On the Narrowing of Particle-Size Distributions in Staged Vessels with Classified Product Removal

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A well-known, but quite inefficient, representation of dead time in a continuous process is that of a series of staged vessels with equal time constants. Buckley (*1*) compares such a series approximation for dead time, τ_D, with other methods of dead time representation. The transfer function for this approximation (equivalent to k well-mixed stages in series) is given as

$$G_D = \frac{1}{\left(\frac{\mathrm{T}_D s}{k} + 1\right)^k} \tag{1}$$

The transfer function given by Equation (1), applied to the problem of residence-time distributions of particles residing in a system of k serially-staged well-mixed vessels, indicates that as the number of tanks in series increases, a uniformity of residence time within the total system occurs. As $k \rightarrow \infty$ the residence-time distribution of plug-flow (pure dead time) is predicted.

Robinson and Roberts (*2*) attacked the problem of predicting crystal size distribution in a staged crystallizer by calculating the residence-time distribution of particles in the system, assuming they grew at the same linear rate in each of the vessels. It was further necessary to assume that all particles entered (were formed) at zero size in the first stage. These authors did not dwell on the narrowing of crystal size distribution expected in such a system. Randolph and Larson (*3*) considered the same problem of crystal size distribution in staged systems, but allowed for particle formation (nucleation) in each of the stages. The resultant population distribution leaving the kth stage was calculated to be

$$n_k = \left[\frac{n^o{}_1 x^{k-1}}{(k-1)!} + \frac{n^o{}_2 x^{k-2}}{(k-2)!} + \ldots \frac{n^o{}_{k-1} x}{1!} + \frac{n^o{}_k}{0!}\right] e^{-x} \tag{2}$$

where $x = \dfrac{L}{rT} = \dfrac{LQ}{rV}$ is a dimensionless particle size. Again, it was necessary to assume that the product of linear growth rate and mean retention time was equal in each stage. Cumulative weight distribution was obtained from population distribution as

$$W_k = \frac{\int_o^x n_k x^3 dx}{\int_o^\infty n_k x^3 dx} \tag{3}$$

The occurrence of nucleation in each stage results in a wider distribution of residence times, and hence wider crystal size distribution, but the above cited reference did not comment on this aspect.

In the general problem of predicting crystal size distribution from a serially-staged crystallization process, one must take into account nucleation-growth rate kinetics as well as a mass balance, which latter constrains the growth rates obtainable. A sufficient set of equations to describe crystal size distribution produced from a general staged crystallization process with segregated particle withdrawal is as follows.

Population balance (*3* to *5*):

$$V_1 \frac{d}{dL}(r_1 n_1) = -Q_1(L) n_1$$

$$V_2 \frac{d}{dL}(r_2 n_2) = -Q_2(L) n_2$$

$$\begin{array}{cc} \cdot & \cdot \\ \cdot & \cdot \\ \cdot & \cdot \end{array}$$

$$V_k \frac{d}{dL}(r_k n_k) = -Q_k(L) n_k$$

Mass balance:

$$Q^T{}_{j-1} C_{j-1} = Q^T{}_j C_j + \rho k_v \int_o^\infty Q_j(L) n_j L^3 dL \tag{5}$$

written for $j = 1, 2, \ldots k$

Nucleation growth rate kinetics (*5*):

$$\begin{aligned} r_j &= r_j(L, s_j) \\ n_j{}^o &= n_j{}^o(s_j) \\ s_j &= C_j - C_j{}^o \end{aligned} \tag{6}$$

or, where $s_j \approx 0$, then only the relationship between nucleation and growth rate is needed. Thus

$$n_j{}^o = n_j{}^o(r_j) \tag{6a}$$

The solution of these equations for a particular system would yield complete information about the system, including concentrations, production rates, and crystal size distribution in each stage. Such calculations can only be meaningful when a large amount of information concerning kinetics of nucleation and growth, as well as particle draw-down rates, $Q(L)$, is available on a particular system.

It is the purpose of this paper to generalize on the form, but not the magnitude, of crystal size distribution obtainable from such serially staged processes. Particle draw-down rates, $Q(L)$, will be represented by a simple, but yet realistic, classification model.

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NARROWNESS OF DISTRIBUTION

A conventional and quite useful way of characterizing the narrowness of a distribution function is the coefficient of variation defined as the ratio of the standard deviation to the mean. Thus,

$$\text{Coefficient of variation} \equiv \frac{\sigma}{\bar{x}} \cdot 100 \tag{7}$$

where

$$\sigma^2 = \int_0^\infty f(x)(x-\bar{x})^2 dx \tag{8}$$

$$\bar{x} = \int_0^\infty x f(x) dx \tag{9}$$

and where $f(x)$ is the normalized distribution function such that

$$\int_0^\infty f(x) dx = 1$$

It is easy to show that for the population distribution given by Equation (2) and for the case of nucleation only in the first stage ($n_j^o = 0$ for $j = 2, 3, \ldots k$) coefficient of variation is given by

$$\text{coefficient of variation of population in } k\text{th stage} = \frac{100}{k^{1/2}} \tag{10}$$

Thus, the population distribution in a single stage has a coefficient of variation of 100%, a wide distribution indeed. Four stages would be required to narrow the distribution to a coefficient of variation of 50%, still a rather wide distribution. The coefficient of variation of weight distribution for the same case is given as

coefficient of variation of weight distribution in kth stage

$$= \frac{100}{(k+3)^{1/2}} \tag{11}$$

Thus a coefficient of variation of 50 on a weight basis is indicated for the single stage mixed crystallizer. To obtain a coefficient of variation of 20, readily obtainable in a batch process with controlled nucleation, would require 22 mixed stages in series! It is apparent that staging by itself is a very inefficient way of narrowing crystal size distribution even assuming that the conditions of no nucleation in any but the first stage can be met.

STAGING AND CLASSIFIED PRODUCT REMOVAL

It has been suggested by Hill (*6*) in a study of continuous sugar crystallization that a combination of staging and classified product withdrawal might be the best practical way of achieving a narrow crystal size distribution in a continuous crystallization process. Sugar crystallization is a classic case in point on the subject of this paper. Market considerations demand a narrow crystal size distribution in the crystal product. This demand, plus the extreme difficulty of continuously nucleating sucrose, have given rise to initially seeded, batch-by-batch processes for sugar crystallization. To compete with the batch process, a continuous process must also produce a narrow distribution, but it is precisely this difficulty of sucrose nucleation which would permit the formation of particles (seeding or nuclei stimulation) only in the first stage, thus permitting the maximum effectiveness of staging to affect narrowing of crystal size distribution.

Hill (*6*) studied the effects on crystal size distribution of the number of stages together with preferential withdrawal of product-size crystals. The effects of recycling undersized particles from the last stage to the first stage was also investigated; the recycle tended to broaden the distribution when compared to returning the undersize to the stage from which they were removed. Hill's study was rather complete, but the cases studied were somewhat particular and difficult to generalize. His most general classification model was unrealistic, in that it did not allow for normal mixed withdrawal of undersize crystals with exit liquor, while his more realistic classification model required analog computation, with subsequent loss of generality.

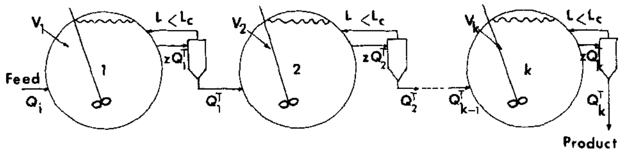

Fig. 1. Schematic design of staged, classified product removal, crystallization process.

The following classification model, an idealization of hydroclone operation, has been proposed to study classified product removal in a single stage (*5*), and will be adopted in this study. The classification device is assumed to have a classification size, L_c, such that:

1. particles greater than L_c are removed proportional to the feed rate to the classifying device, and
2. particles less than L_c are removed proportional to the discharge rate of the classifying device.

This idealization takes into account the fundamental principle of operation of such classification devices, that is, that large particles are excluded from the overflow while small particles split in the same ratio as the fluid in the device.

If the feed to underflow ratio of the classifying device is given as z, then the classification model is defined, in terms of previous nomenclature, as

$$Q_j(L) = Q_j^T \text{ for } L < L_c$$

$$Q_j(L) = zQ_j^T \text{ for } L > L_c$$

This model is also a suitable idealization for such classifying devices as wet screens.

The general system to be simulated is shown in Figure 1 with the number of stages, k, equal four. In the following development, particle size, L, can be taken as any coordinate property attached to the particles which can be given quantitative value and which property advances or retreats in time according to some law at a rate $r = dL/dt$ determined by the state of the system. As described in previous theories of particulate systems (*4, 7, 8*) particle size could mean activity level of a catalyst particle, chemical concentration within a suspended droplet, or age of a particle within the system, but more particularly we can think of the actual size distribution of crystals in a crystallization process as measured by screen analysis. The above mentioned product classification model depends on a real difference in particle size for segregation, hence a generalized particle size has little meaning in this particular study.

Equation (4), adopted to the general staged process shown in Figure 1, is sufficient to predict the form (in particular, coefficient of variation) of resultant particle distributions, and can be written as

$$r_1 V_1 \frac{dn_1}{dL} = -Q^T{}_1 n_1 \text{ for } L < L_c$$

$$r_1 V_1 \frac{dn_1}{dL} = -zQ^T{}_1 n_1 \text{ for } L > L_c$$

$$r_2 V_2 \frac{dn_2}{dL} = Q^T{}_1 n_1 - Q^T{}_2 n_2 \text{ for } L < L_c$$

$$r_2V_2\frac{dn_2}{dL} = z(Q^T{}_1n_1 - Q^T{}_2n_2) \text{ for } L > L_c$$

$$r_kV_k\frac{dn_k}{dL} = Q^T{}_{k-1}n_{k-1} - Q^T{}_kn_k \text{ for } L < L_c$$

$$r_kV_k\frac{dn_k}{dL} = z(Q^T{}_{k-1}n_{k-1} - Q^T{}_kn_k) \text{ for } L > L_c \tag{12}$$

which assumes that r_j is constant. The following boundary conditions hold

$$n_1(0) = n_1{}^o$$

$$n_j(0) = 0 \quad j = 2, 3, \ldots k$$

In addition, it is required that n_j be continuous at L_c. This set of equations can be made dimensionless with the substitutions $y = n/n_1{}^o$, and $x = LQ^T/rV$, making the assumption that $Q^T{}_j = Q^T{}_{j+1} = Q^T$ and $r_jV_j = r_{j+1}V_{j+1}$. With these substitutions, Equation (12) becomes

$$\begin{aligned}
\frac{dy_1}{dx} &= -\,y_1 \text{ for } x < \beta \\
\frac{dy_1}{dx} &= -\,zy_1 \text{ for } x > \beta \\
\frac{dy_2}{dx} &= y_1 - y_2 \text{ for } x < \beta \\
\frac{dy_2}{dx} &= z(y_1 - y_2) \text{ for } x > \beta \\
&\vdots \\
\frac{dy_k}{dx} &= y_{k-1} - y_k \text{ for } x < \beta \\
\frac{dy_k}{dx} &= z(y_{k-1} - y_k) \text{ for } x > \beta
\end{aligned} \tag{13}$$

with boundary conditions

$$y_1(0) = 1; \quad y_j(0) = 0; \quad j = 2, 3 \ldots k$$

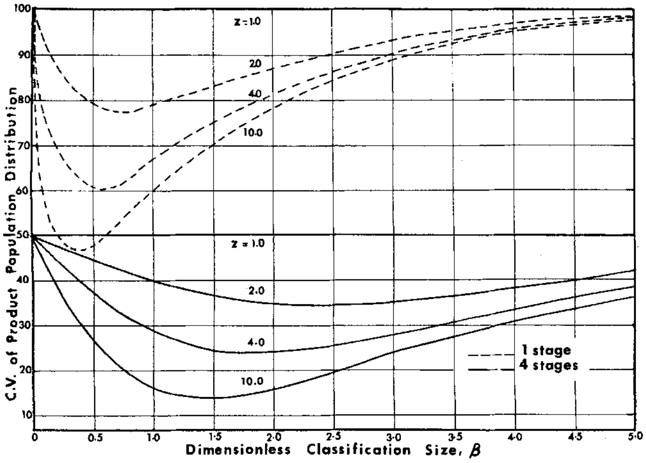

Fig. 2. Coefficient of variation of product population distribution from single and four stage vessels with classified removal.

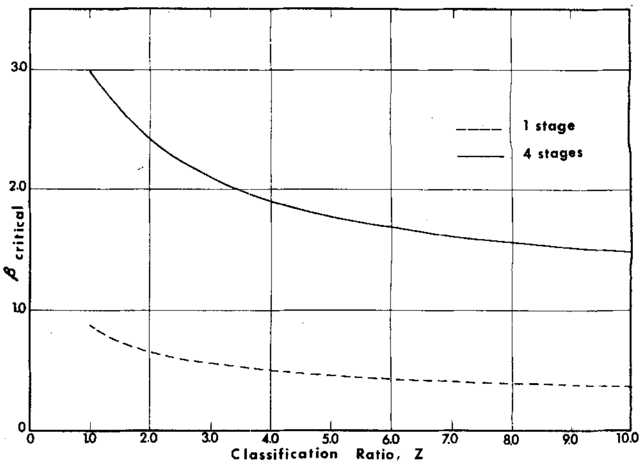

Fig. 3. Dimensionless classification size giving minimum coefficient of variation as a function of classification ratio.

and where $\beta = L_cQ^T/rV$, the dimensionless classification size. The solution to Equation (13), and hence coefficient of variation in the kth stage, is given in terms of the two classification parameters, z and β. The population distribution in the second stage, for example, is given as

$$\begin{aligned}
y_2 &= xe^{-x} \text{ for } x < \beta \\
y_2 &= \{\beta(1-z) + zx\}e^{\beta(z-1)-zx} \text{ for } x > \beta
\end{aligned} \tag{14}$$

while the distribution in the third and fourth stages is given as

$$\begin{aligned}
y_3 &= \frac{x^2}{2!}e^{-x} \text{ for } x < \beta \\
y_3 &= \left\{\beta^2\left(\frac{1}{2} - z + \frac{z^2}{2}\right) + \beta(z - z^2)x + \frac{z^2x^2}{2!}\right\} \\
&\qquad \exp\left[\beta(z-1) - zx\right] \text{ for } x > \beta
\end{aligned} \tag{15}$$

and

$$\begin{aligned}
y_4 &= \frac{x^3}{3!}e^{-x} \text{ for } x < \beta \\
y_4 &= \left\{\beta^3\left(\frac{1}{6} - \frac{z}{2} + \frac{z^2}{2} - \frac{z^3}{6}\right) + \beta^2\left(\frac{z}{2} - z^2 + \frac{z^3}{2}\right)x \right. \\
&\qquad \left. + \beta(z^2 - z^3)\frac{x^2}{2!} + \frac{z^3x^3}{3!}\right\}\exp\left[\beta(z-1) - zx\right] \\
&\qquad \text{for } x > \beta
\end{aligned} \tag{16}$$

Product distribution leaving a given stage is obtained by mixing one part of undersize with z parts of oversize particles. The coefficient of variation was calculated from this product mixture by analytically performing the integrations indicated in Equations (7), (8), and (9). This resulted in a very cumbersome algebraic expression for coefficient of variation in terms of β and z, which equation for product coefficient of variation from the fourth and first stages was evaluated parametrically for various values of β and z on a digital computer. Calculated product coefficient of variation (population basis) for one and four stages are plotted in Figure 2 as a function of classification size β with classification ratio z as a parameter. Notice that for all z as $\beta \to 0$, coefficient of variation $\to$ 50 or 100%, the theoretical coefficient of variation for four unclassified vessels in series or a single vessel. In this case the mean residence time of the particles is $1/z$ times that of the liquor, but the particles all have the same residence time as a function of size and hence coefficient of variation is unchanged. In the case $\beta \to \infty$, for all z, the coefficient of variation again approaches 50 or 100% (4 stage or single stage). In this case the particle population decays to zero as $L \to \infty$ and no classification occurs, thus

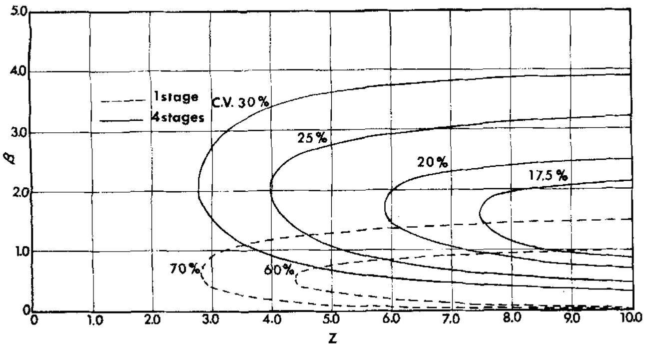

Fig. 4. Contours of constant coefficient of variation as a function of classification size and classification ratio for single and four stage vessels.

reducing identically to the mixed discharge case. An interesting observation from Figure 2 is that there is a critical classification size at which the maximum narrowing of the distribution occurs, given by a minimum coefficient of variation. This minimum in the coefficient of variation occurs at a smaller dimensionless size and is more pronounced as the classification ratio increases. Figure 3 plots this critical classification size, β_c, which gives the minimum coefficient of variation vs. classification ratio for both single and four stage operation. The larger the amount of classification, z, the smaller the classification size should be to produce maximum narrowness.

It is interesting to note that β_c is less than 3 for all classification ratios; this value of 3 is the dominant size (weight basis) produced in a single stage crystallizer.

Figure 4 plots contours of the coefficient of variation in the $\beta - z$ plane for a single and four stage operation. For the case of a four stage operation it is observed that a classification ratio of nearly 6 is required to produce a narrow distribution with a coefficient of variation of 20%. However, this is not an unobtainably large classification ratio in systems with low solids concentration. In the single stage system, a coefficient of variation of 20% can not be produced with any reasonable classification ratio, z. Thus, it appears that the combination of staging together with segregated product removal is an efficient way of narrowing particle-size distributions (under the previous assumptions as to particle formation in only the first tank) as compared to either staging or segregated withdrawal alone. It is possible that even greater narrowing of particle-size distribution could be obtained if classification at different sizes in each vessel were assumed. However, it is doubtful if the assumptions of equal r_jT_j equal Q_j^T, and equal β_j affect the results nearly as much as the assumption of nucleation only in the first tank. These former assumptions were made to enable analytical solution of the population balance equations, thus permitting generalization of the results. The assumption of nucleation (seeding) only in the first stage is much more critical to the central point of this paper, that is, the narrowing of the distribution. Most ion-pair inorganics nucleate very easily and would not be expected to follow this assumption. However, there are a variety of organic materials, sucrose being the classic example, as well as complex double salt inorganics, which are difficult to nucleate at the low supersaturation obtained in a continuous backmixed suspension. Such materials could be produced with a narrow size distribution in a continuous process as indicated in this paper. Any specific engineering simulation of particle-size distributions should involve rigorous solution of the combined population balances, mass balance, and nucleation-growth rate kinetics, with completely empirical product draw-down rates, $Q(L)$.

It should be remembered that weight distributions calculated from the above population distributions will have lower coefficient of variations than that calculated for the population distribution. Visually, of course, the uniformity one observes in a particle sample is closely related to the coefficient of variation on a weight basis, as the volume of a particle is exposed to view. It has been observed in practice that a few oversize particles in a distribution give the sample (visually) a much more heterogeneous appearance than an even greater weight of undersize particles which, in effect, are hidden within the other particles. If customer acceptance of the uniformity of a crystalline product is a marketing requirement, this often necessitates scalping the oversize particles from the product.

ACKNOWLEDGMENT

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NOTATION

C_j = concentration in jth stage, lb./cu.ft.
C_j^o = solubility concentration in jth stage, lb./cu.ft.
$C.V.$ = coefficient of variation, (standard deviation/mean) × 100
G_D = transfer function for dead time
k_V = volumetric shape factor, cu.ft./(length)^3
L = particle size, ft.
L_c = particle classification size, ft.
n_k = population density in kth stage, no./ft.-cu.ft.
n_j^o = nuclei density in jth stage, no./ft.-cu.ft.
Q_j^T = total liquor discharge rate from jth stage, cu.ft./hr.
$Q_j(L)$ = liquor drawdown rate from jth stage associated with particle size L, cu.ft./hr.
r_j = linear particle growth rate in jth stage, ft./hr.
s = Laplace transform variable, hr.$^{-1}$
s_j = supersaturation in jth stage, lb./cu.ft.
T = mean retention time in vessel, V/Q, hr.
t = time, hr.
V_j = liquor volume of jth stage, cu.ft.
W_k = cumulative weight fraction distribution in kth stage
x = dimensionless particle size, LQ/rV
$\bar{x}$ = mean of a distribution
y_j = dimensionless population density in jth stage, n_j/n_1^o
z = feed to underflow ratio (liquor basis) of classifying device

Greek Symbols

β = dimensionless classification size, L_cQ^T/rV
β_c = critical classification size for minimum c.v.
ρ = crystal density, lb./cu.ft.
σ = standard deviation of a distribution
τ_D = process dead time, hr.

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