

# Control of particle size distribution in emulsion polymerization using mid-course correction under structural plant-model mismatch<sup>\*</sup>

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**Abstract:** This paper suggests a method to control the particle size distribution in semi-batch emulsion homopolymerizations under structural plant-model mismatch. In this approach, firstly a nominal monomer feed input trajectory is applied to the plant up to a predefined time instant after the start of the batch (mid-course). By means of a calorimetric observer, all states of the system except the particle size distribution are estimated using the available measurements. The estimated states and the measured PSD at the mid-course of the process are used as the initial condition for an optimization which is done to compute the trajectory of the monomer feed from the mid-course up to the end of the batch. In this optimization, considering a structural plant-model mismatch, a hybrid model which comprises the nominal model of emulsion polymerization and an empirical component that corrects the predictions of this nominal model is used.

*Keywords:* Emulsion polymerization, Particle size distribution, Population balance equation, Mid-course correction, Hybrid model

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## 1. INTRODUCTION

Emulsion polymers are used in a wide range of applications such as adhesives, inks, paints, coatings, gloves and cosmetics. The process of emulsion polymerization belongs to the family of free radical polymerizations where the initiation process usually starts by dissociation of the initiator molecules in the water phase. This process is one of the common polymerization techniques to produce high molecular weight latexes. In emulsion polymerization, the probability of termination of the growing radicals is reduced by the compartmentalization of the radicals in the particles. This results in having a high polymerization rate even at high molecular weights while the viscosity of the latex does not increase drastically.

Monomer, surfactant, initiator and water are the main ingredients of the emulsion polymerization process. The process starts by dispersing the monomer in water using a stirrer. Additionally, in order to prevent the droplets from coalescing in the reactor, a surfactant is used to cover the droplets. When the amount of the surfactant exceeds the critical micelle concentration (CMC), micelles of surfactant are formed within the system; these are monomer swollen aggregates of surfactant. In order to bring the resulting dispersion of monomer in water into the appropriate condition for starting the reaction, the emulsion is heated up, usually to around 50 to 80°C, depending on the type of the monomer. After reaching the desired temperature, a water soluble initiator is added to the dispersion where it decomposes to form radicals

which start the reaction with the small amount of free monomer molecules which are dissolved in the water phase. These free monomer molecules are outside of the monomer droplets covered by the surfactant. The product of initiator radicals and monomer are oligomeric radicals which can either propagate with the rest of the free monomer that is present in the water phase or they can terminate with each other. If they do not terminate in the water phase, they propagate to reach a certain chain length of  $j_z$  after which they will enter into micelles of surfactant and reacting there with the monomer, the result of which is the occurrence of micellar nucleation where the precursor particles are formed. The newly formed particles are then converted into stable ones either via propagation (growth by consuming monomer) or coagulation.

The end-use properties of the polymers produced by emulsion polymerization processes such as film forming, adhesion, and viscosity are highly correlated with the particle size distribution (PSD). Therefore controlling the PSD is well motivated. To control the PSD, a rigorous model of the emulsion polymerization process is usually adopted where the population balance equation (PBE) model of emulsion polymerization is used to predict the evolution of the PSD (Vale and McKenna, 2005). Hosseini et al. (2012, 2013a) proposed to use the Fokker-Planck equation model of emulsion polymerization instead of PBE model as it predicts the observation of the broadening of the PSDs in experiments significantly better. Hence, in this work, the Fokker-Planck model of emulsion polymerization is used to describe the temporal PSDs.

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In general, for batch and semi-batch processes, different control approaches such as online, batch-to-batch and combinations of them (depending on the availability of the off/online measurements and the level of sophistication needed and/or desired) can be used. Feedforward control (Immanuel and Doyle III (2002); Rajabi-Hamane and Engell (2007)) is the simplest scheme where the optimal input trajectories are computed by performing an offline optimization or they are repeated from a golden batch. The corresponding optimizations are usually performed using mechanistic models. The obtained optimal input trajectory is implemented at the plant without considering feedback. As mechanistic models cannot cover all aspects of the real processes, in the presence of plant-model mismatch and/or disturbances the optimal input trajectory computed by this method cannot conduct the process exactly to the desired target due to the lack of a mismatch/disturbance rejection mechanism. Batch-to-batch control (Dokucu and Doyle III (2008); Doyle III et al. (2003)) is a relatively simple approach to improve the quality of offline control strategies. Using the results of offline measurements taken at the end of a batch, a correction is computed. This correction is then considered in the offline optimization which is performed to calculate the input trajectory of the next batch. However, in this method of batch optimization, due to the absence of the in-batch feedback, the disturbances are not adequately treated. To overcome the deficiencies of the offline and batch-to-batch control approaches, online measurements can be used under the framework of nonlinear model predictive control (NMPC) like the work of Mansour et al. (2011). When frequent measurements are not available to perform closed-loop control, mid-course correction control policies (Flores-Cerrillo and MacGregor (2002)) can be used instead of NMPC approaches. This methods are compromises between offline and online control. Hosseini et al. (2013b,c) proposed an approach to perform the mid-course correction to control the PSD in emulsion polymerization under parametric plant-model mismatch. In this approach, assuming the availability of quasi-continuous solid (polymer) content measurements, a state estimator was incorporated to estimate the lumped state of the system at the mid-course of the process. Furthermore, an empirical model was added to improve the predictions of the nominal model in comparison to a virtual plant when performing an optimization to obtain the optimal monomer flow rate trajectory, from the mid-course up to the end of the batch, that brings the PSD of the virtual plant to a desired target. The virtual plant was considered to be the nominal model of emulsion polymerization with different key parameters (i.e. propagation rate constant, termination rate constant, initiator decomposition rate constant, and the entry of radicals into the particles rate constant). In the previous work, the coagulation phenomenon was neglected in the nominal model as well as in the virtual plant.

In this paper, the seeded emulsion homopolymerization of styrene is considered as the example process for which, based on the mid-course correction idea, a method to control the PSD under the structural plant-model mismatch is proposed. To describe the behavior of the real plant, a virtual plant is considered where it is assumed that in contrast to the nominal model, in the virtual plant coagulation occurs. The flow rate of the monomer feed is

considered as the manipulated variable to control the PSD. The structure of this paper is as follows: first we briefly introduce the model of emulsion polymerization in section 2. The main idea behind the proposed control structure is presented in section 3. The control structure is then simulated. Finally conclusions are presented in section 4.

## 2. PROCESS MODEL

To describe the evolution of the PSD in emulsion polymerization, considering a seeded process and neglecting the nucleation phenomenon, the model of Hosseini et al. (2013a) is used. In this model, to overcome the inadequacies of conventional PBE models of emulsion polymerization to describe the evolution of the broadening of experimental PSD, the Fokker-Plank Equation (FPE) is employed as follow:

$$\frac{\partial}{\partial t} n(r, t) = -\frac{\partial}{\partial r} \left[ \left( G(r, t) + \frac{dD(r)}{dr} \right) n(r, t) \right] + \frac{\partial^2}{\partial r^2} (D(r)n(r, t)) + \mathfrak{R}_{coag.}, \quad (1)$$

where  $n$  is the density function,  $r$  is the particle radius (the only internal coordinate which is considered in the FPE),  $D$  is the dispersion coefficient. The growth kernel can be expressed as follows:

$$G(r, t) = \frac{dr}{dt} = \frac{k_p M_{wt}}{4\pi r^2 \rho_p N_A} \bar{n}(r, t) [M]^p, \quad (2)$$

where  $k_p$  is the propagation rate constant,  $M_{wt}$  is the molecular weight of the monomer,  $\bar{n}$  is the average number of radicals per particle,  $[M]^p$  is the monomer concentration in the particle phase,  $\rho_p$  is the density of the polymer and  $N_A$  is the Avagadro constant. The coagulation rate is calculated as follows (Vale and McKenna, 2005):

$$\mathfrak{R}_{coag.} = \frac{1}{V} \int_{r_{nuc.}}^{(r/2)^{1/3}} \beta(r', r'', t) n(r', t) n(r'', t) \frac{r^2}{(r^3 - (r')^3)^{2/3}} dr' - n(r, t) \int_{r_{nuc.}}^{r_{max}} \beta(r, r', t) n(r', t) dr', \quad (3)$$

in which  $\beta$  is the coagulation kernel defined for two interacting particles with the swollen radii of  $r_s$  and  $r'_s$  as:

$$\beta = \frac{2k_B T}{3\eta W_{rr'}} \left( 2 + \frac{r_s}{r'_s} + \frac{r'_s}{r_s} \right), \quad (4)$$

where  $\eta$  is the viscosity,  $k_B$  is the Boltzman constant and  $W_{rr'}$  is the stability ratio which is a measure of the stability of the latex; the higher the stability ratio the more stable is the latex. Here a simple stability ratio is used,

$$W_{rr'} = \left( \frac{(rr')^3}{r_{min}^6} \right)^S, \quad (5)$$

in which  $r$  and  $r'$  are the radius of the interacting particles,  $r_{min}$  is the lower limit of the internal coordinate (here the particle radius) and  $S$  is a parameter. In this model, by decreasing the parameter  $S$  (here considered to be 1.8), the particles are simulated to coagulate more.

In what follows, the dynamic balances of the lumped states of the system for a semi-batch process are briefly introduced.

### Monomer balance

The monomer balance for a semi-batch reactor leads to:

$$\frac{d[M]}{dt} = -r_{ip} - \frac{[M]}{V} \frac{dV}{dt} + \frac{\dot{V}_M}{V} \frac{\rho_m}{M_{wt}} x_{M,F}, \quad (6)$$

where  $r_{ip}$  is the reaction rate,  $V$  is the volume of the reactor content,  $\rho_m$  is the monomer density,  $\dot{V}_M$  is the monomer flow rate and  $x_{M,F}$  is the monomer feed purity.

### Initiator balance

The water soluble initiator (usually a persulfate) decomposes in the aqueous phase and its concentration balance is

$$\frac{d[I]}{dt} = -fk_I[I] - \frac{[I]}{V} \frac{dV}{dt} + \frac{\dot{V}_I}{V} x_{I,F}, \quad (7)$$

in which  $f$  is the initiator decomposition efficiency,  $k_I$  is the initiator decomposition rate coefficient,  $\dot{V}_I$  is the initiator flow rate and  $x_{I,F}$  is the initiator feed purity.

### Radicals in the water phase balance

One can consider a single overall balance for all types of radicals in the water phase (Rawlings and Ray, 1988),

$$\begin{aligned} \frac{d[R]^w}{dt} = & 2fk_I[I] + \int_{r_{min}}^{r_{max}} n(r)k_d(r)\bar{n}(r)dr - \\ & \frac{4\pi k_{mp}[R]^w V N_A}{V_w} \int_{r_{min}}^{r_{max}} r_s^2 n(r)dr - k_t^w ([R]^w)^2 \frac{V^w}{V} - \\ & 4\pi r_m^2 k_{mm} N_m [R]^w \frac{V^w}{V} - \frac{[R]^w}{V} \frac{dV}{dt}, \end{aligned} \quad (8)$$

here  $k_{mp}$  is the rate constant of radicals entry to particles,  $V^w$  is the volume of the water phase,  $k_{mm}$  is the rate of radicals entry to the micelles of surfactant,  $r_m$  is the radius of the micelles,  $N_m$  is the number of micelles,  $k_t^w$  is the water phase termination rate constant and  $k_d$  is the desorption rate coefficient.

### Volume balance

The mass balance of the reactor content leads to:

$$\frac{dV}{dt} = \dot{V}_M + \dot{V}_I + \dot{V}_S - \underbrace{\left( \bar{V}_M - \frac{M_{wt}}{\rho_p} \right)}_{\text{Considering shrinkage}} r_{ip} V^p, \quad (9)$$

where  $\bar{V}_M$  is the molar volume of the monomer and  $V^p$  is the total volume of particle phase.

### Heat balance reactor side

$$\begin{aligned} \frac{d(\rho_r V c_{p_r} T_r)}{dt} = & -\Delta H_r V r_{ip} + kA(T_j - T_r) + \\ & \dot{V}_M \rho_m c_{p_m} (T_{r,in} - T_r), \end{aligned} \quad (10)$$

where  $\rho_r$  is the density of the reactor content,  $c_{p_r}$  is the specific heat capacity of the reactor content,  $T_r$  is the reactor temperature,  $T_{r,in}$  is the monomer inlet temperature,  $\Delta H_r$  is the enthalpy of the polymerization reaction,  $k$  is the heat transfer coefficient,  $A$  is the heat transfer area,  $T_j$  is the jacket temperature, and  $c_{p_m}$  is the specific heat capacity of monomer.

### Heat balance jacket side

$$\frac{d(\rho_w V_j c_{p_w} T_j)}{dt} = \dot{V}_W \rho_w c_{p_w} (T_{j,in} - T_j) + kA(T_r - T_j), \quad (11)$$

where  $\rho_w$  is the density of water,  $c_{p_w}$  is the specific heat capacity of water,  $V_j$  is the volume of the jacket,  $\dot{V}_W$  is

the water flow rate, and  $T_{j,in}$  is the temperature of water at the jacket inlet.

The discretized form of equation (1) in combination with the dynamic balances of the lumped states constitute a set of differential algebraic equations (DAE), the integration of which provides the dynamic evolution of the PSD and of the other states of the system.

## 3. CONTROL STRUCTURE

In this paper, a practical control strategy based on the mid-course correction idea is proposed to control the PSD in a semi-batch seeded emulsion homopolymerization process under structural plant-model mismatch (to resemble the structural plant-model mismatch, no coagulation is considered in the nominal model whereas in the (virtual) plant coagulation takes place). In this approach, firstly a nominal input trajectory of the monomer flow rate which is obtained either by experiments or from an offline optimization is applied at the plant up to a certain time (mid-course of the batch) after the start of the batch. Using a calorimetric state estimator and incorporating the available measurements, the lumped states (i.e. all states except of the PSD) of the emulsion polymerization model are estimated. The estimated states together with the PSD measured at the mid-course of the process constitute the complete state vector at the mid-course of the process which is used as the initial condition for an optimization that is performed to compute the optimal trajectory of the monomer feed from the mid-course up to the end of the batch. The difference between the PSD predicted by the nominal model and the PSD of the virtual plant as well as the reduction in the number of the particles due to the coagulation cannot simply be compensated by fitting the parameters of the nominal model to the experimental data (obtained by simulation of the virtual plant) because intuitively the nominal model without considering coagulation/nucleation delivers constant number of particles. Apart from that, the rigorous model of coagulation is not reliable in reacting conditions (Vale and McKenna, 2005) and even if it was reliable, the simulation of the FPE model considering the coagulation is computationally demanding such that one cannot use the model for the optimization purposes. Hence, in this work it is proposed to use an empirical model to compensate for the coagulation in the nominal model and the resulting hybrid model is used to perform the above mentioned optimization. The empirical model maps the state of the system at mid-course to the residual of the states (the difference between model prediction and plant) at the end of the batch. This residual is used to correct the predictions of the nominal model during the optimization.

### 3.1 STATE ESTIMATION

To estimate the lumped states of the system at the mid-course of the process, an Extended Kalman Filter based on the nominal model (model without coagulation) of emulsion polymerization is used. The available measurements (reactor temperature, jacket temperature, and volume of the reactor content) obtained from a virtual plant are used to estimate the non-measured lumped states of the system

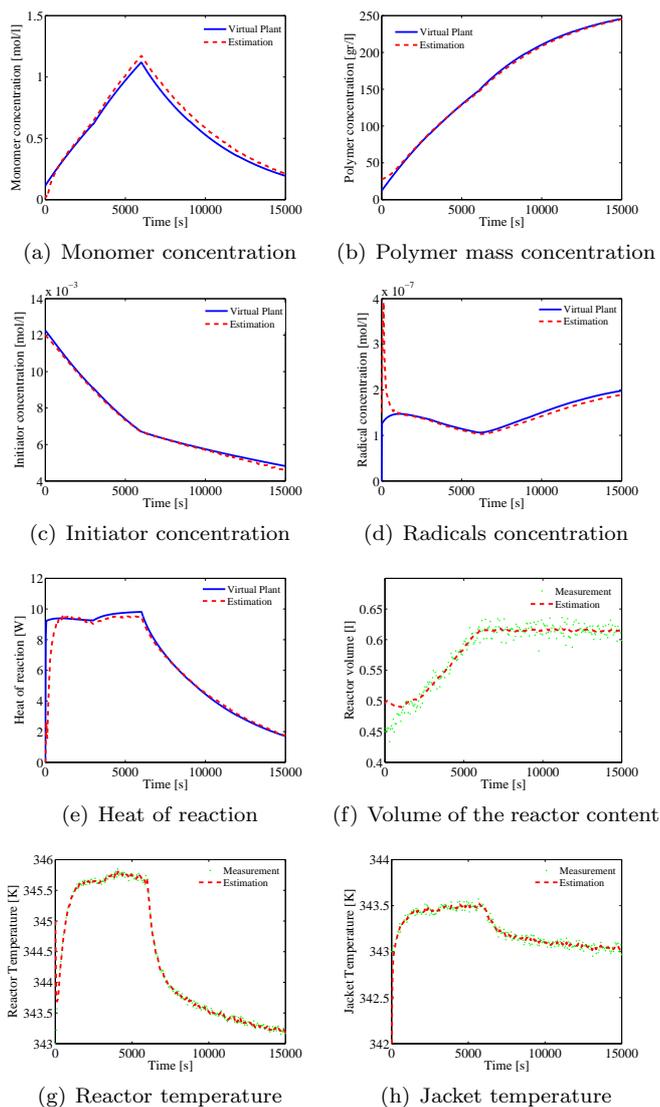


Fig. 1. Results of the state estimation. The diagonal values of the matrixes of model error covariance ( $Q$ ), initial condition error covariance ( $P_0$ ) and the measurement error covariance ( $R$ ) for the monomer concentration, polymer mass concentration, initiator concentration, radicals in the water phase concentration, the heat of the reaction, volume of the reactor content, the reactor temperature, and the jacket temperature are  $Q = [10^{-5}, 0.4, 1.5 \times 10^{-7}, 10^{-8}, 0.1, 1.3 \times 10^{-4}, 0.5, 0.5]$ ,  $P_0 = [10^{-4}, 0.8, 1.5 \times 10^{-7}, 1.2 \times 10^{-7}, 0.06, 10^{-3}, 0.4, 0.4]$ , and  $R = [0.01, 0.5, 0.5]$ .

at the mid-course of the process. To simulate the plant-model mismatch, it is assumed that in the virtual plant (model of the plant) coagulation occurs whereas no coagulation is considered in the nominal model. Apart from this structural mismatch, the parameters of the virtual plant and the nominal model are considered to be the same. The elements of the covariance matrices of the initial state and the state noise,  $P_0$  and  $Q$ , were tuned by performing simulations.  $Q$  was considered to be diagonal and time invariant. The result of the state estimation is shown in figure 1. As one can see, despite the uncertain initial con-

ditions, the concentrations of the monomer (figure 1(a)), polymer (figure 1(b)), initiator (figure 1(c)), radicals in the water phase (figure 1(d)), the heat of the reaction (figure 1(e)) are estimated correctly and the volume of the reactor content (figure 1(f)), the temperature of the reactor (figure 1(g)), and temperature of the jacket (figure 1(h)) are properly filtered.

### 3.2 HYBRID MODEL

In the control structure proposed above, a hybrid model with two components, the nominal model (model without coagulation) and an empirical model which corrects the predictions of the nominal model at the end of the batch based upon the estimated/measured states of the system at the mid-course, is used to compute the optimal input trajectory of the monomer from the mid-course up the end of the batch.

The batch history needed to build the empirical component of the hybrid model is obtained by simulating the virtual plant using different monomer input trajectories which are obtained by perturbing the feed trajectory around the nominal input trajectory (16 experiments were created). The empirical model maps the states of the system at the mid-course and the parameterized monomer flow rate trajectory from the mid-course up to the end of the process to the state residuals (difference between the predictions of the nominal model and the virtual plant) at the end of the batch. Linear models like partial least squares (PLS) were not able to capture the nonlinearities of the above mapping. Therefore, a nonlinear model, a partial least square based radial basis function neural network (RBF-PLS) (Walczak and Massart, 1996) is used where firstly the activation matrix of the RBF component of this black-box model is calculated using the input matrix, and to connect the activation matrix to the output matrix, instead of weights (as in conventional RBF networks), a PLS model is used. RBF-PLS enjoys the dual advantage of capturing the nonlinearities by its RBF component while treating the high dimensionality of the data with the PLS model. After selecting the centers (k-means clustering is used to obtain the RBF centers) and the standard deviation of activation functions, the activation matrix of the RBF component of the empirical model is calculated using the input matrix  $\mathbf{X}$  as follows:

$$\Phi = \begin{bmatrix} \varphi_1(\mathbf{X}_1) & \varphi_2(\mathbf{X}_1) & \dots & \varphi_{N_c}(\mathbf{X}_1) \\ \varphi_1(\mathbf{X}_2) & \varphi_2(\mathbf{X}_2) & \dots & \varphi_{N_c}(\mathbf{X}_2) \\ \vdots & \vdots & \dots & \vdots \\ \varphi_1(\mathbf{X}_N) & \varphi_2(\mathbf{X}_N) & \dots & \varphi_{N_c}(\mathbf{X}_N) \end{bmatrix}, \quad (12)$$

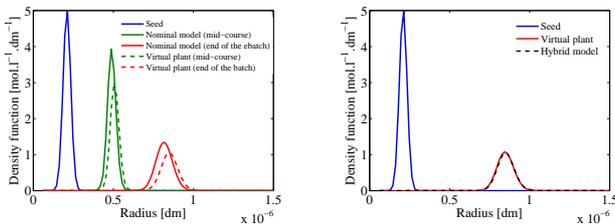
where  $\varphi_j(\mathbf{X}_i) = \exp\left(-\frac{\|\mathbf{X}_i - \mathbf{C}_j\|_2^2}{2\sigma_r^2}\right)$  in which  $\mathbf{X}_i (1 \times 15)$  consists of the states of the system at the mid-course (8 estimated states, number of particles and first 2 moments of the distribution obtained from the measured PSD) and of the feed flow rate trajectory from the mid-course up to the end of the process (monomer flow rate trajectories parameterized by 4 parameters) for experiment  $i$ ,  $\mathbf{C}_j$  is  $j$ th center,  $N_c$  is the number of centers,  $N (=16)$  is the number of experiments and  $\sigma_r$  is the standard deviation of the activation functions. The activation matrix  $\Phi (15 \times N_c)$  is then mapped to the residuals of the states at the end of the batch (the first two moments of the PSD,

number of particles and the monomer concentration for each experiment, i.e. the residual matrix is  $\mathbf{R}(15 \times 4)$  using the PLS model as follows:

$$\Phi = \mathbf{T} \cdot \mathbf{P}^t + \mathbf{E}, \quad \mathbf{R} = \mathbf{U} \cdot \mathbf{Q}^t + \mathbf{F}, \quad \mathbf{U} = \mathbf{K} \cdot \mathbf{T} + \mathbf{H} \quad (13)$$

where  $\mathbf{T}(15 \times N_l)$  and  $\mathbf{U}(15 \times N_l)$  are the scores of the predictor and response,  $\mathbf{P}(N_c \times N_l)$  and  $\mathbf{Q}(4 \times N_l)$  are the loadings,  $\mathbf{K}(15 \times 15)$  is the regression matrix,  $\mathbf{E}(15 \times N_c)$ ,  $\mathbf{F}(15 \times 4)$ , and  $\mathbf{H}(15 \times N_l)$  are the error matrices, and  $N_l$  is the number of PLS latent variables. The loading, score, regressor, and error matrixes of the PLS model are computed using the NIPALS algorithm (Geladi and Kowalski, 1986). The predictions of the nominal model are then corrected using the residuals obtained from the RBF-PLS model (e.g. for the first moment of the distribution  $\mathbf{M}_1^{Hybrid}(t_{end}) = \mathbf{M}_1^{FPE}(t_{end}) + \mathbf{R}_{M_1}$ ). To build the RBF-PLS model the data-sets were divided into two parts for the training and the validation. The performance of the empirical model is evaluated by the predictability index ( $PI = 1 - \sum_{i=1}^k (Residual_i^{predicted} -$

$Residual_i^{real})^2 / \sum_{i=1}^k (Residual_i^{real})^2$ ) computed for the validation data-sets. In the RBF-PLS model,  $N_c$ ,  $\sigma_r$ , and  $N_l$  are degrees of freedom. To obtain the best combination of these parameters, firstly, it is assumed that  $N_c$  and  $\sigma_r$  vary in the ranges of [3-10] and [0.1-2] respectively. Then for each pair of  $N_c$  and  $\sigma_r$  the optimal number of latent variables of the PLS model is obtained using Monte Carlo cross-validation. To avoid over-fitting, the minimum number of RBF components which gives  $PI > 0.95$  is selected.  $N_c = 6$ ,  $\sigma_r = 1.7$  and  $N_l = 6$  were found to provide very good performance with the average prediction ability of 0.96 for this problem. As one can see in figure 2(a) there is an offset between the PSD predictions of the nominal model and the virtual plant when simulating both models using a nominal monomer flow rate input trajectory. There is a 22% reduction in the number of particles based on the considered coagulation in the virtual plant. The significance of these differences depends mainly on the application of the latex and the required preciseness of the PSD. In this work, simulations are used to show the capability of the control approach. The hybrid model predicts the final PSD of the virtual plant with a very good accuracy as it is illustrated in figure 2(b).



(a) Nominal model vs. virtual plant (b) Hybrid model vs. virtual plant

Fig. 2. PSD predictions of the nominal and hybrid model versus virtual plant.

### 3.3 MID-COURSE CORRECTION

The monomer input trajectory is discretized over the whole emulsion polymerization batch horizon (here considered to be 15000 seconds) using a control vector parametrization. The batch time is divided into 5 equal periods of time for each of which the flow rate of the monomer is kept constant. In this study, the mid-course correction is considered to be computed when one fifth of the whole batch time (i.e. 3000 seconds) has passed. This means that the correction is performed at the end of the first step of the parameterized control vector.

Using the hybrid model presented in section 3.2, an optimization problem is solved to compute the optimal input trajectory from the mid-course up to the end of the batch:

$$\begin{aligned} \text{Min}_{\dot{\mathbf{V}}_M} \quad J = & w_1 \sum_{i=1}^2 (M_i^{Hybrid} - M_i^{Target})^2 / \sum_{i=1}^2 (M_i^{Target})^2 + \\ & w_2 (N^{Hybrid} - N^{Target})^2 / (N^{Target})^2 + \\ & w_3 \sum_{i=2}^5 (\dot{V}_{M,i} - \dot{V}_{M,i}^{Nominal})^2 / \sum_{i=2}^5 (\dot{V}_{M,i}^{Nominal})^2, \end{aligned} \quad (14)$$

subject to  $\dot{\mathbf{x}} = f(\mathbf{x}(t), \mathbf{u}(t))$ ,  $\mathbf{x}(t = t_{mid}) = \mathbf{x}_{mid}$ ,

$$\dot{\mathbf{V}}_M^{min} \leq \dot{\mathbf{V}}_M \leq \dot{\mathbf{V}}_M^{max}, [M]_{t_{end}}^{Hybrid} \leq [M]_{t_{end}}^{max}, \sum_{i=1}^5 \dot{\mathbf{V}}_M^i \Delta t_i <$$

$V_{max}^{tot, fed}$ , and  $\dot{\mathbf{Q}} < \dot{\mathbf{Q}}_{max}$ , where  $M_i^{Hybrid}$  are the  $i$ th moments of the distribution at the end of the batch predicted by hybrid model,  $M_i^{Target}$  is the  $i$ th moment of the target PSD,  $N^{Hybrid} = \int_{r_{min}}^{r_{max}} n_{end}^{Hybrid}(r, t_{end}) dr$ ,  $N^{Target} = \int_{r_{min}}^{r_{max}} n^{Target}(r, t) dr$ ,  $\dot{V}_{M,i}$  is the parameterized monomer flow rate,  $\dot{V}_M^{Nominal}$  is the nominal input trajectory,  $V_{max}^{tot, fed}$  is the maximum amount of monomer to be fed into the reactor,  $\dot{\mathbf{x}}(t)$  is the model of emulsion polymerization,  $\mathbf{x}_{mid}$  is the state of the system at the mid-course,  $[M]_{t_{end}}^{Hybrid}$  is the monomer concentration at the end of the batch predicted by the hybrid model,  $\dot{\mathbf{Q}}$  is the heat of the reaction, and  $w_1 = 1$ ,  $w_2 = 0.5$ , and  $w_3 = 0.25$ .

In general, there are always concerns regarding the residue of the unreacted monomer at the end of the batch in polymerization processes as the contamination of the final product with the excess monomer is restricted. Furthermore, the postprocessing which has to be done for removing the unreacted monomer is costly and time consuming. Therefore, the concentration of the monomer should be reduced to an acceptable level (here considered to be  $[M]_{t_{end}} \leq 0.2 \text{ mol/l}$ ). Moreover, due to the economical issues the amount of monomer consumed in the batch has to lie within a certain range. Considering these arguments, the monomer concentration at the end of the batch and the total amount of the monomer fed to the reactor are taking into account as end point constraints in the formulation of the optimization problem. The heat removal capacity of the jacket is another constraint. This is treated here as a path constraint ( $\dot{\mathbf{Q}}_{max} = 10 \text{ J/s}$ ). Due to the operational limitations, a maximum allowable range is considered for the parameterized control vector ( $\dot{\mathbf{V}}_M^{max} = 1 \text{ ml/s}$ ).

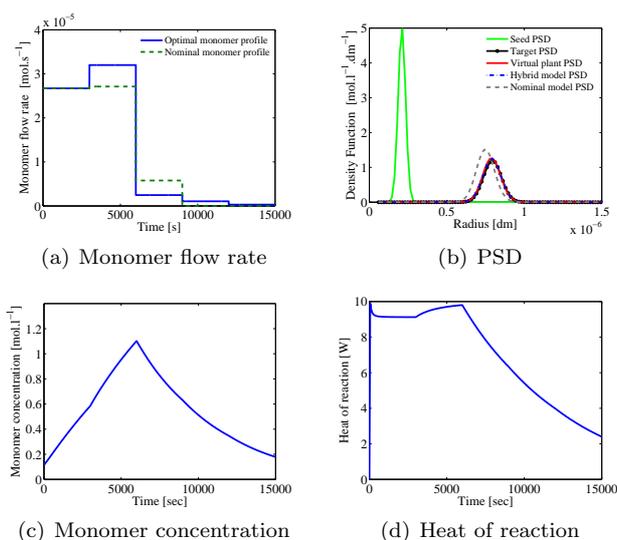


Fig. 3. The result of the mid-course correction using the hybrid model. Mid-course correction is done when one fifth of the batch time has passed.

The above optimization problem is solved using the *NPSOL* solver of TOMLAB and the corresponding results are presented in figure 3. As one can see in figure 3(b), by applying the obtained optimal inlet flow rate of monomer from the mid-course up to the end of the batch (shown in figure 3(a)) to the virtual plant, the PSD of the virtual plant converges to the target PSD. The same behavior is observed when the optimal input trajectory is implemented at the hybrid model which once more shows the efficiency of the hybrid model in the prediction of the PSD of the virtual plant. To illustrate the inadequacy of the nominal model for the optimization purpose in the presence of the structural plant-model mismatch, the optimal trajectory of monomer is implemented at the nominal model and as one can see in figure 3(b) there is a significant mismatch between the prediction of the nominal model and the target PSD. Moreover, the constraints of the above optimization problem are satisfied as it is depicted in figures 3(c) and 3(d). It can be concluded from this figure that employing the proposed mid-course control strategy enables one to produce a latex with a predefined target PSD despite uncertain initial conditions (see figure 1) and a structural mismatch between the nominal model and the virtual plant.

#### 4. CONCLUSIONS

A practical approach to perform a mid-course correction under structural plant-model mismatch in a semi-batch emulsion polymerization process to achieve a polymer with a predefined target PSD was developed. In this method, firstly a nominal parameterized monomer flow rate trajectory is applied at the plant up to the mid-course of the batch while the available measurements are used to estimate the lumped states of the emulsion polymerization model using an EKF. The estimated states together with the measured PSD at the mid-course of the process are used as the initial condition for an optimization which is done to compute the trajectory of the monomer feed from the mid-course up to the end of the process. In this optimization, a hybrid model which comprises the

nominal model of the emulsion polymerization process and an empirical component that maps the state of the system at mid-course to the residual of the states at the end of the batch, is used. It was shown that using this method one can effectively control the PSD in a seeded emulsion polymerization in the presence of uncertain initial conditions and significant structural plant-model mismatch (e.g. when unlike the nominal model coagulation occurs in the virtual plant).

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