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NOTATION

X_i = normalized concentration of species i
P = Lk/v
f_i = normalized rate expression for the i^{th} reaction
r = recycle ratio
u = fraction of total catalyst concentration devoted to first catalyst
$u_m(\tau)$ = policy in singular segment
T_i, S_i = parameters in rate expressions
k = rate constant for the first forward reaction
v = linear superficial velocity
Z = reactor coordinate
L = reactor length

Greek Letters

α, β, γ = ratios of rate constants
$\zeta, \eta, \lambda, \mu$ = parameters in rate expressions
ξ_1 = normalized extent variable for i^{th} reaction
ξ_{1F} = ξ_1 at reactor inlet
ξ_{1E} = ξ_1 at reactor exit
τ = normalized reactor coordinate = (Z/L)
τ_1, τ_2 = first and second switching points

Subscripts

M = mono
D = di
T = tri
A = acetate
B = acetyl phosphate

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Magma Density and Dominant Size for Size Dependent Crystal Growth

F. P. O'DELL and R. W. ROUSSEAU

Department of Chemical Engineering
North Carolina State University
Raleigh, North Carolina 27607

The design or control of mixed-suspension mixed-product removal (MSMPR) crystallizers using population balance techniques is dependent on an accurate representation of the crystal size distribution (CSD). As illustrated by Moyers and Randolph (1973), CSD is important not only as a characterization of the output from a crystallization operation, but also in determining the nucleation and growth characteristics within the crystallizer.

Suspension density is a primary variable in correlating nucleation rates, and dominant crystal size is an important characteristic of the crystalline product. The calculation of these quantities when the crystal growth rate is size dependent can be quite difficult. The Abegg-Stevens-Larson (ASL) model (1968) has been used successfully to correlate growth rate with crystal size; a method is herein described for the determination of suspension density and dominant crystal size when the ASL model can be used to describe crystal growth rate.

SIZE INDEPENDENT GROWTH

For an MSMPR crystallizer operating at steady state, Randolph and Larson (1971) show that the general population balance equation reduces to

$$\frac{\partial(nG)}{\partial L} = -\frac{n}{\tau} \tag{1}$$

For size independent growth ($\partial G/\partial L = 0$) Equation (1) may be integrated to give

$$n = n^\circ \exp\left[-L/G\tau\right] \tag{2}$$

where n° is $\lim\limits_{L \to 0} n$, the nuclei population density.

The mass of crystals in a size range dL is

$$dM = \rho k_v L^3 n dL \tag{3}$$

so the suspension density can be calculated as

$$M_T = \rho k_v \int_0^\infty nL^3 dL = 6\rho k_v n^\circ (G\tau)^4 \tag{4}$$

and the mass distribution is given by

$$m(L) = \frac{dM}{dL} = \rho k_v L^3 n^\circ \exp\left[-L/G\tau\right] \tag{5}$$

The maximum of the mass distribution, called the dominant size of the CSD, L_D, can be found by maximizing $m(L)$ from Equation (5), yielding

$$L_D = 3G\tau \tag{6}$$

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SIZE DEPENDENT GROWTH

In many cases, growth is not independent of size. Of the many models proposed for size dependent growth, the ASL model has been particularly successful at correlating growth rates:

$$G = G^\circ\ (1 + \gamma L)^b; \quad b < 1 \tag{7}$$

where G° is $\lim\limits_{L \to 0} G$, the nuclei growth rate, and γ and b are constants. Use of the ASL model in the steady state MSMPR population balance [Equation (1)] yields

$$n = n^\circ\ (1 + \gamma L)^{-b} \exp\left[\frac{1 - (1 + \gamma L)^{1-b}}{G^\circ \tau \gamma (1 - b)}\right] \tag{8}$$

Jancic and Garside (1976) present methods of determining the ASL model parameters from population density data.

For this model, the nucleation rate can be determined as

$$B^\circ = N_T/\tau = \frac{1}{\tau}\int_0^\infty n\,dL = n^\circ G^\circ \tag{9}$$

since at steady state, nucleation rate equals production rate, and the suspension of crystals is removed on the average during one residence time.

The suspension density is not easily obtained when the ASL model is used. After some mathematics, the suspension density reduces to

$$M_T = \frac{3\rho k_v n^\circ G^\circ \tau}{\gamma^3 (1 - b)} \exp\left[\frac{1}{G^\circ \tau \gamma (1 - b)}\right] \int_1^\infty \left(\psi^{\frac{2+b}{1-b}} - 2\psi^{\frac{1+b}{1-b}} + \psi^{\frac{b}{1-b}}\right) \exp\left[-\frac{\psi}{G^\circ \tau \gamma (1 - b)}\right] d\psi \tag{10}$$

where ψ is $(1 + \gamma L)^{1-b}$. The integral is a function of b and $(G^\circ \tau \gamma)$. The suspension density can be calculated by evaluating the integral numerically for specified values of b and $(G^\circ \tau \gamma)$.

The mass distribution is given by

$$m(L) = \rho k_v L^3 n^\circ\ (1 + \gamma L)^{-b} \exp\left[\frac{1 - (1 + \gamma L)^{1-b}}{G^\circ \tau \gamma (1 - b)}\right] \tag{11}$$

Garside and Jancic (1976) show that the dominant crystal size, found by maximizing $m(L)$ from Equation (11), can be determined from

$$L\left[\frac{(1 + \gamma L)^{1-b}}{G^\circ \tau} + \gamma(b - 3)\right] - 3 = 0 \tag{12}$$

This equation can be solved to find L_D by the Newton convergence scheme

$$L_{D,i+1} = L_{D,i} - \frac{F(L_{D,i})}{\left[\dfrac{dF}{dL}\right]_{L_{D,i}}} \tag{13}$$

where $F(L)$ is Equation (12). The dominant particle size size is a function of b, γ, and $(G^\circ \tau)$.

A satisfactory representation of CSD data can often be obtained by letting $\gamma = 1/G^\circ \tau$. This reduces the number of parameters in the ASL model by one. The population density expression of Equation (8) now becomes

$$n = n^\circ \left(1 + \frac{L}{G^\circ \tau}\right)^{-b} \exp\left[\frac{1 - \left(1 + \dfrac{L}{G^\circ \tau}\right)^{1-b}}{1 - b}\right] \tag{14}$$

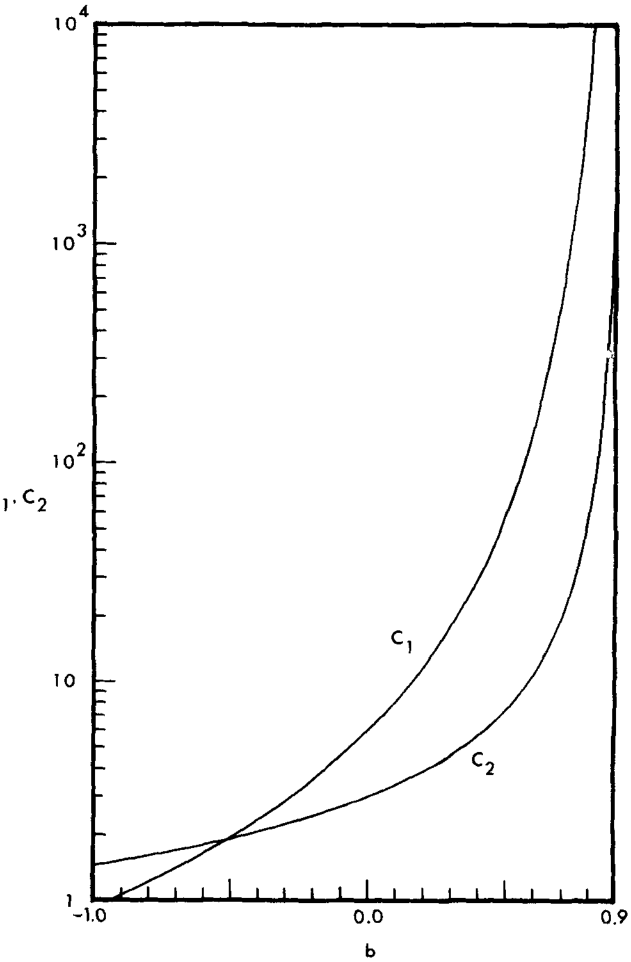

Fig. 1. Constants for Equations (16) and (21).

The suspension density given in Equation (10) now becomes

$$M_T = \frac{3\rho k_v n^\circ (G^\circ \tau)^4}{(1 - b)} \exp\left[\frac{1}{1 - b}\right] \int_1^\infty \left(\psi^{\frac{2+b}{1-b}} - 2\psi^{\frac{1+b}{1-b}} + \psi^{\frac{b}{1-b}}\right) \exp\left[-\frac{\psi}{1 - b}\right] d\psi \tag{15}$$

with ψ being defined as before. The integral is only a function of b. Thus one can write the suspension density as

$$M_T = C_1 \rho k_v n^\circ (G^\circ \tau)^4 \tag{16}$$

where C_1 is only a function of b. Values of C_1 calculated for different b's are presented in Table 1 and are plotted in Figure 1. The integral in Equation (15) was evaluated as the difference of the integrals for ψ from 0 to ∞ and from 0 to 1 using the following equations:

$$\int_0^\infty \psi^p \exp(-a\psi)\, d\psi = \Gamma(p + 1)/a^{p+1} \tag{17}$$

$$\int_0^1 \psi^p \exp(-a\psi)\, d\psi = \left[(p + 2 + a)\exp(-a) + a^2 \int_0^1 \psi^{p+2} \exp(-a\psi)\, d\psi\right] \Big/ [(p + 1)(p + 2)] \tag{18}$$

The integral on the right-hand side of Equation (18) was evaluated numerically. This expanded formula was used because of problems with numerical integration when p was between -1.0 and 1.0. The same method can be used to evaluate the integral in Equation (10) to determine the suspension density when the general ASL model is employed.

The mass distribution is given by

$$m(L) = \rho k_v L^3 n^\circ \left(1 + \frac{L}{G^\circ\tau}\right)^{-b} \exp\left[\frac{1 - \left(1 + \frac{L}{G^\circ\tau}\right)^{1-b}}{1-b}\right] \tag{19}$$

Garside and Jancic (1976) show that the dominant crystal size, found by maximizing $m(L)$ from Equation (19), can be determined from

$$C_2[(1 + C_2)^{1-b} + b - 3] - 3 = 0 \tag{20}$$

where C_2 is $L/G^\circ\tau$. The dominant crystal size can then be written

$$L_D = C_2 G^\circ\tau \tag{21}$$

where C_2 is only a function of b. Values of C_2 vs. b are presented in Table 1 and are plotted in Figure 1. The desired value of C_2 can be found by a Newton convergence scheme

$$C_{2,i+1} = C_{2,i} - \frac{F(C_{2,i})}{\left[\frac{dF}{dC_2}\right]_{C_{2,i}}} \tag{22}$$

where $F(C_2)$ is Equation (20). The convergence scheme had problems for $|b| > 0.5$ unless the first guess was in the neighborhood of the correct value. Use of Table 1 or Figure 1 for interpolation will avoid that problem.

Note that the case of $\gamma = L/G^\circ\tau$ and $b = 0$ corresponds to size-independent growth; the values for C_1 and C_2 are 6 and 3, respectively, as they should be according to Equations (4) and (6).

When γ is taken as $1/G^\circ\tau$, the ratio of two suspension densities reduces to

$$\frac{M_{T2}}{M_{T1}} = \frac{C_{1,2}\, n_2^\circ}{C_{1,1}\, n_1^\circ}\left(\frac{G_2^\circ\, \tau_2}{G_1^\circ\, \tau_1}\right)^4 \tag{23}$$

and the ratio of two dominant crystal sizes becomes

$$\frac{L_{D2}}{L_{D1}} = \frac{C_{2,2}\, G_2^\circ \tau_2}{C_{2,1}\, G_1^\circ \tau_1} \tag{24}$$

where C_1 and C_2 depend on the ASL parameter b. If b does not vary when system conditions are changed, the constants (C_1 and C_2) cancel; Equations (23) and (24) then become identical to those for size independent growth.

Often, nucleation rates are correlated by the power law model

$$B^\circ = k_N\, G^{\circ i} M_T{}^j \tag{25}$$

The nuclei population density can thus be determined as

$$n^\circ = k_N\, G^{\circ i-1}\, M_T{}^j \tag{26}$$

using Equation (9). If the residence time is held constant, the ratio of two dominant crystal sizes can be related to the ratio of suspension densities by manipulation of Equations (23), (24), and (26).

$$\frac{L_{D2}}{L_{D1}} = \left(\frac{C_{1,1}}{C_{1,2}}\right)^{\frac{1}{i+3}} \frac{C_{2,2}}{C_{2,1}}\left(\frac{M_{T2}}{M_{T1}}\right)^{\frac{1-j}{i+3}} \tag{27}$$

The ASL model is often used to describe a CSD when growth is size-dependent. For systems in which a satisfactory representation of CSD is obtained for γ defined as $1/G^\circ\tau$, Table 1 can be used for easy determination of suspension density and dominant crystal size. In cases where γ can not be taken as $1/G^\circ\tau$, the full expressions derived in Equations (10) and (12) must be employed.

Table 1. Constants for Equations (16) and (21)

$$G = G^\circ\left(1 + \frac{L}{G^\circ\tau}\right)^b$$

$$M_T = C_1 \rho k_v n^\circ\ (G^\circ\tau)^4$$

$$L_D = C_2\, G^\circ\tau$$

b	C_1	C_2
0.9	5 841 000	1 681
0.8	6 205	57.00
0.7	539.0	19.03
0.6	140.9	10.75
0.5	57.75	7.431
0.4	29.93	5.688
0.3	17.86	4.622
0.2	11.70	3.904
0.1	8.177	3.389
0.0	6.000	3.000
−0.1	4.569	2.696
−0.2	3.583	2.452
−0.3	2.877	2.252
−0.4	2.356	2.084
−0.5	1.961	1.942
−0.6	1.656	1.819
−0.7	1.414	1.712
−0.8	1.221	1.618
−0.9	1.064	1.535
−1.0	0.9341	1.461
−2.0	0.3438	1.000
−5.0	0.0668	0.5435
−10.0	0.0164	0.3256

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NOTATION

a = constant used in Equations (17) and (18)
b = constant in growth rate expression, Equation (7)
B° = nucleation rate
C_1 = constant in suspension density expression, Equation (16)
C_2 = constant in dominant crystal size expression, Equation (21)
F = function for Newton convergence, Equations (13) and (22)
G = crystal growth rate, dL/dt
G° = nuclei growth rate
i = power of G° in power law model, Equation (25)
j = power on M_T in power law model, Equation (25)
k_v = crystal shape factor
k_N = nucleation constant for power law, Equation (25)
L = crystal size
L_D = dominant crystal size
m = mass distribution
M = mass concentration
M_T = suspension density
n = population density
n° = nuclei population density
N_T = total number of crystals per unit volume
p = constant used in Equations (17) and (18)

Greek Letters

γ = constant in growth rate expression, Equation (7)
Γ = gamma function
ρ = crystal density
ψ = dummy variable in Equations (10) and (15), $(1+\gamma L)^{1-b}$
τ = residence time

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Hydrodynamics of Drop Formation From a Hydrocarbon Film Around a Sphere Placed in a Moving Aqueous Phase

The study of the coalescence of secondary dispersions passing through a granular packing has led to the consideration of drop formation from a hydrocarbon film around a single sphere placed in the flux of an aqueous phase. An analogue mock-up study led to a mathematical model for relating the diameter of the drop to various parameters participating in the phenomenon. A relationship enabling reasonably accurate calculation of the diameter of a drop formed by means of such a sphere placed in a stationary or mobile aqueous phase for a wide range of Reynolds numbers and Bond numbers is proposed.

JEAN P. CALTEAU
YVES AURELLE
and
HENRI L. ROQUES

Department Chimie, I.N.S.A.
Avenue de Rangueil, 31077 Toulouse
Cedex, France

The efficiency of granular packing coalescence is independent of the nature of the packing for low mass velocities. In the case of packings such as oleophilic resin, ion exchange resins with detergents fixed to them by ionic bonds, or a styrene-divinyl benzene copolymer, this efficiency diminishes and becomes zero for mass velocities greater than the critical velocity. For these velocities, the discharge consists of a dispersion with highly uniform particle size. Study of this has shown that it is generated by the packing and is independent of the input dispersion Even if the experimental conditions of dispersion generation could be described in detail, this would not automatically give an insight into the mechanism of dispersion formation. Among the various possible mechanisms, we consider that which corresponds to drop formation from a continuous film of a dispersed phase surrounding the packing elements as provided by the geometry of the arrangement.

The analogue study leads to a relationship of three dimensionless groups (dg/dS, $\gamma_i/gd_s^2\Delta\rho$, $U_f d_s/\nu_f$) which enable a description of this phenomenon to be made.

Under static conditions, with low values for the dispersed phase flow rate, the proposed relationship enables the diameter of the drops formed from a sphere to be calculated to an accuracy of within 7%.

Under dynamic conditions, the relationship for calculating the drop diameter is established within a wide range of Reynolds number and Bond number variation. The level of accuracy is once again very good.

A wide difference is found between calculated and experimental average size distribution of microdrops emitted by a coalescer; this leads to a rejection of this model for the formation of microdrops in the packing. *This result demonstrates that the microdrops do not arise* from the lamination of a continuous film of a dispersed phase flowing around spherical particles. In addition, this result casts some doubt on the existence of a continuous film which surrounds the materials having a residual hydrophilic character. Parallel studies have shown that hydrophobic packings, for which the condition for the formation of a continuous film is optimal, do not lead to the formation of dispersions in the discharge under the same operating conditions.

The coalescence of secondary dispersions by passage through a porous medium has been known for quite some time. Nevertheless, studies of this process have until now been based only on a system approach, without gaining a deeper understanding of the mechanism of the various stages in experiments, that is, interception of

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