

CONTROL OF PARTICLE SIZE DISTRIBUTION IN EMULSION CO-POLYMERIZATION PROCESSES

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Abstract: A mid-course correction (MCC) policy has been shown as a practical approach to compensate the effects of the new disturbances on the final particle size distribution (PSD) in the emulsion polymerization process. However, the development of control model remains immature in the practical sense. In this paper, a control strategy to control the bi-modal particle size distribution in an emulsion copolymerization process within the MCC approach is presented. The strategy proposes a controlled adaptive perturbation (CAP) to develop the MCC control model while minimizing the off-specification batches generation during the perturbation. The scheme utilizes the particle size polydispersion index (PSPI) as the control objective to simplify the development process. In addition, it is also shown that the final PSD can be estimated by PLS model with an adequate accuracy by using on-line calorimetry-based conversion measurements as predictor. This eliminates the requirement of off-line analysis thus faster predictions can be made.
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1. INTRODUCTION

Emulsion polymerization is an important process for the production the higher value products. The qualities of these products are defined by several specific characteristics which are greatly influenced by the particle size distribution. Eventually, PSD has become an important control objective in the emulsion polymerization process. In emulsion polymerization reactions, the main process variations arise from different start-up conditions and changes in the quality of raw materials [1]. To compensate for the effects of these disturbances on the final product quality, the mid-course correction policies (MCC) has been proposed [2]. A specific application of MCC approach to control PSD in emulsion semi-batch polymerization has been reported [1].

There are two important steps in the MCC approach. The first step is to predict the final product quality and the second step to invoke the control action if necessary. In the predicting step, it has been shown that with a simple energy balance, a good regression model could be built to predict the final average particle size [3]. However for predicting the final bi-modal PSD, off-line analysis are necessary to attain a

prediction with acceptable accuracy [1]. This results in a time delay (not suitable for fast process) and it is extremely sensitive to any sampling and measurement error due to a single analysis. In most cases, the initial condition variations will have a significant influence on the nucleation process and has a direct influence to the primary modal. Statistically, a normal common variation will produce in-state of control PSD. However, if the variation magnitude is quite significant, the nucleation rate is being affected substantially and this will eventually lead to out-state of control PSD. This substantial change in the nucleation process has a direct impact on the conversion rate and particle composition at that particular period. Therefore, if a good on-line conversion measurement is available, a fast and accurate final PSD could be predicted. Furthermore, it also reduces the risk of depending on a single analysis. In bi-modal PSD, the modal of larger size particles is basically shaped by the primary nucleation whereas the modal of smaller size particles is greatly influenced by the secondary nucleation. Therefore, with very early prediction, more corrective choices can be performed to reshape either the modals of the smaller or larger size particles. The intermediate analysis elimination also

makes MCC implementation possible for a very fast semi-batch process because whole analysis process might take a few hours from site sampling to result endorsing.

In the second step, the control action will be invoked if the predicted PSD is statistically out of state control. If some significant variations are observed in the manipulated variables during the normal operation, these manipulated variables can be included in building the model to predict the final quality parameters. In another case, it can be assumed that the significant changes in manipulated variables are available which resemble empirical control actions taken by operators when the quality properties are not in target [1]. However, in practice, both cases are very rare. In normal operation, most variables are kept at specific trajectory with very minimal variations, whereas in the off-target product the quality analysis is only available at the end of the batch. If some changes are made by the operators, the changes are very random in term of timing and variables selected. As a result, it is less useful for a control algorithm development. Therefore, an appropriate perturbation must be carried out on some selective manipulated variables. Unless a good quantitative knowledge is available, a random perturbation must be avoided because it might create large off-specification batches. Unlike in a continuous process, where the effect of each perturbation can be promptly observed, in semi-batch process, its accumulative magnitude effect on the final quality parameters is unknown until at the end of the batch.

In this paper, a mid-course correction (MCC) policy is utilized to compensate the effects of the new disturbances on the final particle size distribution (PSD) with application to emulsion copolymerization processes. The MCC strategy is developed based on the particle size polydispersion index (PSPI) as the control objective thus simplifying the overall development. This strategy allows for a practical control model development that minimizes the off-specification batches generation during the perturbation process. In addition, it will be shown that the final PSD can be estimated using a PLS model with an adequate accuracy by using on-line calorimetry-based conversion measurements as a predictor. This eliminates the requirement of off-line analysis thus a faster prediction can be made. To illustrate the proposed strategy, a case study of styrene/MMA emulsion copolymerization semi-batch process is utilized [4].

2. PSD PREDICTION

In this work, PLS is used to predict the final PSD. PLS has been recognized as an efficient tool to estimate important properties in correlated data environments. In addition the PLS model considerably robust to noises because a number of

predictor components utilized is smaller than the original data dimension. The detail descriptions of PLS model building for regression can be referred to the seminal paper by Geladi and Kowalski [5].

As in other MCC approaches, the PSD prediction model is developed based on the historical data of previous batches. In this work, the final PSD is predicted with an assumption that the on-line conversion measurements are available based on calorimetry approach with acceptable accuracy and sensitivity. Calorimetry-based conversion measurements have been successfully exploited in many emulsion polymerization applications. In [6], an approach had been developed to estimate the conversion and copolymer composition in semi-continuous emulsion copolymerization systems based on calorimetric measurements. A successful of composition control based on this approach had also been reported [7]. It had also been demonstrated, that the desired copolymer product were successfully produced by controlling the inferential conversion based on calorimetry [8]. Furthermore, in [9] the inference of the terpolymer composition from calorimetric measurements was studied and experimentally validated. In later works, the control of emulsion polymerization process based on calorimetry were carried out [10, 11]. For the specific case of styrene/MMA emulsion copolymerization semi-batch process, the development of calorimetry-based conversion measurement is referred to the original publication [12].

An emulsion polymerization process is conveniently divided into three intervals [13]. The first interval is a rapid period with an increasing rate of reaction primary due to particle nucleation. Any significant variations or contamination in initial conditions will have significant effect on the nucleation activities. Thus, the conversion measurements should cover the interval I with as many as possible of the measurement samples. The actual number of samples is very dependent on the process reaction rate. Since calorimetry approaches utilize only temperature and flow rate measurements, which are readily available online, and the availability of fast computation engine at the present time, an adequate number of conversion measurements of the interval I should be possible.

Let the matrix X represents a data matrix with m number of batches and n number of conversion observations. The matrix Y represents a data matrix with m number of batches and p number of PSD parameters. Generally, the continuous PSD can be discretized into a finite number of particle sizes. In this case, p is the number of particle sizes classes. For a fixed target of bi-modal polymer product, the p dimension can be significantly reduced by modeling the bi-modal PSD as two symmetric Gaussian distributions. If the two distributions are independently modeled by taking the local minima as

the separating point between the two, the PSD can be described as:

$$W(r, p) = \max(k_i e^{-\frac{1}{2}(r-\mu_i)^2/\sigma_i}) \quad \text{Eq. (1)}$$

where $p = \{\mu_i, \sigma_i, k_i | i=1,2\}$ are the PSD parameters, that is, particle size means, variances and amplitudes, respectively, of the two modals.

3. CONTROL OBJECTIVES

In a typical operation, under a common variation, the product PSD is rather distributed around the target PSD than exactly a fixed value. Based on the good previous batches, the normal PSD region can be developed. If the continuous PSD is discretized into p number of particle sizes classes, the lower and upper limits of each class can be statistically calculated. When the predicted PSD and the limits are plotted on the same plot, a good visual interpretation on the predicted PSD can be made. To justify whether a corrective action is necessary or not, a control region need to be defined. Based on historical good batches, PCA is performed on the final PSD measurement. Two principal components are considered adequate to summarize the final PSD space [1]. In this work, the particle size polydispersity index (PSPI) is proposed to characterize the final PSD and will become the central focus in the whole strategy. PSPI has been successfully utilized as control objective in controlling the PSD in emulsion polymerization [4, 14]. The utilization of PSPI simplifies the control objective to a single parameter. In addition it provides a directional description which is very useful in the development of the control model as shown later.

The PSPI indicates the spread of the distribution which can be estimated as follows:

$$PSPI = \frac{\langle r^2 \rangle}{\langle r \rangle^2} \quad \text{Eq. (2)}$$

where $\langle r^2 \rangle$ is the mean squared radius. For future batches, as similar to other MCC approaches, a corrective action is only invoked if the predicted PSPI is not within the normal control limit. The lower and upper control limits of predicted PSPI can be estimated by using the t-distribution as follows:

$$\text{Limits} = \bar{x} \pm t_{\alpha/2, N-1} s \quad \text{Eq. (3)}$$

4. CONTROL MODEL DEVELOPMENT

A good control model that relates the relevant measurements of the predicted parameters and manipulated variables is the key element in the successfulness in controlling the final PSD towards the targeted values. In most cases, perturbation is

inevitable in building the control model. In the semi-batch emulsion polymerization process, the accumulative effect of any change during the process on the final quality parameters is hardly observed until a test is performed on the final sample at the end of the batch. Thus, a random perturbation is not preferable unless a good quantitative knowledge is available. A good controlled perturbation can be performed if there is an indicator or objective function that provides a quantitative summary of final PSD. The indicator must be simple and possess a directional property. In addition, the perturbation must be performed within the normal variation limits to avoid off-specification batches. At end, the developed control model should have an extrapolation capability in order to be practically applied in controlling the off-specification predicted PSD.

In this work, a controlled adaptive perturbation (CAP) which utilizes PSPI as the controlled indicator or objective function is proposed to build the control model. In CAP, the manipulated variables are perturbed to move the predicted PSPI to a new target value but remains in the controlled limit as prescribed by the Equation (3). The magnitude of perturbation is derived from a function/model that relates a change between the PSPI and the manipulated variables. However, for the first batch, a reasonable guess must be made since the model is not available. For the second and subsequent batches, the perturbation magnitudes are estimated from the model and the model is re-fitted after each batch completion. This CAP procedure will minimize the off-specification batches and a fast accurate model can be developed. In order to maximize the perturbation magnitude, dual PSPI target values are utilized rather than a single PSPI target. For PSPI mean and controlled limits described by Equation (3), the targets PSPI ($PSPI_t$) are set as follows:

$$PSPI_t = \begin{cases} \bar{x} - kt_{\alpha/2, N-1} s & ; PSPI_p \geq \bar{x} \\ \bar{x} + kt_{\alpha/2, N-1} s & ; PSPI_p < \bar{x} \end{cases} \quad \text{Eq. (4)}$$

where k is a constant between 0 and 0.5 and $PSPI_p$ is the predicted PSPI of the final PSD. If k is set to zero, it reduces the dual target to a single target (the PSPI mean).

5. CASE STUDY

To illustrate the proposed methodology, a simulation case study of styrene/MMA emulsion copolymerization semi-batch process is utilized [4]. Following our previous work, the objective of the process in our formulation is to produce a polymer product with a bi-modal PSD under a known recipe and operating profiles. The process simulations are conducted for 6900 sec run with seeded in the first 1500 sec. The system temperature is controlled at 70°C throughout the run. The control objective is to

control the secondary modal PSD relatively to the primary modal PSD such that the final overall PSD is within the desired shape under initial condition disturbances.

In order to build a normal reference batch set, 50 batch runs are simulated. Since the actual mechanism of initial variation is not fully known, the variation effects are simulated by randomly charging the monomers, surfactant and initiator around the recipe values. It is assumed that the initial charges are normally distributed around the recipe values with some variances. For the normal reference batch set, the variances are set at 10% of the recipe values. Figure 1 shows the 50 batches of the normal reference set. In a typical PSD measurement, the continuous PSD is usually discretized into some particle sizes classes. Therefore, the lower and upper limits of each class can be statistically calculated which give a pictorial boundary of the normal PSD set as shown by the bold dash line. With 99% confidence level, almost all the PSDs reside within the limits.

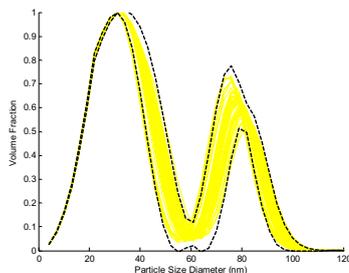


Figure 1: PSD of the reference set

From these reference batches, a PLS model is developed to predict the final PSD from conversion measurements. To bear a resemblance to actual measurements, a random noise with zero mean is added. The variance is set at 1% of the measurement span [0-1]. The final PSD is modeled as two normal distributions by taking local minima as the separating point between the two modals as given by the Equation (1). A major function of the model is to make a good prediction under higher variations. In other word, in order the model to be useful for a control purpose, it must have a good extrapolation capability. Thus, additional 4 batches are randomly generated with higher variance setting (20%) for the surfactant and initiator initial charges. This set is called set B. Figure 2 shows the PSD plots of set B against the reference PSD limits. The comparison plots between the actual and predicted final PSD for this set are shown in Figure 3a-b. For a medium deviation (Figure 3a), the model extrapolation capability is considerably adequate in predicting the final PSD. However, for a very high deviation (Figure 3b), it has a mild extrapolation capability.

Next, the control model is developed under controlled adaptive perturbation, in which the PSPI is

exploited as the objective function. Based on the reference set, a basic statistical analysis of PSPI needs to be performed. Table 1 shows the basic statistics of the reference set. To evaluate whether the predicted PSPI can be sufficiently utilized in CAP, the residual statistics between the predicted and actual PSPI must be performed. Table 2 shows the mean and standard deviation of the residuals for the 50 batches. The most important aspect here is to compare the predicted PSPI standard deviation to the residual standard deviation. This ratio is equivalent to the process capability index which if bigger is better. From Table 1 and 2, the standard deviation ratio is 1.15 which is equivalent to medium relative capability.

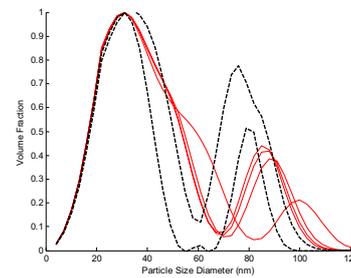


Figure 2: PSD of set B

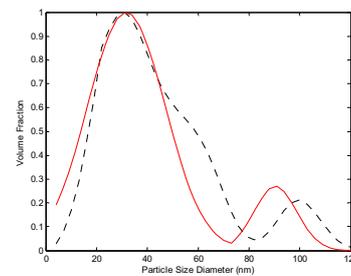
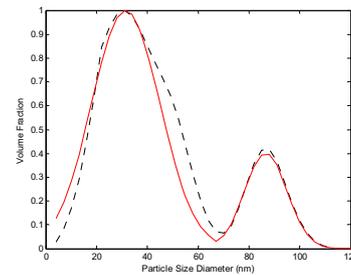


Figure 3a-b: Comparison between the actual and predicted PSD of set B

Table 1: The PSPI statistics

Parameters	Actual PSPI	Predicted PSPI
Min	1.227	1.198
Max	1.25	1.288
Mean	1.241	1.243
Std. Dev	0.00533	0.01821
Interval range (95% CL)	1.231-1.251	1.207-1.279

Table 2: The residual statistics

Mean	0.0026
Std. Dev	0.0158

The PSD of copolymer product can be controlled by manipulating some potential variables such as the reaction temperature and the surfactant, initiator and monomer feed rates. In an earlier work, the control actions of the MCC approach was restricted to manipulate surfactant to control the PSD in styrene emulsion polymerization [1]. However, it has been found that the monomer feed rate has strong effects on PSD and can be used as a practical manipulated variable to control the PSD in the emulsion polymerizations [4, 14]. Along these lines, for our case study, we propose to employ two manipulated variables: the surfactant and monomer feed rates. For the monomer feed rates, an equal magnitude of adjustment is performed on both the styrene and MMA monomer feed rates to maintain an equal ratio of the monomers composition in the polymer product. The perturbations of these two flowrates are sequentially performed to minimize the off-specification products. The first perturbation set is to develop a control model which relates the surfactant flowrate changes to the PSPI changes as given by the below simple equation.

$$\Delta PSPI = a\Delta S^3 + b \quad \text{Eq. (5)}$$

where $\Delta PSPI = PSPI_{final} - PSPI_{predicted}$ and ΔS is the perturbation magnitude. a and b are the fitting coefficients. The model is adapted by refitting after each run until the model errors is reasonably minimized. The nonlinear relationship is employed rather than a linear relationship to improve the model accuracy as the system is expected to be highly nonlinear. The perturbation is only performed starting from 3300 sec as the secondary nucleation in this particular case study is observed taking place from 3500 to 5000 seconds. Because the control model is not available initially, the perturbation magnitude of the first batch is set at 15% of the nominal value. The second and subsequent perturbation will be calculated based on the control model which is adapted from the preceding perturbation batches. From equation (4), dual PSPI target values are utilized to maximize the perturbation magnitude as below:

$$PSPI_t = \begin{cases} 1.235 & ; PSPI_p \geq 1.24 \\ 1.245 & ; PSPI_p < 1.24 \end{cases} \quad \text{Eq. (6)}$$

where $PSPI_p$ is the predicted PSPI.

Once, the effect of surfactant on PSPI has been adequately modeled (results are not shown), the monomer perturbation can be performed. In this case, the surfactant flowrate is adjusted (based on the previously developed model) to bring the final PSPI to some random values between the normal PSPI ranges. Then, the monomers perturbation magnitude is calculated to bring the final PSPI to 1.24. This approach is to ensure the randomness in the direction and magnitude for both surfactant and monomer

perturbations while maintaining the final PSD on the specification. As similar to the surfactant control model, a simple nonlinear model is utilized to relate between the monomers changes to the PSPI changes as follow:

$$\Delta PSPI = a\Delta M^3 + b\Delta S^3 + c \quad \text{Eq. (7)}$$

where $\Delta PSPI = PSPI_{final} - PSPI_{predicted}$ and ΔM and ΔS are the monomers and surfactant perturbation magnitudes, respectively. a , b and c are the fitting coefficients. The first monomers perturbation magnitude is set at 5% of the monomers nominal flowrates values. Similarly, the model is adapted by refitting after each run until the modeling errors are reasonably minimized.

Figure 4 shows the final actual PSPI for 20 batches under the monomers and surfactant perturbations. Except for the first, fourth and fifth batches, all final PSPI are within the typical normal PSPI range (1.23-1.25). The corresponding final PSD are shown in Figure 5. All PSD are within the normal reference limits except for the three batches. This clearly illustrates the functionality of PSPI in the proposed CAP strategy to minimize the off-specification products during the control model development. Since the fourth and fifth batches are outside the normal range, there might be a significant error in predicting the PSPI. Therefore, their information will not be included in fitting the control model.

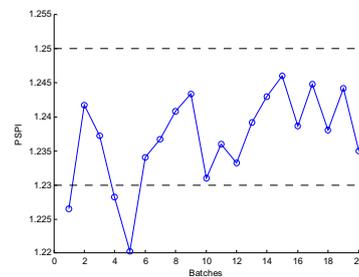


Figure 4: PSPI of perturbed batches

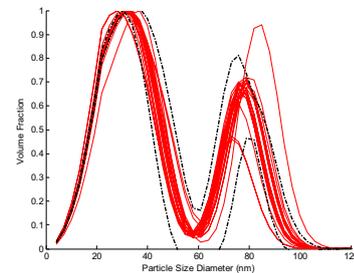


Figure 5: PSD of perturbed batches

Currently, we have one control model and two manipulated variables. In order to have a unique solution, an additional control model is required. This second model can be easily fitted from the above perturbation data. Based on equation (2), instead of

using PSPI the control objective, the position of the primary modal peak is selected as follow:

$$\Delta P = a\Delta M^3 + b\Delta S^3 + c \quad \text{Eq. (8)}$$

where $\Delta P = P_{final} - P_{predicted}$ is the change in the primary modal peak positions.

To assess the performance of the two developed control models, they are tested on set B. Figure 6 shows the final controlled PSD for the 4 batches. Comparing to figure 2, in all cases, there are significant improvements in the PSD with respect to the normal reference limits. For the first three batches, they may be considered as the good products. However, for the fourth batch, the PSD remains outside the normal reference limits. It seems to indicate, that for a very high variation in the initial condition, controlling the generation of the secondary modal only is not adequate to have a relative control of the two modals and a proper adjustment on the generation of the primary modal would be necessary.

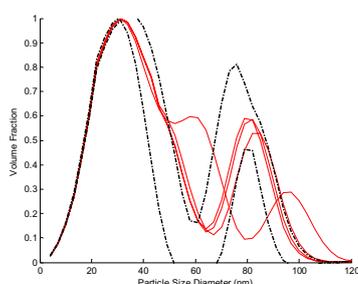


Figure 6: PSD of set B under surfactant and monomers control

6. CONCLUSION

The development of a control strategy to control a bimodal particle size distribution for an emulsion copolymerization process within the mid-course correction policy approach has been proposed. The strategy utilizes the PSPI as the objective function to develop the perturbation scheme which minimizes the off-specification products during the perturbation stage. In estimating the final PSD, a PLS model using on-line calorimetry-based conversion measurements as predictor was developed. The strategy was illustrated with an application to the styrene/MMA emulsion copolymerization process.

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