NOTE

Optimal Seeding in Batch Crystallization

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This is the first comprehensive study on the optimization of seed distribution in a crystallization process. For a batch crystallizer, a dynamic programming formulation optimizes a property of the product crystals over the supersaturation profile and the seed characteristics, namely the mean size of the seed crystals, the seed mass, and the width of the seed distribution. Three optimization objectives are considered: (1) weight mean size, (2) coefficient of variation, and (3) the ratio of the nucleated crystal mass to seed crystal mass. Different objectives lead to substantially different optimal seed distributions. It is shown that optimizing over the seed distribution can have a larger effect on the product crystal size distribution than optimizing over the supersaturation profile.

C'est la première étude complète sur l'optimisation de la distribution des semences dans un procédé de cristallisation. Pour un cristalliseur discontinu, une formulation de programmation dynamique optimise une propriété des cristaux du produit en fonction du profil de sursaturation et des caractéristiques des semences, à savoir la taille moyenne des cristaux de semences, la masse des semences et la largeur de la distribution des semences. Trois objectifs d'optimisation sont considérés : (1) le poids moyen, (2) le coefficient de variation et (3) le rapport entre la masse de cristaux nucléés/germinés et la masse de cristaux de semences. Différents objectifs conduisent à des distributions de semences optimales substantiellement différentes. On montre que l'otpimisation de la distribution de semences peut avoir un effet plus important sur la distribution de taille des cristaux de produit que l'optimisation en fonction du profil de sursaturation.

Keywords: crystallization, optimal control, dynamic programming, batch control.

Crystallization from solution is an industrially important unit operation due to its ability to provide high purity separations. The crystal size distribution (CSD) is a critically important factor in the production of high quality products and for determining the efficiency of downstream operations, such as filtration and washing. Batch crystallizers are heavily used in industry, and a large proportion of these crystallizers are seeded. While it is well-known that the optimal supersaturation profile and the seed characteristics have a strong influence on the crystal size distribution in batch crystallizers (Chianese et al., 1984; Bohlin & Rasmuson, 1992; Rawlings et al., 1993), optimal control studies have only optimized over the supersaturation profile (Ajinkya & Ray, 1974; Chang & Epstein, 1982; Jones, 1974; Jones & Mullin, 1974; Morari, 1980; Miller & Rawlings, 1994; Mullin & N'yvlt, 1971).

This study is the first comprehensive investigation of the effect of the seed distribution on the final CSD properties for a crystallization process. The model equations are based on the moment equations. The seed distribution is parameterized in terms of its width, the mean size, and the seed mass. A dynamic programming formulation optimizes over the supersaturation profile and the seed distribution. Computer simulations of an industrial-scale batch crystallizer indicate that the seed distribution has a large effect on the final CSD properties, even when the supersaturation profile is optimal. In fact, it is shown that optimizing the seed distribution can have a larger effect on the final crystal properties than optimizing the supersaturation profile, which was the focus of earlier studies.

Batch crystallization model

Here, the model of a batch crystallizer is summarized.

Population balance

The population balance equation (PBE) approach accounts for the crystal distribution in size, location, and other state variables (Hulburt & Katz, 1964; Randolph & Larson, 1988). Assume that the crystals are characterized by one characteristic length L and have symmetrical shape, so that the volumetric shape factor $k_v = \frac{\text{Volume}}{L^3}$ is constant. Also, assume that the crystallizer is well-mixed, and growth dispersion, agglomeration, fracture, and attrition are negligible. Then, the population balance equation for a batch crystallizer is given by:

$$\frac{\partial f(L,t)}{\partial t} + \frac{\partial\{G(S,\theta_g,L)f\}}{\partial L} = B(S,\theta_b) \quad \ldots\ldots\ldots\ldots \quad (1)$$

where $f(L,t)$ is the distribution function for crystals, t is time, $G(S,\theta_g,L)$ is the rate of crystal growth in units of length per time, $B(S,\theta_b)$ is the nucleation rate (number of particles per unit time), $S = (C\text{-}C_{sat})/C_{sat}$ is the relative supersaturation, C_{sat} is the saturation concentration, C is the solute concentration, θ_g and θ_b are the growth and nucleation parameters, respectively.

Moment equations

The method of moments replaces the partial differential Equation (1) by a set of ordinary differential equations, which simplifies the simulation and optimization of the batch crystallizer. Assume that the growth rate is independent of characteristic size L. The moment equations defined on a per mass of solvent basis are given in the following (Hulburt & Katz, 1964):

$$\frac{d\hat{\mu}_0}{dt} = B$$

$$\frac{d\hat{\mu}_j}{dt} = jG\hat{\mu}_{j-1} + Br_0^j, \quad j = 1,2,\ldots \quad \ldots\ldots\ldots\ldots \quad (2)$$

where r_0 is crystal size at nucleation and is assumed to be a constant, and the j^{th} moment is defined by:

$$\hat{\mu}_j \equiv \int_0^\infty L^j \hat{f}(L,t)dL \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

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where $\hat{f}(L,T)$ is the population density distribution function on a per mass of solvent basis.

The final crystals can be characterized in terms of the final amount of nucleated crystal mass relative to seed crystal mass (Jones, 1974). Quantifying this requires determining the final state of the crystals grown from seed. Writing a mass balance only over the seed crystals, and applying the method of moments gives:

$$\frac{d\hat{\mu}'_0}{dt} = 0$$

$$\frac{d\hat{\mu}'_j}{dt} = jG\hat{\mu}'_{j-1}, \quad j = 1,2,\ldots \qquad (4)$$

where the symbol ′ indicates seed.

Mass balance for the continuous phase

Assume constant volume. The amount of solute leaving the solution must be accounted by crystal growth and nucleation:

$$\frac{d\hat{C}}{dt} = -3\rho_c k_v G\hat{\mu}_2 - \rho_c k_v B r_c^3 \qquad (5)$$

where ρ_c is density of the crystal, and the solute concentration $\hat{C}$ is on a per mass of solvent basis.

Nucleation and growth kinetics

Several models for growth kinetics have been developed depending on the crystal growth mechanisms (Garside, 1984; O'Hara & Reid, 1973; Burton et al., 1951). The most popular model is given by (Randolph & Larson, 1988):

$$G = k_g S^g \qquad (6)$$

where k_g and g are the growth parameters.

There are several different types of nucleation mechanisms (Randolph & Larson, 1988). This paper considers secondary nucleation from crystal surfaces, since it is the predominant mechanism taking place in most seeded batch-crystallizers. The nucleation rate is assumed proportional to the collision energy, with the rest of the kinetics being in standard power law form (Nyvlt et al., 1985):

$$B = k_b S^b \hat{\mu}_3 \qquad (7)$$

where k_b and b are the nucleation parameters.

Dynamic programming formulation

Although the dynamic programming framework allows for more complex seed distribution, for specificity here the seed is characterized by its mass m_{seed}, its mean $\bar{L}_0$, and the width of the distribution %width W (see Figure 1). For this study, the seed distribution will be optimized simultaneously with the supersaturation profile, the driving force for crystallization. For specificity we consider the case where the supersaturation is created by reducing the temperature $T(t)$, although other methods of achieving supersaturation such as anti-solvent addition (Charmolue & Rousseau, 1991) can be formulated in a similar manner.

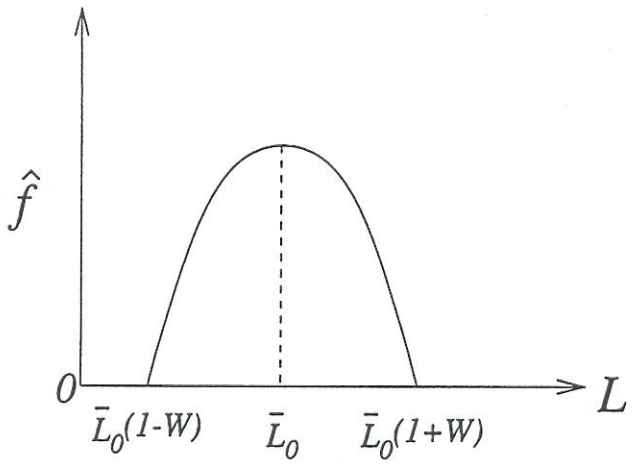

Figure 1 — Seed distribution $\bar{L}_0 = \hat{\mu}_1/\hat{\mu}_0$ is the mean size, $W \in [0, 1]$ quantifies the width of the distribution.

The optimal control formulation is a generalization of (Miller & Rawlings, 1994):

$$\underset{T(t),\, m_{seed},\, \bar{L}_0,\, W}{\text{optimize}} \quad \Phi$$

subject to:

$$\begin{aligned}
g_1(t) &= T_{min} - T(t) \le 0 \\
g_2(t) &= T(t) - T_{max} \le 0 \\
g_3(t) &= \frac{dT(t)}{dt} - R_{max} \le 0 \\
g_4(t) &= R_{min} - \frac{dT(t)}{dt} \le 0 \\
g_5 &= m_{seed,min} - m_{seed} \le 0 \\
g_6 &= m_{seed} - m_{seed,max} \le 0 \\
g_7 &= \bar{L}_{0,min} - \bar{L}_0 \le 0 \\
g_8 &= \bar{L}_0 - \bar{L}_{0,max} \le 0 \\
g_9 &= W_{min} - W \le 0 \\
g_{10} &= W - W_{max} \le 0 \\
g_{11} &= \hat{C}_{final} - \hat{C}_{max} \le 0
\end{aligned} \qquad (8)$$

where Φ is some desired characteristic of the crystals at the end of the batch (details in next section). The temperature constraints $g_1(t)$ to $g_4(t)$ ensure that the temperature profile stays within the operating range of the crystallizer. The constraints g_5 to g_{10} ensure that the seed distribution is practical. For example, for economic reasons the seed mass is usually constrained to be less than 10% of the final crystal mass. Finally, the constraint g_{11} is the minimum yield constraint, as the final solute concentration specifies the amount of crystals produced.

Batch control objectives

Several objectives have been recommended to favor downstream operations or product quality. One can maximize the mean crystal size (Ajinkya & Ray, 1974), the final size of seed crystals (Jones, 1974), the number average size, or the total volume (Chang & Epstein, 1982), or minimize

TABLE 1
Parameters used in the Simulation Study. The Parameters marked by a Dagger are from Miller (Miller, 1993).

Variable	Name	Value	Units
$m_{solvent}$	mass of solvent	7.57×10^3	kg
$\rho_c^\dagger$	density of crystal	2.11×10^3	kg/m^3
$r_0^\dagger$	nucleated crystal size	0	m
T_{max}	maximum T constraint	305.45	K
T_{min}	minimum T constraint	295.15	K
R_{max}	maximum rate of T change	0.0	C/s
R_{min}	maximum rate of T change	–0.1/60	K/s
$m_{seed,max}$	maximum seed mass	110	kg
$m_{seed,min}$	minimum seed mass	5×10^{-3}	kg
$\bar{L}_{0,max}$	maximum mean seed size	600×10^{-6}	m
$\bar{L}_{0,min}$	minimum mean seed size	5×10^{-6}	m
W_{max}	maximum % width of seed CSD	0.95	dimensionless
W_{min}	minimum % width of seed CSD	0.05	dimensionless
$\hat{C}_{sat}^\dagger$	saturation concentration	$0.1286 + 0.00588T + 0.00017217T^2$	kg KNO_3/kg H_2O
$\hat{C}_{max}$	maximum final concentration	0.0342	kg KNO_3/kg H_2O
k_v	volumetric shape factor	1	dimensionless
$k_b^\dagger$	nucleation parameter	4.6401×10^{11}	#/m^3 s
$b^\dagger$	nucleation parameter	1.78	dimensionless
$k_g^\dagger$	growth parameter	1.1612×10^{-4}	*m/s*
$g^\dagger$	growth parameter	1.32	dimensionless

TABLE 2
Optimal Seed Distribution for each Batch Control Objective with Simultaneous Optimization over the Temperature Profile

	weight mean size	coefficient of variation	ratio of nucleation crystal mass to seed crystal mass
m_{seed} (kg)	110	859.26×10^{-3}	110
$\bar{L}_0$ (m)	600×10^{-6}	5×10^{-6}	5×10^{-6}
W	0.95	0.05	0.05
Optimal temperature profile	Figure 2	Figure 4	Figure 3

the ratio of nucleated crystal mass to seed crystal mass (Eaton & Rawlings, 1990). Here three representative properties of the final CSD are investigated: weight mean size, coefficient of variation, and ratio of nucleated crystal mass to seed crystal mass. The three properties can be calculated directly from the moments (Randolph & Larson, 1988) (whether the goal is to maximize or minimize the property is also listed):

$$\text{weight mean size} = \frac{\hat{\mu}_4}{\hat{\mu}_3} \quad \text{(maximize)}$$

$$\text{coefficient of variation} = \sqrt{\frac{\hat{\mu}_2\hat{\mu}_0}{(\hat{\mu}_1)^2} - 1} \quad \text{(minimize)} \quad \ldots (9)$$

$$\frac{\text{nucleated crystal mass}}{\text{seed crystal mass}} = \frac{\hat{\mu}_3 - \hat{\mu}_3'}{\hat{\mu}_3'} \quad \text{(minimize)}$$

Results

The parameters for an industrial-scale potassium nitrate-water batch cooling crystallizer are listed in Table 1. The dynamic optimization (8) was solved for each of the three batch control objectives (9). The moment equations were integrated for a production run of 160 minutes using Gear's stiff method (IMSL, 1997). The cooling profile $T(t)$ was parameterized by a linear spline (Wylie & Barrett, 1995) to reduce the infinite dimensional nonlinear program to a finite dimensional nonlinear program, which was solved using successive quadratic programming (Zhou et al., 1989). Although there is no proof that this optimization procedure converges to the global optimum, extensive runs with a range of starting points with all other parameters fixed always converged to the same local optimum, giving some confidence that the global optima were being computed. The seed distribution optimizing (8) for each of the three batch control objectives (9) are listed in Table 2, with the optimal temperature profiles plotted in Figures 2 to 4.

Note that the optimal operating parameters depend strongly on which batch control objective is selected. Selecting the maximum seed mass suppresses nucleation and maximizes the product weight mean size, but at the cost of increased coefficient of variation (Table 2). Selecting the maximum seed size maximizes the product weight mean size, but at the cost of increased nucleation mass and a larger coefficient of variation. The cooling profiles that maximize the weight mean size and minimize the nucleation mass are very similar, with the temperature being reduced at a relatively low slope initially, but reduced as quickly as possible near the end of the run (Figures 2 and 3). Selecting a cool-

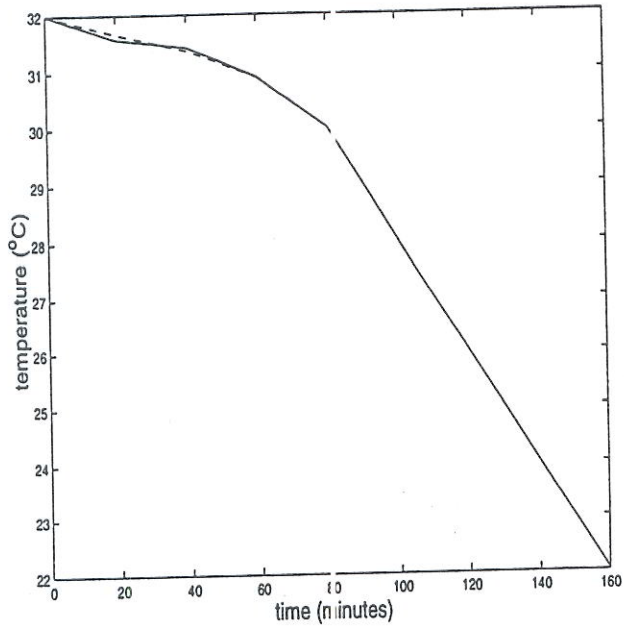

Figure 2 — Optimal cooling profiles for maximizing the weight mean size:
for optimized seed (- - -); for m_{seed} = 400 g, $\bar{L}_0$ = 100 μm, and W = 0.1 (—)

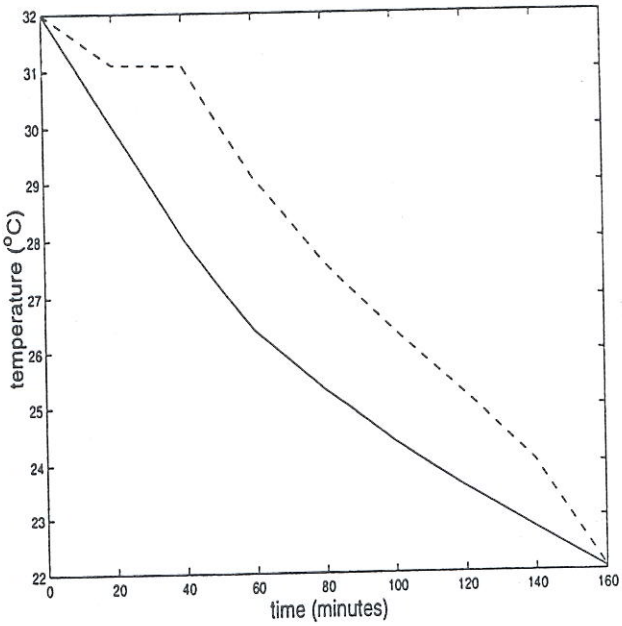

Figure 4 — Optimal cooling profiles for minimizing the coefficient of variation:
for optimized seed (- - -); for m_{seed} = 10 g, $\bar{L}_0$ = 400 μm, and W = 0.2 (—)

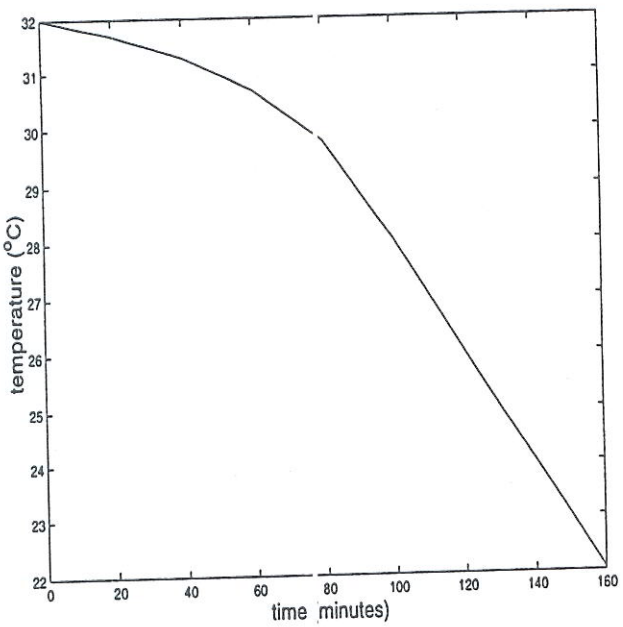

Figure 3 — Optimal cooling profiles for minimizing the ratio of the nucleated crystal mass to seed mass:
for optimized seed (- - -); for m_{seed} = 800 g, $\bar{L}_0$ = 20 μm, and W = 0.125 (—)

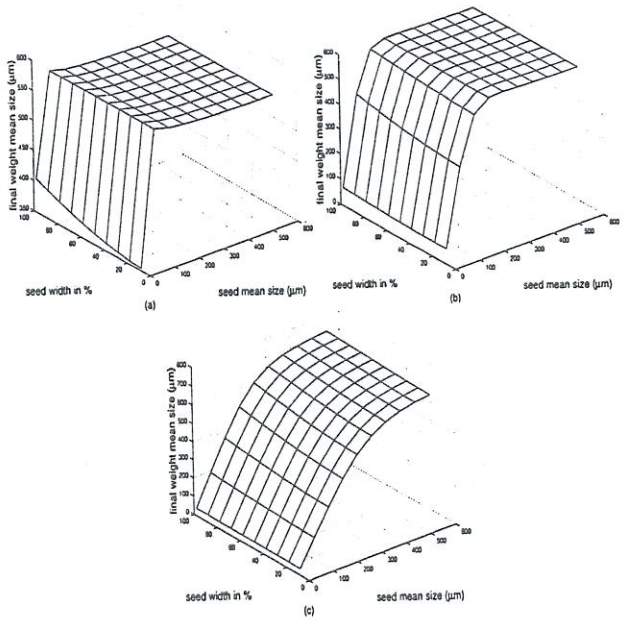

Figure 5 — Plot of weight mean size versus seed mean size and percent width at seed mass:
(a) m_{seed} = 25 g;
(b) m_{seed} = 8000 g;
(c) m_{seed} = 110,000 g.

ing profile that encourages growth over nucleation optimizes both objectives. In contrast, the optimal temperature profile with optimal seeding that minimizes the coefficient of variation rapidly reduces the temperature initially, with the temperature being reduced more gradually as the crystallization proceeds (Figure 4).

To investigate the sensitivity of the optimal cooling profile to changes in the seed distribution, the optimal cooling profile was re-computed with a fixed non-optimal seed distribution and also plotted in Figures 2 to 4. For the objectives of maximizing weight mean size and minimizing the ratio of nucleation mass to seed mass, the cooling profile is relatively insensitive to changes in the seed distribution (Figures 2 and 3). In contrast, the optimal cooling profile is much more dependent on the seed distribution when the objective is to minimize the coefficient of variation (Figure 4).

To investigate the sensitivity of the product CSD properties to changes in the seed distribution, each batch control

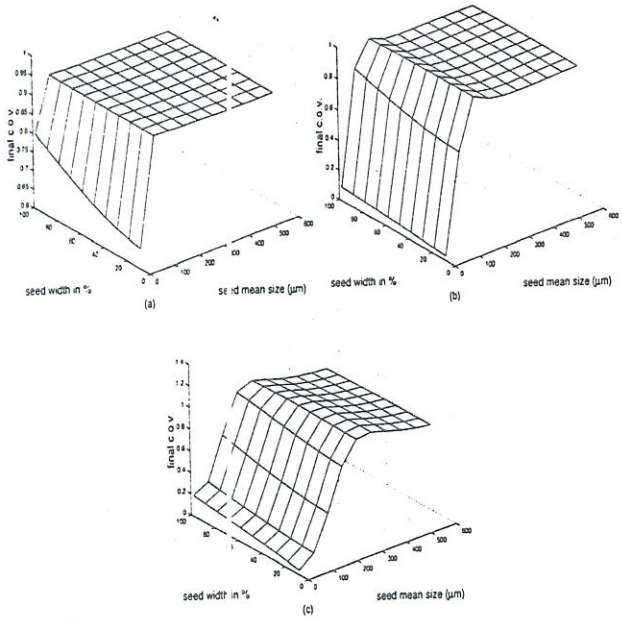

Figure 6 — Plot of coefficient of variation versus seed mean size and percent width at seed mass:
(a) m_{seed} = 25 g;
(b) m_{seed} = 8000 g;
(c) m_{seed} = 110,000 g.

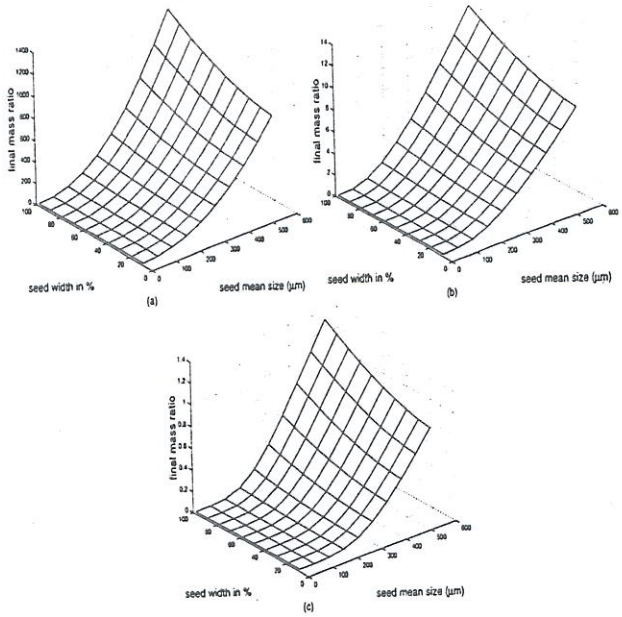

Figure 7 — Plot of ratio of nucleated mass to seed mass versus seed mean size and percent width at seed mass:
(a) m_{seed} = 25 g;
(b) m_{seed} = 8000 g;
(c) m_{seed} = 110,000 g.

objective (9) is plotted over a wide range of feasible seed distributions (see Figures 5 to 7), using the corresponding cooling profiles plotted in Figures 2 to 4. Figure 5 plots the final weight mean size as the batch control objective. It shows that the final weight mean size is a weak increasing function of the width of the seed distribution. On the other hand, maximizing the seed mass enables the production of crystals with higher weight mean size. For a fixed seed mass, there is an optimal intermediate seed mean size, which is the result of two competing effects. For a small enough seed mean size, most of the product crystal mass is grown from the seed crystals, so smaller seed mean size translates to smaller weight mean size. If the seed mean size is too large, then the product is dominated by the nucleated crystals, which have smaller weight mean size than crystals grown from seed. As shown in Figure 5, the optimal seed mean size for seeds of fixed mass increases as the seed mass increases.

The effects of seed distribution on the coefficient of variation are shown in Figure 6. The minimized seed mean size and distribution width produce the crystals of nearly uniform size, but at the cost of a small weight mean size (Figure 5). For fixed seed mean size and distribution width, whether a small, intermediate, or large seed mass minimizes the coefficient of variation depends the values for the seed mean size and distribution width.

The ratio of the mass of nucleated crystals to the mass of seed crystals is minimized by maximizing the seed mass and minimizing the seed mean size and width of distribution (see Figure 7). Increasing the seed mass and decreasing the seed mean size increases the seed surface area for growth, promoting growth over nucleation. For large seed mass and low seed mean size, the dependence of the ratio of the mass of nucleated crystals and the mass of seed crystals on the width of the seed distribution is weak (see Figure7c).

Discussion

Chianese et al. (1984) conducted an experimental study to optimize the weight mean crystal size over several factors, including the cooling profile and the seed mass for the batch crystallization of potassium sulphate in water. Although Chianese et al. considered a different solute, the experimental results regarding the effect of seed mass are qualitatively consistent with Figure 5.

Bohlin and Rasmuson (1992) studied the effect of seed mass and cooling profile on weight mean size and the coefficient of variance for citric acid and potassium sulphate batch crystallizations. The cooling profiles that were studied did not correspond to optimizing a batch control objective, but to maintaining a constant rate of nucleation (Mullin & N'yvlt, 1971). One of their main conclusions was that the product weight mean size and the coefficient of variation may increase or decrease with increasing seed mass depending on the governing kinetics. Figures 5 and 6 imply that this statement can hold, even for the same system, depending only on the magnitude of the seed mass.

Publications which consider only optimal cooling profiles for batch crystallizers tend to report improvements of 30 to 50% in the batch control objective under study, compared to natural or linear cooling (Ajinkya & Ray, 1974; Jones, 1974; Jones & Mullin, 1974; Miller & Rawlings, 1994; Mullin & N'yvlt, 1971). It was shown here that the effect of optimizing the seed distribution is significantly more important than optimizing the supersaturation profile. For example, from Figure 5 we see that changing the seed mass can have an order of magnitude effect on the final weight mean size. From Figure 6, we see that changing any of the seed distribution parameters can have a huge effect (up to orders of magnitude) on the coefficient of variation. This illustrates the importance of optimizing over the seed distribution parameters as well as the supersaturation profile during-

batch crystallization, and likely explains why crystallization experts in industry focus much more on the seed characteristics than on the supersaturation profile (Johnson et al., 1997).

Conclusions

It was shown that optimizing over the seed distribution can have a larger effect on the crystal product than optimizing over the supersaturation profile. In the simulations performed, the product crystal properties can change by an order-of-magnitude with a change in a seed distribution parameter. This illustrated the importance of optimizing over the seed distribution parameters, as well as the supersaturation profile, during batch crystallization.

Some general conclusions can be made about the selection of batch control objectives for dynamic optimization. First, minimizing the coefficient of variation can result in very poor operations in terms of the other two batch control objectives, as it can favor nucleation over growth. Second, while minimizing the ratio of the mass of the nucleated crystal to seed crystal and maximizing the weight mean size resulted in similar cooling profiles, the objectives resulted in very different optimal seed distributions. For all three objectives, the optimal operating parameters depend strongly on which batch control objective is selected. Because of this, it is important to select an objective that correlates well with the actual crystal product property of interest, e.g., filterability.

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Nomenclature

B = nucleation rate, (# of particles/m s)
b = nucleation parameter, (dimensionless)
C = solute concentration, (kg/m^3 solvent)
C_{sat} = saturation concentration, (kg/m^3 solvent)
$\hat{C}$ = solute concentration on a per mass of solvent basis, (kg/kg solvent)
$\hat{C}^{\dagger}_{sat}$ = saturation concentration from Miller (Miller, 1993), (kg/kg solvent)
$\hat{C}_{max}$ = maximum final concentration, (kg/kg solvent)
$f(L, t)$ = population density distribution function, (# of particles/m)
$\hat{f}(L, t)$ = population density distribution function on a per mass of solvent basis, (# of particles/kg solvent)
G = rate of crystal growth, (m/s)
g = growth parameter, (dimensionless)
$g_1(t), \ldots, g_4(t)$ = temperature constraints
$g_4, \ldots, g_{10}$ = constraints on the seed distribution
g_{11} = maximum yield constraint
k_b = nucleation parameter, (# of particles/m^3 s)
k_g = growth parameter, (m/s)
k_v = volumetric shape factor, (dimensionless)
L = characteristic length of the crystal, (m)
$\bar{L}_0$ = mean seed size, (m)
$\bar{L}_{0,max}$ = maximum mean seed size, (m)
$\bar{L}_{0,min}$ = minimum mean seed size, (m)
m_{seed} = seed mass, (kg)
$m_{seed,max}$ = maximum seed mass, (kg)
$m_{seed,min}$ = minimum seed mass, (kg)
$m_{solvent}$ = mass of solvent (kg)
r_0 = nucleated crystal size, (m)
R = rate of T change, (K/s)
R_{max} = maximum rate of T change, (K/s)
R_{min} = minimum rate of T change, (K/s)
S = relative supersaturation, (dimensionless)
T = temperature profile, (K)
T_{max} = maximum temperature constraint, (K)
T_{min} = minimum temperature constraint, (K)
W = % width of seed CSD, (dimensionless)
W_{max} = maximum % width of seed CSD, (dimensionless)
W_{min} = minimum % width of seed CSD, (dimensionless)

Greek letters

θ_g = growth parameters
θ_b = nucleation parameters
$\hat{\mu}_j$ = j^{th} moment
$\hat{\mu}'_j$ = j^{th} moment of seed crystals
ρ_c = density of crystal, (kg/m^3)
Φ = some desired characteristics of the product crystals

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