Reactor Modeling and Recipe Optimization of Polyether Polyol Processes

Spring 2013 EWO Meeting

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Introduction

Project timeline

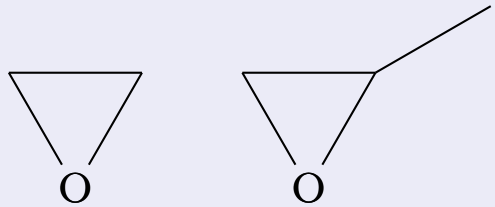
Development of systematic optimization methods of batch processes

- Nov. 2009 - Dec. 2011
  - Proof-of-concept: integration of scheduling and dynamic optimization
  - Y. Nie, L.T. Biegler, and J.M. Wassick. Integrated Scheduling and Dynamic Optimization of Batch Processes Using State Equipment Networks. *AIChE Journal*, 2012.
- Jan. 2012 - Dec. 2012
  - 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
  - Y. Nie, L.T. Biegler, C.M. Villa, and J.M. Wassick. Reactor Modeling and Recipe Optimization of Polyether Polyol Processes: Polypropylene Glycol. *submitted for publication*, 2013.
  - 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)

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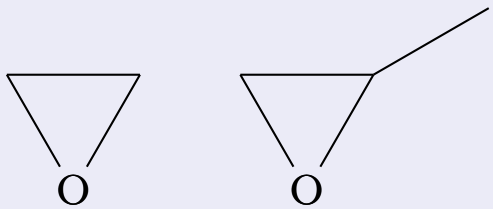

  - Molecules containing active hydrogen atoms (alcohols, amines)

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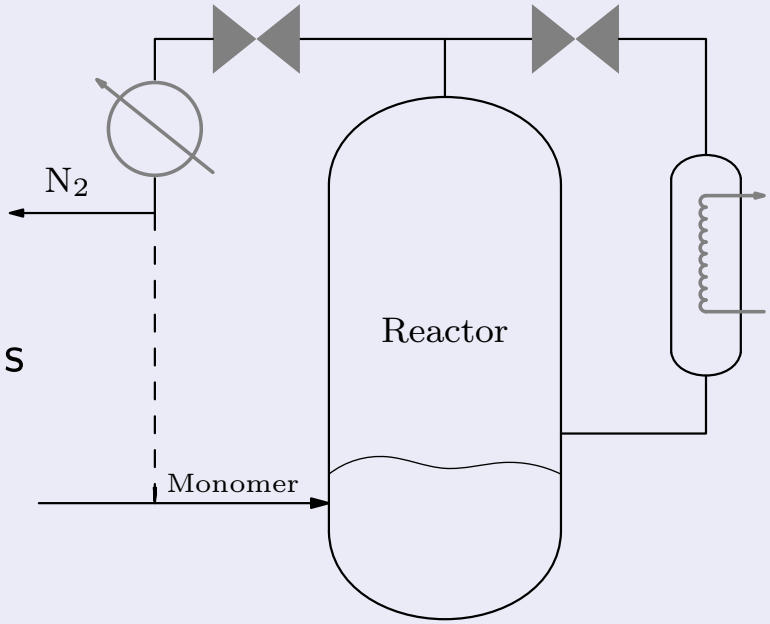
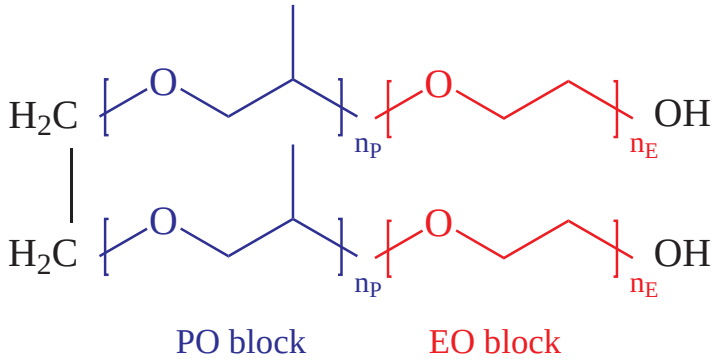


- Typical procedures used
  - Starters are first mixed with catalyst in the liquid phase
  - Alkylene oxides in the liquid phase are fed in controlled rates
  - The reactor temperature is controlled by the heat exchanger
  - Allowed maximum reactor pressure guarded by the vent system control valve

Process Dynamic Modeling

Modeling reaction kinetics

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



EO/PO block copolymer

- Challenge: the effect of chain ends on chain growth

Propagation scheme	Rate constant
$\ldots \mathrm{EO}^* + \mathrm{EO} \rightarrow \ldots \mathrm{EO}^*$	k_p^{EE}
$\ldots \mathrm{EO}^* + \mathrm{PO} \rightarrow \ldots \mathrm{PO}^*$	k_p^{EP}
$\ldots \mathrm{PO}^* + \mathrm{EO} \rightarrow \ldots \mathrm{EO}^*$	k_p^{PE}
$\ldots \mathrm{PO}^* + \mathrm{PO} \rightarrow \ldots \mathrm{PO}^*$	k_p^{PP}

Terminal unit is designated by $*$

$$k_p^{EE} > k_p^{EP} > k_p^{PE} > k_p^{PP}$$

Process Dynamic Modeling

Modeling EO/PO copolymerization processes

- Reaction scheme: EO/PO copolymer

Initiation:

$$\mathrm{G_{0,0} + EO \xrightarrow{k_i^E} G^E_{0,1}}$$
$$\mathrm{Q_{0,0} + EO \xrightarrow{k_i^E} Q^E_{0,1}}$$
$$\mathrm{G_{0,0} + PO \xrightarrow{k_i^P} G^E_{1,0}}$$
$$\mathrm{Q_{0,0} + PO \xrightarrow{k_i^P} Q^E_{1,0}}$$

Propagation:

$$\mathrm{G^P_{n_P,n_E} + PO \xrightarrow{k_p^{PP}} G^P_{n_P+1,n_E}} \quad (n_P + n_E \geqslant 1)$$
$$\mathrm{Q^P_{n_P,n_E} + PO \xrightarrow{k_p^{PP}} Q^P_{n_P+1,n_E}} \quad (n_P + n_E \geqslant 1)$$
$$\mathrm{G^P_{n_P,n_E} + EO \xrightarrow{k_p^{PE}} G^E_{n_P,n_E+1}} \quad (n_P + n_E \geqslant 1)$$
$$\mathrm{Q^P_{n_P,n_E} + EO \xrightarrow{k_p^{PE}} Q^E_{n_P,n_E+1}} \quad (n_P + n_E \geqslant 1)$$
$$\mathrm{G^E_{n_P,n_E} + PO \xrightarrow{k_p^{EP}} G^P_{n_P+1,n_E}} \quad (n_P + n_E \geqslant 1)$$
$$\mathrm{Q^E_{n_P,n_E} + PO \xrightarrow{k_p^{EP}} Q^P_{n_P+1,n_E}} \quad (n_P + n_E \geqslant 1)$$
$$\mathrm{G^E_{n_P,n_E} + EO \xrightarrow{k_p^{EE}} G^E_{n_P,n_E+1}} \quad (n_P + n_E \geqslant 1)$$
$$\mathrm{Q^E_{n_P,n_E} + EO \xrightarrow{k_p^{EE}} Q^E_{n_P,n_E+1}} \quad (n_P + n_E \geqslant 1)$$

Transfer:

$$\mathrm{G^P_{n_P,n_E} + PO \xrightarrow{k_t} D^P_{n_P,n_E} + Q_{0,0}} \quad (n_P, n_E \geqslant 0)$$
$$\mathrm{G^E_{n_P,n_E} + PO \xrightarrow{k_t} D^E_{n_P,n_E} + Q_{0,0}} \quad (n_P, n_E \geqslant 0)$$
$$\mathrm{Q^P_{n_P,n_E} + PO \xrightarrow{k_t} R^P_{n_P,n_E} + Q_{0,0}} \quad (n_P, n_E \geqslant 0)$$
$$\mathrm{Q^E_{n_P,n_E} + PO \xrightarrow{k_t} R^E_{n_P,n_E} + Q_{0,0}} \quad (n_P, n_E \geqslant 0)$$

Exchange:

$$\mathrm{G^P_{n_P,n_E} + D^P_{m_P,m_E} \xrightarrow{k_e} D^P_{n_P,n_E} + G^P_{m_P,m_E}} \quad (n_P, n_E, m_P, m_E \geqslant 0)$$
$$\mathrm{G^P_{n_P,n_E} + D^E_{m_P,m_E} \underset{k_e}{\overset{k_e}{\rightleftharpoons}} D^P_{n_P,n_E} + G^E_{m_P,m_E}} \quad (n_P, n_E, m_P, m_E \geqslant 0)$$
$$\mathrm{G^E_{n_P,n_E} + D^E_{m_P,m_E} \xrightarrow{k_e} D^E_{n_P,n_E} + G^E_{m_P,m_E}} \quad (n_P, n_E, m_P, m_E \geqslant 0)$$
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$$\mathrm{G^E_{n_P,n_E} + R^E_{m_P,m_E} \underset{k_e}{\overset{k_e}{\rightleftharpoons}} D^E_{n_P,n_E} + Q^E_{m_P,m_E}} \quad (n_P, n_E, m_P, m_E \geqslant 0)$$

Material

Starter	Low MW diol
Catalyst	KOH
Monomer	EO and PO

Notation

$\mathrm{G_n}$	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 (PO and EO)

Superscript

E,P	terminal units

Polyol chains in the reactor

	living	dormant
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

$$\frac{\mathrm{d}(V[\mathrm{X}^{\mathrm{P}}_{\mathrm{n_P},\mathrm{n_E}}])}{\mathrm{d}t} = V(k_p^{PP}[\mathrm{G}^{\mathrm{P}}_{\mathrm{n_P}-1,\mathrm{n_E}}] + k_p^{EP}[\mathrm{G}^{\mathrm{E}}_{\mathrm{n_P}-1,\mathrm{n_E}}])[\mathrm{PO}] - V(k_p^{PP}[\mathrm{PO}] + k_p^{PE}[\mathrm{EO}])[\mathrm{G}^{\mathrm{P}}_{\mathrm{n_P},\mathrm{n_E}}]$$

$$\frac{\mathrm{d}(V[\mathrm{X}^{\mathrm{E}}_{\mathrm{n_P},\mathrm{n_E}}])}{\mathrm{d}t} = V(k_p^{PE}[\mathrm{G}^{\mathrm{P}}_{\mathrm{n_P},\mathrm{n_E}-1}] + k_p^{EE}[\mathrm{G}^{\mathrm{E}}_{\mathrm{n_P},\mathrm{n_E}-1}])[\mathrm{EO}] - V(k_p^{EP}[\mathrm{PO}] + k_p^{EE}[\mathrm{EO}])[\mathrm{G}^{\mathrm{E}}_{\mathrm{n_P},\mathrm{n_E}}]$$

$$\frac{\mathrm{d}(V[\mathrm{Y}^{\mathrm{P}}_{\mathrm{n_P},\mathrm{n_E}}])}{\mathrm{d}t} = V(k_p^{PP}[\mathrm{Q}^{\mathrm{P}}_{\mathrm{n_P}-1,\mathrm{n_E}}] + k_p^{EP}[\mathrm{Q}^{\mathrm{E}}_{\mathrm{n_P}-1,\mathrm{n_E}}])[\mathrm{PO}] - V(k_p^{PP}[\mathrm{PO}] + k_p^{PE}[\mathrm{EO}])[\mathrm{Q}^{\mathrm{P}}_{\mathrm{n_P},\mathrm{n_E}}]$$

$$\frac{\mathrm{d}(V[\mathrm{Y}^{\mathrm{E}}_{\mathrm{n_P},\mathrm{n_E}}])}{\mathrm{d}t} = V(k_p^{PE}[\mathrm{Q}^{\mathrm{P}}_{\mathrm{n_P},\mathrm{n_E}-1}] + k_p^{EE}[\mathrm{Q}^{\mathrm{E}}_{\mathrm{n_P},\mathrm{n_E}-1}])[\mathrm{EO}] - V(k_p^{EP}[\mathrm{PO}] + k_p^{EE}[\mathrm{EO}])[\mathrm{Q}^{\mathrm{E}}_{\mathrm{n_P},\mathrm{n_E}}]$$

  - Algebraic equations

$$\mathrm{X}^{\mathrm{S}}_{\mathrm{n_P},\mathrm{n_E}} n_c = \mathrm{G}^{\mathrm{S}}_{\mathrm{n_P},\mathrm{n_E}}(n_i + n_u), \quad S \in \{P, E\}$$

$$\mathrm{Y}^{\mathrm{S}}_{\mathrm{n_P},\mathrm{n_E}} n_c = \mathrm{Q}^{\mathrm{S}}_{\mathrm{n_P},\mathrm{n_E}}(n_i + n_u), \quad S \in \{P, E\}$$

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

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

    2000 MW diol $>$ 1400 differential equations + 1400 algebraic equations

Process Dynamic Modeling

Population balances vs. method of moments

- Definition of moments: kth order moment of polymeric species

$$\lambda_k = \sum_{n_\mathrm{P}+n_\mathrm{E}\geqslant 1}^{\infty} (n_\mathrm{P}+n_\mathrm{E})^k \mathrm{X}_{n_\mathrm{P},n_\mathrm{E}}, \quad \zeta_k = \sum_{n_\mathrm{P}+n_\mathrm{E}\geqslant 1}^{\infty} (n_\mathrm{P}+n_\mathrm{E})^k \mathrm{G}_{n_\mathrm{P},n_\mathrm{E}}, \quad k=0,1,\ldots$$

$$\mu_k = \sum_{n_\mathrm{P}+n_\mathrm{E}\geqslant 1}^{\infty} (n_\mathrm{P}+n_\mathrm{E})^k \mathrm{Y}_{n_\mathrm{P},n_\mathrm{E}}, \quad \nu_k = \sum_{n_\mathrm{P}+n_\mathrm{E}\geqslant 1}^{\infty} (n_\mathrm{P}+n_\mathrm{E})^k \mathrm{Q}_{n_\mathrm{P},n_\mathrm{E}}, \quad k=0,1,\ldots$$

- Moment model (MM)
  - Differential equations

$$\frac{\mathrm{d}\lambda_k^\mathrm{P}}{\mathrm{d}t} = V^{-1}(k_i^\mathrm{P}\mathrm{G}_0\mathrm{PO} + k_p^\mathrm{PP}\sum_{i=0}^{k-1}\binom{k}{i}\zeta_i^\mathrm{P}\mathrm{PO} + k_p^\mathrm{EP}\sum_{i=0}^{k}\binom{k}{i}\zeta_i^\mathrm{E}\mathrm{PO} - k_p^\mathrm{PE}\zeta_k^\mathrm{P}\mathrm{EO})$$

$$\frac{\mathrm{d}\lambda_k^\mathrm{E}}{\mathrm{d}t} = V^{-1}(k_i^\mathrm{E}\mathrm{G}_0\mathrm{EO} + k_p^\mathrm{EE}\sum_{i=0}^{k-1}\binom{k}{i}\zeta_i^\mathrm{E}\mathrm{PO} + k_p^\mathrm{PE}\sum_{i=0}^{k}\binom{k}{i}\zeta_i^\mathrm{P}\mathrm{EO} - k_p^\mathrm{EP}\zeta_k^\mathrm{E}\mathrm{PO})$$

$$\frac{\mathrm{d}\mu_k^\mathrm{P}}{\mathrm{d}t} = V^{-1}(k_i^\mathrm{P}\mathrm{Q}_0\mathrm{PO} + k_p^\mathrm{PP}\sum_{i=0}^{k-1}\binom{k}{i}\nu_i^\mathrm{P}\mathrm{PO} + k_p^\mathrm{EP}\sum_{i=0}^{k}\binom{k}{i}\nu_i^\mathrm{E}\mathrm{PO} - k_p^\mathrm{PE}\nu_k^\mathrm{P}\mathrm{EO})$$

$$\frac{\mathrm{d}\mu_k^\mathrm{E}}{\mathrm{d}t} = V^{-1}(k_i^\mathrm{E}\mathrm{Q}_0\mathrm{EO} + k_p^\mathrm{EE}\sum_{i=0}^{k-1}\binom{k}{i}\nu_i^\mathrm{E}\mathrm{PO} + k_p^\mathrm{PE}\sum_{i=0}^{k}\binom{k}{i}\nu_i^\mathrm{P}\mathrm{EO} - k_p^\mathrm{EP}\nu_k^\mathrm{E}\mathrm{PO})$$

  - Algebraic equations

$$\lambda_k^S n_c = \zeta_k^S(n_i+n_u), \quad S=\{\mathrm{P},\mathrm{E}\}$$
$$\mu_k^S n_c = \nu_k^S(n_i+n_u), \quad S=\{\mathrm{P},\mathrm{E}\}$$

- Pros and cons
  - \+ Model size does not increase with polymer MW
    $0^{th}-2^{nd}$ moments $=$ 12 differential equations + 12 algebraic equations
  - – No detailed distribution

Copolymerization Case Study

Production of EO capped diol

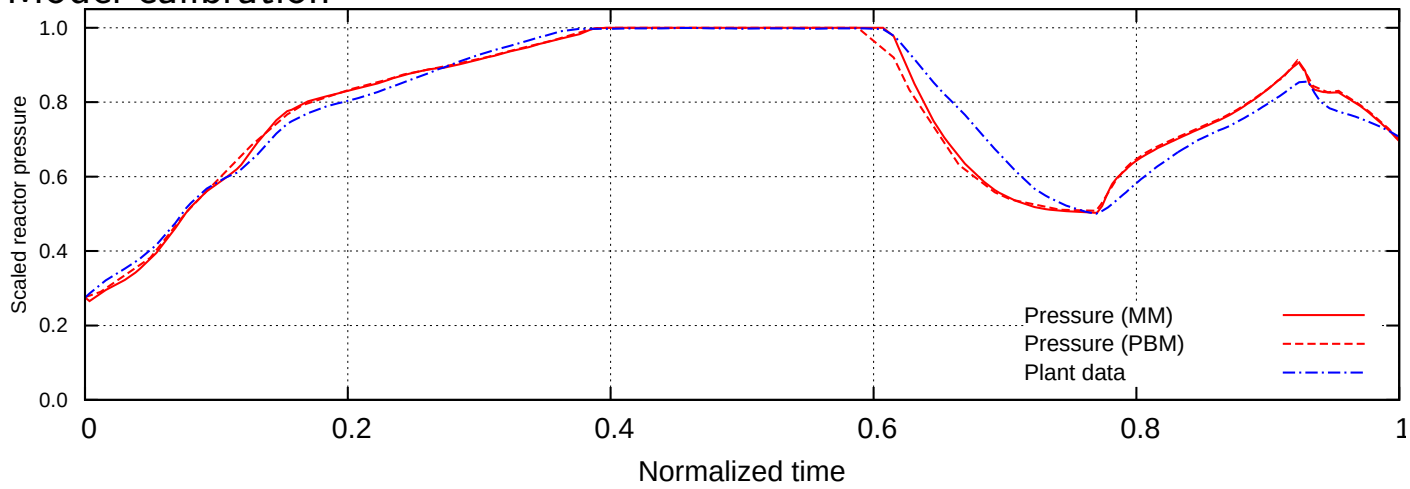
- Process specifications
  - Charge condition

Initiator:	PPG
Catalyst:	KOH
Monomer:	PO and EO

  - Process constraints*
    - ★ Product molecular weight $\geqslant 2000$ g/mol
    - ★ Product unsaturation value $\leqslant 0.02$ mmol/g polyol
    - ★ Heat exchanger load $\leqslant UA(T - T_w)$ kW
    - ★ Adiabatic end temperature $\leqslant (T_b + 90)^\circ$C
    - ★ Capping ratio $\geqslant 70\%$ (% 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



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- Optimization results
  - Optimization model statistics and solution

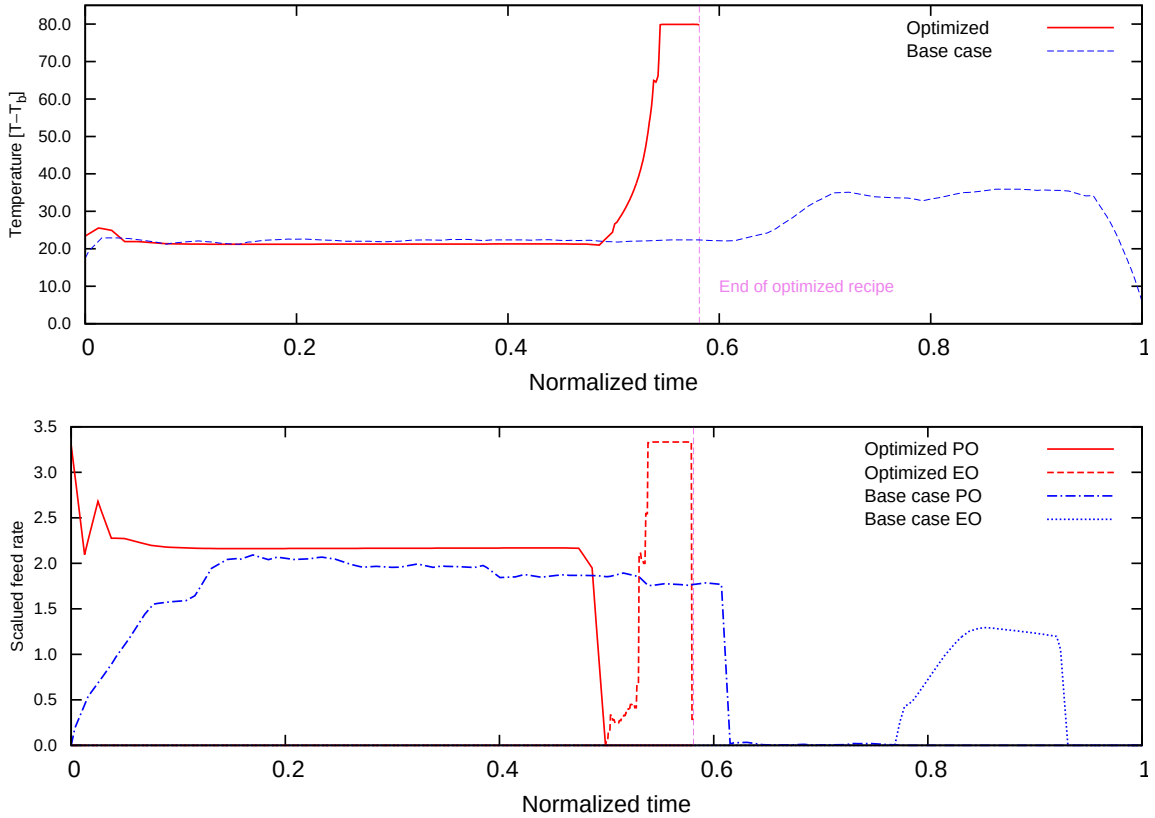
Opt. soln	MW (g/mol)	Unsat (mmol/g)	Capping(%)	# of var.	# of con.	CPU (s)
0.580	2000	0.02	70	11,248	11,121	22

    - ★ 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

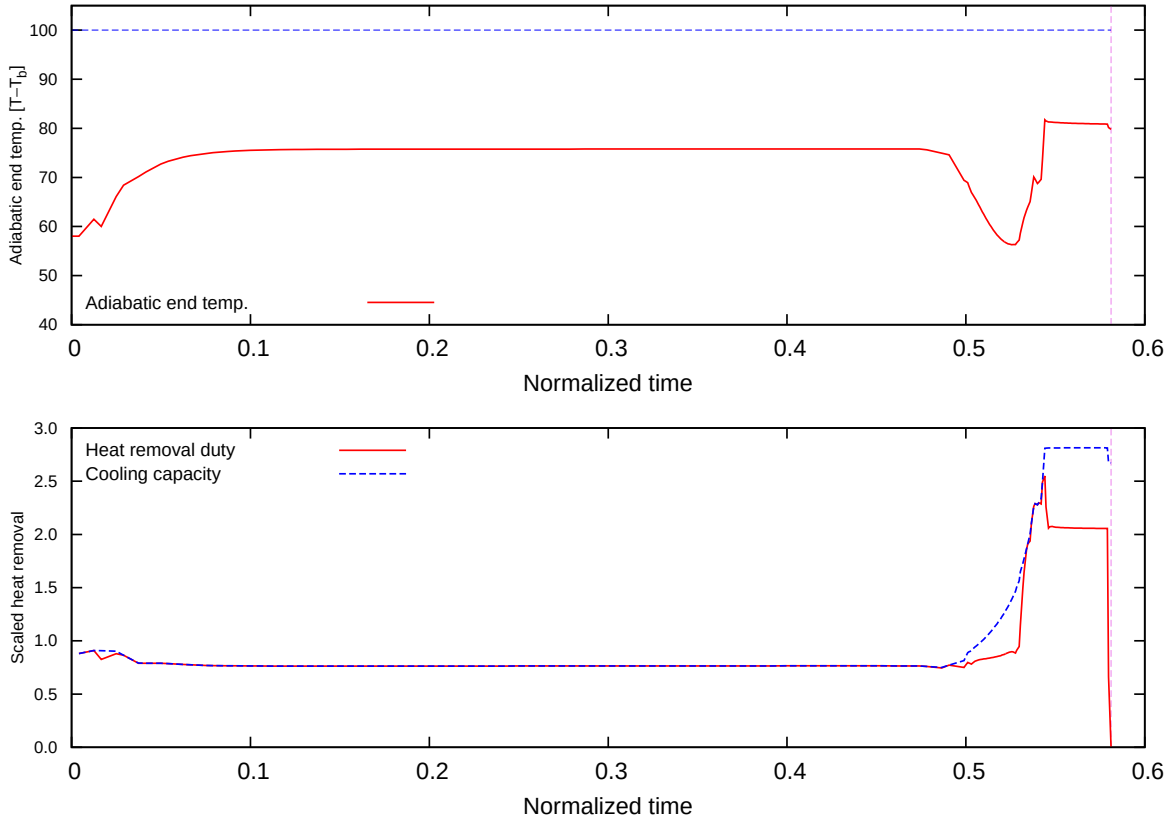


- Important remarks
  - Piecewise linear control profiles with continuity on finite element boundaries
  - Rising temperature for PO digestion and EO feeding
  - Flat feed rates for both monomers: no need for ramping

Copolymerization Case Study Results

Process constraint profiles

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

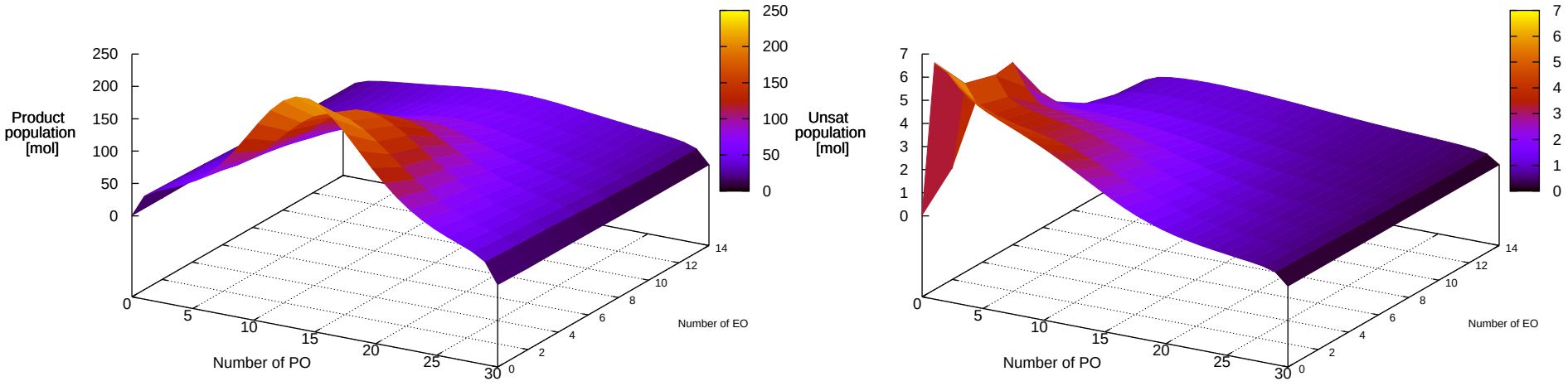


- Important remarks
  - Constraint on the adiabatic temp. is inactive
  - Heat exchanger capacity is the major constraining factor

Copolymerization Case Study Results

Optimal product molecular weight distributions (MWD)

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



- Important remarks
  - Similar optimal solution obtained from the PBM

Opt. soln	MW (g/mol)	Unsat (mmol/g)	Capping(%)	# of var.	# of con.	CPU (s)
0.588	2000	0.02	70	191,408	185,147	5221

  - Optimization over PBM is computationally expensive

Conclusions

Project timeline

Development of systematic optimization methods of batch processes

- Jan. 2012 - Dec. 2012
  - 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 copolyol
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    2. Hypothetical optimization case study: over 40% batch time reduction
- Jan. 2013 - May. 2014
  - 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