

## INFLUENCE OF COOLING PROFILE ON THE PRODUCT PROPERTIES IN COOLING CRYSTALLIZERS

A. BORSOS<sup>✉</sup>, B. G. LAKATOS

University of Pannonia, Department of Process Engineering, H-8200 Egyetem Street 10, HUNGARY  
<sup>✉</sup>E-mail: borsosa@fmt.uni-pannon.hu

Batch cooling crystallization process is investigated using different cooling procedures through mathematical modelling and computer simulation. The main element of the mathematical model is the population balance equation which contains both process and kinetic parameters. In the mathematical model of crystallizer the population balance equation is completed with the ordinary differential equations governing the mass balances of solute and solvent, as well as the heat balances of the crystalline suspension and the cooling medium. From the population balance model a set of differential equations was obtained for the first four moments of the size variable of crystals and the mass and heat balances, and the resulted equation system was solved in MATLAB environment. The dynamic properties and behaviour of the crystallizer depending on the cooling procedures was studied by numerical experimentation the results of which are presented and analysed.

**Keywords:** Cooling crystallization, Population balance model, Moment method, Cooling method, Simulation.

### Introduction

Crystallization is an important unit operation of chemical and process industry and it is a suitable method for formulation of solid particles, and separation and purification of chemical components. In industrial practice there exist special demands for well-designed crystalline products what requires developing more precise operation methods. Batch cooling crystallization is an often used method in industry, especially in the pharmaceutical industry hence well designed and operated batch processes seem to have great advantage in producing appropriately tailored crystalline products. Naturally, the detailed knowledge of these processes provides an elementary requirement for success.

Investigation by properly constructed mathematical models is a feasible tool for process design of crystallization. The balance equations which contain process and kinetic parameters as constitutive expressions are coming into view by development of computer science and technology. In the case of crystallization the fundamental balance equation describes the behaviour of crystal population by means of which the size distribution of crystals and dynamics of crystallizer can be investigated [1-5].

The population balance equation is often solved by applying the moment method [6-8]. The moment equations of low order moments describe some important properties of crystals such as the number of crystalline particles, the total crystal volume in solution, the size distribution and mean crystal size of the product. A well designed moment equation model beside the properties

of crystalline population involves information also on the mass and heat balance and dynamics of crystallizer.

The aim of this paper is to investigate the effects of cooling procedures of a batch cooling crystallizer on the properties of crystalline product by using a suitable model. The population balance equation is completed with the mass and energy balances and is converted into the set of moment equations for the first four moments having physical meaning. The properties of the crystalline product and dynamic behaviour of the crystallizer, obtained by numerical experimentation carried out by using a computer program in MATLAB environment are presented and analysed.

### Population balance model

The population balance equation which describes the kinetic and transport processes in a perfectly mixed crystallizer is written in the following form:

$$\frac{\partial n(L, t)}{\partial t} + \frac{\partial G(L, c, c_s) n(L, t)}{\partial L} = \frac{q}{V} [n_{in}(L, t) - n(L, t)] + B(L_0, c, c_s) \quad (1)$$

where  $G$  denotes the growth rate of crystals,  $n$  is the population density function,  $L$  stands for the crystal size, and  $c$  and  $c_s$  are, respectively, the concentration of solution and the equilibrium solubility concentration. Further, in eq. (1)  $q$  is the volumetric flow rate,  $V$  means the volume of suspension, and the variable  $B$  describes the nucleation process.

$$B(L_0, c, c_s) = e_p B_p(L_0, c, c_s) + e_b B_b(L_0, c, c_s) \quad (2)$$

where  $L_0$  denotes the size of nuclei,  $B_p$  and  $B_b$  are the primary and secondary nucleation rates while  $e_p$  and  $e_b$  are binary existence variables by means of which the primary and secondary nucleation rates, depending on the actual process conditions can be selected.

The mass and energy balance equations are part of the mathematical model. These equations are required to complete the population balance equation to obtain a full crystallizer model for determining and calculating the cooling profiles.

The mass balance of solute is governed by the following equation

$$\begin{aligned} \frac{d[\varepsilon c + (1-\varepsilon)\rho_c]}{dt} &= \frac{q}{V} [\varepsilon_{in} c_{in} + (1-\varepsilon_{in})\rho_c] \\ &- \frac{q}{V} [\varepsilon c + (1-\varepsilon)\rho_c] \end{aligned} \quad (3)$$

where  $\varepsilon$  is the volumetric ratio of solution,  $\rho$  is the density.

The mass balance equation of solvent is

$$\frac{d(\varepsilon c_{sv})}{dt} = \frac{q}{V} (\varepsilon_{in} c_{sv,in} + \varepsilon c_{sv}) \quad (4)$$

while the heat balance consists two equation. One of those is the heat balance of suspension

$$\begin{aligned} \frac{d[\varepsilon(C_{sv}c_{sv} + C_c c) + (1-\varepsilon)C_c \rho_c]T}{dt} \\ = \frac{q}{V} [\varepsilon_{in}(C_{sv}c_{sv,in} + C_c c_{in}) + (1-\varepsilon_{in})C_c \rho_c]T_{in} \\ - \frac{q}{V} [\varepsilon(C_{sv}c_{sv} + C_c c) + (1-\varepsilon)C_c \rho_c]T \\ - Ua(T - T_h) + (-\Delta H_c)R_{mc} \end{aligned} \quad (5)$$

where parameters  $C$  are the heat capacities of crystals and solvent,  $T$  is the temperature of suspension and  $U$  is the overall heat transfer coefficient. The second equation expresses the heats balance of fluid in the cooling jacket:

$$\frac{d(C_h \rho_h T_h)}{dt} = C_h \rho_h \frac{q_h}{V_h} (T_{h,in} - T_h) + \frac{UaV}{V_h} (T - T_h) \quad (6)$$

The volumetric ratio of solution  $\varepsilon$  is related to the total volume of crystals in a unit volume of suspension as

$$\varepsilon(t) = 1 - \int_0^{\infty} v_c(L)n(L,t)dL \quad (7)$$

where  $v_c(L)$  denotes the volume of a single crystal having linear size  $L$  expressed as

$$v_c(L) = k_v \cdot L^3 \quad (8)$$

where  $k_v$  denotes the volume shape factor.

The mathematical model of the crystallizer consists of the partial differential equation (1) and the set of ordinary differential equations. (3)-(6). It can be solved by using the boundary conditions

$$\lim_{L \rightarrow L_0} G(c, c_s, L)n(L, t) = 0, \quad t \geq 0 \quad (9a)$$

$$\lim_{L \rightarrow \infty} n(L, t) = 0, \quad t \geq 0 \quad (9b)$$

and the appropriately specified initial conditions. BC (9a) denotes that there is no crystal flux through  $L=0$ , while the BC (9b) assures the absence of too large crystals.

### Moment equation model

The properties of crystalline particles in the crystallization process and behaviour of the crystallizer are determined by the population balance model (1)-(7). Numerical solution of the population balance equation (1) is a complex time consuming procedure but the moment method provides an alternative way of treatment of problem. This method is widely used in modelling of disperse systems.

The moment method is a suitable one for computing and investigating the behaviour of a number of parameters characterizing the crystal size distribution such as the particle number, mean crystal size and dispersion of the crystal population. Besides, this method provides also a way for approximating the crystal size distribution.

The moments of the crystal size variable  $L$  weighted by the population density function are given as

$$\mu_k(t) = \int_0^{\infty} L^k n(L, t) dL, \quad k = 0, 1, 2, \dots \quad (10)$$

where  $k=0, 1, 2, 3, \dots$  denotes the order of moment.

Taking eq. (8) into consideration the total volume of crystals in a unit volume of suspension is expressed by means of the third order moment  $\mu_3$  as

$$V_c(t) = k_v \mu_3(t) = k_v \int_0^{\infty} L^3 n(L, t) dL \quad (11)$$

Therefore the mass and heat balances can be formulated by means of the third order moment of the linear crystal size using the relation (7).

The third order moment can be determined from the following infinite hierarchy of moment equations

$$\frac{d\mu_0}{dt} = \frac{q}{V} (\mu_{0,in} - \mu_0) + e_p B_p + e_b B_b \quad (12a)$$

$$\frac{d\mu_k}{dt} = \frac{q}{V} (\mu_{k,in} - \mu_k) + kG\mu_{k-1}, \quad k = 1, 2, 3, \dots \quad (12b)$$

using the sequence of equations for moments  $\mu_0, \mu_1, \mu_2$  in turn.

As a consequence, the ordinary differential equations for moments  $\mu_0, \mu_1, \mu_2$  and  $\mu_3$  together with the mass and heat balance equations (3)-(7) provide a closed model consisting only of ordinary differential equations, representing, in principle, a dynamic system governing the behaviour of continuous cooling crystallizers.

This system of equations involves also the models of batch cooling crystallizers taking the volumetric flow rate zero in all differential equations, i.e.  $q=0$ . Then the

whole process is determined by the initial conditions and the cooling rate controlled by eq. (8).

### Scaling

The moment equation model needs scaling of variables for numerical solution since there are differences of several orders of magnitude between the kinetic rates of nucleation and crystal growth and, consequently, between the values of moments. The rates of temporal changes of the moments can be reduced to similar orders of magnitude by defining suitable scaling factors [8].

Applying these scale factors

$$s_0 := 6k_v k_{g0}^3 s_t^{-3} s_c^{-3g}, \quad s_1 := 6k_v k_{g0}^2 s_t^{-2} s_c^{-2g}$$

$$s_2 := 3k_v k_{g0} s_t^{-1} s_c^{-g}, \quad s_3 := k_v, \quad s_c := \frac{1}{\max\{c\}}$$

$$s_T := \frac{1}{\max\{T\}}, \quad s_V = \frac{1}{V}, \quad s_t = \frac{1}{\max\{t\}}$$

where  $s_t$ ,  $s_c$ ,  $s_T$  and  $s_V$  can be chosen arbitrary, we introduce the following set of dimensionless variables

$$x_m = s_m \mu_m, \quad m = 0, 1, 2, 3, \quad y_{sv} = s_c c_{sv}, \quad y = s_c c, \quad y_s = s_c c_s$$

$$z = s_T T, \quad z_h = s_T T_h, \quad \xi = s_t t, \quad v = s_V V$$

and scaled parameters

$$\alpha = \rho_c s_c, \quad D_{ap} = 6k_v k_{p0} k_{g0}^3 s_t^{-4} s_c^{-3g}$$

$$D_{ab} = 6k_v^{1-j} k_{b0} k_{g0}^3 s_t^{-4} s_c^{-3g-b}, \quad \beta_g = \frac{E_g s_T}{R}$$

$$\beta_p = \frac{E_p s_T}{R}, \quad \beta_b = \frac{E_b s_T}{R}, \quad b_0 = s_c a_0, \quad b_1 = \frac{s_c a_1}{s_T}$$

$$b_2 = \frac{s_c a_2}{s_T^2}, \quad \kappa = \frac{s_c U a}{s_t C_h}, \quad \gamma = -\frac{s_T \Delta H_c}{C_h}$$

$$\phi = (1 - x_3) \left( \frac{C_{sv}}{C_h} y_{sv} + \frac{C_c}{C_h} y \right) + \frac{C_c}{C_h} \alpha x_3$$

by means of which the scaled mathematical model of the batch cooling crystallizer is as follows.

Moment equations:

$$\frac{dx_0}{d\xi} = e_p \Theta_p + e_b \Theta_b \quad (13)$$

$$\frac{dx_1}{d\xi} = \Theta_g x_0 \quad (14)$$

$$\frac{dx_2}{d\xi} = \Theta_g x_1 \quad (15)$$

$$\frac{dx_3}{d\xi} = \Theta_g x_2 \quad (16)$$

Mass balance for solute:

$$\frac{dy}{d\xi} = -\frac{\alpha - y}{1 - x_3} \Theta_g x_2 \quad (17)$$

Mass balance for solvent:

$$\frac{dy_{sv}}{d\xi} = \frac{y_{sv}}{(1 - x_3)} \Theta_g x_2 \quad (18)$$

Heat balance for the crystalline suspension:

$$\frac{dz}{d\xi} = -\frac{\kappa}{\phi} (z - z_h) + \frac{\alpha \gamma}{\phi} x_2 \exp\left(-\frac{\beta_g}{z}\right) \left(\frac{y - y_s}{y_s}\right)^g \quad (19)$$

Heat balance for the cooling medium:

$$\frac{dz_h}{d\xi} = \frac{1}{\xi_{zh}} (z_{h,in} - z_h) + \frac{\kappa v}{v_h \alpha_h} (z - z_h) \quad (20)$$

In eqs. (13)-(20) the scaled rate expressions of growth, primary and secondary nucleation are:

$$\Theta_g = \left(\frac{y - y_s}{y_s}\right)^g \exp\left(-\frac{\beta_g}{z}\right) \quad (21)$$

$$\Theta_p = D_{ap} \exp\left(-\frac{\beta_p}{z}\right) (1 - x_3) \exp\left(-\frac{k_e}{\ln^2\left(\frac{y}{y_s}\right)}\right) \quad (22)$$

$$\Theta_b = D_{ab} \exp\left(-\frac{\beta_b}{z}\right) \left(\frac{y - y_s}{y_s}\right)^b x_3^j \quad (23)$$

The dependence of saturation concentration on the temperature is described by the expression

$$y_s(z) = b_0 + b_1 z + b_2 z^2 \quad (24)$$

### Simulation

Numerical solution of the set of scaled differential equations (13)-(20) was carried out in MATLAB environment using the ODE solvers. In numerical experiments the temporal temperature profile was simulated using the function [9]

$$T_{prof} = \left( \frac{-t^{\frac{1}{bn}}}{t_{c,end}^{\frac{1}{bn}}} + 1 \right) (T_{start} - T_{end}) + T_{start} \quad (25)$$

where when fixing the start and end values the shape of the profile was controlled by changing the parameter  $bn$ .

For illustration some examples of temperature profiles are shown in Fig. 1 as a function of the parameter  $bn$ . Here, for the sake of making possible real comparisons, the profile marked by  $bn=1.655$  was used in all simulation runs. This profile has been chosen optimal when the goal function in optimizing experiments was the mean size value of crystals. Further, also for the sake of real

comparisons, identical initial conditions were used in all simulation runs given in turn of eqs. (13)-(20): 1.2e-1, 6.2e-2, 3.2e-2, 1.8e-2, 0.1, 8.1, 1.0, 0.2.

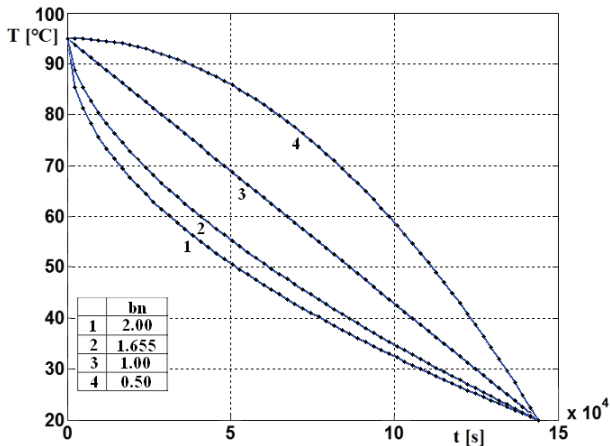


Figure 1: Temperature profiles depending on the parameter  $bn$  of function (25)

The effects of four cooling procedures were studied by applying the temperature profile given by eq. (25) at different places of the thermal system as controlled temperature programs. These are as follows.

- This program is called perfect cooling of crystallizer. In this case the temperature of the crystalline suspension was controlled following the cooling profile.
- In this case the temperature of the cooling medium in the jacket, assumed to be perfectly mixed, was changed in accordance of the cooling profile.
- The inlet temperature of the cooling medium was controlled following the cooling profile.
- In this case the inlet temperature of the cooling medium was kept constant temperature 18 °C.

The process and kinetic parameters used in numerical experimentation are listed in *Tables 1* and *2*.

Table 1: Process parameters used simulation

$V=10 \text{ m}^3$	$V_h=3 \text{ m}^3$	$q_{in}=1.1e-3 \text{ m}^3 \text{ s}^{-1}$
$c_{in}=221 \text{ kg m}^{-3}$	$q_h=1 \text{ m}^3 \text{ s}^{-1}$	$c_{svin}=870 \text{ kg m}^{-3}$
$T_{in}=95 \text{ °C}$	$T_h=20 \text{ °C}$	$Ua=2.1e4 \text{ J m}^{-2} \text{ s}^{-1} \text{ K}^{-1}$

Table 2: Kinetic parameters used simulation

$k_{g0}=4.0e-2 \text{ ms}^{-1}$	$g=1, b=3$	$b_0=1.448$
$k_{p0}=1.6e30 \text{ \#m}^{-3} \text{ s}^{-1}$	$k_e=5$	$b_1=-0.666$
$k_{b0}=2.0e25 \text{ \#m}^{-3} \text{ s}^{-1}$	$\Delta H_c=-4.5e4 \text{ J kg}^{-1}$	$b_2=0.5548$
$\rho_c=1760 \text{ kg m}^{-3}$	$\rho_{sv}=1000 \text{ kg m}^{-3}$	$\rho_h=1000 \text{ kg m}^{-3}$
$E_g=3.2e4 \text{ J mol}^{-1}$	$E_p=1.0e5 \text{ J mol}^{-1}$	$E_b=6.5e5 \text{ J mol}^{-1}$

Fig. 2 shows how the temperature of crystalline suspension depends on the cooling methods (b)-(d). Large differences are seen between those. Since the properties of the crystalline product and behaviour of kinetic processes, i.e. nucleation and growth of crystals strongly depend on evolution of the temperature of suspension these processes produce products of different quality.

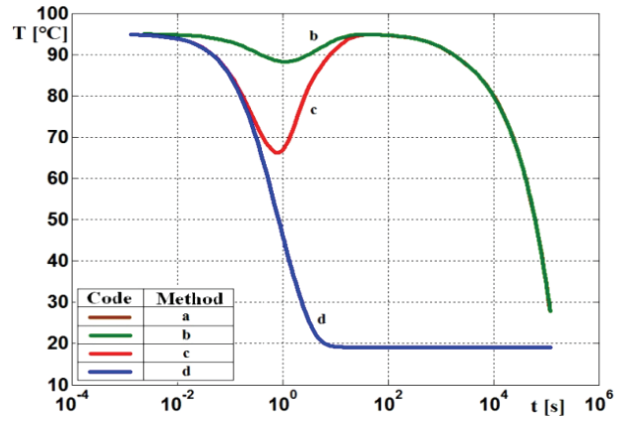


Figure 2: Evolution of the temperature of crystalline suspension for different cooling methods

Fig. 2 shows that the cooling capacities in the case of cooling methods b) and c) prove to be insufficient to eliminate the temperature rise induced by primary nucleation.

Fig. 3 presents temporal evolutions of the temperature of cooling medium in the jacket when using the cooling methods (c) and (d). The plots in Fig. 3 illustrates well that in the case of method (c) the temperature of the cooling medium achieves practically that of the crystalline suspension increasing rather sharply. This figure gives evidence of that in the case of method c) the heat capacity of the cooling medium is insufficient to cool the system monotonously, i.e. such a method appears to be strongly inadequate.

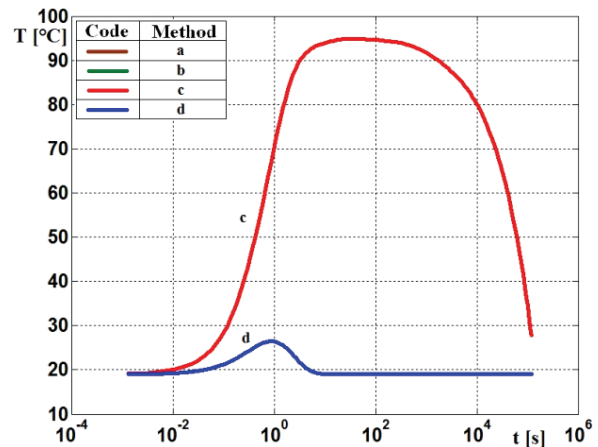


Figure 3: Temperature histories of cooling medium in the case of the (c) and (d) cooling methods

Evolutions of the zero order moment  $\mu_0$  are presented in Fig. 4 for different cooling methods. This moment, in principle, provides the total number of crystals in a unit volume of suspension. It is seen well that the method (c) produces about one order of magnitude more crystals than the other methods.

Histories of the third order moment  $\mu_3$  which is related to the total volume of crystals in a unit volume of suspension is shown in Fig. 5. Here significant differences are observed in the transients produced by the cooling methods applied while the final volume of

the crystalline product becomes of nearly the same value at the end of the process.

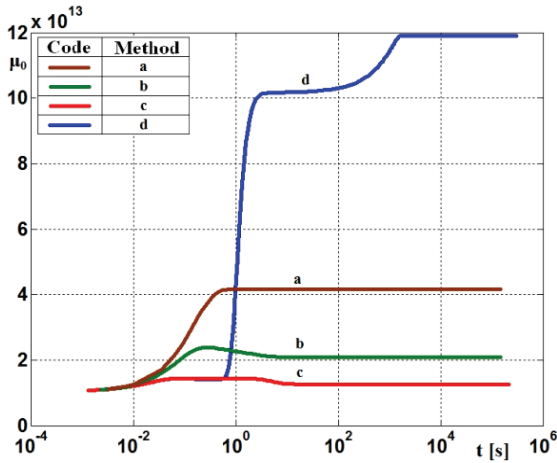


Figure 4: Evolution of the zero order moment  $\mu_0$ , i.e. the total number of crystals in a unit volume of suspension for different cooling methods

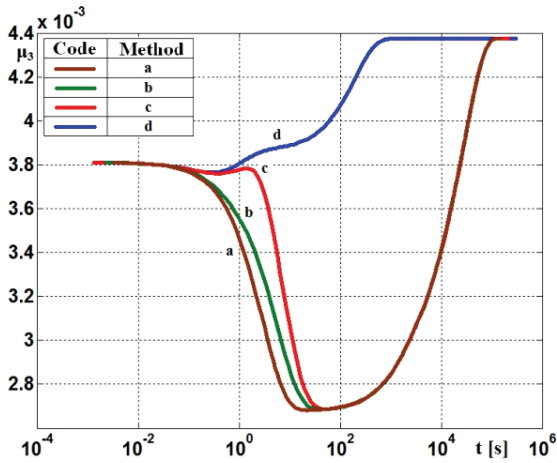


Figure 5: Evolution of the third order moment  $\mu_3$  relating to the total volume of crystals in a unit volume of suspension for different cooling methods

Fig. 5 shows clearly that in the case of cooling programs a), b) and c) the total amount of crystals in the crystallizer is decreased through some period of time. This phenomenon is the result of the initial condition that the initial temperature of the crystallizer was too high compared with the solute concentration. As a consequence, a part of crystals being initially in the crystallizer dissolve before the crystallization process starts.

Temporal evolutions of the mean size of crystals  $\bar{L}_{23}$ , defined as

$$\bar{L}_{23} = \frac{\mu_3}{\mu_2} \quad (26)$$

are presented in Fig. 6. This variable was computed using the actual values of the third order and second order moments.

The graphs in Fig. 6 illustrate well that the temporal evolutions of the mean crystal size exhibit significant differences in transients in accordance with the changes in time shown in Figs 4 and 5. The constant temperature

cooling method, i.e. method (d) produced the smallest final mean crystal size of the crystalline product as it was expected. Using this processing method nucleation of crystals has become very intensive as it is illustrated by the results in Fig. 4. At the same time, the largest mean crystal size was obtained using the method (c) although its advantage over the method (b) proves to be rather small.

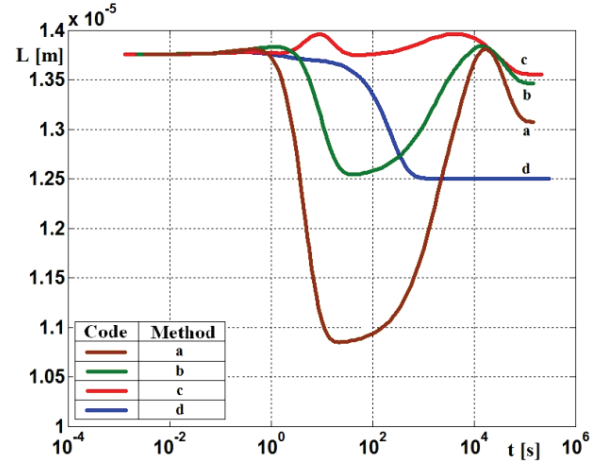


Figure 6: Temporal evolutions of the mean crystal size for different cooling methods

## Conclusions

A population balance model was developed and applied for a detailed study of batch cooling crystallization. Using the population balance equation a moment equation model was obtained for the first four moments of crystal size variable weighted by the population density function. These equations coupled with the mass and heat balances of the crystalline suspension and cooling medium form a suitable model for investigating both the dynamic and steady state behaviour of cooling processes of either continuous or batch crystallizers.

For making possible real comparisons of the cooling methods studied well defined cooling profiles were applied in all simulation runs but changing their placing in the thermal processes of crystallizer. The effects of these methods were compared also with those of the natural cooling method keeping the temperature of cooling feedstock constant.

The results of numerical experimentation revealed that significant differences could be observed between the numbers of crystals produced by means of the cooling methods studied while the final volumes of crystals have become practically of the same value. This means that nucleation of crystals was the dominant process in the case of all cooling methods.

Analysing the simulation results presented allows concluding that the product properties can be predicted well computer experimentation. The mathematical and computer models developed make possible also of optimizing the system and choosing the optimal cooling profiles for producing crystalline products having the required product properties.

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## SYMBOLS

$a$	- surface area of heat transfer, $m^2$
$B$	- nucleation rate, $\# m^{-3} s^{-1}$
$b$	- kinetic parameter
$bn$	- optimization variable
$C$	- heat capacity, $J kg^{-1} K^{-1}$
$c$	- concentration, $kg m^{-3}$
$D_a$	- dimensionless parameter
$E$	- Energy, $J mol^{-1}$
$e$	- binary existence variable
$G$	- growth rate, $m s^{-1}$
$\Delta H$	- crystallization heat, $J kg^{-1}$
$k$	- kinetic coefficient
$k_v$	- volume shape factor
$L$	- size variable, $m$
$L_0$	- size of nuclei, $m$
$n$	- population density function, $\# m^{-4}$
$q$	- volumetric flow rate, $m^3 s^{-1}$
$R_{mc}$	- rate of crystallization, $kg s^{-1}$
$s$	- scale factor
$s_c$	- scale factor of concentration
$T$	- temperature, $K$
$t$	- time, $s$
$U$	- heat transfer coefficient, $J m^{-2} s^{-1} K^{-1}$
$V$	- volume, $m^3$
$x_k$	- dimensionless $k^{th}$ order moment
$y$	- dimensionless concentration
$z$	- dimensionless temperature

## GREEK SYMBOLS

$\alpha$	- dimensionless parameter
$\beta$	- dimensionless parameter
$\varepsilon$	- volumetric ratio of solution
$\kappa$	- dimensionless parameter
$\gamma$	- dimensionless parameter
$\Theta$	- scaled (dimensionless) growth rate
$\mu_k$	- $k^{th}$ order moment
$\xi$	- dimensionless time
$\rho$	- density, $kg m^{-3}$

## INDICES

$b$	- secondary nucleation
$c$	- crystal
$g$	- growth
$h$	- cooling phase
$in$	- inlet
$p$	- primary nucleation
$s$	- equilibrium saturation concentration
$sv$	- solvent

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