Recovering the Crystal Size Distribution from the Moment Equations

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Batch crystallizers pose a unique problem in their design and analysis because the simplest isothermal cases require solution of a partial differential population balance equation to generate information about the crystal size distribution (CSD). It is common to solve only the moment transformation equations of the population balance to describe the statistical parameters of the crystal size distribution, thereby losing the detailed information of the nature of the CSD. The choices one has to obtain the detailed CSD are to: solve the partial differential equation; solve a very large number of moment equations and recover an approximate form (Hulburt and Katz, 1964; Randolph and Larson, 1988); or to assume a functional form, such as a gamma distribution, and generate the required parameters from the moments (for example, Nikolakis et al., 1998).

A numerical technique is presented and illustrated for batch crystallizer design and analysis by which the crystal size distribution function can be recovered after solving only the first three moment transformation equations of the population balance (or four, if the nucleation function requires it). It is shown that the computational scheme required to carry out this recovery is flexible, straightforward, and efficient.

Background

The basis of the technique described below stems from an experimental technique reported at the 1980 International Zeolite Association meeting (Zhdanov and Samulevich, 1980). Although the technique is described in that reference, it also is readily available, and clearly described, in the text by Professor Barrer (Barrer, 1982, especially on pp. 145–147). We also learned, through private correspondence, that the approach had been discussed much earlier (Bransom et al., 1949, p. 98), but not used or cited elsewhere to our knowledge.

In a batch crystallization, if one measures the evolving size of the largest crystals in the population (say the largest 20 or so observed) and the final CSD at the termination of the crystallization, one can calculate the nucleation rate history for the crystallization in the following way. The number of crystals in the final CSD between $L \rightarrow L + dL$ was born within a certain time $t \rightarrow t + dt$. The corresponding birth time can be determined by going back a distance L from the terminal size of the largest crystals, and noting the time at which those crystals were nucleated. By determining the "birth time" for all crystals in all size ranges, dL, in the final population in that way, the entire nucleation profile can be developed. Although this is laborious in experimental investigations, this concept can be used to recover the crystal size distribution for design, analysis, and experimental verification purposes in a very similar way. This involves solving what we shall refer to as the "inverse problem," not that presented previously.

As illustrated by Zhdanov and Samulevich (1980), and shown below, the time evolution of the largest growing crystals does not have to be constant. That is, changes of the crystal growth rate G, as the supersaturation changes with time, can be accounted for. The overwhelming evidence in most crystallizations is that McCabe's ΔL law is obeyed; that is, crystal growth is size-invariant. Therefore, we have assumed that crystal growth does not depend on crystal size L.

Inverse Problem

Whereas the previous studies cited inferred the nucleation history from the final crystal size distribution, we report here the prediction of the evolving crystal size distribution by solving the moment equations, then solving the "inverse problem."

The moment transformation of the population balance equation for the batch crystallizer with size-independent crystal growth is given by (Randolph and Larson, 1988)

$$dm_0/dt = B(C_P) \tag{1}$$

$$dm_i/dt = iG(C_P)m_{i-1} \tag{2}$$

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Table 1. Parameter Values Used in the Simulations

b	6.0
C_{sat}	8.77×10^{-7} mol/cm^3
f_v	1.0
k_A	1.0×10^{-4}
k_P	9.0×10^{-7}
k_b	2.153×10^{30} [with B(s) in cm^{-3} h^{-1}]
k_g	442.7 [with $G(s)$ in μm/h]
ρ	0.028 mol/cm^3

where $i = 1$, 2, and 3. These four moments of the CSD correspond to the total number of crystals m_0, length m_1, surface area m_2, and volume (or mass) m_3. To these ordinary differential equations, we added a growth rate function linear in supersaturation, a nucleation function proportional to supersaturation to the 6th power, and a reversible precursor reaction to represent a system that creates supersaturation by a chemical reaction (that is, $A \leftrightarrow P$). The supersaturation was presumed to be in terms of species P [that is, $s = (C_P - C_{sat})$], which precipitates to the crystalline phase. Solute balances accounted for the reaction of A going to P, and the consumption of P by nucleation and crystal growth.

The CSD was determined by using the inverse of the scheme summarized above. The nucleation rate function $B(t)$ accounted for the birth of some number of crystal nuclei/volume at various times. These nuclei grew at some rate, accounted for by determining $G(t)$ from the solution of the moment equations, until some final crystallization time t. The CSD was then developed by accounting for enough small time intervals in the nucleation and growth histories to draw a smooth size distribution function $n(L, t)$. The required nucleation and growth rate trajectories were determined from the simultaneous solution of the moment equations, the solute balance, and the birth and growth functions, $B(C_P)$ and $G(C_P)$, respectively.

The model equations were solved using MathCad. A copy of the working part of the program is in the Appendix. In the program, the quantity m_4 is the concentration of the precipitating phase C_P. The values of constants used are provided in Table 1.

Results and Discussion

Figure 1 shows the results of a typical solution, in which the simulation of a batchwise crystallization has been carried out. The results from some of the moment equations and mass balances are shown in Figure 1a–c. The evolution of the total number of particles is shown in Figure 1a. The CSD was computed from the simultaneous consideration of the evolution of crystal size by growth, Figure 1b, and their nucleation rate in Figure 1c. Those crystals nucleated at the earliest times grew for the remainder of the crystallization (that is, the longest time). Those nucleated later grew for a comparatively shorter time.

In a time interval Δt, the growth G of the crystals was known. In fact, $G(t)$ for all time intervals up to the final time t_f was known from the simultaneous solution of the moment equations and the auxiliary equations. The summation of the differential growths from the "birth time" to the final time for a crystal cohort, multiplied by the growth time from its birth to completion, would determine the size of that cohort of crystals; that is

$$L(t) = \sum \Delta L = \sum [G(t)\Delta t] \tag{3}$$

for each cohort of crystals in the population. The number in the cohort $n(L)$ was found from the number born in that Δt by the birth function, Figure 1c.

In Figure 2 we show the time evolution of the CSD, computed at various times during the crystallization. The procedure was the same as discussed previously, except that the "final time" was allowed to vary from very short times to much longer times. The values of the other dependent variables

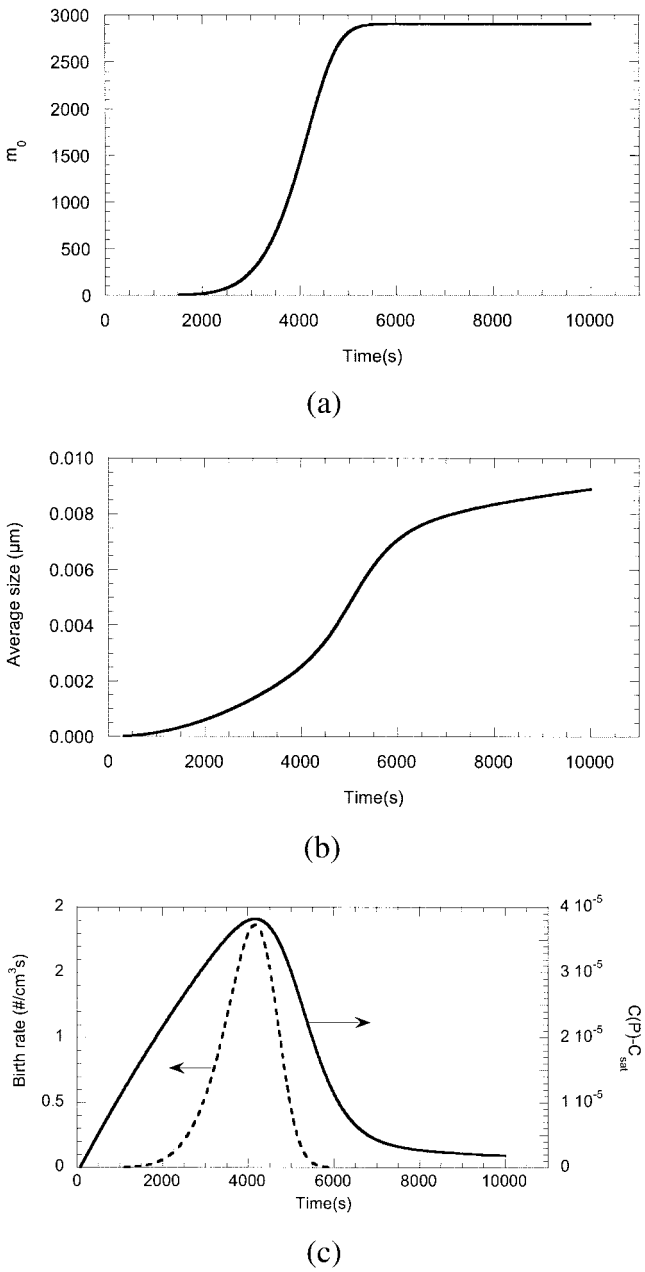

Figure 1. Results of simulation of batch crystallization using the parameter values in Table 1.

Simulations result from solution of only the moment transformation equations: (a) number concentration of crystals, (b) average crystal sizes, and (c) supersaturation and nucleation rate.

changed correspondingly. For example, the concentration of the intermediate P continued to approach its equilibrium value C_{sat}, at very long times, whereas the concentration of the primary reactant A continued to decrease toward its equilibrium value governed by the relative magnitudes of k_A and k_P. This feature of the technique is interesting because it shows how the CSD would be expected to develop at early times, and move along the size axis at later times.

The CSDs for three different starting solute concentrations C_A are shown in Figure 3. This modeling approach could be used to analyze a large number of parameter variations very quickly, given that the technique is not computationally demanding. This technique could also be used to predict the effects that changes in system parameters should have on the final CSD, and test models for nucleation and growth functions.

Conclusions

A very simple, but accurate and expedient, technique has been developed to recover the crystal size distribution, CSD, by solving only the moment transformation equations of the population balance, with the associated auxiliary equations. Once the moment equations have been solved together with the solute balance, the nucleation function, and the growth function, the nucleation and growth trajectories are used to determine the evolving crystal size distribution. The technique has been applied to a batch crystallizer in which the supersaturation changes with time, although crystal growth is independent of crystal size.

We anticipate that the technique will be of benefit to: (1) evaluate nucleation and growth rate functions in experimental studies, and (2) facilitate design and selection of operating parameters for crystallization systems for which control of the CSD is important. We also expect this technique to be of benefit in further batch studies of secondary nucleation.

Acknowledgments

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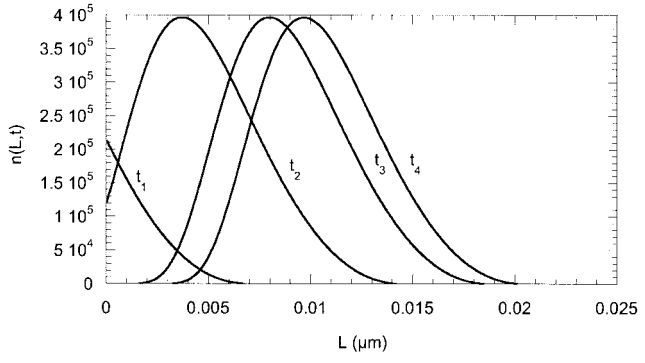

Figure 2. CSD, $n(L, t)$, computed from the results in Figure 1 for various crystallization times.

Times t_1 through t_4 are: 3,300, 5,000, 10,000, and 30,000 s, respectively.

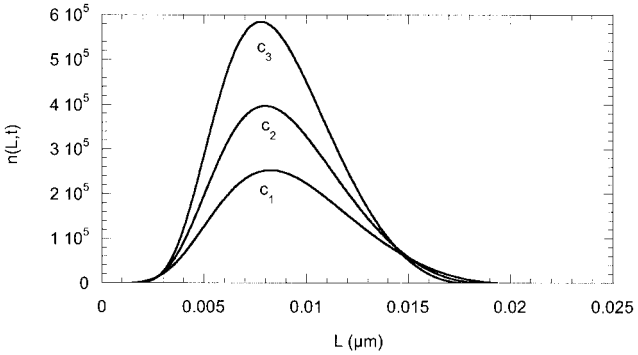

Figure 3. Number density function, $n(L, t)$, for three simulated crystallizations having different starting solute concentrations.

Concentrations c_1 through c_3 are: 1.0×10^{-4}, 1.24×10^{-4}, and 1.5×10^{-4} mol/cm^3, respectively.

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Appendix: MathCad Program

This Appendix contains a MathCad program used to calculate the moments of the crystal size distribution, then recover the evolving crystal size distribution for batch crystallizers.

$$kb := \frac{2.153 \cdot 10^{30}}{3600} \quad kg := \frac{4.427 \cdot 10^{2}}{3600}$$

$$kA := 0.0001 \quad kP := 0.0000009$$

$$\text{Csat} := 8.77 \cdot 10^{-7} \quad b := 6 \quad fv := 1 \quad rho := 0.0281$$

$$Q(m) := \begin{cases} 0 \text{ if } m_4 < \text{Csat} \\ kg \cdot (m_4 - \text{Csat}) \text{ otherwise} \end{cases}$$

$$B(m) := \begin{cases} 0 \text{ if } m_4 < \text{Csat} \\ kb \cdot (m_4 - \text{Csat})^b \text{ otherwise} \end{cases}$$

$$D(t,m) := \begin{pmatrix} B(m) \\ Q(m)\cdot m_0 \\ 2\cdot Q(m)\cdot m_1 \\ 3\cdot Q(m)\cdot m_2 \\ \begin{cases} kA\cdot m_5 - kP\cdot m_4 - 3\cdot fv\cdot rho\cdot Q(m)\cdot m_2 \text{ if } m_5 > 0 \wedge m_4 > \text{Csat} \\ kA\cdot m_5 - kP\cdot m_4 \text{ if } m_5 > 0 \wedge m_4 < \text{Csat} \\ -kP\cdot m_4 - 3\cdot fv\cdot rho\cdot Q(m)\cdot m_2 \text{ if } m_5 < 0 \wedge m_4 > \text{Csat} \\ 0 \text{ otherwise} \end{cases} \\ \begin{cases} 0 \text{ if } m_5 < 0 \\ -kA\cdot m_5 + kP\cdot m_4 \text{ otherwise} \end{cases} \end{pmatrix} \quad m := \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1.24\cdot 10^{-4} \end{pmatrix}$$

$Z := \text{rkfixed}(m,0,10000,1000,D) \quad n := 0..1000$

$$G_n := \begin{cases} 0 \text{ if } Z_{n,5} < \text{Csat} \\ \text{kg}\cdot(Z_{n,5} - \text{Csat}) \quad \text{otherwise} \end{cases} \qquad L_n := \sum_{p=n}^{1000} G_p \cdot \frac{(10000-0)}{1000}$$

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