

IDENTIFIABILITY ANALYSIS OF A LIQUID-LIQUID PHASE-TRANSFER CATALYZED REACTION SYSTEM

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Abstract: Identifiability is a structural property of mathematical models. A model is identifiable if the model parameters can be uniquely identified from input-output behaviour. This work focuses on the application of a novel methodology for testing differential algebraic equation systems for identifiability. In this work, a non-linear, differential algebraic model of a liquid-liquid phase-transfer reactor is tested for identifiability using a linearization-based approach. This approach is shown to be useful for the testing of identifiability even for inherently non-linear models. Furthermore, this approach allows the effect of system parameters on the non-linear system to be qualitatively analyzed.

1. INTRODUCTION

Mathematical models are commonly used in almost every area of science and engineering. These models are often characterized by unknown parameters. In order to predict the behaviour of physical systems, these parameters must often be determined experimentally from the input-output behaviour of physical systems. Lack of ability to estimate parameters may be due to several reasons including noisy data, plant-model mismatch, poor choice of experiments, or poor choice of models. In this last case, the model itself is deficient and model parameters cannot be estimated regardless of the quality or quantity of input-output data obtained.

One common model deficiency is lack of identifiability. Consider a mathematical model

$$\mathcal{M}(p) : \mathcal{U} \rightarrow \mathcal{Y}$$

mapping from a set of input signals to a set of output signals and depending on a parameter vector $p \in \mathcal{P} \subseteq \mathbb{R}^s$. Note that this representation of an input-output behaviour implies the existence

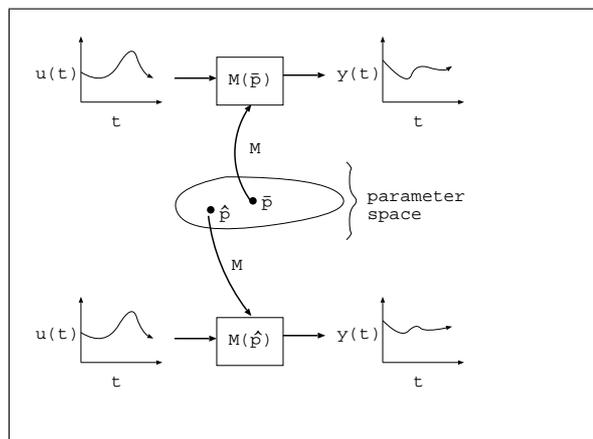


Figure 1.1: Idealized Input-Output Framework

of a mapping $\mathcal{M} : p \rightarrow \mathcal{M}(p)$ that takes a particular parameter p and maps to a particular input-output behaviour $\mathcal{M}(p)$. The situation is summarized in Figure 1.1. It is the properties of the mapping \mathcal{M} that describe the effect of the system parameters on the input-output behaviour. Indeed, Walter and Pronzato (1995) have proposed the following definition for identifiability

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Definition 1. (Structural Global Identifiability). A model \mathcal{M} is *structurally globally identifiable* if for almost any $\bar{p}, \hat{p} \in \mathcal{P}$,

$$\mathcal{M}(\bar{p}) = \mathcal{M}(\hat{p}) \Rightarrow \bar{p} = \hat{p}$$

where the words *almost any* imply that the identifiability condition holds at every point on a dense subset of \mathcal{P} .

Similarly, viewing \mathcal{P} as a subset of \mathbb{R}^s we can define the property of local identifiability as

Definition 2. (Structural Local Identifiability). A model \mathcal{M} is *structurally locally identifiable* if for almost any $\bar{p} \in \mathcal{P}$, and \hat{p} such that $\|\bar{p} - \hat{p}\| < \epsilon$ for any $\epsilon > 0$ the following holds

$$M(\bar{p}) = M(\hat{p}) \Rightarrow \bar{p} = \hat{p}$$

2. LINEAR TIME-INVARIANT DIFFERENTIAL ALGEBRAIC MODELS

Consider the following system.

$$E(p)x'(t) + M(p)x(t) + B(p)u(t) = 0 \quad (1a)$$

$$y(t) = C(p)x(t) \quad (1b)$$

where $x(t) \in \mathbb{R}^n$, $u(t) \in \mathbb{R}^\gamma$, $y(t) \in \mathbb{R}^m$ and $E(p)$, $M(p)$, $B(p)$ and $C(p)$ are appropriately sized matrices whose entries are continuously differentiable functions on \mathcal{P} . It has been shown by Brennan et al. (1989) that System 1 has a solution if and only if there exists a scalar $\lambda \in \mathbb{C}$ such that

$$\det(E(p)\lambda + M(p)) \neq 0$$

From now on, it will be assumed that System 1 is solvable for every $p \in \mathcal{P}$.

We now turn to the problem of expressing $\mathcal{M}(p)$ for system 1 in terms of the system equations. We may take the Laplace transform of System 1, starting from the steady state solution $x(0) = 0$, $u(0) = 0$, $x'(0) = 0$ to obtain the following Laplace-domain input-output representation.

$$Y(s) = C(p)(E(p)s + M(p))^{-1}B(p)U(s)$$

where the transfer function $T(p, s) = C(p)(E(p)s + M(p))^{-1}B(p)$ can be seen as taking an input U to an output Y . For finite dimensional, multi input, multi output (MIMO) systems, $T(p, s)$ can be represented by a matrix of rational transfer functions. Without loss of generality, we may

assume that each of the transfer functions has a monic denominator, and no poles that are also zeros (i.e., all of the possible pole-zero cancellations have been carried out). Let $s_{ij}(p) = [c_{ij1}(p), \dots, c_{ij\alpha_{ij}}(p)]^T \in \mathbb{R}^\alpha$ be a vector whose entries are the coefficients of the ij^{th} entry in $T(p, s)$. It has been shown by Bellman and Astrom (1970) that

$$\mathcal{M}(\bar{p}) = \mathcal{M}(\hat{p}) \Leftrightarrow s_{ij}(\bar{p}) = s_{ij}(\hat{p}) \\ i = 1 \dots m, \quad j = 1 \dots \gamma$$

which implies that, by definition 1, for identifiability one need only check that for every $i = 1 \dots m$, $j = 1 \dots \gamma$,

$$s_{ij}(\bar{p}) = s_{ij}(\hat{p}) \Rightarrow \bar{p} = \hat{p} \quad (2)$$

The above computations have the advantage that they are relatively easy to perform using computer algebra software such as *Maple*TM.

3. THE PHASE-TRANSFER CATALYZED REACTOR SYSTEM

Chen et al. (1991) proposed a model to describe the behaviour of a liquid-liquid phase-transfer catalyzed reactor (PTC) system. The reactor system and kinetic scheme are shown schematically in Figure 3.1. The model proposed by Chen et al. (1991) is batch, however, in this work, the model is extended to a continuous stirred tank reactor (CSTR) model. A more comprehensive discussion of the model is available in Ben-Zvi et al. (in press 2004). The corresponding model is shown in Table 1. Equations f_1 to f_6 in Table 1 are first-order ordinary differential equations (ODEs), and equations g_1 to 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 (tetrabutylammonium 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 tetrabutylammonium (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 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 g_5 describes the ionization equilibrium for TBA chloride (QX_w). 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.

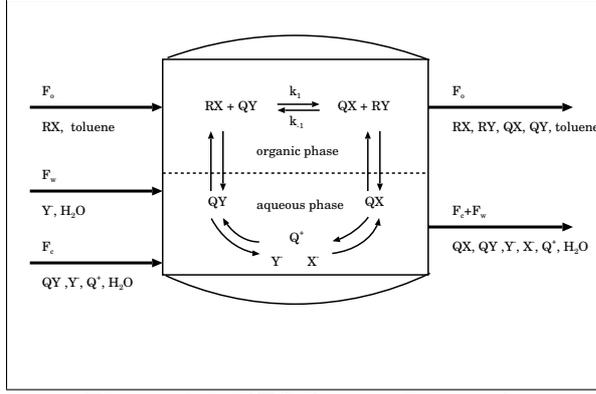


Figure 3.1: PTC Reactor Schematic

Table 1. Continuous PTC Reaction Model

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

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

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

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

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

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

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

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

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

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

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

$$0 = QX_o - m_{QX} QX_w \quad (g_6)$$

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

The batch-reactor model originally developed by Chen et al. (1991) is a special case 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 equations f_4 to f_6 . 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.

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

Table 2. Parameter Values

Estimated parameters from Chen et al. (1991) and specified quantities for PTC reaction model.

Variable	Value	Units
Parameters		
k_1	2.51×10^{-2}	$m^3/mol \cdot min$
k_{-1}	1.68×10^{-1}	$m^3/mol \cdot min$
$V_o^{-1} AK_{QY}$	1.42×10^5	$mol/m^3 \cdot min$
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

in their model of the system. These parameters are listed in Table 2. 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 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 behaviour 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 behaviour of the PTC reactor system. However, it is not known whether alternative sets of parameter values could give exactly the same model predictions. Indeed, for the parameter estimates obtained by Chen et al. (1991) to be meaningful, the parameter estimates obtained must be unique.

4. LINEARIZATION OF THE PTC MODEL

The reactor equations listed in Table 1 were linearized about the nominal parameter and state values listed in Table 3. Note that the parameter values listed in Table 3 match those estimated by Chen et al. (1991).

The resulting linear time-invariant (LTI) DAE system is given by

$$E\dot{x}(t) + M(p)x(t) + B(p)u(t) = 0 \quad (3a)$$

$$y(t) = Cx(t) \quad (3b)$$

where $\dot{x}(t) = \frac{dx}{dt}(t)$, $M(p) = -[\partial f/\partial x, \partial g/\partial x]_{t=0}^T$, $B(p) = -[\partial f/\partial u, \partial g/\partial u]_{t=0}^T$, and

Table 3. State and Input Values

Symbol	Definition	Initial Value	Units
States			
RX_o	$BzCl_o$	9.82×10^2	mol/m^3
QY_o	$TBABr_o$	1.40×10^{-1}	mol/m^3
RY_o	$BzBr_o$	1.02×10^3	mol/m^3
n_Y	Cl_{both}	2.99×10^{-1}	mol/m^3
n_X	BR_{both}	1.50×10^{-1}	mol/m^3
n_Q	TBA_{both}	1.41×10^{-2}	mol/m^3
QY_w	$TBABr_w$	1.40×10^{-1}	mol/m^3
QX_w	$TBACl_w$	5.69×10^{-2}	mol/m^3
QX_o	$TBACl_o$	3.76×10^{-3}	mol/m^3
Y_w^-	Br_w^-	1.49×10^3	mol/m^3
X_w^-	Cl_w^-	5.09×10^2	mol/m^3
Q_w^+	TBA_w^+	9.37×10^1	mol/m^3
Inputs			
F_o	feed flow	2.08×10^{-7}	m^3/min
F_w	feed flow	3.96×10^{-7}	m^3/min
F_c	catalyst feed	2.08×10^{-8}	mol/m^3
RX_{in}	reactant in feed	2.00×10^3	mol/m^3
QY_{in}	catalyst in feed	1.88×10^3	mol/m^3
Y_{in}	reactant in feed	2.00×10^3	mol/m^3

$$x(t) = [RX_o, QY_o, RY_o, n_Y, n_X, n_Q, QY_w, Y_w^-, X_w^-, Q_w^+, QX_w, QX_o]^T \quad (4)$$

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

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

$$E = \begin{bmatrix} I_6 & 0 \\ 0 & 0 \end{bmatrix} \quad C = [I_2 \quad 0] \quad (5)$$

where I_j is the j by j identity matrix. The values of $x(t)$ and $u(t)$ are the deviation in value of the states and parameters, respectively, from the values, listed in Table 3, about which the system was linearized. 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, for example 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 five. 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.

This system is an index one LTI DAE system that is solvable when evaluated at the nominal parameter values listed in Table 2.

5. IDENTIFIABILITY ANALYSIS OF THE PTC SYSTEM

The identifiability of (the linearized) System 3 was checked using Condition 2. However, using modest computational tools, including a Toshiba Satellite laptop running at 2.66 GHz, and 512Mb of RAM memory, the computation involved in

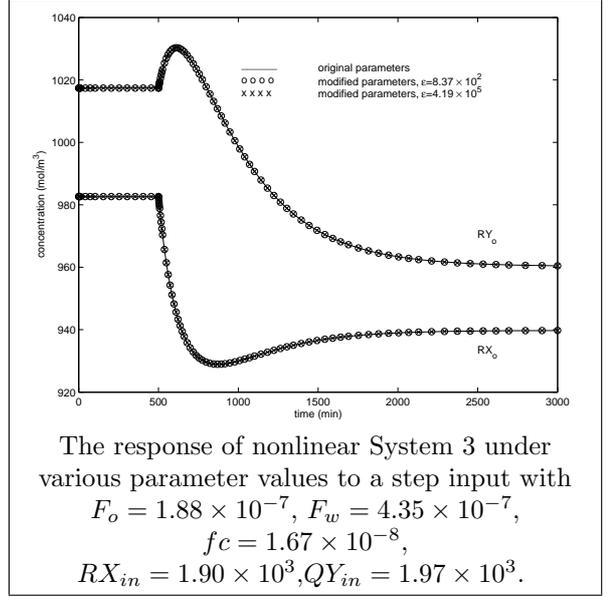


Figure 5.1: Simulation Results

The response of nonlinear System 3 under various parameter values to a step input with

$$F_o = 1.88 \times 10^{-7}, F_w = 4.35 \times 10^{-7},$$

$$f_c = 1.67 \times 10^{-8},$$

$$RX_{in} = 1.90 \times 10^3, QY_{in} = 1.97 \times 10^3.$$

checking Condition 2 became intractable. However, locally in the parameter space, Condition 2 can be checked by examining the rank of the Jacobian matrix

$$\mathcal{J}_0 = \left. \frac{\partial [s_{11}(p), \dots, s_{m\gamma}(p)]^T}{\partial p} \right|_{p=p_0}$$

at p_0 , the nominal values listed in Table 3. This computation can easily be carried out numerically even using modest computer hardware. Using Matlab version 6.5, it was found that the rank of \mathcal{J}_0 was six, up to the limit of machine precision. It was therefore determined that the PTC system is not identifiable.

The null-space of the matrix \mathcal{J}_0 , which is the set of all vectors w in \mathbb{R}^7 such that $\mathcal{J}_0 w = 0$, was found to be spanned by the vector

$$v = -[-3.71 \times 10^{-12}, -5.41 \times 10^{-10}, -1.46 \times 10^{-8}, 1.90 \times 10^{-9}, 7.89 \times 10^{-8}, 2.38 \times 10^{-3}, 1.00]^T$$

which implies that, $\mathcal{M}(p_0 + \epsilon v) \rightarrow \mathcal{M}(p_0)$ as $|\epsilon|^2 \rightarrow 0$. This behaviour is illustrated in Figure 5.1 where ϵ values of 8.37×10^2 and 4.19×10^5 were used to perturb the parameters, and the resulting step response of the original, nonlinear PTC model was plotted. As can be seen from Figure 5.1, even for large values of ϵ , the system behaviour remained virtually identical. This fact shows that even if the system parameters were identifiable, they are not practically estimable, up to machine precision. This is especially relevant in light of the fact that the simulations were performed using no plant-model mismatch, and no added noise.

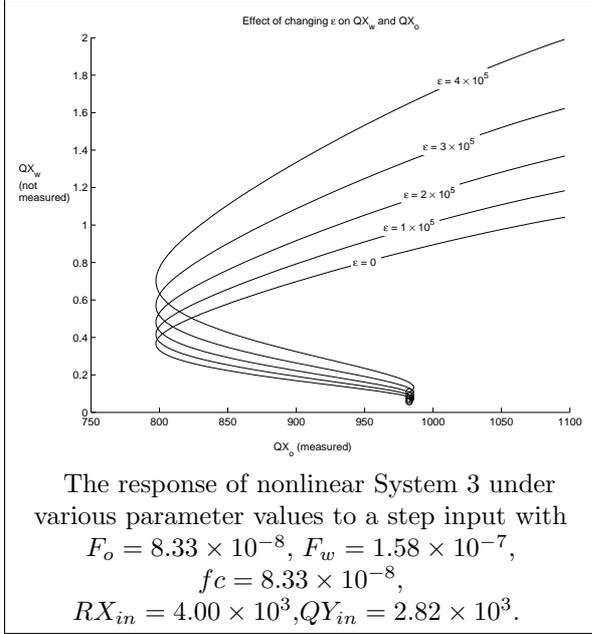


Figure 6.1: Simulation Results

6. IDENTIFIABILITY ANALYSIS OF THE ORIGINAL, NONLINEAR PTC SYSTEM

Lack of identifiability of the linearized system does not, in general imply lack of identifiability of the original, nonlinear system. Although the parameter estimates obtained by Chen et al. (1991) have been shown, by example in Figure 5.1, to be suspect, the simulation results themselves do not prove lack of identifiability. In addition, even if the original, nonlinear system is assumed to be un-identifiable, it is not clear from the results of the rank test done on the linear system what is the cause of this lack of identifiability and what can be done to correct this problem.

In order to get some insight into whether the PTC system is identifiable, we make note of the following fact: The largest entry by far in v , both in absolute terms, and relative to the size of the nominal parameter estimates, corresponds to the value of K_{QX}^D . According to Equation g_5 , K_{QX}^D affects the ionization of QX_w in the aqueous phase. In addition, we note that none of the aqueous phase concentrations have been directly measured by Chen et al. (1991). In order to determine the effect of different values of ϵ on QX_w , the trajectory of the System in the $QX_w - QX_o$ plane, in response to a step input was examined. This trajectory is shown for different values of ϵ in Figure 6.1.

The observed response of the PTC system corresponds to the horizontal axis in Figure 6.1. This implies that the experimenter would observe only the horizontal coordinate of the trajectories depicted in Figure 6.1. The trajectories shown in Figure 6.1 are identical except for a vertical translation at every point. This suggests that the

trajectories of the PTC system are different for different ϵ values, but produce identical input-output behaviour because the effect of varying ϵ lies entirely in the unobserved states.

In order to test whether some alternative state trajectories can be generated using parameter values different than the ones estimated by Chen et al. (1991), we define new variables describing the unmeasured aqueous-phase concentrations \widetilde{Q}_w^+ , \widetilde{X}_w^- , and \widetilde{QX}_w . We also define new, alternative parameter values \widetilde{K}_{QY}^D and \widetilde{m}_{QX} . Using Equations g_4 to g_6 , and insist that $\widetilde{Q}_w^+ + \widetilde{QX}_w = Q_w^+ + QX_w$ and $\widetilde{X}_w^- + \widetilde{QX}_w = X_w^- + QX_w$ so that the input-output behaviour of System 3 remains the same (Ben-Zvi et al., in press 2004), we obtain the following set of five algebraic equations

$$0 = Q_w^+ / K_{QY}^D - \widetilde{Q}_w^+ / \widetilde{K}_{QY}^D \quad (6)$$

$$0 = \widetilde{Q}_w^+ \widetilde{X}_w^- - (K_{QX}^D + \epsilon) \widetilde{QX}_w \quad (7)$$

$$0 = \widetilde{m}_{QX} \widetilde{QX}_w - m_{QX} QX_w \quad (8)$$

$$0 = \widetilde{Q}_w^+ + \widetilde{QX}_w - (Q_w^+ + QX_w) \quad (9)$$

$$0 = \widetilde{X}_w^- + \widetilde{QX}_w - (X_w^- + QX_w) \quad (10)$$

in the five unknowns \widetilde{Q}_w^+ , \widetilde{K}_{QY}^D , \widetilde{X}_w^- , \widetilde{QX}_w , and \widetilde{m}_{QX} . Solving the Equations 6 to 10 we have

$$\begin{aligned} \widetilde{Q}_w^+ &= Q_w^+ + (QX_w - \psi(\epsilon)) \\ \widetilde{K}_{QY}^D &= K_{QY}^D \frac{Q_w^+ + QX_w - \psi(\epsilon)}{Q_w^+} \\ \widetilde{X}_w^- &= X_w^- + (QX_w - \psi(\epsilon)) \\ \widetilde{QX}_w &= \psi(\epsilon) \\ \widetilde{m}_{QX} &= m_{QX} QX_w \psi(\epsilon)^{-1} \end{aligned} \quad (11)$$

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

$$0 = \psi^2 - ((K_{QX}^D + \epsilon) + Q_w^+ + 2QX_w + X_w^-) \psi + Q_w^+ QX_w + QX_w^2 + Q_w^+ X_w^- + X_w^- QX_w \quad (12)$$

Equation 12 has two roots for each value of ϵ . For $\epsilon = 0$, these roots are $0.569 \frac{mol}{m^3}$ and $8.38 \times 10^5 \frac{mol}{m^3}$. The first of these roots corresponds to the nominal value of QX_w , while the second is an un-realistic concentration. We will therefore consider only the values of Ψ which correspond to the lower root of Equation 12.

The value of $\psi(\epsilon)$ is a measure of how different the new and old variables are. Note that, given $\epsilon = 0$, the quantity $\psi(\epsilon) = QX_w$, and the old and new parameter and state values are the same. Also note that changing the value of $\psi(\epsilon)$ amounts to scaling of the unobserved state QX_w . Given small values of ϵ , Equation 12 can be solved for ψ so that new values of parameters \widetilde{K}_{QY}^D , \widetilde{m}_{QX} , along with $K_{QX}^D + \epsilon$ will generate the same input-output behaviour as the nominal parameter values.

Several conclusions can be drawn from the above result. First, System 3 is not strongly locally identifiable. Secondly, if one is not interested in estimating every parameter, but rather in describing the input-output behaviour of the system, then the value of $\psi(\epsilon)$ can be fixed at the nominal value of m_{QX} so that m_{QX} , which is the extractive-equilibrium constant, is effectively set to unity, and removed from the model equations. Note that this re-parameterization is not unique. An alternative re-parameterization is obtained by setting the value of $\psi(\epsilon)$ to $(K_{QY}^D)^{-1}$ in order to eliminate the parameter K_{QY}^D from the model equations. This action corresponds to setting the dissociation constant K_{QY}^D to unity. A third alternative is to set the value of $\psi(\epsilon)$ to $\psi(K_{QX}^D - 1)$ in order to eliminate the dissociation constant K_{QX}^D by arbitrarily setting it to unity. Each of the proposed re-parameterizations will yield parameter estimates that describe the input-output behaviour, are unique to that input-output behaviour, 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, QX_w , at some time (for example, at the initial condition) is obtained then the value of $\psi(\epsilon)$ 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. Once again, the additional information required to accurately estimate the system parameters is not unique. One could also use measurements of Q_w^+ , or X_w^- at some time to accurately estimate each of the model parameters.

7. CONCLUSIONS

Identifiability is a desirable property of a mathematical model. Each of the parameters in an identifiable model can be uniquely identified from input-output data. 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. This lack of identifiability implies that several parameter values produce identical input-output behaviour in the model. Furthermore, this lack of identifiability

in the parameters also implies lack of identifiability of a subset of the un-observed states.

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