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Identification of Chemical Reaction Process

Takeichiro TAKAMATSU
Faculty of Engineering, Kyoto University
and Hayatoshi SAYAMA
Department of Industrial Science

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The identification or model building of system is the important problem for the dynamic optimization of chemical plant and it is desired that this mathematical model can be determined as quickly and as exactly as possible from experimental or operating data. Recently the identification of linear system has been studied, but there have been few papers on nonlinear systems. Especially, no approaches can be found to identify effectively a chemical reaction process which is a nonlinear and nonisothermal system. Except for the case in which the linearized model is enough to represent the approximate dynamic behaviour of the plant, system should be directly represented by nonlinear mathematical model in general.

In this paper, the gradient method was applied to identify a nonlinear system. In this method, the parameters to be chosen optimally are regarded as time-invariant control variables and they are numerically determined by using a high speed digital computer (KDC-I). As a numerical example, we choose a continuous stirred tank reactor with the first order exothermic reaction and show the procedure to determine the three parameters, that is, the order of reaction, the values of activation energy and frequency factor. It should be emphasized that this approach makes it possible to construct the mathematical model of non-isothermal chemical reaction processes only from input and output data.

§ 1. Introduction

The key to solve a dynamic optimization problem is to build a mathematical model of the systems and to calculate a dynamic optimal path of control variables by using the mathematical model. Moreover it is desirable to build a mathematical model of the system from as little as possible experimental data. In general, chemical kinetics are quite complex and it is difficult to represent chemical reaction processes by the reasonable mathematical model[1]. In order to determine the parameters of chemical process equations, many experimental data under the condition of constant pressure or constant temperature have been usually required.

In adaptive control, a mathematical model should be constructed from input-output data of a process under any transient state. For the purpose of identification of the system, the gradient method or the steepest ascent method has been used in several papers[2), 3), 4)] and also the gradient method as developed by Kelley[5)] and Bryson[6)] has been successfully applied to optimization problems.

In this paper, the parameters in the process equation to be identified are considered as time-invarying control variables, and the degree of agreement between the measured and calculated values of state variables is considered as the performance index of the system, and then the identification of the chemical process can be performed by some modification of the gradient method of Bryson[6)].

§ 2. Computing Procedures of Gradient Method

In general, chemical reactions are complex systems, and their performances are strongly dependent upon the reaction temperature and the concentrations of chemical species. Therefore the exactness of process model will be strongly required not only for computer control but also for reaction engineering itself. Usually, chemical reaction processes are identified by analog simulation. The values of parameters in a reaction equation are varied by trials and error, comparing this simulation output with the experimental data obtained under constant temperature and constant pressure. But it may be impossible by this method to build an exact process for a complex reaction system. The

gradient method or the steepest ascent method is applied to determine the optimum parameters of the chemical process equation from transient data in a continuous stirred tank reactor (CSTR).

Let the system be described by a set of first order ordinary differential equations:

$$\frac{dx_i}{dt}=f_i(x_1, \cdots x_n, p_1, \cdots p_m, t),\ i=1, \cdots, n \quad (1)$$

where x_i is the i-th state variable, p_j is the j-th parameter to be chosen optimally, and f_i is a known function with x_i and p_j. The proplem under consideration is the adjustment of the kinetic parameters to match the measured output values of concentration and temperature. The performance index which defines the degree of agreement of the equation with the specified data is given by

$$\phi=\int_{t_o}^{t_f}\{\sum_{i=1}^{n} W_i[x_{id}(t)-x_i(t)]^2\}\,dt \quad (2)$$

where $x_{id}(t)$ is a desired response function and W_i is a weighting factor. Since the parameters are constants over the interval of integration in the following calculations, they are considered as the control variables which do not vary with time. Equations of the gradient method were obtained by Kelley[5] and Bryson[6] and the iteration feature for this identification problem can be expressed as follows:

$$(p_j)_{NEW}=(p_j)_{OLD}+dp_j, \quad (3)$$

where $$dp_j=\frac{I_j}{W_j(I)^{1/2}}dS, \quad (4)$$

$$(dS)^2=\sum_{j=1}^{m} W_j(dp_j)^2\,, \quad (5)$$

$$I_j=\int_{t_0}^{t_f}\sum_{i=1}^{n}\lambda_i\left(\frac{\partial f_i}{\partial p_j}\right)dt\,,$$

$$I=\sum_{j=1}^{m} W_j^{-1}(I_j)^2, \quad (6)$$

$$\frac{d\lambda_k}{dt}=-\sum_{i=1}^{n}\left(\frac{\partial f_k}{\partial x_i}\right)\lambda_i\,,\quad k=1, \cdots, n \quad (7)$$

and dS is the length of step size.

The gradient method for obtaining the solution is summerized as follows:

(a). Estimation of a set of nominal parameters, p_j.

(b). Integration of Eq. (1).

(c). Determination of I_j and I along trajectories from integration of Eq. (7) with boundary conditions $(\partial\phi/\partial x_i)_{tf}$

(d). Selection of a value of dS in Eq. (5):

(e). Calculation of the quantities, dp_j in Eq. (4).

(f). Determination of $(p_j)_{NEW}$ from Eq. (3) and repetition of the process (b) through (f) until I becomes so small that possible further improvement is not significant.

There are many gradient methods which have been applied to model building or the identification of a process and the method described above is an example of solution for obtaining unknown parameters. Although the parameters to be adjusted are considered as constants in this paper, there are continuously varying parameters in many chemical processes. The gradient method seems to be a very powerful tool for continually updating the mathematical dynamic model with varying parameters.

§ 3. Numerical Example

The chemical reaction process under consideration is a single CSTR with a first order exothermic reaction $M_1 \longrightarrow M_2$. It is assumed that this reactor operates without any cooling. The mass and heat balances for CSTR is given by

$$\frac{dx_1}{dt}=\frac{F}{V}(x_1^0-x_1)-k_0x_1\exp(-E/RT), \quad (8)$$

$$\frac{dT}{dt}=\frac{F}{V}(T_0-T)-\frac{(\Delta H)}{\rho c_p}k_0x_1\exp(-E/RT) \quad (9)$$

The following numerical values were taken in the calculations[7]:

V = volume of reactor = 1, 000 cc

F = feed-flow rate = 10 cc/sec.

E = activation energy = 28, 000 cal/mole

k_0 = frequency factor = 7.86×10^{12} sec^{-1}.

ΔH = heat of reacton = −27, 000 cal/mole°K

ρ = density of solution = 1.0 g/cc.

c_p = heat capacity of solution = 1.0 cal/mole°K

x_1^0 = feed concentration of reactant M_1 = 0.0065 mole/liter

T^0 = feed temperature = 350°K

The initial conditions of the process are

$x_{10}(t_0)=35.31\times10^{-5}$ mole/liter

$T_0(t_0)=440.91$°K

Fig. 1 shows the available information on values of $x_{1d}(t)$ and $T_d(t)$ which was obtained from numerical solution of the process equations with true parameters. The performance index to be minimized is given by

$$\phi=\int_{t_0}^{t_f}\{W_{x1}[x_{1d}(t)-x_1(t)]^2 + W_T[T_d(t)-T(t)]^2\}dt \quad (10)$$

where the weighting factors in the performance

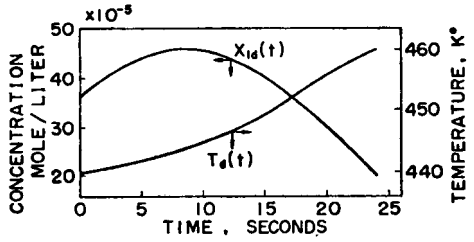

Figure 1. Response function of concentration and temperature.

index were taken as $W_{x1}=10^6$ and $W_T=10^{-4}$ in order to cause deviations in concentration and temperature to be of about the same order of magnitude. In this experiment the form of kinetic expressions are known but the numerical values of parameters in the kinetic equation are not known. The kinetic expression has the form

$$k_0 x_1^n \exp(-E/RT)$$

In this expression, k_0, E and n, the order of reaction, are the unknown kinetic parameters. It is necessary to select a reasonable value of dS in the following equation:

$$(dS)^2 = W_{k0}(dk_0)^2 + W_E(dE)^2 + W_n(dn)^2 \quad (11)$$

Let initial approximations be

$$k_0=6.5\times10^{12},\ E=3\times10^4 \text{ and } n=1.3$$

The weighting factors were taken as

$$W_{k0}=10^{-9},\ W_E=5\times10^9 \text{ and } W_n=3\times10^{17}$$

so that small perturbations of the parameters are expressed in numbers of about the same order of magnitude and the value of dS is selected as

$$dS=4.0\times10^7$$

The reaction order is assumed to be known and 3 parameters k_0, E and n are adjusted to match the calculated values with the data during the reaction time of 6 secs. Fig. 2 and 3 show the approach of concentration and temperature to

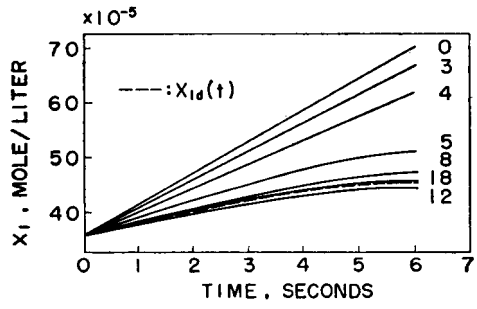

Figure 2. Successive approximations to true concentration trajectory.

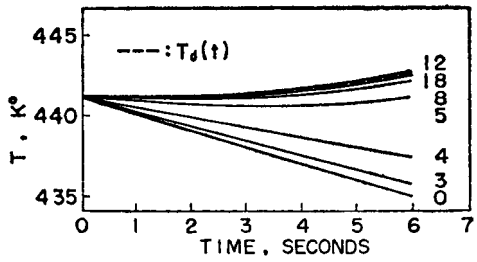

Figure 3. Successive approximations to true temperature trajectory.

their true values on successive iterations. After 18 iteations, the desired result was obtained. Although a constant value of dS was used during the above calculations, the rate of convergence should be much faster by automatic adjustment of step size[4]. The results of this experiment are summerized in Table 1. When

Table 1 Sequence of parameter estimation

Iteration Number	$E\times10^{-4}$	$k_0\times10^{-12}$	n	$\phi\times10^6$
0	3.0000	6.5070	1.3000	1.35×10^5
1	2.9570	6.9881	1.2525	1.32×10^5
2	2.9141	7.0639	1.2050	1.24×10^5
3	2.8711	7.3289	1.1574	1.05×10^5
4	2.8282	7.5842	1.1098	6.67×10^4
5	2.7855	7.8306	1.0621	9.82×10^3
8	2.7749	7.8901	1.0500	1.16×10^3
12	2.7696	7.9196	1.0440	1.36×10
18	2.7703	7.9159	1.0447	1.72
True Values	2.8000	7.8600	1.0000	0

the total duration of the reaction was taken to be as small as 0.5sec, the results of the calculations showed almost the same characteristic of of convergence as shown in Table 1. Then the gradient method will be able to estimate the kinetic parameters from the data for the short time period the reaction. From Eqs. (8) and (9), the relation between the temperature and the concentration is obtained as follows:

$$\frac{dx_1}{dt}-\frac{F}{V}(x_1^0-x_1) = -\frac{\rho c_p}{(\Delta H)}\left[\frac{dT}{dt}-\frac{F}{V}(T^0-T)\right] \quad (12)$$

The left term of this equation is the function of concentration and right term is the function of temperature. Therefore the mathematical models of this simple chemical reaction process can be built from measurements of either tempera-

ture or concentration, ie, $W_{x1}=0$ or $W_T=0$ in Eq. (10) during chemical reaction.

Difficulties will arise when the mathematical form of the models used to describe the behavior of reaction process is wrong and the measured responses taken during early operation are colored with process noise. Such complicated problems will be discussed in the forthcoming paper.

§ 4. Conclusion

The study mentioned above is one of the fundamental approch to the model building of chemical reaction processes and in this paper, the simple chemical reaction is discussed for the identification of parameters of kinetic eqations. But there are many problems for practical reaction processes which remains unsolved, for example, polymerization processes and flow model building for the nonlinear processes. We believe that the accumulation of the results of these fundamental studies leads the practical application of computer control system to their successful use in industry. On the basis of the above theoretical investigation, the experimental studies are being carried out for a chemical reaction process.

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