Dynamic Modeling and Recipe Optimization of Polyether Polyol Processes

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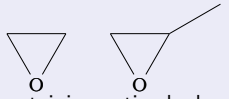
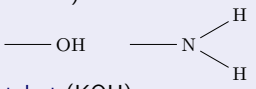
Introduction

Semi-batch polyether polyol process description

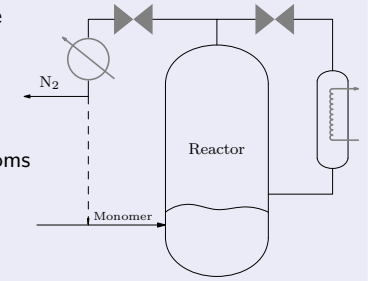
- Key ingredients
  - Epoxides (ethylene oxide (EO), propylene oxide (PO))



  - 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:

$$H_2O + PO \xrightarrow{k_h} P_0OH$$

Initiation:

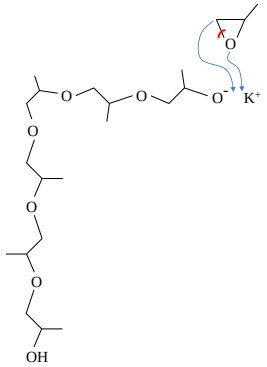
$$P_0O^-K^+ + PO \xrightarrow{k_i} P_1O^-K^+$$

Propagation:

$$P_nO^-K^+ + PO \xrightarrow{k_p} P_{n+1}O^-K^+$$

Exchange:

$$P_nO^-K^+ + P_mOH \xrightarrow{k_e} P_nOH + P_mO^-K^+$$



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

Notation

P_n $CH_3(PO)_n$

Process Dynamic Modeling

Modeling reaction kinetics

- Reaction scheme: Polypropylene glycol

Hydrolysis:

$$H_2O + PO \xrightarrow{k_h} P_0OH$$

Initiation:

$$P_0O^-K^+ + PO \xrightarrow{k_i} P_1O^-K^+$$

Propagation:

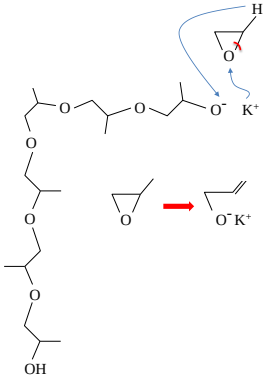
$$P_nO^-K^+ + PO \xrightarrow{k_p} P_{n+1}O^-K^+$$

Exchange:

$$P_nO^-K^+ + P_mOH \xrightarrow{k_e} P_nOH + P_mO^-K^+$$

Transfer:

$$P_nO^-K^+ + PO \xrightarrow{k_t} P_nOH + U_0O^-K^+$$



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

Notation

P_n $CH_3(PO)_n$

U_n $CH_2=CHCH_2(PO)_n$

Process Dynamic Modeling

Modeling reaction kinetics

- Reaction scheme: Polypropylene glycol

Hydrolysis:

$$\mathrm{W} + \mathrm{M} \xrightarrow{k_\mathrm{h}} \mathrm{D}_0$$

Initiation:

$$\mathrm{G}_0 + \mathrm{M} \xrightarrow{k_\mathrm{i}} \mathrm{G}_1$$
$$\mathrm{Q}_0 + \mathrm{M} \xrightarrow{k_\mathrm{i}} \mathrm{Q}_1$$

Propagation:

$$\mathrm{G}_\mathrm{n} + \mathrm{M} \xrightarrow{k_\mathrm{p}} \mathrm{G}_{\mathrm{n}+1} \quad (\mathrm{n} \geqslant 1)$$
$$\mathrm{Q}_\mathrm{n} + \mathrm{M} \xrightarrow{k_\mathrm{p}} \mathrm{Q}_{\mathrm{n}+1} \quad (\mathrm{n} \geqslant 1)$$

Transfer:

$$\mathrm{G}_\mathrm{n} + \mathrm{M} \xrightarrow{k_\mathrm{t}} \mathrm{D}_\mathrm{n} + \mathrm{Q}_0 \quad (\mathrm{n} \geqslant 0)$$
$$\mathrm{Q}_\mathrm{n} + \mathrm{M} \xrightarrow{k_\mathrm{t}} \mathrm{R}_\mathrm{n} + \mathrm{Q}_0 \quad (\mathrm{n} \geqslant 0)$$

Exchange:

$$\mathrm{G}_\mathrm{n} + \mathrm{D}_\mathrm{m} \xrightarrow{k_e} \mathrm{D}_\mathrm{n} + \mathrm{G}_\mathrm{m} \quad (\mathrm{n}, \mathrm{m} \geqslant 0)$$
$$\mathrm{Q}_\mathrm{n} + \mathrm{R}_\mathrm{m} \xrightarrow{k_e} \mathrm{R}_\mathrm{n} + \mathrm{Q}_\mathrm{m} \quad (\mathrm{n}, \mathrm{m} \geqslant 0)$$
$$\mathrm{G}_\mathrm{n} + \mathrm{R}_\mathrm{m} \underset{k_e}{\overset{k_e}{\rightleftharpoons}} \mathrm{D}_\mathrm{n} + \mathrm{Q}_\mathrm{m} \quad (\mathrm{n}, \mathrm{m} \geqslant 0)$$

Material

Starter	Propylene glycol (PG)
	Water
Catalyst	KOH
Monomer	PO

Notation

M	monomers (PO)
W	water
G_n	growing product chains ($\mathrm{P_nO^-K^+}$)
D_n	dormant product chains ($\mathrm{P_nOH}$)
Q_n	growing unsat chains ($\mathrm{U_nO^-K^+}$)
R_n	dormant unsat chains ($\mathrm{U_nOH}$)
P_n	$\mathrm{CH_3(PO)_n}$
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 exchange reactions
  → Stiff differential equations

A nullspace projection method for reformulating equilibrium reactions

- A generic reaction system with irreversible and equilibrium reactions

$$\dot{x} = \begin{bmatrix} A_1 & A_2 \end{bmatrix} \begin{bmatrix} r_1(x) \\ \sigma r_2(x) \end{bmatrix} + g(t), \qquad \sigma \gg 1 \text{ for fast equilibrium rates}$$

- Multiplying with a non-singular matrix $\begin{bmatrix} \mathcal{Y}^\mathrm{T} & \mathcal{Z}^\mathrm{T} \end{bmatrix}^\mathrm{T}$,

where, $(\mathcal{Z}^\mathrm{T}A_2 = 0, \sigma\mathcal{Y}^\mathrm{T}A_2 r_2(x) = \begin{bmatrix} 0 \\ \sigma f(x) \end{bmatrix})$

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

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

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

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

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

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

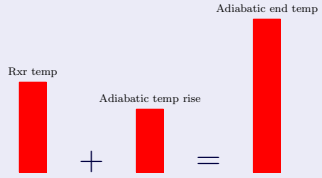
Process Recipe Optimization

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 number
  - Final time monomer concentration
- Process safety constraints
  - Heat removal duty
  - Adiabatic end temperature due to loss of cooling



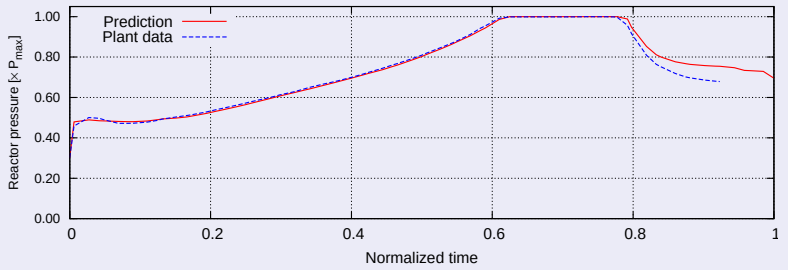
Control variables Reactor temperature and monomer feed rate

Solution strategy The simultaneous collocation method

Case Study

Model calibration: matching reactor pressure profiles

Reactor pressure: model prediction vs. plant data



Model parameter adjustments

1. Open literature parameters
2. Speed up the propagation rate by 70%
3. Increase water and PG activities and lower the hydrolysis rate
4. Estimate released nitrogen during venting

Case Study

Production of polypropylene glycol

Process specifications

- Initial charge condition

Initiator:	PG and Water
Catalyst:	KOH
Monomer:	PO

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

Optimization results

- Optimization model statistics and solution

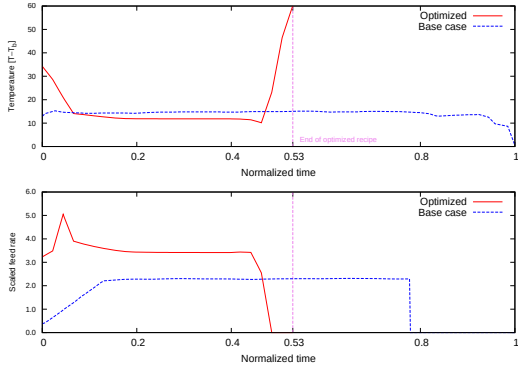
Opt. soln	MW (g/mol)	Unsat (mmol/g)	PO(ppm)	# of var.	# of con.
0.575	950	0.028	120	10946	11043

  - Batch time reduced by 42.5% (base case batch time is normalized to 1)
  - Constraints are satisfied at the end of the operation

Case Study Results

Optimal control profiles of the process

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

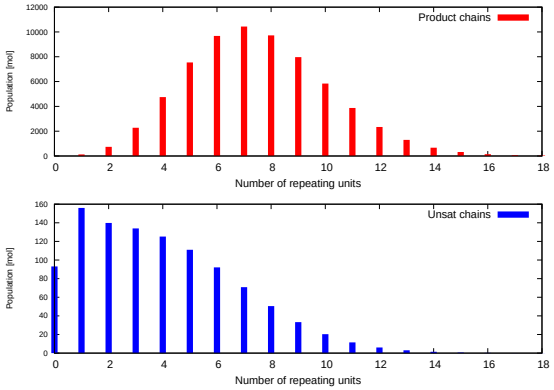


- Important remarks
  - Piecewise linear control profiles with continuity on finite element boundaries
  - U-shape temperature profile and higher average feed rates
  - Merging the feeding and digestion periods

Case Study Results

Optimal product molecular weight distributions (MWD)

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

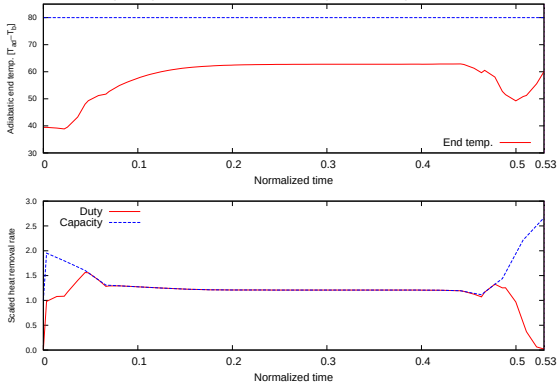


- Important remarks
  - Near *Poisson* distribution for the product polymers
  - Flat distribution for the unsat polymers

Case Study Results

Process constraint profiles

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

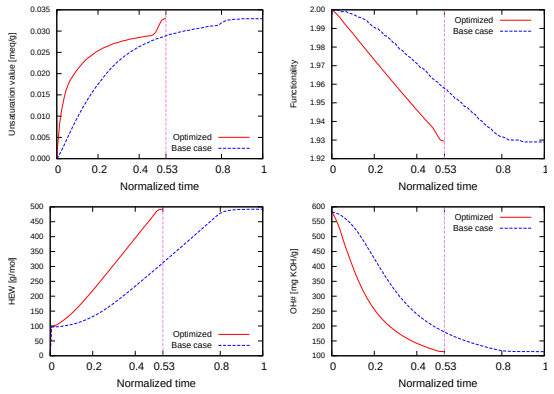


- Important remarks
  - Heat exchanger capacity is the main constraining factor
  - The adiabatic end temperature constraint is also limiting process performance

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

Concluding remarks and future work

- Concluding remarks
  - Developed a detailed and computationally efficient dynamic model for alkoxylation processes
  - Model validation against plant data
  - Dynamic optimization for process recipe improvement
    - Merged feeding and digestion: changing recipe design pattern
- Future work
  - Extension of the model: copolymerization, multi-step products, etc.
  - Simultaneous scheduling and dynamic optimization
    - Multiple reactors
    - Real-time constraints on shared resources
  - Other applications at Dow