Uniqueness and Multiplicity in Isothermal CMSMPR Crystallizers

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While the occurrence of instabilities and sustained oscillations in crystallizers has attracted widespread attention in the literature (Randolph and Larson, 1962; Sherwin et al., 1979; Nyvlt and Mullin, 1970; Yu and Douglas, 1975; Ishii and Randolph, 1980; Epstein and Sowul, 1980; Jerauld et al., 1983; Lakatos and Sapundzhiev, 1990; Buevich et al., 1991a, b), less attention has been paid to the possible appearance of multiple steady states. Jerauld et al. (1983), studying the appearance of sustained oscillations, have stated that in the case of primary nucleation isothermal CMSMPR crystallizers exhibit unique steady states over the entire range of parameters, while Lakatos and Sapundzhiev (1990) have shown that this property is preserved also for size-dependent crystal growth rate. They used Volmer's model to describe the kinetics of nucleation, but did not take into consideration the possible dependence of the nucleation rate on properties of the crystal magma. Tavare and Garside (1985), as well Tavare et al. (1985) and Tavare (1989), have shown that in CMSMPR crystallizers with magma-dependent secondary nucleation, multiplicity of steady states may indeed occur under some circumstances. They considered both isothermal and nonisothermal, as well as reaction crystallizers, but only size-independent crystal growth rate has been taken into account. They also included into the conditions for uniqueness and multiplicity the steady-state values of the dependent variables, obtaining in this way rather implicit criteria.

The object of the present work is to derive, based on a rigorous moment equations model, stricter explicit criteria for uniqueness and multiplicity of steady-states of isothermal CMSMPR crystallizers for both primary and secondary nucleation, as well as for size-dependent crystal growth rate. Regions in parameter space over which multiple steady states occur are derived, and the effects of the size-dependent crystal growth rate, of the rate of nucleation, and of the dilution of feed on the steady-state solutions are analyzed.

Steady-State Equations

The mathematical model of a CMSMPR crystallizer consists of the population balance equation for crystals, the balance equations for solvent and crystallizing substance, and the equations describing the variation of the equilibrium saturation concentration. In the present analysis, the crystallizer is assumed to be isothermal; thus, the equilibrium saturation concentration is constant during the course of the process. Besides, we assume the solvent concentration to be constant as well.

If the crystallizer is unseeded the crystals can be characterized by a linear dimension L, all new crystals are formed at a nominal size $L_n \approx 0$, crystal breakage and agglomeration is negligible, no growth rate fluctuations occur, and the size-dependence of the overall growth rate of crystals G is linear in crystal size L and has the form of power law expression:

$$G = k_g(c - c^*)^g(1 + aL). \tag{1}$$

where c is the concentration of the crystallizing substance, c^* denotes the saturation concentration, and k_g and a are constants. Then the population balance equation describing the size distribution can be converted into an infinite system of recursive algebraic equations for moments which, however can be closed by the mass balance equation of solute at that for the 3rd order moment. In consequence, the steady-state behavior of the crystallizer is governed by the set of nonlinear algebraic equations:

$$-x_0 + B_\nu = 0, \quad \nu = p, s \tag{2}$$

$$-x_m + y^g(x_{m-1} + m\beta x_m) = 0, \quad m = 1,2,3 \tag{3}$$

$$\frac{y_{\text{in}} - y - (\alpha - y)y^g(x_2 + 3\beta x_3)}{1 - x_3} = 0, \tag{4}$$

given with scaled dimensionless variables, where

$$B_p = D_{\text{ap}}(1 - x_3)\exp\left(-\frac{F}{y^2}\right) \tag{5}$$

denotes the primary nucleation rate, and

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$$B_s = D_{as} y^s x_3^j \tag{6}$$

describes the rate of secondary nucleation. The details of the model represented by Eqs. 2–6 are presented by Lakatos et al. (1994). In dimensionless Eqs. 2–6, x_m denotes the mth order ordinary moment of the population density function n of crystals, defined as:

$$x_m = s_m \int_0^\infty L^m n dL, \quad m = 0, 1, 2, 3 \tag{7}$$

with scale factors $s_0 = 6k_v k_g^3 \tau^3 \ (\max\{c_{in}\} - c^*)^{3g}$, $s_1 = 6k_v k_g^2 \tau^2 \ (\max\{c_{in}\} - c^*)^{2g}$, $s_2 = 3k_v k_g \ \tau(\max\{c_{in}\} - c^*)^g$ and $s_3 = k_v$, where k_v is the volume shape factor of crystals, and y stands for the dimensionless supersaturation concentration, defined as $y = (c - c^*)/(\max\{c_{in}\} - c^*)$, where c_{in} denotes the feed concentration of solute, while $\max\{c_{in}\}$ is the maximal value of that. The dimensionless parameters of Eqs. 2–6 are given as:

$$F = k_e c^{*2} (\max\{c_{in}\} - c^*)^{-2}, \alpha = (\rho - c^*)(\max\{c_{in}\} - c^*)^{-1},$$

$$\beta = k_g a \tau (\max\{c_{in}\} - c^*)^g, D_{ap} = 6k_p k_v k_g^3 \tau^4 (\max\{c_{in}\} - c^*)^{3g},$$

$$\text{and} \quad D_{as} = D_{ap} k_s k_p^{-1} k_v^{-j} (\max\{c_{in}\} - c^*)^s,$$

where k_p and k_e are constants of Volmer's model, k_s, s and j are the coefficient, exponent of supersaturation, and exponent of solids concentration in the power law model, respectively, and ρ stands for mass density of crystals.

In models 2–6, the state of the crystallizer is represented by the vector of variables (x_0, x_1, x_2, x_3, y) of the five-dimensional phase space $\mathfrak{R}_5$. The variables, however, are bounded by the inequality constraints (Lakatos et al., 1994):

$$0 \le x_0 \le x_{0m}, \quad 0 \le x_1 \le A_1 x_{0m}^{2/3}, \quad 0 \le x_2 \le A_2 x_{0m}^{1/3},$$

$$0 \le x_3 \le 1, \quad 0 \le y \le y_{in} \tag{8}$$

where $x_{0m} = x_0 \ (0) + \tau s_0 \max\{B_v\}$, and A_1 and A_2 are real constants depending on the scale factors of moments. Moreover, the parameters, which in the case of primary nucleation are given as the vector of real numbers $p_p = (y_{in}, \alpha, g, \beta, D_{ap}, F)$, while in the case of secondary nucleation they form the vector $p_s = (y_{in}, \alpha, g, \beta, D_{as}, s, j)$, are also bounded:

$$0 \le y_{in} \le 1, \quad \alpha \ge 0, \quad g \ge 0, \quad \beta \ge \beta_{min}, \quad D_{ap} \ge 0,$$

$$D_{as} \ge 0, \quad F \ge 0, \quad s \ge 0, \quad j \ge 0 \tag{9}$$

where the minimal value $\beta_{min} < 0$ depends on the maximal size of crystals. Hereafter, domains 8 and 9 of states and parameters will be referred to as the feasible region of the crystallizer.

Primary Nucleation

If an isothermal CMSMPR crystallizer operates with high supersaturation and low magma density, new particles are born dominantly by primary nucleation. Then the nucleation rate is given by Eq. 5, and expressing y from the set of Eqs. 2–4, we obtain a single nonlinear equation:

$$\psi_1 \psi_2 \psi_3 (y_{in} - y) = D_{ap} (\alpha - y_{in}) y^{3g} \exp\left(-\frac{F}{y^2}\right), \tag{10}$$

where $\psi_k = 1 - k\beta y^g$, $k = 1, 2, 3$.

The righthand side of Eq. 10 is a monotonic increasing function of y, while the lefthand side decreases monotonically from y_{in} to 0 in the interval [0, min $\{\sqrt[g]{1/3\beta}, y_{in}\}$]. Therefore, since both sides are continuous functions of their arguments, there exists at least one steady-state solution satisfying $0 \le y \le y_{in}$ for any set of parameters. In addition, this solution is unique whenever condition $\beta < 1/2 y_{in}^g$ is satisfied.

In the case of $\beta > 1/2 y_{in}^g$, the righthand and lefthand sides of Eq. 10 may have two or even three intersections, implying two or three solutions in the interval $(0, y_{in})$. However, only roots y_r of Eq. 10, which satisfy the inequality $y_r \le \sqrt{1/3\beta}$, yield feasible solutions of Eqs. 2–4, since the larger ones yield negative lower-order moments which are not realizable physically. This appears to be valid only for the smallest root y_1, as illustrated in Figure 1. Here, the dependence of solutions of Eq. 10 as a function of parameter β is presented, and it is seen that at the limit point $\beta \simeq 0.11757$ two new solutions of Eq. 10 arise. These, however, are always greater than $1/3\beta$ which, in the present case, describes the boundary of the feasible region. Therefore, for an isothermal CMSMPR crystallizer operating with primary nucleation represented by Eq. 5 models 2–4 predicts a unique steady state over the entire possible region of parameters.

Secondary Nucleation

In the case of low supersaturation and high magma density, secondary nucleation appears to be the dominating process producing new crystals in a CMSMPR crystallizer. The

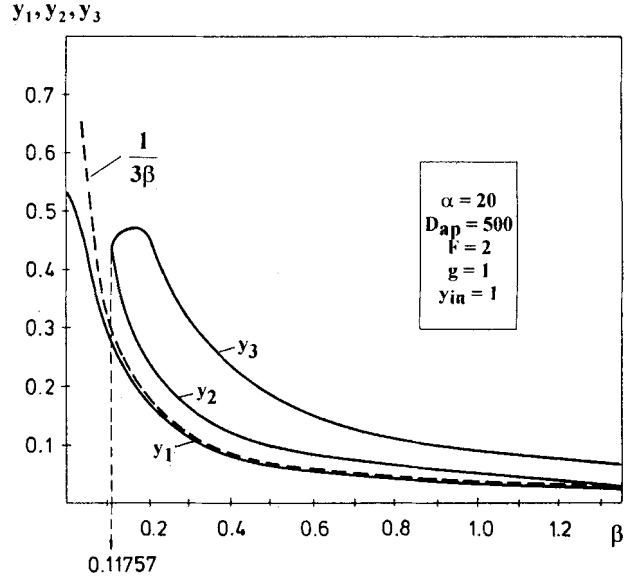

Figure 1. Steady-state solutions of Eq. 10 as a function of parameter β.

The curve $1/3\beta$, denoted by broken line, marks the boundary of the feasible region of solutions of model (Eqs. 2–4).

nucleation rate is now expressed by Eq. 6, and, since $s > 0$ and $j > 0$, the set of Eqs. 2–4 has a trivial (boundary) solution, $\{x_m = 0,\ m = 0,\ 1,\ 2,\ 3,\ y = y_{in}\}$, as can be shown by direct substitution. Then, there is no crystallization, and both the inflow and outflow consist of pure solution. This steady state is termed "washout" and is always a possibility for an unseeded crystallizer with secondary nucleation rate given by Eq. 6 when $j > 0$. As a consequence, the existence of a solution to the set of Eqs. 2–4 other than the boundary one at once implies multiple steady states for the crystallizer for all $j > 0$.

Criteria for $j < 1$

The set of Eqs. 2–4 can be algebraically reduced to the single equation for supersaturation y:

$$\psi_1\psi_2\psi_3(y_{in} - y)^{1-j} = D_{as}(\alpha - y)^{1-j}y^{3g+s}, \qquad (11)$$

provided that the trivial solution of the system of Eqs. 2–4 is precluded. The righthand side of Eq. 11 has two zeros: at $y = 0$ and at $y = \alpha > y_{in}$, and a maximum between them at $y^r_{max} = [\alpha(3g + s)]/(3g + s + 1 - j)$. Since the lefthand side of Eq. 11, which is a continuous function of y, decreases monotonically from y_{in} to 0 in $[0, \min\{\sqrt[g]{1/3\beta}, y_{in}\}]$, there thus exists always a nontrivial solution of Eq. 11 on $(0, y_{in})$. Based on simple arguments, however, we come to the conclusion that in the present case there is no other feasible nontrivial solution.

Consequently, for $j < 1$ the crystallizer exhibits two steady states over the entire possible region of parameters.

Criteria for $j = 1$

Now the equation for the steady-state concentration becomes:

$$\psi_1\psi_2\psi_3 = D_{as}y^{3g+s}, \qquad (12)$$

which appears to be independent on parameter α. The righthand side of Eq. 12 is a monotonic increasing function of y, which the behavior of the lefthand side strongly depends on β. For $\beta \le 0$ it is monotonic on $[0, \infty]$, but for $\beta > 0$ has local minimum at $y_{min} = \sqrt[g]{(11 - \sqrt{13})/18\beta}$, and local maximum at $y_{max} = \sqrt[g]{(11 + \sqrt{13})/18\beta}$.

Consequently, we can establish that the trivial solution is unique, if and only if the following conditions are satisfied:

$$\sqrt[g]{(11 - \sqrt{13})/18\beta} > y_{in}, \qquad (13a)$$

$$R_{12}(y_{in}) > L_{12}(y_{in}), \qquad (13b)$$

where for the sake of simplicity, $R_{12}(y_{in})$ and $L_{12}(y_{in})$ denote, respectively, the righthand and lefthand sides of Eq. 12 at y_{in}. When $\beta = 0$, then the condition (Eq. 13b) takes the simple form:

$$\sqrt[3g+s]{1/D_{as}} > y_{in}. \qquad (14)$$

If one of the conditions 13 is violated, then the crystallizer exhibits two steady states: one is the trivial; the other is given by the solution of Eq. 12.

The regions of single and two steady states on the (y_{in}, D_{as}) plane are presented in Figure 2. It is seen that with increasing size-dependence as represented by parameter β, the region of "washout" steady state is greatly increased, and at more diluted inflow higher intensity of nucleation D_{as} is needed for "ignition" of the crystallizer. In mechanically stirred crystallizers, for instance, this means that since D_{as} is an increasing function of the stirrer rotation rate (Ottens and de Jong, 1973), only more intensive stirring may maintain the crystallizer in a working state.

Criteria for $j > 1$

When the exponent j of the secondary nucleation rate is greater than 1, then the equation for supersaturation y takes the form:

$$\psi_1\psi_2\psi_3(\alpha - y)^{j-1} = D_{as}(y_{in} - y)^{j-1}y^{3g+s}, \qquad (15)$$

The righthand side of Eq. 15 has two zeros: at $y = 0$ and $y = y_{in}$, and it passes through a maximum at $y^r_{max} = [y_{in}(3g + n)]/(3g + n + 1 - j)$. The lefthand side is monotonic for $\beta \le 0$, but exhibits some extrema on $(0, \infty)$ for $\beta > 0$. Depending on the values of parameters, single, two or even three steady states are now possible.

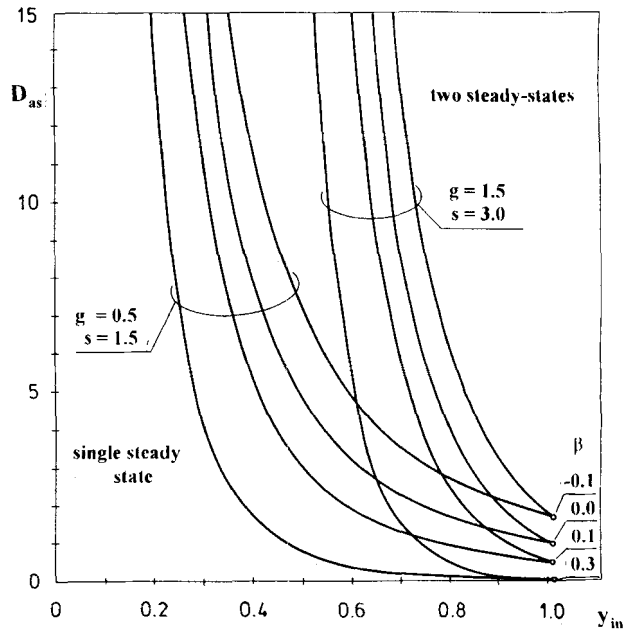

Figure 2. Regions of unique and two steady states in plane (y_{in}, D_{as}) in secondary nucleation for $j = 1$.

It is evident from the relative dispositions of the graphs of the lefthand and righthand sides of Eq. 15 that the crystallizer has three steady states if:

$$L_{15}(y_t) < R_{15}(y_t) \tag{16}$$

where y_t stands for the tangential point of the lefthand and righthand sides Eq. 15, given as such solution of equation:

$$-\{(3g+s)y_t^2 - [(3g+s)(\alpha + y_{in}) + (j-1)(\alpha - y_{in})]y_t + (3g+s)y_{in}\alpha\} = \beta g(y_{in} - y_t)(\alpha - y_t)y_t^g \sum_{k=1}^{3} \frac{k}{1 - k\beta y_t^g} \tag{17}$$

which lies in interval $(0, y_{in})$. Equation 17 has been obtained by equating the first derivatives of both sides of Eq. 15 to zero, and substituting into the resulting equation (Eq. 15).

Now the necessary conditions for the crystallizer to have three steady states are satisfying the criteria:

$$j > 1 \quad \text{and} \quad \beta < 1/3y_{in}^g, \tag{18}$$

Thus the necessary and sufficient conditions for having three steady states are criteria 17–18. Uniqueness is guaranteed, if the inequality beside conditions 18

$$L_{15}(y_t) > R_{15}(y_t) \tag{19}$$

holds, while two steady states exist, if the lefthand and righthand sides of Eq. 15 are equal at y_t, or instead of inequalities we have

$$j > 1 \quad \text{and} \quad \beta \geq 1/3y_{in}^g. \tag{20}$$

Figure 3 shows a bifurcation diagram $\beta - y$ with regions of all possible steady-state configurations. Two steady-state bifurcations occur: the first at $\beta = 1/3$ is independent on parameter D_{as}, while the second bifurcation point is affected by D_{as} significantly. Between them, there exist three steady-state solution branches from which the upper and lower ones are always stable, while the middle branch, formed by states of saddle node character (Lakatos et al., 1994), is always unstable. At $\beta = 1/3$, the boundary solution bifurcates; thus, the number of solutions is changed here by one.

Curves separating the regions of unique and three steady states on the $y_{in} - D_{as}$ plane have been plotted in Figure 4 as a function of β. We see that for every value of intensity of nucleation there exists a sufficient dilution of feed, differing from zero, which gives rise to the extinction of the crystallization process.

When $\beta = 0$, Eq. 17 reduces to a quadratic algebraic equation, and y_t can be expressed explicitly. Now two steady states exist only at the boundary points between the regions of unique and three steady states, since $\alpha > y_{in}$ and, consequently, $L_{15}(y_{in}) > 0$ always holds.

Discussion

The analysis indicates that an isothermal CMSMPR crystallizer, depending on the dominant mechanism of nucleation, and consequently on the governing kinetic equations, may exhibit a wide variety of steady-state behavior. This may be explained by the interaction of supersaturation auto-inhibition (negative feedback) with the closed cycle of moments $x_0 \to x_1 \to x_2 \to x_3 \to x_0$ of crystal-size distribution (positive feedback), revealed by the models 2–6.

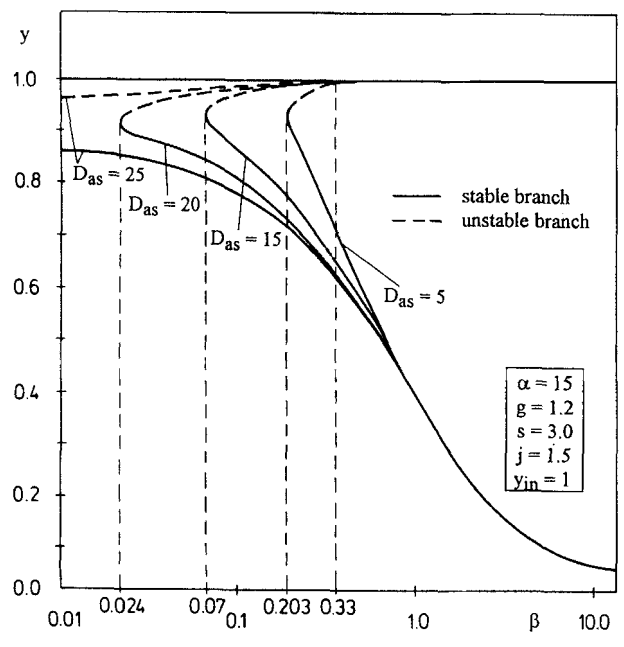

Figure 3. Bifurcation diagram β-y for the crystallizer in secondary nucleation with variation of parameter D_{as}.

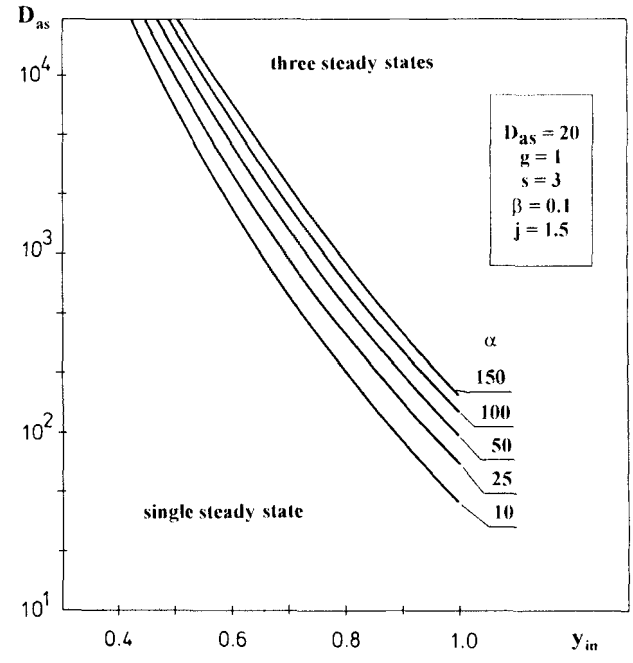

Figure 4. Regions of unique and three steady states in plane (y_{in}, D_{as}) in secondary nucleation with various parameters α.

For primary nucleation, the model predicts a unique steady state over the entire possible region of system parameters, but in the case of secondary nucleation, the crystallizer may have one, two, or three steady states depending on the values of parameters. The steady state termed "washout" is always a possibility in such crystallizers. If the exponent j of the solids concentration term in the nucleation rate equation is not greater than one, then the crystallizer may have at most two steady states, one inside the feasible region and the other on its boundary. However, for $j > 1$ even three steady states are possible, which is a stricter prediction than that of Tavare and Garside (1985).

The size dependence of the crystal growth rate as represented by parameter β significantly modifies the regions over which unique and multiple steady states occur. Increasing size dependence leads to a unique steady state representing the great extent of crystallization for all values of the remaining parameters.

By means of the general analytical criteria, developed for the prediction of uniqueness and multiplicity of steady states as a function of system parameters, the status of the desired states of the crystallizer to be designed can be easily checked.

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