Deterministic and Stochastic Optimal Control of a Batch Cooling Crystallizer

Submitted by

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Certificate

This is to certify that the project report entitled Optimal Control of Seeded Batch Crystallizer submitted by Tushar Gupta (13CH30023) towards partial fulfilment for the award of the degree of Master of Technology in Chemical Engineering to the Department of Chemical Engineering of the Indian Institute of Technology Kharagpur is an original bona fide research work carried out by him under my guidance and supervision and that the results contained in it have not been submitted in partial or full to any other university for the award of any degree.

Date: 30th April 2018

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Abstract

Minimization of operation costs and the enhancement in product quality have been major concerns for all industrial processes. The field under study here is batch crystalllization which is affected heavily by the uncertainities in measurements and other errors.

The current work aims to study Deterministic and Stochastic methods for Optimum Control in batch crystallization. All the methods involve maximising an objective function by manipulating the cooling profile. At first, the Deterministic approach uses experimental kinetic parameters, which is then extended to Stochastic optimization to incorporate uncertainities in them. Lastly, a novel approach named Polynomial Chaos Expansions is implemented which has been applied successfully to other domains for Nonlinear Model Predictive Control but was not explored in detail in the field of batch cooled crystalllization. It successfuly includes probability distributions for the parameters into the model to provide a more robust optimization srategy.

Acknowledgements

Contents

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.

A common goal of a crystallization process is to obtain a narrower Particle size distribution (PSD) with high crystal purity. The PSD has a strong 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. 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 optimal control for a cooling crystallization process described by using the population balance equations and obtain the solution for the optimal temperature profile using deterministic and probabilistic methods.

Deterministic Optimal Control aims at finding the an optimum temperature profile to maximise an objective function selected to achieve a desired volume of the product. Herein, the experimental kinetic parameters are employed to simulate a batch crystallization process.

Stochastic Optimal Control undertakes the task of quantifying the uncertainites which creep in due to experimentation. It aims to achive a maximum expected value for the desired product, simultaneously incorporating randomness in the process parameters into the model. Namely, Two methods **Ito Process** and **Polynomial Chaos**

Expansions are employed for this purpose.

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.[12], the data and knowledge from which have been used in further work in this project . Grosso et al.[13] presented a stochastic approach for modeling PSD and comparative assessments of different models. Ma et al.[14] 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 $= \Delta C/C_s = S$

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.

- **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 the practical driving forces of a crystallization process. Depending upon the conditions, either nucleation or growth may be predominant over the other, dictating crystal size.

Two other phenomena which 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

This is the initial process for the formation of a crystals in a solution, a liquid, or a vapour, in which a small number of ions, atoms, or molecules become arranged in a characteristic pattern of a crystalline solid, and subsequently form 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 of 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] are defined by :

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

Growth Kinetics[5−7] are given by:

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

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].

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

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

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

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

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 :

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

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 :

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

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

n : nucleated crystal , s: seeded crystal , 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]

$$\frac{d\mu_0^n}{dt} = B(t) \tag{3.10}$$

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

2. Seeded crystals[5][7]

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

$$\mu_0^s = constant \tag{3.13}$$

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[10] :

$$\frac{dy_1}{dt} = -3\rho k_v G(t)(y_4 + y8) \tag{3.14}$$

$$\frac{dy_2}{dt} = 0 \tag{3.15}$$

$$\frac{dy_3}{dt} = G(t)y_2 \tag{3.16}$$

$$\frac{dy_4}{dt} = 2G(t)y_3 \tag{3.17}$$

$$\frac{dy_5}{dt} = 3G(t)y_4 \tag{3.18}$$

$$\frac{dy_6}{dt} = B(t) \tag{3.19}$$

$$\frac{dy_7}{dt} = G(t)y_6 \tag{3.20}$$

$$\frac{dy_8}{dt} = 2G(t)y_7 \tag{3.21}$$

$$\frac{dy_9}{dt} = 3G(t)y_8 \tag{3.22}$$

$$\tag{3.23}$$

Here the state variables y_i are given by :

$$y_i = \begin{bmatrix} C & \mu_0^s & \mu_1^s & \mu_2^s & \mu_3^s & \mu_0^n & \mu_1^n & \mu_2^n & \mu_3^n \end{bmatrix}$$

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

$$C_s \leqslant C \leqslant C_m$$

C_m is the metastable concentration described by Equation(3.5) The state variables can be represented as :

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

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. A two-point boundary-value-problem is constructed using state equations and additionally defined adjoint equations which has been explained in detail futher.

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 :

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

The state variables and objective function can be described as :

$$\max_{T(t)} \{y_5(t_f) - y_9(t_f)\}$$

$$\frac{dy_i}{dt} = f(y_i, t, T)$$

$$\frac{dz_i}{dt} = \sum_{j=1}^{9} z_j \frac{\partial f(y_i, t, T)}{\partial y_i} = f(y_i, z_i, t, T)$$

with the following initial conditions:
$t_0 = 0$ and $t_f = 1800s$ (batch time)

$$y_i(t_0) = \begin{bmatrix} 0.1743 & 66.66 & 1.83 \times 10^4 & 5.05 \times 10^6 & 1.93 \times 10^9 & 0.867 & 0 & 0 & 0 \end{bmatrix}$$

$$z_i(t_f) = \begin{bmatrix} 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & -1 \end{bmatrix}$$

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 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 :

$$\theta = \frac{dy_i}{dT} \quad and \quad \phi_i = \frac{dz_i}{dT} \tag{4.2}$$

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

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

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

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 kinetic parameters were used in the deterministic optimization.

TABLE 4.1: Parameter Values for Batch Crystallizer[5, 7]

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

- 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.

- A tolerance value of 10^{-2} is used for computation of the Hamiltonian Derivative profile. The value of M was selected suitably after experimentation.
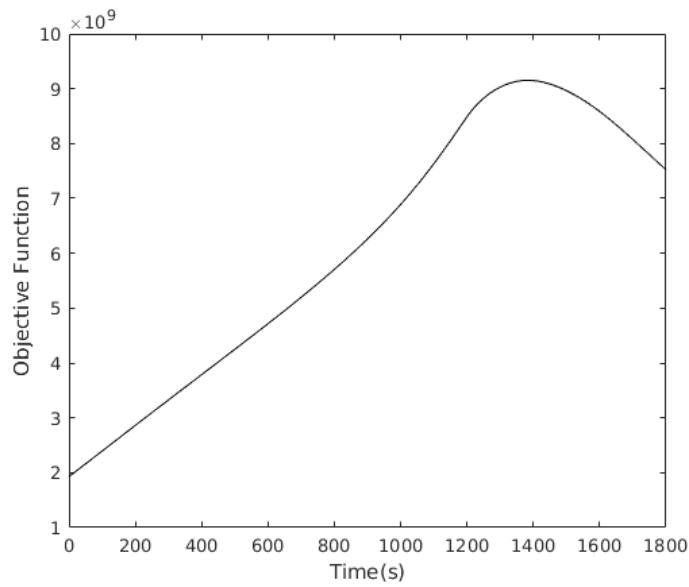
The following results were obtained:

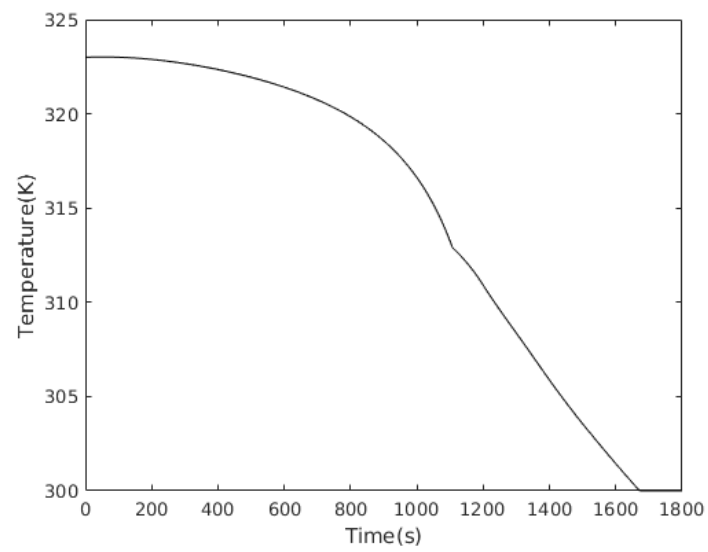FIGURE 4.1: Objective Function $(\mu_3^s(t) - \mu_3^n(t))$

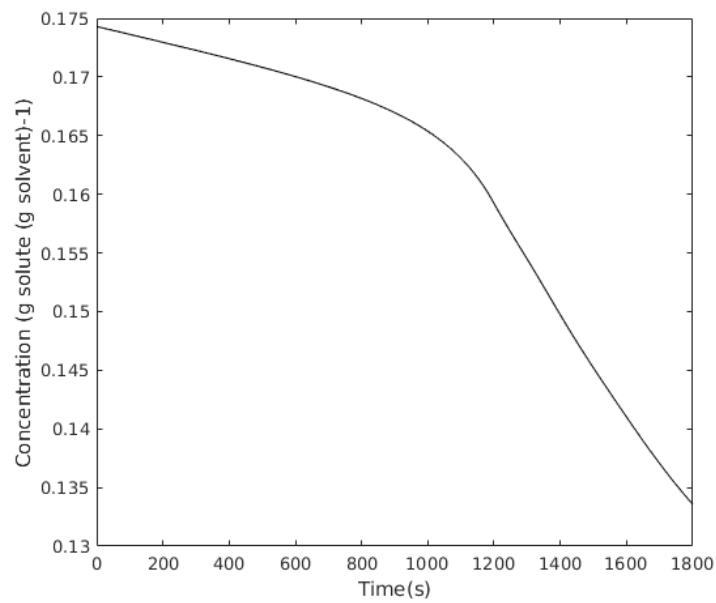FIGURE 4.2: The cooling profile for the controlled variable T(t) obtained at the final iteration

FIGURE 4.3: The Concentration profile as obtained.

The change of the Hamiltonian Derivative($\frac{dH}{dT}$) after each iteration is shown below :
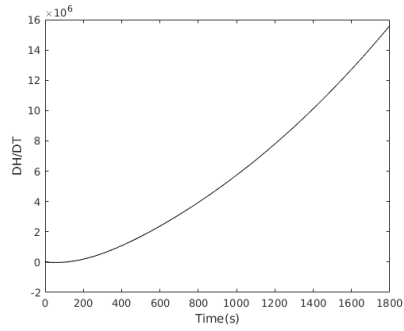

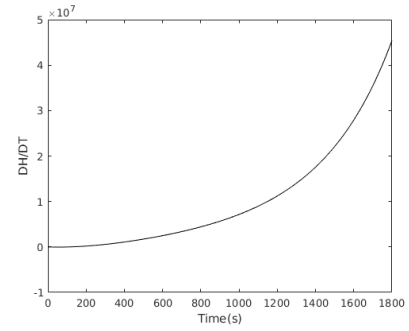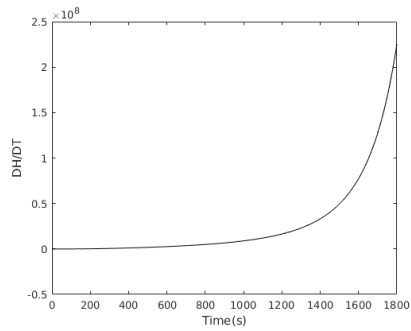FIGURE 4.4: Iteration 1
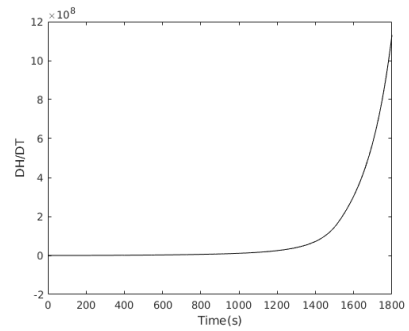

FIGURE 4.5: Iteration 2
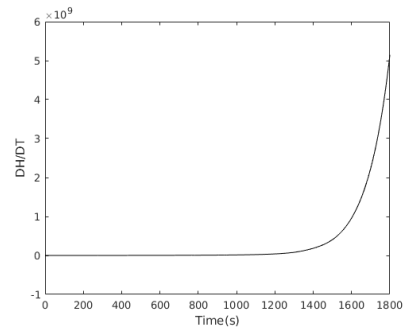

FIGURE 4.6: Iteration 3
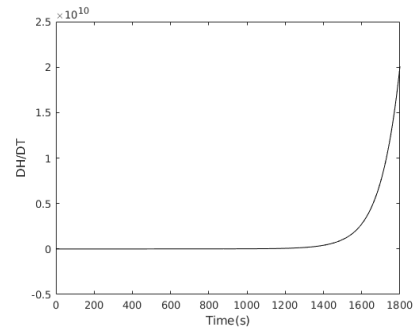

FIGURE 4.7: Iteration 4

FIGURE 4.8: Iteration 5

FIGURE 4.9: Iteration 6

Chapter 5

Optimal Control using Uncertainity 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. Two methods are discussed here to quantify these uncertainities and thereby perform build a more robust dynamic optimization.

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[15] and batch distillation,[8], can be represented using stochastic processes called as the Ito processes. We characterize the time-dependent uncertainties in the state variables using 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:

$$dy = a(y,t)dt + b(y,t)dz \tag{5.1}$$

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, equation(5.1) has been used to incorporate the uncertainties into the moment equations which are[10] :

$$dy_1 = [-3\rho k_v G(t)(y_4 + y8)]\,\Delta t + g_1\varepsilon_1\sqrt{\Delta t} \tag{5.2}$$

$$dy_2 = 0 \tag{5.3}$$

$$dy_3 = (G(t)y_2)\Delta t + g_3\varepsilon_3\sqrt{\Delta t} \tag{5.4}$$

$$dy_4 = (2G(t)y_3)\Delta t + g_4\varepsilon_4\sqrt{\Delta t} \tag{5.5}$$

$$dy_5 = (3G(t)y_4)\Delta t + g_5\varepsilon_5\sqrt{\Delta t} \tag{5.6}$$

$$dy_6 = (B(t))\Delta t + g_6\varepsilon_6\sqrt{\Delta t} \tag{5.7}$$

$$dy_7 = (G(t)y_6)\Delta t + g_7\varepsilon_7\sqrt{\Delta t} \tag{5.8}$$

$$dy_8 = (2G(t)y_7)\Delta t + g_8\varepsilon_8\sqrt{\Delta t} \tag{5.9}$$

$$dy_9 = (3G(t)y_8)\Delta t + g_9\varepsilon_9\sqrt{\Delta t} \tag{5.10}$$

$$\tag{5.11}$$

$a(y,t)$ in each equation is replaced by the corresponding deterministic function for the state variable.

Here, the g_i values represent the variance in the variable for which they are associated. They are calculated by recording the variance of the differences in y_i, which is divided by the time interval Δt, and then the square root of this value is taken.

Objective Function for the stochastic formulation now becomes :

$$\max_T L = \mathbf{E}\left[\mu_3^s(t_f) - \mu_3^n(t_f)\right] \tag{5.12}$$

$\mathbf{E}$ is the expected value of the variable.

The **Active Constraints** and **Initial Conditions** remain the same as mentioned in Section (4.1).

5.1.1 Solution Technique : Stochastic Steepest Ascent Hamiltonian

The Hamiltonian for this section is modified to incorporate the uncertainities as[10] :

$$H = \sum_{i=1}^{9}\left(z_i f_i + \omega_i\frac{g_{y_i}^2}{2}\right) \tag{5.13}$$

f_i are the deterministic parts for the eq (5.2-5.11). ω_i is an additional adjoint variable defined to calculate the Hamiltonian for the **Stochastic Maximum Principle** formulation[16].

The **Algorithm** for the method remains same as mentioned in Section (4.1.1) with minor changes.

1. Steps (1-4) are repeated.

2. The variable i corresponds to each of the state variable yi and the variable i corresponds to each of the adjoint variable zi , i corresponding to each i respectively.

3. 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, ψ_i for each ω_i respectively.

4. The Hamiltonian derivative is now calculated at each time step as :

$$\theta = \frac{dy_i}{dT} \quad \phi_i = \frac{dz_i}{dT} \quad \psi = \frac{d\omega_i}{dT} \tag{5.14}$$

$$\frac{dH}{dT} = \sum_{i=1}^{9} \left(\frac{dH}{dy_i}\right)\left(\frac{dy_i}{dT}\right) + \sum_{i=1}^{9} \left(\frac{dH}{dz_i}\right)\left(\frac{dz_i}{dT}\right) + \sum_{i=1}^{9} \left(\frac{dH}{dw_i}\right)\left(\frac{dw_i}{dT}\right) \tag{5.15}$$

5. The convergence criteria and the constraints remain same as the above referenced method.

5.1.2 Results

The following values were used as the coefficients for uncertainities for the state variables :

TABLE 5.1: State Variable Uncertainity Coefficients[10]

Parameters	Values
g_1	2.659×10^{-5}
g_2	0
g_3	25.882
g_4	1.517×10^4
g_5	6.57×10^6
g_6	0.5486
g_7	25.9
g_8	1382.34
g_9	8.753×10^4

- The stochastic differential equations are integrated using stochastic calculus through **SDE Tools** Library available in **Matlab**.A strong Taylor approximation from the **Euler Maruyama** scheme has been used to integrate the equations which has an order of convergence of 0.5.

The following profiles were obtained as a result :
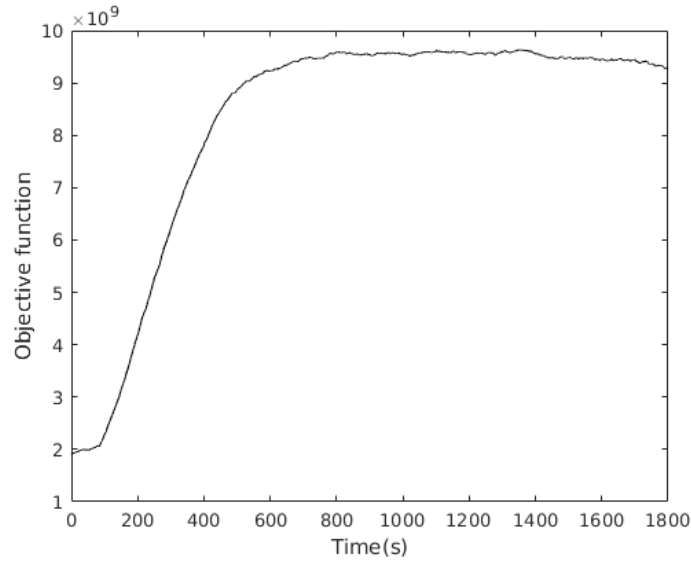

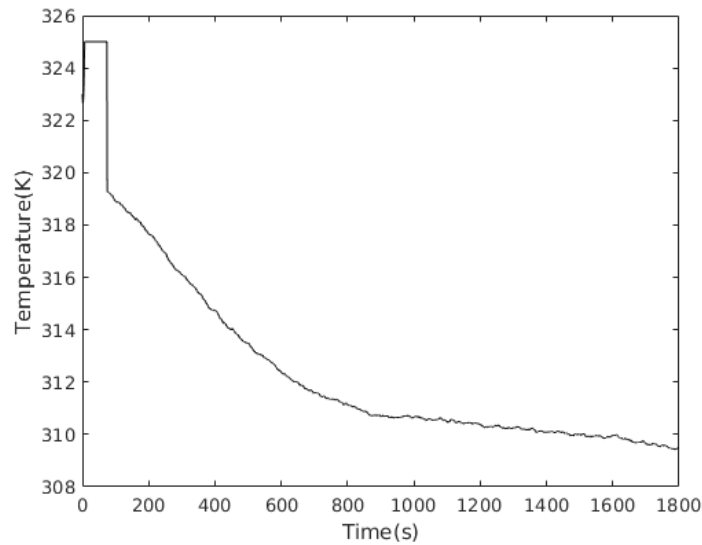FIGURE 5.1: Objective Function ($\mathbf{E}\left[\mu_3^s(t) - \mu_3^n(t)\right]$)

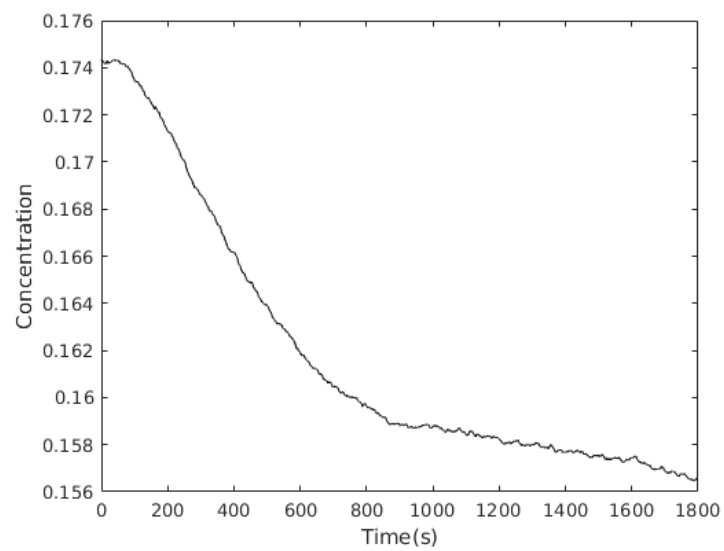FIGURE 5.2: The cooling profile for the controlled variable T(t) obtained at the final iteration

FIGURE 5.3: Concentration Profile as obtained

5.2 Stochastic Optimal Control using Polynomial Chaos Expansions

5.2.1 Introduction

A Polynomial Chaos Expansion (PCE) describes a random process as a spectral expansion of random variables(θ_i), using orthogonal basis functions, Φ_i (Ghanem and Spanos, 1990,Ghanem and Spanos, 1997). For example, any second-order (finite variance) random process y^d, can be described using a PCE as follows:

$$y^d = a_0^d \phi_0 + \sum_{i_1=1}^{\infty} a_{i_1}^d \phi_1(\theta_{i_{i_1}}) + \sum_{i_1=1}^{\infty} \sum_{i_2=1}^{i_1} a_{i_1 i_2}^d \phi_2(\theta_{i_1}, \theta_{i_2}) \tag{5.16}$$

where $a_{i_1}^d$ are deterministic coefficients for each term in the expansion. The number of independent sources of random variables $(\theta_{i_1}, \theta_{i_2})$, generally defines the dimensionality, n_0. For practical application these expansions can be truncated to a finite number of terms. Then the maximum polynomial order for the basis function, q needs to be defined. The number of terms now become $P_{PCE} = \frac{(n_0+q)!}{n_0!q!} - 1$.

Using these notations a truncated PCE expansion can be represented as follows:

$$y^d \approx \sum_{i=1}^{P_{PCE}} a_i^d \phi_\theta \tag{5.17}$$

The orthogonality property of the basis functions(ϕ_i) is used for the calculation of the coefficients when propagating uncertainty from the input random variables$(\theta_{i_1}, \theta_{i_2})$, to the output random variables (y^d).

The choice of the basis functions ϕ_i depends on the type of stochastic distribution to be represented, i.e. normal or uniform. In our case the parameters follow a Gaussian distribution[10], which uses Hermite Polynomials to describe the probability distribution in the least number of terms.

Thus, given a process model with uncertain output, $y = X(x, \lambda)$, where x is the uncertain input and λ is the uncertain parameter, the aim is to quantify uncertainty in $y(\theta)$ from $x(\theta), \lambda(\theta)$ using the process model. Then the first step is to construct PCEs of $x(\theta)$, and $\lambda(\theta)$, by determining their PCE coefficients x_i and λ_i.

$$x(\theta) = \sum_{i=1}^{P_{PCE}} x_i \phi(\theta) \qquad \lambda(\theta) = \sum_{i=1}^{P_{PCE}} \lambda_i \phi(\theta) \tag{5.18}$$

$$x_i = \frac{\int x\phi_i(\theta)g(\theta)d\theta}{\langle \phi_i^2 \rangle} \quad \lambda_i = \frac{\int \lambda\phi_i(\theta)g(\theta)d\theta}{\langle \phi_i^2 \rangle} \tag{5.19}$$

where $g(\theta)$ is probability distribution function (pdf) of θ. The next step is to develop PCE for $y(\theta)$ from $x(\theta)$, and $\lambda(\theta)$, which can be done by evaluating the inner product of $y(\theta)$ with each basis functions ϕ_i to determine the ith- PCE coefficient.

$$y_i = \frac{\langle f(x, \lambda)\phi_i \rangle}{\langle \phi_i^2 \rangle} \tag{5.20}$$

Evaluating the inner product $\langle y\phi_i \rangle$, requires computation of multi-dimensional integrals which can be performed by one of two approaches referred to as **non-intrusive** and **intrusive**.

The work under consideration here uses a non-intrusive approach. The model $y = X(x, \lambda)$ is represented by the modelling equations of Section(3.2). x are the state variables and λ's are the kinetic parameters.

5.2.2 Usage of PCE in Batch Crystallization

The model under consideration is composed of the state equations and kinetics mentioned in Section(3.2), which are :

$$\frac{dy_1}{dt} = -3\rho k_v G(t)(y_4 + y8) \tag{5.21}$$

$$\frac{dy_2}{dt} = 0 \tag{5.22}$$

$$\frac{dy_3}{dt} = G(t)y_2 \tag{5.23}$$

$$\frac{dy_4}{dt} = 2G(t)y_3 \tag{5.24}$$

$$\frac{dy_5}{dt} = 3G(t)y_4 \tag{5.25}$$

$$\frac{dy_6}{dt} = B(t) \tag{5.26}$$

$$\frac{dy_7}{dt} = G(t)y_6 \tag{5.27}$$

$$\frac{dy_8}{dt} = 2G(t)y_7 \tag{5.28}$$

$$\frac{dy_9}{dt} = 3G(t)y_8 \tag{5.29}$$

$$\tag{5.30}$$

Here, the state varibles(y_i) act as the uncertain outputs which is caused by errors in process parameters used to calculate the Growth rate $\left(G(t) = k_g \exp\left(-E_g/RT\right) \left(\frac{C - C_s(T)}{C_s(T)}\right)^g \right)$

and the Nucleation rate $(B(t) = k_b \exp(-E_b/RT) \left(\frac{C - C_s(T)}{C_s(T)}\right)^b \mu_3)$. As a result, uncertainities in the parameters λ (k_g, E_g, g, k_b, E_b, b) are propogated into the model using P.C.E during optimal control.

A non-intrusive approach is followed for the above task where the integrals are calculated by generating samples of the above process and evaluating the model at these pre-determined points.

Algorithm is as follows :

1. Following the general representation, y_i can be written as :

$$y_i = f(x(\theta), \lambda_i(\theta))$$

   where x is the input temperature(T), λ_i's are process the parameters and θ is the random variable.

2. The process model consists of 6 uncertainities which computationally prohibits the evaluation. Thus, an approximation of $n_0 = 2$ is taken by employing a joint distribution of the parameters.

3. Samples are generated for the model at N points. The sampling technique used is the Gaussian Quadratures along with Hermite Polynomials to represent state variables (y_i) into Eq(5.17).

4. For each of the above sample $y_i^j = f(T^j(\theta), \lambda(\theta))$, the optimization problem is solved using the Steepest Ascent Hamiltonian method discussed in Section(4.1.1).

5. The optimum value of the input temperature $T^j(\theta)$ at these samples is used to construct the PCE's for $T(\theta)$ and $\lambda(\theta)$ as given by Equations(5.18).

6. y_i^j's for each sample are used to evaluate :

$$y_i = \frac{1}{\langle \phi_i^2 \rangle} \frac{1}{N} \sum_{j=1}^{N} y^j \phi_i(\theta) \tag{5.31}$$

   Here, ϕ_i are the coefficients of the orthogonal polynomials being used for PCE estimation.

7. As the above Equation averages over N samples, the resultant y_i maximises the objective function, given by $\mathbf{E}\{y_5 - y_9\})$.

The kinetic parameter values used for the above model are given below :

TABLE 5.2: Kinetic Parameter Uncertainities[5–7]

Parameters	Experimental Values	Range of Values
Growth Kinetics		
k_g	$1.44 \times 10^8 \mu m s^{-1}$	$1.368 - 1.512 \times 10^8$
E_g/R	$4859K$	$4606.15 - 5101.95$
g	1.5	$1.425 - 1.575$
Nucleation Kinetics		
k_b	$285(s\mu m^3)^{-1}$	$270.75 - 299.25$
E_b/R	$7517K$	$7141.15 - 7892.85$
b	1.45	$1.3775 - 1.5225$

5.2.3 Results

- The method was implemented in pyhton using the **chaospy** library[17] for Polynomial Chaos Expnasions.

The following profiles were obtained :
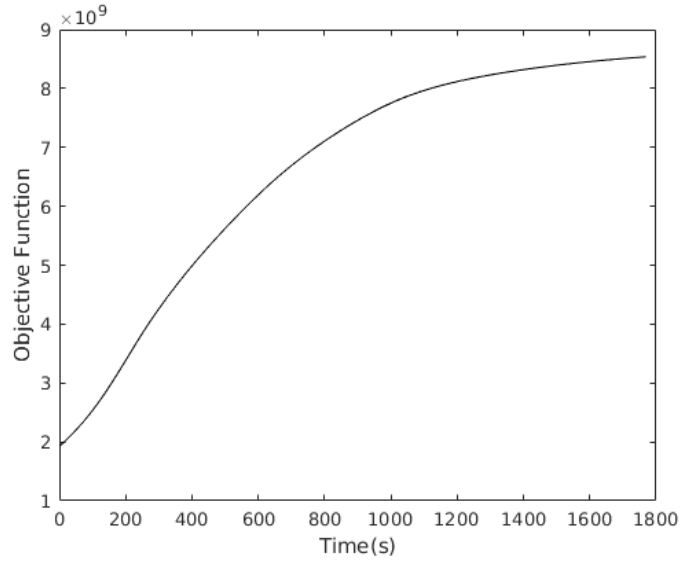
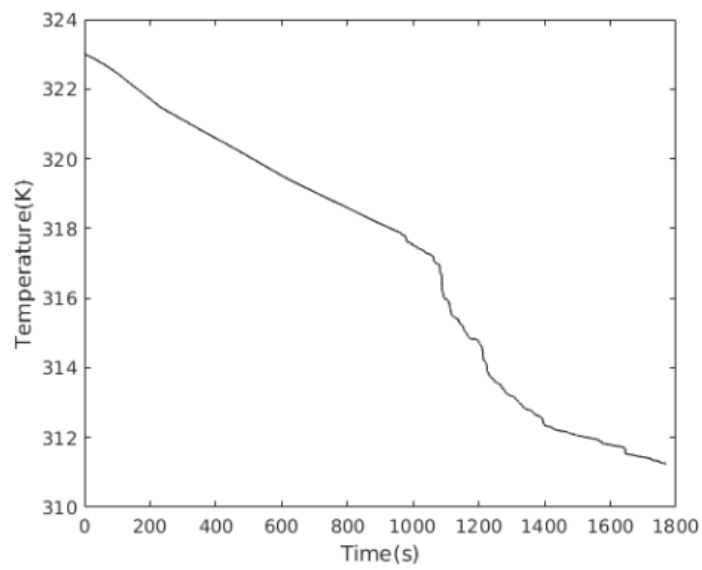FIGURE 5.4: Objective Function ($\mathbf{E}\left[\mu_3^s(t) - \mu_3^n(t)\right]$)

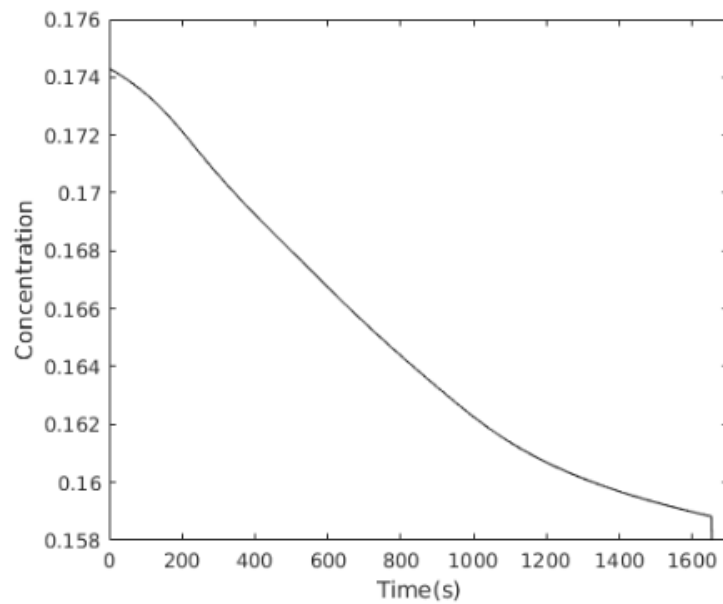FIGURE 5.5: The cooling profile for the controlled variable T(t) obtained at the final iteration

FIGURE 5.6: The concentration profile as obtained.

5.3   Conclusions

- The same process was optimized using 3 different methods of Optimization. This achieves the aim of maximising the volume of the product obtained.

- The Temperature profile for all the 3 cases was obtained as a decreasing one and thus follows the principle of batch cooling crystallization.

- Polynomial Chaos Expansions, when applied to crystallization performs at par with the existing methods in optimizing the process by efficiently incorporating uncertainities.

- After comparing the final values of the objective functions$(\mu_3^s - \mu_3^n)$[particle volume] the following values were obtained :

  1. Deterministic : $9.153 \times 10^9 \mu m^3$

  2. Expected value for Stochastic involving Ito Processes : $8.978 \times 10^9 \mu m^3$

  3. Expected value for Stochastic case involving PCE : $8.64 \times 10^9 \mu m^3$

- The decrease of values can be attributed to the presence of errors or uncertainities in the kinetic parameters. Thus, the model becomes helpful in predicting the expected values for volume of crystals taking care of the process uncertainities.

Chapter 6

Stochastic Optimization using Polynomial Chaos Expansions : Unseeded Crystallization

Aim   To build a predictive model for unseeded batch crystallization of L-Asparagine Monohyrdate(LAM).

6.1   Optimal Control Problem

The population balance equations(PBE) given by 3.1 are used here to model the kinetics of crystal formation. The Nucleation rate expression for LAM crystals is given by[18] :

$$B = k_{j_1} S \exp\left(-k_{j_2} \frac{\ln^3 C_c/C^*}{\ln^2 S}\right) \tag{6.1}$$

C_c representys the molar density of LAM. kJ1 and kJ2 are empirical parameters. The following power-law expression is used to describe the growth rate[19][20]:

$$G = k_g(S - 1)^g \tag{6.2}$$

The supersaturation ratio, S, is defined as :

$$S = C/C^* \tag{6.3}$$

C* represents the saturation concentration of LAM. The solubility of LAM in can be expressed as:

$$C^* = 5 \times 10^{-5}T^2 - 0.001T + 0.0236 \tag{6.4}$$

Method of Moments has been used to reduce the PBE to ODE's as stated in Section 3.2. The mass balance for LAM crystals also remains the same from there, with the difference being the absence of seeded crystals.

The ODEs for the model are given by :

$$\frac{du_0}{dt} = B \tag{6.5}$$

$$\frac{du_j}{dt} = jG\mu_{j-1} \tag{6.6}$$

for $j = 1, 2, 3, 4$

The determination of the optimal temperature profile for maximizing the weight mean size is a highly studied objective for a crystallization process.Thus,

Objective Function becomes :

$$\max_{T(t)} \phi = \mu_4/\mu_3 \quad at \quad t_f \tag{6.7}$$

Constraints

$$T_{min} \leqslant T(t) \leqslant T_{max} \tag{6.8}$$

$$\frac{dT}{dt} \leqslant 0 \tag{6.9}$$

The state variables can be represented as :

$$y_i = \begin{bmatrix} C & \mu_0 & \mu_1 & \mu_2 & \mu_3 & \mu_4 \end{bmatrix}$$

Here we do not divide the moments in seeded and nucleated ones.

The Hamiltonian method described in the previous sections was employed to solve the optimaization problem along with the uncertainity quantification being done using Polynomial Chaos Expansions. The new state equations, constraints and kinetics as described above are used to define the problem.

6.2 Solution Technique : Hamiltonian Steepest Ascent with PCE

Equations(6.5-6.6) take place as the new state equations and the uncertain parameters are mentioned in Table 6.1. The constraint(Eq 6.9)) depicts a cooling profile for the

crystallizer. The obejective function here (Eq 6.7) differs from the one used in Section(4.1) so as to calculate the final maximum mean size of the crystals.

Key Differences :

- The batch time for the model was taken to be 240 min(t_f).

- An initial concentration value of 0.073 g/L was taken to obtain the cooling profile. All the moments were intialised to 0.

- The ODEs were integrated using Python **scipy's odeint** integrator.

TABLE 6.1: Kinetic Parameters[21]

Parameters	Experimental Values	Range of Values
Growth Kinetics		
$\ln(k_g)$	3.41 ± 0.28	$\mu m \, min^{-1}$
g	1.48 ± 0.04	$-$
Nucleation Kinetics		
$\ln(k_{j_1})$	24.74 ± 0.73	$No. per m^3 min$
k_{j_2}	$2.7 \times 10^{-2} \pm 3.2 \times 10^{-3}$	$-$

Algorithm

1. The process model consists of 4 uncertainities which computationally prohibits the evaluation. Thus, the experiment has been done on k_g and g, employing a joint distribution of the parameters.

2. Samples are generated using the distribution using Gaussian Quadrature Scheme.

3. The function is evaluated at each of these samples to evalute the integrals numerically to determine the PCE coefficients.

4. At each sample, optimization of the model is performed using the Determinstic Approach explained in Section(4.1).

5. The convergence criteria and the constraints remain same as the above referenced method.

6.3   Results

The value for the concentration profile for the time horizon was obtained as :

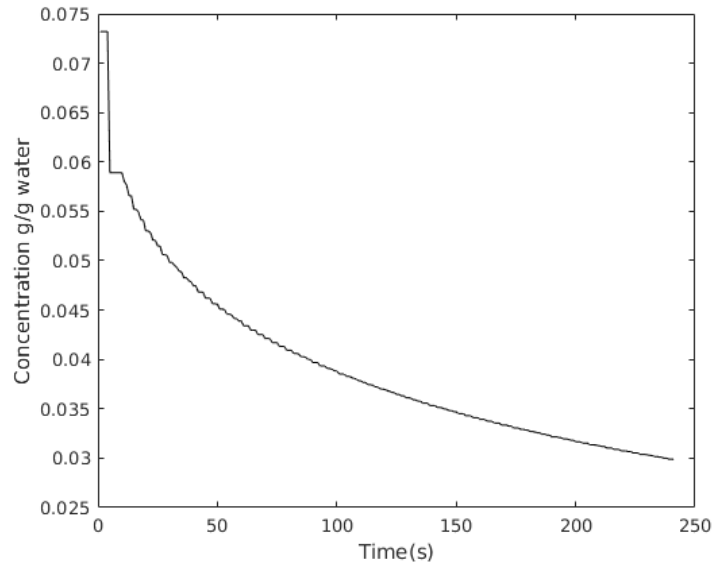The value for the temperature profile was obtained as :
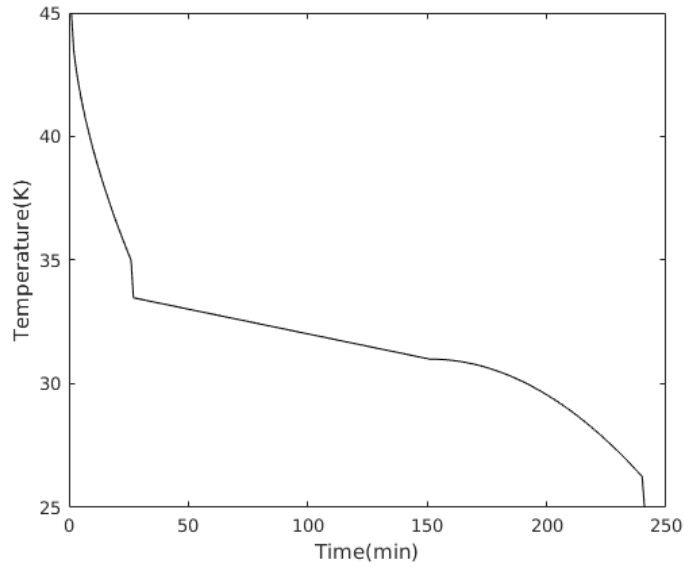
FIGURE 6.1: Concentration Profile

FIGURE 6.2: Temperature Profile

6.4 Conclusion

- The final value of the objective function(μ_4/μ_3), ie. the mean crystal size was obtained at : $300\mu m$

- The model performs at par with other cooling policies such as cubic cooling policy($251\mu m$)[21]. This proves the efficacy of P.C.E in the field of batch crystallization.

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