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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.

Keywords: Distributed chemical reactors, Variants and invariants, Reaction extents, Kinetic identification

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 $(\tilde{\cdot})$ 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 $\mathbf{x}_{r,f}(0,t) = \mathbf{0}_{r_f}$, $\mathbf{x}_{m,f}(0,t) = \mathbf{0}_m$.

Identification of reaction rates $\mathbf{r}_f$. The identification of the rate expression for the ith reaction $r_{f,i}$ ($\forall i = 1, ..., r_f$) and the estimation of the parameters $\boldsymbol{\theta}_{r,f,i}$ are carried out by solving the regression problem:

$$\min_{\boldsymbol{\theta}_{r,f,i}} \sum_{p=1}^{P} \sum_{h=1}^{H} \left(\tilde{x}_{r,f,i}(z_p, t_h) - x_{r,f,i}(z_p, t_h, \boldsymbol{\theta}_{r,f,i}) \right)^2$$

$$\text{s.t. } \frac{\partial}{\partial t}\left(\epsilon_f \, x_{r,f,i}(z,t,\boldsymbol{\theta}_{r,f,i})\right) + \frac{\partial}{\partial z}\left(\epsilon_f \, v_f \, x_{r,f,i}(z,t,\boldsymbol{\theta}_{r,f,i})\right)$$

$$= \epsilon_f \, r_{f,i}(\tilde{\mathbf{c}}_f(z,t), \boldsymbol{\theta}_{r,f,i}),$$

$$x_{r,f,i}(z,0,\boldsymbol{\theta}_{r,f,i}) = x_{r,f,i}(0,t,\boldsymbol{\theta}_{r,f,i}) = 0. \quad (9)$$

Identification of mass-transfer rates $\boldsymbol{\phi}_{m,f}$. The identification of the rate expression for the jth mass transfer $\phi_{m,f,j}$ ($\forall j = 1, ..., m$) and the estimation of the parameters $\boldsymbol{\theta}_{m,f,j}$ are carried out by solving the regression problem:

$$\min_{\boldsymbol{\theta}_{m,f,j}} \sum_{p=1}^{P} \sum_{h=1}^{H} \left(\tilde{x}_{m,f,j}(z_p, t_h) - x_{m,f,j}(z_p, t_h, \boldsymbol{\theta}_{m,f,j}) \right)^2$$

$$\text{s.t. } \frac{\partial}{\partial t}\left(\epsilon_f \, x_{m,f,j}(z,t,\boldsymbol{\theta}_{m,f,j})\right)$$

$$+ \frac{\partial}{\partial z}\left(\epsilon_f \, v_f \, x_{m,f,j}(z,t,\boldsymbol{\theta}_{m,f,j})\right)$$

$$= \epsilon_f \, \phi_{m,f,j}(\tilde{\mathbf{c}}_l(z,t), \tilde{\mathbf{c}}_g(z,t), \boldsymbol{\theta}_{m,f,j}),$$

$$x_{m,f,j}(z,0,\boldsymbol{\theta}_{m,f,j}) = x_{m,f,j}(0,t,\boldsymbol{\theta}_{m,f,j}) = 0. \quad (10)$$

Obviously, the accuracy of the identification/estimation improves if concentrations can be measured frequently at many locations along the tubular reactor. While the former condition is generally fulfilled, the latter condition – measurements along the reactor – is difficult to achieve in practice. Although, in recent years, research in the field of process intensification and development of stacked plate reactors have made possible the measurements of concentrations along the spatial coordinate, see Kockmann et al. (2011), concentrations are more commonly measured only at the entry ($z = 0$) and exit ($z = z_e$). Hence, the next section considers some common simplifications.

3. SIMPLIFIED IDENTIFICATION PROBLEM

The following simplifications are commonly found/made in experimental studies of distributed reaction systems:

(1) the reactions are only significant in one phase, say in phase L, hence, $\mathbf{N}_g^{\mathrm{T}} \epsilon_g \mathbf{r}_g(z,t) = \mathbf{0}_{s_g}$,
(2) the mass transfers are sufficiently fast to be considered at steady state, thence $\boldsymbol{\phi}_{m,l} = \boldsymbol{\phi}_{m,g} = \boldsymbol{\phi}_m$,
(3) the reactions and mass transfers are significantly slower than the advection, thus the volumetric fractions ϵ_l and ϵ_g are constant,
(4) the velocity is the same for the two phases and remains constant, namely, $v_l(z,t) = v_g(z,t) = v$,[3]
(5) the boundary conditions $\mathbf{c}_{l,in}$ and $\mathbf{c}_{g,in}$ are constant.

3.1 Material Balance Equations

On the basis of the simplifications (1)-(5), one can rewrite the PDE system (1) as the ODE system:[4]

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[3] The two fluid phases are treated as an incompressible quasi-single phase flow.
[4] To an observer sitting on a *particle* of velocity v, the concentrations $\mathbf{c}(z,t)$ are viewed as $\mathbf{c}_p(\tau)$, with $z = v\tau$ and $t = \tau$. It follows from $\mathbf{c}_p(\tau) = \mathbf{c}(z,t)$ that $\frac{d\mathbf{c}_p}{d\tau} = \frac{\partial \mathbf{c}}{\partial z}\left(\frac{dz}{d\tau}\right) + \frac{\partial \mathbf{c}}{\partial t}\left(\frac{dt}{d\tau}\right) = \frac{\partial \mathbf{c}}{\partial z}v + \frac{\partial \mathbf{c}}{\partial t}$.

$$\frac{d}{d\tau}\mathbf{c}_p(\tau) = \mathbf{N}^{\mathrm{T}}\mathbf{r}(\tau) + \mathbf{E}_m\boldsymbol{\phi}_m(\tau), \quad (11)$$

where τ is the time spent in the reactor up to position z, $\mathbf{c}_p = \begin{bmatrix} \mathbf{c}_{p,l} \\ \mathbf{c}_{p,g} \end{bmatrix}$, $\mathbf{N}^{\mathrm{T}} = \begin{bmatrix} \mathbf{N}_l^{\mathrm{T}} \\ \mathbf{0}_{s_g \times r} \end{bmatrix}$ and $\mathbf{E}_m = \begin{bmatrix} +\mathbf{E}_{m,l} \\ -\mathbf{E}_{m,g} \end{bmatrix}$, with $\mathbf{c}_p(0) = \mathbf{c}_{in} = \begin{bmatrix} \mathbf{c}_{l,in} \\ \mathbf{c}_{g,in} \end{bmatrix}$.

3.2 Transformation to Extents

The right-hand side of (11) has two contributions that are associated with the reactions and the mass transfers, respectively. Deviation variables $\delta\mathbf{c}_p = \mathbf{c}_p - \mathbf{c}_{in}$ are introduced to remove the effect of the boundary conditions.

Let rank $\left(\begin{bmatrix} \mathbf{N}^{\mathrm{T}} & \mathbf{E}_m \end{bmatrix} \right) = r + m$ and consider the matrix $\mathcal{T} = \begin{bmatrix} \mathbf{N}^{\mathrm{T}} & \mathbf{E}_m & \mathbf{P} \end{bmatrix}^{-1}$, where $\mathbf{P}$ describes the null space of the matrix $\begin{bmatrix} \mathbf{N}^{\mathrm{T}} & \mathbf{E}_m \end{bmatrix}^{\mathrm{T}}$.[5] Then, $\mathcal{T}$ partitions $\delta\mathbf{c}_p$ into three contributions, namely, r extents of reaction $\mathbf{x}_{p,r}$, m extents of mass transfer $\mathbf{x}_{p,m}$ and $q = (s_l + s_g) - (r + m)$ invariants $\mathbf{x}_{p,iv}$:

$$\begin{bmatrix} \mathbf{x}_{p,r}(\tau) \\ \mathbf{x}_{p,m}(\tau) \\ \mathbf{x}_{p,iv}(\tau) \end{bmatrix} = \mathcal{T}\,\delta\mathbf{c}_p(\tau) = \begin{bmatrix} \mathcal{T}_r \\ \mathcal{T}_m \\ \mathcal{T}_{iv} \end{bmatrix} \delta\mathbf{c}_p(\tau), \quad (12)$$

with which the dynamic equations (11) give:

$$\frac{d}{d\tau}\mathbf{x}_{p,r}(\tau) = \mathbf{r}(\tau), \qquad \mathbf{x}_{p,r}(0) = \mathbf{0}_r \quad (13)$$

$$\frac{d}{d\tau}\mathbf{x}_{p,m}(\tau) = \boldsymbol{\phi}_m(\tau), \quad \mathbf{x}_{p,m}(0) = \mathbf{0}_m \quad (14)$$

$$\mathbf{x}_{p,iv}(\tau) = \mathbf{0}_q. \quad (15)$$

Pre-multiplying (12) by $\mathcal{T}^{-1} = \begin{bmatrix} \mathbf{N}^{\mathrm{T}} & \mathbf{E}_m & \mathbf{P} \end{bmatrix}$, considering that $\mathbf{x}_{p,iv}(\tau) = \mathbf{0}_q$, and using the definition of $\delta\mathbf{c}_p$ yields

$$\mathbf{c}_p(\tau) = \mathbf{N}^{\mathrm{T}}\mathbf{x}_{p,r}(\tau) + \mathbf{E}_m\mathbf{x}_{p,m}(\tau) + \mathbf{c}_{in}. \quad (16)$$

3.3 Model Identification

Transformation (12) requires the measurements of $\mathbf{c}_p(\tau_k)$ for various values of τ_k. We show next that $\mathbf{c}_p(\tau_k)$ can be obtained by measuring the concentrations at the reactor exit corresponding to the velocity $v_k = \frac{z_e}{\tau_k}$.

From $z = v\tau$ and $t = \tau$, one can write $\mathbf{c}(z,t) = \mathbf{c}_p(\tau) = \mathbf{c}_v(z)$, with the latter indicating the concentration profile associated with the velocity v. Note that a different velocity will lead to a different concentration profile. Furthermore, from $\tau = \frac{z}{v} = \frac{\alpha z}{\alpha v}$, with $\alpha > 0$, one can write $\mathbf{c}_p(\tau) = \mathbf{c}_v(z) = \mathbf{c}_{\alpha v}(\alpha z)$. In particular, for $\alpha v = v_k$ and $\tau_k = \frac{z_e}{v_k}$, it follows that $\mathbf{c}_p(\tau_k) = \mathbf{c}_{v_k}(z_e)$.

Hence, if concentrations are measured at the reactor exit for K values τ_k, that is, for K velocities $v_k = \frac{z_e}{\tau_k}$, and the rank condition associated with transformation (12) is satisfied, the measured concentrations can be transformed in the $r + m$ variant contributions $\tilde{\mathbf{x}}_{p,r}$ and $\tilde{\mathbf{x}}_{p,m}$.

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[5] Provided that the rank condition is satisfied, the dimension of $\mathbf{c}_p$ can be reduced to $s_l + s_g \geq r + m$.

As described in Section 2.3, each extent is used to identify a corresponding rate model by comparing, in the least-squares sense, the 'experimental' and 'modeled' extents.

Identification of reaction rates $\mathbf{r}$. The identification of the rate expression for the ith reaction r_i ($\forall i = 1, ..., r$) and the estimation of the parameters $\boldsymbol{\theta}_{r,i}$ are carried out by solving the regression problem:
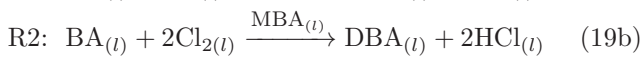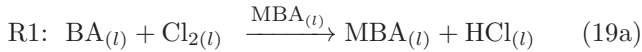
$$\min_{\boldsymbol{\theta}_{r,i}} \sum_{k=1}^{K} \left(\tilde{x}_{p,r,i}(\tau_k) - x_{p,r,i}(\tau_k, \boldsymbol{\theta}_{r,i}) \right)^2$$

$$\text{s.t.} \quad \frac{d}{d\tau} x_{p,r,i}(\tau, \boldsymbol{\theta}_{r,i}) = r_i\left(\tilde{\mathbf{c}}_{p,l}(\tau), \boldsymbol{\theta}_{r,i} \right), \quad x_{p,r,i}(0) = 0 \quad (17)$$

Identification of mass-transfer rates $\boldsymbol{\phi}_m$. The identification of the rate expression for the jth mass transfer $\phi_{m,j}$ ($\forall j = 1, ..., m$) and the estimation of the parameters $\boldsymbol{\theta}_{m,j}$ are made by solving the regression problem:

$$\min_{\boldsymbol{\theta}_{m,j}} \sum_{k=1}^{K} \left(\tilde{x}_{p,m,j}(\tau_k) - x_{p,m,j}(\tau_k, \boldsymbol{\theta}_{m,j}) \right)^2$$

$$\text{s.t.} \quad \frac{d}{d\tau} x_{p,m,j}(\tau, \boldsymbol{\theta}_{m,j}) = \phi_{m,j}\left(\tilde{\mathbf{c}}_{p,l}(\tau), \tilde{\mathbf{c}}_{p,g}(\tau), \boldsymbol{\theta}_{m,j} \right),$$

$$x_{p,m,j}(0) = 0 \quad (18)$$

4. ILLUSTRATIVE EXAMPLE

Incremental model identification is applied to the simulated example of the chlorination of butanoic acid (BA). This reaction system takes place in an organic solvent at 25°C and involves two parallel auto-catalytic reactions producing mono- and di-chlorobutanoic acid (MBA and DBA). The system is composed of $s_g = 2$ species in the gas phase and $s_l = 5$ species in the liquid phase that are involved in $r = 2$ reactions and $m = 2$ mass transfers (Cl$_2$ and HCl). The reactions read:

$$\text{R1:} \quad \text{BA}_{(l)} + \text{Cl}_{2(l)} \xrightarrow{\text{MBA}_{(l)}} \text{MBA}_{(l)} + \text{HCl}_{(l)} \quad (19a)$$

$$\text{R2:} \quad \text{BA}_{(l)} + 2\text{Cl}_{2(l)} \xrightarrow{\text{MBA}_{(l)}} \text{DBA}_{(l)} + 2\text{HCl}_{(l)} \quad (19b)$$

with the reaction rate $\mathbf{r}$ expressed in kmol/(m^3 s):

$$r_1 = k_1 \, c_{l,\text{BA}} \, c_{l,\text{Cl}_2} \, \sqrt{c_{l,\text{MBA}}} \quad (20a)$$

$$r_2 = k_2 \, r_1 \, c_{l,\text{Cl}_2} \quad (20b)$$

and the rate constants $k_1 = 1.3577$ (m^3)$^{1.5}$/(kmol$^{1.5}$ s) and $k_2 = 0.6788$ m^3/kmol. The steady-state rates of mass transfer $\boldsymbol{\phi}_m$ expressed in kmol/(m^3 s) are:

$$\phi_{m,\text{Cl}_2} = k_{\text{Cl}_2} \, a \, \left(c^\star_{\text{Cl}_2} - c_{l,\text{Cl}_2} \right) \quad (21a)$$

$$\phi_{m,\text{HCl}} = k_{\text{HCl}} \, a \, \left(c^\star_{\text{HCl}} - c_{l,\text{HCl}} \right) \quad (21b)$$

with $c^\star_{\text{Cl}_2} = \frac{p_{\text{Cl}_2}}{H_{\text{Cl}_2}}$ and $c^\star_{\text{HCl}} = \frac{p_{\text{HCl}}}{H_{\text{HCl}}}$, where $k_{\text{Cl}_2} = 0.6660 \cdot 10^{-4}$ and $k_{\text{HCl}} = 0.8450 \cdot 10^{-4}$ m/s are the mass-transfer coefficients, $a = 5 \cdot 10^3$ m^{-1} is the specific interfacial area (finely dispersed gas bubbles in liquid), $c^\star_{\text{Cl}_2}$ and $c^\star_{\text{HCl}}$ are the equilibrium concentrations at the interface, $H_{\text{Cl}_2} = H_{\text{HCl}} = 70.33$ (bar m^3)/kmol are Henry's constants, and p_{Cl_2} and p_{HCl} are the partial pressures (in bar) in the gas phase calculated using the ideal gas law from the concentrations in the gas phase.

For the sets of species $\mathcal{S}_l = \{\text{Cl}_{2(l)}, \text{BA}_{(l)}, \text{MBA}_{(l)}, \text{HCl}_{(l)}, \text{DBA}_{(l)}\}$ and $\mathcal{S}_g = \{\text{Cl}_{2(g)}, \text{HCl}_{(g)}\}$, the matrices $\mathbf{N}_l^{\text{T}}$, $\mathbf{E}_{m,l}$, $\mathbf{N}_g^{\text{T}}$ and $\mathbf{E}_{m,g}$ read:

$$\mathbf{N}_l^{\text{T}} = \begin{bmatrix} -1 & -2 \\ -1 & -1 \\ 1 & 0 \\ 1 & 2 \\ 0 & 1 \end{bmatrix}, \; \mathbf{E}_{m,l} = \begin{bmatrix} 1 & 0 \\ 0 & 0 \\ 0 & 0 \\ 0 & 1 \\ 0 & 0 \end{bmatrix}, \; \mathbf{N}_g^{\text{T}} = \mathbf{0}_{2\times2}, \; \mathbf{E}_{m,g} = \mathbf{I}_2$$
$$(22)$$

Assuming that the velocity of the advective flow is sufficiently large, the effects of diffusion can be neglected and the tubular reactor can be treated as one dimensional.

4.1 Dynamic Experiments

Concentrations of all species $\mathbf{c}_f(z_p, t_h)$ in the liquid and gas phases are assumed to be measured at $P = 11$ different values of z equally distant between the entry ($z = 0$) and exit ($z_e = 1$ m) of a reactor composed of 10 stacked plates and for $H = 25$ different values of t equally spaced between 0 and 5 s. The velocity v_f at the entry is 0.2 m/s for both phases and varies according to the total mass of each phase along z and t.[6] The volumetric fractions at the entry are $\epsilon_l = 0.79$ and $\epsilon_g = 0.21$ and vary according to the composition of the phase along z and t.[7] Both v_f and ϵ_f are assumed to be available at the points (z_p, t_h) where $\mathbf{c}_f$ is measured.

The boundary conditions at the entry point are assumed to be constant at $\mathbf{c}_{l,in} = \begin{bmatrix} 0 & 1.82 & 10^{-6} & 0 & 0 \end{bmatrix}^{\text{T}}$ and $\mathbf{c}_{g,in} = \begin{bmatrix} 4.07 & 0 \end{bmatrix}^{\text{T}}$ kmol/m^3. The initial conditions $\mathbf{c}_{f,0}(z)$ are chosen as the steady-state values obtained with the aforementioned boundary conditions.

The concentrations $\mathbf{c}_f(z,t)$ are simulated by integrating (1) with varying $v_f(z,t)$ and $\epsilon_f(z,t)$ and using the rate expressions (20) and (21).[8] Simulated concentrations are reduced to $P \times H$ points in space and time, and corrupted with 2% zero-mean Gaussian noise with respect to each maximal concentration, as shown in Figure 1a.

The extents are obtained from the measured concentrations $\tilde{\mathbf{c}}_f(z_p, t_h)$ by subtracting $\tilde{\mathbf{c}}_{ibc,f}(z_p, t_h)$ that result from the integration of (2) to obtain $\delta\tilde{\mathbf{c}}_f(z_p, t_h)$, and applying transformation (4). Figure 1b shows the resulting extents of reaction $\tilde{\mathbf{x}}_r(z_p, t_h)$ and extents of mass transfer $\tilde{\mathbf{x}}_{m,l}(z_p, t_h)$ and $\tilde{\mathbf{x}}_{m,g}(z_p, t_h)$. Note that $\tilde{\mathbf{x}}_{m,l}$ and $\tilde{\mathbf{x}}_{m,g}$ only differ due to the variation of ϵ_l and ϵ_g along z and t.

For each extent of reaction $\tilde{x}_{r,i}(z_p, t_h)$ ($i = 1, 2$), several rate expressions $r_i(\tilde{\mathbf{c}}_l(z_p, t_h), \boldsymbol{\theta}_{r,i})$ are postulated and the regression problem (9) solved for each rate expression – using $\tilde{v}_f(z_p, t_h)$ – as shown in Table 1. Based on the sum of squared errors (SSE), the rate models $\hat{r}_1^{(4)}$ and $\hat{r}_2^{(4)}$, which correspond to the rate expressions (20a) and (20b) that were used to generate the concentration data, are correctly identified.

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[6] The velocities vary due to changes in density. The variation $\frac{\partial}{\partial z} v_f(z,t)$ is computed from the mole balance equation (1) and knowledge of the molecular weights.

[7] The volumetric fractions vary due to changes in concentrations. The variation $\frac{\partial}{\partial z}\epsilon_f(z,t)$ is computed from the concentrations and knowledge of the molar volumes.

[8] A stiff integration method was used for the time coordinate and the space coordinate was discretized in 100 intervals from 0 to $z_e = 1$.
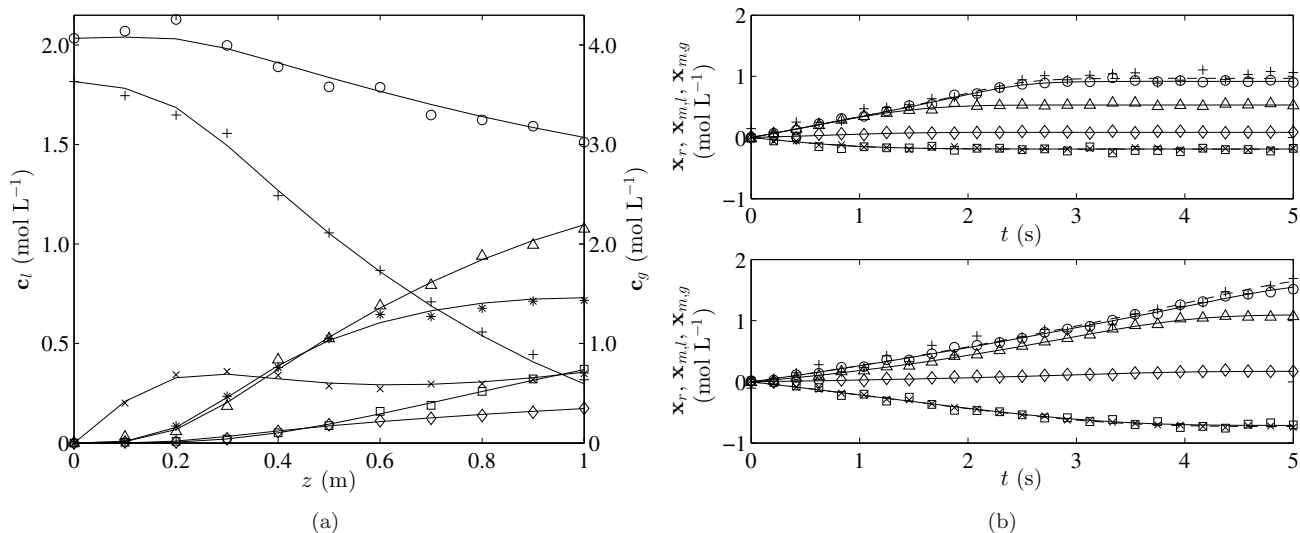
Figure 1. (a) Simulated (noise-free, continuous lines) and experimental (noisy) concentrations of the gas species $Cl_{2(g)}$ (◦) and $HCl_{(g)}$ (□) on the right axis, and of the liquid species $Cl_{2(l)}$ (×), $BA_{(l)}$ (+), $MBA_{(l)}$ (△), $HCl_{(l)}$ (∗) and $DBA_{(l)}$ (◊) on the left axis at $t = 5$ s; (b) Modeled (with the identified models, continuous lines) and experimental (noisy) extents of reaction and mass transfer $x_{r,1}$ (△), $x_{r,2}$ (◊), $x_{m,l,1}$ (Cl_2, ◦), $x_{m,l,2}$ (HCl, □), $x_{m,g,1}$ (Cl_2, +) and $x_{m,g,2}$ (HCl, ×) at $z = 0.5$ m (above) and $z = 1$ m (below).
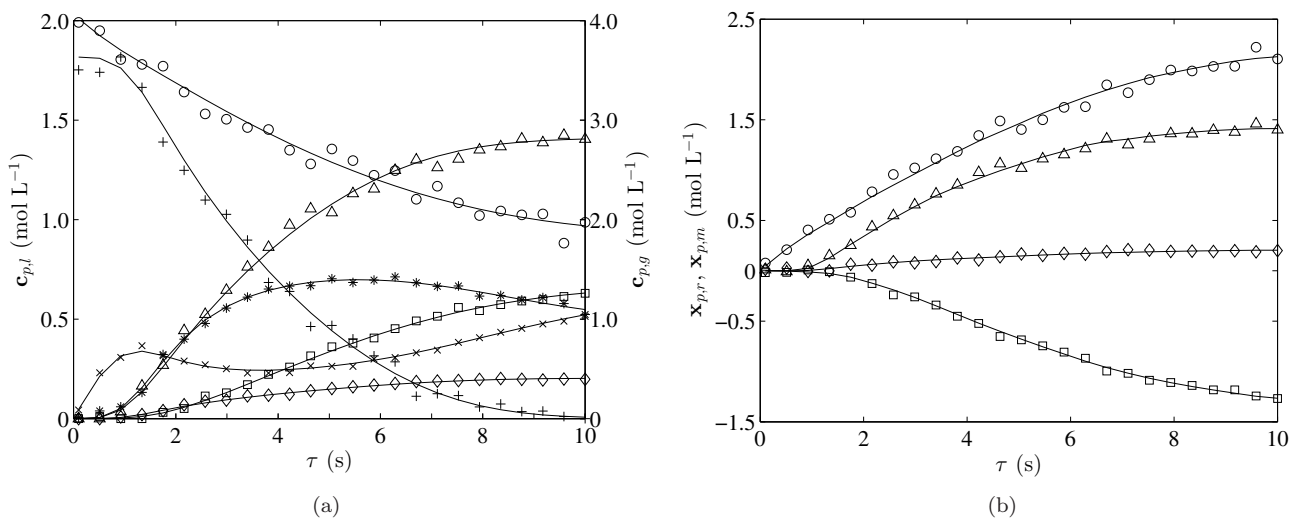

Figure 2. (a) Simulated (noise-free, continuous lines) and experimental (noisy) concentrations of the gas species $Cl_{2(g)}$ (◦) and $HCl_{(g)}$ (□) on the right axis, and of the liquid species $Cl_{2(l)}$ (×), $BA_{(l)}$ (+), $MBA_{(l)}$ (△), $HCl_{(l)}$ (∗) and $DBA_{(l)}$ (◊) on the left axis; (b) Modeled (with the identified models, continuous lines) and experimental (noisy) extents of reaction and mass transfer $x_{p,r,1}$ (△), $x_{p,r,2}$ (◊), $x_{p,m,1}$ (Cl_2, ◦) and $x_{p,m,2}$ (HCl, □).

Table 1. Incremental model identification of reactions R1 and R2 based on the extents of reaction, with the corresponding sum of squared errors (SSE).

R1	Rate expression	SSE		R2	Rate expression	SSE	
		$x_{r,1}(z_p, t_h)$	$x_{p,r,1}(\tau_k)$			$x_{r,2}(z_p, t_h)$	$x_{p,r,2}(\tau_k)$
$\hat{r}_1^{(1)}$	$k_1 c_{l,Cl_2}$	0.923	1.270	$\hat{r}_2^{(1)}$	$k_2 k_1 c_{l,BA} c_{l,Cl_2}$	0.153	0.018
$\hat{r}_1^{(2)}$	$k_1 c_{l,BA} c_{l,Cl_2}$	5.120	0.563	$\hat{r}_2^{(2)}$	$k_2 k_1 c_{l,BA} c_{l,Cl_2}^2$	0.131	0.017
$\hat{r}_1^{(3)}$	$k_1 c_{l,BA} c_{l,Cl_2} c_{l,MBA}$	2.013	0.320	$\hat{r}_2^{(3)}$	$k_2 k_1 c_{l,BA} c_{l,Cl_2}^2 c_{l,MBA}$	0.107	0.010
$\hat{r}_1^{(4)}$	$k_1 c_{l,BA} c_{l,Cl_2} \sqrt{c_{l,MBA}}$	**0.089**	**0.026**	$\hat{r}_2^{(4)}$	$k_2 k_1 c_{l,BA} c_{l,Cl_2}^2 \sqrt{c_{l,MBA}}$	**0.049**	**0.005**

Note that, in this example, the mass-transfer rate expressions are assumed to be known, thus limiting the identification to the estimation of the parameters.

As shown in Table 2, the rate parameters k_1, k_2, k_{Cl_2} and k_{HCl} are correctly estimated. Mass-transfer coefficients can be estimated either from $\tilde{\mathbf{x}}_{m,l}$ or $\tilde{\mathbf{x}}_{m,g}$.

4.2 Steady-State Experiments

Assuming simplifications (1)–(5) in Section 3 can be made, concentrations of all species $\mathbf{c}_p(\tau_k)$ in the liquid and gas phases are measured at steady state at the entry and exit ($z_e = 1$ m) of the reactor for $K = 25$ different values τ_k equally spaced between 0.1 and 10 s, and corresponding velocities $v_k = \frac{z_e}{\tau_k}$. The boundary conditions are identical to those described in Section 4.1.

The vectors $\mathbf{c}_{p,l}(\tau)$ and $\mathbf{c}_{p,g}(\tau)$ are concatenated into the vector $\mathbf{c}_p(\tau)$ according to (11), with the matrices $\mathbf{N}^{\mathrm{T}} = \left[\frac{\mathbf{N}_l^{\mathrm{T}}}{\mathbf{0}_{s_g \times r}} \right]$ and $\mathbf{E}_m = \left[\frac{+\mathbf{E}_{m,l}}{-\mathbf{E}_{m,g}} \right]$.

The concentrations $\mathbf{c}_p(\tau)$ are simulated by integrating (11) using the rate expressions (20) and (21). After reduction to K points, the simulated concentrations $\mathbf{c}_p(\tau_k)$ are corrupted with 2% zero-mean Gaussian noise with respect to each maximal concentration (Figure 2a).

The extents are obtained from the measured concentrations $\tilde{\mathbf{c}}_p(\tau_k)$ by subtracting the boundary conditions $\mathbf{c}_{in}$ to obtain $\delta\tilde{\mathbf{c}}_p(\tau_k)$ and applying transformation (12). Figure 2b shows the resulting extents of reaction and mass transfer $\tilde{\mathbf{x}}_{p,r}(\tau_k)$ and $\tilde{\mathbf{x}}_{p,m}(\tau_k)$.

For each extent of reaction $\tilde{x}_{p,r,i}(\tau_k)$ ($i = 1, 2$), several rate expressions $r_i(\tilde{\mathbf{c}}_{p,l}(\tau_k), \boldsymbol{\theta}_{r,i})$ are postulated and the regression problem (17) solved for each rate expression (see Table 1). According to the sum of squared errors (SSE), the rate models $\hat{r}_1^{(4)}$ and $\hat{r}_2^{(4)}$ are identified, similarly to Section 4.1. As shown in Table 2, the rate parameters are also correctly estimated.

Table 2. Estimated rate constants for reactions R1 and R2 and mass-transfer coefficients for Cl_2 and HCl, with the corresponding 99% confidence intervals (C.I.).

Rate	Const.	True	Fitting	Estimated [99% C.I.]
r_1	k_1	1.3577	$x_{r,1}(z_p, t_h)$	1.3612 [1.3551, 1.3672]
			$x_{p,r,1}(\tau_k)$	1.3540 [1.3441, 1.3640]
r_2	k_2	0.6788	$x_{r,2}(z_p, t_h)$	0.6757 [0.6610, 0.6904]
			$x_{p,r,2}(\tau_k)$	0.6725 [0.6658, 0.6792]
ϕ_{Cl_2}	$k_{Cl_2} \cdot 10^4$	0.6660	$x_{m,l,1}(z_p, t_h)$	0.6661 [0.6634, 0.6688]
			$x_{m,g,1}(z_p, t_h)$	0.6667 [0.6580, 0.6754]
			$x_{p,m,1}(\tau_k)$	0.6665 [0.6552, 0.6778]
ϕ_{HCl}	$k_{HCl} \cdot 10^4$	0.8450	$x_{m,l,2}(z_p, t_h)$	0.8476 [0.8353, 0.8600]
			$x_{m,g,2}(z_p, t_h)$	0.8421 [0.8369, 0.8473]
			$x_{p,m,2}(\tau_k)$	0.8460 [0.8362, 0.8558]

5. CONCLUSION

This paper has provided a novel transformation to extents of reaction and mass transfer for the case of two-phase distributed reaction systems. The transformed system is well suited to decoupled kinetic identification using an extent-based incremental approach. Experimental simplifications of distributed reaction systems have also been reviewed, and their implications on the formulation of the identification problem have been discussed.

The applicability of this incremental identification method has been demonstrated via the simulated example of a two-phase tubular reactor described in a one-dimensional coordinate system. Although the identification of kinetic models in distributed reaction systems formally requires measurements along the spatial and time coordinates, accurate identification can also be performed using steady-state measurements at the reactor exit only, when a number of simplifying assumptions hold.

The method described in Section 2 can be extended to distributed reaction systems with diffusion, by adapting the transformation to extract the extents of diffusion, as proposed in Rodrigues et al. (2015), and then modeling individually each rate of diffusion. However, the method of Section 3 does not apply in case of diffusion.

Industrially relevant applications of the proposed method include the identification of distributed reaction-separation systems such as reaction-absorption or reaction-distillation columns, or reaction systems in three dimensions such as tubular reactors or micro-reactors.

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