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

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Outline

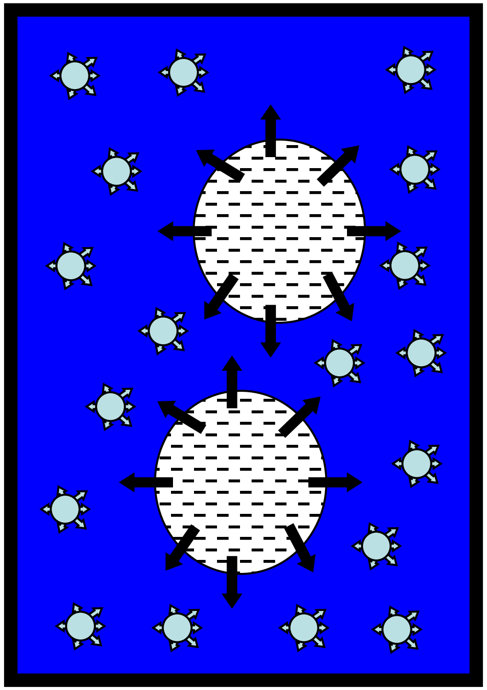
- Emulsion polymerization
- Control approach
- Conditions for time-optimal operation
- Estimation approach – uncertainties
- Performance of the control approach
- Summary

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:

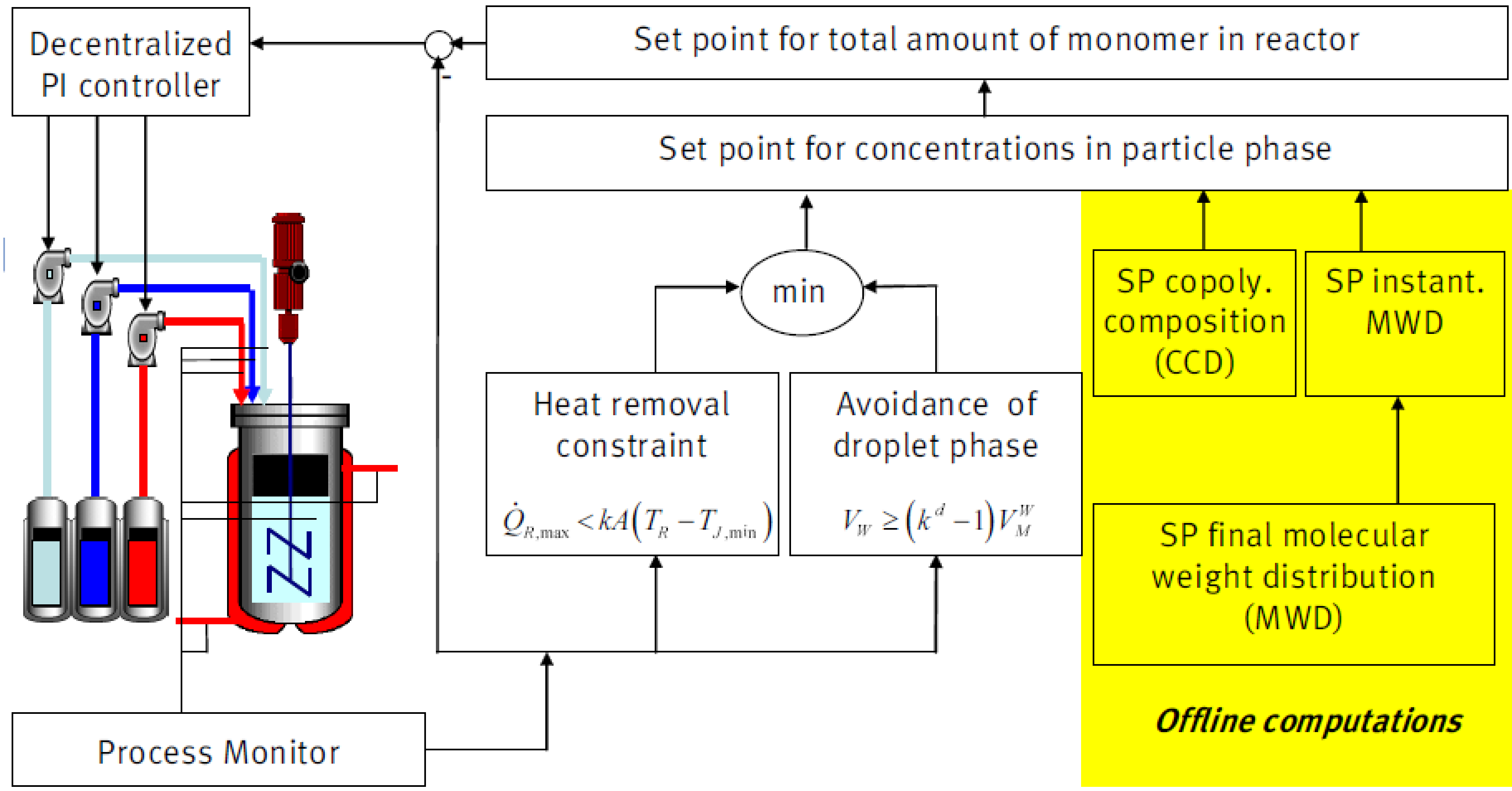
- Time-optimal control while achieving quality constraints:
  - *M*olecular *W*eight *D*istribution (MWD)
  - *C*opolymer *C*omposition *D*istribution (CCD)

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

[1] R. Gesthuisen, S. Krämer and S. Engell (2004). Hierarchical control scheme for time-optimal operation of semibatch emulsion polymerizations. *Ind. Eng. Chem. Res.* 43, p. 7410.

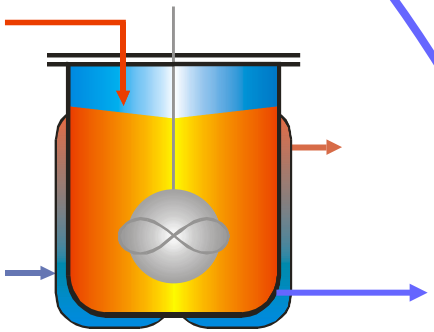
Control concept



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

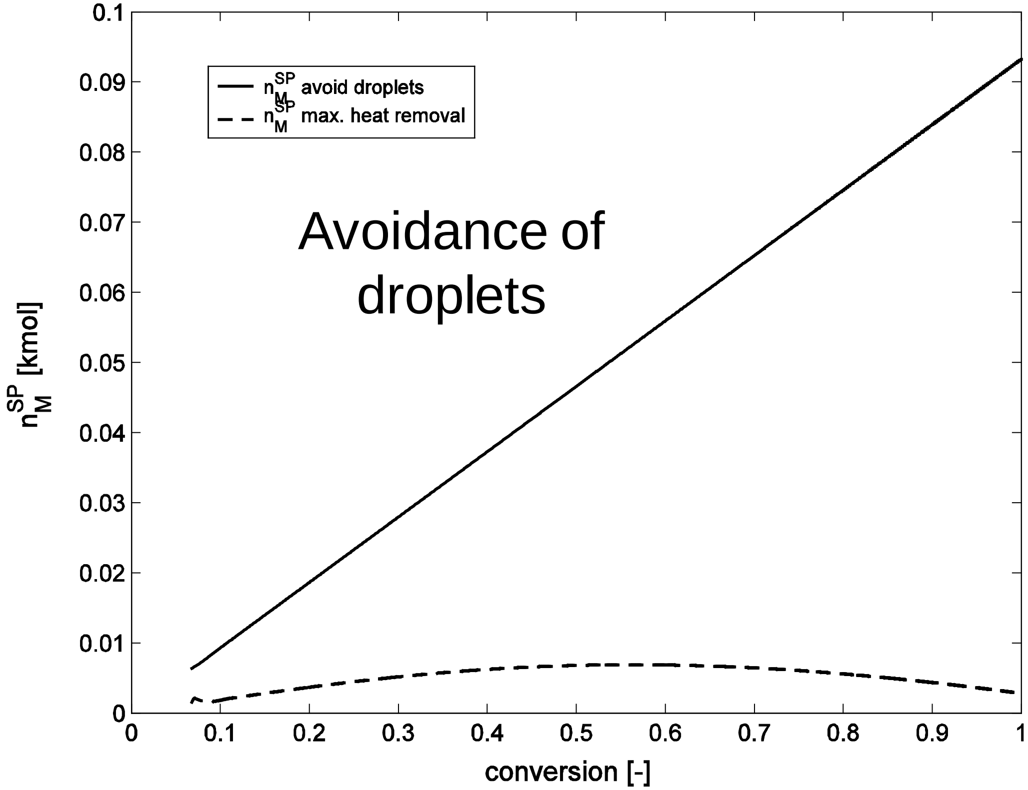
$$[M]_{\max}^{p} = \left(\sum_i \dot{V}_{in,i} \rho_i c_{p,i} \left(T_R - T_{in,i} \right) + kA \Delta T_{\max} \right) \frac{[M]^p}{Q_R}$$

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

to be estimated

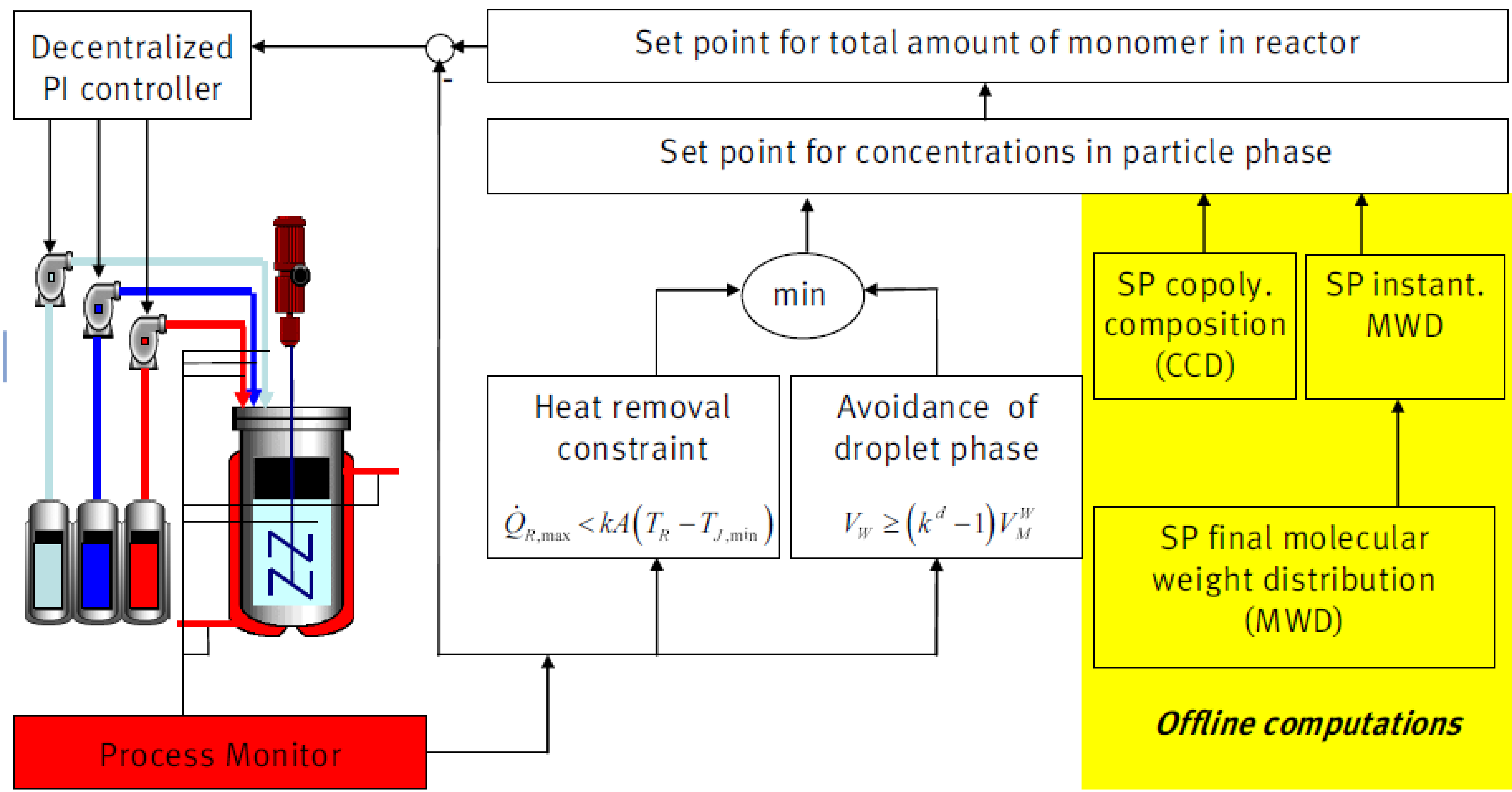
Limitations of the Monomer Holdup

- Seeded semi batch emulsion polymerisation of Styrene (simulation)

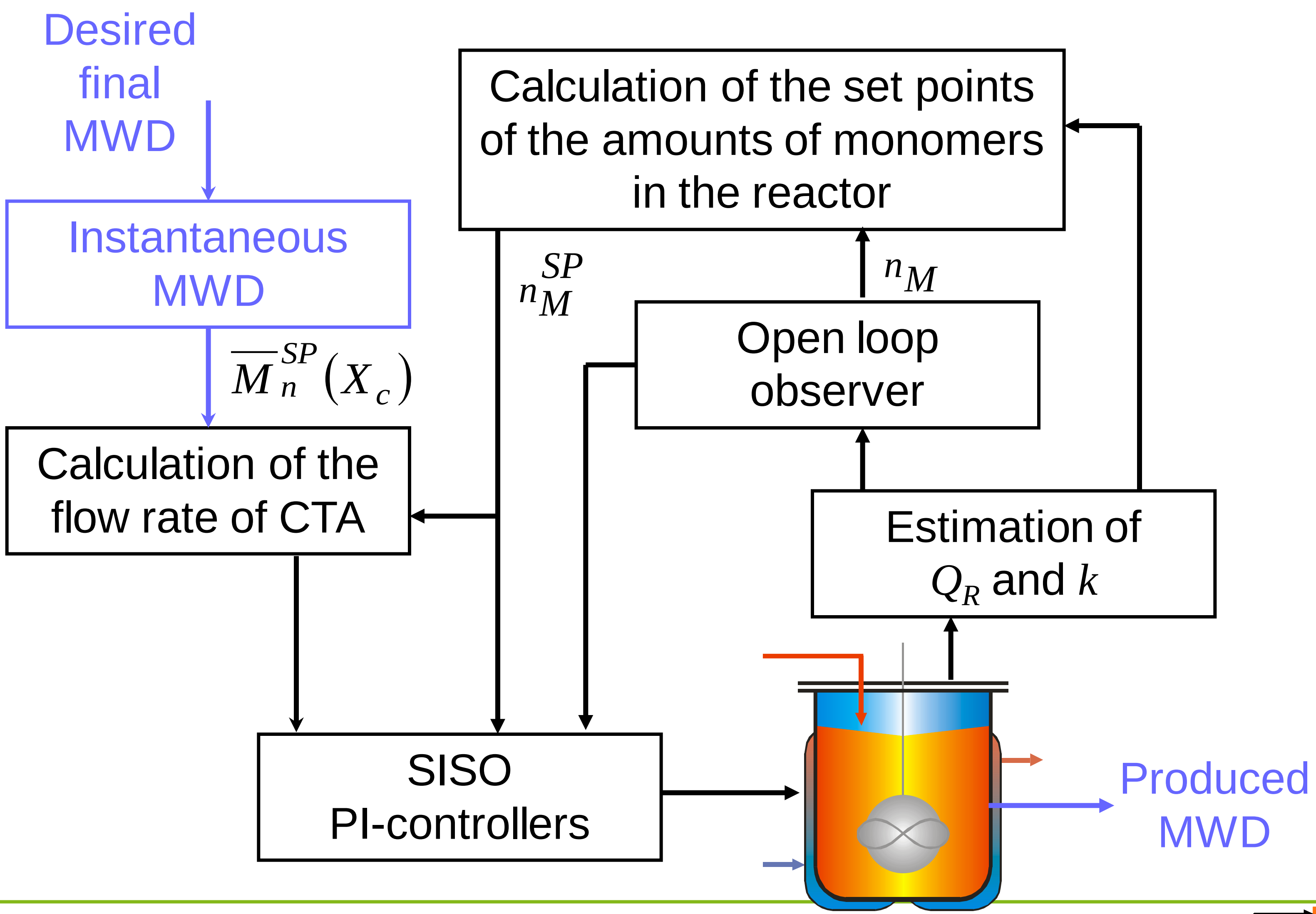


Limited heat removal capacity

Control concept



Hierarchical control approach (II)



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
$$\frac{d[i]^R}{dt} = \frac{1}{V^R}\left(-R_i - \frac{dV^R}{dt}[i]^R + \dot{n}_i\right) \text{ with } R_i = \sum_{j=1}^{n} k_{Pji} P_j [M^i]^p \frac{\bar{n} N_T}{N_A}$$

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

Volume Balances
$$\frac{dV^R}{dt} = \sum_i \dot{n}_i \overline{V_i} + \sum_i R_i M_i \left(\frac{1}{\rho_{Pol}} - \frac{1}{\rho_i}\right) \quad , \quad \frac{dV_P}{dt} = \sum_i \frac{R_i M_i}{\rho_{Pol}}$$

Temperature Balance
$$\frac{dT_R}{dt} = \frac{1}{C_S}\left(\sum_i R_i(-\Delta H_i) + \sum_i \dot{n}_i M_i c_{p_i}(T_{Rin} - T_R) + kA(T_J - T_R)\right)$$

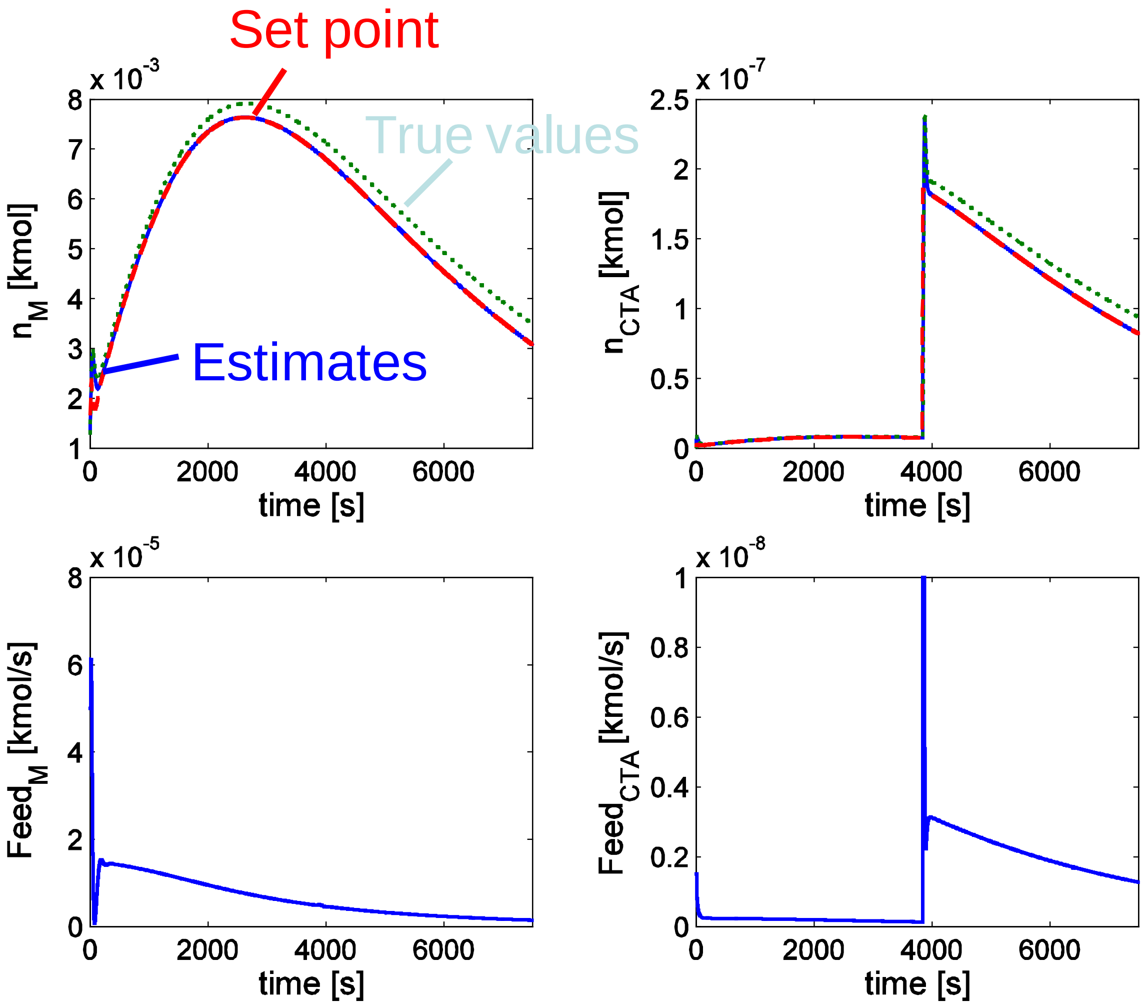
$$\frac{dT_J}{dt} = \frac{1}{C_J}\left((T_{Jin} - T_J) - kA(T_J - T_R)\right)$$

+ Phase distribution equations
+ Temperature dependent rate constants

Simulation Study Homopolymerization

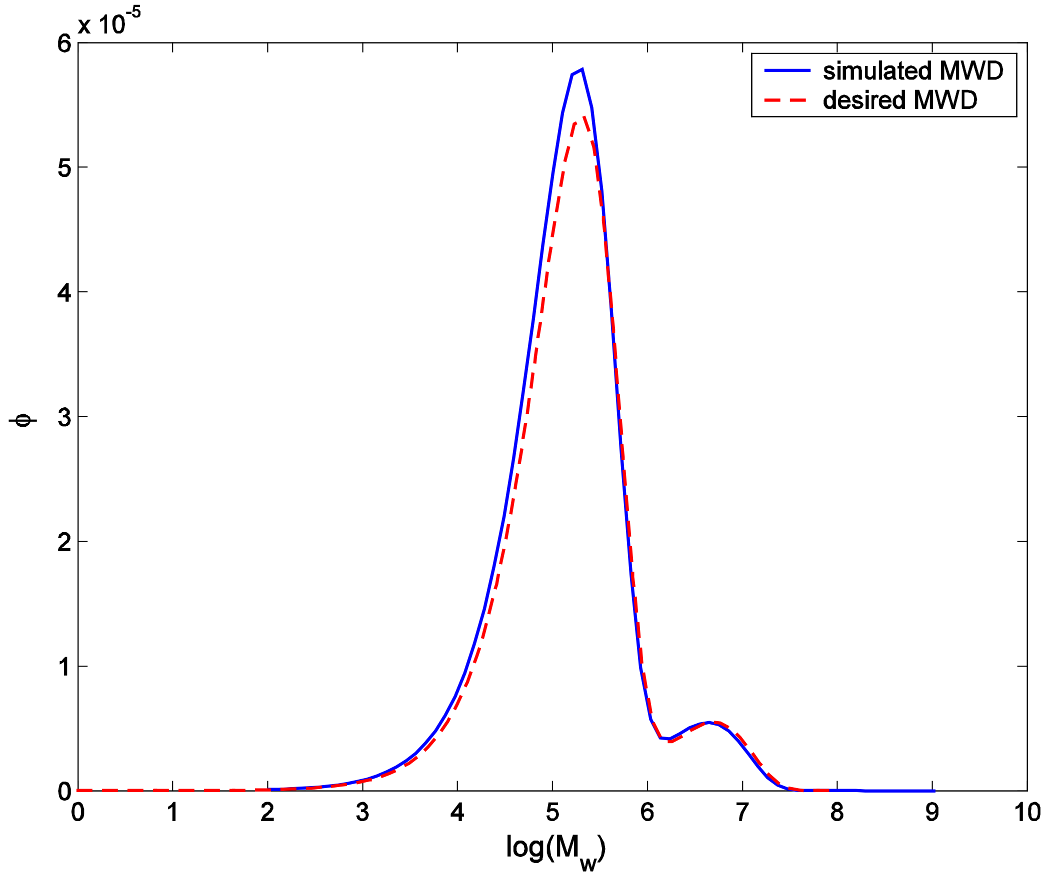
- Optimal trajectories of the molar amounts of monomer and CTA

- Discrete time PI-controllers
- Anti-wind-up
- Trajectories are tracked well
- Difference between estimates and true values



Simulation Study

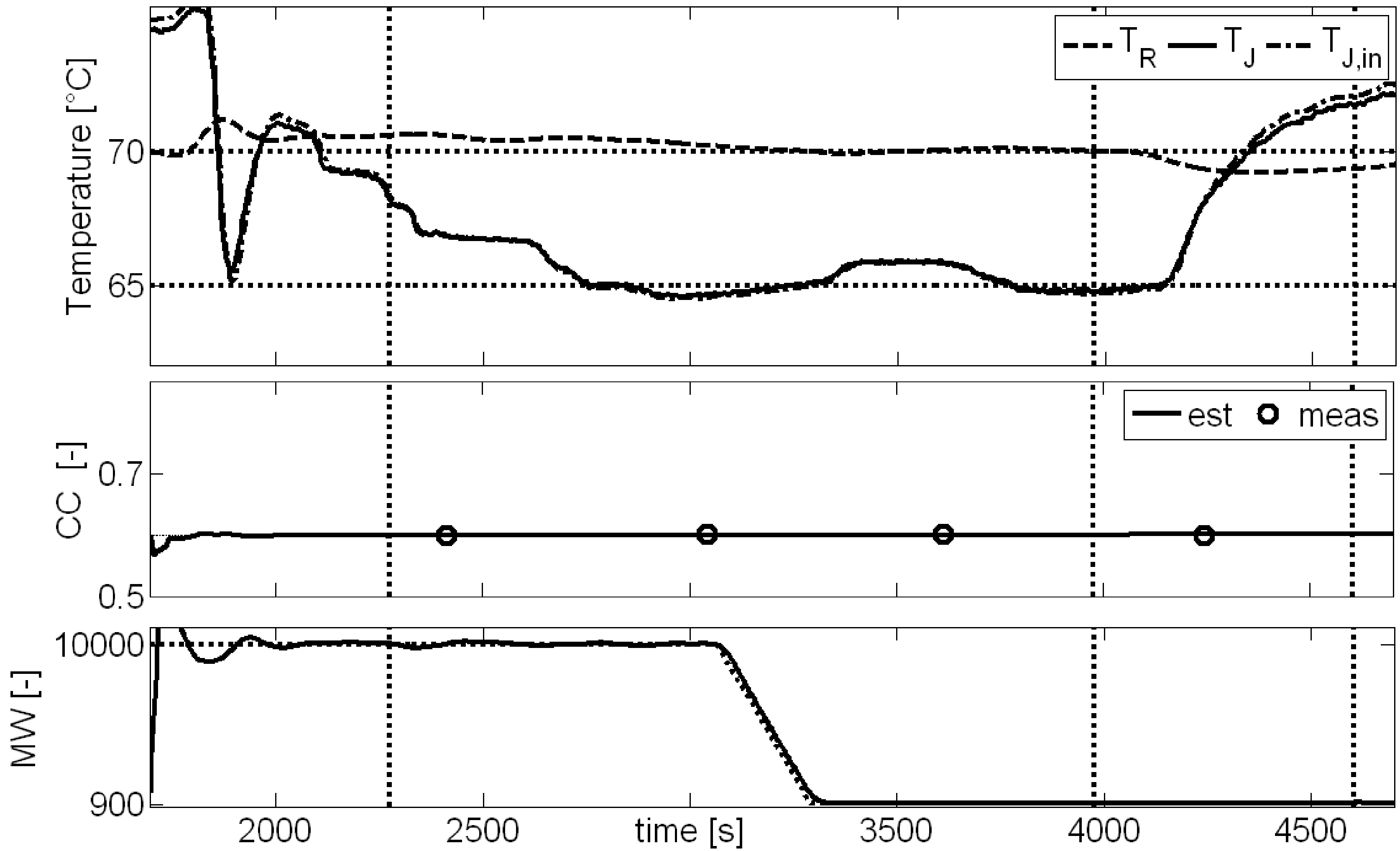
- Comparison of produced and desired MWD



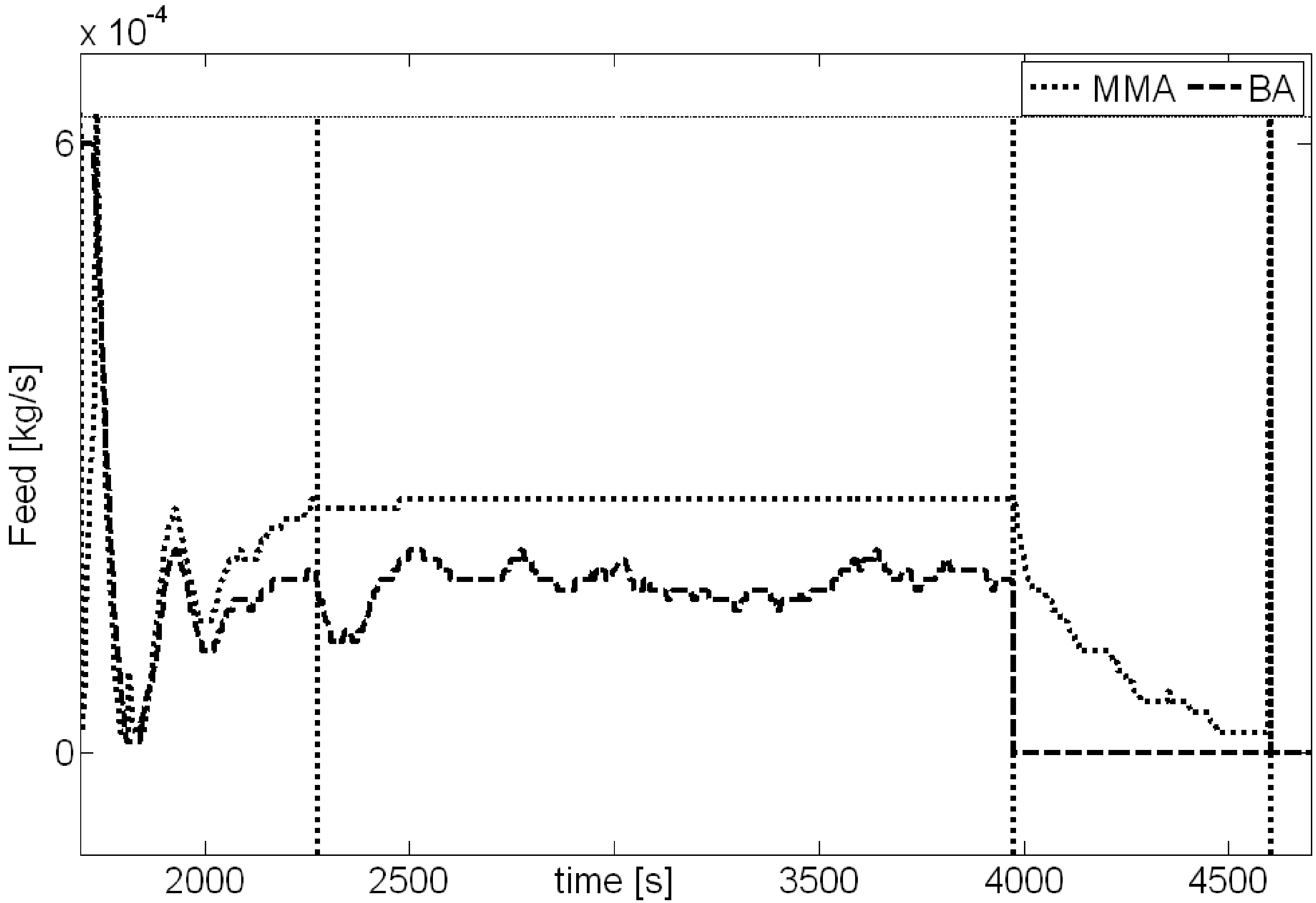
Experimental Work by Wolfgang Mauntz

Copolymerization of MMA with BA

Results at the 10 l Pilot Plant



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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