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On the Crystal Size Intensity Function and Interpreting Population Density Data from Crystallizers

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In recent literature the application of the ideal mixed suspension, mixed product removal (MSMPR) crystallizer concept to the analysis of crystal size distribution (CSD) data obtained from experimental or plant crystallizers has been considered. Several excellent reviews are available. Notable have been the works of Randolph (1965), Randolph and Larson (1971), Canning (1970), Nyvlt (1969, 1971), and Mullin (1972). Examination of previous work shows that there still exist many unsolved problems between the various model-oriented interpretations and the actual population density CSD data. There has been criticism of these interpretations from industrial workers as "giving little insight to the actual mechanism" to the real crystallization process involved (Canning, 1970). In addition, many possible combinations of these specific interpretations, such as size-dependent growth rate (Abegg et al., 1968; Bransom, 1960; Canning and Randolph, 1967; and Margolis et al., 1971), size-dependent supersaturation (Estrin, et al., 1969), size-dependent residence time (Randolph and Larson, 1971), and crystal breakage (Rosen and Hulburt, 1971) can apparently fit the same population density CSD data. A typical example is the case of CSD data showing linear sections of different slopes in a semi-log population density distribution plot, $\ln n(L)$ versus L.

In this note, several different interpretations of population density CSD data from crystallizers are re-examined. The crystal size intensity function (CSIF) concept as suggested by the analogous residence time intensity function of Noar and Shinnar (1963) is introduced. It is suggested that this CSIF can be conveniently used together with the population density distribution function developed by Randolph and Larson (1962) in the analysis of CSD data. It makes a distinction among different possible mechanisms leading to similar CSD plots and gives better understanding of implications of previous publications. Certain new insights to clarify the apparent anomalies existing in previous interpretations are also discussed.

CRYSTAL SIZE INTENSITY FUNCTION

It has been shown that steady state crystal size distributions from a continuous MSMPR crystallizer for a number of systems satisfy the solution of the population balance equation (Randolph and Larson, 1962)

$$n = \frac{(rn)^0}{r} \exp\left[- \int_0^L \frac{dL}{rT} \right] \tag{1}$$

For the case of size-independent growth rate, (1) becomes

$$n = n^0 \exp[- L/rT] \tag{2}$$

The simplifying assumptions incorporated in the development of these expressions are well known (Randolph and Larson, 1962 and 1971). The physical meaning of $n(L)$ is as follows: $n(L)dL$ represents the total number of crystal particles of all possible sizes in a unit volume of slurry in the crystallizer that will leave the unit volume of slurry within a particle size between L and $(L + dL)$. If, alternatively, $n(L)$ is considered as a properly normalized probability density distribution function, then, on viewing crystal particles with all possible sizes which have just entered the unit volume of slurry with a particle size between L and $(L + dL)$ is equal to $n(L)dL$. Thus, the population density distribution function $n(L)$ characterizes the CSD for all possible particle sizes.

Consider now a situation where knowledge about the CSD and its related probability information for crystal particles of a specific size is desired. For example, when a selective fines trap is added to a continuous MSMPR crystallizer (Nauman, 1971), knowledge about crystal particles with the specific fines destruction size is particularly important. In this case, a more general problem may be posed: suppose crystal particles with a specific size L have already stayed in a unit volume of slurry in the crystallizer, one desires to know the probability of their leaving the unit volume of slurry within the next size increment dL after growth. Let this conditional prob-

ability be denoted by $\Lambda(L)dL$. The specification to the latter can be obtained simply from the Bayes rule in probability. Thus the probability $n(L)dL$ is the product of two other terms: (1) the probability of the crystal particles of all possible sizes not leaving the unit volume of slurry with a particle size L or less; (2) the probability of their leaving the unit volume of slurry with a particle size between L and $(L + dL)$, that is, $\Lambda(L)dL$. For the simple case of size-independent growth rate in a continuous MSMPR crystallizer, such a Bayes rule, can be written as

$$Qn(L)dL = [Vn(L)r]\,[\Lambda(L)dL]$$

or

$$\Lambda(L) = \frac{1}{rT} \tag{3}$$

From (1) and (3), it is noted that $\Lambda(L)$ is related to the well-known slope $-1/rT$ of the population density plot, $\ln n(L)$ versus L, the possibility of using $\Lambda(L)$ together with $n(L)$ in interpreting CSD data from crystallizers is apparent. This conditional probability distribution function $\Lambda(L)$ is actually known as the intensity function in statistics (Gumbel, 1958, p. 20) and the analogous concept in the framework of residence time distribution theory has been introduced earlier by Noar and Shinnar (1963). The latter has been discussed in detail by Himmelblau and Bischoff (1968). Except in the work of Han and Shinnar (1968) where the related residence time intensity function concept was used to study the steady state behavior of crystallizers with classified product removal, however, there has been apparently no attempt in the literature to apply this CSIF concept to crystallization problems. It is thus worthwhile to consider more clearly the theoretical significance and experimental implications of this proposed CSIF $\Lambda(L)$ in interpreting population density data from crystallizers.

It is known in statistics that there exists a unique relationship between the population density distribution function $n(L)$ and the CSIF $\Lambda(L)$ defined by (Gumbel, 1958, p. 20)

$$1 - \int_0^L n(L)dL = \exp\left[- \int_0^L \Lambda(L')dL' \right]$$

or

$$n(L) = \Lambda(L) \exp\left[- \int_0^L \Lambda(L')dL' \right] \tag{4}$$

Thus, (1) and (4) indicate that in a population density CSD plot, $\ln(L)$ versus L, the intercept of the plot gives the CSIF for crystal particles of size L, $\Lambda(L)$, while the slope of the plot gives a measure of the average CSIF $\overline{\Lambda(L)}$ over the size interval 0 to L, that is,

$$\begin{cases} [\text{intercept}] = \Lambda(L) \\ -[\text{slope}] = \dfrac{1}{L}\displaystyle\int_0^L \Lambda(L')dL' = \overline{\Lambda(L)} \end{cases} \tag{5}$$

As defined, the CSIF $\Lambda(L)$ gives the escaping probability of crystal particles with a specific size L within the next size increment dL in a unit volume of slurry in a crystallizer. (5) suggests that by considering the whole possible size interval of crystal particles as a sequence of size increments, the comparison of $\Lambda(L)$ and $\overline{\Lambda(L)}$ obtained from the population density plot will yield a more natural indication of possible mechanisms leading to the deviation from the ideal exponential population density distribution behavior suggested by the McCabe's delta L law. The latter ideal case is indeed as expected since both $\Lambda(L)$ and $\overline{\Lambda(L)}$ are independent of particle size and equal to $1/rT$ from (2) and (3). In the general case, as $\Lambda(L)$ may depend explicitly on particle size or implicitly through the effects of diffusional process, flow configuration, kinetic process, etc., it is thus not surprising to note that so many model-oriented interpretations can apparently fit the same population density CSD data. In the following, a number of such interpretations taken from the literature are discussed. Special attention is devoted to demonstrating the advantages of using both $n(L)$ and $\Lambda(L)$ together in the analysis of CSD data.

EXAMPLES

Size-Dependent Growth Rate

For the size-dependent growth rate expression of Abegg et al. (1968),

$$r = r^0 P(L) \tag{6}$$

$$= r^0(1 + \gamma L)^b \quad b < 1 \quad L \geq 0 \tag{7}$$

and defining

$$X = \frac{L}{r^0 T} \quad \alpha_1 = \gamma r^0 T \quad y = \frac{n}{n^0}$$

(1) gives

$$y = \frac{1}{P(X)} \exp\left[- \int_0^X \frac{1}{P(X)} dX \right] \tag{8}$$

$$= \frac{1}{(1 + \alpha_1 X)^b} \exp\left[\frac{-(1 + \alpha_1 X)^b}{\alpha_1(1 - b)} + \frac{1}{\alpha_1(1 - b)} \right] \tag{9}$$

where $P(X) = (1 + \alpha_1 X)^b$. Thus, (5) can be written as

$$\Lambda(X) = \frac{1}{(1 + \alpha_1 X)^b} \tag{10}$$

$$\overline{\Lambda(X)} = \frac{(1 + \alpha_1 X)^{1-b} - 1}{\alpha_1(1 - b)X} \tag{11}$$

This explicit dependence of escaping probability of crystal particles on the particle size is therefore consistent with the resulting curved population density plot. A possible physical mechanism leading to such a size-dependent growth behavior has recently been discussed in the work of Lieb and Osmers (1973). These authors study the effects of diffusive mass transfer on the CSD in a continuous, MSMPR crystallizer. In all cases examined, the growth rate can be expressed in the form of (6), with $P(L)$ being the quotient of two size-dependent functions representing the effects of mass transfer limitation. When the diffusional effect is not extremely significant, the size dependence of the denominator in the quotient is found to be usually higher than that of the numerator. This implies that there exist local maxima in both curves of $n(L)$ and $\Lambda(L)$, thus permitting an easy identification of such behavior.

A special case of the growth rate model (7) when $b = 0$ is of particular interest. (9) gives the dimensionless form of the classical population density distribution function in the ideal, continuous MSMPR crystallizer,

$$y = \exp[-X] \tag{12}$$

and the corresponding intensity functions, (10) and (11), are

$$\Lambda(X) = \overline{\Lambda(X)} = \text{constant} = 1 \tag{13}$$

The constancy of the escaping tendency for crystal parti-

cles of all possible sizes in the given slurry in the crystallizer represented by such CSIF's results in the well-known linear population density plot.

As an intermediate between the above two cases, consider the recent experimental results of Margolis et al. (1971). These authors observed curved population density distribution behavior for the small particle size interval in the population density plot of the study of crystallization of ice in a continuous MSMPR crystallizer. Such behavior was postulated as a result of the size-dependent growth rate. However, for large particle sizes, their data indicated the ideal, exponential population density distribution. The population density distribution functions were given by

$$n = \begin{cases} n^0 \exp\left[-\int_0^{L_0} \frac{dL}{r_1 T} \right] & 0 \leq L \leq L_0 \quad (14) \\ (n^0)' \exp\left[-\frac{L}{r_2 T} \right] & L_0 \leq L \quad (15) \end{cases}$$

(14) shows that in most cases the analytical form of the crystal size intensity function for describing the nonideal population density distribution behavior may not be easily obtained. However, an understanding of the CSIF concept and its implications on interpreting population density data will be very useful in the analysis of CSD data. The next example will thus indicate how the CSIF concept can give clear a priori knowledge about the resulting population density distribution behavior for a specific crystallization system without any mathematical complications.

Crystal Breakage

Consider the kinetic model of crystallization of potassium sulfate including the effect of crystal breakage proposed by Rosen and Hulburt (1971). These authors assume crystals grow until they reach some critical characteristic particle size X_c at which they become strong enough to withstand the possibility of breakage, and thus breakage occurs only in some of the crystals with sizes smaller than X_c. It is further assumed that probabilities of breakage for such crystals are the same and the growth rate of crystals is independent of particle size. It is then expected that the CSIF $\Lambda(X)$ for $X \geq X_c$ is given by (13) due to the constant growth rate without crystal breakage as in the case of the ideal MSMPR crystallizer. For $X < X_c$, the postulated constant and identical escaping probability for crystals in a given slurry due to breakage events adds to the constant escaping probability of the crystals due to the size-independent growth process. Thus, this kinetic model implies a population density plot with two linear sections. The difference between slopes of these two straight lines will give a measure of the average CSIF due to breakage events only. In fact, the population density distribution functions given by these authors

$$n = \begin{cases} 0 & L < L_0 \quad (15) \\ \frac{1}{rTV_0} \exp\left[\frac{L_0(1+\beta)}{rT} \right] \exp\left[-\frac{L}{rT}(1+\beta) \right] & L_0 \leq L < L_c \quad (16) \\ \frac{1}{rTV_0} \exp\left[\frac{(1-\beta)L_0 - \beta L_c}{rT} \right] \exp\left[-\frac{L}{rT} \right] & L_c \leq L \quad (17) \end{cases}$$

can be written as

$$y = \begin{cases} 0 & X < X_0 \quad (18) \\ \exp[-(1+\beta)X] & X_0 \leq X < X_c \quad (19) \\ \exp[-X] & X_c \leq X \quad (20) \end{cases}$$

where

$$n^0 = \begin{cases} \frac{1}{rTV_0} \exp\left[\frac{L_0(1+\beta)}{rT} \right] & L_0 \leq L < L_c \\ \frac{1}{rTV_0} \exp\left[\frac{(1-\beta)L_0 - \beta L_c}{rT} \right] & L_c \leq L \end{cases}$$

(18) to (20) obviously confirm the above intuitive conclusion based on the crystal size intensity function concept. The parameter β denoting the breakage contribution of the escaping probability can be determined experimentally for such a specific kinetic model. It should be emphasized, however, that the form of the population density distribution function, (18) to (20), has essentially been obtained simply a priori by the intuitive CSIF concept; while in the original work of Rosen and Hulburt (1971), it was derived by lengthy mathematical manipulations using Laplace transforms.

Size-Dependent Supersaturation or Residence-Time

It is interesting to note, however, that other model-oriented interpretations of population density CSD data based on size-dependent supersaturation (Estrin, et al., 1969), size-dependent residence time (Canning, 1970; Randolph and Larson, 1971; Nauman, 1971; Nauman and Szabo, 1971), etc., would imply a similar population density plot of linear sections with different slopes as represented by (18) to (20). For example, the Equation (5) in the paper of Estrin et al. can be written as

$$y = \begin{cases} \exp[-X] & 0 \leq X < X_0 \\ \exp[-(X - X_0)] & X_0 \leq X \end{cases} \quad (21)$$

where

$$X = \begin{cases} \frac{L}{k_1 S_1{}^a T} & 0 \leq L < L_0 \\ \frac{L}{k_2 S_2{}^b T} & L_0 \leq L \end{cases}$$

and

$$n^0 = \begin{cases} n^0 & 0 \leq L < L_0 \\ n^0 \exp\left[-\frac{L_0}{k_1 S_1{}^a T} \right] & L_0 \leq L \end{cases}$$

(21) is in the form of (18) to (20).

The existence of such apparent anomalies calls attention to further studies of the effects of diffusional process, flow configuration, kinetic process, etc., on the CSD. The usual macroscopic approach based only on the population density distribution function $n(L)$ gives little insight to the real mechanism leading to the deviation from the ideal exponential population density distribution behavior observed in a continuous, MSMPR crystallizer. The introduction of the CSIF, $\Lambda(L)$, does, however, provide an additional conceptual basis for interpreting population density data from crystallizers. This is particularly true when the deviation from the ideal population density distribution behavior is due to the existence of size-dependent residence time such as the international or unintentional fines dissolution, stagnant zones, dead corners or bypassing in the crystallizer. By following the similar procedures well established in the residence time distribu-

tion theory (Himmelblau and Bischoff, 1968, p. 71; Noar and Shinnar, 1963), the use of the CSIF concept makes a distinction among possible mechanisms leading to these cases very simply. It is unfortunate, however, that this useful idea has apparently not been used before in crystallization practice.

CONCLUDING REMARKS

Although the intensity function concept is not new in the chemical engineering literature, this note has demonstrated for the first time the theoretical significance and experimental implications of the CSIF concept in the analysis of CSD data. The effects of kinetic process, flow configuration, diffusional process, particle breakage, etc., on the CSD have been considered within the same framework of the unifying CSIF concept. The illustrative examples have indicated that the CSIF concept allows physical insights into both a priori formulation and a posteriori interpretation of population density distribution functions. These results suggest that it is reasonable to point out the recent argument in interpreting the nonideal population density distribution behavior by either a size-dependent growth rate model or a size-dependent supersaturation expression is only a simple possible extreme in reflecting real mechanisms involved in leading to such a deviation.

The use of the CSIF concept will also provide a rational approach to the study of effects of mixing processes on the CSD (Noar and Shinnar, 1963; Lieb, 1973; Becker and Larson, 1969). By extending the similar concepts available in recent residence time distribution studies (Chen, 1971; McCord, 1972), the effects of micromixing on the transient and steady state CSD from crystallizers have been studied and will be reported separately.

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NOTATION

L, L' = crystal particle size (X, X')
L_0 = lower limit of the crystal particle size interval (X_0)
L_c = critical particle size in the crystal breakage model (X_c)
$n(L)$ = population density crystal size distribution function
n^0, $(n^0)'$ = lower limit of the population density crystal size distribution function $n(L)$ in a specific particle size interval
$P(L)$ = term in the size-dependent growth rate expression
Q = flow rates of feed and effluent streams of the crystallizer
r, r_1, r_2 = crystal growth rate
r^0 = term in the size-dependent growth rate expression
S, S_1, S_2 = supersaturation
T = residence time
V, V_0 = characteristic volume of the crystallizer
y = dimensionless population density crystal size distribution function, n/n^0 or $n/(n^0)'$
$\Lambda(L)$ = crystal size intensity function $(\Lambda(X))$
$\overline{\Lambda(L)}$ = average crystal size intensity function $(\overline{\Lambda(X)})$

Notations written within parentheses in the above list refer to the corresponding dimensionless forms. Other undefined notations appearing in the text such as a, b, β, γ are all constant parameters in the specific equations.

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