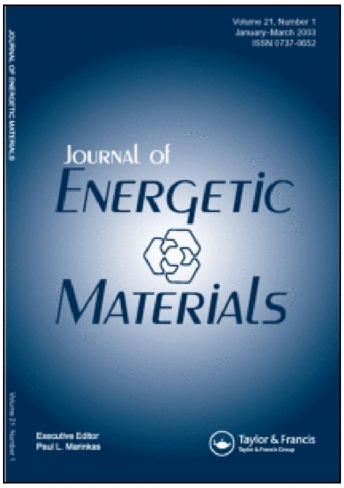

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Mathematical Model for a Fed-Batch Crystallization Process for Energetic Crystals to Achieve Targeted Size Distributions

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Mathematical Model for a Fed-Batch Crystallization Process for Energetic Crystals to Achieve Targeted Size Distributions

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In the manufacture of energetic materials including RDX, HMX, CL-20, it is a challenge to obtain the targeted size distribution. Generally blending is costly and regrinding of the crystals increases the defect densities to give rise to increased sensitivity. The ability to predict apriori the size distribution of various energetic crystalline materials upon recrystallization as a function of the operating conditions, allows the optimization of the process parameters to achieve the desired size distribution without having to regrind or blend different size populations. Here a comprehensive mathematical model of the fed-batch crystallization process consisting of two groups of equations is presented. These include first the dynamic material and energy equations, and second, a population balance model

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for the prediction of the number density of crystals as a function of time and size as functions of the nucleation and growth kinetics for the particles. A numerical solution to the general problem, which involves the alternate solution of the equations at each time step, was developed considering that the reactor volume changes with each time step. Typical results are presented to demonstrate the utility of the mathematical model of the recrystallization process.

Keywords: CL-20, fed-batch crystallization process, HMX, RDX, particle size

Introduction

A typical fed-batch crystallization process is shown in Fig. 1. In the fed-batch crystallization process a hot solution consisting of solvents and the energetic material is fed to the crystallizer at a

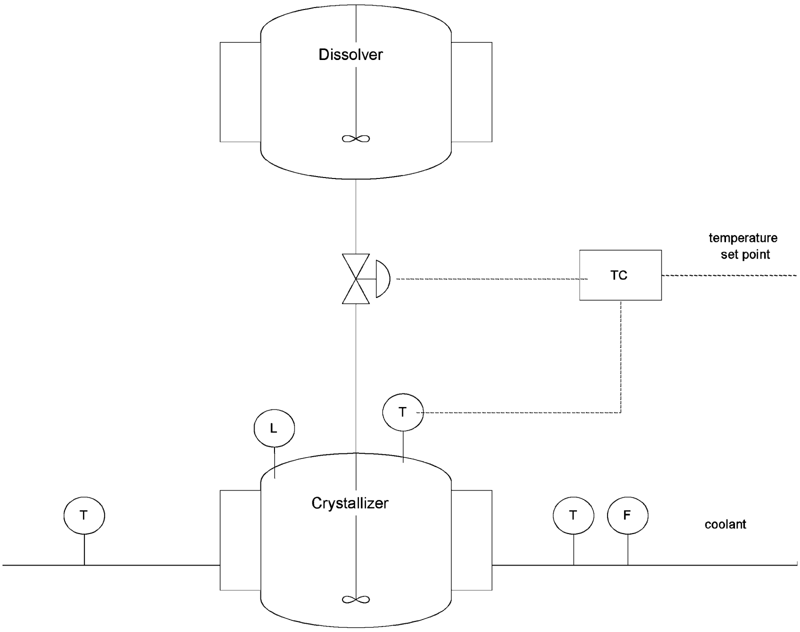
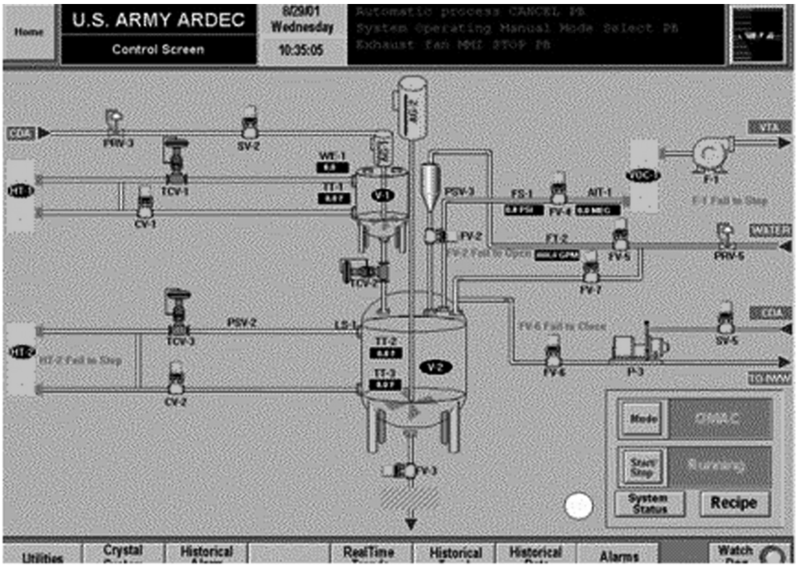


Figure 1. Typical fed-batch crystallizer system.

rate such that the temperature is maintained at the desired set point. A jacket to the crystallization vessel can be provided to furnish better control of the crystallization temperature. The crystallizer is generally loaded with a water heel such that a high degree of supersaturation results when the dissolver solution is added, thus inducing crystallization. The crystallizer can also be initially seeded. The proper selection of the parameters including the feeding rates, supersaturation conditions including the concentrations of the antisolvent and temperature, the quantity of the seed crystals is necessary to allow the achievement of a targeted particle size distribution of the energetic crystals. The dynamics of the process is also affected by the presence of a process controller and the parameters selected for the control law to govern the process controller (Fig. 2). A realistic mathematical model of the process should provide a predictive understanding of the process dynamics and the resultant size distributions [1]. For the prediction of the population distributions of the crystals dispersed in the



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Automatic process CANCEL PB
System Operating Manual Mode Select PB
Exhaust fan MMI STOP PB
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Figure 2. Typical control system for crystallization.

solvent/anti-solvent mixtures population balance modeling is used [1–4]. To our knowledge, such population balance methods have not been applied to the crystallization of the energetic materials.

The Basic Tenets of the Process Model

The problem of simulating the behavior of the fed-batch process involves two distinct systems; *one*, the dynamics of the crystallizer and the dissolver discharge which serves as a feed system to the crystallizer, and *two*, the crystallization process for a crystallizer in which the volume varies with time.

The dynamics problem involves the simultaneous solution of crystallizer material balances, energy balances, the cooling jacket, and the process control equations. The crystallizer can be modeled as a constant volume batch process for a very short time increment. These equations must all be solved simultaneously along with a set of supporting equations such as, mean heat capacities, mean densities, solubility of the energetic material in mixtures which vary with the state of the process, and other miscellaneous equations. The simultaneous solution of this set of equations can be avoided, however, if one assumes that, for a single time step, the two major systems are independent of each other, and therefore they can be solved sequentially. The solution technique is as follows:

1. Set up initial conditions for the dynamic equations and the batch crystallizer (the seeding).
2. For a single time step solve the dynamic equations.
3. Apply the solution of the dynamic equations for the calculation of solution supersaturation which is required to calculate the growth and nucleation rates for the crystallizer.
4. Solve the crystallizer equations for this time step.
5. Use the third moment of the distribution function to calculate the mass of crystals in solution and adjust the material balance calculated from the dynamic equations.

The solution proceeds by incrementing to the next time step and using the current solution as the initial conditions for the next step.

Dynamics of the Process

The solution of the process dynamics problem involves the simultaneous solution of the describing equations as a function of time. These equations are as follows:

Overall Material Balance

$$\rho A \frac{dh}{dt} = F_D \tag{1}$$

Here ρ, is the density of the crystallizer solution, A is the cross sectional area of the crystallizer, h is the height of fluid in the crystallizer, and F_D is the feed rate from the dissolver tank.

Crystallizer Component Material Balances

$$\text{Solvent} \qquad \rho A \frac{d(x_a h)}{dt} = y_a F_D \tag{2}$$

$$\text{Solute} \qquad \rho A \frac{d(x_s h)}{dt} = y_s F_D \tag{3}$$

$$\text{Antisolvent} \qquad x_a + x_s + x_w = 1 \tag{4}$$

Here x_a, x_s, and x_w are the mass fractions of solvent, solute, and antisolvent respectively in the crystallizer, and y_a and y_s are the mass fractions of the solvent and solute in the dissolver.

Crystallizer Energy Balance

$$\rho A h c_c \frac{dT_C}{dt} = F_D c_D (T_D - T_C) - Q_W - \lambda y_S F_D \tag{5}$$

Here C_c and T_c refer to specific heat and temperature of crystallizer and dissolver respectively by subscripts c and D. Q_W is the heat removed by the coolant, and λ is the heat of fusion of the solute.

Coolant Energy Balances

$$Q_W = F_W c_W (T_{WI} - T_{WO}) \tag{6}$$

$$Q_W = UA(T_c - T_{W_{avg}}) \tag{7}$$

Here F_W is the coolant flow rate, T_{WI} and T_{WO} are the inlet and outlet coolant temperatures, $T_{W_{avg}}$ is the average coolant temperature, and U is the overall heat transfer coefficient between the crystallizer contents and the coolant.

PI Controller – Velocity Form

$$p = p_0 + k_c\left[(e - e_0) + \frac{\Delta t}{\tau} e\right] \tag{8}$$

Here k_c and τ are the standard PI controller tuning parameters, i.e., the gain and the derivative time settings and e and p are the current time values of the controller error and the controller output. When subscripted with 0, they refer to the previous time step values, where Δt refers to the size of a time step.

Controller Set Point Error

$$e = T_{SET} - T_C \tag{9}$$

Here the controller error is defined as the difference between the set point temperature, T_{SET} and the crystallizer temperature T_C.

Control Valve Equation

$$F_D = K_V p \tag{10}$$

Here K_V represents a linear valve constant.

The unknowns corresponding to the ten equations above are as follows:

F_D = flow rate of material leaving dissolver
h = height of fluid in crystallizer

x_a = mass fraction of acetone in crystallizer
x_s = mass fraction of solute(liquid) in crystallizer
x_W = mass fraction of water in crystallizer
T_C = temperature of fluid in crystallizer
T_{WO} = temperature of cooling water leaving crystallizer
Q_W = coolant duty
p = controller output
e = controller's set point error

The ten equations include linear, non-linear, and differential equations. In our solution methodology all derivatives are written as backward differences in time. The equations are repeatedly solved by taking a single time step into the future. The solution technique requires that initial conditions be provided for all derivatives. At the first time step, the initial conditions must be provided externally, but for each subsequent time step, the initial conditions are the solution from the previous time step. When the equations are written in numerical form at any time step, they become a set of ten simultaneous non-linear equations, which are solved by the Newton-Raphson method.

The Batch Crystallizer Equations

The basis for the modeling of a batch crystallizer is the well known partial differential equation, developed by Randolph, relating the number distribution function of the crystals, n, to their characteristic length l, and time, shown below [3].

$$\frac{\partial n}{\partial t} + \frac{\partial (gn)}{\partial l} = 0 \tag{11}$$

It is clear that the effects of agglomeration, breakage and additional nucleation are assumed to be negligible. Such terms can be incorporated for individual processes upon comparison of the model predictions with time dependent data on particle size distributions collected during the course of the crystallization process. The distribution function n is defined as dN/Vdl, where N is the number of crystals per unit volume V, and l is the characteristic length and the growth rate g, is defined as dl/dt.

The growth rate is obtained from experimental data and is usually correlated in an Arrhenius form given by Equation (12) below:

$$g = a_g \Delta C^{b_g} \tag{12}$$

where a_g and b_g are experimentally determined parameters and ΔC is supersaturation i.e., the difference between the solution concentration and its solubility. The nucleation rate b, is defined as $(dN/dt)_{l=0}$ is also usually correlated by an Arrhenius form given by Equation (13) below where a_b and b_g are:

$$b = a_b \Delta C^{b_b} \tag{13}$$

experimentally determined parameters.

The solution to Randolph's Equation requires initial conditions, which must be given as the distribution function of the seed crystals, and the boundary condition at $l = 0$, which must be given as a distribution function as well. At the boundary the relationship

$$b = n^0 g \tag{14}$$

applies, where n^0 is the nuclei distribution function.

In this formulation it is assumed that the spatial variations in the concentrations of the solute and the solvent/antisolvent mixture are negligible. The fluid mechanics in the crystallizer is also scale dependent and is also ignored in this analysis. The equations can be written in a discretized implicit form, which is convenient for solution numerically. The solution can be visualized as a matrix of numbers where time is increasing down the y axis and characteristic length increase along the x axis. The following formulations for the derivatives provide a set of linear simultaneous equations at each time step. For $\partial n/dl$ a central difference can be written as follows:

$$\frac{\partial n}{\partial l} = \frac{n_{t,l+\Delta l} - n_{t,l-\Delta l}}{2\Delta l} \tag{15}$$

For $\partial n/dt$ a backward difference can be written as follows:

$$\frac{\partial n}{\partial t} = \frac{n_{t,l} - n_{t-\Delta t,l}}{\Delta t} \tag{16}$$

Substitution of the difference formulations into Randolph's Equation gives

$$\frac{g\Delta t}{2\Delta l}n_{t,l+\Delta l} + n_{t,l} - \frac{g\Delta t}{2\Delta l}n_{t,l-\Delta l} = n_{t-\Delta t,l} \tag{17}$$

This equation shows that all discretized points at a typical point in time depends only on their adjacent points in length and the point at the previous time. The last length point however, cannot employ a $l + \Delta l$ point since it does not exist, therefore the central difference approximation for $\partial n/dl$ is replaced with a backward difference as follows:

$$\frac{\partial n}{\partial l} = \frac{n_{t,l} - n_{t,l-\Delta l}}{\Delta l} \tag{18}$$

and Randolph's Equation becomes:

$$\left(1 + g\frac{\Delta t}{\Delta l}\right)n_{t,l} - \frac{g\Delta t}{\Delta l} = n_{t-\Delta t,l} \tag{19}$$

When these equations are written for any time point they take the familiar tri-diagonal form shown in Table 1, below, for ten increments in l.

Table 1

Tri-diagonal matrix structure

Tri-diagonal matrix										n(t,l)	rhs
B	C	0	0	0	0	0	0	0	0	n(t,1)	R
A	B	C	0	0	0	0	0	0	0	n(t,2)	R
0	A	B	C	0	0	0	0	0	0	n(t,3)	R
0	0	A	B	C	0	0	0	0	0	n(t,4)	R
0	0	0	A	B	C	0	0	0	0	n(t,5)	R
0	0	0	0	A	B	C	0	0	0	n(t,6)	R
0	0	0	0	0	A	B	C	0	0	n(t,7)	R
0	0	0	0	0	0	A	B	C	0	n(t,8)	R
0	0	0	0	0	0	0	A	B	C	n(t,9)	R
0	0	0	0	0	0	0	0	A	B	n(t,10)	R

Note that in the general solution matrix, the first value of n, i.e., at l = 0 for all t, n is the boundary condition given by Equation (14). This system of equations is readily solved by the Thomas Algorithm. In the tri-diagonal matrix, when the l increment refers to the first row, l=1, the values of the coefficients are given below.

$$A = 0$$

$$A = 0 \qquad\qquad B = 1$$

$$B = 1 \qquad C = \frac{g\Delta t}{2\Delta l}$$

$$R = n_{t,0}, \quad \text{the boundary condition } \frac{b}{g}.$$

For all values of l, except the last row the coefficients are.

$$A = -\frac{g\Delta t}{2\Delta l}$$

$$B = 1$$

$$B = 1 \quad C = \frac{g\Delta t}{2\Delta l}$$

$R = n_{t-\Delta t,l}$, the value of n at l at the previous time step.

For l = L, the last row the coefficients are.

$$A = -\frac{g\Delta t}{\Delta l}$$

$$B = 1 + \frac{g\Delta t}{\Delta l}$$

$$C = 0$$

$C = 0 \quad R = n_{t-\Delta t,l}$, the value of n at l at the previous time step.

A complete solution requires the simultaneous solution of the dynamic and crystallization equations. In this development the equations are solved in an alternating manner for a single time step. At the conclusion of one step of the dynamic equations, a material balance yields ΔC, and b and g are evaluated. These values are employed in the tri-diagonal matrix solution of the crystallizer equations for the current time step. The material crystallized, M_T is then calculated using the third moment of the distribution function, Equation (20),

$$M_T = \alpha \rho_c \int_0^\infty n l^3 dl \tag{20}$$

which is used to correct the composition of the solution in the crystallizer to initiate the next step in the dynamics.

Solution Implementation

A source code was written to incorporate the set of equations described above. Separate subroutines are used for the calculation of nucleation and growth rates according to the Arrhenius formulations. However, since ΔC is virtually zero initially, the use of a global Arrhenius type correlation for growth and nucleation is questionable. Similarly, there exists a subroutine for the solubility of the solute in the solvent and antisolvent mixture. The latent heat of fusion of the solute as well as the other thermal properties of both the solute and the solvent, and the overall heat transfer coefficient for the cooling jacket and coil have to be determined apriori. In addition to these data it is necessary to provide the particle size distribution data for the seed crystals in the form of distribution function.

A sample run of the process dynamics solution is given in Table 2 for RDX and a mixture of acetone and water, i.e., acetone is the solvent and water is the antisolvent. One may observe that the performance of the control system, even though not optimally tuned, is excellent. The typical results for temperature control are shown in Fig. 3, upon a step change in the feed temperature to return back to the steady state condition without oscillations. Thus one may conclude that if the method of control for the process employed in the model is adopted in the field, an excellent degree of repeatability in the performance of the process can be expected.

The crystal mass increases by an order of magnitude over the entire length of the run. One may also note that, due to the nature of the fed-batch process, ΔC has a tendency to

Table 2

Typical process dynamics over a short time span

Time	Coolant T deg. F	Duty btu/hr	Crystallizer T deg. F	Height ft.	Mass frac. acetone	Mass frac. solute	Mass frac. water	Feed rate lbs/hr	Valve position	Set point error	Crystal mass	Delta-C g/cm^3
0.01	70.08	100845	80.54	2.072	0.013	0.002	0.985	15465	0.910	5.458	4.E-07	0.141
0.02	70.44	104413	81.04	2.102	0.025	0.004	0.971	14703	0.865	4.962	4.1E-07	0.270
0.03	70.77	107737	81.49	2.131	0.036	0.006	0.958	13885	0.817	4.510	4.1E-07	0.389
0.04	71.08	110833	81.90	2.158	0.046	0.008	0.946	13116	0.772	4.100	4.1E-07	0.498
0.05	71.37	113715	82.27	2.183	0.055	0.010	0.935	12397	0.729	3.727	4.1E-07	0.599
0.06	71.64	116396	82.61	2.207	0.063	0.011	0.925	11726	0.690	3.388	4.2E-07	0.692
0.07	71.89	118891	82.92	2.230	0.071	0.013	0.916	11101	0.653	3.079	4.2E-07	0.778
0.08	72.12	121212	83.20	2.252	0.079	0.014	0.907	10521	0.619	2.799	4.2E-07	0.858
0.09	72.34	123372	83.46	2.273	0.086	0.015	0.899	9983	0.587	2.544	4.2E-07	0.933
0.10	72.54	125383	83.69	2.292	0.092	0.016	0.891	9485	0.558	2.313	4.3E-07	1.002
0.11	72.73	127255	83.90	2.311	0.098	0.017	0.884	9025	0.531	2.102	4.3E-07	1.067
0.12	72.90	129000	84.09	2.329	0.104	0.018	0.877	8601	0.506	1.911	4.3E-07	1.128
0.13	73.06	130627	84.26	2.346	0.110	0.019	0.871	8210	0.483	1.737	4.3E-07	1.186

0.14	73.21	132146	84.42	2.362	0.115	0.020	0.865	7850	0.462	1.579	4.4E-07	1.240
0.15	73.36	133565	84.56	2.378	0.119	0.021	0.859	7520	0.442	1.435	4.4E-07	1.290
0.16	73.49	134893	84.70	2.393	0.124	0.022	0.854	7217	0.425	1.304	4.4E-07	1.339
0.17	73.61	136136	84.81	2.408	0.128	0.023	0.849	6938	0.408	1.186	4.4E-07	1.384
0.18	73.73	137302	84.92	2.422	0.133	0.023	0.844	6684	0.393	1.078	4.4E-07	1.428
0.19	73.84	138398	85.02	2.435	0.136	0.024	0.839	6451	0.379	0.980	4.5E-07	1.470
0.20	73.94	139428	85.11	2.448	0.140	0.025	0.835	6238	0.367	0.891	4.5E-07	1.509
0.21	74.04	140399	85.19	2.461	0.144	0.025	0.831	6044	0.356	0.809	4.5E-07	1.547
0.22	74.13	141316	85.26	2.473	0.147	0.026	0.827	5866	0.345	0.736	4.5E-07	1.584
0.23	74.22	142182	85.33	2.485	0.151	0.027	0.823	5705	0.336	0.669	4.6E-07	1.619
0.24	74.30	143004	85.39	2.497	0.154	0.027	0.819	5558	0.327	0.608	4.6E-07	1.653
0.25	74.38	143784	85.45	2.508	0.157	0.028	0.815	5424	0.319	0.553	4.6E-07	1.686
0.26	74.45	144525	85.50	2.519	0.160	0.028	0.812	5302	0.312	0.502	4.6E-07	1.718
0.27	74.52	145233	85.54	2.530	0.163	0.029	0.808	5192	0.305	0.457	4.6E-07	1.749
0.28	74.59	145908	85.58	2.541	0.166	0.029	0.805	5092	0.300	0.415	4.7E-07	1.779
0.29	74.66	146555	85.62	2.551	0.169	0.030	0.801	5001	0.294	0.377	4.7E-07	1.808
0.30	74.72	147175	85.66	2.561	0.172	0.030	0.798	4919	0.289	0.343	4.7E-07	1.836

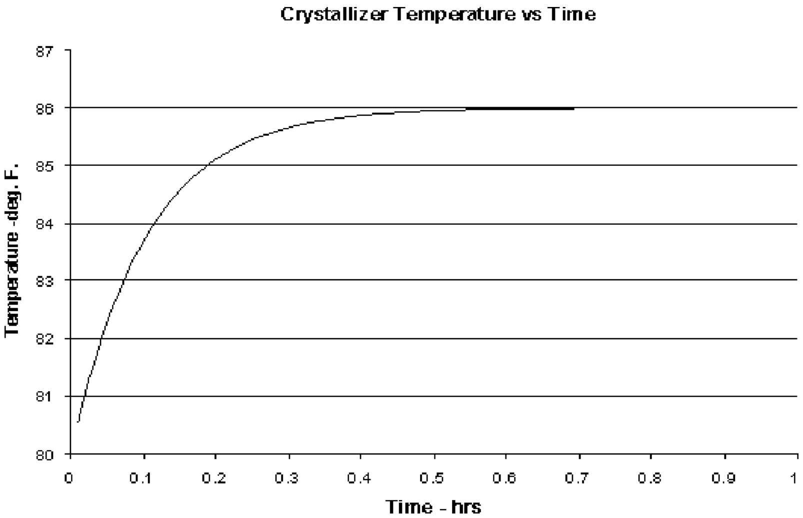

Figure 3. Crystallizer temperature control.

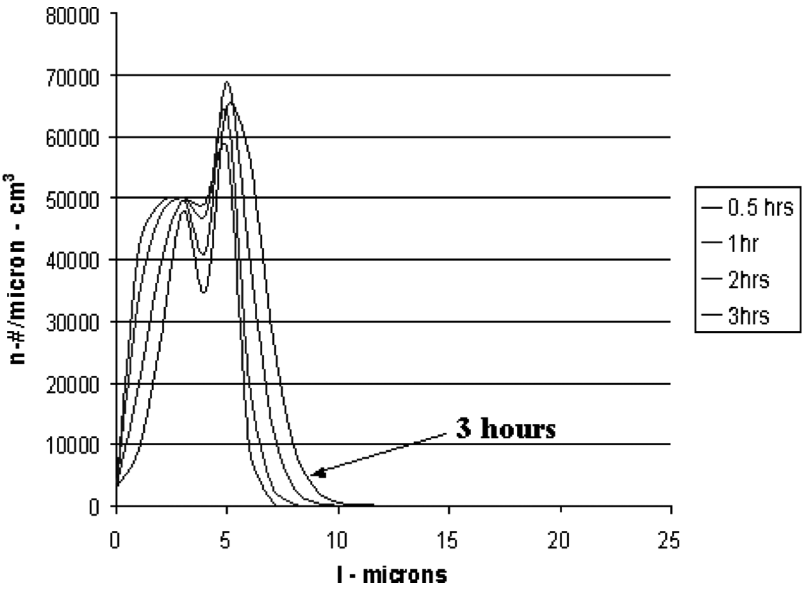

Figure 4. The particle size distribution function.

increase with time, the exact opposite of batch crystallization, depending upon the rate of addition of dissolver fluid and the buildup of crystal mass. After the addition ceases, ΔC will eventually go to zero.

The development of the size distribution of the RDX crystals with time during the course of the crystallization process is shown in Fig. 4 (over a relatively short time span). There is a significant degree of freedom in the process to allow changes in the operating parameters and the control parameters to be made during the course of the crystallization process to allow the tailoring of the particle size distribution.

Conclusions

A mathematical model of the crystallization from solution process for energetic materials is provided. Such population balance method based models allow the tailoring of the particle size distribution as a function of the process conditions and controller tuning parameters in industrial scale crystallizers and their use in the energetics materials industry should be encouraged.

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