Incremental Model Identification of Gas - Liquid Reaction Systems with Unsteady-State Diffusion

Benoit Cretegny, Sriniketh Srinivasan, Julien Billeter and Dominique Bonvin

1. SIMULATION OF THE SYSTEM

Assumptions: Homogeneous bulks, only a liquid film, $D \neq f(t,c)$ and $L \neq f(t)$.

Mole balance for bulk b:

$$\dot{\mathbf{n}}_b(t) = \mathbf{N}_b^{\mathrm{T}}\, V_b(t)\, \mathbf{r}_b(t) \pm \mathbf{W}_{m,b}\, \zeta_b(t) + \mathbf{W}_{in,b}\, \mathbf{u}_{in,b}(t) - \frac{u_{out,b}(t)}{m_b(t)}\, \mathbf{n}_b(t)$$

$$\mathbf{n}_b(0) = \mathbf{n}_{b0}$$

The film is discretized using Fick's First and Second laws. The bulks mole balances are used as boundary conditions:

$$\frac{d\mathbf{c}_f(x,t)}{dt} = D\left(\frac{\mathbf{c}_f(x+\triangle x,t) - 2\mathbf{c}_f(x,t) + \mathbf{c}_f(x-\triangle x,t)}{(\triangle x)^2}\right)$$

$$x = \triangle x, \ldots, L - \triangle x$$

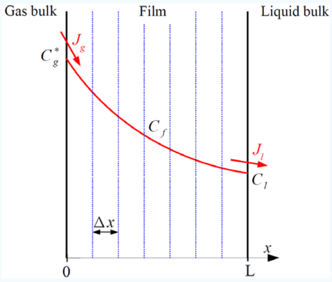
$$\mathbf{J}_g(t) = \mathbf{J}(0,t) = -\mathbf{D}\left(\frac{\mathbf{c}_f(\triangle x,t) - \mathbf{c}_f(0,t)}{\triangle x}\right)$$

$$\mathbf{c}_f(0,t) = \mathbf{c}_g^*(t)$$

$$c_{g,i}^*(t) = \frac{p_{g,i}(t)}{k_{H,i}} \quad i = 1, \ldots, S_g$$

$$\mathbf{J}_l(t) = \mathbf{J}(L,t) = -\mathbf{D}\left(\frac{\mathbf{c}_f(L,t) - \mathbf{c}_f(L-\triangle x,t)}{\triangle x}\right)$$

$$\mathbf{c}_f(L,t) = \mathbf{c}_l(t)$$



2. INCREMENTAL MODEL IDENTIFCATION

The identification is decomposed into sub-problems by transforming the numbers of moles into extents, which are then modeled individually.

Each extent describes the effect of a single reaction, mass transfer or inlet:

$$\begin{bmatrix} \mathbf{x}_{r,b}(t) \\ \mathbf{x}_{m,b}(t) \\ \mathbf{x}_{in,b}(t) \\ x_{ic,b}(t) \end{bmatrix} = \begin{bmatrix} \mathbf{N}_b^{\mathrm{T}} & \pm\mathbf{W}_{m,b} & \mathbf{W}_{in,b} & \mathbf{n}_{b,0} \end{bmatrix}^{+} (\mathbf{n}_b(t) - \mathbf{n}_{b,0})$$

$$rank\left(\begin{bmatrix} \mathbf{N}_b^T & \pm\mathbf{W}_{m,b} & \mathbf{W}_{in,b} & \mathbf{n}_{b,0} \end{bmatrix}\right) = R_b + p_m + p_{in,b} + 1$$

If the rank condition is not fulfilled, a reaction and mass-transfer variant form is used:

$$\begin{bmatrix} \mathbf{x}_{r,b}(t) \\ \mathbf{x}_{m,b}(t) \end{bmatrix} = \begin{bmatrix} \mathbf{N}_b^T & \pm\mathbf{W}_{m,b} \end{bmatrix}^{+} \mathbf{n}_b^{RMV}(t)$$

$$rank\begin{bmatrix} \mathbf{N}_b^T & \pm\mathbf{W}_{m,b} \end{bmatrix} = R_b + p_m$$

2a. Mass-transfer Parameters Estimation

The diffusion coefficients of the diffusing species as well as the film thickness can be estimated by resolving a minimization problem:

$$\min_{\mathbf{D},L}\left(\sum_{i=1}^{p_m}\left(q_i\|x_{m,g,i}(t) - \hat{x}_{m,g,i}(t,D_i,L)\|^2 + (1-q_i)\|x_{m,l,i}(t) - \hat{x}_{m,l,i}(t,D_i,L)\|^2\right)\right)$$

Calculation of $\hat{x}_{m,g,i}(t,D_i,L)$ and $\hat{x}_{m,l,i}(t,D_i,L)$:

1. Construction of $\hat{c}_f(x,t,D_i,L)$ using experimental values as boundary conditions:

   $$\hat{c}_{f,i}(0,t,D_i,L) = c_{g,i}^*(t)$$
   $$\hat{c}_{f,i}(L,t,D_i,L) = c_{l,i}(t)$$

2. Calculation of the corresponding fluxes:

   $$\hat{c}_f(x,t,D_i,L) \rightarrow \hat{J}_{b,i}(t,D_i,L) \rightarrow \hat{\zeta}_{b,i}(t,D_i,L)$$

3. Integration of $\hat{\zeta}_{b,i}(t,D_i,L)$ to obtain $\hat{x}_{m,b,i}(t,D_i,L)$:

   $$\dot{\hat{x}}_{m,b,i}(t,D_i,L) = \hat{\zeta}_{b,i}(t,D_i,L) - \frac{u_{out,b}(t)}{m_b(t)}\,\hat{x}_{m,b,i}(t,D_i,L)$$

2b. Kinetic Parameters Estimation

The reaction rate parameters can be estimated using a similar approach. For a power rate law with a forward and a backward reaction, the problem is expressed as follows:

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

$$r_{b,i}(t) = k_{b,i}\prod_{j=1}^{S_b}(c_{b,j}^{n_{b,i,j}}) - k_{b,i,r}\prod_{j=1}^{S_b}(c_{b,j}^{n_{b,i,r,j}})$$

3. ABSORPTION OF CO_2 IN AN AQUEOUS SOLUTION

Two competitive reactions in the liquid phase consuming CO_2:

$$R_2R'N + H_2O + CO_2 \xrightarrow{k_1} R_2R'N^+H + HCO_3^-$$
$$RR'NH + H_2O + CO_2 \xrightarrow{k_2} RR'N^+H_2 + HCO_3^-$$

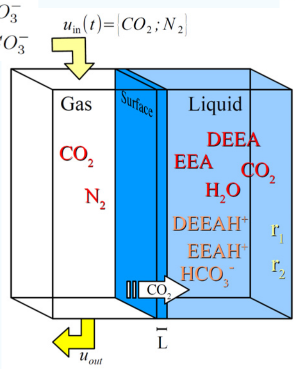
$R_2R'N$ = N,N-diethylethanolamine (DEEA)
$RR'NH$ = N-ethylethanolamine (EEA)

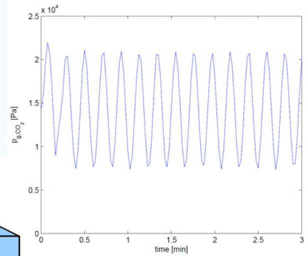
$R = -C_2H_5$
$R' = -CH_2CH_2OH$

Rate laws:

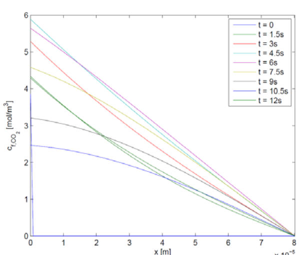
$$r_1 = k_1 c_{l,DEEA} c_{l,CO_2}$$
$$r_2 = k_2 c_{l,EEA} c_{l,CO_2}$$

The inlet flow rate varies periodically over time to ensure unsteady-state mass transfer.

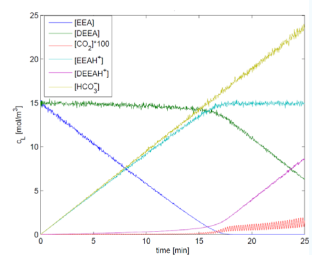




Gas phase partial pressure

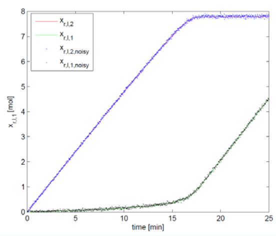


Film concentration profile

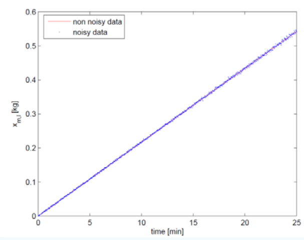


Liquid phase concentrations

Extents of reactions



Extent of mass transfer (L)

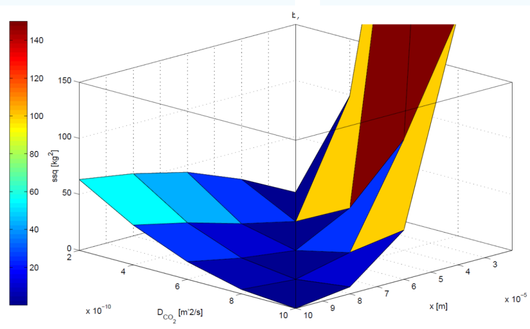


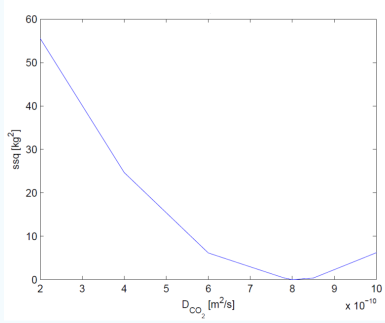
3a. Estimation of Mass-transfer Parameters

If both the diffusion coefficient and the film thickness are unknown, only the ratio between the two can be estimated (left figure).

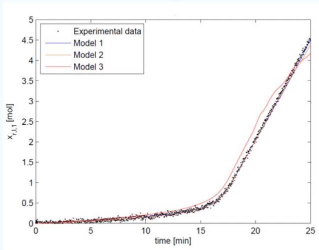
If the film thickness is known, the diffusion coefficients can be estimated individually (right figure).

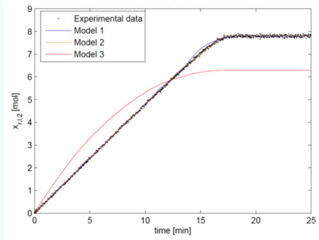
	$D\ [m^2/s] \cdot 10^{10}$
Estimated	8.1 ± 0.002
Simulated	8.02





3b. Estimation of Kinetic Parameters





- Reaction 1
  - Model 1: $r_{11} = k_{11} c_{DEEA} c_{CO_2} c_{H_2O}$
  - Model 2: $r_{12} = k_{12} c_{DEEA} c_{CO_2}$
  - Model 3: $r_{13} = k_{13} {c_{DEEA}}^2 c_{CO_2}$
- Reaction 2
  - Model 1: $r_{21} = k_{21} c_{EEA} c_{CO_2} c_{H_2O}$
  - Model 2: $r_{22} = k_{22} c_{EEA} c_{CO_2}$
  - Model 3: $r_{23} = k_{23} {c_{EEA}}^2 c_{CO_2}$
- Both model 1 and 2 fit the data for each reaction
- H_2O is in large excess =>
  - $k_{12} \cong k_{11} \cdot c_{H_2O}$ and $r_{11} \cong r_{12}$
  - $k_{22} \cong k_{21} \cdot c_{H_2O}$ and $r_{21} \cong r_{22}$

	$k_1\ [(m^3/mol)^2 s^{-1}]$	$k_2\ [(m^3/mol)^2 s^{-1}]$
Estimated (Model 2)	0.170 ± 0.026	8.21 ± 0.06
Simulated	0.173	8.04

Laboratoire d'Automatique

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE