Multiplicity in Continuous MSMPR Crystallizers

Part II: Temperature Multiplicity in a Cooling Crystallizer

This paper demonstrates the application of the theory of temperature multiplicity to the continuous mixed-suspension, mixed-product removal (MSMPR) cooling crystallizer as described by the coupled solute and energy balances along with the associated population balance transformed into moment equations. Exact uniqueness and multiplicity criteria are developed. Applications to specific cases together with diagrams depicting the effects of the important variables on the regions of multiplicity and uniqueness are presented.

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SCOPE

Almost all the published studies of crystal size distribution (CSD) dynamics considering, for example, different crystallizer configurations, high- or low-yield systems, and various crystallization kinetic models, are confined to isothermal conditions. In this paper the nonisothermal case is considered. By analogy with the continuous stirred tank reactor (CSTR) in reaction engineering the theory of concentration multiplicity and stability as applied to a simple MSMPR crystallizer was developed in Part I (Tavare and Garside, 1985) of this paper. In this second part the same analogy is extended to develop a theory of temperature multiplicity for a cooling crystallizer by incorporating the energy balance in a macroscopic lumped-parameter model description of an MSMPR crystallizer. The crystallization kinetics are described by power law growth and power law magma-dependent nucleation models incorporating Arrhenius type temperature-dependent rate constants. A linear stability analysis of the dynamic balance equations using small perturbations around the steady state is also presented.

CONCLUSIONS AND SIGNIFICANCE

Temperature multiplicity of a continuous MSMPR cooling crystallizer is determined by the intersections of the dimensionless characteristic heat generation function and the dimensionless heat removal line defined by the slope parameter and intercept on the reduced temperature axis. The kinetic orders, dimensionless activation and heat transfer parameters, and reduced operating temperatures characterize the dimensionless heat generation function, while the slope parameter of the heat removal line depends on the physical parameters, rate coefficients, mean residence time, and feed concentration. The necessary and sufficient conditions for the existence of temperature multiplicity together with the uniqueness criteria are defined in terms of important quantities which characterize the heat generation and heat removal functions. Multiple steady states of temperature are possible over certain ranges of kinetic, physical, and operating parameters, given the proviso of a high-order nucleation rate with respect to magma density. Effects of the important variables on the regions of multiplicity and uniqueness are delineated. The middle of the three possible steady states for temperature is normally unstable, as can be demonstrated by means of simple linear stability analysis of the dynamic balances using a small perturbation around the steady state.

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INTRODUCTION

The problem of crystal size distribution (CSD) dynamics in continuous crystallizers has been analyzed by many researchers (Randolph and Larson, 1965; Sherwin et al., 1967, 1969; Hulbert and Stefango, 1969; Lei et al., 1971; Anshus and Ruckenstein, 1973; Randolph et al., 1973, 1977; Randolph, 1980; Epstein and Sowul, 1980). Crystallizer configurations studied have ranged from the simple MSMPR (mixed-suspension, mixed-product removal) system to more complex units having one or more combinations of process modifications such as fines destruction, clear liquor advance, and product classification; both high- and low-yield systems have been considered. A simple power law growth rate model, with or without a size-dependent term, and a range of nucleation models including simple power law, Miers, Volmer, and magma-dependent power law have been used in these CSD dynamics studies. In general most of the analytical crystallizer stability work has centered around the dynamic population balance over the configuration together with the associated mass balance under isothermal conditions alone. Linear stability analysis has been used to delineate the stability regions of such crystallizer configurations over a range of kinetic and process parameters, but the interaction of the energy content with the dynamic behavior has been ignored.

The subject of reactor stability has been extensively investigated and the chemical engineering literature is replete with both theoretical and experimental stability studies of chemical reactors (Aris, 1969, 1975; Perlmutter, 1972; Denn, 1975; Himmelblau and Bischoff, 1968). One aspect of such work is the concept of multiplicity in the operation of a chemical reactor (Frank-Kamenetskii, 1947; van Heerden, 1953; Bilous and Amundson, 1955; Stewart and Villadsen, 1969; Furusawa et al., 1969; Vejtasa and Schmitz, 1970; Luss, 1971; Hlavacek et al., 1976, Lin, 1979).

In Part I of this paper (Tavare and Garside, 1985) an analogy with the isothermal well-mixed CSTR (continuous stirred tank reactor) of reaction engineering has demonstrated the application of the theory of concentration multiplicity and stability to the isothermal continuous MSMPR crystallizer described by the population balance equation together with power law growth and magma-dependent power law nucleation kinetics. The object of this second part is to extend the same analogy by incorporating the energy balance in addition to the solute balance in the description of the simple MSMPR cooling crystallizer and to develop a theory that will enable predictions of the regions of multiplicity. Discussion is confined to the simple MSMPR crystallizer configuration in which supersaturation is achieved by cooling a hot feed to the working temperature. The specific aim of the paper is to present some exact uniqueness and multiplicity criteria together with the stability analysis in terms of the solute concentration and working temperature of a continuous MSMPR crystallizer. The analysis will simulate most real continuous crystallizers operated in this mode and should be useful in the identification of ranges of parameters within which temperature multiplicity can be expected.

THEORY

Crystallizer Description

The analogy of the classical CSTR as analyzed by a macroscopic description which leads to a model involving a lumped-parameter set of ordinary differential equations will be used to describe the crystallizer. The dynamic solute balance as written for the solution in a continuous MSMPR cooling crystallizer of the type shown in Figure 1 can be formulated as

$$\tau \frac{dc}{dt'} = c_f - c - M_T \tag{1}$$

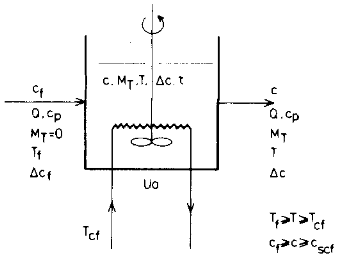

Figure 1. Schematic representation of a continuous MSMPR cooling crystallizer.

and the energy balance as

$$c_p \tau \frac{dT}{dt'} = c_p(T_f - T) + (-\Delta H_c)M_T - \frac{Ua}{Q}(T - T_{cf}) \tag{2}$$

A basic premise of the above description is that both the concentration and the temperature are uniform throughout the crystallizer and the heat capacity of the adiabatic vessel itself is negligible. The final term in Eq. 2 arises from the need to allow for heat transfer across the boundary of the system by means in addition to the material flows. Ua is thus the overall heat transfer coefficient in units which include the area of heat transfer surface. It is not necessarily the true overall heat transfer coefficient in a conventional heat transfer sense, but rather a phenomenological model parameter used to simplify the representation; its value depends on fluid properties, fluid conditions, and the heat generation term. c_p is the representative value of solution specific heat. For simplicity its variation with temperature and solid content is neglected.

The crystallization kinetics of the system will be described empirically by:

overall linear growth rate: $G = k_{GO} \exp(-E_G/RT)\Delta c^g$ (3)

nucleation rate: $B = k_{BO} \exp(-E_B/RT)\, \Delta c^b M_T^j$ (4)

Both these rate expressions incorporate an Arrhenius temperature dependence with activation energies E_G and E_B, and a power law supersaturation effect with orders g and b, respectively. The power law term, M_T^j, in the nucleation rate expression accounts for secondary nucleation effects occurring within the crystallizer. Effects of variables other than temperature, supersaturation, and suspension density on the kinetics are lumped into the rate coefficients k_{GO} and k_{BO}; examples of such variables include slurry hydrodynamics and the presence of impurities.

Using the dimensionless variables

$$x = \frac{c}{c_f}$$

$$y = \frac{Tc_p}{c_f(-\Delta H_c)}$$

$$t = \frac{t'}{\tau}$$

$$\delta = \frac{Ua}{Qc_p}$$

the dimensionless dynamic solute and energy balances, Eqs. 1 and 2 may be rewritten as

$$\frac{dx}{dt} = 1 - x - \frac{M_T}{c_f} \tag{5}$$

$$\frac{dy}{dt} = y_f - y + \frac{M_T}{c_f} - \delta(y - y_{cf}) \tag{6}$$

The parallel between the two dynamic conservation equations is more obvious in these dimensionless forms. The corresponding steady state equations can be obtained by setting the time derivatives in Eqs. 5 and 6 to zero, so giving

$$1 - x - \frac{M_T}{c_f} = 0 \tag{7}$$

$$(y_f - y) + \frac{M_T}{c_f} - \delta(y - y_{cf}) = 0 \tag{8}$$

If the solubility relation for the crystallizing salt over the range of interest is expressed as a linear function of temperature:

$$c_s = mT + e \tag{9}$$

then the equivalent in dimensionless form is

$$x_s = \beta y + \xi \tag{10}$$

where $\beta = m(-\Delta H_c)/c_p$ and $\xi = e(-\Delta H_c)/c_p$

Using the steady state solute and energy balances, Eqs. 7 and 8, along with the solubility relation in the definition of the difference in supersaturation values

$$\frac{\Delta c - \Delta c_f}{c_f} = \frac{c - c_f}{c_f} + \frac{c_{sf} - c_s}{c_f} \tag{11}$$

the relationship between the reduced supersaturation and reduced temperature can be established as

$$\Delta x = \Delta x_f + (1 + \beta)(y_f - y) - \delta(y - y_{cf}) \tag{12}$$

while that between the reduced concentration and the reduced temperature is

$$1 - x = (y - y_f) + \delta(y - y_{cf}) \tag{13}$$

For the steady state continuous MSMPR crystallizer operating with a clear feed and negligible crystal agglomeration and breakage, the suspension density obtained from the moment transformation of the population balance equation is given by (Randolph and Larson, 1971)

$$M_T = 6k_v \rho \tau^4 G^3 B \tag{14}$$

Using Eqs. 3, 4, 12, and 13, the dimensionless characteristic heat generation function, $H(y)$, used in multiplicity analysis may be expressed as a function of y alone as

$$\begin{aligned} H(y) &= \frac{M_T}{c_f \alpha} \\ &= \exp\left(-\frac{\gamma}{y}\right)(\Delta x)^k (1 - x)^j \\ &= \exp\left(-\frac{\gamma}{y}\right)(s_2 - s_1 y)^k \left(\frac{y - \phi}{\eta}\right)^j \end{aligned} \tag{15}$$

where

$$\alpha = 6k_v \rho \tau^4 k_{BO} k_{GO}^3 c_f^{k+j-1} \tag{16}$$

$$\gamma = \frac{(E_B + 3E_G)c_p}{R(-\Delta H_c)c_f} \tag{17}$$

$$k = b + 3g \tag{18}$$

$$s_1 = 1 + \beta + \delta \tag{19}$$

$$s_2 = \Delta x_f + (1 + \beta)y_f + \delta y_{cf} \tag{20}$$

$$\phi = (y_f + \delta y_{cf})\eta \tag{21}$$

$$\eta = \frac{1}{1 + \delta} \tag{22}$$

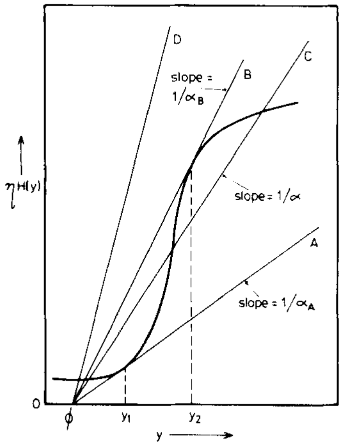

Figure 2. Schematic representation of the van Heerden diagram.

In addition to the above crystallizer description there exist two physical limitations on a cooling crystallizer which may be expressed by

$$x_{scf} \leqslant x \leqslant 1 \tag{23}$$

and

$$y_f \geqslant y \geqslant y_{cf} \tag{24}$$

Equation 23 sets the limits on the reduced exit concentration, Eq. 24 on the reduced working temperature. However, if Eq. 13 is incorporated in inequality Eq. 23 to yield

$$\phi < y < \phi + \eta(1 - x_{scf}) = \phi + \eta(1 - \beta y_{cf} - \xi) \tag{25}$$

then Eq. 25 sets less conservative limits on the reduced working temperature than those represented by Eq. 24.

Multiplicity Analysis

It is evident from the steady state energy balance Eq. 8 that the characteristic function $H(y)$ is proportional to the dimensionless heat generation term due to the crystallization process, and the other two terms to the heat removal from the crystallizer. Thus Eq. 8 may be rewritten as

$$\text{Heat generation} = \text{Heat removal}$$

$$\eta H(y) = \frac{y - \phi}{\alpha} \tag{26}$$

For a graphical solution of Eq. 26 it is necessary to plot the heat generation and heat removal functions against y on the same plot when the intersection(s) of the curve representing the dimensionless function $H(y)$ with the straight line representing the heat removal term yields a steady state solution(s). This classic representation is known as the van Heerden diagram. The nature of the function $H(y)$ depends on many parameters and with certain sets of parameters will have a sigmoid shape as shown schematically in Figure 2. When the heat removal function is superimposed on the same diagram it is evident that the equality of the heat removal and generation terms can define one or more steady states at the intersection points, depending on the system parameters that determine the position of the heat removal line as characterized by its slope $(1/\alpha)$ and intercept (ϕ) on the y axis. Examination of Figure 2 shows clearly that a crystallizer steady state can be very sensitive to small changes in parameters if the conditions are close to those that produce the triple intersection. It would perhaps be expected that the relatively high sensitivity associated with the multiple state ought to be avoided and indeed this would be a reasonable basis so long as the unique steady states that are attainable are satisfactory as regards performance.

Conditions for Multiplicity

From Figure 2 it is evident that if the slope $(1/\alpha)$ of the heat removal line is not within the range of slopes of the tangents to the function $\eta H(y)$ from the point $(\phi,0)$, only one steady state will exist. Hence a necessary condition is that it must be possible to draw two tangents to $\eta H(y)$ from the point $(\phi,0)$. A sufficient condition is that the slope of the straight line through $(\phi,0)$ (i.e., $1/\alpha$) should lie between the slopes of the two tangents to the function $\eta H(y)$ from the point $(\phi,0)$, i.e., from Figure 2

$$\frac{1}{\alpha_A} < \frac{1}{\alpha} < \frac{1}{\alpha_B} \tag{27}$$

The slope parameter α as defined by Eq. 16 depends on many quantities, in particular the kinetic rate constants, mean residence time, and feed concentration. Some of these are rather difficult to assign a priori with precision. Thus the slope parameter may be eliminated in deciding the region of multiplicity by taking the ratio of the derivative of $H(y)$ to $H(y)$ which, after using Eq. 15, gives

$$\begin{aligned}\frac{\dot H(y)}{H(y)} &= \frac{1}{y-\phi} \\ &= \frac{\gamma}{y_2} - \frac{k\,s_1}{(s_2 - s_1 y)} + \frac{j}{(y-\phi)}\end{aligned} \tag{28}$$

Simplification of Eq. 28 yields a cubic equation in y as

$$\begin{aligned}y^3 + y^2 &\left[\frac{(1-j)s_2 + \gamma s_1 - k\phi\, s_1}{(k+j-1)s_1}\right] \\ &-y\left[\frac{\gamma s_2 + \gamma\phi s_1}{(k+j-1)s_1}\right] + \left[\frac{\gamma\phi s_2}{(k+j-1)s_1}\right] = 0\end{aligned} \tag{29}$$

If this cubic equation in y has two real and distinct roots within the range of y specified by Eq. 25, then these two roots will set the limits on the range of multiplicity.

Conditions for Uniqueness

If the desirable flexibility is available it would be worthwhile to explore the effects of parameter choices to determine the conditions which always produce a unique steady state. The energy balance characteristic function from Eq. 26 can be defined as

$$F(y) = -\frac{y-\phi}{\alpha} + \eta H(y) = 0 \tag{30}$$

Differentiating Eq. 30 with respect to y gives

$$\dot F(y) = -\frac{1}{\alpha} + \eta \dot H(y) \tag{31}$$

The lefthand side of Eq. 31 can never be zero if

$$\dot H(y) < 0 \tag{32}$$

Since $H(y)$ can only be positive, Eq. 32 will be satisfied if the following inequality from Eq. 28 is satisfied:

$$\frac{\gamma}{y^2} + \frac{j}{y-\phi} < \frac{ks_1}{(s_2 - s_1 y)} \tag{33}$$

Equation 33 represents a system uniqueness criterion and provides the sufficient condition which guarantees a unique solution to the choices of the parameters contained within it for nonzero positive $H(y)$. Equation 32 is safe but quite conservative, a sufficient but not a necessary uniqueness criterion. It is important to note that although multiple solutions require $\dot F(y)$ to be zero at some value of y, the converse is not true. Having accepted the $\dot F(y) < 0$ inequality, it follows exactly from Eq. 31 that $\dot H(y) < 1/\eta\alpha$ rather than the correct but simplified Eq. 32. An interesting physical interpretation of the inequality can be made as

$$\eta \dot H(y) < \frac{1}{\alpha} \tag{34}$$

i.e., (slope of dimensionless heat generation curve)
< (slope of dimensionless heat removal line)

In otherwords, an MSMPR crystallizer will have a unique steady state if the slope of the heat removal line in Figure 2 is larger than the slope of the heat generation curve over the entire range of interest (line ϕD in Figure 2).

The question of uniqueness may be explored in further detail by returning to the inequality represented by Eq. 34 and recognizing that it can be satisfied by a less conservative relationship than Eq. 32. The derivative $\dot H(y)$ need not necessarily be negative so long as it is less than a positive number, i.e., Max $|\dot H(y)| < 1/\eta\alpha$.

STABILITY ANALYSIS

The concept of uniqueness and stability must be carefully distinguished. It is a property of a given equation to have or not to have a unique solution. It is the property of any one solution to be stable or unstable. Questions of uniqueness or multiplicity of the steady state can be resolved by the study of the steady state equations whereas the question of stability requires consideration of the dynamic equations. However the steady state equations do permit certain limited and usually negative statements to be made about stability.

The dynamic energy balance around the crystallizer may be rewritten from Eqs. 6 and 26 as

$$\eta\frac{dy}{dt} = \phi - y + \alpha\eta H(y) \tag{35}$$

The steady state value (denoted by subscript s) obtained by letting $dy/dt = 0$ in Eq. 35 and subtracting the steady state equation from Eq. 35 results in

$$\eta\frac{d\epsilon}{dt} = -\epsilon + \alpha\eta[H(y) - H(y_s)] \tag{36}$$

where ϵ represents the deviation from the steady state and is defined as

$$\epsilon = y - y_s \tag{37}$$

For small perturbations from the steady state the term in the square bracket of Eq. 36 can be linearized using a Taylor series expansion as

$$[H(y) - H(y_s)] = \epsilon \dot H(y_s) \tag{38}$$

Substituting Eq. 38 into Eq. 36 and integrating the result gives

$$\epsilon = \epsilon_o \exp(-qt) \tag{39}$$

where ϵ_o is the value of the deviation at $t = 0$, and q is given by

$$q = 1 - \alpha\eta \dot H(y_s) \tag{40}$$

For a steady state to be stable the perturbation ϵ must decay with time. This is possible for $q > 0$. It can be shown that q is negative for the range $y_1 < y < y_2$ (see Figure 2) and so the steady state lying within this region is unstable. Normally the middle of the three steady states is one such case for which $q < 0$. The inequality Max $[\dot H(y)] < 1/\eta\alpha$ guarantees a positive value to q and hence a unique and stable solution.

TABLE 1. PARAMETERS USED IN THE ANALYSIS

Parameter	
Cooling fluid temperature, T_{cf}, K	298
Crystallizer feed temperature, T_f, K	348
Solubility, c_s, kg salt/kg solvent	$0.004T - 1.0$
Feed concentration, c_f, kg salt/kg solvent	$0.004T_f - 1.0 = 0.392$
Growth rate order, g	1.0
Nucleation order, b	2.0
Exponent of magma density, j	2.0
Activation energy for nucleation, E_B, kJ/kmol	6×10^4
Activation energy for growth, E_G, kJ/kmol	5×10^4
Ratio of overall heat transfer coefficient to heat capacity of crystallizer feed, δ	5.0
Ratio of heat of crystallization to specific heat, $-\Delta H_c/c_p$, K	50.0

The foregoing linear stability analysis utilizing an infinitesimal perturbation is based on the dynamic energy balance alone. However both dynamic balances should be considered for the stability analysis. If then Eqs. 5 and 6 are rewritten as

$$\frac{dx}{dt} = 1 - x - \alpha\eta H(x,y) \tag{41}$$

$$\eta\frac{dy}{dt} = \phi - y + \alpha\eta H(x,y) \tag{42}$$

an identical procedure to that outlined above enables Eqs. 41 and 42 to be linearized in a Taylor series as

$$\frac{d\epsilon_1}{dt} = -[1 + \alpha\eta\dot{H}_x(x_s,y_s)]\,\epsilon_1 - [\alpha\eta\dot{H}_y(x_s,y_s)]\epsilon_2 \tag{43}$$

$$\eta\frac{d\epsilon_2}{dt} = [\alpha\eta\dot{H}_x(x_s,y_s)]\,\epsilon_1 + [-1 + \alpha\eta\dot{H}_y(x_s,y_s)]\epsilon_2 \tag{44}$$

where ϵ_1 and ϵ_2 are the deviation variables for x and y, and $\dot{H}_x$ (x_s,y_s) and $\dot{H}_y(x_s,y_s)$ are the partial derivatives of $H(x,y)$ with respect to x and y evaluated at the steady state, respectively.

In order to examine the stability of the steady state it is necessary to examine the roots of the characteristic equations derived from the determinant of the characteristic matrix $A = |J - \lambda I|$ of Eqs. 43 and 44 where J is the Jacobian matrix, λ the eigenvalues, and I the identity matrix. The characteristic equation is

$$\lambda^2 - (a_{11} + a_{22})\lambda + (a_{11}a_{22} - a_{12}a_{21}) = 0 \tag{45}$$

where a_{ij} are the elements of the characteristic matrix and are defined from Eqs. 43 and 44 as

$$\begin{aligned} a_{11} &= -[1 + \alpha\eta\dot{H}_x(x_s,y_s)], a_{12} = -\alpha\eta\dot{H}_y(x_s,y_s), \\ a_{21} &= \alpha\eta\dot{H}_x(x_s,y_s), \qquad a_{22} = -1 + \alpha\eta\dot{H}_y(x_s,y_s) \end{aligned} \tag{46}$$

For the steady state to be stable both the roots λ_1 and λ_2 need to have negative real parts. This is true if and only if

TABLE 2. EQUIVALENT DIMENSIONLESS QUANTITIES USED IN THE ANALYSIS

$\beta = 0.2$	$\xi = -0.02$
$y_f = 17.755$	$y_{cf} = 15.204$
$x_f = 1.0$	$\Delta x_f = 0.0$
$k = 5.0$	$j = 2.0$
$\gamma = 1{,}288.0$	$\delta = 5.0$
$\phi = 15.629$	$\eta = 0.166$
$s_1 = 6.2$	$s_2 = 97.327$
$y_{\min} = 15.629$	$y_{\max} = 15.714$
$y_{\eta H(y)=0} = 15.698$	$\dot{H}(y)\|_{\max} = 8 \times 10^{-40}$

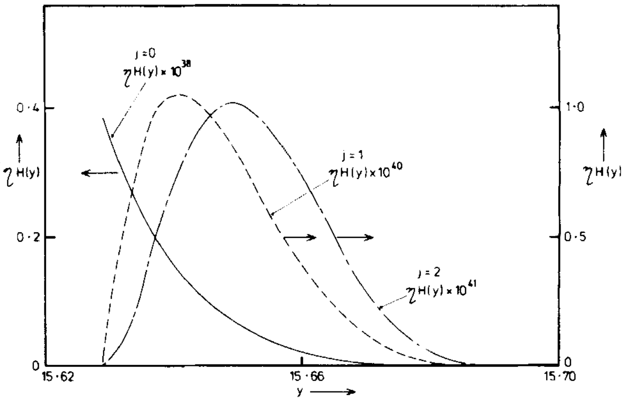

Figure 3. Characteristic function $\eta H(y)$. Data used in the calculations are given in Tables 1 and 2.

$$a_{11} + a_{22} < 0 \tag{47}$$

$$a_{11}a_{22} - a_{12}a_{21} > 0 \tag{48}$$

Equations 47 and 48 are commonly known as the dynamic ($tr\,|J|$ < 0) and static or slope ($det\,|J| > 0$) conditions of the linear stability respectively. Normally these conditions are always satisfied for the lower and upper steady states. The middle steady state however violates these conditions and is therefore unstable.

For the occurrence of oscillations it is necessary that the static condition, Eq. 48, should be satisfied while the dynamic condition, Eq. 47, be violated.

APPLICATION

The dimensionless characteristic heat generation function, $H(y)$, depends on the kinetic orders (k,j), dimensionless activation energy (γ) and heat transfer (δ) parameters, and the operating reduced temperatures $(y$, y_f and $y_{cf})$, while the slope of the heat removal

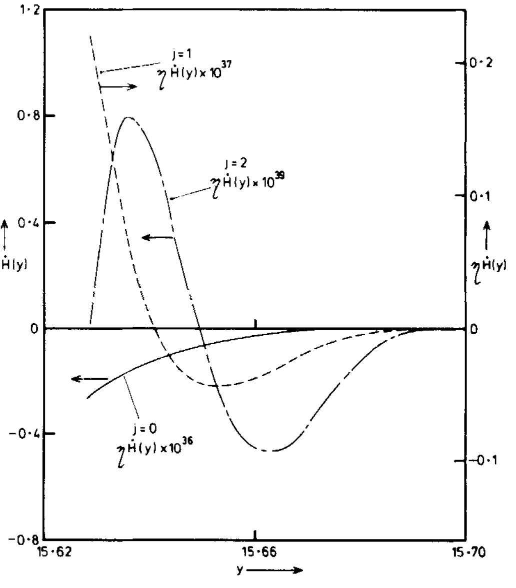

Figure 4. The function $\eta\dot{H}(y)$. Data used in the calculations are given in Tables 1 and 2.

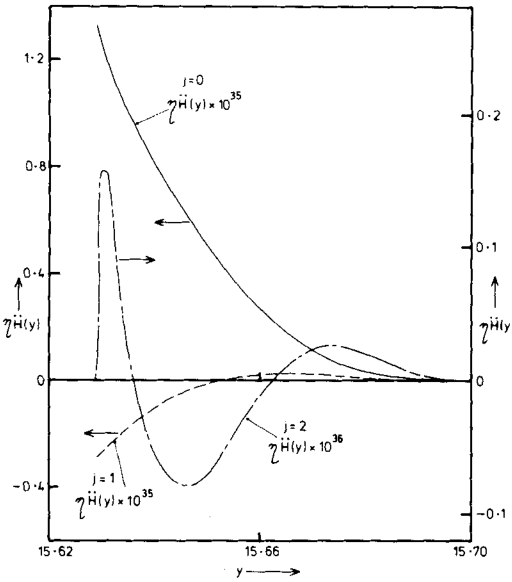

Figure 5. The function $\eta\ddot{H}(y)$. Data used in the calculations are given in Tables 1 and 2.

line $(1/\alpha)$ is characterized by the physical parameters (k_v,ρ), rate coefficients (k_{BO},k_{GO}), mean residence time (τ), and feed concentration (c_f). The necessary conditions are made independent of α and depend mostly on the parameters in $H(y)$. As several parameters are involved in the foregoing general analytical formulation, a typical set of actual parameter values, Table 1, was chosen for numerical analysis; the corresponding equivalent dimensionless quantities are given in Table 2.

Plots of $\eta H(y)$ against y for $j = 0$, 1, and 2 are depicted in Figure 3 and those of $\eta\dot{H}(y)$ and $\eta\ddot{H}(y)$ in Figures 4 and 5, respectively. When $j = 0$ (no secondary nucleation effects) a monotonically decreasing $\eta H(y)$ guarantees a unique steady state without any possibility of multiplicity. A graphical solution of Eq. 29 indicates no regions of multiplicity. The uniqueness criterion, Eq. 33, and dynamic and static stability criteria, Eqs. 47 and 48, are satisfied over the entire range of y defined by Eq. 25, confirming a unique and stable steady state for this case. Although the function $\eta H(y)$ for $j = 1$ passes through a maximum and the uniqueness and stability criteria are not satisfied in the region very close to $y = \phi$, the graphical solution of Eq. 29 does not yield any other root within the range of y defined by Eq. 25, and so indicates no possibility of multiple solutions. However this possibility does exist for $j = 2$, as the graphical solution provides a region of multiplicity. The uniqueness and stability criteria are violated over the overlapping range of y, indicating the possibility of multiple unstable solutions.

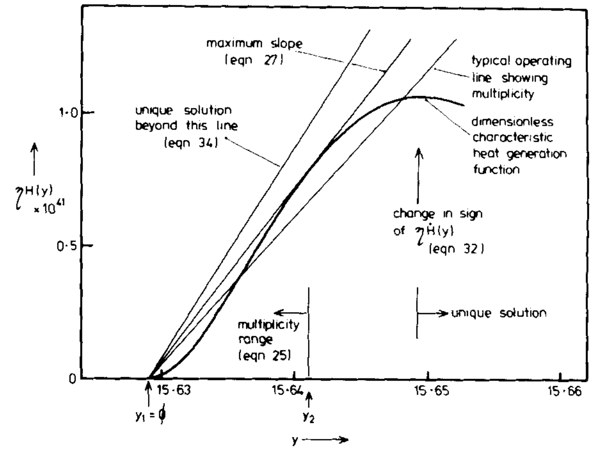

Figure 6. Characteristic function $\eta H(y)$ showing region near $y = \phi$ for $j = 2$. Other data as in Tables 1 and 2.

Confirmation of these observations can be obtained from Figures 4 and 5. For $j = 2$ both the derivatives $\eta\dot{H}(y)$ and $\eta\ddot{H}(y)$ yield three roots, while for $j = 0$ only one and for $j = 1$ only two roots are possible. Thus a possibility of multiplicity exists if the slope condition, Eq. 27, is satisified.

An enlargement of that part of the dimensionless characteristic heat generation function near $y = \phi$ as displayed in Figure 6 shows a sigmoid shape and demonstrates the possibility of multiplicity within this region. The slope parameter α defined by Eq. 16 has several adjustable parameters, in particular the mean residence time, the kinetic rate coefficients, and the feed concentration. Also included in Figure 6 are the regions defining the unique solution. This shows clearly how conservative and safe estimates are obtained by these criteria.

The effect of the dimensionless heat transfer parameter δ on the regions of multiplicity and uniqueness for $k = 5$ and $j = 2$ is depicted in Figure 7. Other parameters are as shown in Table 2. The

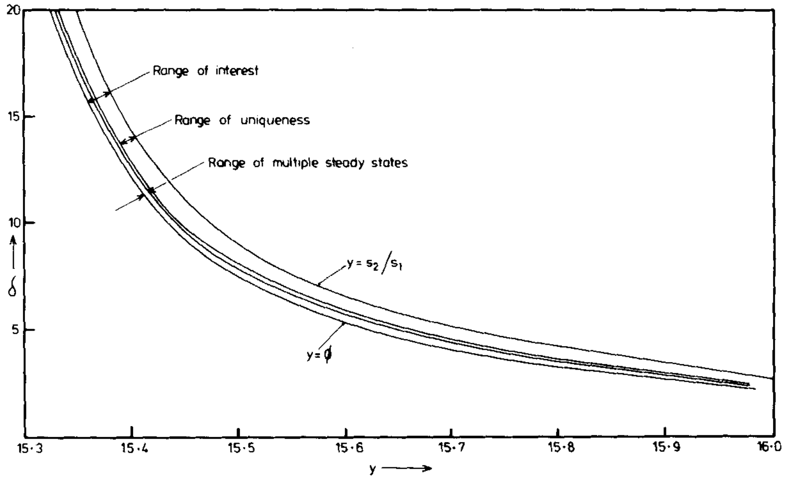

Figure 7. Effect of the heat transfer parameter δ on the regions of multiplicity and uniqueness for $j = 2$. Other data as in Tables 1 and 2.

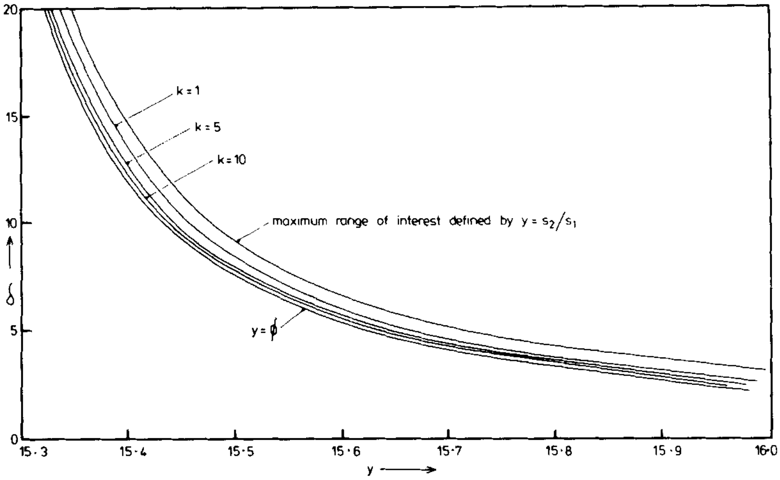

Figure 8. Effect of the kinetic orders parameter *k* on the region of multiplicity for *j* = 2. Other data as in Tables 1 and 2.

lowermost curve, $y = \phi$, and the uppermost curve, $y = s_2/s_1$, represent lower and upper bounds on $\eta H(y)$ for the potential region of interest; $\eta H(y) = 0$ on the bounds. The possibility of multiplicity exists in the region between the two lowermost curves while the region of uniqueness lies between the uppermost curves. The stability criteria, Eqs. 47 and 48, predict a stable solution in this region of uniqueness. All the regions show slight increase with decrease in δ. The uniqueness, Eq. 33, and stability criteria, Eqs. 47 and 48, present a safe and conservative estimate over the entire range of δ.

The effect of the kinetic orders parameter k on the region of multiplicity can be seen by using k as a parameter on the plot of δ against y as shown in Figure 8. As k increases the region of multiplicity reduces and that of uniqueness and stability increases while the trend of safe but conservative estimates for uniqueness and stability is retained in each case. The activation energy parameter, γ, showed no effect on the regions over a range $600 < \gamma < 1{,}850$ and the general behavior of the system was found to be independent of temperature range. A high temperature difference between feed and cooling fluid was specifically chosen to obtain large regions, as the regions are reduced for small temperature differences.

DISCUSSION

As in the case of concentration multiplicity (Tavare and Garside, 1985) this analysis based on the steady state balances alone shows the possible existence of multiplicity for a continuous MSMPR crystallizer, in this case temperature multiplicity for a cooling crystallizer. A high-order term of magma density in the nucleation model, Eq. 4, is again the crucial parameter, in this case exerting a significant influence on the form of the dimensionless characteristic heat generation function $\eta H(y)$. Unique and stable behavior of the MSMPR configuration for a low-order magma-dependent term in the nucleation model is predicted.

As Eqs. 5 and 6 in the present model are normally nonlinear and coupled, a number of possible routes to stability analysis are open (Perlmutter, 1972; Himmelblau and Bischoff, 1968). Solution by direct computer simulation of these equations may be possible. On the other hand the stability can be examined by considering small perturbations around steady states. The foregoing stability analysis attempts to place quantitative limits on the system parameters which would insure stable operation. Normally the dynamic ($tr|J| < 0$) and static or slope ($\det|J| > 0$) conditions of the stability are satisified for the upper and lower steady states. The middle steady state violates these conditions and therefore is unstable. For the occurrence of sustained cycles the static condition is satisfied but the other dynamic condition may be violated. Detailed dynamic studies of the configuration may be necessary to provide more information and better understanding. In the present stability analysis the dimensionless heat generation function $\eta H(y)$ was evaluated from the magma density term obtained from the steady state analysis ignoring its dynamic behavior. A more rigorous analysis involving evaluation of the characteristic matrix for the set of differential equations describing the dynamic moments of the CSD along with the dynamic solute and energy balance, as presented in Appendix 1 to Part 1 of this paper, would be rather complex.

As can be seen from Figure 7, the maximum potential temperature range of interest for analysis is ~0.075 in dimensionless terms; this corresponds to ~1.5 K in real temperature, whereas the corresponding multiplicity range is ~0.5 K. Using the analogy with the CSTR in reaction engineering, the temperature range over which multiplicity might occur is likely to be much higher in reactors than in crystallizers. In the crystallizer operating mode considered here, there has to be some cooling of the feed as a prerequisite of the operation; hence the crystallizer would normally be operated at a temperature lower than that of the feed but higher than that of the cooling fluid. Such a constraint is unnecessary in chemical reactors. Further, heats of reaction would normally be much higher than those of crystallization, the latter being usually less than about 400 kJ/kg.

Finally, it is important to assess the practical implications of the present work. Temperature multiplicity is possible for a high-order magma density term in the secondary nucleation kinetic expression over a narrow range of operating parameters, although such high-order magma-dependent nucleation kinetics seem rare in published crystallization kinetics (Garside and Shah, 1980). One of the important inferences that can be drawn from this work is that the designer should be aware of a possibility of multiple steady states over some choices of operating system parameters whereby the crystallizer might operate at conditions quite removed from those intended. Although such regions may be rather drastic, *a priori* knowledge of operating conditions and crystallizer parameters within which multiple steady states are possible is beneficial in design, start-up, and control. Extreme parametric sensitivity in the region close to multiplicity is another characteristic which may be limited to a narrow region, to special cases, or to localized situations in the crystallizer.

NOTATION

A = characteristic matrix, = $|J - \lambda I|$
a_{ij} = elements of the characteristic matrix, Eqs. 45–48
b = nucleation order
B = nucleation rate, no/s·kg solvent
c = concentration of solute, kg solute/kg solvent
c_p = specific heat, kJ/kg·K
e = constant, Eq. 9
E_B = activation energy for nucleation, kJ/kmol
E_G = activation energy for growth, kJ/kmol
$F(y)$ = dimensionless characteristic energy balance function, Eq. 30
g = growth rate order
G = overall linear growth, m/s
$H(y)$ = dimensionless characteristic heat generation function, $= M_T/c_f\alpha$, Eq. 15
$|\dot{H}_x(x,y)$ = partial derivative of $H(x,y)$ with respect to x at x,y
$|\dot{H}_y(x,y)$ = partial derivative of $H(x,y)$ with respect to y at x,y
$-\Delta H_c$ = heat of crystallization (exothermic), kJ/kg
i,j = index integers
I = identity matrix
j = exponent of magma density, Eq. 4
J = Jacobian matrix
k = kinetic orders parameter, $= b + 3g$
k_{BO} = nucleation rate constant, no/s·kg solvent $(\text{kg/kg})^{b}$·$(\text{kg/kg})^{j}$
k_{GO} = growth rate constant, m/s$(\text{kg/kg})^{g}$
k_v = volume shape factor
m = solubility temperature coefficient, Eq. 9
M_T = suspension density, kg crystal/kg solvent
Q = mass flowrate, kg/s
q = constant, Eq. 40
R = gas constant, 8.314 kJ/kmol·K
s_1,s_2 = constants, Eqs. 19 and 20
t' = time, s
t = dimensionless time, t/τ
T = temperature, K
Ua = overall heat transfer coefficient, kJ/s·K
x = dimensionless concentration, c/c_f
y = dimensionless temperature, $Tc_p/c_f(-\Delta H_c)$

Greek Letters

α = slope parameter, Eq. 16
α_A,α_B = extreme slope parameters, Eq. 27
β = dimensionless solubility coefficient, Eq. 10
γ = activation energy parameter, Eq. 17
δ = heat transfer parameter, Ua/Qc_p
Δ = difference between actual and corresponding saturation quantities
ϵ = deviation variable, Eq. 37
ϵ_1,ϵ_2 = deviation variables for x and y
ξ = constant, Eq. 10
η = $1/(1 + \delta)$
λ = eigenvalues of the characteristic matrix
ρ = density of crystals, kg/m^3
τ = mean residence time, s
ϕ = intercept on y axis of heat removal line

Subscripts

f = feed
cf = cooling fluid
o = initial
s = saturation, steady state

Superscript

= derivative with respect to x or y

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