Dynamic Modeling and Recipe Optimization of Polyether Polyol Processes

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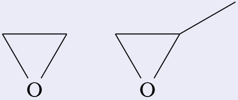
Introduction

Polyether polyol process description

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



  - Molecules containing active hydrogen atoms (alcohols, amines)

  - A basic catalyst (KOH)

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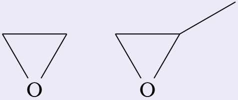
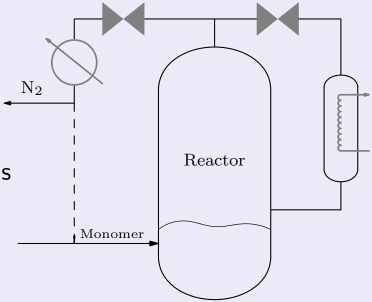


  - Molecules containing active hydrogen atoms (alcohols, amines)

  - 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

Hydrolysis:

$$\mathrm{W + M \xrightarrow{k_h} D_0}$$

Initiation:

$$\mathrm{G_0 + M \xrightarrow{k_i} G_1}$$
$$\mathrm{Q_0 + M \xrightarrow{k_i} Q_1}$$

Propagation:

$$\mathrm{G_n + M \xrightarrow{k_p} G_{n+1} \quad (n \geqslant 1)}$$
$$\mathrm{Q_n + M \xrightarrow{k_p} Q_{n+1} \quad (n \geqslant 1)}$$

Transfer:

$$\mathrm{G_n + M \xrightarrow{k_t} D_n + Q_0 \quad (n \geqslant 0)}$$
$$\mathrm{Q_n + M \xrightarrow{k_t} R_n + Q_0 \quad (n \geqslant 0)}$$

Exchange:

$$\mathrm{G_n + D_m \xrightarrow{k_e} D_n + G_m \quad (n, m \geqslant 0)}$$
$$\mathrm{Q_n + R_m \xrightarrow{k_e} R_n + Q_m \quad (n, m \geqslant 0)}$$
$$\mathrm{G_n + R_m} \underset{k_e}{\overset{k_e}{\rightleftharpoons}} \mathrm{D_n + Q_m \quad (n, m \geqslant 0)}$$

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

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

Index	
n, m	repeating units

Process Dynamic Modeling

A first-principle dynamic model

Model equations

- Population balances

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

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

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

Process Dynamic Modeling

Reformulation of the first-principle model

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

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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

Process Dynamic Modeling

Reformulated propoxylation model

- Two pseudo-species introduced: $\mathrm{X} = \mathrm{G} + \mathrm{D} \quad \mathrm{Y} = \mathrm{Q} + \mathrm{R}$
- Population balances

$$\frac{\mathrm{d}(V[\mathrm{X_n}])}{\mathrm{d}t} = Vk_p([\mathrm{G_{n-1}}] - [\mathrm{G_n}])[\mathrm{M}]$$
$$\frac{\mathrm{d}(V[\mathrm{Y_n}])}{\mathrm{d}t} = Vk_p([\mathrm{Q_{n-1}}] - [\mathrm{Q_n}])[\mathrm{M}]$$

- Quasi-steady states of the equilibrium reactions

$$\mathrm{X}_n n_c = \mathrm{G}_i(n_i + n_u)$$
$$\mathrm{Y}_n n_c = \mathrm{Q}_i(n_i + n_u)$$

n_c	total moles of catalyst
n_i	total moles of initiator
n_u	total moles of unsaturated chains

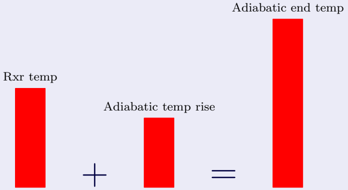
- Important remarks
  - Complete with additional equations: monomer balance, VLE, etc.
  - An index-one DAE system
  - \+ Fewer differential variables and equations
  - \+ Less stiff differential equations

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 $\geqslant 950\ \mathrm{g/mol}$
  - Product unsaturation value $\leqslant 0.032\ \mathrm{mmol/g\,polyol}$
  - Unreacted PO $\leqslant 120\ \mathrm{ppm}$
  - Heat exchanger load $\leqslant H_{max}\ \mathrm{kW}$
  - Adiabatic end temperature $T_{ad} - T_b \leqslant 80^\circ\mathrm{C}$

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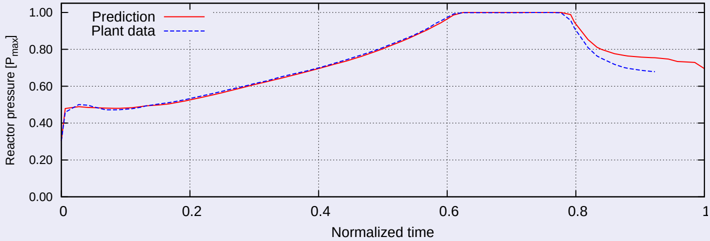
Model validation on reactor pressure: model prediction vs. plant data



Case Study

Production of polypropylene glycol

Optimization results

- Optimization model statistics and solution

Opt. soln	MW (g/mol)	Unsat (mmol/g)	PO(ppm)	# of var.	# of con.
0.575	950	0.028	120	10946	11043

  - Batch time reduced by 42.5% (base case batch time is normalized to 1)
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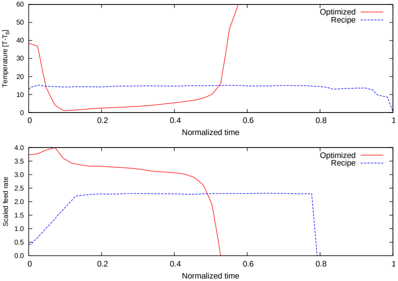
- Reactor temperature (top) and monomer feed rate (bottom) profiles

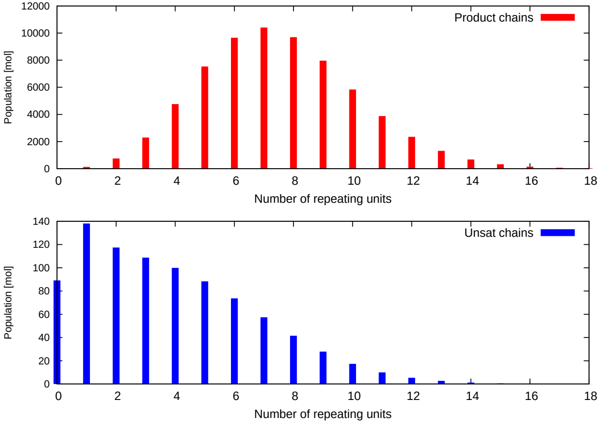


- Important remarks
  - Piecewise linear control profiles with continuity on finite element boundaries
  - U-shape temperature profile and higher average feed rates
  - Merging the feeding and digestion periods

Case Study Results

Optimal product molecular weight distributions (MWD)

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

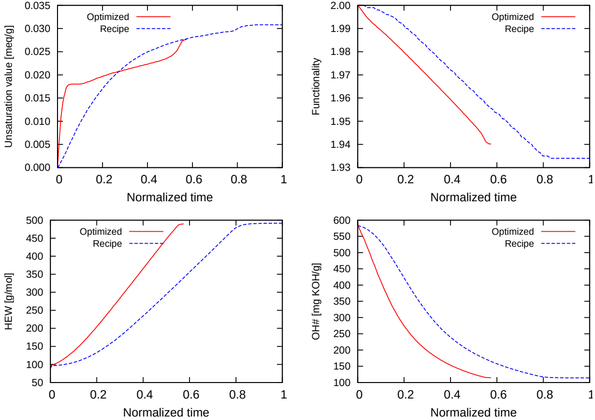


- Important remarks
  - Near *Poisson* distribution for the product polymers
  - Flat distribution for the unsat polymers

Case Study Results

Optimal product polymer property profiles

- Unsat number, functionality, HEW, and OH number



- 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
- Jan. 2012 - May. 2012
  - Application at Dow: polyether polyols
    - First-principle reactor model development
    - Optimization case study: 3000-MW product of PO and glycerol
- Jun. 2012 - Aug. 2012
  - Polyol process: reactor model development con't
    1. VLE model and reactor pressure calculations
    2. Model calibration against plant data
    3. Copolymerization of EO and PO and multi-step products
  - Optimization case study: polypropylene glycol
    - Recipe design pattern change
- Sep. 2012 - Dec. 2013
  - 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
  - Methodology generalization and further extensions

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Thank you

I am glad to take any questions

Backup Slides

The nullspace projection method

Method development

- A generic reaction system with irreversible and equilibrium reactions

$$\dot{x} = \begin{bmatrix} A_1 & A_2 \end{bmatrix} \begin{bmatrix} r_1(x) \\ \sigma r_2(x) \end{bmatrix} + g(t)$$

- Multiplying with a non-singular matrix $\begin{bmatrix} \mathcal{Y}^{\mathrm{T}} & \mathcal{Z}^{\mathrm{T}} \end{bmatrix}^{\mathrm{T}}$ $(\mathcal{Z}^{\mathrm{T}} A_2 = 0)$

$$\begin{bmatrix} \mathcal{Y}_a^{\mathrm{T}} \\ \mathcal{Y}_b^{\mathrm{T}} \\ \mathcal{Z}^{\mathrm{T}} \end{bmatrix} \dot{x} = \begin{bmatrix} \mathcal{Y}_a^{\mathrm{T}} \\ \mathcal{Y}_b^{\mathrm{T}} \\ \mathcal{Z}^{\mathrm{T}} \end{bmatrix} A_1 r_1(x) + \begin{bmatrix} 0 \\ \sigma f(x) \\ 0 \end{bmatrix} + \begin{bmatrix} \mathcal{Y}_a^{\mathrm{T}} \\ \mathcal{Y}_b^{\mathrm{T}} \\ \mathcal{Z}^{\mathrm{T}} \end{bmatrix} g(t)$$

- Stable solution needs $f(x) = 0$, when $\sigma \to \infty$
- Reformulated system

$$\begin{aligned} \mathcal{Y}_a^{\mathrm{T}} \dot{x} &= \mathcal{Y}_a^{\mathrm{T}} A_1 r_1(x) + \mathcal{Y}_a^{\mathrm{T}} g(t) \\ f(x) &= 0 \\ \mathcal{Z}^{\mathrm{T}} \dot{x} &= \mathcal{Z}^{\mathrm{T}} A_1 r_1(x) + \mathcal{Z}^{\mathrm{T}} g(t) \end{aligned}$$

Backup Slides

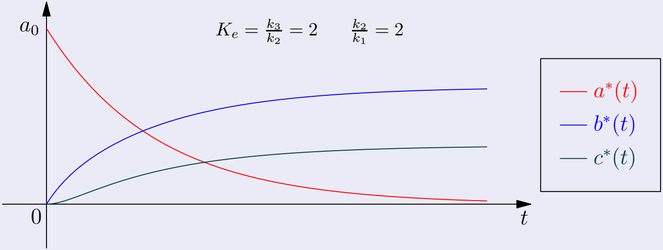
The nullspace projection method

A toy example

- Reaction system $\mathrm{A} \xrightarrow{\mathrm{k_1}} \mathrm{B} \underset{k_3}{\overset{k_2}{\rightleftharpoons}} \mathrm{C}$
- Mass balance equations

$$\begin{aligned} \dot{a} &= -k_1 a & a(0) &= a_0 \\ \dot{b} &= k_1 a - k_2 b + k_3 c & b(0) &= 0 \\ \dot{c} &= k_2 b - k_3 c & c(0) &= 0 \end{aligned}$$

- Analytical solution



Backup Slides

The nullspace projection method

A toy example

- Reformulation matrix $\mathcal{Y}^{\mathrm{T}} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix}$ $\mathcal{Z}^{\mathrm{T}} = \begin{bmatrix} 0 & 1 & 1 \end{bmatrix}$
- Reformulated system

$$\begin{aligned} \dot{a} &= -k_1 a \\ \dot{b} &= k_1 a - k_2 b + k_3 c \\ \dot{c} &= k_2 b - k_3 c \end{aligned} \quad \Longrightarrow \quad \begin{aligned} \dot{a} &= -k_1 a & a(0) &= a_0 \\ \dot{s} &= k_1 a & s(0) &= 0 \\ s &= b + c & k_2 b &= k_3 c \end{aligned}$$

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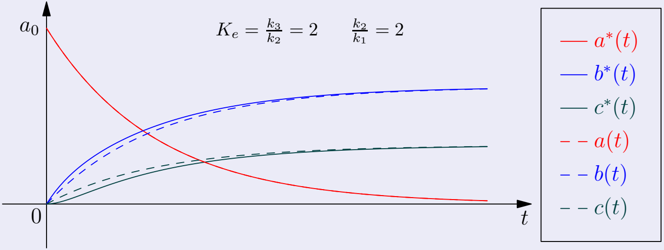

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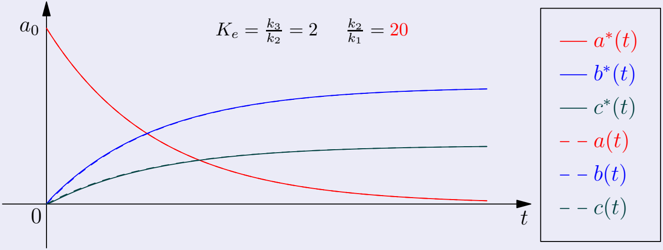
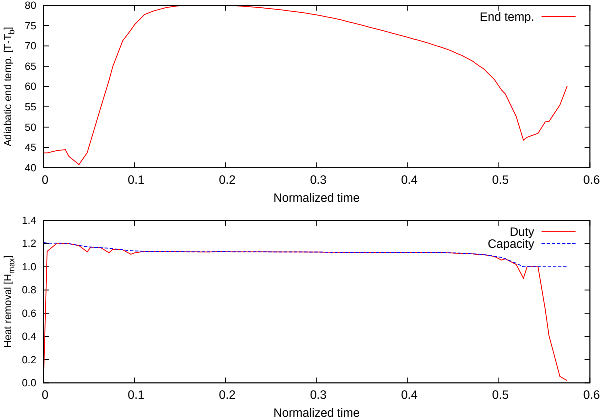


Backup Slides

Process constraint profiles

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



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