STABILITY CONDITIONS AND OBSERVER DESIGN FOR A CONTINUOUS CRYSTALLIZER

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Abstract

The population balance equation is used to describe the dynamics of a continuous crystallizer. A simple condition to guarantee the stability of a mixed suspended mixed product removal crystallizer is derived based on the population balance. A novel discretization scheme solves the population balance and the resulting discretized population balance is shown to be equivalent to the original population balance. The obtained condition is tested by simulations of the crystallization process. Furthermore an observer based estimator is developed to estimate the crystal growth rate and the simulation results show that the estimator is able to track its true value.

Keywords

Stability, Continuous Crystallizers, Population Balance, Discretization, Observer, Estimator.

Introduction

Crystallization is a typical chemical process that yields a particulate product characterized by shape and size (Randolph and Larson, 1988). The population balance equation was initially formalized from a statistical mechanical perspective by Hulburt and Katz (1964). Since then a considerable amount of research in the area of crystallizer dynamics followed. Some work was motivated by the occurrence of limit-cycle behavior in continuous crystallizers (Randolph, 1980). Two explanations for the crystal size distribution (CSD) instability were given by studying population balance. The first explanation depends greatly on the sensitivity of the nucleation rate. Instability is induced by the high order kinetic relationship between nucleation rate and super saturation (Juzaszek et al., 1977). In the second case, CSD stability is explained by classified crystal withdrawal (Beckman and Randolph, 1977). Yu et al. (1975) obtained a condition for the occurrence of sustained oscillations in the continuous crystallizers by linearizing the system at certain steady states. Jerauld et al. (1983) introduced new dimensionless groups that depend on physical properties and control parameters and derived a simpler condition by excluding the effect on the steady-state values of the state variables. Yin et al. (2003) investigated the influence of size dependent crystal growth rate on the stability and dynamics of continuous crystallizer using the similar approach. Du and Ydstie (2011) derived the global stability property of a specific particulate process using an entropy based energy function. The equivalent condition for discretized population balance is also obtained in their work.

Numerous investigations have addressed the problem of stabilizing an oscillating crystallizer using feedback control. Early studies proposed to measure the moments of CSD on-line and to adjust the flow rate of the fines destruction system (Lei et al. 1971). Beckman and Randolph (1977) demonstrated that oscillation could be eliminated by manipulating the flow. Hashemi and Epstein (1982) linearized the set of ordinary differential equations resulting from the method of moments and used singular value decomposition to define controllability and observability indices. Myerson et al. (1987) developed a nonlinear optimal stochastic control scheme with an extended Kalman filter for state estimation. Rawlings and Ray (1987) showed that the residence time and radical

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desorption rate are found to be key parameters governing reactor stability. Eaton and Rawlings (1990) developed a model predictive control strategy for a batch crystallizer. Furthermore Eaton et al. (1993) reviewed the development of parameter estimation and presented a new method based on nonlinear optimization. A number of parameter estimation methods for batch crystallization were also summarized by Tavare (1995). Semino and Ray (1995) showed that CSD is controllable through the manipulation of feed concentrations in a continuous crystallizer. Dochain (2003) developed a class of observers do not require the knowledge of the process kinetics which are suitable for crystallization processes because it is difficult to obtain their reaction kinetics. Recently Christofides et al. (2008) provided a comprehensive overview of model based feedback control for crystallization processes.
Huang et al. (2010) analyzed the nominal and robust stability for nonlinear recursive observers. Furthermore, they developed a fast moving horizon estimation strategy for online applications.

The structure of this paper is as follows. The population balance is used to describe the dynamics of a continuous crystallizer. An energy function is developed to study the stability property of the particle phase. The condition to eliminate self-sustained oscillations is derived by investigating the energy function behavior in Section 2. A novel discretization scheme solves the population balance. We further demonstrate the equivalence of the discrete population balance with the classic one as the total number of discrete intervals increases. A condition is obtained using Tellegen's theorem for the discretized population balance in Section 3. Finally we design an observer-based estimator to estimate the kinetic parameter of the continuous crystallization process in Section 4.

Stability Condition of the Population Balance

In a mixed suspension mixed product removal (MSMPR) crystallizer, the dynamics of the crystals is described by the population balance. It relates the crystal distribution function relates to deposition, agglomeration, attrition, seeding and withdrawal. For a MSMPR crystallizer with a volume we have

$$\frac{\partial n}{\partial t} + \frac{\partial Gn}{\partial l} = \frac{F_{in}}{V} n_{in} - \frac{F}{V} n_{out} + B - D \quad (1)$$

where $n(l,t)$ is the number density of particles as a function of crystal size l and time t. l is the characterized length of crystals which are assumed to be spherical in this work. n_{in} is the number density of seed crystals whereas F_{in} is the volumetric seeding rate. n_{out} is the number density of particles in the product. F is the volumetric removal rate. G is the particle growth rate which is given by McCabe's law. B and D are the birth and death rates which represent agglomeration and attrition. Such crystallizer behaves as though it is perfectly mixed. Further it has unclassified withdrawal which means that the size distribution of the product crystals is the same as that in the crystallizer, $n_{out}(l) = n(l)$.

Crystallization from solution is a two-step process. The first step is the birth of new crystals whereas the next is the growth of these crystals to larger sizes. Those two processes are known as nucleation described by Volmer's model and crystal growth by McCabe's law (Jerauld et al., 1983). Here we assume that agglomeration or attrition is neglected and no seed crystals are feeding in.

Equation (1) is thereby rewritten so that we get the partial differential equation,

$$\frac{\partial n}{\partial t} + \frac{\partial Gn}{\partial l} = B - \frac{F}{V} n_{out} \quad (2)$$

where G the growth rate and B the nucleation rate are expressed respectively as,

$$G = k_1(c - c_s) \quad (3)$$

$$B = \epsilon\, k_2 e^{-\frac{k_3 c_s^2}{(c-c_s)^2}} \quad (4)$$

here k_1 is the growth constant and $c - c_s$ is the supersaturation of the mother liquid, which is the driving force of the crystal growth. ϵ is the volume fraction of liquid phase. k_2 and k_3 are the kinetic constant of the nucleation rate.

Substituting equation (3) and (4) into the population balance we get

$$\frac{\partial n}{\partial t} + G\frac{\partial n}{\partial l} = \epsilon\, k_2 e^{-\frac{k_3 c_s^2}{(c-c_s)^2}} - \frac{F}{V} n \quad (5)$$

The following theorem provides conditions for the stable operation of the particulate phase in the FBR. Simulation studies show that the condition is necessary in the sense that oscillations occur if it is violated.

Theorem: The population balance in equation (5) converges to stable steady state $n^*(l)$ provided

$$\frac{V}{F} < \frac{l_{min}}{6G} \quad (6)$$

where V is the crystallizer volume, F is the particle withdrawal rate, G is the particle growth rate and l_{min} is the minimum radius of the seeds feeding the bed. Otherwise the steady state is unstable.

Proof: The relationship between the number density and the mass density of particles is given by

$$m(l) = \frac{4}{3}\pi \left(\frac{l}{2}\right)^3 \rho\, n(l) \quad (7)$$

The mass density based population balance for spherical particles is obtained by substituting equation (7) into equation (5)

$$\frac{\partial m}{\partial t} + G\frac{\partial m}{\partial l} = \epsilon\, k_2 e^{-\frac{k_3 c_s^2}{(c-c_s)^2}} \frac{4}{3}\pi \left(\frac{l_{min}}{2}\right)^3 \rho - \frac{F}{V}m + G\frac{m}{l} \tag{8}$$

The deviation form of the mass density of particles is defined

$$\bar{m}(l) = m(l) - m^*(l) \tag{9}$$

where $m^*(l)$ is mass density at steady state. The parameters G, F, V remain unperturbed so that the deviation form of population balance is written

$$\frac{\partial \bar{m}}{\partial t} + G\frac{\partial \bar{m}}{\partial l} = \bar{\epsilon}\, k_2' - \frac{F}{V}\bar{m} + 6G\frac{\bar{m}}{l} \tag{10}$$

An energy function is now defined so that

$$W(t) = \frac{c_s}{V\rho\Theta}\int_{l_{min}}^{l_{max}} \overline{m(l)}^2\, dl \tag{11}$$

where c_s is the concentration of a saturated solution, ρ is the density of crystals and Θ represents the granular temperature. The derivative of the energy function is obtained by differentiating $W(t)$ and use equation (10) to get,

$$\frac{dW}{dt} = \frac{2\, c_s}{V\rho\Theta}\int_{l_{min}}^{l_{max}} \bar{m}\, \frac{d\,\bar{m}}{dt}\, dl$$

$$\leq\ 2\left(\frac{6G}{l_{min}} - \frac{F}{V}\right)W(t) \tag{12}$$

Such that

$$W(t) \leq e^{-2\left(\frac{F}{V} - \frac{6G}{l_{min}}\right)}W(0) \tag{13}$$

In order to guarantee the particle phase is stable, it is therefore sufficient that the following condition is satisfied,

$$\frac{V}{F} < \frac{l_{min}}{6G}$$

The energy function converges exponentially if the above condition is satisfied and this results in L_2 stability for the system according to the definition of $W(t)$ in equation (11).

Discretized Population Balance

The population balance in equation (5) is approximated with a system of ordinary differential equations by partitioning the crystal size into a finite number of intervals. The mass balance and the number balance were then established for each size interval to obtain a discrete version of the population balance. The approach ensures that conservation laws are maintained at all discretization levels and facilitates computation without additional discretization. The details of discretization scheme are in White et al. (2006).

The mass balance in each interval is expressed as

$$\frac{dM_i}{dt} = r_i + f_{i-1} - f_i + q_i \tag{14}$$

where M_i is the mass of crystals in the interval i, r_i is the mass based growth rate and it is proportional to the surface area available for deposition,

$$r_i = N_i a_i k_m (c - c_s) \tag{15}$$

where N_i is the number of crystals and a_i is the crystal surface area in the interval i. k_m is the reaction constant. An extra term Q is added in the mass balance for the first size interval due to nucleation as shown in Figure 1.

The crystals are assumed to be spherical, then the relationship between M_i and N_i is written as,

$$M_i = N_i \frac{4}{3}\pi \left(\frac{l_i}{2}\right)^3 \rho \tag{16}$$

As the crystals grow they move from on size interval to the next. The rate of transition is represented by f_{i-1} for flow into and f_i for flow out of interval i. By comparing the mass balance and number balance in the same interval

$$f_i = \frac{m_{i+1}}{m_{i+1} - m_i} r_i \tag{17}$$

The deposition rate is proportional to the surface area and the mass transfer coefficient such that

$$r_i = k_m c\, N_i a_i \tag{18}$$

The discrete version of population balance in equation (14) converges to the continuous population balance (5) as the number of size intervals approaches to infinity. Du and Ydstie (2011) have proven the resulting discretized population balance is equivalent to the continuous population balance in equation (1). From the proof of equivalence of the population balance and its discrete version, it is shown that

$$k_m = k_1 \rho \tag{20}$$

The discretized population balance is represented in the format of a process network shown in Figure 1.

The state of the network is given by

$$Z = [M_1, M_2, \dots, M_K]^T$$

where K is the total size intervals, which determines the accuracy of the discretization scheme.

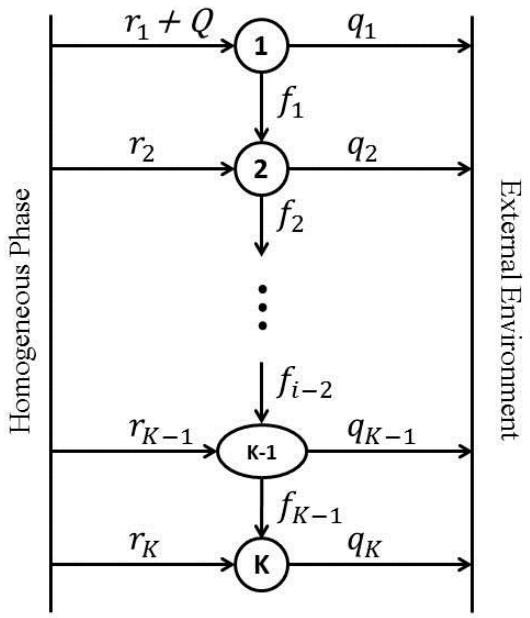

Figure 1. Network representation of the discretized population balance

Stability Condition for the Discretized Population Balance

The entropy based energy function is defined as

$$A(Z) = \sum_i A_i(Z) \quad (21)$$

$$A_i(Z) = A_i(Z^*) + w_i^{*T} Z - S_i(Z) \quad (22)$$

where Z^* is the desired steady state and $S_i(Z)$ is the entropy function in each discrete interval. w is the conjugated variable of Z and defined as

$$w = \frac{\partial S(Z)}{\partial Z} \quad (23)$$

Alonso and Ydstie (2001) have shown that $A_i(Z_i)$ is positive $\forall\, w_i \neq w_i^*$. Therefore $A(Z)$ is positive $\forall\, w \neq w^*$ due to the additive property of entropy.

The derivative of $A(Z)$ is calculated as

$$\frac{dA(Z)}{dt} = \sum_i \frac{d\, A_i(Z)}{dt} = \sum_i (w_i^* - w_i) \frac{dZ_i}{dt} \quad (24)$$

where w^* is the corresponding conjugated variable to the stationary steady state Z^*.

The conjugated variable at each node of the networked representation is selected as the mass density of size interval i , i.e. $\frac{M_i}{V}$. Substituting it into equation (24) and combining the discretized population balance in equation (14), we obtain,

$$\frac{dA}{dt} = -\frac{l_1^2}{l_2^3 - l_1^3}\frac{6ck_1}{\rho}\overline{M_1}\,\overline{M_1} - \cdots - \frac{l_{K-1}^2}{l_K^3 - l_{K-1}^3}\frac{6ck_1}{\rho}\overline{M_K}\,\overline{M_K} - \frac{e^{-\frac{k_3 c_s^2}{(c-c_s)^2}}}{\rho V}\overline{M_1}\,\overline{M_1} - \cdots - \frac{e^{-\frac{k_3 c_s^2}{(c-c_s)^2}}}{\rho V}\overline{M_1}\,\overline{M_K} + \frac{l_2^2}{l_2^3 - l_1^3}\frac{6ck_1}{\rho l_1}\overline{M_1}\,\overline{M_2} + \cdots + \frac{l_K^2}{l_K^3 - l_{K-1}^3}\frac{6ck_1}{\rho l_{K-1}}\overline{M_{K-1}}\,\overline{M_K} - \frac{F}{V}\overline{M_1}\,\overline{M_1} - \cdots - \frac{F}{V}\overline{M_K}\,\overline{M_K}$$

Using eigenvalue analysis we are able to obtain the critical value of particle residence time $\frac{V}{F}$ to guarantee the stability for the discretized population balance.

We will compare those conditions for the population balance equations in different forms. Moreover we will show that once the number of total size intervals is properly chosen, the critical value of particle residence time calculated from the discretized PB converges to that from the continuous PB in the next section.

Simulation Results

We apply the proposed method to a MSMPR crystallizer. In this crystallizer, no crystals are fed and nucleus is produced by nucleation. The kinetic parameters of nucleation rate and growth rate are listed in the table 1.

Table 1. The process parameters of the crystallizer

Parameters	Values
V	$1\ m^3$
k_m	$0.005\ m^4/(kg \cdot s)$
c	$1000\ kg/m^3$
c_s	$980\ kg/m^3$
k_2	$50\ 1/s$
k_3	0.001
ρ	$1800\ kg/m^3$
l_{min}	$0.4\ mm$
l_{max}	$4\ mm$
K	20

From the previous derivation to show the equivalence between the population balance and the discretized one, we find out the relationship between k_1 and k_m,

$$k_1 = k_m/\rho \quad (19)$$

Based on the parameters given in the table 1, k_1 is then calculated.

Recall the stability condition in equation (6) and (15), we find out the sufficient condition for the elimination of limit cycles for the crystallizer. The simulation results for stable and oscillating behaviors are shown in Figure 2 and 3. Here $F = 0.8\ m^3/s$ is calculated from equation (20).

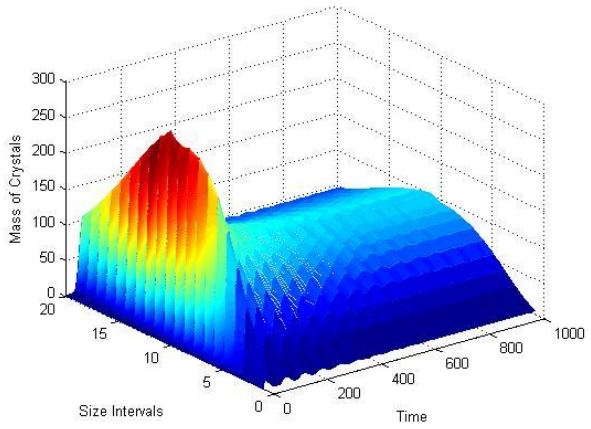

Figure 2.The oscillating behavior with $F= 0.1\ m^3/s$

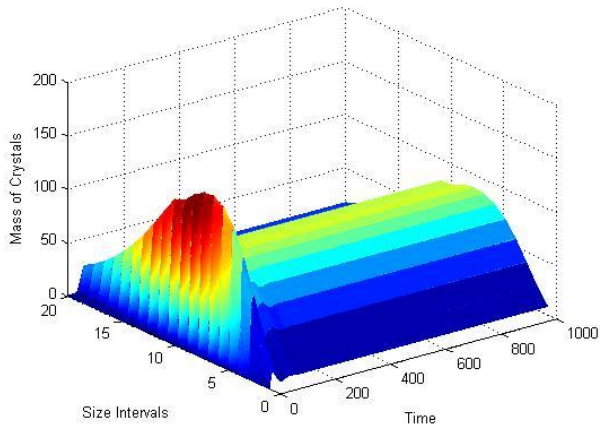

Figure3. The steady state behavior with $F= 0.8\ m^3/s$

Using the parameters provided in Table.1, the stability condition for the continuous population balance is plotted on the left in Fiugre 3. The domain below the straight line is stable. In this example, the minimal size of the particles is 0.4 mm and hence the critical value for particle residence time is obtained. As to that for discretized population balance , the graph on the right shows that the particle residence time converges to the critical value for the continuous population balance as we increase the total number of size intervals for the scenario that minimal size equals 0.4mm.

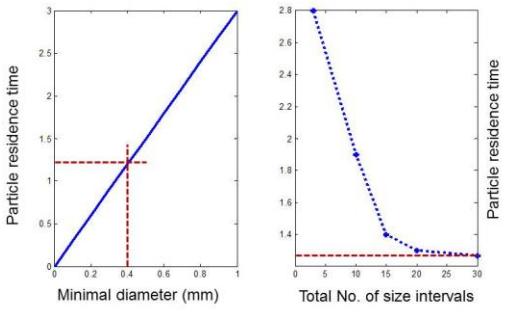

Figure 4. Stability condition for the crystallizer

An Observer Based Estimator Design

The observer based estimation scheme uses information from the measured states and follows the line of reasoning for the design of Luenberger observers. An important difference with respect to the extended Luenberger is that the measured variables don't appear as estimates in the observer equations but with their measured values. In our case, the total crystal mass can be measured on-line. It is unlikely to have a complete knowledge of the reaction kinetics for chemical reactors. Here the mass transfer rate from continuous phase to solid phase is not known so that it has to be estimated. Based on the dynamics of the crystals described in equation (14), the dynamics of total mass of the crystals is

$$\frac{dM}{dt} = \sum_i r_i + Q - \frac{F}{V}M \qquad (20)$$

Using the total crystal mass M as the measurement and the reaction kinetic $k = k_m(c - c_s)$ as the unknown parameter which needs to be estimated, the resulting estimator is

$$\frac{d\widehat{M}}{dt} = \sum_i a_i \cdot \hat{k} + Q - \frac{F}{V}M - C_1 \cdot (M - \widehat{M})$$
$$\frac{d\hat{\hat{k}}}{dt} = \sum_i a_i \cdot\ C_2 \cdot \left(M - \widehat{M}\right) \qquad (21)$$

Since $\sum_i a_i$ is the total surface area which is positive, it is a regressor which is persistently excited. We choose that $C_2 = \frac{C_1^2}{4}$ to control the convergence speed.

Figure 5 illustrates the kinetics parameter estimation for k_m and state estimation for M, the total mass of crystals for the simulation shown on the top and bottom respectively. Simulation results show that the estimated

value of k_m tracks the true value and the state estimator gives off-set free estimation of total mass of the crystals.

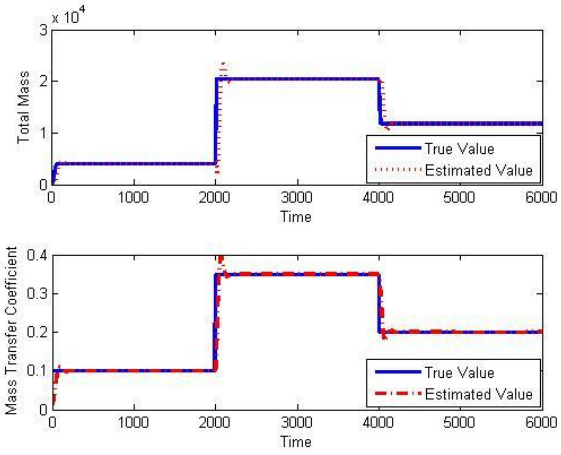

Figure 5.Parameter tracking and state estimation for the crystallizer.

Conclusion

In this work we derive the stability conditions for a MSMPR crystallizer and design an observer based estimator for the crystallization process. An energy function is developed to develop the condition for the population balance which describes the dynamics of the crystals. Furthermore the condition for the equivalent discretized population balance is also developed. The conditions are tested by simulations. An observer based estimator is developed to estimate the reaction kinetics of the growth rate. The simulation shows the effectiveness of the observer.

References

Alonso, A. A. and Ydstie, B. E. (2001), Stabilization of Distributed Systems using Irreversible Thermodynamics, Automatica, Vol. 37, 1739-1755

Beckman, J. R. and Randolph, A. D. (1977), Crystal Size Distribution Dynamics in a Classified Crystallizer, *AIChE Journal*, Vol. 23, 510-520.

Christofides, P. D., El-Farrac,N., Li M. and Mhaskar P.(2008), Model Based Control of Particulate Processes, *Chemical Engineering Science*, Vol.63, 1156-1172.

Dochain, D. (2003), State and Parameter Estimation in Chemical and Biochemical Processes, a tutorial, *J. of Proc. Cont.*, Vol. 13, 801-818.

Du, J. and Ydstie, B. E. (2011), Modeling and Control of Particulate Systems and Application to Poly-Silicon Production, *Chemical Engineering Science*, Vol. 67, 120-130.

Eaton, J. W. and Rawlings, J. B. (1990), Feedback Control of Chemical Processes Using On-Line Optimization Techniques, *Computers & Chemical Engineering*, Vol. 14, 469-479.

Hashemi, R. and Epstein, M. A. (1982), Observability and Controllability Consideration in Crystallization Process Design. *AIChE Symp. Ser.*, Vol. 78, 81-90.

Huang, R., Patwardhan, S. and Biegler, L. (2010), Stability of a Class of Discrete-time Nonlinear Observers, *J. of Proc. Cont.*, Vol. 20, 1150-1160.

Huang, R., Biegler, L. and Patwardhan, S. (2010), Fast Offset-free Nonlinear Model Predictive Control based on Moving Horizon estimation, *Ind. Eng. Chem. Res.*, Vol. 49, 7882-7890.

Hulburt, H. M. and Katz, S. (1964), Some Problems in Particle Technology: A Statistical Mechanical Formulation, *Chemical Engineering Science*, Vol. 19, 555-574.

Jerauld, G. R., Vasatis, Y. and Doherty, M. (1983), Simple Conditions for the Appearance of Sustained Oscillations in Continuous Crystallizers, *Chemical Engineering Science*, Vol. 38, 1675-1681.

Juzaszek, P. and Larson, M. A.(1977), Influence of fines dissolving on crystal size distribution in an MSMPR crystallizer, *AIChE Journal*, Vol. 23, 460-468.

Lakatos, B. G. (1994), Stability and Dynamics of Continuous Crystallizers, *Computers & Chemical Engineering*, Vol. 18, 427-431.

Lei, S., Shinnar, R. and Katz, S. (1971), The Stability and Dynamic Behavior of a Continuous Crystallizer with a Fines Trap, *AIChE Journal*, Vol. 17, 1459-1470.

Myerson, A. S., Rush, S., Schork, F. J. and Johnson, J. L. (1987), Control of Crystallization Processes, *In Industrial Crystallization 87, Elsevier*: Amsterdam, 407-410.

Randolph, A. D. and Larson, M. A. (1988). Theory of Particulate Process: Analysis and Techniques of Continuous Crystallization, *Academic Press*, San Diego, CA.

Randolph, A. D. (1980), CSD Dynamics, Stability and Control (A Review Paper), *AIChE Journal*.

Rawlings, J. B. and Ray, W. H.(1987), Stability of Continuous Emulsion Polymerization Reactors: a Detailed Model Analysis, *Chemical Engineering Science*, Vol. 42, 2767-2777.

Rawlings, J. B., Miller, S. M. and Witkowski, W. R. (1993), Model Identification and Control of Solution Crystallization Processes: A Review. *Industrial Engineering Chemistry Research*, Vol. 32, 1275-1296.

Semino, D. and Ray, W. H. (1995), Control of Systems Described by Population Balance Equations, *Chemical Engineering Science*, Vol. 50, 1805-1839.

Tavare, N. S. (1995), Industrial Crystallization: Process Simulation Analysis and Design, Plenum, New York.

White, W. C. (2007), Modeling for Design and Control of Particulate Systems, *Carnegie Mellon University*.

Yin, Q. , Song, Y. and Wang, J. (2003), Analysis of Stability and Dynamics Patterns of a Continuous Crystallizer with a Size Dependent Crystal Growth Rate, *Industrial Engineering Chemistry Research*, Vol.42, 630-635.

Yu, K. M. and Douglas, J. M. (1975), Self-Generated Oscillations in Continuous Crystallizers: Part I. Analytical Prediction of the Oscillating Output, *AIChE Journal*, Vol.21, 917-930.