MATHEMATICAL MODELING FOR ADIPIC ACID CRYSTALLIZATION PROCESS

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Abstract: This work is part of a study aiming to improve crystallization processes. The batch crystallization of adipic acid is chosen as a case study, a process in which the supersaturation necessary for the crystals to appear and grow is generated by the cooling of the solution. This part of the study involves the process modeling and an analysis of the influence of the process variables on the final crystal size distribution (CSD) and on the quantity of solids. The results have shown that the developed model is a good representation of the process, being able to reproduce literature results. *Copyright © 2004 IFAC*

Keywords: Mathematical models, Solids processing, Process models, Dynamic Behaviour, Temperature profiles

1. INTRODUCTION

Crystallization is an ancient unit operation and is widely used, since solids of high purity can be obtained. Batch crystallization is specially used in the production of high value added products, mainly because it offers flexible and simple processing steps for plants with frequently changing recipes and product lines (Zhang and Rohani, 2003; Rawlings *et al.*, 1993). For this kind of material, product purity and the crystal size distribution (CSD) are of prime importance. Furthermore, the crystals produced through a crystallization process have a decisive influence on the downstream processing and, therefore, the CSD should be reproducible in each operation and regular as much as possible (Ma *et al.*, 2002). Therefore, the variables that affect the crystallization process must be known and controlled so as to be kept within an acceptable range, in order to satisfy the requirements concerning the final product quality and the production process (Rawlings *et al.*, 1993).

This work is part of a study aiming to improve the performance of batch crystallization processes. The batch cooling crystallization of adipic acid is chosen as a case study. In a well-mixed batch crystallizer, the final crystal product is determined by the supersaturation profile, the initial seed mass, and the seed crystal size distribution (Ma *et al.*, 2002). The supersaturation evolution during batch crystallization processes determines the magnitude of the many kinetic phenomena that comprise the process. In order to perform a successful study of the process, the accurate modelling of the process is crucial. It turns possible the calculation of further on-line optimal operating policies, as well as real time applications (Zhang and Rohani, 2003). In order to analyse the performance of suitable control structures and to perform control calculations, an accurate modelling is necessary to be developed.

Seeding is frequently applied to avoid a supersaturation peak at the beginning of the process (Giulietti *et al.*, 2001). This occurs because the supersaturation values sufficient for crystal growth are lower than the necessary ones for spontaneous nucleation. So, if the system could be kept at a region in the metastable zone with not so high supersaturation values, and with addition of seeds, just seeds growth will occur (Mullin, 1993; Rawlings *et al.*, 1992).

In this work, the developed mathematical modeling of the adipic acid crystallization process is presented. The role of the several process variables in the final product is evaluated as part of the study of ways to improve the process.

2. MATHEMATICAL MODELING

In order to completely model a crystallization process, mass balance, energy balance and a description of the crystal size distribution are necessary. This description is necessary because the process produce a mass of particles of many sizes, whose description of size distribution is crucial to its characterization. The models used in this description are called population balance models. According to Puel *et al.* (2003), the population balance modeling is firmly established as a basic theoretical framework for all particle processes.

Two phenomena dominate the crystallization kinetics: nucleation and crystal growth. Both phenomena consume the mass of the desired material during the crystallization process and are, therefore, competing mechanisms. They are different in the manner they consume material: nucleation involves the formation of new crystals while in crystal growth the crystals become larger with the deposition of material onto the existing crystals (Lang *et al.*, 1999). Apart from nucleation and growth, other phenomena, such as agglomeration and breakage, may occur during the process.

2.1 Population Balance – The Method of Classes.

Population Balance equation (PBE) is a hyperbolic partial differential equation, which involves all the crystallization kinetic phenomena. Being strongly nonlinear, the PBE do not possess an analytical solution in most cases, requiring the development and adaptation of numerical techniques. According to Wulkow *et al.* (2001), in the present state of PBE studies, no standard numerical method has been established for population balance models and none of the presently available methods produce an efficient and accurate solution for a broad class of models. Discretization sizing techniques appear to be robust. Marchal *et al.* (1988) developed the Method of Classes, a method that transforms the partial differential equation into an ordinary differential equations system by discretizing the range of variation of the variable L, related to the crystal size. The obtained differential equations are then no longer written with population density functions but with absolute numbers of crystals in each class (Nallet *et al.*, 1998). In a recent work, Puel *et al.* (2003) also used the Method of Classes to solve the population balance equation, but they extended the method to consider two characteristic dimensions.

In the Method of Classes, the particles sizes are defined as L_0, L_1, L_2,...., L_N, where L_0 is the size of the nuclei and L_N is the size of the largest crystals. This sizes determine the existence of N granulometric classes C_i, whose widths are defined by $\Delta C_i = L_i - L_{i-1}$ and the characteristic size of the class C_i is $S_i = (L_{i-1}+L_i)/2$ (see Figure 1).

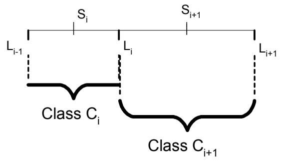

Fig. 1. Division of Classes.

The population of crystals is described by the number density function Ψ. Ψ(L,t)dL is the number of crystals of size between L and L+dL per unit volume at time t (Nallet *et al.*, 1998). Ni(t), the number of crystals per unit of volume in the *ith* class (C_i) at time t, is given by:

$$N_i(t) = \int_{L_{i-1}}^{L_i} \Psi(L,t)\,dL \qquad (1)$$

The model assumes that the number density function is constant at each class, turning possible the transformation of the population balance equation into a system of ordinary differential equations:

$$\begin{cases} \dfrac{dN_1}{dt} + \dfrac{1}{V_{susp}}\dfrac{dV_{susp}}{dt}N_1 + \dfrac{Q_s N_1 - Q_e N_{1e}}{V_{susp}} + \dfrac{G(L_1)}{2\Delta C_2}N_2 + \dfrac{G(L_1)}{2\Delta C_1}N_1 = r_N + R_{A,1} - R_{B,1} \\ \dfrac{dN_i}{dt} + \dfrac{1}{V_{susp}}\dfrac{dV_{susp}}{dt}N_i + \dfrac{Q_s N_i - Q_e N_{ie}}{V_{susp}} + \dfrac{G(L_i)}{2\Delta C_{i+1}}N_{i+1} + \dfrac{G(L_i) - G(L_{i-1})}{2\Delta C_i}N_i \\ -\dfrac{G(L_{i-1})}{2\Delta C_{i-1}}N_{i-1} = R_{A,i} - R_{B,i} \\ \dfrac{dN_N}{dt} + \dfrac{1}{V_{susp}}\dfrac{dV_{susp}}{dt}N_N + \dfrac{Q_s N_N - Q_e N_{Ne}}{V_{susp}} + \dfrac{-G(L_{N-1})}{2\Delta C_N}N_N \\ -\dfrac{G(L_{N-1})}{2\Delta C_{N-1}}N_{N-1} = R_{A,N} - R_{B,N} \end{cases} \qquad (2)$$

In the development of the modelling of the batch cooling crystallization process, the Method of Classes was chosen, because it is an efficient method widely used in literature, including in modelling of growth-dominated processes. Puel *et al.* (2003) stress that this numerical technique reliability is confirmed by three different papers dealing with bi-dimensional balance equations where discretization methods were used, despite differences in the formalism and the application area. However, the number of classes considered is the major key to guarantee the accurate solution, as was pointed out by Puel *et al* (2003). This was also observed in the present work.

Growth Mechanism. The expression for the growth rate developed by Marchal *et al.* (1988) is based on the film model and may be written as:

$$G = \frac{dL}{dt} = \frac{k_a MM\, k_c}{3\rho_c k_v}\eta_r (c - c^*)^{j'} \qquad (3)$$

The effectiveness factor, η_r, which expresses the diffusional limitations in crystal growth, causing a distribution of the growth rates among the classes, is found by the solution of equation (4). The mass transfer coefficient, k_d, is evaluated through the expression for Sherwood (equation (5)).

$$\left[\frac{k_c}{k_d}(c - c^*)^{j'-1}\right]\eta_r + \eta_r^{1/j'} - 1 = 0 \qquad (4)$$

$$Sh = \frac{k_d L}{D} = 2{,}0 + 0{,}47\left[\frac{L^{4/3}\varepsilon^{1/3}}{\nu}\right]^{0{,}62}\left[\frac{Diam}{Diam_T}\right]^{0{,}17}\left[\frac{\nu}{D}\right]^{0{,}36} \qquad (5)$$

From the equation (5), it is easy to note that each granulometric class has a value for the mass transfer coefficient, what means that the growth rate is size dependent.

The data of solubility of adipic acid in water were extracted from Postnikov and Nalivaiko (1971).

Nucleation Mechanism. Both primary and secondary nucleation are considered. Their expressions are respectively given by equations (6) and (7):

$$\mathrm{r}_{\mathrm{N1}} = A\exp\left[-\frac{B}{\ln^2\left[\frac{(HR)}{(HR)^*}\right]}\right] \tag{6}$$

$$\mathrm{r}_{\mathrm{N2}} = \mathrm{k}'_{\mathrm{N}}\left[(HR)-(HR)^*\right]^{i'} C_s^{\mathrm{k}'} \tag{7}$$

Agglomeration Mechanism. Still in the work of Marchal *et al.* (1988), a model for the agglomeration mechanism is proposed, considering only the agglomeration of two particles. The agglomeration is considered as chemical reaction of particle *m* and particle *n*, leading to the formation of a crystal of size *q*. Considering that the pseudo-chemical reaction describing the agglomeration can be schematically represented by equation (9), its stoichiometric coefficient may be found by $\nu_{est} = (S_m^3+S_n^3)/S_q^3$. The class q, where the agglomerate fits, is found by the relation: $L_{q-1}<(S_m^3+S_n^3)^{1/3}\leq L_q$.

$$\textcircled{m} + \textcircled{n} \longrightarrow \nu\,\textcircled{q} \tag{8}$$

All possible agglomerations between two particles (*m* and *n*, $n \geq m$) can be arranged in a series, assuming a rank $l_{m,n}$ that represents its position in this series. For N granulometric classes, N(N+1)/2 different binary agglomerations are present and the series are represented by (1,1), (1,2) ... (1,N), (2,2), (2,3) .... (m,n) .... (N,N). The position $l_{m,n}$ of the agglomeration of a particle *m* with a particle *n* is found by relation (9):

$$l_{m,n} = N(m-1) - \frac{m(m-1)}{2} + n \tag{9}$$

This agglomeration will affect class *i*, only if *i* is equal to *m*, *n* (in both cases, $\nu_{est} = -1$) or *q* (with $\nu_{est} = (S_m^3+S_n^3)/S_q^3$). In this way, an overall stoichiometric coefficient of class i, with respect to agglomeration of rank *l* can be computed:

$$\nu_{est\,l,i} = \left(\frac{S_m^3+S_n^3}{S_q^3}\right)\delta_{i,q} - \left(\delta_{i,m}+\delta_{i,n}\right) \tag{10}$$

where $\delta_{ij} = 1$ if $i = j$ and $\delta_{ij} = 0$ if $i \neq j$.

The net rate of particle production by agglomeration in the *i*th class is calculated by equation (11), where r(*l*) is the intrinsic rate of agglomeration of rank *l*, being a function of the number of collisions per unit volume per time and of the supersaturation.

$$R_{A,i} = \sum_{l=1}^{\frac{N(N+1)}{2}} \nu_{est\,l,i}\, r(l) \tag{11}$$

David *et al.* (1991) proposed an expression for the calculation of the intrinsic rate of agglomeration (equation 12), based on phenomenological and fluid mechanical considerations, taking into account the concentration of particles, the supersaturation, the power dissipation per mass unit, the crystallizer size and of the crystals being agglomerated. The agglomeration contribution in the developed software is computed through equation (12).

$$r = k'_A S_m\left(1+\frac{S_n}{S_m}\right)^2 N \quad Diam \quad f\left(\frac{S_n}{S_m}\right)\left[1-\frac{(S_n+S_m)^2}{\lambda_e^2}\right]k'_d(c-c^*) \\ \times N_n N_m (S_m-\delta) \quad H\left(\lambda_e - S_n - S_m\right) \tag{12}$$

where H(*x*) = 1 for $x \geq 0$ and H(*x*) = 0 for $x < 0$. The coefficient k_d’ is calculated by the same expression for k_d (Eq. 5), but the size of crystal considered must be the size of the agglomerate (S_m + S_n). The f function represents a relative shape function of both crystals. Considering both particles as spheres:

$$f\left(\frac{S_n}{S_m}\right) = \frac{4\left(1+\frac{S_n}{S_m}-\sqrt{\left(\frac{S_n}{S_m}\right)^2-1}\right)}{\frac{1}{3}+\frac{S_n}{S_m}-\sqrt{\left(\frac{S_n}{S_m}\right)^2-1}-\left(\frac{S_n}{S_m}-\sqrt{\left(\frac{S_n}{S_m}\right)^2-1}\right)^2\left(\frac{2\frac{S_n}{S_m}}{3}+\frac{\sqrt{\left(\frac{S_n}{S_m}\right)^2-1}}{3}\right)} \tag{13}$$

λ_e is defined as Lagrangian microscale, which is taken as having the same magnitude as the Taylor microscale, calculated by:

$$\lambda_e = 0{,}3\,\pi\,N\,Diam\left(\frac{60\nu}{10\varepsilon}\right)^{1/2} \tag{14}$$

The calculation of further on-line optimal operation policies takes an advantage with the inclusion of agglomeration in the model, compared to most batch optimization studies encountered in literature. Most of them neglect agglomeration and considers just nucleation and growth, which may be a poor consideration, as is the case with adipic acid, a classic-known substance that tends to agglomerate during crystallization processes.

2.2 *Mass Balance – Batch Crystallizer.*

The material balance of the solute is made based on the fact that a change in the solution concentration results in a change of the mass of crystals per unit volume.

Since the simulated crystallizer is a batch one, the solute present in the solution in the beginning of the batch is the whole mass of adipic acid available for crystallization. The mass balance is made using the dissociation constant of adipic acid, considered as a monoacid: the concentration of solid in the suspension can be connected with the concentration of protons in the solution (Marchal *et al.*, 1988):

$$V_o C_o = \frac{(H^+)^2}{K}\left[1+\frac{K}{(H^+)}\right]V_o + \frac{V_o}{1-\frac{MM}{\rho}C_s}C_s \tag{15}$$

2.3 *Energy Balance.*

The energy balance must take into account the differences in enthalpy of the streams in and out, the heat of crystallization and the heat removed by the cooling system. In the case study, batch crystallization, the energy balance equation is:

$$\rho C_p V \frac{dT}{dt} = -\Delta H_c 3 \rho_c k_v V_{susp} \int_0^\infty n L^2 G dL - U A_c (T - T_c) \qquad (16)$$

Using the Method of Classes, the integral present in the previous equation is substituted by a summation over all granulometric classes.

The heat of crystallization of adipic acid was extracted from Postinikov and Nalivaiko (1971).

The specific heat of the slurry is considered to be not so different from the water, since the process considered is the crystallization from solution, which is characterized to have not so high concentrations of solids.

3. MODEL VALIDATION

In order to test the validity of the constructed model, results from the literature were reproduced. The results obtained by Marchal *et al.* (1988) are compared with the ones generated with the developed model with the same data. To illustrate this point, Figure 2 depicts a comparison between the results for evolution of the relative supersaturation during the crystallization. The results generated by the developed software fit pretty well to the results obtained by Marchal *et al.* (1988), both for crystallization considering agglomeration or not. Considering the availability of data, the model is validated by the similarities of plots, not only for supersaturation evolution, but also for solids concentration evolution, CSD in number and in mass at the end of the batch and effectiveness factor for three granulometric classes during the batch.

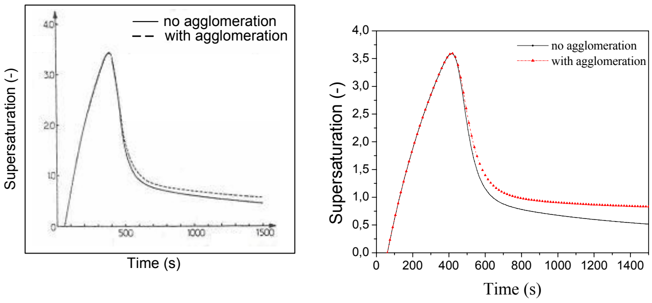

Fig.2: Comparison between Marchal *et al.* (1988) result (left) and model predictions (right)

4. SIMULATIONS – PROCESS VARIABLES INFLUENCE

Some simulations were made in order to evaluate the influence of several process variables. The main results are presented here. They are concerned to seeding, cooling rate, influence of the global heat transfer coefficient and of the power dissipation. It should be pointed that the effect of model uncertainties (i.e., model parameters) on the accuracy of the model predictions should be analysed. It was evaluated, through analysis of the effect of model parameters variations (±15%) on the final response through experimental design. The study showed that the model uncertainties do not affect the analysis that can be extracted from the influence of the process variables: the same qualitative results illustrated in Figures 3 – 5 are obtained.

The first result is the influence of the seeding in the process. In order to analyze the influence of seeding, the plots on Figure 3 are presented. It shows the results of operation trajectories, solution temperature evolution and supersaturation evolution for two batches that differ each other only in the seeding: the first one (non-seeded) has insignificant amount of seeds, while the second one has a considerable mass of crystals working as seeds. At these two simulations, a parabolic profile of coolant temperature, with negative second derivative, was employed.

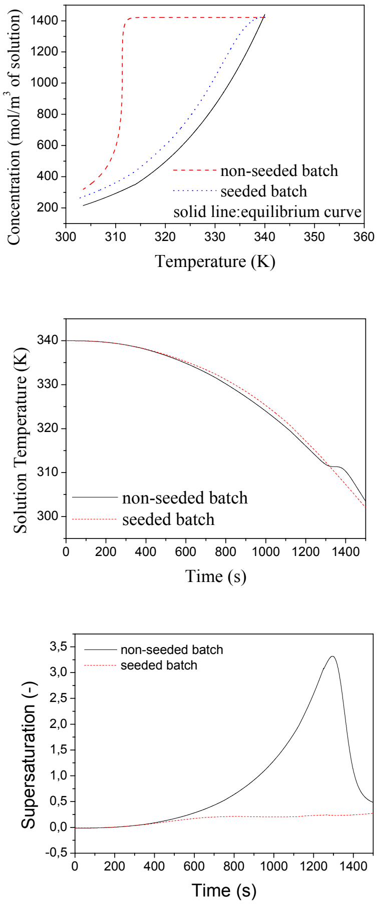

Fig. 3: Operation curve, evolution of the solution temperature and evolution of the supersaturation for a non-seeded and a seeded batch crystallization

The first plot in Figure 3 illustrates the operation curves (trajectories) for the two simulations. The operation trajectory is formed by the pairs of values of solution concentration and temperature followed during the batch time. The difference in the path followed during the process in the two cases is extremely visible. When no seeds are added to the crystallization process, the solution is cooled with constant concentration until the metastable zone limit is probably reached. An enormous quantity of crystals is generated by nucleation, releasing great amount of heat of crystallization (exothermic reaction), making the solution temperature to rise (second plot of Fig. 3) – what means that the cooling system was not able to remove all the heat released. As a consequence of the operation curve, a great peak of supersaturation is noted (last plot of Fig. 3).

On the other hand, if the crystallization is conducted the same way, except by the addition of seeds, the cooling of the solution happens softly, while the concentration of adipic acid in solution decreases (first plot of Fig. 3), probably keeping the operation far from the metastable zone limit. It is kept at a reasonable distance from the equilibrium line (Lang *et al.*, 1999). Not so high values of supersaturation are reached in the process (last plot of Fig. 3) and the nucleation is disfavoured. There is no great release of heat of crystallization and so there is no increase of solution temperature (second plot of Fig. 3).

Apart from the influence of the seeding, other important factor in the crystallization performance is the rate of cooling during all the process. According to Mullin (1993), the use of natural cooling is not the best choice. By natural cooling, one understands that the coolant is passed through the exchange device at constant both temperature and flow rate. If natural cooling is used, the temperature inside the crystallizer decreases exponentially, making the supersaturation to increase very fast at the first moments of the process, favouring nucleation. As a result, at the end of the batch small crystals and a large CSD are obtained. But, if the cooling profile is characterized to have a soft decrease at the early stages and a more pronounced one at the end of the process, the operation is favoured (Mullin, 1993).

Two seeded simulations that differ in the coolant temperature profile illustrate appropriately this feature. In the first one, natural cooling is simulated (coolant temperature and flow rate are both constant). In the next simulation, the same amount of seed is used, but a parabolic profile of coolant temperature, with negative second derivative, is employed. This last cooling rate is characterized to have a soft decrease at the early stages and a more pronounced one at the end of the process. The results of the two simulations can be observed in Fig. 4. When natural cooling is employed, a great number of fines is obtained (last plot in Fig. 4). A great peak of supersaturation occurs at the early stages of the crystallization process, what causes the appearance of thousands of nuclei. The concentration of solids in the suspension increases too fast in the first moments (first plot of Fig. 4). Except for the disadvantage of the great number of fines, this kind of cooling has the advantage of being able of extracting a great amount (mass) of solute of the solution, bringing them into crystals.

When a negative parabolic temperature profile is employed, much less number of fines is obtained and the solid concentration evolves softly (see Fig. 4), with seeds growth and not so many fines being generated. This is a consequence of the evolution of the supersaturation during the batch, showing that it is desirable to avoid peak supersaturation in order to favour growth. This confirms the results from literature (Lang et al, 1999), indicating that the optimum temperature profile would produce no peak in supersaturation at all, being almost flat. However, the slow evolution of the process when the supersaturation is kept low implies in less extraction of solute from the solution (less mass is obtained compared to natural cooling).

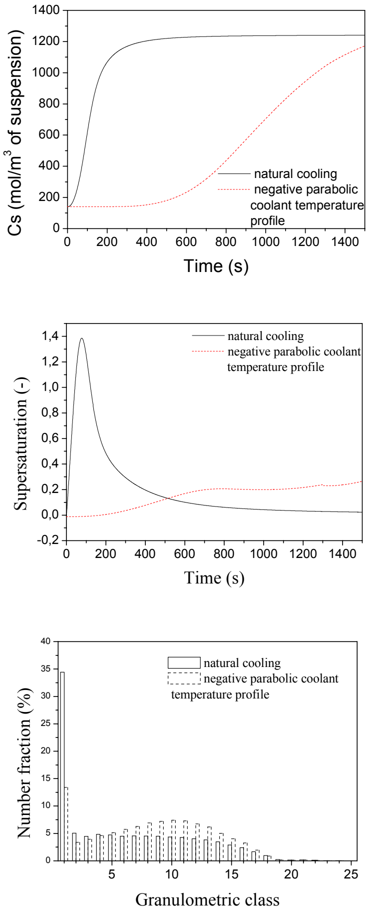

Fig. 4: Evolutions of solid concentration and supersaturation, as well as the CSD in number at the end of the batch in a seeded crystallization with natural cooling and with a negative parabolic coolant temperature profile.

At the study of the influence of the global heat transfer coefficient, its variation would express a variation in the coolant flow rate: the grater the value of the global heat transfer coefficient, the greater the coolant flow rate. The study showed that an increase in the fluid flow rate would be advantageous only in cases where the coolant temperature profile decreases slowly in early stages and sharper latter in time, what means to pass the coolant fluid with lower temperature and higher flow rate as the batch time passes. In this way, more mass is obtained in the process.

The role of the power dissipation is evaluated in the present work and this variable has shown itself to be important in the distribution of crystals in the various classes (Fig. 5). It is an expected result, since the power dissipation is present in the expression of the mass transfer coefficient, which influences the growth rate in each class, as well as the intrinsic rate of agglomeration. It has shown to be not so important in the amount (mass) of crystals obtained.

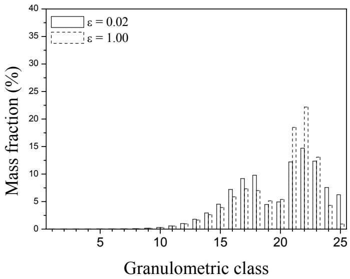

Fig. 5: CSD in mass at the end of the batch in two simulations (ε = 0.02 and ε = 1.00).

5. BATCH OPTIMIZATION STUDY

In order to control batch cooling crystallization processes, it is necessary to have an off-line optimized cooling profile (set point profile), which is calculated through optimal control theory. The accurate model of the process is essential in obtaining this set point profile, because it is obtained through the solution of a non-linear optimization problem. A general non-linear optimization problem subjected to equality and inequality constraints h (x) and g (x), respectively, may be defined as:

$$\begin{array}{ll} \text{Min} & f(x) \\ \text{s. t.:} & h_j(x) = 0,\ j = 1, 2, ..., m \\ & g_k(x) \leq 0,\ k = 1, 2, ..., p \end{array} \tag{17}$$

In the batch cooling crystallization optimization, the function to be minimized is set as a function of the final CSD and the problem constraints are the model equations, as well as physical constraints.

On-line batch optimal operating policies are calculated through the use of a model-based controller, which uses the process model to predict future answers of the process and take actions in order to obtain the best product at the end of the batch.

The optimal operating profiles may be successfully obtained by the proposed model together with the optimal control theory.

6. CONCLUSIONS

The developed model proved to be a good one, expressing representative results of the process. Literature results were satisfactory reproduced from the available information. The predictions generated through the model allow analyzing the impact of the process variables in the system behaviour. The proposed model may be used in a non-linear optimization problem, in order to find out the optimal cooling profile.

7. ACKNOWLEDGEMENTS

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