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Supersaturation Control using Analytical Crystal Size Distribution Estimator for Temperature Dependent in Nucleation and Crystal Growth Phenomena

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Abstract. The specification of the crystal product is usually given in terms of crystal size distribution (CSD). To this end, optimal cooling strategy is necessary to achieve the CSD. The direct design control involving analytical CSD estimator is one of the approaches that can be used to generate the set-point. However, the effects of temperature on the crystal growth rate are neglected in the estimator. Thus, the temperature dependence on the crystal growth rate needs to be considered in order to provide an accurate set-point. The objective of this work is to extend the analytical CSD estimator where Arrhenius expression is employed to cover the effects of temperature on the growth rate. The application of this work is demonstrated through a potassium sulphate crystallisation process. Based on specified target CSD, the extended estimator is capable of generating the required set-point where a proposed controller successfully maintained the operation at the set-point to achieve the target CSD. Comparison with other cooling strategies shows a reduction up to 18.2% of the total number of undesirable crystals generated from secondary nucleation using linear cooling strategy is achieved.

1. Introduction

In crystallisation processes, the need to achieve the desired crystal products, particularly crystal size distribution (CSD) and to consistently improve the product quality requires an understanding of the fundamentals of crystallisation processes [1-2]. The fundamental driving force of the crystallisation process is supersaturation, where the most common method to achieve supersaturation is by cooling operation. During the cooling process, it is also essential to maintain operation within the metastable zone which is bounded by the saturation and metastable concentrations. This is due to the fact that if the crystallisation operation exceeds the metastable concentration then, the high supersaturation is expected which results in excessive nucleation. The excessive nucleation is undesirable in the crystallisation because the new crystals produced usually are considered fine particles at relatively low size. The production of these new crystals also affects the downstream process, such as fouling problem [2]. Therefore, it is necessary to generate necessary set-point for crystallisation operation.

Two approaches could be considered for generating set-point, namely the model-based design approach and direct design control approach [3]. In the model-based design approach, the set-point profile is obtained using dynamic optimisation, where it requires a detailed first principle model with



accurate model parameters, such as nucleation and growth kinetics. Thus, these approaches depend on the model accuracy which may not be possible to obtain. In direct design control, the optimal set-point is obtained from analytical CSD estimator and subsequently a feedback control system can be used to maintain the operation at its set-point. This approach does not require a detailed first principle model and close to optimal set-point can be obtained relatively fast [2].

The analytical CSD estimator originally developed by Nagy and Aamir [3] is able to generate the set-point that consists of both the supersaturation and the total batch time. It is computationally efficient and can be applied for size independent or size dependent crystal growth rates [3-4]. However the crystal growth kinetic neglects the dependence of temperature and thus the parameters are assumed constant. In the pharmaceutical crystallisation, the crystal growth kinetic is dependent on the temperature of crystallisation operation and thus the kinetic must be extended. Therefore the objective of this work is to extend the current analytical CSD estimator to cover the temperature dependence crystal growth rate. The application of this extended analytical CSD estimator is highlighted using potassium sulphate crystallisation where the set-point needed to achieve the desired target CSD is generated using the extended estimator. The performance of closed-loop simulation is also evaluated in terms of its ability to maintain the operation at the generated set-point and to achieve the target CSD. In addition, the performance comparison with other cooling strategies is also demonstrated.

2. Analytical CSD Estimator

Analytical CSD estimator has been developed based on the assumptions of constant supersaturation throughout the entire batch operation and based on the crystal growth dominant phenomena [2-4]. It consists of two main equations, firstly being the final CSD, followed by final characteristic length. Due to the size independence crystal growth, the shape of CSD is not changed but only the size of CSD will be increased. This estimator is applied to generate a supersaturation set-point that yields a target CSD on the condition the initial seed distribution and growth rate kinetics of the crystallisation are specified. However, the crystal growth kinetic neglect the dependence of temperature and thus the parameters are assumed constant. In this study, the Arrhenius expression is included in the crystal growth kinetic for the temperature dependent cases. The analytical CSD estimator model equations for temperature independent and temperature dependent crystal growths are shown in table 1.

Table 1. Analytical CSD estimators for the case of temperature independence/dependence crystal growths.

Characteristic	Final CSD	Final Characteristic Length
Crystal growth temperature independence $G_x = k_{gx} S^{gx}$	$f_{n,i} = f_{n0,i}$	$L_{x,i} = L_{x0,i} + k_{gx} S^{gx} t_c$
Crystal growth temperature dependence $G_x = k_{gx0} \exp(-E_g / RT) S^{gx}$	$f_{n,i} = f_{n0,i}$	$L_{x,i} = L_{x0,i} + k_{gx0} \exp(-E_g / RT) S^{gx} t_c$

The set-point candidates can be generated from the analytical CSD estimators in table 1 and the optimal set-point is then obtained by solving the model-based optimisation problem in Eqs. (1) to (2). The objective function is to minimise the sum of squares of relative errors between the predicted CSD obtained from the analytical CSD estimator and the desired target CSD.

$$\text{Minimise} \quad F_{obj} = \sum_{i=1}^N \left(\frac{f_{n,i} - f_{n,i,target}}{f_{n,i,target}} \right)^2 \quad (1)$$

$$\text{Subject to:} \quad S_{sp,min} \leq S_{sp} \leq S_{sp,max}; \quad t_{c,min} \leq t_c \leq t_{c,max}; \quad c_f \leq c_{f,batch} \quad (2)$$

Where N is the number of discretisation points, $f_{n,i}$ is the predicted CSD that is obtained from the analytical CSD estimator and $f_{n,i,target}$ is the desired target CSD, $c_{f,batch}$ is the expected solute concentration at the end of the batch and c_f represents the maximum acceptable solute concentration at the end of the batch to achieve the required yield [2].

3. Model Applications: Potassium Sulphate Crystallisation Case Study

3.1 Modelling of a Batch Crystallisation Process

The mathematic model of potassium sulphate crystallisation process is generated from the generic multi-dimensional model-based framework [5]. The population balance equation (PBE) is obtained based on these assumptions; the volume is constant, no effects of agglomeration and breakage are considered. The PBE obtained is solved using the method of classes [5] as shown in Eqs. (3)–(5).

$$\text{For } i = 1; \quad \frac{dN_1}{dt} + \frac{G_x}{2\Delta Cl} N_1 = B_{nuc} \quad (3)$$

$$\text{For } 1 < i < n; \quad \frac{dN_i}{dt} + \frac{G_x}{2\Delta Cl} N_i - \frac{G_x}{2\Delta Cl} N_{i-1} = 0 \quad (4)$$

$$\text{For } i = n; \quad \frac{dN_n}{dt} + \frac{G_x}{2\Delta Cl} N_n - \frac{G_x}{2\Delta Cl} N_{n-1} = 0 \quad (5)$$

The overall mass balance for potassium sulphate concentration in the solution is shown below:

$$\frac{dc}{dt} = -\frac{\rho_c k_v V}{m_w} \left(\sum_{i=1}^{i=N} S_{xi}^3 \frac{dN_i}{dt} \right) \quad (6)$$

The energy balance used for this operation is shown in Eq. (7).

$$\rho V c_p \frac{dT}{dt} = -\Delta H_c \rho_c k_v V \left(\sum_{i=1}^{i=N} S_{xi}^3 \frac{dN_i}{dt} \right) - U_1 A_1 (T - T_w) \quad (7)$$

The saturation and metastable concentrations for potassium sulphate are generated based on the following polynomial expressions as the function of the solution temperature [6].

$$c_{sat} = 6.29 \times 10^{-2} + 2.46 \times 10^{-3} T - 7.14 \times 10^{-6} T^2 \quad (8)$$

$$c_{met} = 7.76 \times 10^{-2} + 2.46 \times 10^{-3} T - 8.10 \times 10^{-6} T^2 \quad (9)$$

The temperature dependence nucleation and crystal growth rates are shown in Eqs. (10)–(11):

$$B_{nuc} = k_b \exp(-E_b / RT) S^b \quad (10)$$

$$G_x = k_g \exp(-E_g / RT) S^g \quad (11)$$

Where the relative supersaturation (S) is applied as $S = (c - c_{sat}) / c_{sat}$. The initial seed distribution of the seeded batch crystalliser is assumed to be a parabolic distribution as shown in Eqs. (12)–(13).

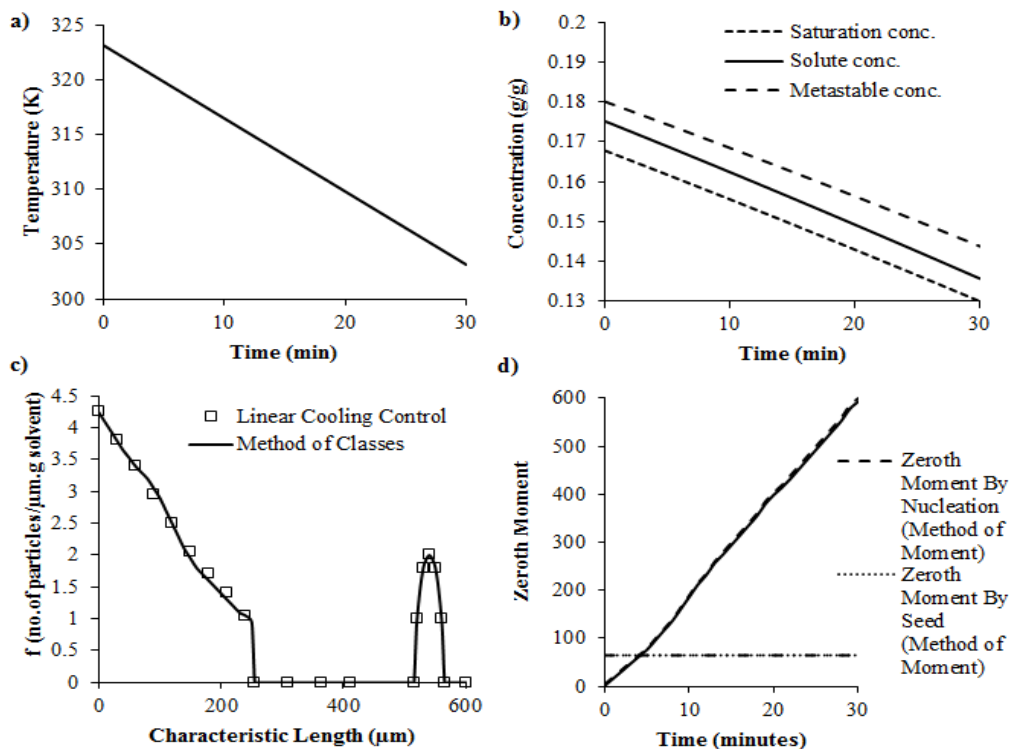
$$\text{For } 250 \mu\text{m} \leq L \leq 300 \mu\text{m}: \quad f(L,0) = 0.032(300 - L)(L - 250) \quad (12)$$

$$\text{For } L < 250 \mu\text{m}, L > 300 \mu\text{m}: \quad f(L,0) = 0 \quad (13)$$

The mathematical model for the potassium sulphate crystallisation process is developed in MATLAB 2014a software and is solved using the “ode15s” solver. Table 2 shows the parameter values used to solve the mathematical model. The open-loop simulation is validated with literature data [6-7] using the same operating conditions and parameters. Although the mathematical model used in this study is similar as published in the literature [6-7], in this work the PBE is solved using the method of classes.

Table 2. Parameter values for the seeded batch cooling crystalliser [6-7]

Parameters	Values	Units
Nucleation order, b	1.45	-
Kinetic coefficient for nucleation, k_b	285.01	$\mu\text{m}^3/\text{s}$
Growth order, g	1.5	-
Kinetic coefficient for crystal growth, k_g	1.44×10^8	$\mu\text{m}/\text{s}$
Arrhenius equation for nucleation, E_b/R	7517	K
Arrhenius equation for crystal growth, E_g/R	4859	K

**Figure 1.** Open-loop simulation for a) Temperature profiles, b) Concentration profiles, c) CSD comparison, d) Zeroth moment comparison

Based on the simulation results, figure 1a) shows the temperature is cooled down linearly from 323.15 K to 303.15 K. The potassium sulphate concentration in figure 1b) also follows the same trends where the concentration initially at 0.1742 g/g and is dropped steadily until 0.1372 g/g at the end of operation. Figure 1c) shows the final CSD obtained from method of classes is in good agreement with literature data, indicating the method of classes is indeed reliable. As shown in figure 1c), there are two peaks existing where the peak on the right is the crystals grown from initial seed and the other peak indicates the crystals formed by secondary nucleation. Although the seed of CSD has been grown from mean characteristic length of 275 μm to 512 μm , but the number of crystals produced from secondary nucleation is relatively high. The number of crystals produced from secondary nucleation is able to be determined by method of classes considering there is a clear gap between those peaks as shown in figure 1d). The total number of crystal seeds remains constant at 70 until the end of operation. This is due to no agglomeration and breakage is considered and thus the total number of crystal seeds is not changing. Meanwhile the total number of crystals formed from secondary nucleation is approximately 600 indicating the crystallisation process is also dominated by nucleation phenomena. Nevertheless, the model has been tested by comparing with the results of Shi et al. [6] and a good agreement has been achieved between both methods in terms of the final CSD.

3.2 Direct Design Control

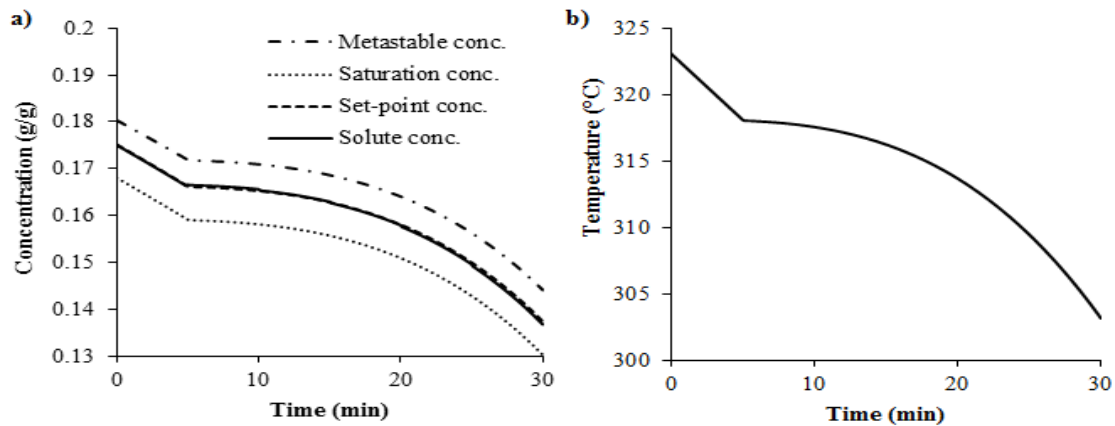


Figure 2. Closed-loop simulation for a) Concentration profiles, b) Temperature profiles

Based on the open-loop simulation, it is clearly shown that the linear cooling profile causes a production of a large number of crystals at relatively low characteristic length, which is undesirable in crystallisation process. Therefore, the direct design control using analytical CSD estimator is employed in order to reduce the total number of crystals produced from secondary nucleation while maintaining the desired final CSD. In this study, the final CSD obtained in figure 1c) is chosen as the target CSD. The model-based optimisation problem in Eqs. (1) to (2) is solved using a sequential quadratic programming (SQP) in order to obtain the optimal set-point. The optimal set-point consisting of the supersaturation set-point of 0.042 g/g that is to be maintained and the total crystallisation time of 30 minutes are obtained. A closed-loop simulation is then performed, where a proportional-integral (PI) controller has been employed in order to maintain the potassium sulphate concentration at the generated optimal set-point. Based on the closed-loop simulation results, it can be concluded that the potassium sulphate concentration initially started at 0.1742 g/g was successfully maintained at the set-point using the PI controller in figure 2a). Approximately, 0.1367 g/g of potassium sulphate concentration remains by the end of the operation. Figure 2b) shows the temperature initially decreased linearly from 323.15 K to 318.15 K and then further decreased steadily to 303.15 K at 30 minutes.

The evolution of CSD is shown in figure 3. Figure 3a) shows the seed of CSD at the start of the crystallisation operation where the aims to achieve the target CSD. At time of 20 minutes, the seed of CSD has been grown from initially mean characteristic length of 275 μm to 415 μm in figure 3b). Due to the sharp increase of temperature profiles in figure 2b), the potassium sulphate concentration is also decreased where the solute has been transferred into the seeds of crystal which explains the growth of crystal seeds. Meanwhile the nucleation effect is also dominant which explains the increment of the secondary peak from time frame of 0 to 30 minutes. Figure 3c) shows the CSD obtained from simulation is very close to the desired target at the final time of 30 minutes. This indicates the generated set-point is reliable for achieving the target CSD. The final CSD obtained is also compared with different cooling strategies; the linear cooling strategy and dynamic optimisation strategy. Figure 2d) shows the final CSD obtained is approximately similar except the secondary peak produced by the secondary nucleation. Among these three different cooling strategies, the optimal cooling strategy from direct design control shows the secondary peak has been reduced up to 18.2% compare to the peak produced from linear cooling strategy but approximately similar with dynamic optimisation. In this case, the lower secondary peak is preferred due to the fact that less number of new crystals has been produced. However, the CSD obtained from dynamic optimisation only gives the optimal cooling profile without the implementation of the feedback control and thus the CSD might differ. Meanwhile the direct design control considers both implementation covering the optimal cooling profile and closed-loop implementation involving PI control indicating its practicality.

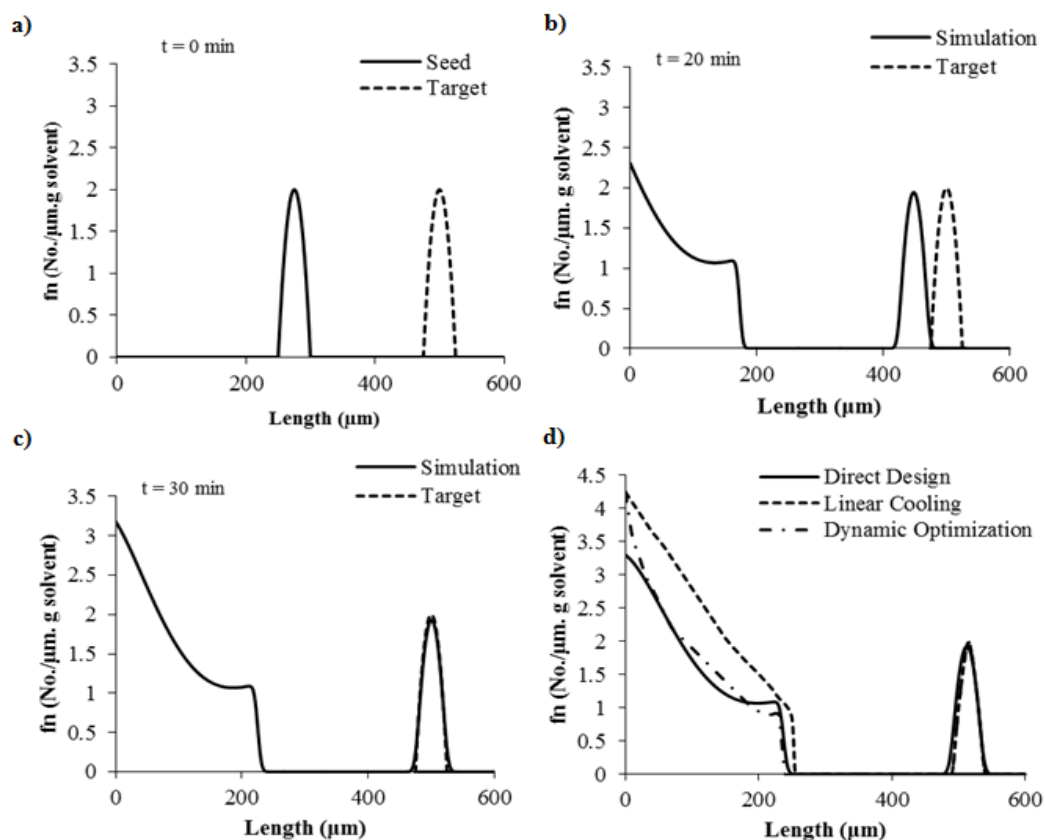


Figure 3. Evolution of CSD for a) At the start of the process, b) At time of 20 minutes, c) At the final time, d) Comparison using different cooling strategies

4. Conclusions

The application of extended analytical CSD estimator for achieving the desired target CSD is highlighted through potassium sulphate crystallisation. The extended estimator is covering the effects of temperature on the crystal growth rate. The open-loop simulation has been performed for potassium sulphate crystallisation and a good agreement has been obtained with literature data. The final CSD obtained in open-loop simulation is then used as the target CSD and the optimal set-point consisting of supersaturation set-point of 0.042 and 30 minutes crystallisation time has been generated from extended estimator. In the closed-loop simulation, the PI controller is successfully maintaining the operation at its set-point which results in achieving the desired target CSD. Comparison with other cooling strategies also indicated the optimal cooling strategy using direct design control manages to reduce the total number of crystals from secondary nucleation compared to linear cooling strategy.

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