Efficient crystal size distribution estimation approach for growth dominated crystallisation processes

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The paper presents a novel methodology for the estimation of the shape of crystal size distribution (CSD) during crystallization processes. The approach is based on the combination of quadrature method of moment (QMOM) and method of characteristics (MOCH). The computationally efficient solution of the population balance equation allows the fast prediction of the dynamic evolution of the CSD for the entire batch. Furthermore, under the assumption that for supersaturation controlled crystallization the main phenomenon is growth, an analytical CSD estimator is derived for generic size dependent growth kinetics. The approaches are evaluated for the crystallization of potassium alum in water. The model parameters are identified based on industrial experimental data, obtained using an efficient implementation of supersaturation control. The proposed approach is able to predict and reconstruct the dynamic evolution of the CSD during the batch. The technique can serve as a soft sensor for predicting CSD or as a computationally efficient algorithm for off-line design or on-line adaptation of operating policies based on full CSD data.

1. Introduction

Crystallization from solution is an industrially important unit operation due to its ability to provide high purity separation. It is widely used in industries such as petrochemicals, pharmaceuticals, microelectronics and food processing. Batch cooling crystallization provides the advantages of being simple, flexible, and generally requiring less process development and investment than many other separation/purification techniques. Many problems in downstream processes can be attributed to poor particle characteristics established in the crystallization step. Most of the product qualities are directly related to the crystal size distribution (CSD). The control objectives for batch crystallization processes can be defined in terms of product purity, crystal habit, morphology, average particle size, crystal size distribution, bulk density, product filterability, and dry solid flow properties, which all depend on the CSD. The main difficulty in batch crystallization is to accomplish uniform and reproducible CSD [BRA02]. On-line control during the process allows for improved crystalline product quality, shorter process times, and reduction or elimination of compromised batches. Even if some of the objectives can be expressed in terms of the moments of the distribution, knowing and predicting the entire shape of the distribution allow the design and adaptation of operating policies to achieve improved product quality.

One way to enhance the control of CSD is to use supersaturation control, which drives the process within the metastable zone to avoid nucleation ([FUJ05], [NAG08]). Although this approach can provide improved consistency of the CSD, the actual prediction and estimation of the shape of CSD at the end of the batch can provide useful information for monitoring or designing the operating curve for the supersaturation controller. Model-based approaches can be used for better control [NAG03] but also for product design by reverse engineering the process to achieve desired CSD [HOU06].

Population balance models have been widely used for modelling crystallization processes ([HUL64], [RAN71]). The solution of generic population equation (PBE) usually requires computationally expensive complex numerical solution techniques. The variety of solution approaches proposed
from PBE ranges from standard method of moments (SMM), quadrature method of moments (QMOM) [MCG97], method of characteristics (MOCH), method of classes (MOC), to direct numerical solution (DNS) approaches, such as finite volume and finite difference schemes, or dynamic Monte Carlo (DMC) simulation approaches [RAM00]. The first two methods only provide average characteristics of the CSD expressed in low order moments (e.g. mean and standard deviation), whereas the last two methods are usually computationally too expensive for on-line real time applications. Both SMM and QMOM provide efficient solution of the PBE, and have been widely used in the literature for optimization and control purposes ([FU05], [NAG03]). However, these approaches only provide the moments of CSD and not the entire distribution. Several techniques are available to reconstruct the distribution from its moments. Linear or nonlinear inversion approaches can be used. These techniques have the disadvantage that they require a larger number of moments and generally suffer from solution multiplicity and ill-conditioning problems. Approximate distribution functions (e.g. polynomial, normal, gamma or lognormal), or weighted sum of distributions, using for example orthogonal polynomials as weighting functions, can also be used to approximate the shape of the distribution based on the moments ([RAN71], [FLO02]). However, the solution of the inversion problems is usually not unique. There is also a lack of systematic methodologies for the choice of the suitable type and number of base functions and distributions. Hence the approximate distribution functions resulted from both categories of reconstruction approaches are subject to spurious oscillations, and the correctness of the resultant shape of distribution is difficult to evaluate in most practical cases. The method of characteristics (MOCH) in combination with the SMM has been used successfully for processes with size independent growth and nucleation [HOU06]. However this approach does not apply in the more generic case of PBE with size dependent growth or when breakage and agglomeration mechanisms are also considered.

The approach presented in the paper combines the advantages of (QMOM) with the (MOCH) to provide a computationally efficient technique for the prediction of the entire CSD. The algorithm can be applied for the solution of population balance equations with generic size dependent growth and nucleation kinetics. The method has been used to identify the kinetic parameters for the batch cooling crystallization of potash alum from water using industrial experimental data. An analytical CSD estimator is also presented, which can be used in conjunction with the supersaturation control in the case of growth dominated processes. It is shown that the proposed approach provides a computational efficient CSD estimation technique, which can be used for off-line parameter estimation, crystallization design or for on-line estimation and control.

2. Combined QMOM-MOCH Approach for the Efficient Solution of Generic PBEs

Considering a single growth direction with one characteristic length \(L\), and a well-mixed crystallizer with growth and nucleation as the only dominating phenomena the population balance equation (PBE) has the form

\[
\frac{\partial f_n(L,t)}{\partial t} + \frac{\partial (G(S,L;\theta_g) f_n(L,t))}{\partial L} = B(S;\theta_b) \delta(r_0, L),
\]

where \(f_n(L,t)\) is the crystal size distribution expressed in the number density function (number of crystal per unit mass of slurry), \(t\) is time, \(G(S,L;\theta_g)\) is the rate of crystal growth, \(B(S;\theta_b)\) is the nucleation rate, \(S = (C - C_{sat})\) is the absolute supersaturation, \(C\) is the solute concentration, \(C_{sat} = C_{sat}(T)\) is the saturation concentration with \(T\) being the temperature, \(r_0\) is the size of nuclei, \(\delta(L_0, L)\) is the Kronecker delta (\(\delta = 1\) if \(L = r_0\) and \(\delta = 0\) if \(L \neq r_0\)) and \(\theta_g\) and \(\theta_b\) are vectors of growth and nucleation kinetic parameters, respectively. The solution of (1) is an initial value problem with initial condition given by the size distribution of seed, \(f_n(L,0) = f_{n,0}(L_0)\).
Equation (1) can be transformed into a system of ODEs by applying the standard method of moments (in the case of size independent growth and nucleation) or the quadrature method of moments (in more generic cases including size dependent growth, breakage and aggregation). Both methods calculate the moments of the distribution defined by,

\[ \mu_k = \int_0^{+\infty} f_n(L)L^k dL, \quad k = 1, 2, \ldots, \infty. \] (2)

The quadrature method of moments (QMOM) is a generic solution approach of the PBE [MCG97]. It employs a quadrature approximation of the distribution function

\[ f_n(L,t) \approx \sum_{i=1}^{N_q} w_i(t)\delta(L_i(t),L), \] (3)

where \( N_q \) is the number of quadrature points and the corresponding weights \( w_i(t) \) and abscessas \( L_i \) can be determined through the product-difference (PD) algorithms [GOR68] or via direct solution of a differential-algebraic (DAE) system, based on the idea of minimizing the error committed by replacing the integral from the moment definition with its quadrature approximation,

\[ \mu_k = \int_0^{+\infty} f_n(L)L^k dL \approx \sum_{i=1}^{N_q} w_i L_i^k. \] (4)

Applying the moment transformation to (1) with the quadrature approximation (4) the resulting moment equations have the form

\[ \frac{d\mu_0}{dt} = B(S;\theta_h), \]

\[ \frac{d\mu_i}{dt} = j \sum_{i=1}^{N_q} w_i L_i^{-1} G(S,L_i;\theta_g) + B(S;\theta_h) r_i^j, \quad j = 1, 2, 3... \] (5)

The generic PBE (1) can be reduced to a system of ODEs by applying the method of characteristics (MOCH). The aim of the MOCH is to solve the PBE by finding characteristic curves in the \( L-t \) plane that reduce the partial differential equation to a system of ODEs. The \( L-t \) plane is expressed in a parametric form by \( L = L(Z) \) and \( t = t(Z) \), where the parameter \( Z \) gives the measure of the distance along the characteristic curve. Therefore, \( f_n(L,t) = f_n(L(Z),t(Z)) \), and applying the chain rule gives:

\[ \frac{df_n}{dZ} = \frac{dL}{dZ} \frac{df_n}{dL} + \frac{dt}{dZ} \frac{df_n}{dt}. \] (6)

In the case of generic growth kinetics, (1) can be rewritten in the form of

\[ \frac{\partial f_n(L,t)}{\partial t} + G(S,L;\theta_g) \frac{\partial f_n(L,t)}{\partial L} = -f_n(L,t) \frac{dG(S,L;\theta_g)}{dL} + B(S;\theta_h)\delta(r_0,L). \] (7)

Comparing equations (6) and (7) it can be shown that \( Z = t \) and the characteristic equations are given by the following system of ODEs:

\[ \frac{dL}{dt} = G(S,L;\theta_g), \] (8)

\[ \frac{df_n(L,t)}{dt} = -f_n(L,t) \frac{dG(S,L;\theta_g)}{dL} + B(S;\theta_h)\delta(r_0,L), \] (9)
with initial conditions $L = L_0$ and $f_n(L,0) = f_{n,0}(L_0)$. To obtain the dynamic evolution of the crystal size distribution $f_n(L,t)$, the system (8)-(9) with given nucleation and growth expressions can be integrated repeatedly for different initial values $[L_0,f_{n,0}(L_0)]$. The number of integrations of the system will determine the resolution of the obtained distribution. For the solution of (8)-(9) it is considered that at the moment of nucleation, nuclei can have any size between 0 and $r_0$. This is described by the modified delta function defined as

$$\delta(r_0, L) = \begin{cases} 1 & \text{if } L \in [0, r_0] \\ 0 & \text{if } L \notin [0, r_0] \end{cases}.$$  (10)

The use of the modified delta function in the model may yield multiple nucleation events with different initial sizes of the nuclei within the size range $[0, r_0]$. To model the contribution to the overall distribution function of the potential nucleation events, which may occur later during the batch, the system (8)-(9) has to be initialized also with values $L_0 \leq 0$, for which $f_{n,0}(L_0) = 0$ or the time when the new nucleation will occur has to be estimated from the previous simulation and used as the initial condition for the time integration. The system (8)-(9) is integrated with the condition (10) and considering $f_n(L,t) = 0$ for any $L < 0$. The initial conditions are calculated by choosing a discretization interval $\Delta L_0$ and using $L_0 = L_{0,\max} - k\Delta L_0$, $k = 0,1,\ldots,N$, where $N$ corresponds to the maximum $L_0$ value for which all $L$ values resulting from the integration of (8)-(9) are negative for the entire batch period. The growth and nucleation rates are functions of the supersaturation, $S$, which can be calculated from the material balance. The solute concentration is given by

$$C(t) = C(0) - k_v\rho_v(\mu_3(t) - \mu_3(0)),$$  (11)

where $\rho_v$ is the density of crystals and $k_v$ the volumetric shape factor. The secondary nucleation rate, which is a dominating phenomenon in the case of seeded crystallization, is generally given as a function of supersaturation and the volume of exiting crystals (represented by the third order moment of the size distribution),

$$B = k_v S^b \mu_3.$$  (12)

The solution of (8)-(9) requires a priori knowledge of the dynamic evolution of the supersaturation, $S(t)$ and/or the third moment $\mu_3(t)$, which can be obtained by using the moment transformation of (1) using the SMM or QMOM. The main steps of the proposed algorithm are shown in Figure 1.

3. Analytical CSD Estimator for Growth Dominated Crystallization Systems

The traditional way of controlling cooling crystallization processes is to follow a predetermined temperature profile in time. Recent developments in the direct design of crystallization systems have lead to a widespread application of supersaturation control. The direct design approach is based on the idea of operating the system within the metastable zone bounded by the nucleation and solubility curves (see Figure 2). In this technique a supersaturation setpoint profile is chosen...
experimentally and it is followed in the phase diagram using a supersaturation controller based on concentration measurement. The supersaturation profile is usually chosen to be constant and with the application of properly designed control algorithms, in the case of seeded crystallization the process is maintained at the desired constant supersaturation throughout the entire batch. For supersaturation controlled seeded crystallization, seed is added to suppress nucleation, and the operation will be dominated by growth, which occurs at constant supersaturation. Considering the generic case of size dependent growth given by

\[ G = k_\gamma S^\gamma (1 + \gamma L)^\theta, \]

where \( \theta = [k_\gamma, g, \gamma, p] \) is the growth parameter vector, for growth dominated systems \( (B = 0) \) the model (8)-(9), reduces to the form:

\[ \frac{dL}{dt} = k_\gamma S^\gamma (1 + \gamma L)^\theta, \]

\[ \frac{df_n(L,t)}{dt} = -k_\gamma S^\gamma \gamma p(1 + \gamma L)^{p-1} f_n(L,t). \]

In the case of well-controlled constant supersaturation, which follows the desired set-point value, \( S_{wp} \), the system (14)-(15), can be solved analytically, with the solution:

\[ L = \left( \frac{(1 + \gamma L_0)^{1-p} + k_\gamma S^\gamma \gamma (1 - p)t)\left(1 + \gamma L_0\right)^{1-p} - 1}{\gamma} \right), \]

\[ f_n(L) = f_{n,0}(L_0) \left[ 1 + \frac{k_\gamma S^\gamma \gamma (1 - p)t^p}{(1 + \gamma L_0)^{1-p}} \right]. \]

Discretizing the initial distribution \( f_{n,0}(L_0) \) for different values of \( L_0 \), equations (16)-(17) can be used to compute the dynamic evolution of the CSD for a generic growth dominated process (the solution is valid for \( p \neq 1 \) and \( \gamma \neq 0 \); for \( p = 1 \) and/or \( \gamma = 0 \) the analytical expressions can also be derived).

4. Experimental and Simulation Results

The QMOM-MOCH approach has been validated for the batch cooling crystallization of the inorganic compound, potash alum \( (KAl(SO_4)_2) \) in water. The experimental data were obtained using a crystallization system located at BASF (Ludwigshafen, Germany). A supersaturation controller was implemented in the process and seeded experiments were carried out at constant supersaturation set-point. The CSD was measured at different time intervals using laser-diffraction, whereas concentration measurements were obtained based on density measurements of the slurry. The results from two experimental runs (experiments A and B) are shown in Figure 3. Experiment A was conducted at a supersaturation set-point \( S_{wp} = 0.6\% \) (weight percent, kg solute/kg slurry), whereas experiment B at \( S_{wp} = 0.3\% \) (weight percent). Seed was introduced in both cases shortly after the supersaturated state had been reached. In the case of experiment A it can be seen that the supersaturation controller exhibits an overshoot during the initial part of the operating curve, which leads to secondary nucleation. Since experiment A captures both the growth and nucleation mechanisms, it was used for model parameter identification using the QMOM-MOCH described in Section 2, whereas experiment B was used for validation of the
analytical estimator. For the potash alum system size dependent growth has been reported in the literature \cite{BRE80}, and was observed experimentally. Hence a generic size dependent growth expression given by (13) was used in the model identification.

The nucleation and growth parameters were determined to capture the dynamic evolution of the shape of the size distribution, as well as the experimental concentration profile. The optimization problem for the parameter estimation is given by,

$$\min_{\theta} \left\{ \sum_{k=1}^{K} \sum_{l=1}^{N_d} \left( f_{v,k}^{\text{L}}(L_l) - f_{v,k}^{\text{exp}}(L_l) \right)^2 + \sum_{k=1}^{K} \left( C_k - C_k^{\text{exp}} \right)^2 \right\},$$

subject to

$$\theta_{\min} \leq \theta \leq \theta_{\max},$$

with $\theta = [g, \gamma, p, b, b_k]$, being the model parameter vector with the growth and nucleation kinetic parameters, $\theta_{\min}$ and $\theta_{\max}$ are vectors with specified minimum and maximum bounds for each parameter, respectively, $C_k$ and $C_k^{\text{exp}}$ are the simulated and experimental concentration values at the discrete time steps $k = 1, \ldots, K$, $f_{v,k}^{\text{L}}$ and $f_{v,k}^{\text{exp}}$ are the values of the simulated and experimental volume probability distribution functions, corresponding to the discretized size $L_l$, $l = 1, \ldots, N_d$, with $N_d$ being the number of experimental size bins, and $\alpha_f$, $\alpha_C$ are scaling factors.

The optimization problem is solved using a sequential quadratic programming (SQP) approach implemented in the Matlab function fmincon. The resulted model parameters for the potash alum system are presented in Table 1. The dynamic evolutions of the modelled and experimental CSDs are in very good agreement during the entire batch (see Figure 4).

Table 1. Size-dependent growth and nucleation parameters for the crystallisation of potash alum in water (unit of $S$ is $(kg \text{ solute})/(kg \text{ slurry})$).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth rate constant ($k_g$)</td>
<td>8.570</td>
<td>$\mu$m s$^{-1}$</td>
</tr>
<tr>
<td>Growth constant ($\gamma$)</td>
<td>0.005</td>
<td>$\mu$m$^{-1}$</td>
</tr>
<tr>
<td>Growth constant ($p$)</td>
<td>1.577</td>
<td>-</td>
</tr>
<tr>
<td>Growth order constant ($g$)</td>
<td>1.000</td>
<td>-</td>
</tr>
<tr>
<td>Nucleation rate constant ($b_k$)</td>
<td>0.038</td>
<td># $\mu$m$^{-3}$ s$^{-1}$</td>
</tr>
<tr>
<td>Nucleation order constant ($b$)</td>
<td>3.417</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 3. Experimental results in the case of supersaturation controlled experiments; (A) - $S_y = 0.6 \text{ wt\%}$, experiment used for parameter identification, (B) - $S_y = 0.3 \text{ wt\%}$, experiment used for validation.

Figure 4. Dynamic evolution of modelled and experimental CSD for experiment A.
Figure 5 shows the comparison between the experimental and modelled concentration and weight mean size along the batch, which are also in good agreement. The combined QMOM-MOCH can be used not only for the model identification but also for CSD prediction. The simulation time for the reconstruction of the entire evolution of the CSD during the batch, only takes a few seconds. For even better computational performance the analytical estimator given by equations (16)-(17) can be used. Figure 6 shows the CSD for the seed, selected samples during the batch and the final CSD for experiment B in the case of applying the analytical estimator with initial concentration, temperature profile and seed distribution from the experiments. In this case the supersaturation was well maintained at its constant setpoint. The simulated and experimental CSD are in good agreement overall. However, the experimental CSD shows evidence of secondary nucleation during the batch, indicated in Figure 6 by the secondary CSD peak developed during the crystallization. The analytical estimator is derived based on the assumption of constant supersaturation and neglecting nucleation. Therefore, initializing it with the seed CSD and applying it in open-loop, the analytical estimator is not able to predict the development of the secondary peak. However, in the case of many practical applications the online measurement of the CSD is available (e.g. by using focused beam reflectance measurement coupled with inverse geometric modelling to transform chord length distribution into size distribution). In these cases the analytical estimator can be used in closed-loop, initializing it with the new CSD measurement every time it becomes available. Figure 7 illustrates the results when the estimator was initialized with the measure CSD after 30 min. The effect of the secondary nucleation, which occurred in the first 30 minutes of the batch, on the final CSD is partially predicted. The proposed method can be used as an efficient estimator for monitoring and predicting the CSD at the end of the batch or in off-line or on-line optimization approaches for designing crystallization systems to produce consistently the desired final CSD.
5. Conclusions

The paper describes a new methodology of solving population balance equations. The approach combines the quadrature method of moments (QMOM) with the method of characteristics (MOCH), and provides an computationally efficient method of reconstructing the crystal size distribution (CSD). Applying the approach in conjunction with supersaturation control at constant supersaturation, analytical expressions can be derived for the estimation of the CSD for growth dominated processes. The QMOM-MOCH approach and the analytical CSD estimator are evaluated in the case of the seeded crystallization of potash alum in water with size dependent growth. Experimental and simulation results demonstrate the efficiency of the proposed approach.

6. References


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