Reactor Modeling and Recipe Optimization of Polyether Polyol Processes

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Development of systematic optimization methods of batch processes

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

  - Application on polyether polyol processes at Dow
  - Homopolymerization: polypropylene glycol
    1. First-principle reactor model: population balances, kinetics, VLE, etc.
    2. Hypothetical optimization case study: over 40% batch time reduction
  - Copolymerization: block copolymer polyol
    1. Reactor modeling with the method of moments
    2. Hypothetical optimization case study: over 40% batch time reduction
Introduction
Polyether polyol process description

- **Key ingredients**
  - **Epoxides** (ethylene oxide (EO), propylene oxide (PO))
  - Molecules containing active hydrogen atoms (alcohols, amines)
  - A basic **catalyst** (KOH)

![Epoxide structures](image-url)
Polyether polyol process description

- **Key ingredients**
  - **Epoxides** (ethylene oxide (EO), propylene oxide (PO))
  - Molecules containing active hydrogen atoms (alcohols, amines)
  - A basic catalyst (KOH)

- **Typical procedures used**
  - 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

- Many polyether polyol products are copolymers
  - Example: EO capped diols

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{O} \quad \text{H}_2\text{C} \quad \text{O} \\
\text{H}_2\text{C} & \quad \text{O} \quad \text{H}_2\text{C} \quad \text{O} \\
\text{PO block} & \quad \text{EO block}
\end{align*}
\]

EO/PO block copolymer

- Challenge: the effect of chain ends on chain growth

<table>
<thead>
<tr>
<th>Propagation scheme</th>
<th>Rate constant</th>
<th>\[ k_p^{EE} &gt; k_p^{EP} &gt; k_p^{PE} &gt; k_p^{PP} ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \ldots \text{EO}^* + \text{EO} \rightarrow \ldots \text{EO}^* )</td>
<td>( k_p^{EE} )</td>
<td></td>
</tr>
<tr>
<td>( \ldots \text{EO}^* + \text{PO} \rightarrow \ldots \text{PO}^* )</td>
<td>( k_p^{EP} )</td>
<td></td>
</tr>
<tr>
<td>( \ldots \text{PO}^* + \text{EO} \rightarrow \ldots \text{EO}^* )</td>
<td>( k_p^{PE} )</td>
<td></td>
</tr>
<tr>
<td>( \ldots \text{PO}^* + \text{PO} \rightarrow \ldots \text{PO}^* )</td>
<td>( k_p^{PP} )</td>
<td></td>
</tr>
</tbody>
</table>

Terminal unit is designated by ^*

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### Process Dynamic Modeling

**Modeling EO/PO copolymerization processes**

#### Reaction scheme: EO/PO copolymer

**Initiation:**
- \( G_{0,0} + EO \xrightarrow{k_E} G_{0,1} \)
- \( Q_{0,0} + EO \xrightarrow{k_E} Q_{0,1} \)
- \( G_{0,0} + PO \xrightarrow{k_P} G_{1,0} \)
- \( Q_{0,0} + PO \xrightarrow{k_P} Q_{1,0} \)

**Propagation:**
- \( GP_{n,p,q} + PO \xrightarrow{k_{FP}} DP_{n+1,p,q} \) (\( n_p + n_E \geq 1 \))
- \( GP_{n,p,q} + PO \xrightarrow{k_{FP}} EP_{n+1,p,q} \) (\( n_p + n_E \geq 1 \))
- \( GP_{n,p,q} + EO \xrightarrow{k_{FE}} DP_{n,p,q+1} \) (\( n_p + n_E \geq 1 \))
- \( GP_{n,p,q} + EO \xrightarrow{k_{FE}} EP_{n,p,q+1} \) (\( n_p + n_E \geq 1 \))

**Transfer:**
- \( GP_{n,p,q} + PO \xrightarrow{k_s} DP_{n,p,q} + Q_{0,0} \) (\( n_p, n_E \geq 0 \))
- \( GP_{n,p,q} + PO \xrightarrow{k_s} EP_{n,p,q} + Q_{0,0} \) (\( n_p, n_E \geq 0 \))
- \( QP_{n,p,q} + PO \xrightarrow{k_s} RP_{n,p,q} + Q_{0,0} \) (\( n_p, n_E \geq 0 \))

**Exchange:**
- \( GP_{n,p,q} + DP_{m,p,q} \xrightarrow{k_e} DP_{n+m,p,q} + GP_{m,p,q} \) (\( n_p, n_E, m_p, m_E \geq 0 \))
- \( GP_{n,p,q} + DP_{m,p,q} \xrightarrow{k_e} EP_{n+m,p,q} + GP_{m,p,q} \) (\( n_p, n_E, m_p, m_E \geq 0 \))
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**Material**
- **Starter**: Low MW diol
- **Catalyst**: KOH
- **Monomer**: EO and PO

**Notation**
- \( G_n \) growing product chains (\( P_n O^- K^+ \))
- \( D_n \) dormant product chains (\( P_n OH \))
- \( Q_n \) growing unsat chains (\( U_n O^- K^+ \))
- \( R_n \) dormant unsat chains (\( U_n OH \))

\( P_n = CH_3(PO)_n \)
\( U_n = CH_2 = CHCH_2(PO)_n \)

**Index**
- \( n, m \) repeating units (PO and EO)

**Superscript**
- \( E, P \) terminal units

**Polyol chains in the reactor**

- **Normal**
  - \( G^P, G^E \)
  - \( D^P, D^E \)

- **Unsaturated**
  - \( Q^P, Q^E \)
  - \( R^P, R^E \)

- **Total products**
  - \( X = G^P + G^E + D^P + D^E \)

- **Total byproducts**
  - \( Y = Q^P + Q^E + R^P + R^E \)
Process Dynamic Modeling
Population balances vs. method of moments

- Population balance model (PBM)
  - Differential equations

\[
\frac{d(V[X_{nP,nE}^P])}{dt} = V(k_p^{PP}[G_{nP-1,nE}^P] + k_p^{EP}[G_{nP-1,nE}^E])[PO] - V(k_p^{PP}[PO] + k_p^{PE}[EO])[G_{nP,nE}^P]
\]
\[
\frac{d(V[X_{nP,nE}^E])}{dt} = V(k_p^{PE}[G_{nP,nE-1}^P] + k_p^{EE}[G_{nP,nE-1}^E])[EO] - V(k_p^{EP}[PO] + k_p^{EE}[EO])[G_{nP,nE}^E]
\]
\[
\frac{d(V[Y_{nP,nE}^P])}{dt} = V(k_p^{PP}[Q_{nP-1,nE}^P] + k_p^{EP}[Q_{nP-1,nE}^E])[PO] - V(k_p^{PP}[PO] + k_p^{PE}[EO])[Q_{nP,nE}^P]
\]
\[
\frac{d(V[Y_{nP,nE}^E])}{dt} = V(k_p^{PE}[Q_{nP-1,nE}^P] + k_p^{EE}[Q_{nP-1,nE}^E])[EO] - V(k_p^{EP}[PO] + k_p^{EE}[EO])[Q_{nP,nE}^E]
\]

- Algebraic equations

\[
X_{nP,nE}^S n_c = G_{nP,nE}^S (n_i + n_u), \quad S \in \{P, E\} \quad n_c \quad \text{total moles of catalyst}
\]
\[
Y_{nP,nE}^S n_c = Q_{nP,nE}^S (n_i + n_u), \quad S \in \{P, E\} \quad n_i \quad \text{total moles of initiator}
\]
\[
\quad n_u \quad \text{total moles of unsaturated chains}
\]

- Pros and cons
  + Revealing full MWD spectrum
  - Computationally demanding

2000 MW diol > 1400 differential equations + 1400 algebraic equations
Population balances vs. method of moments

Definition of moments: $k$th order moment of polymeric species

\[
\lambda_k = \sum_{n_P + n_E \geq 1}^\infty (n_P + n_E)^k \chi_{n_P,n_E}, \quad \zeta_k = \sum_{n_P + n_E \geq 1}^\infty (n_P + n_E)^k G_{n_P,n_E}, \quad k = 0, 1, \ldots
\]

\[
\mu_k = \sum_{n_P + n_E \geq 1}^\infty (n_P + n_E)^k \gamma_{n_P,n_E}, \quad \nu_k = \sum_{n_P + n_E \geq 1}^\infty (n_P + n_E)^k Q_{n_P,n_E}, \quad k = 0, 1, \ldots
\]

Moment model (MM)

- Differential equations

\[
\frac{d\lambda_k^P}{dt} = V^{-1} (k_i^P G_0^P \rho_O + k_{PP}^P \sum_{i=0}^{k-1} \binom{k}{i} \zeta_i^P \rho_O - k_{PP}^P \zeta_k^P \rho_O)
\]

\[
\frac{d\lambda_k^E}{dt} = V^{-1} (k_i^E G_0^E \rho_O + k_{PE}^P \sum_{i=0}^{k-1} \binom{k}{i} \zeta_i^E \rho_O - k_{PE}^P \zeta_k^E \rho_O)
\]

\[
\frac{d\mu_k^P}{dt} = V^{-1} (k_i^P Q_0^P \rho_O + k_{PP}^P \sum_{i=0}^{k-1} \binom{k}{i} \nu_i^P \rho_O - k_{PP}^P \nu_k^P \rho_O)
\]

\[
\frac{d\mu_k^E}{dt} = V^{-1} (k_i^E Q_0^E \rho_O + k_{PE}^P \sum_{i=0}^{k-1} \binom{k}{i} \nu_i^E \rho_O - k_{PE}^P \nu_k^E \rho_O)
\]

- Algebraic equations

\[
\chi_k^S n_c = \zeta_k^S (n_i + n_u), \quad S = \{P, E\}
\]

\[
\mu_k^S n_c = \nu_k^S (n_i + n_u), \quad S = \{P, E\}
\]

Pros and cons

- Model size does not increase with polymer MW

0th - 2nd moments = 12 differential equations + 12 algebraic equations

- No detailed distribution
Copolymerization Case Study
Production of EO capped diol

- Process specifications

  ▶ Charge condition
  - Initiator: PPG
  - Catalyst: KOH
  - Monomer: PO and EO

  ▶ Process constraints*
  - Product molecular weight $\geq 2000$ g/mol
  - Product unsaturation value $\leq 0.02$ mmol/g polyol
  - Heat exchanger load $\leq UA(T - T_w)$ kW
  - Adiabatic end temperature $\leq (T_b + 90)\, ^\circ$C
  - Capping ratio $\geq 70\%$ (% of EO ended chains in total chains)

* The set of constraints has been chosen to illustrate the use of dynamic optimization technology and does not include all possible constraints or necessarily reflect the true capability of the plant.

- Model calibration
Copolymerization Case Study
Production of EO capped diol

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- Optimization results
  - **Optimization model statistics and solution**
    - | Opt. soln | MW (g/mol) | Unsat (mmol/g) | Capping(%) | # of var. | # of con. | CPU (s) |
      |------------|------------|---------------|------------|----------|----------|---------|
      | 0.580      | 2000       | 0.02          | 70         | 11,248   | 11,121   | 22      |
  - ★ Optimized with the moment model
  - ★ Batch time reduced by 42.0% (base case batch time normalized to 1)
  - ★ Product quality constraints are satisfied at the end of the operation
  - ★ More details...
Copolymerization Case Study Results

Optimal control profiles of the process

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

![Graph showing reactor temperature and monomer feed rate profiles]

- Important remarks
  - Piecewise linear control profiles with continuity on finite element boundaries
  - Rising temperature for PO digestion and EO feeding
  - Flat feed rates for both monomers: no need for ramping
Copolymerization Case Study Results

Process constraint profiles

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

![Graph showing adiabatic temperature and heat removal over time]

- Important remarks
  - Constraint on the adiabatic temp. is inactive
  - Heat exchanger capacity is the major constraining factor
Copolymerization Case Study Results

Optimal product molecular weight distributions (MWD)

- **MWD of the product (left) and unsat (right) polymers**

![MWD Graphs]

- **Important remarks**
  - Similar optimal solution obtained from the PBM
  - Optimization over PBM is computationally expensive

<table>
<thead>
<tr>
<th>Opt. soln MW (g/mol)</th>
<th>Unsat (mmol/g)</th>
<th>Capping (%)</th>
<th># of var.</th>
<th># of con.</th>
<th>CPU (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.588 2000 0.02</td>
<td></td>
<td>70</td>
<td>191,408</td>
<td>185,147</td>
<td>5221</td>
</tr>
</tbody>
</table>

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Conclusions

Project timeline

Development of systematic optimization methods of batch processes

  - Application on polyether polyol processes at Dow
    - Homopolymerization: polypropylene glycol
      1. First-principle reactor model: population balances, kinetics, VLE, etc.
      2. Hypothetical optimization case study: over 40% batch time reduction
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  - Simultaneous scheduling and dynamic optimization
    - Multiple reactors and possible incorporation of finishing trains
    - Real-time constraints on shared resources
  - Methodology generalization and further extensions

Thank you

I am glad to take your questions