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ESTIMATION OF CRYSTAL SIZE DISTRIBUTION OF A BATCH CRYSTALLIZATION PROCESS USING A GROWTH SIZE DEPENDENT MODEL

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Abstract: A high gain observer was designed to estimate the Crystal Size Distribution in batch crystallization processes. This observer is based on a model where growth kinetics depend on crystal size. The observer is based on the discretization of population balance equations solved by the finite difference method. A reduction of the number of state variables was done in order to reduce the computation time. The observer's output allows to estimate the moments of the CSD, which are interesting for control purposes.

Keywords: Crystallization processes, high gain observer, population balance equations, crystal size distribution, finite difference method.

1. INTRODUCTION

The crystallization represents one of the most important processes in the industry. The control of such processes is a real challenge because of modelling complexity, lack or reproducibility and the difficulty of measuring the CSD (Crystal Size Distribution). The problem of measuring CSD remains an open field of research.

The CSD is an important characteristic of the final solid end-use properties. In line calorimetric or turbidimetric measurements have been used, together with off line image analysis for the modelling of the time variation of CSD during batch solution crystallizations by (Kleizen *et al.*, 1993) and (Monnier *et al.*, 1997). However it is important to note that no reliable on line CSD measurements were available when such modelling studies were done. Using the Mc Cabe hypothesis, the model of batch crystallization process could be considerably simplified. The growth kinetic became size independent. A high gain observer and a continuous-discrete observer were designed ((Bakir *et al.*, 2005) and (Bakir *et al.*, 2006*b*)) in order to reconstruct the whole CSD using population balance equations (PBE). This model was also used in (Bakir *et al.*, 2006*a*) in order to reconstruct the two CSD's in polymorphic crystallization and in line partial measurements.

The aim of the present work is the use of a more precise model to estimate the whole CSD. The crystallization rate depends on two mechanisms: nucleation and crystal growth (Ramkrishna, 2000). These two kinetics are computed using solute concentration and crystallizer temperature. The used model also exhibits a growth kinetic which depends on crystal size.

Since the observer is based on the PBE describing the time variations of the CSD, it is essential to use a well adapted method to solve these PBE. The different moments of the distribution are known to describe well the the main dynamic fea-

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tures of the process. Using the different moments of the CSD, the control of such process had been explored by (Jones, 1974), (Rohani, 1990) and (Zoltan and Richard, 2004).

In this work, the measurement used to perform the observer is the number of nuclei (smallest stable crystals). A reduced high gain observer is developed. Different state reductions are studied which allows to considerably reduce computation time. The paper is organized as follows, first the batch crystallization model is briefly described. The principle of discretization of the PBE is then exposed in section 3. Section 4 is devoted to the observer synthesis. Finally, the estimation technique is validated through simulation.

2. MODEL DEVELOPMENT

The population balance approach applied to the batch crystallizer yields the following partial differential equation:

$$\frac{\partial n(x,t)}{\partial t} + \frac{\partial G(x,t)n(x,t)}{\partial x} = 0 \qquad (1)$$

where $n(x,t)$ represents the CSD which defines the number of crystals of size x per unit volume of suspension. In this model, only nucleation and growth are considered. Agglomeration and breakage are not taken into account. The growth term $G(x,t)$ is size dependent. The solute concentration balance describing the mass transfer from the liquid to the solid phase is:

$$\frac{dV_t(t)C(t)}{dt} + \frac{dV_T(t)C_s(t)}{dt} = 0 \qquad (2)$$

$C(t)$ represents the solute concentration and $V_T(t)$ is the suspension volume. The variation of this volume du to the mass transfer is very small and can be neglected. the solid concentration $C_s(t)$ is deduced from the crystal size distribution (CSD):

$$C_s(t) = \frac{K_v \rho_s}{M_s} \int_0^\infty x^3 n(x,t)dx \qquad (3)$$

where K_v is a shape factor. For sphere $K_v = \frac{\pi}{6}$. M_s is the molecular weight of solid, ρ_s is the density of the solid and $V_t(t)$ is the solution volume (i.e. the continuous phase) calculated from the following expression:

$$V_t(t) = V_T(t)(1 - \frac{M_s}{\rho_s}C_s(t)) \qquad (4)$$

The crystallizer temperature is described by the energy balance around the jacket wall:

$$\sum_{i=1}^{3} Cp_i n_i \frac{\partial T_{cr}}{\partial t} = -\triangle H_c V_T \frac{dC_s}{dt} - UA(T_{cr} - T_j) \qquad (5)$$

The solubility, which refers to the solute concentration under saturated conditions, is assumed to obey Van't Hoff equation:

$$C_{sat}(T) = a_{sat} \exp(\frac{-\Delta H_f}{RT}) \qquad (6)$$

The absolute supersaturation $(C - C_{sat})$ is the driving force of the crystallization process. The overall growth rate, including possible diffusive limitations, is assumed to be represented by the following simple power low. Exponential values of exponent J_2 where generally found to lie between 1 and 2:

$$G(x,t) = \frac{M_s}{2\rho_s} K_c \eta(x)(C(t) - C_{sat}(t))^{J_2} \qquad (7)$$

where K_c represents growth rate coefficient, η represents the effectiveness factor which is the solution of the following equation:

$$\frac{K_c}{K_d(x)}(C - C_{sat})^{g-1}\eta(x) + \eta(x)^{\frac{1}{g}} - 1 = 0 \qquad (8)$$

$K_d(x)$ represents the mass transfer coefficient and is size dependent:

$$K_d(x) = \frac{D}{x}(2.0{+}0.47(\frac{x^{\frac{4}{3}}\epsilon^{\frac{1}{3}}}{\nu})^{0.62}(\frac{D_a}{T_R})^{0.17}(\frac{\nu}{D})^{0.36}) \qquad (9)$$

With:
D: solute diffusivity ($\frac{m^2}{s}$)
ϵ: dissipated energy per unit of suspension mass (W/kg)
ν: cinematic viscosity of the solution ($\frac{m^2}{s}$)
D_a: stirrer diameter (m)
T_R: crystallizer diameter (m)

Analytical solution of equation (8) is available if g is equal to 1 or 2. A numerical solution can be considered in the other case. B is the result of two competitive nucleation mechanisms. Primary nucleation takes place in the absence of any crystal in the solution:

$$B_1 = a_{N1} \exp(\frac{b_{N1}}{\ln^2(\frac{C}{C_{sat}})}) \qquad (10)$$

Secondary nucleation, which may occur at lower supersaturation level, is favored by the presence of solid in suspension (i.e. added in the crystallizer through seeding or generated through primary nucleation):

$$B_2 = a_{N2} M_T^i (C - C_{sat})^j \qquad (11)$$

a_{N1} is the primary nucleation parameter required to be identified on line , a_{N2} and b_{N1} are constant parameters and M_T is the crystal mass in the solution. The boundary condition for equation (1) is usually set as follows:

$$n(x_1,t) = \frac{B(x_1,t)}{G(x_1,t)} \simeq \frac{B(t)}{G(x_1,t)} \qquad (12)$$

3. DISCRETIZATION OF THE PBE

Many discretization methods were developed for solving PBE by (Kumar and Ramkrishna, 1997) and (Liu and Cameron, 2003). To our concern, two methods are applied: finite difference method and collocation method (Villadsen and Stewart, 1966) that are widely developed in numerical analysis books. The first method gives a model under a canonical form of observability. Indeed, the state matrix has tri-diagonal form. Moreover it agrees with the physical behavior of the system. Collocation method gives a polynomial approximation based on a mathematical correlation between the different states not describing physical phenomena. Therefore, we use the finite difference method is used for the observer development.

After the discretization of the PBE, the final system of equations gives:

$$\begin{cases} \dot{n_x} = \dfrac{1}{\Delta x} A(u,t) n_x \\ y = C n_x \end{cases} \tag{13}$$

with: $n_x = \begin{pmatrix} n_{x_1} \\ n_{x_2} \\ \vdots \\ n_{x_{N-1}} \\ n_{x_N} \end{pmatrix}$, $C = \begin{pmatrix} 1 & 0 & \dots & 0 \end{pmatrix}$,

$$A(u,t) = \begin{pmatrix} -G(x_1,t) & G(x_2,t) & 0 & \dots & 0 \\ -\dfrac{G(x_1,t)}{2} & 0 & \dfrac{G(x_3,t)}{2} & \ddots & \vdots \\ 0 & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & -\dfrac{G(x_{N-2},t)}{2} & 0 & \dfrac{G(x_N,t)}{2} \\ 0 & \dots & 0 & 0 & 0 \end{pmatrix},$$

with $n_x \in \mathbb{R}^N$, $A \in \mathbb{R}^N \times \mathbb{R}^N$ and $C \in \mathbb{R}^N$. The moments of the estimated CSD can be calculated and compared to those of the model. The expression of the moments is the following:

$$\mu_i = \int_{x^*}^{x_\infty} x^i n(x,t) dL \tag{14}$$

The moments computation allows the evaluation of certain values that characterize the CSD like the number mean size L_{pop} and the variation coefficient VC_{pop} which are calculated as follow:

$$L_{pop} = \frac{\mu_1}{\mu_0} \tag{15}$$

$$VC_{pop} = \sqrt{\frac{\mu_0 \mu_2}{\mu_1^2} - 1} \tag{16}$$

4. HIGH GAIN OBSERVER SYNTHESIS

The system 20 has the following form:

$$\begin{cases} \dot{z} = f(z,t) \\ y = h(x) = Cx \end{cases} \tag{17}$$

with $z \in \mathbb{R}^N, y \in \mathbb{R}^m$. The system is clearly observable due to its triangular form. For the conception of the high gain observer for this system, the following assumptions must be verified :
The time varying parameter in 20 is positif:

$$\exists \gamma, \xi : 0 < \gamma \leq \xi, \forall t \leq 0 : \gamma I_{d_N} \leq A_G(t) \leq \xi I_{d_N} \tag{18}$$

In the case of continuous measurements, a candidate exponential observer for this system is given by a variant of (Farza *et al.*, 1997) and (Gauthier *et al.*, 1992):

$$\begin{cases} \dot{\hat{n}}_x(t) = \dfrac{1}{\Delta x} A(u,t) \hat{n}_x \\ \quad - \dfrac{1}{\Delta x} S_\theta^{-1} C^T (C\hat{n}_x - y)) \\ \dot{S}_\theta(t) = -\theta S_\theta(t) - A^T(u,t) S_\theta(t) \\ \quad - S_\theta(t) A(u,t) + C^T C \end{cases} \tag{19}$$

The convergence of this observer can be easily proved using 18.

In the case of unseeded solution, we took N equal to 200 to improve the model precision. This number could be reduced for the observer to a half ($N_{observer} = 100, ratio = 2$). This task is motivated by the reduction of the computation time. In this case, the following matrix of the system is generated for the observer synthesis:

$$A_{2_{obs}}(u,t) = \begin{pmatrix} -\dfrac{G(x_1,t)}{ratio} & \dfrac{G(x_2,t)}{ratio} & 0 & \dots & 0 \\ -\dfrac{G(x_1,t)}{2ratio} & 0 & \dfrac{G(x_3,t)}{2ratio} & \ddots & \vdots \\ 0 & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & -\dfrac{G(x_{N-3},t)}{2ratio} & 0 & \dfrac{G(x_N,t)}{2ratio} \\ 0 & \dots & 0 & 0 & 0 \end{pmatrix},$$

With:
$ratio = \frac{N}{N_{observer}}$
So:
$A_{2_{obs}} = \frac{A_{obs}}{ratio}$

The new equations system is:

$$\begin{cases} \dot{n}_{x_{obs}} = \dfrac{1}{\Delta x} A_{2_{obs}}(u,t) n_{x_{obs}} \\ \qquad = \dfrac{1}{ratio \Delta x} A_{obs}(u,t) n_{x_{obs}} \\ y = C_2 n_{x_{obs}} \end{cases} \tag{20}$$

The structure remains unchanged. The new number of components of the gain matrix S is $(1 + N_{obs})\frac{(N_{obs}-1)}{2}$.

5. SIMULATION RESULTS

The simulation concerns a batch crystallization with unseeded initial solution. In this simulation, the observer is run with a reduced number of states. This simulation was performed using a concentration measurement with added noise of about ($\pm 2\%$) which is a reasonable choice regarding the range of concentration $(0-1500)\frac{mol}{m^3}$. The solubility curve (C_{sat}) and the solute concentration profile during the crystallization are presented in figure 1.

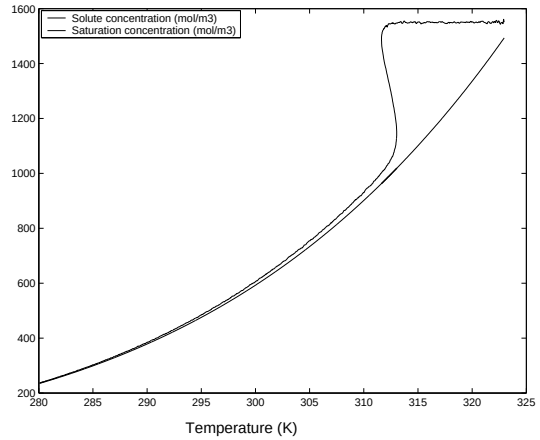

Fig. 1. solubility and solute concentration versus temperature

Nuclei produced by the primary nucleation grow with the increase of the supersaturation due to decreasing temperature. Temperature increases at this time because the crystal growth is exothermic. The secondary nucleation also takes place due to the presence of crystals. A simulation problem due to noise appears when the supersaturation becomes small. Some noisy solute measurements are lower than the concentration at saturation (C_{sat}). This error introduces a change of the model (from growth kinetics to dissolution kinetics). Knowing the process behavior, this error is set equal to zero.

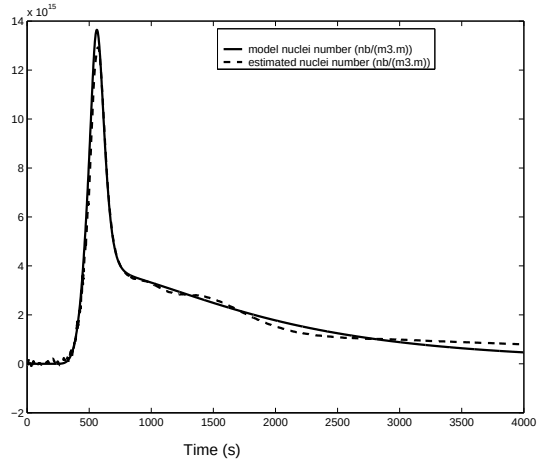

Fig. 2. Germ number (nuclei)

The significant interval where an important production of nuclei occurs is presented in figure (2). The generation of nuclei in the remaining interval is less important. Sampling period is equal to 2 seconds. This period is small because of fast system dynamic. Greatest sampling periods yield to important estimation error.

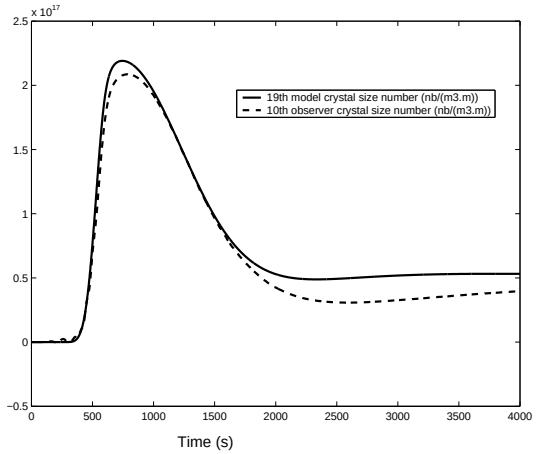

Fig. 3. 19th model crystal size and equivalent 10th observer crystal size

The $10th$ crystal class observer corresponds to the ($19th$) crystal model class. There evolution with time is presented in figure 3. It is shown that this crystal size is estimated with acceptable precision. The choice of such crystal size was arbitrary. The other crystal sizes exhibit the same estimation accuracy.

The $3D$ figures 4 and 5 represent the growth size dependent model and observer. These tow figures show that the Mc Cabe hypothesis leads to neglecting important growth kinetic difference between small and large crystals. Growth for small crystals is about 10 to 20 times greater than the growth for large crystals. This justifies the use of a more complex model. Figure 5 represents the growth kinetic obtained by the observer. It was computed using noised solute concentration.

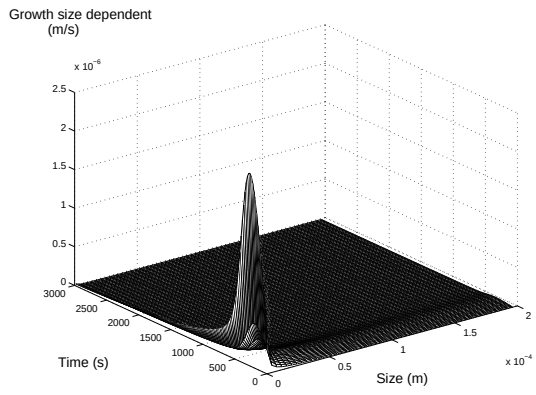

Fig. 4. Growth size dependent for the model

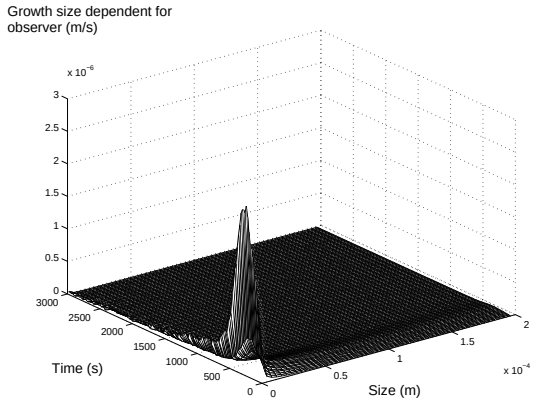

Fig. 5. Growth size dependent for the observer

The last two $3D$ figures (6) and (7) represent respectively the CSD model and its estimation. An estimation error can be seen. It is justified by the huge number of estimated variable.

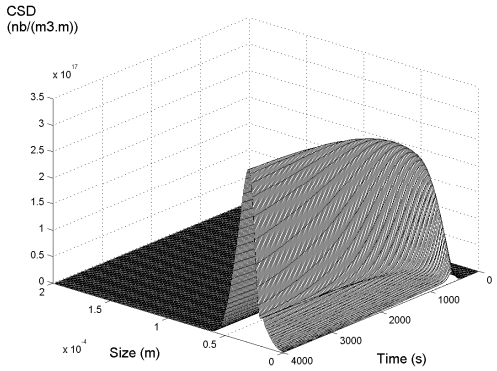

Fig. 6. model CSD

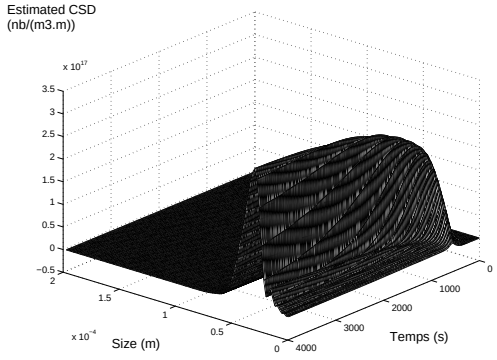

Fig. 7. CSD Observer

6. CONCLUSION

The model used in order to estimate the CSD is more complex than those used before. The PBE discretization yields to a change of model structure and thus the observer structure.

In spite of the great number of variables (crystal sizes) to be estimated, and the availability of only germs number, a high gain observer allowed the estimation of the CSD. In the observers realized above, the accuracy of the CSD estimation is acceptable. The reduction of the variable number involved a less number of variables to integrate and therefore a reduced computation time.

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