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ON THE CONTROL OF CRYSTAL SIZE IN A SEMIBATCH CRYSTALLIZER

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Abstract—Optimal programming of input flow rate to a solventing-out batch crystallizer was studied to find the maximum or the minimum average particle size while keeping the total amounts of solventing-out agent and crystals constant. For salt-water-ethanol system the maximum difference of average particle size was calculated to be about 20 percent. The difference was confirmed by experiment. The maximum difference was found by model calculation to become very large for a limited range of birth functions.

INTRODUCTION

Batch crystallization is widely used for production of specialty chemicals in solid forms. Product crystal size is often an important factor in such operations. Since batch processes are operated in transient state, the system is more difficult to analyze and control [1-3] than steady state crystallization processes. The crystal size distribution control problem has been investigated for continuous MSMPR (Mixed Suspension Mixed Product Removal) crystallizers [4-9], but less work has been done on the control of batch crystallization process.

Mullin and Nyvlt [10] studied the cooling curve which gave the maximum average product size. Jones and Mullin [11] carried out a similar investigation with a slightly different set of equations. Jones [12] applied Pontryagin's maximum principle [13] to calculate the optimal cooling program. Chang and Epstein [14] proposed a method for the calculation of optimal temperature program to maximize the average product size or the volume of solid product.

In this investigation, a solventing-out batch crystallization system is studied to obtain the input flow rate program of solventing-out agent which maximize or minimize the weight mean size of crystals. The method is applied in the salt-water-ethanol system and compared with experimental values.

STATE EQUATIONS

We consider a well-mixed concentrated salt solution into which a second solvent is introduced at a volumetric flow rate Q_{in} and causes the solute to solvent-out.

The moment transformed population balance equation is often used for the analysis of crystal size distribution [3]. When the growth rate is independent of crystal size, first five moments m_0, m_1, m_2, m_3 and m_4 of the population density function are given as follows.

$$\frac{dm_0}{dt}=B_0-\frac{\gamma}{\tau}m_0 \tag{1}$$

$$\frac{dm_1}{dt}=Gm_0-\frac{\gamma}{\tau}m_1 \tag{2}$$

$$\frac{dm_2}{dt}=2Gm_1-\frac{\gamma}{\tau}m_2 \tag{3}$$

$$\frac{dm_3}{dt}=3Gm_2-\frac{\gamma}{\tau}m_3 \tag{4}$$

$$\frac{dm_4}{dt}=4Gm_3-\frac{\gamma}{\tau}m_4 \tag{5}$$

where the mean residence time τ is given as a function of input volumetric flow rate and the system volume V which in turn depends on γ.

$$\tau=\frac{V}{Q_{in}}=\frac{Vo+\int_0^t \gamma Q_{in}dt}{Q_{in}} \tag{6}$$

γ reflects the volume change rate of the slurry system as the feed flows in [15].

$$\gamma=\lim_{\Delta t\to 0}\frac{\Delta V}{\Delta V_{in}}=\frac{dV/dt}{Q_{in}} \tag{7}$$

The mean residence time τ is constant in the continuous MSMPR crystallizer, but it is time-dependent in batch crystallization processes. γ/τ may be expressed as follows.

$$f=\gamma/\tau=(\underline{V}_{in}/V)\,Q_{in}+3k_vGm_2(1-\rho_c\underline{V}_S) \tag{8}$$

where $\underline{V}_{in}$ is defined as

$$\underline{V}_{in}=\underline{V}_Sw_S+\underline{V}_Ww_W+\underline{V}_Ew_W \tag{9}$$

Here $\underline{V}_S$, $\underline{V}_W$ and $\underline{V}_E$ are partial specific volumes of component S, W and E, respectively and w's are weight fractions of components.

We also need mass balance equations for solute S and solvents E and W to calculate the solubility and volumetric properties. Following forms are found convenient.

$$\frac{dW_s}{dt}=Q_{in}C_{Sin}-3\rho_cK_vGm_2V \tag{10}$$

$$\frac{dW_E}{dt}=Q_{in}C_{Ein} \tag{11}$$

$$\frac{dW_W}{dt}=Q_{in}C_{Win} \tag{12}$$

OPTIMUM INPUT PROGRAMS

Now we like to find the input flow rate program which maximize or minimize the average particle size defined as,

$$r_{av}=m_4/m_3 \tag{13}$$

subject to some constraints. For this purpose it is convenient to define a performance index in the form,

$$P=b_1r_{av}+b_2(K_v\rho_cm_3V-M_S)^2+b_3\int Q_{in}dt \tag{14}$$

where b's are weighting factors and M_S is final value for total mass of solid. Minimization of P results in a minimum particle size when b_1 is greater than zero and a maximum size when b_1 is less than zero.

When the maximum principle is applied to the solution of the problem, a singular problem is suspected which can be very difficult to handle [16]. Here we apply a nonlinear programming method or a nonlinear minimization method. In this method a fixed time interval is devided into three equal parts and a constant flow rate $Q_{in,i}$ in each time interval is optimized using the performance index given by Eq. (14) subject to following constraints.

$$Q_{min}\leq Q_{in,i}\leq Q_{max}\quad (i=1,2,3) \tag{15a}$$

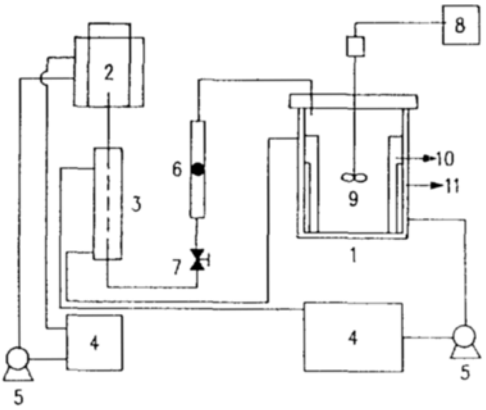

Fig. 1. Schematic diagram of crystallization system.

$$Q_{in,1}+Q_{in,2}+Q_{in,3}=\text{const} \tag{15b}$$

A global minimization routine together with a Runge-Kutta integration routine from the ISML library is used for computation.

EXPERIMENTS

The experimental apparatus, schematically shown in Fig. 1, consisted of a preheater to preheat the entering solution, water jacket to maintain the constant temperature, a Master servodyne system to maintain the impeller speed and a capillary valve to change the input flow rate. The crystallizer was 200 mm in height and 140 mm in the internal diameter. Four baffles were installed, each of which was 180 mm high and 27 mm wide, separated from the inner wall of the crystallizer by 3.8 mm to reduce dead zones and edding. A 50 mm diameter standard three-blade marine propeller, located 50 mm from the bottom of the crystallizer, was used to mix the suspension.

Initially 1 liter of saturated aqueous salt solution was introduced into the crystallizer which was held at 25℃, and 96% EP grade ethanol was then pumped into the crystallizer. The impeller speed was maintained at 2700 rpm. A total of 800 ml of ethanol was introduced in 40 minutes.

At 40 minutes after the start of crystallization, 100 ml of the sample was collected and the crystals were separated from the mother liquor using a ASTM 10-15 M glass filter. The filtered crystals were washed repeatedly with aceton and then dried in a desicator at 40℃. The mother liquor was dried in a desicator at 60℃. Then the mass of completely dried crystals and that of salt in the mother liquor were determined. The crystals larger than 140 ASTM mesh size were classified using 40, 60, 80, 100, 120 and 140 mesh standard sieves. Each fraction of dried crystals was weighed. The size distribution of crystals smaller than 140 ASTM mesh were measured using a SKA-5000 Micro Photo Sizer.

PROPERTIES AND SALT-ETHANOL -WATER SYSTEM

We summarize thermodynamic properties and rate informations for salt-ethanol-water system which are needed for calculation. We define R and S as

$$R=W_E/(W_E+W_W);\quad S=W_S/(W_E+W_W) \tag{16}$$

where subscripts S, E and W indicate salt, ethanol and water respectively. Mass concentration of salt in the saturated solution, C_S^*, and specific solution volume of the mixture, V_f, are fitted to data at 25℃ [17] and represented as follows.

$$C_S^*=0.30203-0.4759W+0.03995W^2-0.1581W^3+0.02283W^4 \tag{17}$$

$$V_f=(V_{f0}+V_{f1})/(1-S) \tag{18}$$

where

$V_{f0}=0.3554$
$V_{f1}=-0.06287+0.1924W-0.2331W^2+0.1559W^3-0.05566W^4$

Then the total system volume is calculated,

$$V=V_f(W_S+W_E+W_W)/(1-K_v m_3) \tag{19}$$

where the denominator is the fraction of fluid in the solid fluid mixture. Partial specific volumes in Eq. (9) are calculated from Eq. (19),

$$\underline{V}_i=\partial[V_f(W_S+W_E+W_W)]/\partial W_i \tag{20}$$

where i stands for S, E or W.

We use the nucleate birth function B^0 given by Shin et al. [18]. The growth function G is also of the same form but we modified the rate constant to improve fitting. They are given below.

$$G=k_g\,\Delta C \tag{21}$$

$$B^0=k_B\,\Delta C(2\Delta C+M_T) \tag{22}$$

where $\Delta C=C_S-C_S^*$,

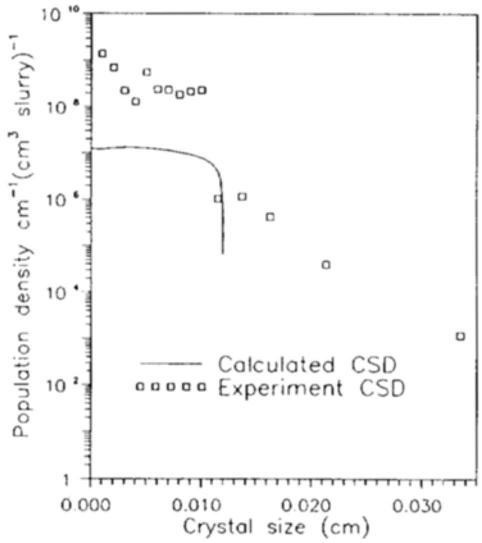

Fig. 2. Comparison of calculated CSD and experimental CSD in batch crystallizer after startup at 40 min ($U=20-20-20$ cm^3 min^{-1}).

$M_T=\rho_c K_v m_3$
$j=1.0$
$k_g=0.015$[cm(cm^3 solution)min^{-1} (g solute)$^{-1}$],
$k_B=3.2\times10^6$ [(cm^3 solution)min^{-1} (g solute)$^{-2}$].

Without ΔC term in the parenthesis of Eq. (22), one has to assume an arbitrary number of nuclei to start.

RESULT AND DISCUSSION

With the informations given above we can compute the optimal flow rate program to maximize or minimize the average particle size as defined by Eq. (13). Initially 360g of salt was dissolved in 1 kg of water and placed in a well stirred vessel. For 40 minutes 96% ethanol solution was introduced into the vessel. The total volume of ethanol solution fed to crystallizer was 800 cm^3. Q_{min} and Q_{max} were 5 ml/min and 50 ml/min respectively. The process is operated at 25℃.

For an arbitrarily selected input program, we compared experimental crystal size distribution with calculated results in Fig. 2. The agreement is only qualititative. Tavare and Garside [19] reported the similar comparison but the agreement is not as good as ours. Average size for different input program is cömpared in the group I of Table 1. They indicate that the system response is very insensitive to the input program.

Group II of the Table 1 gives the comparison of optimization calculation with experimental data. Since we also want the amount of solid to be large, we put a small number in b_2 of Eq. (14). Larger flow rate in

Table 1. Comparison of crystal size with the input velocity sequence in the salt-water-ethanol system

		Input velocity (ml/min^{-1})			Ave. size (μm)		Solid recovery (g)	
		$Q_{1,in}$	$Q_{2,in}$	$Q_{3,in}$	Cal.	Exp.	Cal.	Exp.
I	1	20	20	20	88	86	102	87
	2	5	20	35	94	90	95	86
	3	35	20	5	84	88	106	93
II	Max	5	45	10	93	86	105	92
	Min	50	5	5	81	83	106	86

the initial period induced a large number of nuclei and the average size is slightly smaller. In both program the flow rate is very small in the third period. This may indicate that particles need time to grow. The average particle size difference which is defined $(W_{Max} - W_{Min})/W_{Min}$ is 14.8 percent. By optimal programing we could reduce the minimum size.

Such an insensitivity to input program cannot be generally true. Therefore we varied growth and birth function arbitrarily and did some model calculations. The results are summarized in Table 2. In the first set of variation (group I) we changed the rate constant, in the second set (group II) the power to ΔC in the growth function, in the third set (group III) the rate constant and in the fourth set (group VI) the power to M_T in the birth function. We find the average particle size difference is approximately in the range of values given in Table 1.

Instead of Eq. (22) we use the following usual form of birth function to see the effect of optimal calculation.

Table 2. Model calculation of crystal size with the input velocity sequence using the varied growth and birth function

		Input vel.(ml/min^{-1})			Ave. size(μm)	Solid recov.(g)	$\frac{W_{Max} - W_{Min}}{W_{Min}}$ (%)
		$Q_{1,in}$	$Q_{2,in}$	$Q_{3,in}$	Calculated	Calculated	
I-1	Max	5	5	50	192	104	12.28
	Min	50	6	4	171	107	
I-2	Max	50	7	3	23	10	0.00
	Min	49	10	1	23	10	
II-1	Max	49	10	1	45	57	2.27
	Min	46	12	2	44	55	
II-2	Max	5	5	50	180	107	24.14
	Min	50	5	5	145	107	
III-1	Max	13	22	25	143	78	2.14
	Min	5	41	14	140	77	
III-2	Max	5	45	10	58	105	18.36
	Min	50	6	4	49	106	
IV-1	Max	8	38	14	82	104	7.98
	Min	35	5	20	76	103	
IV-2	Max	5	45	10	94	104	14.63
	Min	49	5	6	82	106	

I-1: $k_g=0.15$, $g=1.0$; I-2: $k_g=0.0015$, $g=1.0$, II-1: $k_g=0.015$, $g=1.5$; II-2: $k_g=0.015$, $g=0.5$, III-1: $k_B=3.2\times10^5$, $j=1.0$; III-2: $k_B=3.2\times10^7$, $j=1.0$, IV-1: $k_B=3.2\times10^6$, $j=0.5$; IV-2: $k_B=3.2\times10^6$, $j=1.5$

Table 3. Model calculation of crystal size with the input velocity sequence using the varied birth function with constant kg (0.032)

		Input vel.(ml/min^{-1})			Ave. size(μm)	Solid recov.(g)	$\frac{W_{Max} - W_{Min}}{W_{Min}}$ (%)
		$Q_{1,in}$	$Q_{2,in}$	$Q_{3,in}$	Calculated	Calculated	
I-1	Max	7	43	10	148	105	23.23
	Min	49	5	6	120	106	
I-2	Max	6	16	38	105	102	45.83
	Min	50	7	3	72	107	
II-1	Max	5	50	5	57	107	42.50
	Min	50	5	5	40	107	

Table 3. Continued

		Input vel.(m*l*/min^{-1})			Ave. size(μm)	Solid recov.(g)	$\frac{W_{Max}-W_{Min}}{W_{Min}}$ (%)
		$Q_{1,in}$	$Q_{2,in}$	$Q_{3,in}$	Calculated	Calculated	
II-2	Max	5	38	17	149	104	22.13
	Min	50	5	5	122	106	
III-1	Max	5	50	5	168	106	127.03
	Min	50	9	1	74	107	
III-2	Max	5	46	9	155	105	241.41
	Min	50	5	5	45	107	
IV-1	Max	5	48	7	148	106	236.36
	Min	50	7	3	44	107	
IV-2	Max	12	43	5	170	106	33.86
	Min	49	7	4	127	106	

I-1: $k_B'=3.2\times10^{10}$, i=3.0, j=1.0; I-2: $k_B'=3.2\times10^{11}$, i=3.0, j=1.0
II-1: $k_B'=3.2\times10^{11}$, i=3.0, j=0.5; II-2: $k_B'=3.2\times10^{11}$, i=3.0, j=1.5
III-1: $k_B'=3.2\times10^{21}$, i=10.0, j=1.0; III-2: $k_B'=3.2\times10^{22}$, i=10.0, j=1.0
IV-1: $k_B'=3.2\times10^{21}$, i=10.0, j=0.5; IV-2: $k_B'=3.2\times10^{21}$, i=10.0, j=1.0

$$B^0=k_B'\,\Delta C^i\,M_T^j \tag{23}$$

The calculated results are summarized in Table 3. We find the average crystal size difference can become very large for a large value of the power to ΔC. Such values of k_B' and i are in the range found in the literature [20]. Although not reported here, growth function is relatively insensitive to the results.

Although no general criteria can be drawn from this model calculation, it is evident that optimal programming is possible for maximum or minimum average particle size while keeping the total amount of solventing-out agent and the total amount of solids in the crystallizer constant.

CONCLUSION

1. Optimum programming of input flow rate is feasible for calculation of the maximum or minimum average particle size in a solventing out batch crystallization. In salt-water-ethanol system, the maximum average crystal size differences is about 20 percent.

2. The maximum average particle size difference is sensitive to the nucleation function and can become very large for limited cases.

NOMENCLATURE

B^0 : birth function [min^{-1} (cm^3 slurry)$^{-1}$]
b_1, b_2, b_3 : weighting factor
C_{Ein} : ethanol concentration in feed stream [g ethanol (cm^3 solution)$^{-1}$]
C_{Sin} : solute concentration in feed stream [g solute (cm^3 solution)$^{-1}$]
C_{Win} : water concentration in feed stream [g H_2O (cm^3 solution)$^{-1}$]
ΔC : supersaturation [g solute (cm^3 solution)$^{-1}$]
G : crystal growth function [cm min^{-1}]
g : power of growth rate [supersaturation]
i : power of nucleation [supersaturation]
j : power of nucleation [suspension density]
k_g : growth rate constant [cm (cm^3 solution) min^{-1} (g solute)$^{-1}$]
k_B : nucleation rate constant [(cm^3 solution) min^{-1} (g solute)$^{-2}$]
k_B' : nucleation rate constant [(cm^3 solution) min^{-1} (g solute)$^{-1}$ (cm^3 slurry)$^{-1}$]
k_v : volumetric shape factor
m_i : ith moment
M_S : final value of total mass of solid [g]
M_T : suspension density [g solute (cm^3 slurry)$^{-1}$]
P : performance index
Q_{in} : input flow rate of solution [(cm^3 solution) min^{-1}]
Q_{Max} : maximum input flow rate of solution [(cm^3 solution) min^{-1}]
Q_{Min} : minimum input flow rate of solution [(cm^3 solution) min^{-1}]
R : defined by Eq. (17)
r_{av} : average particle size defined by Eq. (13)
S : defined by Eq. (17)
t : time [min]
dt : time increment [min]
V : volume of slurry [cm^3]
V_0 : initial volume of solution [cm^3]
ΔV_{in} : volume increment by input flow [cm^3]
ΔV : volume increment in the crystallizer [cm^3]

$\underline{V}_E$: partial specific volume of component E
$\underline{V}_m$: defined by Eq. (9)
V_f : defined by Eq. (18)
V_{f0} : defined by Eq. (18)
V_{f1} : defined by Eq. (18)
$\underline{V}_S$: partial specific volume of component S
$\underline{V}_W$: partial specific volume of component W
W_E : weight fraction of component E
W_S : weight fraction of component S
W_W : weight fraction of component W

Greek Letters

γ : defined by Eq. (10)
ρ_c : crystal density [g cm^{-3}]
τ : mean residence time [min]

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