Time-optimal Control of Emulsion Co-polymerization by Tracking Necessary Conditions of Optimality

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Outline

- Emulsion polymerization
- Control approach
- Conditions for time-optimal operation
- Estimation approach – uncertainties
- Performance of the control approach
- Summary
Emulsion polymerization

- Important industrial process for production of dispersed macromolecules
- Environmentally friendly due to use of water as a solvent
- High degrees of polymerization possible
- Relatively low-viscosity product
- Favorable chemical properties (e.g. high molecular weights)

Applications
- Adhesives
- Paints
- Polymer films
  - ……
Emulsion Polymerization

1. Mixing of water and monomer
   • Formation of two liquid phases with relatively large droplets (µm – mm)

2. Addition of emulsifier
   • Very small droplets (micelles, d≈10nm) develop

3. Addition of water-soluble initiator
   • Reaction starts in the water phase
   • Polymer chains are formed

4. Polymer precipitates and forms particles
   • Particles are the main location of polymerization
   • Monomer and radicals diffuse through the water phase into the particles
   • Monomer phase vanishes (starved conditions)

- Multiphase semi-batch process
- Products-by-Process: End-use properties are determined by process conditions
Goal

- Development of a control strategy for emulsion co-polymerization featuring
  - Time-optimal operation to increase productivity
  - Satisfaction of quality constraints (copolymer composition, molecular weight distribution)
  - Capability to cope with fast disturbances (e.g. stirrer breakdown, feed pump failures)
  - Capability of coping with slow disturbances (e.g. caused by fouling)
  - Ease of implementation
  - Acceptable for operators
Time optimal control

Task:
- Time-optimal control while achieving quality constraints:
  - *Molecular Weight* Distribution (MWD)
  - Copolymer Composition Distribution (CCD)

Concept:
- Drive the process along the constraints [1]:
  - Limited heat removal capacity of the reactor
  - Avoidance of a droplet phase because the reaction rate becomes uncontrollable if droplets are present

Control concept

- Decentralized PI controller
- Set point for total amount of monomer in reactor
- Set point for concentrations in particle phase
- Heat removal constraint
  \[ \dot{Q}_{R,\text{max}} < kA(T_R - T_{J,\text{min}}) \]
- Avoidance of droplet phase
  \[ V_W \geq (k^d - 1)V_M^W \]
- Offline computations
  - SP copoly. composition (CCD)
  - SP instant. MWD
  - SP final molecular weight distribution (MWD)
Off-line optimization

Desired MWD and Copolymer Composition

Model-based computation of a feed strategy for the monomers and the chain transfer agent taking the constraints into account

Produced Polymer
Conditions for time optimal operation (I)

- **Avoidance of droplets**
  - The monomers distribute among the phases
  - Monomer is not well soluble in water, excess monomer forms droplets
  - From the phase distribution, conditions for the total holdups of the monomers in the reactor can be derived
  - The volume of the polymer and of the monomer and the water in the reactor must be computed
  - This is done by forward (open-loop) simulation based upon the estimated (total) conversion
Conditions for time optimal operation (II)

- Limited heat removal capacity of the jacket cooling
  - Limited by the heat transfer coefficient $k$
  - Reaction rate depends on the monomer concentrations in the polymer and the volume of the polymer

\[
[M]_{\text{max}}^p = \left(\sum_i \dot{V}_{\text{in},i} \rho_i c_{p,i} (T_R - T_{\text{in},i}) - kA \Delta T_{\text{max}}\right) \frac{[M]^p}{Q_R}
\]

\[
n_M^{SP} = \varphi [M]_{\text{max}}^p \frac{V_{\text{Pol}}}{1 - [M]_{\text{max}}^p \bar{V}}
\]

to be estimated
Limitations of the Monomer Holdup

- Seeded semi batch emulsion polymerisation of Styrene (simulation)

Avoidance of droplets

Limited heat removal capacity
Control concept

Decentralized PI controller

Set point for total amount of monomer in reactor

Set point for concentrations in particle phase

Heat removal constraint
\[ \dot{Q}_{R,\text{max}} < k A (T_R - T_{I,\text{min}}) \]

Avoidance of droplet phase
\[ V_W \geq (k^d - 1) V_M \]

SP copoly. composition (CCD)

SP final molecular weight distribution (MWD)

SP instant. MWD

Offline computations

Process Monitor
Hierarchical control approach (II)

Desired final MWD

Instantaneous MWD

$\overline{M}_n^{SP} (X_c)$

Calculation of the flow rate of CTA

Calculation of the set points of the amounts of monomers in the reactor

$SP$

$n_M$

Open loop observer

Estimation of $Q_R$ and $k$

SISO PI-controllers

Produced MWD
Simulation Study

Investigated Process:

- Seeded semi batch emulsion polymerisation of Styrene (M) with Butylmaleate (CTA)
- Kinetic model based on Vicente et al. 2001, Li & Brooks 1993:
  - Differential equations for M, CTA, initiator, volumes of polymer & water, radical conc. in the water phase, average number of radicals per particle, conversion, MWD
  - Algebraic equations, e.g. phase distribution
Model Equations

Monomer Balance
\[
\frac{d[i]^R}{dt} = \frac{1}{V^R} \left( -R_i - \frac{dV^R}{dt} [i]^R + \dot{n}_i \right) \text{ with } R_i = \sum_{j=1}^n k_{pj} M^j \frac{nN_T}{N_A}
\]

Initiator Balance
\[
\frac{d[I]^R}{dt} = \frac{1}{V^R} \left( -2 \alpha k_d [I]^R - \frac{dV^R}{dt} [I]^R \right)
\]

Volume Balances
\[
\frac{dV^R}{dt} = \sum_i \dot{n}_i \bar{V}_i + \sum_i R_i M_i \left( \frac{1}{\rho_{pol}} - \frac{1}{\rho_i} \right) \quad , \quad \frac{dV_p}{dt} = \sum_i \frac{R_i M_i}{\rho_{pol}}
\]

Temperature Balance
\[
\frac{dT_R}{dt} = \frac{1}{C_s} \left( \sum_i R_i (-\Delta H_i) + \sum_i \dot{n}_i M_i c_p \left( T_{rin} - T_R \right) + kA \left( T_J - T_R \right) \right)
\]
\[
\frac{dT_J}{dt} = \frac{1}{C_J} \left( (T_{jin} - T_J) - kA \left( T_J - T_R \right) \right)
\]

+ Phase distribution equations
+ Temperature dependent rate constants
Simulation Study Homopolymerization

- Optimal trajectories of the molar amounts of monomer and CTA
- Discrete time PI-controllers
- Anti-wind-up
- Trajectories are tracked well
- Difference between estimates and true values
Simulation Study

- Comparison of produced and desired MWD

![Graph showing comparison of simulated MWD and desired MWD]
Experimental Work by Wolfgang Mauntz

Copolymerization of MMA with BA
Results at the 10 l Pilot Plant

- Temperature [°C]
- CC [-]
- MW [-]

Graph showing time-optimal control of Emulsion Co-polymerization.
Results at the Pilot Plant
Summary

- Emulsion polymerization is a challenging multiphase process
- New time-optimal control scheme based on the estimation of the monomer holdups and $kA$
- Simple SISO controllers used to implement the desired set-points, no nonlinear controllers needed
- Process constraints are met
- Product quality was good

- Future work: Transfer to industrial application
- Robustification by additional measurements
- Modeling and control of the particle size distribution
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