Nucleation, Growth, and Aggregation Rates from Steady-State Experimental Data

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This note describes a technique by which the product size distribution from a continuous mixed-suspension, mixed-product-removal crystallizer (CMSMPRC) may be calculated when simultaneous nucleation, growth, and aggregation take place. In such systems the size distribution is most conveniently represented by a population density function, $n(L)$; the nucleation rates are given by B_0, and the linear rate of growth is denoted G. At steady state these variables are related by the population balance, Eq 1.

$$G\frac{dn}{dL} + \frac{n}{\tau} - B_0\delta(L) - B + D = 0 \qquad (1)$$

The birth and death terms included in this equation are given by

$$B(L) = \frac{L^2}{2}\int_0^L \cdot \frac{\beta[(L^3-\lambda^3)^{1/3},\lambda]\, n\,[(L^3-\lambda^3)^{1/3}]\, n\,(\lambda)}{(L^3-\lambda^3)^{2/3}}\, d\lambda \qquad (2)$$

$$D(L) = n(L)\int_0^\infty \beta(L,\lambda)\, n(\lambda)\, d\lambda \qquad (3)$$

The aggregation kernel, β, is a frequency factor containing information about the occurrence of collisions and their success in forming aggregates. In the analysis of the CMSMPRC it is usual, in the absence of better information, to assume that the kernel is independent of particle size. Under these circumstances, Eqs. 2 and 3 become

$$B(L) = \frac{\beta_0 L^2}{2}\int_0^L \frac{n\,[(L^3-\lambda^3)^{1/3}]\, n(\lambda)}{(L^3-\lambda^3)^{2/3}}\, d\lambda \qquad (4)$$

$$D(L) = \beta_0\, n(L) m_0 \qquad (5)$$

In this last expression, m_0 is the zero moment, defined by

$$m_0 = \int_0^\infty n(L)\, dL$$

In general, the jth moment is defined by Eq 6.

$$m_j = \int_0^\infty L^j n(L)\, dL \qquad (6)$$

For cases in which $j/3$ is an integer, the technique of Randolph and Larson (1988) may be used to transform the population balance into a series of algebraic equations in terms of the moments. The two results of value here are

$$\frac{\beta_0}{2} m_0^2 + \frac{m_0}{\tau} - B_0 = 0 \qquad (7)$$

$$3\,G\,m_2 - \frac{m_3}{\tau} = 0 \qquad (8)$$

In situations where aggregation does not occur, these last two equations may be used to determine the nucleation and growth rates, B_0 and G, from experimentally determined size distributions; the moments are determined readily from the distribution. If aggregation occurs, an additional equation is required. In what follows in this note, just such an additional equation is developed.

Nondimensionalizing the Population Balance

In nondimensionalizing Eq. 1, appropriate characteristic particle size and crystal number must be selected. If these are, respectively, $G\tau$ and $B_0\tau$, the following dimensionless quantities

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may be defined:

$$x = \frac{L}{G\tau}; \quad f(x) = \frac{G}{B_0} n(L)$$

In terms of these variables Eq. 1 becomes

$$\frac{df}{dx} + f - \delta(x) - b + d = 0 \tag{9}$$

where

$$b(x) = K\frac{x^2}{2}\int_0^x \frac{f[(x^3 - \epsilon^3)^{1/3}]f(\epsilon)}{(x^3 - \epsilon^3)^{2/3}}\,d\epsilon \tag{10}$$

$$d(x) = Kf(x)\int_0^\infty f(\epsilon)\,d\epsilon = Kf(x)\tilde{m}_0 \tag{11}$$

and K is a new aggregation parameter,

$$K = B_0\beta_0\tau^2 \tag{12}$$

The dimensionless moments are defined as

$$\tilde{m}_j = \int_0^\infty x^j f(x)\,dx$$
$$= \frac{1}{(G\tau)^j}\frac{1}{B_0\tau}m_j \tag{13}$$

From the form of Eq. 9 it is apparent that the dimensionless population density is a function only of size, x, and the aggregation parameter, K.

By combining the definition of the aggregation parameter with Eq. 7, the zero moment may be related directly to K.

$$m_0 = \frac{\sqrt{1 + 2K} - 1}{\beta_0\tau} \tag{14}$$

So,

$$\tilde{m}_0 = \frac{\sqrt{1 + 2K} - 1}{K} \tag{15}$$

One might proceed now to investigate solutions of the population balance in terms of the aggregation parameter, K. It is more convenient, however, to work in terms of the index of aggregation defined by Hounslow (1990),

$$I_{Agg} = 1 - \frac{m_0}{B_0\tau} \tag{16}$$

The index of aggregation has the advantage that it is bounded on the domain (0, 1), with $I_{Agg} = 0$ corresponding to no aggregation and $I_{Agg} = 1$ indicating complete aggregation of every crystal formed. Further, the index of aggregation is independent of the model of aggregation chosen: it is a true characteristic of a system.

Combining the definition of I_{Agg}, Eq. 16 with Eq. 14, the index of aggregation becomes

$$I_{Agg} = \frac{K + 1 - \sqrt{1 + 2K}}{K} \tag{17}$$

It follows then, that the dimensionless population density, f, is a function of size and the index of aggregation.

General Solution to the Population Balance

The population balance, Eq. 1, was solved using the technique of Hounslow (1990). Figures 1 and 2 present the solutions obtained in dimensionless form, for various values of I_{Agg}. In both figures the results are displayed as cumulative number oversize (COS). In Figure 1 the results are normalized to give COS = 1 at $x = 0$. The result for $I_{Agg} = 0$ is a straight line, corresponding to the well-known exponential solution for nucleation and growth. In Figure 2, the results are normalized by the characteristic number used above, $B_0\tau$. The results shown in this figure might be achieved by a CMSMPRC operating with constant nucleation and growth rates but varying values of the aggregation kernel. Figure 2 clearly shows the reduction in total numbers associated with increasing the aggregation rate. It is also apparent that the limiting slope, as size tends to zero, is constant. It must be concluded then that $n(0) = B_0/G$ irrespective of the value of I_{Agg}. Such a result follows directly from Eq. 1, with $n(0^-) = 0$ as the boundary condition.

It is also apparent from Figure 2 that the mean size and standard deviation of the size distribution vary with the index of aggregation. It seems likely that the coefficient of variation also

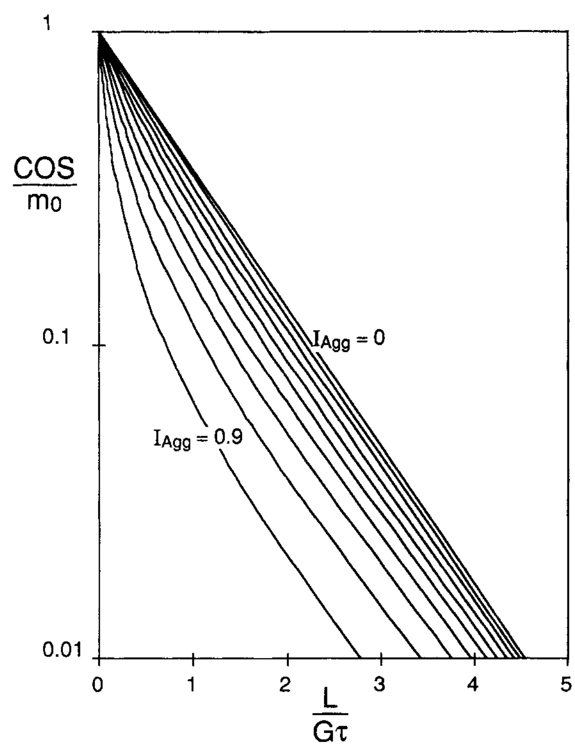

Figure 1. Dimensionless size distribution with index of aggregation varying from 0 to 0.9 in increments of 0.1.

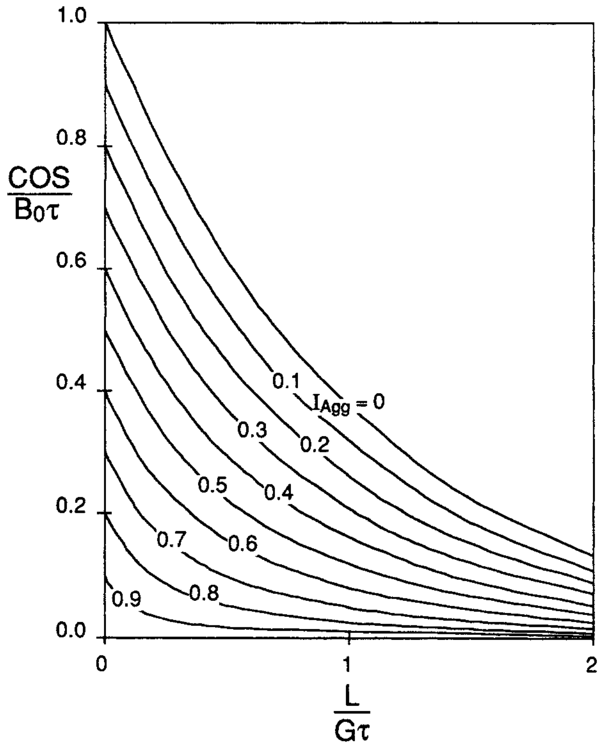

Figure 2. Variation in size distribution with aggregation rate for constant nucleation and growth rates.

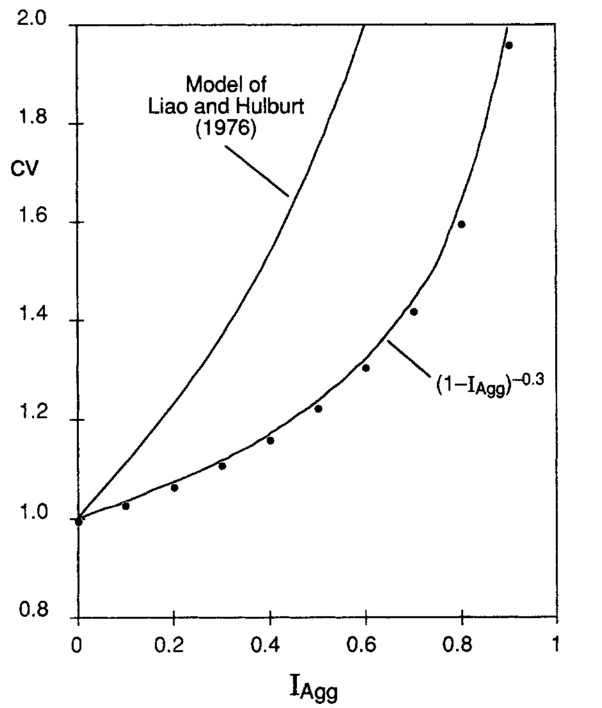

Figure 3. Effect of extent of aggregation on coefficient of variation.

● Solution to Eq. 9

varies with I_{Agg}.

$$cv = \sigma/\overline{L} = \left(\frac{\tilde{m}_0\,\tilde{m}_2}{\tilde{m}_1^2} - 1\right)^{1/2} \tag{18}$$

Now, since the normalized moments are functions only of K, or I_{Agg}, it follows that the coefficient of variation is also a function only of K.

The dependence of cv on I_{Agg} may be determined from the size distributions displayed in Figure 2. In Figure 3, cv is plotted against I_{Agg}; also shown is an empirical line of good fit,

$$cv = (1 - I_{Agg})^{-0.3} \tag{19}$$

The relationship displayed in Figure 3, or as described by Eq. 19, is the additional equation referred to in the previous section.

Extracting the Rates

The procedure to be adopted in determining the three rate parameters, B_0, G, and β_0, is a simple one. Having first determined the moments of the experimental size distribution, one proceeds as follows. From Eq. 8

$$G = \frac{m_3}{3\,\tau\,m_2} \tag{20}$$

By inverting Eqs. 19 and 17 one obtains

$$I_{Agg} = 1 - cv^{-10/3} \tag{21}$$

$$K = \frac{2\,I_{Agg}}{I_{Agg}^2 - 2\,I_{Agg} + 1} \tag{22}$$

From Eq. 14, the aggregation kernel may be isolated.

$$\beta_0 = \frac{\sqrt{1 + 2K} - 1}{m_0 \tau} \tag{23}$$

Finally, from the definition of the aggregation parameter, Eq. 12, the nucleation rate may be determined.

$$B_0 = \frac{K}{\beta_0\,\tau^2} \tag{24}$$

As an example, consider the results of Tavare et al. (1985). For their data the moments are:

$m_0 = 5.4 \times 10^7$
$m_1 = 2.02 \times 10^9$
$m_2 = 3.05 \times 10^{11}$
$m_3 = 8.91 \times 10^{13}$

From Eqs. 20, 18, 21, and 22

$G = 389\ \mu$m/h
$cv = 1.75$
$I_{Agg} = 0.84$,
$K = 69$

By means of Eqs. 23 and 24 $\beta_0 = 801 \times 10^{-9}$ L/h and $B_0 = 1.38 \times 10^9$ 1/h · L. In Figure 4 the experimental data are compared with the dimensionless solution to the population balance. The data lie predominantly between the curves corresponding to I_{Agg} values of 0.8 and 0.9, a result consistent with the calculated value of $I_{Agg} = 0.84$.

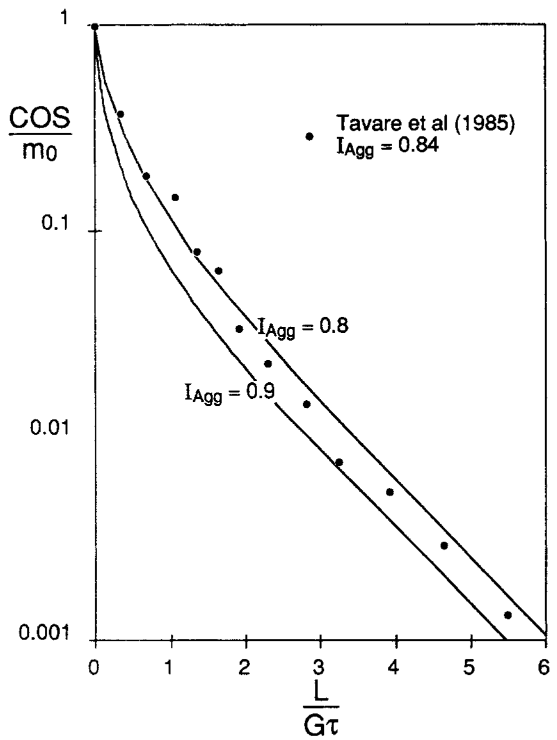

Figure 4. Comparison of experimental and estimated particle size distributions.

The rate parameters calculated above are almost identical to those produced by Hounslow (1990) using least squared error parameter estimation: $B_0 = 1.67 \times 10^9$ 1/h · L, $G = 388$ μm/h, and $\beta_0 = 800 \times 10^{-9}$ L/h.

It is very unlikely that these two sets of results are significantly different; while the higher moments can be calculated quite easily from experimental data, there is significant uncertainty in the value for m_0 in particular. An assessment of how this uncertainty propagates through the calculated results may be deduced from the sensitivity matrix. If a dependent variable, y, depends on an independent variable x, the sensitivity of y to x is

$$S_{x,y} = \frac{x}{y}\frac{\partial y}{\partial x} \tag{25}$$

If there is a small uncertainty in x, δx, the uncertainty in y is

$$\delta y = S_{x,y}\, \delta x \tag{26}$$

For the solution given above, the values of sensitivity displayed in Table 1 were deduced. From this table it may be deduced that a 10% uncertainty in m_0 will lead to a 32% uncertainty in B_0 and a 16% uncertainty in β_0. Further, both of these variables are even more sensitive to uncertainty in the first moment, although the severity of this effect is diminished by the lower value of that moment's uncertainty.

Table 1. Sensitivity Matrix

x/y	B_0	G	β_0
m_0	3.2	0	1.6
m_1	−4.4	0	−5.3
m_2	2.2	−1	2.6
m_3	0	1	0

Approximate Model of Liao and Hulburt

The experimental data discussed above, those of Tavare et al., were analyzed by those authors using the approximate method of Liao and Hulburt (1976), yielding much lower values for the nucleation and growth rates: $B_0 = 0.65 \times 10^9$ 1/h · L and $G = 131$ μm/h, both of which are low by a factor of about 3. In a previous paper, Hounslow (1990) advanced qualitative arguments suggesting that nucleation and growth rates deduced from the approximate model of Liao and Hulburt are substantially in error. By virtue of the material presented in this paper, it is now possible to quantify that error.

With their model Liao and Hulbert seek to remove the complexity associated with the nonlinear components of the birth and death rates, consequently they replace Eqs. 4 and 5 by

$$B(L) = \frac{A}{2}\int_0^L n(L-\lambda)\, n(\lambda)\, d\lambda \tag{27}$$

$$D(L) = A\, n(L)\, m_0 \tag{28}$$

In these equations A is an aggregation parameter, similar in significance to the aggregation kernel of the current work. The significance of these replacements is that they change aggregation from being a volume-conserving phenomenon to one that conserves crystal length.

It can be shown that the length-conserving population balance implies an index of aggregation and a coefficient of variation given by Eqs. 29 and 30.

$$I_{Agg} = 1 - \frac{\sqrt{1 - 2AB_0\tau^2} - 1}{AB_0\tau^2} \tag{29}$$

$$cv = \sqrt[4]{2AB_0\tau^2 + 1} \tag{30}$$

from which it is possible to deduce that

$$I_{Agg} = \frac{cv^2 - 1}{cv^2 + 1} \tag{31}$$

This last result is shown as the upper result in Figure 3.

The errors inevitably associated with the approximate model of Liao and Hulburt are now apparent. A particle size distribution contains a large amount of information, it may, however, be characterized by the total number of particles, m_0, the value of the density function at zero size, $n(0) = B_0/G$, and an appropriate shape factor, such as the coefficient of variation, cv. With this in mind we may reflect on the efficacy of the approximate model.

Consider the case where values for A, B_0, and G are to be selected to produce a size distribution with specified characteristics, for either analysis or design purposes. A value of cv may be used to deduce a value of I_{Agg}, which in turn implies a value for the nucleation rate, B_0. If the model of Liao and Hulburt is used, Figure 3 demonstrates that I_{Agg} will be substantially underesti-

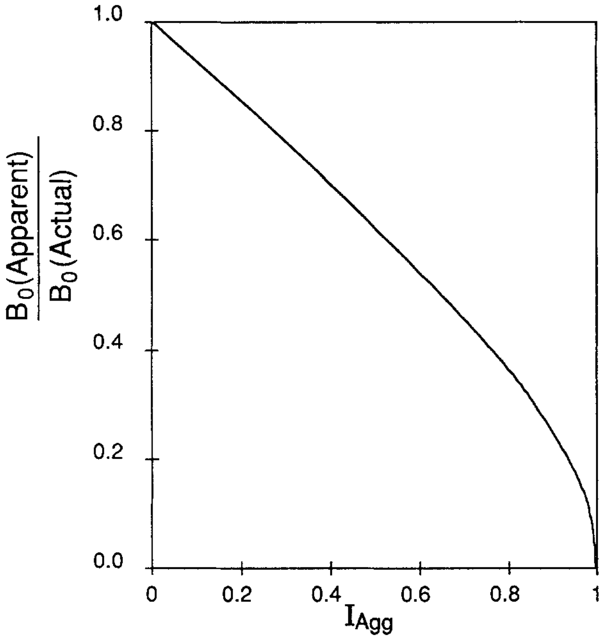

Figure 5. Error in calculated nucleation rate if the model of Liao and Hulburt (1976) is used.

mated. Indeed, Figure 5 shows that values for B_0 produced by this model are low by more than a factor of two, for values of I_{Agg} greater than 0.65. Now, in order to produce the desired value of the density function in zero size, B_0/G must be kept in correct proportion. Consequently, if B_0 is low by a factor of two or more, so is the growth rate, G.

Acknowledgment

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Notation

A = aggregation parameter in model of Liao and Hulburt (1976)
b = dimensionless birth rate
B = birth rate, $1/\mu m \cdot L \cdot h$
B_0 = nucleation rate, $1/L \cdot h$
cv = coefficient of variation
COS = cumulative oversize, $1/L$
d = dimensionless death rate
D = death rate $1/\mu m \cdot L \cdot h$
f = normalized population density function
G = linear rate of growth, $\mu m/h$
I_{Agg} = index of aggregation
K = aggregation parameter
L = particle size, μm
$\bar{L}$ = mean size, μm
m_j = jth moment, $\mu m^j/L$
n = population density function, $1/\mu m \cdot L$

Greek letters

β = coalescence kernel, L/h
β_0 = size-independent portion of coalescence kernel, L/h
δ = Dirac delta function
ϵ = dimensionless variable of integration
λ = variable of integration (length)
σ = standard deviation
τ = draw-down time

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