The Steady State Behavior of Crystallizers with Classified Product Removal

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Many industrial crystallizers incorporate some classifying devices. This paper deals with the steady state behavior of such systems. A method is described by which the particle size distribution can be calculated for any classifier, provided the crystallizer itself can be considered as a mixed vessel. The method is based on the use of residence time distribution and the escape probability or intensity function introduced by Shinnar and Naor. The effect of classification on crystallizer performance is discussed with the help of some illustrative examples.

Many industrial crystallizers have some kind of classification device incorporated into their design. In general, there are two types of classifying crystallizers available. In the first, the crystallizer itself is designed with some classifying action, as in the Oslo crystallizer, where the crystals are maintained during their growth in a fluidized bed that has a classifying action. In the second the classification occurs in an additional external device; the growth occurs in a well mixed region and very little growth occurs in the classifying device. The crystal magma is circulated through a classifier which removes only the larger crystals, whereas the smaller crystals are recirculated to the growth section.

The first type of crystallizer is very hard to treat analytically, because the conditions in the fluidized bed where the growth and nucleation occur are spatially nonuniform. In the second type of crystallizer the crystallizing section is well mixed, therefore one can attempt to treat it as a completely mixed crystallizer. As pointed out in a previous paper (*1*) one must be much more careful in applying the concept of an ideal mixed vessel to a crystallizer than to a chemical reactor. Any continuously fed agitated vessel has a finite mixing time for the incoming feed. If this mixing time is small as compared to the residence time, the contribution of these nonmixed regions to a regular chemical reaction is very small. In a crystallizer, however, one is dealing with a very high nonlinear phenomenon, such as nucleation. Even at very small mixing times the supersaturation in the nonmixed regions could in some circumstances be the main source of nucleation. For some practical situations in crystallizers, however, the assumption of ideal mixing will be a relatively good one.

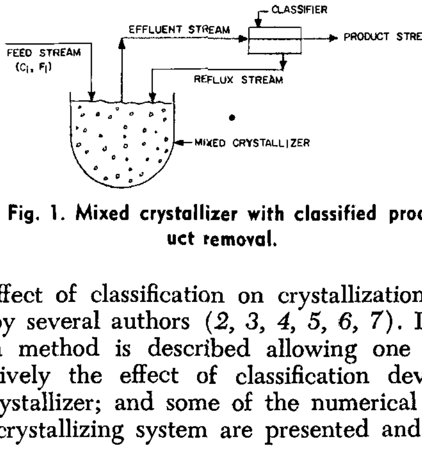

Fig. 1. Mixed crystallizer with classified product removal.

The effect of classification on crystallization has been treated by several authors (*2, 3, 4, 5, 6, 7*). In the next section a method is described allowing one to predict quantitatively the effect of classification devices on a mixed crystallizer; and some of the numerical results for a given crystallizing system are presented and discussed.

DEVELOPMENT OF SYSTEM EQUATIONS FOR THE STEADY STATE BEHAVIOR

In order to derive a mathematical model let us first make some simplifying assumptions and define a few suitable terms. If all crystals have a similar geometric form we can define an equivalent radius r such that the volume of the crystal is equal to kr^3 and the area to $3kr^2$ (similar treatment can be made for crystals which grow in only one or two dimensions). The growth rate of the crystal, $G = dr/dt$, is in the case of ideal mixing assumed to be a function of radius r and concentration C only and is independent of the spatial coordinates. (In a dense crystal suspension, G also depends on the properties of the crystal magma due to the effect of particles on the turbulence. If this effect is quantitatively known it can be incorporated in the treatment as will be shown later.) It is further assumed that the nuclei size is negligibly small.

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If we now look at the size distribution of crystals inside the crystallizer, as in the case of ideal mixing, $G(c, r)$ is independent of the spatial coordinates and therefore there is a unique relation between the age of a crystal and its size, which we can write

$$r = \varphi(t)$$

or

$$t = \psi(r)$$

If the growth rate is independent of size r, then $r = \varphi(t) = G(C)t$.

If $A(t)$ denotes the cumulative age distribution of particles inside the crystallizer and $Q(r)$ is their cumulative size distribution then

$$A(t) = Q[r = \varphi(t)] \tag{1}$$

In other words $A(t)$ is the fraction of particles (by number count) whose age is less than t and this is obviously the fraction of particles whose radius is less than Gt if the growth rate is independent of r or less than $\varphi(t)$ if G depends on r. In the same way if one looks at the product stream and designates its cumulative size distribution as $P(r)$ and its residence time distribution as $F(t)$ then

$$F(t) = P[r = \varphi(t)] \tag{2}$$

Now in an ideally mixed vessel $F(t) = A(t)$ and therefore $P(r) = Q(r)$. If the product stream passes through a classifier before leaving the vessel, then $F(t)$ and $A(t)$ are not equal but related to each other by

$$A(t) = \int_o^t \frac{1}{E_f(t)} F^*(t)\ dt \tag{3}$$

where $E_f(t)$ is the expected value of t in the product given by

$$E_f(t) = \int_o^\infty t\ f(t)\ dt = \int_o^\infty F^*(t)\ dt \tag{4}$$

$f(t)$ in Equation (4) is the density function of the residence time distribution defined as $dF(t)/dt$ and $F^*(t)$ is $1 - F(t)$. If we can derive $F(t)$ for the product stream, we can then derive $A(t)$, $P(r)$, and $Q(r)$ which, as we will see later, together with the mass balance and nucleation rate completely define the system.

A simple way to derive $F(t)$ from the properties of the classifier is by using the intensity function introduced by Shinnar and Naor (*8*) as

$$\lambda(t) = -\frac{d \ln F^*(t)}{dt} \tag{5}$$

The physical meaning of $\lambda(t)$ is the following: The probability of a particle which is still in the vessel at time t to exit the vessel between t and $t + \Delta t$ is given by $\lambda(t)\Delta t$. Now in a mixed vessel any particle has the same probability to enter the classifier in a fixed time interval. This probability per unit time is equal to the ratio of the volumetric recirculation rate to the total crystallizer volume which will be designated as η. Now, once a particle enters the classifier it may enter the product stream with a probability ξ or return to the vessel with a probability $1 - \xi$. In an ideal classifier, ξ would be unity above a certain desired product size $r > r_c$, and zero for any particle smaller than r_c. For a real classifier $\xi(r)$ is a continuous function of r (see Figure 2), which can be either calculated or measured experimentally. Then, the probability of a particle of size r to escape the vessel per unit time is the product of $\xi(r)$ and η. A particle of the size r has an age of $\psi(r)$ and therefore one can write

$$\lambda[t = \psi(r)] = \eta\ \xi(r) \tag{6}$$

Integration of Equation (5) by the use of the relation $F^*(t) = 1 - F(t)$ results in

$$F(t) = 1 - \exp\left[-\int_o^t \lambda(t')dt'\right] \tag{7}$$

which allows us to calculate

$$\begin{aligned} P(r) = F\left\{t = \psi(r)\right. &= 1 - \exp\left[\int_o^t \lambda(t = \psi(r))\, dt'\right] \\ &= 1 - \exp\left[-\int_o^r \eta\zeta(r)\frac{d\psi(r)}{dr}\,dr'\right] \end{aligned} \tag{8}$$

which for G independent of r becomes

$$P(r) = 1 - \exp\left[-\int_o^r \eta\xi(r)\frac{dr}{G}\right] \tag{8a}$$

and also $A(t)$ and $Q(r)$ can be obtained in a similar way. It should be pointed out that completely equivalent results can be obtained from a population balance (*1*) that for this case becomes

$$\frac{\partial[G(r, C)N_vq(r)]}{\partial r} = B\epsilon(r) - \eta\xi(r)N_vq(r)$$

We note here that the steady state particle size distribution is a unique function of $G(r, C)$ and therefore concentration C, and $\zeta(r)$ and η which are design parameters of the classifier. Equation (8a) therefore gives the particle size distribution as a function of solute concentration in an implicit form. Now, solute concentration in the vessel at any time is not an independent variable, but dependent on feed rate and feed concentration C_i. This dependence can be obtained from a mass balance.

For the continuous steady state case the conservation of mass can be derived as follows: The overall material balance of solute is given by

$$F_iC_i = F_pC + S \tag{9}$$

where F_i is the volumetric rate, and F_p the volumetric liquid removal rate and S the production rate of crystals. In the absence of evaporation the overall material balance is given by

$$F_i\rho_i = F_p\rho_p + S \tag{10}$$

where ρ_i is the density of the feed and ρ_p the density of the solution removed from the crystallizer. ρ_p is actually a function of C, but as in most crystallizers the supersaturation is very small, one can safely assume that ρ_p is equal to the density of the saturated solution.

If the mass of solute consumed to form the nuclei themselves can be neglected, the production rate of crystals from the crystallizer P must also be equal to the deposition rate of crystals on the growing particles, given as

$$P = N_v\rho \int_o^\infty 3kr^2G(C, r)q(r)dr \tag{11}$$

where $q(r)$ is the density function of $Q(r)$, the size distribution inside the crystallizer, and N_v is the total number of particles in the crystallizer. Thus if G is independent of r, Equation (11) becomes

$$P = N_v\,\rho\, 3K\ \mu_2[q(r)]G \tag{12}$$

where μ_2 is the second moment of $q(r)$. P is also given by

$$P = \rho\, N_p\, k\, \mu_3[p(r)] \tag{13}$$

where $\mu_3(p(r))$ is the third moment of $p(r)$ and N_p is the number of particles removed per unit time as a final product. Now N_p is related to N_v by

$$\frac{N_v}{N_p} = E_f(t) \qquad (14)$$

the average residence time of a particle in the product stream.

It should be pointed out that $E_f(t)$ is the average residence time of a particle in the product stream. It is different from the average residence time of the product stream itself defined as

$$\tau_s = \frac{V(1-\epsilon)}{S/\rho} \qquad (15)$$

In mixed crystallizers the solid residence time and the overall residence time $\tau = V/F$ are equal and τ_s is $\frac{1}{4}E_f(t)$. In a classified crystallizer this is not true as ϵ depends on the adjustment of the classifier. In the case that the volumes of solid and solution are additive

$$\tau_s = \frac{V/F_i\,(1-\epsilon)}{1-\dfrac{\rho-C_i}{\rho-C}} \qquad (16)$$

Now, in the absence of crystals in the feed liquor, N_p (the number of particles in the product stream) must be equal to the number of nuclei produced in the vessel; they are related to each other by

$$N_p = B(C)V\epsilon \qquad (17)$$

Where $B(C)$ is the nucleation rate per unit of free volume, and ϵ the fraction of free volume in the vessel given by

$$V(1-\epsilon) = N_v k\ \mu_3[q(r)] = N_p E_f(t) k\ \mu_3[q(r)] \qquad (18)$$

It is assumed here that $B(C)$ is a function of concentration only. The system equation from Equations (9), (10), (13), (17), and (18) results in

$$\frac{F_i(C_i - C/\rho_i/\rho_p)}{(1-C/\rho_p)} = \frac{B(C)Vk\rho\mu_3(p_r)}{1+B(C)kE_f(t)\ \mu_3(q_r)} \qquad (19)$$

$\mu_3(p_r)$ and $\mu_3(q_r)$ denote $\mu_3[p(r)]$ and $\mu_3[q(r)]$ respectively, and they are unique functions of $G(C, r)$ and therefore concentration C. Equation (19) gives C as an implicit function of the crystallizer operating parameters V/F_i or overall residence time, and inlet concentration C_i, and the saturation concentration which determines the form of $G(C)$ and $B(C)$. $\mu_n(p_r)$ and $\mu_n(q_r)$ can be calculated from η and ξ as follows:

$$\mu_n(p_r) = \int_0^\infty r^n p(r)\,dr = n\int_0^\infty r^{n-1}P^*(r)\,dr$$
$$= n\int_0^\infty r^{n-1}\exp\left(-\int_0^r \eta\xi(r')\frac{d\psi(r')}{dr}dr'\right)dr \qquad (20)$$

by the use of Equation (8), and

$$\mu_n(q_r) = \int_0^\infty r^n q(r)\,dr = \frac{1}{E_f(t)}\int_0^\infty r^n$$
$$\exp\left(-\int_0^r \eta\xi(r')\frac{d\psi(r')}{dr}dr'\right)\frac{d\psi(r)}{dr}dr \qquad (21)$$

by the use of Equations (3) and (8), since

$$q(r) = \frac{1}{E_f(t)}F^*[t=\psi(r)]\frac{d\psi(r)}{dr}$$

For G independent of r, Equation (20) and (21) become

$$\mu_n(p_r) = n\int_0^\infty r^{n-1}\exp\left[-\int_0^r \eta\xi(r)\,dr/G\right]dr \qquad (22)$$

and

$$\mu_n(q_r) = \frac{1}{E_f(t)\,G}\int_0^\infty r^n \exp\left[-\int_0^r \eta\xi(r)\,dr/G\right]dr \qquad (23)$$

Therefore, Equations (20) and (21), or Equations (22) and (23) can be used to obtain any order of moments of particle size distribution function, $P(r)$, and that inside the crystallizer, $q(r)$.*

As initially said, $\xi(r)$ can either be estimated from the design parameters of the classifier or measured experimentally by studying the classifier above. η can be estimated from the agitator design by known methods. One can also try to measure experimentally $\eta\xi(r)$ directly by a suitable tracer experiment. In this case one would have to prepare several closely sieved size fractions of inert tracer particles of different average size, and measure the residence time distribution of each size fraction. The tracer particles should preferably have the same density and shape as the crystals. By using tracer particles of different color one can also apply a pulse of different sized particles simultaneously.

It is generally not too difficult to measure $G(r, C)$ experimentally. It is however, rather difficult to measure the nucleation rate $B(C)$, but for the present purpose it can be estimated from the performance of a mixed crystallizer without classification.

Previously it was assumed that the growth rate $G(r, C)$ and the nucleation rate are functions of a supersaturation, and independent of the free volume and the nature of the crystal magma. It is well known, however, that this is an oversimplification. If the growth rate is diffusion controlled, the average mass transfer coefficient depends not only on r but on the properties of the magma itself. However if one wants to evaluate the performance of a classification on crystallizer performance, one normally deals with a fairly narrow range of magma properties. Over this range the assumption that G is a function of r and c only is not so bad, as long as this dependence is measured in a similar magma. In the same way it is well known that in a crystallizer the nucleation is often heterogeneous and therefore depends on the total crystal surface. Again the experimental evidence indicates that while in the absence of seed crystals, an addition of a small amount of seed crystals increases the nucleation rate significantly, a further increase of seed crystals produces only a minor effect. It is therefore advisable to measure both G and B in a magma. Data for B that is measured in pure solution cannot be used in the above calculation. Should more exact data for B and G be available which show the effect of free volume, average particle size, and crystal surface, then this information could be utilized as follows. The dependence of B and G on the properties of the crystal dispersion could be expressed quantitatively in terms of the moments of $q(r)$. In Equation (19), $B(C)$ would then depend on the moments of $q(r)$. As these moments depend on $G(r, C, \mu_n[q(r)]$ the solution of Equation (19) becomes a quite complex but feasible interaction procedure.

While Equation (19) can be solved numerically for any arbitrary function of $\xi(r)$, $G(r, C)$, and $B(C)$, some simplifying assumptions are often justified and some special cases are discussed in the following section.

It was previously stated that Equation (11) holds only if the nuclei are negligibly small. If this is not the case Equations (19) through (23) are still correct, as they contain only the size distribution of the product stream. The finite size of the nuclei can be taken into account in the function $t = \psi(r)$. The relations between $A(t)$ and $F(t)$ and therefore $a(r)$ and $p(r)$ are still correct, and are independent of this assumption.

SIMPLIFIED MODELS OF THE MIXED CRYSTALLIZER WITH CLASSIFIED INPUT

While the method is not restricted to any form of $G(C, r)$, it is often assumed that $G(G, r)$ is independent of particle size and has the form

$$G = K_1\,(C - C_s) \tag{24}$$

where C_s is the saturation concentration of solution. In the following example nucleation rate will be assumed to have the well known Volmer relation

$$B(C) = K_2 \exp[-K_3/(\ln C/C_s)^2] \tag{25}$$

but as pointed out previously any relation of B and C (and μ_2, μ_3) can be used.

A Real Classifier with Finite Reflux

A typical form of $\xi(r)$ for a real classifier is given in Figure 2. Now, if the classifier becomes very efficient, it will approach a step function such that $\xi = 1$ for $r > r_c$ and $\xi(r) = 0$ for $r < r_c$. One way of approximating $\xi(r)$ is by a step function such that

$$\begin{cases} \xi(r) = 1, & r > r_c \\ \xi(r) = \beta, & r < r_c \end{cases} \tag{26}$$

where β is a small constant less than unity, which takes into account that small particles have a finite chance of entering the product stream. η is the reciprocal of the recirculation time and can have any value from 0 to ∞. The escape probability of a particle will therefore be

$$\lambda[t = \psi(r)] = \begin{cases} \eta & ; \quad r > r_c \\ \beta\eta & ; \quad r < r_c \end{cases} \tag{27}$$

From this one can write

$$1 - F(t) = F^*(t) = \begin{cases} \exp(-\beta\eta t) \ ; \ t < r_c/G \\ \exp(-\beta\eta r_c/G)\exp[-\eta(t - r_c/G)];\ t > r_c/G \end{cases} \tag{28}$$

and

$$E_f(t) = \int_o^\infty t\, f(t)\,dt = \int_o^\infty F^*(t)\,dt$$

$$= \frac{1}{\beta\eta} - \frac{1}{\eta}\left(\frac{1}{\beta} - 1\right) e^{-\beta\eta r_c/G} \tag{29}$$

which for small values of β becomes equal to

$$E_f(t) = \frac{r_c}{G} + \frac{1}{\eta} \tag{30}$$

or equal to the growth time plus the recirculation time. The size distribution of the product $P(r)$ can now be written

$$P(r) = \begin{cases} 1 - e^{-\beta\eta r/G} \ ; \ r < r_c \\ 1 - e^{-\beta\eta r_c/G}\, e^{-\eta(r - r_c)/G} \ ; \ r > r_c \end{cases} \tag{31}$$

and the average particle size in the product is then $r_{\text{avg.}} = GE_f(t)$ which for the case $\beta = 0$ is equal to $r_c + G/\eta$. The size distribution inside the crystallizer becomes

$$q(r) = \frac{1}{G\,E_f(t)}\,F^*(t) = P(r)/r_{\text{avg.}} \tag{32}$$

Now, for solving Equation (19) we need $\mu_3(p_r)$ and $\mu_3(q_r)$ which can now be obtained from Equations (22) and (23) respectively:

$$\mu_3(p_r) = 3G^3\left\{e^{-\beta\eta r_c/G}\left[\left(\frac{r_c}{G}\right)^2\frac{1}{\eta}\left(1 - \frac{1}{\beta}\right) + 2\left(\frac{r_c}{G}\right)\frac{1}{\eta^2}\left(1 - \frac{1}{\beta^2}\right) + \frac{2}{\eta^3}\left(1 - \frac{1}{\beta^3}\right)\right] + \frac{2}{(\beta\eta)^3}\right\} \tag{33}$$

and

$$\mu_3(q_r) = \frac{G^3}{E_f(t)}\left\{e^{-\beta\eta r_c/G}\left[\left(\frac{r_c}{G}\right)^3\frac{1}{\eta}\left(1 - \frac{1}{\beta}\right) + 3\left(\frac{r_c}{G}\right)^3\frac{1}{\eta^2}\left(1 - \frac{1}{\beta^2}\right) + 6\left(\frac{r_c}{G}\right)\frac{1}{\eta^3}\left(1 - \frac{1}{\beta^3}\right) + \frac{6}{\eta^4}\left(1 - \frac{1}{\beta^4}\right)\right] + \frac{6}{(\beta\eta)^4}\right\} \tag{34}$$

which for the case $\beta = 0$ simplifies to

$$\mu_3(p_r) = \frac{3G^3}{\eta}\left[\left(\frac{r_c}{G}\right)^2 + \frac{2}{\eta}\left(\frac{r_c}{G}\right) + \frac{2}{\eta^2}\right] + r_c^3$$

$$\mu_3(q_r) = \frac{G^4}{E_f(t)\eta}\left[\left(\frac{r_c}{G}\right)^3 + \frac{3}{\eta}\left(\frac{r_c}{G}\right)^2 + \frac{6}{\eta^2}\left(\frac{r_c}{G}\right) + \frac{6}{\eta^3}\right] + \frac{r_c^4}{4\,E_f(t)\cdot G} \tag{35}$$

A knowledge of $\mu_3(p_r)$ and $\mu_3(q_r)$ as a function of G allows one to compute the behavior of the crystallizer in terms of its parameters.

Now, $r_{\text{avg.}}$ in Equation (32) is the number of average particle size in the product. Industrial specifications are normally given by the sieve analysis, and a better measure of product size is therefore given by the weight average diameter which, in terms of particle size distribution, is given by $\mu_4(p_r)/\mu_3(P_r)$ (*1*). The uniformity of the size distribution is best expressed by the coefficient of variation γ^2 which for the weight distribution is given by

$$\gamma^2 = \frac{(\mu_5/\mu_3) - (\mu_4/\mu_3)^2}{(\mu_4/\mu_3)^2} \tag{36}$$

For the above case μ_4 and μ_5 are given by

$$\mu_4(p_r) = 5G^4\left\{e^{-\beta\eta r_c/G}\left[\left(\frac{r_c}{G}\right)^3\frac{1}{\eta}\left(1 - \frac{1}{\beta}\right) + 3\left(\frac{r_c}{G}\right)^2\frac{1}{\eta^2}\left(1 - \frac{1}{\beta^2}\right) + 6\left(\frac{r_c}{G}\right)^3\frac{1}{\eta^3}\left(1 - \frac{1}{\beta^3}\right) + \frac{6}{\eta^4}\left(1 - \frac{1}{\beta^4}\right)\right] + \frac{6}{(\beta\eta)^4}\right\} \tag{37}$$

and

$$\mu_5(p_r) = 5G^5\left\{e^{-\beta\eta r_c/G}\left[\left(\frac{r_c}{G}\right)^4\frac{1}{\eta}\left(1 - \frac{1}{\beta}\right) + 4\left(\frac{r_c}{G}\right)^3\frac{1}{\eta^2}\left(1 - \frac{1}{\beta^2}\right) + 12\left(\frac{r_c}{G}\right)^2\frac{1}{\eta^3}\left(1 - \frac{1}{\beta^3}\right)\right.$$

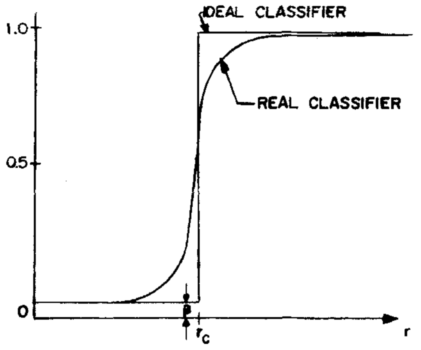

Fig. 2. Forms of $\xi(r)$ in a classified crystallizer.

$$+ 24\left(\frac{r_c}{G}\right)\frac{1}{\eta^4}\left(1-\frac{1}{\beta^4}\right)+\frac{24}{\eta^5}\left(1-\frac{1}{\beta^5}\right)\Bigg]+\frac{24}{(\beta\eta)^5}\Bigg\} \qquad (38)$$

and again for $\beta = 0$ this simplifies to:

$$\mu_4(p_r) = \frac{4G^4}{\eta}\left[\left(\frac{r_c}{G}\right)^3+\frac{3}{\eta}\left(\frac{r_c}{G}\right)^2+\frac{6}{\eta^2}\left(\frac{r_c}{G}\right)+\frac{6}{\eta^3}\right]$$

$$\mu_5(p_r) = \frac{5G^5}{\eta}\Bigg[\left(\frac{r_c}{G}\right)^4+\frac{4}{\eta}\left(\frac{r_c}{G}\right)^3 + \frac{12}{\eta^2}\left(\frac{r_c}{G}\right)^2+\frac{24}{\eta^3}\left(\frac{r_c}{G}\right)+\frac{24}{\eta^4}\Bigg] \qquad (39)$$

The Ideal Classifier with Infinite Reflux

If β is very small and η is large, $P(r)$ approaches a step function as the range of r for which $(r - r_c)/G$ is not negligible is very narrow. For those cases a further simplification is possible. If $\eta \to \infty$ such that

$$\lambda[t = \psi(r)] = \begin{cases} \eta\xi(r) = 0 \ ; \ r < r_c \\ \eta\xi(r) = 1 \ ; \ r > r_c \end{cases} \qquad (40)$$

We obtain the very simple relation for $P(r)$:

$$\begin{cases} P(r) = 0 \ ; \ r < r_c \\ P(r) = 1 \ ; \ r > r_c \end{cases} \qquad (41)$$

The characteristics of the classified crystallizer are not immediately apparent from Equation (19). Due to the complex nature of the dependence of B on C it is impossible to write an explicit equation for product size and production rate as a function of residence time. The effects of different variables on crystallizer performance are therefore best discussed by specific examples. First some general features of such crystallizers are worth mentioning.

Most continuous crystallizers have the peculiar property that if one disregards particle size, the yield is fairly insensitive to residence time over a wide range of flow rates. The total production rate in this range is therefore almost directly proportional to residence time. This is due to the fact that most salt solutions can only sustain a very small supersaturation and at high supersaturations the nucleation rate becomes very high. This increases the available surface for growth and thus compensates for the reduced residence time. If C_i and C_s in a mixed crystallizer are fixed the particle size decreases with increasing production rate, therefore the desired particle size and not the yield determines the production rate. In a classified crystallizer particle size can be independently controlled (over some range) by adjusting the operation of the classifier.

We now have an additional degree of freedom and can obtain the same particle size over a range of residence times. By changing the classifier at fixed feed rate we control the residence time of the solid, as particles which are too small are fed back to the crystallizer. If we increase the particle size that can pass through the classifier into the product stream we increase the residence time of the solid, as a particle now needs a larger time to grow to the critical size. This increase in solid residence time is further amplified by the fact that in order to increase the particle size in the product the nucleation rate has to be reduced. This means the steady state operation of the crystallizer will now be at a lower supersaturation, resulting in a smaller growth rate and therefore a longer residence time.

Now the solid residence time is uniquely related to the

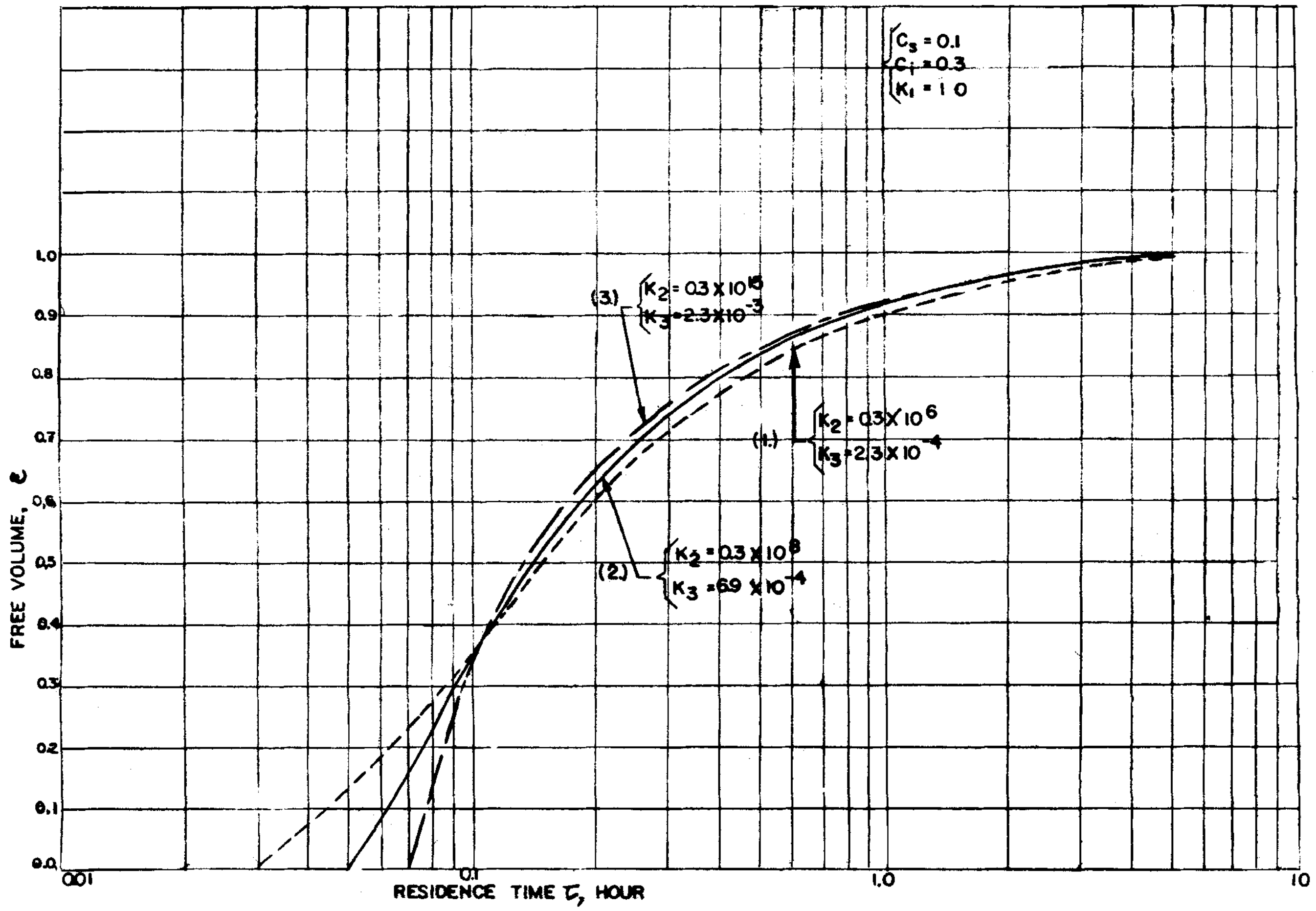

Fig. 3. Effect of free volume on residence time in the ideal classifier with infinite reflux.

free volume ϵ by Equation (16). Increasing the solid residence time with the help of the classifier while keeping the feed rate constant causes the free volume to decrease. Our ability to control the solid residence time depends on how much we can decrease the free volume. If the values of C_i and C_s are such that even without classification the free volume is rather small (about 60 to 70%), then any further decrease would also effect the fluidity of the crystal magma and make the crystallizer hard to operate. If the free volume based on equal residence time of liquid and solid is large (above 80%) then, an increase in solid residence time is possible and often advantageous.

The range of residence time that can be used to achieve a desired product size at fixed C_i and C_s is rather limited and depends mainly on how much one can decrease ϵ while maintaining a sufficient fluidity in the crystal magma.

The exact relations of ϵ vs. F_i or overall residence time $t = V/F_i$ depend very strongly on the nature of the dependence of B and G on supersaturation [and possibly moments of $q(r)$]. They may therefore vary from case to case. Some examples for the case where B and G have the form given in Equations (24) and (25) are given in Figure 3.

For the three cases given the parameters, K_2 and K_3, are adjusted so that the nucleation rate is the same at a concentration of $C - C_s = 0.011$. This concentration corresponds to a residence of 0.1 hr. At the residence time higher than 0.1 hr., there is little effect of nucleation parameters on the free volume vs. residence time relationship; while at the residence time lower than 0.1 hr., there is a significant difference in the free volume vs. residence time relationship among three curves shown in Figure 3. For example, at the residence time of 0.07 hr. (at very high feed rate) curve 1 has the free volume ϵ close to zero, curve 2 has $\epsilon = 0.15$, and curve 3 has $\epsilon = 0.28$. This indicates that the smaller the K_2 and K_3 values are, the higher the value of free volume would be at the same residence time (at the same feed rate or same production rate).

As compared to a mixed crystallizer with the same average particle size and the same feed rate, a classified crystallizer has to operate at a slightly lower supersaturation to reduce nucleation. This is due to the fact that for the same particle size (by weight) the Poisson distribution contains about ten times more particles by number. The necessary reduction in C to obtain this reduced nucleation rate necessitates a longer growth time of the crystal as G is reduced. As the dependence of $B(C)$ on C is normally very steep, this difference in G is normally quite small. Now, in a regular crystallizer ϵ is fixed, whereas here ϵ is adjustable by changing $\theta = V/F_i$. For systems which have a high value of ϵ in the mixed case (low inlet concentration), the classified crystallizer will actually increase the production rate and not decrease it as stated previously (*1*).

In Table 1 a comparison is made for a specific example, using the same parameters as curve 3 in Figure 3. It can be seen that at the same production rate the free volume is slightly less in the classified case, but if it is permissible to reduce the free volume further, the production rate can be significantly increased. Thus, for example, it can be seen from curve 1 in Figure 4 that if the free volume is decreased from 0.85 to 0.7 the overall residence time changes from 0.5 to 0.25 hr. or the production rate almost doubles.

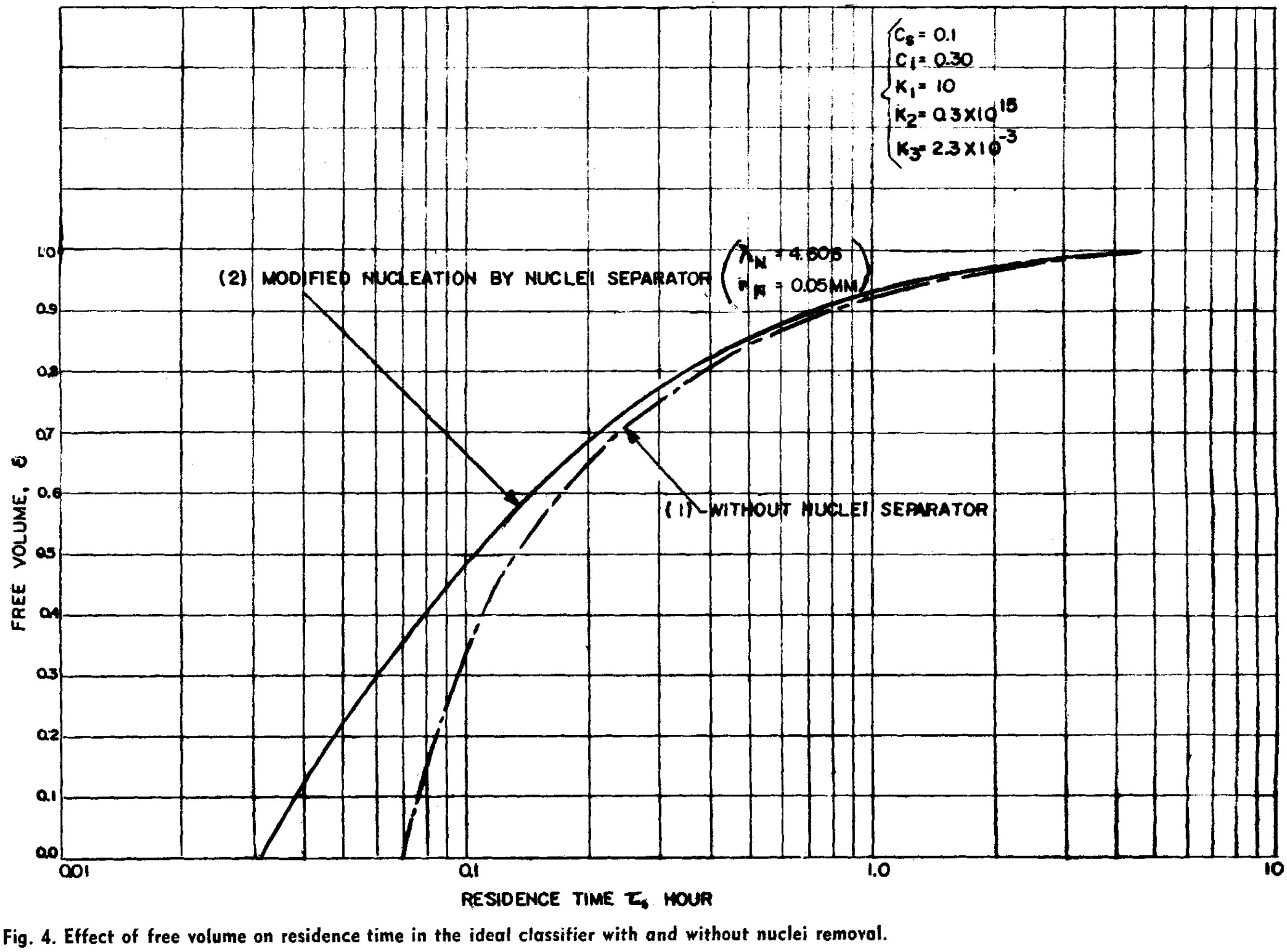

Fig. 4. Effect of free volume on residence time in the ideal classifier with and without nuclei removal.

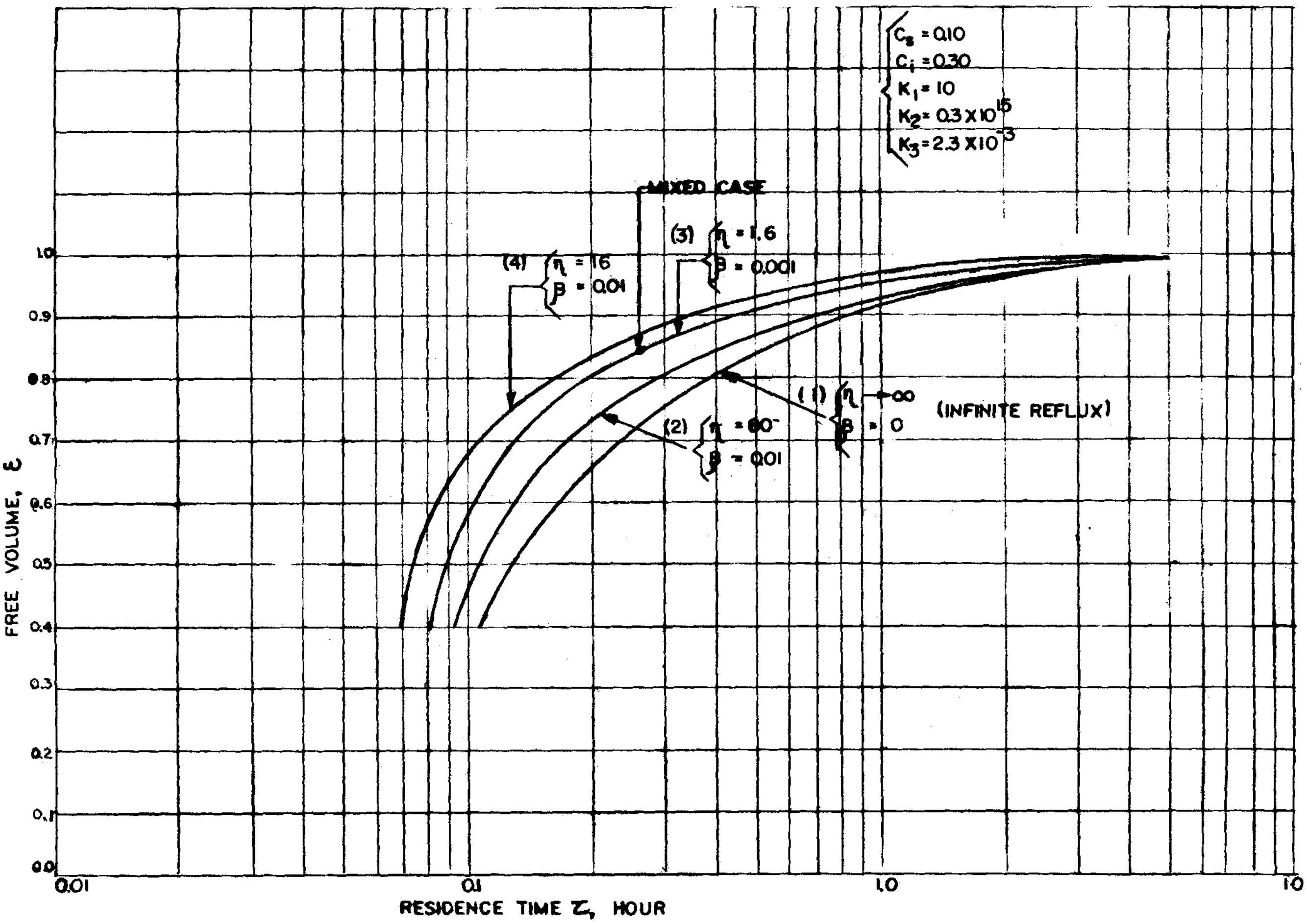

Fig. 5. Effect of free volume on residence time with different values of the escape probability.

In Figure 5 the effects of escape probability are shown on the free volume vs. residence time relationship. Curves 2, 3, and 4 are for an ideal classifier with finite reflux whose escape probability is given in Equation (27). Curve 1 is for an ideal classifier with infinite reflux ($\eta = \infty$, $\beta = 0$), curve 2 for $\eta = 80$ and $\beta = 0.01$, curve 3 for $\eta = 1.6$ and $\beta = 0.01$, and curve 4 for $\eta = 16$ and $\beta = 0.01$. It can be seen that as η becomes larger and β smaller the ideal classifier with finite reflux approaches to the classifier with infinite reflux.

In Table 1 a comparison is also made for the case of an imperfect classifier with finite reflux. It is seen that for moderately high values of η and small values of β the ideally classified crystallizer with infinite reflux is a very good approximation of the real case.

TABLE 1. COMPARISON OF MIXED CRYSTALLIZER WITH THE IDEAL AND NONIDEAL CLASSIFIED CRYSTALLIZER

	Mixed case without classifier	Ideal classifier with infinite reflux	Ideal classifier with finite reflux
Free volume,	0.895	0.855	0.086
Weight average particle size, mm.	0.5	0.5	0.504
Coefficient variation	0.5	0.0	0.086
Residence time, hr.	0.5	0.5	0.5

** $\eta = 16.0$
$\beta = 0.01$

STEADY STATE CHARACTERISTICS OF CLASSIFIED CRYSTALLIZER WITH NUCLEI REMOVAL

In order to increase the particle size it is most important to reduce the nucleation rate. One way of achieving this is by removing nuclei from the system in some kind of elutriation device (3), through which the crystal magma is recirculated. The larger crystals are returned to the crystallizer whereas the smaller crystals are redissolved in the solution.

The chance of a small crystal to be removed from the solution again depends on its size. For simplicity one can assume that this probability is equal to a constant λ_N for crystals below a critical size r_N and zero for particles larger than r_N. Again there is no special difficulty of handling a more complicated dependence of the probability on particle size.

Now the effective nucleation rate $B^*(C)$ is equal to the total nucleation rate multiplied by the probability of a particle to reach r_N without being removed as a nuclei. For the case defined above the probability of entering the nuclei trap (in unit time) will be λ_N for $r > r_N$ and zero for $r < r_N$. The fraction of nuclei growing to r_N is then given by $\exp(-\lambda_N t_{r_N})$, where t_{r_N} is equal to $\psi(r_N)$ or the time needed for the crystal to grow to size r_N. Now the time needed for a nucleated crystal to reach the critical survival size r_N depends on the growth rate $G(C, r)$. If again $G(C, r)$ is independent of r and given by Equation (24) then the modified nucleation rate becomes

$$B^*(C) = B(C) \exp\left(-\frac{\lambda_N r_N}{K(C - C_s)}\right) \qquad (42)$$

If the total mass of solid removed from the crystal magma in the nuclei removal unit is negligible, then one can treat a classified crystallizer with nuclei removal in the same way as without nuclei removal by substituting the modified nucleation rate Equation (42) [instead of Equation (25)] into the system Equations (19) through (23). Neglecting the mass of the destroyed nuclei will be a justifiable assumption for most practical cases.

In Figure 4 the effect of nuclei removal on the performance characteristics of a mixed crystallizer with classified output is illustrated by a typical numerical example. The operating curve, free volume vs. overall residence time, is plotted with and without nuclei removal for one of the cases given in Figure 3. In plotting this curve it was assumed that the nuclei trap is adjusted at each residence time to remove 10% of the nuclei formed.

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NOTATION

$A(t)$ = the cumulative age distribution of particles inside the crystallizer defined as the fraction of particles whose age is less than t
$B(C)$ = nucleation rate, no. of particles/cc. of mother liquor/hr.
$B^*(C)$ = modified nucleation rate defined as $B^* = B\ \exp(-\lambda_N r_N/G)$
C = concentration of effluent stream
C_i = concentration of feed stream
C_s = concentration of saturated solution
$E_f(t)$ = average residence time defined as the expected value of t
F = the fraction of particles in the product stream possessing a residence time t or less
f = the density function defined as the probability of a residence time being found between t and $t + dt$
F^* = the fraction of particles in the product stream whose residence time exceeds $t (= 1 - F)$
F_i = feed rate
F_p = effluent flow rate of mother liquor
G = linear growth rate
k = shape factor of a crystalline particle
K_1 = growth rate constant
K_2, K_3 = nucleation rate constants
$P(r)$ = cumulative size distribution of the product stream
$p(r)$ = the density function of size distribution of the product stream
$Q(r)$ = the cumulative size distribution of particles inside the crystallizer
$q(r)$ = the density function of size distribution of particles inside the crystallizer
N_p = the total number of particles in the product stream per unit time
N_v = the total number of particles in the crystallizer
r = the radius of a particle
$r_{\text{avg.}}$ = average particle size in the product
r_c = sieve size of ideal classifier
r_N = particle size of the nuclei removed by nuclei separator
S = production rate of solid
t = age of crystal
V = total volume of crystallizer

Greek Letters

ρ = density of a crystal
ρ_p = density of effluent stream of mother liquor
ρ_i = density of feed stream
ϵ = free volume of the crystallizer
$\lambda(t)$ = escape probability defined in Equation (5)
η = the ratio of the volumetric recirculation rate to the total crystallizer volume
$\xi(r)$ = probability of a particle entering the classifier exits as a product stream
β = a value of $\xi(r)$ in the ideal classifier with finite reflux as defined in Equation (26)
$\mu_n(p_r)$ = n-th moment of the density function $p(r)$
$\mu_n(q_r)$ = n-th moment of the density function $q(r)$
γ^2 = coefficient of variation as defined in Equation (36)
τ = residence time defined as V/F_i
τ_s = residence time of solid, $S/\rho V$
λ_N = probability of entering the nuclei trap of size r_N

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APPENDIX
MOMENTRELATIONS

Consider the density function of a residence time distribution $f(f)$ The cumulative distribution of residence times can be described either from below

$$F(t) = \int_0^t f, \text{ so that } f(t) = \frac{dF(t)}{dt}$$

or from above

$$F^*(t) = 1 - F(t) = \int_0^\infty f, \text{ so that } f(t) = \frac{dF^*(t)}{dt}$$

Now all the moments of the residence time distribution

$$\mu_n = \int_0^\infty t^n f(t)dt; \qquad n = 1,2,3, \ldots\ldots$$

must be finite (as a physical meaning can be attributed to them). Therefore, $f(t)$ must $\rightarrow o$ (as $t \rightarrow \infty$) faster than t^{-n} for any n. The cumulative distribution of tails $F^*(t)$ must likewise $\rightarrow o$ faster than any t^{-n}. An integration by parts then shows that

$$\mu_n = -\int_0^\infty t^n \frac{dF^*(t)}{dt} dt$$

$$= t^n F^*(t) \Big/ \begin{matrix} t - \infty \\ t = o \end{matrix} + n \int_0^\infty t^{n-1} F(t)dt$$

$$= n \int_0^\infty t^{n-1} F^*(t)dt; \qquad n = 1,2,3, \ldots\ldots$$

The boundary term at $n \rightarrow \infty$ vanishing for the reasons just noted (and the boundary term at o vanishing because of the t^n). In particular

$$\mu_1 = E_f(t) = \int_0^\infty tf(t)dt = \int_0^\infty F^*(t)dt$$

where $E_f(t)$ is the average residence time of a single crystal, as distinct from τ_s, the average residence time of the crystal mass.