Indian Institute of Technology,Kharagpur

Optimal Control of Seeded Batch Crystallizer

by

Author Name

A thesis submitted in partial fulfillment for the
degree of Doctor of Philosophy

in the

Faculty Name
Department of Chemical Engineering

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Acknowledgements

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

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Abbreviations

LAH **L**ist **A**bbreviations **H**ere

Physical Constants

Speed of Light $c = 2.997\ 924\ 58 \times 10^8\ \mathrm{ms}^{-\mathrm{S}}$ (exact)

Symbols

a	distance	m
P	power	W (Js^{-1})
ω	angular frequency	$rads^{-1}$

For/Dedicated to/To my...

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 :
Supersaturation $= \Delta C = C - C_s$
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 kisnetics, *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 :

$$\frac{\partial n(r,t)}{\partial t} + \frac{\partial G(r,t)n(r,t)}{\partial r} = B \tag{3.1}$$

where **n** is the number density distribution, **t** is the time, **r** represents the characteristic dimension for size measurements, **G** is the crystal growth rate, and **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] :

$$\mathrm{B(t)} = \mathrm{k}_b \exp\left(-E_b/RT\right) \left(\frac{C-C_s(T)}{C_s(T)}\right)^b \mu_3$$

Appendix A

An Appendix

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