub>j</sub>  | : B-spline basis function on j-th space                                |
| C               | : product, chemical species in Diels-Alder reaction, adduct            |
| C <sub>j</sub>  | : concentration of component j [ $mol/m^3$ ]                           |
| C <sub>p</sub>  | : specific heat [ $J/mol\ K$ ]   |
| D <sub>j</sub>  | : dispersion coefficient of component j [ $m^2/s$ ]                    |
| D               | : dispersion coefficient [ $m^2/s$ ]                                   |
| Da              | : Damköhler number [-]   |
| E               | : activation energy [ $J/mol$ ]  |
| f <sub>j</sub>  | : reaction rate based on species j [ $mol/m^3\ s$ ]                    |
| $\Delta H_r$    | : heat of reaction [ $J/mol$ ]   |
| J <sub>LS</sub> | : least-square objective function                                      |
| k               | : order of piecewise polynomial  |
| k               | : thermal conductivity [ $J/s\ m\ K$ ]                                 |
| K <sub>eq</sub> | : equilibrium constant [ $m^3/mol$ ]                                   |

|          |   |
|----------|---|
| $k_1$    | : forward reaction rate constant [ $\text{m}^3/\text{mol s}$ ]            |
| $k_b$    | : frequency factor of forward reaction [ $\text{m}^3/\text{mol s}$ ]      |
| $l$      | : reactor length [m]  |
| $l$      | : number of intervals in piecewise polynomial                             |
| $m$      | : number of collocation points of piecewise polynomial                    |
| $M$      | : number of partial differential equations                                |
| $M$      | : number of chemical species  |
| $M_{AB}$ | : ratio of initial concentration A to B                                   |
| $M_{AC}$ | : ratio of initial concentration A to C                                   |
| $P$      | : perimeter of tubular reactor, $R/2$ [m]                                 |
| $p$      | : vector of estimating parameter  |
| $p_i$    | : i-th parameter  |
| $Pe_h$   | : Peclet Number for heat, $V l \rho C_p/k$ [-]                            |
| $Pe_m$   | : Peclet Number for mass, $V l/D$ [-]                                     |
| $Q$      | : heat input by thermal pulse [ $\text{J}/\text{m}^3 \text{ s}$ ]         |
| $R$      | : gas constant  |
| $r_k$    | : dimensionless reaction rate based on species k, $f_k/f_{k_0}$ [-]       |
| $t$      | : time [s]  |
| $T$      | : temperature [K]   |
| $u$      | : dimensionless temperature   |
| $U$      | : overall heat transfer coefficient [ $\text{J}/\text{s m}^2 \text{ K}$ ] |
| $V$      | : velocity [m/s]  |
| $v$      | : dimensionless concentration [-]   |
| $x$      | : breakpoint sequence used in B-spline specification                      |
| $x$      | : axial position in the reactor   |

### Greek Letters

|                |  |
|----------------|--|
| $\alpha_{j,1}$ | : B-spline coefficient at j-th space for concentration                               |
| $\alpha_{j,2}$ | : B-spline coefficient at j-th space for temperature                                 |
| $\beta$        | : dimensionless adiabatic temperature rise, $(-\Delta H_r) C_{k_0}/\rho C_p T_r$ [-] |
| $\gamma$       | : dimensionless activation energy, $E/R T_r$ [-]                                     |
| $\delta$       | : dimensionless heat transfer coefficient, $U P l / \rho C_p V A$ [-]                |
| $\Theta$       | : dimensionless heat of reaction, $(-\Delta H_r)/R T_r$ [-]                          |
| $\mu$          | : dimensionless heat input by pulse [-]  |
| $v_j$          | : stoichiometric coefficient for component j   |
| $v$            | : number of continuity condition at breakpoint                                       |
| $\xi$          | : dimensionless axial position in the reactor, $x/l$ [-]                             |
| $\xi_i$        | : collocation points   |
| $\rho$         | : density [ $\text{mol}/\text{m}^3$ ]  |

|          |  |
|----------|--|
| $\tau$   | : dimensionless time, $t V/l$ [-]                      |
| $\omega$ | : spline coefficients corresponding to initial profile |

### Superscripts

|      |   |
|------|---|
| (0)  | : initial state in parameter estimation     |
| calc | : calculated value                          |
| (k)  | : iteration counter in parameter estimation |
| obs  | : observed value                            |

### Subscripts

|         |                                 |
|---------|---------------------------------|
| A, B, C | : chemical species A, B and C   |
| i       | : i-th parameter for estimation |
| init    | : initial condition             |
| k       | : key chemical species          |
| o       | : inlet condition               |
| w       | : reactor wall                  |

### REFERENCES

1. de Boor, C.: "A Practical Guide to Splines", Springer-Verlag (1978).
2. Varma, A. and Aris, R.: in "Chemical Reactor Theory, A Review" (Edited by Lapidus, L. and Amundson, N. R.), Prentice-Hall, p. 79 (1977).
3. Sparks, B. G. and Poling, B. E.: *AIChE J.*, **29**, 534 (1983).
4. Lee, Y. C.: MS Dissertation, Chonnam National University, Korea (1986).
5. Davis, M. E.: "Numerical Methods and Modeling for Chemical Engineers", John Wiley & Sons (1984).
6. Seinfeld, J. H. and Lapidus, L.: "Mathematical Methods in Chemical Engineering Volume 3, Process Modeling, Estimation and Identification", Prentice-Hall, p. 382 (1974).
7. Garbow, B. S., Hillstrom, K. E. and More, J. J.: MINPACK Project, Argonne National Laboratory (1980).
8. Edgar, T. F. and Himmelblau, D. M.: "Optimization of Chemical Processes", McGraw-Hill (1988).
9. Park, C. Y., Ryu, M. S., Lee, K. J., Kim, T. S., Sohn, E. S. and Cho, J. H.: *Hwahak Konghak*, **28**, 358 (1990).
10. Park, C. Y., Ryu, D. W. and Cho, J. H.: *Hwahak Konghak*, **29**, 358 (1991).
11. Thompson, P. F., Bertrand, G. L. and Poling, B. E.: *Ind. & Eng. Chem. Fundam.*, **24**, 386 (1985).
12. Park, C. Y. and Jung, H. J.: *KJChE*, in Preparation.