Dynamics and control of continuous reactive crystallization processes

Hsing-Yu Wang, Jeffrey D. Ward*

Department of Chemical Engineering, National Taiwan University, Taipei 106-07, Taiwan

ARTICLE INFO

ABSTRACT

Control of two continuous reactive crystallization processes, one for the production of barium sulfate and one for the production of L-glutamic acid, is investigated. In both processes, the crystal mass production rate and the volume mean size of the product are controlled by manipulating the reactant inlet volumetric flow rates and the holdup in the crystallizer. The reactant inlet concentration, nucleation rate, and temperature of the crystallizer are considered as disturbances. The control structures provide good performance for 10% changes in disturbance variables and setpoint changes. Furthermore, stability analysis is performed for both processes and operating regions where continuous oscillations in solute concentration and crystal size distribution can occur are identified.

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1. Introduction

Crystallization is often used for solid-liquid separation and purification to produce chemical and pharmaceutical products. Solid crystal products with desired purity, size, and shape can be obtained from an impure feed solution. Recently, continuous crystallization processes have received increasing interest and research effort [1], as companies have sought to increase efficiency and reduce cost.

Though many researchers have studied the control of continuous crystallization processes [2–5], challenges remain due to nonlinearities and complex interactions between phenomena such as nucleation and growth. Most continuous crystallization processes are still designed and controlled based on time-consuming trial-and-error experimentation. [3]

In some cases, reactants that are soluble in some solvent combine to form a product that is sparingly soluble. In this case it is attractive to combine reaction and crystallization in a single step. Reactive crystallization processes have been widely studied by simulation and experiment in the literature. [2,6–9] Many studies focused on determination of crystallization kinetic parameters and simulation of the crystallization process, but only a few have studied design and control of continuous reactive crystallization processes.

Therefore, in this work, feedback control of continuous reactive crystallization processes is studied using two case study systems which are model systems for reactive crystallization that are widely-studied in the literature: production of barium sulfate

[7–14] and production of L-glutamic acid [2,6,15–21]. The remainder of this article is organized as follows: in Section 2, models for the two case studies are presented. In Section 3, results are drawn for both case studies and finally in Section 4 conclusions are presented.

2. Model development

2.1. Model equations for continuous reactive crystallization

For a well-mixed continuous crystallization process neglecting agglomeration and breakage, the population balance equation is [22]

$$\frac{\partial (V(t)n(t,x))}{\partial t} = -\frac{\partial (V(t)G(t,x)n(t,x))}{\partial x} + \dot{V}_{in}(t)n_i(t,x) - \dot{V}_{out}(t)n(t,x) \qquad (1)$$

subject to the left boundary condition: $n(t,0) = B(t)/G(t)$. Here, $V(t)$ is crystallizer volume (m^3), $n(t,x)$ is crystal size distribution (CSD) function (#/m^3−m), $G(t)$ is the crystal growth rate (m/s), $B(t)$ is the nucleation rate (#/m^{3}s), $\dot{V}_{in}(t)$ is the inlet flow rate (m^3/s), $\dot{V}_{out}(t)$ is the outlet flow rate (m^3/s), $n_i(t,x)$ is the inlet CSD function, x is the crystal size (m), and t is time (s).

At steady-state, assuming the growth rate is size-independent, and no crystals are present in the input stream, the population balance equation can be simplified to:

$$0 = -VG\frac{\partial (n(x))}{\partial x} - \dot{V}_{out}n(x) \qquad (2)$$

Integrating Eq. (2) using the boundary condition generates the CSD of a continuous mixed-suspension, mixed-product-removal

* Corresponding author. Tel.: +886 2 3366 3037; fax: +886 2 2369 1314.
  E-mail address: jeffward@ntu.edu.tw, jeffward97@gmail.com (J.D. Ward).

(MSMPR) crystallizer

$$n(x) = \frac{B}{G}e^{-\frac{x}{G\tau}} \tag{3}$$

where $\tau = V/\dot{V}_{out}$ is the residence time (s).

The definition of the moments is:

$$\mu_i(t) = \int_0^\infty x^i n(t,x)dx, i = 0, 1, 2, \ldots \tag{4}$$

where μ_0, μ_1, μ_2, μ_3, are the zeroth, first, second, third moments which are related to the total number, total length, total surface area, and total volume of the crystals. The time derivatives of the moments for a continuous crystallizer if growth rate is size-independent and volume may change with time are

$$\frac{d(\mu_0 V)}{dt} = BV - \mu_0 \dot{V}_{out} \tag{5}$$

$$\frac{d(\mu_i V)}{dt} = iGV\mu_{i-1} - \mu_i \dot{V}_{out}, i = 1, 2, \ldots \tag{6}$$

2.2. Case study systems

Two case study systems are investigated in this work: production of barium sulfate (model modified from Wei and Garside [23]) and production of L-glutamic acid (model modified from Borissova [6] and Scholl [20,21]). The model equations for both systems are summarized in this section.

2.2.1. Production of barium sulfate

Mass balance equations for a continuous reactive crystallization process to produce barium sulfate are adapted from Wei and Garside [23]. It is assumed that the rate of reaction is nearly instantaneous (much faster than crystal growth) so expressions for the reaction rate are not provided. Two inlet streams are continuously fed into the system: barium chloride solution and sodium sulfate solution, and an outlet stream is continuously withdrawn with barium sulfate crystals. The chemical reaction is:

$$Ba^{2+}_{(l)} + SO^{2-}_{4(l)} \rightarrow BaSO_{4\,(s)} \downarrow \tag{7}$$

and the component balance equations for this system are:

$$\frac{d(C_{Ba^{2+}}V)}{dt} = C_{BaCl_2,in}\dot{V}_{BaCl_2,in} - C_{Ba^{2+}}\dot{V}_{out} - \frac{k_v \rho_C}{M_{BaSO_4}}\frac{d(\mu_3 V)}{dt} \tag{8}$$

$$\frac{d(C_{SO_4^{2-}}V)}{dt} = C_{Na_2SO_4,in}\dot{V}_{Na_2SO_4,in} - C_{SO_4^{2-}}\dot{V}_{out} - \frac{k_v \rho_C}{M_{BaSO_4}}\frac{d(\mu_3 V)}{dt} \tag{9}$$

$$\frac{d(C_{BaSO_4}V)}{dt} = -C_{BaSO_4}\dot{V}_{out} + \frac{k_v \rho_C}{M_{BaSO_4}}\frac{d(\mu_3 V)}{dt} \tag{10}$$

$$\frac{dV}{dt} = \dot{V}_{BaCl_2,in} + \dot{V}_{Na_2SO_4,in} - \dot{V}_{out} \tag{11}$$

where $C_{Ba^{2+}}$ is the barium ion concentration (kmol/m^3), $C_{SO_4^{2-}}$ is the sulfate ion concentration (kmol/m^3), $C_{BaCl_2,in}$ is the inlet concentration of barium chloride stream (kmol/m^3), $C_{Na_2SO_4,in}$ is the inlet concentration of the sodium sulfate stream (kmol/m^3), $\dot{V}_{BaCl_2,in}$ is the inlet flow rate of the barium chloride stream (m^3/s), $\dot{V}_{Na_2SO_4,in}$ is the inlet flow rate of the sodium sulfate stream (m^3/s), k_v is the volumetric shape factor of barium sulfate crystals (-), ρ_C is the density of solid barium sulfate (kg/m^3), and M_{BaSO_4} is the molecular weight of barium sulfate (kg/kmol).

Because barium sulfate is an ionic compound, the thermodynamic supersaturation ratio S_a is used and is defined as:

$$S_a = [(c_+^{\upsilon+}c_-^{\upsilon-})/K_{sp}]^{1/\upsilon} \tag{12}$$

Table 1
Parameters in the barium sulfate crystallization process model.

| Description	Symbols	Value	Unit
For $S_a \geq 10^3$			
Nucleation rate parameter	A	2686	–
Nucleation rate coefficient	B_0	10^{36}	no./(m^3 s)
For $S_a < 10^3$			
Nucleation rate parameter	A	67.3	–
Nucleation rate coefficient	B_0	1.46×10^{12}	no./(m^3 s)
Growth rate coefficient	k_g	4.0×10^{-11}	m/s
Growth rate order	g	2	–
Density of crystals	ρ_{BaSO4}	4480	kg/m^3
Density of BaCl$_2$ solution	$\rho_{BaCl2(aq)}$	1154	kg/m^3
Density of Na$_2$SO$_4$ solution	$\rho_{Na2SO4(aq)}$	1088.7	kg/m^3
Volumetric shape factor	k_v	$\pi/6$	–
Molecular weight	M_{BaSO4}	233.4	kg/kmol
Crystallizer diameter	d	1	m
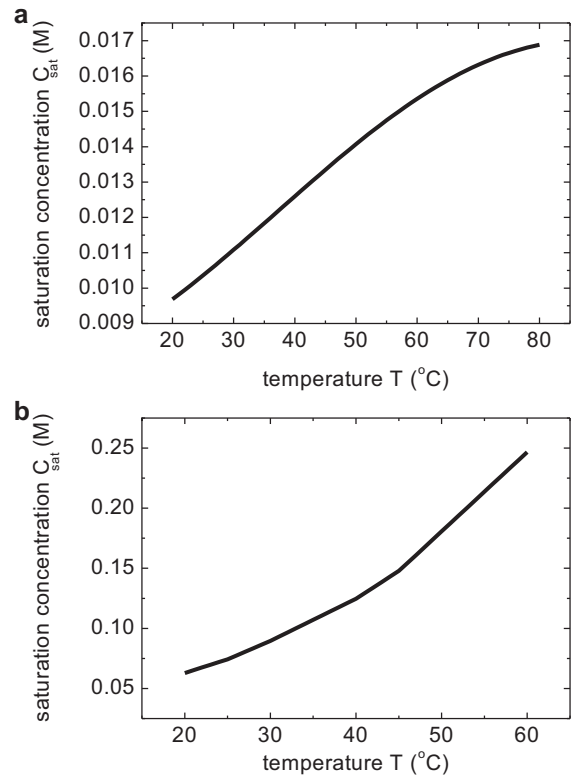
Fig. 1. Solubility as a function of temperature for (a) barium sulfate system and (b) L-glutamic acid system.

where c_+ is cation concentration dissolved in the solution (M), c_- is anion concentration dissolved in the solution (M), υ^+ and υ^- are number of moles of cations and anions respectively if 1 mol solute is dissolved in the solution, and υ is the number of moles of ions if 1 mol of solute is dissolved in the solution.

Semi-empirical power-law expressions are used for the growth rate kinetics and nucleation rate kinetics:

$$G = k_g(S_a - 1)^g \tag{13}$$

$$B = B^0 \exp[-A/\ln^2 S_a] \tag{14}$$

Values of parameters in these equations are given in Table 1 with some values taken from the literature [23]. The solubility as a function of temperature is shown is Fig. 1.