Incremental Model Identification of Reaction Systems

CPAC / ATOCHEMIS Workshop
25 – 27 March 2013, Rome – Italy

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Outline

- Motivation
- Concept of vessel extent
- Homogeneous reaction systems
- Incremental model identification
- Fluid-Fluid reaction systems
- Extensions to calorimetry and spectroscopy
- Perspectives: distributed reaction systems
Model reduction
Separate fast / slow dynamics

○ Discard redundant (invariant) states
  • What is the minimal number of states (variants) ?
  • Batch reactors: $S \rightarrow R$ extents
  • Open reactors: $S \rightarrow R+p+1$ vessel extents
  • Open G-L reactors: $S \rightarrow R+p_m+p+1$ vessel extents

○ Separate fast/slow dynamics
  • Rates are fast/slow, not individual concentrations
    $\rightarrow$ work with extents, not concentrations…

M. Amrhein, PhD dissertation n°1861 (1998), EPFL, Switzerland
Motivation

- Concept of vessel extent
- Homogeneous reaction systems
- Incremental model identification
- Fluid-Fluid reaction systems
- Extensions to calorimetry and spectroscopy
- Perspectives: distributed reaction systems
Definitions
Extent vs vessel extent of reaction

- **Extent of the** \( i \)-th reaction \( \xi_{r,i}(t) \):
  
  number of moles produced by the \( i \)-th reaction
  
  \[
  \xi_{r,i}(t) = \frac{1}{v_{s,i}} \dot{n}_s = r_{v,i}(t) \quad \xi_{r,i}(0) = 0
  \]

- **Vessel extent of the** \( i \)-th reaction \( x_{r,i}(t) \):
  
  number of moles produced by the \( i \)-th reaction still in vessel
  
  \[
  \dot{x}_{r,i}(t) = r_{v,i}(t) - \frac{u_{\text{out}}(t)}{m(t)} x_{r,i}(t) \quad x_{r,i}(0) = 0
  \]

N. Bhatt, PhD dissertation n°5028 (2011), EPFL, Switzerland
Definitions

Extent vs vessel extent of mass transfer

- **Extent of the** $j$-th **mass transfer** $\xi_{m,j}(t)$:
  mass transferred by the $j$-th mass transfer

  **Differential extent of mass transfer**
  
  \[
  \dot{\xi}_{m,j}(t) = \xi_j(t) \quad \xi_{m,j}(0) = 0
  \]

- **Vessel extent of the** $j$-th **mass transfer** $x_{m,j}(t)$:
  mass transferred by the $j$-th mass transfer still in vessel

  **Differential vessel extent of mass transfer**
  
  \[
  \dot{x}_{m,j}(t) = \xi_j(t) - \frac{u_{out}(t)}{m(t)} x_{m,j}(t) \quad x_{m,j}(0) = 0
  \]

N. Bhatt, PhD dissertation n°5028 (2011), EPFL, Switzerland
General concept of vessel extent

A vessel extent indicates the amount of material (number of moles, mass, volume), associated with one phenomenon, that is still in the vessel...

Differential vessel extent (\(i\)-th phenomenon \(f\))

\[
\dot{x}_{f,i}(t) = \dot{\xi}_{f,i}(t) - \frac{u_{out}(t)}{m(t)} x_{f,i}(t) \quad \quad x_{f,i}(0) = 0
\]

N. Bhatt, PhD dissertation n°5028 (2011), EPFL, Switzerland
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Homogeneous reaction systems

Mole balance equations

Homogeneous reaction system consisting of $S$ species, $R$ independent reactions, $p$ independent inlets and one outlet

Mole balances for $S$ species

$$ \dot{n}(t) = N^T r_v(t) + W_{in} u_{in}(t) - \frac{u_{out}(t)}{m(t)} n(t), \quad n(0) = n_0 $$

Mass, volume and concentrations

$$ m(t) = 1^T_S M_w n(t), \quad V(t) = \frac{m(t)}{\rho(t)}, \quad c(t) = \frac{n(t)}{V(t)} $$

Amrhein et al, AIChE J. 56 (2010) 2873
Homogeneous reaction systems
Decomposition in variants and invariants

- Condition: \( \text{rank}(\begin{bmatrix} N^T & W_{in} & n_0 \end{bmatrix}) = R + p + 1 \)

- Vessel extents (variants) and \( q = S - R - p - 1 \) redundant information (invariants)

\[
\begin{align*}
\dot{x}_r(t) &= R N^T r_v(t) + R W_{in} u_{in}(t) - \frac{u_{out}(t)}{m(t)} x_r(t), \quad x_r(0) = 0_R \\
\dot{x}_{in}(t) &= F N^T r_v(t) + F W_{in} u_{in}(t) - \frac{u_{out}(t)}{m(t)} x_{in}(t), \quad x_{in}(0) = 0_p \\
\dot{x}_{ic}(t) &= q N^T r_v(t) + q W_{in} u_{in}(t) - \frac{u_{out}(t)}{m(t)} (1 + x_{ic}(t)), \quad x_{ic}(0) = 0 \\
\dot{x}_{iv}(t) &= Q N^T r_v(t) + Q W_{in} u_{in}(t) - \frac{u_{out}(t)}{m(t)} \dot{x}_{iv}(t), \quad x_{iv}(0) = 0_q
\end{align*}
\]

Amrhein et al, AIChE J. 56 (2010) 2873
Homogeneous reaction systems
Decomposition in variants and invariants

- **Condition:** \( \text{rank} \left( \left[ N^{T} W_{\text{in}} n_{0} \right] \right) = R + p + 1 \)

\[
\begin{bmatrix}
x_{r}(t) \\
x_{\text{in}}(t) \\
x_{\text{ic}}(t) \\
x_{\text{iv}}(t)
\end{bmatrix} \Leftrightarrow \begin{bmatrix} R \\ F \\ q^{T} \\ Q \end{bmatrix} (n(t) - n_{0})
\]

- **Vessel extents (variants) and** \( q = S - R - p - 1 \) **redundant information (invariants)**

\[
\begin{align*}
\dot{x}_{r}(t) &= r_{v}(t) - \frac{u_{\text{out}}(t)}{m(t)} x_{r}(t), \\
\dot{x}_{\text{in}}(t) &= u_{\text{in}}(t) - \frac{u_{\text{out}}(t)}{m(t)} x_{\text{in}}(t), \\
\dot{x}_{\text{ic}}(t) &= -\frac{u_{\text{out}}(t)}{m(t)} - \frac{u_{\text{out}}(t)}{m(t)} x_{\text{ic}}(t), \\
x_{\text{iv}}(t) &= 0_{q}
\end{align*}
\]

\[
x_{r}(0) = 0_{R}, \quad x_{\text{in}}(0) = 0_{p}, \quad x_{\text{ic}}(0) = 0
\]

- **Reconstruction:** \( (n(t) - n_{0}) \cong N^{T} x_{r}(t) + W_{\text{in}} x_{\text{in}}(t) + n_{0} x_{\text{ic}}(t) \)

Amrhein et al, AIChE J. 56 (2010) 2873
Homogeneous reaction systems
Orthogonal spaces in 4-way decomposition

\[
\begin{align*}
\text{space of initial conditions} & \quad n_0 q^T \\
\text{space of reaction extents} & \quad N^T R \\
\text{space of invariants} & \quad Q Q^T \\
\text{space of inlet extents} & \quad W_{in} F \\
\text{S-dim space of the number of moles} & \quad \mathbb{R}^1, \mathbb{R}^q, \mathbb{R}^R, \mathbb{R}^T, \mathbb{R}^p
\end{align*}
\]

Amrhein et al, AIChE J. 56 (2010) 2873
Homogeneous reaction systems
Transformation to RV form

- When \( \operatorname{rank}\left(\begin{bmatrix} \mathbf{N}^T & \mathbf{W}_{\text{in}} & \mathbf{n}_0 \end{bmatrix}\right) < R + p + 1 \) (\( u_{\text{in}}(t) \) and \( u_{\text{out}}(t) \) known), the numbers of moles are rearranged in Reaction Variant (RV) form:

\[
\mathbf{n}^{\text{RV}}(t) = \mathbf{N}^T \mathbf{x}_r(t) = \mathbf{n}(t) - \mathbf{W}_{\text{in}} \mathbf{x}_{\text{in}}(t) - \mathbf{n}_0 \left(1 + \mathbf{x}_{\text{ic}}(t)\right)
\]

- The \( R \) vessel extents of reaction are then computed as:

\[
\mathbf{x}_r(t) = \left(\mathbf{N}^T\right)^+ \mathbf{n}^{\text{RV}}(t)
\]
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  ○ Perspectives: distributed reaction systems
Kinetic investigation
From measurements to rate expressions

1. Simultaneous approach
2. Incremental approach (rate-based)
3. Incremental approach (extent-based)

Incremental model identification
Extent-based method

- The kinetic problem is decomposed into sub-problems of lower complexity that are solved individually.

- The model identification proceeds in two steps:
  - Transformation to extents (v+iv)
    Computation of the contribution of each dynamic effect (reaction, inlets and outlets) as extents
  - Model identification (Parameter estimation)
    Individual model identification of each effect from its corresponding extent with the integral method of parameter estimation.
Extent-based model identification
Model identification and parameter estimation

A dynamic model is postulated for each extent of interest and a regression problem is solved individually using the integral method of parameter estimation.

Example: fitting of $R$ extents of reaction

![Graph showing extent of reaction over time](image-url)
Extent-based model identification
Model identification and parameter estimation

A dynamic model is postulated for each extent of interest and a regression problem is solved individually using the integral method of parameter estimation.

Example: fitting of $R$ extents of reaction

$$\min_{\theta_{r,i}} \left\| x_{r,i}(t) - \hat{x}_{r,i}(t, \theta_{r,i}) \right\|^2$$

s.t. $$\dot{\hat{x}}_{r,i}(t, \theta_{r,i}) = r_{v,i}(t, \theta_{r,i}) - \frac{u_{out}(t)}{m(t)} \hat{x}_{r,i}(t), \quad \hat{x}_{r,i}(0) = 0$$

$$\theta_{r,i}^L \leq \theta_{r,i} \leq \theta_{r,i}^U$$

Homogeneous reaction systems
Ethanolysis of phthalyl chloride in a CSTR

Ethanolysis of phthalyl chloride (A) comprising seven species ($S = 7$), three reactions ($R = 3$), two inlets ($p = 2$) and 1 outlet

$$\begin{align*}
N &= \begin{bmatrix}
-1 & -1 & 1 & 1 & 0 & 0 & 0 \\
0 & -1 & -1 & 1 & 1 & 0 & 0 \\
0 & -1 & 0 & -1 & 0 & 1 & 1 \\
\end{bmatrix} \\
W_{in} &= \begin{bmatrix}
w_{in,A} & 0 & 0 & 0 & 0 & 0 & 0 \\
w_{in,B} & 0 & 0 & 0 & 0 & 0 & 0 \\
\end{bmatrix}^T
\end{align*}$$

A + B $\rightarrow$ C + D
C + B $\rightarrow$ E + D
$D + B \leftrightarrow F + G$

Extents of reaction?

N. Bhatt, PhD dissertation n°5028 (2011), EPFL, Switzerland
Homogeneous reaction systems
Ethanolysis of phthalyl chloride in a CSTR

\[ R = 3 \text{ Extents of reaction} \]

\[ \mathbf{N}, W_{\text{in}}, n_0 \]

Number of moles

Each extent of reaction can then be modeled individually, that is, independently from all the other phenomena / extents…
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Fluid-Fluid reaction systems

Mole balance equations

Fluid-Fluid reaction system consisting of:

- **Phase L**: \( S_\ell \) species with \( R_\ell \) reactions, \( P_m \) mass transfers, \( P_\ell \) inlets and 1 outlet
- **Phase G**: \( S_g \) species with \( R_g \) reactions, \( P_m \) mass transfers, \( P_g \) inlets and 1 outlet

Mass transfer described by various models…

Mole balances on phase \( B \)

\( R_b \) reactions, \( P_m \) mass transfers, \( P_b \) inlets, 1 outlet

\[
\dot{n}_b(t) = N_b^T \mathbf{r}_{v,b}(t) \pm W_{m,b} \zeta_b(t) + W_{in,b} \mathbf{u}_{in,b}(t) - \frac{u_{out,b}(t)}{m_b(t)} n_b(t), \quad n_b(0) = n_{0,b}
\]

\( (S_b \times 1) \) \( (S_b \times R_b)(R_b \times 1) \) \( (S_b \times P_m)(P_m \times 1) \) \( (S_b \times P_b)(P_b \times 1) \) \( (S_b \times 1) \)

Fluid-Fluid reaction systems
Decomposition in variants and invariants

- Condition: \( \text{rank} \left( \begin{bmatrix} N_b^T & W_{m,b} & W_{in,b} & n_{0,b} \end{bmatrix} \right) = R_b + P_m + p_b + 1 \)

\[
\begin{bmatrix}
  x_r (t) \\
  x_m (t) \\
  x_{in} (t) \\
  x_{ic} (t) \\
  x_{iv} (t)
\end{bmatrix} = \begin{bmatrix}
  R_b \\
  M_b \\
  F_b \\
  q_b^T \\
  Q_b
\end{bmatrix} \left( n_b (t) - n_{0,b} \right) \quad b \in \{ \ell, g \}
\]

- Vessel extents (variants) and \( q_b = S_b - R_b - P_m - p_b - 1 \) invariants

\[
\begin{align*}
  \dot{x}_{r,b} (t) &= R_b N_b^T r_{v,b} (t) \pm R_b W_{m,b} \zeta_b (t) + R_b W_{in,b} u_{in,b} (t) - \frac{u_{out,b}(t)}{m_b(t)} x_{r,b} (t), \quad x_{r,b} (0) = 0_{R_b} \\
  \dot{x}_{m,b} (t) &= M_b N_b^T r_{v,b} (t) \pm M_b W_{m,b} \zeta_b (t) + M_b W_{in,b} u_{in,b} (t) - \frac{u_{out,b}(t)}{m_b(t)} x_{m,b} (t), \quad x_{in,b} (0) = 0_{p_m} \\
  \dot{x}_{in,b} (t) &= F_b N_b^T r_{v,b} (t) \pm F_b W_{m,b} \zeta_b (t) + F_b W_{in,b} u_{in,b} (t) - \frac{u_{out,b}(t)}{m_b(t)} x_{in,b} (t), \quad x_{in,b} (0) = 0_{p_b} \\
  \dot{x}_{ic,b} (t) &= q_b^T N_b^T r_{v,b} (t) \pm q_b^T W_{m,b} \zeta_b (t) + q_b^T W_{in,b} u_{in,b} (t) - \frac{u_{out,b}(t)}{m_b(t)} (1 + x_{ic,b} (t)), \quad x_{ic,b} (0) = 0
\end{align*}
\]
Fluid-Fluid reaction systems
Decomposition in variants and invariants

- Condition: \( \text{rank} \left( \begin{bmatrix} N_b^T & W_{m,b} & W_{in,b} & n_{0,b} \end{bmatrix} \right) = R_b + P_m + p_b + 1 \)

\[
\begin{bmatrix}
\dot{x}_r(t) \\
\dot{x}_m(t) \\
\dot{x}_{in}(t) \\
\dot{x}_{ic}(t) \\
\dot{x}_{iv}(t)
\end{bmatrix} = \mathcal{L}_b
\begin{bmatrix}
R_b \\
M_b \\
F_b \\
q_b \\
Q_b
\end{bmatrix}
\begin{bmatrix}
(n_b(t) - n_{0,b})
\end{bmatrix} \quad b \in \{\ell, g\}
\]

- Vessel extents (variants) and \( q_b = S_b - R_b - P_m - p_b - 1 \) invariants

\[
\begin{align*}
\dot{x}_{r,b}(t) &= r_{v,b}(t) - \frac{u_{out,b}(t)}{m_b(t)} x_{r,b}(t), & x_{r,b}(0) &= 0_{R_b} \\
\dot{x}_{m,b}(t) &= \zeta_{b}(t) - \frac{u_{out,b}(t)}{m_b(t)} x_{m,b}(t), & x_{in,b}(0) &= 0_{P_m} \\
\dot{x}_{in,b}(t) &= u_{in,b}(t) - \frac{u_{out}(t)}{m_b(t)} x_{in,b}(t), & x_{in,b}(0) &= 0_{P_b} \\
\dot{x}_{ic,b}(t) &= -\frac{u_{out,b}(t)}{m_b(t)} - \frac{u_{out,b}(t)}{m_b(t)} x_{ic,b}(t), & x_{ic,b}(0) &= 0 \\
\end{align*}
\]

with \( x_{iv,b}(t) = 0_{q_b} \)

\[
(n_b(t) - n_{0,b}) \overset{\mathcal{L}_b^{-1}}{=} N_b^T x_{r,b}(t) \pm W_{m,b} x_{m,b}(t) + W_{in,b} x_{in,b}(t) + n_{0,b} x_{ic,b}(t)
\]
Fluid-Fluid reaction systems
Orthogonal spaces in 5-way decomposition

space of initial conditions

space of reaction extents

space of mass-transfer extents

space of invariants

space of inlet extents

$S_b$-dim space of the number of moles in phase $B$

Fluid-Fluid reaction systems
Transformation to RMV form

○ When \( \text{rank} \left( \begin{bmatrix} N_b^T & W_{m,b} & W_{in,b} & n_{0,b} \end{bmatrix} \right) < R_b + P_m + p_b + 1 \) (\( u_{in,b}(t) \) and \( u_{out,b}(t) \) known), the numbers of moles are rearranged in Reaction Mass-transfer Variant (RMV) form:

\[
\begin{align*}
  n_b^{\text{RMV}}(t) &= N^T x_{r,b}(t) \pm W_{m,b} x_{m,b}(t) = \begin{bmatrix} N^T & \pm W_{m,b} \end{bmatrix} \begin{bmatrix} x_{r,b}(t) \\ x_{m,b}(t) \end{bmatrix} \\
  &= n_b(t) - W_{in,b} x_{in,b}(t) - n_{0,b} \left( 1 + x_{ic,b}(t) \right)
\end{align*}
\]

○ The \( R_b \) vessel extents of reaction and \( P_m \) extents of mass transfer are then computed as:

\[
\begin{bmatrix} x_{r,b}(t) \\ x_{m,b}(t) \end{bmatrix} = \left[ N^T \pm W_{m,b} \right]^+ n_b^{\text{RMV}}(t)
\]
Chlorination of butanoic acid comprises $S_\ell = 5$ (BA, MBA, DBA, Cl$_2$, HCl) and $S_g = 3$ (Cl$_2$, HCl, air) species, $R_\ell = 2$ reactions, $p_\ell = 1$ and $p_g = 1$ inlets and 2 outlets.

\[
\begin{align*}
\text{Phase } G & : \text{Cl}_2, \text{HCl}, \text{Air} \\
\text{Phase } L & : \text{BA, MBA, DBA, Cl}_2, \text{HCl}
\end{align*}
\]

\[
\begin{align*}
BA + Cl_2 & \xrightarrow{\text{cat}} MBA + HCl & \text{(R1)} \\
BA + 2Cl_2 & \xrightarrow{\text{cat}} DBA + HCl & \text{(R2)}
\end{align*}
\]

Extents of reaction?  

N. Bhatt, PhD dissertation n°5028 (2011), EPFL, Switzerland
Fluid-Fluid reaction systems
Chlorination of butanoic acid in a CSTR

\[ T \begin{bmatrix} R_m \\ M_m \end{bmatrix} = T \begin{bmatrix} R_m \\ M_m \end{bmatrix} + T \begin{bmatrix} q_m \\ Q_m \end{bmatrix} \]

Number of moles in liquid phase

\[ N_l, W_m, W_{in}, n_0, \ell \]

\[ R = 2 \text{ Extents of reaction} \]

\[ p_m = 2 \text{ Extents of m.t.} \]

N. Bhatt, PhD dissertation n°5028 (2011), EPFL, Switzerland
Fluid-Fluid reaction systems
Chlorination of butanoic acid in a CSTR

○ Identification of the rate expression for the main reaction R1

○ Rate expression candidates

\[
\begin{align*}
    r_1^{(1)} &= k_1 \ c_{\ell,BA} \ c_{\ell,Cl_2} \\
    r_1^{(2)} &= k_1 \ c_{\ell,Cl_2} \\
    r_1^{(3)} &= k_1 \ c_{\ell,BA} \ c_{\ell,Cl_2} \ c_{\ell,MBA} \\
    r_1^{(4)} &= k_1 \ c_{\ell,BA} \ c_{\ell,Cl_2} \ \sqrt{c_{\ell,MBA}}
\end{align*}
\]

○ Identified rate expression

\[
\begin{align*}
    r_1^{(4)} &= 1.3543 \ c_{\ell,BA} \ c_{\ell,Cl_2} \ \sqrt{c_{\ell,MBA}}
\end{align*}
\]
Fluid-Fluid reaction systems
Chlorination of butanoic acid in a CSTR

- Identified rate expressions

\[ r_1 = k_1 c_{\text{BA}} c_{\ell,\text{Cl}_2} \sqrt{c_{\ell,\text{MBA}}} \]
\[ r_2 = k_2 r_1 c_{\ell,\text{Cl}_2} \]
\[ \zeta_{\text{Cl}_2} = k_{\text{Cl}_2} A_s V_\ell M_{w,\text{Cl}_2} (c_{\text{Cl}_2}^* - c_{\ell,\text{Cl}_2}) \]
\[ \zeta_{\text{HCl}} = k_{\text{HCl}} A_s V_\ell M_{w,\text{HCl}} (c_{\ell,\text{HCl}} - c_{\text{HCl}}^*) \]

- Results of curve fitting (2% noise level)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Simulated value</th>
<th>Estimated value</th>
<th>95% Confidence interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1)</td>
<td>1.3577</td>
<td>1.3543</td>
<td>[1.3207 – 1.3879]</td>
</tr>
<tr>
<td>(k_2)</td>
<td>0.1</td>
<td>0.105</td>
<td>[0.0884 – 0.1216]</td>
</tr>
<tr>
<td>(k_{\text{Cl}_2})</td>
<td>0.666\cdot10^{-4}</td>
<td>0.594\cdot10^{-4}</td>
<td>[0.514\cdot10^{-4} – 0.674\cdot10^{-4}]</td>
</tr>
<tr>
<td>(k_{\text{HCl}})</td>
<td>0.845\cdot10^{-4}</td>
<td>0.813\cdot10^{-4}</td>
<td>[0.763\cdot10^{-4} – 0.863\cdot10^{-4}]</td>
</tr>
</tbody>
</table>

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Recent extensions
Rank augmentation of conc. data by calorimetry

○ Homogeneous reaction systems

\[
\mathbf{n}_{\text{aug}}^{\text{RV}}(t) := \begin{bmatrix} \mathbf{n}_{a}^{\text{RV}}(t) \\ Q_r(t) \end{bmatrix} = \begin{bmatrix} \mathbf{N}_{a}^{T} \\ -\Delta H_{r}^{T} \end{bmatrix} \mathbf{x}_{r}(t) := \mathbf{N}_{\text{aug}}^{T} \mathbf{x}_{r}(t)
\]

\[
\mathbf{x}_{r}(t) = \left(\mathbf{N}_{\text{aug}}^{T}\right)^{+} \mathbf{n}_{\text{aug}}^{\text{RV}}(t)
\]

○ Fluid-Fluid reaction systems

\[
\mathbf{n}_{\text{aug}}^{\text{RMV}}(t) := \begin{bmatrix} \mathbf{n}_{\ell,a}^{\text{RMV}}(t) \\ Q_{rm}(t) \end{bmatrix} = \begin{bmatrix} \mathbf{N}_{\ell,a}^{T} \\ -\Delta H_{r,\ell}^{T} & -\Delta H_{m,\ell}^{T} \end{bmatrix} \begin{bmatrix} \mathbf{x}_{r,\ell}(t) \\ \mathbf{x}_{m,\ell}(t) \end{bmatrix} := \mathbf{N}_{\ell,\text{aug}}^{T} \begin{bmatrix} \mathbf{x}_{r,\ell}(t) \\ \mathbf{x}_{m,\ell}(t) \end{bmatrix}
\]

\[
\begin{bmatrix} \mathbf{x}_{r,\ell}(t) \\ \mathbf{x}_{m,\ell}(t) \end{bmatrix} = \left(\mathbf{N}_{\ell,\text{aug}}^{T}\right)^{+} \mathbf{n}_{\text{aug}}^{\text{RMV}}(t)
\]

Recent extensions
Construction of calibration models in spectroscopy

\[
\begin{align*}
&\text{Required measurements} \\
&\begin{aligned}
&\left( C_{l,\text{cal}}, A_{\text{cal}} \right) \\
&\mathcal{S}_{\text{cal}}^{\text{RMV}} \\
&c_{g,\text{cal}}(t)
\end{aligned} \\
&\text{RMV} \\
&\mathcal{S}_{\text{cal}}^{\text{RV}} \\
&\text{CAL} \\
&\mathcal{F}^{\text{RMV}} \\
&\text{CAL} \\
&\mathcal{F}^{\text{RV}} \\
&\left( C_{l,\text{cal}}, A_{\text{cal}} \right) \\
&\text{Calibration model}
\end{align*}
\]

RMV, RV : transformation to RMV-, RV-form
CAL : construction of calibration model
\[
\mathcal{S}_{\text{cal}}^{\text{RMV}} = \{u_{\text{in},l,\text{cal}}(t), u_{\text{out},l,\text{cal}}(t), m_{l,\text{cal}}(t), V_{l,\text{cal}}(t), W_{\text{in},l,\text{cal}}, n_{0,\text{cal}}, A_{\text{in,cal}}, a_{0,\text{cal}}\}
\]
\[
\mathcal{S}_{\text{cal}}^{\text{RV}} = \{u_{\text{in},f,\text{cal}}(t), u_{\text{out},f,\text{cal}}(t), m_{f,\text{cal}}(t), V_{f,\text{cal}}(t), W_{\text{in},f,\text{cal}}, W_{\text{in},f,\text{cal}}, n_{0,\text{cal}}, A_{\text{in,cal}}, a_{0,\text{cal}}, A_{m,\text{cal}}\}
\]
Recent extensions
Prediction of concentrations from spectral data

\[ \begin{align*}
\text{Required measurements} & \quad \text{Predicted concentrations of calibrated species} & \quad \text{Predicted extents} & \quad \text{Predicted concentrations} \\
RMV & \quad a_{RMV}(t) & \quad F_{RMV} & \quad \hat{e}_{l,c}^{RMV}(t) & \quad L_{RMV} & \quad \left( \begin{array}{c}
\hat{x}_r(t) \\
\hat{x}_{m,i}(t) 
\end{array} \right) & \quad R_{RMV} & \quad \hat{e}_l(t) \\
& \quad S_{RMV}^1 & & & & \\
& \quad S_{RMV}^2 & & & & \\
\text{RV} & \quad a_{RV}(t) & \quad F_{RV} & \quad \hat{e}_{l,c}^{RV}(t) & \quad L_{RV} & \quad \left( \begin{array}{c}
\hat{x}_r(t) \\
\hat{x}_{m,i}(t) \\
\hat{\lambda}_i(t)
\end{array} \right) & \quad R_{RV} & \quad \hat{e}_l(t) \\
& \quad S_{RV}^1 & & & & \\
& \quad S_{RV}^2 & & & & \\
& \quad c_g(t) & & & & \\
\end{align*} \]

- \( F \), \( F_{RV}, F_{RMV} \): prediction via calibration
- \( L, L_{RV}, L_{RMV} \): linear transformation to extents
- \( R, R_{RV}, R_{RMV} \): reconstruction of all concentrations from extents
- RMV, RV: transformation to RMV-, RV-form

- \( S_{RMV}^1 = \{u_{in,i}(t), u_{out,i}(t), m_i(t), V_i(t), W_{in,i}, u_0\} \)
- \( S_{RMV}^2 = \{A_{in}, a_0\} \)
- \( S_{RV}^1 = \{u_{in,f}(t), u_{out,f}(t), m_f(t), V_f(t), W_{in,f}, W_{in,f}, n_{f0}\} \), where \( f \in \{g,l\} \)
- \( S_{RV}^2 = \{A_{int}, A_{in}, a_0\} \)
Outline

✓ Motivation
✓ Concept of vessel extent
✓ Homogeneous reaction systems
✓ Incremental model identification
✓ Fluid-Fluid reaction systems
✓ Extensions to calorimetry and spectroscopy

○ Perspectives: distributed reaction systems
Perspectives
Distributed reaction systems

Bonvin et al, TFMST, Lyon, July 13–16, 2013 (to be published)
**Perspectives**

**Distributed reaction systems**

How to decouple reaction, convection and diffusion phenomena?

PDE: \[ \frac{d}{dt} \mathbf{c}(t, x) = N^T \mathbf{r}(t, x) - v_x \frac{d}{dx} \mathbf{c}(t, x) + D \frac{d^2}{dx^2} \mathbf{c}(t, x), \]

How to decouple reaction, convection and diffusion phenomena?

- \( \mathbf{c}(0, x) = \mathbf{c}_{t=0}(x) \) (IC)
- \( \mathbf{c}(t, 0) = \mathbf{c}_{x=0}(t) \) (BC)
- \( \mathbf{c}(t, \delta) = \mathbf{c}_{x=L}(t) \) (BC)
Laboratoire d’Automatique

Prof. Bonvin, Prof. Longchamp, Prof. Jones, Dr. MER Karimi
6 Postdocs + 20 PhD students + technical / administrative staff
Model reduction
- M. Amrhein, PhD dissertation n°1861 (1998), EPFL, Switzerland

Transformation to variants/invariants (extents)
- N. Bhatt, PhD dissertation n°5028 (2011), EPFL, Switzerland
- Amrhein et al, AIChE J. 56 (2010) 2873
- Bonvin et al, TFMST, Lyon, July 13–16, 2013 (to be published)

Incremental model identification

Rank augmentation by calorimetric data

Incremental kinetic modeling of spectroscopic data