Incremental Model Identification of Distributed Two-phase Reaction Systems

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Abstract A transformation to variant and invariant states, called extents, is used to decouple the dynamic effects of reaction systems and serves as basis for incremental model identification, in which kinetic models are identified individually for each dynamic effect. This contribution introduces a novel transformation to extents for the incremental model identification of two-phase distributed reaction systems. Distributed reaction systems are discussed for two cases, namely, when measurements along the spatial coordinate are available and when they are not. In the second case, several measurements made under appropriate operating conditions are combined to overcome the lack of measurements along the spatial coordinate. This novel method is illustrated via the simulated example of a two-phase tubular reactor.

1. INTRODUCTION

Dynamic models of reaction systems represent the cornerstone of monitoring, control and optimization of industrial chemical processes. If it can be assumed that each phase is well mixed, the models describe the state evolution over time by means of *ordinary differential equations* (ODE) expressing the conservation of mass and energy. The identification of rate expressions (or kinetic models) for the various dynamic effects at work often represents a challenge. The difficulty arises from the coupling between the different physical effects, as in the case of reaction systems with two phases, where reaction and mass-transfer phenomena are interdependent (inherently coupled).

Identification problems are commonly solved in one step using a simultaneous method, where an overall kinetic model comprising rate expressions for all dynamic effects is identified. This method suffers from combinatorial complexity and can lead to convergence problems and high parameter correlation, Bhatt et al. (2012). As an alternative, the incremental methods break down the original identification problem into a set of subproblems of lower complexity, which allows the individual modeling of each dynamic effect, Marquardt (2005). The incremental methods exist in two variants, (a) the rate-based approach that relies on a differential method of parameter estimation via rates, Brendel et al. (2006); Jia et al. (2012), and (b) the extent-based approach that uses an integral method of parameter estimation via extents. This latter approach, which is discussed in this article, is based on two steps: (i) the computation of the contributions of each dynamic effect in the form of extents, Rodrigues et al. (2015), and (ii) the identification of each kinetic model by comparing individually the computed and modeled extents, Srinivasan et al. (2012); Billeter et al. (2013).

In this article, the assumption of perfect mixing within each phase is relaxed, and the model identification in two-phase distributed reaction systems (resolved in time and space) is considered from a methodological standpoint, Rodrigues et al. (2015). Inhomogeneity can either result from a technical flaw, as in reactors with poor mixing (dead zones), or be the consequence of a technical choice, as in tubular reactors. Such reaction systems are described by *partial differential equations* (PDE), which complicates the identification task.

The paper is organized as follows. Section 2 presents a novel transformation to extents for two-phase distributed reaction systems described by PDE and discusses the use of these extents for incremental identification. Section 3 proposes experimental conditions that lead to a simplified identification problem using ODE. Section 4 discusses a simulated example of a two-phase tubular reactor, while Section 5 concludes the paper.

2. INCREMENTAL MODEL IDENTIFICATION

As a working example, let us consider a one-dimensional tubular reactor of length z_e resolved in time t and space z containing two fluid phases, L and G, at constant temperature. Each phase $F \in \{L, G\}$ contains s_f species, $f \in \{l, g\}$, which are subjected on one hand to advection (forced convection) and on the other hand to r_f reactions and m mass transfers between the phases. Assuming the velocity is sufficiently high, diffusion is neglected and the velocity profile is in a plug-flow regime, which allows treating the tubular reactor as one dimensional.

2.1 Material Balance Equations

The dynamics of the distributed reaction system outlined above can be described by a set of PDE representing the material balance of all species involved in the phase F:

$$\frac{\partial}{\partial t}\big(\epsilon_f\,\mathbf{c}_f(z,t)\big) + \frac{\partial}{\partial z}\big(\epsilon_f\,v_f\,\mathbf{c}_f(z,t)\big) =$$
$$\mathbf{N}_f^{\mathrm{T}}\,\epsilon_f\,\mathbf{r}_f(z,t) \pm \mathbf{E}_{m,f}\,\epsilon_f\,\boldsymbol{\phi}_{m,f}(z,t) \quad (1)$$

with the initial conditions $\mathbf{c}_f(z,0) = \mathbf{c}_{f,0}(z)$ and the boundary conditions $\mathbf{c}_f(0,t) = \mathbf{c}_{f,in}(t)$, see Friedly (1972).

In (1), $\mathbf{c}_f$ denotes the s_f-dimensional vector of concentrations, ϵ_f the volumetric fraction of phase F such that $\epsilon_l + \epsilon_g = 1$, $\mathbf{N}_f$ the $r_f \times s_f$ constant stoichiometric matrix, $\mathbf{r}_f$ the r_f-dimensional vector of reaction rates, $\mathbf{E}_{m,f}$ the $s_f \times m$ mass-transfer matrix containing ones for species transferring via a given mass transfer and zeros for all others, a positive sign $(+)$ being used for the phase L and a negative sign $(-)$ for the phase G (by convention), $\boldsymbol{\phi}_{m,f}$ the m-dimensional vector of mass-transfer rates, and v_f the velocity of the advective flow. The rates $\mathbf{r}_f$ and $\boldsymbol{\phi}_{m,f}$ are expressed in units of concentration per unit of time. For the sake of conciseness, the dependence of v_f and ϵ_f on z and t is omitted, that is, v_f and ϵ_f stand for $v_f(z,t)$ and $\epsilon_f(z,t)$.

2.2 Transformation to Extents

Equation (1) has three contributions that are associated with advection, reactions and mass transfers. Since the corresponding terms $\frac{\partial}{\partial z}(\epsilon_f v_f \mathbf{c}_f)$, $\epsilon_f \mathbf{r}_f$ and $\epsilon_f \boldsymbol{\phi}_{m,f}$ appear linearly, the principle of superposition is satisfied and each contribution can be computed separately.

The effect that advection has on the initial and boundary conditions in absence of all other dynamic effects is obtained by solving the differential equation

$$\frac{\partial}{\partial t}\big(\epsilon_f\,\mathbf{c}_{ibc,f}(z,t)\big) + \frac{\partial}{\partial z}\big(\epsilon_f\,v_f\,\mathbf{c}_{ibc,f}(z,t)\big) = \mathbf{0}_{s_f} \quad (2)$$

with $\mathbf{c}_{ibc,f}(z,0) = \mathbf{c}_{f,0}(z)$ and $\mathbf{c}_{ibc,f}(0,t) = \mathbf{c}_{f,in}(t)$.

The effect of advection on the initial and boundary conditions is removed by writing concentrations as deviation variables, $\delta\mathbf{c}_f = \mathbf{c}_f - \mathbf{c}_{ibc,f}$, and (1) becomes:

$$\frac{\partial}{\partial t}\big(\epsilon_f\,\delta\mathbf{c}_f(z,t)\big) + \frac{\partial}{\partial z}\big(\epsilon_f\,v_f\,\delta\mathbf{c}_f(z,t)\big) =$$
$$\mathbf{N}_f^{\mathrm{T}}\,\epsilon_f\,\mathbf{r}_f(z,t) \pm \mathbf{E}_{m,f}\,\epsilon_f\,\boldsymbol{\phi}_{m,f}(z,t) \quad (3)$$

with $\delta\mathbf{c}_f(z,0) = \mathbf{0}_{s_f}$ and $\delta\mathbf{c}_f(0,t) = \mathbf{0}_{s_f}$.

Let $\mathrm{rank}\left(\begin{bmatrix} \mathbf{N}_f^{\mathrm{T}} & \pm\mathbf{E}_{m,f}\end{bmatrix}\right) = r_f + m$ and consider the matrix $\mathcal{T}_f = \begin{bmatrix} \mathbf{N}_f^{\mathrm{T}} & \pm\mathbf{E}_{m,f} & \mathbf{P}_f \end{bmatrix}^{-1}$, where $\mathbf{P}_f$ is the null space of the matrix $\begin{bmatrix} \mathbf{N}_f^{\mathrm{T}} \pm \mathbf{E}_{m,f}\end{bmatrix}^{\mathrm{T}}$.[1] Then, $\mathcal{T}_f$ transforms $\delta\mathbf{c}_f$ into three contributions, namely, r_f extents of reaction $\mathbf{x}_{r,f}$, m extents of mass transfer $\mathbf{x}_{m,f}$, and $q_f = s_f - (r_f + m)$ invariants $\mathbf{x}_{iv,f}$:

$$\begin{bmatrix} \mathbf{x}_{r,f}(z,t) \\ \mathbf{x}_{m,f}(z,t) \\ \mathbf{x}_{iv,f}(z,t) \end{bmatrix} = \mathcal{T}_f\,\delta\mathbf{c}_f(z,t) = \begin{bmatrix} \mathcal{T}_{r,f} \\ \mathcal{T}_{m,f} \\ \mathcal{T}_{iv,f} \end{bmatrix}\delta\mathbf{c}_f(z,t). \quad (4)$$

With this transformation, the material balance equations (3) are split into the three sets of equations:

$$\frac{\partial}{\partial t}\big(\epsilon_f\,\mathbf{x}_{r,f}(z,t)\big) + \frac{\partial}{\partial z}\big(\epsilon_f\,v_f\,\mathbf{x}_{r,f}(z,t)\big) = \epsilon_f\,\mathbf{r}_f(z,t) \quad (5)$$

$$\frac{\partial}{\partial t}\big(\epsilon_f\,\mathbf{x}_{m,f}(z,t)\big) + \frac{\partial}{\partial z}\big(\epsilon_f\,v_f\,\mathbf{x}_{m,f}(z,t)\big) = \epsilon_f\,\boldsymbol{\phi}_{m,f}(z,t) \quad (6)$$

$$\mathbf{x}_{iv,f}(z,t) = \mathbf{0}_{q_f} \quad (7)$$

with all initial and boundary conditions equal to zero.[2]

Pre-multiplying (4) by $\mathcal{T}_f^{-1} = \begin{bmatrix} \mathbf{N}_f^{\mathrm{T}} & \pm\mathbf{E}_{m,f} & \mathbf{P}_f \end{bmatrix}$, considering the fact that $\mathbf{x}_{iv,f}(z,t) = \mathbf{0}_{q_f}$, and using the definition of deviation variables, $\mathbf{c}_f = \delta\mathbf{c}_f + \mathbf{c}_{ibc,f}$, the concentrations can be reconstructed from the extents as:

$$\mathbf{c}_f(z,t) = \mathbf{N}_f^{\mathrm{T}}\,\mathbf{x}_{r,f}(z,t) \pm \mathbf{E}_{m,f}\,\mathbf{x}_{m,f}(z,t) + \mathbf{c}_{ibc,f}(z,t) \quad (8)$$

The meaning of the extents introduced in (5)-(7) is as follows:

Extents of reaction $\mathbf{x}_{r,f}$ The extent of reaction $x_{r,f,i}$ $(\forall i = 1,...,r_f)$ indicates the amount in concentration units at position z and time t that has been produced by the ith reaction. The ith extent of reaction is decoupled from all the other extents (in particular from the other extents of reaction).

Extents of mass transfer $\mathbf{x}_{m,f}$ The extent of mass transfer $x_{m,f,j}$ $(\forall j = 1,...,m)$ indicates the amount in concentration units at position z and time t that has been transferred between phases by the jth mass transfer.

Invariants $\mathbf{x}_{iv,f}$ The q_f invariants $\mathbf{x}_{iv,f}$ represent variables that are orthogonal (by construction) to all the other extents and therefore invariant in time and space. These variables represent true invariants since they remain identically equal to zero.

For each extent, the term $\frac{\partial}{\partial z}(\cdot)$ accounts for the amount of material that has been transported by advection over time to a farther position.

2.3 Model Identification

Incremental model identification in its extent-based form consists in two steps: first, measured concentrations are transformed into individual contributions (called extents) of each dynamic effect; in a second step, the rate expressions are identified one at a time and the corresponding rate parameters are estimated.

If concentrations are measured at P positions and H time instants and the rank condition associated with transformation (4) is satisfied, these measurements can be transformed into $r_f + m$ variant contributions, namely, the extents $\tilde{\mathbf{x}}_{r,f}(z,t)$ and $\tilde{\mathbf{x}}_{m,f}(z,t)$, where the superscript $(\tilde{\ })$ is used to denote a quantity associated with measurements. Each extent is used to identify the corresponding rate expression $r_{f,i}$ or $\phi_{m,f,j}$ by comparing, in the least-squares sense, the 'experimental' extents, obtained by transformation of the concentration measurements via (4), and the 'modeled' extents, obtained by integration of the postulated rate model via (5) or (6). The identification problems are formulated as follows.

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[1] Provided that the rank condition is satisfied, the dimension of $\mathbf{c}_f$ can be reduced to $s_f \geq r_f + m$.

[2] That is $\mathbf{x}_{r,f}(z,0) = \mathbf{0}_{r_f}$, $\mathbf{x}_{m,f}(z,0) = \mathbf{0}_m$, and $\mathbf{x}_{r,f}(0,t) = \mathbf{0}_{r_f}$, $\mathbf{x}_{m,f}(0,t) = \mathbf{0}_m$.