Using Discrete Distributions to Analyze CSD Data from MSMPR Crystallizers

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A novel technique for treating continuous mixed-suspension, mixed-product removal (MSMPR) crystal-size distribution (CSD) data uses a discrete probability distribution to represent the growth rate distribution of crystals in a crystallizer. It is based on the premise that individual crystals in a population each have their own intrinsic growth rate, but the growth rates of crystals in the population may vary. Treatment of CSD data using this discrete distribution technique enables the calculation of crystallizer kinetics data, including the nucleation rate and characterization of the nuclei growth rate distribution and using both graphical representation and descriptive statistics. Previously published data for a system exhibiting growth rate dispersion is used to demonstrate the efficacy of the technique. Furthermore, the results of the data analysis using the discrete distribution technique are compared to the results of data analysis using the continuous distribution technique.

Introduction

Continuous mixed suspension, mixed-product removal (MSMPR) crystallizers (Randolph and Larson, 1971) are particularly useful when trying to understand crystallization processes because key process conditions are fixed at steady state. Therefore, the nucleation and growth rates that are calculated are representative of a crystallizer operating at those conditions.

Using the assumption that no particles are present in the feed stream to a continuous MSMPR crystallizer yields the well-known expression for a MSMPR crystallizer operating at steady state (Randolph and Larson, 1971)

$$\frac{d(Gn)}{dl} + \frac{n}{\tau} = 0 \tag{1}$$

By assuming that McCabe's ΔL law (McCabe, 1929) is valid, one can take G outside of $d(Gn)/dl$ as a constant and solve the differential equation for the population density as a function of size (Randolph and Larson, 1972)

$$n = n^o \exp\left(-\frac{l}{g\tau}\right) \tag{2}$$

When CSD data from an MSMPR experiment is plotted as $\ln(n)$ vs. crystal size l, the result, if these assumptions hold true, is a straight line, where the slope of the line equals $-1/g\tau$ and the y-intercept is $\ln(n^o)$. When analyzing CSD data, one may observe that while the plot of $\ln(n)$ vs. l is linear at large sizes, it curves upward as size approaches zero (Randolph and Larson, 1971). Concave-upward curvature of the semi-logarithmic plot at small crystal sizes is nonideal behavior that occurs because crystals in the population grow at different rates.

Various theories have been used to explain deviation from the ΔL law. The three most popular theories include random fluctuations (RF), size-dependent growth (SDG), and intrinsic growth rate dispersion. The RF theory assumes that a crystal's growth rate fluctuates randomly around a mean value. The RF theory (Randolph and White, 1977), when applied to a continuous MSMPR crystallizer, yields the same linear plot of $\ln(n)$ vs. l (Zumstein and Rousseau, 1987) that one would get if the ΔL law (McCabe, 1929) were valid (Randolph and Larson, 1971). Because the RF theory is not capable of modeling nonideal behavior in continuous MSMPR crystallizers, it does not make a good theory on which to base a phenomenological understanding of growth rate behavior.

The size-dependent growth (SDG) theory postulates that a crystal's growth rate is an intrinsic function of its size $G(l)$. Abegg et al. (1968) proposed a form for $G(l)$ that was successfully used to fit nonideal data from a continuous MSMPR crystallizer exhibiting upward curvature at small sizes. Despite this success, it is difficult to accept the SDG model and its underlying assumption that a crystal's growth rate is a direct function of its size. Direct observation of individual crystals has demonstrated that a crystal's growth rate is independent of its size and each crystal has its own intrinsic growth rate (Garside, 1979; Girolami and Rousseau, 1985; Ramanarayanan, 1982; Berglund et al., 1983; Shanks and Berglund, 1985; Mathis-Lilley and Berglund, 1985; Jones and Larson, 1999). Furthermore, it has been demonstrated that the size-dependent growth function is mathematically equivalent to the conditional mean growth rate at a given size calculated using the intrinsic growth rate dispersion theory (Rojkowski, 1993). Because the basic postulate of the SDG theory is inconsistent with direct observation of crystal growth rates, SDG makes a poor choice as a basis for understanding growth rate phenomena in a continuous MSMPR crystallizer.

The theory of intrinsic growth rate dispersion, or constant crystal growth rate dispersion, postulates that each crystal is born with its own intrinsic growth rate and that crystals retain that growth rate as long as they remain in the crystallizer (Ramanarayanan, 1982). The growth rates of a population of crystals in a crystallizer can be described using a growth rate distribution. The intrinsic growth rate dispersion theory has been used successfully to model nonideal crystallizer behavior in both batch and continuous crystallization processes (Larson et al., 1985; Zumstein and Rousseau, 1987; Berglund and Larson, 1984; Girolami and Rousseau, 1985; Wang et al., 1990). The intrinsic growth rate dispersion model can account for nonideal behavior in both batch and continuous crystallizer processes and is consistent with observations of the growth rates of individual crystals. This makes it a desirable theory for providing a fundamental understanding of growth processes on which to base CSD analysis methods.

Intrinsic growth rate dispersion theory

For a population of crystals in a continuous MSMPR crystallizer, the crystals have a bivariate probability distribution $f(g,l)$ with respect to size l and growth rate g, which are both continuous random variables (Janse and de Jong, 1976). The bivariate distribution can be represented using Eq. 3 (Janse and de Jong, 1976; Berglund and Larson, 1984; Larson et al., 1985)

$$f(g,l) = \frac{1}{g\tau}\exp\left(\frac{-l}{g\tau}\right)f_G(g) \tag{3}$$

The function $f_G(g)$ is the marginal growth rate distribution, which represents the distribution of growth rates for all crystals present in the crystallizer. The marginal size distribution in a MSMPR crystallizer, representing the size distribution of all crystals in the crystallizer, is calculated in Eq. 4 (Janse and de Jong, 1976; Berglund and Larson, 1984; Larson et al., 1985)

$$f_L(l) = \int_0^\infty \frac{1}{g\tau}\exp\left(\frac{-l}{g\tau}\right)f_G(g)\,dg \tag{4}$$

The function $f_L(l)$ is the normalized population density n/N_T, where n is the population density at a given size l and N_T is the total number of crystals in the crystallizer per unit volume.

The normalized population density can be rewritten in terms of the conditional growth rate distribution at size zero, as in Eq. 5,

$$f_L(l) = \int_0^\infty \frac{1}{g_o\tau}\exp\left(\frac{-l}{g\tau}\right)f(g|l=0)\,dg \tag{5}$$

where g_o is the conditional mean growth rate at zero size (Janse and de Jong, 1976; Berglund and Larson, 1984; Larson et al., 1985; Zumstein and Rousseau, 1987).

Rojkowski (1993) demonstrated that the function $G(l)$ within the population balance equation for a continuous MSMPR crystallizer

$$n\frac{dG(l)}{dl} + G(l)\frac{dn}{dl} + \frac{n}{\tau} = 0 \tag{6}$$

is mathematically equivalent to the conditional mean growth rate at a given size $E(g|l)$. The proof is shown below:

Proof. Using the assumption that the intrinsic growth rate dispersion theory is valid, the conditional mean growth rate (CMGR) at a given size $E(g|l)$ can be calculated using Eq. 7

$$E(g|l) = \int_0^\infty \frac{1}{\tau f_L(l)}\exp\left(\frac{-l}{g\tau}\right)f_G(g)\,dg \tag{7}$$

By taking the derivative of the CMGR with respect to crystal size l

$$\frac{dE(g|l)}{dl} = -\int_0^\infty \frac{\frac{1}{g\tau^2}\exp\left(\frac{-l}{g\tau}\right)f_G(g)f_L(l) + \frac{1}{\tau}\exp\left(\frac{-l}{g\tau}\right)f_G(g)f_L'(l)}{(f_L(l))^2} \times dg \tag{8}$$

and using Leibnitz's formula for differentiating under the integral sign yields Eq. 9

$$\frac{dE(g|l)}{dl} = \frac{-1}{\tau} - \frac{f_L'(l)}{f_L(l)}E(g|l) \tag{9}$$

This equation can be rearranged to give

$$f_L(l)\frac{dE(g|l)}{dl} + E(g|l)\frac{df_L(l)}{dl} + \frac{f_L(l)}{\tau} = 0 \tag{10}$$

Multiplying through by N_T yields the population balance equation in Eq. 11

$$n\frac{dE(g|l)}{dl}+E(g|l)\frac{dn}{dl}+\frac{n}{\tau}=0 \tag{11}$$

which is Eq. 6, where $G(l)$ has been replaced with $E(g|l)$.

Using continuous distributions to characterize growth rate dispersion

Berglund and Larson (1984) and Larson et al. (1985) described a technique that uses continuous growth rate distributions to characterize the marginal distribution of growth rates in a continuous MSMPR crystallizer. Using the mean and variance of the CSD, one can calculate the mean and variance of the marginal growth rate distribution. Conversely, estimates of the mean and variance of the marginal growth rate distribution can be used to calculate the mean and variance of the CSD. Once the mean and variance of the marginal growth rate distribution are identified, one can specify a probability density distribution function like the gamma, inverse gamma, and normal distributions to represent the marginal growth rate distribution, $f_G(g)$. The CSD can then be calculated using Eq. 4.

The continuous distribution method requires the evaluation of a number of probability density functions in order to determine which one provides the best fit to the data and also the best representation of the marginal growth rate distribution. Even after trying many different probability density distribution functions, one may not find an expression that provides an adequate fit. Subsequent calculations of other useful parameters, distributions, and statistics using the continuous distribution method often require numerical integration. For example, calculating the nuclei growth rate distribution and its characterizing statistics using the continuous distribution technique almost always requires numerical integration.

Computational time and complexity, ease of use, performance, and flexibility are all issues when deciding whether to use the continuous distribution technique.

Crystallizer kinetics

Obtaining crystallizer kinetics requires both the calculation of the nucleation rate and characterization of the nuclei growth rate distribution (NGRD) for a given set of crystallizer conditions. The NGRD, or the conditional growth rate distribution at zero size, is the growth rate distribution of interest when generating kinetics data. If nuclei were formed and grown in a batch crystallizer under the same fixed conditions as in a continuous MSMPR crystallizer, the growth rate distribution of crystals in the batch crystallizer would be the same as the NGRD in the MSMPR crystallizer.

The marginal growth rate distribution describes the growth rate distribution for all of the crystals in the crystallizer. The marginal growth rate distribution is useful because its moments can aid in the calculation of the moments of the CSD. One can conceptualize the marginal growth rate distribution in another way by thinking of it as the NGRD transformed by the residence time distribution of the crystals in the crystallizer. In a batch crystallizer, where all of the crystals are nucleated and grown at the same time and under the same conditions, there will not be a residence time distribution; hence, the NGRD would be the same as the marginal growth rate distribution in that case. The conditional growth rate distribution (CGRD) at a given size characterizes the growth rate distribution of crystals in the population as a function of size. At small sizes, the CGRD is dominated by nuclei growth rates, and, at large sizes, crystals with the fastest growth rates dominate the CGRD.

In most cases it is neither convenient nor particularly useful to characterize growth rate distributions solely as a mathematical expression that describes the probability density distribution. One can plot the distributions for comparison, but comparison is then more qualitative rather than quantitative. Instead, it is more useful to calculate statistics that describe the distribution. Four statistics are used in this article to characterize a growth rate distribution: mean, variance, skewness, and kurtosis. The mean characterizes the average value for the distribution. The variance characterizes the spread of the distribution around the mean; the standard deviation is the square root of the variance. The skewness characterizes the symmetry of the distribution about the mean. Positive values of skewness indicate skew right distributions, and negative values indicate skew left distributions. A skewness of zero indicates a perfectly symmetrical distribution. The kurtosis characterizes the heaviness of the distribution's tail relative to the standard normal distribution. The coefficient of variation (CV) calculated as the standard deviation divided by the mean, is also used to describe the spread of the distribution. The CV is useful for comparing the spread of distributions with different means. These statistics are used to characterize the crystal-size distribution as well.

Technique and Theory

Discrete probability distributions

Let's assume that the continuous NGRD and marginal growth rate distributions can be well represented by a discrete probability distribution. Looking first at the marginal growth rate distribution, if g is a discrete random variable, the function given by $f_G(g=g_i)$ for each g_i within the range of g is called the probability distribution of g. The discrete function $f_G(g)$ must satisfy the following conditions:

(1) $f_G(g_i)\geq 0$ for each value in its domain.

(2) $\sum_{g_i} f(g_i)=1$, where the summation extends over all values in the domain.

The probability that a crystal will have growth rate g_i is given by the probability distribution $f_G(g_i)$. For the purposes of fitting crystal-size distribution data, the number of growth rates in the domain $[0,\infty]$ with nonzero probabilities is finite. The values of g, where the probability is nonzero, are denoted by g_i.

Thus, by using a discrete probability distribution to represent the marginal growth rate distribution, the equation representing the normalized population density function $f_L(l)$ is

$$f_L(l)=\sum_i \frac{1}{g_i\tau}\exp\left(\frac{-l}{g_i\tau}\right)f_G(g_i) \tag{12}$$

The nuclei growth rate distribution (NGRD), or the conditional growth rate distribution at zero size, can be written in terms of the marginal growth rate distribution

$$f(g_i|l=0)=\frac{1}{f_L^o g_i \tau} f_G(g_i)=\frac{g_o}{g_i} f_G(g_i) \tag{13}$$

where g_o is the CMGR at zero size. The NGRD is also a discrete probability distribution function by definition. The crystal-size distribution can also be described in terms of the population density

$$n(l)=\sum_i n^o \exp\left(\frac{-l}{g_i \tau}\right) f(g_i|l=0)=\sum_i n_i \exp\left(\frac{-l}{g_i \tau}\right) \tag{14}$$

Because crystallizer data is usually collected in terms of population density at a given size, in most cases Eq. 14 is the most effective for treating CSD data. One plots $\ln(n)$ vs. l for both experimental data and the fitted curve from Eq. 14. Increasing the number of growth rates with nonzero probabilities will reduce the error in the model, as each new term in the sum takes up two degrees of freedom, although increasing the number of terms also increases the complexity of the data regression process. One also reaches a point where the new terms are no longer statistically significant, making the addition of new terms relatively meaningless.

At the end of the regression process, one will obtain a set of n_i's and g_i's. The conversion from n_i's to probabilities in the discrete NGRD and marginal growth rate distributions is straightforward. The discrete marginal growth rate distribution and the discrete conditional growth rate distribution at zero size at g_i's with nonzero n_i's are

$$f_G(g_i)=\frac{g_i n_i}{g_o n^o} \tag{15}$$

$$f(g_i|l=0)=\frac{n_i}{n^o} \tag{16}$$

where n^o, the population density at zero size is

$$n^o=\sum_i n_i \tag{17}$$

and g_o the conditional mean growth rate at zero size is

$$g_o=\frac{\sum_i n_i g_i}{\sum_i n_i} \tag{18}$$

Crystal-size distribution

CSDs are characterized in much the same way as growth rate distributions, using descriptive statistics. It is also useful to be able to transform number based CSD data into length, area, and mass distributions. All of these things are easily calculated once the growth rate distribution has been defined following data regression.

The moments of the size distribution can be calculated using the following generalized equation where $E(l^j)$ is the jth moment of the size distribution

$$E(l^j)=j!\tau^j \frac{\sum_i n_i g_i^{j+1}}{\sum_i n_i g_i} \tag{19}$$

The weighted mean sizes can be calculated using

$$L_{h,h-1}=\frac{h!}{(h-1)!}\tau \frac{\sum_i n_i g_i^{h+1}}{\sum_i n_i g_h} \tag{20}$$

For example, the dominant particle size $L_d=L_{3,2}$, is

$$L_d=3\tau \frac{\sum_i n_i g_i^4}{\sum_i n_i g_i^3} \tag{21}$$

The total number of crystals per unit crystallizer volume is

$$N_T=\sum_i n_i g_i \tau \tag{22}$$

The total length per unit crystallizer volume is

$$L_T=\sum_i n_i (g_i \tau)^2 \tag{23}$$

The total surface area per unit crystallizer volume is

$$A_T=2k_a \sum_i n_i (g_i \tau)^3 \tag{24}$$

The suspension density in mass per unit crystallizer volume is

$$M_T=6k_v \rho \sum n_i (g_i \tau)^4 \tag{25}$$

The nucleation rate can be calculated using the CMGR at zero size and the population density at zero size n^o

$$B^o=g_o n^o=\sum_i n_i g_i \tag{26}$$

Growth rate distributions

The normalized discrete marginal growth rate distribution can be calculated using

$$f_G(g_i)=\frac{n_i g_i}{\sum_i n_i g_i} \tag{27}$$

and the normalized conditional growth rate distribution at zero size is

$$f(g_i|l=0) = \frac{n_i}{\sum_i n_i} \tag{28}$$

The moments of the NGRD can be calculated using

$$E(g^j|l=0) = \frac{\sum_i n_i g_i^j}{\sum_i n_i} \tag{29}$$

The moments of the marginal growth rate distribution can be calculated using

$$E(g^j) = \frac{\sum_i n_i g_i^{j+1}}{\sum_i n_i g_i} \tag{30}$$

The jth moment about the conditional mean growth rate at zero size is given by

$$E\left[(g-g_o)^j|l=0\right] = \frac{\sum_i n_i (g_i - g_o)^j}{\sum_i n_i} \tag{31}$$

The variance of the NGRD is the second moment about the CMGR at zero size. The skewness measures the asymmetry present in the distribution, where a value of zero indicates that the distribution is perfectly symmetrical about the mean like in a normal distribution. Values less than zero indicate a skew left distribution and values greater than zero indicate a skew right distribution like in a gamma or inverse gamma distribution. The skewness of the NGRD can be calculated using Eq. 32

$$\mathbf{skewness}(g|l=0) = \frac{E\left[(g-g_o)^3|l=0\right]}{\left\{E\left[(g-g_o)^2|l=0\right]\right\}^{1.5}} \tag{32}$$

The kurtosis is a measure of the heaviness of the tail using a normal distribution as reference. The fourth moment of the growth rate about the mean divided by the variance squared is three for a normal distribution. The kurtosis of the NGRD can be calculated using Eq. 33

$$\mathbf{kurtosis}(g|l=0) = \frac{E\left[(g-g_o)^4|l=0\right]}{\left\{E\left[(g-g_o)^2|l=0\right]\right\}^2} - 3 \tag{33}$$

The coefficient of variation measures the relative spread of the distribution and is calculated by

$$CV = \frac{\sigma}{\mu} \times 100 \tag{34}$$

The conditional expected value of g^j at a given crystal size is then given by

$$E(g^j|l) = \frac{\sum_i n_i g_i^j \exp\left(\frac{-l}{g_i \tau}\right)}{\sum_i n_i \exp\left(\frac{-l}{g_i \tau}\right)} \tag{35}$$

The CMGR at a given size can be calculated using $j=1$. The jth moment about $E(g|l)$ is given by

$$E\left\{[g - E(g|l)]^j|l\right\} = \frac{\sum_i n_i [g_i - E(g|l)]^j \exp\left(\frac{-l}{g_i \tau}\right)}{\sum_i n_i \exp\left(\frac{-l}{g_i \tau}\right)} \tag{36}$$

The variance of the conditional growth rate at a given size $\mathrm{Var}(g|l)$ is the second moment about $E(g|l)$. The skewness is the third moment about $E(g|l)$ divided by $\mathrm{Var}(g|l)^{3/2}$. The kurtosis is the fourth moment about $E(g|l)$ divided by $\mathrm{Var}(g|l)^2$ subtracted by three; subtracting by three makes the kurtosis zero for a normal distribution.

Example

Rojkowski published CSD data from a continuous MSMPR crystallizer with a volume of 0.01 m^3 crystallizing aluminum ammonium alum from water at 20°C with a residence time of 2,290 s (Rojkowski, 1993).

Data regression

Specification of the discrete growth rate distribution begins with specifying the number of growth rates that will have nonzero probabilities. Each growth rate with a probability greater than zero uses up two degrees of freedom, one for each g_i and one for each n_i, from the total available degrees of freedom $N-1$. N is the total number of data points. There are 31 data points in this example, which means the total available degrees of freedom $N-1$ is 30. The maximum number of growth rates with nonzero probabilities that can be specified for this example is fifteen. The actual number of growth rates with nonzero probabilities that are specified depends upon the desired quality of the fit. Increasing the number of terms will increase the quality of the fit as the degrees of freedom are used up. The reward from increasing the quality of the fit is balanced out by the penalty for having to regress additional parameters to the data. When only one term is used in the discrete probability distribution, that is, one g_i and one n_i, the CSD reduces to the ideal MSMPR case in Eq. 1.

In this example, five terms were used to specify the discrete growth rate distribution. Values of the five n_i's and five g_i's were determined using MS-Excel's Solver routine to fit the experimental data to Eq. 6, although the nonlinear fit tool within JMP also worked well for that purpose and yielded the same result. The program that is used to perform the regression will likely depend upon what is available and what the user is most familiar with. MS-Excel will be discussed here, because it is a readily available and a familiar application for most chemical engineers. MS-Excel Solver uses a nonlinear optimization technique to minimize the sum of squared residuals (SSR) by manipulating the g_i's and the n_i's

$$SSR = \sum_{k=1}^{N} \left[\log(n_k) - \log(\hat{n}_k)\right]^2 \tag{37}$$

One may also choose to define the SSR alternatively as

$$SSR = \sum_{k=1}^{N} (n_k - \hat{n}_k)^2 \tag{38}$$

Although in this example, however, the former definition for SSR was used.

Because Eq. 6 is nonlinear, the success of the iteration process is dependent upon the choice of initial values for the n_i's and g_i's. For this example, initial guesses were input and changed until the fitted curve began to resemble the CSD data, that is, $\ln(n)$ vs. l data was plotted along with the fitted curve using Eq. 6. At that point, the Solver routine was initiated. If it failed to converge, then the guesses were refined, and the iteration was tried again. This process was repeated until it converged.

Within Solver, the "Automatic Scaling" and "Assume Non-Negative" options should be selected. Constraints were placed on the g_i's, $0 < g_I < 1.5 \times 10^{-7}$ m/s and on the n_i's, 1.0×10^{12} No./m^4 < n_i < 1.0×10^{19}/m^4. Using the proper constraints helps the routine to converge. Depending on the CSD data, one may try selecting different options for the search, derivative, and estimate selections to help the Solver routine converge more quickly.

Results

The results of the regression are shown in Table 1. The n_i's are also shown in Table 1 having been converted into the discrete probabilities for the marginal growth rate distribution and the conditional growth rate distribution at zero size using Eqs. 15 and 16. Figure 1 shows the plot of the experimental CSD data with the fitted curve that was solved for using the discrete distribution technique. The Pearson product moment correlation, or R^2 value, for the population density using the discrete distribution method was 0.9996.

The discrete NGRD and marginal growth rate distributions were converted into a continuous form by assigning the discrete probabilities to bins with centers around the specified g_i's. This can be useful if one wishes to assign a continuous probability distribution function to the NGRD or for comparing the results of the discrete distribution technique with the results of using a continuous distribution technique (Larson et al., 1985). The bin sizes were calculated by starting at zero and using the value of the growth rate center point in the first bin to set the size of the first bin 2^*g_1. The size of the first bin and the next center point were then used to determine the size of the second bin $2^*(g_2 - 2^*g_1)$ and so on. The discrete probability was then divided by the size of the bin to calculate the probability density for that bin. The continuous representations of the discrete NGRD and marginal growth rate distributions found using this procedure are shown in Figure 2.

The calculated normalized mass $m(l) = \rho^* k_v^* l^{3*} n/M_T$, area, $a(l) = k_a^* l^{2*} n/A_T$, length $l(l) = l^* n/L_T$, and number $f_L(l) = n/N_T$, distributions are shown in Figure 3. These distributions can all be represented by continuous functions.

Statistics that characterize the marginal size and marginal growth rate distributions and the conditional growth rate distribution at zero size are shown in Table 2. The mean speci-

Table 1. Fitted Parameters Describing Discrete Marginal and Discrete Conditional Growth Rate Distribution at Zero Size

i	g_i (m/s)	n_i (No./m^4)	$f_G(g_i)$	$f(g_i \mid l=0)$
1	8.35×10^{-10}	1.53×10^{18}	7.94×10^{-1}	9.28×10^{-1}
2	2.48×10^{-9}	1.15×10^{17}	1.77×10^{-1}	6.97×10^{-2}
3	1.14×10^{-8}	3.30×10^{15}	2.34×10^{-2}	2.01×10^{-3}
4	2.65×10^{-8}	3.32×10^{14}	5.47×10^{-3}	2.02×10^{-4}
5	6.46×10^{-8}	1.36×10^{13}	5.48×10^{-4}	8.28×10^{-6}

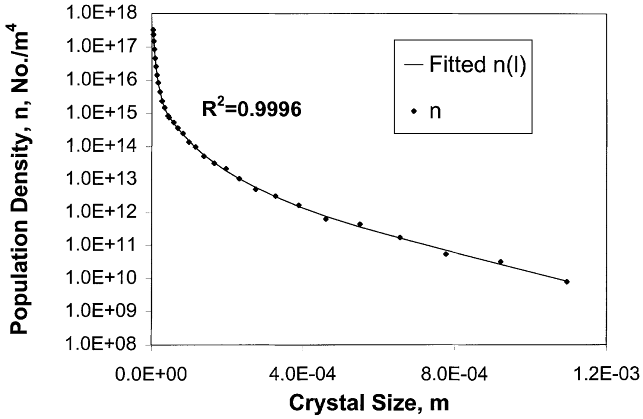

Figure 1. Experimental data with fitted curve for $n(l)$ using a discrete distribution method.

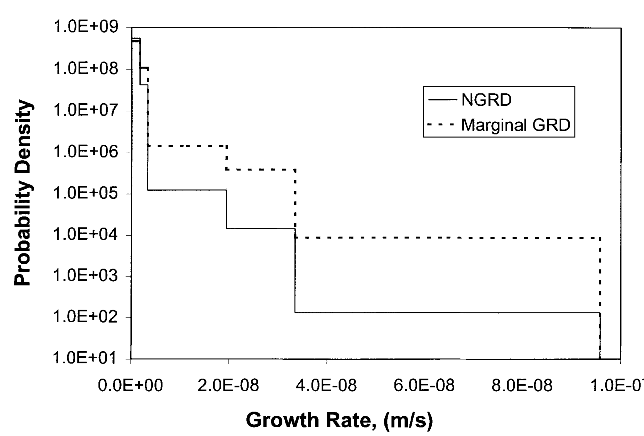

Figure 2. Calculated probability density distribution of NGRD and marginal growth rate distribution calculated from the discrete NGRD and marginal growth rate distributions.

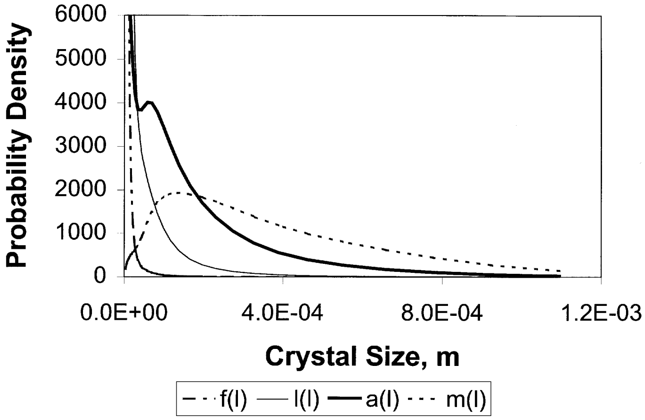

Figure 3. Calculated normalized number, length, area, and mass probability density distributions using discrete distribution method.

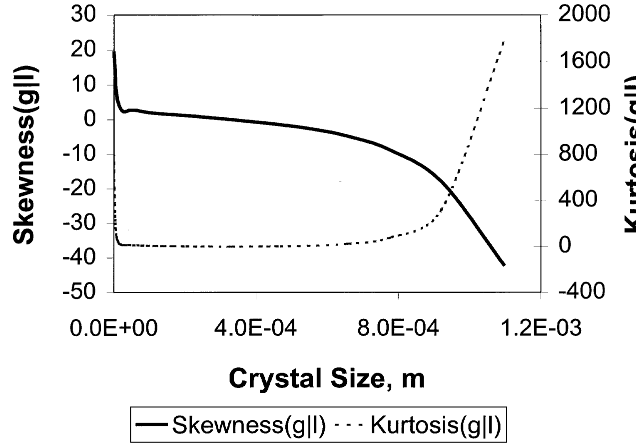

Figure 4. Skewness and kurtosis of the conditional growth rate distribution with respect to varying crystal size.

fies the average value. The variance measures the spread of the distribution. The CV is a measure of the relative spread of the distribution. The skewness measures the asymmetry of the distribution with increasing magnitude indicating an increased degree of asymmetry. The sign of the skewness indicates whether the distribution is skew left, negative values, or skew right, positive values. A normal distribution is perfectly symmetrical and has a skewness of zero. The kurtosis measures the heaviness in the tail of the distribution relative to a normal distribution. Kurtosis greater than zero indicates that the distribution is becoming more tail-heavy than a normal distribution. A kurtosis less than zero indicates a distribution that is less tail-heavy than a normal distribution. The NGRD is more asymmetrical and has a heavier tail than the marginal growth rate distribution. The NGRD has a lower mean growth rate, variance, and CV than the marginal growth rate distribution.

Key crystallizer kinetics data calculated using the discrete distribution technique are presented below:

- The nuclei mean growth rate g_o is 9.76×10^{-10} m/s.
- The nucleation rate B^o is 1.61×10^{9} No./m^3/s.
- The population density at zero size n^o is 1.64×10^{18} No./m^4.
- The total number density N_T is 3.68×10^{12} No./m^3.

Using Eqs. 32 and 33, the skewness and kurtosis of the conditional growth rate distribution at a given size were calculated and plotted. The trends in Figure 4 demonstrate how the nuclei growth rate distribution is affected by the residence time distribution of crystals in the crystallizer. The skewness of the conditional growth rate distribution actually becomes skew left with increasing size. The kurtosis of the CGRD decreases quickly from its value at size zero and then increases as the size increases.

Table 2. Normalized Marginal Size Distribution, Marginal Growth Rate Distribution, and Conditional Growth Rate Distribution at Zero Size

	f_L [l/(m)]	f_G [g(m/s)]	f [g(m/s)|$l=0$]
Mean	3.54×10^{-6}	1.55×10^{-9}	9.76×10^{-10}
Variance	1.01×10^{-10}	8.39×10^{-18}	5.57×10^{-19}
Skewness	19.4	10.1	19.2
Kurtosis	794.8	153.4	787.0
CV	283.1	187.3	76.4

Using Eqs. 35 and 36, the mean and coefficient of variation of the conditional growth rate distribution with respect to varying size were calculated and plotted as shown in Figure 5. The smallest crystals have growth rates with the largest CV, or relative spread. The CV of the CGRD decreases with increasing size. The conditional mean growth rate at a given size increases from g_o to an asymptotic value with increasing crystal size. This implies that only crystals with high growth rates ever reach a large size in the crystallizer.

The results from using the discrete distribution technique were also compared to the results found using the continuous growth rate distribution technique described by Larson et al. (1985). The gamma, inverse gamma, and normal distributions

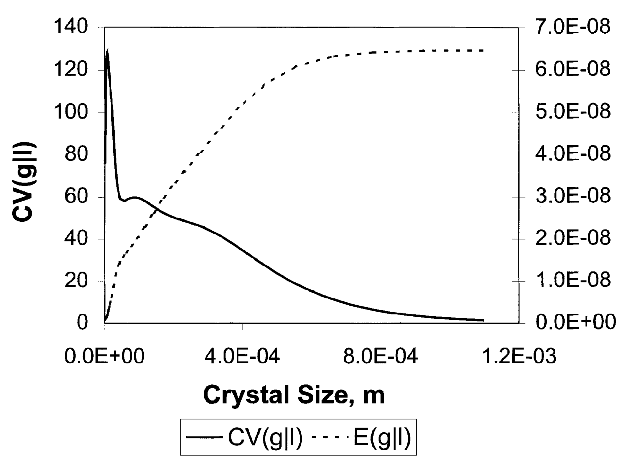

Figure 5. Mean and coefficient of variation of the conditional growth rate distribution with respect to varying crystal size.

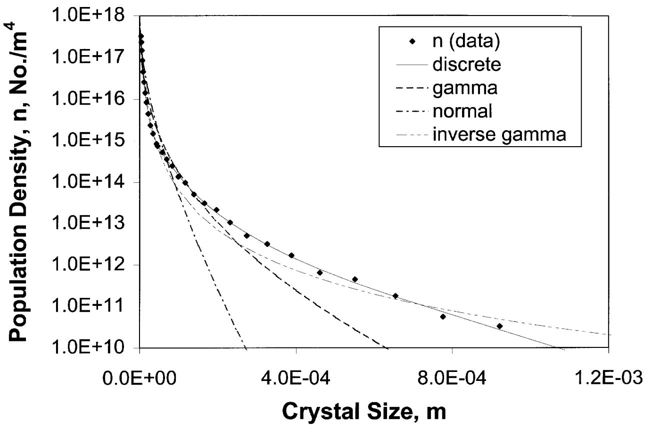

Figure 6. Comparison of CSD fits using discrete, gamma, normal, and inverse gamma distributions to represent the growth rate distribution.

were all evaluated in order to determine which of these would provide the best data fit. The CSDs predicted using the continuous distribution method are shown in Figure 6. The normal and gamma distributions provided poor fits to the CSD experimental data of $\ln(n)$ vs. l. The inverse gamma distribution provided the best fit of the three continuous distributions that were analyzed. However, none of the three continuous distributions approached the quality of fit that the discrete distribution method was able to deliver.

Figure 7 shows the mass distribution as a function of size $n(l)*l^3$ vs. l, comparing results using the continuous and discrete methods with the experimental data. The mass distributions calculated using the three continuous distributions all do a very poor job of fitting the experimental data. The inverse gamma distribution, which was found to provide the best fit of $\ln(n)$ vs. l of the three continuous distributions tested, provides, arguably, the poorest fit to the mass distribution. Conversely, the discrete distribution method was able to fit the mass distribution very well.

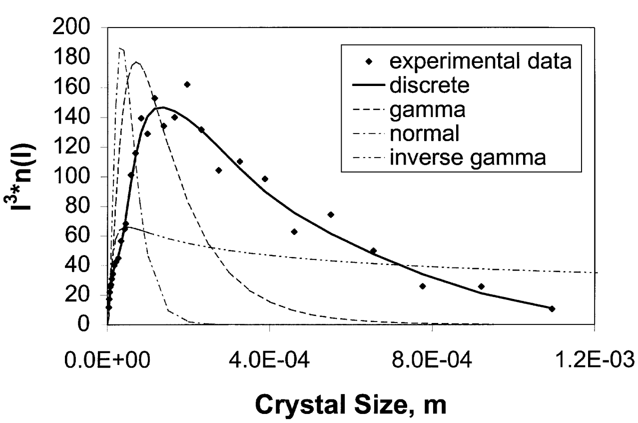

Figure 7. Comparison of mass distributions using discrete, gamma, normal, and inverse gamma distributions to represent the growth rate distribution.

Summary and Conclusions

A technique that uses discrete probability distributions to characterize relevant growth rate distributions and calculate crystallizer kinetics data has been proposed and its efficacy has been demonstrated. This technique is consistent with the assumption that intrinsic growth rate dispersion is responsible for nonideal CSD behavior in continuous MSMPR crystallizers.

A previously defined data set (Rojkowski, 1993) was analyzed using the discrete distribution technique. The mean, variance, CV, skewness and kurtosis of the size, marginal growth rate, and nuclei growth rate distributions were calculated to quantitatively characterize those distributions. A continuous representation of the marginal growth rate and nuclei growth rate distributions was also determined. The discrete distribution technique yielded a continuous equation for $n(l)$ that fit the experimental data with an R^2 value of 0.9996. The normalized length, area, and mass distributions were also calculated.

Comparison of the discrete and continuous distribution methods demonstrated that using the discrete distribution technique had the following advantages over using the continuous distribution technique:

- It did not require evaluating several different types of distributions.
- It provided a better fit to the data implying better representation of the growth rate distributions.
- Efficient calculation of key crystallizer parameters and distribution statistics using summations.
- Continuous representation of the number, length, area, and mass distributions.
- No numerical integration necessary.
- Better fit of number, length, area, and mass distributions.

The only negative aspect of using the discrete distribution method was that nonlinear regression was required; however, this work has demonstrated that it is quite feasible.

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Notation

A_T = the cumulative crystal area per unit volume
$a(l)$ = normalized area distribution
B^o = nucleation rate
$f_G(l)$ = normalized marginal growth rate distribution
$f_L(l)$ = normalized marginal crystal-size distribution
g_o = conditional mean growth rate for crystals at zero size
g = growth rate
k_a = area shape factor
k_v = volume shape factor
l = crystal size
$l(l)$ = normalized length distribution
L_d = dominant particle size
L_T = the cumulative crystal area per unit volume
m_G = moment of the marginal growth rate distribution
m_L = moment of the marginal crystal size distribution
$m(l)$ = normalized mass distribution
M_T = cumulative crystal mass per unit volume or slurry density

N_T = cumulative crystal number per unit volume
n = population density
n^o = population density at zero size
V = crystallizer volume
τ = residence time

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