ON-LINE PARTICLE SIZE DISTRIBUTION CONTROL STRATEGY IN AN EMULSION COPOLYMERIZATION REACTOR

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Abstract: Model order reduction is applied to a population balance equation (PBE) describing the particle size distribution in an emulsion copolymerization reactor. The reduced order model is used in linear model predictive control. The performance of controllers with different controlled outputs is compared in the presence of two classes of disturbances, one related to the nucleation mechanism and the other affecting the growth rate, to determine the most robust control strategy for the regulation of the distribution at the final time.

Keywords: Reference trajectory tracking, on-line feedback-based control, model order reduction, particle size distribution.

1. INTRODUCTION

Several control strategies for polymer properties, including molecular weight distribution, copolymer composition, and particle size distribution, have been developed to improve the end-use properties of a polymer product. Some of strategies are based on the tracking of trajectories calculated off-line using optimization methods (Choi and Butala, 1989; Saldivar and Ray, 1997; Crowley *et al.*, 2000) and on-line feedback algorithms have been applied to overcome the limitations of open-loop optimal trajectory tracking (Kozub and MacGregor, 1992; Echevarria *et al.*, 1998; Vicente *et al.*, 2001). However, on-line feedback-based control of particle size distribution (PSD) in particulate systems is rarely reported as the process is highly nonlinear and numerical solution techniques for the population balance equation lead to a high dimension problem. Therefore, most research work has focused on the control of lumped properties (Zeaiter *et al.*, 2002; Chiu and Christofides, 1999).

In this study, model order reduction based on principal component analysis (PCA) is applied to the first-principles model, and a control strategy is developed for tracking the reference trajectory in an effort to control the final PSD in an emulsion copolymerization system. This modeling and control is more difficult than the homopolymerization case because the two monomers influence the stability of the particle in different manners.

2. SEMIBATCH VAC/BUA EMULSION COPOLYMERIZATION REACTOR

A mechanistic model of a semibatch VAc/BuA emulsion copolymerization reactor developed by Immanuel *et al.* (2002) is summarized in Table 1. This model has several advantages in that the size-dependent growth rate is taken into account and the average number of radicals per particle is calculated via a balance between the rates of entry, desorption and termination of

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Table 1. Model equations for a semibatch emulsion copolymerization system

Mass balance equations	
Oxidizer	$d([I_w]V_{aq})/dt = -k_{d1}[I_w][Y_1^r] + v_{I_w}$
Reducer	$d([Y_2]V_{aq})/dt = -r_I k_{d1}[I_w][Y_1^r] + v_{Y_2}$
Initiator radical	$d([R_w]V_{aq})/dt = k_{d1}[I_w][Y_1^r] - V_{aq}\sum_{i=1}^{2} k_{ri}[R_w][M_i]_w - V_{aq}k_{tav}^w[R_w]\left(\sum_{l=0}^{j_{cr}-1}[P_w]^l + [R_w]\right)$
Monomers	$\frac{dM_j}{dt} = v_{M_j} - \sum_{i=1}^{2}(k_{pij}^w + k_{trij}^w)p_{wi}[P_w][M_j]_w V_{aq} - \sum_{i=1}^{2}(k_{pij} + k_{trij})p_i[M_j]_p \int_{r_{nuc}}^{r_{\max}} \bar{n}(r,t)F(r,t)dr$
Population balance equation	
Density function	$\frac{\partial}{\partial t}F(r,t) + \frac{\partial}{\partial r}\left(F(r,t)R_{growth}(r,t)\right) = R_{nuc}(r,t) + R_{coag}(r,t)$
Growth rate	$R_{growth}(r,t) = \frac{dr}{dt} = \frac{3}{4\pi r^2 \rho_p}\sum_{i=1}^{2}\sum_{j=1}^{2} k_{pij}p_i\frac{\bar{n}(r,t)}{N_A}[M_j]_p MW_j$
Nucleation rate	$R_{nuc} = R_{micellar} + R_{homo} = \sum_{l=0}^{j_{cr}-1}\sum_{i=1}^{2} e_{i,micelle}^l p_{wi}[P_w]^l C_{micelle}V_{aq} + k_{pav}^w[P_w^{j_{cr}-1}]V_{aq}$
Coagulation rate	$R_{coag}(r,t) = H(r_{uppper} - r)R_{formation}(r,t) - H(r_{cutoff} - r)R_{depletion}$
	$R_{formation}(r,t) = \frac{1}{V_{aq}}\int \beta(r',r'')F(r',t)F(r'',t)\frac{r^2}{\left(r^3-(r')^3\right)^{2/3}}dr'$
	$R_{depletion}(r,t) = \frac{1}{V_{aq}}\int_{r_{nuc}}^{r_{\max}} \beta(r,r')F(r,t)F(r',t)dr'$ where $\beta(r,r') = c_1 4\pi D_0(r+r')/W_s$
Output functions	
Weight averaged PSD	$W(r_i,t) = r_i^3 F_i \big/ \sum_i r_i^3 F_i$ where $F_i = \int_{r_{b,i-1}}^{r_{b,i}} F(r,t)dr$
Total particle number	$N_p = N_A \sum_i F_i$ Solid content $S_c = N_A\left(\sum_i 4\pi r_i^3 \rho_p F_i/3\right)/m_T$

radicals. The kinetic rate constants and physical constants were drawn from the literature (see Immanuel *et al.*, 2002 and references) and Immanuel *et al.* (2002) investigated the parametric sensitivity on the distribution at the final time of the batch.

The population balance equation (PBE) is solved numerically using the solution technique proposed by Immanuel and Doyle III (2003*a*), in which the continuous PSD is divided into a finite number of sections within which an integral quantity of the distribution is defined. To discretize the population balance equation for the particle density function (*cf.* Table 1), 250 elements (or grids) with a width of 2 nm are used and ordinary differential equations for mass balance equations of two monomers, aqueous phase volume, surfactant, oxidizer, reducer and initial radicals are calculated using the ODE solver (ode45) in MATLAB.

3. MODEL ORDER REDUCTION

The finite discretization of the governing PBE leads to very high order, ill-conditioned and uncontrollable dynamical systems, thus motivating the application of model order reduction (MOR) methods to the mechanistic model for semibatch VAc/BuA copolymerization. In general, MOR methods involve the projection of the full order states onto a state space with a suitable reduced order through a linear transformation:

$$x = \mathbf{P}z \tag{1}$$

where z is a q-th order projection of state $x \in R^N$ in the reduced order state space, and $\mathbf{P}$ represents an orthonormal matrix for a transformation from the reduced one to the original state space. There are a number of methods to select the transformation matrix $\mathbf{P}$. In the present study, principal component analysis (PCA) (Sharaf *et al.*, 1986) is applied. PCA is one of several multivariate statistical projection techniques in which the original number of (possibly) correlated variables are transformed into a (smaller) number of uncorrelated variables known as *principal components*. This technique has several advantages in that it addresses limitations due to measurement noise, correlated variables and unknown variables, and the data set dimensionality problem can be managed.

Some key issues in applying the transformation matrix to a nonlinear system are associated with storage and evaluation (Park and Doyle III, 2004). To solve this problem, the nonlinear model is linearized at every sample time using a nominal point and the zero-order hold is used to calculate discrete system matrices ($\mathbf{A}_k$, $\mathbf{B}_k$, and $\mathbf{H}_k$) under the assumption that the state between sample times is not changed significantly (Garcia, 1984; Gattu and Zafiriou, 1992). The transformation matrix $\mathbf{P}$ in Eq. (1) is applied to the linearized model and consequently the following reduced order model is obtained:

$$\bar{z}_{k+1} = \mathbf{A}_k^r \bar{z}_k + \mathbf{B}_k^r \bar{u}_k \ \text{ and } \ \bar{y}_k = \mathbf{H}_k^r \bar{z}_k \tag{2}$$

where $\mathbf{A}_k^r = \mathbf{P}^T\mathbf{A}_k\mathbf{P}$, $\mathbf{B}_k^r = \mathbf{P}^T\mathbf{B}_k$ and $\mathbf{H}_k^r = \mathbf{H}_k\mathbf{P}$, respectively. The over-bar represents the deviation from the nominal value.

4. RESULTS AND DISCUSSION

In order to generate the database for the calculation of the linear transformation matrices, pseudo random multi-level signals are introduced to the plant (the first principles model) with the assumption that this signal produces representative responses over the region of interest. At every sample time, the input is changed with the probability of 7% and the value is chosen

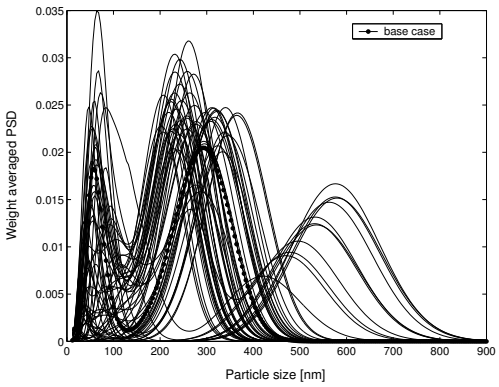

Fig. 1. Weight averaged particle size distribution at the final time generated by pseudo random 4-level signals (60 batches).

among 4-level values (0, 3.5×10^{-4}, 7.0×10^{-4}, 1.05×10^{-3} for u_1 and 0, 1.66×10^{-4}, 3.32×10^{-4}, 4.97×10^{-3} for u_2). The corresponding responses, including states and outputs, are saved in the database at every sample time (1 min). Experimental conditions and additional details are listed in Table 2.

Table 2. Conditions for semibatch VAc/BuA copolymerization system

Initial reactor charge	
Water	1.0L
VAc	52g
Ferrous ammonium sulphate	0.1g
Sodium benzoate	1.12g
Reactor temperature	67.5°C
Flow rates of feed solutions [mol/s]	
BuA feed	$2.81 \times 10^{-4} \rightarrow 0$ at 94 min
Oxidizer feed	$5.4 \times 10^{-4} \rightarrow 9.0 \times 10^{-4}$ at 107 min
Reducer feed	$4.86 \times 10^{-4} \rightarrow 8.09 \times 10^{-4}$ at 107 min
Operating range of inputs [mol/s]	
VAc flow rate (u_1)	$0 \sim 1.05 \times 10^{-3}$
surfactant flow rate (u_2)	$0 \sim 4.97 \times 10^{-3}$ mol/s

Figure 1 shows the results of weight averaged particle size distribution at the final time for 60 batches. Since the inputs are specified between upper and lower bounds, this figure accounts for the reachable region of the system under the current operation condition. Due to the slow supply of surfactant, the amount of free surfactant in the reactor is below the critical micelle concentration (cmc), thus only homogeneous nucleation takes place in the early stage while micellar nucleation becomes dominant after the surfactant concentration exceeds the cmc (Immanuel *et al.*, 2002). Hence the PSD at the final time shows a bimodal distribution; the primary peak in right-hand side by homogeneous nucleation and the secondary peak in left-hand side by micellar nucleation.

To simplify the calculations of the linear time varying transformation matrices, all the data are mean-centered and scaled to unit variance. For the principal component analysis, the Statistics Toolbox for MATLAB is used. The number of principal components (PCs) is determined so that the transformation matrix constitutes more than 99.9% of the total variance because the PCs for 90.0% fail to approximate the entire distribution (Park and Doyle III, 2004). In general, the PCs for 80% or 90% variance predict the behavior of original system in most of the results reported in the literature, while the PCs for 99.9% are used in this system. It is worth emphasizing that PCA approach described in this paper employs the nonlinear fundamental model directly, hence the unusually large variance is reasonable. If, on the other hand, data were employed to generate the PCs, a lower variance would be more practical to avoid capturing noise effects (Park and Doyle III, 2004). The number of PCs for the particle density function (F) is chosen to be 16 at every sample time while the number of PCs for the weight averaged PSD that predicts more than 99.9% cumulative variance is determined to be 15. The state variables for the mass balance equations, such as monomer concentration, are not projected to the latent variable space but are normalized as $x_{normalized} = (x - x_{\min})/(x_{\max} - x_{\min})$. After the transformation matrices are obtained, the reduced order model is used in the prediction equation of linear model predictive control (MPC).

Immanuel and Doyle III (2003*b*) suggested a control strategy where time varying reference trajectories for the total number of particles (N_p) and solid content (S_c) can be used for the control of the nucleation rate and the growth rate, respectively. They applied the Nondominated Sorting Genetic Algorithm (NSGA) (Bhaskar *et al.*, 2000) to calculate the optimal input trajectories to track the reference trajectories for N_p and S_c. Meanwhile, Park and Doyle III (2004) introduced a control strategy that drives the weight averaged particle size distribution directly to its time varying reference trajectory using a model predictive control based on the reduced order model. In this study, the performance of these strategies is evaluated for the case when a disturbance or a model mismatch exists in the system.

Three control strategies are compared in this study: (*strategy* 1) the utilization of N_p and S_c time varying reference trajectories; (*strategy* 2) the utilization of weight averaged PSD time varying reference trajectory; and (*strategy* 3) the utilization of all of the reference trajectories. For all cases, it is assumed that the state variables are available by feedback and the 250 original state variables in the particles density function (F) are projected onto the latent variable space. The total number of particles is scaled using the normalization method with high and low bounds as 1×10^{18} and 0, respectively, and the weight averaged PSD is reduced using PCA.

The controller is tuned to exhibit acceptable performance in rejecting a disturbance in the surfactant feed concentration (the concentration of surfactant feed in the plant is less than that in the model by 10%), and the weighting matrices are determined by trial and error (listed in Table 3). State variables are assumed to be available by state feedback. For all strategies, the prediction and control horizons are 25 and 15, respec-

Table 3. Weighting matrices for each control strategy

weights on the control error (Λ^y)	
Strategy 1	$81 \times \mathbf{I}_{15\times 15}$
Strategy 2	$diag([5.5 \times 10^3, 1.0 \times 10^3])$
Strategy 3	$diag([94 \times \mathbf{I}_{15\times 15}, 5.5 \times 10^3, 1.0 \times 10^3])$
weights on the control input (Λ^u)	
Strategy 1	$diag([0.1, 0.51])$
Strategy 2	$diag([0.1, 0.12])$
Strategy 3	$diag([0.1, 0.22])$

tively, and the sampling time is 1 min. Constraints on the input magnitude are specified with the operating range given in Table 2, and the rate of input change is constrained as follows:

Constraints on the rate of input change

$$\begin{aligned} -4.0 \times 10^{-4} \leq \Delta u_1 \leq 4.0 \times 10^{-4} \quad [\mathrm{mol/s}] \\ -2.0 \times 10^{-3} \leq \Delta u_2 \leq 2.0 \times 10^{-3} \quad [\mathrm{mol/s}] \end{aligned} \tag{3}$$

Figures 2–4 illustrate the controlled distribution at the final time of the batch and the corresponding input trajectories determined by each strategy. As the results in Figure 2 indicate, the direct feedback of variables that are sensitive to the disturbances leads to the use of both inputs to eliminate the disturbance. The controller in strategy 2 uses the flow rate of surfactant feed solution primarily to drive the total number of particles to its time varying reference trajectory as the disturbance in the surfactant feed solution mainly effects N_p. As a result, different levels of control performance are observed between strategies 1 and 2, in that strategy 1 shows better performance in the secondary peak than the primary peak, while strategy 2 results in satisfactory performance in both peaks. Considering the characteristics of the controller as well as the system, the different results of the controllers are attributed to the limitations of each controller; strategy 1 has a disadvantage in that different control weights cannot be used for different peaks because the distribution is projected to a latent variable space, and the shortcoming of strategy 2 is that, even after the deviated trajectories of N_p and S_c due to the disturbance are converged to their respective reference trajectories, the effect of deviations in the early stage still remains in the weight averaged particle size distribution at the final time.

To compensate for the disadvantages of each controller in strategies 1 and 2, all the outputs (the distribution, N_p, and S_c) are utilized in the strategy 3 and the result is indicated in Figure 4. It is noted that the same control weights as those in the previous strategy are used for N_p and S_c, but the VAc feed flow rate between 20 and 40 min shows higher values while the surfactant feed flow rate becomes smaller compared to the input trajectories in strategy 2. This feature indicates that the utilization of the distribution as a controlled output compensates for the error in strategy 2 and consequently, the controlled distribution in strategy 3 shows a better level of performance than those of strategies 1 or 2.

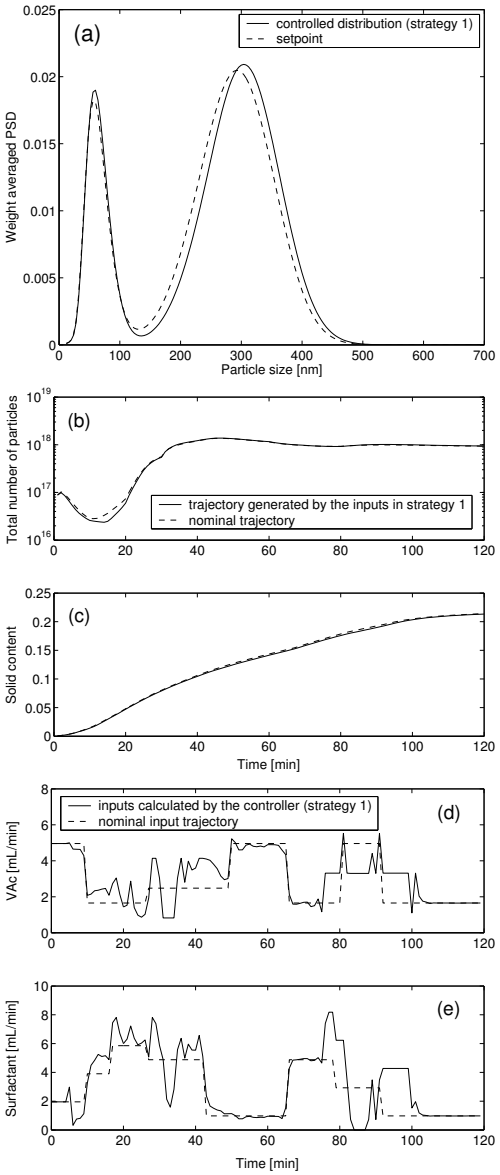

Fig. 2. The performance of the controller in strategy 1 (a) the weight averaged particle size distribution (b) the total number of particles (c) the solid content (d) the input trajectory (VAc) (e) the input trajectory (surfactant).

To evaluate robustness, the performance of the controllers is compared when disturbance magnitudes are varied (controller tuning is fixed). The following relative error is used for comparison

$$\frac{\|W_i(t_f) - W_{i,\mathrm{desired}}\|_2^2}{\|W_{i,\mathrm{desired}}\|_2^2} \tag{4}$$

where W_i denotes the sampled version of the weight averaged PSD and the result is presented in Figure 5 (surfactant disturbance). When the disturbance is less than 0.9, the performance of strategy 1 becomes worse and the magnitude of the difference in relative errors between strategies 1 and 2 is increased. Therefore, utilization of the distribution hinders the performance of strategy 3 compared to that of strategy 2. However,

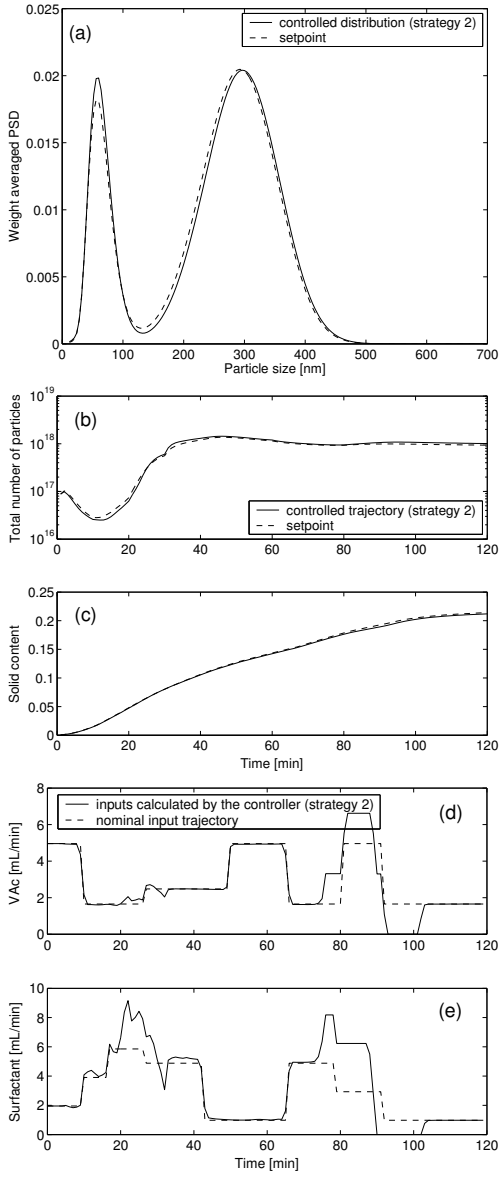

Fig. 3. The performance of the controller in strategy 2 (a) the weight averaged particle size distribution (b) the total number of particles (c) the solid content (d) the input trajectory (VAc) (e) the input trajectory (surfactant).

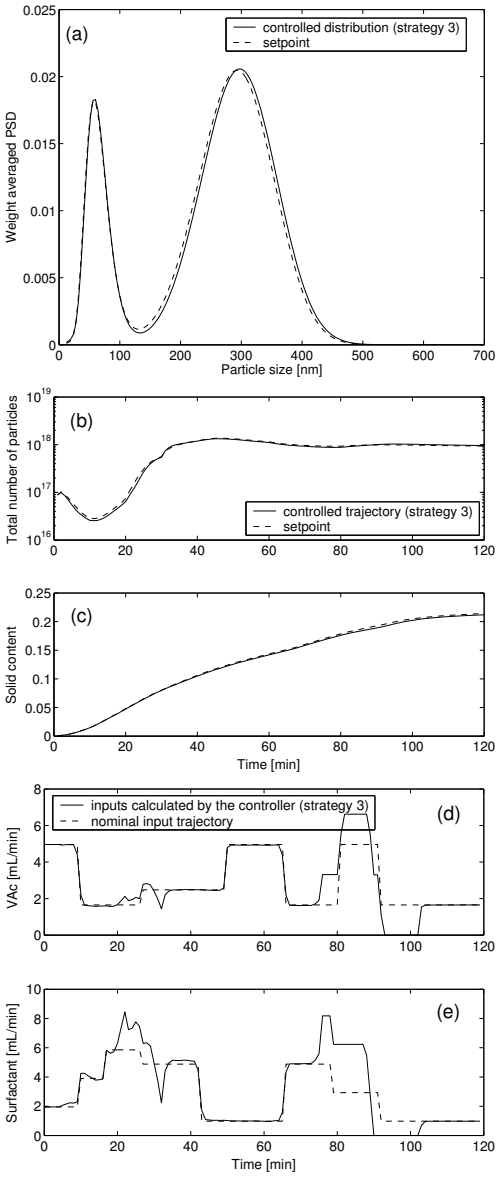

Fig. 4. The performance of the controller in strategy 3 (a) the weight averaged particle size distribution (b) the total number of particles (c) the solid content (d) the input trajectory (VAc) (e) the input trajectory (surfactant).

in the region of disturbance larger than 1.0 (nominal case), the performance of strategy 1 becomes best whereas strategy 2 as well as 3 (including N_p and S_c) performs worse. As the magnitude of the disturbance is increased, the output trajectories for N_p and S_c deviate from the reference trajectories and then converge to them again. However, the deviation of lumped parameters in the middle of the reaction causes a deviation of the PSD at the final time. Therefore, the utilization of lumped parameters in the controlled outputs results in worse performance compared to the direct tracking of the PSD reference trajectory. From the results, it is inferred that the direct use of the distribution in the controller is robust to the different magnitudes of disturbances.

Figure 6 shows the performance of strategies when a different disturbance from the previous case is im-

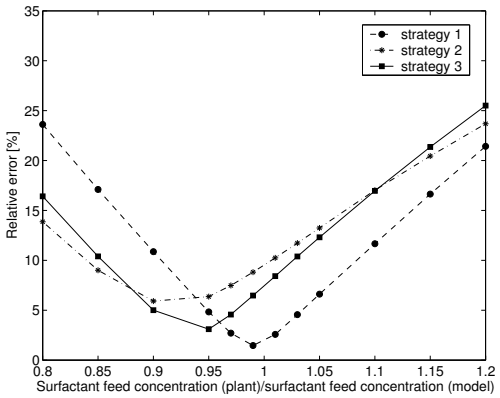

Fig. 5. Comparison of performance between strategies in the presence of a disturbance in the surfactant feed.

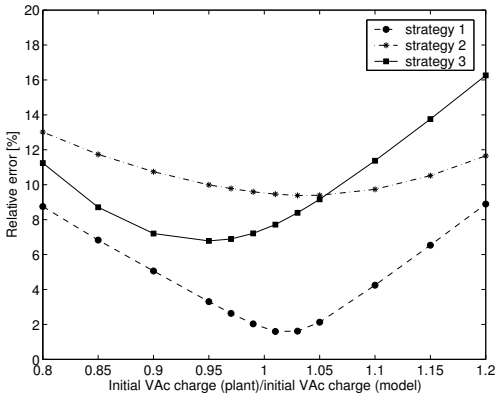

Fig. 6. Comparison of performance between strategies in the presence of a disturbance in the initial VAc charge.

posed on the system. In this case, a disturbance is introduced in the initial charge of VAc. This type of disturbance brings about an error in the growth rate while the disturbance in the previous case is related to the nucleation rate. In this case, the result also shows the effectiveness of strategy 1 since it utilizes most effectively both control inputs. The presence of the disturbance in the early stage of the reaction is also responsible for the inferior performance of strategies 2 and 3 because the tracking of N_p and S_c trajectories produces a deviation in the initial stage.

5. SUMMARY

A model order reduction method based on principal component analysis (PCA) is applied to a nonlinear mechanistic model for a semibatch VAc/BuA emulsion copolymerization reactor. The resulting model is used to design a model predictive controller. Strategies using different controlled outputs are compared in the presence of disturbances on the basis of particle size distribution at the final time of the reaction. The results show that the performance of the controller utilizing lumped parameters is satisfactory in the region of "optimal" tuning. However, compared to the strategy utilizing the direct measurement of particle size distribution, a lumped parameter-based method leads to inferior performance for various disturbances (a practical situation for the application of the controller to industrial processes). In summary, the strategies using the reduced order model and trajectory tracking for the distribution are proven to be most effective for the generation of a desired distribution at the final time.

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