Parameter estimation and model discrimination of batch solid-liquid reactors

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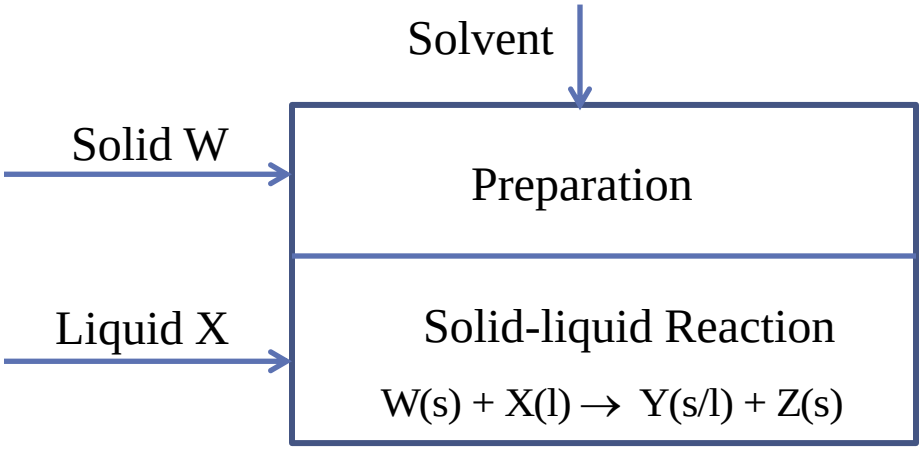
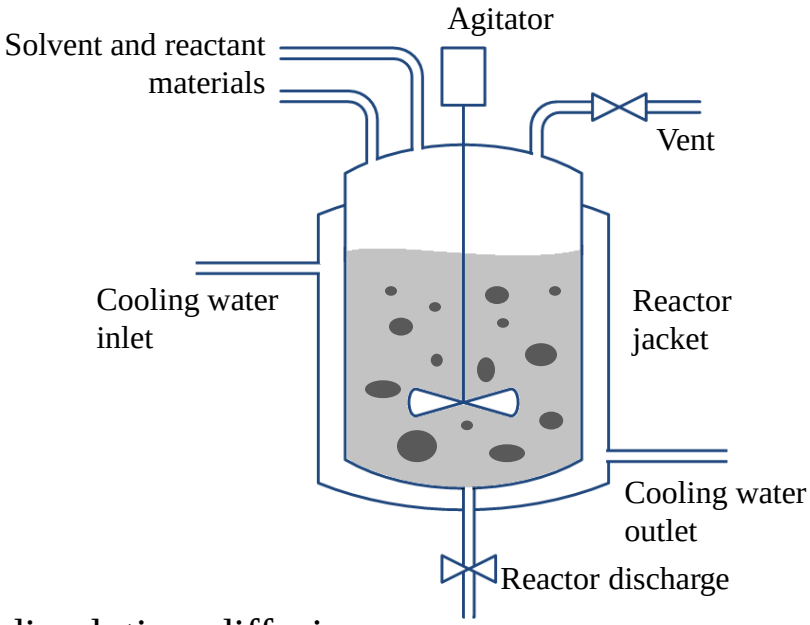
Enterprise-wide Optimization Meeting

Problem Statement & Motivation

- Batch reactor



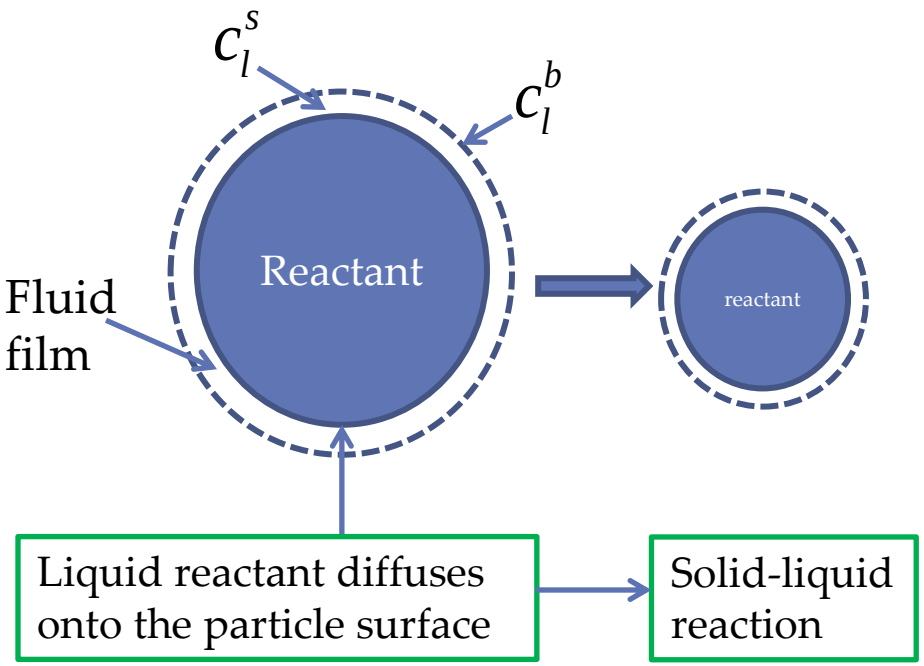


- **Unknown reaction mechanism –** Surface reaction, dissolution, diffusion
  Different particle shapes and sizes
  Product effects
- **Limited information –** Lack of concentration measurements

➡ **An over-parameterized model without enough data**

Reaction Mechanisms

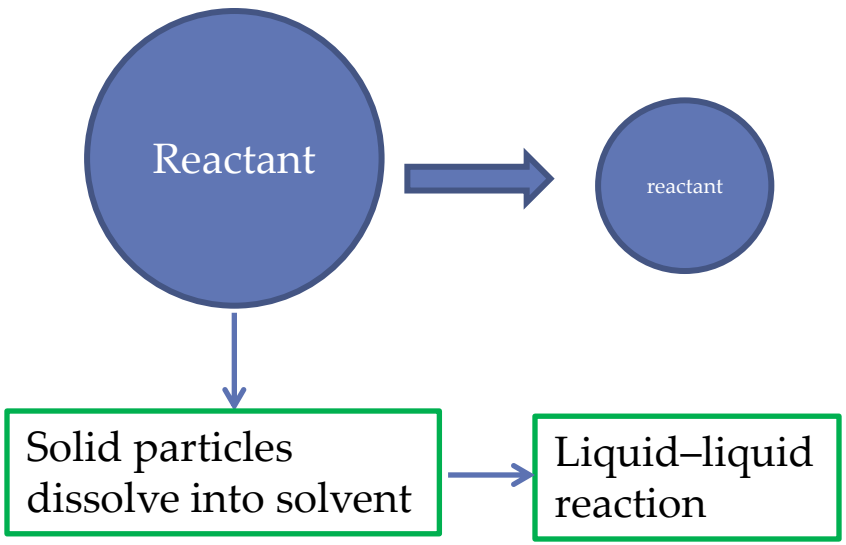
Shrinking particle model (SPM)



Solid product breaks off from reaction surface.

Dissolution model (DM)

Assume dissolution is the rate limiting step.



Products precipitate into solid phase.

Reaction rate of SPM depends on liquid reactant concentration while DM doesn't.

Batch Reactor Model

Total surface area is related to total amount and the shape of particles[1]. $S = \frac{aM_s}{\rho_s R_0} N_{s0}^{1/a} N_s^{1-1/a}$

SPM $\frac{dN_s}{dt} = \upsilon_s SR = \upsilon_s \frac{aM_s}{\rho_s R_0} N_{s0}^{1/a_s} N_s^{1-1/a_s} k_0 e^{-\frac{E_a}{RT}} (c_l^s)^{\alpha}$

DM $\frac{dN_s}{dt} = -kS = \upsilon_s \frac{aM_s}{\rho_s R_0} N_{s0}^{1/a_s} N_s^{1-1/a_s} k_0 e^{-\frac{E_a}{RT}}$

Solid reactant	$\frac{dN_W}{dt} = -\nu_W \mathbf{A} N_{W0}^{1-\mathbf{E}} N_W^{\mathbf{E}} exp(\mathbf{B}(1-\frac{Tr}{T})) C_{s,X}^{\mathbf{F}}$
Liquid reactant	$\frac{dN_X}{dt} = F_{in,X} - \nu_X \mathbf{A} N_{W0}^{1-\mathbf{E}} N_W^{\mathbf{E}} exp(\mathbf{B}(1-\frac{Tr}{T})) C_{s,X}^{\mathbf{F}}$
Product	$\frac{dN_Y}{dt} = \nu_Y \mathbf{A} N_{W0}^{1-\mathbf{E}} N_W^{\mathbf{E}} exp(\mathbf{B}(1-\frac{Tr}{T})) C_{s,X}^{\mathbf{F}}$
Volume	$\frac{dV}{dt} = Q_{in}$
Temperature	$\frac{dT}{dt} = \frac{\sum \Delta H_j r_j V + \sum F_k Mw_k Cp_k (T_{in} - T) + \mathbf{U} a_{jac} (\bar{T}_{jac} - T)}{\sum N_i Mw_i Cp_i}$
Diffusion	$\mathbf{D}(C_{b,X} - C_{s,X}) - exp(\mathbf{B}(1-\frac{Tr}{T})) C_{s,X}^{\mathbf{F}} = 0$
Heat transfer	$U = \phi(T, \mathbf{U_A}, \mathbf{U_B}, \mathbf{U_C})$

- Parameters

$A = \frac{aMw}{\rho_p R_0} k(Tr)$

$B = \frac{Ea}{RTr}$

$D = \frac{k_d}{k(Tr)}$

$E = 1 - \frac{1}{a}$

$F = \alpha$

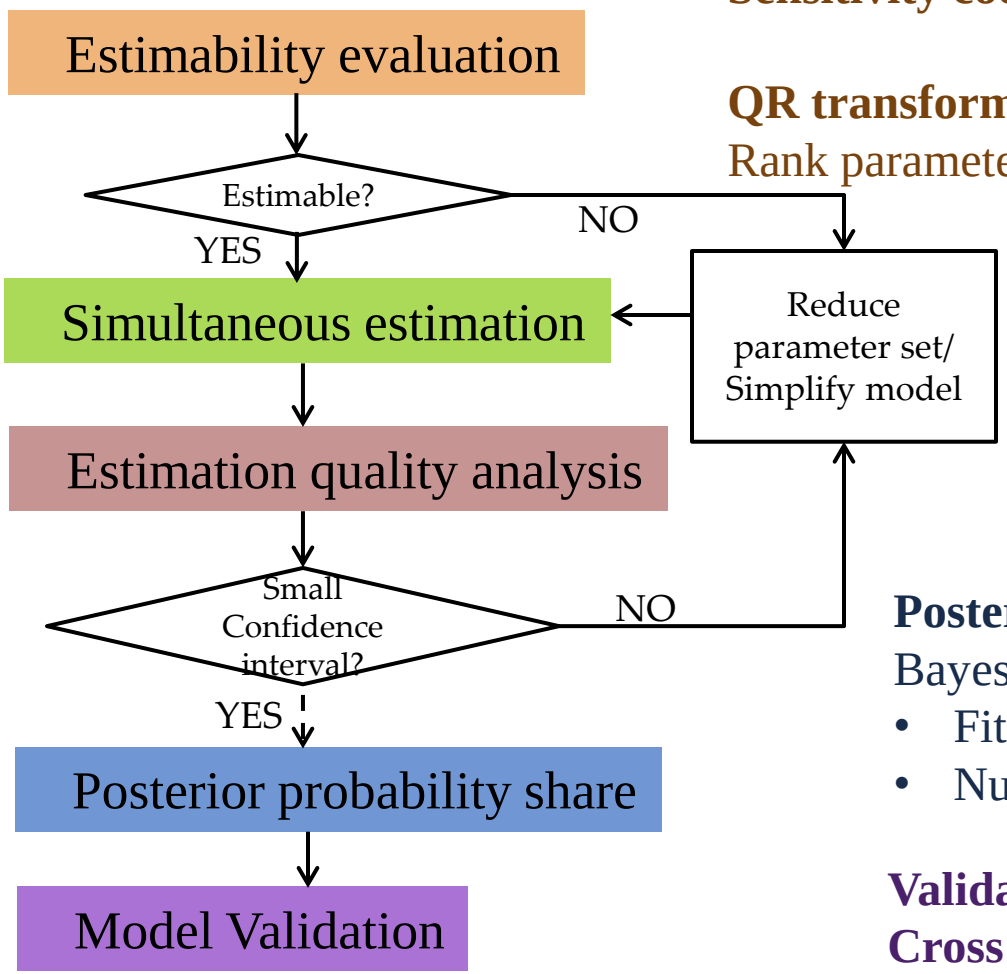
$U = \phi(U_A, U_B, U_C)$

- Model indicator

F=0 → DM
F>0 → SPM

[1] Salmi, Tapio, et al. "New modelling approach to liquid–solid reaction kinetics: From ideal particles to real particles." Chemical Engineering Research and Design 91.10 (2013): 1876-1889.

Parameter Estimation



Sensitivity coefficient matrix

$$S = \begin{pmatrix} \frac{\theta_1^* \partial \eta_1}{\sigma_{\eta_1} \eta_1^* \partial \theta_1}|_{t=t_1} & \cdots & \frac{\theta_p^* \partial \eta_1}{\sigma_{\eta_1} \eta_1^* \partial \theta_p}|_{t=t_1} \\ \vdots & \ddots & \vdots \\ \frac{\theta_1^* \partial \eta_R}{\sigma_{\eta_R} \eta_R^* \partial \theta_1}|_{t=t_1} & \cdots & \frac{\theta_p^* \partial \eta_R}{\sigma_{\eta_R} \eta_R^* \partial \theta_p}|_{t=t_1} \\ \frac{\theta_1^* \partial \eta_1}{\sigma_{\eta_1} \eta_1^* \partial \theta_1}|_{t=t_2} & \cdots & \frac{\theta_p^* \partial \eta_1}{\sigma_{\eta_1} \eta_1^* \partial \theta_p}|_{t=t_2} \\ \vdots & \ddots & \vdots \\ \frac{\theta_1^* \partial \eta_R}{\sigma_{\eta_R} \eta_R^* \partial \theta_1}|_{t=t_f} & \cdots & \frac{\theta_p^* \partial \eta_R}{\sigma_{\eta_R} \eta_R^* \partial \theta_p}|_{t=t_f} \end{pmatrix}$$

QR transformation with column permutation

Rank parameters by their individual variance contribution

EVM formulation > WLS formulation

- Data reconciliation
- Parameter estimation

Estimation covariance matrix

Reduced Hessian – confidence region

Posterior probability share

Bayes' theorem $p(M_j|Y,\Sigma) \propto p(M_j) 2^{-n_{\theta_j}/2} exp(-\hat{F}_j/2)$

- Fitting
- Number of parameters

Validation by unseen batch data

Cross validation

Industrial Case Study

Solid-liquid batch reactor

- Batch k k = 1 … NS
- Measured input u_{kj}^*
- Measured output η_{ki}^*
- Normally distributed measurements

$$u_{kj}^* = \bar{u}_{kj} + \xi_{kj} \qquad \xi_{kj} \sim \mathcal{N}(0, \sigma_{kj}^2)$$

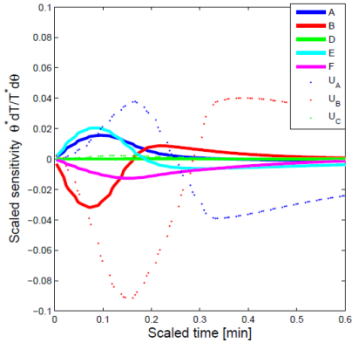
$$\eta_{ki}^* = \bar{\eta}_{ki} + \epsilon_{ki} \qquad \epsilon_{ki} \sim \mathcal{N}(0, \sigma_{ki}^2)$$

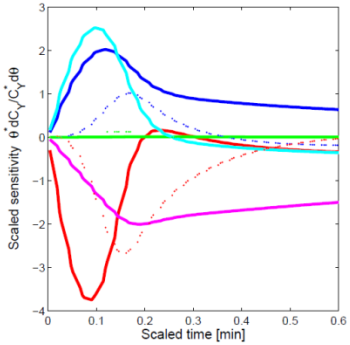
- **Jacket temperatures**
- **Inlet flowrates**
- **Reactor weights**
- **Reactor temperatures**
- **Concentrations**

➢ Estimability evaluation

Rank parameters by QRcp of scaled sensitivity matrix

	Selected point 1		Selected point 2	
Parameter	Scaled value	Scaled variance contribution	Scaled value	Scaled variance contribution
A	0.5	1.99×10^4	0.5	0.0456
B	0.45	5.68×10^{-4}	0.3	1.11×10^{-3}
D	1	1.61×10^3	0.01	20.4
E	0.95	19.42	0.8	0.2046
F	1	0.0075	0.5	744.3
U_A	0.03	4.48×10^{-5}	10	2.90×10^{-3}
U_B	0.37	8.37×10^{-8}	0.75	2.5×10^{-9}
U_C	0.05	2.03×10^{-6}	0.46	9.301×10^{-11}





- Parameter rankings at different points are different
- All parameters are included in the estimation

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➢ Simultaneous estimation -- EVM

Measured output errors

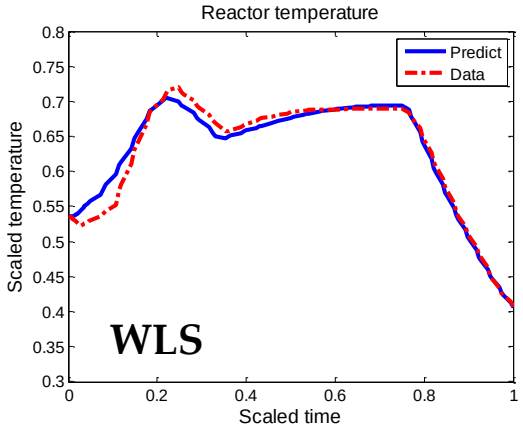
$$\min_{\theta} \quad \frac{1}{2}\sum_{k=1}^{NS}\sum_{i\in\mathcal{T}_k}(\eta_k(t_i)-\eta_{ki}^*)^T\Sigma_{\eta ki}^{-1}(\eta_k(t_i)-\eta_{ki}^*)$$

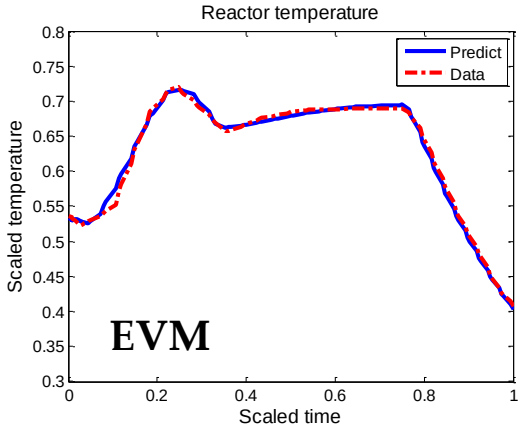
Measured input errors

$$+\frac{1}{2}\sum_{k=1}^{NS}\sum_{j\in\mathcal{J}_k}(u_k(t_j)-u_{kj}^*)^T\Sigma_{ukj}^{-1}(u_k(t_j)-u_{kj}^*)$$

$$\begin{aligned} s.t. \quad & \frac{dz_k}{dt} = f(z_k, y_k, u_k, \theta, t) \\ & 0 = g(z_k, y_k, u_k, \theta, t) \\ & \eta_k(t_i) = h(z_k(t_i), y_k(t_i)) \qquad i \in \mathcal{I}_k \\ & z_k(0) = z_{k0} \\ & \theta^L \le \theta \le \theta^U \end{aligned}$$

- **Reactor temperatures**
- **End-point concentrations**
- **Jacket temperatures**
- **Weights and flowrates**





- EVM does parameter estimation and data reconciliation simultaneously
- **Better output data fitting** Accumulated squared errors of EVM is reduced by 44% compared with WLS
- **Intensive computational load** EVM has 15771 variables and 13830 equation constraints

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➢ Estimation quality analysis

Parameter	Estimated value $\theta_i^\star$	Scaled variance $H^{-1}(i,i)$	Reliability factor $\beta_i = \frac{\sigma_i}{\lvert\theta_i^\star\rvert}$
A	0.11	2.21×10^{-5}	0.0428
B	0.38	1.05×10^{-4}	0.0270
D	0.27	0.14	1.3793
E	0.74	1.19×10^{-4}	0.0147
F	0.06	1.20×10^{-3}	0.5829
U_A	10	UB*	UB*
U_B	0.71	2.40×10^{-4}	0.0218
U_C	0.37	9.91×10^{-4}	0.0844

UB*: parameter at its upper bound. the reduced Hessian is extremely small and evaluated reliability factor is not meaningful.

- **Set $C_{b,X} = C_{s,X}$**
- **Set F = 0 → dissolution model**
- **Fix parameter U_A**
  Linearly temperature-dependent U

➢ Posterior probability share $p(M_j|Y,\Sigma) \propto p(M_j)2^{-n_{\theta_j}/2}exp(-\hat{F}_j/2)$

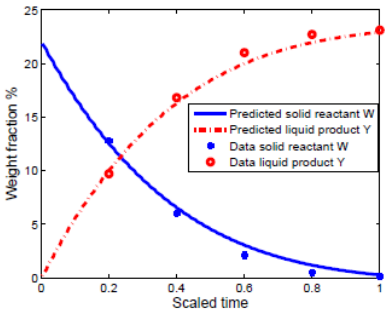
	Description	A	B	D	E	F	U_A	U_B	U_C
Model 1	Full model, Nonlinear U	√	√	√	√	√	√	√	√
Model 2	Nonlinear U, Fixed D	√	√		√	√	√	√	√
Model 3	Nonlinear U, Fixed D and F	√	√		√		√	√	√
Model 4	Nonlinear U, Fixed D, F and U_A	√	√		√			√	√
Model 5	Linear U, Fixed D and F	√	√		√		√	√	

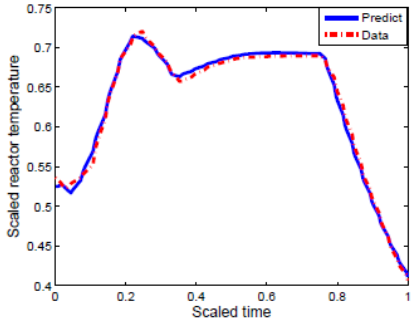
	Objective values	CPU time (sec)	Number of parameters	Posterior probability
Model 1	1419.7	508	8	0.2199
Model 2	1419.9	233	7	0.2546
Model 3	1421.1	67	6	0.1085
Model 4	1420.1	10	5	0.4170
Model 5	1445.3	52	5	1.4×10^{-6}

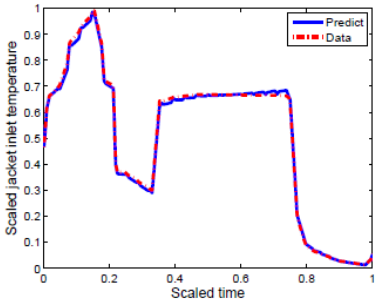
Industrial Case Study

- Estimation results

Parameter	Estimated value $\theta_i^\star$	Scaled variance $H^{-1}(i,i)$	Reliability factor $\beta_i = \frac{\sigma_i}{\lvert\theta_i^\star\rvert}$
A	0.10	1.05×10^{-5}	0.0323
B	0.38	1.01×10^{-4}	0.0264
E	0.77	1.39×10^{-4}	0.0153
U_B	0.83	4.24×10^{-4}	0.0248
U_C	0.5	1.80×10^{-3}	0.0848

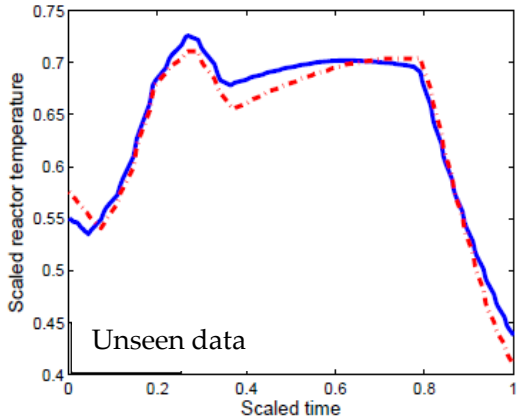




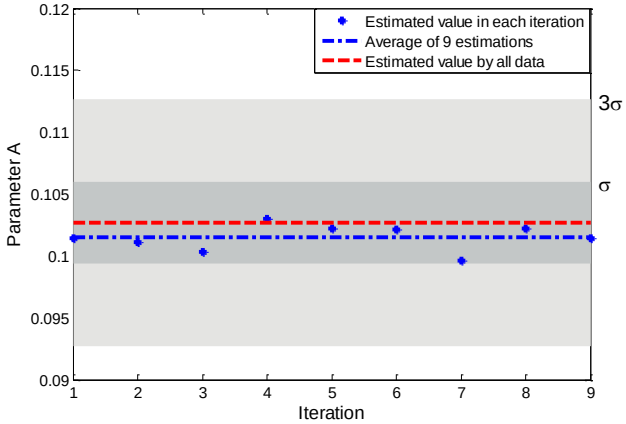


- Model Validations

New data



9-fold cross validation



Conclusions & Significance

- Discussed two potential models for a solid-liquid reaction in a batch reactor
- Built a uniform dynamic model with an indicating parameter to discriminate two mechanisms
- Introduced a parameter estimation procedure
- Applied parameter estimation to the solid-liquid batch reactor model
- Conducted model validation to examine the model capability of predicting system behaviors

➢ Optimal control will be conducted based on estimated model to reduce the batch time