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Cite as: AIP Conference Proceedings 2124, 020042 (2019); <https://doi.org/10.1063/1.5117102>
Published Online: 24 July 2019

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Evaluation of Controlled Cooling for Seeded Batch Crystallization Incorporating Dissolution

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Abstract. Crystallization is an essential solid-liquid separation technique which is widely used in the industry such as in pharmaceuticals, pigments, food, plastics, semi-conductors and others due to its capability to produce high quality of crystals. The final specification of the crystal product usually is given in terms of crystal size distribution (CSD), shape and purity. However achieving the target CSD for the case of batch seeded cooling crystallization is always a challenge due to the limited control on the production of fine crystals. Generally crystallization process is controlled to be operated in the metastable zone where the crystal particles will grow until the end of the operation. If the crystallization process is operated beyond the metastable concentration, excessive nucleation is expected due to the high supersaturation. As a consequence the target crystal product is able to achieve but there is unnecessary amount of fine crystals by the end of the operation. This unnecessary nucleation can be reduced by incorporating the crystallization process with dissolution phenomena where the temperature of the solution is controlled so that the solution is operated in the undersaturated condition. This condition is enabling the grown crystal particles to dissolve back into solution. Thus reducing the amount of fine crystals in the overall CSD. Therefore the objective of this study is to develop and evaluate controlled cooling for batch seeded crystallization of potassium nitrate incorporating dissolution phenomena. The mathematical model for potassium nitrate crystallization is developed and simulated in MATLAB software where it is validated against experimental data. The optimization algorithm is then developed in order to determine the set-point trajectory for closed-loop control. Based on this optimal trajectory a closed-loop control is proposed to maintain the crystallization operation at its set-point using two types of controller which consists of Proportional (P) and Proportional-Integral (PI) controllers. Two important criteria are measured in the closed-loop simulation which are the performance of PI controller to follow the given set-point trajectory and the achievement of target CSD. Based on the closed-loop control it is shown that the PI control is more superior than P control by maintaining the operation at its set-point and successfully achieved the desired CSD. In addition the production of fines particle is greatly reduced indicating this new optimal trajectory is capable of producing the target CSD and minimizes the effects of nucleation.

INTRODUCTION

Crystallization technique is considered favorable and widely used in variety industry due to its capability to produce high quality crystals [1]. Due to extensive use of this application, the needs of optimal operation and efficient process control strategy is highly demanding in order to achieve better performance in terms of product quality [2]. The quality of product which generally demonstrated by crystal size distribution (CSD) is an important control factor in crystallization because it has a significant effect on the efficiency of the downstream operations such as filtration and drying [3-7].

Understanding on the fundamentals of crystallization is an essential tool in generating necessary set-point trajectory for crystallization operation. In order to produce good quality of crystals, the crystallization process needs to be operated within metastable zone which is bounded by saturation concentration and metastable concentration. In this metastable zone, the supersaturation which is a driving force of crystallization process can be generated by cooling operation. Theoretically, the supersaturation level is essential for shaping the desired CSD. However, one of the most common problems during cooling crystallization process is to maintain the operation within the metastable

zone. If the crystallization operation exceeds the metastable concentration, the high supersaturation is expected to results in excessive nucleation. The excessive nucleation is undesirable in the crystallization because the new crystals produced usually are considered fine particles at relatively low size and may cause fouling in the downstream process [5-6]. On the contrary, the crystallization process operates near to saturation concentration line may results in longer operational time due to the low supersaturation level which contributing to the insufficient growth of crystal seeds [4]. Therefore, appropriate set-point trajectory generation for crystallization should be employed in order to produce desired CSD.

Several studies in batch crystallization under open-loop optimal control are known to perform better than uncontrolled natural cooling but it is subjected to severe robustness problems. Without applying appropriate kinetics and accurate control, the crystallization may results in producing smaller product crystals and excessive fine particles [4-5]. To simplify the model development, most batch crystallization studies in the literature only consider crystal growth and nucleation kinetics as such no dissolution is allowed. Although desired CSD is obtained, the amount of fine crystals produced is also significantly high. Dissolution if properly designed into the model, would become beneficial in terms of dissolving fine crystals produced by the secondary nucleation. The crystals particles grown from both seed crystals and secondary nucleation will dissolve according to the dissolution kinetics during reheating cycle.

In this paper, the study of seeded batch cooling crystallization for potassium nitrate is demonstrated using simulation under open-loop and closed-loop condition. Open-loop simulation represents the nominal cooling profile and the parameter estimation for the model is developed and validated against published literature [5]. The optimization algorithm to reduce secondary nucleation through dissolution is employed to determine the set-point trajectory for closed-loop control which is used to control the crystallization operation using Proportional (P) and Proportional-Integral (PI) controllers. The performance of the controllers in terms of its ability to maintain the operation at the generated set-point and achieving desired CSD is evaluated further in the next section.

MATHEMATICAL MODEL OF POTASSIUM NITRATE CRYSTALLIZATION PROCESS

The mathematical model of potassium nitrate crystallization process is generated from the generic multi-dimensional model-based framework [8]. The process conditions and assumptions as reported by Seki & Su [5] have been used for model validation. Firstly, the population balance equations (PBEs) to be used are selected. In the PBE formulation, the assumption for this model is size dependent growth of the one-dimensional PBE. Also, the dissolution phenomenon is considered.

$$\frac{\partial f_n(L,t)}{\partial t} + \frac{\partial G(L,S)f_n(L,t)}{\partial L} = B_{nuc} \quad (1)$$

This one-dimensional PBE is solved by using method of classes as shown in Equations (2)-(4). It is important to note that the solution of PBE in this work is different with the one used by Seki & Su [5]. The use of method of classes in this work is to demonstrate the capability of this method to incorporate the dissolution terms and to generate the CSD accurately.

For $i = 1$,

$$\frac{dN_1}{dt} + \frac{G_{x1}}{2\Delta Cl_2} N_2 + \frac{G_{x1} - G_{x0}}{2\Delta Cl_1} N_1 = B_{nuc} \quad (2)$$

For $1 \leq i \leq n$,

$$\frac{dN_i}{dt} + \frac{G_{xi}}{2\Delta Cl_{i+1}} N_{i+1} + \frac{G_{xi} - G_{xi-1}}{2\Delta Cl_i} N_i + \frac{G_{xi-1}}{2\Delta Cl_{i-1}} N_{i-1} = 0 \quad (3)$$

For $i = n$,

$$\frac{dN_n}{dt} + \frac{G_x}{2\Delta Cl} N_n + \frac{G_{x1} - G_{x0}}{2\Delta Cl} N_n = 0 \quad (4)$$

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

$$\frac{dc}{dt} = -\frac{\rho_c k_v V}{m_w} \left(\sum_{i=1}^{i=N} S_{xi}^3 \frac{dN_i}{dt} \right) \quad (5)$$

The energy balance used for this operation is shown in Equation (6).

$$\rho V c_p \frac{dT}{dt} = -\Delta H_c \rho_c k_v V \left(\sum_{i=1}^{i=N} S_{xi}^3 \frac{dN_i}{dt} \right) - U_1 A_1 (T - T_w) \quad (6)$$

The saturation concentrations for potassium nitrate is generated and adapted based on the following polynomial expressions as the function of solution temperature [5].

$$c_{sat} = 0.129 + 5.88 \times 10^{-3} T - 1.72 \times 10^{-4} T^2 \quad (7)$$

Secondary nucleation is assumed while the effect of agitation is neglected in the nucleation, crystal growth and dissolution equations. It has been assumed the crystal is grown or dissolved based on size dependent rate. The dissolution kinetics as well as the size dependence of the growth are fictional as suggested by Seki & Su [5]. The dissolution rate is set to have the same order of magnitude as the growth rate and a first-order dependence on the degree of under saturation is assumed. The models for secondary nucleation, crystal growth and dissolution rates are shown in Equations (8)-(10):

$$B_{nuc} = k_b S^b V \quad (8)$$

For $S \geq 0$,

$$G = k_g S^g (1 + \alpha_g L)^{\beta_g} \quad (9)$$

For $S < 0$,

$$G_d = k_d S^d (1 + \alpha_d L)^{\beta_d} \quad (10)$$

Where the relative supersaturation (S) is applied as $S = (c - c_{sat}) / c_{sat}$. The initial seed distribution used for this seeded operation is based on the uniform distribution adapted in [5-6] where it is characterized by the mass C_s , the average mean size L_s , and the percentage of width w of the distribution. The initial mean characteristic length is set to be 300 μm as shown in Fig. 1.

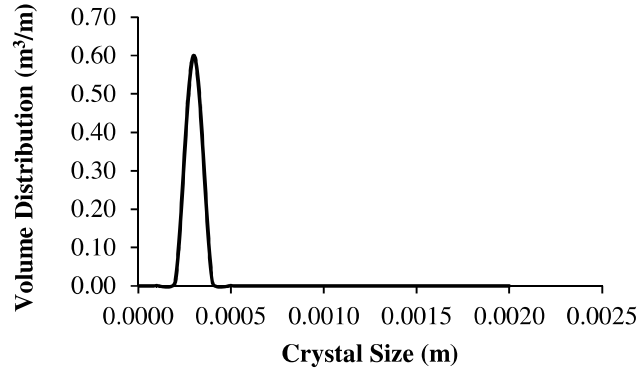


FIGURE 1. Initial seed of CSD

In addition to validate the model with experimental data, parameter estimation could also been developed and estimated as shown in the following equation:

$$F_{obj} = \min_{\theta} \left\{ \omega_T \sum_{i=1}^n \left(\frac{T_{calculated} - T_{exp}}{T_{exp}} \right)^2 + \omega_c \sum_{i=1}^n \left(\frac{c_{calculated} - c_{exp}}{c_{exp}} \right)^2 \right\} \quad (11)$$

This optimization algorithm can be used to predict the kinetic parameters of nucleation, crystal growth and dissolution rate. In total, there are 10 parameters that need to be estimated, such as $k_b, b, k_g, g, \alpha_g, \beta_g, k_d, d, \alpha_d, \beta_d$. These parameters are subjected to the $\theta_{min} < \theta < \theta_{max}$ and model equations as shown in Equations (8-10). From the equation, θ represents the parameter to be estimated, where θ_{min} is the lower bound of parameter and θ_{max} is the upper bound of parameter. The weightages used for temperature, ω_T and potassium nitrate concentration, ω_c are set at 0.5 and 0.2 respectively.

MODEL APPLICATIONS OF POTASSIUM NITRATE CRYSTALLIZATION CASE STUDY

The mathematical model for the potassium nitrate crystallization process is developed in MATLAB 2014b software and is solved using backward differentiation formula (BDF) method known as 'ode15s' solver using the initial conditions in Table 1. Also, the model parameters are estimated using Equation (11) and the optimization algorithm is solved using 'fmincon' solver available in MATLAB 2014b software and based on the simulation the objective function obtained is 4.5×10^{-05} . The parameters are then compared with literature data [5] as shown in Table 2. A good agreement has been achieved where the estimated kinetic parameters obtained in this work are very close with the expected value in literature. In addition, the confidence interval is also calculated and the intervals for each parameter are shown in Table 2. Overall, the confidence intervals shown in Table 2 exhibit significantly high level of confidence as the values are all narrow which show less uncertainty towards the true value. Apart from that, the open-loop simulation results for potassium nitrate crystallization process using estimated kinetic parameters are shown in Figs. 2 and 3.

TABLE 1. Operating conditions and major constraints used for optimization problem [5-6]

Nomenclature		Values
T_{feed}	Saturation temperature of feed, °C	30.0
T_{fin}	Final temperature, °C	20.0
t_{cool}	Cooling duration, min	120
t_{batch}	Batch time, min	150
C_s	Seed loading ratio, %	0.5
L_s	Seed size, μm	200
w	% Width of distribution, %	10
T_s^{\max}	Upper limit of seeding temperature, °C	30.0
T_s^{\min}	Lower limit of seeding temperature, °C	27.0
T^{\max}	Upper limit of crystallizer temperature, °C	30.5
T^{\min}	Lower limit of crystallizer temperature, °C	20.0
$c_0 = c_{sat}(30.0^\circ\text{C})$	Initial feed concentration, g/ g-water	0.459
ρ_c	Density, kg/ m^3	2.11×10^3
k_v	Volumetric shape factor	1

TABLE 2. Comparison of estimated nucleation, crystal growth and dissolution kinetic parameters versus crystallizer model parameters [5-6]

Parameters	Units	[5-6]	This work	Confidence Interval
Nucleation parameter k_b	#/s/g-water	4.64×10^5	4.21×10^5	0.51×10^5
Nucleation parameter b	-	1.78	1.59	0.31
Growth parameter k_g	m/s	1.1612×10^{-4}	1.0741×10^{-4}	0.023×10^{-4}
Growth parameter g	-	1.32	1.28	0.11
Growth parameter α_g	1/m	1000	1000	10
Growth parameter β_g	-	0.5	0.5	0.02
Dissolution parameter k_d	m/s	1.16×10^{-4}	1.19×10^{-4}	0.08×10^{-4}
Dissolution parameter d	-	1	1	0.01
Dissolution parameter α_d	1/m	1000	1000	10
Dissolution parameter β_d	-	-1.0	-1.0	0.01

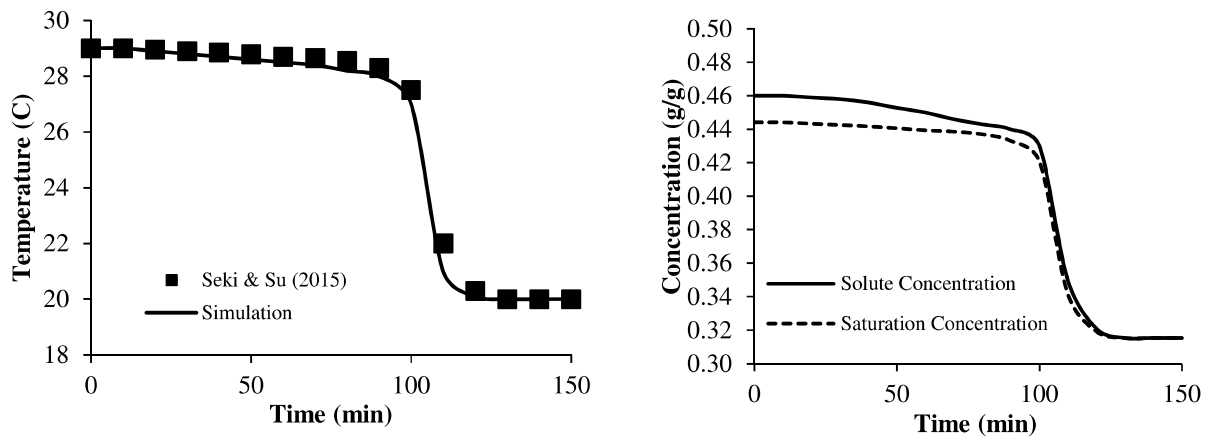


FIGURE 2. Temperature (left) and potassium nitrate concentration (right) profiles

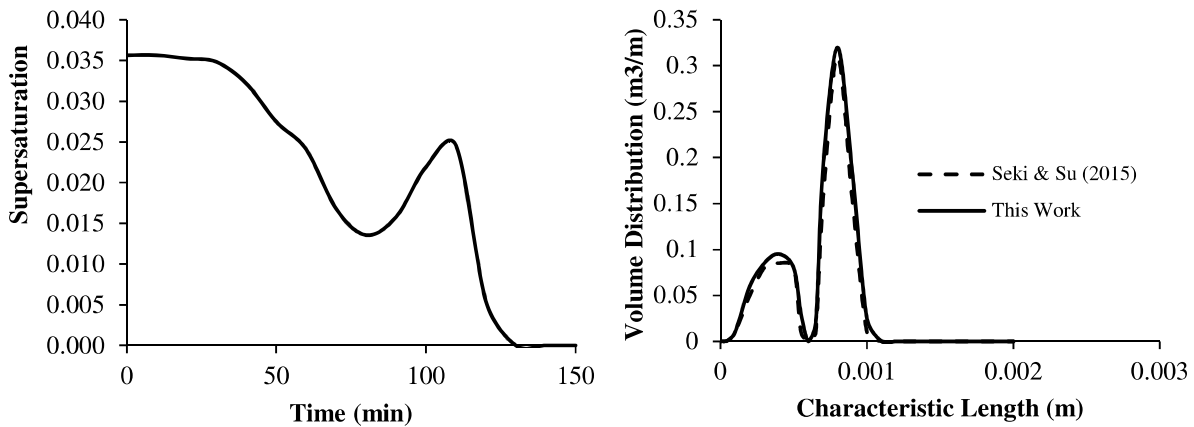


FIGURE 3. Supersaturation (left) and CSD obtained at final time (right) profiles

Based on the open-loop simulation results, Fig. 2 shows the temperature and concentration profiles of potassium nitrate crystallization. The temperature profile shows that the process is being cooled down gradually from 29°C to 20°C. It is noted that the generated temperature profile from this simulation is in good agreement with literature [5] indicating the model from this work is comparable with experimental data. The concentration profile has a similar trend with temperature profile where it has been dropped gradually from 0.46 g/g until it reaches 0.32 g/g at the end of the operation. It is also clearly shown that there are significant gap between solute concentration (potassium nitrate) and saturation concentration profile which shows that the crystallization starts exactly at the beginning of the process as supersaturation condition already reached.

The supersaturation profile as shown in Fig. 3 is initially decreasing as the temperature dropped and starts to increase again at approximately 80 minutes which is reflected from the sharp steepness of temperature profiles. From operational time of 0-80 minutes, the solute concentration operates far from saturation concentration where the high supersaturation level is obtained. This high supersaturation level increases the nucleation and crystal growth rate which promoting the production of crystal particles and growth of the crystal particles from the seed crystals. As the temperature profiles decreased sharply after 80 minutes, the supersaturation level is observed to have an increment in which is expected to contribute to the excessive production of fine particles due to the nucleation rate. Initially, as shown in Fig.1 there is only seed particles with the mean crystal size of 300 μm exist. At the end of crystallization process, as shown in Fig. 3 two peaks of CSD exist. Two peaks from the CSD profile are from the crystals grown from initial seed (right) and the lower value mean crystal size (left) formed from the secondary nucleation as the operation proceeds. After 120 minutes, a low supersaturation at the end of the process result in low

crystal growth rate as the solute concentration operates closer to the saturation concentration. Overall, the supersaturation profiles visibly shows that the supersaturation is positive which indirectly means that there is no dissolution of crystals involve in this case.

Also, Fig. 3 shows that the crystals have grown from mean crystal size of 300 μm to approximately 800 μm as the results from high supersaturation level. High supersaturation level contributes to the high nucleation and crystal growth rate but literally shown from Fig. 3, nucleation has become dominant that the number of crystals produced from secondary nucleation (left peak) is also significantly high at around mean crystal size of 300 μm . The highest peak of the initial seed which is 0.6 m^3/m is decreasing to 0.3 m^3/m at the end of the operation is believed to be subjected to the fact that crystals grown from initial seed dependently grow according to its initial size throughout the process following the concentration profiles and the solubility conditions which agrees with crystallization kinetics' properties of size dependent growth. Large crystals have higher crystal growth rate and vice versa. Thus, producing relatively low height of the distribution due to the difference in crystal growth rate.

In summary, the model developed for this work is similar and comparable with the cited literature as the temperature profiles and the final CSD agrees with each other as shown in Fig. 3. Thus, the simulation of the mathematical model for this case study is validated and can be used for further application. However, high secondary nucleation indicated by the left peak of the CSD profile need to be reduced. Theoretically, this high secondary nucleation may diminish by implying proper cooling profiles incorporating dissolution phenomena which is proposed then as a new optimal cooling control strategy. As a start, the optimization algorithm as shown in Equation (12) is used to minimize the CSD that fall under the size of 500 μm . The objective function is set to reduce the production of small crystals from nucleation phenomena. This equation is subjected to $T_{\min} \leq T \leq T_{\max}$ where the value for minimum and maximum temperature is listed in Table 1. The optimal temperature trajectory obtained in this way is shown in Fig. 4 where it is served as temperature set-point for the controller.

$$F_{obj} = \min f_n(500\mu\text{m}) \quad (12)$$

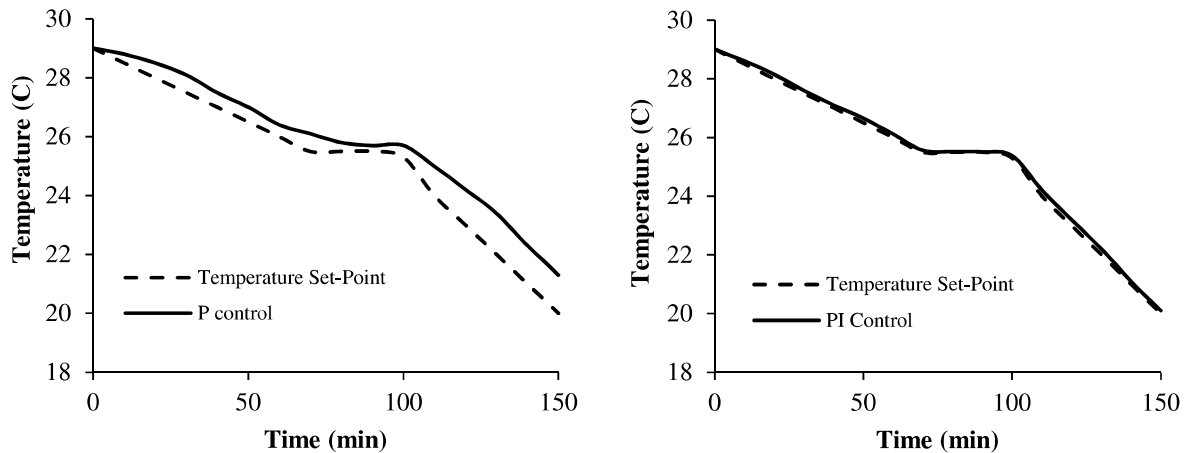


FIGURE 4. Temperature profiles using P controller (left) and PI controller (right)

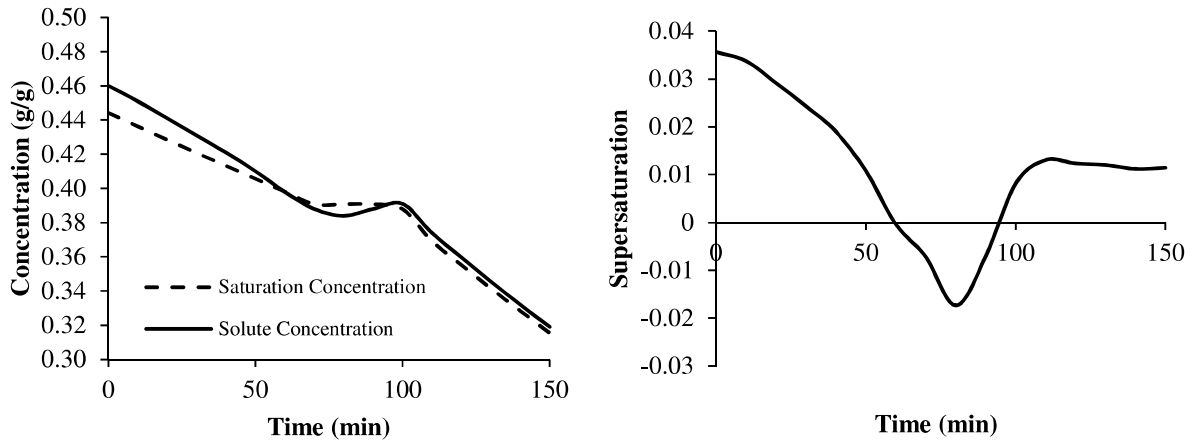


FIGURE 5. Concentration (left) and supersaturation (right) profiles using PI controller

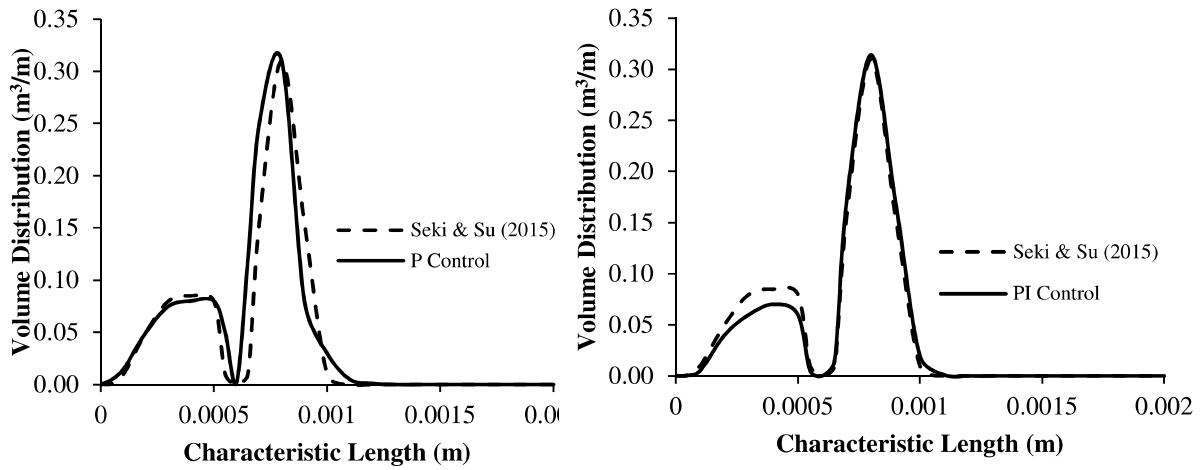


FIGURE 6. CSD profiles using P controller (left) and PI controller (right) at the final time

Using the same model, parameters and the operating constraints as the previous case, the simulation of potassium nitrate crystallization is performed again under closed-loop condition using both P and PI controllers. The cooling profile generated from optimization algorithm in Equation (12) is used as the set-point for both controllers and the temperature of crystallizer is maintained at its set-point by manipulating the water inlet temperature of the crystallizer. The controller parameters for P and PI controllers are calculated from Internal Model Control (IMC) tuning method where the proportional gain (K_c) for both controllers are 33 and integral time (τ_i) for PI controller is 2.3 respectively.

The proposed cooling profile (dashed line) shown in Fig. 4 decreases linearly from 29°C to 26°C at 0 to 70 minutes and then is maintained at 26°C from 70 to 100 minutes. After 100 minutes, the temperature profile is decreased again until it reaches 20°C at 150 minutes. Also as shown in Fig. 4, it is noted that PI controller serves better in terms of following the temperature set-point closely compared to P controller. PI controller is expected to perform better as it is known that this controller would give advantage by effectively eliminates the steady state error resulted from the deviation of variable temperature versus temperature set-point, but with slow response time due to its integral mode. Since controlling and maintaining the temperature is already a slow process, PI controller perform at its best in this case study.

Meanwhile, Fig. 5 demonstrates the concentration and supersaturation profile generated from the closed-loop simulation results under PI controller. The concentration profile is similar as the temperature profile due to the fact

that concentration depends on the temperature as shown in Equation (7). As the process begins at 0 to 70 minutes, it is evidently seen from the concentration profile that the solute concentration is significantly dropped accordingly but far from the saturation concentration. This means that the crystallization starts from the starting point of 0 minute until 70 minutes as the huge gap between those two concentration profiles indicates high supersaturation which promotes nucleation and crystals growth phenomena. This condition stimulates the production of new crystal particles and the growth of the crystal particles from the seed crystals. Then, from 70 to 100 minutes as the solution is maintained at 26°C, it can be seen that the solute concentration is operated below the saturation concentration based on the concentration profile. Also, it is observed that the supersaturation level is trending down until -0.02 following the concentration profiles. Both low solute concentration from saturation concentration and rock-bottomed supersaturation conditions are called undersaturated condition whereby this condition forces the crystals to stop growing and dissolve. Small crystals formed by secondary nucleation in the previous high supersaturation level dissolved faster than those of bigger crystals grown from the seed crystals due to the fact that small size of particles have higher surface area than big size of particles. This disappearance of crystals is called dissolution phenomena where it benefits in producing less fines for the overall CSD theoretically. Subsequently, the solution is rapidly being cooled from 100 minutes until the end of the crystallization process to provide more room for crystals to grow sufficiently to achieve desired CSD. Apart from that, the supersaturation profile also shows that the profile have both positive and negative values which means that all the crystallization phenomena which is crystal growth, nucleation and dissolution occur accordingly.

The comparison of the performance for P and PI controllers is shown in Fig. 6. The optimization done by using temperature controller to obtain temperature profiles in this case study shows slight improvement in terms of reduction of fine crystals, especially by using PI controller. The closed-loop simulation using PI controller is able to reduce notable amount of crystal fines compared with the cited literature [5]. Hence, this closed-loop simulation using PI controller serves better to control and achieve the desired CSD for this crystallization process.

CONCLUSIONS

This paper discusses two approaches for the study of batch seeded cooling crystallization for potassium nitrate which is open-loop and closed-loop controlled cooling. The one-dimensional mathematical model adopted from [6] is used to compute open-loop cooling trajectory. The open-loop simulation results show that the parameters estimated in this work have shown good agreement with the published crystallization data, thereby validating the model and experimental data reported by others. In addition, the model is also extended to incorporate dissolution along with nucleation and crystal growth phenomena for the selected crystallization system. The closed-loop temperature control using P and PI controllers are demonstrated. By incorporating dissolution through proposed cooling profiles, PI controller shows notable improvements in terms of controlling the temperature and thus, positively achieving desired CSD and reduce the amount of crystal fines instead of only using P controller.

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