

# Incremental model identification of reaction systems

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- Models of reaction systems and concept of extents
  - Homogeneous reaction systems
  - Distributed reaction systems
  - Generalization to other reaction systems
  - Applications of extents
- Model identification
  - Simultaneous model identification
  - Incremental model identification
  - Example
- Conclusions

# Homogeneous reaction systems

## Balance equations

Nonisothermal homogeneous reaction system consisting of  $S$  species,  $R$  independent reactions,  $p$  inlet streams, and  $1$  outlet stream

### Mole balances for $S$ species

$$\dot{\mathbf{n}}(t) = \mathbf{N}^T \mathbf{r}_v(t) + \mathbf{W}_{in} \mathbf{u}_{in}(t) - \omega(t) \mathbf{n}(t), \quad \mathbf{n}(0) = \mathbf{n}_0$$

$$(S) \quad (S \times R) \quad (R) \quad (S \times p) \quad (p) \quad \mathbf{r}_v(t) := V(t) \mathbf{r}(t), \quad \omega(t) := \frac{u_{out}(t)}{m(t)}$$

### Mass $m$ , volume $V$ and molar concentrations $\mathbf{c}$

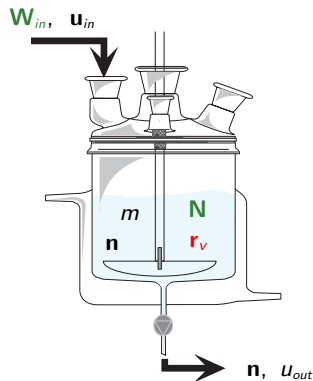
$$m(t) = \mathbf{1}_S^T \mathbf{M}_w \mathbf{n}(t), \quad V(t) = \frac{m(t)}{\rho(t)}, \quad \mathbf{c}(t) = \frac{\mathbf{n}(t)}{V(t)}$$

$$\dot{m}(t) = \mathbf{1}_p^T \mathbf{u}_{in}(t) - u_{out}(t), \quad m(0) = m_0$$

Global macroscopic view

Valid regardless of temperature, catalyst or solvent

Redundant information  $m(t)$



# Homogeneous reaction systems

Objective: Decoupled reaction system in terms of vessel extents

- S-dimensional model equations

$$\dot{\mathbf{n}}(t) = \mathbf{N}^T \mathbf{r}_v(t) + \mathbf{W}_{in} \mathbf{u}_{in}(t) - \omega(t) \mathbf{n}(t), \quad \mathbf{n}(0) = \mathbf{n}_0$$

- Decoupled reaction model in terms of vessel extents

$$\begin{aligned} \dot{x}_{r,i}(t) &= r_{v,i}(t) - \omega(t) x_{r,i}(t) & x_{r,i}(0) &= 0 & i &= 1, \dots, R \\ \dot{x}_{in,j}(t) &= u_{in,j}(t) - \omega(t) x_{in,j}(t) & x_{in,j}(0) &= 0 & j &= 1, \dots, p \\ \dot{x}_{ic}(t) &= -\omega(t) x_{ic}(t) & x_{ic}(0) &= 1 \end{aligned}$$

- **Vessel extents** are extents discounted by the amount of material that has left the reactor
- System of dimension  $d := (R + p + 1)$
- Only apparent decoupling as  $r_{v,i}(t)$  is an **endogenous input** and not an independent input!

# Homogeneous reaction systems

Procedure: Four-way decomposition into extents and invariants<sup>1</sup>

- Model **with zero initial conditions**

$$\dot{\mathbf{n}}(t) = \mathbf{N}^T \mathbf{r}_v(t) + \mathbf{W}_{in} \mathbf{u}_{in}(t) + \mathbf{n}_0 \delta(t) - \omega(t) \mathbf{n}(t), \quad \mathbf{n}(0) = \mathbf{0}_s$$

- Assumption:  $\text{rank}([\mathbf{N}^T \ \mathbf{W}_{in} \ \mathbf{n}_0]) = R + p + 1$ . Linear transformation

$$\begin{bmatrix} \mathbf{x}_r(t) \\ \mathbf{x}_{in}(t) \\ x_{ic}(t) \\ \mathbf{x}_{iv}(t) \end{bmatrix} = \mathcal{T} \mathbf{n}(t) \quad \mathcal{T} = [\mathbf{N}^T \ \mathbf{W}_{in} \ \mathbf{n}_0 \ \mathbf{P}]^{-1} \quad [\mathbf{N}^T \ \mathbf{W}_{in} \ \mathbf{n}_0]^T \mathbf{P} = \mathbf{0}_{d \times q}$$

- Vessel extents** of reaction  $\mathbf{x}_r$ , inlet  $\mathbf{x}_{in}$ , initial conditions  $x_{ic}$ , and invariants  $\mathbf{x}_{iv}$

$$\dot{\mathbf{x}}_r(t) = \mathbf{r}_v(t) - \omega(t) \mathbf{x}_r(t) \quad \mathbf{x}_r(0) = \mathbf{0}_R$$

$$\dot{\mathbf{x}}_{in}(t) = \mathbf{u}_{in}(t) - \omega(t) \mathbf{x}_{in}(t) \quad \mathbf{x}_{in}(0) = \mathbf{0}_p$$

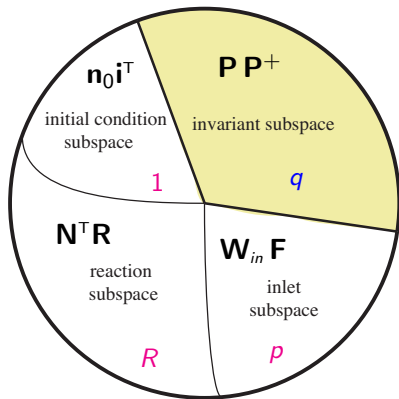
$$\dot{x}_{ic}(t) = -\omega(t) x_{ic}(t) \quad x_{ic}(0) = 1$$

$$\mathbf{x}_{iv}(t) = \mathbf{0}_q$$

<sup>1</sup>Rodrigues, D. et al. *Comp. Chem. Eng.* **2015**, *73*, 23–33.

# Homogeneous reaction systems

Four subspaces, transformation possible if  $S \geq R + p + 1$



S-dimensional space of species

$d = R + p + 1$  variants

$q = S - R - p - 1$  invariants

$$\mathcal{T} = \begin{bmatrix} \mathbf{R} \\ \mathbf{F} \\ \mathbf{i}^T \\ \mathbf{P}^+ \end{bmatrix} = [\mathbf{N}^T \ \mathbf{W}_{in} \ \mathbf{n}_0 \ \mathbf{P}]^{-1}$$

$$\begin{bmatrix} \mathbf{x}_r(t) \\ \mathbf{x}_{in}(t) \\ x_{ic}(t) \\ \mathbf{x}_{iv}(t) \end{bmatrix} = \mathcal{T} \mathbf{n}(t)$$

$$\mathbf{n}(t) = \mathbf{N}^T \mathbf{x}_r(t) + \mathbf{W}_{in} \mathbf{x}_{in}(t) + \mathbf{n}_0 x_{ic}(t)$$

$$\mathbf{x}_{iv}(t) = \mathbf{P}^+ \mathbf{n}(t) = \mathbf{0}_q$$

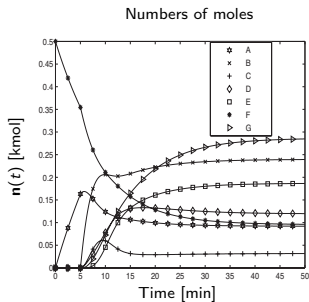
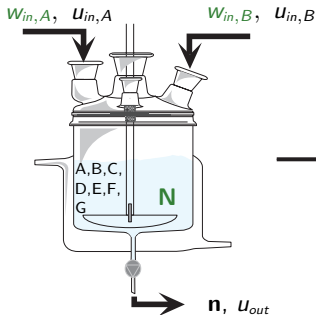
# Homogeneous reaction systems

Example: Ethanolysis reaction in an homogeneous CSTR

- Seven species ( $S = 7$ ), three reactions ( $R = 3$ ), two inlets ( $p = 2$ ) and one outlet
- Stoichiometric matrix  $\mathbf{N}$ , inlet-composition matrix  $\mathbf{W}_{in}$  and initial conditions  $\mathbf{n}_0$ :

$$\mathbf{N} = \begin{bmatrix} -1 & -1 & 1 & 1 & 0 & 0 & 0 \\ 0 & -1 & -1 & 1 & 1 & 0 & 0 \\ 0 & -1 & 0 & -1 & 0 & 1 & 1 \end{bmatrix}$$

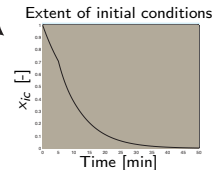
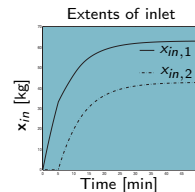
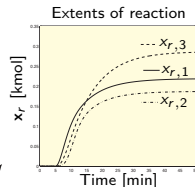
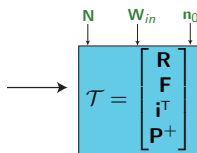
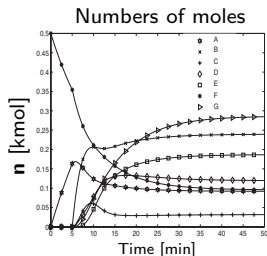
$$\mathbf{W}_{in} = \begin{bmatrix} w_{in,A} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & w_{in,B} & 0 & 0 & 0 & 0 & 0 \end{bmatrix}^T \quad \mathbf{n}_0$$



Reaction extents?

# Homogeneous reaction systems

Example: Computation of extents



- Fewer extents than numbers of moles

- Extents are more prone to have mathematically well-defined shapes such as monotonicity, convexity/concavity

One invariant  $x_{iv}(t) = P^+ n(t) = 0$



# Distributed reaction systems

## Plug-flow reactor: balance equations<sup>2</sup>

- Mole balances for  $S$  species:

$$\frac{\partial \mathbf{c}(z, t)}{\partial t} + v \frac{\partial \mathbf{c}(z, t)}{\partial z} = \mathbf{N}^T \mathbf{r}(z, t), \quad \mathbf{c}(0, t) = \mathbf{c}_{in}(t), \quad \mathbf{c}(z, 0) = \mathbf{c}_0(z)$$

- To an observer sitting on a *particle* of velocity  $v$ ,  $\mathbf{c}(z, t)$  and  $\mathbf{r}(z, t)$  are viewed as  $\mathbf{c}_p(\tau)$  and  $\mathbf{r}_p(\tau)$ , with  $z = v\tau$  and  $t = \tau$ , where  $\tau$  is the time spent in the reactor up to position  $z$
- It follows that  $\frac{d\mathbf{c}_p}{d\tau} = \frac{\partial \mathbf{c}}{\partial z} \left( \frac{dz}{d\tau} \right) + \frac{\partial \mathbf{c}}{\partial t} \left( \frac{dt}{d\tau} \right) = \frac{\partial \mathbf{c}}{\partial z} v + \frac{\partial \mathbf{c}}{\partial t}$ , and the system of PDEs becomes a system of ODEs:

$$\frac{d}{d\tau} \mathbf{c}_p(\tau) = \mathbf{N}^T \mathbf{r}_p(\tau), \quad \mathbf{c}_p(0) = \mathbf{c}_{in}(0)$$

- Deviation variables  $\delta \mathbf{c}_p := \mathbf{c}_p - \mathbf{c}_{in}(0)$  without effect of boundary conditions:

$$\frac{d}{d\tau} \delta \mathbf{c}_p(\tau) = \mathbf{N}^T \mathbf{r}_p(\tau), \quad \mathbf{c}_p(0) = \mathbf{0}_S$$

<sup>2</sup>Rodrigues, D. et al. *Chem. Eng. Sci.* **2017**, submitted; Rodrigues, D. et al. In *IFAC ADCHEM'15*, Whistler, 2015.

# Distributed reaction systems

Plug-flow reactor: two-way decomposition<sup>3</sup>

- Let  $\text{rank}(\mathbf{N}^T) = R$  and consider the matrix  $\mathcal{T} = [\mathbf{N}^T \ \mathbf{P}]^{-1}$ , where  $\mathbf{NP} = \mathbf{0}_{R \times q}$ . Then,  $\mathcal{T}$  partitions  $\delta \mathbf{c}_p$  into two contributions:

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

- Dynamic equations:

$$\begin{aligned} \frac{d}{d\tau} \mathbf{x}_{p,r}(\tau) &= \mathbf{r}_p(\tau), & \mathbf{x}_{p,r}(0) &= \mathbf{0}_R \\ \mathbf{x}_{p,iv}(\tau) &= \mathbf{0}_q \end{aligned}$$

- Reconstruction:

$$\mathbf{c}_p(\tau) = \mathbf{N}^T \mathbf{x}_{p,r}(\tau) + \mathbf{c}_{in}(0)$$

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<sup>3</sup>Rodrigues, D. et al. In *IFAC ADCHEM'15*, Whistler, 2015

# Generalization to other reaction systems

- Homogeneous reaction systems with heat balance<sup>4</sup>
  - Additional heat balance equation
  - Additional decoupled extent of heat exchange
- Gas-liquid reaction systems<sup>5</sup>
  - Balance equations for both the gas and liquid phases
  - Additional decoupled extents of mass transfer
- Reaction systems with instantaneous equilibria<sup>6</sup>
  - Balance equations for components conserved by equilibria
  - Extents of kinetically controlled reactions

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<sup>4</sup>Rodrigues, D. et al. *Comp. Chem. Eng.* **2015**, *73*, 23–33.

<sup>5</sup>Bhatt, N. et al. *Ind. Eng. Chem. Res.* **2010**, *49*, 7704–7717.

<sup>6</sup>Srinivasan, S. et al. *Ind. Eng. Chem. Res.* **2016**, *55*, 8034–8045.

- **Linear state transformation**
  - From concentrations and temperatures to **decoupled extents**
  - Systematic generation of **invariant relationships**
- **Minimal dimensionality**
  - Redundant states can be eliminated → model-order reduction
  - Invariant relationships → algebraic constraints for data reconciliation
- **Decoupled states**
  - Each state is related to a single rate process
  - Rates can be identified individually → incremental approach with fewer parameters → global optimization
  - Possibility of having additional ( $0^{th}$ ,  $1^{st}$  and  $2^{nd}$ -order) constraints on the extents → improved data reconciliation, state estimation, ALS, etc.

- Useful for the investigation of reaction systems:
  - **Kinetic model identification**
    - State reconstruction via invariant relationships<sup>7</sup>
    - Data reconciliation via invariant relationships and shape constraints<sup>7</sup>
    - State estimation via invariant relationships and shape constraints<sup>8</sup>
    - Control via rate estimation<sup>9</sup>
    - Static RTO via rate estimation<sup>10</sup>
    - Model reduction via singular perturbation<sup>10</sup>
- Generally applicable
  - To most reaction systems and reactor types
  - In principle, to systems with more balance equations than rates

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<sup>7</sup>Srinivasan, S. et al. *Comp. Chem. Eng.* **2017**, *101*, 44–58.

<sup>8</sup>Srinivasan, S. et al. In *DYCOPS 2016*, Trondheim, 2016.

<sup>9</sup>Rodrigues, D. et al. In *PSE-12/ESCAPE-25*, Copenhagen, 2015.

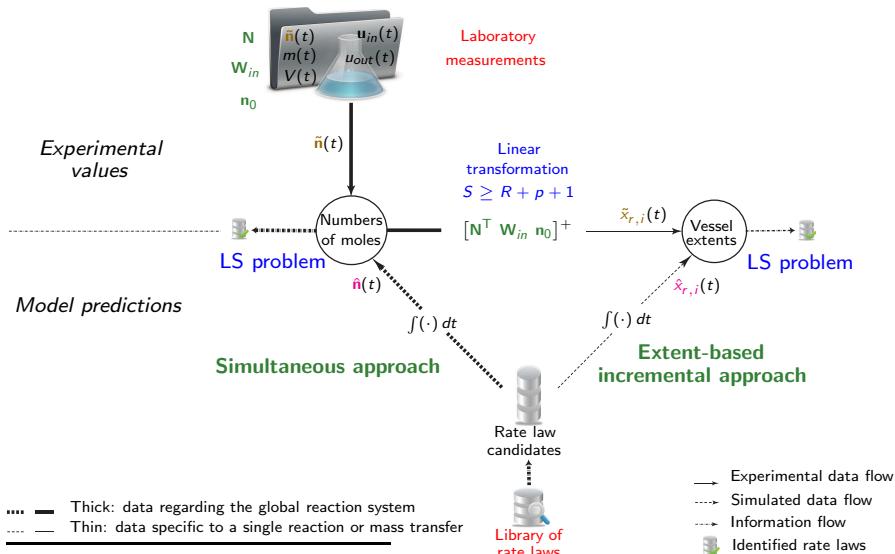
<sup>10</sup>Bonvin, D. et al. In *FOCAPO-CPC 2017*, Tucson, 2017.

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- Given **experimental** concentrations
- Identify unknown functions for the **reaction rates**
- Subject to a set of **candidate models** for all reactions

# Model identification

## Simultaneous and incremental approaches<sup>11</sup>



<sup>11</sup>Bhatt, N. et al. *Ind. Eng. Chem. Res.* **2011**, *50*, 12960–12974.



# Simultaneous model identification

- Define a model candidate for all rate processes
- Estimate parameters in the model by solving the following problem:

$$\begin{aligned} \min_{\theta} \quad & \sum_{h=1}^H \left( \tilde{\mathbf{n}}(t_h) - \hat{\mathbf{n}}(t_h, \theta) \right)^T \mathbf{W}(t_h) \left( \tilde{\mathbf{n}}(t_h) - \hat{\mathbf{n}}(t_h, \theta) \right) \\ \text{s.t.} \quad & \dot{\hat{\mathbf{n}}}(t, \theta) = \mathbf{N}^T \mathbf{V}(t) \mathbf{r}(\hat{\mathbf{c}}(t, \theta), \theta) + \mathbf{W}_{in} \mathbf{u}_{in}(t) - \omega(t) \hat{\mathbf{n}}(t, \theta), \quad \hat{\mathbf{n}}(0, \theta) = \mathbf{n}_0 \\ & \hat{\mathbf{c}}(t, \theta) = \frac{\hat{\mathbf{n}}(t, \theta)}{\mathbf{V}(t)} \end{aligned}$$

- Repeat the procedure for all combinations of model candidates
- The set of model candidates with the best fit is chosen

# Model identification

## Simultaneous and incremental approaches

- **Simultaneous model identification** leads to optimal parameter estimates in a maximum-likelihood sense for correct model structure
- But it is computationally costly:
  - The procedure must be repeated for all combinations of rate candidates
  - Convergence is difficult due to the large number of parameters
- **Rate-based incremental model identification** was initially proposed to identify the correct model structure efficiently<sup>12</sup>
- **Extent-based incremental model identification** provides tighter confidence intervals and improved model discrimination<sup>13</sup>

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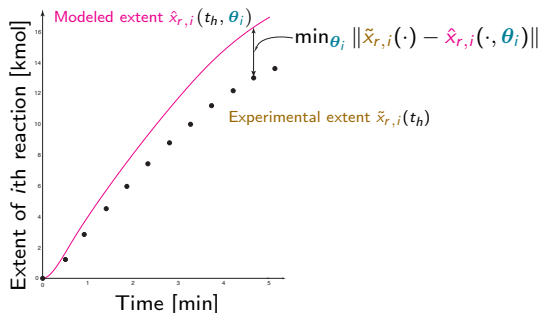
<sup>12</sup>Bardow, A.; Marquardt, W. *Chem. Eng. Sci.* **2004**, *59*, 2673–2684; Brendel, M. et al. *Chem. Eng. Sci.* **2006**, *61*, 5404–5420.

<sup>13</sup>Bhatt, N. et al. *Chem. Eng. Sci.* **2012**, *83*, 24–38.

# Incremental model identification

- For the  $i$ th reaction, estimation of kinetic parameters  $\theta_i$  by comparing the experimental extent  $\tilde{x}_{r,i}$  with the modeled extent  $\hat{x}_{r,i}$ , which approximates

$$\dot{x}_{r,i}(t) = V(t) r_i(\mathbf{c}(t), \theta_i) - \omega(t) x_{r,i}(t) \quad x_{r,i}(0) = 0.$$



- Experimental extent  $\tilde{x}_{r,i}(t_h)$  is given by a linear transformation of  $V(t_h)\tilde{\mathbf{c}}(t_h)$
- Requires measurements  $\tilde{\mathbf{c}}(t_h)$ ,  $V(t_h)$ ,  $\omega(t_h)$

# Incremental model identification (IMI<sub>n</sub>)

- Compute  $\mathbf{x}_r(t)$  for all  $R$  reactions
- Identify the model for each reaction individually<sup>14</sup>

$$\begin{aligned} \min_{\theta_i^{(m_i)}} J(\theta_i^{(m_i)}) &= \sum_{h=1}^H \left( \tilde{x}_{r,i}(t_h) - \hat{x}_{r,i}^{(m_i)}(t_h, \theta_i^{(m_i)}) \right) W_i(t_h) \left( \tilde{x}_{r,i}(t_h) - \hat{x}_{r,i}^{(m_i)}(t_h, \theta_i^{(m_i)}) \right) \\ \text{s.t. } \dot{\hat{x}}_{r,i}^{(m_i)}(t, \theta_i^{(m_i)}) &= V(t) \hat{f}_i^{(m_i)}(\tilde{\mathbf{c}}(t), \theta_i^{(m_i)}) - \omega(t) \hat{x}_{r,i}^{(m_i)}(t, \theta_i^{(m_i)}), \quad \hat{x}_{r,i}^{(m_i)}(0, \theta_i^{(m_i)}) = 0. \end{aligned}$$

- Model  $m_i$  with the least objective function is the best model
- Use simultaneous approach as final step for optimal parameter estimates

<sup>14</sup>Bhatt, N. et al. *Ind. Eng. Chem. Res.* **2011**, *50*, 12960–12974.

# Incremental model identification (IMI<sub>n</sub>)

## Simplified identification problem

- If a reaction rate law  $r$  is linear in  $L$  parameters  $\alpha$  and nonlinear in  $\theta$ :

$$r(\mathbf{c}(t), \alpha, \theta) = r_0(\mathbf{c}(t), \theta) + \sum_{\ell=1}^L \alpha_{\ell} r_{\ell}(\mathbf{c}(t), \theta)$$

- Assuming the  $i$ th reaction rate is  $r$ , the integral solution of  $x_{r,i}$  is:

$$x_{r,i}(t) = V(t)d_0(t) + \sum_{\ell=1}^L \alpha_{\ell} V(t)d_{\ell}(t),$$

where  $d_{\ell}(t) := \int_0^t \frac{V(\tau)}{V(t)} r_{\ell}(\mathbf{c}(\tau), \theta) e^{-\int_{\tau}^t \omega(\zeta) d\zeta} d\tau$  is estimated as  $\hat{d}_{\ell}(t_h, \theta)$  from  $\hat{r}_{\ell}(\tilde{\mathbf{c}}(t_h), \theta)$ ,  $V(t_h)$ ,  $\omega(t_h)$

- Modeled extent  $\hat{x}_{r,i}(t_h, \alpha, \theta) := V(t_h)\hat{d}_0(t_h, \theta) + \sum_{\ell=1}^L \alpha_{\ell} V(t_h)\hat{d}_{\ell}(t_h, \theta)$  is linear in  $\alpha$

# Incremental model identification (IMI<sub>n</sub>)

## Simplified identification problem

- The identification problem is

$$\min_{\alpha, \theta} J(\alpha, \theta) = \sum_{h=1}^H \frac{1}{H} \left( \frac{\hat{x}_{r,i}(t_h, \alpha, \theta) - \check{x}_{r,i}(t_h)}{V(t_h)} \right)^2$$

- The cost function is quadratic in  $\alpha$ :  $J(\alpha, \theta) = c(\theta) + 2\alpha^T \mathbf{g}(\theta) + \alpha^T \mathbf{H}(\theta) \alpha$
- The optimal parameters  $\alpha$  for each  $\theta$  are  $\hat{\alpha}(\theta) = -\mathbf{H}(\theta)^{-1} \mathbf{g}(\theta)$ , and the optimization problem is reformulated with only the decision variables  $\theta$ :

$$\min_{\theta} \bar{J}(\theta) = J(\hat{\alpha}(\theta), \theta) = c(\theta) - \mathbf{g}(\theta)^T \mathbf{H}(\theta)^{-1} \mathbf{g}(\theta)$$

- Problem with few decision variables, solved efficiently to global optimality<sup>15</sup>

<sup>15</sup>Rodrigues, D. et al. In *ESCAPE-27*, Barcelona, 2017.

# Incremental model identification (IMI<sub>x</sub>)

- Identify the model **for each reaction individually**, by postulating rate expressions with extents as arguments<sup>16</sup>

$$\begin{aligned} \min_{\theta_i^{(m_i)}} J(\theta_i^{(m_i)}) &= \sum_{h=1}^H \left( \tilde{x}_{r,i}(t_h) - \hat{x}_{r,i}^{(m_i)}(t_h, \theta_i^{(m_i)}) \right) W_i(t_h) \left( \tilde{x}_{r,i}(t_h) - \hat{x}_{r,i}^{(m_i)}(t_h, \theta_i^{(m_i)}) \right) \\ \text{s.t. } \dot{\hat{x}}_{r,i}^{(m_i)}(t, \theta_i^{(m_i)}) &= V(t) \varphi_{x,i}^{(m_i)}(\hat{x}_{r,i}^{(m_i)}(t, \theta_i^{(m_i)}), \tilde{x}_{r,\mathcal{J}}(t), \theta_i^{(m_i)}) - \omega(t) \hat{x}_{r,i}^{(m_i)}(t, \theta_i^{(m_i)}), \\ &\hat{x}_{r,i}^{(m_i)}(0, \theta_i^{(m_i)}) = 0. \end{aligned}$$

- $\tilde{x}_{r,\mathcal{J}}$  are the  $(R - 1)$  measured extents that need to be interpolated
- Model  $m_i$  with the least objective function is the best model
- Use simultaneous approach as final step for optimal parameter estimates

<sup>16</sup>Srinivasan, S. On Decoupling Chemical Reaction Systems - Methods, Analysis and Applications., Doctoral thesis No. 7376, EPFL, Switzerland, 2017.

# Incremental model identification

## Plug-flow reactors<sup>17</sup>

- Identification of the rate expression  $r_i$  and estimation of the parameters  $\theta_i$ :

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

$$\text{s.t. } \frac{\partial}{\partial t} (\hat{x}_{r,i}(z, t, \theta_i)) + v \frac{\partial}{\partial z} (\hat{x}_{r,i}(z, t, \theta_i)) = \hat{r}_i(\tilde{c}(z, t), \theta_i), \quad \hat{x}_{r,i}(z, 0, \theta_i) = \hat{x}_{r,i}(0, t, \theta_i) = 0$$

- Accurate for frequent measurements along the reactor: difficult in practice
- But  $\tilde{c}_p(\tau_h)$  are concentrations at the reactor exit  $z_e$  with the velocity  $v_h = \frac{z_e}{\tau_h}$
- Identification problem reformulated as:

$$\min_{\theta_i} \sum_{h=1}^H \left( \tilde{x}_{p,r,i}(\tau_h) - \hat{x}_{p,r,i}(\tau_h, \theta_i) \right)^2$$

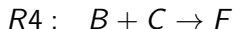
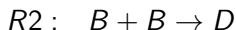
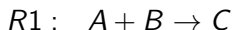
$$\text{s.t. } \frac{d}{d\tau} \hat{x}_{p,r,i}(\tau, \theta_i) = \hat{r}_{p,i}(\tilde{c}_p(\tau), \theta_i), \quad \hat{x}_{p,r,i}(0, \theta_i) = 0$$

<sup>17</sup>Rodrigues, D. et al. In *IFAC ADCHEM'15*, Whistler, 2015.



## Example: Acetoacetylation of pyrrole

- Consider the acetoacetylation of pyrrole in a semi-batch reactor
- The reaction system consists of seven species ( $S = 7$ ) involved in four independent reactions ( $R = 4$ )



- Reactions R1, R2 and R4 are catalyzed by species K
- The reactor initially contains 4 mol of A, 0.5 mol of B, 0.1 mol of C and 1 mol of catalyst K
- Pure diketene (B) is fed into the reactor at the constant volumetric flowrate  $0.1 \text{ L min}^{-1}$

## Example: Acetoacetylation of pyrrole

- Material balance equations:

$$\dot{n}_A(t) = -V(t) r_1(t)$$

$$\dot{n}_B(t) = -V(t) r_1(t) - 2V(t) r_2(t) - V(t) r_3(t) - V(t) r_4(t) + w_{in,B} u_{in}(t)$$

$$\dot{n}_C(t) = V(t) r_1(t) - V(t) r_4(t)$$

$$\dot{n}_D(t) = V(t) r_2(t)$$

$$\dot{n}_E(t) = V(t) r_3(t)$$

$$\dot{n}_F(t) = V(t) r_4(t)$$

$$\dot{n}_K(t) = 0$$

- The simulated numbers of moles of each species are corrupted by additive zero-mean Gaussian noise of standard deviation corresponding to  $\alpha$  % of its maximum value
- Data sets are generated for 1000 different noise realizations

# Example: Acetoacetylation of pyrrole

- A list of rate candidates is available for each reaction

Table: Rate candidates for the acetoacetylation of pyrrole system.

R1	R2	R3	R4
$r_1^{(1)} = k_1 c_A c_B c_K$	$r_2^{(1)} = k_2 c_B^2 c_K$	$r_3^{(1)} = k_3 c_B$	$r_4^{(1)} = k_4 c_B c_C c_K$
$r_1^{(2)} = k_1 c_B$	$r_2^{(2)} = k_2 c_B$	$r_3^{(2)} = k_3 c_B^2$	$r_4^{(2)} = k_4 c_C$
$r_1^{(3)} = k_1 c_A$	$r_2^{(3)} = k_2 c_B^2$	$r_3^{(3)} = k_3 c_B c_K$	$r_4^{(3)} = k_4 c_B$
$r_1^{(4)} = k_1 c_K$	$r_2^{(4)} = k_2 c_B c_K$	$r_3^{(4)} = k_3 c_B^2 c_K$	$r_4^{(4)} = k_4 c_B c_C$
$r_1^{(5)} = k_1 c_A c_B$	$r_2^{(5)} = k_2 c_K$	$r_3^{(5)} = k_3 c_K$	$r_4^{(5)} = k_4 c_C c_K$
$r_1^{(6)} = k_1 c_A c_K$			
$r_1^{(7)} = k_1 c_B c_K$			
$r_1^{(8)} = k_1 c_A^2 c_K$			

# Example: Acetoacetylation of pyrrole

Table: Comparison between the extent-based incremental approaches  $\text{IMI}_n$  and  $\text{IMI}_x$  using different noise levels and  $H = 61$  sampling points.

Reaction	$k_{true}$	Data set	$\alpha$	$\text{IMI}_n$			$\text{IMI}_x$		
				#/1000	$k^*$	$\sigma_{k^*}$	#/1000	$k^*$	$\sigma_{k^*}$
R1	0.0530	D1	1%	995	0.0529	0.0009	1000	0.0530	0.0005
		D2	5%	733	0.0523	0.0041	942	0.0529	0.0023
		D3	10%	483	0.0519	0.0075	731	0.0530	0.0045
R2	0.1280	D1	1%	992	0.1275	0.0013	1000	0.1279	0.0007
		D2	5%	764	0.1250	0.0059	940	0.1271	0.0028
		D3	10%	425	0.1218	0.0114	924	0.1265	0.0059
R3	0.0280	D1	1%	983	0.0280	0.0001	984	0.0280	0.0001
		D2	5%	870	0.0279	0.0006	818	0.0279	0.0006
		D3	10%	833	0.0278	0.0011	756	0.0278	0.0010
R4	0.0030	D1	1%	749	0.0035	0.0032	999	0.0028	0.0001
		D2	5%	335	0.0038	0.0056	994	0.0028	0.0001
		D3	10%	236	0.0035	0.0059	866	0.0028	0.0002

- $\text{IMI}_x$  performs better than  $\text{IMI}_n$  in identifying the model structures

- Models of reaction systems and concept of extents
  - Homogeneous reaction systems
  - Distributed reaction systems
  - Generalization to other reaction systems
  - Applications of extents
  
- Model identification
  - Simultaneous model identification
  - Incremental model identification
  - Example
  
- **Conclusions**

- Divide-and-conquer strategy – decoupling provided by extents enables model identification of **one reaction at a time**
- Incremental approach allows **correct model discrimination** and **estimates accurately the parameter values**
- This approach **avoids the drawbacks** of the simultaneous approach
- Can the incremental approach yield **optimal parameter estimates** and **maintain its advantages**? How and in which case?

## Thank you for your attention!

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