SOME ASPECTS OF PROCESS DESIGN OF CONTINUOUS CRYSTALLIZERS: A THEORETICAL ANALYSIS

Ramanarayanan, K. A.
Chemical Engineering
University of South Florida
Tampa, FL 33620

Paper to be presented at the 1985 Joint Meeting of the
Central and Peninsular Florida Sections of the
American Institute of Chemical Engineers

25 May, 1985

SOME ASPECTS OF PROCESS DESIGN OF CONTINUOUS CRYSTALLIZERS: A THEORETICAL ANALYSIS

Ramanarayanan, K. A.
Chemical Engineering
University of South Florida
Tampa, FL 33620

INTRODUCTION

Crystallization is a commonly used unit operation for the separation of a solid product from solution and for the purification of a wide variety of industrially important organic and inorganic materials. In addition to achieving the required production rate and purity specifications, the crystalline product should also meet requirements of shape and the crystal size distribution (CSD). These properties affect the flow, handling, storage and packaging characteristics of the crystalline product. One of the main factors which determines the CSD is the crystallization kinetics viz. nucleation and growth rates. Thus, the control of the product quality effectively means the control of the nucleation and growth steps in the crystallizer.

The product CSD is determined primarily by three factors in a continuous crystallizer. These are:

1. The birth size dispersion (BSD) of the crystals
2. The growth rate dispersion (GRD) of the crystals and
3. The residence time distribution (RTD) of the crystals.

Each of the above factors can be mathematically characterized by a statistical distribution with parameters related to the mean and the variance of the distributions. The birth size dispersion can be generally characterized by a uniform distribution with all the crystals assumed to be born near zero size. This assumption is valid in many crystallization systems since the product crystal sizes are relatively large compared to the birth sizes of the nuclei. The growth rate dispersion function can be characterized say by a two parameter "Inverse Gamma Distribution" (Larson et al., 1985). The RTD for the case of a well mixed crystallizer is an exponential function with a mean equal to the mean residence time of the crystals in the crystallizer. For an actual crystallizer, the RTD may not be an exponential function and can be conveniently represented by a Gamma Distribution. This distribution offers the advantage of representing the extreme cases of backmixed and plugflow situations. (Ramanarayanan and Howard, 1985).

THE CONSTANT CRYSTAL GROWTH (CCG) MODEL

The CCG model is a macroscopic engineering model that relates the final product size of a crystal to its initial size, growth rate and the residence time. This model has been verified for a number of inorganic and organic systems using photomicroscopy (Ramanarayanan et al., 1985). According to this model crystals exhibit birth size and growth rate dispersions; the crystal growth rates are size independent and have no correlation to their initial sizes. The CCG model can be represented in a statistical-mathematical form with the following equation:

$$\ell = \ell_o + g\,t \qquad (1)$$

where ℓ_o, g and t are random independent variables and ℓ_o and g are independent of each other.

GENERALIZED CSD MODEL FOR CONTINUOUS CRYSTALLIZERS

This section derives a generalized model for predicting the CSD from a continuous crystallizer for crystallizing systems exhibiting growth rate dispersion and non-ideal residence time distribution with the following assumptions:

1. The size of the product crystals is very large compared to their initial birth size.
2. There is no subsequent breakage nor agglomeration of crystals in the crystallizer.
3. The crystals follow the CCG Model.
4. The residence time of the crystals in the crystallizer and the growth rate of the crystals are independent of their size.

According to the CCG Model,

$$\ell = \ell_o + gt \tag{1}$$

Let θ be the Laplace Transform variable with respect to size. From Equation (1),

$$\exp(-\theta\ell) = \exp(-\theta\ell_o) \cdot \exp(-\theta g t) \tag{2}$$

Taking the expected values of both sides of Equation (2),

$$E[\exp(-\theta\ell)] = E[\exp(-\theta\ell_o)] \cdot E[\exp(-\theta g t)] \tag{3}$$

It is assumed that ℓ_o, g and t are random independent variables. From the statistical-mathematical background presented in Table 1 (Ramanarayanan, 1982),

$$\Psi_L(\theta) = \Psi_{L_o}(\theta) \cdot E[\exp(-\theta g t)] \tag{4}$$

or

$$\Psi_L(\theta) / \Psi_{L_o}(\theta) = E[\exp(-\theta g t)] \quad (5)$$

The $E[\exp(-\theta g t)]$ can be evaluated from the knowledge of the distribution functions $f_G(g)$ and $f_T(t)$ for the growth rate 'g' and the residence time 't' respectively (Ramanarayanan et al., 1984). Noting that the random variables 'g' and 't' are >=0,

$$E[\exp(-\theta g t)] = E[E[\exp(-\theta g t)\,|_t]]$$

$$= E[\Psi_G(\theta t)] \text{ for all t's}$$

$$= \int_0^\infty \Psi_G(\theta t)\, f_T(t)\, dt \quad (6)$$

or

$$\frac{\Psi_L(\theta)}{\Psi_{L_o}(\theta)} = \int_0^\infty \Psi_G(\theta t)\, f_T(t)\, dt \quad (7)$$

$$= \int_0^\infty \left[\int_0^\infty \exp(-\theta g t) f_G(g)\, dg \right] f_T(t)\, dt \quad (8)$$

$$= \int_0^\infty \left[\int_0^\infty \exp(-\theta g t)\, f_T(t)\, dt \right] f_G(g)\, dg \quad (9)$$

$$\frac{\Psi_L(\theta)}{\Psi_{L_o}(\theta)} = \int_0^\infty \Psi_T(\theta g)\, f_G(g)\, dg \quad (10)$$

For the special case when $\ell_o = 0$,

$$\Psi_{L_o}(\theta) = 1 \quad (11)$$

$$\Psi_L(\theta) = \int_0^\infty \Psi_T(\theta g)\, f_G(g)\, dg \quad (12)$$

Consider the RTD to be a Gamma Distribution with parameters α and β. From Table 2,

$$f_T(t) = \frac{1}{\beta^{\alpha}\ \Gamma(\alpha)}\ t^{\alpha-1}\ \exp\ (\ -\ t/\beta\ ) \qquad (13)$$

and

$$\Psi_T(\theta g) = 1/\ (\beta\theta g+1)^{\alpha} \qquad (14)$$

From Equations (11), (14) and (10),

$$\Psi_L(\theta) = \int_0^{\infty} \frac{f_G(g)\ dg}{(\beta\theta g\ +\ 1)^{\alpha}} \qquad (15)$$

Inverting equation (15) into the size domain yields,

$$f_L(\ell) = \frac{\ell^{\alpha-1}}{\beta^{\alpha}\ \Gamma(\alpha)} \int_0^{\infty} g^{-\alpha}\ \exp\ (\ -\ell\ /\beta\ g)\ f_G(g)\ dg \qquad (16)$$

For the special case when $\alpha = 1$ (exponential RTD) and $g = \bar{g}$ (no growth rate dispersion), Equation (16) reduces to the case of the ideal MSMPR crystallizer given by Equation (17).

$$f_L(\ell) = \frac{1}{\beta\ \bar{g}}\ \exp\ (\ -\ \ell\ /\beta\ \bar{g}\ ) \qquad (17)$$

where 'β' corresponds to the mean residence time of the crystals. A plot of $\ell n\ [f_L(\ell)]$ versus ℓ should be a straight line for an ideal MSMPR crystallizer (Randolph and Larson, 1971). Any deviation from this linear nature of the population density plot can be attributed to the relaxation of the assumptions made in deriving the ideal MSMPR model. Hence, the generalized CSD model given by Equation (16) is valid for a number of realistic situations and can be used to predict the CSD from the knowledge of the growth rate dispersion kinetics and the parameters for the RTD.

Equation (16) represents the CSD from a continuous crystallizer for which:

(a) the RTD is represented by a Gamma distribution with parameters (α,β); $\alpha = 1$ corresponds to a backmixed RTD with a mean residence time, β.

(b) the growth dispersion characteristics of the system are represented by an arbitrary distribution function $f_G(g)$.

Thus by knowing the parameters (α,β) and the growth rate distribution function $f_G(g)$, the CSD $f_L(\ell)$ can be calculated.

Recently Larson et al. (1985) considered the following two parameter distributions to characterize growth rate dispersion.

(a) Normal distribution
(b) Gamma Distribution and
(c) Inverse Gamma Distribution

The two parameters commonly used to determine the form of the growth rate distribution function are the mean growth rate $\bar{g}$ and the variance of the growth rate distribution, σ_G^2. Experimental methods to obtain these parameters are available in the literature (Blem and Ramanarayanan, 1985). Larson et al. (1985) observed that the CSD's predicted for a continuous well-mixed crystallizer were practically identical to each other even though the three different forms mentioned above were used to characterize $f_G(g)$. Thus it seems reasonable to assume any one of the three distributions viz. Normal, Gamma or the Inverse Gamma to arbitrarily represent the growth rate distribution function.

For the sake of analytical ease, consider the Inverse Gamma distribution the form and properties of which are listed in Table 4 (Larson et al., 1985). Substituting for $f_G(g)$ from Table 4 and integrating with respect to 'g' between 0 and ∞, yields,

$$f_L(\ell) = (a\beta)^{k-1} \frac{\Gamma(\alpha+k-1)}{\Gamma(\alpha)\ \Gamma(k-1)} \quad \frac{\ell^{\alpha-1}}{(\ell + a\beta)^{\alpha+k-1}} \qquad (18)$$

$$\alpha > 0 \text{ and } k > 3$$

The properties of the CSD represented by Equation (18) are listed in Table 4. Figure 3 shows a plot of the crystal size distribution for a given set of growth rate dispersion kinetic parameters. The parameters assumed for the growth rate distribution were 'a=10' and 'k=5' which correspond to a mean growth rate of 3.33 and a variance of 5.56. Curve 1 corresponds to the backmixed case whereas the curve 5 corresponds to plug flow behavior. It can be seen that there is substantial difference in the CSD predicted for the extreme situations of backmixed and plug flow behavior. Intermediate curves such as 3 and 4 represent RTD's between complete mixing and ideal plug flow. Figure 4 depicts CSD's for small deviations from the MSMPR case. This case corresponds to small deviations of α values from unity such as α = 2 and 0.5. These induce substantial curvature to the population density plots from continuous crystallizers.

This suggests that the nonlinear population density plots for continuous crystallizers may be due to growth rate dispersion and/or due to the deviation of the RTD from complete mixing. One popular method to account for these nonlinearities has been the use of the size dependent growth model proposed by Abegg, Stevens and Larson (1968). This model is empirical in nature and experimental evidence in support of size dependent growth is scanty in the literature (Garside, 1985). It is therefore important to establish the macroscopic mechanisms for birth and growth of crystals using photomicroscopy for the rational interpretation of CSD data from continuous crystallizers.

Starting with Equation (18), the j th moment of the CSD can be calculated as follows:

$$M_L(j) = \int_0^\infty \ell^j f_L(\ell)\, d\ell \qquad (19)$$

$$= (a\beta)^j \frac{\Gamma(\alpha+j)\,\Gamma(k-j-1)}{\Gamma(\alpha)\,\Gamma(k-1)} \qquad (20)$$

$$k > 3,\ j < k$$

$$M_L(1) = \bar{\ell} = \frac{a\,\alpha\,\beta}{k-2} = \bar{g}\,\tau \qquad (21)$$

$$M_L(2) = \frac{\alpha(\alpha+1)(a\beta)^2}{(k-2)(k-3)} \qquad (22)$$

or

$$\sigma_L^2 = M_L(2) - M_L^2(1) \qquad (23)$$

$$= (\bar{g}\,\tau)^2 \left[\frac{\alpha+1}{\alpha}\,\frac{k-2}{k-3} - 1\right] \qquad (24)$$

For an ideal MSMPR ($\alpha = 1$) and no growth rate dispersion ($k \to \infty$),

$$\bar{\ell}_{\text{ideal}} = \bar{g}\,\tau \qquad (25)$$

$$\sigma^2_{L\ \text{ideal}} = (\bar{g}\,\tau)^2 \qquad (26)$$

Hence,

$$\Phi_L = \bar{\ell} / \bar{\ell}_{\text{ideal}} = 1 \qquad (27)$$

$$\Phi_V = \sigma_L^2 / \sigma^2_{L\ \text{ideal}} = \frac{\alpha+1}{\alpha}\,\frac{k-2}{k-3} - 1 \qquad (28)$$

where Φ_L and Φ_V represent the nonideality factors for the mean and the variance of the CSD respectively. Since $\Phi_L = 1$, it can be concluded that neither the residence time distribution nor the growth rate dispersion characteristics have an effect on the mean size from the continuous crystallizer. However, the variance factor is determined by the RTD and the GRD parameters 'α' and 'k'. When $k \to \infty$ and $\alpha = 1$, the variance factor reduces to unity.

The weight distribution $\omega(\ell)$, which represents the fraction of the weight of the crystals between size ℓ and $\ell + d\ell$, is given by the the

derivative of the cumulative undersize weight distribution W(ℓ) defined as:

$$W(\ell) = \int_{0}^{\ell} \ell^3 f_L(\ell)\, d\ell \;/\; \int_{0}^{\infty} \ell^3 f_L(\ell)\, d\ell \qquad (29)$$

$$= \frac{\Gamma(\alpha+k-1)}{\Gamma(\alpha+3)\Gamma(k-4)} (a\beta)^{k-4} \int_{0}^{\ell} \frac{\ell^{\alpha+2}}{(\ell + a\beta)^{\alpha+k-1}} d\ell \qquad (30)$$

$$\omega(\ell) = \frac{d}{d\ell} W(\ell) = \frac{\Gamma(\alpha+k-1)}{\Gamma(\alpha+3)\Gamma(k-4)} (a\beta)^{k-4} \frac{\ell^{\alpha+2}}{(\ell + a\beta)^{\alpha+k-1}} \qquad (31)$$

and the dominant size of the weight distribution 'ℓ_D' (defined as the crystal size at which ω(ℓ) is maximum) is given by,

$$\ell_D = \frac{(\alpha + 2)\, a\, \beta}{k - 3} \qquad (32)$$

$$= \frac{\alpha + 2}{\alpha} \frac{k - 2}{k - 3} \bar{g}\, \tau \qquad (33)$$

For the case of the backmixed continuous crystallizer with no growth rate dispersion ($\alpha = 1$, $\beta = \tau$ and $k \to \infty$), the dominant size reduces to $3\,\bar{g}\,\tau$ as per the case of the MSMPR model of Randolph and Larson (1971). From Equation (33), it can be seen that the dominant crystal size depends not only on the RTD parameters 'α' and 'τ' but also on the GRD parameter 'k' for a given set of operating conditions. Thus the interpretation of CSD's from continuous crystallizers need to be done with caution while scaling up crystallizers. The RTD of the crystallizer needs to be established and the kinetics of growth rate dispersion need to be determined for the rational design of crystallizers.

CONCLUSIONS

A generalized mathematical model accounting for growth rate dispersion and the residence time distribution for a continuous crystallizer is presented. Expressions are derived for the weight distribution and for the dominant crystal size of the size distribution. The dominant crystal size is affected not only by the RTD characteristics of the crystallizer but also the growth rate dispersion characteristics. Care should be taken while interpreting CSD's from continuous pilot plant crystallizers since nonidealities of the CSD with respect to the MSMPR model may be due to the effects of RTD and GRD and not due to size dependent growth behavior of the system.

ACKNOWLEDGEMENT

The financial support provided by International Minerals and Chemicals Corporation, New Wales Operation is gratefully acknowledged.

NOTATION

a	parameter for the growth rate distribution
CV	coefficient of variation
$E[x]$	expected value of the random variable 'x'
$f_X(x)$	probability density function for the random variable 'x'
g	linear growth rate of a crystal, random variable
$g(x)$	moment generating function
k	parameter for the growth rate distribution
ℓ	characteristic size of a crystal, random variable
ℓ_o	initial size of a crystal, random variable
ℓ_D	dominant crystal size
$m_X(j)$	jth moment about the origin of the probability density function $f_x(x)$
t	residence time of a crystal in a crystallizer
$\omega(\ell)$	weight distribution function
$W(\ell)$	cumulative weight distribution function

Greek Letters

α	parameter for the residence time distribution
β	parameter for the residence time distribution
$\Gamma(n)$	Gamma function
$\Gamma(\alpha,\beta)$	Gamma probability density function with parameters α and β
$I\Gamma(a,k)$	Inverse Gamma probability density function with parameters a and k
$\Psi_X(\theta)$	Laplace transform of the probability density function $f_X(x)$ with respect to the random variable 'x'
Φ	nonideality factors
θ	Laplace variable for size

σ_X^2 variance of the random variable 'x'

τ mean residence time of the crystals in the crystallizer

Subscripts

G growth rate distribution

ideal well mixed continuous crystallizer with no growth rate dispersion

L product crystal size distribution

L_o initial or birth distribution

T residence time distribution

Superscripts

$\bar{}$ mean of the distribution

LITERATURE CITED

Abegg, C. F., J. D. Stevens and M. A. Larson, "Crystal Size Distributions in Continuous Crystallizers when Growth is Size-dependent", AIChEJ, 14(1), 118 (1968).

Blem, K. E. and K. A. Ramanarayanan, "Crystallization Kinetics in the Presence of Birth Size and Growth Rate Dispersions", Paper to be submitted to the AIChE J., 1985.

Garside, J., "Industrial Crystallization from Solution", Chem. Eng. Sci., 40(1), 3 (1985)

Larson, M. A., E. T. White, K. A. Ramanarayanan and K. A. Berglund, "Growth Rate Dispersion in MSMPR Crystallizers", AIChEJ, 31(1), 90 (1985)

Ramanarayanan, K. A., "Growth Rate Dispersion in Batch and Continuous Crystallizers", Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1982.

Ramanarayanan, K. A., K. A. Berglund and M. A. Larson, "Growth Rate Dispersion in Batch Crystallizers", Accepted for Publication in Chemical Engineering Science, 1985.

Ramanarayanan, K. A. and W. K. Howard, "A Physical Interpretation for the Gamma Distribution", Paper submitted to AIChE J., 1985.

Ramanarayanan, K. A. and M. A. Larson, "Statistical-Mathematical Modeling of Continuous and Batch Crystallizers" AIChE Symposium Series, 80 (240), 75 (1984).

Randolph, A. D. and M. A. Larson, "Theory of Particulate Processes", Academic Press, New York, 1971.

TABLE 1 Statistical Background Material

Probability density function $f_X(x)$ is defined such that if 'x' is a random variable, the probability that $x \in (x, x + dx) = f_X(x)dx$.

Expected value of x^j is defined as,

$$E[x^j] = \int_{-\infty}^{\infty} x^j f_X(x)dx = M_X(j)$$

Note that the $E[x^j]$ is also the jth moment of the probability distribution about the origin, $M_X(j)$.

In crystallization, the random variable 'x' is generally the particle size or the linear growth rate, both of which cannot be negative. Hence,

$$E[x^j] = \int_0^{\infty} x^j f_X(x)dx = M_X(j)$$

where: $M_X(j)$ = jth moment about the origin of $f_X(x)$.

Similarly, the expected value of a function g(x) can be defined as,

$$E[g(x)] = \int_0^{\infty} g(x)f_X(x)dx$$

Consider the special case when

$$g(x) = \exp(-\theta x)$$

thus,

$$E[\exp(-\theta x)] = \int_0^{\infty} \exp(-\theta x)f_X(x)dx = \psi_X(\theta)$$

$\psi_X(\theta)$ is the Laplace Transform of the probability density function, f(x) and 'θ' is the Laplace variable for the random variable 'x'.

TABLE 2 Properties of the Gamma Residence Time Distribution

Form : $$f_T(t) = \frac{1}{\beta^{\alpha}\ \Gamma(\alpha)}\ t^{\alpha-1}\ \exp\ (\ -\ t/\beta\ )$$

$\alpha > 0,\ \beta > 0$

---

1 $$\int_0^{\infty} f_T(t) = 1$$

2 $f_T(t=0) = 0$

3 Mean Residence Time, $\tau = \alpha\beta$

4 Variance, $\sigma_T^2 = \alpha\ \beta^2$

5 $(CV)_T = (\alpha)^{-\ 0.5}$

6 The j th moment of $f_T(t)$ about the origin :

$$M_T(j) = \frac{\beta^j\ \Gamma\ (\ \alpha + j\ )}{\Gamma\ (\ \alpha\ )}$$

7 $$\Psi_T\ (\ \theta\ ) = \frac{1}{(\ \beta\ \theta + 1\ )^{\alpha}}$$

where θ is the Laplace Transform variable for 't'.

TABLE 3 Properties of the Inverse Gamma Growth Rate Distribution

---

Form: $$f_G(g) = \frac{a^{k-1}}{\Gamma(k-1)} g^{-k} \exp\left(\frac{-a}{g}\right)$$

$a > 0, k > 3$

---

1 $$\int_0^\infty f_G(g)\, dg = 1$$

2 $f_G(g = 0) = 0$

3 Mean Growth Rate, $\bar{g} = \frac{a}{k-2}$

4 Variance, $\sigma_G^2 = \frac{a^2}{(k-2)^2 (k-3)}$

5 $(CV)_G = \frac{1}{k-3}$

6 The j th moment about the origin is:

$$M_G(j) = a^j \frac{\Gamma(k-1-j)}{\Gamma(k-1)}$$

TABLE 4 Properties of the Crystal Size Distribution from a Continuous Crystallizer for which the Residence Time Distribution is $\Gamma(\alpha,\beta)$ and the Growth Rate Distribution is $I\Gamma(a,k)$

Form: $$f_L(\ell) = (a\beta)^{k-1} \frac{\Gamma(\alpha+k-1)}{\Gamma(\alpha)\ \Gamma(k-1)} \quad \frac{\ell^{\alpha-1}}{(\ell + a\beta)^{\alpha+k-1}}$$

$$a > 0,\ K > 3$$

---

1 $$\int_0^\infty f_L(\ell)\, d\ell = 1$$

2 $$f_L(\ell = 0) = 0$$

3 Mean Length, $$\bar{\ell} = \frac{a\ \alpha\ \beta}{k - 2} = \bar{g}\ \tau$$

4 Variance, $$\sigma_L^2 = (g\ \tau)^2 \left[\frac{\alpha + 1}{\alpha} \frac{k - 2}{k - 3} - 1 \right]$$

5 $$(CV)_L = \left[\frac{\alpha + 1}{\alpha} \frac{k - 2}{k - 3} - 1 \right]^{0.5}$$

6 The j th moment of the CSD about the origin is,

$$M_L(j) = = (a\beta)^j \frac{\Gamma(\alpha+j)\ \Gamma(k-j-1)}{\Gamma(\alpha)\ \Gamma(k-1)}$$

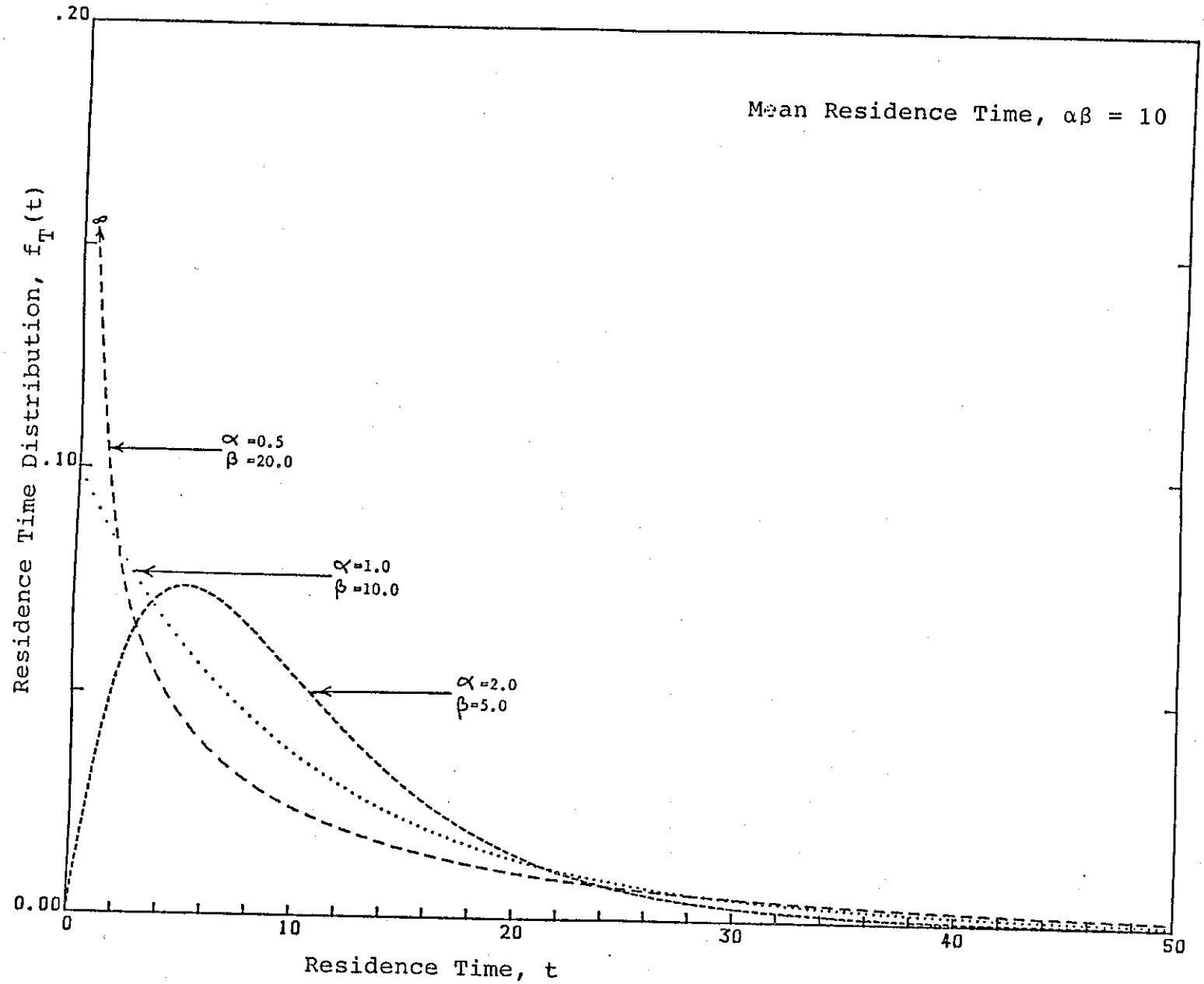

Figure 1: Typical RTD for small deviations from complete backmixing ($\alpha \cong 1$)

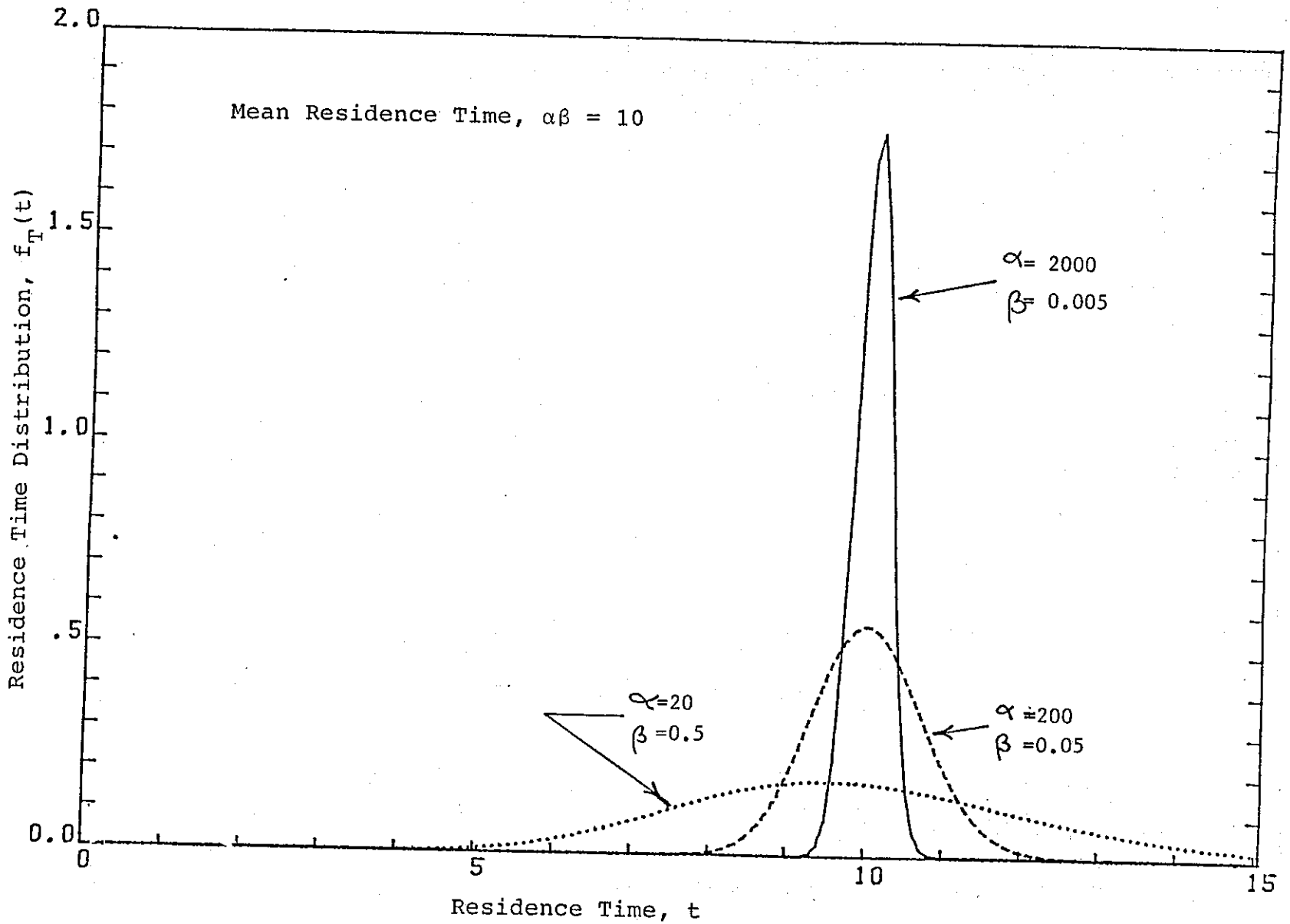

Figure 2: Typical RTD for large deviations from complete backmixing ($\alpha >> 1$)

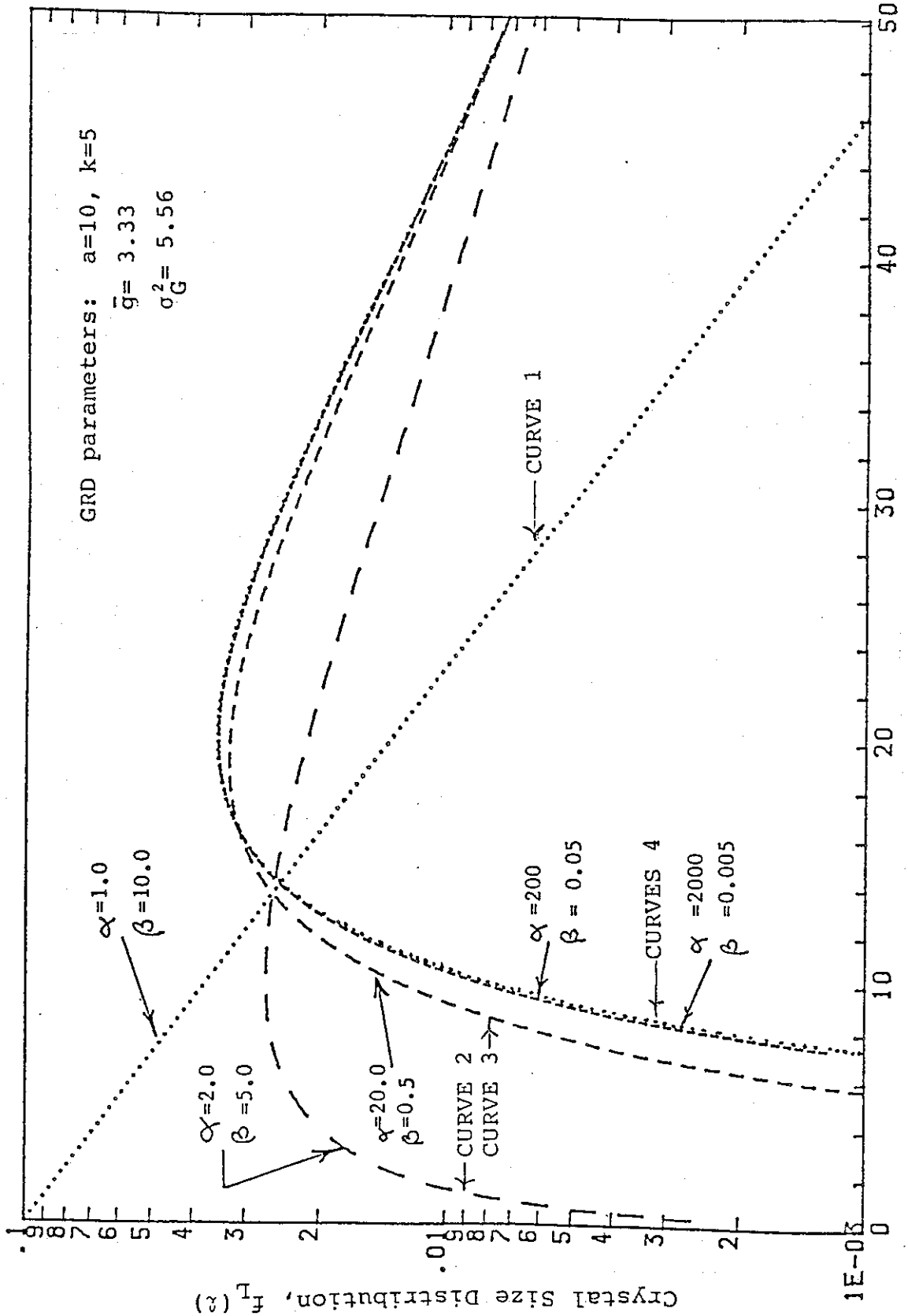

Figure 3: CSD's from continuous crystallizer for large deviations from complete backmixing ($\alpha>1$)

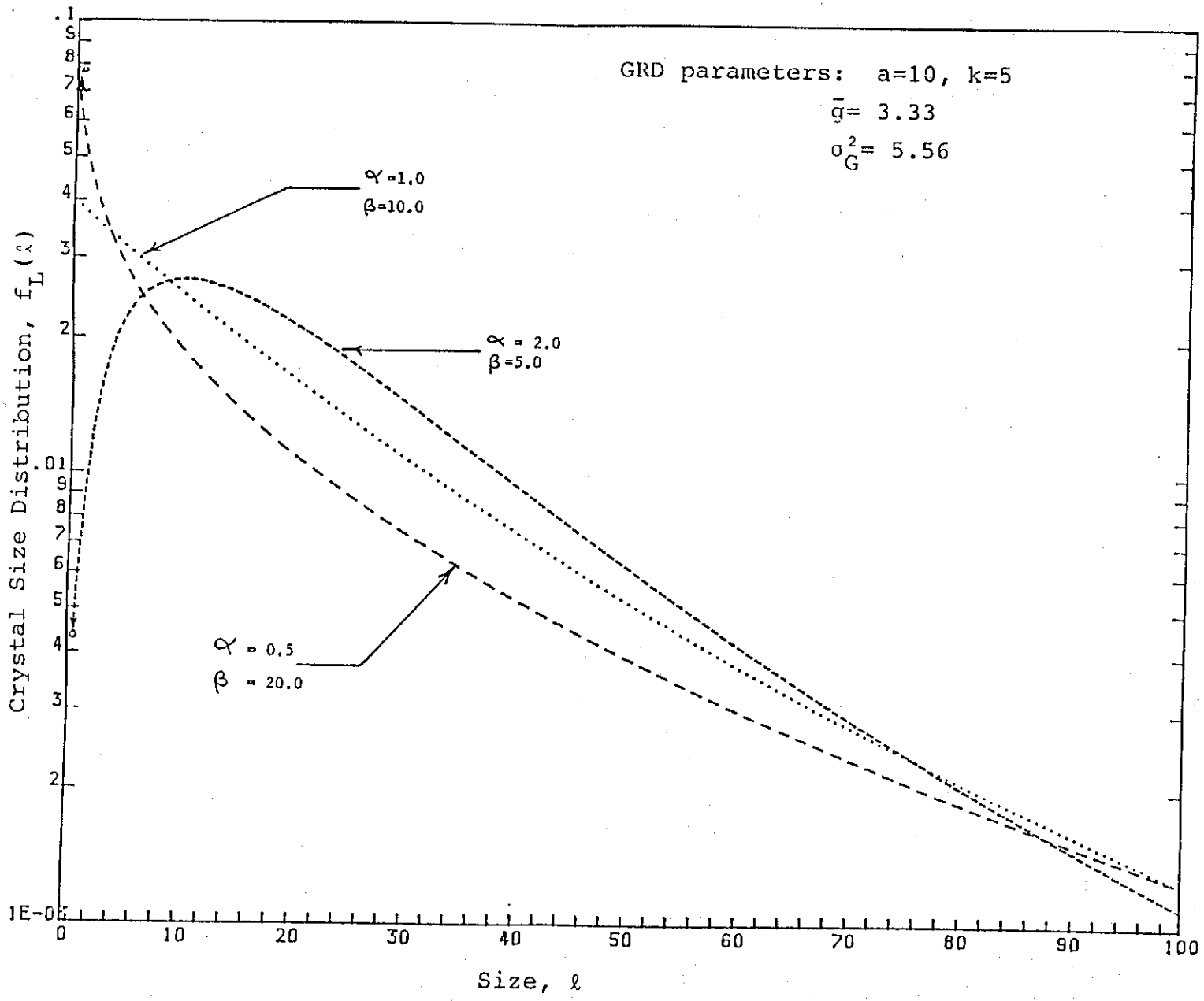

Figure 4: CSD's from continuous crystallizer for small deviations from complete backmixing ($\alpha \cong 1$)