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L. I. Salcedo[a]; M. Serna[a]; A. J. Castro[a]; E. Bolaños[b]; P. A. Quintana[c]
[a] Facultad de Ingeniería Química, UMSNH, Morelia, Michoacán, México [b] Instituto Tecnológico de Orizaba, Orizaba, Veracruz, México [c] Instituto Tecnológico de Celaya, Celaya, Guanajuato, México

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Mathematical Model of the Dissolution Stage in Cooling Batch Crystallization

L. I. Salcedo, M. Serna, and A. J. Castro
Facultad de Ingeniería Química, UMSNH, Morelia, Michoacán, México

E. Bolaños
Instituto Tecnológico de Orizaba, Orizaba, Veracruz, México

P. A. Quintana
Instituto Tecnológico de Celaya, Celaya, Guanajuato, México

Abstract: Experiments were performed in a cooling batch crystallizer to develop a phenomenological model that represents the dissolution stage in crystallization. Two models were used: a theoretical and a black box, comparing their results with the experimental ones through the simulation of these models (use the mean and the standard deviation of crystal size like comparative means). The theoretical model was obtained by population's balance, mass and energy balances, and constitutive relations (decrease speed and production-reduction speed). The black box model consisted of a set of equations, which are functions of the mean, standard deviation, agitation speed and time.

Keywords: Dissolution, crystallization, simulation, model

INTRODUCTION

The crystallization process has been used from antiquity. In our days it is a separation method very commonly used in the chemical industry. It is used in the production of drugs, sugar, electronic, and photography materials. In

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Address correspondence to L. I. Salcedo, Doctor en Ciencias en Ingeniera Quimica, Division de Estudios de Postgrado, Facultad de Ingeniería Química, Universidad Michoacana de San Nicolas de Hidalgo, Morelia, Michoacán, México. E-mail: lisalcedofiq@yahoo.com.mx

spite of its old roots and their extensive use, the modeling and control of the process of continuous crystallization show many technological problems requiring fundamental investigation (1).

One of the basic challenges in characterizing and controlling the crystallization process is its distributed nature. The distributed systems are processes with parameters and states varying in space and in the case of crystallization also distributed in the crystal population.

The objective of this work is to obtain a theoretical or semi-empirical model and a black box model that reproduce the experimental data of the dissolution stage of the batch crystallization process with the general objective of being able to use it in the process control.

Two factors have motivated the study of batch crystallization processes. First, the crystallization is used in new pharmaceutical, photography, and electrical processes, where products of high added value are involved, the reason why still small improvements in the yield have a positive impact on the profitability. Second, the batch crystallization processes have been studied less compared to the studies done on continuous processes. A wide range of chemical industries handles this type of processes, without really knowing the phenomenological behavior or reason why its control, if they have it (they apply heuristic rules), is very poor or deficient. Due to the abovementioned facts, the crystallization as separation process and the dissolution as a result of the same one requires fundamental investigations that contribute with new knowledge to solve the problems related to their industrial operation.

Most of the research on control of crystal size distribution (CSD) has taken place based on a cooling temperature with a constant agitation speed. The profiles of cooling (natural, linear, cubic) have been determined without considering the effects of agitation speed variations on the average saturation of the system, which modifies the wanted CSD, and they have not contemplated the dissolution stage in the crystallization process, when the system temperature is increased to control the product size.

In this work the effect of the agitation speed is studied and a semi-linear profile for cooling or heating temperature is used. These two manipulated variables have an effect in the final CSD. Three different agitation trajectories were employed producing specific CSD. By means of the parameters optimization method, the kinetic parameters of the decrease and production-reduction speed for dissolution were obtained using the program GREG that uses the estimation procedures of Stewart et al. (2).

In addition, an alternative black box model as a function of the mean and variance was employed.

The crystallization process and their basic concepts have been studied widely (3, 4).

Dissolution in Batch Crystallizers

The dissolution process is being considered as the process opposite to the one of crystallization. The dissolution appears when the solution with crystals

already formed is warmed up, taking place as a diminution in the CSD. It is necessary to mention that this process has been poorly investigated as far as its mathematical model.

Batch Crystallization

Crystallization processes are classified as "continuous" and "discontinuous" or "batch."

The continuous operations are commonly employed, because their conditions of operation can be fit finely to obtain the best results in terms of energy use and product characteristics. For productions bigger than 50 ton/day its use is justified.

The batch operations have applications for small productions and when the materials are very expensive. Commonly they are used in the production of fine chemicals and in the pharmaceutical industry (5).

The batch operations offer a good business for plants that constantly are changing to the lines of product or the process (6).

Mathematical Models

The studies in mathematical models for cooling batch crystallization have focused basically in the crystallization stage (3, 1, 7) and they consisted of population, mass and energy balances, and constitutive relations. Normally population balance and constitutive relations are simplified. In contrast, the research on dissolution modeling is scarce.

Methodology

A glass-made crystallizer; Pignat Dn 159Bx, of 2.5 L capacity, was used. CSD, temperatures (in the crystallizer and in the jacket), density, and agitation rate can be read on-line. Cooling-heating water flow and agitation rate were manipulated through a PC control system program. Figure 1 shows the equipment used in this investigation. A Mastersizer "S" of Malvern Instruments (size range 0.05–3500 μm) was adapted in order to measure CSD on-line. Density was measured with an Anton Paar densitometer DPRn427. Cooling and heating fluid was obtained from a 16-L Huber HS40 (temperature range −40 to 150°C and internal circulating rate of 18 L per minute). Agitation was done with a motor RW20DZM (speed range 240 to 2000 rpm).

Experimental data were obtained for crystallization and dissolution in two steps. First, a saturated solution of ammonium sulfate was prepared at 40°C and agitated at 400 rpm for 30 min, and then process temperature was increased to 43°C for another 30 min in order to guarantee a complete

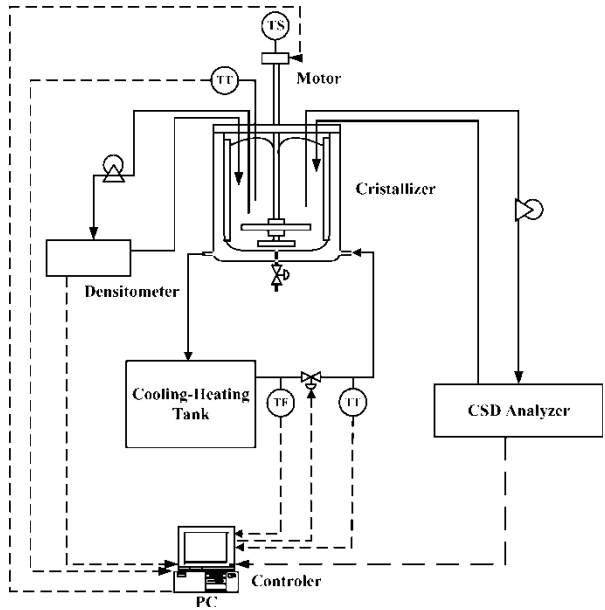

Figure 1. Equipment used.

dissolution of crystals. Process temperature was settled back to 30.5°C in order to start the crystallization process (semi-linear profile). Temperature, density, and CSD were measured until temperature reached 30°C and 30 min after. At this point a new dissolution cycle of 13°C was induced with the same procedure described previously. In both processes, data from the mean and standard deviation were obtained using the CSD analyzer and the densitometer connected to the crystallizer as shown in Fig. 1.

Theoretical Model and Crystallization Kinetics

The theoretical model was developed by means of the population, mass and energy balances, and the constitutive relations for our specific system (ammonium sulfate, 99.5%). Although this model is not the most general, since this would imply to study it in three dimensions.

Comparing both processes (crystallization and dissolution) a mathematical dissolution model can be developed based on the crystallization model but with opposite mass and energy flows. This model has seven parameters obtained from multivariable adjustment (2).

Experimental data was obtained through the experimental design shown in Table 1. Three levels were used: 200, 300, and 400 rpm. Below 200 and above 400 rpm there are mixing and formation of bobbles problems,

Table 1. Experimental design

Rpm	Experimental sequence		
200	1	5	9
300	2	6	7
400	3	4	8

respectively. The experiments were performed in a random way (1, 5, 9, 2, 6, 7, 3, 4, and 8).

Black Box Model

Using the obtained data of the experimental design an equation of the particle size is obtained as a function of time, with the form

$$N = \phi(t, N_r, T) \tag{1}$$

In order to find the black box model, the means and the standard deviations for each experiment were employed with the following relations:

$$\mu = \phi(N_r, t) \tag{2}$$

$$\sigma = \phi(N_r, t) \tag{3}$$

At a specific time and agitator speed, the CSD can be obtained using its mean and standard deviation values with the expression

$$F(L) = \frac{1}{\sigma L\sqrt{2\pi}} e^{(-0.5((\ln(L)-\mu)/\sigma)^2)} \tag{4}$$

RESULTS

Theoretical Model

Summarizing the equations that model the dissolution in a cooling batch crystallizer, without chemical reaction, seeded or fines dissolution are the following.

Populational Balance

$$\frac{\partial(nV)}{\partial t} + V\frac{\partial(B_d n)}{\partial L} = V\alpha(L) \tag{5}$$

Boundary condition:

$$L = L_0 \rightarrow n(L_0, t) = 0 \tag{6}$$

Initial condition:

$$t = 0 \rightarrow n_0(L) = n(L, t) = n(L, 0) \neq 0 \tag{7}$$

Equation (5) is for when L is bigger than L_o. For when L is similar to L_o the boundary condition is used [Eq. (6)].

Mass Balance

$$R_d = -\delta_C K_V V\left[3\int_0^\infty B_d\, n\, L^2\, dL\right] \tag{8}$$

$$\frac{d(\hat{C})}{dt} = -\delta_C K_V h\left[3\int_0^\infty B_d\, n\, L^2\, dL\right] \tag{9}$$

Initial condition:

$$t = 0 \quad \rightarrow \quad \hat{C}(0) = \hat{C}0 \tag{10}$$

Energy Balance

Inside the crystallizer

$$\frac{dT}{dt} = -\frac{\Delta H_d}{M\ Cp}\delta_C K_V\ V\left(3\int_0^\infty B_d\ n\ L^2\ dL\right) - \frac{U_0 A_0}{M\ Cp}(T - Tr) \tag{11}$$

Initial condition:

$$t = 0 \quad \rightarrow \quad T(0) = T_0 \tag{12}$$

Cooling jacket

$$\delta_a V_a Cp_a \frac{dTr}{dt} = F_a \delta_a Cp_a (Tr_0 - Tr) + U_0 A_0 (T - Tr) \tag{13}$$

Initial condition:

$$Tr(0) = Tr_0 \tag{14}$$

Constitutive Relations

Decrease speed:

$$-B_d = k_d S_r^m N_r^e \tag{15}$$

Production-reduction speed:

$$\alpha(L) = k_a S_r^c M_{TC}^k N_r^d \times FTM \tag{16}$$

where:

$$M_{TC} = \delta_C K_V m_3(t) \tag{17}$$

$$m_3(t) = \int_0^\infty L^3 n(t, L) dL \tag{18}$$

$$FTM = \Delta L \left(\frac{n_i}{n_T} \right) \times 1000 \tag{19}$$

In Figs. 2, 3, and 4 the results are reported for the crystal size standard deviation at 200, 300, and 400 rpm, respectively, and in Figs. 6, 7, and 8 are reported results of the crystal size mean at 200, 300, and 400 rpm, respectively. Notice that experimental values in terms of its mean and standard deviation are practically constant. The only way to see the dissolution is in terms of CSD shown in Fig. 5.

The values for parameters of Eqs. (15) and (16) are reported in Table 2; all are equal independently of the agitation speed. For that reason, just one column is reported in Table 2.

Black Box Model

The mean and the standard deviation of crystal size in Eqs. (2) and (3) were modeled as constant functions independent of time in order to reproduce the experimental behavior shown in Figs. 2–4 and 6–8:

$$Y(t) = B \tag{20}$$

The Eq. (20) mathematically indicates that dissolution does not exist, since practically the mean or the standard deviation do not change, but as

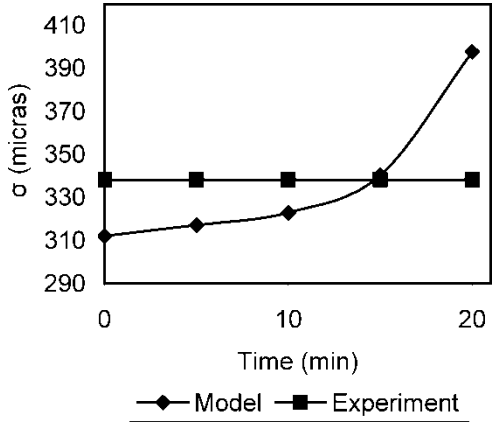

Figure 2. Standard deviation at 200 rpm.

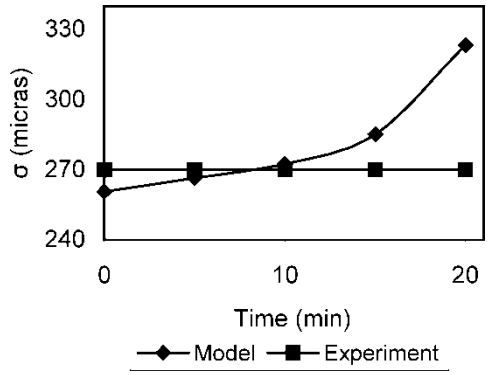

Figure 3. Standard deviation at 300 rpm.

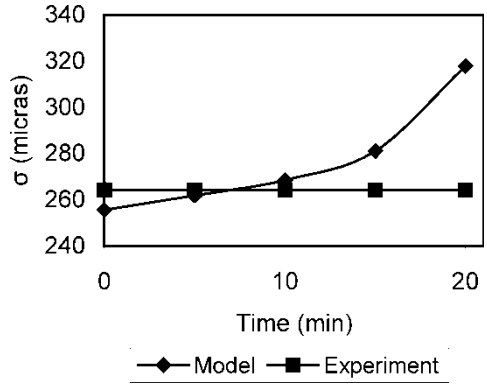

Figure 4. Standard deviation at 400 rpm.

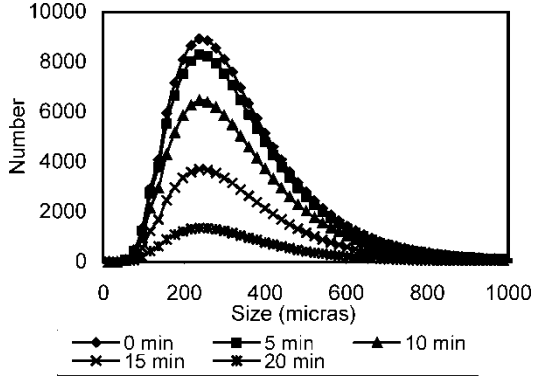

Figure 5. CSD at 200 rpm.

Table 2. Parameters of the theoretical model

Parameter	Rpm
kd	5.00E−04
m	5.00E−03
e	5.00E−02
ka	1.00E−03
c	1.00E−02
k	1.00E−01
d	5.00E−02

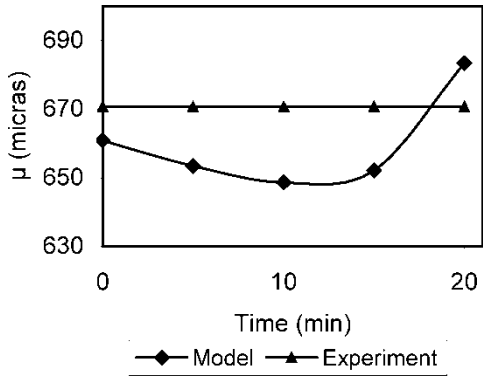

Figure 6. Mean at 200 rpm.

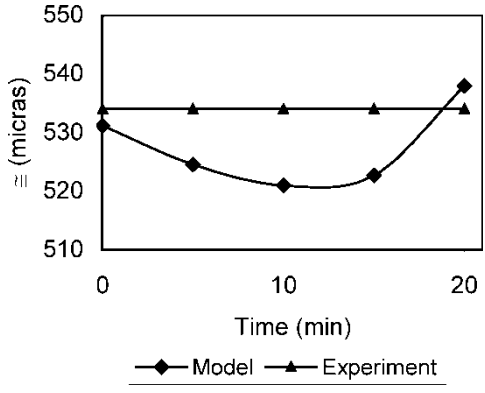

Figure 7. Mean at 300 rpm.

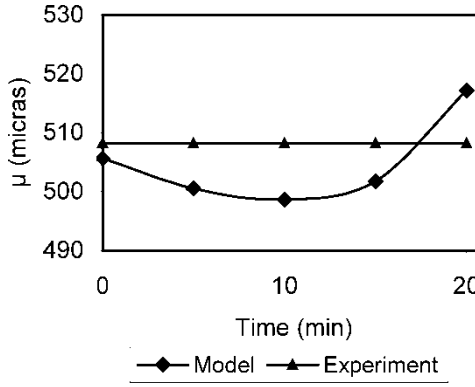

Figure 8. Mean at 400 rpm.

Table 3. Parameters for the mean

Parameter	200 rpm	300 rpm	400 rpm
B	670.73	534.03	508.26

Table 4. Parameters for the standard deviation

Parameter	200 rpm	300 rpm	400 rpm
B	338.39	269.95	264.29

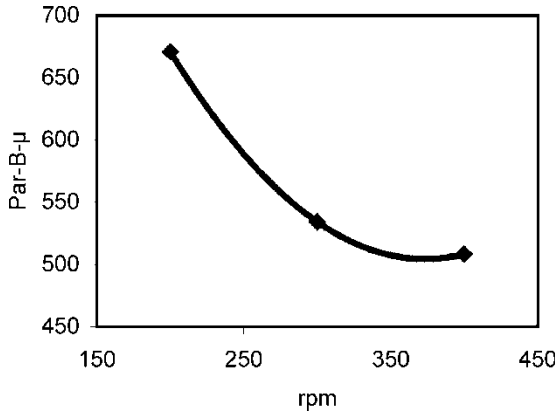

Figure 9. Parameter B for the mean.

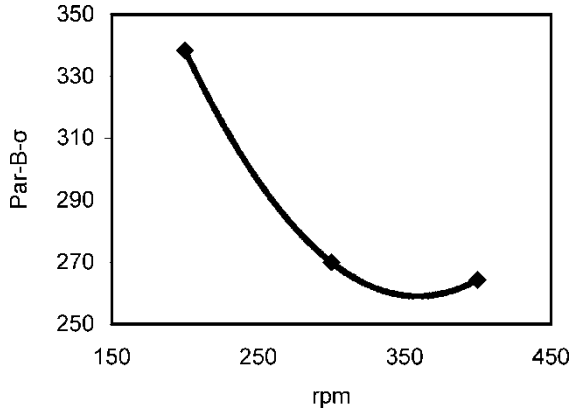

Figure 10. Parameter B for the standard deviation.

seen in Fig. 5, we can demonstrate that there is dissolution in terms of CSD profiles, for example at 200 rpm.

In Tables 3 and 4 are reported the parameters found for the mean and the standard deviation, respectively. In Figs. 9 and 10 are shown the fittings of the parameters B for the mean and the standard deviation, respectively. Continuous line represent the best fitting represented by the Eqs. (21) and (22).

$$B = 0.0055(rpm)^2 - 4.1403(rpm) + 1276.9 \tag{21}$$

$$B = 0.0031(rpm)^2 - 2.2539(rpm) + 663.61 \tag{22}$$

Notice that the fitting is perfect. The reason why is that using these values of mean and standard deviation in Eq. (4), the experimental data are reproducing better than using the theoretical model.

CONCLUSIONS

- The theoretical mathematical model and their solution method reproduced the experimental data appropriately. The parameters were obtained through a multivariable adjustment.
- The black box model was simpler mathematically than the theoretical model and reproduced in a better way the experimental data.
- For the dissolution stage, there is no variation of the mean and the standard deviation for the experiments. They remain approximately constant, but there is a change in the number of particles as a function of time.
- The mean and the standard deviation of crystal size decreased monotonically with the agitation speed.

NOMENCLATURE

	Name	Units
$\hat{C}$	Solute concentration	gr of sulfate/gr of water
$\hat{C}_o$	Initial concentration solute	gr of sulfate/gr of water
μ	Mean	cm
σ	Standard deviation	cm
$\alpha(L)$	Production-reduction speed	no. part./$cm^3 \cdot$ liquor $\cdot$ cm $\cdot$ min
δ_a	Water density	gr/cm^3
δ_c	Crystal density	gr/cm^3
ΔH_d	Dissolution enthalpy of liquor	cal/gr
ΔL	Spaced of crystal size	cm
A_0	Total area of transfer inside the crystallizer	cm^2
B	Parameter	cm
B_d	Decrease speed	cm/min
c	Exponent	none
Cp	Heating capacity of the suspension	cal/gr. °C
Cp_a	Heating capacity of the water	cal/gr $\cdot$ °C
d	Exponent	none
e	Exponent	none
F(L)	Crystal size distribution	cm
F_a	Flow of water in the entrance of jacket	cm^3/min
FTM	Factor of mesh transformation	cm
h	Conversion factor	cm^3/gr of water
k	Exponent	none
k_a	Constant	no. part./$cm^3 \cdot$ liquor $\cdot$ $cm^2 \cdot$ min $\cdot$ $(gr/cm^3)^k \cdot (rpm)^r$
k_d	Constant	cm/min.$(rpm)^q$
K_v	Form factor	none
L	Size of crystal	cm
L_O	Size of nucleus	cm
m	Exponent	none
$m_3(t)$	Moment 3	no. of particles
M	Mass of the suspension	gr
M_{TC}	Total mass of crystals	gr/cm^3
n	Populational density (number)	no. part./cm^3.liquor.cm
N	Populational density (number)	no. part. (gr of water)/cm^3.liquor.cm
n_0	Populational density (number) initial	no. part./$cm^3 \cdot$ liquor $\cdot$ cm
n_i	Populational density (number) from $L = Li$ to $Li + 1$.	no. part./$cm^3 \cdot$ liquor $\cdot$ cm

N_r	Agitation speed	rpm
n_T	No. of total crystals/cm^3 licor · cm	no. part./cm^3 · liquor · cm
R_d	Global speed of mass transfer of solute (liquid) and crystals (solid) for dissolution	gr of sulfate/min
Sr	Relative super saturation	none
t	Time	min
T	Temperature of liquor	°C
T_0	Initial temperature of liquor	°C
T_r	Temperature of cooling water in the jacket	°C
Tr_0	Temperature of water in the entrance of the jacket	°C
U_0	Coefficient of heat transfer (liquor-crystal-water)	cal/°C · min · cm^2
V	Total volume of liquor	cm^3
V_a	Volume of water	cm^3
Y(t)	Mean or standard deviation	cm

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