Convergence Results for Continuous Crystallizers

Juan Du and B. Erik Ydstie*

* Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213 USA (e-mail: ydstie@ cmu.edu).

Abstract: We derive global stability results for continuous crystallizers using convergence analysis. The sufficient condition for exponential stability is derived in the analytical expression. The analytical condition offers a lower bound of the nucleus size and an upper bound of the largest size that crystals can grow. These conditions ensure that all the trajectories of the crystallizer converge to a single trajectory which is not necessarily known beforehand.

Keywords: Global stability, Convergence analysis, Continuous crystallization, Particle size distribution, Self-sustained oscillation.

1. INTRODUCTION

Crystallization is a typical chemical process that yields a particulate product characterized by shape and size as pointed out by Randolph and Larson (1988). As no two particles have exactly the same size, they need to be characterized by particle size distribution. Population balance represents a number balance in particles of a specific state according to Ramkrishna (2000). The population balance approach to analysis of crystallizers was formalized from a statistical mechanical perspective by Hulburt and Katz (1964).

Most of the work on stability analysis was mainly motivated by the occurrence of limit-cycle behavior of crystallizers observed both in laboratory and industry. Different explanations for the crystal size distribution instability were provided by studying population balance. Lei et al. (1971) showed that instability is induced by the high order kinetic relationship between nucleation rate and super saturation. Beckman and Randolph (1977) demonstrated that the instability can also be caused by classified crystal withdrawal at product sizes. The resulting CSD has a narrower distribution than that generated by mixed suspension mixed product removal type. Yu and Douglas (1975) obtained a condition for the occurrence of sustained oscillations in the continuous crystallizers by linearization at certain steady states. Jerauld et al. (1983) introduced new dimensionless groups that depend on physical properties and control parameters and derived a simpler condition by obscuring the effect on the steady-state values of the state variables. Rawlings and Ray (1987a) developed a simplified emulsion polymerization model and derived analytical solution to the distribution of particle sizes and radical numbers. Ralwings and Ray (1987b) used orthogonal collocation on finite elements to approximate population balance and studied bifurcation structure of continuous emulsion polymerization. Rawlings (1990) also compared the analytical solutions of particle size distribution and radical numbers to their numerical solutions of complex models. Lakatos (1994) showed that steadystate multiplicity was caused by secondary nucleation in

continuous crystallizers. Yin et al. (2003) investigated the influence of size dependent crystal growth rate on the stability and dynamics of continuous crystallizer using linearization approach. Du and Ydstie (2011) derived the global stability property of a particulate process using an entropy based energy function and obtained the condition to guarantee the stable operation.

Lohmiller and Slotine (1998) showed that convergence analysis provides global stability property of nonlinear systems. A nonlinear dynamic system is convergent if all the trajectories of the perturbed system converge to their nominal behavior with an exponential convergence rate. Pavlov et al. (2007) used convergence analysis to obtain global stability of a generalized convection-diffusionreaction processes. Lohmiller and Slotine (2000) remarked that the extension above to a state dependent metric coordinate transformation was expected for further research. Aggarwal (2009) presented the stability analysis of a multicomponent reactive flash operating under equilibrium using contraction theory. The analysis can be easily extended to study process networks like the distillation column as he pointed out.

In this paper, we present new results in global stability of continuous crystallizers. The sufficient condition for global exponential stability is derived in analytical form. The prerequisite on crystal nucleation and growth rate is given to achieve convergence results. The analytical condition offers the lower bound of nuclei size and the upper bound of largest size that crystals can grow. We believe these are new findings in the study of stability property of continuous crystallizers. These obtained conditions ensure that all the trajectories of the crystallizer converge to a single trajectory other than an equilibrium point. The existence and uniqueness of a steady state trajectory is guaranteed by convergence theory.

2. PROCESS DESCRIPTION

Consider an isothermal crystallizer with a constant volume V_T . The mother liquor with inlet concentration c_{in} is

fed into the crystallizer at the volumetric flow rate F. The difference between the solute concentration c and its saturation concentration c_s results in supersaturation. The supersaturation is the driving force for crystal nucleation and the consequent growth. The crystallizer behaves as though it is perfectly mixed and has unclassified product withdrawal. Crystals and liquor are removed continuously at the flow rate F. In the current work we use the crystal diameter to represent the characteristic length of crystals. The nucleation occurs at the smallest size l_{min} and l_{max} is the largest possible size that crystals can grow in the crystallizer. There is no crystal agglomeration and attrition.

The dynamics of the crystals are described by population balance

$$\frac{\partial M_s(l)}{\partial t} + \frac{\partial}{\partial l} GM_s(l) = Q + \frac{6G}{l} M_s(l) - \frac{M_s(l)}{\tau} \quad (1)$$

The mass balance of the solute dissolved in the mother liquor is given by

$$\frac{dM_l}{dt} = F_{in}c_{in} - \frac{M_l}{\tau} - \int_{l_{min}}^{l_{max}} [Q + \frac{6G}{l}M_s(l)]dl \quad (2)$$

where $M_s(l)$ is crystal mass distribution and M_l is total mass of the solute. τ denotes the residence time and is inversely proportional to the volumetric flow rate F so that,

$$\tau = \frac{V_T}{F} \tag{3}$$

The nucleation rate Q and the growth rate G govern mass transfer rate in the crystallizer. The complete model for the crystallization process is shown in Definition 1.

Definition 1. The primary state variables of an isothermal crystallizer is given by:

$$Z = \begin{bmatrix} V_l, & M_l, & V_T, & M_s(l) \end{bmatrix}^T$$

where V_l is the liquid phase volume and V_T is total volume of the crystallizer. M_l denotes total mass of the solute whereas M_s is crystal mass distribution with respect to the diameter l. Their time evolutions are governed by

$$\frac{dV_T}{dt} = F_{in} - F$$

$$\frac{\partial M_s(l)}{\partial t} = -\frac{\partial}{\partial l} GM_s(l) + Q + \frac{6G}{l} M_s(l) - \frac{M_s(l)}{\tau}$$

$$\frac{dM_l}{dt} = F_{in}c_{in} - \frac{M_l}{\tau} - \int_{l_{min}}^{l_{max}} Q + \frac{6G}{l} M_s(l) dl$$

$$\frac{dV_l}{dt} = \frac{d}{dt} \left(V_T - \int_{l_{min}}^{l_{max}} \frac{M_s(l)}{\rho} dl \right)$$

3. THE ENTROPY FUNCTION

An entropy function is constructed to investigate the stability property of the crystallizer,

$$S(Z) = M_l \ln\left(\frac{ec_0 V_l}{M_l}\right) + \int_{l_{min}}^{l_{max}} M_s(l) \ln\left(\frac{em_0(l)V_T}{M_s(l)}\right) dl$$
(4)

where c_0 and m_0 are basis values for solute concentration on mass basis and crystal mass density to make S(Z) positive. e is the base of the natural logarithm. The conjugate variable of Z is obtained by

$$\omega(Z) = \frac{\partial S(Z)}{\partial Z}$$
$$= \left[\frac{M_l}{V_l}, \quad \ln\left(\frac{c_0 V_l}{M_l}\right), \quad \frac{M_s(l)}{V_T}, \quad \ln\left(\frac{m_0(l) V_T}{M_s(l)}\right)\right]^{\mathrm{T}}$$

Proposition 1. The entropy function S(Z) in (4) is homogeneous degree of 1 and concave. Furthermore

$$MZ = 0 \tag{5}$$

where $M = \frac{\partial^2 S(Z)}{\partial Z_i \partial Z_j}$ is a negative semi-definite Hessian matrix.

Proof 1. We first show that it is a homogeneous function by multiplying S with a scalar $\lambda > 0$

$$\begin{split} \lambda S(Z) &= \lambda M_l c_0 - \lambda M_l \ln \frac{M_l}{V_l} \\ &- \int\limits_{l_{min}}^{l_{max}} \left(\lambda M_s(l) m_0(l) - \lambda M_s(l) \ln \frac{M_s(l)}{V_T} \right) \mathrm{d}l \\ &= \lambda M_l c_0 - \lambda M_l \ln \frac{\lambda M_l}{\lambda V_l} \\ &- \int\limits_{l_{min}}^{l_{max}} \left(\lambda M_s(l) m_0(l) - \lambda M_s(l) \ln \frac{\lambda M_s(l)}{\lambda V_T} \right) \mathrm{d}l \\ &= S(\lambda Z) \end{split}$$

Next calculate the second order derivative of S(Z) with respect to Z,

$$M = \frac{\partial^2 S(Z)}{\partial Z_i \partial Z_j}$$
$$= \begin{bmatrix} -\frac{M_l}{V_l^2} & \frac{1}{V_l} & 0 & 0\\ \frac{1}{V_l} & -\frac{1}{M_l} & 0 & 0\\ 0 & 0 & -\frac{M_s(l)}{V_T^2} & \frac{1}{V_T}\\ 0 & 0 & \frac{1}{V_T} & -\frac{1}{M_s(l)} \end{bmatrix}$$

The eigenvalues of the symmetric matrix M are

$$\lambda = \left\{ 0, \quad -\frac{1}{M_l} - \frac{M_l}{V_l^2}, \quad 0, \quad -\frac{1}{M_s(l)} - \frac{M_s(l)}{V_T^2} \right\}$$

so that M is negative semi-definite and hence S(Z) is concave. Multiplying M by the primary state vector Z gives (5).

4. THE ENTROPY BASED DISTANCE FUNCTION

In order to measure the difference between any two neighboring trajectories of an isothermal crystallizer, we construct a distance function based on the entropy function. *Definition 2.* The entropy based distance function is defined as

$$\mathbf{D} = -\delta\omega^{\mathrm{T}}\delta Z + \delta Z^{\mathrm{T}}K_{c}\delta Z \tag{6}$$

where δZ is the distance between the primary states of two neighboring trajectories and is given as,

$$\delta Z = Z_1(t) - Z_2(t)$$

Correspondingly $\delta \omega$ is the distance between the conjugate variables of Z and is obtained as,

$$\delta\omega(Z,\delta Z) = \frac{\partial\omega}{\partial Z}\delta Z + \mathbf{O}(\|\delta Z\|^2)$$
(7)

A positive semi-definite matrix K_c is chosen so that K_c-M is positive definite.

Theorem 1. The distance function is in the form of

$$\mathbf{D} = \delta Z^{\mathrm{T}}(K_c - M)\delta Z + \mathbf{O}(\|\delta Z\|^3)$$
(8)

Moreover $\mathbf{D} > 0$ if $\|\delta Z\| \neq 0$; $\mathbf{D} = 0$ if $\|\delta Z\| = 0$. *Proof 2.* As the conjugate variable ω is defined

$$\omega = \frac{\partial S(Z)}{\partial Z}$$

and (7) shows that

$$\delta\omega = M\delta Z + \mathbf{O}(\|\delta Z\|^2) \tag{9}$$

Substitute it into Definition 2, we obtain (8). As K_c is selected so that $K_c - M$ is positive definite, we have

$$\begin{aligned} \mathbf{D} &> 0 & \forall \|\delta Z\| \neq 0 \\ \mathbf{D} &= 0 & \text{if } \|\delta Z\| = 0 \end{aligned}$$

Theorem 2. The time derivative of the distance function \mathbf{D} is given by

$$\frac{d\mathbf{D}}{dt} = -2\delta\omega^{\mathrm{T}}\frac{d}{dt}\delta Z + 2\delta Z^{\mathrm{T}}K_{c}\frac{d}{dt}\delta Z + \mathbf{O}(\|\delta Z\|^{2}) \quad (10)$$

Proof 3. We calculate the time derivative of \mathbf{D} in (6),

$$\frac{d\mathbf{D}}{dt} = -\delta\omega^{\mathrm{T}}\frac{d\delta Z}{dt} - \delta Z^{\mathrm{T}}\frac{d\delta\omega}{dt} + 2\delta Z^{\mathrm{T}}K_{c}\frac{d}{dt}\delta Z$$

Apply the chain rule to (9), we have

$$\frac{d\delta\omega}{dt} = \frac{d}{dt}(M\delta Z) + \mathbf{O}(\|\delta Z\|^2)$$
$$= \frac{dM}{dt}\delta Z + M\frac{d\delta Z}{dt} + \mathbf{O}(\|\delta Z\|^2)$$

Multiply it by δZ^{T}

$$\delta Z^{\mathrm{T}} \frac{d\delta\omega}{dt} = \delta Z^{\mathrm{T}} \frac{dM}{dt} \delta Z + \delta \omega^{\mathrm{T}} \frac{d\delta Z}{dt} + \mathbf{O}(\|\delta Z\|^{3})$$

We obtain its explicit form,

$$\frac{d\mathbf{D}}{dt} = -2\delta\omega^{\mathrm{T}}\frac{d}{dt}\delta Z - \delta Z^{\mathrm{T}}\frac{dM}{dt}\delta Z + 2\delta Z^{\mathrm{T}}K_{c}\frac{d}{dt}\delta Z + \mathbf{O}(\|\delta Z\|^{3})$$

Denote

$$\delta Z^{\mathrm{T}} \frac{dM}{dt} \delta Z \sim \mathbf{O}(\|\delta Z\|^2)$$

Then we have $\frac{d\mathbf{D}}{dt}$ as shown in (10).

In order to achieve the exponential convergence, we need to show that there exists a a > 0 so that

$$\frac{d\mathbf{D}}{dt} \le -a\mathbf{D}$$

5. APPLICATION FOR THE ISOTHERMAL CRYSTALLIZER

The distance of the process state Z is in the form of

$$\delta Z = \begin{bmatrix} \delta V_l, & \delta M_l, & \delta V_T, & \delta M_s(l) \end{bmatrix}^{\mathrm{T}}$$
(11)
we the crystallizer under investigation is constant-

Since the crystallizer under investigation is convolume, then δZ is simplified as

$$\delta Z = V_T \begin{bmatrix} \delta \epsilon, & \delta(\epsilon c), & 0, & \delta m(l) \end{bmatrix}^{\mathrm{T}}$$
(12)

Those primary variables are related to the secondary variables such as solute concentration c, crystal mass density m(l) and the liquid volume fraction ϵ as follows:

$$c = \frac{M_l}{V_l}$$
$$m(l) = \frac{M_s(l)}{V_T}$$
$$\epsilon = \frac{V_l}{V_T}$$

Substitute those constitutive relations into the conjugate variable ω in (5), we have

$$\omega = [c, \ln(c_0/c), m(l), \ln(m_0(l)/m(l))]^{\mathrm{T}}$$
(13)

The resulting variation of ω is thus in the form of

$$\delta\omega = \left[\delta c, \quad -\frac{\delta c}{c}, \quad \delta m(l), \quad -\frac{\delta m(l)}{m(l)}\right]^{1} + \mathbf{O}(\|\delta Z\|^{2})$$
(14)

The explicit forms of the distance function and its time derivative are given as,

$$\mathbf{D} = V_T \left(\frac{\epsilon}{c} \delta c \delta c + \int_{l_{min}}^{l_{max}} \frac{1}{m} \delta m \delta m dl \right) + \mathbf{O}(\|\delta Z\|^3) \quad (15)$$
$$\frac{d\mathbf{D}}{dt} = 2V_T \left(-\delta c \frac{d}{dt} \delta \epsilon + \frac{\delta c}{c} \frac{d}{dt} \delta(\epsilon c) + \int_{l_{min}}^{l_{max}} \frac{\delta m}{m} \frac{d}{dt} \delta m dl \right)$$
$$+ \mathbf{O}(\|\delta Z\|^2)$$

6. THE SUFFICIENT CONDITION FOR EXPONENTIAL CONVERGENCE

Before presenting the stability results, we make the following assumption on the nucleation and growth rates to facilitate further analysis.

Assumption 1. Assume that the crystal growth rate G only depends on the degree of supersaturation $c - c_s$:

$$G = g(c - c_s) \tag{16}$$

The nucleation rate Q is a function of the liquid volume fraction ϵ and the degree of supersaturation so that

$$Q = q(\epsilon, (c - c_s))\delta_D(l_{min}) \tag{17}$$

 $\delta_D(l_{min})$ is the Dirac delta function which represents that nucleation only occurs at l_{min} . Furthermore we assume that

$$k_1 = \frac{\partial G}{\partial c} > 0 \tag{18}$$

$$k_{2}^{'} = \frac{\partial Q(\epsilon, c - c_{s})}{\partial \epsilon} \ge 0 \tag{19}$$

$$k_2^{''} = \frac{\partial Q(\epsilon, c - c_s)}{\partial c} > 0 \tag{20}$$

It is worth noting that k_1 , k'_2 and k''_2 can be positive functions of c and ϵ , other than constants. Now we show the sufficient condition to guarantee exponential convergence of all the trajectories to a single trajectory. *Theorem 3.* The sufficient condition for exponential convergence of all the trajectories of an isothermal crystallizer is:

$$l_{min} \ge \frac{6k_1(c-c_s)}{\frac{1}{\tau} - \alpha} \tag{21}$$

$$L \le \min_{l} \left\{ \frac{4((1 - \frac{c}{\rho})(\epsilon k_{2}^{''} + \int_{l_{min}}^{l_{max}} \frac{6k_{1}m}{l} dl) + \frac{\epsilon}{\tau} - \epsilon\alpha)(\frac{1}{\tau} - \frac{6k_{1}(c - c_{s})}{l})}{cm((\frac{1}{c} - \frac{1}{\rho})(\frac{k_{2}^{'}}{\rho} - \frac{6k_{1}(c - c_{s})}{l}) + \frac{6k_{1}}{l} + \frac{\epsilon k_{2}^{''}}{m})^{2}} \right\}$$
(22)

where L denotes $l_{max} - l_{min}$. If the above conditions are satisfied then the storage function decays with an exponential rate α such that

$$\frac{d\mathbf{D}}{dt} < -2\alpha\mathbf{D}$$

The upper bound for the exponential decay rate α is

$$(1 - \frac{c}{\rho})(k_2'' + \frac{1}{\epsilon} \int_{l_{min}}^{l_{max}} \frac{6k_1m}{l} dl) + \frac{1}{\tau} \ge \alpha$$
(23)

If nucleation rate depends on the volume fraction ϵ then the foregoing conditions are only sufficient but not necessary.

Proof 4. We use the differential form of continuity equations in the appendix and combine like terms,

$$\frac{1}{V_T} \frac{d\mathbf{D}}{dt} = -\left(\left(\frac{1}{c} - \frac{1}{\rho}\right) \left(\int_{l_{min}}^{l_{max}} \frac{6k_1m}{l} dl + \epsilon k_2''\right) + \frac{\epsilon}{c} \frac{1}{\tau} \right) \delta c \delta c$$

$$+ \int_{l_{min}}^{l_{max}} \left(\left(\frac{1}{c} - \frac{1}{\rho}\right) \left(\frac{k_2'}{\rho} - \frac{6k_1(c - c_s)}{l}\right) + \frac{6k_1}{l} + \frac{\epsilon k_2''}{m} \right) \delta m \delta c dl$$

$$- \int_{l_{min}}^{l_{max}} \frac{1}{m} \left(\frac{1}{\tau} - \frac{6k_1(c - c_s)}{l}\right) \delta m \delta m dl$$

$$- \int_{l_{min}}^{l_{max}} \frac{k_2'}{\rho m} \delta m dl \int_{l_{min}}^{l_{max}} \delta m dl$$
(24)

For any given τ , we can choose a proper l_{min} and a small positive numbers α such that

$$\frac{1}{\tau} - \frac{6k_1(c-c_s)}{l} \ge \alpha \qquad \forall l$$

Rewrite $\frac{d\mathbf{D}}{dt}$ as

$$\frac{d\mathbf{D}}{dt} = -2\alpha\mathbf{D} + \Gamma \tag{25}$$

where

 $\frac{\Gamma}{V_T} = -\int_{l_{min}}^{l_{max}} \frac{\frac{1}{\tau} - \frac{6k_1(c-c_s)}{l} - \alpha}{m} \delta m \delta m \, \mathrm{d}l$

$$\frac{21}{l_{min}} + \int_{l_{min}}^{l_{max}} \left((\frac{1}{c} - \frac{1}{\rho})(\frac{k_2'}{\rho} - \frac{6k_1(c - c_s)}{l}) + \frac{6k_1}{l} + \frac{\epsilon k_2''}{m} \right) \delta m \delta c dl$$

$$\frac{\frac{6k_1(c - c_s)}{l}}{l} \\ \frac{\frac{6k_1(c - c_s)}{l}}{\frac{\epsilon_2'}{2})^2} \\ \left\{ - ((\frac{1}{c} - \frac{1}{\rho})(\int_{l_{min}}^{l_{max}} \frac{6k_1m}{l} dl + \epsilon k_2'') + \frac{\epsilon}{c\tau} - \frac{\epsilon \alpha}{c}) \delta c \delta c \right\}$$

$$-\int_{l_{min}} \frac{k_2}{\rho m} \delta m dl \int_{l_{min}} \delta m dl$$
(26)

Denote

$$\mu = \epsilon k_2^{''} + \int_{l_{min}}^{l_{max}} \frac{6k_1m}{l} \mathrm{d}l$$

Hence μ is positive. Rewrite $\frac{\Gamma}{V_T}$ as

$$\begin{split} \frac{\Gamma}{V_T} &= -\int\limits_{l_{min}}^{l_{max}} \frac{k_2'}{\rho m} \delta m dl \int\limits_{l_{min}}^{l_{max}} \delta m dl \\ &- \int\limits_{l_{min}}^{l_{max}} ((\frac{1}{c} - \frac{1}{\rho})\mu + \frac{\epsilon}{c\tau} - \frac{\epsilon\alpha}{c})/L\delta c\delta c \\ &+ (\frac{1}{\tau} - \frac{6k_1(c-c_s)}{l} - \alpha)/m\delta m\delta m \\ &- ((\frac{1}{c} - \frac{1}{\rho})(\frac{k_2'}{\rho} - \frac{6k_1(c-c_s)}{l}) + \frac{6k_1}{l} + \frac{\epsilon k_2''}{m})\delta m\delta c \ dl \\ &= - \int\limits_{l_{min}}^{l_{max}} \frac{k_2'}{\rho m} \delta m dl \int\limits_{l_{min}}^{l_{max}} \delta m dl - \int\limits_{l_{min}}^{l_{max}} \Lambda dl \end{split}$$

The sufficient and necessary condition to make matrix Λ positive semi-definite is

$$\frac{1}{L} \ge \max_{l} \frac{\left(\left(\frac{1}{c} - \frac{1}{\rho}\right)\left(\frac{k_2'}{\rho} - \frac{6k_1(c-c_s)}{l}\right) + \frac{6k_1}{l} + \frac{\epsilon k_2''}{m}\right)^2 m(l)}{4\left(\left(\frac{1}{c} - \frac{1}{\rho}\right)\mu + \frac{\epsilon}{c\tau} - \frac{\epsilon\alpha}{c}\right)\left(\frac{1}{\tau} - \frac{6k_1(c-c_s)}{l}\right)}$$

That condition ensures the negativeness of Γ .

In order to guarantee that L is positive, the denominator of max needs be positive, that means

$$(\frac{1}{c}-\frac{1}{\rho})\mu+\frac{\epsilon}{c\tau}\geq \frac{\epsilon\alpha}{c}$$

That provides the upper bound of α as shown in (24).

If the nucleation rate is independent of volume fraction ϵ , $\frac{d\mathbf{D}}{dt}$ is then simplified as

$$\begin{split} &\frac{1}{V_T}\frac{d\mathbf{D}}{dt} = -\int\limits_{l_{min}}^{l_{max}} \frac{1}{m} (\frac{1}{\tau} - \frac{6k_1(c-c_s)}{l}) \delta m \delta m \, \mathrm{d}l \\ &+ \int\limits_{l_{min}}^{l_{max}} \left((\frac{1}{c} - \frac{1}{\rho}) (-\frac{6k_1(c-c_s)}{l}) + \frac{6k_1}{l} + \frac{\epsilon k_2^{''}}{m} \right) \delta m \delta c \, \mathrm{d}l \\ &- \left((\frac{1}{c} - \frac{1}{\rho}) (\int\limits_{l_{min}}^{l_{max}} \frac{6k_1m}{l} \mathrm{d}l + \epsilon k_2^{''}) + \frac{\epsilon}{c} \frac{1}{\tau} \right) \delta c \delta c \end{split}$$

So if the symmetric matrix Λ is positive semi-definite, the system is exponentially convergent. The sufficient and necessary condition to make Λ positive semi-definite is given in (22) and (23).

7. NUMERICAL EXPERIMENTS

We carry out numerical experiments to verify the analytical conditions of exponential stability for continuous crystallizer. The sufficient and necessary condition is about the size that nucleation occurs and the largest possible size crystals grow. The nuclei size for stable operation can be calculated using (22). Unfortunately it is difficult to obtain the exact value of the upper bound for the largest size based on (23). Numerical study demonstrates that simulation results are in good agreement with the analytical conditions derived in the previous section. The process parameters and physical properties are listed in the table. As we derive two analytical conditions to guarantee

Table 1. Simulation parameters

Variables	Meanings	Values
c_{in}	inlet concentration of solute	$1000 \ mol/m^3$
c_s	saturation concentration	$980.2 \ mol/m^{3}$
ho	crystal density	$1770 \ kg/m^{3}$
au	crystal residence time	0.05 h
k_1	constant for growth	$0.05065 \ m^4/kg \cdot h^4$
k_2	constant for nucleation	$7.958 \ h^{-1}$
k_3	dimensionless constant for nucleation	0.001217

Table 2. Nomenclature

Variables	Meanings	Units
l	crystal diameter	\overline{m}
m(l)	mass density distribution of crystals	kg/m^3
M_s	total mass of crystals	Kg
M_l	total mass of liquid	Kg
V_T	crystallizer volume	m^{3}
V_l	total volume of mother liquid	m^3
ϵ	volume fraction of mother liquid	
c	concentration of mother liquid	kg/m^3
F	volumetric withdrawal rate	m^3/s
F_{in}	volumetric feeding rate	m^3/s
c_s	saturation concentration	mol/m^3
ho	crystal density	kg/m^3
au	crystal residence time	s

convergence, simulations are conducted based on three different scenarios based on the same initial conditions: (a) Both inequality (22) and (23) are satisfied so that we have stable open-loop dynamics as in Fig. 1. The initial condition is $c(t = 0) = 981 mol/m^3$ and m(l, t = 0) = 0. (b) Inequality (22) holds while inequality (23) is not valid. Self-sustained oscillations occur as shown in Fig. 2. The



Fig. 1. The stable dynamics of an isothermal crystallizer when two conditions are satisfied



Fig. 2. The oscillatory dynamics of an isothermal crystallizer when only the condition in inequality (22) is satisfied



 $g \cdot F$ ig. 3. The oscillatory dynamics of an isothermal crystallizer when neither of the two conditions is satisfied

-initial condition is $c(t = 0) = 981 mol/m^3$ and m(l, t = 0) = 0.

(c) Neither of the two conditions hold so that self-sustained oscillations appear, seen in Fig. 3. The initial condition is $c(t = 0) = 981 mol/m^3$ and m(l, t = 0) = 0.

8. CONCLUSION

We derive the sufficient and necessary conditions for the convergence of all the trajectories in a continuous crystallizer to a time-varying equilibrium point. Regardless of initial conditions and temporary disturbances, all the trajectories converge to a nominal motion that is not necessarily known ahead of time. The relations between particle size and stability is revealed by an explicit analytical expression. A generalized distance function is constructed so that the stability result can be easily extended to particulate processes.

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Appendix A. THE MODEL IN DIFFERENTIAL FORM

Lemma 1. The differential form of continuity equations on the basis of mass density of crystals and solute is written as

$$\frac{\partial \delta m(l)}{\partial t} + \frac{\partial}{\partial l} \delta(Gm(l)) = k_2' \delta \epsilon + \epsilon k_2'' \delta c - \frac{1}{\tau} \delta m(l) + \frac{6k_1 (c - c_s)}{l} \delta m(l) + \frac{6k_1 m}{l} \delta c$$
(A.1)

$$\frac{d}{dt}\delta(\epsilon c) = \int_{l_{min}}^{l_{max}} \left(\frac{k_2'}{\rho} + \frac{c}{\rho\tau} - \frac{6k_1(c-c_s)}{l}\right) \delta m$$
$$- \left(\frac{\epsilon k_2'' + \frac{\epsilon}{\tau}}{l_{max} - l_{min}} + \frac{6k_1m}{l}\right) \delta c \, \mathrm{d}l \qquad (A.2)$$

The rate of the change of the liquid volume fraction is

$$\rho \frac{d}{dt} \delta \epsilon = \int_{l_{min}}^{l_{max}} -k_2^{'} \delta \epsilon - \epsilon k_2^{''} \delta c - \frac{6k_1 m}{l} \delta c - (\frac{6k_1 (c-c_s)}{l} - \frac{1}{\tau}) \delta m \, \mathrm{d} l$$
(A.3)

Proof 5. Total mass transfer rate from liquid to solid phase is the sum of the growth and nucleation rates,

$$Q + \int_{l_{min}}^{l_{max}} \frac{6G}{l} m(l) dl = \frac{d}{dt} \int_{l_{min}}^{l_{max}} m(l) dl + \frac{1}{\tau} \int_{l_{min}}^{l_{max}} m(l) dl + \int_{l_{min}}^{l_{max}} \frac{\partial}{\partial l} Gm(l) dl \qquad (A.4)$$

The relation between the liquid volume fraction and crystal mass density is given by

$$\frac{d}{dt} \int_{l_{min}}^{l_{max}} m(l) dl = -\rho \frac{d\epsilon}{dt}$$
$$\frac{1}{\tau} \int_{l_{min}}^{l_{max}} m(l) dl = \frac{\rho}{\tau} (1 - \epsilon)$$

Substituting those relationships into equation (A.4), total mass transfer rate is

$$Q + \int_{l_{min}}^{l_{max}} \frac{6G}{l} m(l) dl = -\rho \frac{d\epsilon}{dt} + \frac{\rho}{\tau} (1-\epsilon)$$

That simplifies solute mass balance in equation (2) as

$$\frac{d}{dt}(\epsilon c) = \frac{F_{in}}{V_T}c_{in} - \frac{1}{\tau}\epsilon c - (1-\epsilon)\frac{\rho}{\tau} + \rho\frac{d\epsilon}{dt}$$

The differential forms for the mass balances of the crystals and the solute are

$$\frac{\partial \delta m(l)}{\partial t} + \frac{\partial}{\partial l} \delta(Gm(l)) = \delta Q + \frac{6}{l} \delta(Gm(l)) - \frac{1}{\tau} \delta m(l)$$
$$\frac{d}{dt} \delta(\epsilon c) = \rho \frac{d\delta \epsilon}{dt} - \frac{1}{\tau} \delta(\epsilon c) + \frac{\rho}{\tau} \delta \epsilon + \frac{1}{\tau} \delta c_{in}$$

The constitutive relations are given as,

$$\delta \epsilon = -\frac{1}{\rho} \int_{l_{min}}^{l_{max}} \delta m(l) dl$$

$$\delta(Gm(l)) = k_1(c - c_s) \delta m(l) + k_1 m(l) \delta c$$

$$\delta Q = k_2 \exp\left(-\frac{k_3 c_s^2}{(c - c_s)^2}\right) \delta \epsilon$$

$$+ \epsilon k_2 \exp\left(-\frac{k_3 c_s^2}{(c - c_s)^2}\right) \frac{2k_3 c_s^2}{(c - c_s)^3} \delta c$$

The time derivative of $\delta \epsilon$ is

$$\rho \frac{d}{dt} \delta \epsilon = -\int_{l_{min}}^{l_{max}} \delta Q + \frac{6}{l} \delta \left(Gm \right) - \frac{\delta m}{\tau} \mathrm{d}l$$

Substituting these constitutive relations into it, we get the complete differential form of the solute.