Estimation of Batch Precipitation Kinetics by a Simplified Differential Method

Iztok Livk and Ciril Pohar
Faculty of Chemistry and Chemical Technology, University of Ljubljana, 1000 Ljubljana, Slovenia

Dean Ilievski
AJ Parker CRC for Hydrometallurgy, CSIRO Minerals, Perth WA 6102, Australia

Crystallization from solution is a unit operation of great economic importance in the chemical industry. The uses of this separation and purification technique range from the small-scale manufacture of fine chemicals to bulk production, such as the precipitation of aluminum trihydroxide in the Bayer process. In addition to the purity and shape of crystals, the crystal-size distribution (CSD) is usually a key quality consideration for a crystallization product. The product CSD is determined by the relative rates of crystal growth, agglomeration and nucleation, which are controlled by the process conditions and the chemistry of the system. A population-balance (PB)-based model, the theory for which can be found in Randolph and Larson (1988), provides a mathematical tool to describe the relationship between the CSD and process conditions.

This research note describes a method based on a discretized PB to estimate the rates of growth, agglomeration, and nucleation from experimental batch CSD data. This so-called "inverse" problem is posed as a nonlinear optimization, where an objective function based on the difference between the experimental and model-predicted values is minimized with respect to the kinetic parameters. It is shown that in the case when the objective function is formulated in terms of the time derivatives of the measured variables, the original problem can be reduced into three smaller subproblems that can be rapidly solved.

The method is illustrated using data from a batch aluminum trihydroxide precipitation experiment. The validity of the estimates is evaluated by comparing the experimental CSD with that obtained from the simulation using the estimated kinetics. Estimates from our method are also compared to the estimates obtained using the differential technique of Bramley et al. (1996).

Batch Crystallization Model

The PB for a batch crystallizer is generally represented by an integro-partial differential equation that can be discretized (Marchal et al., 1988; Hounslow et al., 1988) in order to facilitate the solution. For a batch crystallization process involving nucleation, growth, and agglomeration, a discretized form of the population balance for the ith size interval can be written as (Marchal et al., 1988):

$$\frac{dN_i}{dt} = \left[G(L_i) n(L_i) - G(L_{i+1}) n(L_{i+1}) \right] + R_{a,i} + B_{u,i} \qquad i = 1, \ldots, m \tag{1}$$

$$G = G(\boldsymbol{\theta}_G, x, L) \tag{2}$$

$$R_{a,i} = R_{a,i}(\beta_{\upsilon,\lambda}, N_\upsilon, N_\lambda); \qquad \beta_{\upsilon,\lambda} = \beta_{\upsilon,\lambda}(\boldsymbol{\theta}_\beta, x, L) \tag{3}$$

$$B_{u,i} = B_{u,i}(\boldsymbol{\theta}_B, x) \tag{4}$$

$$\boldsymbol{\theta}^T = \left[\boldsymbol{\theta}_G^T \;\; \boldsymbol{\theta}_\beta^T \;\; \boldsymbol{\theta}_B^T \right], \tag{5}$$

where G is the linear growth rate; $R_{a,i}$ is the net rate of change of the number of particles per unit volume in the ith size interval due to aggregation resulting from binary collisions, and is proportional to the product of the number of particles in respective size intervals. The aggregation kernel, $\beta_{\upsilon,\lambda}$, is a measure of the frequency at which crystals of size, $\bar{L}_\upsilon$ and $\bar{L}_\lambda$ collide and form an agglomerate. There are a number of different formulations for $R_{a,i}$ available in the literature (Hounslow et al., 1988; Marchal et al., 1988; Litster et al., 1995). The source function, $B_{u,i}$, accounts for the crystals entering into the field of view of the particle-size analyzer, represented by the first size interval of a discretized model, and is nonzero only for $i = 1$.

The kinetics G, β, and B_u depend on the physicochemical nature of the system, and on operational conditions such as supersaturation, temperature, and hydrodynamics. In some systems, G and β can also depend on crystal size. Therefore kinetic models usually involve a vector of empirical parameters, $\boldsymbol{\theta}$, vector of process states, x, and size domain, L. They are commonly expressed as power-law equations.

Correspondence concerning this article should be addressed to C. Pohar.

The crystallizer model must also be consistent with the mass balance, which for an isothermal batch crystallizer can be expressed in a discretized form as:

$$\epsilon\frac{dc}{dt} = -\rho_s k_v \frac{d\mu_3}{dt} = -3\rho_s k_v \sum_{i=1}^{m} G\bar{L}_i^2 N_i - \rho_s k_v \bar{L}_1^3 B_{u,1} \tag{6}$$

$$\mu_3 = \sum_{i=1}^{m} \bar{L}_i^3 N_i, \tag{7}$$

where c is the concentration of the crystallizing species, and μ_3 is the third moment of the discrete CSD. In many cases the contribution of nucleation to the total mass is negligible and the last term on the righthand side of Eq. 6 can be neglected. Together with the initial conditions, $N_i(0)$ and $c(0)$, the preceding model can be solved using any of the available integration procedures.

Kinetic Parameter Estimation

Viewed as a nonlinear optimization problem, the estimation of the kinetics parameter set, $\boldsymbol{\theta}$, is carried out by minimizing an objective function, which is a measure of the deviation between the model and experiment. The transient behavior of batch crystallization enables the values of the kinetic parameters to be estimated from a single-experiment data set. Although there are many different ways of expressing the objective function, $\boldsymbol{\Phi}$, the weighted-least-square form is a common choice:

$$\boldsymbol{\Phi}(\boldsymbol{\theta}) = \sum_j \sum_k \omega_j \left[y_{k,j}^{\text{exp}} - y_{k,j}(\boldsymbol{\theta}) \right]^2. \tag{8}$$

The elements of the measurement vector, y, may involve any process variable, such as N_i, supersaturation, or moments of CSD, as a function of time instant k. Using the model equations (Eqs. 1–6), Eq. 8 can be estimated in two different ways (Bard, 1974). These are: (1) by using the experimental data and numerical integration of the model equations (*integral approach*), or (2) by differentiating the experimental data with respect to time and using the differential PB model equations (*differential approach*). In the second case, the derivatives of the measurement vector, $\dot{y}$, for example, $\dot{N}_{i,k}$ would be used in Eq. 8.

The integral approach has been widely used to estimate crystallization kinetics (Ilievski and White, 1994; Rawlings et al., 1993; Hostomsky and Jones, 1991). A disadvantage of this approach is that it is computationally intensive and requires all kinetic parameters to be determined simultaneously. This can further initiate problems with the convergence and uniqueness of the solution. On the other hand, it is well known that numerical differentiation of experimental data can introduce significant errors. Despite this fact, a number of successful applications based on the method of moments have been reported by Tavare and Garside (1986, 1993), Nývlt and Karel (1993), and Ilievski and White (1996). Recently, Bramley et al. (1996) developed a differential method, which uses the time derivatives of the zeroth moment, the third moment, and of the number of particles in the first size interval.

In the current work, we show that when the differential approach is used to estimate unknown parameters, the original problem from Eq. 8 can be reduced into three subproblems, which can then be solved sequentially.

Simplified Differential Method

The differential approach is faster than the integral one and also enables the initial problem to be reduced into three lower dimensional subproblems, one for each set of kinetic parameters. The objective functions that define these reduced order subproblems can be stated as

$$\boldsymbol{\Phi}_1(\boldsymbol{\theta}_G) = \sum_{k=1}^{m_s} \left[\dot{c}_k^{\text{exp}} - \dot{c}_k(\boldsymbol{\theta}_G) \right]^2 \tag{9}$$

$$\boldsymbol{\Phi}_2(\boldsymbol{\theta}_G, \boldsymbol{\theta}_\beta) = \sum_{k=1}^{m_s} \left[\sum_{i=2}^{m} \dot{N}_{i,k}^{\text{exp}} - \sum_{i=2}^{m} \dot{N}_{i,k}(\boldsymbol{\theta}_G, \boldsymbol{\theta}_\beta) \right]^2 \tag{10}$$

$$\boldsymbol{\Phi}_3(\boldsymbol{\theta}_G, \boldsymbol{\theta}_\beta, \boldsymbol{\theta}_B) = \sum_{k=1}^{m_s} \left[\dot{N}_{k,1}^{\text{exp}} - \dot{N}_{k,1}(\boldsymbol{\theta}_G, \boldsymbol{\theta}_\beta, \boldsymbol{\theta}_B) \right]^2. \tag{11}$$

In the absence of accurate information on the measurement uncertainties, unity weights were used in the formulation of Eqs. 9 to 11. It is assumed that the errors in the measurement of all N_{ik} are of similar magnitude, similarly for c_k.

The first objective function, stated in Eq. 9, is deduced from the solute mass balance (Eq. 6) with the assumption that the contribution of nucleation to the crystal mass is negligible. The second and third criteria, stated in Eqs. 10 and 11, are formulated on the basis of Eq. 1. The three objective functions are minimized sequentially. First, the growth-rate parameters, $\boldsymbol{\theta}_G$, are estimated by minimizing $\boldsymbol{\Phi}_1(\boldsymbol{\theta}_G)$. Next, the agglomeration parameters, $\boldsymbol{\theta}_\beta$, are estimated by minimizing $\boldsymbol{\Phi}_2(\boldsymbol{\theta}_G, \boldsymbol{\theta}_\beta)$, using the $\boldsymbol{\theta}_G$ values determined in the previous step. Finally, the source function rate parameters, $\boldsymbol{\theta}_B$, are obtained in the same manner by minimizing $\boldsymbol{\Phi}_3(\boldsymbol{\theta}_G, \boldsymbol{\theta}_\beta, \boldsymbol{\theta}_B)$, using the estimates of $\boldsymbol{\theta}_G$ and $\boldsymbol{\theta}_\beta$. This computation scheme has good convergence properties and is illustrated for each minimization in Figure 1. Note that the supersaturation and particle-size distribution, used to evaluate the derivatives at each step, do not depend on values of kinetic parameters.

In the case where the growth rate, agglomeration kernel, and source function rate are all size-independent, the preceding nonlinear optimization problem can be reduced to a sequence of three algebraic equations that can be solved explicitly for G, β, and B_u at each time instant. This is essentially the approach introduced in the work of Bramley et al.

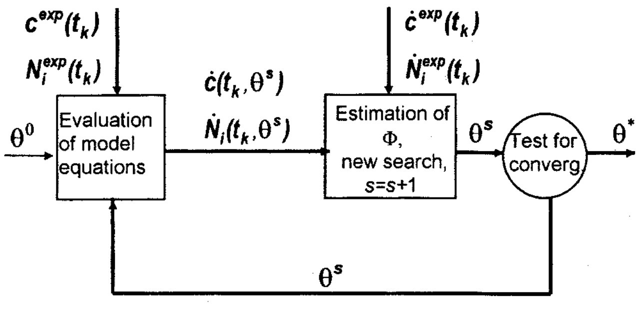

Figure 1. Calculation flow for estimating kinetic parameters using the differential method.

(1996), where the authors derived their method for a specific size discretization scheme with $L_{i+1} = \sqrt[3]{2}\,L_i$. Unlike their technique, however, the method proposed here uses the rates of change of the individual numbers of particles in an interval rather than the moments.

Estimation of Batch Aluminum Trihydroxide Precipitation Kinetics

The aluminum trihydroxide crystal growth rate is size-independent, and the agglomeration-rate kernel can be described by a size-independent model (Ilievski and White, 1994). This enables a direct comparison of parameter estimates from our method with the estimates from the differential technique of Bramley et al. (1996). In Figure 2, the values of kinetic rates, estimated from batch experimental data by both methods, are presented as a function of supersaturation. Figure 3 shows the simulated evolution of the CSD using the estimated kinetics and the experimental CSD.

As can be seen in Figure 2, the two methods give similar results for the investigated system. Compared to the method of Bramley et al., our method slightly overestimates the kinetic parameters. This is a consequence of neglecting the nucleation term in the mass balance. In general, the difference between the two methods will depend on the relative rates of crystal growth and nucleation for a given system, and on the characteristic length chosen for the first size interval. The difference between both methods diminishes as $\bar{L}_1 \to 0$.

Conclusions

The differential technique proposed here enables a successive determination of the growth-agglomeration-, and nucleation-rate parameters from dynamic crystallization data. Posed as a nonlinear optimization problem, the proposed method is not restricted to any specific model formulation and has good convergence properties. The CSD predicted by the model using the estimated kinetics matches well with the experimental CSD. The values of the aluminum trihydroxide precipitation kinetics, obtained in our work, are in good agreement with estimates obtained using another kinetics estimation technique reported in the literature. However, the applicability of differential methods in practice will depend on the quality of experimental data.

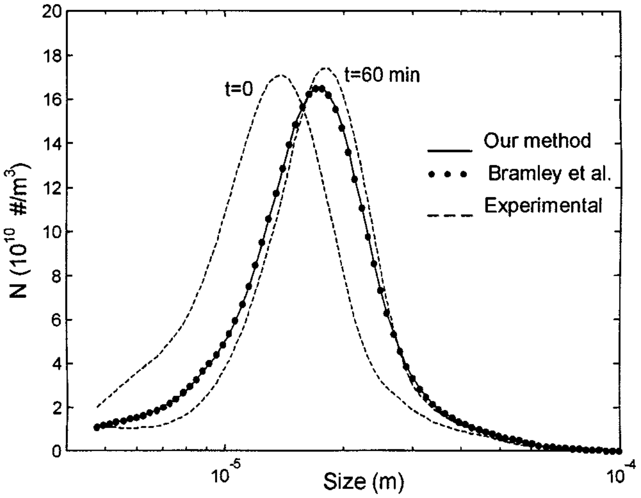

Figure 3. Comparison of experimental and simulated particle-size distributions.

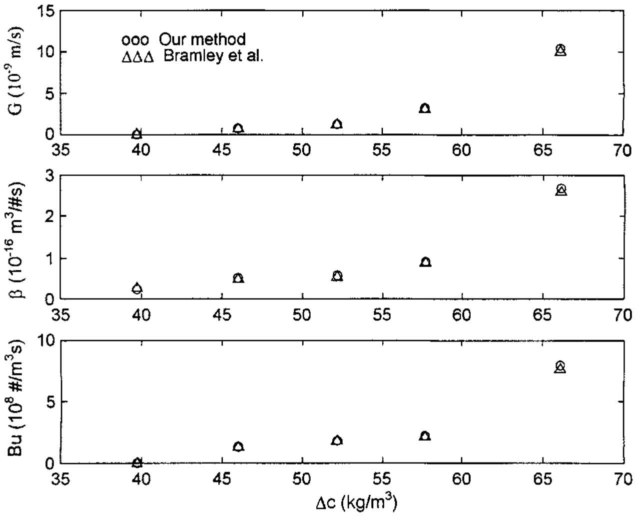

Figure 2. Estimates of the growth rate, agglomeration kernel and source function as a function of supersaturation obtained by the reported method and the Bramley method.

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Notation

$\dot{c}$ = time derivative of solution concentration, kg·m^{3}s^{-1}
k_v = volume shape factor
$\underline{L}_i$ = lower limit of the ith size interval, m
$\bar{L}_i$ = mean size of the ith size interval, m
n = population density function defined as dN/dL, m^{-4}
N = number of particles, # m^{-3}
N_i = number of particles per unit volume of slurry in the ith size interval, # m^{-3}
m = number of size intervals or the number of measured variables (Eq. 8)
m_s = number of sampling instants (Eq. 8)
t = time, s
Δc = supersaturation ($c - c_{eq}$), kg·m^{-3}
ϵ = conversion factor equal to the volume of solution per volume of slurry
μ_3 = time derivative of third moment, m^3·m^{-3}s^{-1}
θ^* = vector of optimal kinetic parameters
ρ_s = density of the crystal solid, kg·m^{-3}
ω_i = weight for the ith measurement (Eq. 8)

Superscripts and subscripts

k = sampling time
exp = experimental values
s = step number
0 = initial value

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