

REACHABILITY ANALYSIS OF PARTICLE SIZE DISTRIBUTION IN SEMIBATCH EMULSION POLYMERIZATION

Yang Wang*, Francis J. Doyle III*,†

* Department of Chemical Engineering, University of California at Santa Barbara, CA 93106, U.S.A.

† Corresponding author: doyle@engineering.ucsb.edu

Keywords: Particle size distribution control, population balance model, reachability, nonlinear programming, emulsion polymerization.

Abstract

Emulsion polymerization is an economically important method of producing a number of polymer products, where particle size distribution (PSD) is an essential property of the latex produced. A programming-based approach has been proposed for reachability analysis of PSD for a general particulate system described by population balance models, along with application to a semibatch styrene homopolymerization system. The reachable region is defined for both the nominal and perturbed cases, with final PSDs characterized as multi-Gaussian distributions. The evolution of the reachable region in the case of mid-course correction shows the best in-batch control performance achievable given limited PSD measurements.

1 Introduction

Emulsion polymerization is a multi-phase reaction system in which the main reacting components are in the dispersed organic phase. The amphiphilic surfactant molecules are used to stabilize the dispersed phases. Polymerization is initiated in the aqueous phase by water-soluble (ionic) initiators. The oligomers formed in the aqueous phase nucleate new particles either by entering into micelles, which are aggregates of surfactant molecules (micellar nucleation), or by precipitating out of the aqueous phase (homogenous nucleation). The polymer chains inside the particle propagate at very high rates compared to that in the aqueous phase, causing the particles to grow in size. The growth dynamics depend on the number of polymer chains within the particles. Particles can also increase in size by coalescence with other particles, either due to insufficient stabilization by surfactants or due to the shear stress imparted on the particles by the mixing in the reactor [5, 6]. The economic value of emulsion polymerization is dependent on the production of high-quality polymers, where the particle size distribution (PSD) is essential to determine the quality of end-point products such as its rheological properties, adhesion, drying characteristics and film-forming properties. These depend upon the entire PSD rather than the average properties indicated by a small number of moments. Therefore, the control of the entire PSD as an end-objective in emulsion polymeriza-

tion is well motivated in industrial practice (see, for example, the recent review by Congalidis and Richards [2]). Distribution control is also facilitated by recent advancements in measurement techniques and computational approaches [4]. The various applications of the emulsions target different particle size distributions, usually complex and multi-modal. However, the classes of distributions that can be potentially produced might be limited, depending not only on the polymerizing system, but also on the process constraints and on the initial conditions. It is therefore imperative to identify the class of PSDs that are potentially reachable, i.e., can be produced by the particulate process.

There is a rich literature on modelling emulsion polymerization processes. In contrast, there have been relatively few analysis results published for the control of PSD, where its evolution is described by population balance models to account for the nucleation events, particle growth due to polymerization, and growth due to coagulation. The complexity of the underlying mathematical framework (or even its discretized version in terms of ODEs) precludes a rigorous mathematical analysis. Two notable exceptions are the work of Liotta et al. [7] and Semino and Ray [9]. In the former, a lumped dynamic model was developed for the diameter ratio of a bimodal distribution, and the reachable region for such a controlled property was analysed based on sensitivity work to key kinetic and physical parameters. The latter work considers the controllability of emulsion systems in both the constrained and unconstrained cases. A key insight obtained there is that the controllability properties of the reactor are strongly influenced by both constraints on the manipulated variables and by the structure of the controller (e.g., PI vs. PID). However, the assumption of particle age as the only internal coordinate (so as to guarantee an analytical solution) actually excludes its implementation to most practical particulate systems.

In the current work, a systematic reachability study of PSDs has been performed based on recipe optimization. The testbed in this work is a styrene semibatch emulsion homopolymerization system described by a ‘zero-one’ model [1]. A definition of ϵ -reachability is introduced for general particulate system based on an equivalent recipe optimization problem. This is followed by a parametric characterization of the targeted final PSDs as multi-Gaussian distributions. The subsequent section discusses the reachable regimes for both unimodal and bimodal distributions, as well as the influence of reaction time. Finally,

the re-mapping of the reachable distributions in the face of disturbances and uncertainties is discussed.

2 Reachability of the particulate system

Emulsion polymerization is representative of particulate systems described by population balance equations, which also include crystallization, precipitation and granulation. The system is modeled by the evolution of the distribution of number of particles per unit volume, $n(r, t)$. It is assumed in the following study that particle size r is the only internal coordinate (i.e., the location in property space).

2.1 Zero-One emulsion polymerization system

The so-called ‘zero-one’ model is a multi-distribution population balance model based on the assumption that the rate of radical-radical bimolecular termination within a latex particle is very fast relative to the rate of radical entry into the particles [5]. As a result, latex particles contain either zero or one radical at a given instant.

In brief, the particle size population is divided into a population containing zero radicals, $n_0(r)$, and a population containing one radical, $n_1(r)$. The one-radical population is further divided into a population containing a polymer radical, $n_1^p(r)$, which would not readily diffuse out of the particle due to its size, and a population containing a monomer radical formed from chain transfer reaction, $n_1^m(r)$, which presumably can readily exit the particles. The balance equations for these populations in a semibatch reactor are given by:

$$\frac{\partial n_0(r)}{\partial t} = \rho(r)[n_1^p(r) + n_1^m(r) - n_0(r)] + k_0(r) \cdot n_1^m(r) \quad (1)$$

$$\frac{\partial n_1^p(r)}{\partial t} = \rho_{init}(r) \cdot n_0(r) - [\rho(r) + k_{tr}C_p]n_1^p(r) + k_p C_p n_1^m(r) - \frac{\partial}{\partial r}[G(r) \cdot n_1^p(r)] + \sum_{i=z}^{j_{crit}-1} k_{em,i}[Micelle][IM_i]\delta(r - r_{nuc}) \quad (2)$$

$$n_1^m(r) = \frac{k_{e,E}[E]n_0(r) + k_{tr}C_p n_1^p(r)}{\rho(r) + k_{pe}C_p + k_0(r)} \quad (3)$$

$$n(r) = n_1^p(r) + n_1^m(r) + n_0(r) \quad (4)$$

where the particle growth rate is given by

$$G(r) = \frac{k_p C_p w_m}{4\pi r^2 \rho_P N_A} \quad (5)$$

Here, the quasi-steady state assumption is applied to n_1^m to derive an algebraic expression for this population. $\rho(r)$ represents an overall radical entry rate into particles, $k_0(r)$ the radical exit rate and ρ_{init} is the entry rate of initiator derived polymer radicals only (no monomer radicals). k_p is the propagation rate constant, C_p the monomer concentration in polymer particles. $\delta(r - r_{nuc})$ in the expression for n_1^p denotes that nucleation of

particles occurs only at a minimum size, r_{nuc} . The partial differential equations are discretized to yield ordinary differential equations (ODEs) using orthogonal collocation on finite elements (OCFE). Model details and the numerical solution techniques are described in [1, 3].

The ‘zero-one’ kinetics focuses on the early stage of emulsion polymerization where particle size is small and particles are rich in monomer. Unlike the later regimes (interval II & III in [3]) dominated by particle growth, the system incorporates current theory on particle nucleation, particle growth due to propagation, and growth due to coagulation. Although the coalescence is assumed to be negligible in this study due to the relatively high surfactant concentrations and the low solids concentrations, it is in consistent with the control practice of minimizing, instead of manipulating, the coalescence phenomenon.

2.2 Reachability of final PSD

For a general dynamic system, given fixed values of the initial time, t_0 , and the terminal time, t_f , a *reachable region* is defined as the envelope of $x(t_f)$ that can be reached from $x(t_0)$ through the use of admissible control [7, 10]. However, the absence of a general approach to solve population balance systems has precluded the possibility of a rigorous analysis of reachability for these systems. For instance, the multiple-distributions and interactions based on statistical reaction mechanisms do not admit closed form solutions via the method of characteristics. There is no way to trace a deterministic growth path for any individual particle.

In the context of the current work, reachability is defined in an equivalent, programming-based manner, as the existence of a feasible solution to a recipe optimization problem to reach the targeted final PSD at specified time, t_f . However, the exact reachability condition is difficult to ascertain for more practical PSD control problems, given the existence of inherent limitations including the reaction mechanism, and the uncertainties in determining the target PSD. Also, to account for external limitations such as model mismatch, parameter uncertainties, inconsistent measurement, as well as the inaccurate control vector parameterization, the concept of ϵ -reachability is introduced here.

The recipe optimization problem is formulated to minimize the sum of the squared deviation between the targeted final PSD, $n^{target}(r)$, and that predicted by model, $n^{model}(r, t_f)$:

$$\min_u J_1 = \frac{\sum_k [n^{model}(r_k, t_f) - n^{target}(r_k)]^2}{n_{scale}} \quad (6)$$

where n_{scale} is a standardization factor given by

$$n_{scale} = \sum_k [n^{target}(r_k)]^2 \quad (7)$$

Definition Given a threshold value ϵ , the targeted final PSD is defined to be ϵ -reachable if the recipe optimization result J_1 satisfies

$$J_1 \leq \epsilon \quad (8)$$

For this specified styrene emulsion homopolymerization system, surfactant and initiator feed rates are chosen as the manipulated variables. When solving above recipe optimization problem, each of them is discretized as 10 equal-spaced heaviside functions, with the amplitudes of the piecewise constant control actions as decision variables. The terminal time t_f has been fixed at 2 hrs. It is expectable that the reachability of the final PSD will be strongly influenced by the free terminal time.

Unless mentioned otherwise, the reachability results presented here refer to the ϵ -reachability, rather than the exact reachability. A value of $\epsilon = 0.05$ is used in this study as an acceptable neighborhood around the original target.

2.3 Parametric characterization of final PSD

For visualization purpose, the targeted final PSDs are characterized in a finite dimensional parametric space. Given the unimodal and bimodal distributions as the most interesting cases in application, the final PSDs (for coagulation-free cases) are described by multi-Gaussian distributions:

$$n^{target}(r, p) = k_1 \cdot e^{-\frac{(r-a_1)^2}{\sigma_1}} + k_2 \cdot e^{-\frac{(r-a_2)^2}{\sigma_2}} \quad (9)$$

where the parameters $p = \{a_i, k_i, \sigma_i | i = 1, 2\}$ are the mean radii, amplitudes and variances for primary and secondary modes, respectively. All the final PSDs are subject to a fixed solids concentrations at the terminal time, which is described by an equality constraint.

$$\int_{r_{nuc}}^{r_{max}} r^3 \cdot n^{target}(r, p) dr = constant \quad (10)$$

3 Results for nominal system

3.1 Effect of the initial reaction conditions

A nominal bimodal distribution is set as the targeted final PSD in the recipe optimization problem. In the first formulation, the initial moles of surfactant, $S(t_0)$ is predetermined as $2.5 \times 10^{-3} mol$. Given the later input profiles as decision variables, the recipe optimization result (Figure 1 in [11]) shows that the number density of the primary mode (large particle size) is always larger than the targeted value, while the secondary mode (small particle size) is well reachable. Consequently, the final PSD is unreachable.

An analysis of the solution reveals that at early time, the optimized surfactant input is at its lower bound of 0, which suggests that the lack of reachability is caused by high initial surfactant mole number, $S(t_0)$. As a result, $S(t_0)$ is included into the decision variables in an extended formulation, which leads to the attainment of the targeted final PSD, with a smaller $S(t_0) = 1.51 \times 10^{-3} mol$. In summary, the influence of initial conditions may be critical, and is not always rectifiable by later inputs due to the irreversibility inherent in the process.

Since the total amount of surfactant feed remains comparable between the two optimization results, it also suggests that not only the amount, but also the timing, of input profiles is critical for the reachability of a targeted PSD. This is a strong nonlinearity that may affect the solution of the recipe optimization problems. Unless mentioned otherwise, $S(t_0)$ will be included into the decision variables in the following studies.

3.2 Reachable region for the unimodal PSDs

A set of unimodal final PSDs described by a single Gaussian distribution

$$n(r, p) = k_1 \cdot e^{-\frac{(r-a_1)^2}{\sigma_1}} \quad (11)$$

is considered, which renders a 2-dimensional map of the reachable region (Figure 1) in the parameter space. All the PSD candidates are chosen around one reference PSD, which is characterized by $k_1 = 1.558$, $a_1 = 46.94 nm$ and $\sigma_1 = 14.37 nm^2$. The reference PSD is known to be well reachable with a standardized residual $J_1 = 9.51 \times 10^{-4}$. The equality constraint of certain solid concentration at the terminal time is used to determine the amplitudes, k_1 , of all the candidate PSDs.

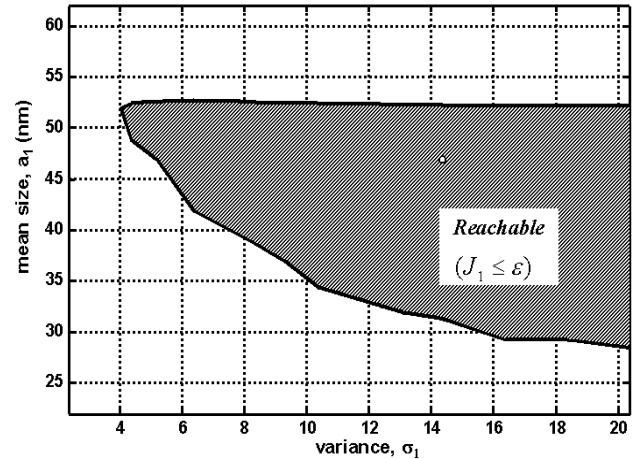


Figure 1: Map of reachable region for the nominal system with $\epsilon = 0.05$.

Given the current ϵ -specification, the reachable region (the shaded area in Figure 1) corresponds to all the achievable final products under the allowable operating conditions. According to the map, there are drastic changes of reachability around both large and small a_1 . The following discussion will connect these results to both sensitivity studies and kinetic analysis.

An analysis of a representative case (corresponding to $a_1 = 56.94 nm$ and $\sigma_1 = 12.37 nm^2$) shows that, for this unreachable PSD, a high $S(t_0) = 1.77 \times 10^{-3} mol$ (See Table 1) along with later surfactant input have been applied to start the micellar nucleation as early as possible while avoiding the undesired secondary mode. The optimized recipe could achieve only the small-size mode of the desired distribution. This is attributed to limited particle growth rate.

$\sigma_1 = 12.37$		J_1	$S(t_0)$	<i>reachable</i>
$a_1 = 56.9$	old k_p	0.339	1.8×10^{-3}	No
	doubled	0.0009	6.5×10^{-5}	Yes
$a_1 = 61.9$	old k_p	0.838	1.3×10^{-3}	No
	doubled	0.0096	1.6×10^{-5}	Yes

Table 1: Sensitivity study of doubled k_p .

To validate this hypothesis, the recipe optimization is reformulated with the value of the propagation rate constant, k_p , (Equation 5) doubled. As a result, the particle growth rate will also be doubled, given sufficient monomer in the reactor. Solving the new recipe optimization problem shows that the previously unreachable PSD now becomes reachable. Similar sensitivity studies have been performed for a value of k_p equal to $\frac{1}{2}$ the original value. All of these results suggest that the particle growth rate is the dominant factor for reachability, which can be used to explain the boundary around the large a_1 and part of the small a_1 . Thus, the reachable region can be significantly improved by manipulating the particle growth rate. One possibility to achieve this is through non-isothermal operation as suggested by [8]. Another easier way is to manipulate the monomer concentration in reactor [7]. However, the latter operation might challenge the assumptions underlining the current ‘zero-one’ model.

3.3 Effect of a flexible terminal time, t_f

In addition to manipulating the reactor temperature and monomer concentration, the reaction/terminal time, t_f , can also be changed to regulate the final PSD. This may be required in the presence of disturbances or mismatch in the initial charge. Here the reachable region of the final PSD is investigated for different terminal times of $t_f = 2, 2.5$ and 3 hrs, respectively. As the reaction time becomes longer with constant control interval (10 min), more decision variables from control vector parameterization are introduced for the new recipe optimization problems. Meanwhile, the reagent feed rates are constrained to be zero for the last 20 min of reaction, as done in the real operation.

The resulting reachability maps (Figure 2) reveal that the reachable region moves to the area of large particle size as the reaction time is extended. This is consistent with the longer evolution of particle nucleation and growth. It is also observed that the reachable region actually is reduced for the mode of small size particles, which could be attributed to two factors. First, due to the cutting of surfactant supply during the last 20 min of reaction, the current system has certain limitations on the achievable small size particles. Second, to generate a mode of small size particles under an extended reaction time, the particle nucleation has to be significantly delayed in time. From the viewpoint of reachability analysis, the system is losing the manipulation capability on the initial charge of reagents (such as surfactant), which could be beneficial in generating the desired final PSD.

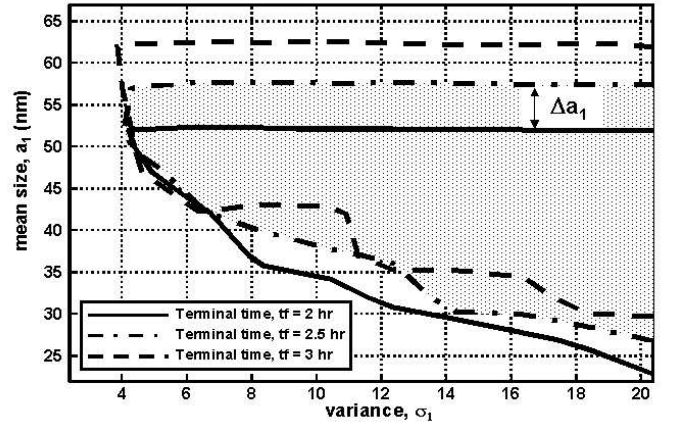


Figure 2: Influence of the reaction time, t_f , on the reachable regions of final PSD.

Clearly, by including t_f as a manipulated variable, the reachable region will be significantly extended along the direction of large mean size (a_1), which will cover each of the above reachable regions obtained with fixed terminal times. Furthermore, it is useful to consider whether the quantitative criterion could be developed for the extension in the direction of mean size (i.e., the Δa_1 in Figure 2), particularly in the case of mid-course correction.

Due to the surplus of monomer in the current reaction system, particle growth rate becomes essentially time-independent. As a result, an upper bound can be determined for a_1 from the targeted final PSD.

Quantitative criterion

The calculation is based on the following observations: compared with the targeted PSD $n^0(r)$ as a function of $p_0 = \{k_1, a_1, \sigma_1\}$, a secondary PSD can be found to provide the largest left shift regarding the location of a specified critical point, while maintaining the deviation between these two distributions below tolerance ϵ . The secondary PSD, which is labelled as $n^1(r)$, will be the easiest one to achieve considering the limited particle growth rate. Then, the critical point on $n^1(r)$ will be used to determine whether the distribution can be reached under the current operating conditions. The detailed derivation is given as follows:

- Given a specified tolerance β , the critical point α is determined for standard normal distribution $\dot{n}(r) = e^{-r^2}$ so that

$$\int_{\alpha}^{\infty} [\dot{n}(r)]^2 dr \leq \beta \cdot \int_{-\infty}^{\infty} [\dot{n}(r)]^2 dr \quad (12)$$

- Given the threshold value ϵ , parameters $p_1 = \{\bar{k}_1, \bar{a}_1, \bar{\sigma}_1\}$ of the unimodal distribution $n^1(r) = \bar{k}_1 \cdot e^{-\frac{(r-\bar{a}_1)^2}{\bar{\sigma}_1}}$ are solved via following NLP problem:

$$\min_{p_1} \bar{a}_1 + \alpha \cdot \bar{\sigma}_1 \quad (13)$$

$$s.t. \int_{-\infty}^{\infty} [\dot{n}(r) - n^1(r)]^2 dr \leq \epsilon \int_{-\infty}^{\infty} [\dot{n}(r)]^2 dr$$

- The critical point of the original targeted PSD $n^0(r)$ will be located at

$$r^* = a_1 + \sigma_1 \cdot (\bar{a}_1 + \alpha \cdot \bar{\sigma}_1) \quad (14)$$

Criterion 1 Assuming surplus of monomer in the *ab initio* reactor throughout the batch, it is impossible to reach a uni-modal final PSD at time t_f , if

$$r^* > [r_{nuc}^3 + \frac{3k_p C_p w_m}{4\pi \rho_P N_A} (t_f - t_0)]^{1/3} \quad (15)$$

4 Results for perturbed system

In the previous section we have discussed the reachable uni-modal PSDs for a known zero-one system. However, in real applications, this map of achievable products could be dramatically changed due to inevitable disturbances from upstream supply, as well as the uncertainties in the original model. From an industrial perspective, it is even more important to understand how the reachable region will change against the perturbations in the key reaction kinetics.

4.1 Sensitivities to parametric mismatches

A sensitivity study of the reachable region has been performed for following parametric mismatches:

- +50% mismatch in Langmuir adsorption constant a_s and b_s of the surfactant partition model given by:

$$\begin{aligned} S &= S_{ad} + [S]_w v_w \\ S_{ad} &= \frac{S_{par} + 3v_d/r_d}{a_s N_A} \cdot \frac{b_s [S]_w}{1 + b_s [S]_w} \end{aligned} \quad (16)$$

- +25% mismatch in Critical Micelle Concentration ($[S_{CMC}]$), which plays a key role in determine the micelle concentration, and in turn determine the micellar nucleation rate.

$$[Micelle] = \frac{\ln(e^{10^4 \cdot ([S]_w - [S]_{CMC}) + 1})}{10^4 \cdot n_{agg}} \quad (17)$$

In addition to their importance in polymerization mechanism, these parameters are also among the most difficult to be identified.

The results of the sensitivity analysis are shown in Figure 3 by dashed, dash-dotted, and dotted lines, respectively, in comparison with the nominal reachable region bounded by solid line (i.e., the shadowed area). Despite the variability of the reachable region, the changes due to the parametric mismatches are not dramatic compared with the overall reachable region. Namely, the current system shows a certain level of robustness in the achievable products, given accurate information of the current model mismatch at the start of the reaction.

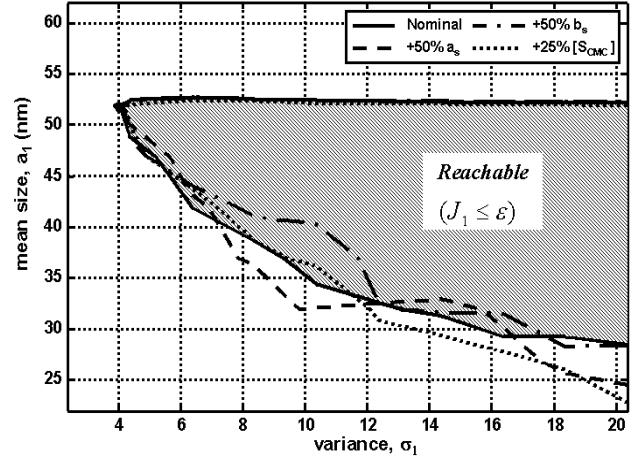


Figure 3: Sensitivity of the reachable region to key parametric mismatches.

4.2 Reachability in case of mid-course correction

Another interesting issue pertains to the in-batch feedback control of PSD, i.e., the identification of the key disturbance and the subsequent compensation for its influence by mid-course correction.

Mid-course correction is a control policy frequently applied to semibatch processes with irregular measurements and excessive measurement delays. In detail, the reactor is charged and operated based on a standard recipe until a specified moment, at which time a latex sample is collected and lab analyses are performed. Once the intermediate PSD information is available, a model-based estimator is used to identify the disturbances and predict the final PSD. If the prediction falls within a region (specified by ϵ) around the original target, then no mid-course adjustment is needed. Otherwise, the reachability analysis results is used to decide a proper PSD control strategy under the current situation. If the original target becomes unreachable, i.e., it is impossible to correct the influence of the current disturbance by later inputs, disturbance would be recorded and handled by a batch-to-batch control. If the PSD remains reachable, the best profiles for the future inputs will be determined by iterative recipe optimization.

The formulation and assessment of the ϵ -reachability under mid-course correction (i.e., the *mid-course reachability*) is identical to Equations 6-8, with an implicit assumption of perfect knowledge of the current disturbances, and the initial conditions, except a reduced reaction time.

Here a complete evolution of the reachable region has been investigated and sampled every 10 min during the first 40 min of reaction in presence of a +25% mismatch in $[S_{CMC}]$. To assess the reachable region, the exact model mismatch is assumed to be identified immediately after the sampling moment. According to the reachability maps (Figure 4), shortly after $t=40$ min, the original targeted PSD (indicated by the arrowed trace)

will fall outside the reachable region. Namely, the reachable region declines so dramatically that if no corrective action has been taken prior to $t=40$ min, the original targeted PSD can never be reached.

Considering the fact that one has only a few opportunities to obtain the intermediate PSD measurement, as well as the competition between the identifiability of disturbance and the mid-course reachability, the reachability analysis is essential to determine the optimal sampling moments as well as in-batch control action.

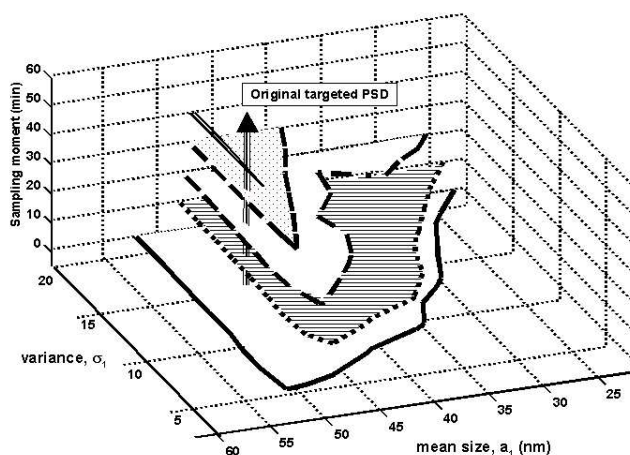


Figure 4: Evolution of the reachable region in case of +25% mismatch in $[S_{CMC}]$.

5 Conclusion

A programming-based approach has been proposed for reachability analysis of general particulate systems described by population balance models. In this study, it has been applied to a semibatch styrene emulsion polymerization process, which is modeled in a ‘zero-one’ framework. The reachable region is determined for both the nominal and perturbed cases, for final PSDs characterized as multi-Gaussian distributions.

The discussion indicates the importance of proper initial reaction condition as well as the nonlinearity inherent in the recipe optimization problems. For the reachability of unimodal PSDs, more dominant factors such as reaction temperature and terminal time are identified, along with a quantitative criteria for the reachable regions. The study also reveals a certain level of robustness in the reachable region against uncertainties in the surfactant partition parameters and the CMC values. The reachability studies in the case of mid-course correction have highlighted the importance of early PSD measurements, and proper early corrective action.

Acknowledgment

The authors gratefully acknowledge funding from the Chemical Division at Air Products and Chemicals Inc.

References

- [1] E. M. Coen, R. G. Gilbert, B. R. Morrison, H. Leube, and S. Peach. Modeling particle size distributions and secondary particle formation in emulsion polymerization. *Polymer*, 39(26):7099–7112, 1998.
- [2] J. P. Congalidis and J. R. Richards. Process control of polymerization reactors: An industrial perspective. *Polymer Reaction Engineering*, 6(2):71–111, 1998.
- [3] T. J. Crowley, E. S. Meadows, A. Kostoulas, and F. J. Doyle. Control of particle size distribution in semibatch emulsion polymerization by surfactant addition. *J. Process Control*, 10:419–432, 2000.
- [4] F. J. Doyle, M. Soroush, and C. Cordeiro. Control of product quality in polymerization processes. In *Proceeding of CPC - VI, Tucson, AZ*, pages 290–306, 2001.
- [5] R. G. Gilbert. *Emulsion polymerization: A mechanistic approach*. Academic Press, San Diego, 1995.
- [6] C. D. Immanuel, C. F. Cordeiro, S. Sundaram, E. S. Meadows, T. J. Crowley, and F. J. Doyle. Modeling of particle size distribution in emulsion co-polymerization: Comparison with experimental data and parametric sensitivity studies. *Comp. Chem. Engng.*, 26(7-8):1133–1152, 2002.
- [7] V. Liotta, C. Georgakis, and M. S. El-Aasser. Control-liability issues concerning particle size in emulsion polymerization. In *Proceeding of DYCORD, Helsingør, Denmark*, pages 299–304, 1995.
- [8] E. S. Meadows, T. Crowley, C. D. Immanuel, and F. J. D. III. Nonisothermal modeling and sensitivity studies for batch and semibath emulsion polymerization of styrene. *Ind. Eng. Chem. Res.*, 42:555–567, 2003.
- [9] D. Semino and W. H. Ray. Control of systems described by population balance equations - I. Controllability analysis. *Chem. Eng. Sci.*, 50(11):1805–1824, 1995.
- [10] R. F. Stengel. *Stochastic Optimal Control: Theory and Application*. John Wiley and Sons, New York, 1986.
- [11] Y. Wang, C. D. Immanuel, and F. J. Doyle. Reachability of particle size distribution in emulsion batch polymerization under mid-course correction policies. In *Proceeding of ACC, Denver, CO*, pages 2491–2496, 2003.