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CRYSTALLIZATION OF PARA-XYLENE IN A BATCH COOLING CRYSTALLIZER

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Crystallization of para-xylene in a batch cooling crystallizer was investigated by means of computer simulation. The mathematical model used in this modelling study consists of the population balance equation for crystals completed with the differential equations governing the mass balance of solute and the heat balance of the crystalline suspension. The population balance equation was reduced to a finite set of ordinary differential equations for moments of the crystal size variable using the standard moment method. The resulted finite system of ordinary differential equations was solved in MATLAB environment. The simulation results revealed that both the dynamic trajectories of the crystallizer and the final properties of the crystalline product depend strongly on the cooling profiles. Using the numerical model presented the batch crystallization system can be optimized by choosing the best temperature profile for producing a crystalline product exhibiting the required properties.

Keywords: Para-xylene, Cooling crystallization, Population balance model, Moment method, Optimization, Simulation

Introduction

Xylenes are widely used materials in industry since the three xylene isomers are important components of diverse paints and varnishes and also of the gasoline and fuel of airplanes. The leather industry consumes xylenes in great amounts too.

Xylene as a mixture of three isomers, i.e. orto-xylene, meta-xylene and para-xylene is produced mostly from petroleum. These isomers have the same chemical formula $C_6H_4(CH_3)_2$ but different structural configuration.

Among the xylene isomers para-xylene plays important role since it is the principal precursor to terephthalic acid and dimethyl terephthalate. Both monomers are used in the production of polyethylene terephthalate (PET) which is a widely used raw material of polyesters. Some modern technologies use PET-based materials to produce vehicle parts as engineering resins often in combination with glass fibre [1].

After the first steps in crude oil separation technology the isomers and other components are in the same phase and that needs a further separation step for producing pure para-xylene. The three xylene isomers exhibit rather close boiling points but taking advantage of differences in the melting points cooling crystallization is a well suited separation technique for producing pure para-xylene product [2].

Crystallization is an important, often used unit operation of chemical industry as a separation and purification technique. During the course of process solid particles are formulated from solution. The driving force for crystallization is supersaturation which is, in essence, the difference between the actual and the equilibrium saturation concentration of solute depending on temperature.

In crystallization, the crystalline product exhibits size distribution (CSD) even under ideal process conditions. This is an important quality parameter in processing. CSD depends on the degree of supersaturation that influences the nucleation and growth of crystals significantly.

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 population balance equation describes the behaviour of the crystal population by means of which the size distribution of crystals and dynamics of crystallizer can be investigated.

The population balance equation is often solved by applying the moment method [3-9]. 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 the solution, the size distribution and the mean size of the crystalline product. A well designed moment equation model beside the properties of crystalline population involves information also on the mass and heat balance and dynamic behaviour of crystallizer [10, 11].

The aim of this paper is to investigate the para-xylene crystallization process by using a controlled cooling profile in a batch crystallizer. The process is described by a suitable population balance model, and the population balance equation is solved by means of the moment method. The properties of the crystalline product and dynamic behaviour of the crystallizer obtained by numerical experimentation in MATLAB environment are presented and analysed.

Population balance model

Consider a stirred batch crystallizer in which supersaturation is generated by cooling as it is illustrated in *Fig. 1*. In this case, the crystallizer is considered as a two phase operational unit having liquid and solid phases. Assuming that:

- Crystals are characterized by a linear dimension L;
- All new crystals are formed at a nominal size $L_n \geq 0$ so that we take $L_n \approx 0$;
- Crystal breakage and agglomeration are negligible;
- No growth rate fluctuations occur,

then the set of process equations, termed population balance model consists of the following balance equations. Population balance equation:

$$\frac{\partial n(L,t)}{\partial t} + \frac{\partial G(w_c, w_s, T) n(L,t)}{\partial L} = 0 \tag{1}$$

subject to the initial and boundary conditions

$$n(L, t=0) = n_0(L) \tag{2}$$

$$\lim_{L \to 0} G(w_c, w_s, T) n(L,t) = B(w_c, w_s, T) \tag{3}$$

$$\lim_{L \to \infty} n(L,t) = 0 \tag{4}$$

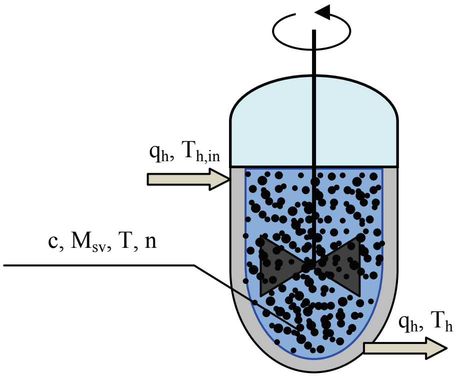

Figure 1: Schematics of a cooling crystallizer cooled by means of a jacket

In Eq.(1), B denotes the nucleation rate given by the power law expression

$$B(w_c, w_s, T) = k_{b0} \exp\left(-\frac{E_b}{RT}\right)\left(\frac{w_c - w_s}{w_s}\right)^b \tag{5}$$

where k_{b0} is the constant kinetic coefficient, E_b is the energy of nucleation, T is the temperature of crystalline suspension, w_c is the concentration of solute and w_s denotes the equilibrium saturation concentration.

The growth rate of crystals is calculated by the following equation

$$G(w_c, w_s, T) = k_{g0} \exp\left(-\frac{E_g}{RT}\right)\left(\frac{w_c - w_s}{w_s}\right)^g \tag{6}$$

where k_{g0} denotes the constant kinetic coefficient.

The equilibrium saturation concentration w_s, i.e. the solubility of para-xylene is given by the second order polynomial

$$y_s(T) = b_0 + b_1 T + b_2 T^2 \tag{7}$$

obtained by fitting to the measurement data published by de Geode [13]. The results of fitting of Eq.(7) to the experimental data of equilibrium saturation concentration of para-xylene dissolved in a mixture of xylene isomers is presented in *Fig. 2*. Further thermodynamic properties of xylene isomers are listed in *Table 1*.

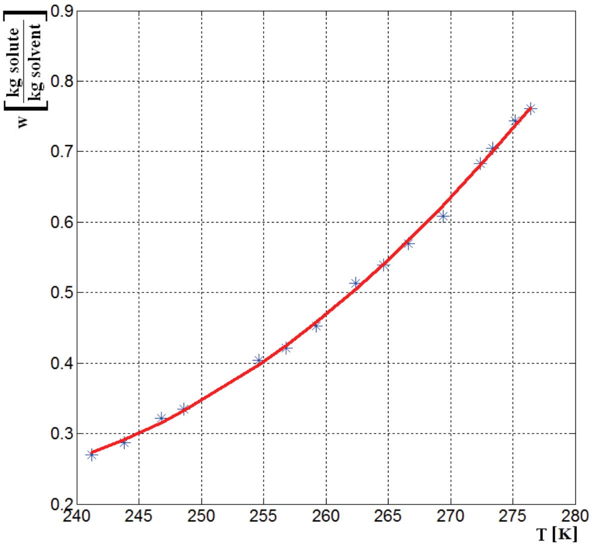

Figure 2: Equilibrium saturation concentration of para-xylene in solution of xylenes

Table 1: Thermodynamic properties of xylene isomers

	Melting point (°C)	Boiling point (°C)
para-xylene	13.3	138.5
ortho-xylene	-25.2	144.0
meta-xylene	-47.9	139.3

The mass and energy balance equations are also parts of the mathematical model. These equations are required to complete the population balance equation to obtain a full crystallizer model for computing the cooling profile, crystallization process and the properties of the product.

The solute mass balance is given as

$$M_{sv} \frac{dw_c}{dt} = -3 k_V \rho_c M_{sv} G \mu_2 \tag{8}$$

where M_{sv} denotes the total mass of solvent in the crystallizer, k_V is the volumetric shape factor, ρ_c is the density of crystals and μ_2 is the second order moment from the raw moments of the crystal size variable L weighted by the population density function defined as

$$\mu_k(t) = \int_0^{L_{\max}} L^k n(L,t)dL, \;\; k = 0,1,2,3. \tag{9}$$

Naturally, here the mass M_{sv} of solvent is constant. The heat balance equation for the crystalline suspension is expressed as

$$\begin{aligned}(C_{sv} + C_c m_c)M_{sv}\frac{dT}{dt} &= Ua_V V_{sv}(T_{control} - T)\\ &= Ua_V \frac{M_{sv}}{\rho_{sv}}(T_{control} - T)\end{aligned} \tag{10}$$

where C_c and C_{sv} are the heat capacities of crystals and solvent, $T_{control}$ denotes the controlled temperature of fluid medium in the jacket, U is the overall heat transfer coefficient and a_V is the heat transfer surface in a unit volume of suspension. In Eq.(10), m_c denotes the total mass of solute and crystals in a unit volume of suspension

$$m_c = w_c + k_V \rho_c \mu_3 \tag{11}$$

assuming that the heat capacities of crystals and solute are the same value.

Moment equation model

The population balance model (1)-(11) describes the properties of crystalline particles and the behaviour of crystallizer but the numerical solution of the population balance equation (1) is a complex time consuming procedure. The moment method provides an alternative way of handling the problem. This is a widely used method in studying the disperse systems which often provides exact results.

The mass and heat balances are formulated by means of the third order moment which can be determined from the set of equations for the first four leading moments in the moment equation hierarchy:

$$\frac{d\mu_0(t)}{dt} = B(w_c, w_s, T) \tag{12}$$

$$\frac{d\mu_1(t)}{dt} = G(w_c, w_s, T)\mu_0(t) \tag{13}$$

$$\frac{d\mu_2(t)}{dt} = 2G(w_c, w_s, T)\mu_1(t) \tag{14}$$

$$\frac{d\mu_3(t)}{dt} = 3G(w_c, w_s, T)\mu_2(t) \tag{15}$$

As a consequence, the ordinary differential equations for moments μ_0, μ_1, μ_2 and μ_3 together with the mass and heat balance equations (8) and (10) provide a closed model consisting of six ordinary differential equations, as well as of the kinetic equations (5) and (6) and the constitutive expression (7) describing the solubility of para-xylene in a xylene solution.

Simulation results and discussion

Numerical solution of the set of differential equations (8), (10) and (12)-(15) were solved using the ODE solvers in MATLAB environment. In numerical experiments the temporal temperature profile was simulated by means of the following function

$$T_{control} = \left(\frac{-t_c^{\frac{1}{bn}}}{t_{c,end}^{\frac{1}{bn}}} + 1 \right)(T_{start} - T_{end}) + T_{start} \tag{16}$$

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

Fig. 3 presents some possible temperature profiles depending on the value of parameter *bn*. The thin lines present the evolution of temperature in the suspension while the thick lines show the temperature changes in the jacket. The differences reflect, in principle, the dynamics of the crystalline suspension coupled with the wall of the crystallizer.

The process and kinetic parameters used in numerical experimentation are listed in *Tables 2* and *3*. The kinetic parameters were chosen as published by Mohameed et al. (2006)

Table 2: Process parameters used in simulation

V=10 m^3	V_h=3 m^3	T_0=5 °C
Ua_v=1,1e3	q_h=1 m^3 s^{-1}	T_{end}=-18 °C
b_0=0.6943	b_1=0.02	b_2=0.0002

Table 3: Kinetic parameters used in simulation

k_{g0}=28.5 ms^{-1}	g=3.95
k$_v$=0.52	b=0.89
k_{b0}=812.6 #m^{-3}s^{-1}	ρ_h=1000 kg m^{-3}
ρ_c=1100 kg m^{-3}	ρ_{sv}=1000 kg m^{-3}
E_g=785. J mol^{-1}	E_b=-56.37 J mol^{-1}

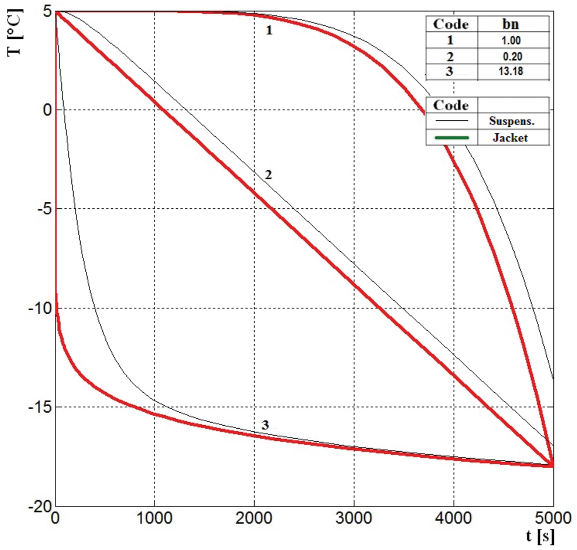

Figure 3: Temperature profiles by Eq.(16)

A number of numerical experiments have been carried out to choose the so called optimal temperature profile which provide the maximum final mean size of crystals $\overline{L}_{32}$ defined as

$$\overline{L}_{32}(t_{end}) = \frac{\mu_3(t_{end})}{\mu_2(t_{end})} \tag{17}$$

where t_{end} denotes the final moment of time corresponding to the final temperature T_{end}.

Fig. 4 shows the temporal profiles of solute concentration and the equilibrium saturation concentration corresponding to the temperature profiles in Fig. 3. The evolutions of the zero order moment μ_0 are presented in *Fig. 5* for the cooling methods shown in Fig. 3. This moment provides, in principle, the total number of crystals in a unit volume of suspension. Differences are observed in the final values of the number of crystals as a function of the cooling profiles. The optimal cooling profile produced the lowest value of crystal number.

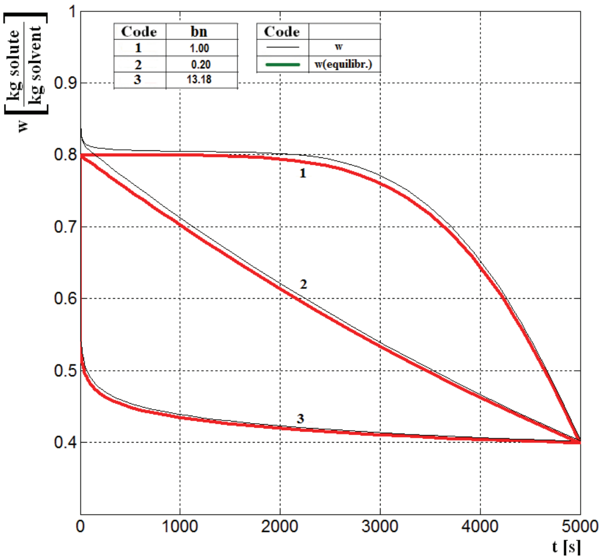

Figure 4: Solute and saturation concentration

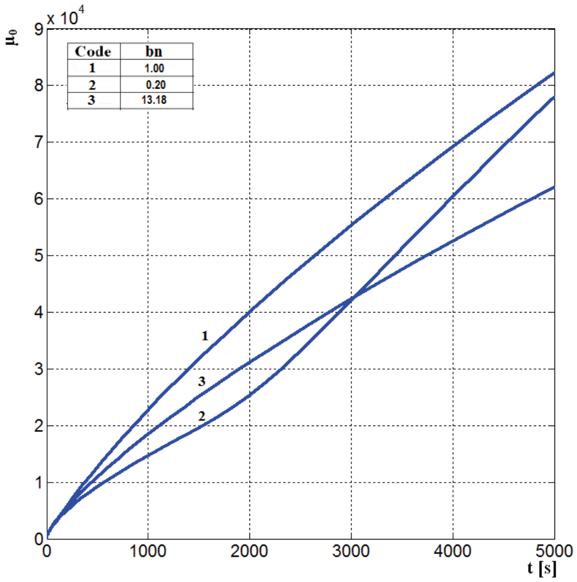

Figure 5: Evolution of the zero order moment μ_0

The histories of the third order moment μ_3 as a function of time are shown in *Fig. 6*. This moment is related to the total volume of crystals in a unit volume of suspension from which the mass of the crystalline product can be obtained by multiplying that with the density of crystals. There are significant differences in the time profiles but the final volumes of the crystalline product becomes of nearly the same value at the end of the process.

Temporal evolutions of the mean size of crystals $\overline{L}_{23}$, defined by Eq.(15) are presented in *Fig. 7*. The graphs in Fig. 7 illustrate well that variation of the mean crystal size exhibit significant differences during the course of the batch process. The optimal cooling profile gives the largest mean crystal size in accordance with the results shown in Figs *5* and 6. The other two cooling methods produced nearly the same mean sizes.

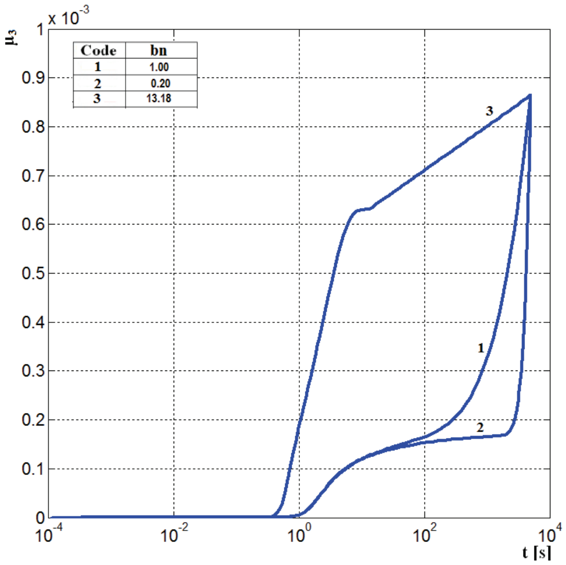

Figure 6: Evolution of the third order moment μ_3 relating to the total volume of crystals in a unit volume of suspension for different cooling methods

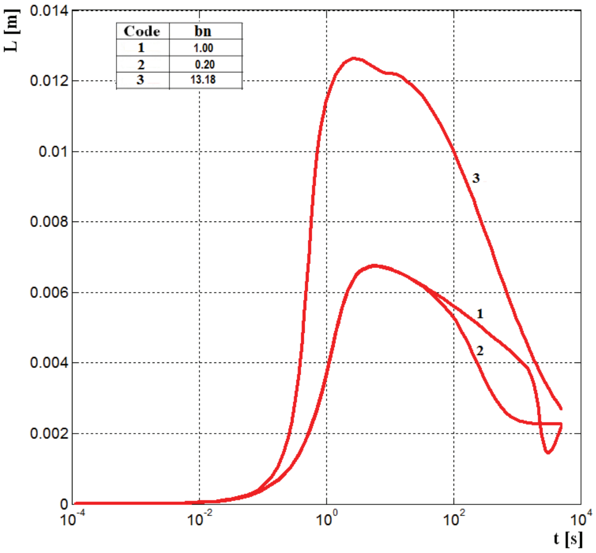

Figure 7: Temporal evolutions of the mean crystal size $\overline{L}_{32}$ depending on the cooling methods of Fig. 3

It should be noted that the temporal evolution of the mean crystal size passes through maximum in each case as it is shown in Fig. 7. It is a consequence of that although all the moments increase monotonously in time the rates of their increase differ leading to such an unusual phenomenon.

Similar phenomena can be observed in *Fig. 8* comparing the temporal evolutions of the mean crystal size $\overline{L}_{32}$ with that of $\overline{L}_{10}$ defined as

$$\overline{L}_{10}(t) = \frac{\mu_1(t)}{\mu_0(t)} \qquad (18)$$

Both graphs presented in Fig. 8 were computed applying the linear temperature profile. The corresponding evolutions of the first order moment are shown in *Fig. 9* for the sake of illustration that these moments also increase monotonously in time.

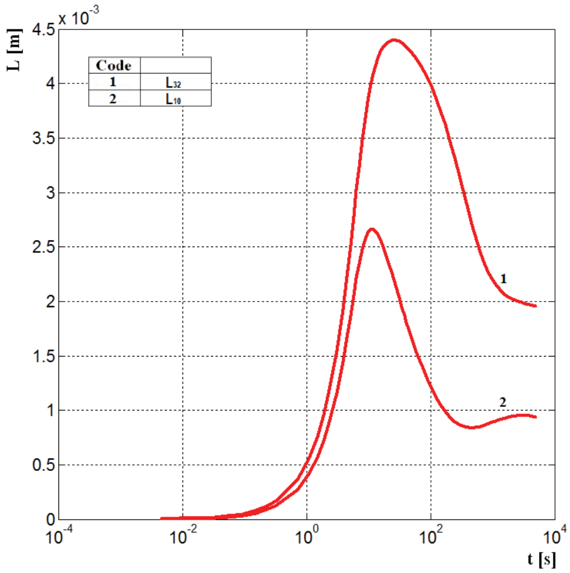

Figure 8: Temporal evolution of the mean sizes $\overline{L}_{32}$ and $\overline{L}_{10}$

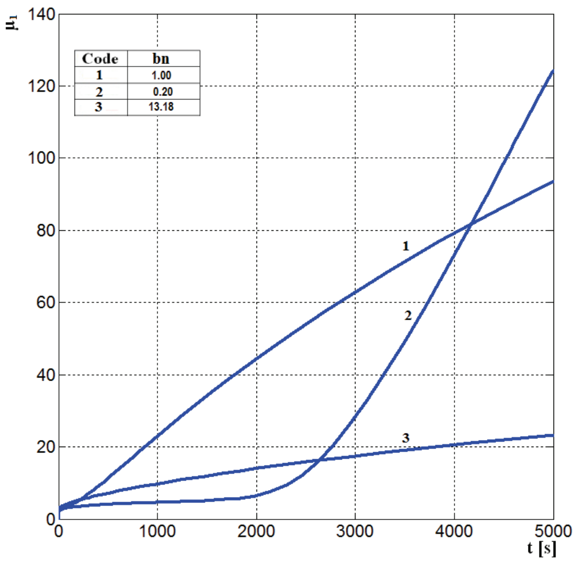

Figure 9: Evolution of the first order moment μ_1

It seems to be interesting to note that the mean crystal size $\overline{L}_{32}$ is greater than $\overline{L}_{10}$ at each moment of time during the course of the process leading to greater value even at the final moment.

Mohameed et al. (2006) published kinetic parameters differing to some extent, obtained by fitting their model to experimental data produced by using diverse cooling profiles. A second set of their kinetic parameters is shown in *Table 4*. The differences between the processes of crystal mean sizes obtained by using the original parameters listed in Table 3 and those in Table 4 are shown in *Fig. 10*.

Table 4: Kinetic parameters used in simulation

k_{g0}=16.25 ms^{-1}	g=4.74
k$_v$=0.52	b=0.71
k_{b0}=345.59 #m^{-3}s^{-1}	ρ_h=1000 kg m^{-3}
ρ_c=1100 kg m^{-3}	ρ_{sv}=1000 kg m^{-3}
E_g=370.23 J mol^{-1}	E_b=-63.37 J mol^{-1}

Fig. 10 illustrates well that the time histories of the mean crystal sizes differ from each other significantly but the final mean sizes of the crystalline product exhibit just about 10% difference. This means that the parameters obtained from different experiments reflect different dynamic behaviour of the batch crystallizer but rather similar final product properties.

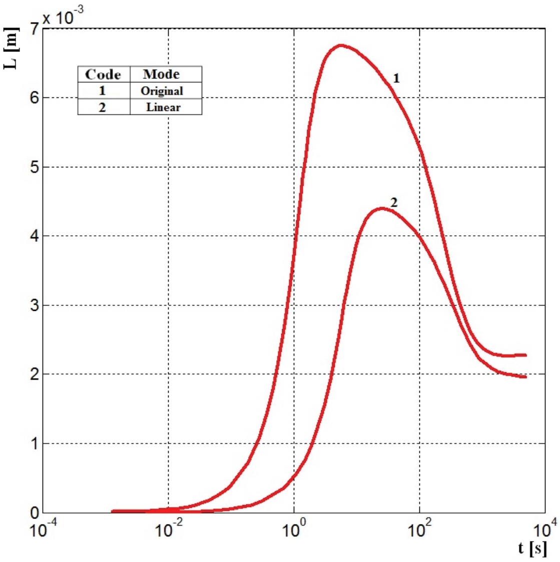

Figure 10: Evolution of the mean size $\overline{L}_{32}$ by using the kinetic parameters in Tables 3 and 4

Conclusions

A population balance model was developed and applied for simulation of batch cooling crystallization of para-xylene. In order to apply the moment method a moment equation hierarchy was generated from the population balance equation. The set of equations for the first four moments coupled with the mass and energy balance equations proved suitable to investigate the dynamic behaviour of the crystallizer and to predict the product properties of the cooling crystallization process.

The applied model allowed simulating the heat transfer through the wall of crystallizer by using a controlled jacket cooling method. In this case, there was negligible difference in the product values from the perfectly controlled crystallizer and that when the controlled jacket temperature model was applied.

The results of numerical experimentations revealed that different cooling profiles generate significant differences in the characteristic values of the crystalline product. Analysis of the simulation results allows concluding that the product properties can be computed and designed successfully by using a mathematical model and numerical experimentation.

By means of the numerical model presented the batch crystallization system can be optimized by choosing the best temperature profile for producing a crystalline product exhibiting the required properties.

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SYMBOLS

a_V - heat transfer surface in a unit volume, $m^2\ m^{-3}$
B - nucleation rate, # $m^{-3}\ s^{-1}$
b - kinetic parameter
bn - optimization variable, Eq.(14)
C - heat capacity, $J\ kg^{-1}\ K^{-1}$
E - Energy, $J\ mol^{-1}$
G - growth rate, $m\ s^{-1}$
k - kinetic coefficient
L - size variable, m
n - population density function, # m^{-4}
T - temperature, K
t - time, s
U - heat transfer coefficient, $J\ m^{-2}\ s^{-1}\ K^{-1}$
V - volume, m^3
w - concentration, kg_solute kg_solvent^{-1}

GREEK SYMBOLS

ε - volumetric ratio of solution
μ_k - k^{th} order moment
ρ - density, $kg\ m^{-3}$

INDICES

b - nucleation
c - crystal
g - growth
in - inlet
s - equilibrium saturation concentration
sv - solvent

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