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สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
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MODEL PREDICTIVE CONTROL FOR SEMI-BATCH REACTIVE CRYSTALLIZATION PROCESS

Miss Aritsara Saengchan

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By	Miss Aritsara Saengchan
Field of Study	Chemical Engineering
Advisor	Associate Professor Paisan Kittisupakorn, Ph.D.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

…………………………………….Dean of the Faculty of Engineering
(Associate Professor Boonsom Lerdhirunwong, Dr.Ing.)

THESIS COMMITTEE

……………………………………Chairman
(Associate Professor Tharathon Mongkhonsi, Ph.D.)

……………………………………Advisor
(Associate Professor Paisan Kittisupakorn, Ph.D.)

…………………………………… Examiner
(Soorathep Kheawhom, Ph.D.)

……………………………………External Examiner
(Veerayut Lersbamrungsuk, D.Eng.)

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กระบวนตกผลึกที่มีปฏิกิริยาเป็นกระบวนการที่ใช้สำหรับผลิตสารเคมีมูลค่าเพิ่มสูง เช่น ยา ตัวเร่งปฏิกิริยา เซรามิก เม็ดสีและเครื่องสำอางค์ ในกระบวนการตกผลึกทั่วไป การกระจายขนาดผลึกมีผลต่อกระบวนการในขั้นตอนถัดไป เช่น การกรอง การทำให้แห้งและการเก็บรักษา วัตถุประสงค์ของกระบวนการตกผลึกคือการได้ผลึกที่มีขนาดเฉลี่ยตามความต้องการ

งานวิจัยนี้นำเสนอการประยุกต์ใช้เทคนิคการออปติไมซ์แบบพลวัตในกระบวนการตกผลึกแบบเซมิแบตช์ที่มีปฏิกิริยาเพื่อหาภาวะความเข้มข้นที่เหมาะสมในการดำเนินงานที่ทำให้ได้ผลึกขนาดใหญ่ที่สุด โดยสอดคล้องตามเงื่อนไขข้อกำหนดคุณภาพผลิตภัณฑ์ เช่น ค่าความแปรปรวนของขนาดผลึก การควบคุมแบบโมเดลพรีดิกทีฟ ซึ่งเป็นการควบคุมแบบไม่เชิงเส้น ได้นำมาประยุกต์ใช้เพื่อควบคุมติดตามภาวะดำเนินการที่เหมาะสมที่ได้ออกแบบไว้ โดยตัวควบคุมแบบโมเดลพรีดิกทีฟนั้นต้องการข้อมูลป้อนกลับที่แต่ละช่วงเวลาเพื่อใช้ในระเบียบวิธีการคำนวณและใช้ตัวกรองคาลมานส่วนเพิ่มเติมเพื่อประมาณค่าภาวะของระบบที่ไม่สามารถวัดได้และเพื่อประมาณค่าคงที่ทางจลนศาสตร์ที่มีค่าไม่แน่นอน ผลจากการจำลองกระบวนการแสดงให้เห็นว่าเทคนิคการควบคุมแบบโมเดลพรีดิกทีฟร่วมกับตัวกรองคาลมาลส่วนเพิ่มเติมจะสามารถควบคุมให้ได้ผลึกเฉลี่ยที่มีขนาดใหญ่เพิ่มขึ้น 30% เมื่อเทียบกับเทคนิคการควบคุมโดยการป้อนสารแบบคงที่ สมรรถนะการควบคุมของถังตกผลึกแบบเซมิแบตช์สามารถปรับปรุงให้ดีขึ้นได้โดยใช้การควบคุมแบบโมเดลพรีดิกทีฟร่วมกับตัวกรองคาลมานส่วนเพิ่มเติม

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต

สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก

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Reactive crystallization or precipitation is widely used for the production or purification of valuable substances such as catalysts, ceramics, pigments, cosmetics and pharmaceuticals. In the crystallization process, the size distribution of crystals can affect subsequent operations such as filtration, drying and storage. Normally, the objective of the crystallization process is to achieve a specified the average crystal size.

This research presents the implementation of a dynamic optimization strategy in a semi-batch reactive crystallization process to determine an optimal operating concentration policy maximizing an average crystals size subject to a product quality constraint, i.e., the requirement of coefficient of variation. Instead of assuming the perfect tracking of the optimal concentration profile, a nonlinear model predictive control (MPC) is applied to track the obtained optimal concentration policy. As feedback information of states at each time step is required in the MPC algorithm, an extended Kalman filter (EKF) is incorporated to provide the estimate of non-measurable states and uncertain kinetic model parameters in the MPC algorithm. Simulation results demonstrate that the average crystal size is increased by 30% compared with the constant feed rate control strategy. The robustness of the semi-batch reactive crystallizer control is improved by the MPC control integrated with the EKF.

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LIST OF ABBREVIATIONS

b	nucleation rate exponent
B	nucleation rate, *no.crystal /[s kg solvent]*
C	solution concentration, *kmol solute/kg solvent*
C_s	saturation concentration, *kmol solute kg solvent*
CV	coefficient of variation
E	activation energy
F	feed flow rate, *kg/s*
g	growth rate exponent
G	growth rate, *m/s*
k_b	birth rate coefficient, *no.crystal/[kg s (mol/kg)*^{b}*]*
k_g	growth rate coefficient, *m/[s (mol/kg)*^{g}*]*
k_v	volumetric shape factor
k_r	rate constant, *kg/kmol*
K	Kalman gain matrix
K_{SP}	solubility product
L	characteristic crystal length or crystal size, *µm*
M_C	molecular weight of crystal
Q	mass of reactant, *kg*
r	rate of reaction, *kmol/kg solvent s*
S	relative supersaturation
S_a	thermodynamic supersaturation
t	time, *sec*
Δt	sampling time, *sec*
u	the control vector
V	capacity of reactor, *kg*
v	the measurement noise
w	the process noise

x	the system state vector
y	the observation vector

Greek Symbols

ν	the number of mole of ion in 1 mol of solute
ν^-	the number of mole of anion in 1 mol of solute
ν^+	the number of mole of cation in 1 mol of solute
ρ_C	density of crystals, kg/m^3
μ_i	the i moment of crystal size, $no.m^j/kg$ *solvent*

CHAPTER I

INTRODUCTION

A crystallization process plays an important role in many industries. In chemical engineering, crystallization is used in the petrochemical industry for the manufacture of polymers. In a specialty chemical industry, crystallization is utilized for solid-liquid separation and purification of high-valued chemicals and household products. In a pharmaceutical industry, protein crystallization is required for drug design. In addition, applications of crystallization have been found in a microelectronic industry for silicon production and chemical vapor deposition for semiconductor manufactures. Crystallization is also applied in food industries, e.g., in the production of butter, cheese, ice cream, sugar, and salt (Patience, 2002). Crystallization can generally be operated in continuous and batch operation modes. Continuous crystallizers are typically used for large-scale production. However, since batch crystallizers can produce a narrow crystal size distribution and a large mean crystal size production, they are often used especially in the production of low-volume and high-value products. Moreover, process operation in the batch mode is quite flexible and allows for changing product specification.

Reactive crystallization or precipitation is a key production step for a wide range of industrial process. Many substances such as fine and bulk chemicals, pharmaceuticals, biochemicals, catalysts, pigments, photographic materials or ceramics are produced by reactive crystallization.

There is currently a great deal of interest in the development and use of alternative non-conventional techniques that allow both the separation and purification of the compounds obtained during a process and the use of systems that combine reaction and separation into a single process unit to improve process performance. Reactive crystallization is a very complex process and much effort has been directed towards understanding and interpreting the interplay between the reaction, crystallization and mixing kinetics. However, further exploitation of the interplay between these kinetic processes for the optimal operation of reactive crystallizers remains a scarcely researched area.

Semi-batch operation for a reactive crystallization process offers the advantages of easily controllable feed rates, which can lead to significant improvement in product quality than traditional batch operation. During a semi-batch reactive crystallization, two liquid reactants are brought into close contact in a single feed or double feed operation, and the crystalline product or precipitate is formed by a chemical reaction in concentrations exceeding the solubility of the solute (supersturation). Thus, the mixing mechanism and the feed flow rates of the reactants exert significant influence on the characteristics of the product crystals.

The crystal size distribution (CSD) is one of the most important properties to control in these processes. CSD is typically characterized by the mean and variance, or sometimes upper and lower particle sizes, but the entire shape of the distribution can affect the product’s material and processing properties. It is the usual practice to control the CSD by controlling its characteristic variables (e.g. the mean) or other easily measured variables (e.g. temperatures, pressures, and concentrations) of the bulk phase. Recent development of on-line instrumentation for particle sizing makes it possible to use on-line CSD data and on-line feedback control of CSD is becoming a realistic possibility. Even with an accurate on-line CSD measurement, the use of a conventional feedback control strategy (e.g. multi-loop PID control) may be unsuitable, because the CSD for different size ranges cannot all be controlled independently. In addition, characteristics of most particulate systems are nonlinear and time-varying; a fixed parameter controller based on an off-line-data-fitted model may perform poorly over a course of large time period. The problem is better handled by using an optimization-based control technique coupled with state estimation (Rawlings et al., 1993). However, it requires an on-line optimization calculation at each time step and hence the computational burden is not always manageable. Significant simplification of the model or the simulation/optimization algorithm may be needed for on-line control.

A model-based feedback controller known as a model predictive control (MPC) has found to be successful in industrial applications because of its ability to handle nonlinear processes, multivariable interactions, constraints, and optimization requirements. A nonlinear model predictive control has been applied to various process systems. In a MPC algorithm, a dynamic process model is used to predict and optimize the future behavior of the process. The basic concept is that it calculates future controls based on current measurements via the solution of an optimal control problem. Then, the states are measured and used as initial conditions in order to recalculate the control action.

In this work a semi-batch reactive crystallization that developed by Tavare and Garside (1990) is considered. A model predictive control (MPC) with the Extended Kalman filter is designed and implemented for control of crystal size distribution (CSD) described by population balance models, and its performance has been evaluated and compared with conventional controller.

1.1. Research Objective

The objective of this research is to design a MPC, a modelbased control, for a semi-batch reactive crystallization to track optimal operating condition. The model predictive control (MPC) is incorporated with the extended Kalman filter (EKF) to estimate unknown parameter. The designed MPC with EKF is then tested and evaluated in cases of plant/model mismatches.

1.2. Scope of Research

1. A semi-batch reactive crystallization process by Tavare and Garside (1990) is considered.
2. A mathematical model of a semi-batch reactive crystallization process is studied.
3. A model predictive control approach is implemented for the semi-batch reactive crystallization process.
4. The performance of model predictive controller is compared with conventional controller.

5. Programs written to simulate and control the process are based on MATLAB Program and MATLAB Toolbox.

1.3. Contributions

1. A computational program to simulate the performance of a semi-batch reactive crystallization has been developed.
2. A semi-batch reactive crystallization has been controlled via using the model predictive controller to achieve a desire objective.
3. Unmeasurable state variable and unknown parameter of a semi-batch reactive crystallization have been estimated.

1.4. Activity plan

1. Study and collect the information relating to the research
    - A conventional semi-batch reactive crystallization process
    - Optimization techniques
    - Model predictive control strategy
    - System identification
2. Study MATLAB programming software
3. Apply the developed MPC for the control of the semi-batch reactive crystallization process.
4. Compare the performance of the model predictive control with the conventional control strategy.
5. Analyze and summarize the result of the research

1.5. Research Framework

This thesis is organized as follows: First, the literature reviews related to the reactive crystallization process, the model predictive control and the extended Kalman filter are presented in Chapter II. Second, the theories of the reactive crystallization process, the model predictive control and the parameter estimation approach are explained in Chapter III. Next, the application of the model predictive control for semi-batch reactive crystallization and simulation results are presented in Chapter IV. Finally, the conclusions and the recommendations for future work are given in Chapter V.

CHAPTER II

LITERATURE REVIEW

2.1 Semi-batch reactive crystallization

Reactive crystallization or precipitation is used commercially for the production or purification of valuable substances such as catalysts, ceramics, pigments, cosmetics, pharmaceuticals and photographic emulsion.

The effects of different mixing and process parameters on the formation of crystals obtained from semi-batch precipitation and the influence of feed time, feed concentration, feed tube diameter and impeller type on particle morphology of the crystal are discussed in many research for example Aslund and Rasmuson (1992) carried out an experimental study of the semi-batch reactive crystallization of benzoic acid. They comprehensively investigated the effects of feed addition time, feed concentration, feed point location, stirrer type and mixing intensities on the product characteristics of crystals. Houcine et al. (1997), Mahajan and Kirwan (1996), and Baldyga et al. (2007) investigated the influence of mixing conditions on the precipitation process. Torback and Rasmuson (2004) reviewed the influence of the stirring rate and the feed rate on the mean-crystal size in semi-batch reaction crystallization processes, Wong et al. (2001) investigated the effect of reactive ions in a semi-batch reactor on the crystal size distribution (CSD), mean sizes and morphology.

A study of barium sulfate precipitation in a double-feed, semi-batch mode was conducted by Wong et al. (2003). The effects of addition mode, feed location, feed molar ratio and stirrer speed on the precipitate characteristics were investigated. It was found that stirrer speed had only a limited effect. The most important parameter was the local, initial molar ratio of reactants, hence the local supersaturation.

2.2 Optimization

There has been extensive research on the modeling and analysis of reactive crystallization through simulation and experimentation. Tavare and Garside (1990) simulated a general reactive process in semi-batch crystallizer and concluded that variations in the reactant addition profiles can be used to exercise significant control over the product-size distribution.

Not very much research has been directed toward mathematical optimization of reaction crystallization processes. Semi-batch operation for a reactive crystallization process offers the advantages of easily controllable feed rates, which can lead to significant improvement in product quality than traditional batch operation. Many studies have been conducted to investigate the effect of feed position, the diameter of the feed-pipe, the feeding rate and profile, the hydrodynamic within the vessel, and the time of feeding on the CSD in reactive crystallization processes. Experimental studies show that feed rates do have an effect on the final product CSD (Philips et al. (1999), Torbacke and Rasmuson (2004), and Mukhopadhyay and Epstein (1980)) in such process. In addition, under certain conditions the importance of mixing, and in particular, the effects of micromixing can be neglected.

Recently an optimization of semi-batch reactive crystallization process has received considerable attention as it is a useful tool to design an optimal operating temperature which has a direct effect on the final-time CSD. The majority of the studies focused on understanding the interplay between mixing and crystallization kinetics.

The study of Choong and Smith (2004) presented a stochastic optimization framework, based on Simulated Annealing for optimizing semi-batch reactive crystallization processes. The optimization is sought with respect to thee reactants feed profiles that maximize the crystal size subject to a specified maximum coefficient of variation (CV), or minimize CV subject to a specified minimum crystal size. The control strategies that produce the largest average crystal size usually lead to high CV. Results indicate that the optimized operation produced significant improvement in the overall crystal quality compared with the conventional semi-batch operation of constant feeding rate.

2.3 Model Predictive Control

Model predictive control (MPC) refers to a class of control strategies in which control inputs are computed based on an optimization criterion that is formulated over a prediction horizon, using an explicit model to predict the effect of future inputs on system states or outputs. MPC incorporates feedback by dynamically updating the optimization problem to include the effects of process measurements.

MPC approach has found to be successful in industrial applications. This is due to the outstanding characteristics of the MPC for couple with inherent nonlinear processes, multivariable systems, and constraints on processes. In general, model predictive control can be divided into two classes: linear model predictive control and nonlinear model predictive control. Linear MPC refers to a family of MPC schemes in which linear models are used to predict the system dynamics even though the dynamics of the system is nonlinear, while nonlinear MPC refers to the general cases in which the dynamic system models, performance objective, and constraints may be in nonlinear function of state, input and output variables.

Even though, a construction of nonlinear process models is sometime very difficult and time-consuming task, they can be used to describe the system in a wide range of operation condition. Moreover, due to advanced numerical techniques for optimization and powerful computer, it is possible to solve the nonlinear programming problem resulting from the formulation of nonlinear MPC.

Nonlinear MPC has been applied to a wide variety of process systems. For instance, Lee and Lee (1997) proposed a novel model predictive control algorithm designed specially for nonlinear batch processes. Unlike existing MPCs which duplicate the same control error in the repeated batches, the proposed algorithm can achieve perfect tracking despite model uncertainty as the number of batch runs increases. As a special case, they also propose a maximum horizon algorithm which ensures convergence just as infinite horizon MPC does for continuous processes.

The proposed of Ju et al. (2000), a nonlinear MPC is applied to control a fabric filtration process. The control algorithm formulated in a multiple-objective optimization framework takes an economic factor into consideration. The global optimization technique is used to compute a manipulated input profile. Simulation results showed that the proposed MPC is especially suitable to the filtration process where the set point change and process disturbance occur frequently.

The nonlinear MPC based on a successively linearized nonlinear model is formulated and applied to an industrial polypropylene semi-batch reactor process as well as to a high density polyethylene (HDPE) continuous stirred tank reactor process by Seki et al. (2002). For the semi-batch reactor, the nonlinear MPC successfully prevented thermal runaway of the reactor temperature control. For the continuous reactor, the nonlinear MPC improved the closed loop performance during the grade changeover operation, compared with the conventional linear MPC.

Cerrillo and MacGregor (2005) presented a latent variable model predictive controller (LV-MPC) for use in tracking set point trajectories in batch and semi-batch processes. The performance of the LV-MPC is shown to be very good in comparison to traditional PI controllers, not only for achieving tighter trajectory tracking, but also by doing so with much less effort in the manipulated variables.

In case of continuous operation of the crystallizers, the objective is often stabilization, and the presence of constraints on the manipulated input variables limits the set of initial conditions starting from where stabilization can be achieved. For batch processes, in contrast, the expression of performance considerations in the form of appropriate constraints or in the objective function, and achieving a desired product size distribution, are more important issues. Shi et al. (2005) proposed the control of a batch protein crystallization process. A predictive controller is designed to achieve the objective of maximizing the volume-averaged crystal size while respecting constraints on the manipulated input variables and on the process state variables. Simulation results showed that the proposed predictive controller was able to increase the volume-averaged crystal size by 30% and 8.5% compared with the constant temperature control and constant supersaturation control strategies, respectively, and the number of fine crystal is reduced. Moreover; in the presence of plant-model mismatch, this method is robust in comparison to open-loop optimal control strategies.

Shi et al. (2006) concentrated on an optimization-based predictive control strategy, which incorporated constraints explicitly in the controller design in continuous and batch crystallizers. For continuous mode, the objective of stabilization under constraints is considered. Using this strategy, a continuous crystallizer at an open-loop unstable can be successfully stabilized. On the other hand, the objective is to achieve a desired particle size distribution under control and product quality constraints for the batch mode. The strategy is shown to be able to reduce the total volume of fine crystals by 13.4% compared to a linear cooling strategy.

In the present of Paengjuntuek (2007), the implementation of a dynamic optimization strategy in a batch crystallization process to determine an optimal operating temperature policy minimizing the nucleation of fine crystals subject to a product quality constraint. An on-line dynamic optimization and advance control technique known as Model Predictive Control (MPC) technique have been implemented to achieve a desired crystal size distribution (CSD) and an extended Kalman filter (EKF) has also been incorporated to provide estimates of non-measurable states.

Ricker (1990) developed a state space formulation of the multivariable model predictive controller with provisions for state estimation. Hard constraints on the manipulated variables and outputs were accommodated, as in Quadratic Dynamic Matrix Control (QDMC) and related algorithms. For unconstrained problems, a low order analytical form of the controller is obtained. The potential benefits of MPC with state estimation are demonstrated for the case of dual-composition, LV control of the high-purity distillation column problem studied previously by Skogestad and Morari, which is an especially challenging problem for MPC-type algorithms. It is shown that the use of the state estimator with a single tuning parameter (beyond that required for standard MPC) provides robust performance equivalent to the best p-optimal controller designed by Skogestad and Morari.

Eaton and Rawlings (1992) purposed Model Predictive Control (MPC) a scheme in which an open-loop performance objective is optimized over a finite moving time horizon. MPC is shown to provide performances superior to conversional feedback control for nonminimum phase systems or systems with input constraints when future set points are known. Stabilizing unstable linear plants and controlling nonlinear plants with multiple steady state are also discussed.

Sistu et al., (1993) discussed the implementation of different nonlinear strategies in a MPC framework to control an exothermic continuous stirred tank reactor. The computational efficiency of a MPC strategy depends on the method used to predict model outputs within the optimization loop. The computational requirements of collocation and numerical-based methods to solve nonlinear differential modeling equations are compared with the nonlinear quadratic dynamic matrix control (NLQDMC) formulation. The convolution coefficients for NLQDMC are obtained using analytical and numerical methods and their computational time requirements are compared.

Patwardhant and Madhavan (1993) presented the development of an approximate second-order perturbation model, which can be used for single step and multistep predictive control. The algorithm has been successfully implemented on two continuously stirred tank reactors (CSTRs) control problem where the control objective is to operate the reactor at an extremum point. The control problem is associated with the singular nature of the operating point has been successful tackled by the purposed algorithm. The MPC algorithm based on the proposed second-order model is shown to improve the closed loop performance when compared to other nonlinear MPC algorithms. The proposed algorithm has been found to be robust for moderate variations in the kinetic parameters.

Masoud et al., (1995) used the short horizon nonlinear model predictive control that concerns nonlinear model predictive control of the multivariable, open-loop stable processes whose delay-free part is minimum-phase. The control law is derived by using a discrete-time state-space formulation and the shortest useful prediction horizon for each controlled output. This derivation allows to establish the theoretical connections between the derived nonlinear model predictive control law and the discrete-time globally linearizing control, and to deduce the conditions for nominal closed-loop stability under the model predictive control law. Under the nonlinear model predictive controller, the closed-loop system is partially governed by the zero dynamics of the process, which is the nonlinear analog of placing a subset of closed-loop poles at the zeros of a process by a model algorithmic controller.

Phupaichitkun (1998) applied model predictive control (MPC) to control the temperature of a batch reactor with exothermic reactions and its performance is compared with generic model control (GMC) to that of individually/simultaneously plant/model mismatches. In addition, Kalman Filter that used to estimate the heat released of chemical reactions is incorporated into the MPC and GMC. Simulation studies are shown that MPC to be as good as GMC for all cases for which both controllers are well tuned.

Ruksawid (1999) used model predictive control (MPC) with Kalman filter for the control of the temperature and the concentration of a reversible exothermic. The design MPC with Kalman filter which can give a good control performance and guarantee the stability of closed loop nonlinear continuous time systems subject to constraints. Several different problems have been considered, such as control performance, disturbance rejection, set point tracking and parametric model/plant mismatch. Simulation results have shown that the MPC with Kalman filter provides better control performances than the conventional PID controller does for the control of the temperature and the concentration f a continuous stirred tank reactor in the cases of disturbance rejection and set point tracking. In addition, the MPC is more robust than the PID in presence of model/ plant mismatch.

Ralhan and Badgwell (2000) presented two robust model predictive control algorithms for linear integrating plants described by a state space model. The first formulation focused on steady state offset whereas the second minimizes output deviations over the entire prediction horizon. The input matrix parameters of the plant are assumed to lie in a set defined by an ellipsoidal bound. Robustness is achieved through the addition of constraints that prevent the sequence of the optimal controller costs from increasing for the true plant. The resulting optimization problems solved at each time step are convex and highly structured. Simulation example compared the performance of these algorithms with those based on minimizing the worst-case controller cost.

Tongmeesee (2000) presented the application of MPC to control the temperature of a batch polymerization reactor. The performance of MPC with Kalman filter is compared to that of a simple nonlinear control technique named generic model control (GMC). Simulation results have shown in normal case and presence of plant/model mismatch (decrease in heat transfer coefficient and rate of termination reaction and increase of the monomer concentration and heat of reactions), MPC with Kalman filter give a better control performance than GMC with Kalman filter.

Brempt et al. (2001) presented the advanced model predictive control technology bsed on rigorous dynamic models. Key requirements of the new technology are the realization of a flexible process operation, a large bandwidth control enabling tight quality control and low application costs. The flexible operation is realized by the combination of a dynamic optimizer over a rigorous model together with a model predictive controller in delta-mode. A large band width control is enabled by the used of high frequent prediction models. Ultimately, reuse of large parts of rigorous models for different applications together with low frequency testing on these rigorous models for different applications together with low frequency testing on these rigorous models reduces the application cost. The application of the before mentioned technology is shown successfully on a polyethylene gasphase reactor simulator. A considerable economic benefit can be obtained optimizing the transition trajectory as will as the throughput at that time.

In the present of Paengjuntuek (2007), the implementation of a dynamic optimization strategy in a batch crystallization process to determine an optimal operating temperature policy minimizing the nucleation of fine crystals subject to a product quality constraint. An on-line dynamic optimization and advance control technique known as Model Predictive Control (MPC) technique have been implemented to achieve a desired crystal size distribution (CSD) and an extended

Kalman filter (EKF) has also been incorporated to provide estimates of non-measurable states.

2.4 Parameter Estimation Approach

In most industrial processes, the process parameters and state variables are not all measurable or, not with sufficient accuracy for control purposes. Furthermore, measurements that are available often contain significant amounts of random noise and systematic errors.

State variables of a process determine uniquely the state of the process and are either measured directly or estimated using a state estimator. On the other hand, process parameters provide a mathematical model with flexibility to fit process measurements, are often of great physical importance, and are usually not measured directly. Information on unknown process parameters can be obtained indirectly by means of a parameter estimator: In 1960, Kalman published a famous paper decribing a recursive solution to the discrete data linear filtering problem. The Kalman filter has been the subject of extensive research and application, particularly in the area of autonomous or assisted navigation.

The nucleation and growth parameters for a KNO_3-H_2O system and a photochemical-heptane system are estimated by Rawlings et al. (1993), and Matthews et al. (1996) respectively. The results show that information obtained from the continuous phase (the concentration measurement) is not enough to determine the parameter uniquely. In order to reduce the limits of uncertainty in the parameter values, it is also necessary to use information on the solid phase (transmittance measurement).

Then, in 1995 Livk et al. determined the nucleation, growth and agglomeration kinetic parameters for sodium perborate (SPB) precipitation process by applying an optimization estimation procedure posed as a nonlinear programming problem. Successive quadratic programming (SQP) has been used to solve this problem. Optimal values of parameters were calculated based on either concentration or size distribution data. The least squares objective function was used. First type of the objective function is written as a sum of the weighted square-deviations between measured and calculated CSD. Another type can be stated in terms of solute concentration. The results show that agglomeration kinetics and CSD can not be predicted using the concentration information. When both criteria of the objective function is formed; however, no significant improvement is observed. The reason is that the first objective function already includes the concentration criteria and the CSD information. The values of some parameters (growth parameters) are close to those obtained by experiments implying isolation methods.

A model based experimental design procedure is applied in a KNO_3-H_2O crystallization process by Chung et al. (2000) to estimated nucleation and growth parameters. Initial parameters estimates are used to compute the first experimental design. The collected data are used to compute improved parameter estimates for the next laboratory experiment. The procedure was repeated until the relative error in each kinetic parameter was less than 2%. The parameter estimation problem is posed as a nonlinear optimization problem. The measurements are concentration and transmittance (related to the second moment). Highly accurate estimation of these parameters can be obtained with four batch experiments. The seed characteristics have a much stronger effect on the quality of the parameter estimates.

Yang and Wei (2006) said that the traditional empirical correlations obtain from experimental data using assumed functional forms cannot give reliable predictions, as the highly nonlinear behavior of crystallization kinetics. Hence, a neural network model, which is able to reproduce the system behavior with its nonlinearities and parameter interaction effects, is developed to predict crystal nucleation, growth, and agglomeration rates for a ciprofloxacin hydrochloride, water, and ethanol system. The results demonstrated that the neural network approach can predict the complex interplays of influential factors in the crystallization process result in more accurate prediction of the crystallization kinetics.

On the other hand, in order to perform the on-line optimization strategy, the knowledge of current states and/or process parameters in the process model is required. However, some of these variables cannot be known exactly, it is important to include an on-line estimator to estimate these process variables using available process measurement as well. As is several estimation techniques, an Extended Kalman Filter (EKF) has been widely employed as it is relatively straightforward to implement. It has been found that the EKF can be applied to a number of chemical process applications with great success.

Model Predictive Control (MPC) incorporated with an EKF is presented by Kittisupakorn and Hussain to control and estimate the unmeasured a concentration in a reactor. The simulation results have been shown that the estimated concentration can approach the actual value. Hence, the MPC with EKF can control the reactant concentration at the desired set point with less drastic control action and within the reactor temperature constraint.

An on-line dynamic optimization strategy incorporated with EKF to modify optimal temperature set point profile for batch reactor. The EKF is used to updated current states, reactant concentrations, from their delayed measurement, to estimate the reaction rate constants, and to estimate unmeasurable state variables, heat released of reactions (Q_r). The simulation results have been shown that the EKF provides an excellent estimation of the heat release. In addition, the EKF gives good estimations of reactant concentrations and reaction rate constants. Hence, the performance of the batch reactor in terms of the amount of a desired product and batch operation time can be improved significantly by the proposed strategy.

In the crystallization process, the EKF is used as a state estimator to estimates for the unmeasured states in the research of Zhang and Rohani (2003), The EKF is used as an on-line state estimator to provide estimates for the unmeasured states, and to reduce the effect of measurement noise in an on-line optimal control of a seeded batch cooling crystallizer. The simulation results have been demonstrated that the predicted values of *i*th moments and the size of seeded crystals converge to the actual values quickly with small offset, which indicate that the EKF can provide good predictions of the unmeasured state variables.

In the present of Paengjuntuek (2007), the implementation of a dynamic optimization strategy in a batch crystallization process to determine an optimal operating temperature policy minimizing the nucleation of fine crystals subject to a product quality constraint. An on-line dynamic optimization and advance control technique known as Model Predictive Control (MPC) technique have been implemented to achieve a desired crystal size distribution (CSD) and an extended Kalman filter (EKF) has also been incorporated to provide estimates of non-measurable states.

CHAPTER III

THEORY

The continuous development of the chemical process industry has been accompanied by rising demands for product quality. Crystallization is one of the methods to produce particulate material in the chemical industry. In the twenties, the first definition of crystallization as a unit operation appeared (Walker et al., 1923). This concept was used until the sixties when Randolph and Larson (1971) took population balance into account for mathematical treatment for crystallization analysis and design. After that, crystallization became recognized as a more complex field and as a part of the chemical engineering sciences. Many approaches appeared to establish the foundations of industrial crystallization, including chemical precipitation (Nielsen, 1964; Strickland-Constable, 1968; Nývlt, 1971; Mullin, 1972 and Garside, 1985).

3.1 Crystallization process

The motivation for modeling a process is to gain an accurate mathematical representation of the behavior of the physical system. The developed process model can be employed as a useful tool to study, design and improve the systems. Furthermore, the model can be used in the formulation of advanced model-based control techniques.

This chapter outlines a semi-batch crystallizer model using a population balance equation (PBE) to describe the evolution of a crystal size distribution (CSD). The PBE is augmented by mass and energy balances that model the dynamics of the solute concentration in the solution phase and the system temperature, respectively. Semi-batch crystallization is driven by the kinetic processes of crystal nucleation and growth.

The PBE is a partial differential equation in time and crystal size. Consequently, the crystallization model is solved numerically. Although the population model can be directly solved, its implementation in an optimization problem is very time-consuming. Therefore, the moment model of crystallizers is used to formulate the optimization problem in this study.

Crystallization

Crystallization is the formation of solid particles within a homogeneous phase. It is widely applied for a separation process in inorganic chemical industries, particularly where salts are recovered from aqueous media. In the production of organic chemicals, crystallization is also used to recover product, to refine intermediate chemicals and to remove undesired salts. The feed to a crystallization system consists of a solution from which solute is crystallized or precipitated via one or more variety of processes. The solids are normally separated from the crystallizer liquid, washed, and discharged to downstream equipment for additional treatment. High recovery of refined solute is generally the desired design objective, although sometimes the crystalline product is a residue (Rousseau, 1987). The solid phase is characterized in part by its inherent habit and size distribution. The natural habit of the solid phase is important since it influences product purity, yield and capacity of the crystallizer system.

Crystallization offers the following advantages:

1. Pure product (solute) can be recovered in one separation stage.
2. A solid phase is formed that is subdivided into discrete particles. Generally, conditions are controlled so that the crystals have the desired physical form for direct packaging and sale.
3. The capital and operating cost are relatively low.

However, the major disadvantages of crystallization are:

1. Purification of more than one component is not normally attainable in one stage.
2. The phase behavior of crystallizing systems prohibits full solute recovery in one stage; thus, the use of additional equipment to remove solute completely from the remaining crystallizer solution is necessary.

Crystallization occurs only if the system is supersaturated. In the formation of a crystal two steps are required: (1) the birth of a new particle called nucleation and (2) its growth to macroscopic size. In a crystallizer, the CSD is determined by the interaction of the rates of nucleation and growth, and the overall process is complicated kinetically. The driving potential for both rates is the nonequilibrium state of the system. The nonequilibrium state is measured by the relative supersaturation, S, where

$$S = \frac{C - C_s(T)}{C_s(T)} \tag{3.1}$$

where C_s is the saturation concentration corresponding to the solution temperature, T .

The technique employed to generate supersaturation is strongly influenced by the phase-equilibrium characteristics of the system. The common techniques for producing solids from a solution include:

1. If the solubility of the solute increases strongly with increase in temperature, as is the case with many common inorganic salts and organic substances, a saturated solution becomes supersaturated by simple cooling and temperature reduction.

2. If the solubility is relatively independent of temperature, as is the case with common salt, supersaturation may be generated by evaporating a portion of the solvent.

3. If neither cooling nor evaporation is desirable, as when the solubility is very high, supersaturation may be generated by adding a third component. The third component may act physically by forming, with the original solvent, a mixed solvent in which the solubility of the solvent is sharply reduced. This process is called salting.

4. If a nearly complete precipitation is required, a new solute may be created chemically by adding a third component that will react with the original solute and form an insoluble substance. This process is called precipitation.

3.2 Reactive Separation Process

Reactive separation processes are unique in that they couple chemical reactions and physical separations into a single unit operation. This fusion of reaction and separation operations into one combined operation is prized for the simplicity and novelty this approach brings to the process flowsheet. These reactive separations are also coveted for the investment and operating cost savings garnered on successful scale-up to commercial operations. Reactive separation processes as a whole are not a new concept. Numerous applications have been commercialized for traditional separation methods over the course of six decades. However, the academic and industrial communities have taken renewed interest in the development and commercialization of reactive separations in recent years in response to economic opportunities and pressures exerted, which have caused the emergence of new industries and decline of existing industries, the emergence of new separation and process technologies, the demand for higher building block purities for food, pharmaceutical, polymer, and electronics products, changes in the availability and pricing of key resources, and the growing concern for protecting our environment. This interest is reflected in the increased volume of literature issued on the development and design of reactive separations and the increasing number of technical conferences devoted to the subject.

The applications of reactive separation process design are numerous and span a broad range of process operations. The development and application of reactive separations is not new. For example, reactive absorption has long been practiced for the removal of acid gases in the petroleum production and refining industries, and acid/base extractions and reactive distillations have long been practiced in the purification of chemicals. However, mention the phrase “reactive separations” and chemists and engineers will likely point to the more recent commercialization of reactive distillation technologies for the esterification of acetic acid to methyl acetate and the etherification of methanol with isobutylene to methyl tertiary butyl ether (MTBE) as examples of the art of reactive separation design.

The potential advantages for implementation of reactive separations are numerous. Perhaps the most sought-after goals in the development of reactive separations are the linking of chemical “sources” and “sinks” to enhance reaction rates, conversions, or selectivities. Transport of desirable reaction products away from the catalyst may lead to enhanced reaction rates and increased feed conversion to products in equilibrium-controlled reaction regimes. Elimination of intermediates and suppression of side reactions may lead to higher yields of desirable byproducts, resulting in lower feedstock costs as a consequence of better feedstock utilization.

3.3 Reactive crystallization

Reactive crystallization, also called precipitation, is an area for which crystallization as well as reaction engineering aspects are important. Classically, crystals are obtained from a solution by (a) cooling, (b) increasing the concentration of the solute through solvent evaporation, (c) combining these two processes when the solvent evaporation is used both for cooling and for concentrating, or (d) by salting or drowning-out with the help of a cosolvent.

Reactive crystallization differs from these classical processes in that the supersaturation, which is required for the crystallization, no longer results from an action on the physical properties of the solution. It is obtained by a chemical reaction between two soluble components leading to a less soluble product which crystallizes.

The reactants can be molecules or ions. The reaction crystallization may proceed via a third intermediate, a dissolved molecule, which becomes solid afterwards. Alternatively, the reactants can directly lead to a very sparingly soluble precipitate. The generated solids can be crystalline or amorphous. Reticulation of the suspended, solid particles may take place, and the suspension is then called a gel.

Hence, the study of reactive crystallization is more difficult than that of classical crystallization, because the crystal generation depends on several processes, which all have their own kinetics (e.g., chemical reaction, crystallization, and mixing). The competition between these three steps generally results in (a) rapid crystallization and especially nucleation, which is very problematic to keep under control, and (b) multiple zones in the apparatus showing different mixing conditions and, consequently, very different crystallization and reaction conditions, therefore, it is necessary to spit the reactor into ideal zones, each zone having given mixing parameters, global reactive crystallization kinetics, and subsequent mechanisms influenced by mixing.

Due to the complexity of the reaction crystallization, the following steps are to be studied:

1. The kinetics of the chemical reaction leading to the supersaturation. These kinetics are often very fast, especially when combining ionic species or for acid-base reactions, leading, in turn, to high local supersaturation. In some cases, this kinetics can be complex, for gas-liquid reactions or for organic reactions between molecules, for example.

2. The kinetics of crystallization, including primary and secondary nucleation, growth, agglomeration and Ostwald ripening, which can be considered as important mechanisms during the reactive crystallization of very small particles. The species are often ionic components and, as an example, growth can be considered as a rather complicated step, because on has to take into account the surface integration and the diffusion of two ions.

3. The kinetics of mixing, which can have a high effect on both reaction and crystallization kinetic rates if the are of the same order of magnitude.

Driving force of reactive crystallization

Two possibilities are to be considered, and we will find this duality in all our discussions:

1. The chemical reaction leads to a more or less soluble molecule P, which then crystallizes. This is the case for many compounds.

$$\mathrm{A+B} \rightleftarrows \mathrm{P} \rightleftarrows \mathrm{S\,(solid)}$$

The first reaction can either be at equilibrium or with finite rates in both directions. For such problems, the solubility of component P can be described as the molar concentration of P in the solution at the thermodynamic solid-liquid equilibrium. This concentration is a function of temperature.

2. The chemical reaction does not lead to any intermediate soluble species, and the solid crystallizes directly from the reactants. This is the case of many ionic reactions, leading to a sparingly soluble salt, between a cation and an anion

$$\mathrm{xA^{z+} + yB^{z'-}} \longleftrightarrow \mathrm{A_xB_y\,(solid)}$$

with the electroneutrality condition $xz=yz'$

3.4 The control of crystallizers

The objective in the operation of a crystallization process is to meet product specifications: (a) a narrow crystal size distribution (CSD), (b) maximum crystal purity, (c) high yield, and (d) acceptable crystal morphology. Moreover, the manufacturer’s requirements for economic and trouble-free operation should be met. Depending on the type of the product, one of the above objectives may be critical. For example, in the production of fertilizers, less significance is ascribed to product purity is of utmost importance. A narrow CSD is always required; however, the desirable mean crystal size varies depending on the type of the product. Maximum yield with a given driving force is to be achieved under all circumstances subject to constraints on crystal quality. Finally, well-formed crystals with uniform morphology not susceptible to breakage are desirable.

It has been demonstrated that a generalized theory for the analysis and prediction of the CSD is available; however, the birth and death rates in the population equation are poorly understood. The principal reason for this is that presently we are unable to make a general prediction of agglomeration, attrition, and breakage rates. This is also true for the rates of nucleation. As a rule, the true supersaturation in the crystallizer is not known and can oscillate even in continuous crystallizers.

Furthermore, the process interrelations that determine the CSD in mixedmagma crystallizers are extremely complicated. In this information flow diagram the population balance is the central equation with reference to the CSD. Besides agglomeration and attrition, the rates of nucleation and growth are the main kinetic parameters that determine the size distribution. These kinetic parameters depend strongly on supersaturation and impurities present in the solution. The true supersaturation is influenced not only by the balances of mass and energy but also by the kinetics of the crystallization process. The picture becomes even more complicated if such processes as clear-liquor advance, fines destruction, and classified product removal are taken into account.

As discussion in earlier sections, crystallization from solution can be brought about by various mechanisms, such as cooling, evaporation, salting out, and reaction using a batch or continuous mode of operation. The common feature among these is the existence of the crystallization driving force (i.e., supersaturation). The method by which supersaturation is generated and various factors affecting its “local” and “average” values have a strong influence on all properties of a crystalline material. Note that the local and average values of supersaturation affect growth, nucleation, and aggregation rates, which, in turn, determine population density and the CSD. The crystal size distribution, on the other hand, determines specific surface area and magma density, which strongly affect growth rate, rate of secondary nucleation, aggregation rate, and solute mass balance in a feedback fashion. Irrespective of the mechanism of generation of supersaturation, impurities exert a strong effect on the width of the metastable zone. Impurities also influence crystallization kinetics, crystal purity, crystal morphology, and aggregation rate. Other disturbances affecting crystal properties are the intensity of mixing, heat losses from the crystallizer, variations in the crystallizer head pressure and feed temperature and composition.

Any attempt to control a crystallization process to meet the above mentioned product qualities should be directed toward generating and maintaining a mild and homogeneous supersaturation in the crystallizing magma at the local and average levels. This favors growth rate and prevents spontaneous nucleation. In industrial crystallizers, this objective is achieved by improving the design of crystallizers as well as controlling some of the easily measurable process variables, like temperature, pressure, level, and flow rates. Such an approach is not sensitive to frequent variations in the feed composition feed temperature, impurities, and local degree of mixedness. Consequently, in the presence of disturbances, off-specification product is to be expected. Improvement in product quality can be assured if advanced control algorithms incorporating sophisticated sensors for on-line measurement or inference of product properties using state estimators (the extended Kalman filter) are employed. The control algorithm should have knowledge of the prevailing local and average supersaturation. If supersaturation is generated in regions where a sufficient crystal surface area does not exist, the available supersaturation will be relieved in primary nucleation and/or leads to encrustation and fouling. Moreover, the likelihood of capturing impurities either in the lattice or in the form of mother liquor inclusion is increased.

Control over crystal morphology is a very complex process. It can be realized either by a controlled growth rate through proper adjustment of supersaturation or by the addition of certain habit modifiers. The habit modifiers are either surface-active agents that adhere to a specific crystal surface retarding its growth rate or are tailor-made additives that would be incorporated in the crystal lattice at one end and slow down further growth a their other end. There is growing interest in the design and manufacture of habit modifiers, which are often product dependent.

Accordingly, in this section, the main emphasis is placed on the control of the CSD, crystal purity, and crystal yield from a suspension. Moreover, control strategies used in melt crystallization will not be considered. Conventional control strategies utilized in industrial crystallizers and recent advances in academic research to improve the CSD and product purity for batch and continuous operations are summarized. It should be borne in mind that product quality in industrial crystallizers is affected not only by the crystallizer but also by the upstream and especially downstream processes (i.e., dewatering, filtration, and drying steps). Discussion on the nature and extent of such effects, however, is beyond the scope of this chapter. Conventional sensors used in the existing control strategies are explained briefly.

3.5 Model Predictive Control

In the previous study, it is demonstrated that the performance of the on-line optimal temperature policy has more robustness than the off-line optimal policy as it able to cope with the external disturbance. Hence, an on-line optimal policy is the superior control strategy in real applications. Furthermore, in the operation of crystallization processes, constraints regarding physical limitations on the capacity of actuators and/or the state variables, i.e., temperature and concentration for safety and/or product quality requirement are inevitably considered. For these reasons, a control technique that provides both on-line optimization computation and ability to handle constraints should be considered.

A model-based feedback controller known as a model predictive control (MPC) has been found to be a successful control strategy in several industrial applications because of its ability to handle nonlinear processes, multivariable interactions, constraints, and optimization requirements (Qin and Badqwell, 2000). For a continuous crystallization process, normally, a key control objective is to stabilize the system at a specified condition. In the presence of constraints on the manipulated input variables, the performance of the controlled system is limited to the conditions which stabilization can be achieved. For a batch process, in contrast, the expression of performance considerations in the form of appropriate constraints and the achievement of the desired size distribution of a product are much more needed.

In a MPC algorithm, a mathematical model of a process is used to determine and optimize its future dynamic behavior. The feedback control action is then calculated based on state values at each time step. In a crystallization process, on-line measurements are not all available; only concentration and temperature can be measured directly. Hence, an on-line estimator should be incorporated in the MPC formulation to estimate un-measurable states. In this study, the implementation of MPC algorithm is proposed to achieve the desired crystal size distribution (CSD) subject to a product quality constraint. In addition, an EKF is incorporated into the proposed algorithm to estimate un-measurable states; the quality of crystals in terms of the *i*th moments. Furthermore, as a model-based control algorithm, MPC requires an accurate model to predict exact process behavior and design the controller maximizing product quality. Generally, an optimization approach has attracted attention for kinetic model identification by a number of authors such as Rawlings et al. (1993), Livk et al. (1995), Matthews et al. (1996), Monnier et al. (1996), Chung et al. (2000), Tadayon et al. (2002), Hu et al. (2005a). The concept of a nonlinear optimization technique, which is used to generate successive guesses of kinetic parameters, is that for each guess, the dynamic equations describing the process are solved and the resulting measurement predictions are compared to the data according to an optimization criterion which is generally a measure of the prediction errors. However, due to unknown disturbances and batch to batch variations in each batch operation, the kinetic parameters obtained from an experiment as mentioned earlier may not suitable to describe real processes. To overcome this problem, an EKF is also designed to on-line estimate these uncertain parameters.

The concept of MPC is to determine a control profile for a whole time horizon minimizing an objective function subject to a dynamic process model with path and/or end point constraints. At each control interval, an open-loop sequence of the manipulated variables is computed in such a way to optimize the future behavior of the plant. Only initial value of the control profile is applied and then the optimization procedure, based on new information at the next sampling time, is repeated to modify a new input profile with the control and prediction horizons moving forward one sampling time step.

3.5.1 The Principle of Model Predictive Control

There are two basic components in MPC approach. A dynamical model represents process behavior, and an optimization algorithm modifies the optimal solution to the manipulated variables with respect to some performance criterion. The optimization procedure is specified by the model structure. For linear model, dynamic matrix control (DMC) is an early approach in MPC (Morari and Lee, 1999).

On the contrary, nonlinear model predictive control (NMPC) is implemented using a nonlinear process model. The optimization problem is solved using a nonlinear programming approach. The basic principle of model predictive control is shown in Figure 3.1. Based on measurements obtained at time t, the controller predicts the future dynamic behavior of the system over a prediction horizon, T_p, and determines the input (manipulated variable), u, over the control horizon, T_c. Usually, the prediction horizon is greater than the control horizon ($T_c \leq T_p$). If there were no disturbances and no model-plant mismatch, and if the optimization problem could be solved for infinite horizons, then one could apply the sequence of the control input profile calculated at time t to the system for all times. However, in reality due to disturbances and model-plant mismatch, the system behavior is different from the predicted behavior. In order to incorporate some feedback mechanism, only the initial value of the control profile is applied and then the optimization procedure, which obtains new information at the next sampling time, is repeated to modify a new control input with the control and prediction horizons moving forward one sampling time step. This causes a feedback control law.

3.5.2 Problem Formulation

A sequence of control moves is computed to minimize an objective function (performance index) which includes predicted future values of the controlled variables. The optimization is solved subject to constraints on input and output variables. This formulation yields an open-loop optimal controller. Feedback is included by implementing only the manipulated inputs computed for the present time step, and then moving the prediction horizon forward one step and resolving the problem using new process measurements. Calculation of the manipulated input sequence requires the on-line solution of a nonlinear programming problem.

Optimization Problem

The nonlinear process model is assumed to have the discrete-time representation.

$$x(k+1) = F\left[x(k), u(k)\right] \tag{3.2}$$

$$y(k) = h\left[x(k)\right] \tag{3.3}$$

where x is a n-dimensional vector of state variables, u is a m-dimensional vector of manipulated variables, and y is a p-dimensional vector of controlled variables.

The optimization problem for the nonlinear model predictive control formulation is

$$\min_{u(k|k),u(k+1|k),\ldots,u(k+T_c-1|k)} J \tag{3.4}$$

where $u(k+j\,|\,k)$ is the input $u(k+j)$ calculated from information available at time k, and J are nonlinear function chosen to satisfy a wide variety of objectives, including minimization of overall process cost.

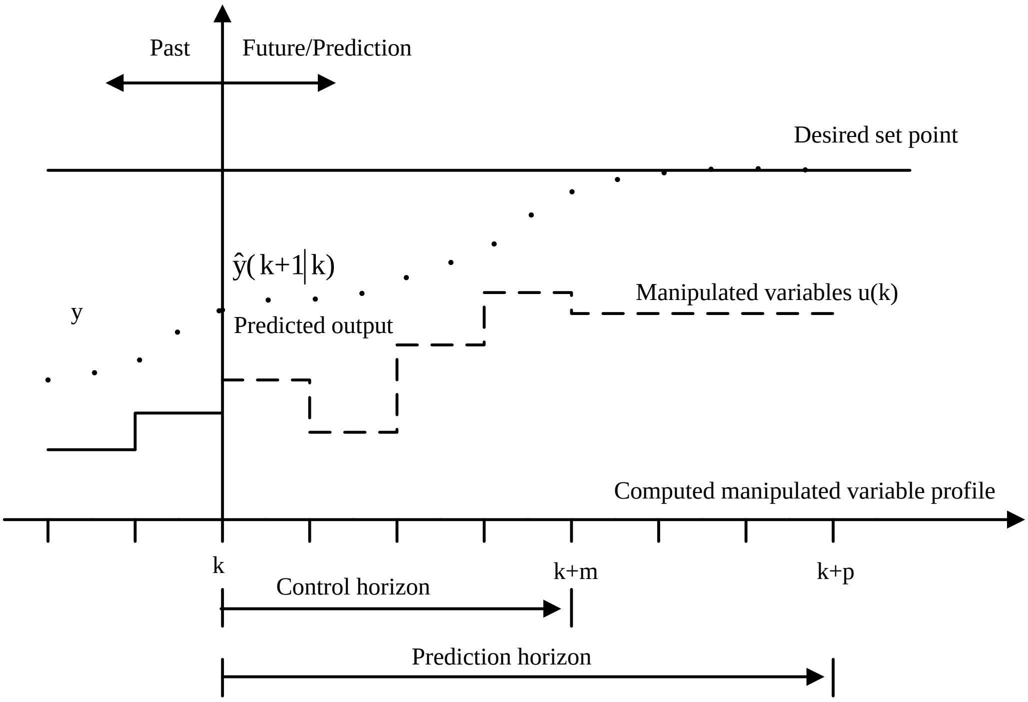

Figure 3.1 Model predictive control approach

The predicted outputs are obtained from the nonlinear process model, Equation (3.2)-(3.3). Successive iterations of the model equations yield

$$
\begin{aligned}
y(k+1|k) &= h\left[x(k+1|k)\right] \\
&\equiv G_1\left[x(k), u(k|k)\right]
\end{aligned}
$$

$$
\begin{aligned}
y(k+2|k) &= G_1\left[x(k+1|k), u(k+1|k)\right] \\
&\equiv G_2\left[x(k), u(k|k), u(k+1|k)\right]
\end{aligned}
$$

.

.

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$$
y(k+j|k) = G_j\left[x(k), u(k|k), u(k+1|k), ..., u(k+j-1|k)\right]
$$

where $x(k|k) = x(k)$ is a vector of current state variables. If the control horizon is less than the prediction horizon, the output predictions are generated by setting inputs beyond the control horizon equal to the last computed value, $u(k+j\,|\,k)=u(k+T_c\,|\,k)$, $T_c \leq j \leq T_p$.

Solution of the nonlinear model predictive control (NMPC) problem yields the input sequence $\left\{u(k\,|\,k), u(k+1\,|\,k), \ldots, u(k+T_c\,|\,k)\right\}$. Only the first input vector in the sequence is actually implemented, $u(k)=u(k\,|\,k)$. Then the prediction horizon is moved forward one time step, and the problem is resolved using new process measurements. This receding horizon formulation yields improved closed-loop performance in the presence of unmeasured disturbances and modeling errors.

Process Constraints

An important characteristic of process control problems is the presence of constraints on input and output variables. Such constraints take the form.

$$u_{\min} \leq u \leq u_{\max}$$

$$\Delta u_{\min} \leq \Delta u \leq \Delta u_{\max}$$

$$y_{\min} \leq y \leq y_{\max}$$

where $u_{\min}$ and $u_{\max}$ are the minimum and maximum values of the inputs, respectively, $\Delta u_{\min}$ and $\Delta u_{\max}$ are the minimum and maximum values of the rate change of the inputs, respectively, and $y_{\min}$ and $y_{\max}$ are the minimum and maximum values of the outputs, respectively. The state constraints may be specified if appropriate.

A major advantage of NMPC when compared to other nonlinear control strategies is that it provides the constraint handling capability. This is achieved by solving the nonlinear optimization problem, Equation (3.4), subject to the following inequality constraints.

$$u_{\min} \leq u(k+j\,|\,k) \leq u_{\max}, \qquad 0 \leq j \leq T_c - 1 \tag{3.5}$$

$$\Delta u_{\min} \leq \Delta u(k+j\,|\,k) \leq \Delta u_{\max}, \qquad 0 \leq j \leq T_c - 1 \tag{3.6}$$

$$y_{\min} \leq y(k+j\,|\,k) \leq y_{\max}, \qquad 1 \leq j \leq T_p \tag{3.7}$$

It is important to note that input constraints are hard constraints in the sense that they must be satisfied. Conversely, output constraints can be viewed as soft constraints because their violation may be necessary to obtain a feasible optimization problem.

3.6 Extended Kalman Filter (EKF)

In the formulation of the MPC controller, the knowledge of current states is required in order to compute the solution of an on-line optimal control problem. However, in practice, not all states can be measured directly. Hence, the estimation of un-measurable state is needed and incorporated into the MPC algorithm. Extended Kalman Filter (EKF), one of state estimation techniques, is a technique where the states of a dynamic system are estimated by balancing the contribution made by a deterministic dynamic process model with that given by a measurement model. The advantage of the EKF is that it requires information only from the previous sampling time and allows previous knowledge of a system via process model to be used for the estimation. Several successful applications of an EKF for estimation of uncertain/un-measurable state and/or parameter have been reported in Kittisupakorn and Hussain (2000), Zhang and Rohani (2003), and Arpornwichanop et al. (2005). In this work, the EKF is designed to determine the non-measurable *i*th moments and uncertain kinetic parameters form the measurable concentration and temperature states. The EKF algorithm can be stated as follows:

The nonlinear crystallization model can be expressed by differential equations

State equation

$$\dot{x} = \Psi(x(t), u(t)) + w(t) \tag{3.8}$$

Output equation

$$y = \Phi(x(t)) + v(t) \tag{3.9}$$

where Ψ and Φ are a vector of system and measurement function , respectively, *w* describes process noise with covariance Q , and *v* represents measurement noise , with covariance *R*.

The EKF algorithm requires only the estimated state from the previous time step and the current measurement to compute the estimate for the current state. It consists of two phases; prediction and correction as shown in Figure 5.2.

In the prediction phase, the estimates of the current states ($\dot{\hat{x}}$) and the error covariance matrix (*P*) are calculated based on the previous time step estimates.

$$\dot{\hat{x}}_{k/k-1} = F(\hat{x}_{k-1/k-1}, u_{k-1}) \tag{3.10}$$

$$P_{k/k-1} = A_{k-1}P_{k-1/k-1} + P_{k-1/k-1}A_{k-1}^T + Q_{k-1} \tag{3.11}$$

In the correction phase, the Kalman gain (*K*) is computed, and measurement information from the current time step is used to refine the prediction to achieve more accurate estimates. Additionally, the estimate covariance is updated.

$$K_k = P_{k/k-1}C_k^T (C_k P_{k/k-1} C_k^T + R_k)^{-1} \tag{3.12}$$

$$\hat{x}_{k/k} = \hat{x}_{k/k-1} + K_k(y_k - C_k\hat{x}_{k/k-1}) \tag{3.13}$$

$$P_{k/k} = (I - K_kC_k)P_{k/k-1} \tag{3.14}$$

where *A* and *C* are the Jacobians matrices of function Ψ and Φ with respect to the state vector, respectively.

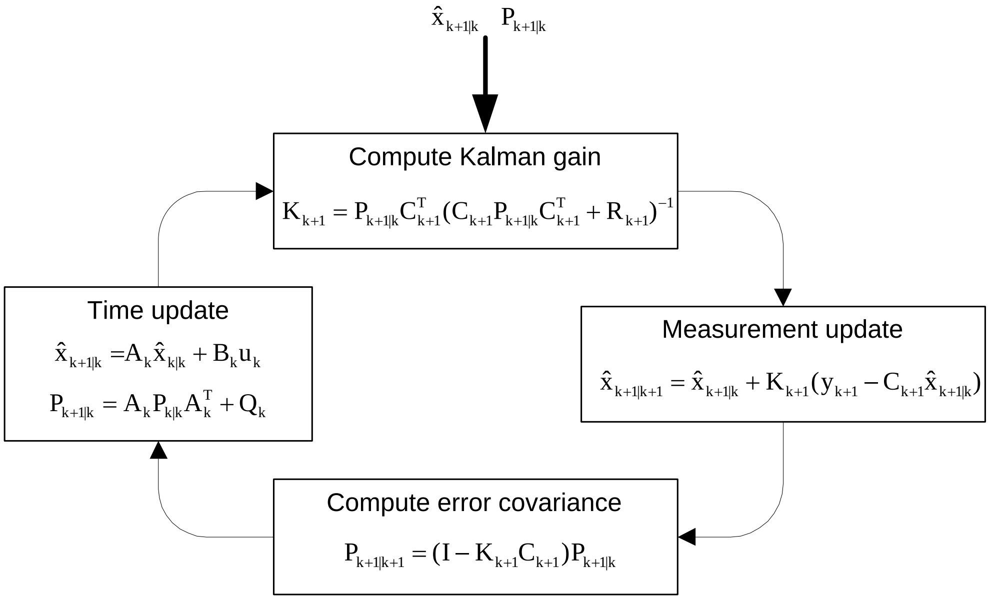


Figure 3.2 The computational structure of the EKF

CHAPTER IV

SEMI-BATCH REACTIVE CRYSTALLIZATION

During a semi-batch reactive crystallization, two liquid reactants are brought into close contact in a single jet or double jet operation, and the crystalline product or precipitate is formed by a chemical reaction in concentrations exceeding the solubility of the solute (supersturation). If the chemical reaction is fast, and the solubility of the product crystal is low compared to the reactant concentrations, the supersaturation at the feed point becomes high, which results in rapid nucleation and fast crystal growth. Thus, the mixing mechanism and the feed flow rates of the reactants exert significant influence on the characteristics of the product crystals, and an optimized crystallization process is required to produce a desired CSD.

4.1 Mathematical model of semi-batch reactive crystallization

The mathematical modeling of semi-batch reactive crystallization is more complex than that of non-reactive crystallization. This complexity is due to the chemical reaction kinetics and the nature of the crystallization. The supersaturation that is the main driving force for crystallization is generated by the chemical reaction. However, the definition of the supersaturation is dependent on the system. According to Klein and David (1995), there are generally two categories of reactive crystallization, Categories I and II.

Category I refers to chemical reaction that leads to a more or less soluble molecule P, which then crystallizes. The supersaturation is simply expressed as $\Delta C = C_s - C$. Category II refers to chemical reaction that does not lead to an intermediate soluble species. The solid crystallizes directly from the reaction. This is normally the case for ionic reactions. In this case, the thermodynamic supersaturation is commonly used to describe the driving force for the crystallization processes.The mathematical model developed will include systems of both categories.

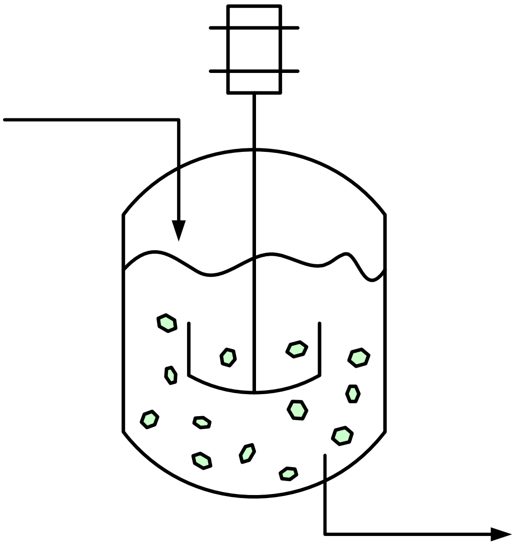


Figure 4.1 The schematic diagram of Semi-batch crystallizer

$C_{A,f},C_{B,f}$

4.1.1 Population Balance

Crystallization is a particulate process and any description of a crystallizing system is incomplete without a population balance, which characterizes the particulate material by the distribution of size of its particles. The particle size distribution (PSD) can be the major determining factor in the ultimate use of a particulate material; hence, it is one of the most important design objectives in a crystallization process. Randolf and Larsan (1962) first for malized rational techniques for the prediction of PSD, based on the population balance in crystallizers. The PSD data are commonly presented in several different ways, such as the cumulative totals (or cumulative fractions), or the density, of a measured quantity such as the crystal number, area, or mass, plotted against the particle size.

The exact shape of the distribution depends on the crystallizer system, and is obtained by solving the population balance equation. The complete population balance for a size range ∂L, for a crystallizer under transient conditions can be given as

$$\frac{\partial n}{\partial t} + \frac{\partial (Gn)}{\partial L} + D(L) - B(L) + \sum_k \frac{V_i n_i}{V} = 0 \tag{4.1}$$

The term $\partial n / \partial t$ gives the change in number density with respect to time in the batch crystallizer and disappears in the case of a continuously operated, steady-state apparatus. The expression $\partial (Gn) / \partial L$ describes the difference between crystals growth rate $G = dL / dt$. The term $n(\partial V / \partial t)$ describes the difference between crystal volume with respect to time. The parameters $D(L)$ and $B(L)$ represent the death rate and birth rate, respectively, which arise due to the agglomeration of crystals. Finally, the term $\sum_k (V_i n_i / V)$ gives the sum of all particle flows entering and leaving the crystallizer.

Assuming that agglomeration and breakage are negligible the population balance equation for such a semi-batch reactive crystallizer is

$$\frac{\partial (nV)}{\partial t} + G \frac{\partial (nV)}{\partial L} = 0 \tag{4.2}$$

where G is the overall linear growth rate, taken to be size independent. The crystal size distribution (CSD) is described by the popular moment equations (Randolph and Larson, 1988). The moment is based on unit solvent. The rate of change of the zeroth moment can hence be expressed as follows:

$$\frac{d(\mu_0 V)}{dt} = B_p V \tag{4.3}$$

The remaining moments of the crystals adopt the following form of differential equation. For crystal growth that is independent of the crystal size:

$$\frac{d(\mu_j V)}{dt} = j\mu_{j-1} G V \qquad j = 1, 2, 3... \tag{4.4}$$

The moment model has some significant limitations. First, the CSD cannot be easily reconstructed by solving a finite set of moment equations because the inverse problem is ill-conditioned. A second disadvantage is the inability to close the model equations when general size-dependent functions are included in the integral terms. At the same time, for many systems the advantages of the moment formulation outweigh its disadvantages. First, the conventional reduction of the PBE to a closed set of four coupled ODE's allows the model to be solved quickly, efficiently, and to a specified accuracy by general ODE solution codes. Second, if the CSD cannot be measured quantitatively, its calculation is not strictly necessary. Third, as the moments have physical meanings, that is,

μ_0 : crystal number
μ_1 : crystal length
μ_2 : crystal surface area
μ_3 : crystal volume

, measurable quantities may often be represented in terms of the moments. Lastly, considering size-dependent phenomena, moment-compatible models are available to allow preliminary investigations of growth rate dispersion, size-dependent growth, crystal breakage, and agglomeration.

4.1.2 Mass Balance

A perfectly mixed, isothermal semi-batch crystallizer are considered, where two feed streams, A and B, react together homogeneously to produce C, which then precipitates as solid crystal as the liquid phase becomes supersaturated with respect to component C. The chemical reaction is assumed to follow first-order kinetics with respect to each of the reacting components. The chemical reaction is normally described by the following reaction kinetics.

$$A + B \rightarrow C \downarrow + D \tag{4.5}$$

$$r_C = k_r C_A C_B \tag{4.6}$$

The rate constant, k_r can be dependent on temperature and can be expressed in the form of the Arrhenius equation:

$$k_r = k_0 \exp(-E_a / RT) \tag{4.7}$$

For semi-batch operation, the capacity of the crystallizer varies with time.

$$\frac{dV}{dt} = F_A + F_B \tag{4.8}$$

The mass balance of the reacting species therefore takes the following form of ordinary differential equations:

$$\frac{d(C_A V)}{dt} = C_{A,f} F_A - r_A V \tag{4.9}$$

$$\frac{d(C_B V)}{dt} = C_{B,f} F_B - r_B V$$

(4.10)

$$\frac{d(C_C V)}{dt} = r_C V - \frac{k_v \rho_c}{M_C} \frac{d(\mu_3 V)}{dt} \tag{4.11}$$

$$\frac{d(C_D V)}{dt} = r_D V \tag{4.12}$$

where C_i is the concentration of various reactive components, $C_{i,f}$ is the concentration of the component i in the feed stream, F_i is the feed rate, V is the capacity of the crystallizer, ρ_c is the density of crystals, k_v is the volume shape factor of the crystals, and μ_3 is the third moment of the CSD.

4.1.3 Crystal Nucleation

The birth of a crystal nucleation, can be caused by various mechanisms. Primary nucleation occurs in the absence of existing crystals and may occur spontaneously in a pure solution (homogeneous nucleation) or be included by foreign particles such as dust or impurities (heterogeneous nucleation). Secondary nucleation occurs due to the presence of existing crystals. Figure 4.2 gives an overview of the different types of nucleation mechanisms.

In primary nucleation, solid collisions of single molecules occur stochastically, thus leading to a formation of crystals. The higher the supersaturation, the higher the probability of such collisions and crystal formation. Further collisions of such a crystal with crystals lead to the growth of the crystals. If the crystal reaches a critical size, it becomes thermodynamically stable. Classical thermodynamic theory and empirical observation both suggest that primary nucleation mechanisms are only initiated by very levels of supersaturation, well outside the typical operating regimes of solution crystallizers. Moreover, poor crystal quality and control difficulties, the primary nucleation have been unsuccessful to predict and scale-up. Secondary nucleation, which is more easily controlled than primary nucleation and occurs at relatively low levels of supersaturation conductive to good crystal quality, is the dominant form of crystal birth in industrial and lab-scale crystallizations.

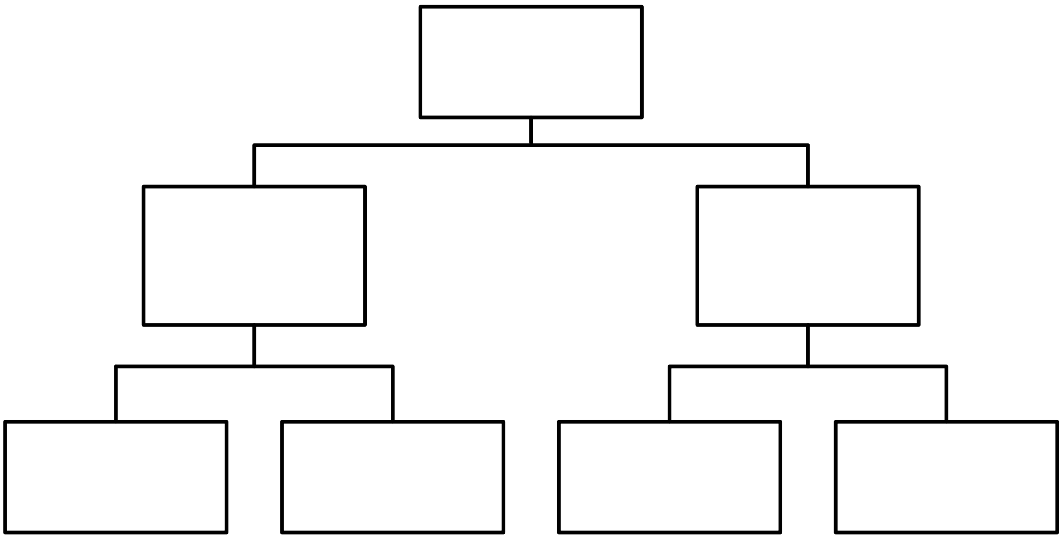


Figure 4.2 Nucleation mechanisms

In reactive crystallization processes, normally the predominant mode of nucleation is through a primary mechanism. There are various expressions for primary nucleation. The most common descriptions of primary nucleation are expressed by the following equations:

$$B_p = k_p \Delta C^p \tag{4.13}$$

$$B_p = B^0 \exp[-A_p / \ln^2 S_a] \tag{4.14}$$

Eq. (4.13) is an empirical equation that is commonly used in non-reactive crystallization. However, Eq. (4.13) has been used to describe primary nucleation of reactive crystallization in numerous literature studies (Tavare and Garside, 1990; Baldyga et al., 1995; Uehara-Nagamine and Armenante, 2001). Eq. (4.14) is based on the theoretical derivation of the primary nucleation expression. This theoretical expression of the primary nucleation has found relatively widespread use in reactive crystallization. S_a is the thermodynamic supersaturation ratio, which is commonly used, in ionic reactive crystallization. The thermodynamic supersaturation is defined as follows (Zauner and Jones, 2000; Wei et al., 2001; Mullin, 2001):

$$S_a = [(c_+^{\nu+} c_-^{\nu-}) / K_{sp}]^{1/\nu} \tag{4.15}$$

Both c_+ and c_- refer to the concentrations of the cation and anion that are formed from the product crystal when it dissociates in the solution. The variable ν refers to the number of mole of ions in 1 mol of solute. Variables $\nu+$ and $\nu-$ are the number of moles of cations and anions in 1 mol of solute. Eq. (4.13) is more commonly used for Category I, as the behavior of the solute in this category is similar to that in non-reactive crystallization. As for ionic reactive crystallization in Category II, Eq. (4.14) has been extensively used in both simulation and data fitting in experiments.

4.1.4 Crystal Growth

A crystal face is a planar surface that grows as existing steps or kinks on the surface area augmented by the incorporation of new solute molecules. Layers spread progressively across the face as new molecules attach themselves to the accessible and energetically favorable leading edges. At the microscopic level, solute molecules moving from the bulk solution adsorb on the crystal solid surface and are incorporated into the crystal lattice. A crystal face is a planar surface that grows as existing steps or kinks on the surface are augmented by the incorporation of new solute molecules. Surface adsorption and diffusion determine whether a solute molecule is incorporated into the crystal or returns to the bulk phase. The observed growth rate is then caused by the flow of steps across the surface.

The overall linear crystal growth rate can be described by several forms of expression. Two of the most common forms are the semi-empirical power law equations:

$$G = k_g \Delta C^g \tag{4.16}$$

$$G = k_g (1 - S_a)^g \tag{4.17}$$

The occurrence of secondary nucleation in reactive crystallization is generally considered insignificant (Mullin, 2001). In addition, the supersaturation level in reactive crystallization is usually high and this causes the predominance of the primary nucleation. The reactive crystallization system is treated as an isothermal system in this work. The heat effect of the crystallization is normally negligible.

In order to evaluate the performance of a perfectly mixed reactive crystallization system, the performance of the reactive crystallization is normally assessed in terms of its product quality: average crystal size and coefficient of variation. Similar to non-reactive crystallization, the desirable crystal characteristics are large crystals with narrow crystal size distribution. Genck (2000) stated that when it comes to crystal size, the larger the better. The average crystal size can be quantified based on number, surface area, volume and weight. A similar basis of definition is applied to the coefficient of variation. Generally, the definitions of the average crystal size and coefficient of variations are expressed as follows:

$$L_j = \frac{\mu_{j+1}}{\mu_j} \tag{4.18}$$

$$CV_j = \sqrt{\frac{\mu_j \mu_{j+2}}{\mu_{j+1}^2} - 1} \times 100, \quad j = 0, 1, 2, 3. \tag{4.19}$$

4.1.5 Nominal Operating Conditions

During the semi-batch operation, the reactants A and B are charged into the crystallizer in a period of 10,000 s. The parameters for physical properties, reaction and crystallization kinetics of the system are given in Table 4.1. Following Choong and Smith (2004), we consider in the case of double feeds with the same addition rates. The concentration profile in the conventional constant feed rate case is shown in Fig 4.3.

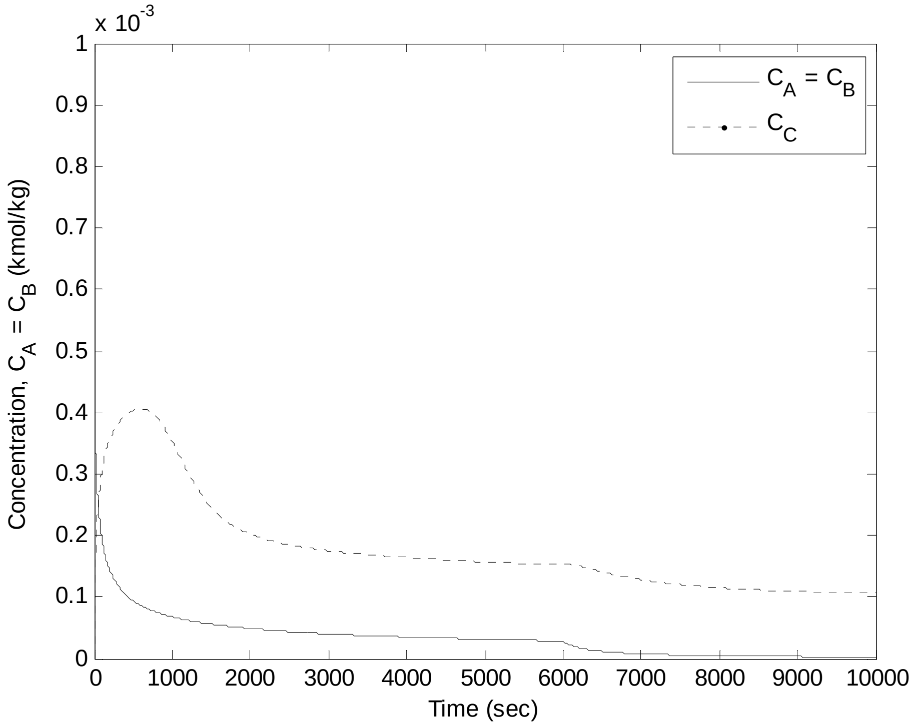


Figure 4.3 The concentration profile under constant feed rate control

Table 4.1. Parameters for physical properties, reaction and crystallization kinetics of the system.

Variables	Values
k_r, kg/kmol s	100
C_S, kmol/kg	1×10^{-4}
k_b, no./[kg s(mol/kg)^b]	3.1×10^{10}
b	4.5
k_g, m/[s (mol/kg)^g]	7.5×10^{-8}
g	1.5
k_v	0.52
ρ_c, kg/m^3	2000
M_C	100
$C_{A0} = C_{B0}$, kmol/kg	1×10^{-3}
Amount of reactant A, kg	100
Amount of reactant B, kg	100

4.2 Dynamic Optimization Study

The purpose of a dynamic optimization is to determine control trajectories that optimize a performance index for a dynamic system. In semi-batch reactive crystallization processes, a large average crystal size favors product quality. On the other hand, the large coefficient of variation obtained should be kept in possible lower limit as they may cause difficulties in downstream operations e.g. filtration and drying. From this reason, the aim of a dynamic optimization is to maximize the average crystal size (L_w) whereas keeping the coefficient of variations (CV_w) small.

In this work, a MATLAB program is written to solve the optimization problem by using a successive quadratic programming (SQP) algorithm in Matlab Optimization Toolbox. The written program is tested to determine an optimal concentration of the isothermal semi-batch crystallizer studied by Tavare and Garside (1990). The optimization results show that this program is effective and applicable to determine an optimal concentration of this work.

4.2.1 Dynamic Optimization Formulation

The semi-batch reactive cyrstallization studied by Tavare and Garside (1990) is considered. The reaction can be written as:

$$A + B \rightarrow C \downarrow + D$$

where C is the crystalline product

The objective function is to maximize the final average crystal size of a semi-batch reactive crystallization process at the specified final time. The objective function can be written as:

$$\underset{Q_A(t),Q_B(t)}{\text{Maximize}} \; L_W = \frac{\mu_4}{\mu_3} \tag{4.20}$$

Subject to

$$CV_W = \sqrt{\frac{\mu_3\mu_5}{\mu_4^{\,2}} - 1} \times 100 \le 18.1\%$$

$$Q_A(t_f) = 100 \;\; kg$$

$$Q_B(t_f) = 100 \;\; kg$$

$$t_f = 10,000 \text{ s}$$

where μ_3, μ_4, and μ_5 are obtained by solving the moments models of Eqs.(4.3)-(4.4). The inequality constraints allow the consideration of maximum allowable CV_w (18.1 %). These values correspond to the properties of the product CSD obtained in an operation with constant rate of feeding. Thus, these constraints ensure that the results of the present study are better than those obtained in operations with constant feed rate. The equality constraints ensure that the total reactants added is exactly equal to the total amount of fresh feed that is available. In the simulation t_f is 10^4 s.

The aim of the optimization problem is to compute the optimal concentration profile represented by a set of discrete values; the batch operation time is divided into a finite number of equally spaced intervals and a constant concentration value is assumed in each interval. A sequential optimization approach is used to solve the dynamic optimization problem. With the initial conditions and a given set of control parameters (the concentration in each interval), the model equations are solved with a differential algebraic equation solver at each iteration and the value of objective function and constraints is computed. The nonlinear programming problem (NLP) is solved by a sequential quadratic programming (SQP) method using the fmincon routine in Matlab optimization toolbox in order to compute new set of control parameters. The sequence continues until the optimal value of the objective function is found satisfying a specified accuracy.

4.2.2 Dynamic Optimization Results

Since the dynamic optimization computes the optimal control trajectory by optimizing the objective function, defining such a function for best process optimization is important.

The optimal concentration profile have been solved using time interval with equal length varied from 1 to 25 intervals to discretize the profile. The switching time is fixed and the length of each interval is specified by dividing the batch operation time (t_f) by a number of time intervals. Thus, the problem is to seek an optimal temperature value (decision variables) in each subinterval.

Simulation results with different time interval are reported in Table 4.2. Optimal concentration profile for each case is shown in Fig. 4.4. As shown in Table 4.2, when one time interval is used, the average crystal size (L_w) at the final time (t_f = 10,000 s) is $14.7071\,\mu m$ and the optimal concentration set point is 9.7737 whereas using ten time interval, the average crystal size is $28.9604\,\mu m$. It was found from these results that the amount of the average crystal size increases as a number of interval increases. This is due to that as the number of intervals enlarges, the approximated optimal profile with piecewise constant policy is closer to the actual optimal profile.

Table 4.2 Summary of the results: off-line optimization and perfect tracking

Time interval	$L_w(\mu m)$	$CV_w(\%)$	Computation Time (s)
1	14.7071	18.1	30
2	23.1673	18.1	32
5	27.6853	18.1	66
10	28.9604	18.1	99
16	29.5787	18.1	189
20	29.7540	18.1	169
25	29.8929	18.1	271

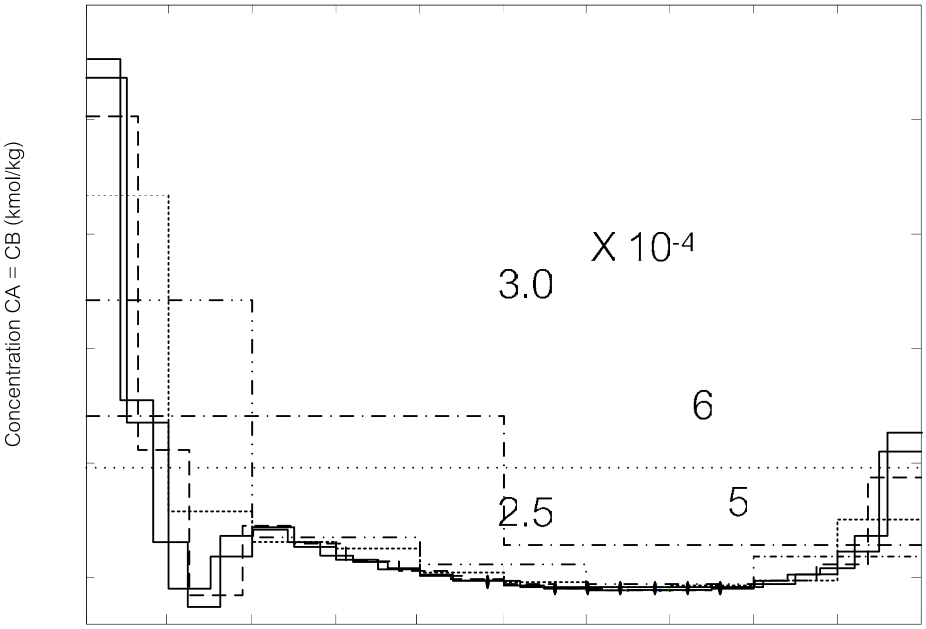


Figure 4.4 Optimal concentration profile: 1 interval (1), 2 intervals (2), 5 intervals (3), 10 intervals (4), 16 interval (5), 20 interval (6)

4.3 Control Study

The purpose of this study is to design the model predictive control for a semi-batch crystallization process to track the crystallizer concentration set point. A feed flow rate is used to control the crystallizer concentration at its desired trajectory. Due to the total feed amount of reactant A and B is limited to 100 kg.

4.3.1 Model Predictive Control (MPC) Configuration

A model-based feedback controller known as a model predictive control (MPC) has been found to be a successful control strategy in several industrial applications because of its ability to handle nonlinear processes, multivariable interactions, constraints, and optimization requirements (Qin and Badqwell, 2000). For a continuous crystallization process, normally, a key control objective is to stabilize the system at a specified condition. In the presence of constraints on the manipulated input variables, the performance of the controlled system is limited to the conditions which stabilization can be achieved. For a batch process, in contrast, the expression of performance considerations in the form of appropriate constraints and achieving the desired size distribution of a product are much more needed.

In a semi-batch crystallization process, the size distribution of crystals can affect subsequent operations such as filtration, drying, transport, and storage. Since fine crystals cause difficulties in downstream processes and affect product quality, the control objective of the process is to determine an concentration profile maximizing the average crystals size, $L_w(t_f)$, whereas the coefficient of variation, $CV_w(t_f)$, has to satisfy the product quality requirement. Hence, the optimal control problem can be formulated as:

$$\underset{Q_A(t),Q_B(t)}{\text{Maximize}} \; L_W = \frac{\mu_4}{\mu_3} \tag{4.21}$$

Subject to

$$CV_W = \sqrt{\frac{\mu_3\mu_5}{\mu_4{}^2} - 1} \times 100 \le 18.1\%$$

$$Q_A(t_f) = 100 \;\; kg$$

$$Q_B(t_f) = 100 \;\; kg$$

$$t_f = 10,000 \, \text{s}$$

In the MPC algorithm, the crystallizer models consist of the moments model Equations (4.3)-(4.4), coupled with the mass balances, Equations (4.9)-(4.12). Assuming the reactor Concentration trajectory can be tracked perfectly as in previous studies. Considering the time elapsed in the determination of the optimal control problem, with 25 time interval,

4.3.2 MPC with extended Kalman Filter

Since the quality of product crystals in terms of the *i*th moments cannot be on-line measured for the MPC computation, the EKF is developed to estimate the values of the moments of the CSD based on the measurable concentration and temperatures. Moreover, process parameters such as nucleation and growth rate exponent (b and g) typically determined by experiments may not sufficiently accurate in the control point of view. Therefore, the estimation of these process parameters is required. Here, state equations appended for states and parameters estimation are:

State estimation:

$$\frac{d(\hat{\mu}_0 V)}{dt} = \hat{B}(t)V(t) \tag{4.22}$$

$$\frac{d(\hat{\mu}_{\mathrm{i}} V)}{dt} = i\hat{G}(t)\hat{\mu}_{\mathrm{i}-1}(t)V(t) \qquad i = 1,2,3,... \tag{4.23}$$

Parameter estimation:

$$\frac{d\hat{b}}{dt} = 0 \tag{4.24}$$

$$\frac{d\hat{g}}{dt} = 0 \tag{4.25}$$

where $\hat{B}$ and $\hat{G}$ are the estimates of nucleation and growth rates computed using the estimated values of $\hat{\mu}_i V$, $\hat{b}$ and $\hat{g}$. The tuning parameters of the EKF are given in Table 4.3.

Table 4.3 The tuning parameters in the EKF algorithm

Estimate $\mu_i V$ using C_C and V
P = diag[100 100 100 100 100 100 100 100] Q = diag[1000 1000 1000 1000 1000 1000 1000 1000] R = diag[10 10]
Estimate b and g using C_C and V
P = diag[100 100 100 100]
Q = diag[1000 1000 1000 1000]
R = diag[10 10]

The control strategy proposed in this study is shown in Figure 4.5. The EKF is introduced to on-line estimate un-measurable $\mu_i V$. With these estimates, the MPC determines the manipulated input variable (F). The performance of the MPC controller in the control of the semi-batch crystallizer is evaluated under nominal and plant/model mismatch cases. In the nominal case, it is assumed that all parameters in the crystallization process are known exactly as given in Table 4.1 whereas in the plant/model mismatch case, a mismatch in kinetic parameters (k_b and k_g) is introduced in the formulation of the MPC controller.

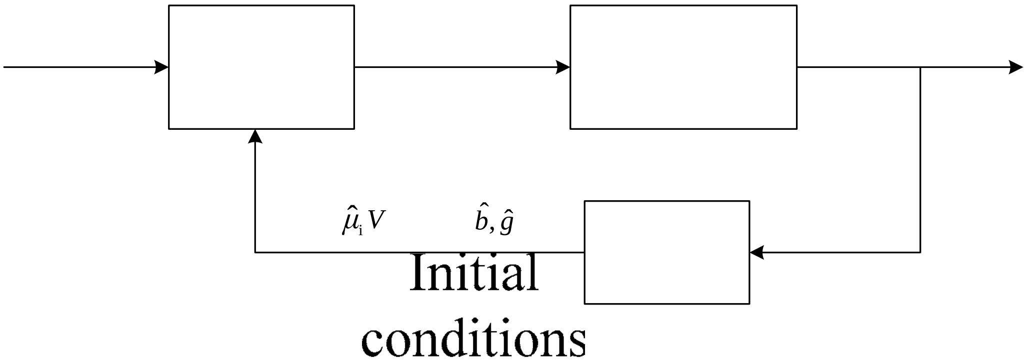


Figure 4.5 The robust MPC control strategy for on-line state measurement and parameters estimation

4.3.3 Control Results

Nominal Case

The control response of a MPC controller in the nominal case is illustrated in Figure 4.6. These results are compared with an open-loop control using conventional constant feed rate policy. The final product quality in terms of the average crystal size is presented in Table 4.4. It is observed that the MPC controller gives better product quality compared with the constant feed rate policy. Simulation results have demonstrated that the average crystal size, L_w is increase by 30% compared with the constant feed rate strategy.

In addition, Figure 4.7 shows a comparison of the $\mu_i V$ between the actual values from the process and the estimated values from the EKF. The results demonstrate that the EKF gives good estimations; small differences are observed. Additionally, this can also be implied that the moment model is reasonably employed to describe the dynamic of the first four moments of the population density function of the actual process.

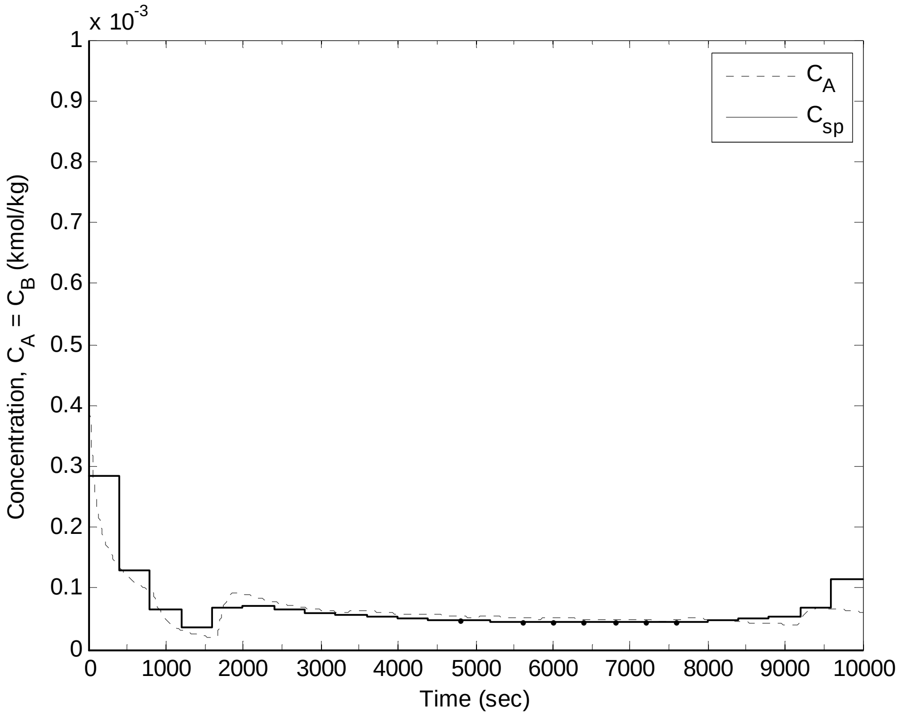
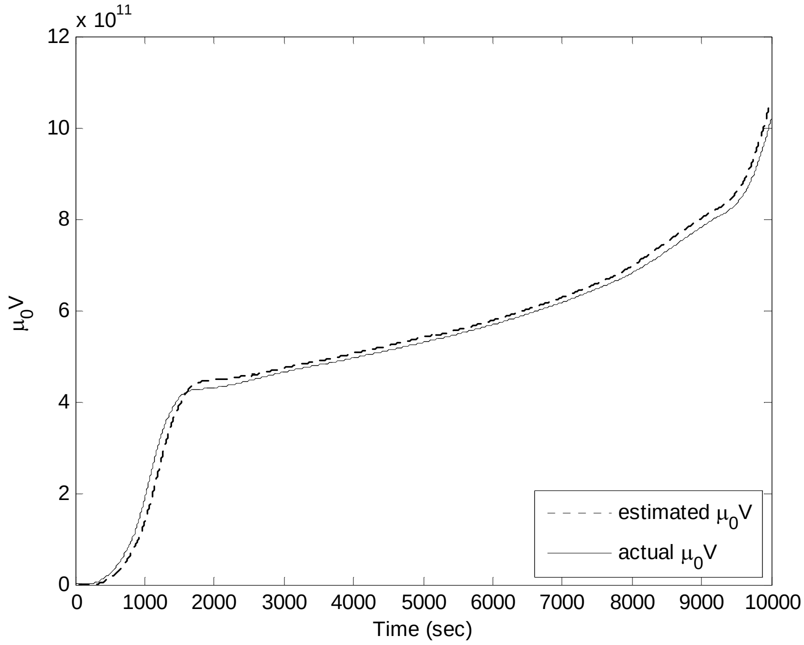


Figure 4.6 The concentration profiles under MPC control with EKF for state estimation

Table 4.4 Comparison of the crystal quality in different control strategies

Control strategy	$L_w(t_f)$, μm	$CV(t_f)$, %
Constant feed rate	15.8233	18.1
MPC with EKF for states estimation	20.4103	15.6


x 10^11
12
10
8
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4
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μ0V
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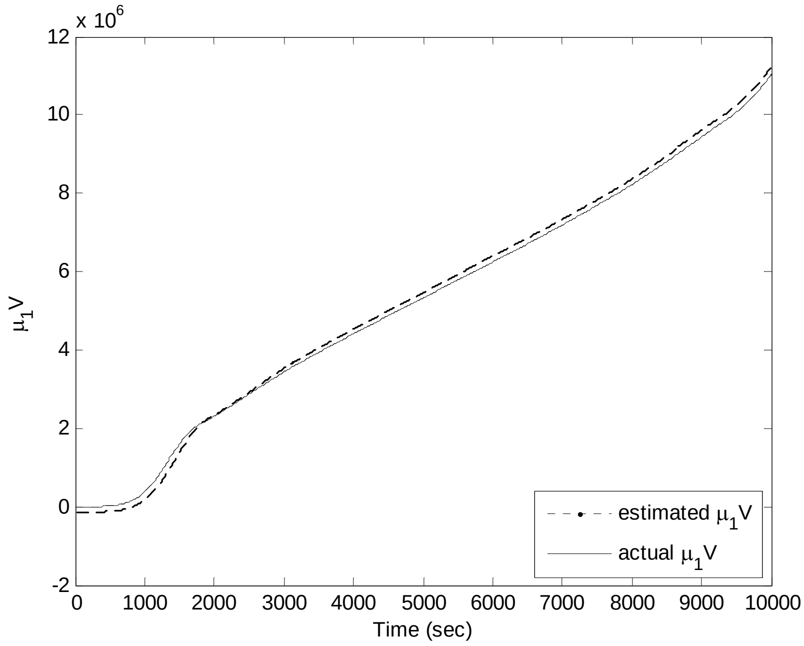
Time (sec)
estimated μ0V
actual μ0V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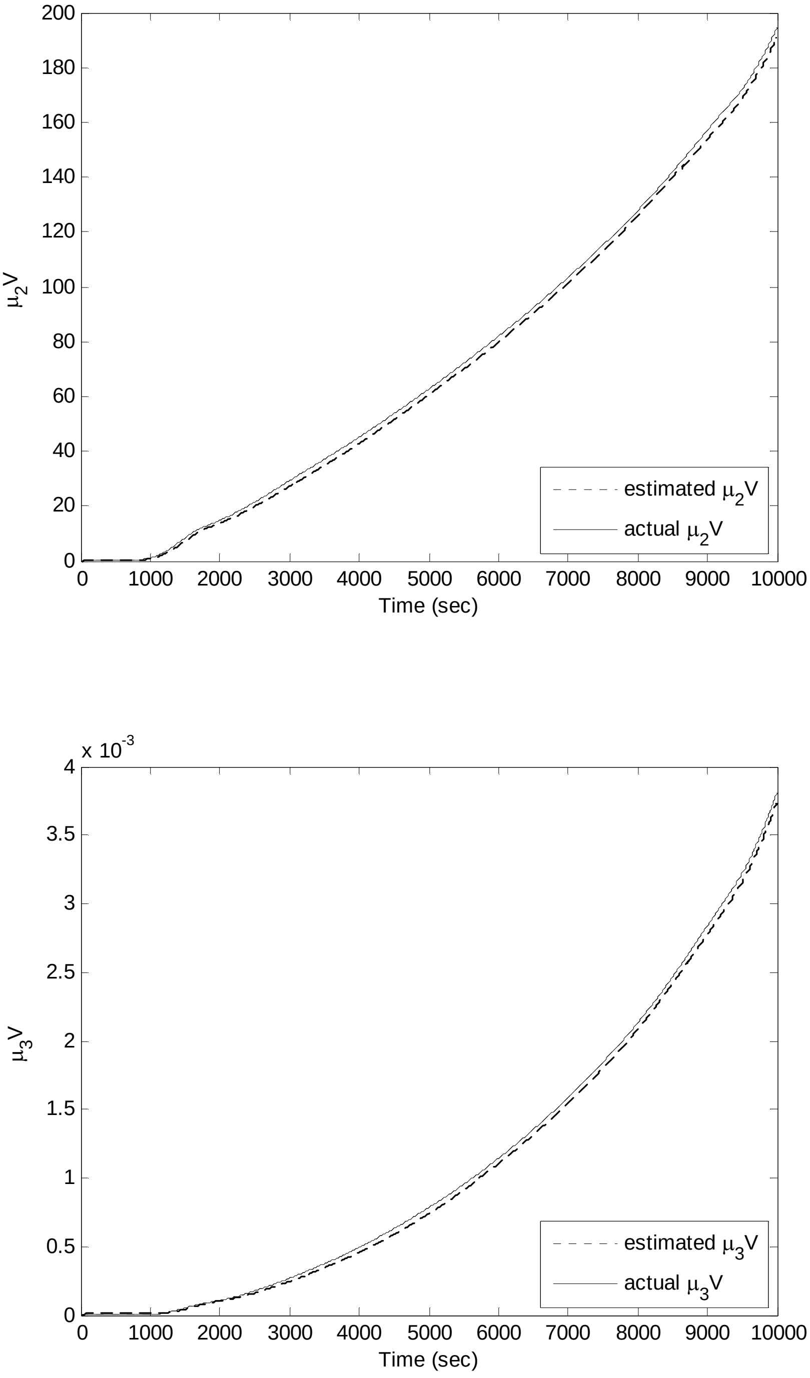

Figure 4.7 Comparison between the actual and estimated values of the $\mu_i V$

Model-Plant Mismatch Case

It has been known that the uncertainty in kinetic parameters is normally occurred when implementing a model-based control technique to real processes. Table 4.5 shows the variation of parameter that effect to the objective function. The result show that the nucleation and growth rate exponent can most effect to the objective function. Here, the proposed control strategy is tested in the presence of model mismatch in kinetic parameters (b and g) in the moment model. Here it is assumed that the nucleation and growth rate exponent are decrease 20% and increases 20% from its actual value respectively. The result shows that the final crystal product obtained is less than the specification ($CV_w \geq 18.1\%$); the average crystal size (L_w) is 11.2315. The EKF is used to estimate the state and parameters mismatch for robust control Figure 4.8 shows the performance of the EKF to estimate uncertain parameters. It can be seen that the EKF can estimate the uncertain parameters close to the actual values and thus the model mismatch is eliminated during batch operation. The MPC control action is quite similar to the nominal case. As a result of this, the requirement of crystal quality is satisfied as shown in Table 4.6.

Table 4.5 The kinetic parameter testing

Parameters or variables	% changed	L_w	% Changed
Nominal case	0	15.8233	
b	+30	21.3379	34.85
	-30	11.2623	28.82
g	+30	12.1114	23.46
	-30	20.8762	31.93
k_b	+30	15.0925	4.62
	-30	16.8751	6.65
k_g	+30	17.8523	12.82
	-30	13.4389	15.07
k_r	+30	15.8583	0.22
	-30	15.7725	0.32
k_v	+30	15.0925	4.62
	-30	16.8751	6.65

Table 4.6 The crystal qualities under MPC control in the kinetic mismatch case

Control strategy	$L_w(t_f)$, μm	$CV_w(t_f)$, %
MPC with EKF for states estimation		
Case I : b mismatch -20%	16.2240	19.0%
Case II: g mismatch +20%	16.5234	22.1%
MPC with EKF for states and parameters estimation		
Case I : b mismatch -20%	18.63	16.1%
Case II: g mismatch +20%	18.91	17.5%

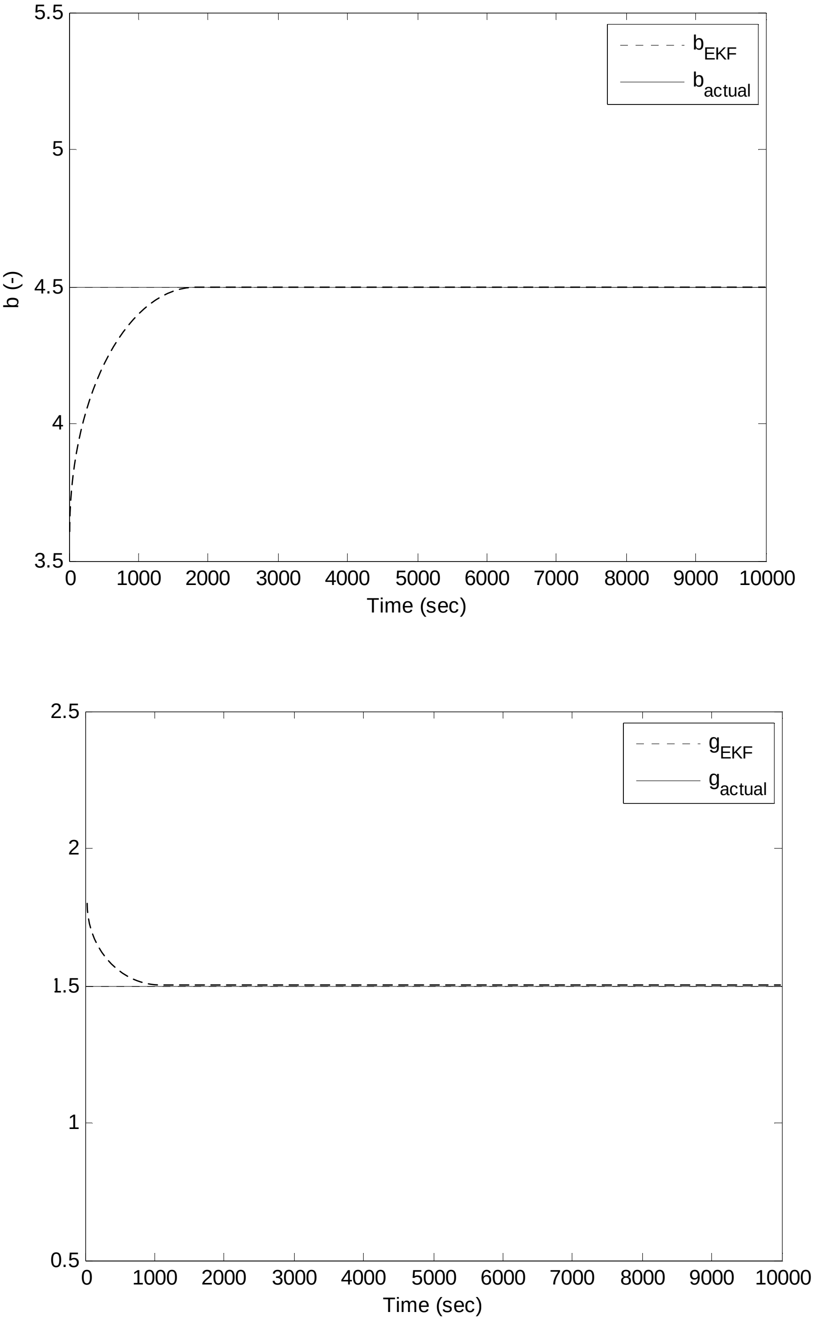

Figure 4.8 The estimate values of $\hat{b}$ and $\hat{g}$ in the mismatch case

4.3.4 Conclusion

A model predictive control (MPC) incorporated with an extended Kalman Filter (EKF) is designed and implemented to control the concentration of a semi-batch reactive crystallizer. The aim is to maximize the average crystals size that affect both product quality and downstream processing equipment; however, the coefficient of variation should satisfy the product quality requirement. Simulation results have demonstrated that the average crystal size, L_w is increase by 30% compared with the constant feed rate strategy. Since the MPC is a model-based controller, accurate model parameters are necessary in order to obtain the optimal operating condition. Furthermore, the EKF performance depends on the model accuracy. The results show that when incorrect values of nucleation and growth rate exponent are used in the MPC model, the final crystal product does not satisfy the quality specification, and the EKF gives poor performance. For this reason, the EKF is proposed in this work to estimate the uncertain parameters. When the MPC control action and state estimation are computed using the estimated kinetic parameters, the $\mu_i V$ approach the actual values and the requirement of crystal quality is satisfied. These results demonstrate that the robustness of the semi-batch reactive crystallizer control is improved using the MPC control integrated with the EKF for estimating unmeasurable states and uncertain parameters.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Reactive crystallization or precipitation is a key production step for a wide range of industrial process. Many substances such as fine and bulk chemicals, pharmaceuticals, biochemicals, catalysts, pigments, photographic materials or ceramics are produced by reactive crystallization. As the widespread utilization of crystallization processes, the optimal operation and efficient control strategy are necessary in order to enhance their performance in terms of product quality and energy usage.

In this research, the semi-batch reactive crystallization process has been studied. The goal is to develop and implement a dynamic optimization approach for specifying an optimal operating condition of a semi-batch reactive crystallization process to obtain a desired quality of crystal product. Apart from specifying the optimal set point profile, a control system implemented to track such a profile is an important issue to be considered. Generally, such a system is characterized as a nonlinear and complex system in nature. Therefore, a nonlinear control strategy based on a the model predictive control (MPC) incorporated with extended Kalman Filter (EKF) for unmearurable state estimation is implemented to control the crystallizer concentration satisfying the quality requirement. Simulation results have demonstrated that the average crystal size is increased by 30% compared with the constant feed rate control strategy. Since the MPC is a model-based controller, accurate model parameters are necessary in order to obtain the optimal operating condition. Furthermore, the EKF performance depends on the model accuracy. However, due to unknown disturbances, the kinetic parameters obtained by an experiment may not suitable to describe the real process. The results show that when incorrect values of nucleation and growth rate exponent are used in the MPC model, the final crystal product does not satisfy the quality specification, and the EKF gives poor performance. For this reason, the EKF is also proposed in this work to estimate the uncertain parameters. When the MPC control action and state estimation are computed using the estimated kinetic parameters, the $\mu_i V$ moments approach the actual values and the requirement of crystal quality is satisfied. These results demonstrate that the robustness of the semi-batch reactive crystallizer control is improved by using the MPC control integrated with the EKF for estimating unmeasurable states and uncertain parameters.

5.2 Recommendations

In general, the first step in developing a system is a process simulation design based on a mathematical model. In addition, before a complex control system is implemented on a process, it is normally tested by simulation. However, experimentally optimized system is an interesting idea that is recommended for future study. Moreover, the proposed control methodology impacts the way in which crystallization processes are designed and will enable more effective control of crystal quality that can provide benefit when apply to the real processes.

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APPENDICES

APPENDIX A

SUCCESSIVE QUADRATIC PROGRAMMING (SQP)

Successive quadratic programming (SQP) method solved a sequence of quadratic programming approximation to nonlinear programming problem. Quadratic Programs (QPs) have a quadratic objective function and linear constraints, and there exist efficient procedures for solving them

Problem formulation with equality constraints

To derive SQP, we again consider a general NLP

$$\begin{aligned} &Minimize: f(x) \\ &Subject\ to: g(x) = b \end{aligned} \tag{A.1}$$

The Langrangian function for this problem is

$$L(x,\lambda) = f(x) + \lambda^T (g(x) - b) \tag{A.2}$$

and the KTC are

$$\nabla_x L = \nabla f(x) + \sum_{i=1}^{m} \lambda_i \nabla g_i(x) = 0 \tag{A.3}$$

and

$$g(x) = b \tag{A.4}$$

The equation (A.1)-(A.2) is a set of $(n+m)$ nonlinear equations in the n unknowns x and m unknown multipliers λ. Linearization of (A.2) – (A.3) with respect to x and λ

$$\nabla_x L - \nabla_x^2 L \Delta x + \nabla g^T \Delta\lambda = 0 \tag{A.5}$$

$$g + \nabla g \Delta x = 0 \tag{A.6}$$

For problem with only equality constraints, we could simply solve the linear equations (A.2)-(A.3). To accommodate both equalities and inequality, an alternative viewpoint is useful. Consider the quadratic programming problem

$$\begin{aligned} &\text{minimize:} \quad \nabla L^T \Delta x + \frac{1}{2}\Delta x^T \nabla_x^2 L \Delta x \\ &\text{Subject to:} \quad \mathrm{g} + \nabla g \Delta x = 0 \end{aligned} \tag{A.7}$$

If we call the Lagrange multipliers for (A.7) $\Delta\lambda$, the Lagrangian for the QP is

$$L_1(\Delta x, \Delta\lambda) = \nabla L^T \Delta x + \frac{1}{2}\Delta x^T \nabla_x^2 L \Delta x + \Delta\lambda^T (g + \nabla g \Delta x) \tag{A.8}$$

Inclusion of the both equality and inequality constraints

When the original problem has a mixture of equalities and inequalities, it can be transformed into a problem with equalities and simple bounds by adding slacks, so the problem has and objective function f, equalities (A.1), and bounds

$$I \le x \le u \tag{A.9}$$

This system is the KTC for the QP in (A.7) with the additional bound constraints

$$I \le \overline{x} + \Delta x \le u \tag{A.10}$$

Here the QP sub problem now has both equality constraints and must be solved by some iterative QP algorithm.

The approximate Hessiain

Solving a QP with a positive-definite Hessian is fairly easy. Several good algorithm all converge in finite number of iteration. However, the Hessian of the QP presented in (A.7) and (A.10) is $\nabla_x^2 L(\overline{x}, \overline{\lambda})$ is an optimal point. In addition, to compute $(\overline{x}, \overline{\lambda})$ is an optimal point. In addition, to compute $\nabla_x^2 L$ by positive-definite quasi-Newton approximate B, whith is updated using only values of L and $\nabla_x L$. Most SQP algorithms use Powell's modification of BFGS update. Hence the QP subproblem becomes $QP(\overline{x}, B)$

$$\begin{aligned} &\text{minmize} : \nabla L^T \Delta x + \frac{1}{2} \Delta x^T B \Delta x \\ &\text{Subject to: } \nabla g \nabla x = -g, \quad I \le \overline{x} + \Delta x \le u \end{aligned} \tag{A.11}$$

The SQP line search

To arrive at a reliable algorithm, one more difficulty must be over come. Newton and quasi-Newton method may not converge if a step of 1.0 is used at each step. Both trust region and time search versions of SQP have been developed that converge reliablitity. A widely used line search strategy is to use the L_1 exact penalty function ($P(x,w)$. In a line search SQP algorithm, $P(x,w)$ is used only to determine the step size along the direction determined by the QP subproblem $QP(\overline{x}, B)$. The L_1 exact penalty function for the NLP problem is

$$P(x,w) = f(x) + \sum_{i=1}^{m} w_i \left| g_i(x) - b_i \right| \tag{A.12}$$

where a separate penalty weight w_i is used for each constraint. The SQP line search chooses a positive step size α to find an approximate minimum of

$$r(\alpha) = P(x + \alpha \Delta x, w) \tag{A.13}$$

A typical line search algorithm, which uses the derivative of $r(\alpha)$ evaluated at $\alpha = 0$ denote by $r'(0)$, is

1. $\alpha \leftarrow 1$
2. if $r(\alpha) < r(0) - 0.1\alpha r'(0)$ (A.14)

   stop and return the current α value
3. Let α_1 be the unique minimum of the convex quadratic function that passes through $r(0)$, $r'(0)$ and $r(\alpha)$. Take the new estimate of α as

   $\alpha \leftarrow \max(0.1\alpha, \alpha_1)$ (A.15)
4. Go to step 2.

SQP algorithm

Base on this line search and the QP subproblem $QP(\overline{x}, B)$

1. Initialize: $B^0 \leftarrow I, x^0 \leftarrow x, k \leftarrow 0$
2. Solved the QP subproblem $QP(\overline{x}, B)$, yieldiging a solution Δx^k and Langrange multiplier estimates λ^k
3. Update the penalty weights in penalty function
4. Apply the line search algorithm, yielding a positive step size α^k
5. $x^{k+1} = x^k + \alpha^k \Delta x^k, \lambda^{k+1} = \lambda^k$

6. Evaluated all problem function and their gradients at new point. Update matrix B^k
7. Replace k by $k+1$, and go to step 2

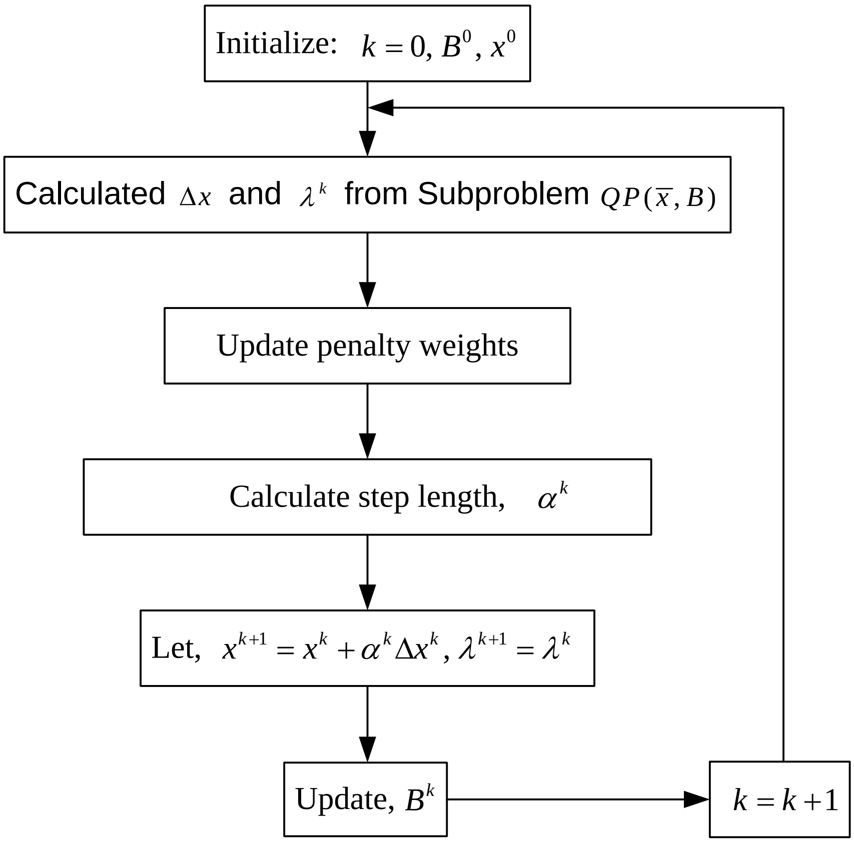

Figure A.1 Flowchart of SQP algorithm

APPENDIX B

DYNAMIC OPTIMIZATION ARRROACH

B.1 Dynamic Optimization

Dynamic optimization, also known as an optimal control problem, requires the determination of control trajectories that optimize some performance index for a dynamic system. Some examples of dynamic optimization problems are the determination of optimal operating policies for chemical plants subject to safety, operational, and environmental constraints. The dynamic system is usually represented by sets of differential and algebraic equations (DAEs). The differential equations typically arise from dynamic material and energy balances, while the algebraic equations arise from thermodynamic and kinetic relationships (Edgar and Himmelblau, 2001).

The general formulation of the dynamic optimization problem is as follows:

$$\min \;\; \Psi\left(x(t_f), y(t_f), u(t_f), t_f, p\right) \tag{B.1}$$

subject to

$$\frac{dx(t)}{dt} = F\left(x(t), y(t), u(t), p, t\right) \tag{B.2}$$

$$h\left(x(t), y(t), u(t), p, t\right) = 0 \tag{B.3}$$

initial condition:

$$x(0) = x_0 \tag{B.4}$$

bounds:

$$\begin{aligned}
&x(t) \in [x_l, x_u] \\
&y(t) \in [y_l, y_u] \\
&u(t) \in [u_l, u_u] \\
&p(t) \in [p_l, p_u] \\
&t_f(t) \in [t_{fl}, t_{fu}]
\end{aligned} \tag{B.5}$$

where Ψ is a scalar objective function, h are algebraic equation constraints, x are differential state variables, x_0 are the initial values of x, y are algebraic state variables, u are control variables, p are time independent parameters, and t_f is a final time.

B.2 Solution of Dynamic Optimization

Numerical methods for the solution of dynamic optimization problems are usually classified into two categories: indirect and direct methods, as described in Figure B.1.

B.2.1 Indirect Method

The indirect or variational approach is based on the solution of the first order necessary conditions for optimality. For problems without inequality constraints, the optimality conditions can be formulated as a set of differential-algebraic equations. Obtaining a solution to these equations requires careful attention to the boundary conditions. Often the state variables are specified at an initial condition whereas adjoint variables are determined at a final condition. This leads to a two-point boundary value problem (TPBVP) that can be solved by different approaches, i.e., single shooting, invariant embedding, multiple shooting or some discretization methods such as collocation on finite elements or finite differences. In general, the indirect method requires an analytical differentiation to derive the necessary conditions and the application of this approach is more difficult when state

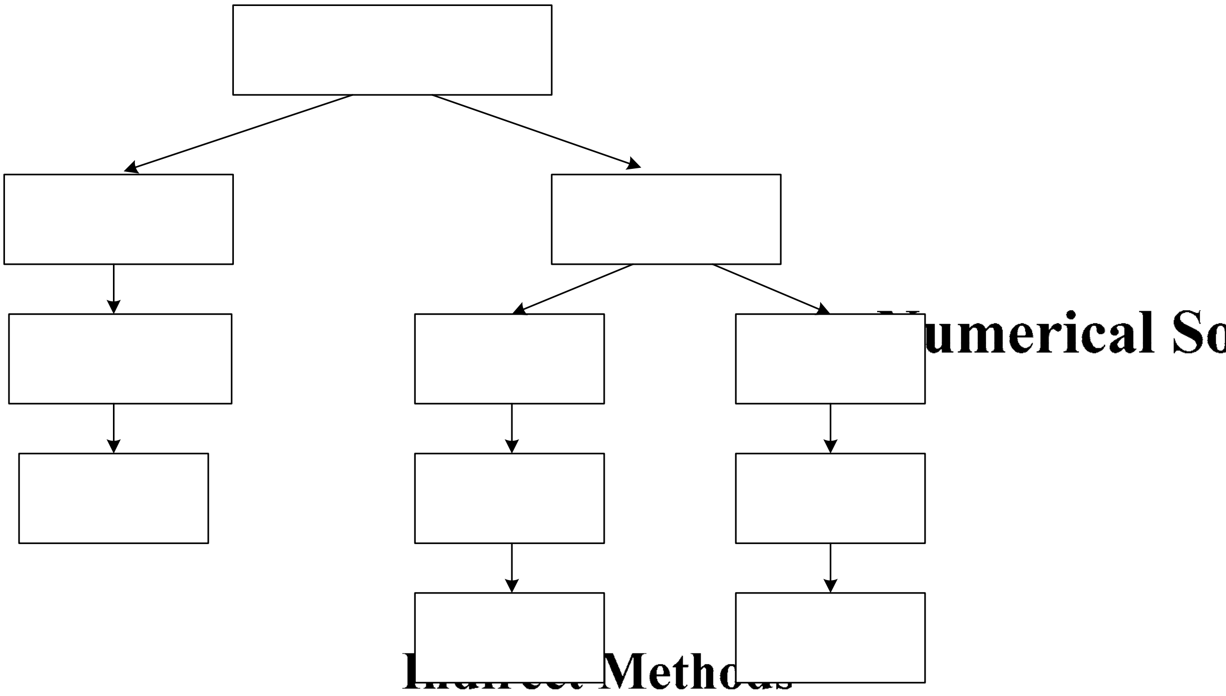

Figure B.1 Numerical solution of dynamic optimization problems

constraints are present in the dynamic optimization problem (Kameswaran and Biegler, 2006).

B.2.2 Direct Method

Deterministic Direct Methods

The concept of this method is to transform an original dynamic optimization problem into a finite dimensional optimization problem, typically a nonlinear programming problem (NLP), using discretization techniques on either only control variables (partial discretization) or both state and control variables (complete discretization). Based on this consideration, two solution strategies can be classified.

Sequential strategy

In the sequential strategy, also called a control vector parameterization (CVP), only a control (manipulated) variable profile is discretized as a piecewise constant, a piecewise linear, or a piecewise polynomial function over a time interval. Computational procedure of this strategy is shown in Figure B.2. With the initial conditions and a given set of control parameters, the model equations are solved with a differential algebraic equation solver at each iteration. The value of an objective function and constraints is computed and then a NLP solver determines a new set of the control parameters and sends it back to the model solver. This procedure is repeated until the optimal value of the objective function satisfies a specified accuracy.

Sequential strategies are relatively easy to construct and apply as they contain the component of reliable NLP solvers. The main advantage of this strategy is that the control profile is discretized and considered as a decision variable and thus, the obtained NLP is a small scale problem. However, since the state variables are not directly included in the NLP, a constraint on state variables (path constraints) is difficult to handle.

Simultaneous strategy

In this strategy, both state and control variable profiles are discretized by approximating functions and treated as decision variables in the optimization problem. The dynamic process model and the optimization problems are solved at one step, which avoids solving the model equations at each iteration in the optimization algorithm as in the sequential strategy. With this approach, the dynamic process model constraints are transformed to a set of algebraic equations that is posed as equality constraints in NLP.

Since the constraints can be included directly in the optimization problem as additional constraints, this approach has a capability in handing constraints on state variables. However, due to the discretization on both state and control variables, a large scale NLP problem is obtained, compared with the sequential approach

Stochastic Direct Methods

As a NLP problem arising from the application of direct approaches is frequently multimodal, deterministic (gradient based) local optimization techniques may converge to local optima, especially if they are started far away from a global solution. Adaptive stochastic methods have been suggested as robust alternatives to overcome these difficulties. Other types of stochastic algorithms have also been used, including different random search algorithms and genetic algorithms. These algorithms; however, would be slower than most other gradient-based algorithms.

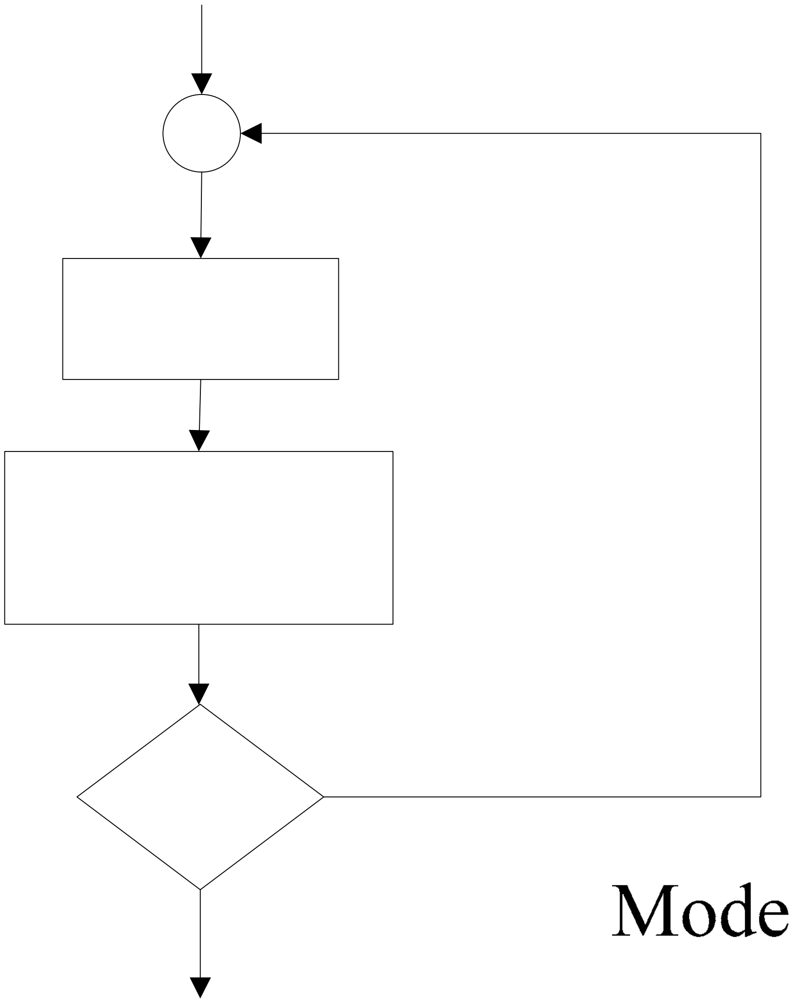

Figure B.2 Dynamic optimization via the sequential strategy

VITA

Miss Aritsara Saengchan was born in Bangkok on April 25, 1985. She received a Bachelor of Engineering degree in Chemical Engineering from Suranaree University of Technology in May 2007. She began her graduate studies in June 2004 when she entered the Graduate School of Chulalongkorn University and joined the process control engineering group in the Department of Chemical Engineering.