$$Nu_{x,N} = 2\left[\frac{1}{2}\left(\frac{3}{10}\right)^{\frac{1}{n}} f(n)\right]^{\frac{n}{3n+1}} \left[\frac{2n+1}{3n+1}\right]^{\frac{n}{3n+1}} Gr_x^{\frac{1}{2(n+1)}} Pr_{x,N}^{\frac{n}{3n+1}} \quad (21)$$

for pure free convection heat transfer to power law fluids as given by Shenoy and Ulbrecht (1979).

Thus, it can be easily seen that the correlating equation for mixed convection flow of Newtonian fluids suggested by Churchill (1977) and later established by Ruckenstein (1978), using the approximate interpolation procedure, holds good even for non-Newtonian power law fluids.

The resulting equation is again

$$Nu_{x,M}^3 = Nu_{x,F}^3 + Nu_{x,N}^3 \quad (22)$$

except for the new definitions of $Nu_{x,F}$ and $Nu_{x,N}$ as given by Equation (20) and (21) respectively.

Finally, it is worth mentioning that, as an assumption of large Prandtl numbers was necessary to obtain the present solution, it would be natural to expect the results from the above equations to be more correct for non-Newtonian fluids (which generally have higher consistencies, implying larger Prandtl numbers) then Newtonian fluids. It is unfortunate that due to lack of experimental data in the literature on combined laminar forced and free convection heat transfer to power law fluids past an isothermal vertical flat plate, a comparison cannot be made to validate the propriety of the above equations.

NOTATION

a = function of n in Equation (16)
a_1 = function of n in Equation (15a)
a_2 = function of n in Equation (15b)
A = constant in Equation (1)
u_1 = velocity component for forced convection in the direction along the plate
u_2 = velocity component for free convection in the direction along the plate
U_∞ = free stream velocity for forced convection
v = velocity component for mixed convection in the direction normal to the plate
v_1 = velocity component for forced convection in the direction normal to the plate
v_2 = velocity component for free convection in the direction normal to the plate
x = distance along the plate from the leading edge
y = distance normal to the plate

Greek Letters

α = thermal diffusivity of the fluid
β = expansion coefficient of the fluid
δ_T = thermal boundary layer thickness
ρ = density of the fluid

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Stability of the High Yield MSMPR Crystallizer with Size-Dependent Growth Rate

T. ISHII and ALAN D. RANDOLPH

Department of Chemical Engineering
University of Arizona
Tucson, Arizona 85721

Cycling behavior of well-stirred isothermal crystallizers occurs in both laboratory-scale and commercial plants, and has been studied as summarized by Randolph and Larson (1971 Chap. 5) and in a recent review paper (Randolph 1977).

The high yield, mixed suspension, mixed product removal (MSMPR) crystallizer has the well-known stability criterion $d(\log B^0)/d(\log G) < 21$. This idealized crystallizer serves as a reference case to judge stability in other configurations and/or systems. Sherwin, Shinnar and Katz (1969), and Randolph, Beer and Keener (1973) investigated the stability limits of mixed suspension classified product removal (MSCPR) crystallizers. They found the stable region is significantly reduced, compared with the MSMPR case. Size-dependent growth rate affects CSD in a manner qualitatively the same as size-dependent product removal; both result in varying slopes on a semi-log population density plot, depending on growth and/or removal rate at that size. Thus the question naturally arises, "Does size-dependent growth rate also destabilize CSD?"

The limiting case of such size-dependent growth rates has been studied. Sherwin, Shinnar and Katz (1967) predicted that increasing growth rate with increasing size raises the system stability limits. Their model assumed that growth rate was linearly proportional to the crystal size. Anshus and Ruckenstein (1973) observed that the CSD stability region narrows when the growth rate is mass transfer controlling, that is, size-dependent and inversely proportional to a power of the size (below the

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Ishii is on sabbatical leave from Department of Chemical Engineering, Yokohama National University, Ohka, Minami-ku, Yokohama, Japan 232. Address correspondence to A. D. Randolph.

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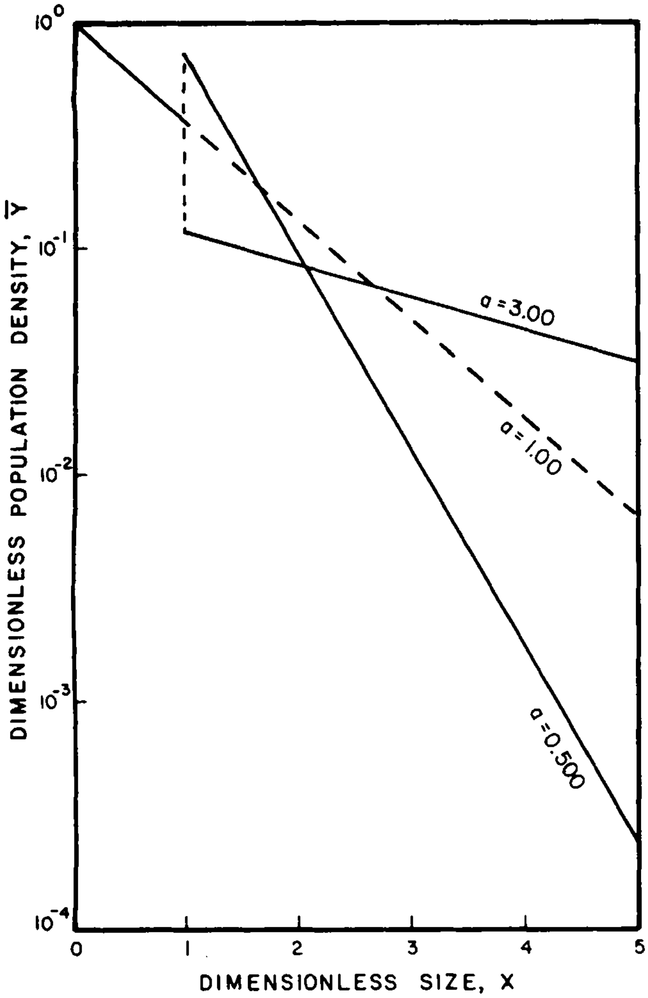

Figure 1. Dimensionless CSD for assumed growth rate model.

critical size) and size-independent for larger sizes (greater than the critical size).

Our purpose in this note is to establish the MSMPR crystallizer stability limits of Class II (high-yield) systems, having different growth rates below and beyond a critical size. The technique consists of linearizing the system equations followed by a formal spectral density analysis. The work closely follows that of Randolph, Beer and Keener (1973). Consult their work for mathematical details of the spectral analysis. The summary of system equations is

Population Balance

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial L}(Gn) + \frac{n}{\tau} = 0 \qquad (1)$$

Mass Balance Constraint

$$G^0 = \frac{K}{\int_0^\infty nL^2 d1} \qquad (2)$$

Growth Rate

$$G = G^0 g(L) \text{ where } g(L) = \begin{cases} 1 & L \leqq L_1 \\ a & L > L_1 \end{cases} \qquad (3)$$

Boundary Condition

$$n_0 = n(0, t) = k_N G^{i-1} \qquad (4)$$

These equations are rearranged into dimensionless form, using the following dimensionless variables.

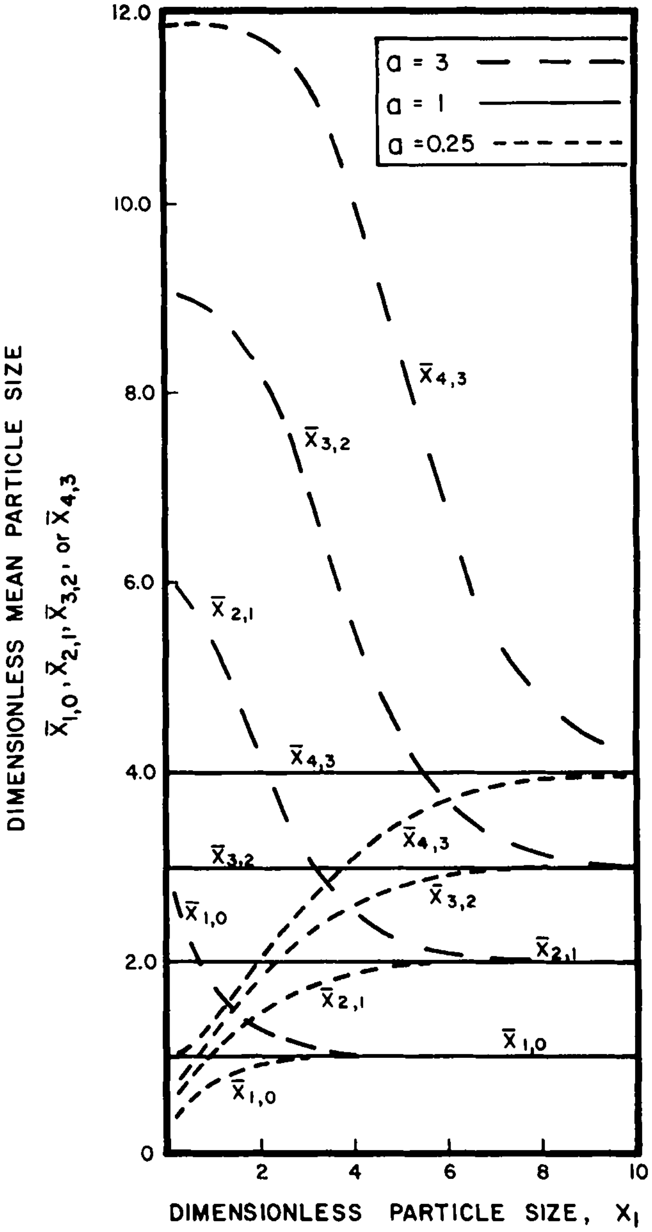

Figure 2. Dimensionless mean sizes for size-dependent model.

$$\theta = \frac{t}{\tau},\ x = \frac{L}{G_0^0 \tau},\ y = \frac{n}{n^0},\ \phi = \frac{G^0}{G_0^0},\ f_j = \frac{\int_0^\infty x^j y\,dx}{\int_0^\infty x^j \bar{y}\,dx}$$

where $(\bar{\ })$ and $(_0)$ represent the steady state and initial values. Thus, the dimensionless set becomes

$$\frac{\partial y}{\partial \theta} + \phi \frac{\partial (gy)}{\partial x} + y = 0 \qquad (5)$$

$$\phi = \frac{G^0}{G_0^0} = \frac{\int_0^\infty \bar{y} x^2 dx}{\int_0^\infty y x^2 dx} = \frac{1}{f_2} \qquad (6)$$

$$y(0, \theta) = \phi^{i-1} \qquad (7)$$

The dimensionless equations are then linearized by substitution of the perturbation variables $y = \bar{y} + y'$ and $f_2 = 1 + f_2'$.

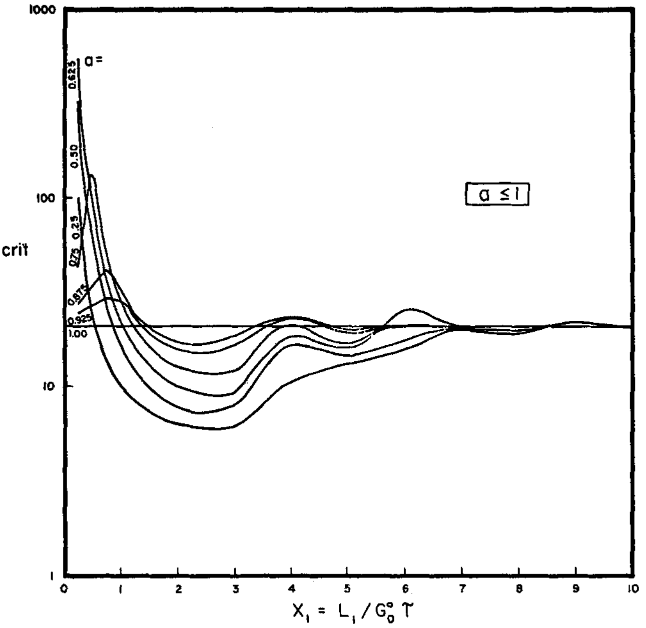

Figure 3. Stability regime for growth rate parameter less than unity.

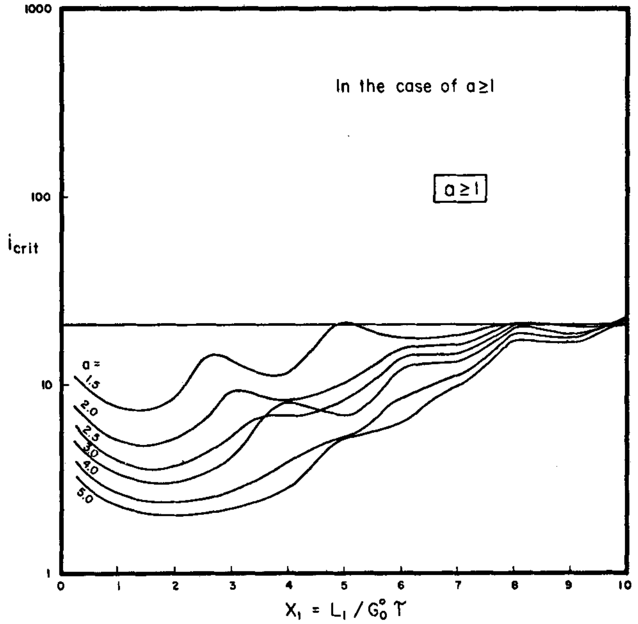

Figure 4. Stability regime for growth rate parameter greater than unity.

The dimensionless linearized perturbation equations describing size-dependent growth rate in a Class II MSMPR crystallizer are summarized as

$$\left.\begin{aligned} \frac{\partial y'}{\partial \theta} + \frac{\partial (gy')}{\partial x} - \frac{\partial (g\bar{y})}{\partial x} f_2' + y' = 0 \\ y'(\theta, 0) = (1-i)f_2' \\ y'(0, x) = 0 \end{aligned}\right\} \qquad (8)$$

Details of the spectral density stability analysis of this equation set are not shown in this note (see Randolph, Beer and Keener 1973).

DISCUSSION OF RESULTS

Figure 1 plots the semi-log population density plot for this idealized size-dependent growth model for the cases "a" less than, greater, or equal to unity. Figure 2 plots the dimensionless mean size $\bar{x}_{1,0}$, $\bar{x}_{2,1}$, $\bar{x}_{3,2}$ and $\bar{x}_{4,3}$ as a function of the dimensionless growth rate model parameters x_1 and a.

Figure 3 plots values of the critical nucleation sensitivity parameter, $i = d(\log B^0)/d(\log G^0)$, as a function of dimensionless critical size x_1 at which an assumed sudden change in growth rate occurs, for values of $a \leqq 1$. Note that CSD is stabilized if the growth rate change occurs at sizes smaller than ca. $G_0^0\tau$. Thus, the phenomenon of slow-growing fines observed in many systems using electronic particle counters (e.g. Randolph and Sikdar 1976, Garside and Jancic 1976) would be predicted to stabilize the system. If, however, the growth rate change (decrease) occurs at about the dominant (mass) particle size, $x_1 \simeq$ 2-3, then significant CSD destabilization is predicted. This latter result is consistent with the CSD destabilizing effects of product classification in the region of the mean (mass) particle size. Accelerated product removal and decreased growth rate produce similar effects on the steady state form of CSD. Finally, for values of $x_1 \to \infty$ the stability response asymptotes to the well-known value of $i_{crit} = 21$.

Figure 4 presents the stability response for the case $a \geq 1$, that is, increased growth rate at increased particle size. This situation holds for several crystallization systems, e.g. for alum or K_2SO_4. For this case, the stability region is severely restricted for example, ($i_{crit} \simeq$ 2-7) when such growth rate increases occur around the population or area mean size ($x_1 \simeq$ 1.5-3.0, See Figs. 4 and 2). Again, $i_{crit} \to 21$ as $x_1 \to \infty$.

CONCLUDING REMARKS

These calculations reveal yet another situation in which the stability criterion is less than the restrictive stability criterion of the Class II MSMPR Crystallizer. The physical situations which have previously been studied and which permit CSD oscillation within a more reasonable regime (i.e. lower values of the stability parameter i_{crit}) are summarized below.

For Class I behavior with per-pass yields in the order of 50%, the mass balance is highly coupled with the population balance and the system equations are 4'th order ODE's rather than 3'rd order. Such higher order systems are predictably more unstable.

For Miers-type nucleation kinetics, $i_{crit} = i(C - C_s)/(C - C_m)$ and can easily exceed the critical value of 21 as the concentration level approaches the metastable concentration, i.e. $C \to C_m$. Long retention times lower the steady state concentration and can bring such systems into a cycling mode.

In the case of size-dependent product removal, when accelerated removal occurs at a size in the region of the mass-average (product) size, significant destabilization of CSD is predicted. This case has received extensive theoretical attention and is likely the cause for sustained CSD limit cycles observed in some large-scale industrial crystallizers, e.g. KCl and $(NH_4)_2SO_4$ crystallizers.

All of the above causes of instability were predicted from one form or another of the linearized system equations. The principle of superposition indicates that all of these conditions could combine and make their respective contribution to over-all system instability. Further, such linearized stability analyses only predict the onset of unstable (positive) roots to the system equations. It is quite possible that experimentally observed CSD "limit cycles" could have occurred in regions where the system equations were mathematically stable, but actual responses to upsets were of long-term slowly-damped oscillatory character. It would be virtually impossible to experimentally distinguish such undamped oscillations from true sustained limit cycles.

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NOTATION

a = growth rate parameter
C_m = metastable concentration
C_s = solubility concentration
f_2 = dimensionless normalized second moment
f_2' = dimensionless perturbed normalized second moment
$g(L)$, $g(x)$ = size-dependent growth rate function
G = growth rate
G_0^0 = steady state growth rate
i = nucleation sensitivity parameter
L = crystal size
L_1 = crystal size where growth rate changes
n = population density
n_0 = steady state population density
n^0 = nuclei density
V = crystallizer volume
x = dimensionless crystal size = $L/G^0{}_0\tau$
x_1 = dimensionless crystal size = $L_1/G^0{}_0\tau$
$\bar{x}_{i,j}$ = dimensionless mean size as ratio of i'th and j'th dimensionless moments.
y = dimensionless population density n/n^0
$\bar{y}$ = dimensionless steady state population density
y' = dimensionless perturbed population density

Greek Letters

ϕ = dimensionless growth rate = $G^0/G^0{}_0$
θ = dimensionless time = t/τ
τ = residence time, V/Q

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On the Concentration Dependence of Diffusion Coefficients in Zeolites

D. GELBIN and K. FIEDLER

Central Institute of Physical Chemistry
Academy of Sciences of German Democratic Republic
Berlin, GDR

Ruthven (1976) published thermodynamic and kinetic data on the adsorption of five gases in zeolites over a wide range of temperatures and concentrations. We have described zeolite diffusivities with a model based on the discrete structure of zeolite crystals and a statistic-thermodynamic evaluation of equilibrium measurements (Fiedler and Gelbin 1978). Prof. Ruthven has kindly sent us tables of results for all systems in his paper, which we analyze below.

THE MODEL DESCRIBED

According to statistical thermodynamics, adsorption equilibrium may be calculated as

$$\theta_a = \frac{a}{N_c} = \sum_{i=1}^{m} i\ \theta_i \tag{1}$$

$$\theta_i = \frac{\left(\dfrac{P/P_0}{T/T_0}\right)^i \exp\left[i\ (S_i T - E_i)/RT\right]}{1 + \displaystyle\sum_{j=1}^{m} \left(\dfrac{P/P_0}{T/T_0}\right)^j \exp\left[j\ (S_j T - E_j)/RT\right]} \tag{2}$$

By curve-fitting equilibrium isotherms at several temperatures, the N_c, E_i and S_i may be determined and used to calculate the θ_i. A distribution of cages holding different numbers of molecules at any average condition is commonly observed. We therefore describe molecular transport between cages by the equation

$$\theta_i p_i + \theta_{j-1} \rightleftharpoons \theta_{i-1} + \theta_j p_j \tag{3}$$

Equation (3) states that a mobile molecule jumps from a cage holding i molecules to one holding $j-1$ molecules, leaving a cage holding $i-1$ molecules and one holding j molecules, one of which is mobile. Local equilibrium between mobile and localized molecules is established immediately. The possibility of more than one molecule in a cage being mobile at any instant is neglected.

Using standard methods and straightforward mathematics we derive

$$D_z = \frac{\displaystyle\sum_{i=1}^{m} D_{i,i-1} p_i \theta_i \theta_{i-1} + 2 \sum_{i=2}^{m} \sum_{j=1}^{i-1} D_{i,j-1} p_i \theta_i \theta_{j-1}}{\displaystyle\sum_{i=1}^{m} i\ (i-\theta_a)\ \theta_i} \tag{4}$$

where

$$\frac{\partial \theta_a}{\partial(\mu/RT)} = \sum_{i=1}^{m} i\ (i-\theta_a)\ \theta_i \tag{5}$$
