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Product quality improvement of batch crystallizers by a batch-to-batch optimization and nonlinear control approach

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Abstract

Batch crystallization is one of the widely used processes for separation and purification in many chemical industries. Dynamic optimization of such a process has recently shown the improvement of final product quality in term of a crystal size distribution (CSD) by determining an optimal operating policy. However, under the presence of unknown or uncertain model parameters, the desired product quality may not be achieved when the calculated optimal control profile is implemented. In this study, a batch-to-batch optimization strategy is proposed for the estimation of uncertain kinetic parameters in the batch crystallization process, choosing the seeded batch crystallizer of potassium sulfate as a case study. The information of the CSD obtained at the end of batch run is employed in such an optimization-based estimation. The updated kinetic parameters are used to modify an optimal operating temperature policy of a crystallizer for a subsequent operation. This optimal temperature policy is then employed as new reference for a temperature controller which is based on a generic model control algorithm to control the crystallizer in a new batch run.

Keywords: Batch crystallization; Batch-to-batch optimization; Parameter estimation; Generic model control

1. Introduction

A crystallization process is one of the major processes for product separation in fine chemical, food, mineral, petrochemical, and pharmaceutical industries [1]. Considering the operation of crystallizers, a batch process is preferable as a larger mean crystal size and narrower crystal size distribution (CSD) can be achieved. In general, the CSD which is typically characterized by the mean and variance of crystal size is a key property to control this process because it directly affects final product qualities. Therefore, finding an optimal operating condition and effective control strategy to obtain the crystals with a desired CSD is significant in order for improving the performance of batch crystallization processes and at the same time reducing difficulties in downstream processing [2].

In the formation of a crystal, a driving potential is the nonequilibrium state of the system measured by a relative supersaturation. For case of batch crystallizations, a solution temperature profile affects the supersaturation profile which has a strong effect on the CSD via kinetic phenomena (i.e., growth and nucleation of crystals), and therefore is often employed to indirectly control this process [3,4]. In the past years, various cooling strategies such as linear, natural, and controlled cooling have been widely investigated. Hojjati and Rohani [5], for example, investigated the effect of cooling rate policy on the level of supersaturation for batch crystallization of ammonium sulfate production. Four cooling strategies consisting of a natural, linear, controlled, and impulse change in natural cooling policy were investigated and the results showed that at low seed loading, the controlled cooling policy is needed in order to ensure narrow final CSD with large mean size.

Recently, an optimization of batch crystallization processes has received considerable attention as it is a useful tool to design an optimal operating temperature which has a direct effect on the final-time CSD. Many previous studies have been focused on the computation and solution of such an optimization problem. Miller and Rawlings [6] proposed an open-loop optimal control strategy on a bench-scale potassium nitrate–water system. Implementation of the optimal cooling policy on this system leads to an increase in the weight mean size of crystal product. Costa et al. [2] proposed the optimal cooling methodology to improve product quality in an adipic acid crystallization process.

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Nomenclature

A	total heat transfer surface area (m^2)
b	nucleation rate exponent
B	nucleation rate (no. crystal s^{-1} g solvent^{-1})
C	solution concentration (g solute g solvent^{-1})
C_{m}	metastable concentration (g solute g solvent^{-1})
C_p	heat capacity of the solution (kJ kg^{-1} K^{-1})
C_{pj}	heat capacity of cooling water (kJ kg^{-1} K^{-1})
C_{s}	saturation concentration (g solute g solvent^{-1})
E	activation energy
f	population density of crystals (no. of crystals µm^{-1} g solvent^{-1})
F_j	cooling water flow rate (m^3 s^{-1})
g	growth rate exponent
G	growth rate (µm s^{-1})
ΔH	heat of crystallization (kJ kg^{-1})
k_{b}	birth rate coefficient (s^{-1} µm^{-3})
k_{g}	growth rate coefficient (µm s^{-1})
k_{v}	volumetric shape factor
K_1, K_2	GMC tuning parameters
L	characteristic crystal length (µm)
M	mass of solvent in the crystallizer (kg)
R	gas constant
t	time (min)
T	reactor temperature (K)
T_j	cooling jacket temperature (K)
$T_{j\mathrm{sp}}$	set point of the jacket temperature (K)
U	overall heat transfer coefficient (kJ m^{-2} h^{-1} K^{-1})
V_j	jacket volume (m^3)

Greek symbols

μ	moment of the CSD
μ_0	zeroth moment of the CSD (no. of crystals g solvent^{-1})
μ_1	first moment of the CSD (µm g solvent^{-1})
μ_2	second moment of the CSD (µm^2 g solvent^{-1})
μ_3	third moment of the CSD (µm^3 g solvent^{-1})
ρ	density of crystals (g µm^{-3})
ρ_j	density of cooling water (kg m^{-3})

Superscripts

n	nucleation
s	seeded crystal

Hu et al. [7] studied the optimization of batch-seeded crystallizers. The results show that the optimal cooling profile is able to reduce the volume of fine crystals. Most of these optimal temperature profiles rely on the accuracy of a crystallization process model which can be described by either a population balance model (PBE) or a moment model (the reduced order model of the PBE) coupled with mass and energy balances. However, from the view point of modeling, the growth and nucleation kinetics are the most important uncertain parameters. It was demonstrated that even such kinetic parameters can be typically determined by experiments, they are likely to have substantial errors [8].

Due to the presence of uncertain kinetic parameters, the calculated optimal control profile may not give an optimal performance when applied to real processes. To overcome this problem, an estimation of kinetic parameters may be required. According to Hu et al. [3], many research activities have been focused on the development of various methods such as polynomial fitting and optimization procedure, for the kinetic parameter estimation in batch crystallization processes. It has been known that all the state variables cannot be measured. This is especially for the CSD of which the on-line measurement is difficult and inaccurate. Thus, the developed techniques to estimate the parameter of the model should be based on the available and reliable measurements.

In this study, we propose a batch-to-batch optimization strategy integrated with an on-line nonlinear control methodology for controlling a crystallizer process, choosing the seeded batch crystallization of potassium sulfate as a case study. As the batch process is repetitive in nature, it would be possible to exploit information of previous batch results to improve the operation of a new batch. Here, an off-line measurement of a crystal size distribution which is obtained with reliability and accuracy through experimental analysis at the end of run is used to update kinetic parameters by solving a parameter optimization problem. These updated kinetic parameters are then used to modify the optimal operating temperature policy for a subsequent operation. Since the deviation from the desired optimal profile might cause an off-spec product, an on-line feedback control system should be considered [7]. However, only a few studies have focused on this topic; for example, Zhang and Rohani [9] applied a conventional PI control to track the optimal cooling temperature of a batch crystallizer. As it has been shown from the previous studies [10,11] that a generic model control (GMC) as a nonlinear model-based control algorithm is more effective and robust in tracking the optimal temperature profile than conventional PID controllers. Thus, in this study a generic model control (GMC) is integrated to the batch-to-batch optimization approach to control the crystallizer temperature following the desired profile.

2. Mathematical model of a seeded batch crystallizer

The classical framework for modeling batch crystallization processes consists of the population balance equation (PBE) describing a conservation equation for a number of crystals in a population. Based on the following basic assumptions; volume change in the system is assumed to be negligible; crystal agglomeration or breakage phenomena are neglected [12], the PBE can be mathematically expressed as

$$\frac{\partial f(L,t)}{\partial t}+G(t)\frac{\partial f(L,t)}{\partial L}=0 \tag{1}$$

where $f(L, t)$ is the population density of crystals at a characteristic length, L and time, t.

As the nucleation and growth of crystals rely on the liquid phase properties, the mass balance is used to explain the concentration change of the solute and can be shown in the following equation:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = -3\rho_{\mathrm{c}} k_{\mathrm{v}} G(t)\mu_2(t) \tag{2}$$

The energy balances for a batch crystallizer and jacket are as follows:

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -3\frac{\Delta H_{\mathrm{c}}}{C_p}\rho_{\mathrm{c}} k_{\mathrm{v}} G(t)\mu_2(t) - \frac{UA}{MC_p}(T(t) - T_j(t)) \tag{3}$$

$$\frac{\mathrm{d}T_j}{\mathrm{d}t} = \frac{F_j}{V_j}(T_{j\mathrm{sp}}(t) - T_j(t)) + \frac{UA}{\rho_j V_j C_{pj}}(T(t) - T_j(t)) \tag{4}$$

The *i*th moment of the population density is defined in terms of the population density function by

$$\mu_i = \int_0^\infty f(L,t)L^i\,\mathrm{d}L \tag{5}$$

In the formation of a crystal, two steps are occurred: the birth of a new particle and its growth to macroscopic size. The driving potential for both rates is the nonequilibrium state of the system measured by a relative supersaturation (*S*):

$$S = \frac{C - C_{\mathrm{s}}(T)}{C_{\mathrm{s}}(T)} \tag{6}$$

The rates of crystal nucleation (*B*) and growth (*G*) can be expressed in Eqs. (7) and (8):

$$B(t) = k_{\mathrm{b}}\,\mathrm{e}^{-E_{\mathrm{b}}/RT} S^{\mathrm{b}}\mu_3(t) \tag{7}$$

$$G(t) = k_{\mathrm{g}}\,\mathrm{e}^{-E_{\mathrm{g}}/RT} S^{\mathrm{g}} \tag{8}$$

The control purpose of a crystallization process is to manage the nucleation and growth rates to achieve the desired crystal size. Well-controlled crystallization processes is usually operated in the metastable zone bounded by the saturation concentration and the metastable limit, $C_{\mathrm{s}} \le C \le C_{\mathrm{m}}$, in order to avoid uncontrolled nucleation of crystals.

In this work, the seeded batch crystallizer of potassium sulfate studied by Shi et al. [13] is considered. The value of the model parameters are shown in Table 1. The following equations are used to calculate the saturation and metastable concentrations corresponding to the solution temperature, *T*:

$$C_{\mathrm{s}}(T) = 6.29 \times 10^{-2} + 2.46 \times 10^{-3}T - 7.14 \times 10^{-6}T^2 \tag{9}$$

$$C_{\mathrm{m}}(T) = 7.76 \times 10^{-2} + 2.46 \times 10^{-3}T - 8.10 \times 10^{-6}T^2 \tag{10}$$

The PBE called “a population model” (Eq. (1)) is solved using a solution methodology proposed by Hu et al. [2,7]. Based on the concept of the population balance that describes the state of the CSD, the PBE is transformed by a finite difference method to a set of algebraic equations. The population densities in the absence of crystal aggregation and breakage at time t_1 and $t_2 = (t_1 + \Delta t)$ can be related by

$$f(L_1, t_1)\Delta L_1 = f(L_2, t_1 + \Delta t)\Delta L_2 \tag{11}$$

Table 1
Model parameters of a seeded batch crystallizer

Parameters	Value
b	1.45
k_{b} (s μm^3)$^{-1}$	285.0
E_{b}/R (K)	7517.0
U (kJ (m^2 h K)$^{-1}$)	1800.0
ΔH (kJ kg^{-1})	44.5
M (kg)	27.0
k_{v}	1.5
V_j (m^3)	0.015
ρ_j (kg m^{-3})	1000.0
g	1.5
k_{g} ($\times 10^8$ μm s^{-1})	1.44
E_{g}/R (K)	4859.0
A (m^2)	0.25
C_p (kJ (kg K)$^{-1}$)	3.8
ρ_{c} ($\times 10^{-12}$ g μm^{-3})	2.66
t_{f} (min)	30.0
F_j (m^3 s^{-1})	0.001
C_{pj} (kJ (kg K)$^{-1}$)	4.184

The definition of growth rate is defined when Δt is small as

$$L_2 \approx L_1 + G(L_1, t_1)\Delta t \tag{12}$$

and

$$L_2 + \Delta L_2 \approx L_1 + \Delta L_1 + G(L_1 + \Delta L_1, t_1)\Delta t \tag{13}$$

Subtracting Eq. (13) by Eq. (12) yields

$$\begin{aligned}\Delta L_2 &\approx \Delta L_1 + (G(L_1 + \Delta L_1, t_1) - G(L_1, t_1))\Delta t \\ &\approx \left(1 + \left.\frac{\partial G(L, t_1)}{\partial L}\right|_{L=L_1}\Delta t\right)\Delta L_1\end{aligned} \tag{14}$$

Substituting Eq. (14) into Eq. (11) gives

$$f(L_2, t_1 + \Delta t) \approx \frac{f(L_1, t_1)}{1 + (\partial G(L, t_1)/\partial L)|_{L=L_1}\Delta t} \tag{15}$$

Therefore, the PBE are defined as algebraic equations for the evaluation of CSD with size L_2 at time t_2 in terms of the CSD with size L_1 at time t_1.

The initial distribution of the seeded crystals in the batch crystallizer is assumed to be a parabolic distribution as the function of the crystal characteristic length ranging from 250 to 300 μm [13]:

$$f(L, 0) = \begin{cases} 0.0032(300 - L)(L - 250) & \text{for } 250\,\mu\mathrm{m} \le L \le 300\,\mu\mathrm{m} \\ 0 & \text{for } L < 250\,\mu\mathrm{m} \text{ and } L > 300\,\mu\mathrm{m} \end{cases} \tag{16}$$

In addition, the boundary condition is defined as the ratio of nucleation and growth rate of crystals with $L = 0$:

$$f(0, t) = \frac{B(t)}{G(t)} \tag{17}$$

It should be noted that although the population model can be directly solved, its implementation in an optimization problem is very time-consuming. Recently, the development in the method of moments leads to a reduced order model (called "the moment model") in which the key dynamics of the crystallization process are taken into account [12]. This method allows the model to be solved quickly and efficiently. As a consequence, in this work the population model represents the actual crystallization process whereas the moment model is used in the formulation of an optimization problem and the design of a nonlinear model-based control.

Following the moment model approach, the population model (Eq. (1)) is transformed to a set of ordinary differential equations (ODEs). The rate equation of moments is derived by determining separately the moments of the seed and nuclei classes for the CSD as in Eqs. (18) and (19):

$$\frac{\mathrm{d}\mu_0^{\mathrm{n}}}{\mathrm{d}t} = B(t), \qquad \frac{\mathrm{d}\mu_i^{\mathrm{n}}}{\mathrm{d}t} = iG(t)\mu_{i-1}^{\mathrm{n}}(t), \quad i = 1, 2, 3 \tag{18}$$

$$\mu_0^{\mathrm{s}} = \text{constant}, \qquad \frac{\mathrm{d}\mu_i^{\mathrm{s}}}{\mathrm{d}t} = iG(t)\mu_{i-1}^{\mathrm{s}}(t), \quad i = 1, 2, 3 \tag{19}$$

The overall ith moments are defined as $\mu_i = \mu_i^{\mathrm{n}} + \mu_i^{\mathrm{s}}$. It is noted that since the crystal breakage or agglomeration model was not considered in the proposed crystallizer model, the total number of the crystals growing from seeds remains constant which is determined by the initial seed size distribution.

3. Batch-to-batch optimization approach

As batch processes are repetitive in nature, it would be possible to use information from the previous batch to improve the operation of a new batch. Here a batch-to-batch optimization approach is proposed to estimate kinetic parameters, i.e., k_{b} and k_{g}, which are important for the prediction of crystal formation. The identification relies on the off-line measurement of a crystal size distribution (CSD) obtained at the end of batch run. Fig. 1 shows the schematic of an integrated batch-to-batch optimization with GMC control proposed in this study. As can be seen from the figure, once the CSD of product at the end of operation is measured, the ith moment of the population density of the crystals ($\mu_{i,\mathrm{process}}$) is calculated using Eq. (5) and compared with that predicted from a moment model ($\mu_{i,\mathrm{model}}$). It is noted here that the crystallization process is represented by the population model while the model of crystallizer, which is used within an optimization and control framework, is based on the moment model. New updated value of the constant kinetic parameters (k_{b} and k_{g}) is determined by solving a dynamic optimization problem with an objective to minimize such an error (Eq. (20)). In this study, a sequential optimization method in which the dynamic optimization is transformed into a nonlinear programming problem is applied to find the new estimate of the kinetic parameters. With the initial guess of the constant kinetic parameters, the crystallizer models consisting of the moment model of crystallization (Eqs. (18)–(19)) and the mass and energy balances (Eqs. (2)–(4)) are integrated using the Matlab ode15 s routine which is based on the backward differentiation formulas (BDFs) and the objective function is then determined. The nonlinear programming problem is solved by a sequential quadratic programming (SQP) method using the fmincon routine in Matlab optimization toolbox in order to compute a new value of the parameters. The sequence continues until the optimal value of the objective function is found satisfying a specified accuracy:

$$\min_{k_{\mathrm{b}},k_{\mathrm{g}}} \sum_{i=0}^{3} \left(\mu_i^{\mathrm{process}}(t_{\mathrm{f}}) - \mu_i^{\mathrm{model}}(t_{\mathrm{f}})\right)^2 \tag{20}$$

subject to

- the moment model of crystallization (Eqs. (18)–(19));
- the mass and energy balances (Eqs. (2)–(4));
- $k_{\mathrm{b}},\ k_{\mathrm{g}} > 0$

It should be noted here that the measured data of the final-time CSD from the last batch is only used to update the kinetic parameters in the proposed method. In the sequence of batch operations, each batch is operated under different optimal cooling policy. Therefore, if all previous batch data are used to identify the parameters, a set of models, with different operating temperature profile, to describe each batch crystallizer is required to predict the value of the ith moments which is compared with that obtained from each batch, resulting in a complicated parameter optimization problem.

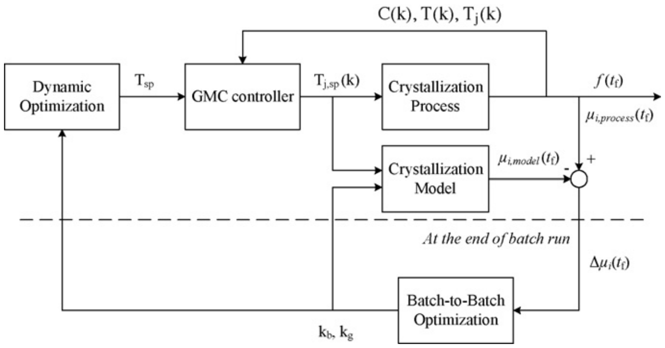

Fig. 1. Control strategy integrated with batch-to-batch optimization for updated kinetic parameter.

3.1. Formulation of a dynamic optimization problem

When the kinetic parameters in the moment model of the seeded batch crystallizer are updated via the batch-to-batch optimization strategy, they are employed for computing an optimal operating temperature policy of the crystallizer for a new batch run. In batch crystallization processes, the fine crystals usually affect both product quality and process economics. Moreover, they can also cause difficulties in downstream processing equipment (i.e., filtration, drying). For this reason, the aim of a dynamic optimization is to determine an optimal temperature profile minimizing the total volume of fine crystals represented by the third moment of crystals, μ_3^{n}, whereas the total volume of seeded crystals has to satisfy the product quality requirement. The dynamic optimization problem can be stated mathematically as follows:

$$\min_{T(t)} \mu_3^{\mathrm{n}}(t_{\mathrm{f}}) \tag{21}$$

subject to

- the crystallizer model equations: Eqs. (2), (18) and (19);
- $C_{\mathrm{s}} \leq C \leq C_{\mathrm{m}}, \quad T_{\min} \leq T \leq T_{\max},$
  $\mu_3^{\mathrm{s}}(t_{\mathrm{f}}) \geq 8.3301 \times 10^9$

where $T_{\min}$ and $T_{\max}$ is chosen as 303 and 323 K, respectively. The final batch time, t_{f}, is 30 min. The performance constraint on the total volume of seeded crystals (μ_3^{s}) is included in the dynamic optimization problem in order to guarantee that the requirement of a final product quality is satisfied.

As in the parameter optimization problem, the sequential optimization approach is also employed to solve the formulated dynamic optimization problem. Since the cooling temperature is the function of operating time, the temperature profile as an optimization variable is approximated by a piecewise constant function. With the initial guess of temperature value in each interval, the crystallizer model equations (Eq. (2), (18) and (19)) are solved and then the objective function is evaluated. The resulting nonlinear programming problem is solved to determine a new set of the temperature value in each time interval. This procedure is repeated until the optimal temperature profile is found.

4. Generic model control algorithm

A generic model control (GMC), one of the nonlinear model-based control algorithms, is successfully applied to a number of chemical processes [10,11]. This is because nonlinear process models can be interpreted straightaway in the GMC control algorithm to generate optimal manipulated inputs, and the controller parameters can be easily tuned [14].

The general form of GMC algorithm can be given as

$$\frac{\mathrm{d}y}{\mathrm{d}t} = K_1(y_{\mathrm{sp}} - y) + K_2 \int_0^{t_{\mathrm{f}}} (y_{\mathrm{sp}} - y)\,\mathrm{d}t \tag{22}$$

where y represents the controlled variables, K_1 and K_2 are the GMC tuning parameters determined by choosing a target profile of the controlled variable [14].

To implement the GMC, an energy balance around the crystallizer as in Eq. (3) is needed. It provides the relation between a controlled variable (crystallizer temperature) and a manipulated variable (jacket temperature). Replacing T for y in Eq. (22) and rearranging to obtain T_j as follows:

$$T_j = T + \frac{MC_p}{UA}\left(K_1(T_{\mathrm{sp}} - T) + K_2 \int_0^{t} (T_{\mathrm{sp}} - T)\,\mathrm{d}t + \left(\frac{\Delta H}{C_p} 3\rho k_{\mathrm{v}} G(t)\mu_2(t)\right)\right) \tag{23}$$

It is note here that the concentration and temperature are assumed to be measured and the second moment (μ_2) can be computed from the moment model. The integral term in Eq. (23) can be approximated by numerical integration. This leads to the discrete-time form of the GMC algorithm as given in the following equation:

$$T_j(k) = T(k) + \frac{MC_p}{UA}\left(K_1(T_{\mathrm{sp}} - T(k)) + K_2 \sum_0^{t} (T_{\mathrm{sp}} - T(k))\Delta t + \left(\frac{\Delta H}{C_p} 3\rho k_{\mathrm{v}} G(k)\mu_2(k)\right)\right) \tag{24}$$

where Δt is the sampling time.

Since the jacket temperature determined from Eq. (24) is an actual temperature in the crystallizer which is not a set point or inlet jacket temperature. In order to compensate the effect of a dynamic of the jacket control system, a first order model with time constant, $\tau_{j,}$ is assumed. The jacket temperature set point can be computed by

$$T_{j\mathrm{sp}}(k) = T_j(k-1) + \tau_j \left(\frac{T_j(k) - T_j(k-1)}{\Delta t}\right) \tag{25}$$

In this work, water is used as coolant, thus the jacket temperature set point is bounded between 293 and 323 K.

5. Simulation results

In the first case study, the effect of cooling modes, i.e., linear and optimal cooling policy, on the control performance of a seeded batch crystallizer in a nominal case where all parameters are known exactly as given in Table 1, is illustrated. Under the conventional linear cooling policy, the temperature set point is cooled down linearly from 323 to 303 K. On the other hand, under the optimal cooling policy, the profile of the temperature set point is determined by solving a dynamic optimization problem as mentioned earlier. It is noted that a piecewise constant function using 60 time interval with equal length is used to approximate the temperature profile. Once the profile of the temperature set point is specified, a GMC controller is implemented to drive the temperature of the crystallizer following the desired set point. Based on the guideline given by [14] for setting the GMC tuning parameters, the values of K_1 and K_2 are chosen as 0.013 and 10^{-10}, respectively.

Figs. 2 and 3 show the crystallizer temperature and the solution concentration profiles under the two cooling policies. Simulation result presents that the solution concentration can be maintained within the metastable zone keeping away from uncontrolled nucleation of crystals. Further, it can be seen from Fig. 3 that at the start of batch run, the optimal temperature set point of the crystallizer cannot be perfectly tracked since the lower bound on the jacket temperature of 293 K is fixed; water is selected as coolant in this case. With the use of other coolants of which the lower limit of the temperature can be determined below 293 K, the temperature set point could be tracked rapidly; however, it might lead to higher operating cost. The product quality in terms of the total volume of fine and seeded crystals is shown in Table 2. The results indicated that the optimal cooling policy with GMC controller gives better final product

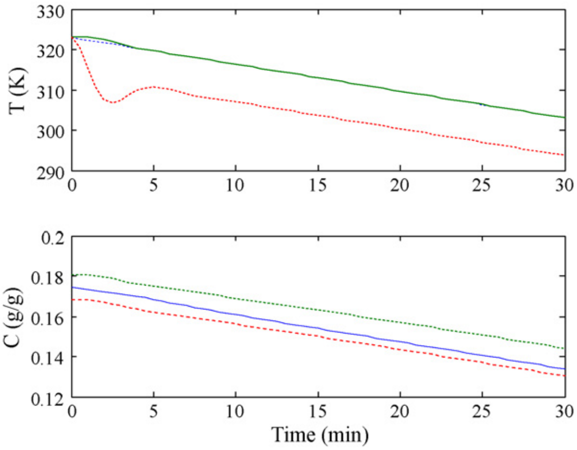

Fig. 2. The reactor temperature (T_{sp}: dotted; T: solid; T_j: dashdot) and concentration profiles (C_s: dotted; C: solid; C_m: dashdot) under conventional linear cooling temperature policy integrated with GMC.

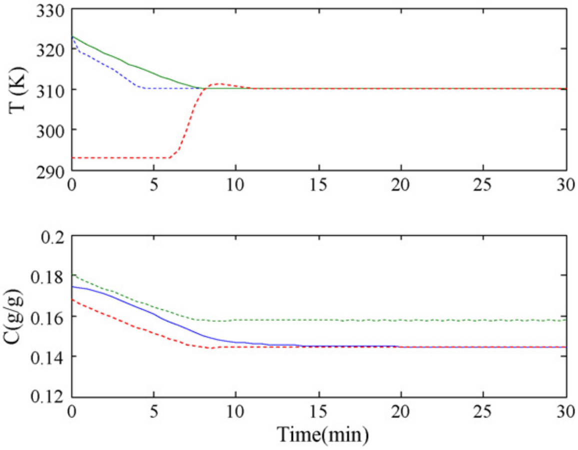

Fig. 3. The reactor temperature (T_{sp}: dotted; T: solid; T_j: dashdot) and concentration profiles (C_s; dotted; C: solid; C_m: dashdot) under off-line optimal cooling temperature policy integrated with GMC.

Table 2
The final product quality in terms of the total volume of fine and seeded crystals in the nominal case

Operating temperature policy	$\mu_3^n(t_f)$ (μm^3 g solvent^{-1})	$\mu_3^s(t_f)$ (μm^3 g solvent^{-1})
Linear cooling with GMC	1.4015×10^9	1.0090×10^{10}
Optimal cooling with GMC	6.3835×10^8	8.3600×10^9

Table 4
The kinetic model parameters used in the moment model

	k_b (s^{-1} μm^{-3})	k_g ($\times 10^8$ μm s^{-1})
Mismatch kinetic parameters (Batch I)	342.0	1.728
Updated kinetic parameters (Batch II)	283.6	1.440

quality compared with the conventional linear cooling policy; the total volume of fine crystals is decreased by 54.4%. Even thought the total volume of seeded crystals decreases when the optimal cooling policy is applied, it still satisfies the requirement of the product quality ($\mu_3^s \geq 8.3301 \times 10^9$). The average product qualities under the optimal operation in terms of the ith moments computed from the CSD at final batch time and those obtained from the moment model are provided in Table 3. Small relative differences of the actual and predicted value with less than 4% are observed. This confirms that the moment model can be reasonably employed to represent crystallization processes.

Next, the performance of the batch-to-batch optimization scheme with GMC is tested in case of a model-plant mismatch. The process condition is the same as the earlier simulation except for the kinetic parameters. We assume that the moment model contains some errors in the kinetic parameters of the nucleation and growth rates; 20% increase of k_b and k_g are introduced. It is found that when implementing the calculated optimal temperature profile obtained by the solution of the dynamic optimization problem with respect to incorrect kinetic parameters to the crystallizer (Batch I), the final crystal product is off-spec; the average total volume of seeded crystal (μ_3^s) of 8.3172×10^9 is less than its specification. To avoid this problem for a new batch run (Batch II), a batch-to-batch optimization approach is considered. Following this approach, information of the CSD measured at the final time from the previous run is used to update the kinetic parameters, i.e., k_b and k_g. That is, the actual ith moments ($\mu_{i,\text{process}}$) are calculated based on the measured CSD and compared with the predicted ith moments ($\mu_{i,\text{model}}$). The dynamic optimization is formulated as described in Section 3 and solved to find new estimated k_b and k_g with an objective to minimize the difference of $\mu_{i,\text{process}}$ and $\mu_{i,\text{model}}$. The updated k_b and k_g is used to modify an optimal cooling policy for the new batch run. It can be seen from Table 4 that the updated kinetic parameters approach the actual values (see Table 1). With these updated values, the optimal temperature profile is re-computed and implemented to control the crystallizer at the subsequent batch. The results in Table 5 show that at the final time, the total volume of seeded crystals satisfies

Table 3
Comparison of the final product properties of crystals predicted from the population model and moment model

ith moments	$\mu_0(t_f)$ (no. of crystals g solvent^{-1})	$\mu_1(t_f)$ ($\times 10^4$ μm g solvent^{-1})	$\mu_2(t_f)$ ($\times 10^7$ μm^2 g solvent^{-1})	$\mu_3(t_f)$ ($\times 10^9$ μm^3 g solvent^{-1})
Population model (actual process)	488	6.7478	2.0968	8.9984
Moment model	501	6.9283	2.0726	8.6510

Table 5
Comparison of the total volume of fine and seeded crystal obtained with/without updating kinetic parameters for next batch operation

	$\mu_3^{\mathrm{n}}(t_{\mathrm{f}})$ ($\times 10^8$ $\mu\mathrm{m}^3$ g solvent^{-1})	$\mu_3^{\mathrm{s}}(t_{\mathrm{f}})$ ($\times 10^9$ $\mu\mathrm{m}^3$ g solvent^{-1})
Mismatch kinetic parameters (Batch I)	6.2742	8.3172
Updated kinetic parameters (Batch II)	6.3789	8.3582

the requirement while the total volume of fine crystals is minimized. From these results, it is clearly indicated that the product quality and process efficiency can be improved by using the batch-to-batch optimization strategy integrated with the GMC control.

6. Conclusion

A batch-to-batch optimization strategy for kinetic parameter estimation is developed and implemented to a seeded batch crystallization of potassium sulfate production in this study. Based on the knowledge in a crystal size distribution of final product, the kinetic parameters involving the nucleation and growth rate of crystals are updated and then used to determine an optimal operating temperature policy for a new batch. The obtained optimal temperature policy is controlled by a generic model control (GMC) algorithm. In the nominal case where all model parameters are exactly known, the performance of the optimal cooling policy is better than that of the linear cooling policy as smaller volume of fine crystals is found at the final time of operation. Under the model-plant mismatch in kinetic parameters, it is demonstrated that the proposed batch-to-batch optimization scheme give a good estimate of the kinetic parameters and can improve the product quality and process efficiency of the seeded batch crystallizer.

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References

[1] P.A. Larsen, D.B. Patience, J.B. Rawlings, Industrial crystallization process and control, IEEE Control Syst. Mag. (2006) 70–80.
[2] C.B. Costa, A.C. Costa, R.M. Filho, Mathematical modeling and optimal control strategy development for an adipic acid crystallization process, Chem. Eng. Process. 44 (2005) 737–753.
[3] Q. Hu, S. Rohani, D.X. Wang, A. Jutan, Optimal control of a batch cooling seeded crystallizer, Powder Technol. 156 (2005) 170–176.
[4] N. Doki, N. Kubota, A. Sato, M. Yokota, Effect of cooling mode on product crystal size in seeded batch crystallization of potassium alum, Chem. Eng. J. 81 (2001) 313–316.
[5] H. Hojjati, S. Rohani, Cooling and seeding effect on supersaturation and final crystal size distribution of ammonium sulphate in a batch crystallizer, Chem. Eng. Process. 44 (2005) 949–957.
[6] S.M. Miller, J.B. Rawings, Model identification and control strategies for batch cooling crystallizers, AIChE J. 40 (1994) 1312–1327.
[7] Q. Hu, S. Rohani, A. Jutan, Modeling and optimization of seeded batch crystallizers, Comp. Chem. Eng. 29 (2005) 911–918.
[8] J.B. Rawlings, S.M. Miller, W.R. Witkowski, Model identification and control of solution crystallization processes: a review, Ind. Eng. Chem. Res. 32 (1993) 1275–1296.
[9] G.P. Zhang, S. Rohani, On-line optimal control of a seeded batch cooling crystallizer, Chem. Eng. Sci. 58 (2003) 1887.
[10] A. Vega, F. Diez, J.M. Alvarez, Programmed cooling control of a batch crystallizer, Comp. Chem. Eng. 19 (1995) 471–476.
[11] N. Aziz, M.A. Hussain, I.M. Mujtaba, Performance of different types of controllers in tracking optimal temperature profiles in batch reactors, Comp. Chem. Eng. 24 (2000) 1069–1075.
[12] H.B. Matthews, Model identification and control of batch crystallization for an industrial chemical system, PhD thesis, University of Wisconsin at Madison, 1997.
[13] D. Shi, N.H. El-Farra, M. Li, P. Mhaskar, P.D. Christofides, Predictive control of particle size distribution in particulate processes, Chem. Eng. Sci. 61 (2006) 268–281.
[14] P.L. Lee, G.R. Sullivan, Generic model control (GMC), Comp. Chem. Eng. 12 (1998) 573–580.