Identifiability Study of a Liquid–Liquid Phase-Transfer Catalyzed Reaction System

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Consistent model parameterization is an important issue when developing mathematical models because it dictates whether parameter values can be estimated uniquely. The problems inherent in model parameterization are presented in an identifiability study of a nonlinear liquid–liquid phase-transfer reactor model. This reactor model was proposed by Chen et al., in a 1991 study, to describe the reaction between organic-phase benzyl chloride and aqueous-phase sodium bromide, using tetrabutylammonium as the phase-transfer catalyst. The model consists of coupled differential and algebraic equations. Existing methods using differential-algebra for testing identifiability of differential-algebraic equation (DAE) models are computationally intensive for models with a large number of states and parameters. A new method for testing DAE systems for identifiability was recently proposed by Ben-Zvi et al. Using this method, the model proposed by Chen et al. is shown to be locally unidentifiable, indicating that it is impossible to uniquely identify all of the model parameters. Two alternatives for simplifying the model to make it identifiable are discussed. © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 2493–2501, 2004

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Introduction

Fundamental mathematical models of physical systems are commonly used in virtually every branch of science and engineering because they can predict the behavior of the physical system over a wide range of operating conditions. These models are particularly beneficial to chemical engineers because they can be used to optimize and control the behavior of dynamic process systems.

Differential-algebraic equation (DAE) systems constitute a common class of first-principle models. These systems consist of a set of coupled differential and algebraic equations that describe the behavior of the states of the system in response to external inputs. The differential equations are usually derived using mass and energy balances on chemical species, whereas the algebraic equations are typically derived using quasi steady-state assumptions or thermodynamic relationships between the process variables. Kumar and Daoutidis (1999) used DAE models to describe the dynamical behavior of chemical processes. Brenan et al. (1989) discussed in detail the numerical solution of DAE models, whereas Pantelides et al. (1988) discussed the initialization and solution of DAEs in a chemical process modeling context.

Most DAE models are parameterized by a set of unknown parameters. These parameters must be determined experimentally by observing the behavior of the physical system. For the DAE model that is the basis of this article, Chen et al. (1991) performed a number of dynamic experiments in a liquid–liquid phase-transfer-catalyzed (PTC) reactor operated in batch mode. The data from these experiments were used to estimate the kinetic and equilibrium parameters in their model of the system. Chen et al. (1991) had difficulties estimating the parameters in their model, so they resorted to a two-stage systematic search technique. Initial values of parameters were selected

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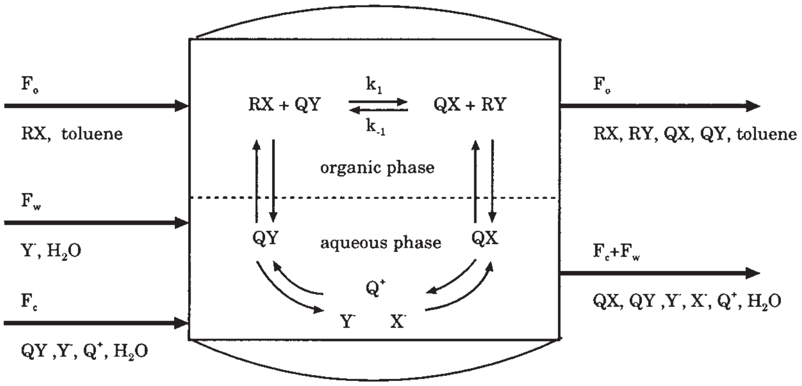

Figure 1. An idealized schematic of the continuous-time PTC reactor system.

using a priori information about the magnitudes of the model parameters. Parameter estimates were refined using a DSC–Powell direct search method. Their goals were to develop a model that can predict the behavior of the system, and to obtain "representative and physically meaningful parameters" (Chen et al., 1991). Comparison of the predictions of their model with experimental data confirmed that the model could capture the behavior of the PTC reactor system. However, it is not known whether alternative sets of parameters could give exactly the same model predictions. The current article addresses this issue.

A model is locally identifiable about some nominal value of the parameters if there is a unique relationship between the values of the parameters in the model and the input–output behavior of the model. If a model is not identifiable then it is impossible to obtain unique estimates of the model parameters, even if a large number of well-designed experiments are performed. Specifically, a set of different parameter values will result in the same predicted system behavior and it is therefore impossible to choose the "true" parameter values from this set. As a result, ensuring that a DAE model is identifiable is important for accurate parameter estimation. It is important to note that *identifiability* is a structural property concerned with whether unique parameter estimates can be obtained under idealized conditions in which there is no noise in the system, no plant-model mismatch, and desired inputs can be actuated perfectly for as many experiments as are desired. This is in contrast to the concept of *estimability* (Yao et al., 2003), which is concerned with whether each parameter can be accurately estimated using a particular set of real-life noisy experiments on the physical system. Identifiability is a necessary condition for estimability.

In this work, a continuous PTC reaction model is tested for identifiability using a linearization-based approach and the parameter values proposed by Chen et al. (1991) as initial guesses. It is shown that the linearized model is not identifiable. Next, simulation results are provided to illustrate the lack of identifiability in the original nonlinear model. These simulation results are verified by computing the set of alternative parameter values that produce the same input–output behavior as the values suggested by Chen et al. (1991). A discussion of how to overcome this lack of identifiability by either measuring more variables or reparameterizing the model follows. Finally, the batch PTC reaction model proposed by Chen et al. (1991) is also shown to be unidentifiable.

The PTC Reaction Model

In this work, the importance of checking a model for identifiability is illustrated by testing the identifiability of a PTC reaction model studied by Chen et al. (1991). PTC reaction systems are used to increase the speed of reaction when reactants are not soluble in the same phase. They are used in catalytic hydrogenation and oxidation (Starks, 1987) and for other industrially important reactions (Naik and Doraiswamy, 1998). The PTC reaction model proposed by Chen et al. (1991) is a good test problem for evaluating DAE identifiability tests because the system is sufficiently complex to exhibit qualitative behaviors typically found in reactive systems, such as inverse response or nonminimum phase behavior. The PTC model contains six differential and six algebraic equations involving 12 states and seven parameters. Term explosion can be a major issue when testing identifiability using computer algebra software, using methods such as the nonlinear differential algebra techniques available in the literature (Ljung and Glad, 1994; Xia and Moog, 2003).

A linearization-based approach has recently been proposed to test the identifiability of DAE systems by Ben-Zvi et al. (2004), with the aim of being able to treat larger-scale systems. Herein, this linearization-based approach is applied to a continuous-reactor operation form of the PTC model originally proposed by Chen et al. (1991). This model describes the reaction of organic-phase benzyl chloride with aqueous-phase sodium bromide using tetrabutylammonium (TBA) as the phase-transfer catalyst. In this model, algebraic constraints result from phase-equilibrium assumptions between the organic and aqueous phases, and from ionization equilibria in the aqueous phase. The differential equations are dynamic material balances on reacting species.

The reactor system and kinetic scheme are shown schematically in Figure 1, and the corresponding model is shown in Table 1. Equations f_1–f_6 in Table 1 are first-order ordinary differential equations (ODEs), and Eqs. g_1–g_6 are algebraic. Equations f_1, f_2, and f_3 are organic-phase dynamic material balances for the reactant (benzyl chloride, RX_o), the phase transfer catalyst (TBA bromide, QY_o), and the product (benzyl bromide, RY_o), respectively. Equations f_4, f_5, and f_6 are total balances on the number of moles of bromine atoms (n_Y), chlorine atoms (n_X) and TBA groups (n_Q), respectively, present in all forms, in both phases of the reaction mixture. Equations g_1, g_2, and g_3 define n_Y, n_X, and n_Q, respectively, in terms of the

Table 1. Continuous PTC Reaction Model

$$\frac{dRX_o}{dt} = -k_1 RX_o QY_o + k_{-1} RY_o QX_o + \frac{F_o}{V_o} RX_{in} - \frac{F_o}{V_o} RX_o \tag{f_1}$$

$$\frac{dQY_o}{dt} = -k_1 RX_o QY_o + k_{-1} RY_o QX_o + V_o^{-1} A K_{QY}(m_{QY} QY_w - QY_o) - \frac{F_o}{V_o} QY_o \tag{f_2}$$

$$\frac{dRY_o}{dt} = k_{-1} RX_o QY_o - k_{-1} RY_o QX_o - \frac{F_o}{V_o} RY_o \tag{f_3}$$

$$\frac{dn_Y}{dt} = F_w Y_{in} + F_c QY_{in} - (F_c + F_w)(Y_w^- + QY_w) - F_o(QY_o + RY_o) \tag{f_4}$$

$$\frac{dn_X}{dt} = F_o RX_{in} - F_o(RX_o + QX_o) - (F_c + F_w)(X_w^- + QX_w) \tag{f_5}$$

$$\frac{dn_Q}{dt} = F_c QY_{in} - F_o(QX_o + QY_o) - (F_c + F_w)(QX_w + QY_w + Q_w^+) \tag{f_6}$$

$$0 = n_Y - V_o(RY_o + QY_o) - V_w(Y_w^- + QY_w) \tag{g_1}$$

$$0 = n_X - V_o(RX_o + QX_o) - V_w(X_w^- + QX_w) \tag{g_2}$$

$$0 = n_Q - V_o(QY_o + QX_o) - V_w(Q_w^+ + QX_w + QY_w) \tag{g_3}$$

$$0 = Q_w^+ Y_w^- - K_{QY}^D QY_w \tag{g_4}$$

$$0 = Q_w^+ X_w^- - K_{QX}^D QX_w \tag{g_5}$$

$$0 = QX_o - m_{QX} QX_w \tag{g_6}$$

$$y(t) = [RX_o \quad RY_o]^T \tag{y}$$

moles of pertinent species in both phases. Equation g_4 describes the ionization equilibrium between TBA bromide (QY_w) and its ions in the aqueous phase, and Eq. g_5 describes the ionization equilibrium for TBA chloride (QX_w). Equation g_6 describes equilibrium partitioning of TBA chloride between the two phases. Equation y defines measured outputs as RX_o and RY_o, the organic phase concentrations of benzyl chloride and benzyl bromide, respectively.

The batch-reactor model originally developed by Chen et al. (1991) is a subset of this continuous model. Their batch-reactor model can be obtained by setting inflow rates F_o, F_w, and F_c in the model to zero, along with the accumulation terms in Eqs. f_4–f_6 (see Table 5 below). In their batch-reactor experiments, Chen et al. (1991) also observed n_Y, n_X, and n_Q, the total number of moles of bromine atoms, chlorine atoms, and TBA groups in the system, which remained constant over time.

Estimates of unknown model parameters and known phase volumes, obtained from Chen et al. (1991), are listed in Table 2. The model assumes that during continuous operation, the position of the interface between the two phases is maintained constant so that V_o and V_w, the organic-and aqueous-phase volumes, respectively, remain fixed. Steady-state initial values for all of the state variables and inputs are listed in Table 3. Values of the state variables in Table 3 are typical values from the experiments conducted by Chen et al. (1991). Inflow rates F_o and F_w were chosen to give residence times for both phases of about 6 h and a conversion of about 50%. Feed concentrations of benzyl chloride and sodium bromide (RX_{in} and Y_{in}) correspond to initial concentrations used in the Chen et al. (1991) batch-reactor experiments. The inlet catalyst concentration (QY_{in}) corresponds to the concentration of commercially available 50% TBA chloride in water.

Solvability of the Nonlinear Model Equations

The PTC model equations in Table 1 can be summarized as follows:

$$E\dot{x}(t) = \begin{bmatrix} f(x(t), u(t), p) \\ g(x(t), u(t), p) \end{bmatrix} \tag{1a}$$

$$y(t) = Cx(t) \tag{1b}$$

where $\dot{x}(t) = (dx/dt)(t)$ and

$$x(t) = [RX_o, QY_o, RY_o, n_Y, n_X, n_Q, QY_w, Y_w^-, X_w^-, Q_w^+, QX_w, QX_o]^T$$

$$u(t) = [F_o, F_w, F_c, RX_{in}, QY_{in}, Y_{in}]^T$$

$$p = [k_1, k_{-1}, V_o^{-1} A K_{QY}, m_{QY}, m_{QX}, K_{QY}^D, K_{QX}^D]^T \tag{2}$$

$$E = \begin{bmatrix} I_6 & 0 \\ 0 & 0 \end{bmatrix} \tag{3}$$

$$C = [I_2 \quad 0] \tag{4}$$

Table 2. Parameter Values: Estimated Parameters from Chen et al. (1991) and Specified Quantities for PTC Reaction Model

Variable	Value	Unit
	Parameters	
k_1	4.183×10^{-4}	$m^3\ mol^{-1}\ s^{-1}$
k_{-1}	2.800×10^{-3}	$m^3\ mol^{-1}\ s^{-1}$
$V_o^{-1} A K_{QY}$	2.367×10^3	$mol\ m^3\ s^{-1}$
m_{QY}	6.96×10^{-1}	—
m_{QX}	6.60×10^{-2}	—
K_{QY}^D	6.89×10^5	m^3/mol
K_{QX}^D	8.373×10^5	m^3/mol
	Known Quantities	
V_o	7.50×10^{-5}	m^3
V_w	1.50×10^{-4}	m^3

Table 3. Nominal State and Input Values

Symbol	Definition	Phase	Initial Value	Unit
		States		
RX_o	Benzyl chloride	Organic	9.82×10^2	mol/m^3
QY_o	TBA bromide	Organic	1.40×10^{-1}	mol/m^3
RY_o	Benzyl bromide	Organic	1.02×10^3	mol/m^3
n_Y	Chlorine	Total (both)	2.99×10^{-1}	mol/m^3
n_X	Bromine	Total (both)	1.50×10^{-1}	mol/m^3
n_Q	TBA	Total (both)	1.41×10^{-2}	mol/m^3
QY_w	TBA bromide	Aqueous	1.40×10^{-1}	mol/m^3
QX_w	TBA chloride	Aqueous	5.69×10^{-2}	mol/m^3
QX_o	TBA chloride	Organic	3.76×10^{-3}	mol/m^3
Y_w^-	Bromide ion	Aqueous	1.49×10^3	mol/m^3
X_w^-	Chloride ion	Aqueous	5.09×10^2	mol/m^3
Q_w^+	TBA ion	Aqueous	9.37×10^1	mol/m^3
		Inputs		
F_o	Feed flow	Organic	3.476×10^{-9}	m^3/s
F_w	Feed flow	Aqueous	6.600×10^{-9}	m^3/s
F_c	Catalyst feed	Aqueous	2.08×10^{-8}	mol/m^3
RX_{in}	Reactant in feed	Organic	2.00×10^3	mol/m^3
QY_{in}	Catalyst in feed	Aqueous	1.88×10^3	mol/m^3
Y_{in}	Reactant in feed	Aqueous	2.00×10^3	mol/m^3

where I_j is the $j \times j$ identity matrix.

It will now be shown that System 1 is solvable; that is, it has a unique solution for a sufficiently small time about the nominal state, input, and parameter values given in Tables 2 and 3. After linearization, the solvability of the time-invariant linearized system may be verified by examining the matrix pencil of the linearized system (Brenan et al., 1989). However, to be sure that the original, nonlinear system is solvable, we must show that it can, at least in theory, be transformed into an ODE system, and that this ODE system admits consistent initial conditions (Brenan et al., 1989).

Let $z_1(t) = [RX_o, QY_o, RY_o, n_Y, n_X, n_Q]^T$ be the vector whose entries are the differential variables, and $z_2(t) = [QY_w, QX_w, QX_o, Y_w^-, X_w^-, Q_w^+]^T$ be a vector whose entries are the algebraic variables. The Jacobian matrix $g_{z_2}\,[z_1(0), z_2(0), u(0), p]$ for this PTC system has full rank. By the implicit function theorem, there is at the initial time a unique solution for the initial condition $z_2(0)$ of the algebraic states. This implies that there exists a consistent set of initial conditions for System 1. In addition, the implicit function theorem implies that, locally about the initial conditions, the algebraic variables $z_2(t)$ could be expressed in terms of the dynamic variables $z_1(t)$, the inputs $u(t)$, and the parameters p.

$$z_2(t) = \beta(z_1(t), p, u(t)) \tag{5}$$

As a result, the DAE system could be expressed as an equivalent ODE system given by $\dot{z}_1(t) = f(z_1(t), \beta(z_1(t), p, u(t)), u(t), p)$, with the initial condition $z_1(0)$. Note that in our particular case, β for the PTC model would not involve any of the input variables, given that the algebraic equations do not involve the input variables. As shown by Brenan et al. (1989), if we assume that the input signals are piecewise continuous functions, then System 1 will have a continuous solution and therefore the DAE model is solvable. Finally, this is an index one DAE problem, and it should be remembered that Eq. 5 implies a constraint on the initial conditions for the DAE system.

Using Eq. 5, the algebraic equations in the system could, in theory, be used to eliminate all of the algebraic variables from the system. However, in general β is only defined locally, and it may be impossible to express β using a finite number of terms. As a result, attempting to eliminate all of the algebraic variables is generally unadvisable. One advantage of the test proposed by Ben-Zvi et al. (2004) is that this step is unnecessary.

Identifiability Analysis

System 1 contains six inputs and two outputs. At the initial rest point and nominal parameter values, p, System 1 takes an input signal and produces unique outputs that are measured at a particular observation time. This relationship is called the *input–output mapping* of System 1, given by $\mathbf{io}(p) : (u, t) \mapsto y(t)$. We define the equality $\mathbf{io}(p) = \mathbf{io}(r)$ to mean that $\mathbf{io}(p)(u, t) = \mathbf{io}(r)(u, t)$ for every positive value of time and every imaginable piecewise continuous input signal. In this work, a linear approximation for $\mathbf{io}(p)$ will be used to test System 1 for identifiability.

Definition 1 [Strong local identifiability (Tunali and Tarn, 1987)]. *At the nominal parameter values p, listed in Table 2, System 1 is strongly locally identifiable if and only if the following holds for any candidate vector of parameter values r arbitrarily close to p*:

$$\mathbf{io}(p) = \mathbf{io}(r) \Leftrightarrow p = r$$

This definition implies that System 1 is strongly locally identifiable if and only if all arbitrarily small perturbations in the value of the parameters change the input–output behavior of the system.

Locally identifiable systems may not be globally identifiable. For example, the algebraic system $a = \theta^2 b$, where a is the output, b is the input, and θ is some parameter, is locally identifiable only for $\theta \neq 0$ because the behavior of the system is independent of the sign of θ.

As summarized in Table 4, the nonlinear DAE system is first linearized and then the identifiability of the linearized system is assessed for identifiability. Details of how Steps 2 and 3 are achieved are available in Ben-Zvi et al. (2004).

Step 1: linearization

System 1 is time-invariant, solvable, and can be linearized about a steady-state operating point. As a result, the local identifiability of the linearized system provides a sufficient condition for the local identifiability of the original nonlinear system (Ben-Zvi, 2003a). This condition can be deduced from

Table 4. Summary of Proposed Procedure

Step	Action
1	Linearize the DAE model about a suitable rest point.
2	Express the input–output behavior of the linearized system in terms of input–output transfer functions.
3	Check whether the dependency of the coefficients in the transfer functions on the parameters is unique.

the fact that, as shown by Campbell (1995), a solvable nonlinear DAE system has, locally, an ODE representation, and furthermore the linearization of this ODE representation is nothing but the linearization of the original DAE system. The linearization of the DAE system can therefore be viewed as the linearization of an ODE system. Furthermore, as shown by Grewal and Glover (1976), for ODE systems, identifiability of the linearized system is a sufficient condition for the identifiability of the original, nonlinear system. The identifiability of the linearized DAE system is therefore a sufficient condition for the linearization of the original, nonlinear DAE system. Note that this is not a sufficient condition because some of the parameters appearing in the nonlinear systems may not appear in the linearized system.

At the nominal values listed in Tables 2 and 3, we have $f(x(0), u(0), p) = 0$ and $g(x(0), u(0), p) = 0$ and the system is at steady state. We may linearize about this steady state to obtain

$$E\dot{\bar{x}}(t) + M(p)\bar{x}(t) + B(p)\bar{u}(t) = 0 \tag{6a}$$

$$\bar{y}(t) = C\bar{x}(t) \tag{6b}$$

where $\bar{x}(t) = x(t) - x(0)$, $\bar{u}(t) = u(t) - u(0)$, and $\bar{y}(t) = y(t) - y(0)$; E is given by Eq. 3, C is given by Eq. 4, and

$$M(p) = -\begin{bmatrix} f_x(x(0), u(0), p) \\ g_x(x(0), u(0), p) \end{bmatrix}$$

$$B(p) = -\begin{bmatrix} f_u(x(0), u(0), p) \\ g_u(x(0), u(0), p) \end{bmatrix}$$

Note that the subscript notation denotes partial differentiation, that is,

$$f_x(x(0), u(0), p) = \left.\frac{\partial f(x, u, p)}{\partial x}\right|_{x=x(0), u=u(0)}$$

The technique proposed by Ben-Zvi et al. (2004) requires that $C(p)$ have full row rank and that $B(p)$ have full column rank. This does not limit the generality of the test. Rather, lack of full rank in either $B(p)$ or $C(p)$ simply produces redundant equations that would be discarded in any case. Note that the column rank of the matrix $B(p)$ is five, although $B(p)$ has six columns. This is because the effect of a change in the value of one of the inputs to the aqueous phase, such as the catalyst inlet concentration Y_{in}, can be offset by varying the other three aqueous-phase inputs and consequently the effective number of input degrees of freedom is 5. As a result, for the rest of this work, the value of Y_{in} will be fixed at the nominal value listed in Table 3, and we will assume, without loss of generality, that the other five inputs given by $u(t) = [F_o, F_w, F_c, RX_{in}, QY_{in}]^T$ are adjusted during experimentation. With these inputs, the matrix $B(p)$ has full column rank. All of the symbolic computations involved in the linearization of System 1 were carried out using Maple software (Maplesoft, Waterloo, Ontario, Canada) and can be found in Ben-Zvi (2003b).

Note that the system equations in Table 1 are written such that each parameter multiplies either a state or an input. If the model was instead written with some parameters appearing alone, as opposed to as coefficients of a state or input, such as

$$0 = m_{QX} - QX_o/QX_w \tag{$g6'$}$$

then those parameters not multiplying a state or input (in this case m_{QX}) would not appear in the linearized model and the linearized model could not be used to assess the effect of all of the model parameters on the input–output behavior.

This linearization-based approach is also appropriate for ODE systems. It is therefore possible to compute the underlying ODE associated with System 1 and then use the linearization of the underlying ODE system to check for identifiability. However, in general, this ODE representation is only local, and in addition, may not have a representation with a finite number of terms because of the difficulty in obtaining an explicit expression for the algebraic variables.

As a practical matter, the ODE representation may be difficult to compute and would provide no additional information about the system dynamics. This fact has been noted in the literature (Brenan et al., 1989), as well as in the work of Chen et al. (1991) where, even after considerable manipulation, the batch PTC reactor model is written as a DAE system rather than as an ODE system. It is therefore better—from both a theoretical and a practical perspective—to linearize the original DAE system.

Step 2: transfer-function representation

Following the procedure of Ben-Zvi et al. (2004), we first define the differentiation operator $\delta = d/dt$, which is used to obtain a transfer-function representation for the input–output behavior of the linearized DAE system. A matrix of transfer functions can be obtained using row reduction (Ben-Zvi et al., 2004). An alternative approach is to solve directly for the transfer-function matrix $Q(\delta, p) = C[E\delta + M(p)]^{-1}B(p)$, such that $y(t) = Q(\delta, p)u(t)$. The entries in $Q(\delta, p)$ were computed symbolically using Maple software version 9.00.

Pole-zero cancellations in transfer-function models can pose a challenge for assessing identifiability, since they can cancel the effect of one or more parameters on the input–output behavior. Failing to identify pole-zero cancellations can lead to erroneous conclusions about identifiability. To ensure that $Q(\delta, p)$ contained no transfer functions with zero-pole cancellations, a two-step procedure was used. First, when computing $Q(\delta, p)$ in Maple, the numerator and denominator in each transfer function were factored with respect to δ and any root that was both a pole and a zero was removed from the transfer functions. Next, the poles and zeros of each resulting transfer function were numerically evaluated using Matlab (The MathWorks, Natick, MA) at the state and parameter values listed in Tables 2 and 3. The values of these poles and zeros were compared, using a threshold value of 1×10^{-10}, and it was found that none of the values corresponding to poles of the system was also zero.

Step 3: checking uniqueness of parameters

After the zero-pole cancellation step, the identifiability of System 6 was tested by examining whether unique values of the coefficients in the transfer functions imply unique values of p, that is, whether the mapping $p \mapsto \mathbf{io}_{\mathscr{L}}(p)$ is injective at p, where $\mathbf{io}_{\mathscr{L}}(p)$ is the input–output mapping of the linearized system.

The transfer function $Q(\delta, p)$ describes the input–output behavior of the linearized system. Specifically,

$$\mathbf{io}_{\mathscr{L}}(p) = \mathbf{io}_{\mathscr{L}}(r) \Leftrightarrow Q(\delta, p) = Q(\delta, r)$$

Therefore, by Definition 1, the linearized system is identifiable if and only if

$$Q(\delta, p) = Q(\delta, r) \Leftrightarrow p = r$$

This condition is tested by checking whether the coefficients of the transfer functions in $Q(\delta, p)$ depend uniquely on the parameters.

Each of the entries in $Q(\delta, p)$ is a ratio of polynomial functions in δ. Because we linearized the system about an initial steady state, δ would be replaced by s throughout the transfer-function matrix if we had used a Laplace transform approach to obtain the transfer functions. Without loss of generality we may assume that the polynomial in the denominator of each entry is monic, that is, the coefficient of the highest-order term is one. Each polynomial is of at most order six in δ because there are only six differential equations in the model. As a result, recalling that the denominator is a monic polynomial, the denominator has only five independent coefficients. Because the model is an index one DAE and the algebraic equations are not functions of the inputs, the resulting transfer functions will be strictly proper. Consequently, the highest possible order of the numerator polynomials is five, and the associated polynomials will have six coefficients. We can therefore associate with each entry of $Q(\delta, p)$ a point in $\mathbb{R}^{12}$ corresponding to the coefficient of each power of δ in the numerator and denominator. The matrix $Q(\delta, p)$ is 2×5 and so the total number of possibly independent coefficients is 120. Let $S(p) = [c_1(p), \ldots, c_{120}(p)]^T$ be a vector in $\mathbb{R}^{120}$ whose entries make up the complete list of transfer-function coefficients. It has been shown by Ben-Zvi et al. (2004) that injectivity of $\mathbf{io}_{\mathscr{L}}(p)$ can be confirmed by showing that $S_p(p)$ is of full rank, where $S_p(p)$ is the Jacobian of S with respect to the parameters evaluated at the nominal values listed in Tables 2 and 3.

Computational issues

The main difficulty in applying the procedure outlined in Table 4 is not the symbolic differentiation (Step 1) nor the rank test (Step 3), but rather the symbolic computation of the matrix inverse $[E\delta + M(p)]^{-1}$ (Step 2). The default matrix inversion routines available in Maple failed because of a lack of memory. Instead, the elements of $C[E\delta + M(p)]^{-1}B(p)$ were computed using Cramer's Rule.

An alternative method for testing linear, time-invariant (LTI) DAE systems for identifiability, which uses a generalized Markov parameter approach, was proposed by Ben-Zvi et al. (2003). This earlier method depends on the partitioning of the linearized system into algebraic and dynamical subsystems. Using Maple, and only modest hardware consisting of a Toshiba Satellite laptop with 512 megabytes of (RAM) memory and running at 2.66 GHz, it was found that the algorithm used to partition the system in Maple required more memory than was available. In contrast, symbolic computations required for the differential algebra method used in this article were accomplished using Maple and the same modest hardware.

Results, Simulation, and Discussion

Symbolic differentiation of the transfer-function coefficients was carried out using Maple version 9.00. The evaluation of the rank of S_p at the nominal parameter values was carried out using Matlab version 6.5. All Matlab and Maple work sheets used in this work are available from Ben-Zvi (2003b). At the nominal steady state, the rank of $S_p(p)$ is 6, which is one less than the number of parameters, indicating that the linearized System 6 is not locally identifiable. However, this result does not imply that the original System 1 is not locally identifiable, given that identifiability of the linearized System 1 is a sufficient, but not a necessary, condition for the identifiability of the original, nonlinear system. However, we may use information obtained from $S_p(p)$ to show that System 1 is not identifiable and what action can be taken to make it identifiable.

The null-space of the matrix $S_p(p)$, which is the set of all vectors w in $\mathbb{R}^7$ such that $S_p(p)w = 0$, allows us to find all of the directions in which the parameters can be perturbed from their nominal values without changing the input–output behavior of the linearized model. Using Matlab the null-space of $S_p(p)$ was found to be spanned by the vector

$$v = [-6.18 \times 10^{-14}, -9.02 \times 10^{-12}, -2.43 \times 10^{-10}, \\ 1.90 \times 10^{-9}, 7.89 \times 10^{-8}, 2.38 \times 10^{-3}, 1.00]^T$$

meaning that any vector w in the null space of $S_p(p)$ is a scalar multiple of v.

Furthermore, for a sufficiently small real constant ε, $\mathbf{io}_{\mathscr{L}}(p) = \mathbf{io}_{\mathscr{L}}(p + \varepsilon v)$. As will be shown later, the value of ε for this case need not be very small. However, for the original, nonlinear system, whether $\mathbf{io}(p) = \mathbf{io}(p + \varepsilon v)$ for arbitrary ε is less clear. To examine whether changing the parameters in the direction of v affects the input–output mapping of the nonlinear System 1, the model was simulated, for a step change in the input at $t = 500$ min, using the original parameters as well as new parameters with ε values of 837 and 4.19×10^5, corresponding to 1 and 50%, respectively, of the nominal value of K_{QX}^D. The simulation results, shown in Figure 2, suggest that System 1 is not locally identifiable. To determine whether this is truly the case, the original, nonlinear equations of System 1 must be examined. However, the following facts obtained from the identifiability results for the linearized system can be used to show that System 1 is not identifiable.

(1) The final entry in v, which corresponds to changes in the value of K_{QX}^D, is the largest, both in absolute terms and relative to the size of the nominal parameter estimates.

(2) Equation g_5, which is the only equation containing K_{QX}^D, defines a relationship between concentrations of the species in the aqueous phase.

(3) The aqueous-phase species concentrations are not directly observed by the experimenter.

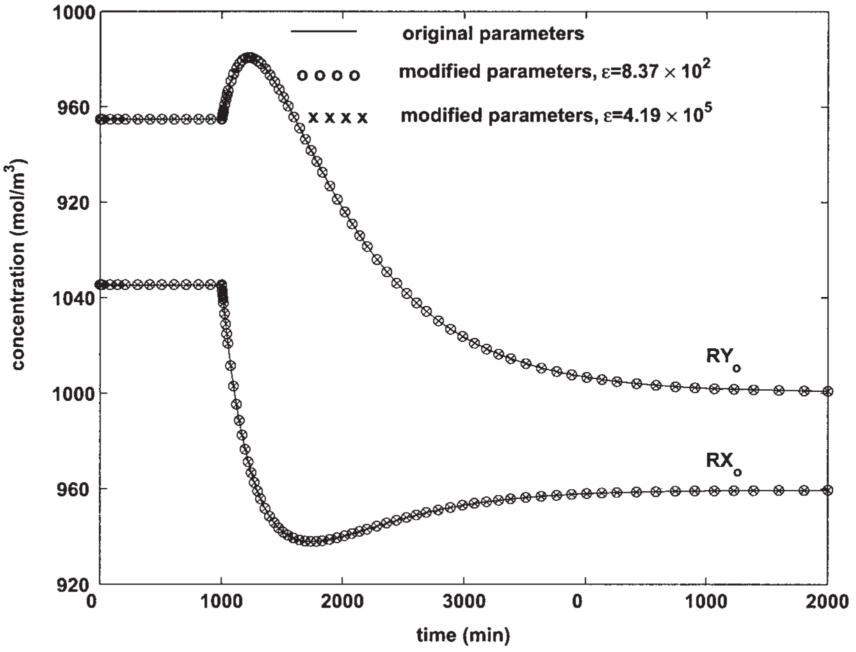

Figure 2. Simulation results.

The response of nonlinear System 1 under various parameter values to a step input with $F_o = 3.13 \times 10^{-9}$ m³/s, $F_w = 7.25 \times 10^{-9}$ m³/s, $F_c = 2.78 \times 10^{-10}$ m³/s, $RX_{in} = 1.90 \times 10^3$ mol/m³, $QY_{in} = 1.97 \times 10^3$ mol/m³.

The above observations suggest that if System 1 is not identifiable, then it is primarily the value of K_{QX}^D that can be changed without affecting the input–output behavior. To better understand how K_{QX}^D is linked to identifiability, we will perturb K_{QX}^D while requiring that the input–output behavior remains unchanged. This perturbation will affect the values of other parameters and unmeasured states. To satisfy Eq. g_5, any change in the value of K_{QX}^D must also imply a change in the value of Q_w^+, X_w^-, or QX_w. For System 1 to be unidentifiable, then, implies that some combination of Q_w^+, X_w^-, and QX_w does not affect the input–output behavior of System 1. Indeed, with the exception of Eqs. g_4 to g_6, the three unmeasured states Q_w^+, X_w^-, and QX_w appear in only two combinations. These combinations are $Q_w^+ + QX_w$ (appearing in Eqs. g_3 and f_6) and $X_w^- + QX_w$ (appearing in Eqs. g_2 and f_5). By ensuring that these sums do not change, we can ensure that the perturbation in K_{QX}^D does not influence the input–output behavior of System 1.

Our goal is to test whether it is possible to perturb the value of K_{QX}^D while affecting only parameters and unmeasured states. We therefore define $\widetilde{K_{QX}^D} = K_{QX}^D + \varepsilon$, using a small perturbation ε chosen so that $\widetilde{K_{QX}^D}$ remains positive. Let $\widetilde{Q_w^+}$, $\widetilde{X_w^-}$, and $\widetilde{QX_w}$ be the new unmeasured aqueous-phase concentrations that satisfy Eq. g_5 along with the perturbed variable $\widetilde{K_{QX}^D}$.

$$0 = \widetilde{Q_w^+}\widetilde{X_w^-} - (K_{QX}^D + \varepsilon)\widetilde{QX_w} \tag{7}$$

To satisfy Eqs. g_4 and g_6, without affecting the values of Y_w^-, QY_w, and QX_o, new parameter values $\widetilde{K_{QY}^D}$ and $\widetilde{m_{QX}}$ are defined.

$$0 = \widetilde{Q_w^+}Y_w^- - \widetilde{K_{QY}^D}QY_w \tag{8}$$

$$0 = QX_o - \widetilde{m_{QX}}\widetilde{QX_w} \tag{9}$$

To express the perturbed variables in terms of the original, unperturbed variables, we can eliminate QY_w and QX_o from Eqs. 8 and 9 using Eqs. g_4 and g_6 to obtain

$$0 = Q_w^+/K_{QY}^D - \widetilde{Q_w^+}/\widetilde{K_{QY}^D} \tag{10}$$

$$0 = \widetilde{m_{QX}}\widetilde{QX_w} - m_{QX}QX_w \tag{11}$$

Furthermore, if we ensure that

$$0 = \widetilde{Q_w^+} + \widetilde{QX_w} - (Q_w^+ + QX_w) \tag{12}$$

and

$$0 = \widetilde{X_w^-} + \widetilde{QX_w} - (X_w^- + QX_w) \tag{13}$$

then Eqs. f_5, f_6, g_2, and g_3 are satisfied without perturbing any additional variables.

By solving Eqs. 7, 10, 11, 12, and 13 for the perturbed variables in terms of the original variables and ε, we obtain

$$\widetilde{Q_w^+} = Q_w^+ + (QX_w - \psi(\varepsilon)) \tag{14}$$

$$\widetilde{K_{QY}^D} = K_{QY}^D \frac{Q_w^+ + QX_w - \psi(\varepsilon)}{Q_w^+} \tag{15}$$

Table 5. Batch PTC Reaction Model

$\frac{dRX_o}{dt} = -k_1RX_oQY_o + k_{-1}RY_oQX_o$	(f_{b1})
$\frac{dQY_o}{dt} = -k_1RX_oQY_o + k_{-1}RY_oQX_o + V_o^{-1}AK_{QY}(m_{QY}QY_w - QY_o)$	(f_{b2})
$\frac{dRY_o}{dt} = k_{-1}RX_oQY_o - k_{-1}RY_oQX_o$	(f_{b3})
$\frac{dn_Y}{dt} = \frac{dn_X}{dt} = \frac{dn_Q}{dt} = 0$	$(f_{b4}$–$f_{b6})$
$0 = n_Y - V_o(RY_o + QY_o) - V_w(Y_w^- + QY_w)$	(g_{b1})
$0 = n_X - V_o(RX_o + QX_o) - V_w(X_w^- + QX_w)$	(g_{b2})
$0 = n_Q - V_o(QY_o + QX_o) - V_w(Q_w^+ + QX_w + QY_w)$	(g_{b3})
$0 = Q_w^+Y_w^- - K_{QY}^DQY_w$	(g_{b4})
$0 = Q_w^+X_w^- - K_{QX}^DQX_w$	(g_{b5})
$0 = QX_o - m_{QX}QX_w$	(g_{6b})
$y(t) = [RX_o, RY_o, n_Y, n_X, n_Q]^T$	(y_b)

$$\widetilde{X_w^-} = X_w^- + (QX_w - \psi(\varepsilon)) \tag{16}$$

$$\widetilde{QX_w} = \psi(\varepsilon) \tag{17}$$

$$\widetilde{m_{QX}} = m_{QX}QX_w\psi(\varepsilon)^{-1} \tag{18}$$

where $\psi(\varepsilon)$ is the solution to

$$0 = \psi^2 - ((K_{QX}^D + \varepsilon) + Q_w^+ + 2QX_w + X_w^-)\psi + Q_w^+QX_w + QX_w^2 + Q_w^+X_w^- + X_w^-QX_w \tag{19}$$

We have now shown that the original, nonlinear system is not identifiable. For any value of ε, Eqs. 14 to 18 give a set of perturbed state and parameter values that differ from the nominal state and parameter values. Because none of the perturbed states is observed, different parameter values produce the same input–output behavior.

For the nominal steady state considered, both roots of Eq. 19 are positive real numbers, for $K_{QX}^D + \varepsilon > 0$. Of the two roots for Eq. 19, one gives a physically unrealistic concentration of $\widetilde{QX_w}$. Note that the results obtained are only local (in the parameter space). If a different set of parameter values was used to compute the steady state of the system and the linearization procedure was repeated, different results may be obtained. For example, if one were to examine the system with $m_{QX} = K_{QX}^D = 0$, the behavior of the system would be qualitatively different. Indeed, it is important to consider whether the steady-state conditions listed in Table 2 are sufficiently generic in an appropriate sense. This is indeed the case because the transformations listed in Eqs. 14 to 18 are independent of the value of the parameters everywhere except for isolated points in the parameter space.

If one is not interested in estimating every parameter in System 1, but rather in describing the input–output behavior of the system, then the value of $\psi(\varepsilon)$ can be fixed at the nominal value of the product m_{QX} QXw so that m_{QX}, which is a partition coefficient, is effectively set to unity, and removed from the model equations. Note that this reparameterization is not unique. An alternative reparameterization is obtained by setting the value of $\psi(\varepsilon)$ to the nominal value $Q_w^+ + QX_w - Q_w^+/K_{QY}^D$to eliminate the parameter K_{QY}^D from the model equations. This action corresponds to setting the dissociation constant K_{QY}^D to unity. Each of the proposed reparameterizations will yield unique parameter estimates that describe the input–output behavior, but are, almost certainly, not close to the true values of the system parameters.

If the experimenter wishes to estimate the value of each parameter accurately then additional information about the system is needed. Specifically, if the value of the aqueous phase TBA chloride concentration, QX_w, at some time (such as at the initial condition) is obtained then the value of $\psi(\varepsilon)$ would be known and it would be possible to determine unique estimates for all parameter values. Furthermore, given an appropriate experimental design, the parameters could be accurately estimated. One could also use a measurement of any of the perturbed states in Eqs. 14 to 18 to uniquely determine all of the model parameters.

Identifiability of the Batch Model

In light of the results showing the continuous model to be unidentifiable, we examine the identifiability of the batch model proposed by Chen et al. (1991). The batch-reactor equations in Table 5 represent a special case of the continuous-reactor equations and it is tempting to conclude that the batch-reactor model is therefore unidentifiable. However, when conducting batch-reactor experiments, the values of n_Y, n_X, and n_Q would most certainly be known from the masses of the various reactants initially charged to the reactor. During the batch experiments, n_Y, n_X, and n_Q would all remain fixed because no bromine or chlorine atoms, and no TBA groups, enter or leave the reactor. To assess the identifiability of the batch-reactor model it is therefore important to consider n_Y, n_X, and n_Q as known outputs. This fact is reflected in Eq. y_b in Table 5.

As in the continuous case, the three states Q_w^+, X_w^-, and QX_w appear only in the two combinations given by $Q_w^+ + QX_w$, appearing in Eq. g_{b3}, and $X_w^- + QX_w$, appearing in Eq. g_2. In addition, none of the batch model outputs provides a direct observation of X_w^-, Q_w^+, or QX_w. Indeed, as in the continuous model, Eqs. g_{b4} and g_{b5}, along with Eqs. 12 and 13, can be used to compute alternative parameter and state values parameterized by $\Phi(\varepsilon)$. This implies that the batch-reactor model, as proposed by Chen et al. (1991), is not identifiable. This result is not unexpected in light of the fact that the continuous-reactor model will be identifiable if and only if one of Q_w^+, X_w^-, or QX_w is observed at some point time, or one of K_{QY}^D, m_{QX}, or K_{QX}^D is known a priori. As shown by Eqs. g_{b1}–g_{b3}, the additional outputs do not allow the experimenter to determine uniquely the value of Q_w^+, X_w^-, or QX_w.

Conclusions

A continuous nonlinear PTC reaction model, based on the batch-reactor model proposed by Chen et al. (1991), was tested for identifiability using a linearization- based approach. The linearized system was found to be unidentifiable. The information gathered from the linearized system, coupled with additional insight into the model equations, was used to show that the continuous nonlinear PTC reaction model is also unidentifiable. Simulation results were used to illustrate this lack of identifiability. Finally, the original batch model proposed in Chen et al. (1991) was also shown to be unidentifiable. A list of parameters that may be eliminated to make the system identifiable is given. In addition, a list of the states whose observation would make the system identifiable is given.

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