

DEVELOPMENT OF NONLINEAR MODEL FOR pH SYSTEM

MOHAMAD FIKHRI BIN NOR AZMAN

SUPERVISOR: DR. K. RAMESH

UNIVERSITI MALAYSIA PAHANG

‘I hereby declare that I have read this thesis is sufficient in terms of scope and quality
for the award of degree of Bachelor of Chemical Engineering’

Signature :

Name of Supervisor : Dr. K. Ramesh

Date :

DEVELOPMENT OF NONLINEAR MODEL FOR pH SYSTEM

MOHAMAD FIKHRI BIN NOR AZMAN

SUPERVISOR: DR. K. RAMESH

A thesis submitted in fulfillment of the requirements for the award of the
degree of Bachelor of Chemical Engineering

FACULTY OF CHEMICAL & NATURAL RESOURCES ENGINEERING

UNIVERSITI MALAYSIA PAHANG

DEC 2010

I declare that this thesis entitled ‘DEVELOPMENT OF NONLINEAR MODEL FOR pH SYSTEM’ is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature :

Name : Mohamad Fikhri Bin Nor Azman

Date : 02 December 2010

For my beloved parent, brother and sister.....

ACKNOWLEDGEMENT

Assalamualaikum wbkt,

A very grateful to the Almighty because gave me all the strengths and guidance to finish this undergraduate research project.

I would like to deliver special thank to my supervisor Dr. K. Ramesh for his valuable comment, guidance, encouragement and useful suggestions that always helped me so much to finish this project. I also wanted to express my deepest thanks for all the time he had spent with me. Without his support, this thesis could not be finish.

My sincere appreciation also extends to all lectures, teaching engineer and my colleagues who helped me in many different ways at various instances of my research. Their support and views are useful indeed. Unfortunately, it is not possible to list all of them in this limited space.

Finally, thank you to Universiti Malaysia Pahang especially Faculty of Chemical Engineering and Natural Resources that gave me this opportunity to conduct my undergraduate research project.

ABSTRACT

The control of pH process is a problem frequently encountered in the chemical process and biotechnology industries. It has been recognized as a challenging problem due to the time varying and nonlinear characteristics of the pH processes. This is particularly true when control has to be achieved in the neutral range (a pH between 6 to 8) when only strong acid and strong bases are present. The objectives of this research are development mathematical model for pH system, simulation studies under steady and unsteady state condition and validation of mathematical model through experimentation. The model of the pH process applied in this paper known as the principle of physico- chemical dynamic modeling. This model used acetic acid and sodium hydroxide for simulating the behavior of a simple pH process in a time optimal control loop. The mathematical model based on first principles is developed from acetate balance, sodium balance, acetic acid equilibrium, water equilibrium and electroneutrality equation. Then, the model equations are solved in MATLAB environment. The results from the MATLAB simulation program are compared with experimental result to validate the developed fundamental model. The results showed that most of the error between the model and experiment result are within 3% which proved the model has the capability to capture the dynamics of the process.

ABSTRAK

Pengendalian proses pH adalah masalah yang sering dihadapi dalam proses kimia dan industri bioteknologi. Ini telah diakui sebagai masalah mencabar kerana masa yang berbeza- beza dan ciri- ciri nonlinear proses pH. Hal ini terutama benar ketika kawalan harus dicapai dalam julat neutral(antara pH 6 hingga 8) ketika hanya asid kuat dan basa kuat hadir. Tujuan dari penyelidikan ini adalah untuk pembangunan model matematik untuk system pH, kajian simulasi pada keadaan steady dan unsteady dan validasi model matematik melalui eksperimen. Model proses pH diaplikasikan dalam masalah ini dikenali sebagai prinsip permodelan dinamik fizik- kimia. Model ini menggunakan asid asetik dan natruim hidroksida untuk mensimulasikan perilaku dari proses pH sederhana dalam loop kawalan masa yang optimum. Model matematik berdasarkan prinsip- prinsip pertama adalah dikembangkan daripada baki asetik, keseimbangan natrium, keseimbangan asid asetik, keseimbangan air dan persamaan neutraliti. Kemudian, persamaan model diselesaikan dalam persekitaran MATLAB. Keputusan dari program simulasi MATLAB dibandingkan dengan keputusan eksperimen untuk mengesahkan kesesuaian model asas yang telah dikembangkan. Keputusan kajian menunjukkan bahawa sebahagian besar kesalahan antara hasil model dan eksperimen dalam julat 3% membuktikan model memiliki kemampuan untuk mengesan proses dinamik.

TABLE OF CONTENT

DECLARATION	ii
DEDICATION	iii
ACKNOWLEDGEMENT	iv
ABSTRACT	v
ABSTRAK	vi
TABLE OF CONTENT	vii
LIST OF TABLES	ix
LIST OF FIGURES	x
LIST OF ABBREVIATIONS	xii
LIST OF NOMENCLATURES	xiii
LIST OF APPENDICES	xiv

CHAPTER	TITLE	PAGE
1	INTRODUCTION	
	1.1 Background of Study	1
	1.2 Problem Statement	2
	1.3 Objectives of Study	3
	1.4 Scope of Study	3
	1.5 Rationale and Significance of Research	4
2	LITERATURE REVIEW	
	2.1 pH Process	5

	2.2 Nonlinear Characteristics of pH Process	6
	2.3 Nonlinear Process Models	8
	2.3.1 Fundamental Models	9
	2.3.2 Empirical Model	11
	2.3.3 Hybrid Model	17
	2.4 Derivation of Dynamic Equations for pH System	18
3	METHODOLOGY	
	3.1 Develop Mathematical Model based on First Principles	20
	3.2 Solving Model Equation in MATLAB Environment (Algorithm)	22
	3.3 Experimental Validation	28
4	RESULTS AND DISCUSSIONS	
	4.1 Validation of Nonlinear Model through Experimentation	29
	4.2 Steady State Titration Curve	33
	4.3 Step Responses of pH Process	35
5	CONCLUSION AND RECOMMENDATION	
	5.1 Conclusion	37
	5.2 Recommendation	37
	REFERENCES	39

LIST OF TABLES

TABLE NO	TITLE	PAGE
1	SSE criteria for applied controller in set- point tracking (Mahmoodi et al, 2008)	15
2	Comparison between linear and the NN model (Dudul and Ghatol, 2005)	16
3	Comparison between experimental data and model (Fa=0.0033 L/s, Fb=0.001667 L/s, Ca=0.01M, Cb=0.1M)	30
4	Comparison between experimental data and model (Fa=0.0033 L/s, Fb=0.0033 L/s, Ca=0.01M, Cb=0.1M)	31

LIST OF FIGURES

FIGURE NO	TITLE	PAGE
1	Three typical titration curves having the most severe gain variation. (a) strong acid-strong base system, (b) weak acid-strong base system, (c) strong acid, weak acid-strong base system (Lee and Park, 2000).	7
2	Step responses of pH process (Mahmoodi et al. 2008)	8
3	Hammerstein model structure (Pearson, 1995)	13
4	Wiener model structure (Pearson, 1995)	13
5	NMPC based on Wiener- Laguerre in comparison with MPC based on Laguerre and Wiener models (Mahmoodi et al, 2008)	15
6	NN Model (4-4-1) (Dudul and Ghatol, 2005)	17
7	pH neutralization process (Valarmathi et al. 2009)	20
8	Graph for comparison between experimental data and model ($F_a=0.0033$ L/s, $F_b=0.001667$ L/s, $C_a=0.01$ M, $C_b=0.1$ M)	30
9	Graph for comparison between experimental data and model ($F_a=0.0033$ L/s, $F_b=0.0033$ L/s, $C_a=0.01$ M, $C_b=0.1$ M)	31
10	Graph for steady state titration curve	34

11	pH response of Fb for $\pm 10\%$ change	35
12	pH response of Fa for $\pm 10\%$ change	36

LIST OF ABBREVIATIONS

A	Generally an arbitrary component, Specifically (strong) acid A
AC	Acetate ion
ANN	Artificial Neural Network
B	Generally an arbitrary component, Specifically (strong) base B
CSTR	Continuous Stirred Tank Reactor
FIR	Finite impulse response
H	Hydrogen ion, proton
HAC	Acetic acid
LMPC	Linear Model Predictive Control
NaOH	Sodium Hydroxide
NARMAX	Nonlinear autoregressive moving average model with exogenous inputs
NFIR	Nonlinear finite impulse response
NMPC	Nonlinear Model Predictive Control
OH	Hydroxide ion
P	Pump
PID	Proportional, integral and derivative control
SQP	Sequential quadratic programming
SSE	Sum square error
V	Valve
VAF	Variance account for
WMPC	Wiener model predictive control

LIST OF NOMENCLATURES

$[i]$	Concentration of i
$\{i\}$	Activity of i
C_1	Concentration of acetate in inlet stream F_1
C_2	Concentration of sodium in inlet stream F_2
C_a	Concentration of the influent stream / Concentration of acid
C_b	Concentration of the titrating stream/ Concentration of base
F_1	Inlet stream 1/ Flowrate of acetic acid
F_2	Inlet stream 2/ Flowrate of sodium hydroxide
F_a	Flowrate of influent system/ Flowrate of acetic acid
F_b	Flowrate of titrating system/ Flowrate of NaOH
K	Chemical equilibrium constant
K_a	Acid equilibrium
K_b	Base equilibrium
K_w	Water equilibrium
u	m - dimensional vector of manipulated input variables
$u(k)$	input sequence
V	Volume of CSTR tank
x	n - dimensional vector of state variables
x_a	Concentration of the acid solution
x_b	Concentration of the base solution
y	p - dimensional vector of controlled output variables
$y(k)$	system response
ζ	$[Na^+]$
ξ	$[HAC]+[AC^-]$

LIST OF APPENDICES

APPENDICES	TITLE	PAGE
A	M-FILE for MATLAB Programming	42
B	Process Diagram For Stirred Tank Reactors In Series	43
C	Table for figure 10, 11 and 12	44

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The pH system is very important in world of chemistry especially in chemical industries. In chemistry, pH is a measure of acidity or basicity of a solution. Normally, at pH equal to 7 the solution is called neutral while at pH above 7 is called base and acid solution is vice versa to the base.

There are two different schools of dynamic pH modeling. The first one is the classical physico- chemical modeling approach presented by McAvoy et al. (1972) and the reaction invariant formulation of the physico- chemical approach presented by Gustafsson and Waller (1982). Both approaches are based on same idea of separating the chemical reaction (equilibrium) from the reaction invariant dynamics. The concept of reaction invariant is referred to the conservation of substance on concentrations. The term was originally introduced by Fjeld et al. 1974. In this thesis, the classical physico-chemical modeling approach is used in development mathematical algorithm.

According to Peter Ylén (2001), pH models are divided into two types. The first type is known as static modeling. Static model are valid when the system has reached the equilibrium. The acid- base unit reactions can be considered instantaneous

and therefore static modeling is a very natural approach. Static models include titration curves and distribution diagrams. Experimental static models are often basic tools for product quality control as well as process state indicators. Experimental methods have been used for both qualitative and quantitative analysis.

The second type of pH model is dynamic modeling. Dynamic modeling is more difficult than static modeling. The difference between static modeling from dynamic modeling is it concentrates only on the equilibrium state where the system does not change as a function of time. In the dynamic modeling procedure the behavior of pH and related phenomena are considered as functions of time. This statement means they will change autonomously even though the changes in the input have already passed. The dynamic pH system can be divided into two categories. First category is when the systems where chemical phenomena are significantly faster than flow and mixing phenomena. The second category is when the system is not in case like category one.

1.2 Problem Statement

pH control is well known as a difficult problem frequently encountered in the chemical process and biotechnology industries. It has been recognized as a challenging problem due to the time-varying and nonlinear characteristics of the pH process. The difficulty arises from the high nonlinearities of the process around the neutralization process. This is true when control has to be achieved in the neutral range (a pH between 6 to 8) when only strong acids and strong bases are present.

Because of the pH process nonlinear characteristic, the linear model cannot predict the process behavior accurately in all operating regions. The steady state gain of pH process shows significant variation with the change of the operating point. This makes it difficult to design a single linear controller to perform accurately in all the

regions. This is because linear model only acceptable when the process operates at a single set point. The problem is many chemical processes including pH process do not operate at single set points. They are often required to operate at different set points depending on the product needed.

1.3 Objectives of Study

- i. Development of mathematical model for pH system based on first principles.
- ii. Validation of mathematical model through experimentation.
- iii. Simulation studies under steady and unsteady state condition.

1.4 Scope of Study

The scopes of study addressed in this research are:

- i. Develop of mathematical model based on first principles
- ii. Develop nonlinear model
- iii. Nonlinear model validation and analysis
- iv. Steady and unsteady state conditions

1.5 Rationale and Significance of Research

pH system is highly nonlinear and time varying process. Based on S- shaped titration curve, the steady state gain shows significant variation with the change in the operating point. This makes it difficult to design a single linear controller to perform satisfactorily in all regions. So, development of nonlinear is necessary to implement Nonlinear Model Predictive Control (NMPC) for pH system in industries.

CHAPTER 2

LITERATURE REVIEW

2.1 pH Process

According to Peter Ylén (2001), pH processes always contain instantaneous reaction kinetics. The protolysation reactions are very fast in general, but there can be slow side reactions that limit the overall speed of reaction kinetics. There is always equilibrium between hydroxide and oxonium ions (ion product of water). The oxonium and hydroxide ions participate in numerous separate reactions and instead of chain reactions there is a net of reactions with the neutralisation or the autoprotolysation reaction as the connecting link.



$$K_w = [\text{H}_3\text{O}^+] \cdot [\text{OH}^-] = 10^{-14} \text{ (mol/l)}^2, \text{ at } 25^\circ\text{C} \quad (2.1)$$

Instead of forming balances for oxonium and hydroxide a more practical solution is to use the charge balance (electro-neutrality equation) and the ion product of water for combining pH phenomena to other reactions. The pH-value is defined as

$$\text{pH} = -\log_{10} \{ \text{H}_3\text{O}^+ \} = -\log [\text{H}_3\text{O}^+] \quad (2.2)$$

The control of pH system is a very important problem in many chemical and biological processes, particularly in effluent wastewater treatment. In wastewater treatment plant, the cell growth rate and the accurate stabilization of pH at an optimal level often determines the efficiency of the bioprocess. It also plays an important role in neutralizing the excess reagents, acidic byproducts and obtaining high yield of selective products. The pH process can be classified as a continuous process, batch process or fed batch process (Bharathi et al. 2007).

2.2 Nonlinear Characteristics of pH Process

In many processes, pH neutralisation is a very fast and simple reaction. In terms of practical control, it is recognized as a difficult control problem (Shinsky 1973; Pishvaie et al. 2000; Wright et al. 1991). The difficulties arise from high process nonlinearity (the process gain can change tens or hundreds of times over a small pH range) and from changes in the pH characteristics due to changes in influent concentration (Karnachi and Waterworth, 2003). The difficulties of pH process nonlinear characteristic also stated by Gomez et al. 2004 in his paper. He stated the difficult task in controlling pH process is when control has to be achieved in the neutral range (a pH between six and eight) when only strong bases are present.

According to Lin and Yu (1993), the non-linearity can be understood from the S-shaped static pH responses with the addition of titrate. The S-shaped titration curve is the primary source of the non-linearity. Ali (2001) also agreed with that statement and stated in his paper the nonlinearity appears in the S-shape titration curve associated with pH processes. The process gain grows drastically at the intermediate region of the S-shape curve, i.e. around the neutralization point. This behavior is the main source of control difficulty. Moreover, the shape of the titration curve is distorted when the feed condition changes.

The titration curve usually considered as a gain variation. Figure 1 show three typical titration curves for which conventional linear controllers suffer from poor performances or instability due to large gain variations.

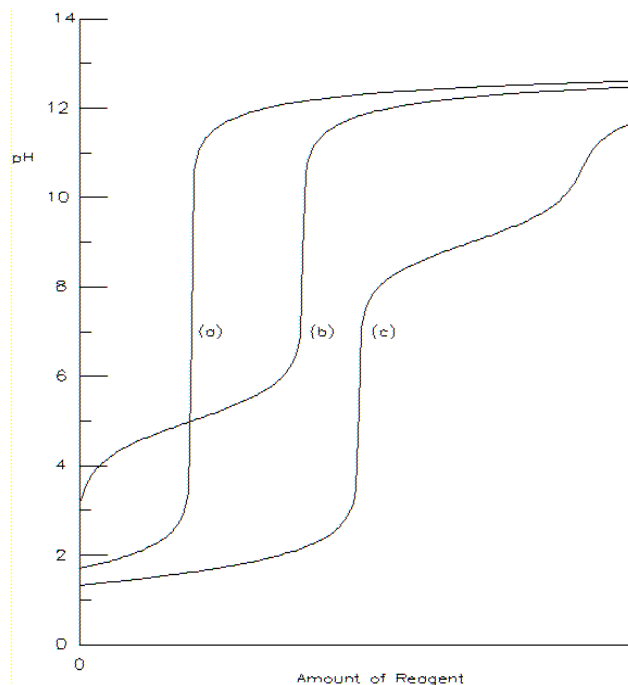


Figure 1: Three typical titration curves having the most severe gain variation. (a) strong acid-strong base system, (b) weak acid-strong base system, (c) strong acid, weak acid-strong base system (Lee and Park, 2000).

The nonlinear behavior of pH process also can be observed through step responses of pH process graph. From figure 2, the different pH value (steady state value – current value) between the same percentages changes of step response are not same. For an example, at 5% change, the different pH value when step response increase by 5% is higher than decrease by 5%. That phenomena show the pH process is nonlinear process. If the process is linear the different pH value for both decreasing and increasing step response should be same.

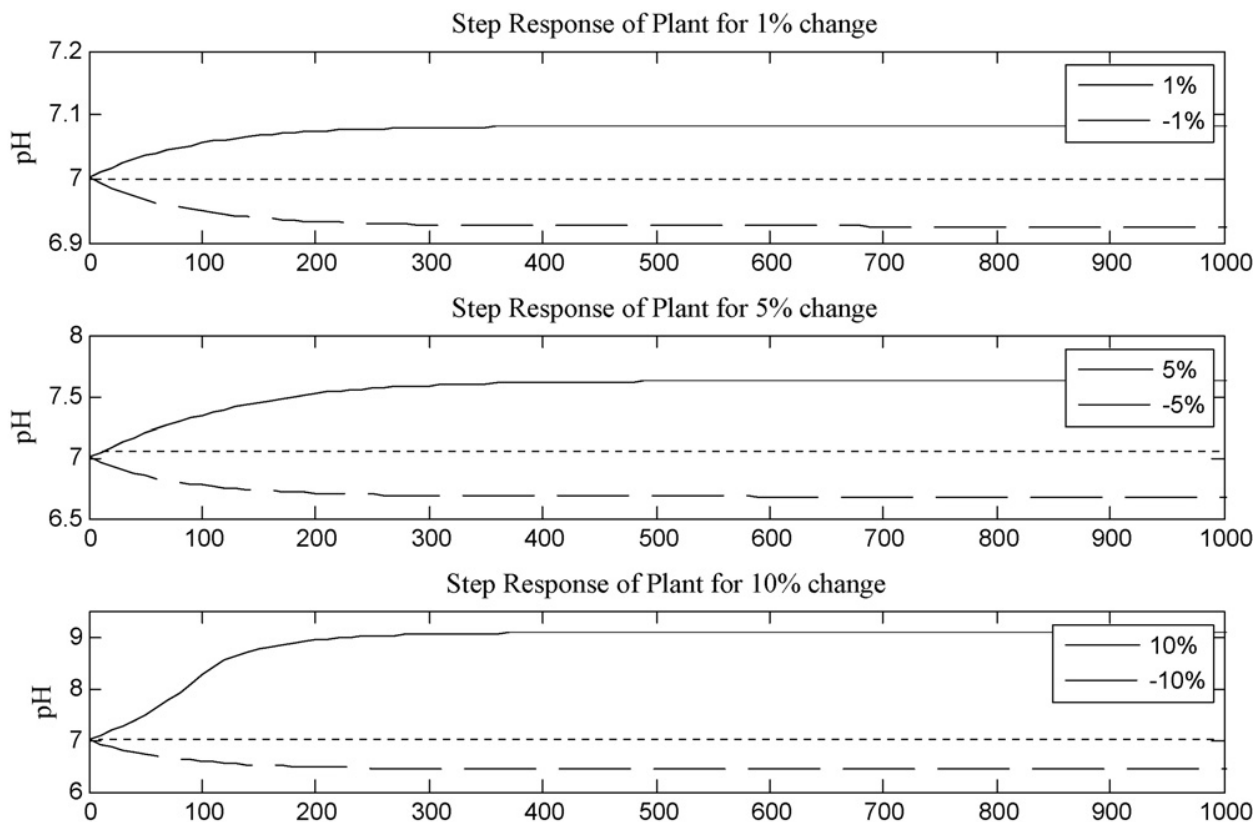


Figure 2: Step responses of pH process (Mahmoodi et al. 2008)

2.3 Nonlinear Process Models

According to Henson (1998), the industrial success of LMPC (Linear Model Predictive Control) is largely attributable to the availability of commercial software packages which can be used to develop linear dynamic models directly from process data (Qin and Badgwell, 1997). These linear empirical models are used by the LMPC controller to predict and optimize process performance. NMPC (Nonlinear Model Predictive Control) requires the availability of a suitable nonlinear dynamic model of the process. Consequently, the development of nonlinear process models is of paramount importance. Due to the complexity of nonlinear systems, it is not possible to

develop nonlinear system identification techniques by straightforward extension of the linear theory (Pearson and Ogunnaike, 1997). As an alternative, the NMPC controller may be based on a fundamental model which is derived from basic conservation laws and constitutive relations.

There are three types of nonlinear models:

1. Fundamental models
2. Empirical models
3. Hybrid models

In this research, the fundamental model of pH system is developed.

2.3.1 Fundamental Models

Fundamental dynamics models are derived by applying transient mass, energy and momentum balances to the process (Ogunnaike and Ray, 1994). In the absence of spatial variations, the resulting models have the general form

$$\dot{x} = f(x, u) \quad (2.3)$$

$$0 = g(x, u) \quad (2.4)$$

$$y = h(x, u) \quad (2.5)$$

where x is a n -dimensional vector of state variables, u is a m -dimensional vector of manipulated input variables and y is a p -dimensional vector of controlled output variables. The ordinary differential equations (2.2) and algebraic equation (2.3) are derived from conservation laws and various constitutive relations, while the output equations (2.4) are chosen by the control system designer. Because NMPC is most

naturally formulated in discrete time, it is necessary to discretize the continuous time differential equations. This is usually achieved by orthogonal collocation or finite elements (Meadows and Rawlings, 1997).

Advantages of fundamental models are highly constrained with respect to their structure and parameters, provides physical interpretation of all the variables involved in the model, less process data is required for development, and model parameters can be estimated from laboratory experiments and routine operating data instead of time-consuming plant tests (Henson, 1998). As long as the underlying assumptions remain valid, fundamental models can be expected to extrapolate to operating regions which are not represented in the data set used for model development (Meadows and Rawlings, 1997). This first-principle model is also valid globally and can predict system dynamics over the entire operating range. However, development of a reliable first-principle model is a difficult and time-consuming task (Mahmoodi et al. 2008). For Pearson (1995), the fundamental model generally gives us more complete process understanding than empirical model and also generally much more complex and requires correspondingly longer to develop.

The disadvantages of this model are lack of process knowledge often leads to disappointing results, since it is hard to capture all relevant phenomena in the model and the resulting dynamic model may be too complex to be useful for NMPC design. But this drawback can be avoided by the use of reduction techniques such as singular perturbations.

The principle of physico-chemical dynamic modelling of a pH-process was first stated by McAvoy et al. in 1972. They used the model (acetic acid and sodium hydroxide) for simulating the behavior of a simple pH-process in a time-optimal control loop. Richter et al. 1974 presented a model including the electro-neutrality condition for many 1-valued acids and bases two years later. Gustafsson and Waller, (1982) and Jutila and Orava, (1981) developed more complex models, closer to practical processes.

The term “reaction invariant” was originally introduced by Fjeld et al. (1974) but the pH process formulation of reaction invariants was presented by Gustafsson and Waller, (1982) as a systematic matrix formulation of the physico-chemical modeling procedure. The stoichiometric chemical reactions and the charge balance form together a set of equations that can be used for determining the reaction invariants with the help of simple linear algebra. More elaborate chemical systems including complex formation and two-phase systems (solid/liquid) are presented by Gustafsson et al, (1995).

2.3.2 Empirical Model

In many applications, lack of process knowledge and/or a suitable dynamic simulator precludes the derivation of a fundamental model. This necessitates the development of empirical nonlinear models from dynamic plant data. According to Henson (1998) the development of empirical nonlinear models from plant data is known as nonlinear system identification. A fundamental difficulty associated with empirical modeling approach is selection of suitable model form. Discrete-time models are most appropriate because plant data is available at discrete instant and NMPC is most naturally formulated in discrete time. The types of discrete time nonlinear model include:

1. Polynomial nonlinear auto-regressive moving average model with exogenous inputs (polynomial NARMAX)
2. Volterra models
3. Artificial neural network (ANN) models
4. Nonlinear FIR (NFIR) MODELS
5. Hammerstein and Wiener models

The development of empirical nonlinear models from plant data is known as nonlinear system identification. Nonlinear system identification in practice involves the following steps:

- 1- Selection of a model structure
- 2- Given a model structure, design of the input sequence, $u(k)$
- 3- Given $u(k)$, generation of the system response $y(k)$
- 4- From the input- output dataset, estimation of the model parameters
- 5- Assessment of identified model quality based on the estimated model parameters
- 6- Iteration and model refinement as necessary

Based on paper write by Henson (1998), as compared to fundamental model models, empirical nonlinear models have several advantages. First, this model not required the detailed process understanding. This is an important consideration for complex industrial process such as polymerization reactors, which are difficult to model from fundamental principles. Because of NMPC requires online solution of a nonlinear programming problem, computational overhead and reliability is intimately connected with the complexity of the nonlinear model. Other advantage of empirical model is that the nonlinear model can be chosen to restrict model complexity (Pearson and Ogunnaike, 1997).

Example of empirical models used for controlling pH system:

- 1) Wiener model

Wiener model are quite similar with Hammerstein model but they are different from the arrangement of static nonlinearity and linear dynamics at their structures.

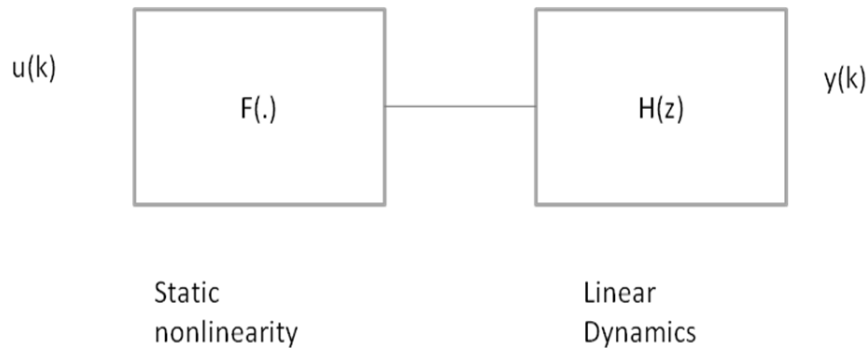


Figure 3: Hammerstein model structure (Pearson, 1995)

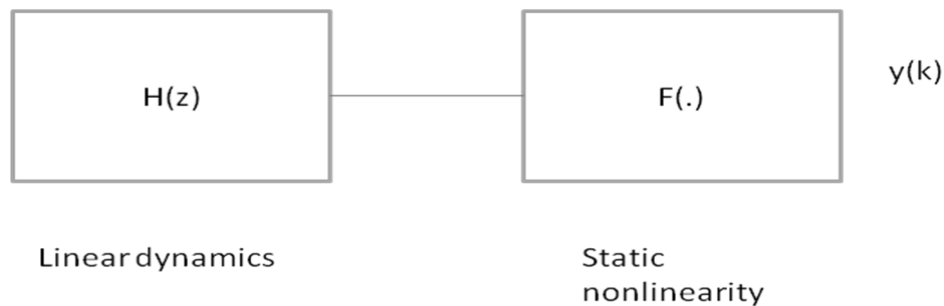


Figure 4: Wiener model structure (Pearson, 1995)

Wiener models have the capability of approximating, with arbitrary accuracy, any fading memory nonlinear time invariant system (Boyd and Chua, 1985), and they have been successfully used to model several nonlinear systems encountered in the process industry, such as distillation columns (Bloemen et al. 2001), and pH processes (Norquay et al. 1998 & 1999, Kalafatis et al. 1995). In the paper wrote by Baeyens et al. (2004), they stated that input-output data from a nonlinear, first principles simulation model of the pH neutralization process are used for subspace-based identification of a black-box Wiener-type model. The proposed nonlinear subspace identification method has the advantage of delivering a Wiener model in a format which is suitable for its use in a standard linear-model-based predictive control scheme. The identified Wiener model is used as the internal model in a model predictive controller (MPC) which is used to control the nonlinear white-box simulation model. To account for the

immeasurable disturbance, a nonlinear observer is proposed. The performance of the Wiener model predictive control (WMPC) is compared with that of a linear MPC, and with a more traditional feedback control, namely a PID control. The WMPC scheme introduced in before this was implemented using the function in the MPC toolbox for use with MATLAB (Morari and Ricker, 1994). Simulation results show that the WMPC outperforms the linear MPC and the PID controllers.

2) Wiener- Laguerre model.

Wiener models are frequently used for identification of nonlinear processes in nonlinear model predictive control systems. Laguerre filters are frequently used as the linear part of Wiener models resulting in the so-called Wiener–Laguerre model. This model structure was used for the identification of a highly nonlinear chemical process with the aim of being used in an NMPC controller.

In the paper wrote by Mahmoodi et al. (2008), they stated that Laguerre filters and simple polynomials are used respectively as linear and nonlinear parts of a Wiener structure. The obtained model structure is the so-called Wiener–Laguerre model. This model is used to evaluate identification of a pH neutralization process. Then the model is used in a nonlinear model predictive control framework based on the sequential quadratic programming (SQP) algorithm. Various orders of Laguerre filters and nonlinear polynomials are tested, and the results are compared for the validation of these models. Validation results for various orders suggest that in order to have a good trade-off between simplicity of the model and its corresponding fitness, a second order nonlinear polynomial along with two Laguerre filters may be selected. The fitness of this model according to variance account for (VAF) criterion is 92.32%, which is completely acceptable for nonlinear model predictive control applications. Then the identified Wiener–Laguerre model is used for nonlinear model predictive control and the results are compared with model predictive control in which just Wiener model was used for identification. It is shown that the use of the Wiener–Laguerre structure

improves the quality of modeling together with the rate of convergence of SQP in a reasonable time. Furthermore, these results are also compared with the performance of a linear model predictive controller based on Laguerre model to provide a fair comparison between linear and nonlinear systems.

Table 1: SSE criteria for applied controller in set- point tracking (Mahmoodi et al, 2008)

Controller	SSE
NMPC (Wiener- Laguerre)	157.1854
MPC (Wiener)	429.9803
MPC (Laguerre)	199.671

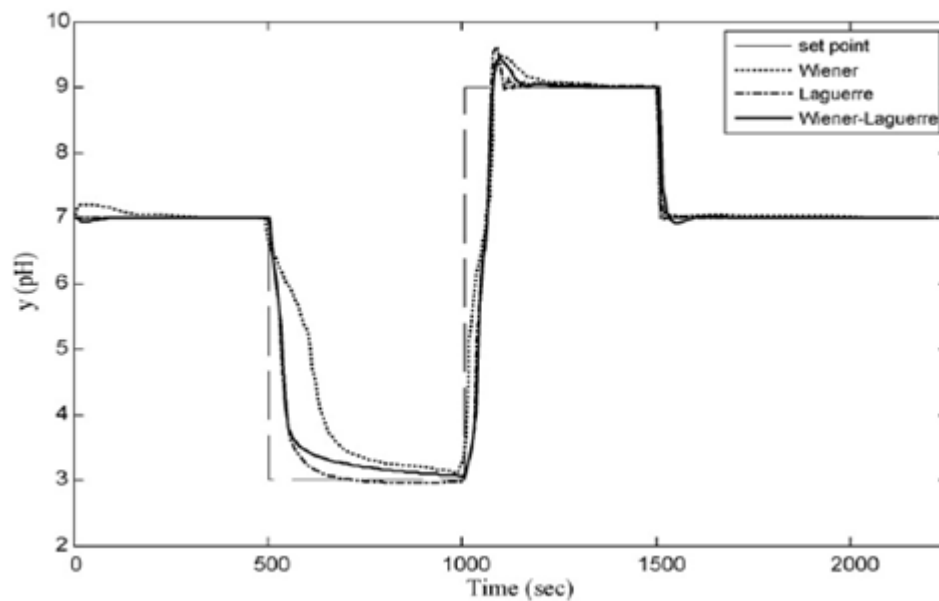


Figure 5: NMPC based on Wiener- Laguerre in comparison with MPC based on Laguerre and Wiener models (Mahmoodi et al, 2008)

Simulation results show that, for the considered application, the Wiener–Laguerre MPC performs slightly better than the MPC based on the linear Laguerre model, but it

performs much better than that corresponding to the Wiener model presented by Baeyens et al. (2004).

3) Neural Network Model

Dudul and Ghatol, 2005 had investigated the identification of the pH Neutralization process in a constant volume stirring tank using a two layer multi-layer perceptron neural network. It is shown that the neural network based state-space innovations form model has clearly outperformed the equivalent linear model in simulation and thus, it is possible to obtain good results for this process with neural network based state-space innovations form model. It is by no means claimed that the optimal solution is found however it is shown that the proposed neural network based model provides a simple means to identify the given nonlinear multi-input-single-output system.

Table 2: Comparison between linear and the NN model (Dudul and Ghatol, 2005)

Model	Fit for One- step Ahead Predictions %	Fit for simulation %	Error
Linear model	64.99%	-125.2%	0.0375719
Neural Network	54.934%	45.168%	0.0381779(FPE) 0.0113365(Train) 0.00557476(Test)

The MSE on a test set (data set not used for training) has been found as 0.00557476 and the fit for simulation is computed as 45.17%, which is clearly higher than that of the state-space model. It is thus observed that the fit for simulation is much better in the case of neuronal model and that it tries to learn the dynamics of the system. Imperfection in the result can be attributed to both the insufficient data and non-linear dynamical behaviour of the system. However, it is possible to obtain good results for a pH neutralization process in a constant volume stirring tank with NN based SSIF model.

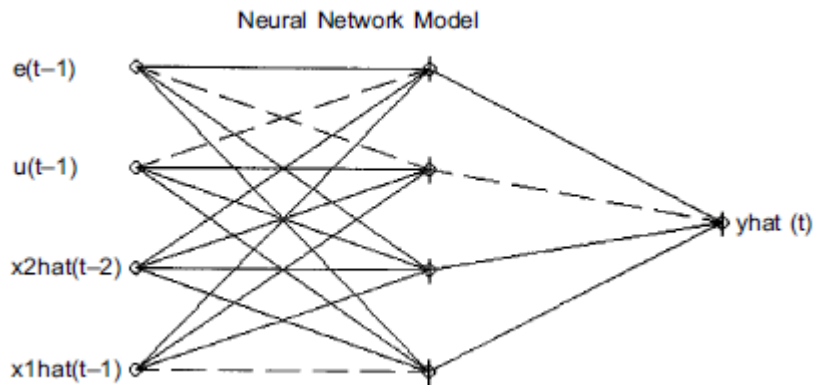


Figure 6: NN Model (4-4-1)(Dudul and Ghatol, 2005)

For the network chosen as 4-4-1 shown in figure 6, the ratio of number of training patterns to the number of weights in the network is 40 and its generalization ability has been improved by means of regularization. This network is trained by Levenberg- Marquardt algorithm.

2.3.3 Hybrid Models

Hybrid nonlinear model are developed by combining the fundamental model and empirical modeling approaches. This allows the advantages of each modeling approach to be exploited. A common method for developing hybrid models is to use empirical models to estimate unknown functions in the fundamental model like reaction rates in a chemical reactor model (Pottmann and Henson, 1997) In this case, steady- state empirical models usually are sufficient. Another possible approach is to utilize a fundamental model to capture the basic process characteristics, and then to describes the residual between the plant and the model using nonlinear empirical model. Both techniques allow the nonlinear model to be constrained by the underlying physics, but

they do not require a complete rigorous model of the plant. While hybrid models hold great promise, their use for NMPC design has not been explored.

2.4 Derivation of Dynamic Equations for pH System

The model derived below is known as classical physico-chemical modeling approach by McAvoy et al. 1972. Consider a stirred tank into which acetic acid of concentration C_1 flows in at a rate F_1 . This acid neutralizes sodium hydroxide of concentration C_2 which flows into the tank at a rate F_2 . The volume of the tank is constant and equal to V . The variable of interest is the pH of the outlet stream. The tank is assumed to be perfectly mixed and isothermal, and the variables to be determined are: $[H^+]$, $[OH^-]$, $[HAC]$, $[AC^-]$, and $[Na^+]$. Once $[H^+]$ is known, the pH can be determined from the expression

$$pH = -\log_{10} [H^+] \quad (2.6)$$

Material balances on hydrogen or the hydrogen ion would be extremely difficult to write down because the dissociation of water and the resultant slight change in water concentration would have to be accounted for. This is especially true if one is interested in almost neutral solutions, as is often the case industrially. However, such balances are not required as is shown below. By making material balances on acetate and sodium, using the acetic acid and water equilibrium relationships and the fact that the solution must be electrically neutral, we can completely formulate the problem.

Letting

$$\xi = [HAC] + [AC^-] \quad (2.7)$$

and

$$\zeta = [\text{Na}^+] \quad (2.8)$$

Then the following equations apply:

Acetate balance

$$F_1 C_1 - (F_1 + F_2) \xi = V d\xi / dt \quad (2.9)$$

Sodium balance

$$F_2 C_2 - (F_1 + F_2) \zeta = V d\zeta / dt \quad (2.10)$$

Acetic acid equilibrium

$$[\text{AC}^-][\text{H}^+] / [\text{HAC}] = K_a \quad (2.11)$$

Water equilibrium

$$[\text{H}^+][\text{OH}^-] = K_w \quad (2.12)$$

Electroneutrality

$$\zeta + [\text{H}^+] = [\text{OH}^-] + [\text{AC}^-] \quad (2.13)$$

Equations 2.6 through 2.13 are a set of seven independent equations in seven unknowns which completely describe the dynamic behavior of the stirred tank.

CHAPTER 3

METHODOLOGY

3.1 Develop Mathematical Model based on First Principles

The pH process consists of neutralization of two monoprotic reagents of a weak acid (acetic acid) and a strong base (sodium hydroxide). The method implements mass balances for components called reaction invariants of the Continuous Stirred Tank Reactor (CSTR) solution. As shown in Figure 7, the CSTR has two inlet streams: the influent process stream and the titrating stream, with one effluent stream at the output. The model of the pH neutralization process used in this work follows Valarmathi et al. 2009 that proposed by McAvoy et al. 1972 and is given below.

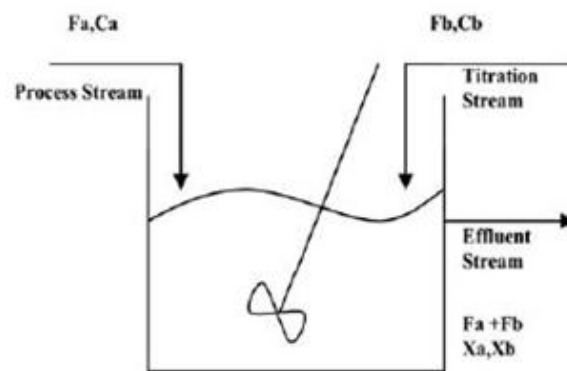


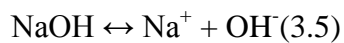
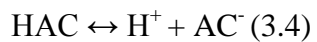
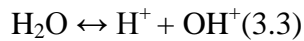
Figure 7: pH neutralization process (Valarmathi et al. 2009)

Assumption of perfect mixing is general in the modeling of pH processes, the volume of tank is constant and the reaction is isothermal. Material balances in the reactor can be given by

$$VdX_a/dt = F_a C_a - (F_a + F_b)X_a \quad (3.1)$$

$$VdX_b/dt = F_b C_b - (F_a + F_b)X_b \quad (3.2)$$

where F_a is the flow rate of the influent stream, F_b is the flow rate of the titrating stream, C_a is the concentration of the influent stream, C_b is the concentration of the titrating stream, x_a is the concentration of the acid solution, x_b is the concentration of the basic solution and V is the volume of the mixture in the CSTR. The above mathematical equations describe how the concentration of the acidic and basic components, x_a and x_b change dynamically with time subject to the input streams, F_a and F_b . The reaction between HAC and NaOH:



Invoking the electroneutrality condition, the sum of the ionic charges in the solution must be zero.

$$[Na^+] + [H^+] = [AC^-] + [OH^-] \quad (3.6)$$

The $[X]$ denotes the concentration of the X ion. The equilibrium relations also hold for water and acetic acid

$$K_a = \frac{[AC^-][H^+]}{[HAC]} \quad (3.7)$$

$$K_w = [H^+][OH^-] \quad (3.8)$$

where $X_a = [HAC] + [AC^-]$ and $X_b = [Na^+]$

The pH value can be determined using equation (3.9)

$$pH = -\log_{10} [H^+] \quad (3.9)$$

where K_a and K_w is the dissociation constant of acetic acid at 25°C ($K_a = 1.778 \times 10^{-5}$ and $K_w = 10^{-14}$).

3.2 Solving Model Equation in MATLAB Environment (Algorithm)

Development of fundamental nonlinear model using MATLAB is based on mathematical model algorithm. In this research, the algorithm is develop from the first principles that proposed by McAvoy et al. 1972. The inputs are F_a , F_b , C_a and C_b while the output is pH value.

Firstly, the acetate and sodium balance equation is integrated.

From acetate balance (equation 3.1):

$$VdX_a/dt = F_a C_a - (F_a + F_b)X_a$$

$$VdX_a = [F_a C_a - (F_a + F_b)X_a]dt$$

$$V \int dX_a = [F_a C_a - (F_a + F_b)X_a] \int dt$$

$$VX_a = [F_a C_a - (F_a + F_b)X_a]t$$

$$X_a \left[\frac{V}{t} + F_a + F_b \right] = F_a C_a$$

$$X_a = \frac{F_a C_a}{\frac{V}{t} + F_a + F_b} \quad (3.10)$$

From sodium balance (equation 3.2):

$$VdX_b/dt = F_b C_b - (F_a + F_b)X_b$$

$$VdX_b = [F_b C_b - (F_a + F_b)X_b]dt$$

$$V \int dX_b = [F_b C_b - (F_a + F_b)X_b] \int dt$$

$$VX_b = [F_b C_b - (F_a + F_b)X_b]t$$

$$X_b \left[\frac{V}{t} + F_a + F_b \right] = F_b C_b$$

$$X_b = \frac{F_b C_b}{\frac{V}{t} + F_a + F_b} \quad (3.11)$$

Note that $X_a = [\text{HAC}] + [\text{AC}^-]$ and $X_b = [\text{Na}^+]$

Then, from water equilibrium (equation 3.8):

$$K_w = [\text{H}^+][\text{OH}^-]$$

$$[\text{H}^+] = K_w / [\text{OH}^-] \quad (3.12)$$

Substitute equation 3.12 into acetic acid equilibrium and electroneutrality equation.

From acetic acid equilibrium (equation 3.7):

$$K_a = \frac{[\text{AC}^-][\text{H}^+]}{[\text{HAC}]} \quad (3.7)$$

$$K_a = [\text{AC}^-] \left(\frac{K_w}{[\text{OH}^-]} \right) / [\text{HAC}]$$

where $[\text{HAC}] = X_a - [\text{AC}^-]$,

$$K_a = \frac{[\text{AC}^-] \left(\frac{K_w}{[\text{OH}^-]} \right)}{X_a - [\text{AC}^-]} \quad (3.13)$$

From electroneutrality equation (3.6):

$$[\text{Na}^+] + [\text{H}^+] = [\text{AC}^-] + [\text{OH}^-] \quad (3.6)$$

$$[\text{Na}^+] + \frac{K_w}{[\text{OH}^-]} = [\text{AC}^-] + [\text{OH}^-] \quad (3.14)$$

From equation (3.14),

$$[\text{AC}^-] = [\text{Na}^+] + \frac{K_w}{[\text{OH}^-]} - [\text{OH}^-] \quad (3.15)$$

Substitute equation (3.15) into (3.13),

$$K_a = \frac{\left([\text{Na}^+] + \frac{K_w}{[\text{OH}^-]} - [\text{OH}^-]\right) \left(\frac{K_w}{[\text{OH}^-]}\right)}{X_a - \left([\text{Na}^+] + \frac{K_w}{[\text{OH}^-]} - [\text{OH}^-]\right)} \quad (3.16)$$

Derive equation (3.16) until;

$$K_a[\text{OH}^-]^3 + (K_w - K_a[\text{Na}^+] + K_a X_a)[\text{OH}^-]^2 + (K_w[\text{Na}^+] - K_a K_w)[\text{OH}^-] - K_w^2 = 0 \quad (3.17)$$

Because of equation (3.17) is cubic equation the roots of $[\text{OH}^-]$ will be determined. The positive root is considered as a concentration of $[\text{OH}^-]$. Then, using equation (3.12), the value of $[\text{H}^+]$ can be calculated. Since the value of $[\text{H}^+]$ is known, pH can be determined using equation (3.9).

In the MATLAB M-File, the development of fundamental nonlinear model is developed using equations (3.9), (3.10), (3.11), (3.12) and (3.17). The program code is shown like below:

```
%assumption:1)tank is perfectly mixed, 2)the process is isothermal
%3)volume of the tank is constant

% fa(L/s),fb(L/s),ca(mol/L),cb(mol/L),v(L) is input

fa=0.00333; fb=0.001667; ca=0.01; cb=0.1; v=1.5;

%ka=acetic acid equilibrium, kw=water equilibrium

ka=1.778*10^(-5);

kw=1*10^(-14);

%t is time, i refer to iteration

for i=1:2400;

t(i)=i;

%xa and xb is concentration of acid & base solution

xa(i)=fa*ca/(v/t(i)+fa+fb);

xb(i)=fb*cb/(v/t(i)+fa+fb);

%OH,Na,H is concentration of ion hydroxide,sodium& hydrogen

%ka(OH^3)+(OH^2)(kw-ka*Na+ka*xa)+OH(-kw*Na-ka*kw)-kw^2=0 where Na=xb

y(i,:)=[ka kw-ka*xb(i)+ka*xa(i) -(kw*xb(i)+ka*kw) -kw^2];

%the true value of OH is the positive value which is real root

z(i,:)=roots(y(i,:));
```

```
OH=z(z>0);
```

```
H(i)=kw/OH(i);
```

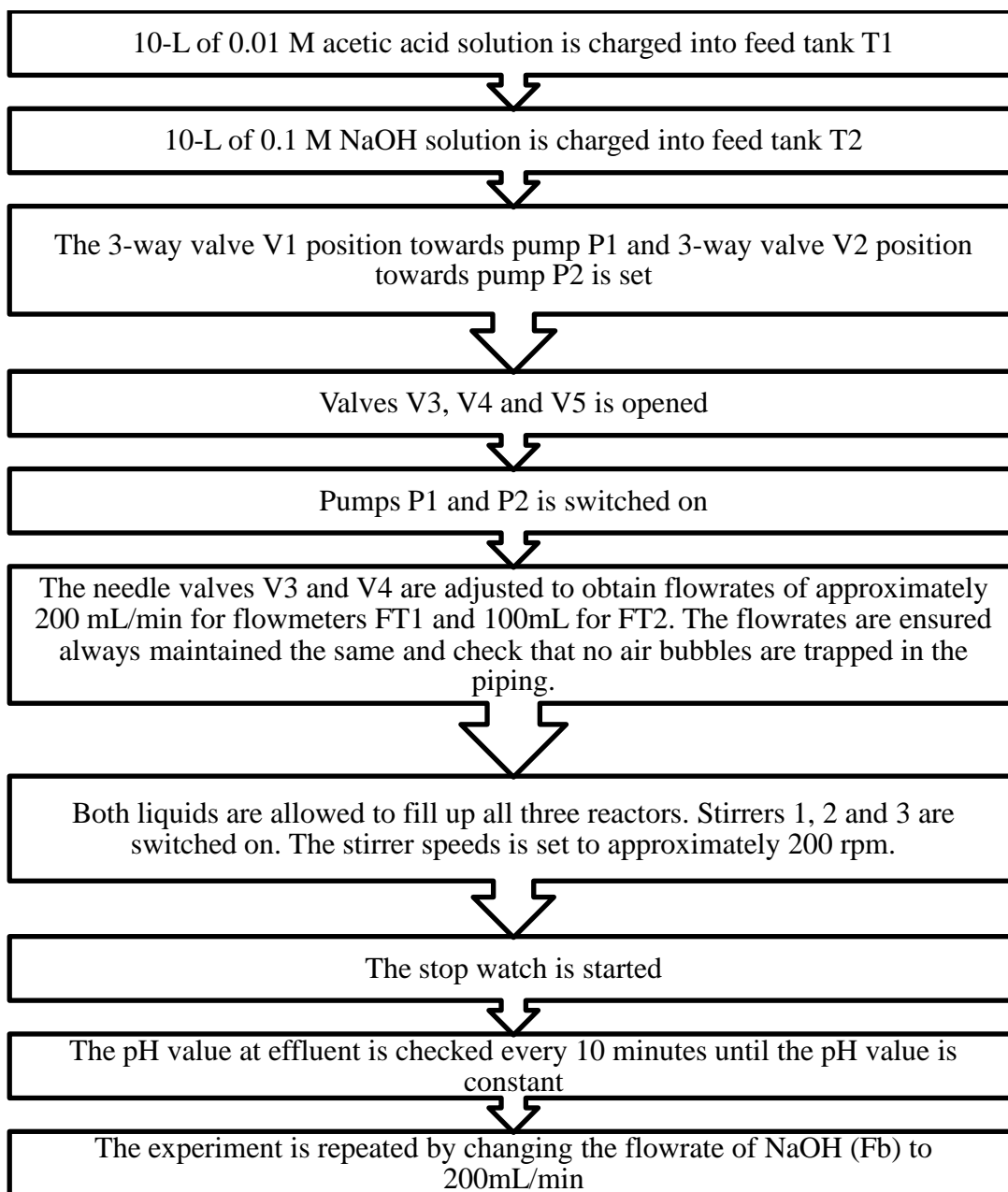
```
ph(i)=-log10(H(i));
```

```
end
```

```
plot(t,ph);
```

3.3 Experimental Validation

The experiment data is taken from the experiment done in the laboratory. The analysis data between the experiment and model will be shown and discussed in chapter 4. These are the experiment procedures for pH process in continuous stirred tank reactor (CSTR):



CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Validation of Nonlinear Model through Experimentation

In this research two experiments has been done in CSTR. The first experiment is done by setting the flowrate of sodium hydroxide (NaOH), F_b at 0.001667 L/s while acetate acid (HAC) flowrate, F_a is set at 0.0033 L/s with concentration of acetate acid, C_a and NaOH, C_b is constant at $C_a = 0.01$ M and $C_b = 0.1$ M. For the second experiment, F_b is increased equal to F_a , 0.0033 L/s which C_a and C_b remain constant. The data is compared with the model data and percentage error is calculated. The result for experiment 1 and 2 is shown at the next page.

Table 3: Comparison between experimental data and model ($F_a=0.0033$ L/s, $F_b=0.001667$ L/s, $C_a=0.01M$, $C_b=0.1M$)

Time(min)	pH (program/model)	pH (experiment)	Error (%)
0	7.00	10.99	36.31
10	12.2503	12.24	0.08
20	12.3395	12.35	0.09
30	12.3593	12.42	0.49
40	12.3753	12.45	0.6

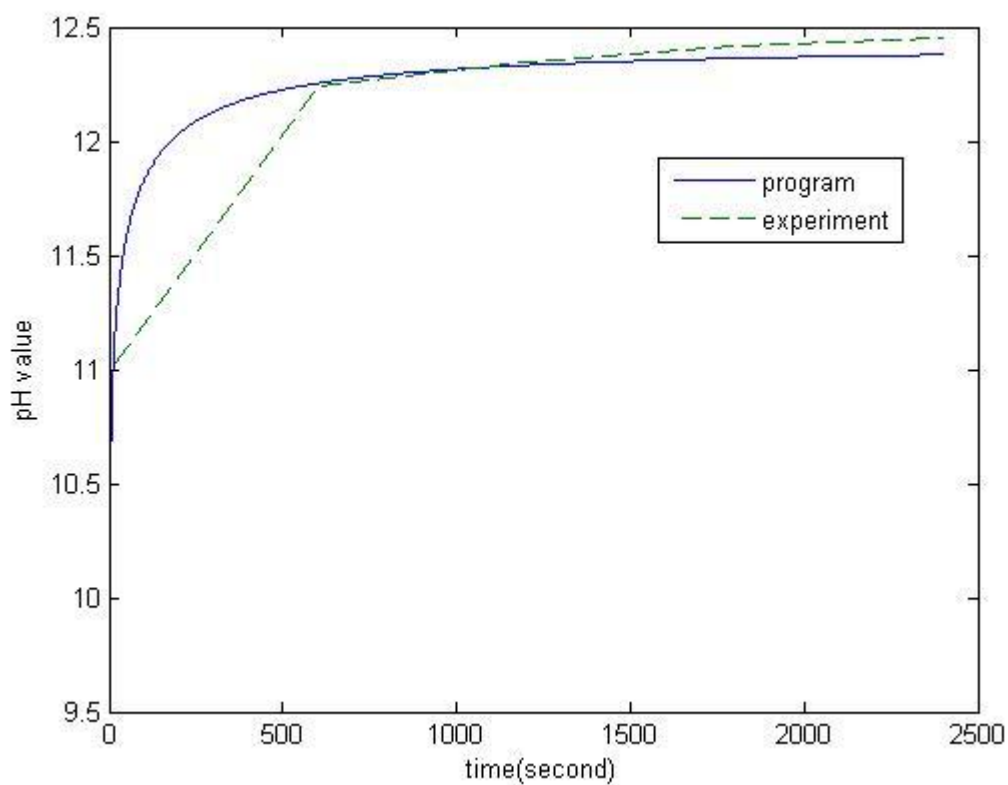


Figure 8: Graph for comparison between experimental data and model ($F_a=0.0033$ L/s, $F_b=0.001667$ L/s, $C_a=0.01M$, $C_b=0.1M$)

Table 4: Comparison between experimental data and model ($F_a=0.0033$ L/s, $F_b=0.0033$ L/s, $C_a=0.01$ M, $C_b=0.1$ M)

Time(min)	pH (program)	pH (experiment)	Error (%)
0	7.00	11.01	36.42
10	12.5148	12.64	0.99
20	12.5785	12.72	1.11
30	12.6020	12.75	1.16
40	12.6143	12.76	1.14

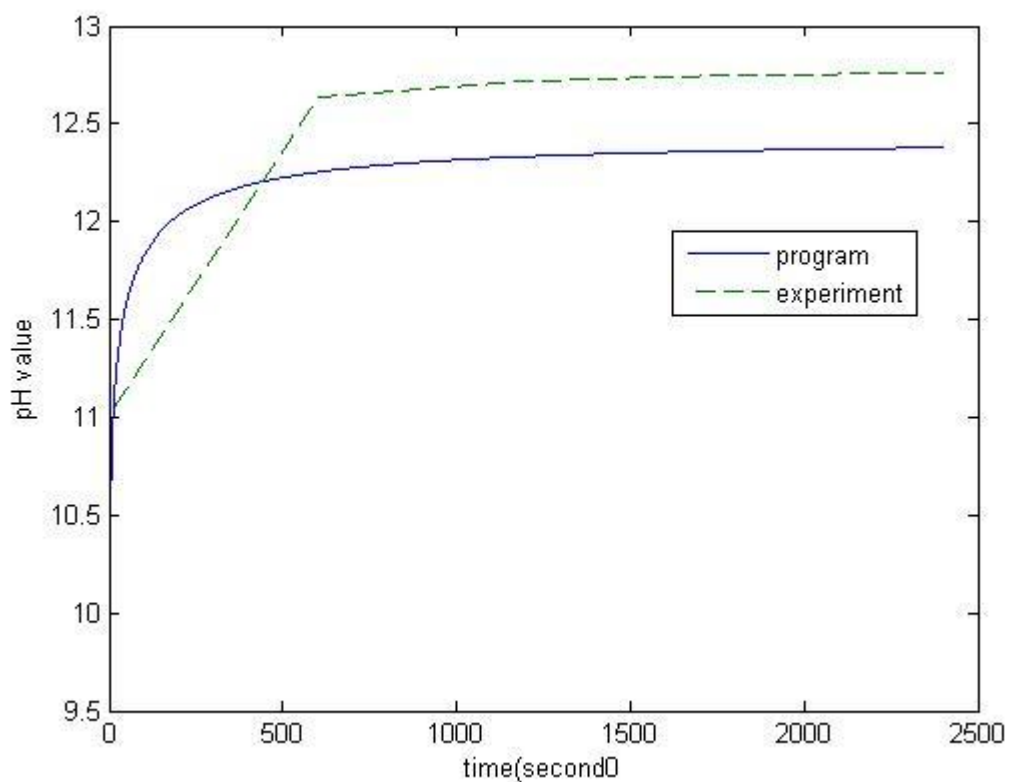


Figure 9: Graph for comparison between experimental data and model ($F_a=0.0033$ L/s, $F_b=0.0033$ L/s, $C_a=0.01$ M, $C_b=0.1$ M)

Based on Table 3, the analysis showed most of the pH values between model and experiment is closed. The errors also showed this model can be accepted because of very small different pH value between model and experiment data. The higher error only occur at time=0 which is the starting of the process. But, the error is decreased when the process starts running. The average error at every point is very small which most of the errors below 1%. The shape of the graph at figure 8 shown the model is almost same to the experiment. The obvious different only occur from 0-550 second when the pH is near neutralization point. This situation shows the nonlinear behavior of pH process. After that point, the model starts to capture accurately the dynamic of pH system which is highly nonlinear process and time- varying.

The error between model and experiment data slightly increased when the flowrate of NaOH, F_b is set equal to flowrate of acetic acid, F_a . Based on Table 4, the highest error also at time=0, same with experiment 1. The same situation occurred during experiment 2. The values of errors also decreased after the process is start. Even though the error is bigger compare to experiment 1, this model is acceptable because most of the error is still lower than 10%. The nonlinear behavior of pH process also can be seen in figure 9. The significance gain variation is showed between times from 0-550 second.

4.2 Steady State Titration Curve

The S- shaped titration curve is the primary source of the pH non-linearity (Lin and Yu, 1993). The non-linearity can be understood from the S- shaped static pH responses with the addition of titrant. In figure 10, the flowrate of acetic acid, F_a is constant while the flowrate of NaOH, F_b is changed. The value of pH is taken at 2400 second at the graph of pH against F_b is plotted in figure 6. From the graph, the steady state gain shows significant variation with the change in the operating point. This makes it difficult to design a single linear controller to perform satisfactorily in all regions. That's why this research develop the nonlinear fundamental model of pH process because this model can predict system dynamics over the entire operating range.

Based on figure 10, the non- linearity appears in the S- shape titration curve associated with pH processes. The process gain grows drastically at the intermediate region of the S- shape curve, i.e. around the neutralization point. At $F_b = 0- 0.4$ L/s, the pH value increased uniformly. But the increasing grows drastically at $F_b = 0.3- 0.4$ L/s because the pH value near the $pH=7$ which is neutralization point. This behavior is the main source of control difficulty which control need to achieve pH around 7. Moreover, the shape of the titration curve is distorted when the feed condition changes. This situation adds more complexity to the control system. For this reason, pH control was and still is the scope of work for many researchers.

For this process, three regions of nonlinear gains can be identified based on figure 10: pH- high, pH- middle and pH- low. pH- high range is starting at point 4.0 L/s and above. Meanwhile, pH- middle range is between 0.3- 0.4 L/s and pH- low range is around 0- 0.3 L/s.

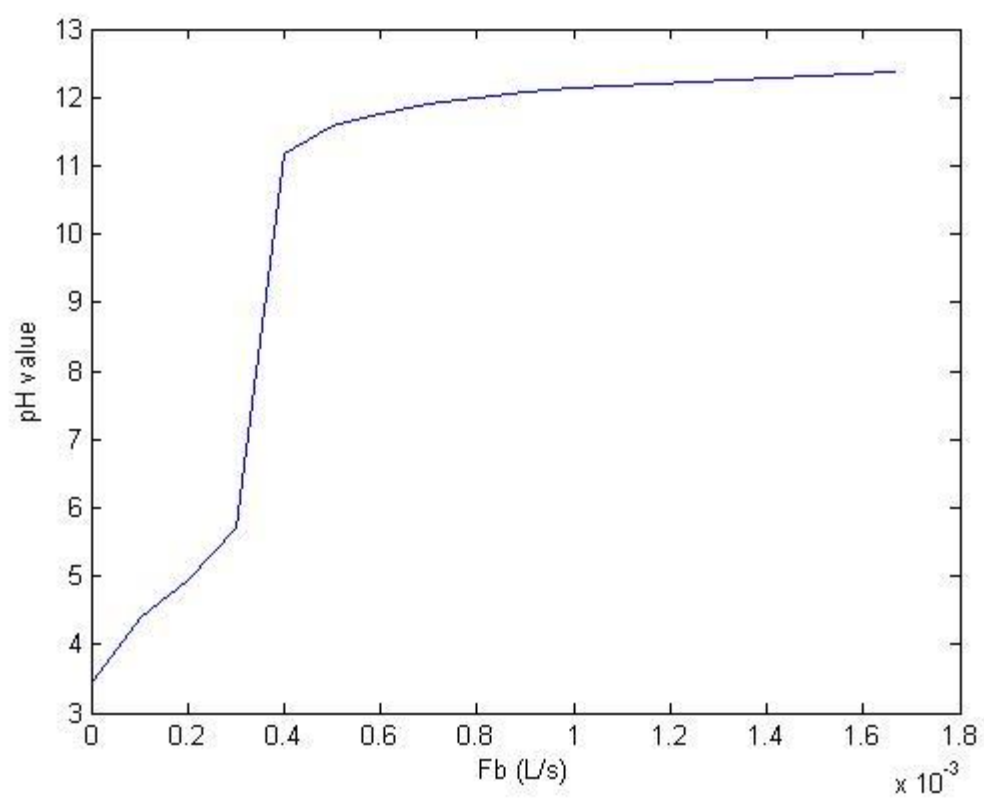


Figure 10: Graph for steady state titration curve

4.3 Step Responses of pH Process

In a step test, the process is operating in open- loop without the model- based controller, each input is stepped separately, and step responses are recorded. The maximum step size can be determined according to process operation experience, and step length should be longer than the settling time of the process. Step tests of pH neutralization process for one step up and one step down with same sizes are shown in figure 11 and 12.

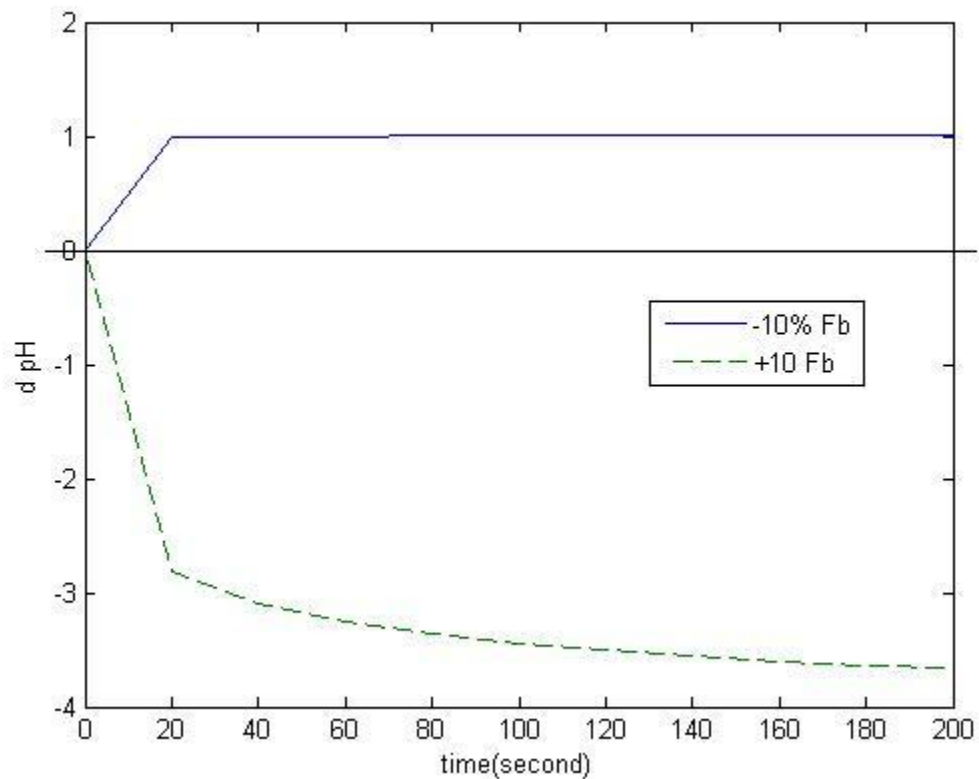


Figure 11: pH response of Fb for $\pm 10\%$ change

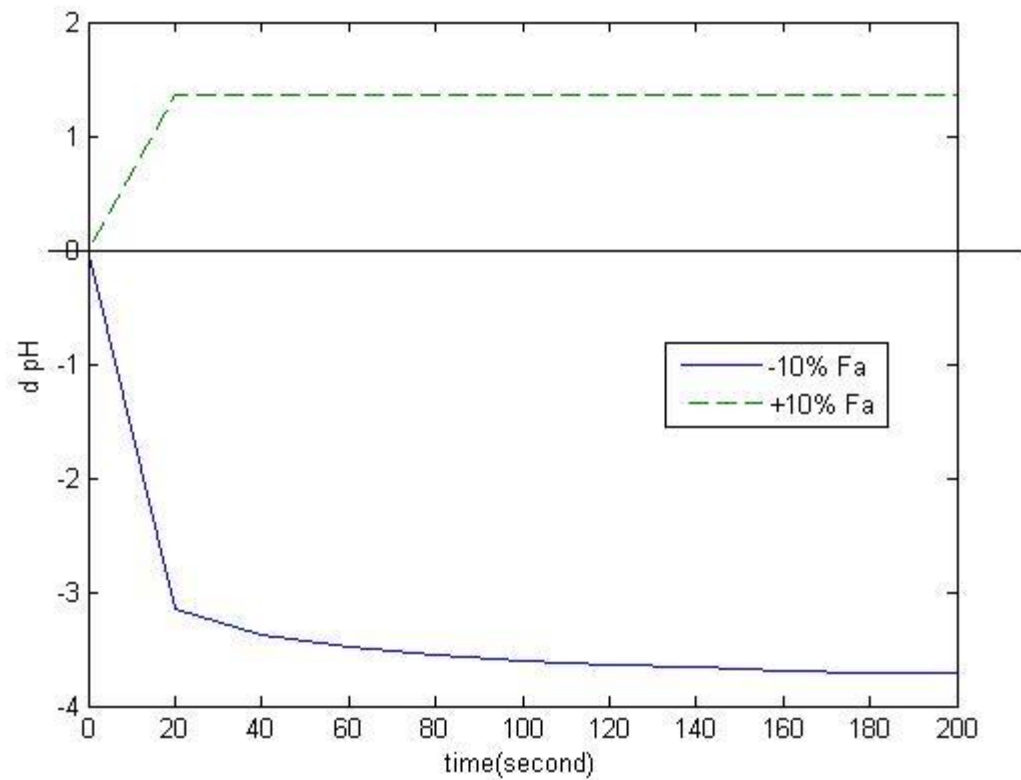


Figure 12: pH response of Fa for $\pm 10\%$ change

Based on figure 11, it is clear that pH neutralization process as a nonlinear system shows different value of $dpH / \Delta pH$ (steady state- current value) for step sizes up to $\pm 10\%$ for changes in base flowrate, F_b . The same phenomena also occurred when flowrate of acetate acid, F_a is changes up to $\pm 10\%$ at figure 12. These two graphs showed that pH process is nonlinear system. This is because, the graph should show same value of ΔpH if the process is linear. Mahmoodi et al. (2008) discussed same thing for pH process nonlinear behavior in their paper. The paper also discussed step responses with different sizes like shown in figure 2.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

A suitable nonlinear fundamental model for pH system is developed, which can capture and predict system dynamics over the entire operating range. This model is developed based on first principle such as conservation laws. The analysis shows the compatibility of the model with experimental results. Based on the result and discussion part, the error between model and experimental data prove that this model can be acceptable.

5.2 Recommendation

This research can be improved by doing more experiments and changes more parameters to prove the compatibility of this model through experimental. The boundary scope of study also can be expanded by doing empirical model of pH system. Even though the first- principle models are valid globally and can predict system dynamics over entire operating range, however, development of a reliable first- principle models is a difficult and time- consuming task. The potential disadvantage is that the resulting dynamic model may be too complex to be useful for NMPC design.

On the other hand, the nonlinear empirical models (black- box models) have certain advantages over the first- principle models in terms of development time and efforts. Thus, from a practical viewpoint, development of an NMPC scheme based on a nonlinear black box model is more attractive choice. For an example, Wiener models are well-known in NMPC because of their simplicity and capability in modeling nonlinear systems, especially those that have linear dynamic and nonlinear output mapping. Wiener models have the capability of approximating, with arbitrary accuracy, any fading memory nonlinear time invariant system, and they have been successfully used to model several nonlinear systems encountered in the process industry for pH process.

REFERENCES

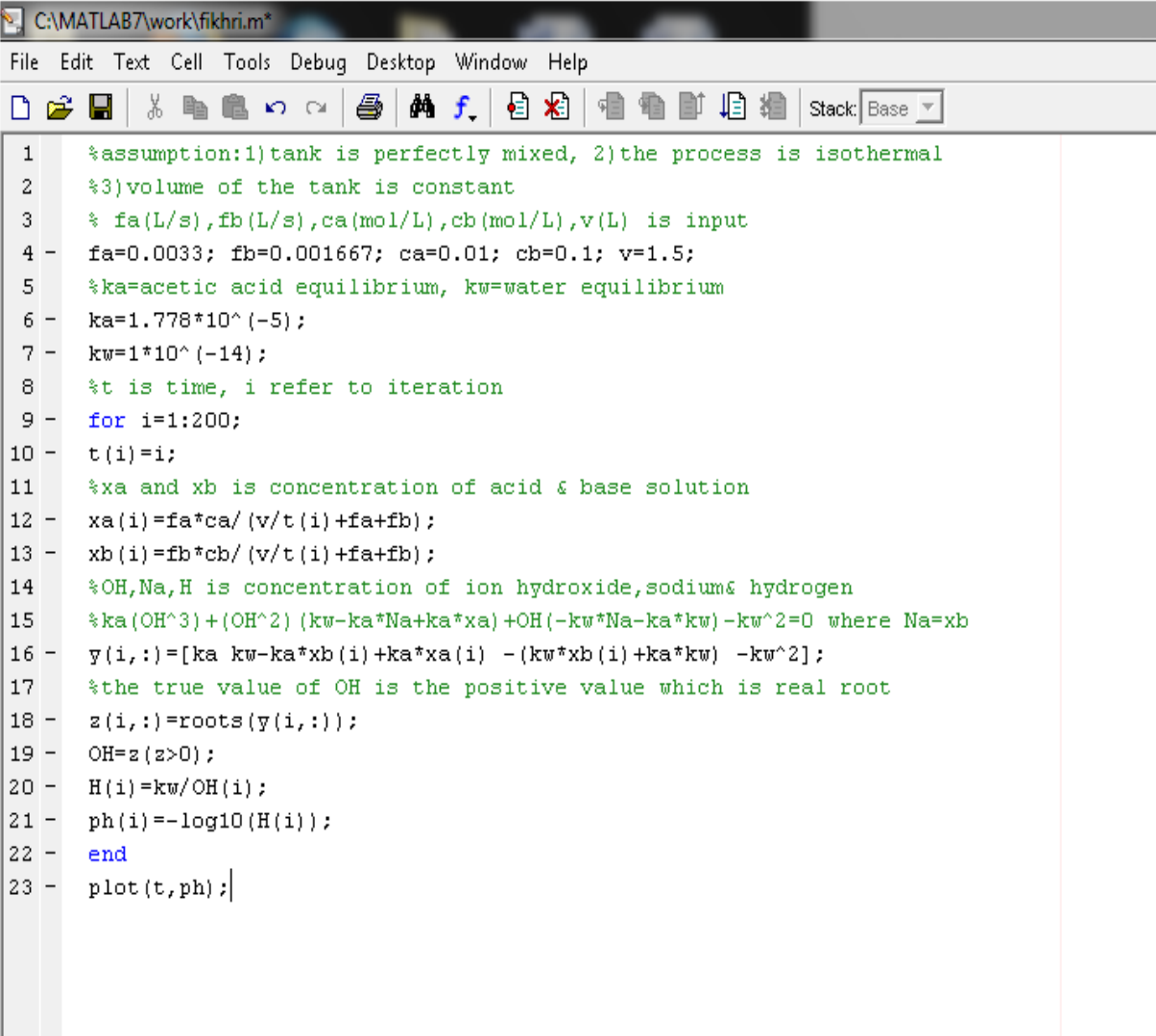
- Ali.E.: 'pH control using PI control algorithms with automatic tuning method', Institution of Chemical Engineers Trans IchemE, vol 79 Patr A, July 2001.
- Baeyens, E., Gomez, J.C., and Jutan, A.: 'Wiener model identification and predictive control of a pH neutralization process', *IEE Proc. Control Theory.*, 2004, pp 329- 334
- Bharathi, N, Shanmugam, J., and Rangaswamy.; 'Intelligent Control of pH in a Neutralization Process', *Asian Journal of Information Technology*, 6(6): 667-673, 2007.
- Bloemen, H., Chou, C., van den Boom, T., Verdult, V., Verhaegen, M., and Backx, T.: 'Wiener model identification and predictive control for dual composition control of a distillation column', *J. Process Control*, 11, pp. 601–620., 2001.
- Boyd, S., and Chua, L.: 'Fading memory and the problem of approximating nonlinear operators with Volterra series', *IEEE Trans. Circuits Syst.*, 32, (11), pp. 1150–1161., 1985
- Dudul, S.V., and Ghatol, A. A.: 'Identification of pH Neutralization Process using the Simplest Neural Network Model', *IE (I) Journal.ID.*, Vol 86, May 2005
- Fjeld, M., Asbjørnsen, O. A., Åström, K. J., Reaction invariants and their importance in for control, *Ind. Eng. Chem. Res.*, 34, 820-827, 1995.
- Gomez, J.C., Jutan, A., and E. Baeyens.: 'Wiener model identification and predictive control of a pH neutralization process', *IEE Proc. Control Theory.*, pp 329- 334., 2004.
- Gustafsson, T. K., Waller, K. V., Dynamic Modelling and Reaction Invariant Control of pH, *Chem. Eng. Sci*, 38(3), 389-398, 1982.
- Gustafsson, T.K., Skrifvars, B. O., Sandström, K. V., Waller, K. V., Modelling of Ph for control, *Ind. Eng. Chem. Res.*, 34, 820-827, 1995

- Henson, M.: 'Nonlinear model predictive control: current status and future directions', *Comput. Chem. Eng*, 23, pp. 187–202., 1998
- Jutila, P., Orava, J., Control and Estimation Algorithms for Physico-Chemical Models of pH-Processes in stirred Tank Reactors, *Int. J. Systems Sci.*, 12(7), 1981
- Kalafatis, A., Arifin, N., Wang, L., and Cluett, W.: 'A new approach to the identification of pH processes based on the Wiener model', *Chem. Eng. Sci*, 50, (23), pp. 3693–3701.,1995
- Karnachi, N.N., Waterworth, G.: 'Non- linear model reference control of pH process: An Experimental Study', *Faculty of Information and Engineering Systems Leeds Metropolitan University*, 2003.
- Lee, J., and Park, H.C.: 'Nonlinear pH control using a three parameter model', *ICASE*, Vol 2, No 2., June 2000.
- Lin, J.H., and Yu, C.C.: 'Automatic tuning and gain scheduling for pH control', *Chemical Engineering Science*, Vol 8, No 18, pp.3159-3171.,1993.
- Mahmoodi, S., Poshtan., J.,Reza, .M., and Montazeri. A.: 'Nonlinear model predictive control of a pH neutralization process based on Wiener- Laguerre model', *Chemical Engineering Journal*, pp 328- 337., 2008.
- McAvoy, T.J Hsu., and S. Lowenthal.: 'Dynamic of pH in a controlled stirred tank reactor', *Industrial & Engineering Chemical Process Design Development*, pp 68-70., 1972.
- Meadows, E.S., and Rawlings, J.B.: Model Predictive control . In: Henson, M.A., & Seborg, D.E. (Eds). *Nonlinear process control, Chapter 5*, (pp. 223-310). Englewood Cliffs, NJ: Prentice-Hall.,(1997)
- Morari, M., and Ricker, N.: 'Model predictive control toolbox-for use with Matlab, user's guide' *The MathWorks, Inc., Natick, MA*, 1994
- Morari, M., and Ricker, N.: 'Model predictive control toolbox-for use with Matlab, user's guide' (The MathWorks, Inc., Natick, MA, 1994)
- Norquay, S., Palazoglu, A., and Romagnoli, J.: 'Application of Wiener Model Predictive Control (WMPC) to a pH neutralization experiment',*IEEE Trans. Control Syst. Technol.*, 7, (4), pp. 437–445.,1997

- Norquay, S., Palazoglu, A., and Romagnoli, J.: 'Model predictive control based on Wiener models', *Chem. Eng. Sci.*, 53, (1), pp. 75–84., 1998 of pH-Processes in stirred Tank Reactors, *Int. J. Systems Sci.*, 12(7), 1981.
- Ogunnaike, B.A., and Ray, W.H.: 'Process dynamics, modeling and control', New York, NY: Oxford Press., 1994
- Pearson, R.K., and Ogunnaike, B.A.: Nonlinear process identification. In: Henson, M.A., & Seborg, D.E. (Eds). *Nonlinear process control, Chapter 2* (pp. 11-110). Englewood Cliffs, NJ: Prentice- Hall., 1997.
- Pearson, R.K.: 'Nonlinear input/output modeling', *J. Proc. Cont.*, pp 197-211., 1995.
- Pishvaie, M. R. and M. Shahrokhii.: 'pH Control using Non-linear Multiple Models, Switching and Tuning Approach', *Ind. Eng. Chem. Res.*, 39, 1311., 2000.
- Pottmann, M., and Henson, M.A.: 'Compactly supported radial basis functions for adaptive process control', *J. Process Control*, 7, 345-356., 1997
- Qin, S.J., and Badgwell, T.A.: 'An overview of industrial model predictive control technology. In: Kantor, J.C Garcia, C.E., & Carnahan, B. (Eds). *Chemical process control V* (pp. 232-256)., (1997).
- Richter, J. D., Fournier, C. D., Ash, R. H., Marcikic, S., Waste neutralization control-digital simulation spots nonlinearities, *Ins. Tech.*, 21, 35-40, 1974
- Shinskey, F. G., *Process Control System: Application, Design and Tuning*, McGraw-Hill, 4th Ed, 1996.
- Shinskey, F. G.: 'pH and PION Control in Process and Waste Streams', *Wiley, New York.*, 1973.
- Valarmathi, K., Devaraj, D., and Radhakrishnan, T.K.: 'Intelligent techniques for system identification and controller tuning in pH process', *Braz. J. Chem. Eng.* vol.26 no.1 São Paulo Jan./Mar. 2009
- Wright, R. A., M. Soroush and C. Kravaris.: "Strong acid equivalent control of pH processes: An experimental study." *Ind. Eng. Chem. Res.*, 30, 2437., 1991.
- Ylen, J.P.: 'Measuring, modeling and controlling the pH value and the dynamic chemical state', *Helsinki University of Technology Control Engineering Laboratory.*, 2001.

APPENDIX A

M- FILE FOR MATLAB PROGRAMMING

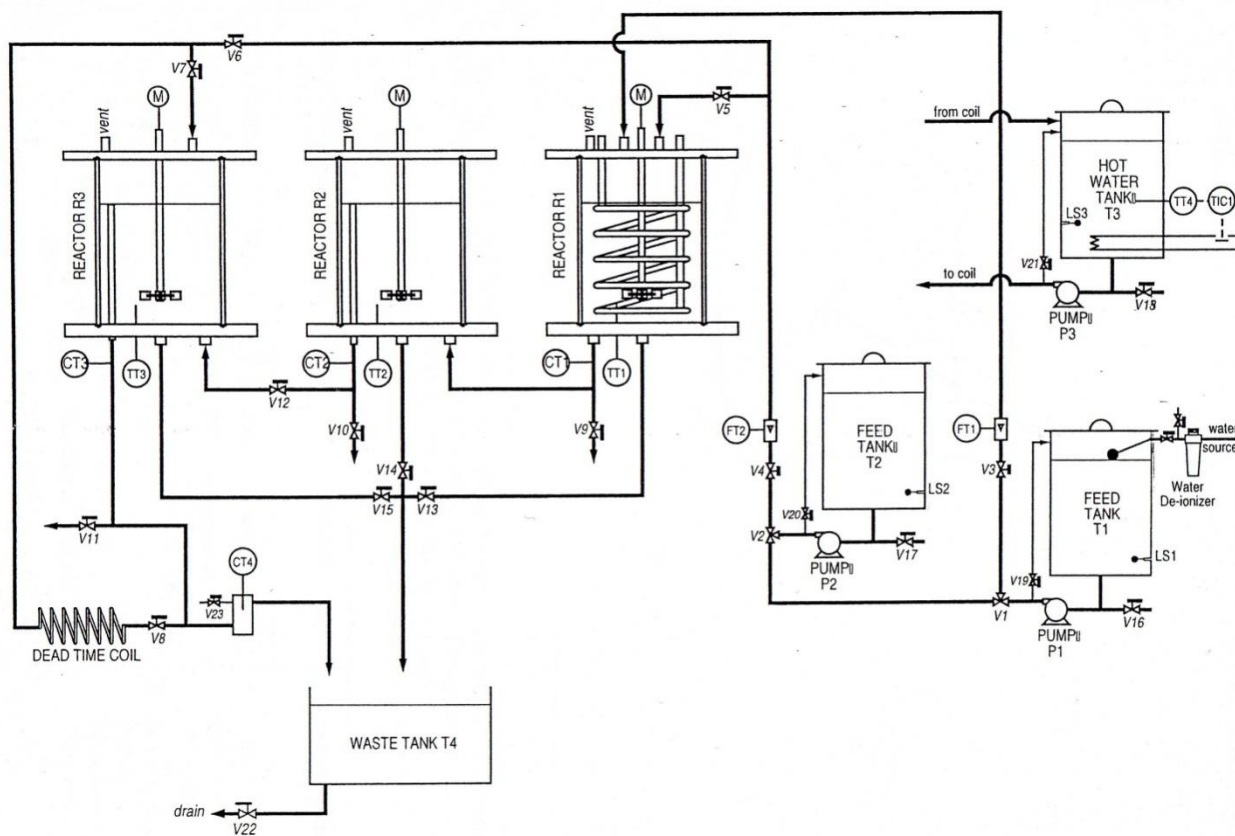


```

C:\MATLAB7\work\fikhri.m*
File Edit Text Cell Tools Debug Desktop Window Help
[Icons] Stack: Base
1 %assumption:1)tank is perfectly mixed, 2)the process is isothermal
2 %3)volume of the tank is constant
3 % fa(L/s),fb(L/s),ca(mol/L),cb(mol/L),v(L) is input
4 - fa=0.0033; fb=0.001667; ca=0.01; cb=0.1; v=1.5;
5 %ka=acetic acid equilibrium, kw=water equilibrium
6 - ka=1.778*10^(-5);
7 - kw=1*10^(-14);
8 %t is time, i refer to iteration
9 - for i=1:200;
10 - t(i)=i;
11 %xa and xb is concentration of acid & base solution
12 - xa(i)=fa*ca/(v/t(i)+fa+fb);
13 - xb(i)=fb*cb/(v/t(i)+fa+fb);
14 %OH,Na,H is concentration of ion hydroxide,sodium& hydrogen
15 %ka(OH^3)+(OH^2)(kw-ka*Na+ka*xa)+OH(-kw*Na-ka*kw)-kw^2=0 where Na=xb
16 - y(i,:)=[ka kw-ka*xb(i)+ka*xa(i) -(kw*xb(i)+ka*kw) -kw^2];
17 %the true value of OH is the positive value which is real root
18 - z(i,:)=roots(y(i,:));
19 - OH=z(z>0);
20 - H(i)=kw/OH(i);
21 - ph(i)=-log10(H(i));
22 - end
23 - plot(t,ph);

```

APPENDIX B
PROCESS DIAGRAM FOR STIRRED TANK REACTORS IN SERIES



APPENDIX C**TABLE FOR FIGURE 10, 11 AND 12****Table for Figure 10**

Fa is constant at 0.0033 L/s

Fb (L/s)	pH
0	3.4224
0.0001	4.3924
0.0002	4.9299
0.0003	5.7099
0.0004	11.1871
0.0005	11.5739
0.0006	11.7680
0.0007	11.8967
0.0008	11.9922
0.0009	12.0674
0.001	12.1291
0.001667	12.3753

Table for figure 11

Fa is constant at 0.0033 L/s, the origin of Fb is 0.00035 L/s and pH value at steady state (t=0)=7

time	ΔpH at -10% changes of Fb = 0.000315 L/s	ΔpH at +10% changes of Fb = 0.000385 L/s
0	0	0
20	0.9872	-2.82
40	0.9965	-3.101
60	0.9996	-3.2579
80	1.0012	-3.3645
100	1.0021	-3.4438
120	1.0028	-3.5061
140	1.0032	-3.5568
160	1.0036	-3.5991
180	1.0038	-3.6351
200	1.004	-3.6662

Table for figure 12

Fb is constant at 0.001667 L/s, the origin of Fa is 0.0171 L/s and pH value at steady state (t=0)=7

time	ΔpH at -10% changes of Fb = 0.01539 L/s	ΔpH at +10% changes of Fb = 0.01881 L/s
0	0	0
20	-3.1432	1.3535
40	-3.3704	1.3554
60	-3.4834	1.356
80	-3.5533	1.3564
100	-3.6013	1.3566
120	-3.6366	1.3567
140	-3.6636	1.3568
160	-3.6851	1.3569
180	-3.7025	1.3569
200	-3.717	1.357