

Indian Institute of Technology, Kharagpur

Optimal Control of Seeded Batch Crystallizer

by

Author Name

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degree of Doctor of Philosophy

in the

Faculty Name

Department of Chemical Engineering

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The Thesis Abstract is written here (and usually kept to just this page). The page is kept centered vertically so can expand into the blank space above the title too...

Acknowledgements

The acknowledgements and the people to thank go here, don't forget to include your project advisor...

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Chapter 1

Introduction

Batch crystallization is widely used in chemical, pharmaceutical, photographic, and other manufacturing processes for the preparation of crystalline products with several desirable attributes.

The batch system helps to obtain a narrower Particle size distribution (PSD) with high crystal purity. The crystallization process has an influence on the downstream processing and, hence, reproducible PSD in each operation is of prime importance. Thus, it is essential to find the variables affecting the process and control them within an acceptable range, so as to satisfy the final product quality requirements. Considering the operation of crystallizers, a batch process is preferable as a larger mean crystal size and narrower Crystal size distribution (CSD) can be achieved. In general, the CSD which is typically characterized by the mean and variance of crystal size is a key property to control this process because it directly affects final product qualities. Therefore, finding effective control strategy to obtain the crystals with a desired CSD is significant in order for improving the performance of batch crystallization processes and at the same time reducing difficulties in downstream processing. In the following work we formulate the problem using the population balance equations and obtain the solution for the optimal Temperature profile using Deterministic and Probabilistic methods

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1.1 Previous Work

The concept of programmed cooling in batch crystallizers was first discussed by Mullin and Nyvlt [1] in 1971. They studied the laboratory-scale crystallization of potassium sulfate and ammonium sulfate using a temperature controller and observed improvement in the crystal size and quality under programmed cooling.

Later, in 1974, A. G. Jones [2] presented a mathematical theory based on moment transformations of population balance equations. He used the continuous maximum principle to predict optimal cooling curves. Rawlings et al. [3] discussed issues in crystal size measurement using laser light scattering experiments and optimal control problem formulation. In 1994, Miller and Rawlings [4] discussed the uncertain bounds on model parameter estimates for a batch crystallization system.

Most importantly optimal temperature prediction for batch crystallization has also been done by Hu et al.[5], Shi et al.[6], Paengjuntuek et al.[7], and Corriou and Rohani.[?]], the data and knowledge from which have been used in further work in this project . Grosso et al.[?]] presented a stochastic approach for modeling PSD and comparative assessments of different models. Ma et al.[?]] presented a worse-case performance analysis of optimal control trajectories by considering features such as the computational effort, parametric uncertainty and control implementation inaccuracies.

The focus of the current work is to be able to handle parametric uncertainties in mathematical formulations of batch crystallization process.

Chapter 2

Theory

Crystallization is the (natural or artificial) process where a solid forms where the atoms or molecules are highly organized in a structure known as a crystal. Some of the ways which crystals form are through precipitating from a solution, melt or more rarely deposited directly from a gas.

Crystal shapes can include cubic, tetragonal, orthorhombic, hexagonal, monoclinic, triclinic, and trigonal. In order for crystallization to take place a solution must be "supersaturated". Supersaturation refers to a state in which the liquid (solvent) contains more dissolved solids (solute) than can ordinarily be accommodated at that temperature.

Supersaturation, can be mathematically defined as :

$$\text{Supersaturation} = \Delta C = C - C_s$$

$$\text{Relative Supersaturation} = \Delta C / C_s$$

C_s : Concentration of solute in saturated solution

C : Concentration of solute in the solution

S : Supersaturation ratio

The crystallization process consists of two major type of kinetics, *nucleation* and *crystal growth* which are driven by thermodynamic properties as well as chemical properties.

- **Nucleation** is the step where the solute molecules or atoms dispersed in the solvent start to gather into clusters, on the microscopic scale (elevating solute concentration in a small region). These stable clusters constitute the nuclei.

nucleation.png

- **Crystal growth** is the subsequent size increase of the nuclei that succeed in achieving the critical cluster size. it is a dynamic process occurring in equilibrium where solute molecules or atoms precipitate out of solution, and dissolve back into solution.

Supersaturation is one of the driving forces of crystallization, as the solubility of a species is an equilibrium process quantified by K_{sp} . Depending upon the conditions, either nucleation or growth may be predominant over the other, dictating crystal size.

Two other phenomena which are rare and are often neglected in the crystallization modelling process are **Agglomeration** and **Breakage**.

Agglomeration occurs when two particles collide and stick together to form a larger particle. Breakage occurs in stirred vessels; the larger particle breaks into smaller fragments, because of attrition .

2.1 Nucleation

The initial process that occurs in the formation of a crystal from a solution, a liquid, or a vapour, in which a small number of ions, atoms, or molecules become arranged in a pattern characteristic of a crystalline solid, forming a site upon which additional particles are deposited as the crystal grows.

Nucleation requires supersaturation, which is obtained usually by a change in temperature (cooling in case of a positive gradient of the solubility curve and heating in case of a negative gradient), by removing the solvent, or by adding a drowning out agent or reaction partners. If the solution contains neither solid foreign particles or crystals of its own type, nuclei are formed only through homogeneous nucleation. If foreign particles are present then nuclei are formed through heterogeneous nucleation.

Both homogeneous nucleation and heterogeneous nucleation are classified as primary nucleation.

2.2 Crystal Growth

Crystal growth occurs as soon as nuclei with radius larger than the critical radius have been formed. There are many proposed mechanisms for crystal growth.

Diffusion theories assume that matter is deposited continuously on the crystal face at a rate proportional to the difference in concentration between the point of deposition and

the bulk of the solution.

When dealing with crystal growth in an ionizing solute, the following steps can be distinguished :

- Bulk diffusion of solvated ions through the diffusion boundary layer
- Bulk diffusion of solvated ions through adsorption layer
- Surface diffusion of solvated or unsolvated ions
- Partial or total desolvation of ions
- Integration of ions into the lattice
- Counterdiffusion through adsorption layer of water released
- Counterdiffusion of water through the boundary layer

The slowest of these steps are rate determining.

A crystal surface grow in such a way that units in a supersaturated solution are first transported by diffusion and convection and then built into the surface of the crystal by integration or an integration reaction , with the supersaturation, ΔC , being the driving force.

Thus, determination of the optimal temperature or supersaturation trajectory for a seeded batch crystallizer is the most well-studied problem in chemical engineering, apart from batch reactors and batch distillation as the evolution of supersaturation in time affects almost all the kinetic phenomena occurring in the crystallization process. For example, growth can be size-independent or size-dependent; it can have a constant value or it may be a function of a thermodynamic parameter such as solubility and thus selection of appropriate kinetics is essential for accurate modelling .

Chapter 3

Modelling a Seeded Batch Crystallizer

3.1 Population Balance Equation

Analysis of a particulate system seeks to synthesize the behavior of the population of particles and its environment from the behavior of single particles in their local environments. The population is described by the density of a suitable extensive variable, usually the **number of particles**, but sometimes by other variables such as the mass or volume of particles. The usual transport equations expressing conservation laws for material systems apply to the behavior of single particles. Particulate processes are characterized by properties such as particle shape, size, surface area, mass, and product purity.

A population balance formulation describes the process of crystal size distribution with time most effectively. Thus, modeling of a batch crystallizer involves the use of population balances to model the crystal size prediction and the mass balance on the system can be modeled as a simple differential equation having concentration as the state variable. The population balance can be expressed as eq :

$$\frac{\partial n(r, t)}{\partial t} + \frac{\partial G(r, t)n(r, t)}{\partial r} = B$$

(3.1)

where \mathbf{n} is the number density distribution, \mathbf{t} is the time, \mathbf{r} represents the characteristic dimension for size measurements, \mathbf{G} is the crystal growth rate, and \mathbf{B} is the nucleation rate. Both growth and nucleation processes describe crystallization kinetics, and their expression may vary, depending on the system under consideration.

3.2 Model Equations

In this work, the system under consideration is potassium sulfate, which has been studied earlier by Hu et al. [5], Shi et al. [6], and Paengjuntuek et al.[7].

Nucleation kinetics⁽⁵⁻⁷⁾ are defined by :

$$B(t) = k_b \exp(-E_b/RT) \left(\frac{C - C_s(T)}{C_s(T)} \right)^b \mu_3 \quad (3.2)$$

Growth Kinetics⁽⁵⁻⁷⁾ are given by:

$$G(t) = k_g \exp(-E_g/RT) \left(\frac{C - C_s(T)}{C_s(T)} \right)^g \quad (3.3)$$

where k_b and k_g are constants of the system, E_b and E_g are activation energies, and b and g are exponents of nucleation and growth, respectively. $C_s(T)$ is the saturation concentration at a given temperature. The following equations are used to evaluate the saturation and metastable concentrations corresponding to the solution temperature T (expressed in units of °C)[6].

$$C_s(T) = 6.29 \times 10^{-2} + 2.46 \times 10^{-3}T - 7.14 \times 10^{-6}T^2 \quad (3.4)$$

$$C_m(T) = 7.76 \times 10^{-2} + 2.46 \times 10^{-3}T - 8.1 \times 10^{-6}T^2 \quad (3.5)$$

The mass balance, in terms of concentration of the solute in the solution, is expressed as :

$$\frac{dC}{dt} = -3\rho k_v G(t) \mu_2(t) \quad (3.6)$$

where ρ is the density of the crystals, k_v the volumetric shape factor, and μ_2 is the second moment of particle size distribution (PSD).

Since $n(r, t)$ represents the population density of the crystals[?], the i th moment of the particle size distribution(PSD) is given by :

$$\mu_i = \int_0^\infty r^i n(r, t) dr \quad (3.7)$$

The above equations along with the Population Balance Equation represent a complete model of a seeded batch crystallizer . Since population balance equations are multidimensional, their implementation in control functions is tedious; hence, much research has been focused on the model order reduction methods.

For simplifying the solution method, we reduce the population balance equations into **Moment balance equations**(ODE). This is done by multiplying the equation (3.1) with r^i on both sides to generate the expression given by equation (3.7). It is also advantageous, since it is difficult and time-consuming to formulate an optimization problem involving PBEs. Thus, the moment method leads to a reduced-order model involving the process dynamics in batch crystallization.

3.3 Solution Methodology

Separate moment equations are used for the seed and nuclei classes of crystals, and they are defined as :

$$\mu_i^n = \int_0^{r_g} r^i n(r, t) dr \quad (3.8)$$

$$\mu_i^s = \int_{r_g}^\infty r^i n(r, t) dr \quad (3.9)$$

n : nucleation , s: seed , r_g : critical radius separating the two

Since, we ignore the agglomeration and breakage phenomena, the number of seeds added to the process (μ_0^s) remain constant.

Fourth and higher order moments are not affected by the lower, which makes it possible for the complete process dynamics to be expressed by the first 4 moments for each of the respective crystals growth patterns.

The moment equations for nucleated and seeded crystals become as follows[10] :

1. Nucleated crystals^{5,7}

$$\frac{du_0^n}{dt} = B(t) \quad (3.10)$$

$$\frac{du_i^n}{dt} = iG(t)u_{i-1}^n(t) \quad i = 1, 2, 3 \quad (3.11)$$

2. Seeded crystals^{5,7}

$$\frac{du_i^s}{dt} = iG(t)u_{i-1}^n(t) \quad i = 1, 2, 3 \quad (3.12)$$

$$\mu_0^s = \text{constant} \quad (3.13)$$

The total moment is obtained as the summation $\mu_i^t = \mu_i^n + \mu_i^s$. The complete set of differential equations are as follows :

Chapter 4

Optimal Control Problems

4.1 Deterministic Optimal Control

Aim To find an optimal temperature trajectory, which minimizes the total volume of fine crystals, represented by the third moment of nucleated crystals (μ_3^n) and maximizes the size of seeded crystals represented by the third moment of seeded crystals (μ_3^s) in order to satisfy the product quality requirements.

Objective Function

$$\max_{T(t)} \{ \mu_3^s(t_f) - \mu_3^n(t_f) \}$$

For uniformity of shape and size in the crystals in a seeded batch crystallization process, it is essential to ensure that the nucleation phenomena occurs to the minimum and mostly the seeded crystals grow to the desired size at a certain rate, which explains the nature of the objective function .

Active Constraints

$$C_s \leq C \leq C_m$$

The state variables can be represented as :

$$y_i = [\quad C \quad \mu_0^s \quad \mu_1^s \quad \mu_2^s \quad \mu_3^s \quad \mu_0^n \quad \mu_1^n \quad \mu_2^n \quad \mu_3^n \quad]$$

Thus, the complete model involving the moment equations consists of nine state equations.

4.1.1 Solution Technique : Steepest Ascent Hamiltonian

The method involves use of the **Maximum Principle** discussed by Diwekar et al.[8] in detail. The algorithm of Steepest Ascent utilizes this principle using the Hamiltonian Derivative to move towards the optimum value of Temperature and maximise the objective function.

The formulation results in two point boundary value problem, since initial conditions for the state variables and final conditions for the adjoint variables are available. The method also involves introduction of nine additional variables, known as adjoints (z_i), corresponding to each of the state variable (y_i), which must satisfy the **Hamiltonian equation** represented by :

$$H = \sum_{i=1}^9 z_i f(y_i, t, T) \quad (4.1)$$

The complete problem can be described as :

$$\begin{aligned} & \max_{T(t)} \{y_5(t_f) - y_9(t_f)\} \\ & \frac{dy_i}{dt} = f(y_i, t, T) \\ & \frac{dz_i}{dt} = \sum_{j=1}^9 z_j \frac{\partial f(y_i, t, T)}{\partial y_i} = f(y_i, z_i, t, T) \end{aligned}$$

with the following initial conditions:

$t_0 = 0$ and $t_f = 1800s$ (batch time)

$$\begin{aligned} y_i(t_0) &= [0.1743 \quad 66.66 \quad 1.83 \times 10^4 \quad 5.05 \times 10^6 \quad 1.93 \times 10^9 \quad 0.867 \quad 0 \quad 0 \quad 0] \\ z_i(t_f) &= [0 \quad 0 \quad 0 \quad 0 \quad 1 \quad 0 \quad 0 \quad 0 \quad -1] \end{aligned}$$

Algorithm

1. An initial temperature $T(t) = 323K$ is assumed for the entire time horizon.
2. The differential equations for state variables are integrated using the initial conditions for a time step of 1s .
3. The value of the adjoint variables are computed by backward integration for the same time step used in the previous.
4. For evaluation of the Hamiltonian derivative, an analytical method proposed by Benavides and Diwekar[9], is used in which we an additional variable corresponding to each of the state and adjoint variable is introduced.

5. The variable θ_i corresponds to each of the state variable y_i and the variable ϕ_i corresponds to each of the adjoint variable z_i , respectively.
6. The Hamiltonian derivative is now calculated at each time step as :

$$\theta = \frac{dy_i}{dT} \quad \text{and} \quad \phi_i = \frac{dz_i}{dT} \quad (4.2)$$

$$\frac{dH}{dT} = \sum_{i=1}^9 \left(\frac{dH}{dy_i} \right) \left(\frac{dy_i}{dT} \right) + \sum_{i=1}^9 \left(\frac{dH}{dz_i} \right) \left(\frac{dz_i}{dT} \right) \quad (4.3)$$

7. The convergence criterion ($\frac{dH}{dT} < \text{tolerance}$) is verified. If it is not satisfied, the temperature $T(t)$ is updated using this gradient[10].

$$T^{new}(t) = T^{old}(t) + M \left(\frac{dH}{dT} \right) \quad (4.4)$$

8. The concentration is evaluated at that time step and compared with first with the saturation concentration (C_s) and the metastable concentration(C_m) to validate the active constraints.
9. Iterations of above steps are repeated.

4.1.2 Results

The following fixed kinetic parameters were used in the deterministic modelling.

Parameters	Experimental Values
Growth Kinetics	
k_g	$1.44 \times 10^8 \mu m s^{-1}$
E_g/R	$4859 K$
g	1.5
Growth Kinetics	
k_b	$285 (s \mu m^3)^{-1}$
E_b/R	$7517 K$
b	1.45

TABLE 4.1: Parameter Values for Batch Crystallizer⁵⁻⁷

- The model was implemented both using **Python** and **Matlab** producing similar results.

- Matlab employed use of **ode15s** for performing the forward and backward integrations which is used to solve stiff-differential equation. In Python it was performed through **Explicit Euler** method.
- A tolerance value of 10^{-2} is used for computation of the Hamiltonian Derivative profile. The value of M was selected suitably after experimentation.

Chapter 5

Optimal Control using Uncertainty Quantification

Kinetic parameters are generally empirical constants determined by fitting experimental data to the model, and, hence, are a source of uncertainty within the system. I discuss two methods here to quantify these uncertainties and as a result build a more robust process dynamics model.

5.1 Stochastic Optimal Control using Ito Processes

From several previous works it has been shown that the dynamic uncertainties such as the batch reactors[12] and batch distillation,[8], can be represented using stochastic processes called as the Ito processes.

The advantage lies in the ability to integrate the equations using the principles of stochastic calculus and the use of stochastic maximum principle to solve for the optimal temperature profile.

In batch crystallization kinetics, the growth and nucleation expressions have empirical constants shown in Table 4.1, they can be assumed to follow a Gaussian distribution[10]. By studying the nature of the dynamic uncertainty plots of the process variables and their correlation to Ito processes, it has been observed that the uncertainties can be best modeled with a simple Ito process known as **Brownian motion** with drift[8][11]. It can be defined as:

$$dy = a(y, t)dt + b(y, t)dz \quad (5.1)$$

where dz is the increment of the Wiener process equal to $\varepsilon_t(\Delta t)^{1/2}$, and $a(y, t)$ and $b(y, t)$ are known functions. The random value ε_t has a unit normal distribution with zero

mean and a standard deviation of 1. To estimate the values of the functions a and b , a generalized method presented by Diwekar[8] has been used.

In this work a simplification of the above equations has been done to incorporate the uncertainties into the moment equations which are[10] :

Appendix A

An Appendix

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