

INFERENTIAL CONTROL OF BORIC ACID PRODUCTION SYSTEM

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ÖZGECAN DERVİŞOĞLU

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submitted by **ÖZGECAN DERVİŞOĞLU** in partial fulfillment of the requirements for the degree of **Master of Science in Chemical Engineering Department, Middle East Technical University** by,

Prof. Dr. Canan Özgen
Dean, Graduate School of **Natural and Applied Sciences** _____

Prof. Dr. Nurcan Baç
Head of Department, **Chemical Engineering** _____

Prof. Dr. Canan Özgen
Supervisor, **Chemical Engineering Dept., METU** _____

Examining Committee Members:

Prof. Dr. İnci Eroğlu
Chemical Engineering Dept., METU _____

Prof. Dr. Canan Özgen
Chemical Engineering Dept., METU _____

Prof. Dr. Kemal Leblebicioğlu
Electrical and Electronics Engineering Dept., METU _____

Assoc. Prof. Dr. Göknur Bayram
Chemical Engineering Dept., METU _____

Dr. Gaye Çakal
Expert, National Boron Research Institute _____

Date: **27.08.2007**

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name : Özgecan Dervişoğlu

Signature :

ABSTRACT

INFERENTIAL CONTROL OF BORIC ACID PRODUCTION SYSTEM

Derviřođlu, Özgecan

M.S., Department of Chemical Engineering

Supervisor: Prof. Dr. Canan Özgen

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Inferential control of boric acid production system using the reaction of colemanite with sulfuric acid in four continuously stirred tank reactors (CSTR) connected in series is aimed. In this control scheme, pH of the product is measured on-line instead of boric acid concentration for control purposes. An empirical correlation between pH and boric acid concentration is developed using the collected data in a batch reacting system in laboratory-scale and this correlation is utilized in the control system for estimator design. The transfer function model of the 4-CSTR system previously obtained is used in the MPC controller design. In the experiments done previously for the modelling of 4-CSTR system, it was observed that the reaction goes complete within the first reactor. Therefore, the control is based on the measurements of pH of the second reactor by manipulating the flow rate of sulfuric acid given to the first reactor, while the flow rate of colemanite fed to the system is considered as disturbance. The designed controller's performance is tested for set-

point tracking, disturbance rejection and robustness issues using a simulation program. It is found that, the designed controller is performing satisfactorily, using the inferential control strategy for this complex reacting system.

Keywords: inferential control, colemanite, boric acid production, model predictive control

ÖZ

BORİK ASİT ÜRETİM SİSTEMİNİN ALGISAL YÖNTEM İLE DENETLENMESİ

Dervişođlu, Özgecan

Yüksek Lisans, Kimya Mühendisliđi Bölümü

Tez Danışmanı: Prof. Dr. Canan Özgen

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Bu çalışmada, kolemanit ve sülfürik asitin tepkimeye girmesiyle borik asit üreten birbirine seri şekilde bağlanmış dört sürekli karıştırıcılı tepkime tankındaki borik asit üretiminin algısal (inferential) yöntem ile denetlenmesi amaçlanmıştır. Denetim sisteminde çıkan ürünlerdeki borik asit derişimi yerine hat-üzerinde ölçülebilen pH değerleri kullanılmıştır. Laboratuvar boyutunda kurulan kesikli bir sistemden elde edilen veriler kullanılarak, pH ile borik asit derişimi arasındaki bağıntı irdelenmiş ve bu bağıntı tahmin edici tasarımında kullanılmıştır. Model Öngörümlü Denetleç tasarımında, dört sürekli karıştırıcılı tepkime tankının daha önceden elde edilmiş aktarım fonksiyonları kullanılmıştır. Modelleme amacı ile yapılan deneylerde, tepkimenin ilk reaktörde tamamlandığı gözlemlendiđi için denetim, ikinci tepkime tankındaki pH değerlerini ölçtükten sonra, birinci tepkime tankına beslenen sülfürik asit akış hızını ayarlayarak gerçekleştirilmiş ve kolemanitin akış hızı sistemde bozan etken olarak kabul edilmiştir. Tasarlanan denetleçin istek değeri takibi, bozan etkenin

ortadan kaldırılması ve gürbüzlük performansı simülasyon çalışmaları ile irdelenmiştir. Yapılan çalışmalar sonucunda bu algısal denetim yönteminin başarı ile kullanılabileceği belirlenmiştir.

Anahtar kelimeler: algısal denetim, kolemanit, borik asit üretimi, model öngörümlü denetim

*To
my dearest family*

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TABLE OF CONTENTS

ABSTRACT.....	iv
ÖZ.....	vi
ACKNOWLEDGEMENTS.....	ix
TABLE OF CONTENTS.....	x
LIST OF TABLES.....	xii
LIST OF FIGURES.....	xiii
LIST OF SYMBOLS.....	xv
CHAPTERS	
1. INTRODUCTION.....	1
2. LITERATURE SURVEY.....	4
2.1. Boric Acid Studies.....	4
2.2. Model Predictive Control Studies.....	6
3. ESTIMATOR AND MODEL PREDICTIVE CONTROLLER DESIGN.....	12
3.1. Estimator Design.....	12
3.2. Model Predictive Controller (MPC) Design.....	21
3.2.1. MPC Strategy.....	22
3.2.2. MPC Tuning (Seborg, 1989).....	24
4. EXPERIMENTAL STUDIES.....	25
4.1. Experimental Set-Up.....	25
4.2. The Variables of the Experimental System.....	27
4.3. Experimental Procedure.....	29
4.3.1. Experimental Procedure for Modelling the Sytem.....	29

4.3.2. Experimental Procedure for Obtaining the Relationship between Boric Acid Concentration and pH.....	30
5. RESULTS AND DISCUSSION	32
5.1. Verification of the Correlation between Boric Acid Concentration and pH Measurement.....	32
5.2. Transfer Function Modelling	34
5.3. MPC Design.....	42
5.4. Simulation Studies	42
5.4.1. Performance of MPC in Set-Point Tracking.....	42
5.4.2. Performance of MPC in Disturbance Rejection.....	45
5.4.3. Performance of MPC for Robustness.....	46
6. CONCLUSIONS AND RECOMMENDATIONS	48
REFERENCES.....	50
APPENDICES	
A. DETERMINATION OF BORIC ACID CONCENTRATION.....	55
B. EXPERIMENTAL DATA	56
C. MPC SIMULATION PROGRAM.....	57

LIST OF TABLES

Table 4.1 The chemical analysis of Hisarcık colemanites (dry basis, wt%).....	27
Table 4.2 Experimental conditions (Aşar, 2004).	29
Table 5.1 The process and disturbance transfer functions obtained from the boric acid concentration responses (Aşar, 2004).	35
Table 5.2 The process and disturbance transfer functions in terms of pH' and inputs.	39
Table 5.3 The parameters of MPC.	42
Table B.1 Amount of colemanite added to the reactor at different R values.....	56
Table B.2 Volume of NaOH consumed and pH at different R values.....	56

LIST OF FIGURES

Figure 3.1 General structure of inferential control configuration (Stephanopoulos, 1984).	13
Figure 3.2 Block-diagram representation of (a) continuous system (b) batch system.	15
Figure 3.3 The strategy of MPC (Garcia et al., 1989).....	23
Figure 3.4 The structure of MPC (Camacho and Borons, 1999).	23
Figure 4.1 Experimental set-up of the boric acid production system (Çakal, 2006). 26	
Figure 4.2 The block diagram of the controlled production system.	28
Figure 5.1 Boric acid concentration as a function of pH.	33
Figure 5.2 Correlation between boric acid concentration and pH.	34
Figure 5.3 Comparison of experimental data with process transfer function model of (a) first reactor (b) second reactor (c) third reactor (d) fourth reactor	36
Figure 5.4 Comparison of experimental data with disturbance transfer function model of (a) first reactor (b) second reactor (c) third reactor (d) fourth reactor.....	37
Figure 5.5 (a) First two reactors with inputs and outputs (b) overall FODT transfer functions for the first two reactors (Aşar, 2004).	40
Figure 5.6 Comparison of second-order transfer function with FODT model and experimental data for (a) process transfer function (b) disturbance transfer function.	41
Figure 5.7 MPC performance in set-point tracking at different f values.	43
Figure 5.8 The comparison of second-order, fourth-order, and FODT models in set-point tracking.	43

Figure 5.9 The MPC performance in set-point tracking in the presence of lower manipulated variable constraint.	44
Figure 5.10 MPC performance in disturbance rejection at different f values.	45
Figure 5.11 The comparison of second-order, fourth-order, and FODT models in disturbance rejection.	46
Figure 5.12 The robustness of MPC in set-point tracking.	47
Figure 5.13 The robustness of MPC in disturbance rejection.	47

LIST OF SYMBOLS

C	Concentration, mole/L
C	Control horizon, min
d_1'	Colemanite flow rate to the first reactor in deviation form, g/min
f	Scalar tuning parameter of MPC
F	Molar flow rate, mole/min
K_a	Dissociation constant of acid
K_{a2}	Second dissociation constant of acid
K_o	Overall gain
m	Mass of matter, g
M	Mass flow rate, g/min
M	Model horizon, min
mw	Molecular weight, g/mole
N	Amount of matter, mole
P	Prediction horizon, min
pH_i'	pH of the i^{th} reactor in deviation form
Q	Volumetric flow rate, L/min
R	$\text{CaO}/\text{SO}_4^{2-}$ molar ratio
t	Time, min
T	Temperature, °C
t_{do}	Overall time delay
u	Process inputs
u_1'	Acid flow rate to the first reactor in deviation form, g/min
V	Volume of liquid in the reactor, mL

W_1	Weighing matrix for predicted errors
W_2	Weighing matrix for control moves
x	Mass ratio
y	Future outputs
y_i'	Boric acid concentration in the i th reactor in deviation form, mol/L

Greek Letters

Δ	Increment
ρ	Density, g/mL
τ_o	Overall time constant

Subscripts

A	Acid
C	Colemanite

Superscripts

'	Variables of batch reactor
*	Amount of matter going into the reaction

Abbreviations

ANN	Artificial Neural Networks
CARIMA	Controlled Auto Regressive Integrated Moving Average
CSTR	Continuously Stirred Tank Reactor
DMC	Dynamic Matrix Control
FDI	Fault Detection and Identification
FODT	First Order with Dead Time
FTMPC	Fault Folerant Model Predictive Control
GLR	Generalized Likelihood Ratios
GPC	Generalized Predictive Control
IAE	Integral Absolute Error
IMC	Internal Model Control
LFT	Linear Fractional Transformation

LMI	Linear Matrix Inequality
MAC	Model Algorithmic Control
MIMO	Multi Input Multi Output
MPC	Model Predictive Controller
MPHC	Model Predictive Heuristic Control
NAMW	Number Average Molecular Weight
NMPC	Nonlinear Model Predictive Control
PID	Proportional Integral Derivative
RPN	Robust Performance Number
SISO	Single Input Single Output
SSE	Sum of Squared Errors

CHAPTER 1

INTRODUCTION

Boric acid as one of the most important semi-finished good in industry is widely used in various manufacturing areas such as glass, soaps, detergents, textile, porcelain, nuclear power, etc. Boric acid is mainly produced by reacting one of the boron minerals, tincal, cernite, ulexide and colemanite, with a strong mineral acid. In our country, it is produced by reacting colemanite with sulfuric acid.

In Turkiye, there are two boric acid production plants one of which is found in Bandırma, Balıkesir and the other one is in Emet, Kütahya. The system in Bandırma is a batch system whereas the process in Kütahya is continuous. Especially, the continuous system in Emet has a newly developing technology. There is a lack of information in this area and the studies on boric acid production from colemanite are rare. Therefore, the studies that will be done on continuous production of boric acid as a result of the reaction between colemanite and sulfuric acid will have important contributions to the improvement of this technology.

Çakal (2004) studied the continuous boric acid production experimentally on a lab-scale system resembling the process in Emet, Kütahya and analyzed the size distribution of gypsum crystals which are the by-product of the reaction between colemanite and sulfuric acid. Aşar (2004) studied the same system by formulating a model from experimental findings. He then, designed a Model Predictive Controller

in order to control the produced boric acid concentration of the product by manipulating the input sulfuric acid flow rate.

In manufacturing, it is very essential to control the process variables and keep them constant at specified values, in order to have efficient production systems. There are many control techniques developed to do so and Model Predictive Control (MPC) technique is one of them, which was originated in the late seventies and has developed considerably since then. It is a control algorithm which makes an explicit use of a model of the process to obtain the control signal by minimizing an objective function (Camacho and Bordons, 1999).

The various MPC algorithms only differ amongst themselves in the model used to represent the process and the noises and the cost function to be minimized. This type of control is of an open nature within which many works have been developed, being widely accepted by the academic world and by the industry (Camacho and Bordons, 1999).

In some control problems, the controlled variable of the process cannot be conveniently measured on-line, as it is in the case of measurement of boric acid concentration which requires the samples to be taken and analyzed in the plant analytical laboratory. In such a situation, where the controlled variable cannot be measured effectively and quickly enough to be used for the feedback control, inferential control is used. In this method, secondary process outputs are used to infer the value of the primary controlled variable (Seborg, 1989).

In Aşar's study (2004), the MPC simulation studies were made according to the direct measurement of boric acid concentration. However, as it is mentioned above, in industrial scale on-line measurement of boric acid concentration is very difficult whereas the measurement of another variable, pH, which is a function of the boric acid concentration, is much easier and more practical. Therefore, in this study the correlation between boric acid concentration and pH is investigated. This knowledge is used in the design of a Model Predictive Controller which is integrated with an

estimator, where pH measurements are used to estimate and control the boric acid concentration of the product.

CHAPTER 2

LITERATURE SURVEY

Literature survey is done on the boric acid studies and Model Predictive Control strategy that is widely used during the last decades.

2.1. Boric Acid Studies

In the world, Turkiye, USA and Russia have large reserves of boron mines. With a share of 72%, Turkiye has a total boron reserves of 563 million tons on the basis of B_2O_3 content (Roskill, 2002). Therefore, many studies are done in Turkiye for the processes that are used to convert these ores to final products. Boric acid is one of the most important of such products that have many usage areas in production.

Gürbüz et al. (1998) investigated the dissolution of colemanite in diluted water and boric acid solutions. The composition of boric acid solutions was selected as 7.5%, 10%, and 20%, respectively. The results showed that the reaction was very fast and all of the boric acid solutions became saturated in the first five minutes. It was also observed that the pH of the medium increased as the colemanite dissolved in distilled water. On the other hand, pH variation was seemed to be constant in boric acid solutions.

Tunç and Kocakerim (1998) studied the dissolution kinetics of colemanite in sulfuric acid solutions. The parameters of the experimental study were chosen as reaction temperature, particle size, acid concentration, stirring rate, and solid/liquid ratio. It was observed that reaction rate increased as the particle size of colemanite and liquid/solid ratio decreased. Increasing the temperature and stirring rate also increased the reaction rate. Moreover, the reaction rate increased with increasing acid concentration up to 1 M but, after exceeding this value it decreased.

Çetin et al. (2001) investigated the formation and growth kinetics of gypsum during the dissolution of colemanite in aqueous sulfuric acid in a batch reactor by varying the temperature (60-90°C), stirring rate (150-400 rpm), and initial concentrations of the reactants. The crystallization of gypsum from the solution was followed by looking at the concentration of calcium ion which was decreased by the formation of calcium sulfate precipitate. The saturation concentration of calcium ion decreased with the increasing temperature up to 80°C, however, further increase in the temperature up to 90°C causes increase in the saturation concentration. The stirring rate was found to have no significant effect on dissolution of colemanite between the values of 150-400 rpm. As the initial concentration of sulfuric acid decreased, the boric acid concentration in the solution also decreased. The rate of gypsum crystallization reaction was found to be second order with respect to saturation level.

The dissolution characteristics of Hisarcık colemanite was also studied by Kalafatoğlu (2000) in sulfuric acid solutions by varying the initial concentration of sulfuric acid. It was observed that as the concentration of sulfuric acid increased, some other kind of impurities present in colemanite also dissolved. Consequently, the optimum value of the acid concentration was investigated and it was found that the dissolution of clay and other impurities was the least when the composition of sulfuric acid was 5%.

Çakal et al. (2006) investigated the size of gypsum crystals which were formed as a by-product of the reaction between colemanite and sulfuric acid as a function of process conditions. Gypsum crystals, which were in the shape of thin needles, must

grow to an easily filterable size in order to increase the production yield and purity of boric acid. In this study, the particle size distributions and the volume-weighted mean diameters of the gypsum crystals obtained in batch and continuous flow systems were compared. The batch and continuous process experiments were performed at a temperature of 85 °C, a stirring rate of 400 rpm, and the inlet CaO to SO_4^{2-} molar ratio of 1.0. Gypsum crystals obtained in the continuous process were wider and longer than the ones obtained in the batch process for long residence time of the solid in the reactor. It was also observed that the boric acid concentration did not vary significantly with an increase in the number of continuous reactors.

Taylan et al. (2007) studied the influence of ultrasound on the dissolution of colemanite in H_2SO_4 solution and on the precipitation of the gypsum during the reaction. Experiments were performed in a batch stirred vessel at 85 °C in the absence and presence of ultrasound. The stirring rates were changed to provide a homogeneous suspension during the reaction. The dynamic concentrations of boric acid and calcium ion in the solution were determined. It was observed that the dissolution of colemanite and precipitation rate of the gypsum in the solution increased with the use of ultrasound after one hour. Moreover, the size of gypsum crystals decreased when ultrasound was used.

2.2. Model Predictive Control Studies

“From the end of the 1970’s various articles appeared showing an implicit interest in MPC in the industry, principally the Richalet et al. (1978) publications presenting Model Predictive Heuristic Control (MPHC) (later known as Model Algorithmic Control (MAC)) and those of Cutler and Ramakter (1979) with Dynamic Matrix Control (DMC). A dynamic process model is explicitly used in both algorithms (impulse response in the first one and step response in the second)”(Camacho and Bordons, 1999).

MPC quickly became popular, particularly in chemical process industries, due to the simplicity of the algorithm and due to the use of the impulse or step response model which can be obtained experimentally (Camacho and Bordons, 1999).

In 1982, mathematical issues for the utilization of MAC analysis were presented by Rouhani and Mehra et al. They defined the fundamental components of the control structure by analyzing the stability and the robustness of both the deterministic and stochastic Single Input Single Output (SISO) systems. In 1983, a SISO predictive controller was compared with a discrete PID controller for three representative process models and for an experimental continuous stirred tank heater by Marchetti et al. The predictive controller performance was found to be better in representative cases, but no improvement was observed in the experimental case.

A new control algorithm called Generalized Predictive Control (GPC) was proposed by Clarke et al. in 1987. They claimed that, this control technique can be applicable to non-minimum phase plants, open-loop unstable plants and plants with unknown dead time and/or order. Control Auto Regressive Integrated Moving Average (CARIMA) model was proposed to model the disturbances.

Garcia et al. (1989) declared that all of the existing MPC algorithms including MPPHC, DMC and Internal Model Control (IMC) belong to the same family of controllers which can be named as Model Predictive Control (MPC).

Psichogios and Ungar (1991) used Artificial Neural Networks (ANN) in model based control. They applied two nonlinear model based control strategies, IMC and Multistep Predictive Control, to control a nonlinear exothermic continuously stirred tank reactor (CSTR). The neural network IMC-type controller, in which the process model was learned using a historical input-output data gave good performance. On the other hand, MPC strategy gave slightly better controller performance than the IMC due to the MPC's ability to handle control action by constraints.

Gobin et al. (1994) studied the MPC for a non-linear process, involving two CSTR's in cascade, in which the polymerization reaction of styrene was taking place. Due to the system's open-loop unstable behavior, the temperature rise should be controlled by manipulating the flow rate of coolant fluid circulating around the jackets of the reactors. A DMC algorithm based on the linearization of the dynamic model around an open-loop stable operating point was designed. The designed DMC was also compared with a conventional PID controller.

Badgwell (1997) studied a new robust MPC algorithm for stable, linear plants which was a direct generalization of the nominally stabilizing regulator proposed by Rawlings and Muske (1993). The control algorithm was applied to a CSTR in which a single irreversible, first-order reaction was taking place. The robust stability was achieved by adding constraints. The simulation studies showed that robust stability was obtained for all possible values of the tuning parameters. It was also noted that the robust stability presented in their study not requiring linearity could also be extended to stable non-linear systems.

A nonlinear model predictive control (NMPC) scheme for open-loop stable systems subject to input and state constraints was introduced by Chen and Allgöwer in 1998. By choosing the appropriate finite prediction horizon, the closed-loop stability was guaranteed. A quasi-finite horizon NMPC scheme was implemented to control a CSTR at optimal yield point. A significant difference was not observed between the achieved control performance and the one in which an NMPC scheme with an infinite prediction horizon was implemented.

Rollins et al. (1998) used a semi-empirical model of an underdamped process in a predictive modelling approach. This approach was found to be very accurate for first-order models. In 1999, Rollins et al. extended this study to demonstrate the ability of the same approach to accurately predict output response of systems with complex dynamics. The control algorithm was simulated for a CSTR having an underdamped second order behavior for changes in coolant flow rate and inverse second order behavior for changes in feed rate. The technique was shown to perform rapidly.

Al-Ghazzawi et al. (2001) developed an automatic on-line tuning strategy for MPC. Their algorithms used explicit expressions of the closed-loop process output response and was sensitized to the MPC tuning parameters. The effectiveness of the technique was illustrated by implementing on a linear model for three-product distillation column and also on a non-linear model for a CSTR. The effectiveness of the proposed tuning method was compared to an existing offline tuning method and showed superior performance.

Santos et al. (2001) implemented a nonlinear MPC (NMPC) algorithm on-line to control the liquid level and temperature in a pilot plant CSTR in which an irreversible exothermic chemical reaction was taking place. The model developed was validated with experimental data. Several sources of model mismatch and unmeasured disturbances were observed. However, the closed loop system followed set-points and rejected disturbances quite well.

Wu (2001) combined robust control technique with MPC in order to develop a methodology which could handle both modelling inaccuracies and hard input/output constraints simultaneously. The developed constrained control technique was studied on an industrial CSTR and compared with conventional MPC. The control objective included set-point tracking and regulation of reactant concentration with respect to disturbances in feed temperature. The simulation results showed that the technique was applicable to industrial problems. Compared with conventional MPC, robust MPC method was stable and also capable of dealing with both model mismatch as well as constraints.

Prasad et al. (2002) applied a multivariable multi-rate nonlinear MPC (NMPC) strategy to styrene polymerization CSTR and the control of polymer properties such as number average molecular weight (NAMW) and polydispersity was considered. The system was assumed to have two sets of measurements which were fast on-line measurements and slow laboratory measurements with significant analysis delay. Therefore, the NMPC was coupled with a multi-rate estimator based on extended Kalman filtering in order to provide inferential control for the system. The results

indicated that the designed multi-rate NMPC algorithm gave good performance when it was compared with linear-rate and nonlinear single-rate MPC algorithms.

Trierweiler and Farina (2003) presented a tuning strategy based on Robust Performance Number (RPN) for MIMO-MPC. The main idea behind the proposed tuning strategy was the correctly scaling the system and weighing matrices. RPN-MPC was applied in the design of the controller of an air separation plant and a CSTR with the Vande Vusse's reaction. It was concluded that the designed tuning strategy was much less sensible to the parameter variation. Moreover, the RPN tuned MPC produced smooth and smaller control action than the untuned MPC indicating that the unconstrained RPN-MPC tuning procedure can also produce good results for the constrained control problem.

Limon et al. (2003) showed that the closed loop formulation of the robust MPC was capable of robustly stabilizing uncertain nonlinear systems subject to constraints. The closed loop formulation was proposed in order to overcome the fact that open loop nature of the predictions might make the controller very conservative. In this case, a sequence of control law was computed so that the reaction of the controller to the uncertainty was incorporated in the prediction. The derived controller algorithm was used to robustly stabilize a CSTR in which an exothermic, irreversible reaction was taking place and satisfactory results were obtained.

Biagiola and Figueroa (2004) studied a nonlinear MPC (NMPC) coupled with nonlinear state estimator based on the measured outputs. An open-loop unstable jacketed exothermic chemical reactor was considered and computer simulations were developed to illustrate performance of both the nonlinear observer and the control strategy. A successful behavior of the whole observer/controller structure was obtained.

Prakash et al. (2005) developed a fault tolerant MPC (FTMPC) scheme integrated with the fault detection and identification (FDI) method based on generalized likelihood ratios (GLR). They demonstrated the controller performance using

simulation and experimental studies on a coupled two CSTR process for temperature control. The difference of FTMPC from conventional MPC was the fact that in the presence of soft faults such as sensor/actuator drifts, the offset between the true value and set points of controlled variables was eliminated and also, the true values of state variables, manipulated inputs as well as measured variables were maintained within their imposed bounds. Thus, due to these advantages of FTMPC, the simulation and experimental studies demonstrated that the proposed controller scheme was robust to unmodeled disturbances of moderate magnitude and had efficient performance for the temperature control of two-CSTR heater system.

Magni and Scattolini (2005) tested the performance of MPC algorithm for a non-linear system, a CSTR in which an irreversible exothermic reaction was taking place. The MPC algorithm solved the tracking problem for asymptotically constant references where the open-loop response was highly non-linear. When the proposed control algorithm together with a standard EKF was used it was observed that the closed-loop equilibrium was stabilized and asymptotic zero-error was regulated satisfactorily.

A dilation of the Linear Matrix Inequality (LMI) characterization was presented by Feng et al. (2007) to address constrained robust MPC for a class of uncertain linear systems with structure time-varying uncertainties. The uncertainty was described in linear fractional transformation (LFT) form. Parameter dependent Lyapunov functions were used and slack variables were introduced in order to reduce the design conservativeness. The proposed approach was applied to an industrial CSTR and through computer simulations, it was investigated that the approach stabilized the system under stronger hard input constraints.

CHAPTER 3

ESTIMATOR AND MODEL PREDICTIVE CONTROLLER DESIGN

In this chapter, estimator design which is based on the correlation between boric acid concentration and pH will be given. Also, the design of MPC will be explained.

3.1. Estimator Design

It sometimes happens that the controlled output of a processing unit cannot be measured directly. Consequently, feedback control or any other configuration which necessitates direct measurement of the controlled variable cannot be used. In such cases, inferential control is the only solution (Stephanopoulos, 1984).

Inferential control is a technique where secondary measurements, which can be obtained easily and rapidly, are used in order to estimate the value of unmeasured primary controlled outputs. In this technique, a mathematical relationship is developed between the unmeasured outputs and the secondary measurements; that is, unmeasured outputs are the functions of secondary measurements, which allows one to determine the values of the unmeasured outputs. The inferential control configuration is shown in Figure 3.1 (Stephanopoulos, 1984).

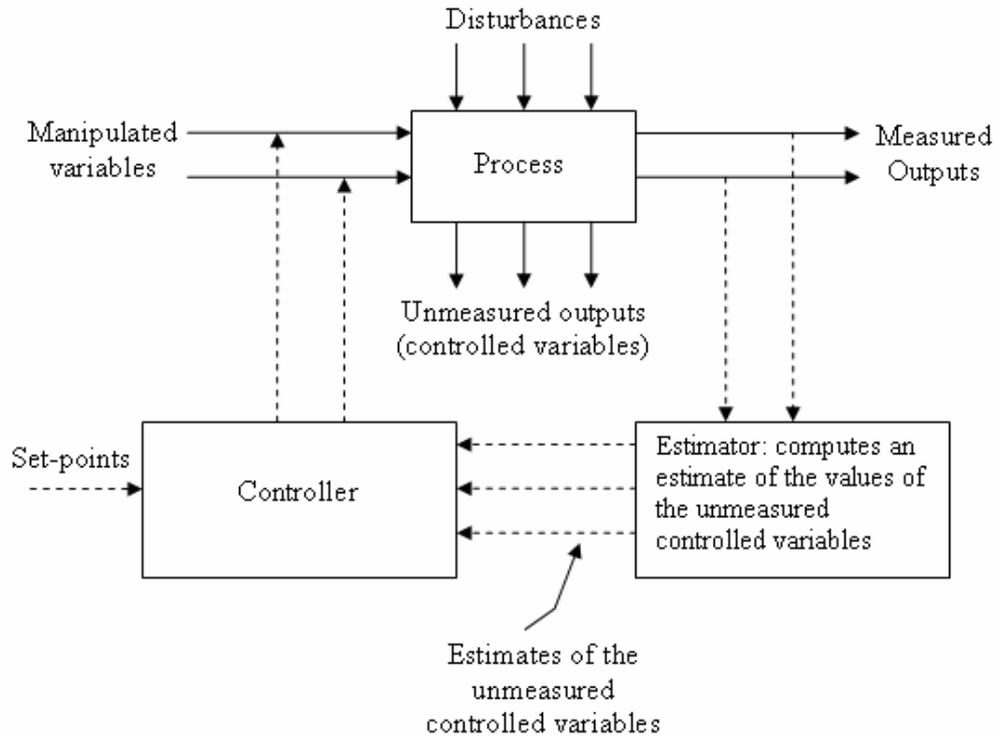


Figure 3.1 General structure of inferential control configuration (Stephanopoulos, 1984).

In this study, the aim is to predict boric acid concentration values by measuring pH, namely, to find out the relationship between boric acid concentration and pH. The boric acid concentration as a function of pH can be obtained by using stoichiometric and analytical chemistry calculations. However, the consistency of this relationship must be checked with the experimental data due to complexity of side reactions taking place.

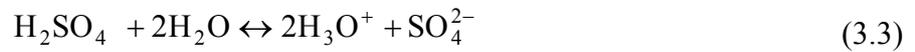
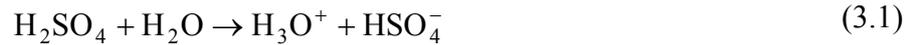
In this section, the derivation of the theoretical equation between boric acid concentration and pH will be given.

The boric acid conversion in 4-CSTR production system is 100% (Çakal, 2004). In the reactors, all of B_2O_3 in colemanite is completely consumed whereas there remains some amount of excess sulfuric acid unreacted. Therefore, the product

coming out of the last reactor mainly contains boric acid, gypsum crystals and also, some amount of sulfuric acid.

In this analysis, effect of other weak acids are considered to be negligible. Sulfuric acid is a strong acid whereas boric acid is very weak. The solubility constant of boric acid at 85°C is in the order of 10^{-10} (Lide, 1993). Therefore, the main factor that effects the pH of the product is the concentration of sulfuric acid ($C_{H_2SO_4}$) in the medium which is the excess amount unreacted. Thus, knowing the input sulfuric acid amount, the excess value determines the boric acid concentration.

Sulfuric acid is unusual in that one of its protons behaves as a strong acid (Equation 3.1) and the other as a weak acid (Equation 3.2) ($K_{a2} = 2.3 \cdot 10^{-3}$ (Marshall et al., 1966)) (Skoog, 1996):



At high sulfuric acid concentrations, the dissociation of HSO_4^- can be neglected due to the large excess of H_3O^+ resulting from the complete dissociation of H_2SO_4 . However, at lower sulfuric acid concentrations, the contribution of the dissociation of HSO_4^- should also be taken into consideration. Therefore, to consider all cases, taking the second dissociation into account, the overall amount of $[H_3O^+]$ can be derived as it is in Equation 3.4 (Skoog, 1996):

$$\frac{[H_3O^+] ([H_3O^+] - C_{H_2SO_4})}{2 C_{H_2SO_4} - [H_3O^+]} = K_{a2} = 2.3 \cdot 10^{-3} \quad (3.4)$$

Considering the definition of pH

$$pH = -\log[H_3O^+] \quad (3.5)$$

and substituting it for $[H_3O^+]$ in Equation 3.4, Equation 3.6 can be obtained as

$$\frac{(10^{-pH}) (10^{-pH} - C_{H_2SO_4})}{2 C_{H_2SO_4} - 10^{-pH}} = 2.3 * 10^{-3} \quad (3.6)$$

This theoretically derived equation has to be checked experimentally. In the 4-CSTR system, for which previous experiments were done, only the boric acid concentration was measured and pH values were not measured. Because the 4-CSTR system was dismantled, another experimental system has to be designed in order to find a correlation between the measured boric acid concentration and pH values. For this purpose, a batch system is planned to be used. However, equivalency of two systems has to be proved.

The block-diagram representation of continuous and batch system are given in Figure 3.2a and Figure 3.2b, respectively. The variables of both continuous and batch system are also given in the figures.

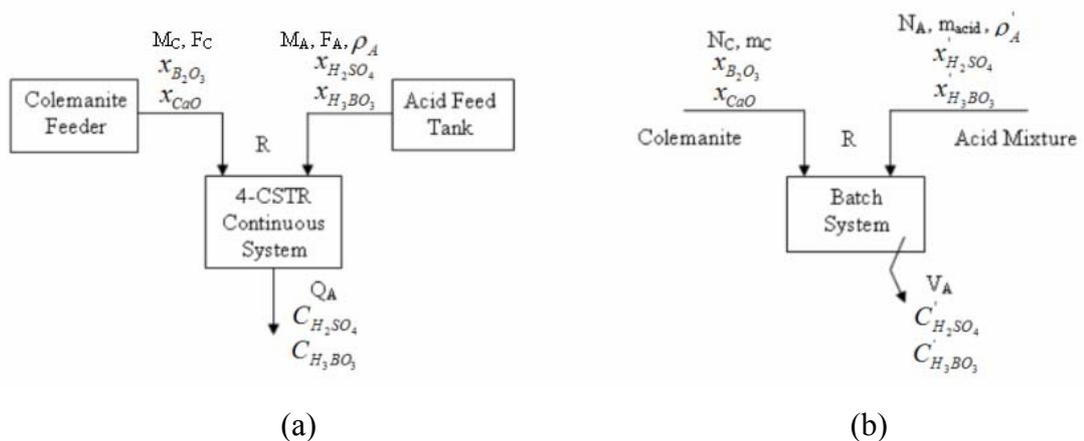


Figure 3.2 Block-diagram representation of (a) continuous system (b) batch system.

The calculations for both continuous and batch system will be made simultaneously.

R is defined as the molar ratio of B₂O₃ coming from colemanite to SO₄²⁻ coming from sulfuric acid:

$$R = \frac{F_{B_2O_3}}{F_{SO_4^{2-}}} = \frac{(M_C)(x_{B_2O_3})}{(mw_{B_2O_3})(F_{H_2SO_4,in})} \quad (3.7)$$

for continuous system, and,

$$R = \frac{N_{B_2O_3}}{N_{SO_4^{2-}}} = \frac{(m_C)(x_{B_2O_3})}{(mw_{B_2O_3})(N_{H_2SO_4,in})} \quad (3.8)$$

for batch system.

Leaving M_C and m_C alone,

$$M_C = \frac{(R)(F_{H_2SO_4,in})(mw_{B_2O_3})}{(x_{B_2O_3})} \quad (3.9)$$

$$m_C = \frac{(R)(N_{H_2SO_4,in})(mw_{B_2O_3})}{(x_{B_2O_3})} \quad (3.10)$$

When the composition of colemanites given in Table 4.1 is analyzed, it is seen that the ratio of B₂O₃/CaO is less than 1.5. That is, as the reaction is completed all of the B₂O₃ is consumed, whereas there remains some amount of CaO unreacted. Therefore, the reacted amount of CaO, x_{CaO}^* , can be calculated by looking at the chemical formulation of colemanite (2CaO·3 B₂O₃·5H₂O) as follows:

$$x_{CaO}^* = \left(\frac{2}{3}\right) \left(\frac{mw_{CaO}}{mw_{B_2O_3}}\right) (x_{B_2O_3}) \quad (3.11)$$

Concentration of H_2SO_4 in the fourth reactor of continuous system and at the end of the reaction in batch system can be calculated by making mass balances as given below, respectively:

$$\begin{aligned} C_{H_2SO_4} &= (F_{H_2SO_4,in} - F_{H_2SO_4,consumed}) \left(\frac{1}{Q_A}\right) \\ &= \left(F_{H_2SO_4,in} - \frac{(2)(M_C)(x_{B_2O_3} + x_{CaO}^*)}{mw_{2CaO.3B_2O_3}}\right) \left(\frac{1}{Q_A}\right) \end{aligned} \quad (3.12)$$

$$\begin{aligned} C'_{H_2SO_4} &= (N_{H_2SO_4,in} - N_{H_2SO_4,consumed}) \left(\frac{1}{V_A}\right) \\ &= \left(N_{H_2SO_4,in} - \frac{(2)(m_C)(x_{B_2O_3} + x_{CaO}^*)}{mw_{2CaO.3B_2O_3}}\right) \left(\frac{1}{V_A}\right) \end{aligned} \quad (3.13)$$

where Q_A is the volumetric flow rate of acid mixture coming from acid feed tank and V_A is the volume of the acid mixture in the batch reactor. The superscript prime denotes the variables of batch system.

Substituting Equations 3.9 and 3.10 into Equations 3.12 and 3.13, respectively,

$$\begin{aligned}
C_{H_2SO_4} &= \left(\frac{F_{H_2SO_4, in}}{Q_A} \right) \left[1 - \frac{\frac{(2)(R)(mw_{B_2O_3})}{x_{B_2O_3}} \left(x_{B_2O_3} + \frac{2}{3} \frac{mw_{CaO}}{mw_{B_2O_3}} x_{B_2O_3} \right)}{mw_{2CaO.3B_2O_3}} \right] \\
&= \left(\frac{F_{H_2SO_4, in}}{Q_A} \right) \left[1 - \frac{(2)(R)}{mw_{2CaO.3B_2O_3}} \left(mw_{B_2O_3} + \frac{2}{3} mw_{CaO} \right) \right]
\end{aligned} \tag{3.14}$$

for continuous system, and for batch system as,

$$C'_{H_2SO_4} = \left(\frac{N_{H_2SO_4, in}}{V_A} \right) \left[1 - \frac{(2)(R)}{mw_{2CaO.3B_2O_3}} \left(mw_{B_2O_3} + \frac{2}{3} mw_{CaO} \right) \right] \tag{3.15}$$

Let

$$\alpha = \frac{F_{H_2SO_4, in}}{Q_A} \tag{3.16}$$

$$\alpha' = \frac{N_{H_2SO_4, in}}{V_A} \tag{3.17}$$

Then, substituting the molecular weight values of B_2O_3 , CaO , and $2CaO \cdot 3B_2O_3$ into Equations 3.14 and 3.15, the concentration of excess sulfuric acid in continuous and batch system can be written as,

$$C_{H_2SO_4} = \alpha(1 - 0.6667R) \tag{3.18}$$

$$C'_{H_2SO_4} = \alpha'(1 - 0.6667R) \tag{3.19}$$

The boric acid concentration, $C_{H_3BO_3}$, in the fourth reactor of the continuous system and batch system can be calculated similar to $C_{H_2SO_4}$ calculation. Again by establishing mass balances for both continuous and batch systems, respectively, these can be written as,

$$\begin{aligned}
 C_{H_3BO_3} &= (F_{H_3BO_3,formed} + F_{H_3BO_3,in}) \left(\frac{1}{Q_A} \right) \\
 &= \left(\frac{(6)(M_C)(x_{B_2O_3} + x_{CaO}^*)}{mw_{2CaO.3B_2O_3}} + F_{H_3BO_3,in} \right) \left(\frac{1}{Q_A} \right) \quad (3.20)
 \end{aligned}$$

$$\begin{aligned}
 C'_{H_3BO_3} &= (N_{H_3BO_3,formed} + N_{H_3BO_3,in}) \left(\frac{1}{V_A} \right) \\
 &= \left(\frac{(6)(m_C)(x_{B_2O_3} + x_{CaO}^*)}{mw_{2CaO.3B_2O_3}} + N_{H_3BO_3,in} \right) \left(\frac{1}{V_A} \right) \quad (3.21)
 \end{aligned}$$

Let

$$\beta = \frac{F_{H_3BO_3,in}}{Q_A} \quad (3.22)$$

$$\beta' = \frac{N_{H_3BO_3,in}}{V_A} \quad (3.23)$$

Then, substituting Equations 3.9, 3.10, and 3.11 and also the molecular weight values of B_2O_3 , CaO , and $2CaO.3B_2O_3$ into Equations 3.20 and 3.21, respectively, one can obtain boric acid concentration in continuous and batch system as,

$$C_{H_3BO_3} = 2\alpha R + \beta \quad (3.24)$$

$$C'_{H_3BO_3} = 2\alpha'R + \beta \quad (3.25)$$

α , α' , β , and β' can be calculated as follows:

$$\alpha = \frac{F_{H_2SO_4,in}}{Q_A} = \frac{\frac{(M_A)(x_{H_2SO_4})}{mw_{H_2SO_4}}}{\frac{M_A}{\rho_A}} = \frac{(x_{H_2SO_4})(\rho_A)}{mw_{H_2SO_4}} \quad (3.26)$$

$$\alpha' = \frac{N_{H_2SO_4,in}}{V_A} = \frac{\frac{(m_{acid})(x'_{H_2SO_4})}{mw_{H_2SO_4}}}{\frac{m_{acid}}{\rho'_A}} = \frac{(x'_{H_2SO_4})(\rho'_A)}{mw_{H_2SO_4}} \quad (3.27)$$

$$\beta = \frac{F_{H_3BO_3,in}}{Q_A} = \frac{\frac{(M_A)(x_{H_3BO_3})}{mw_{H_3BO_3}}}{\frac{M_A}{\rho_A}} = \frac{(x_{H_3BO_3})(\rho_A)}{mw_{H_3BO_3}} \quad (3.28)$$

$$\beta' = \frac{N_{H_3BO_3,in}}{V_A} = \frac{\frac{(m_{acid})(x'_{H_3BO_3})}{mw_{H_3BO_3}}}{\frac{m_{acid}}{\rho'_A}} = \frac{(x'_{H_3BO_3})(\rho'_A)}{mw_{H_3BO_3}} \quad (3.29)$$

If $x'_{H_2SO_4} = x_{H_2SO_4}$ and $x'_{H_3BO_3} = x_{H_3BO_3}$, which makes $\rho_A = \rho'_A$, then $\alpha = \alpha'$ and $\beta = \beta'$. As a result, the concentrations become

$$C_{H_2SO_4} = \alpha(1 - 0.6667R) = C'_{H_2SO_4} \quad (3.30)$$

$$C_{H_3BO_3} = 2\alpha R + \beta = C'_{H_3BO_3} \quad (3.31)$$

Therefore, it can be concluded that the outlet stream of the continuous system can be represented by a batch system having an initial composition of acid mixture in the batch reactor same with that of the acid feed tank of the continuous system.

If the composition of acid mixture fed to the reactor is set as 5.58% sulfuric acid, 8.00% boric acid and 86.42% water in weight percentages, then α and β can easily be calculated. As a result, boric acid concentration ($C_{H_3BO_3}$) in the product and the concentration of excess sulfuric acid ($C_{H_2SO_4}$) for the 4-CSTR system can finally be obtained as given below.

$$C_{H_3BO_3} = 1.1729 * R + 1.3333 \quad (3.32)$$

$$C_{H_2SO_4} = 0.5865 - 0.3910 * R \quad (3.33)$$

Solving Equations 3.6, 3.32 and 3.33 together, the boric acid concentration as a function of pH can finally be obtained as it is in Equation 3.34.

$$C_{H_3BO_3} = 3.0927 - 3 \left(\frac{10^{-2pH} + 2.3 * 10^{-(3+pH)}}{(4.6 * 10^{-3} + 10^{-pH})} \right) \quad (3.34)$$

Thus in the estimator design, Equation 3.34 can be used as the estimator equation to find H_3BO_3 concentration when the input is the on-line measured pH values.

3.2. Model Predictive Controller (MPC) Design

“The term Model Predictive Control (MPC) does not designate a specific control strategy but a range of control methods which make an explicit use of a model of the process to obtain the control signal by minimizing an objective function. The ideas in all the predictive control are basically explicit use of a model to predict the process output at future time instants (horizon), calculation of control sequence minimizing

an objective function and the receding strategy, so that at each instant the horizon is displaced towards the future” (Camacho and Bordons, 1999).

The mathematical formulation of MPC technique is described in various Process Control course books (Seborg, 1989; Camacho and Bordons, 1999). In the following sections, the MPC strategy and MPC tuning together with estimator design will be given briefly.

3.2.1. MPC Strategy

As stated above MPC consists of three major parts which are the process model, optimization, and the receding strategy. The strategy of MPC can be represented by a sequence of steps as shown in Figure 3.3. At the present time n , the future outputs of the system, $y(n)$, $y(n+1)$, ..., $y(n+P)$, over a predetermined prediction horizon (P), are predicted by making use of the model and knowing the past and the future inputs to the process. In the figure, the past inputs ($u(n-1)$, $u(n-2)$, ..., $u(n-M+1)$) are represented by solid lines and the future inputs ($u(n+1)$, $u(n+2)$, ..., $u(n+C)$) are designated by dashed lines where, M and C are the model horizon and control horizon, respectively. The set of future input which minimizes some open loop performance objective is chosen as the control input. Only the first element of this optimal future input set is applied to the process because, at the next sampling time a new measurement of the process is obtained from the plant. Therefore, a new optimization problem is formulated and the procedure is repeated. This repeated optimization, modified at each time step is called the receding strategy (Bahar, 2003).

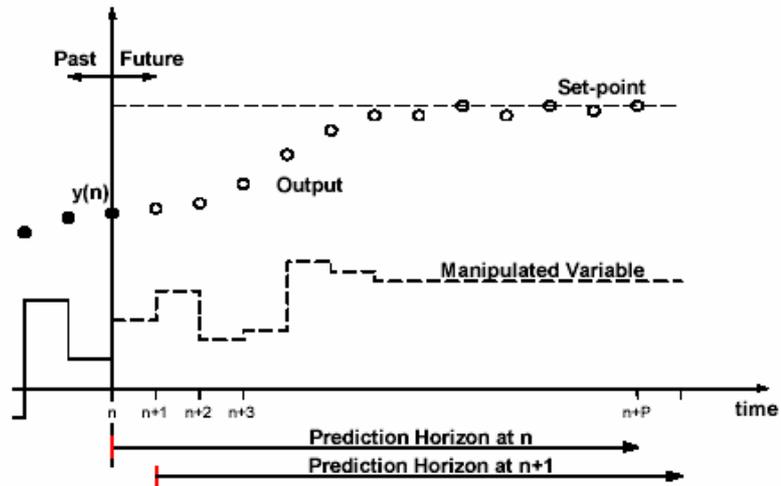


Figure 3.3 The strategy of MPC (Garcia et al., 1989).

The basic structure of MPC can be represented as shown in Figure 3.4. The model takes the past inputs and outputs of the system and predicts the plant's future outputs. Comparing the predicted output with the reference trajectory, the future errors of the plant are calculated at each time step. With this future error information, optimizer determines the best future inputs considering the objective function and the constraints (Camacho and Bordons, 1999).

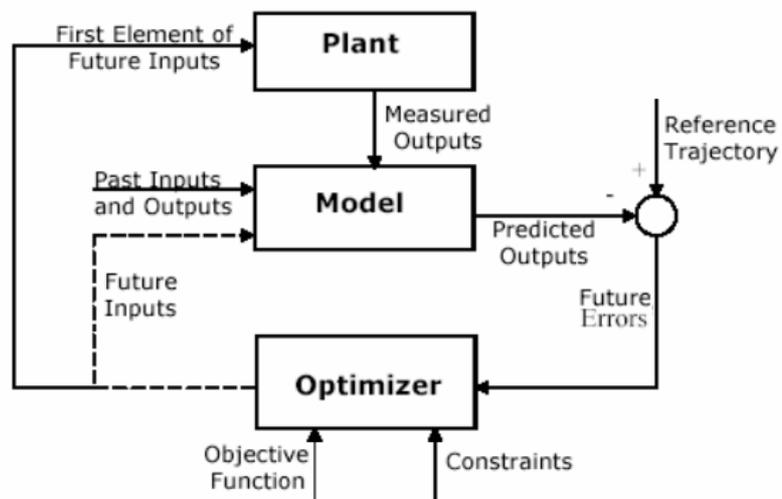


Figure 3.4 The structure of MPC (Camacho and Borons, 1999).

3.2.2. MPC Tuning (Seborg, 1989)

The predictive control technique includes a number of design parameters which can be adjusted to give the desired response as well as an appropriate amount of controller effort. These parameters include model horizon (M), control horizon (C), prediction horizon (P), weighing matrix for predicted errors (W_1), weighing matrix for control moves (W_2) and sampling period (Δt).

The model horizon, M, should usually be selected to be equal to the time for the open-loop step response to be 99% complete. M should be large enough so that no truncation problems arise in calculating the predicted values for the discrete-time model. The control horizon, C, is the number of future control actions that are calculated in the optimization step to reduce the predicted errors. A suitable first guess is to choose C so that it is equal to the time for the open-loop response to be 60% complete. It should be kept in mind that too large values of C results in excessive control action and a smaller value of P leads to a robust controller that is relatively insensitive to model errors. The prediction horizon, P, is the number of predictions that are used in the optimization calculations and it is chosen as 85% of model horizon (Camacho and Bordons, 1999). The weighting matrices W_1 and W_2 contain a potentially large number of design parameters. However, it is usually sufficient to select W_1 as the identity matrix, I, and W_2 as $f \times I$ where f is a scalar design parameter. Larger values of f penalize the control actions more. On the other hand, if $f=0$ the controller gains become very sensitive to C. The value of f must be found by trial and error using simulation. The sampling period Δt must also be selected as part of the design procedure. It should be small enough in order not to lose the important dynamic information. However, if Δt is too small, M must be very large, which is undesirable. The sampling period is not considered to be a tuning parameter because adjustment of M, P, and f is usually quite sufficient to obtain satisfactory closed-loop performance. However, it may be helpful to check the sensitivity of the response to Δt .

CHAPTER 4

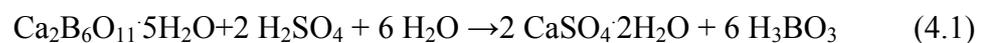
EXPERIMENTAL STUDIES

Model-based controllers have been used for the last 20 years because of their efficient controlling performance in the production processes. In model-based control, a model should be used which can be obtained either theoretically or experimentally. The reaction mechanism of boric acid production is complicated, and in the literature the related data and information are missing. Therefore, experimental modelling is the only way to obtain a model for this system. The experimental set-up and procedure will be given below.

4.1. Experimental Set-Up

The boric acid production system which was designed and established by Çakal (2004) is given in Figure 4.1.

In the system, boric acid is produced by reacting colemanite with sulfuric acid as given in Equation 4.1. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is also formed as a result of the reaction.



In the experimental set-up used by Çakal (2004), there were four CSTR's connected to each other in series, an acid feed tank, a peristaltic pump, a colemanite feeder, a water bath, two temperature controllers and a filtration unit in which gypsum crystals were separated from the mother liquor. The acid feed tank contained a mixture having a composition of 5.58% sulfuric acid, 8.00% boric acid and 86.42% water which were in weight percentages. The density of the acid mixture was 1.03 g/mL. During the experiments the composition in the acid feed tank was kept constant at these specified values. Temperature was also kept constant at 85°C by using temperature controllers and a heated water bath.

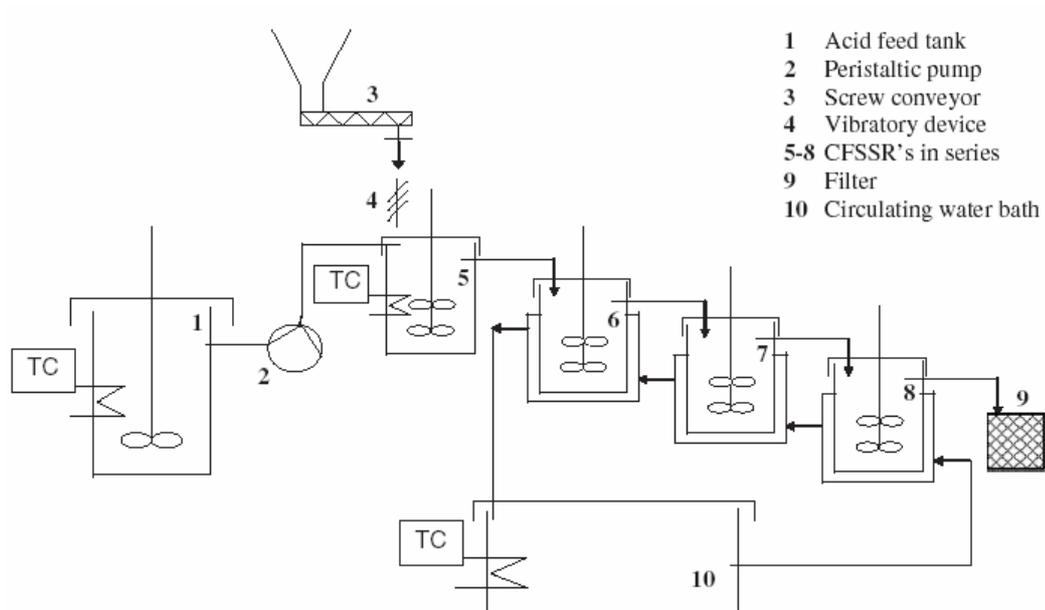


Figure 4.1 Experimental set-up of the boric acid production system (Çakal, 2006).

The chemical analysis of Hisarcık colemanite (provided from a region of Emet, Kutahya, Türkiye) used in the experiments which are numbered according to their B₂O₃ content is given in Table 4.1.

Table 4.1 The chemical analysis of Hisarcık colemanites (dry basis, wt%).

Component	Hisarcık 1 Colemanite	Hisarcık 2 Colemanite	Hisarcık 3 Colemanite
B ₂ O ₃	39.43	43.57	34.61
CaO	25.39	30.90	28.41
Others	35.18	25.53	36.98

The more detailed information about the experimental set-up can be found in the Ph.D. thesis of Çakal (2004).

4.2. The Variables of the Experimental System

The aim of this study is to control the continuous boric acid production system. The most important output of the process is the concentration of boric acid which is obtained as the product. Other process variables should also be kept constant at specified values in order to have an efficient production system. Therefore, the parameters of the production system are analyzed in this section.

The boric acid concentration values which are considered to be the controlled variables in the reactors were measured in the experimental modelling studies done by Aşar (2004). However, in industrial scale, the online measurement of boric acid concentration is very difficult whereas the measurement of pH is much easier and more practical. Therefore, in this study the aim is to design an inferential control system where pH can be used instead of boric acid concentration. Thus, in system modelling and design of MPC, the pH values that can be measurable and related to boric acid concentration by a correlation will be utilized. Therefore, pH is considered to be the secondary controlled variable.

Temperature is another important variable in the system. As it is well known, there is a strong interaction between temperature and concentration due to the exothermic

reaction that is taking place in the reactors (Fogler, 1999). Thus, heat input to each reactor can be considered as a manipulated variable in order to control the temperature in the reactors. However, because of the complexity of the experimental system and difficulty in performing experiments with varying temperature, it is planned to keep temperature at 85°C and to model and design controller only for the control of boric acid concentration in the fourth reactor (Aşar, 2004).

In the system, the boric acid concentration of the product depends on the flow rate of acid coming from acid feed tank, the colemanite flow rate as well as the composition of acid mixture and colemanite. The flow rate of colemanite cannot be fixed continuously at a constant value in the system. Thus, it is the main disturbance to the system. As a result, the manipulated variable can either be chosen as acid mixture concentration or acid flow-rate. However, due to the difficulty of the online measurement of acid concentration, acid flow rate is selected as the manipulated variable for practical means.

The block diagram of the controlled production system is shown in Figure 4.2.

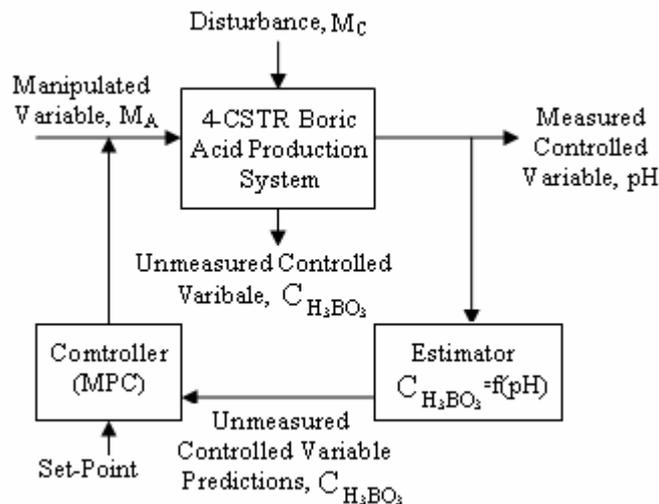


Figure 4.2 The block diagram of the controlled production system.

4.3. Experimental Procedure

Experiments were conducted by Aşar (2004) to find transfer function models of the four reactor system. Also, additional experiments are done in this study to find a relationship between pH and boric acid concentration.

4.3.1. Experimental Procedure for Modelling the Sytem

The experiments were performed by Aşar (2004) in order to obtain the 4-CSTR system model. At different experimental conditions, the response curve of the boric acid concentration in each reactor was obtained by giving a step-change to both manipulated variable (M_A) and disturbance (M_C). The conditions of each experimental run are given in Table 4.2.

Table 4.2 Experimental conditions (Aşar, 2004).

Run No.	$M_{C,initial}$ (g/min)	$M_{C,final}$ (g/min)	$M_{A,initial}$ (g/min)	$M_{A,final}$ (g/min)	$R_{initial}$	R_{final}
1	5.00	-	48.5	50.9	1.13	1.10
2	10.0	-	70.0	72.7	1.58	1.51
3	10.0	11.0	70.0	-	1.25	1.37
4	10.0	11.0	90.0	-	0.97	1.07

Hisarcık 2 colemanite having a size of -250 μm was used in the first two runs, and Hisarcık 3 colemanite having a size of -150 μm was used in the third and fourth runs. The composition of the colemanites is given in Table 4.1.

In Run 1, the acid flow rate was increased from 48.5 g/min to 50.9 g/min, that is, the $\text{B}_2\text{O}_3/\text{SO}_4^{2-}$ ratio (R) was decreased from 1.13 to 1.10. Similarly, acid flow rate was

increased from 70 g/min to 72.7 g/min in Run 2, so that, the R value was decreased from 1.58 to 1.51.

Two more experiments were performed by giving step input to colemanite flow rate. The colemanite flow rate was increased from 10 g/min to 11 g/min in both the third and fourth experimental runs. Due to the difference in colemanite flow rate, R ratio was increased from 1.25 to 1.37 and 0.97 to 1.07, in Run 3 and Run 4, respectively.

In all of the experimental runs, samples were taken at approximately 25-minute time intervals.

4.3.2. Experimental Procedure for Obtaining the Relationship between Boric Acid Concentration and pH

The pH values of the samples were not measured in the experiments performed by Aşar (2004). Therefore, in order to obtain the relationship between pH and boric acid concentration which will be used in the estimator design, additional set of experiments has to be performed in this study. A batch reactor system, which represents the continuous system described in Section 4.1, is designed.

In batch experiments, a 250-mL Erlenmeyer flask is used which is heated by a hot plate with a magnetic stirrer. Seven experimental runs are performed at different R values varying between 0.8 and 1.5 (Table B.1). The R values are not greater than 1.5 because, sulfuric acid is completely consumed and some amount of colemanite remains unreacted in the reactor at R values greater than 1.5. Amount of colemanite is changed in order to obtain different R values. That is, the initial amount of sulfuric acid is kept constant, whereas mass of colemanite is varied at each experimental run. The amount of colemanite added to the reactor at each experimental run is given in Table B.1. Hisarcık 1 colemanite, whose composition is given in Table 4.1, is used in the experiments.

In order to obtain an acid mixture having a composition of 5.58% sulfuric acid, 8.00% boric acid and 86.42% of water in weight percentages, 142.5 g distilled water and 13.2 g boric acid (99.9% b.w.) supplied by Eti Holding A.Ş. are added to Erlenmayer flask initially. This mixture is started to be stirred by the magnetic stirrer which is adjusted to 400 rpm and then, 9.6 g H₂SO₄ (with Merck grade of 96% b.w.) is slowly added to the reactor. Erlenmayer flask is started to be heated to 85°C and this value is kept constant throughout the experiments. When the temperature reaches 85°C, a given amount of colemanite which is also heated to 85°C meanwhile in the oven is fed to the reactor. This time is taken as the starting time of the reaction.

It is waited at least an hour in order the reaction to be completed (Bilal, 2003). Then, the pH electrode is placed in the reactor to measure the pH of the slurry. Samples are taken by 50-mL syringe attached to a glass pipe. This moment is assumed to represent the outlet of the fourth reactor in the 4-CSTR continuous system.

The samples are immediately filtered to a 150-mL Erlenmayer flask by using a filtration capsule. The 150-mL flask is placed into hot water in order to prevent the boric acid solution to crystallize. Solid particles and liquid are collected on filter paper and in the flask, respectively. 5-mL is withdrawn from the liquid portion by the help of micropipettes to measure the boric acid content of the solution. The procedure followed for the determination of boric acid concentration is given in Appendix A.

CHAPTER 5

RESULTS AND DISCUSSION

In this chapter, first, correlation between boric acid concentration and pH will be analyzed by comparing the theoretical derivation (Equation 3.34) with experimental results. Second, determination of transfer functions will be presented. After the parameters for MPC are calculated, the simulation studies for the control system will be given.

5.1. Verification of the Correlation between Boric Acid Concentration and pH Measurement

The results of experimental studies done in batch system, which represents the last reactor of the continuous system, are compared with the theoretical findings in Figure 5.1.

As it is seen from Figure 5.1, there is significant difference between experimental values and the theoretical findings as pH value increases (less acidic). At the same boric acid concentration values, the pH calculated by using Equation 3.34 is lower than the experimental ones. The reason of this difference can be either due to the experimental errors or due to the different boric acid dissociation reactions which

have not been yet well understood (Tossell, 2005) or due to the consumption of sulfuric acid by other impurities found in colemanite (Kalafatoğlu, 2000).

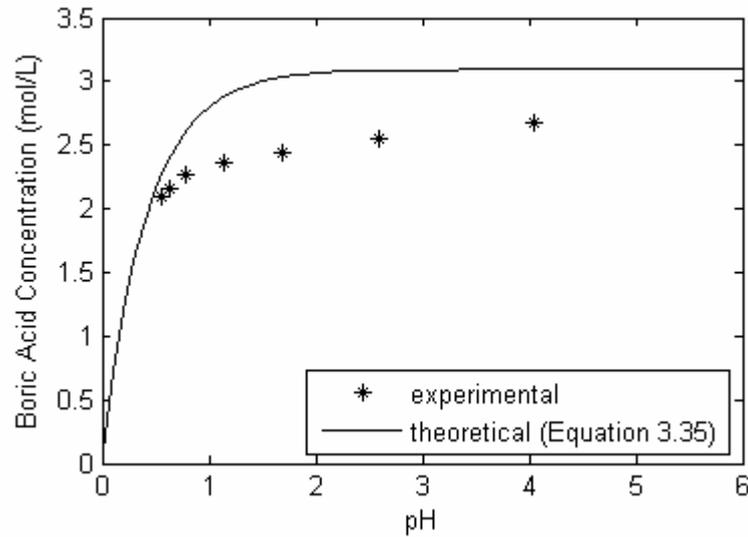


Figure 5.1 Boric acid concentration as a function of pH.

Therefore, the correlation developed between boric acid concentration and pH cannot be used in the MPC algorithm for control purposes. Instead, an empirical correlation between pH and boric acid concentration has to be derived considering the experimental data.

The experimental values are correlated by an equation (Equation 5.1) by using Microsoft Excel and this equation is used in the estimator design. The correlated data is shown in Figure 5.2.

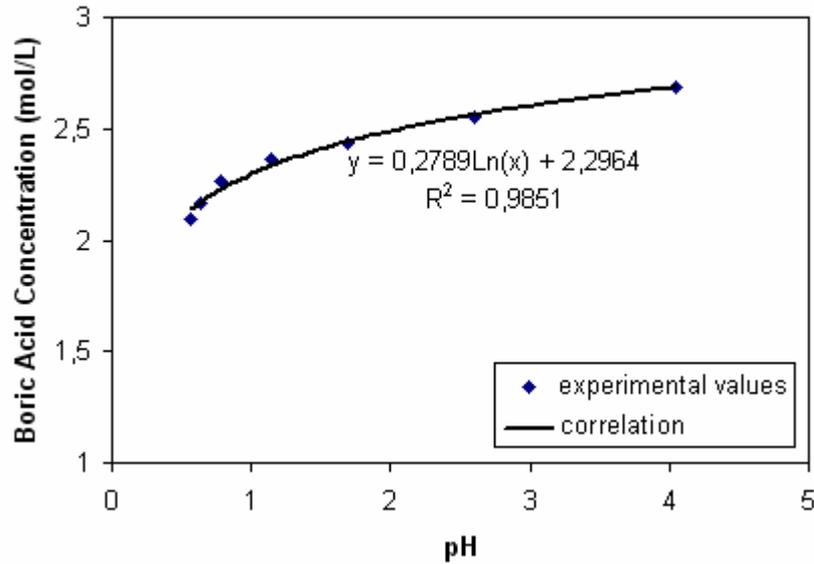


Figure 5.2 Correlation between boric acid concentration and pH.

$$C_{H_3BO_3} = 0.2789 \ln(pH) + 2.2964 \quad (5.1)$$

5.2. Transfer Function Modelling

Aşar (2004), as stated before, obtained the model of the 4-CSTR system in transfer functions using the step inputs to the acid flow rate, M_A , as the manipulated variable and to the colemanite flow rate, M_C , as the disturbance. The response curves experimentally obtained by Aşar (2004) were used to determine the transfer function models of the continuous system.

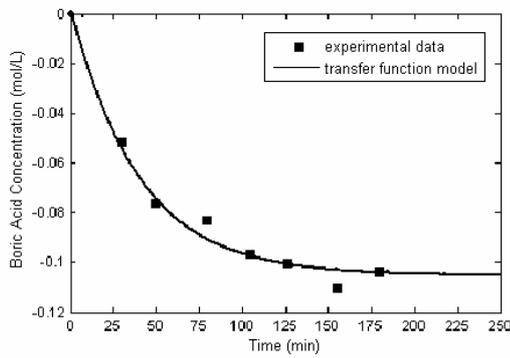
The process and disturbance transfer functions of each reactor were found by Aşar (2004) considering y_i' as the controlled variable (boric acid concentration) in deviation form, u_i' as the manipulated variable (acid flow rate) in deviation form, and d_i' as the disturbance (colemanite flow rate) again in deviation form. The transfer function models obtained by using the data of Run 2 and Run 3 (Table 4.2) are given in Table 5.1.

The response obtained from the second reactor is actually the summation of the responses of first two reactors. Therefore, the transfer function which represents the first two reactors will be of second-order with time delay. In a similar fashion, the response of the third and fourth reactors will be of third and fourth order, respectively, again with dead time.

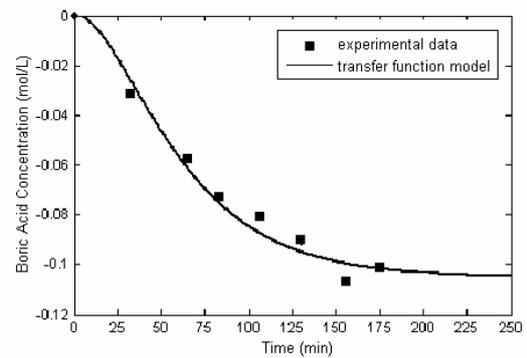
Table 5.1 The process and disturbance transfer functions obtained from the boric acid concentration responses (Aşar, 2004).

Reactor	Process Transfer Function	Disturbance Transfer Function
1	$[y_1]' = \left[\frac{-0.039e^{-s}}{40s+1} \right] [u_1]'$	$[y_1]' = \left[\frac{0.130e^{-s}}{35s+1} \right] [d_1]'$
2	$[y_2]' = \left[\frac{-0.039e^{-2s}}{(40s+1)(25s+1)} \right] [u_1]'$	$[y_2]' = \left[\frac{0.129e^{-2s}}{(35s+1)(15s+1)} \right] [d_1]'$
3	$[y_3]' = \left[\frac{-0.041e^{-3s}}{(40s+1)(25s+1)(15s+1)} \right] [u_1]'$	$[y_3]' = \left[\frac{0.127e^{-3s}}{(35s+1)(15s+1)(8s+1)} \right] [d_1]'$
4	$[y_4]' = \left[\frac{-0.042e^{-4s}}{(40s+1)(25s+1)(15s+1)(5s+1)} \right] [u_1]'$	$[y_4]' = \left[\frac{0.123e^{-4s}}{(35s+1)(15s+1)(8s+1)(7s+1)} \right] [d_1]'$

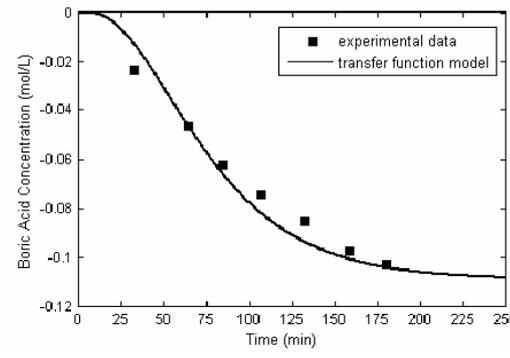
The comparison of the experimentally obtained responses in terms of boric acid concentration with the process transfer function models are given in Figure 5.3 and with the disturbance transfer functions in Figure 5.4, for the first, second, third, and fourth reactors.



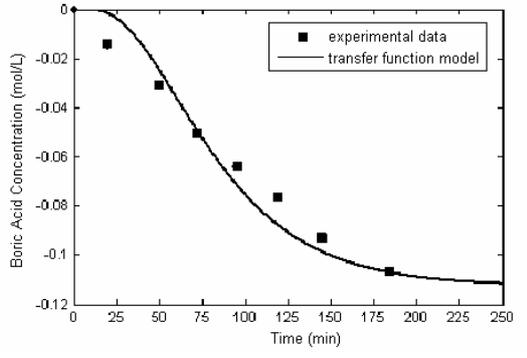
(a)



(b)

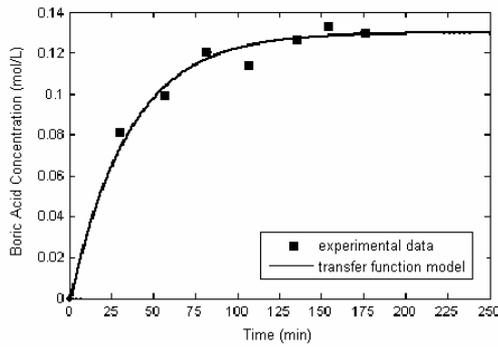


(c)

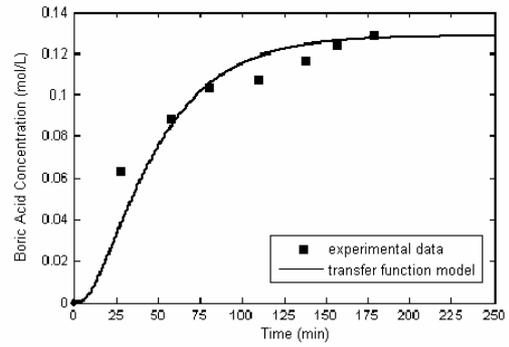


(d)

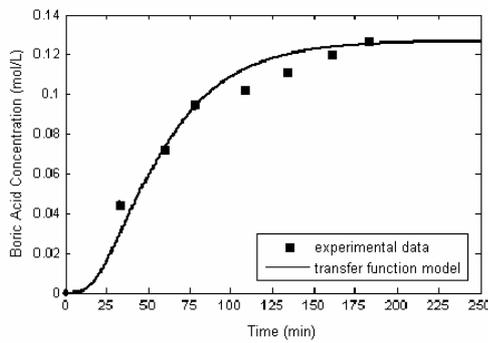
Figure 5.3 Comparison of experimental data with process transfer function model of (a) first reactor (b) second reactor (c) third reactor (d) fourth reactor



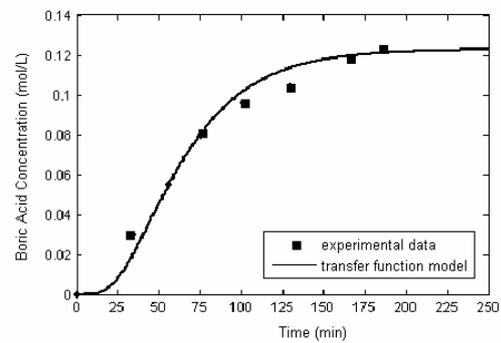
(a)



(b)



(c)



(d)

Figure 5.4 Comparison of experimental data with disturbance transfer function model of (a) first reactor (b) second reactor (c) third reactor (d) fourth reactor

The transfer functions given in Table 5.1 relate boric acid concentrations of each reactor to inputs of the first reactor. However, as stated before, on-line measurement of boric acid is not possible. Therefore, pH has to be used as a secondary variable for control purposes. To analyze the control of such a system the transfer functions have to be derived by using the pH values with the help of Equation 5.1. The process and disturbance transfer functions are obtained from the data of Run 1 and Run 4, respectively (Table 5.2).

As utilized by Aşar (2004), in determining the transfer function models as a first estimate, Sundaresan and Krishnaswamy method is used (Seborg et al., 1989). As an example, the process transfer function obtained for the first reactor is

$$G_1(s) = \frac{-0.48e^{-0.8s}}{52s + 1} \quad (5.2)$$

and the disturbance transfer function for the first reactor is

$$D_1(s) = \frac{0.97e^{-8.9}}{60s + 1} \quad (5.3)$$

Although the delay in the first-order with dead time (FODT) model is 8.9 min, it is observed from the experimental data that delays in the reactors are very small. Thus, one-minute time delay is assumed for the first reactor for the disturbance transfer function model. The same approach is also considered for the other reactors which are in same dimensions with the first reactor. Then, by fine tuning which gives the least Sum of Squared Error (SSE) score, the gain and time constant for the first reactor obtained from Sundaresan and Krishnaswamy method are found and given in Equations 5.4 and 5.5.

$$G_1(s) = \frac{-0.49e^{-0.8s}}{49s + 1} \quad (5.4)$$

$$D_1(s) = \frac{0.97e^{-1.0s}}{40s + 1} \quad (5.5)$$

MATLAB is used in order to find the parameters of the transfer functions and to calculate the SSE scores. Process transfer functions between pH values and acid flow rate, and also the disturbance transfer functions between pH values and colemanite flow rate for all of the reactors are given in Table 5.2.

Table 5.2 The process and disturbance transfer functions in terms of pH' and inputs.

Reactor	Process Transfer Function	Disturbance Transfer Function
1	$[pH_1'] = \left[\frac{-0.49e^{-0.8s}}{49s + 1} \right] [u_1']$	$[pH_1'] = \left[\frac{0.97e^{-s}}{40s + 1} \right] [d_1']$
2	$[pH_2'] = \left[\frac{-0.47e^{-1.6s}}{(49s + 1)(45s + 1)} \right] [u_1']$	$[pH_2'] = \left[\frac{0.92e^{-2s}}{(40s + 1)(10s + 1)} \right] [d_1']$
3	$[pH_3'] = \left[\frac{-0.46e^{-2.4s}}{(49s + 1)(45s + 1)(5s + 1)} \right] [u_1']$	$[pH_3'] = \left[\frac{0.89e^{-3s}}{(40s + 1)(10s + 1)(6s + 1)} \right] [d_1']$
4	$[pH_4'] = \left[\frac{-0.52e^{-3.2s}}{(49s + 1)(45s + 1)(5s + 1)(s + 1)} \right] [u_1']$	$[pH_4'] = \left[\frac{0.90e^{-4s}}{(40s + 1)(10s + 1)(6s + 1)(s + 1)} \right] [d_1']$

Çakal et al. (2006) determined that, the boric acid concentration does not vary significantly with increasing number of CSTR's in series or with increasing residence time in each of the CSTR's. The dissolution of colemanite seems to be completed within the first reactor. Thus, different than Aşar's (2004) study, only the second-order transfer functions, representing the first two reactors will be used as the model in MPC design in this study. That is, the control actions will be considered to be done not after the fourth reactor but after the second reactor.

The first two reactors can also be approximated by a first-order with dead time (FODT) transfer function similar to what was done by Aşar and shown in Figure 5.5.

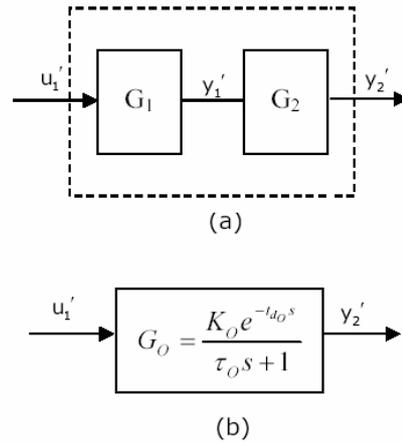


Figure 5.5 (a) First two reactors with inputs and outputs (b) overall FODT transfer functions for the first two reactors (Aşar, 2004).

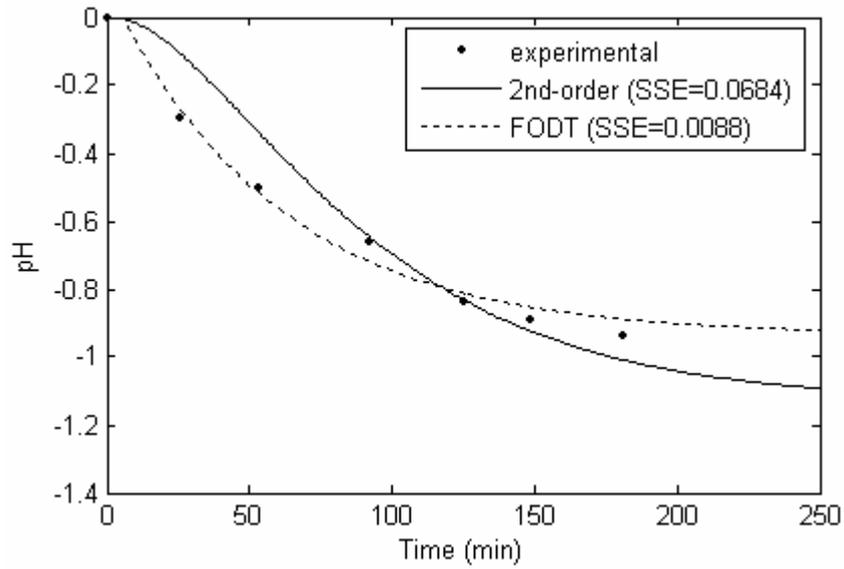
In Figure 5.5, K_o , τ_o , and t_{do} are overall gain, time constant and time delay for the first two reactors, respectively. Thus, by using the Sundaresan and Krishnaswamy method, the approximated process transfer function is found as

$$G_1(s) = \frac{-0.44e^{-17.8s}}{58s + 1} \quad (5.6)$$

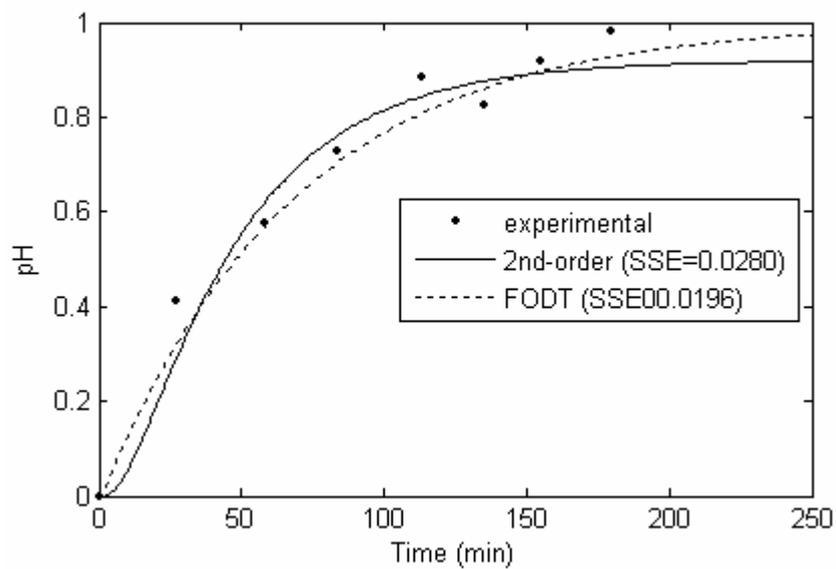
and for the disturbance transfer function as

$$D_1(s) = \frac{1.01e^{-10.6s}}{73s + 1} \quad (5.7)$$

The comparison of FODT model with the second-order transfer functions given in Table 5.2 and also with the experimental data is shown in Figure 5.6.



(a)



(b)

Figure 5.6 Comparison of second-order transfer function with FODT model and experimental data for (a) process transfer function (b) disturbance transfer function.

As it is seen from Figure 5.6, SSE score of FODT model is less than the second-order model. Therefore, in MPC design, FODT model will be used.

5.3. MPC Design

The parameters of MPC, which is designed to control the boric acid concentration of the 4-CSTR system are calculated as it is mentioned in Chapter 3 and the values of the parameters are given in Table 5.3.

Table 5.3 The parameters of MPC.

Model Horizon(M)	110 min
Control Horizon (C)	66 min
Prediction Horizon (P)	94 min
Sampling Time (Δt)	2 min
f	variable

The scalar quantity f is chosen as the varying parameter, in other words, tuning parameter and by this way, the best f value is investigated by trial and error in order to maintain good controller performance.

5.4. Simulation Studies

MPC toolbox in MATLAB is used for the simulation studies. MPC is designed by using the transfer functions given in Equations 5.6 and 5.7. The model horizon, control horizon and prediction horizon are taken as they are indicated in Table 5.3.

5.4.1. Performance of MPC in Set-Point Tracking

The responses of pH and the manipulated input for a set-point change of 2.00 in pH are given in Figure 5.7 for different f values of 1.00, 0.50, 0.10, 0.05, and 0.02. In the figure, only three values of f are shown in a range. The best f value is selected as 0.02 due to small response time and less Integral Absolute Error (IAE) score.

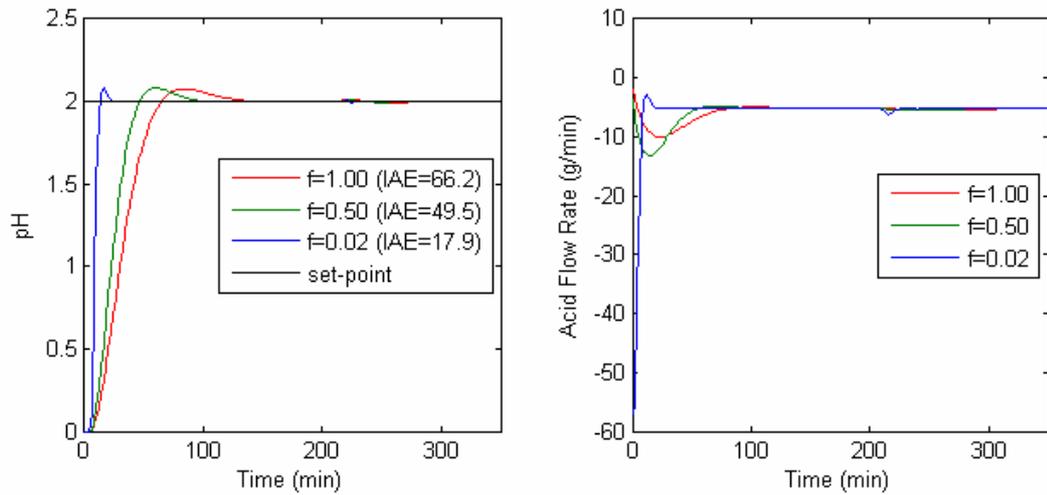


Figure 5.7 MPC performance in set-point tracking at different f values.

The responses of controlled and manipulated variables obtained by using the second-order, fourth-order and also the approximated (FODT) model are compared in Figure 5.8 to test the validity of using only the measurements of the second reactor for control purposes. It can be seen that the response of pH for approximated transfer function model gives less overshoot than that of second and fourth-order models, and it gives better result with small response time and less IAE score.

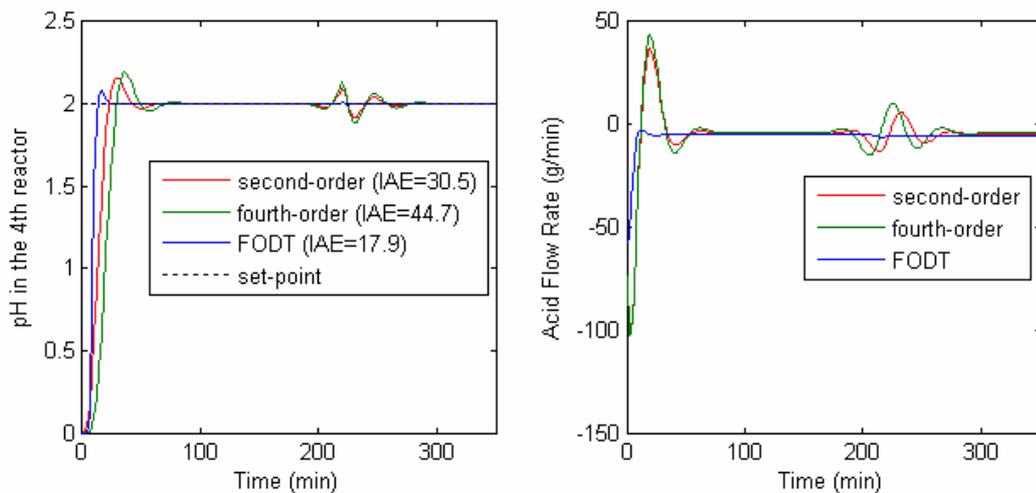


Figure 5.8 The comparison of second-order, fourth-order, and FODT models in set-point tracking.

It is noteworthy to say that the responses obtained by using the second-order and fourth-order models are close to each other which indicates that taking pH measurements after the second reactor in order to control product is not a wrong decision.

Considering Figure 5.7, it is seen that there is an overshoot in acid flow rate in negative direction. This can be reduced by giving a lower constraint to the manipulated variable, acid flow rate.

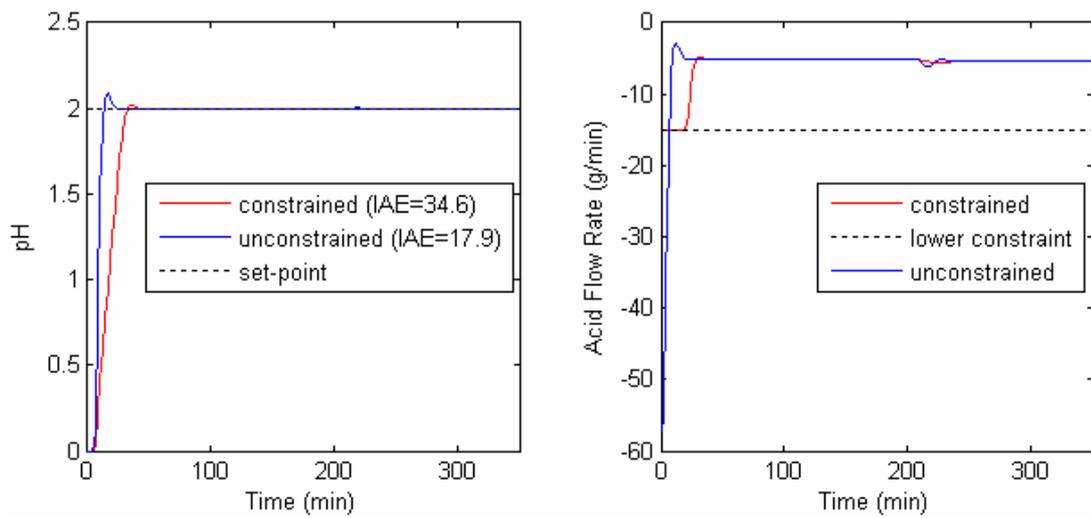


Figure 5.9 The MPC performance in set-point tracking in the presence of lower manipulated variable constraint.

The IAE score of constrained case is greater than that of the unconstrained case as it is shown in Figure 5.9. This is due to the increase in response time. Therefore, it can be concluded that if lower constraint is applied to the acid flow rate, a slower response should be accepted.

5.4.2. Performance of MPC in Disturbance Rejection

The performance of the MPC is investigated for a 10% decrease in colemanite flow rate by again using the FODT model of both process and disturbance transfer functions. Similar runs are done as in set-point tracking to find the f value. The responses of controlled and manipulated variables are shown in Figure 5.10.

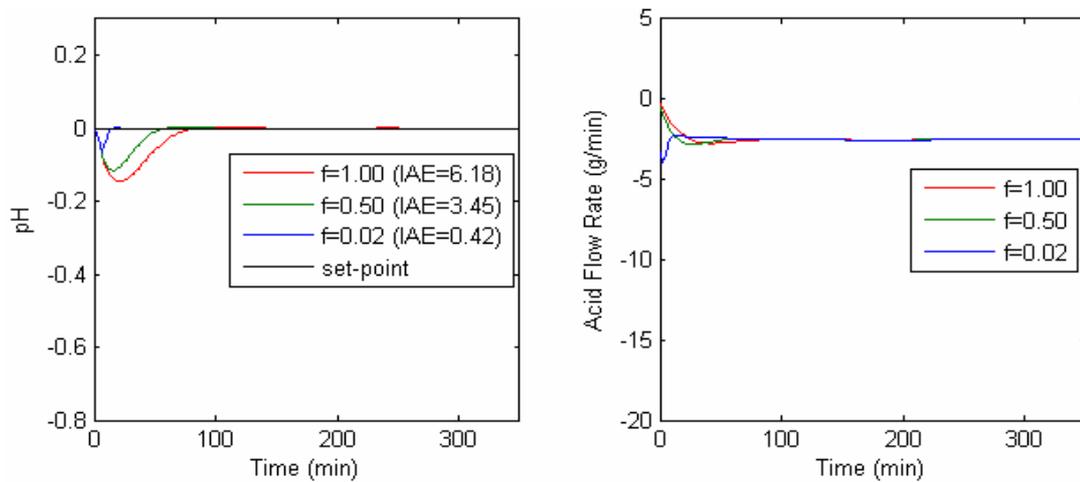


Figure 5.10 MPC performance in disturbance rejection at different f values.

From Figure 5.10, it can be seen that, pH returns to its initial condition for all f values when colemanite flow rate decreases by 10%. However, the best f value is chosen as 0.02 since the response time is fast and IAE score is low.

The changes of controlled and manipulated variables for 10% decrease in colemanite flow rate are compared for second-order, fourth-order and FODT model in Figure 5.11. Again, FODT model gives better result with smaller response and with less overshoot in acid flow rate. A significant difference between the second and fourth-order models is again not observed.

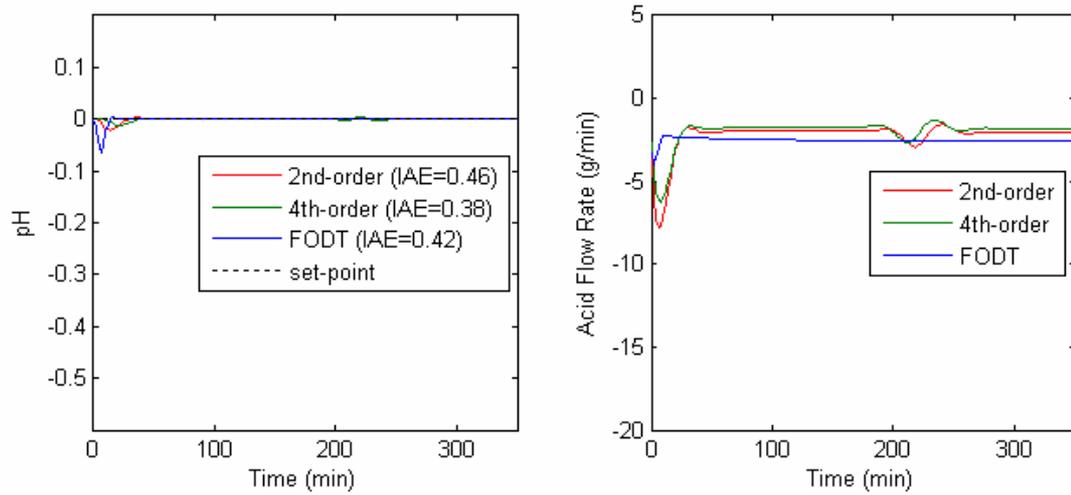


Figure 5.11 The comparison of second-order, fourth-order, and FODT models in disturbance rejection.

5.4.3. Performance of MPC for Robustness

In order to analyze the robustness of MPC, the plant/model mismatch is assumed for -10 % changes in time constant, time delay and gain. Then, the new plant transfer function is expressed as in Equation 5.8:

$$G_2(s) = \frac{-0.40e^{-16.02s}}{52.2s + 1} \quad (5.8)$$

The robustness of designed MPC is analyzed for both setpoint tracking and disturbance rejection. The changes in the responses of controlled and manipulated variables are presented in Figures 5.12 and 5.13. It can be said that the controller is robust in both set point tracking and disturbance rejection.

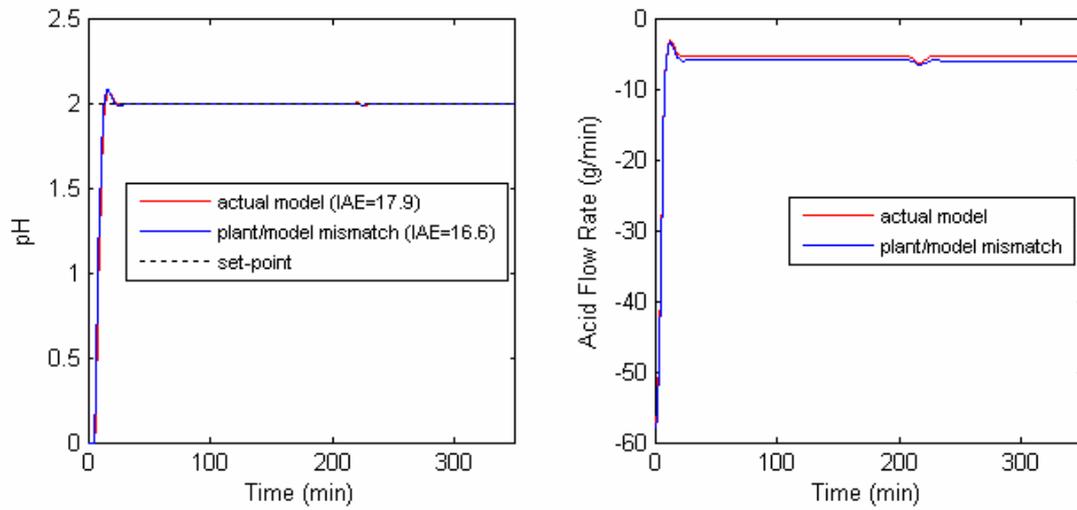


Figure 5.12 The robustness of MPC in set-point tracking.

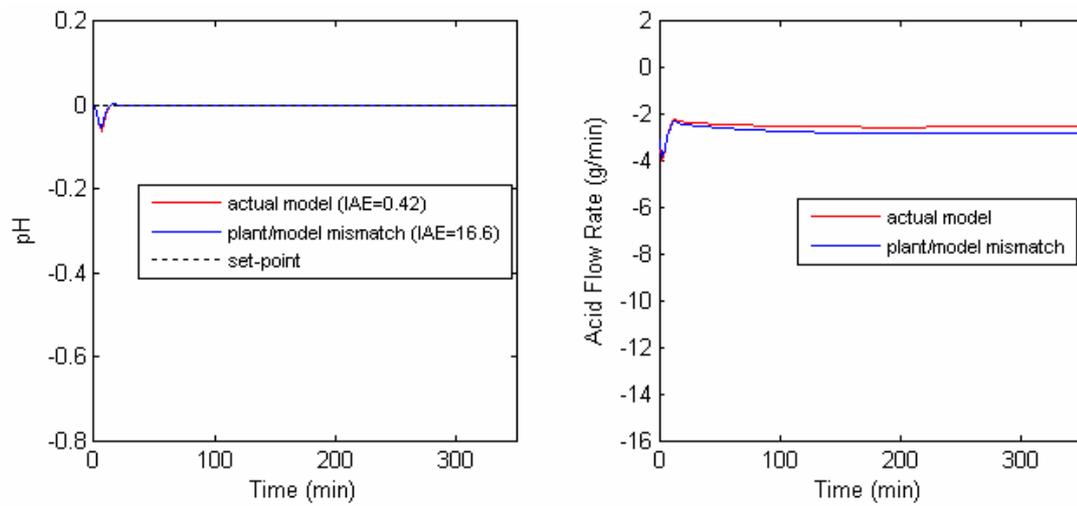


Figure 5.13 The robustness of MPC in disturbance rejection

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

The objective of this study is to inferentially control a 4-CSTR boric acid production system where boric acid is produced by reacting colemanite with sulfuric acid. In the 4-CSTR system, the on-line measurement of pH is much easier and more practical than the measurement of boric acid concentration. Therefore, it is investigated whether pH can be used as the secondary controlled variable instead of boric acid concentration. In the reaction medium, there remains some excess amount of sulfuric acid unreacted. Because sulfuric acid is a strong acid, its concentration is the main factor that specifies the pH of the reaction medium. Thus,

- A theoretical relationship between pH and boric acid concentration is derived by making analytical and stoichiometric calculations and compared with experimentally obtained data. It is found that the difference between theoretical and experimental findings increases significantly as pH increases. The experimentally measured pH values are found to be greater than the theoretical ones.
- The difference between theoretical and experimental findings is attributed to experimental errors or different boric acid dissociation reactions which have not been yet understood well or to the fact that sulfuric acid is not only

consumed by the reaction with $2\text{CaO}\cdot 3\text{B}_2\text{O}_3\cdot 5\text{H}_2\text{O}$ present in colemanite but also, it is consumed by other impurities found in colemanite.

- An empirical correlation between pH and boric acid concentration is obtained considering the experimental findings which is further used in estimator design.
- The second-order model is approximated with a first-order plus dead time (FODT) model and compared with second-order model. It is found that FODT model gives more satisfactory performance.
- The designed MPC is tested for set-point tracking, disturbance rejection and robustness issues by using the second-order transfer function models through the simulation studies and the tuning parameter, f , is found to be 0.02 with the least IAE score.
- As a further study, the application of inferential control technique developed in this study can be considered for the boric production system in Emet, Kütahya.. For this purpose, a new system model can be developed by taking measurements of pH and boric acid concentration from the actual plant located in Emet, Kütahya.
- Furthermore, instead of pH, conductivity can be considered as a secondary measureable controlled variable and the relationship between conductivity and the boric acid concentration can be analyzed for control purposes.

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APPENDIX A

DETERMINATION OF BORIC ACID CONCENTRATION

For boric acid concentration determination, 2-3 drops of methyl red indicator are added to 5-mL filtrate, first. Then the filtrate is titrated with H₂SO₄ solution (1:3 by volume) until the color turns to pink. The solution is titrated with 6 N NaOH solution until the color turns from pink to yellow. As the next step, the solution is titrated with 1 N NaOH solution until the pH becomes 4.5. After phenol-phtaleyn indicator and 2-3 g manitol are added, the solution is again titrated with 1 N NaOH until the pH becomes 8.5 and the volume of the NaOH solution added is recorded. Then the boric acid concentration of the samples are calculated as given below.

$$C_{\text{H}_3\text{BO}_3} = \frac{V_{\text{NaOH}} F_{\text{NaOH}} N_{\text{NaOH}}}{V_{\text{sample}}} \quad (\text{A.1})$$

where V_{NaOH} is volume of NaOH added until the pH becomes from 4.5 to 8.5, N_{NaOH} is the factor of NaOH solution (1), N_{NaOH} is the normality of NaOH solution (1N), and V_{sample} is the volume of the sample (5 mL).

APPENDIX B

EXPERIMENTAL DATA

Table B.1 Amount of colemanite added to the reactor at different R values.

R	Amount of colemanite (g)
0.8	13.3
0.9	14.9
1.0	16.6
1.1	18.2
1.2	19.9
1.3	21.6
1.4	23.2

Table B.2 Volume of NaOH consumed and pH at different R values.

R	Volume of NaOH (mL)	pH
0.8	10.48	0.56
0.9	10.81	0.63
1.0	11.39	0.78
1.1	11.80	1.14
1.2	12.18	1.69
1.3	12.76	2.60
1.4	13.41	4.04

APPENDIX C

MPC SIMULATION PROGRAM

The simulation program written by Aşar(2004) is used in this study as it is given below:

```
% SISO-MPC Design
% Sampling time
deltt=2;
% Truncation time
tfinal=220;
% Model Horizon, N=tfinal/deltt
N=110;
% Process model (first order with dead time)
g11=poly2tfd(-0.44,[58 1],0,17.8);
% Number of Outputs
ny=1;
% Model of transfer function
model=tfd2step(tfinal,deltt,ny,g11);
% Plant/Model Mismatch
plant=model;
% Weights on Outputs
ywt=[1];
% Weights on Inputs
uwt=[0.02];
```

```

% Control Horizon
M=66;
% Prediction Horizon
P=94;
% MPC Gain
Kmpc=mpccon(model,ywt,uwt,M,P);
%-----Set-Point Tracking-----
%Simulation time
tend=300;
%Set Point Change
r=[2.00];
% For unconstrained Case
% MPC Simulation
[y,u]=mpcsim(plant,model,Kmpc,tend,r);
% IAE Calculation
e=abs(r*ones(size(y))-y);
t=0:deltt:tend;
trapz(t,e);
ploteach(y,u,deltt);
%For Constrained MPC
ulim=[-15 0.0001 inf];
ylim=[];
[y,u]=cmprc(plant,model,ywt,uwt,M,P,tend,r,ulim,ylim);
% IAE Calculation
e=abs(r*ones(size(y))-y);
t=0:deltt:tend;
trapz(t,e)
ploteach(y,u,deltt);

%-----Disturbance Rejection-----
%Simulation time
tend=300;
% Disturbance model
gd=poly2tfd(1.01,[73 1],0,10.6);
% Disturbance plant(first order with dead time)
dplant=tfd2step(tfinal,deltt,ny,gd);

```

```

% Disturbance Model
dmodel=dplant;
%Set Point Change
r=[0];
usat=[];
tfilter=[];
% Step Change in Input
dstep=[-1];
%MPC Simulation
[y,u]=mpcsim(plant,model,Kmpc,tend,r,usat,tfilter,dplant,dmodel,dstep);
% IAE Calculation
e=abs(r*ones(size(y))-y);
t=0:deltt:tend;
trapz(t,e)
ploteach(y,u,deltt);

%-----Robustness-----
% A plant/model mismatch was assumed for -10 % changes in time
% constants,
%time delay and gains for each reactor
% Plant model
p11=poly2tfd(0.40,[52.2 1],0,16.02);
% Plant
plant=tf2step(tfinal,deltt,ny,p11);
%Simulation time
tend=300;
%Set Point Change
r=[2.0];
%MPC Simulation
[y,u]=mpcsim(plant,model,Kmpc,tend,r);
% IAE Calculation
e=abs(r*ones(size(y))-y);
t=0:deltt:tend;
trapz(t,e)
ploteach(y,u,deltt);

```