Dynamic Simulation and Optimization of Population Balance Model for Gas Anti-solvent Recrystallization Process


* School of Chemical and Biological Engineering, Institute of Chemical Processes, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 151-744, Republic of Korea

** High Explosives Team, Agency for Defense Development, 462, Jochiwon-gil, Yuseng-gu, Daejeon 305-600, Republic of Korea

Abstract: Crystallization processes are widely used in various applications such as polymers, dyes, pharmaceuticals, and explosives. Novel crystallization processes using supercritical fluids have recently attracted much attention due to the environmental advantage of using environmentally benign carbon dioxide as a solvent. Gas anti-solvent (GAS) process is one of the most common supercritical processes, which utilize the low solubility of the anti-solvent to produce particles. In this work, a mathematical model from a population balance model (PBM) is developed to describe the particle size distribution (PSD) of GAS process and it is numerically solved. The developed PBM involves a set of partial differentials equation with algebraic constraints, which requires effective numerical approaches. A solution scheme based on a high resolution method is proposed to solve the dynamic problem using MATLAB. In addition, the effect of the supercritical CO$_2$ addition rate is investigated. At last, we present the results of open-loop test for the system and propose a nonlinear model predictive control (NMPC) strategy to control the particle size distribution of the GAS process.

1. INTRODUCTION

Crystallization processes have a significant role in producing various chemical products such as polymers, dyes, pharmaceuticals, and explosives. These applications require particles with controlled size and uniform morphology. A narrow particle size distribution (PSD) is one of the requirements. Therefore, controlling the particle size distribution is an important problem in crystallization processes.

Though conventional crystallization techniques have been well established, they have a critical disadvantage that fairly large amounts of toxic solvents are needed for crystallizing and washing processes. New techniques using supercritical fluids overcome this weakness since they use environmentally benign solvents such as carbon dioxide. In addition, supercritical fluids have favorable properties including relatively low viscosity and high diffusivities compared to liquids. These features make the system more convenient to operate. Particle formation processes using supercritical fluids contain rapid expansion of supercritical solutions (RESS) and gas anti-solvent (GAS) recrystallization. In RESS process, particles are initially dissolved in a solvent at high temperature and pressure. It is then heated under supercritical conditions and allowed to expand rapidly through a nozzle into a region of low pressure and temperature which results in the dissolved material precipitating as a fine powder. On the other hand, GAS process initially has loading solution dissolved with the solute. Then, supercritical CO$_2$ is injected into the vessel to crystallize particles which are collected after the process is completed.

In this work, a dynamic model for GAS process is developed and the simulation results are shown. We also examine on optimal control scheme for controlling the particle size distribution in GAS process. Modeling the GAS crystallization process is already proposed in Muhrer [2002]. They modeled the GAS process based on the population balance model (PBM) with the material balance equations. The mathematical model and simulation results of the GAS process is also reported in Dodds [2007] and Bakhbakhi [2009]. However, the study for controlling the particle size distribution in the GAS process is still limited.

While Sheikhzadeh [2008] presents a real-time optimal control method and Nowee [2008] suggests a model-based optimal strategy for anti-solvent crystallization process, optimal control and dynamic simulation of GAS process have not been studied yet. Consequently, we describe the modeling procedure for the GAS process and present an optimal control scheme based on nonlinear model predictive control (NMPC).

This article is organized as follows. Section 2 describes the GAS process modeling procedure based on PBM and presents the solution approach and simulation results. Section 3 provides open-loop test results and a nonlinear model predictive control strategy. Finally, concluding remarks are provided.
2. MATHEMATICAL MODELING AND SIMULATION

2.1 Modeling Procedure

GAS process is schematically described in Fig. 1. The semibatch precipitator with constant volume, V, has one inlet to which the supercritical CO$_2$ is injected and the solution with the dissolved solute is initially loaded in the precipitator. It is assumed that the pressures at gas and liquid phases have the same value during crystallization and the temperature in the vessel is maintained at constant in space so that no energy balance is needed. Besides, the mass transfer between gas and liquid phases is ignored and aggregation and breakage contribution of particles are also neglected.

The general population balance model is in the form of

$$\frac{\partial n}{\partial t} + G \frac{\partial n}{\partial L} = B(L) - D(L)$$  \quad (1)

where $n(t,L)$ [m$^{-4}$] is the population density function which represents the particle size distribution given by $n(t,L)dL$, the number of particles in the size between $L$ and $(L + dL)$ per unit volume of the solution; $G$ [m/s] is the growth rate of particles; and $B(L)$ [m$^{-4}$/s] and $D(L)$ [m$^{-4}$/s] are the birth and death rates of particles, respectively. Disregard for aggregation and breakage of particles contributed to the birth and the death terms simplifies the above equation to

$$\frac{\partial n}{\partial t} + G \frac{\partial n}{\partial L} = 0$$  \quad (2)

Here, we add the third term related to the thermodynamics, thus the equation can be written as (Muhrer [2002])

$$\frac{\partial n}{\partial t} + G \frac{\partial n}{\partial L} + \frac{n}{N_L v_L} \frac{d(N_L v_L)}{dt} = 0$$  \quad (3)

$N_L v_L$ indicates the liquid phase volume, given by the molar hold-up in the liquid phase, $N_L$ [mol], and the molar volume of the liquid phase, $v_L$ [m$^3$/mol]. This term is necessary because the liquid phase volume rapidly expands as the supercritical CO$_2$ is injected to the crystallizer and particle formation occurs in the liquid phase. Finally, PBM describing the GAS process can be obtained as a form of the partial differential equation.

The material balances on the anti-solvent, the solvent, and the solute are given by the following equations

$$\frac{d(N_L x_A + N_V y_A)}{dt} = Q_A$$  \quad (4)

$$\frac{d(N_L x_S + N_V y_S)}{dt} = 0$$  \quad (5)

$$\frac{d(N_P x_P + N_P)}{dt} = 0$$  \quad (6)

where $N_V$ [mol] and $N_P$ [mol] are the molar hold-up in gas and solid phases, respectively; $x_i$ and $y_i$ are the mole fraction of component $i$ in liquid and vapor phases, respectively ($i = A, S, P$); $Q_A$ [mol/s] is the molar flow rate of the anti-solvent. $N_P$ is given by

$$N_P = \frac{N_L v_L k_v m_3}{v_p}$$  \quad (7)

where $k_v$, $v_p$, and $m_3$ are the volume shape factor, the molar volume of the solid phase, and the third moment of the population density function, $n$, respectively. The third moment of the density function is calculated according to the general definition of the ith order moment of a distribution

$$m_i = \int_0^{L_{max}} L^i n(L)dL \quad (i = 3)$$  \quad (8)

The initial condition is entirely arbitrary and may be any realistic population density. The boundary condition for the population balance equation is given as

$$n(t,0) = \frac{B}{G} \quad (t > 0)$$  \quad (9)

where $B$ and $G$ are the nucleation rate and the growth rate, respectively, which are given by the following equations

$$B = B' + B'' \quad (S > 1)$$  \quad (10)

$$B' = 1.5 D(c_p N_A)^{7/3} \sqrt{\frac{\gamma}{kT N_A}} \frac{v_p}{\kappa} \exp \left[ -16\pi \left( \frac{\gamma}{kT} \right)^3 \left( \frac{v_p}{N_A} \right) \left( \frac{1}{\ln S} \right)^2 \right]$$  \quad (11)

$$B'' = \alpha'' a_v D \frac{c_p}{D_M} \exp \left[ -\pi \left( \frac{d_M^2}{kT} \right)^2 \frac{1}{\ln S} \right]$$  \quad (12)

$$c_p = \frac{x_p}{v_L}$$  \quad (13)

$$a_v = k_a n_2$$  \quad (14)

$$D = \frac{kT}{2 \pi \eta d_M}$$  \quad (15)

$$d_M = \frac{\sqrt{v_p}}{N_A}$$  \quad (16)

$$G = K_g (S - 1)^g \quad (S > 1)$$  \quad (17)

where $B'$ is the primary nucleation rate, $B''$ is the secondary nucleation rate, $c_p$ is the solute concentration, $k$ is the Boltzman constant, $\gamma$ is the interfacial tension, $N_A$ is Avogadro’s number, $\alpha''$ is the secondary nucleation rate effectiveness factor, $a_v$ is the specific surface area, $k_a$ is the...
Fig. 2. Finite volume grid

surface shape factor, \( m_2 \) is the second moment of the density function, \( D \) is the solute diffusion coefficient, \( \eta \) is the dynamic viscosity, \( d_M \) is the molecular diameter, and \( k_g \) is the rate constant in the growth rate. The supersaturation is given as

\[
S = \frac{f_{P,L}}{f_{P,P}} \quad (18)
\]

\[
f_{P,P} = f_{P,P}^{0} \exp \left( \frac{v_P (P - P_0)}{RT} \right) \quad (19)
\]

\[
f_{P,L} = f_{P,L}^{0} (P_0, T, x_0) \quad (20)
\]

Thermodynamic behavior of the GAS process is of importance because it determines the supersaturation of the solute. The volumetric expansion of the liquid phase is described by Peng-Robinson equation of state

\[
P = \frac{RT}{v - b} - \frac{a}{v^2 + 2vb - b^2} \quad (21)
\]

\[
a = \sum_i \sum_j x_i x_j a_{ij} \quad (22)
\]

\[
a_{ij} = (1 - k_{ij}) \sqrt{a_i a_j} \quad (23)
\]

\[
b = \sum_i \sum_j x_i x_j b_{ij} \quad (24)
\]

\[
b_{ij} = (1 - l_{ij}) \left( \frac{b_i + b_j}{2} \right) \quad (25)
\]

where \( k_{ij} \) and \( l_{ij} \) are binary interaction coefficients and \( a_i \) and \( b_i \) are related to the critical properties of the pure component

\[
a_i = \frac{0.45724RT_c^2}{P_c} \left[ 1 + \alpha \left( 1 - \left( \frac{T}{T_c} \right)^{1/2} \right) \right]^2 \quad (26)
\]

\[
b_i = \frac{0.07780RT_c}{P_c} \quad (27)
\]

\[
\alpha = 0.37464 + 1.54226 \omega_i - 0.26992 \omega_i^2 \quad (28)
\]

where \( \omega \) is the acentric factor, \( T_c \) and \( P_c \) are the pure component’s critical temperature and pressure, respectively.

\[\text{Equation (3) can be written as the following semi-discrete equation}\]

\[
\frac{\partial n_i}{\partial t} + \frac{1}{\Delta L_i} \left( (Gn)_{i+1/2} - (Gn)_{i-1/2} \right) + \frac{n_i}{(N_{L} v_{L})_i} d(N_{L} v_{L})_i = 0, \quad i = 1, ..., N
\]

The fluxes \( (Gn)_{i+1/2} \) and \( (Gn)_{i-1/2} \) at the boundaries of the control volume are calculated from

\[
(Gn)_{i+1/2} = G_{i+1/2} \left( n_i + \frac{\Delta L_i}{2 \Delta L_i -(1/2)} \phi^\tau (n_{i+1} - n_i) \right) \quad (30)
\]

\[
(Gn)_{i-1/2} = G_{i-1/2} \left( n_{i-1} + \frac{\Delta L_i}{2 \Delta L_i -(1/2)} \phi^\tau (n_i - n_{i-1}) \right) \quad (31)
\]

where

\[
\theta^\tau_i = \frac{n_i - n_{i-1} + \epsilon}{n_{i+1} - n_i + \epsilon} \quad (32)
\]

and

\[
\theta^-_i = \frac{n_{i-1} - n_{i-2} + \epsilon}{n_{i} - n_{i-1} + \epsilon} \quad (33)
\]

The limiting function \( \phi \) is given by

\[
\phi(r) = \frac{|r| + r}{1 + |r|} \quad (34)
\]

The GAS process model obtained from the previous section can be entirely solved with model parameters. However, since the thermodynamic data for the target material, HMX, is insufficient, we use the experimental data for the values of the pressure, the liquid phase volume, and the supersaturation. In the experiment, the pressure varies from 1 to 100 bar, and the temperature is maintained at 31.5 °C. The supercritical CO₂ addition rate lies between 1 and 100 ml/min, and the crystallization is run for 60 s.

2.3 Simulation Results

The GAS crystallization process is simulated for 1 minute with constant input values. The size of actual particles formed ranges from 1 μm to 100 μm and the size of the mesh is chosen to be 1 μm. Computations are performed using MATLAB. Simulation results are shown in Fig. 3. The supercritical CO₂ addition rate varies from 10, 50, to 100 ml/min. As shown in Fig. 3, the particle size distribution becomes narrower and the average particle size is reduced as the CO₂ addition rate increases. Figs. 4, 5, and 6 show 3D plots at each addition rate.

3. OPTIMIZATION AND CONTROL SCHEME

Crystallization process is highly nonlinear and complex, rendering it difficult to control the system. Accordingly, a nonlinear model predictive control strategy is developed for the GAS crystallization process. Before applying the control scheme to this process, we present the results of the optimal open-loop test for the GAS process.
In this system, the input variable is the supercritical CO₂ addition rate and the output variable is the particle size distribution. The CO₂ addition rate is changed between 1, 50, and 100 ml/min (Fig. 7), and we observe the final distributions after 60 s. The open-loop test results are shown in Fig. 8. When the initial CO₂ addition rate is slow, although the rate increases afterwards, the particle size distribution does not change significantly from the PSD with the addition rate at 1 ml/min throughout. The average particle size is almost the same while the addition rate decreases from 100 ml/min to 1 ml/min as observed in cases of input profiles 1 and 2.

3.2 Nonlinear Model Predictive Control (NMPC) Strategy

In this section, the NMPC strategy based on extended predictive self-adaptive control (EPSAC) is developed for the GAS crystallization process by Hermanto [2009]. Nagy
This work was financially supported by Agency for Defense Development of South Korea.

REFERENCES


