Parameter estimation and model discrimination of batch solid-liquid reactors

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Enterprise-wide Optimization Meeting
Problem Statement & Motivation

• Batch reactor

\[
W(s) + X(l) \rightarrow Y(s/l) + Z(s)
\]

• **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)**

- Fluid film
- Liquid reactant diffuses onto the particle surface
- Solid-liquid reaction
- Solid product breaks off from reaction surface.

**Dissolution model (DM)**

- Solid particles dissolve into solvent
- Liquid-liquid reaction
- Products precipitate into solid phase.

Assume dissolution is the rate limiting step.

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\[1\]. \[ S = \frac{aM_s}{\rho_s R_0} N_s^{1/a} N_s^{1-1/a} \]

SPM  \[ \frac{dN_s}{dt} = \nu_s SR = \nu_s \frac{aM_s}{\rho_s R_0} N_s^{1/a} N_s^{1-1/a} k_0 e^{\frac{E_a}{RT}} (c_i^*)^\alpha \]

DM  \[ \frac{dN_s}{dt} = -kS = \nu_s \frac{aM_s}{\rho_s R_0} N_s^{1/a} N_s^{1-1/a} k_0 e^{\frac{E_a}{RT}} \]

Solid reactant  \[ \frac{dN_W}{dt} = -\nu_W A N_W^{1-E} N_W^{E} \exp(B(1 - \frac{Tr}{T})) C_s^{F,X} \]

Liquid reactant  \[ \frac{dN_X}{dt} = F_{in,X} - \nu_X A N_W^{1-E} N_W^{E} \exp(B(1 - \frac{Tr}{T})) C_s^{F,X} \]

Product  \[ \frac{dN_Y}{dt} = \nu_Y A N_W^{1-E} N_W^{E} \exp(B(1 - \frac{Tr}{T})) C_s^{F,X} \]

Volume  \[ \frac{dV}{dt} = Q_{in} \]

Temperature  \[ \frac{dT}{dt} = \sum \Delta H_i r_i V + \sum F_k M_{w_k} C_{p_k} (T_{in} - T) + U_{a,jac} (T_{jac} - T) \]

Diffusion  \[ D (C_{b,X} - C_{s,X}) - \exp(B(1 - \frac{Tr}{T})) C_s^{F,X} = 0 \]

Heat transfer  \[ U = \phi(T, U_A, U_B, U_C) \]

Parameter Estimation

Estimability evaluation

- Estimable?
  - YES → Simultaneous estimation → Estimation quality analysis
  - NO → NO

Simultaneous estimation

Estimation quality analysis

- Small Confidence interval?
  - YES → Posterior probability share → Model Validation
  - NO → NO

Posterior probability share

Sensitivity coefficient matrix

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

Validation by unseen batch data

Cross validation

Problem Statement & Motivation

Reactor Modeling

Parameter Estimation

Industrial Case Study

Significance & Potential Impact
Industrial Case Study

Solid-liquid batch reactor

- Batch \( k \), \( k = 1 \ldots \text{NS} \)
- Measured input \( u_{kj}^* \)
- Measured output \( \eta_{ki}^* \)
- Normally distributed measurements

Estimability evaluation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Selected point 1</th>
<th>Selected point 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Scaled value</td>
<td>Scaled variance contribution</td>
</tr>
<tr>
<td>( A )</td>
<td>0.5</td>
<td>( 1.99 \times 10^4 )</td>
</tr>
<tr>
<td>( B )</td>
<td>0.45</td>
<td>( 5.68 \times 10^{-4} )</td>
</tr>
<tr>
<td>( D )</td>
<td>1</td>
<td>( 1.61 \times 10^3 )</td>
</tr>
<tr>
<td>( E )</td>
<td>0.95</td>
<td>19.42</td>
</tr>
<tr>
<td>( F )</td>
<td>1</td>
<td>( 0.0075 )</td>
</tr>
<tr>
<td>( U_A )</td>
<td>0.03</td>
<td>( 4.48 \times 10^{-5} )</td>
</tr>
<tr>
<td>( U_B )</td>
<td>0.37</td>
<td>( 8.37 \times 10^{-8} )</td>
</tr>
<tr>
<td>( U_C )</td>
<td>0.05</td>
<td>( 2.03 \times 10^{-6} )</td>
</tr>
</tbody>
</table>

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

\[
\begin{align*}
  u_{kj}^* &= \tilde{u}_{kj} + \xi_{kj} \\
  \xi_{kj} &\sim \mathcal{N}(0, \sigma_{kj}^2) \\
  \eta_{ki}^* &= \tilde{\eta}_{ki} + \epsilon_{ki} \\
  \epsilon_{ki} &\sim \mathcal{N}(0, \sigma_{ki}^2)
\end{align*}
\]

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

Simultaneous estimation -- EVM

Measured output errors

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

$$+ \frac{1}{2} \sum_{k=1}^{NS} \sum_{i \in \mathcal{I}_k} (u_k(t_j) - u^*_{kj})^T \Sigma_{u_k}^{-1} (u_k(t_j) - u^*_{kj})$$

s.t.  
\[ \frac{dz_k}{dt} = f(z_k, y_k, u_k, \theta, t) \]  
\[ 0 = g(z_k, y_k, u_k, \theta, t) \]  
\[ \eta_k(t_i) = h(z_k(t_i), y_k(t_i)) \quad i \in \mathcal{I}_k \]  
\[ z_k(0) = z_{k0} \]  
\[ \theta^L \leq \theta \leq \theta^U \]

- 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
Industrial Case Study

- Estimation quality analysis

| Parameter | Estimated value $\theta_i^*$ | Scaled variance $H^{-1}(i, i)$ | Reliability factor $\beta_i = \frac{\sigma_i}{|\theta_i^*|}$ |
|-----------|-------------------------------|--------------------------------|-----------------------------------|
| $A$       | 0.11                          | $2.21 \times 10^{-5}$         | 0.0428                            |
| $B$       | 0.38                          | $1.05 \times 10^{-4}$         | 0.0270                            |
| $D$       | 0.27                          | 0.14                           | 1.3793                            |
| $E$       | 0.74                          | $1.19 \times 10^{-4}$         | 0.0147                            |
| $F$       | 0.06                          | $1.20 \times 10^{-3}$         | 0.5829                            |
| $U_A$     | 10                            | UB*                            | UB*                               |
| $U_B$     | 0.71                          | $2.40 \times 10^{-4}$         | 0.0218                            |
| $U_C$     | 0.37                          | $9.91 \times 10^{-4}$         | 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 $F = 0 \rightarrow$ dissolution model

- Fix parameter $U_A$

Linearly temperature-dependent $U$

- Posterior probability share

\[ p(M_j|Y, \Sigma) \propto p(M_j)2^{-n_{\theta_j}/2}exp(-\hat{F}_j/2) \]

<table>
<thead>
<tr>
<th>Description</th>
<th>A</th>
<th>B</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>$U_A$</th>
<th>$U_B$</th>
<th>$U_C$</th>
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</thead>
<tbody>
<tr>
<td>Model 1 Full model, Nonlinear U</td>
<td>√</td>
<td>√</td>
<td>√</td>
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<tr>
<td>Model 2 Nonlinear U, Fixed D</td>
<td>√</td>
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<td>√</td>
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<td>√</td>
<td>√</td>
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<td></td>
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<tr>
<td>Model 3 Nonlinear U, Fixed D and F</td>
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<td>√</td>
<td>√</td>
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<tr>
<td>Model 4 Nonlinear U, Fixed D, F and $U_A$</td>
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<td>√</td>
<td>√</td>
<td>√</td>
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<td>√</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>Model 5 Linear U, Fixed D and F</td>
<td>√</td>
<td>√</td>
<td>√</td>
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<td>√</td>
<td>√</td>
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</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Objective values</th>
<th>CPU time (sec)</th>
<th>Number of parameters</th>
<th>Posterior probability</th>
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</thead>
<tbody>
<tr>
<td>Model 1</td>
<td>1419.7</td>
<td>508</td>
<td>8</td>
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<tr>
<td>Model 2</td>
<td>1419.9</td>
<td>233</td>
<td>7</td>
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<tr>
<td>Model 3</td>
<td>1421.1</td>
<td>67</td>
<td>6</td>
</tr>
<tr>
<td>Model 4</td>
<td>1420.1</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>Model 5</td>
<td>1445.3</td>
<td>52</td>
<td>5</td>
</tr>
</tbody>
</table>
Industrial Case Study

- Estimation results

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Estimated value $\theta^*_i$</th>
<th>Scaled variance $H^{-1}(i,i)$</th>
<th>Reliability factor $\beta_i = \frac{\theta^<em>_i}{\sigma^</em>_i}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.10</td>
<td>$1.05 \times 10^{-5}$</td>
<td>0.0323</td>
</tr>
<tr>
<td>B</td>
<td>0.38</td>
<td>$1.01 \times 10^{-4}$</td>
<td>0.0264</td>
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<tr>
<td>E</td>
<td>0.77</td>
<td>$1.39 \times 10^{-4}$</td>
<td>0.0153</td>
</tr>
<tr>
<td>$U_B$</td>
<td>0.83</td>
<td>$4.24 \times 10^{-4}$</td>
<td>0.0248</td>
</tr>
<tr>
<td>$U_C$</td>
<td>0.5</td>
<td>$1.80 \times 10^{-3}$</td>
<td>0.0848</td>
</tr>
</tbody>
</table>

- Model Validations

  New data

  9-fold cross validation

Problem Statement & Motivation  Reactor Modeling  Parameter Estimation  Industrial Case Study  Significance & Potential Impact
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