Dynamic Modeling and Recipe Optimization of Polyether Polyol Processes

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September 27, 2012
Introduction
Polyether polyol process description

Key ingredients
- **Epoxides** (ethylene oxide (EO), propylene oxide (PO))

  ![Epoxides](image)

- Molecules containing active hydrogen atoms (alcohols, amines)

  ![Molecules](image)

- A basic **catalyst** (KOH)
Introduction
Polyether polyol process description

Key ingredients
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- Molecules containing active hydrogen atoms (alcohols, amines)
- A basic **catalyst** (KOH)

Basic procedures
- Starters are first mixed with catalyst in the liquid phase
- Alkylene oxides in the liquid phase are fed in controlled rates
- The reactor temperature is controlled by the heat exchanger
- Allowed maximum reactor pressure guarded by the vent system control valve
Process Dynamic Modeling
Modeling reaction kinetics

- **Reaction scheme:** Polypropylene glycol

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolysis</td>
<td>( W + M \xrightarrow{k_h} D_0 )</td>
</tr>
<tr>
<td>Initiation</td>
<td>( G_0 + M \xrightarrow{k_i} G_1 )</td>
</tr>
<tr>
<td></td>
<td>( Q_0 + M \xrightarrow{k_i} Q_1 )</td>
</tr>
<tr>
<td>Propagation</td>
<td>( G_n + M \xrightarrow{k_p} G_{n+1} \quad (n \geq 1) )</td>
</tr>
<tr>
<td></td>
<td>( Q_n + M \xrightarrow{k_p} Q_{n+1} \quad (n \geq 1) )</td>
</tr>
<tr>
<td>Transfer</td>
<td>( G_n + M \xrightarrow{k_t} D_n + Q_0 \quad (n \geq 0) )</td>
</tr>
<tr>
<td></td>
<td>( Q_n + M \xrightarrow{k_t} R_n + Q_0 \quad (n \geq 0) )</td>
</tr>
<tr>
<td>Exchange</td>
<td>( G_n + D_m \xrightarrow{k_e} D_n + G_m \quad (n, m \geq 0) )</td>
</tr>
<tr>
<td></td>
<td>( Q_n + R_m \xrightarrow{k_e} R_n + Q_m \quad (n, m \geq 0) )</td>
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</table>

**Material**
- **Starter:** Propylene glycol (PG)
- **Water:**
- **Catalyst:** KOH
- **Monomer:** PO

**Notation**
- \( M \): monomers (PO)
- \( W \): water
- \( G_n \): growing product chains (\( P_nO^{-}K^+ \))
- \( D_n \): dormant product chains (\( P_nOH \))
- \( Q_n \): growing unsat chains (\( U_nO^{-}K^+ \))
- \( R_n \): dormant unsat chains (\( U_nOH \))
- \( P_n \): \( CH_3(PO)_n \)
- \( U_n \): \( CH_2 = CHCH_2(PO)_n \)

**Index**
- \( n, m \): repeating units
Model equations

- **Population balances**

\[
\frac{d(V[G_n])}{dt} = V(k_p([G_{n-1}] - [G_n])[M] - k_t[G_n][M] - ke[G_n] \sum_{m=0}^{N} ([D_m] + [R_m]) + k_e[D_n] \sum_{m=0}^{N} ([G_m] + [Q_m]))
\]

\[
\frac{d(V[D_n])}{dt} = V(k_h[W][M] + k_t[G_n][M] + ke[G_n] \sum_{m=0}^{N} ([D_m] + [R_m]) - k_e[D_n] \sum_{m=0}^{N} ([G_m] + [Q_m]))
\]

Similar balances for unsat populations (Q and R).

- **Monomer balance**
- **Total mass balance**
- **Volume determination**
- **Vapor-liquid equilibrium**
  - Liquid phase activities: Flory-Huggins theory
  - Vapor pressures: Antoine equation
Characteristics of the obtained model

- A large-scale differential-algebraic equation (DAE) system
- Synergistic fast and slow dynamic modes
  - Caused by fast exchange reactions
  - Stiff differential equations
  - Numerical difficulties in optimization
- A reformulation procedure
Process Dynamic Modeling
Reformulation of the first-principle model

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A nullspace projection method for equilibrium reactions

- Separating fast and slow dynamic components
- Modeling fast dynamics as algebraic equations
  - Systematic procedure based on linear algebra
Two pseudo-species introduced: \( X = G + D \) \( Y = Q + R \)

Population balances

\[
\frac{d(V[X_n])}{dt} = V_k p ([G_{n-1}] - [G_n]) [M] \\
\frac{d(V[Y_n])}{dt} = V_k p ([Q_{n-1}] - [Q_n]) [M]
\]

Quasi-steady states of the equilibrium reactions

\[
X_n n_c = G_i (n_i + n_u) \\
Y_n n_c = Q_i (n_i + n_u)
\]

Important remarks

- Complete with additional equations: monomer balance, VLE, etc.
- An index-one DAE system
- Fewer differential variables and equations
- Less stiff differential equations
Process Recipe Optimization
A dynamic optimization formulation

Objective function
Minimizing the batch time of polymerization

Constraints
- Reformulated process model
- Product quality constraints
  - Target molecular weight
  - Requirement on the unsaturation value
  - Final time monomer concentration
- Process safety constraints
  - Heat removal duty
  - Adiabatic end temperature due to loss of cooling

Control variables
Reactor temperature and monomer feed rate
# Case Study

## Production of polypropylene glycol

### Process specifications

#### Initial charge condition
- **Initiator:** PG and Water
- **Catalyst:** KOH
- **Monomer:** PO

#### Process constraints
- **Product molecular weight** \( \geq 950 \) g/mol
- **Product unsaturation value** \( \leq 0.032 \) mmol/g polyol
- **Unreacted PO** \( \leq 120 \) ppm
- **Heat exchanger load** \( \leq H_{\text{max}} \) kW
- **Adiabatic end temperature** \( T_{ad} - T_b \leq 80^\circ C \)
Case Study
Production of polypropylene glycol

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Model validation on reactor pressure: model prediction vs. plant data

![Graph showing model validation on reactor pressure: model prediction vs. plant data]
Case Study
Production of polypropylene glycol

Optimization results

- Optimization model statistics and solution

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<th>Opt. soln</th>
<th>MW (g/mol)</th>
<th>Unsat (mmol/g)</th>
<th>PO(ppm)</th>
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<th># of con.</th>
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<td>0.575</td>
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- Batch time reduced by 42.5% (base case batch time is normalized to 1)
- Product quality constraints are satisfied at the end of the operation

Important remarks
- Piecewise linear control profiles with continuity on finite element boundaries
- U-shape temperature profile and higher average feed rates
- Merging the feeding and digestion periods

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Case Study

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- Reactor temperature (top) and monomer feed rate (bottom) profiles

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Case Study Results

Optimal product molecular weight distributions (MWD)

- **MWD of the product** (top) and **unsat** (bottom) polymers

![Graph showing MWD of product and unsat polymers]

- **Important remarks**
  - Near *Poisson* distribution for the **product** polymers
  - Flat distribution for the **unsat** polymers

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Case Study Results

Optimal product polymer property profiles

- Unsat number, functionality, HEW, and OH number

![Graphs showing Unsat number, functionality, HEW, and OH number evolution over time.]

- Important remarks
  - All widely used property indexes
  - All in proper ranges at final time
Conclusions and acknowledgments

Project timeline

- Nov. 2009 - Dec. 2011
  - Proof-of-concept: integration of scheduling and dynamic optimization

  - Application at Dow: polyether polyols
    - First-principle reactor model development
    - Optimization case study: 3000-MW product of PO and glycerol

  - Polyol process: reactor model development con’t
    - VLE model and reactor pressure calculations
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    - Copolymerization of EO and PO and multi-step products
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    - Recipe design pattern change

  - Modeling and optimization of copolymers, multi-step products
  - Simultaneous scheduling and dynamic optimization
    - Multiple reactors and possible incorporation of finishing trains
    - Real-time constraints on shared resources
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Thank you

I am glad to take any questions
The nullspace projection method

A generic reaction system with irreversible and equilibrium reactions

\[ \dot{x} = [A_1 \quad A_2] \begin{bmatrix} r_1(x) \\ \sigma r_2(x) \end{bmatrix} + g(t) \]

Multiplying with a non-singular matrix \([Y^T \quad Z^T]^T (Z^T A_2 = 0)\)

\[
\begin{bmatrix} Y_a^T \\ Y_b^T \\ Z^T \end{bmatrix} \dot{x} = \begin{bmatrix} Y_a^T \\ Y_b^T \\ Z^T \end{bmatrix} A_1 r_1(x) + \begin{bmatrix} 0 \\ \sigma f(x) \\ 0 \end{bmatrix} + \begin{bmatrix} Y_a^T \\ Y_b^T \\ Z^T \end{bmatrix} g(t)
\]

Stable solution needs \(f(x) = 0\), when \(\sigma \to \infty\)

Reformulated system

\[
Y_a^T \dot{x} = Y_a^T A_1 r_1(x) + Y_a^T g(t) \\
f(x) = 0 \\
Z^T \dot{x} = Z^T A_1 r_1(x) + Z^T g(t)
\]
A toy example

- **Reaction system** $A \xrightarrow{k_1} B \xrightleftharpoons[k_3]{k_2} C$

- **Mass balance equations**
  \[
  \dot{a} = -k_1 a \quad a(0) = a_0 \\
  \dot{b} = k_1 a - k_2 b + k_3 c \quad b(0) = 0 \\
  \dot{c} = k_2 b - k_3 c \quad c(0) = 0
  \]

- **Analytical solution**
  \[
  K_e = \frac{k_3}{k_2} = 2 \quad \frac{k_2}{k_1} = 2
  \]

\[\text{Graph of } a(t), b(t), c(t)\]
A toy example

- Reformulation matrix
  \[ Y^T = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} \quad Z^T = [0 \ 1 \ 1] \]

- Reformulated system
  \[
  \begin{align*}
  \dot{a} &= -k_1 a \\
  \dot{b} &= k_1 a - k_2 b + k_3 c \\
  \dot{c} &= k_2 b - k_3 c
  \end{align*} \quad \implies \quad \begin{align*}
  \dot{s} &= k_1 a \\
  s &= b + c \\
  k_2 b &= k_3 c
  \end{align*}
  \]

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Backup Slides

The nullspace projection method

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  s &= b + c & k_2 b &= k_3 c \\
  \end{align*}
  \]

\[
K_e = \frac{k_3}{k_2} = 2 \quad \frac{k_2}{k_1} = 20
\]
Process constraint profiles

- **Adiabatic end temp. (top) and hxn. duty (bottom)**

![Graphs showing adiabatic end temperature and heat removal over normalized time]

- **Important remarks**
  - Heat exchanger capacity is the main constraining factor
  - The adiabatic end temperature constraint is also limiting process performance