Online Control of Molar Mass and Particle-Size Distributions in Emulsion Polymerization

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Product quality control is a complex issue in polymerization than in conventional chemical processes. The key polymer properties are related to the polymer particle-size distribution (PSD), and molecular-weight distribution (MWD), which are in turn sensitive to the thermo-kinetic and operating history of the process. Disturbances in operating conditions may cause irreversible changes in the quality of the polymer formed. Therefore, adjustments must be made during the reaction through effective online control schemes. For this purpose, model predictive control (MPC) algorithm for on-line control of polymer PSD and MWD was developed and implemented. An intelligent control hierarchy was formulated for the distributed parameter system at three levels: off-line optimization, on-line MPC and regulatory control successively. The novelty of our approach includes the incorporation of a validated high-order dynamic model as a soft-sensor for on-line feedback of PSD and MWD. The MPC was implemented successfully on a reactor facility, where off-line sample analysis, using CHDF and GPC instruments, were used to update the on-line model predictions. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 1770–1779, 2006

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Introduction

In polymer industry, substantial incentives exist in developing real-time optimal operating schemes that result in the production of polymers with desired properties. The molecular architecture of the polymer and the particle size in the emulsion polymerization processes in particular, play a major role in this context. However, the control of PSD and MWD in emulsion polymerization using closed-loop strategies is a challenging problem.[1] Difficulties associated with on-line measurement of PSD and MWD, together with the complex mechanisms involved in emulsion polymerization systems, limit the options and make control implementation a formidable task. In many cases, conventional control strategies fail to ensure a consistent product quality, with the result that industries rely on traditional "recipes" and experience.

Although a few studies have been published on PSD or MWD control, little information exist on multiobjective optimization of emulsion polymerization. Cawthon and Knaebel[2] studied the optimization problem for both chain and step polymerizations. Their analysis focused on the determination of tradeoffs between polydispersity, composition, number average molar mass and reaction time with the reactor temperature and reactant flow rates as manipulated variables. Hidalgo and Brosilow[3] conducted simulations for the application of nonlinear MPC to free-radical solution polymerization of styrene in a stirred-tank reactor.

Kozub and Macgregor[4] proposed an on-line, nonlinear, inferential feedback control for a semi-batch seeded emulsion copolymerization reactor. The objectives included control of copolymer composition, branching, crosslinking, monomer conversion, average molecular weight and optimal reaction time. Optimal trajectory profiles were calculated for the ma-

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nipulated variables, such as the monomer feedrates, reactor temperature, and the flow rate of the chain transfer agent. Arkun et al.[5] applied a nonlinear MPC algorithm, to control the reactor temperature, and the MW of the polymer in the simulated free radical polymerization of methyl methacrylate (MMA). Ogunnaike[6] applied a control scheme involving a two-task system in which the monomer flow rate and catalyst were used to control the reactant composition at the first level, and at the second level the reactant target values were used to regulate product properties. Deshpande et al.[7] performed a simulation-based study on MPC application to an ethylene-propylene-diene reactor.

Liotta et al.[8] investigated the control of the relative particle growth of a bidispersed polystyrene polymer. The strategy comprised a Kalman filter for state estimation, and a shrinking horizon MPC. Asua et al.[9] used a nonlinear model-based controller to calculate the feed rates of chain transfer agent and monomer required to produce a polymer with desired MWD in styrene polymerization. Crowley and Choi[10] studied the control of weight-chain-length distribution in MMA polymerization. An extended Kalman filter was used for online state estimation. Rhee[11] investigated the use of an extended Kalman filter and nonlinear MPC for control of weight average MW and conversion of MMA. Doyle et al.[12] attempted to control the PSD in emulsion polymerization. Simulations of open-loop optimal trajectories for styrene polymerization were studied in manipulating surfactant feedrate to reactor.

Shi et al.[13,14] focused on the development and application of predictive algorithms for control of PSDs described by PBMs. The control algorithms, subject to manipulated input and product quality constraints, were designed on the basis of finite-dimensional models for particulate processes. Closed-loop simulations demonstrated the effectiveness of the proposed control algorithms. Chiu and Christofides[15] developed nonlinear output feedback controllers with a model reduction procedure to reproduce the dynamics of the particulate process. The nonlinear, low-order, feedback controllers enforce exponential stability in the closed-loop system. The performance and robustness properties of the proposed control, were established through simulations on a continuous crystallizer.

The foregoing indicates that online implementation of advanced multivariable control of particulate product properties is in its early stages of development. To apply advanced control techniques suitable devices/sensors are needed for online information. Recent advances in process understanding, mathematical modeling, soft-sensor technology and model-based control techniques provide opportunities for major improvements in process operation and product quality. A viable approach involves combining these powerful tools into an effective model-based control strategy. In this work, we present the application of MPC to on-line MWD and PSD control in semi-batch styrene emulsion polymerization. The dynamic matrix control (DMC) version of the MPC is presented, including the effects due to process constraints and interactions in the multivariable system. The motive behind selecting MPC is that it is an effective available strategy for incorporating multiple performance criteria efficiently, and is capable of utilising generalized dynamic process models.

Emulsion Polymerization and MPC

Models describing the process kinetics and particle evolution in emulsion polymerization are given in Zeaiter et al.[16] The population balance models (PBM) comprise a series of integropartial differential equations coupled with a set of differential and algebraic equations. The dynamic behaviour of a perfectly mixed semibatch reactor was simulated using gPROMS (Process Systems Enterprise Ltd.) to describe the polymerization of styrene initiated by potassium persulfate and stabilized by sodium lauryl sulfate.

Model testing and validation were carried out over a wide range of operating conditions, such as reaction temperature and monomer feed. Thereafter, the authors conducted a preliminary off-line optimal control study to investigate the use of such detailed mechanistic models in developing advanced control strategies for optimal reactor operation. The dynamic optimization was carried out off-line for the case where a polymer with a very broad PSD was required. Several constraints were included to define the shape of the PSD, and to account for the secondary objectives under specified process and recipe limitations. This control strategy was found, upon experimental implementation, capable of achieving the defined objectives and produced a polymer with the required PSD.

However, the off-line optimization results when applied in practice often become suboptimal due to ever-existing process disturbances. Thus, there is a need for online optimal control to guarantee optimum process operation with robustness to process variability, and the ability to redefine the optimal operating conditions using the information springing continually from the process. The practical hurdle of applying optimal control in an on-line environment within a multivariable model predictive control scheme is addressed in the following section.

Application of MPC to Semi-Batch Emulsion Polymerization

The MPC algorithm uses an input-output model,[17–19] where the step-response coefficients are determined as follows:

- solve for the output using a constant input u^{ss} with help of the dynamic model. The calculated output is designated y^{ss}.
- introduce a consecutive set of step changes and solve the dynamic model 'into the future'. The resultant output is designated y^{step}.

The step response coefficients are calculated as follows

$$a_i = \frac{y^{\text{step}}(k+i) - y^{ss}(k+i)}{u(k+i) - u^{ss}} \tag{1}$$

where u is model input. This model identification involves calculating model predictions estimated every sampling period from the step-response coefficients

$$y(k+1) = \sum_{i=1}^{N} a_i \Delta u(k+1-i) + y^{ss}(k+1) + d(k+1) \tag{2}$$

Modeling error and impact of unmeasured disturbances are included in the last term Eq. 2. After the process output is

measured at a given time, for the linear case, $d(k)$ is estimated by assuming that all future d values are equal

$$d(k) = y^{\text{meas}}(k) - \sum_{i=1}^{N} a_i \Delta u(k-i) - y^{ss}(k) = d(k+1) = \cdots = d(k+N) \quad (3)$$

Application of the above linear configuration to our nonlinear case necessitates further adjustment of the prediction equation. A nonlinear model can be used to determine the effect of the past input excursions or the future control moves on the output prediction. The step-response coefficients are then updated at every sequence, hence, adapting the model to process nonlinearities. Similarly, the disturbance term d can be expressed by combining two terms: d^{ext}, the disturbance due to plant/model mismatch, and d^{nl}, the disturbance due to nonlinearities. The term d^{nl} is determined at every sampling time by minimizing the output prediction error between the linear and nonlinear models.[5]

SISO Control strategy

From Eq. 2, the projection of future outputs is modeled as follows

$$y(k+L) = \sum_{i=1}^{N} a_i \Delta u(k+L-i) + y^{ss}(k+L) + d(k+L) = \sum_{i=1}^{L} a_i \Delta u(k+L-i) + y^{ss}(k+L) + \sum_{i=L+1}^{N} a_i \Delta u(k+L-i) + d(k+L) \quad (4)$$

The part of the prediction output which does not depend on the future inputs is the process free response, and is defined as

$$y^*(k+L) = \sum_{i=L+1}^{N} a_i \Delta u(k+L-i) + y^{ss}(k+L) \quad (5)$$

Substituting Eq. 5 into Eq. 4 gives

$$y(k+L) = \sum_{i=1}^{L} a_i \Delta u(k+L-i) + y^*(k+L)d(k+L) \quad (6)$$

In this formulation, the controller has to calculate the set of control moves (Δu) into the future that allows the system to follow a predefined set point trajectory. This is done by solving for the well-known cost function

$$J = \min_{\Delta u} \left[\sum_{i=1}^{P} \delta(y^{\text{setpoint}}(k+i) - y(k+i))^2 + \sum_{i=1}^{M} \lambda(\Delta u(k+M-i))^2 \right] \quad (7)$$

subject to constraints on the input excursions: $\Delta u(k) \in [\Delta u_{\min}, \Delta u_{\max}]$; constraints on the input: $u(k) \in [u_{\min}, u_{\max}]$; and constraints on the output: $y(k) \in [y_{\min}, y_{\max}]$.

The weight on the error δ, is a $P \times P$ diagonal matrix. Similarly, λ is the weight on the input (suppression move), and is a $M \times M$ diagonal matrix. The optimization is solved at every sampling time when a new prediction is updated by recent feedback measurements. Only the first control move is implemented to the process, although the others could be used in case of loss of measurements. In the absence of constraints, Eq. 7 is equivalent to the least-squares problem with the solution given by

$$\begin{bmatrix} \Delta u(k) \\ \Delta u(k+1) \\ \vdots \\ \Delta u(k+M-1) \end{bmatrix} = [(A^T \delta A + \lambda I)^{-1} A^T \delta] \times \begin{bmatrix} y^{\text{set-point}}(k+1) - y^*(k+1) - d(k) \\ y^{\text{set-point}}(k+2) - y^*(k+2) - d(k) \\ \vdots \\ y^{\text{set-point}}(k+P) - y^*(k+P) - d(k) \end{bmatrix} = \mathbf{K} \times \mathbf{e} \quad (8)$$

where $\mathbf{K}$ is the controller gain and $\mathbf{e}$ is the vector of projected errors.

MIMO Control strategy

The application of the above DMC set of equations to MIMO systems was carried out for a z-output, w-input system, and the model prediction is calculated from

$$\mathbf{y}(k+L) = \sum_{i=1}^{N} \mathbf{a_i} \mathbf{\Delta u}(k+L-i) + \mathbf{y^{ss}}(k+L) + \mathbf{d}(k+L) \quad (9)$$

where $\boldsymbol{y}$ is a z-dimensional vector of outputs $\boldsymbol{a_i}$ is a $z \times w$ matrix of step response coefficients at the i-th interval, $\boldsymbol{\Delta u}$ is a w-dimensional vector of control moves, $\boldsymbol{y^{ss}}$ is the vector of initial conditions, and $\boldsymbol{d}$ the disturbance vector. For $z = w = 1$, Eq. 9 reduces to Eq. 4.

In this case the dynamic matrix A is composed of blocks of $P \times M$ dimensions of step response coefficients matrices as in Eq. 10, relating the i^{th} output to the j^{th} input

$$A = \begin{bmatrix} A_{11} & A_{12} & \cdots & A_{1w} \\ A_{21} & A_{22} & \cdots & A_{2w} \\ \vdots & \vdots & & \vdots \\ A_{z1} & A_{z2} & \cdots & A_{zw} \end{bmatrix} \quad (10)$$

The weighting matrices are defined as in the SISO case

$$\boldsymbol{\lambda} = \underset{M}{\text{diag}}(\lambda_1 \cdots \lambda_1 \lambda_2 \cdots \lambda_2 \cdots \lambda_w \cdots \lambda_w)$$

and

$$\boldsymbol{\delta} = \underset{P}{\text{diag}}(\delta_1 \cdots \delta_1 \delta_2 \cdots \delta_2 \cdots \delta_z \cdots \delta_z) \tag{11}$$

The vector of projection errors becomes

$$\mathbf{E} = [\mathbf{e}_1^T \mathbf{e}_2^T \cdots \mathbf{e}_z^T]^T \tag{12}$$

and the corresponding vector of control excursions is

$$\Delta\mathbf{u}(k) = [\Delta\mathbf{u}_1^T(k) \Delta\mathbf{u}_2^T(k) \cdots \Delta\mathbf{u}_w^T(k)] \tag{13}$$

Control structure

The lack of appropriate online sensors for the measurement of the PSD and MWD is a major challenge in implementing an on-line advanced control strategy. In practice, such measurements require sampling, dilution, off-line analysis (~15–20 min), and data processing, typically with capillary hydrodynamic fractionation (CHDF) for PSD, and gel permeation chromatography (GPC) for MWD. These off-line methods are impractical for online monitoring and control applications. To overcome this, a "soft sensor" approach was employed, with the full dynamic models[16] to provide an on-line estimate of the PSD and MWD. The relevant operating conditions (such as monomer flow rate and reactor temperature) are taken from the reactor at discrete time intervals as on-line measurements. A commercial SCADA system interfaces the reactor to the computer running the MPC (written in Microsoft Visual Basic).

A two-layer control hierarchy was implemented, where PSD and MWD measurements are obtained from the model-based "soft sensor" every 110 s, and fed to the MPC residing in the upper control layer. The MPC calculates the appropriate control actions (optimal trajectories), which are then sent as set point signals to the regulatory controllers in the lower layer of the hierarchical control structure. Off-line samples are also taken from the process every 20 min, and the CHDF/GPC measurements compared to the (model) predicted results. Any modeling error was handled within the MPC algorithm as an unmeasured disturbance, as previously described.

The implementation of the MPC was investigated first for the SISO case for PSD control with monomer flow rate manipulation. The algorithm was tested experimentally for the unconstrained case, and, thereafter, process constraints were added to the formulation. Thereafter, a 2×2 MIMO case was investigated, where the monomer flow rate and reactor temperature were used to control the PSD and MWD simultaneously.

Control Strategy Validation

Unconstrained SISO MPC: PSD control

Since the semi-batch polymerization reactor with PSD as a controlled variable, and the monomer feed rate as manipulated input is a controllable system, we studied the on-line control problem where a specific size distribution is desired for the polymer product. However, owing to their distributed parameter nature, the PBM equations describing the full PSD cannot be directly used for synthesis and implementation of a model-based controller. On the other hand, to determine control strategies which can be applied to the reactor, measurable or observable output variables must be chosen.

The off-line solution of the unconstrained optimal control was investigated.[16] As a result, an optimal trajectory in the monomer feedrate was generated with a particle size polydispersity index (PSPI) profile that ensured the desired broad distribution. The PSPI gives an indication of the width of the distribution, and is defined as the mean squared radius divided by the mean radius squared

$$PSPI = \frac{\langle r^2 \rangle}{\langle r \rangle^2} \tag{14}$$

where the mean squared radius is

$$\langle r^2 \rangle = \frac{\sum_{i=1}^{\Omega} n(i) r(i)^2}{\sum_{i=1}^{\Omega} n(i)} \tag{15}$$

with $n(i)$ is concentration density of particles, and Ω is the number of radial intervals.

For real-time implementation, polymer PSPI is used as the controlled output with the optimal PSPI profile (calculated off-line) being used as a set point for the MPC. The formulation is simplified to the unconstrained case as follows:

- Produce a polymer with a broad PSD (bimodal) with the cost function defined as

$$J = \min_{\Delta u} \left[\sum_{i=1}^{P} \delta(PSPI^{\text{setpoint}}(k+i) - PSPI(k+i))^2 + \sum_{i=1}^{M} \lambda(\Delta F_m(k+M-i))^2 \right] \tag{16}$$

No constraints were included in this case, but a minimum monomer flow rate of 5×10^{-5} mol/s was specified for operational reasons.

A block diagram of the SISO control strategy is given in Figure 1. In this formulation, the PSPI was calculated using the step response method, as described earlier. The prediction horizon, the control moves, and the sampling time were set at 30, 5, and 480 s, respectively. The relatively large magnitude of the sampling time is related to the process dynamics. As the average volume growth rate for particles in emulsion polymerization is small (of the order of 2×10^{-22} L/s), a relatively long sampling time is required to observe discernible changes.

The test for the MPC scheme was carried out off-line (with no feedback) using variable δ and λ. The large magnitude of the PSPI when compared to that of the monomer flow rate was

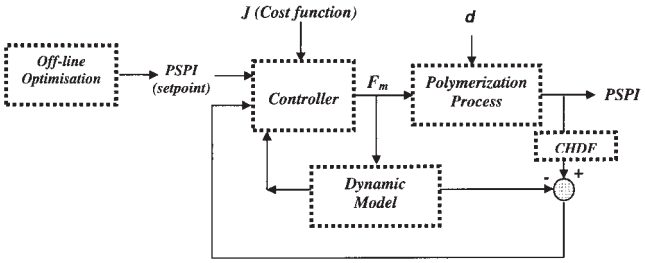


Figure 1. Unconstrained MPC algorithm using the dynamic model as soft-sensor.

expected to skew the optimization results in favor of the projected errors. Hence, δ and λ were chosen to guarantee optimum performance.

Figures 2–3 show that low values of δ and λ resulted in good set point tracking, but aggressive control action. Initially, the PSPI followed the set-point trajectory with a small negative offset, however the controller output was saturated after 8,000 s, and a positive offset was obtained. Using larger values of both δ and λ, however, resulted in deterioration in controller performance. A large negative offset was obtained over the trajectory, and the controller output showing a conservative, sluggish response. Through simulations, the optimum controller settings were found to be $\delta = 100$, and $\lambda = 1 \times 10^{13}$ with the MPC able to track set point trajectory closely. A relatively large value of λ is used to account for the small magnitude of the monomer flow rate.

The MPC strategy was implemented on semi-batch styrene polymerization at 72°C. The reactor was operated with no PSPI control during the batch preperiod of 1,500 s. After the batch period, the MPC was applied to the process with feedback from the soft-sensor, as described previously.

The experimental results are shown in Figures 4–5. Although the PSPI increased throughout the experiment (consequently, the PSD continually broadened), an offset of variable magnitude was observed at every sampling time. Figure 5 shows that the monomer feedrate decreases with time after the batch preperiod, with no controller saturation. The negative offset in the PSPI is caused by the mismatch between the actual monomer flow rate, that is, supplied by the pump, and the flow rate calculated by the MPC. This mismatch was due to the moderate performance exhibited by the monomer pump which was deteriorating during the course of the experiment. The final shape of the PSD was in good agreement with the estimated

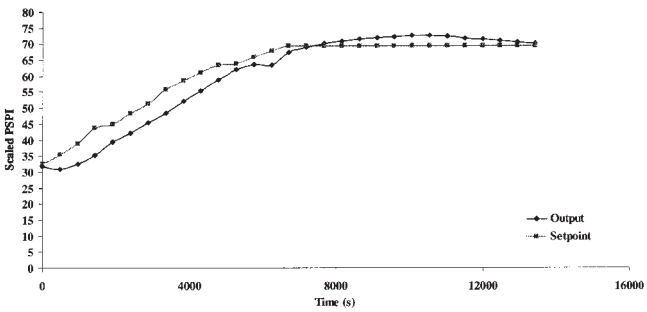


Figure 2. Simulated PSPI using MPC with $\delta = 1 \times 10^{-3}$ and $\lambda = 6 \times 10^{8}$.

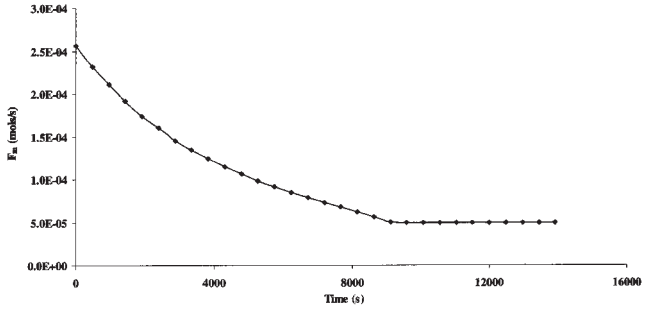


Figure 3. Simulated monomer flow rate using MPC with $\delta = 1 \times 10^{-3}$ and $\lambda = 6 \times 10^{8}$.

soft-sensor result (see Figure 6), showing a broad distribution, as originally defined within the objective of our control strategy.

Constrained SISO MPC: PSD control

The extension of the above approach to include process constraints was examined. Constraints are always present in real life process control. The objective function is setup to fulfill the desired output, while the constraints shaping the feasible region come from the environment. For on-line PSD control several issues were considered:

- what are the constraints,
- what requirements must be met,
- should an inequality or equality type of constraint be used,
- what are the connections among variables.

Although the offline optimization results with constraints on particle concentration were used, this does not imply that the use of PSPI as our control objective would give the desired PSD on-line. This is because it is not feasible to use the particle concentration for the formulation of on-line control. Further, for the same PSPI, different PSD shapes can be tailored. Hence, accurately defining the PSD shape would require the specification of additional polymer attributes.

The average particle radius is an important property which can indicate the process of particle formation and growth. During polymerization, a persistent increase in the average radius is a result of continual growth rate. On the other hand, a decrease in the average radius marks the formation of new particles via secondary nucleation mechanism. To reach the

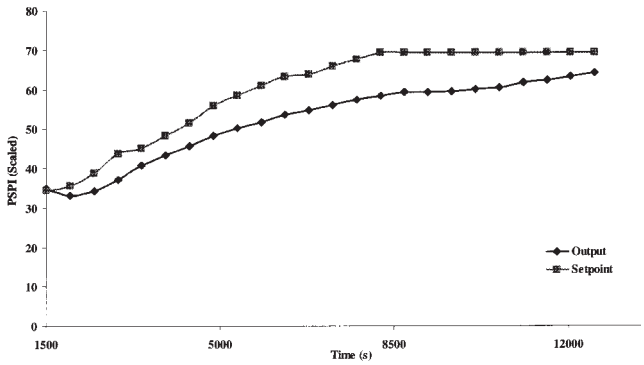


Figure 4. Experimental results for PSPI using online MPC.

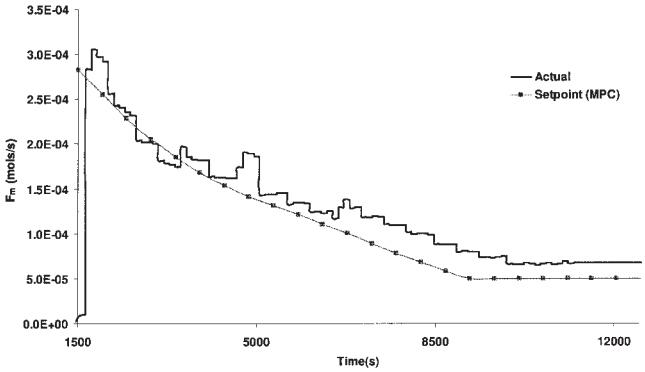


Figure 5. Optimal monomer feed profile.

target solution, the control problem must include the average radius in the formulation. The ε-constraint method was used in the MPC formulation, where the optimal average radius profile generated by the off-line optimization is used to force the particle size to follow the desired trajectory. This is introduced in the form of a hard constraint as follows

$$\sum_{i=1}^{P} (r_{\text{avg}}^{\text{Setpoint}}(k+i) - r_{\text{avg}}(k+i))^2 < \varepsilon_1 \tag{17}$$

where ε_1 is the maximum value the sum of projected particle size errors can take, r_{avg} is the average radius, and $r_{\text{avg}}^{\text{Setpoint}}$ is the set point calculated by off-line optimization.

Solid content is another polymer attribute that was considered. A high solid content is obtained when monomer is added in significant amounts. Under these conditions, large particles are formed and the system resembles bulk polymerization (caused by the dramatic increase in the system viscosity). A desired solids content of approximately 25%, corresponding to a total of 1.6 moles of monomer was specified as a constraint

$$N_{m,T}(P - k + 1) < 1.6 \tag{18}$$

Additional constraints were:

- Constraints on flow rate excursions

$$\Delta F_m(k+i) \in [-1.85 \times 10^{-4}, 1.85 \times 10^{-4}] \tag{19}$$

- Constraints on flow rate

$$F_m(k) \in [5 \times 10^{-5}, 5 \times 10^{-4}] \tag{20}$$

Our tests showed that the designed MPC succeeded under constrained conditions in attaining the desired target. Although some offset was observed, the experimental results agreed well with predictions. The bimodality was minimal because the particle size interval was narrow, and the particles formed were within the "small" size regime (that is, less than 100 nm in diameter). It is usually difficult to produce two peaks over this size range. This process limitation was taken into account when formulating the optimal control strategy.

Constrained MIMO MPC: PSD and MWD control

The coupling between the PSD and MWD occurs through the kinetic equations, and the population balances, both of which are affected by temperature and species concentrations, our manipulated variables. Hence, a MIMO rather than SISO control is desirable. The kinetic growth of particles occurs in three phases: aqueous, monomer and micellar phases, in which a series of competing events occur, such as, aqueous phase propagation and termination, micellar nucleation, secondary nucleation, coagulation and diffusion. For the kinetic system applied, a micelle contains either zero or one active free radical. The population balance equations are given below as a function of time. The parameter values of the equations are given elsewhere.[16]

(1) Population balance for particles containing polymeric radicals

$$\frac{\partial n_1^p(V,t)}{\partial t} = \left(k_{p,aq}^{jcrit-1} C_w IM_{jcrit-1} + \sum_{1}^{jcrit-1} k_{e,micelle} C_{micelle} IM_i \right) + k_p C_p n_1^m + \rho_{init} n_1^o - \rho n_1^p - k_{tr} C_p n_1^p - \frac{\partial (K n_1^p)}{\partial V} \tag{21}$$

(2) Population balance for particles containing no free-radicals

$$\frac{\partial n_o(V,t)}{\partial t} = \rho(n_1^p + n_1^m - n_o) + k_{dm} n_1^m \tag{22}$$

(3) Population balance for monomeric radicals

$$\frac{\partial n_1^m(V,t)}{\partial t} = k_{tr} C_p n_1^p + k_{eE}[E] n_o - (k_p C_p + \rho + k_{dm}) n_1^m \tag{23}$$

$$n = n_o + n_1^m + n_1^p \tag{24}$$

where n_1^p = number of particles containing polymeric radicals, $IM_i^{\bullet}$, where $n > 1$; n_o = number of particles that contain no free-radicals and n_1^m contains monomeric radicals, $IM^{\bullet}$; k are rate-transfer coefficients; C is monomer concentration; K is rate of propagation of volume growth per particle; $\bar{n}$ is average number of radicals per particle; subscripts: *tr* denotes transfer; *P* denote latex particles, *W* is for water phase; *M* stands for monomer; *d* for initiator decomposition; *e* for entry of an oligomeric radical; *p* denotes propagation-rate

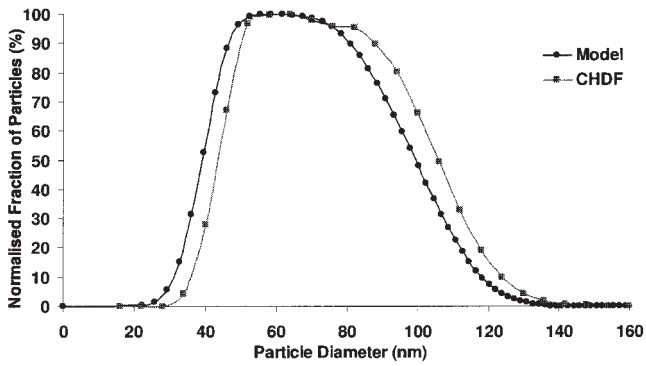


Figure 6. Particle-size distribution controlled in final product.

coefficient in the latex phase; *aq* is for aqueous; superscript: *i* for oligomeric radical of degree "*i*." The instantaneous MWD is calculated using the following equation

$$\frac{\partial \bar{P}(M)}{\partial t} = P(M) = (k_{tr}C_p + \rho_{\text{avg}})\bar{n} \cdot \exp\left(\frac{-(\rho + k_{tr}C_p)}{k_pC_p}\frac{M}{M_w}\right) \tag{1}$$

where M is the molecular weight of the polymer chain, $P(M)$ is the instantaneous MWD, and $\bar{P}(M)$ is the cumulative MWD. The number average molecular weight (NAMW) is given by

$$M_n = \frac{\sum M \cdot P(M)}{\sum P(M)} \tag{26}$$

The attainment of the desired molecular weight is important for the polymerization process, and is coupled with the monomer conversion and the particle number as shown earlier.

To achieve optimal operation of the emulsion polymerization process, all reactor outputs must be maintained within specifications. However, in the multivariable case, the design of the control system requires a suitable strategy which takes into account the extent of interaction and the pairing of manipulated and controlled variables. The MPC was used to solve the control problems associated with a combination of regulation and targeting of terminal conditions. Our strategy was to control the PSPI and MWD by manipulating the monomer flow rate and the reactor temperature, respectively. Thus, the objectives of our 2×2 DMC configuration are:

- to produce a polymer with a broad PSD (targeting) subject to the previously defined constraints.
- to keep the average molecular weight at setpoint (regulation) at all times by adjusting the reactor temperature. This will provide a product which not only has the desired NAMW, but which has a low polydispersity index (narrow MWD).

The earlier objectives were lumped into a single function by assigning appropriate weights to the individual objectives. This was done to render the control problem mathematically manageable for implementation on a real process.

$$J = \min_{\mathbf{\Delta u}}\left[\sum_{i=1}^{P} \boldsymbol{\delta}(\mathbf{y}^{\text{setpoint}}(k+i) - \mathbf{y}(k+i))^2 + \sum_{i=1}^{M} \boldsymbol{\lambda}(\mathbf{\Delta u}(k+\mathbf{M}-i))^2\right] \tag{27}$$

where

$$\boldsymbol{\lambda} = \text{diag}(\underbrace{\lambda_1 \cdots \lambda_1}_{M1}\underbrace{\lambda_2 \cdots \lambda_2}_{M2})$$

and

$$\boldsymbol{\delta} = \text{diag}(\underbrace{\delta_1 \cdots \delta_1}_{P1}\underbrace{\delta_2 \cdots \delta_2}_{P2})$$

In this MIMO MPC two prediction and control horizons were specified

$$\mathbf{P} = [P_1 \quad P_2]$$

and

$$\mathbf{M} = [M_1 \quad M_2]$$

while the outputs and control actions were

$$\mathbf{y} = [\text{PSPI} \quad \text{NAMW}]$$

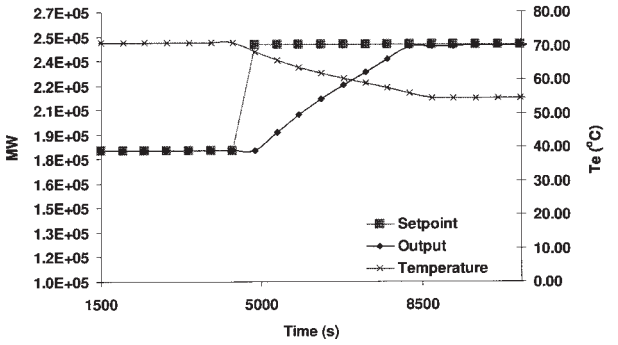
and

$$\mathbf{\Delta u}(k) = [\mathbf{\Delta F}_m^T(k)\mathbf{\Delta T}_e^T(k)]$$

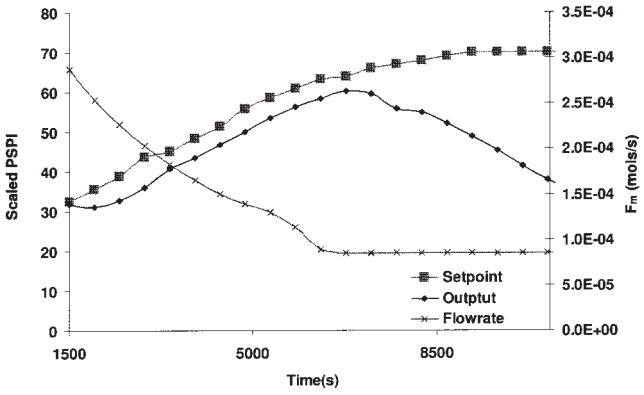
With MIMO MPC, the operation of the polymerization reactor is no longer isothermal and strong interactions between the PSPI and NAMW control exist. Changes in the reactor temperature would affect the reaction rate, overall particle growth, radical transfer rate and chain length. For example, increasing the reactor temperature results in operation in high monomer conversion regime, causing an increase in secondary nucleation (hence, broadening of PSD). At high-conversion, termination becomes diffusion controlled favoring further chain propagation which competes with increasing radical-transfer rate. A decrease in NAMW is observed under these circumstances. However, a decrease in temperature moves the system towards monomer-flooded regime, where particle growth is dominant, resulting in larger particles with a narrow PSD. In addition, larger NAMWs are obtained as radical transfer becomes small compared to chain propagation.

The monomer flow rate marginally affects the NAMW especially at low flow rates where termination becomes diffusion controlled (that is, at high-polymer weight fraction). Process limitation is an important factor to be addressed. As bimodal distribution is not realizable over a small size regime, the use of temperature for MWD control will succeed over a bounded NAMW interval. This interval is defined by the maximum and minimum operating temperatures, of 90°C and 50°C, which produce an NAMW of 80×10^3 and 325×10^3, respectively. In a MIMO configuration, the NAMW interval is further reduced in favor of PSPI control requirements. Thus, obtaining high NAMW will require low limiting values of temperature, thus inducing an undesirable increase in monomer concentration in the reactor (due to decrease in reaction rate) and deterioration in PSPI control.

Prior to on-line implementation, the controllability of PSPI and NAMW was tested with a set of closed-loop control simulations. For PSPI control, the prediction horizon, the control moves, and the sampling time were kept at 30, 5, and 480 s, respectively. The formulation for MW control was less complicated due to the quick response of the MW to temperature changes and the nontransient behaviour exhibited by the NAMW (which characterises the free-radical addition polymerization). A prediction horizon of 8 and a control horizon of 2 were, therefore, used for MW control. Testing of the MPC



(a)



(b)

Figure 7. Offline control of (a) NAMW, and (b) PSPI using multivariable constrained MPC.

scheme was carried out offline using the following optimum settings for $\boldsymbol{\delta}$ and $\boldsymbol{\lambda}$:

- $\delta_1 = 100$ and $\lambda_1 = 1 \times 10^{13}$ for PSPI control
- $\delta_2 = 0.128$ and $\lambda_2 = 2.14 \times 10^7$ for NAMW control

A series of simulations were performed to evaluate the performance of the MPC for set point tracking. Figures 7–8 depict samples of the simulations. The MPC was able to track all setpoint changes in the NAMW. However, as discussed earlier, the controllability of PSPI was conditionally limited. The MPC performance in tracking the optimum PSPI profile worsened when high NAMW set points were specified (Figure 7). The overall performance of the MPC was found to be acceptable when a value below 2×10^5 was set for the NAMW. Thus, for optimum performance an upper bound of 2×10^5 g/mol was set for NAMW.

For online implementation, an additional event must be considered. In the automated reactor facility, the reactor temperature is controlled with hot water supplied by the heating circulator to the jacket.[20] With isothermal operation, the reactor contents are preheated to the desired temperature and no set point changes are introduced thereafter. However, under MPC control, new temperature set points are calculated at every sampling time, and, to achieve good control, the jacket temperature response to set points changes must be acceptable.

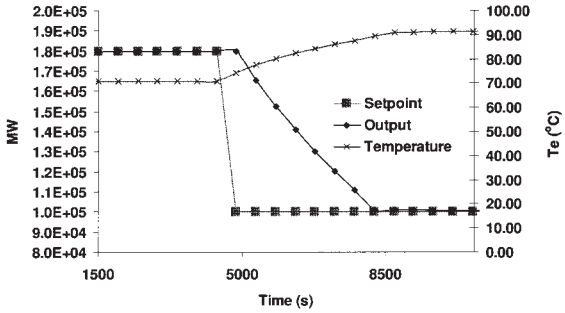
This suggests the use of cascade control, where the MPC acts as the primary (master) controller, and the heating circulator is the secondary (or slave) controller. However, for cascade control to be effective, the dynamics of the secondary loop must be faster than those of the master loop. Through experimental investigations, it was found that the dynamic response of the system during heating is different to that of cooling. The time delay calculated during heating was four times that for cooling. The resulting transfer function models, relating the reactor temperature to that of the jacket, are

$$Gp = \frac{0.831e^{-25s}}{715s + 1} \quad \text{(for cooling)} \tag{28}$$

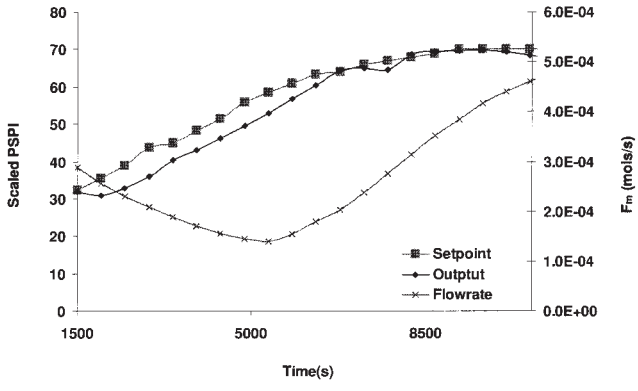
and

$$Gp = \frac{0.856e^{-100s}}{695s + 1} \quad \text{(for heating)} \tag{29}$$

These equations show significant process time-constants due to the slow process dynamics. In addition, the presence of process nonlinearity renders the tuning of the lower layer controller difficult, and these affect the overall controller stability. To circumvent these problems, the MW sampling time must be large enough to cover the secondary closed loop response (including the time delay). Since any offset in the secondary loop is not crucial, a proportional controller with a relatively high gain was used to control the reactor temperature. Further constraints were added to the MPC to reduce the effects of nonlinearity:



(a)



(b)

Figure 8. Offline control of (a) NAMW, and (b) PSPI using multivariable constrained MPC.

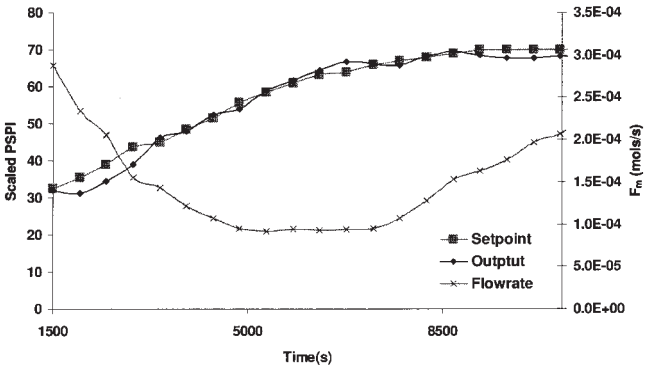


Figure 9. Experimental PSPI using online multivariable constrained MPC.

- Constraints on thermal excursions

$$\Delta T_e(k+i) \in [-5, 5] \tag{30}$$

- Constraints on temperature

$$T_e(k) \in [50, 85] \tag{31}$$

The performance of the control system was evaluated for set point tracking as shown in Figures 9–12. The MPC controller was able to follow the desired product property trajectories with reasonable accuracy to obtain the desired distributions. The PSPI was found to increase during the experiment and the average particle size was at set point for the whole experiment. The NAMW measured by GPC agreed reasonably with results estimated by the soft-sensor. The NAMW was able to reach the desired two set points which were introduced at different time intervals during the experiment. The control excursions for both temperature and monomer flow rates, were also kept within the constraints, as no controller saturations were observed during the entire experiment. The PSD and MWD of the final product were found to support these findings. The final shape of the distribution was in good agreement with the estimated soft-sensor result. Some of the mismatch between theory and experiments is most likely to be the inherent uncertainties with the parameter values which were obtained independently by other investigators working with a similar

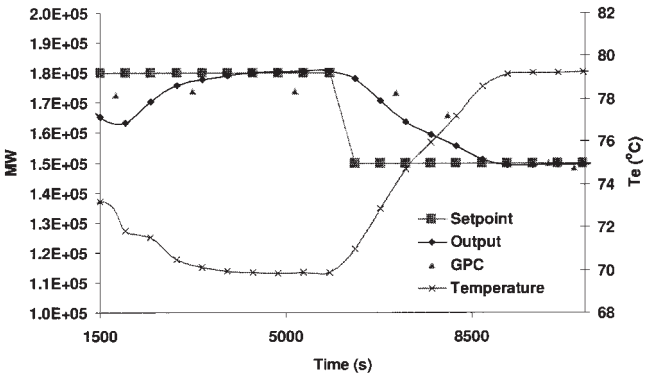


Figure 10. Experimental NAMW using online multivariable constrained MPC.

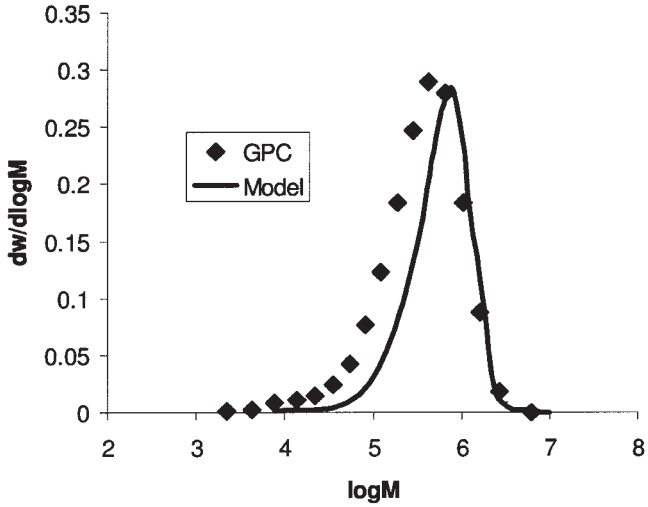


Figure 11. Molecular-weight distribution controlled in final product.

system. Further improvements in the accuracy of these parameters would enable better predictions.

Conclusions

In this work, a strategy is proposed for the online optimal control of key product attributes in emulsion polymerization. The strategy involves application of an MPC control scheme that uses the DMC algorithm to control key polymer properties, the PSD and MWD. The novelty of the proposed strategy is that detailed dynamic models of the semi-batch polymerization reactor, developed and validated in earlier work, was used as an online "soft sensor" for calculating the dynamic step response coefficients of the DMC. The algorithm uses a model generated through linearization around the off-line optimal trajectory.

The control approach was investigated in three consecutive steps where first the unconstrained case of PSD control was investigated. In this situation, the PSPI was the control objective and the manipulated variable was the monomer feedrate. Thereafter, additional constraints were imposed on the input, the input moves and the solids contents. Upon experimental testing, both control schemes were capable of achieving the

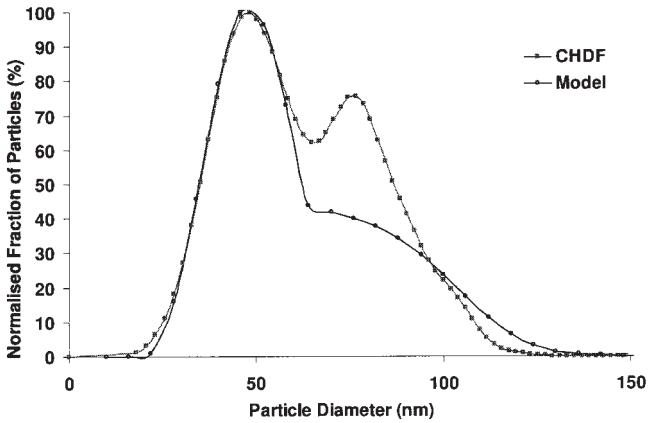


Figure 12. PSD under optimal operation with constrained MIMO MPC.

desired objective without violating the process constraints and showed a high performance in rejecting disturbances in the reactor temperature.

Finally, a multivariable MPC was formulated to solve the control problems associated with a combination of regulation and targeting of terminal conditions. The simultaneous control of the PSPI and MWD by manipulating the monomer flow rate, and the reactor temperature was, therefore, considered. A 2×2 formulation was defined for the multiconstrained optimal control problem for maximising the breadth of the PSD, while maintaining the NAMW at set point. A major improvement in process operation and control of product properties were gained on implementing our multivariable MPC. The manipulation of both the temperature and monomer feed rate increased the degree of freedom and achieved better PSD and MWD tracking.

Acknowledgments

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