Development of a Kinetic Model for Industrial Oxidation of *p*-Xylene by RBF-PLS and CCA

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DOI 10.1002/aic.10113

A novel lumped kinetic model for the liquid-phase oxidation of p-*xylene to terephthalic acid (OXTA) catalyzed by cobaltic, manganic, and bromide salts in industrial continuous stirred-tank reactor (CSTR) was proposed. First, the radial basis functions (RBF) coupled with partial least squares (PLS) approach was used to model the influence of the reaction factors on the rate constants of the lumped kinetic scheme for OXTA in the laboratory semibatch reactor (SBR). Second, to indicate the difference between OXTA in the industrial CSTR and that in the laboratory SBR, the correction coefficients were proposed and introduced into the obtained rate constants models to describe the influence of the reaction factors on OXTA in the industrial CSTR. Third, the kinetics of each of the lumped reactions is assumed to be zeroth-order with respect to gaseous reactants, 0.65-order with respect to* p-*xylene, and first-order with respect to the other liquid reactants, respectively. Based on the lumped kinetic model with unknown correction coefficients and the data obtained in the industrial CSTR, a modified genetic algorithm containing a chaotic variable, designated chaos-genetic algorithm (CGA), was used to obtain the optimum correction coefficients, and the lumped kinetic model for OXTA in the industrial CSTR was developed. Further, the reliability of the model was investigated and the satisfactory results were obtained.* © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 1169–1176, 2004

Keywords: lumped kinetic model, oxidation, p-*xylene, terephthalic acid, continuous stirred-tank reactor, semibatch reactor, radial basis functions, partial least squares, chaos-genetic, algorithms*

Introduction

Aromatic dicarboxylic acids are widely used as polymer intermediates by virtue of their two acid-functional groups. In particular, terephthalic acid (TA) is of outstanding importance in the polymer field and is the starting material for the production of a range of polyesters. In the chemical industry, direct oxidation of petroleum and natural gas feedstock (Prengle and Barona, 1970a,b) is a commercially important reaction for the production of a wide variety of oxygenated compounds, that is, the manufacture of benzaldehyde and benzoic acid from toluene, TA from *p*-xylene, and phenol from isopropylbenzene.

In the 1950s, Mid-Century Corporation developed the well-known process for the liquid-phase catalytic oxidation of *p*-xylene to TA (OXTA) by air or molecular oxygen, in which cobalt and manganese acetates are used as catalysts, acetic acid is used as reaction solvent, and sodium bromide acts as a catalyst promoter to reduce the induction period (Saffer and Barker, 1958). AMOCO bought the ownership of the process and uses it for the commercial production of TA. Accordingly, the process is called the AMOCO process. Because the AMOCO process has the economic advantages such as higher yield, improved selectivity, and milder reaction conditions, many industries use the AMOCO process for the production of TA. To gain a better insight into the reaction mechanism and

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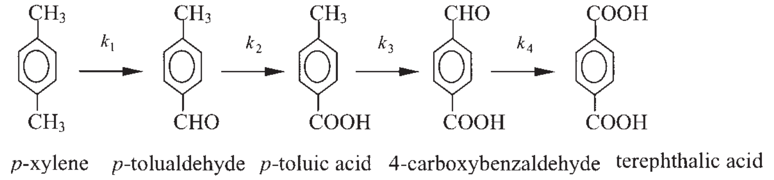

Figure 1. Lumped kinetic scheme for the oxidation of *p*-xylene to terephthalic acid (TA).

identify the effects of different parameters on the progress of reaction, it is essential to study the kinetics. Further, the rational design, optimization, control, and analysis of the OXTA process also require the knowledge of the kinetics. In our work, a lumped kinetic model for OXTA of the AMOCO process was developed.

OXTA occurs through chain elementary reactions, which involve a very large number of radical as well as molecular species (Scheldon and Kochi, 1981). Emanuel and Gal (1986) proposed a detailed radical-chain mechanism of OXTA. However, the complexity of this reacting system clearly prevents the evaluation of the individual values of the kinetic constants by direct fitting of model results against experimental data, mostly because of the inability of measuring the concentration of the radical species. Therefore, the suitable lumping procedure to be adopted is heuristic, founded on an understanding of the basic reacting system and including the minimum number of reactions to describe the behavior of all species of interest.

Generally, the concentrations of all the species of interest need to be monitored as a function of time to obtain a well-balanced estimation procedure for the kinetic parameters (that is, the rate constants and the reaction orders) of the lumped reactions in the experiment in the laboratory semibatch reactor (SBR). The results of previous research demonstrated that the values of the rate constants depend on the values of the reaction factors. In our work, a novel approach founded on radial basis function (RBF) and partial least squares (PLS), introduced by Walczak (Walczak and Massart, 1996), was taken as the method for modeling the rate constants with the reaction factors. At the same time, the results also showed that the oxygen partial pressure has no effect on the reaction rate as long as the oxygen partial pressure does not drop below a minimum value (Mill and Hendry, 1980). That is, it can be assumed that all the reactions are zeroth-order with respect to gaseous reactants under condition that the oxygen partial pressure is more than the minimum value. The effect of the oxygen partial pressure on the reaction rate can be neglected. It is also assumed that all the reactions are 0.65th-order with respect to *p*-xylene and first-order with the other liquid reactants (Cao et al., 1994; Cincotti et al., 1997, 1999; Zhang, 2000). Thus, the lumped kinetic model for OXTA in the laboratory SBR was developed.

However, OXTA of the AMOCO process is in the industrial continuous stirred-tank reactor (CSTR). The time evolution of the concentration of all the species of interest cannot be obtained to estimate the kinetic parameters, and the lumped kinetic model cannot be developed further. At the same time, there is a significant difference between the nature of OXTA in the laboratory SBR and that of OXTA in the industrial CSTR. The lumped kinetic model obtained in the laboratory SBR cannot express the nature of OXTA in the industrial CSTR. To overcome this difficulty, correction coefficients were proposed and introduced into the rate constants to describe the effect of the reaction factors on the reactions in the industrial CSTR. The rate constant model of each of the lumped reactions for OXTA in the industrial CSTR can be developed when the optima of correction coefficients are obtained. Searching the optima of correction coefficients is an optimization problem. A modified genetic algorithm containing a chaotic variable, designated the chaos-genetic algorithm (CGA) (Yan et al., 2002), was used to obtain the optimum correction coefficients. Finally, the lumped kinetic model for OXTA in the industrial CSTR was developed, and the reliability of the model was investigated and satisfactory results were obtained.

Semibatch Reactor Model

Lumped kinetic model of semibatch reactor

The experimental setup and procedure are described in detail by Zhang (2000). Briefly, it consisted of a jacketed titanium reactor maintained at the desired temperature through forced circulation of diathermic oil. The system was also equipped with three jacketed condensers to ensure complete condensation and recycling of the evaporated compounds. In a typical experimental run in the laboratory SBR, the reactor was charged with a proper amount of compounds consisting of liquid reactant (that is, *p*-xylene), solvent (that is, acetic acid), coordination complex catalysts (that is, cobalt and manganese), promoter (that is, bromide), and so forth. After the temperature reached the desired value, air was continuously fed through the liquid. All the experimental runs were performed at a stirring speed of 800–900 rpm, where the influence of stirring on the product distribution becomes negligible (Cao et al., 1994). The reaction products were analyzed and analysis procedure details are reported elsewhere (Zhang, 2000).

By taking into account only the formation of molecular species that represent the most important intermediate and final products, an appropriate lumped kinetic scheme (as shown in Figure 1) was developed for OXTA (Zhang, 2000; Zhou, 1988). The reactions of *p*-xylene to *p*-tolualdehyde and *p*-toluic acid to 4-carboxybenzaldehyde involve the addition of $1O_2$; the reactions of *p*-tolualdehyde to *p*-toluic acid and 4-carboxybenzaldehyde to TA involve the addition of $1/2O_2$. Thus, the following population equations are given as the lumped kinetic model

$$\begin{cases} r_1 = \dfrac{dC_1}{dt} = -K_1 C_1^{n_1} C_{O_2}^{m_1} \\ r_2 = \dfrac{dC_2}{dt} = k_1 C_1^{n_1} C_{O_2}^{m_1} - k_2 C_2^{n_2} C_{O_2}^{m_2} \\ r_3 = \dfrac{dC_3}{dt} = k_2 C_2^{n_2} C_{O_2}^{m_2} - k_3 C_3^{n_3} C_{O_2}^{m_3} \\ r_4 = \dfrac{dC_4}{dt} = k_3 C_3^{n_3} C_{O_2}^{m_3} - k_4 C_4^{n_4} C_{O_2}^{m_4} \\ r_5 = \dfrac{dC_5}{dt} = k_4 C_4^{n_4} C_{O_2}^{m_4} \end{cases} \tag{1}$$

in which the liquid reactants (that is, *p*-xylene, *p*-tolualdehyde, *p*-toluic acid, 4-carboxybenzaldehyde, and terephthalic acid) are denoted 1, 2, 3, 4, and 5, respectively; the concentration of the *i*th liquid reactant is represented by C_i ($i = 1, 2, \ldots, 5$); C_{O_2} represents the concentration of the oxygen in liquid phase; t is residence time; r_i ($i = 1, 2, \ldots, 5$) is the reaction rate of the *i*th lumped reaction; n_i ($i = 1, 2, \ldots, 4$) and m_i ($i = 1, 2, \ldots, 4$) are reaction orders of two reactants of the *i*th lumped reaction; and k_i ($i = 1, 2, \ldots, 4$) is the rate constant of the *i*th lumped reaction.

It is widely known that there are many reaction factors influencing the rate constants k_i ($i = 1, 2, \ldots, 4$). The reaction temperature (x_1, °C), the initial concentration of *p*-xylene in acetic acid solvent (x_2, mol/kg acetic acid), the weight percentage of cobalt in the feed (x_3, %), the weight percentage of manganese in the feed (x_4, %), and the weight percentage of bromine in the feed (x_5, %) are considered as the major reaction factors. The performed experimental runs involve four reaction temperatures, five initial concentrations of *p*-xylene, five concentrations of cobalt catalyst, five concentrations of manganese catalyst, and four concentrations of bromide promoter. The total number of experimental runs is 18 (Zhang, 2000). The values of the kinetic constants are estimated by fitting the time evolution of the experimental product composition of all the experimental runs through a nonlinear least-square procedure. $n_1 = 0.65$, $n_2 = 1$, $n_3 = 1$, $n_4 = 1$, $m_1 = 0$, $m_2 = 0$, $m_3 = 0$, and $m_4 = 0$ are obtained for all the experimental runs, and each experimental run with the different reaction factors has the different rate constants k_i ($i = 1, 2, \ldots, 4$). The values of the rate constants depend on the values of the reaction factors. The reaction factors constitute the independent variables and the rate constants constitute the dependent variables. Thus, RBF-PLS was applied to model the rate constants with the reaction factors because this approach is able to model complex nonlinear systems and can be used without a clearly defined relationship between the independent and dependent variables. When the model of the rate constant of each of the lumped reactions is developed, the lumped kinetic model can be applied to describe the progress of OXTA in the laboratory SBR with various levels of reaction factors.

Radial basis functions–partial least-squares method

Assume that the practical observation vector **p** consists of n independent variables and l dependent variables, the independent variable vector **x** consists of n independent variables, the dependent variable vector **y** consists of l dependent variables, and the data set available for modeling consists of m observation vectors. Thus, the dimension of the independent variable matrix **X** is $m \times n$, and that of the dependent variable matrix **Y** is $m \times l$. In the RBF-PLS method, the Gaussian function is often used as RBF to carry out the nonlinear transformation of **X** to form and activation matrix $\mathbf{X}_A$. The elements of $\mathbf{X}_A$ are defined as

$$a_{ij} = r_j(\mathbf{x}_i) = \exp(-\|c_j - \mathbf{x}_i\|^2/\sigma_j^2) \qquad i, j = 1, 2, \ldots, m \tag{2}$$

where $\mathbf{x}_i$ is a vector consisting of the values of independent variables taken from the *i*th observation, a_{ij} is the element of $\mathbf{X}_A$ at the *i*th row and the *j*th column, r_j is the *j*th radial basis function, $\| \|$ is a norm and denotes the Euclidean distance when the argument is a difference of two vectors, and $\mathbf{c}_j$ and $\boldsymbol{\sigma}_j$ are two parameters (that is, the center and the width) of the *j*th Gaussian function. The parameter $\mathbf{c}_j$ is calculated by

$$c_j = \mathbf{x}_j \qquad j = 1, 2, \ldots, m$$

and the elements of the parameter $\boldsymbol{\sigma}_j$ are calculated by

$$\sigma_{j1} = \sigma_{j2} = \cdots = \sigma_{jn} = \frac{e}{m} \sum_{i=1}^{m} \|\mathbf{x}_i - \mathbf{x}_j\| \qquad j = 1, 2, \ldots, m$$

in which e is a constant, assigned a value of $e > 0$. Thus the diagonal elements of the activation matrix $\mathbf{X}_A$ have a value 1. It is clear that the number of radial basis functions (RBFs) in m, and the RBFs themselves are vector functions, the dimensions of which are all n.

Then, the PLS procedure will be applied to the matrices $\mathbf{X}_A$ and **Y**, and the linear PLS model is set up as

$$\mathbf{Y} = \mathbf{TC} + \mathbf{E} = \mathbf{X}_A\mathbf{UC} + \mathbf{E} \tag{3}$$

in which **T** is the low-dimensional score matrix of $\mathbf{X}_A$ with the dimension of $m \times n_T$, **C** represents the regression coefficient matrix with the dimension of $n_T \times l$, **U** is the transformation matrix of $\mathbf{X}_A$ with the dimension of $n \times n_T$, and **E** is the residuals matrix with the dimension of $m \times l$. Because of the fact that **T** is a linear combination of Gaussian functions (i.e., the row vectors of $\mathbf{X}_A$) that will maximize the covariance between $\mathbf{X}_A$ and **Y**, n_T plays an important role in the predicting ability of the RBF-PLS model. When n_T is determined, the RBF-PLS model can be obtained and used for prediction or other purposes.

In general, before calculating the activation matrix, the variables of the practical observation vectors are always scaled to the range [0, 1]. Assume that a set of independent variable vectors beyond the data used in modeling is chosen to form a matrix $\mathbf{X}_p$ for prediction, and the corresponding dependent matrix $\mathbf{Y}_p$ has not been obtained or is unknown. $\mathbf{X}_p$ will be preprocessed in an identical manner as **X** of the data set used for modeling; that is, its variables are scaled (using the minimum and the maximum values of **X**) and the activation matrix $\mathbf{X}_{Ap}$ of $\mathbf{X}_p$ is calculated keeping the values of centers and widths of Gaussian functions. Finally, the predicted $\mathbf{Y}_p$ is calculated as

$$\mathbf{Y}_p = \mathbf{X}_{Ap}\mathbf{U}\mathbf{C} \tag{4}$$

Modeling the rate constants by RBF-PLS

The practical observation vector represented by **d** consists of five independent variables (that is, the reaction temperature x_1, the initial concentration of *p*-xylene in solvent of acetic acid x_2, the weight percentage of cobalt in feed x_3, the weight percentage of manganese in feed x_4, and the weight percentage of bromine in feed x_5) and four dependent variables [that is, the rate constants k_i ($i = 1, 2, \ldots, 4$)], and the data set **D** available for modeling the rate constants containing 18 observation vectors (that is, $m = 18$) (Zhang, 2000). The RBF-PLS method is used to model the rate constants through the data set **D**. The optimal value for n_T used in the score matrix **T** can be determined by the leave-one-out cross-validated method. The procedure is illustrated as follows:

(1) Assign the initial value $n_T = 1$.

(2) Carry out the leave-one-out cross-validated method; that is, every time leave one observation vector out for validating the model. The other vectors in the data set are used for modeling and thus each observation vector is used as a vector for validating one time and used for modeling $m - 1$ times. Assume that the ith observation vector $\mathbf{d}_i = [\mathbf{x}_i \mathbf{y}_i]$ is left for validating the model, in which $\mathbf{x}_i$ is the ith independent variable vector; $\mathbf{y}_i$ is the ith dependent variable vector; and the data set $\mathbf{D}_i$, used for modeling, consists of the other observation vectors, that is

$$\mathbf{D}_i = \begin{bmatrix} \mathbf{d}_1 \\ \mathbf{d}_2 \\ \vdots \\ \mathbf{d}_{i-1} \\ \mathbf{d}_{i+1} \\ \vdots \\ \mathbf{d}_m \end{bmatrix}$$

RBF-PLS is applied to model the rate constants through the data set $\mathbf{D}_i$ under the current n_T. Further, the model is used to predict the value of $\mathbf{y}_i$ from the value of $\mathbf{x}_i$, that is

$$\mathbf{y}_{pi} = \mathbf{x}_{Ai}\mathbf{U}_i\mathbf{C}_i$$

in which $\mathbf{y}_{pi}$ represents the predicted value of $\mathbf{y}_i$, $\mathbf{x}_{Ai}$ is the activation matrix of $\mathbf{x}_i$, and $\mathbf{U}_i$ and $\mathbf{C}_i$ are obtained through applying the RBF-PLS to the data set $\mathbf{D}_i$. Calculate the mean of square errors (MSE_{n_T}) under the current n_T by

$$MSE_{n_T} = \frac{1}{m}\sum_{i=1}^{m} \|\mathbf{y}_{pi} - \mathbf{y}_i\|^2 = \frac{1}{m}\sum_{i=1}^{m}\sum_{j=1}^{4} (k_{pi,j} - k_{i,j})^2 \tag{5}$$

in which $k_{i,j}$ is the value of the jth dependent variable of $\mathbf{y}_i$ and $k_{pi,j}$ is the predicted value of $k_{i,j}$ by the RBF-PLS model.

(3) As long as n_T is smaller than m, set $n_T = n_T + 1$ and repeat step 2.

(4) Stop the procedure until $n_T \geq m$.

Figure 2 shows the relationship between MSE_{n_T} and n_T. It can be seen from Figure 2 that MSE_{n_T} has the minimum value 0.0173 when $n_T = 4$, which means that the RBF-PLS model has the best predicting ability at this point. Thus the optimal n_T is 4 and the other parameters of the RBF-PLS model (that is, $\mathbf{c}_j$, $\boldsymbol{\sigma}_j$, **U**, and **C**) can be determined through the data set D, and the appropriate RBF-PLS model of the rate constants is obtained and defined as

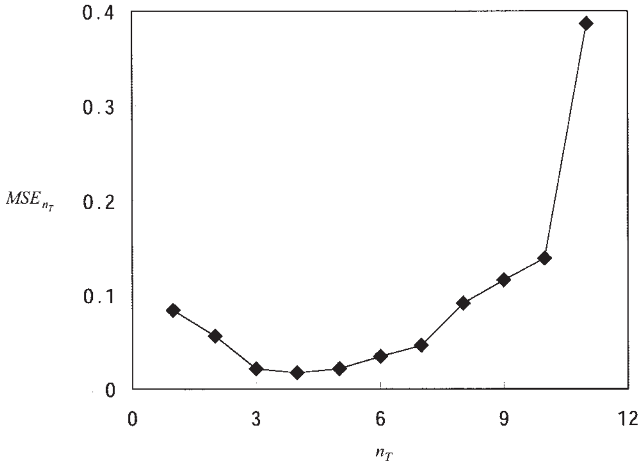

Figure 2 The relationship between MSE_{n_T} and n_T.

$$k_i = f_i^{(\text{RBF-PLS})}(x_1, x_2, x_3, x_4, x_5) \qquad i = 1, 2, \ldots, 4 \tag{6}$$

in which $f_i^{(RBF\text{-}PLS)}(\bullet)$ is the model of the rate constant k_i. When the model of the rate constant of each of the lumped reactions is modeled, the lumped kinetic model can be developed to describe the progress of OXTA in the laboratory SBR with various levels of reaction factors.

Lumped Kinetic Model of Industrial CSTR

AMOCO oxidation process

The AMOCO oxidation process of *p*-xylene to TA mainly consists of three CSTRs connected in parallel and the first crystallizer. The material flow is shown in Figure 3. It can be seen from Figure 3 that TA is manufactured by first preparing the feed including the liquid reactant (that is, *p*-xylene) mixed with catalysts (that is, cobalt and manganese) and promoter (that is, bromide) plus acetic acid solvent. The feed preparation is fed to three CSTRs with air. The liquid-phase catalytic reaction takes place in the three CSTRs to form TA. Then TA slurry from the three CSTRs is supplied to a first crystallizer along with the TA slurry and some further oxidation occurs. The first crystallizer can be regarded as a CSTR to a certain extent. TA is then supplied to a product recovery stage where it is separated and dried. The produced dry TA is then sent to storage.

The lumped kinetic model of the oxidation in each industrial CSTR (including three CSTRs and the first crystallizer) can also be defined as in Eq. 1. However, the time evolution of the concentration of all the species of interest cannot be obtained to estimate the kinetic parameters. Moreover, there is a significant difference between the nature of OXTA in the laboratory SBR and that of OXTA in the industrial CSTR. The lumped kinetic model obtained in the laboratory SBR cannot express the nature of OXTA in the industrial CSTR.

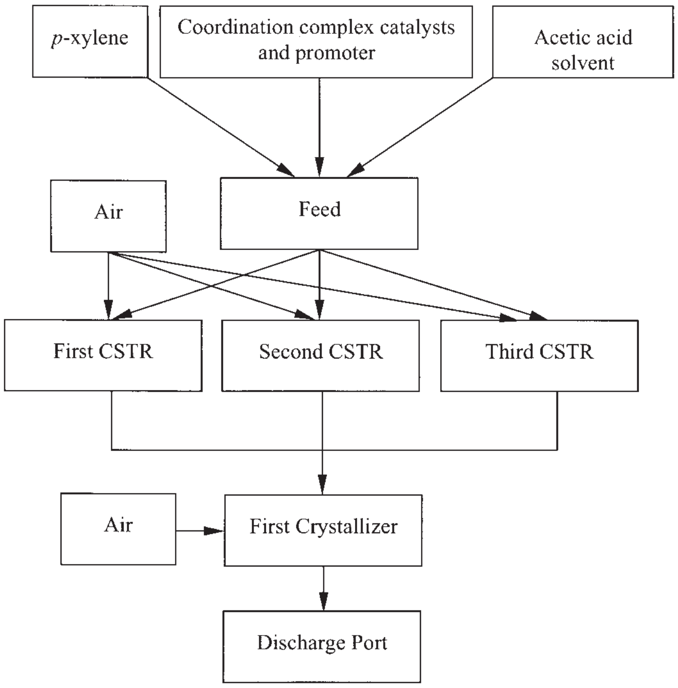

Figure 3 Process for the industrial oxidation of *p*-xylene to TA.

Correction coefficients introduced into the rate constants

To overcome the difficulty and use the kinetic parameters obtained in the laboratory SBR, correction coefficients—introduced into Eq. 6 to describe the effect of the reaction factors on the reactions in the industrial CSTR—were proposed. The rate constants are described as follows

$$k_i^{(\mathrm{CSTR})} = f_i^{(\mathrm{CSTR,RBF\text{-}PLS})}(x_1, x_2, x_3, x_4, x_5, \boldsymbol{\theta}_i) \qquad i = 1, 2, \ldots, 4 \tag{7}$$

where $k_i^{(CSTR)}$ is the ith rate constant of the lumped kinetic model for OXTA in the industrial CSTR, $\boldsymbol{\theta}_i$ is the ith correction vector consisting of q_i correction coefficients for $k_i^{(CSTR)}$, and $f_i^{(CSTR,RBF\text{-}PLS)}(\bullet)$ is the ith function coupling Eq. 6 with $\boldsymbol{\theta}_i$.

Various concrete expressions can be chosen for Eq. 7. By accounting for easily obtaining the values of correction coefficients, a feasible combination expression consisting of Eq. 6 with two linear correction coefficients was also proposed as

$$k_i^{(\mathrm{CSTR})} = a_i f_i^{(\mathrm{RBF\text{-}PLS})}(x_1, x_2, x_3, x_4, x_5) + b_i \qquad i = 1, 2, \ldots, 4 \tag{8}$$

in which $f_i^{(RBF\text{-}PLS)}(\bullet)$ is Eq. 6, a_i and b_i are two linear correction coefficients of the ith rate constant $k_i^{(CSTR)}$.

The rate constant of each of the lumped reactions in the industrial CSTR can be obtained when the optimum correction coefficients a_i and b_i are obtained. Then the lumped kinetic model can be applied to predict the nature of OXTA in the industrial CSTR, and the AMOCO oxidation process can be modeled based on the known lumped kinetic model of each CSTR. In the AMOCO oxidation process, the contents of liquid reactants of interest (i.e., *p*-xylene, *p*-tolualdehyde, *p*-toluic acid, 4-carboxybenzaldehyde, TA) of the slurry from the first crystallizer are analyzed and represented by $C_i^{(4)}$ ($i = 1, 2, \ldots, 5$) (mol/kg acetic acid), in which the superscript 4 refers to the first crystallizer as the fourth CSTR of the AMOCO oxidation process. The specified weight percentages were calculated as follows

$$yw_i = \frac{C_i^{(4)} m_i}{C_5^{(4)} m_5} \times 100 \qquad i = 1, 2, 3, 4 \tag{9}$$

where yw_i denotes the specified weight percentage of the ith liquid reactant in the slurry from the first crystallizer, and m_i is the molecular weight of the ith liquid reactant.

Assume that the reaction temperature of the ith CSTR is represented by $x_1^{(i)}$ ($i = 1, 2, 3, 4$); the residence time of the ith CSTR is represented by $t^{(i)}$ ($i = 1, 2, 3, 4$; the superscript $i = 4$ refers to the first crystallizer as the fourth CSTR of the AMOCO oxidation process); the mass flow of acetic acid fed to the ith CSTR is denoted by $S^{(i)}$ [$i = 1, 2, 3, 4$; in which $S^{(4)} = S^{(1)} + S^{(2)} + S^{(3)}$]; the initial concentrations of *p*-xylene, *p*-tolualdehyde, *p*-toluic acid, 4-carboxybenzaldehyde, and TA in the feed are represented by $C_j^{(0)}$ [$j = 1, 2, \ldots, 5$); $C_1^{(0)} > 0$, $C_2^{(0)} = 0$, $C_3^{(0)} = 0$, $C_4^{(0)} = 0$, and $C_5^{(0)} = 0$]; and the concentrations of the cobalt catalyst, manganese catalyst, and bromide promoter in the feed are represented by x_3, x_4, and x_5, respectively. The practical observed vector $\mathbf{p}_{industrial}$, collected from the AMOCO oxidation process, consists of the following elements: $C_1^{(0)}$, $C_2^{(0)}$, $C_3^{(0)}$, $C_4^{(0)}$, $C_5^{(0)}$, $S^{(1)}$, $S^{(2)}$, $S^{(3)}$, $x_1^{(1)}$, $x_1^{(2)}$, $x_1^{(3)}$, $x_1^{(4)}$, $t^{(1)}$, $t^{(2)}$, $t^{(3)}$, $t^{(4)}$, x_3, x_4, x_5, yw_1, yw_2, yw_3, and yw_4; and the data set $\mathbf{D}_{industrial}$ consists of $m_{industrial}$ practical observed vectors. Thus the procedure of determining the optimal a_i and b_i ($i = 1, 2, 3, 4$) is described as follows:

(1) Assign the initial values a_i and b_i ($i = 1, 2, 3, 4$).

(2) Select a practical observed vector $\mathbf{p}^{l}_{industrial}$ ($l = 1, 2, \ldots, m_{industrial}$) from the data set $\mathbf{D}_{industrial}$; $\mathbf{p}^{l}_{industrial}$ consists of the following elements: $C_1^{(0)}(l)$, $C_2^{(0)}(l)$, $C_3^{(0)}(l)$, $C_4^{(0)}(l)$, $C_5^{(0)}(l)$, $S^{(1)}(l)$, $S^{(2)}(l)$, $S^{(3)}(l)$, $x_1^{(1)}(l)$, $x_1^{(2)}(l)$, $x_1^{(3)}(l)$, $x_1^{(4)}(l)$, $t^{(1)}(l)$, $t^{(2)}(l)$, $t^{(3)}(l)$, $t^{(4)}(l)$, $x_3(l)$, $x_4(l)$, $x_5(l)$, $yw_1(l)$, $yw_2(l)$, $yw_3(l)$, $yw_4(l)$. Further, carry out the following procedure based on the values of the elements of $\mathbf{p}^{l}_{industrial}$ [the following procedures (2A)–(2F) can be considered as the AMOCO oxidation process model].

(2A) Calculate the rate constant of each of the lumped reactions in the jth CSTR: $k_i^{(j)}(l) = a_i f_i^{(RBF\text{-}PLS)}[x_1^{(j)}(l), C_1^{(0)}(l), x_3(l), x_4(l), x_5(l)] + b_i$ ($i = 1, 2, \ldots, 4$; $j = 1, 2, 3$).

(2B) With the known initial concentrations of liquid reactants, the lumped kinetic model can be used to predict the concentrations of the liquid reactants of interest (i.e., *p*-xylene, *p*-tolualdehyde, *p*-toluic acid, 4-carboxybenzaldehyde, TA) in the slurry from the jth CSTR. Assume that the calculated concentrations of the liquid reactants in the slurry from the jth CSTR are represented by $C_i^{(j)}(l)$ ($j = 1, 2, 3$; $i = 1, 2, 3, 4, 5$), in which the superscript j refers to the jth CSTR and the subscript i denotes the ith liquid reactant of interest.

(2C) Calculate the concentrations of the liquid reactants in the mixed slurry supplied to the first crystallizer

$$MC_j(l) = \frac{C_j^{(1)}(l)S^{(1)}(l) + C_j^{(2)}(l)S^{(2)}(l) + C_j^{(3)}(l)S^{(3)}(l)}{\sum_{i=1}^{3} S^{(i)}(l)} \qquad j = 1, 2, 3, 4, 5$$

in which $MC_j(l)$ represents the concentration of the jth liquid reactant of interest in the mixed slurry supplied to the fourth CSTR (i.e., the first crystallizer), and $S^{(i)}(l)$ is the mass flow of acetic acid fed to the ith CSTR.

(2D) Calculate the rate constant of each of the lumped reactions in the first crystallizer

$$k_i^{(4)}(l) = a_i f_i^{(\text{RBF-PLS})}[x_1^{(4)}(l), MC_1(l), x_3(l), x_4(l), x_5(l)] + b_i \qquad i = 1, 2, \ldots, 4$$

(2E) With the calculated initial concentrations of the liquid reactants of interest in the mixed slurry supplied to the first crystallizer [i.e., $MC_j(l)$ ($j = 1, 2, 3, 4, 5$)], the lumped kinetic model can be used to predict the concentrations of the liquid reactants of interest in the slurry from the first crystallizer. Assume that the predicted concentration of the ith liquid reactant of interest is denoted by $PC_i^{(4)}(l)$ ($i = 1, 2, 3, 4, 5$).

(2F) Calculate the specified weight percentages

$$yw_i^{(P)}(l) = \frac{PC_i^{(4)}(l)m_i}{PC_5^{(4)}(l)m_5} \times 100 \qquad i = 1, 2, 3, 4$$

and calculate the following square relative errors

$$SRE(l) = \sum_{i=1}^{4} \left[\frac{yw_i(l) - yw_i^{(p)}(l)}{yw_i(l)} \right]^2 \tag{10}$$

(3) The procedures (2A) to (2F) are applied for each practical observed vector in the data set $\mathbf{D}_{industrial}$ to obtain square relative errors (*SRE*), and calculate mean of square relative errors (*MSRE*) under the current values a_i and b_i ($i = 1, 2, 3, 4$) as follows

$$MSRE_{a_i,b_i} = \frac{1}{m_{industrial}} \sum_{l=1}^{m_{industrial}} SRE(l) \tag{11}$$

(4) Apply an optimal approach for procedures (2) and (3) to search the minimum $MSRE_{a_i,b_i}$ by adjusting correction coefficients a_i and b_i ($i = 1, 2, 3, 4$). Assume that the minimum $MSRE_{a_i,b_i}$ is represented by $MSRE^{\min}_{a_i,b_i}$, and the corresponding optimum correction coefficients are denoted by $a_i^{optimum}$ and $b_i^{optimum}$ ($i = 1, 2, 3, 4$).

It is clear that searching for the minimum $MSRE^{\min}_{a_i,b_i}$ is the problem of optimizing a complex nonlinear system. In our work, a modified genetic algorithm containing a chaotic variable designated the chaos-genetic algorithm (CGA; Yan et al., 2002) was used to search the minimum $MSRE^{\min}_{a_i,b_i}$ and to obtain the optimum correction coefficients.

Chaos-genetic algorithm

Because of the nature of the chaotic variable—that is, pseudorandomness, ergodicity, and irregularity—the evolutional process of CGA makes the individuals of subgenerations distributed ergodically in the defined space and circumvents the prematurity of the individuals of subgenerations. In the literature (Yan et al., 2002), the performance of CGA was demonstrated through two examples and compared with that of the traditional genetic algorithms. The results showed the superior performances of CGA over TGA.

Assume that the working vector containing n optimized variables is denoted by $\mathbf{gx}$. The elements of the working vector $\mathbf{gx}$ are designated as working parameters, denoted by gx_1, gx_2, $\ldots$, gx_n. Thus, the problem of searching for a minimum could be described as

$$\min_{gx} f(gx_1, gx_2, \ldots, gx_n)$$

$$gx_i \in (xlow_i, xhigh_i) \qquad i = 1, 2, \ldots, n \tag{12}$$

where f denotes the function relating the value of optimized variables gx and the dependent variable, which is subject to be optimized. An n-dimensional space S_0 is defined within the region $\{(xlow_i, xhigh_i), i = 1, 2, \ldots, n\}$.

The procedure of executing CGA can be described in the following.

(1) Determine the number of the population n_P, the crossover probability P_c, the mutation probability P_m, and the maximum number of generations t_m. Set the current number of generation $t = 1$, and the first generation of individuals $\mathbf{gx}_1(t)$, $\mathbf{gx}_2(t)$, $\ldots$, $\mathbf{gx}_{n_P}(t)$, which are randomly produced with the values in the space S_0, and are defined by $\mathbf{X}_t^{(1)} = \{\mathbf{gx}_1(t), \mathbf{gx}_2(t), \ldots, \mathbf{gx}_{n_P}(t)\}$.

(2) The chaotic individuals represented by $\mathbf{X}_t^{(2)} = \{\mathbf{gx}_1(t)^{(2)}, \mathbf{gx}_2(t)^{(2)}, \ldots, \mathbf{gx}_{n_P}(t)^{(2)}\}$ are produced through applying the

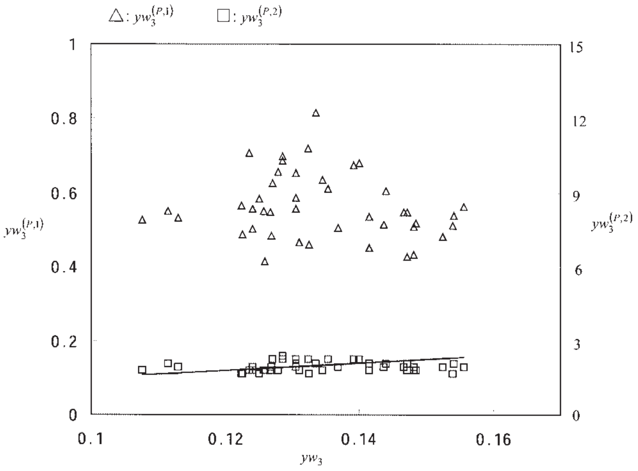

Figure 4 Distributions of $yw_3^{(P,1)}$ vs. $yw_3^{(P,2)}$.

chaotic mapping operator ψ (Yan et al., 2002) to all the individuals of $\mathbf{X}_t^{(1)}$, that is $\mathbf{gx}_i(t)^{(2)} = \psi[\mathbf{gx}_i(t)]$ $(i = 1, 2, \ldots, n_P)$.

(3) Randomly select n_P individuals from the set consisting of $\mathbf{X}_t^{(1)}$ and $\mathbf{X}_t^{(2)}$ to form a reproduction set $\mathbf{X}_t^{(r)}$ using the genetic operation of proportionate reproduction to meet the well-known Darwinian theory of survival of the fittest.

(4) Produce the new population $\mathbf{X}_t^{(3)}$ from $\mathbf{X}_t^{(r)}$ through the arithmetic crossover operation (Michalewicz et al., 1992).

(5) Produce the new population $\mathbf{X}_t^{(4)}$ from $\mathbf{X}_t^{(3)}$ through the mutation operation. There are many kinds of mutation operations for choice, such as the uniform mutation operation of traditional GA, the inconsistent mutation operation introduced by Michalewicz (1992), the adaptive mutation operation (Pan et al., 1996), and others. Here, the uniform mutation operation is used.

(6) Set $t = t + 1$, let $\mathbf{X}_t^{(1)} = \mathbf{X}_{t-1}^{(4)}$, and repeat steps (2) to (5) as long as the number of generations is smaller than the allowable maximum number t_m.

AMOCO oxidation process model with optimum correction coefficients

CGA was used to obtain the optimum correction coefficients based on the data set consisting of 53 practical observed vectors collected from the AMOCO oxidation process. The genetic operation parameters of CGA were taken as $n_P = 500$, $P_c = 1$, $P_m = 0.3$, and $t_m = 2000$. The optimum correction coefficients are $a_1^{optimum} = 0.878$, $a_2^{optimum} = 0.8084$, $a_3^{optimum} = 0.4523$, $a_4^{optimum} = 0.3212$, $b_1^{optimum} = 0.04997$, $b_2^{optimum} = 0.02766$, $b_3^{optimum} = 0.1$, and $b_4^{optimum} = 0.09996$, when the mean square relative error reaches $MSRE_{a_i,b_i}^{optimum} = 0.0615$.

With the optimum correction coefficients, the lumped kinetic model of each CSTR is developed. Based on the known lumped kinetic model of each CSTR, the AMOCO oxidation process model is also developed. When $C_1^{(0)}$, $C_2^{(0)}$, $C_3^{(0)}$, $C_4^{(0)}$, $C_5^{(0)}$, $S^{(1)}$, $S^{(2)}$, $S^{(3)}$, $x_1^{(1)}$, $x_1^{(2)}$, $x_1^{(3)}$, $x_1^{(4)}$, $t^{(1)}$, $t^{(2)}$, $t^{(3)}$, $t^{(4)}$, x_3, x_4, and x_5 are assigned, the AMOCO oxidation process model can be used to predict the concentrations of the liquid reactants of interest in the slurry from the first crystallizer, and to calculate $yw_1^{(P)}$, $yw_2^{(P)}$, $yw_3^{(P)}$, and $yw_4^{(P)}$.

To demonstrate the reliability of the proposed AMOCO oxidation process model consisting of the four lumped kinetic models, another data set, designated the test data set, containing 43 practical observed vectors collected from the AMOCO oxidation process was used. The AMOCO oxidation process model with [i.e., $a_i = a_i^{optimum}$, $b_i = b_i^{optimum}$ $(i = 1, 2, 3, 4)$] and without optimum correction coefficients [$a_i = 1$, $b_i = 0$ $(i = 1, 2, 3, 4)$] were applied to the test data set to calculate the specified weight percentages defined by Eq. 9, respectively, and the specified weight percentages are denoted by $yw_i^{(P,j)}(l)$ $(i = 1, 2, 3, 4; j = 1, 2; l = 1, 2, \ldots, 43)$ with j denoting the model and l denoting the lth practical observed vector. When using the AMOCO oxidation process model with the optimum correction coefficients, $j = 1$; otherwise, $j = 2$.

The entity $yw_i^{(P,j)}(l)$ was compared with the lth practical observed vector $yw_i(l)$ in the test data set, as shown in Figures 4 and 5. Figure 4 shows the distributions of $yw_3^{(P,1)}(l)$ and $yw_3^{(P,2)}(l)$, in which □ denotes $yw_3^{(P,1)}(l)$ and △ denotes $yw_3^{(P,2)}(l)$. Figure 5 shows the distributions of $yw_4^{(P,1)}(l)$ and $yw_4^{(P,2)}(l)$, in which □ denotes $yw_4^{(P,1)}(l)$ and △ denotes $yw_4^{(P,2)}(l)$. Because of the fact that $yw_1^{(P,1)}(l) = yw_1^{(P,2)}(l) = yw_1(l) = 0$ and $yw_2^{(P,1)}(l) = yw_2^{(P,2)}(l) = yw_2(l) = 0$, their results are not shown. The diagonals in Figures 4 and 5 represent the values of the lth practical observed vector $yw_i(l)$ in the test data set. It can be seen from Figures 4 and 5 that the performance of the proposed AMOCO oxidation process model with the optimum correction coefficients is better than that of the traditional model without the correction coefficients.

Conclusions

A lumped kinetic model for OXTA in the industrial CSTR was proposed. First, RBF-PLS was used to model the influence of the reaction rate factors on the rate constants of the lumped kinetic scheme for OXTA in the laboratory semibatch reactor (SBR). Second, to indicate the difference between OXTA in the industrial CSTR and that in the laboratory SBR, the correction coefficients were proposed and introduced into the obtained rate constants models to describe the influence of the reaction factors on OXTA in the industrial CSTR. Third, the kinetics of each of the lumped reactions is assumed to zeroth-order with respect to gaseous reactants, 0.65th-order with re-

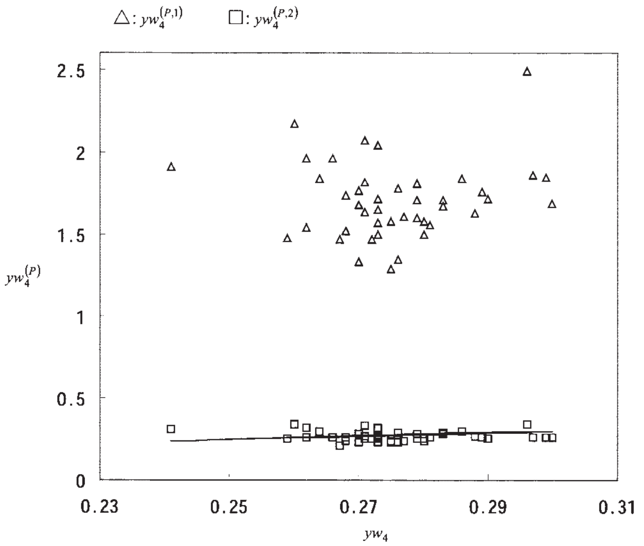

Figure 5 Distributions of $yw_4^{(P,1)}$ vs. $yw_4^{(P,2)}$.

spect to *p*-xylene, and first-order with respect to the other liquid reactants, respectively. Based on the lumped kinetic model with the unknown correction coefficients and the data obtained in the industrial CSTR, a modified genetic algorithm containing a chaotic variable designated chaos-genetic algorithm (CGA) was used to obtain the optimum correction coefficients, and the lumped kinetic model for OXTA in the industrial CSTR was developed. Further, the reliability of the model was investigated and satisfactory results were obtained. Further, a generalized methodology, which applies the RBF-PLS approach to model the rate constants through practical data obtained in the laboratory SBR and subsequently uses CGA to search the optimum values of the correction coefficients, which are introduced into the rate constants to describe the effect of the reaction factors on the reaction rate in the industrial CSTR, was suggested to model the industrial reaction process.

Acknowledgments

The work was supported by the following foundations: the National Nature Science Foundation (60074027) of China, the Fifteen Science and Technology Project (2001BA201A04) of China, the 863 Plan (2001AA413130, 2002AA412110) of China, and the 973 Plan (2002CB312200) of China.

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Manuscript received Apr. 11, 2003, and revision received July 18, 2003