

DEVELOPMENT OF BLOCK-ORIENTED MODEL FOR REACTIVE
DISTILLATION COLUMN: MTBE SYNTHESIS

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ABSTRACT

Reactive distillation is nonlinear in nature and hence, the development of suitable nonlinear models to reactive distillation poses challenging problem to the industry. A good and robust nonlinear model is necessary to study the dynamics of reactive distillation and also to achieve better controller performance using model-based control strategies. A first principle model of reactive distillation column was used as a platform in this research and the model equations are solved in MATLAB environment. The first principle model was validated using plant data. Then, the nonlinear empirical models were developed using the system identification toolbox in MATLAB. The data generated from the validated first principle model was used for the identification of nonlinear empirical block-oriented models namely, Wiener and Hammerstein models. Wiener model consists of linear dynamic block followed by nonlinear static block while Hammerstein model is the reverse connection order of Wiener model. In this research, a comparative study of different block-oriented models namely wavelet based Wiener model, wavelet based Hammerstein model and sigmoidnet based Wiener model was performed. In wavelet based Wiener and Hammerstein models, wavelet nonlinear function was used to describe the nonlinear static block and Output Error (OE) model was used to describe the linear dynamic block. Conversely, in sigmoidnet based Wiener model, sigmoidnet nonlinear function was used to describe the nonlinear static block and Output Error (OE) model was used to describe the linear dynamic block. The selection of input sequence plays an important role in nonlinear model identification. In this research, two types of input sequences namely random Gaussian and random uniform were implemented for the identification of each model and the results were compared. The parameters of the models were estimated using iterative prediction-error minimization method. Sigmoidnet based Wiener model using random Gaussian input sequence was chosen for modeling the reactive distillation column as it shown better agreement with first principle model results compared to other block-oriented models. The model analysis results proved the stability and suitability of sigmoidnet based Wiener model in capturing the dynamics of the reactive distillation column.

ABSTRAK

Penyulingan reaktif adalah tak lurus secara semula jadinya. Oleh sebab itu, pembangunan model tak lurus yang sesuai bagi penyulingan reaktif merupakan permasalahan yang mencabar dalam industri. Model tak lurus yang baik diperlukan untuk mengkaji dinamik penyulingan reaktif dan juga mencapai prestasi kawalan yang lebih baik dengan menggunakan strategi kawalan berasaskan model. Model prinsip pertama telah digunakan sebagai platform dalam kajian ini dan persamaan-persamaan model diselesaikan dalam persekitaran MATLAB. Model prinsip pertama disahkan dengan menggunakan data loji. Kemudian, model empirik tak lurus dibangunkan dengan menggunakan kotak perkakas bagi sistem pengenalpastian dalam MATLAB. Data yang dijana daripada model prinsip pertama yang telah disahkan digunakan dalam pengenalpastian model empirik tak lurus berorientasikan blok iaitu model *Wiener* dan *Hammerstein*. Model *Wiener* terdiri daripada blok lurus dinamik diikuti oleh blok statik tak lurus manakala model *Hammerstein* adalah urutan berbalik kepada model *Wiener*. Dalam kajian ini, perbandingan model-model berorientasikan blok yang berlainan iaitu model *Wiener* berasaskan *wavelet*, model *Hammerstein* berasaskan *wavelet* dan model *Wiener* berasaskan *sigmoidnet* telah dilaksanakan. Dalam model *Wiener* dan *Hammerstein* berasaskan *wavelet*, fungsi tak lurus *wavelet* digunakan untuk mewakili blok statik tak lurus dan model ralat output digunakan untuk mewakili blok dinamik lurus. Sebaliknya, dalam model *Wiener* berasaskan *sigmoidnet*, *sigmoidnet* fungsi tak lurus digunakan untuk mewakili blok statik tak lurus dan model ralat output digunakan untuk mewakili blok dinamik lurus. Pemilihan urutan input memainkan peranan penting dalam pengenalpastian model tak lurus. Dalam kajian ini, dua jenis urutan input iaitu rawak *Gaussian* dan rawak seragam telah digunakan bagi pengenalpastian setiap model dan keputusan-keputusannya dibandingkan. Parameter model dianggarkan dengan menggunakan kaedah lelaran ramalan meminimumkan ralat. Model *Wiener* berasaskan *sigmoidnet* yang menggunakan urutan input rawak *Gaussian* telah dipilih dalam pemodelan turus penyulingan reaktif kerana telah menunjukkan persetujuan yang lebih baik dengan keputusan model prinsip pertama dibandingkan dengan model berorientasikan blok yang lain. Hasil-hasil analisis model membuktikan kestabilan dan kesesuaian model *Wiener* berasaskan *sigmoidnet* dalam mewakili dinamik bagi turus penyulingan reaktif.

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LIST OF SYMBOLS

$A(q)$	Polynomial function in linear model
a_{ij}	Coefficient of polynomial A
as_s	Scaling coefficient
aw_w	Wavelet coefficient
$B(q)$	Polynomial function in linear model
b_{ij}	Coefficient of polynomial B
bs_s	Scaling dilation
bw_w	Wavelet dilation
cs_s	Scaling translation
cw_w	Wavelet translation
d	Output offset
H	Linear dynamic
L	Linear coefficient
$N(\cdot)$	Static nonlinearity
nb	Number of coefficients in $B_1(q^{-1})$ and $B_2(q^{-1})$
na	Number of coefficients in $A_1(q^{-1})$ and $A_2(q^{-1})$
nk	Delay from input to output
P	Linear subspace parameter
Q	Nonlinear subspace parameter
Q_B	Reboiler heat load
r	Regressor mean
R	Reflux flow rate
XD	Top composition

XB Bottom composition

Y measured output

Y^* simulated output

LIST OF ABBREVIATIONS

ANN	Artificial Neural Network
ARMA	Autoregressive Moving Average
ARMAX	Auto-regressive moving average model with exogenous inputs
MISO	Multiple-input-single-output
NARMAX	Nonlinear auto-regressive moving average model with exogenous inputs
NARX	Nonlinear auto-regressive with exogenous inputs
OE	Output Error

CHAPTER 1

INTRODUCTION

1.1 Reactive Distillation Column

In many chemical industries, the chemical reaction and separation are usually performed separately. Instead of conducting reaction and distillation in different units, the performance of this conventional configuration can be significantly improved by the process intensification which combines both reaction and separation in a single unit. This process intensification is called reactive distillation. The integration of reaction and separation in reactive distillation column leads to smaller number of unit operations and higher energy efficiency as compared to the conventional configuration of reactors followed by separators (Taylor and Krishna, 2000; Luyben and Yu, 2008).

In order to describe the reactive distillation column process, let consider an example of a reversible reaction as below:



where the boiling points of the components in the order of $A > C > D > B$

Figure 1.1 demonstrates the schematic representation of a reactive distillation column. The reactive distillation comprises of three sections namely rectifying, stripping and reactive sections. The rectifying and stripping sections are located at the top and bottom sections of the reactive distillation column respectively while reactive section is located at the middle of reactive distillation column. The reactants A and B are fed to the reactive distillation column in which reaction will take place at the

reactive section. The function of the rectifying and stripping section is to separate the product of the reactions, C and D. Reboiler is used to provide heat required for the liquid vaporization in the column while condenser is used to condense the overhead stream of the column (Taylor and Krishna, 2000).

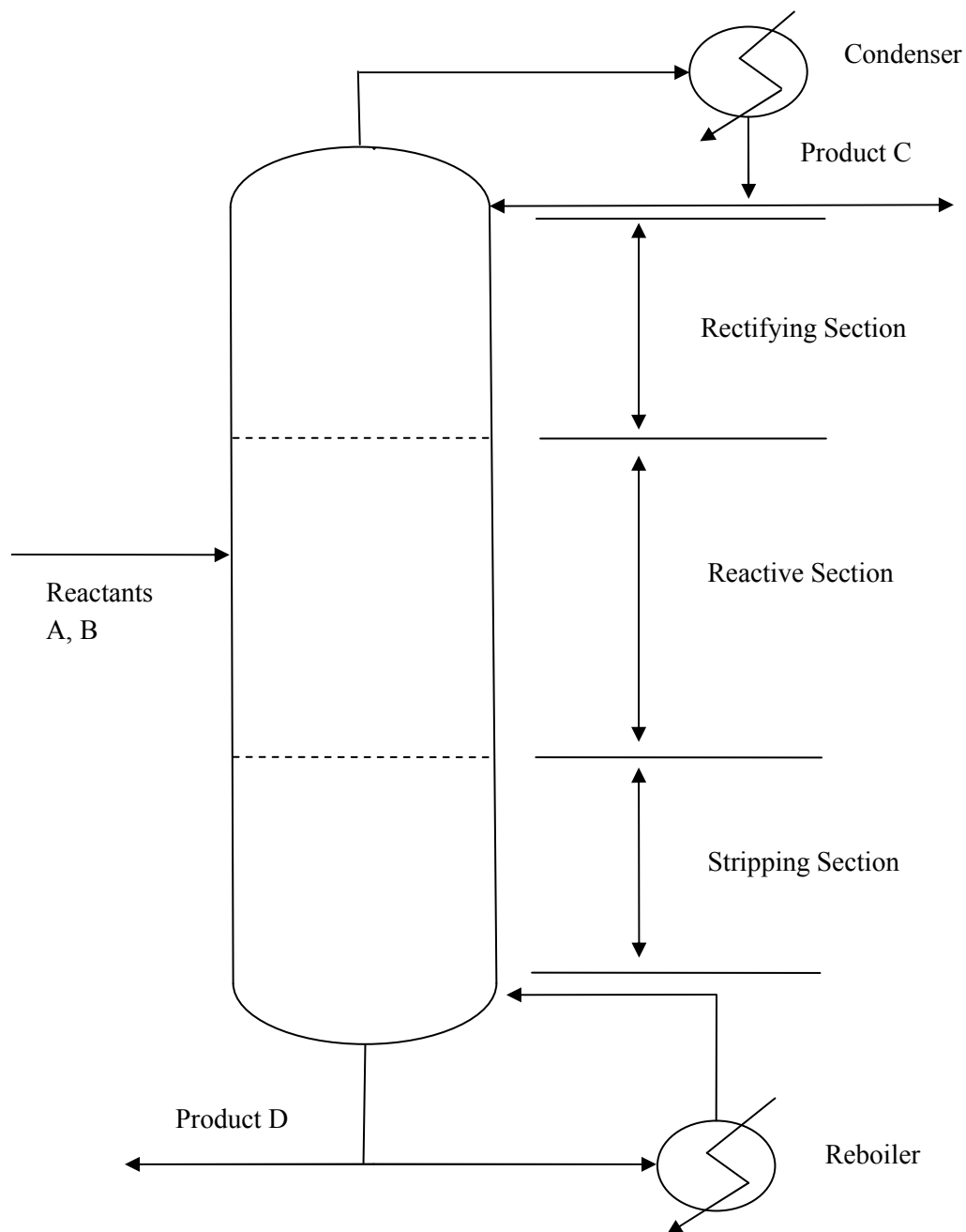


Figure 1.1: Schematic Representation of a Reactive Distillation Column

Reactive distillation offers several benefits over conventional processes which can be summarized as follows: (1) Reduction of unit operations which can result in significant capital savings (2) Enhanced conversion of reactants which can reduce the recycle costs (3) Increased desired product selectivity by removing one of the products from the reaction mixture or maintaining a low concentration of one of the reactants (4) The existence of azeotropes can be avoided by reacting away the azeotropes through reaction (5) Minimizing by-product formation (6) Reduction in reboiler duty in the exothermic reaction case in which heat of reaction can be utilized for liquid vaporization (Taylor and Krishna, 2000).

The advantages of reactive distillation compared to conventional processes have motivated a great interest in the application of reactive distillation technology, which is reflected by the expanding number of patents and publications of reactive distillation (Hiwale *et al.*, 2004). Examples of commercial successes in the development of reactive distillation include nylon 6,6 processes, methyl acetate processes, ethyl acetate processes and methyl tert-butyl ether processes (Doherty and Buzad, 1992). Recently, research on new processes were reported for the synthesis of 2-ethylhexyl dodecanoate (Omota *et al.*, 2003), methyl decanoate (Steinigeweg and Gmehling, 2003) and isopropyl palmitate (Bhatia *et al.*, 2006).

1.2 Reactive Distillation Column Control

Reactive distillation is a complex system which causes a challenging task in control due to the process nonlinearity and complex interaction between vapor-liquid equilibrium and chemical reaction (Sharma and Singh, 2010). Therefore, effective control of reactive distillation have to be developed and applied in order to increase product yield, minimize energy consumption and enhance product quality. Among the control strategies, nonlinear model based control strategy is revealed as an important advanced control technique (Goodwin *et al.*, 2001). There is a growing interest in nonlinear model based control strategy application with the rapid advances in computer technology over the past two to three decades (Pearson, 1999). One of the main challenges in the nonlinear model based control strategy implementation is the development of a suitable nonlinear model which can be used to describe the dynamic

of the process (Qin and Badgwell, 1998). Pearson (1999) explained that the complexity of nonlinear model based control is highly dependent on the structure and complexity of the nonlinear models. Pearson (1999) also explained that an acceptable nonlinear model shall meet the following important criteria: (1) Describe the dynamic of the process from one discrete time to the next discrete time (2) Sufficiently simple for controller design (3) Sufficiently accurate to produce satisfactory controller performance. The first condition is the discrete-time model requirement due to the nature of the computer control which is measured based on discrete-time instant t_k . Subsequently, the control action was formulated from these measurements into manipulated variable changes which were implemented at the next discrete-time instant t_{k+1} . The second condition is the process model complexity. A complex process model leads to complex control problems. Thus, the process model shall be simple enough for controller design. Lastly, the third condition is on the process model accuracy in yielding satisfactory controller performance. One of the important measures to assess the model accuracy is the qualitative agreement between the physical process and the approximate model.

1.3 Nonlinear Models

There are three types of nonlinear model available namely fundamental, empirical and hybrid models. Fundamental or white-box modeling approach generally gives more complete understanding than empirical modeling approach but they are generally complex and require correspondingly longer time to develop. In many nonlinear systems, it is extremely difficult and expensive to derive a suitable model of the process from fundamental modeling approaches. Also, fundamental model is revealed to be too complex for controller design. On the other hand, empirical or black-box modeling approach which is based on input-output data generally does not require the detailed understanding of the process considered, thus render the complexity of the process model can be avoided. Hybrid or grey-box modeling approach which relies on both input/output data and fundamental process understanding can be useful in development of nonlinear model. However, hybrid modeling approach can be only applicable when some physical insight of process is available and some parameters remain to be determined from observed data (Sjoberg, 1995). In addition, it is very difficult to distinguish the particular part of the process to be modeled by using either

fundamental model or empirical model. Due to the complexity of fundamental modeling and fundamental modeling element of hybrid modeling approach reasons, empirical modeling approach is utilised in this research in order to represent the dynamics of the reactive distillation column which can be used with advanced model based controllers. In this research, a case study for the dynamic modeling of an industrial reactive distillation process for the production of methyl *tert* butyl ether (MTBE) is investigated.

1.4 Problem Statement

In current practice of the MTBE industrial reactive distillation, the performance of the controller is determined by linearized dynamic model. Olanrewaju and Al-Arfaj (2005) has compared the performance of linearized dynamic model of a generic reactive distillation system with that of a rigorous nonlinear dynamic model. Their findings indicated that the linear model nicely averages the process nonlinearities of reactive distillation only when the magnitude input change is small which is below 6%. The deviation from base steady state of linear model increases with an increase in the magnitude of input change. Thus, it is important to develop a suitable nonlinear dynamic model that can be applied in model-based control applications on a wider range of operating system.

Several nonlinear black-box models are available in literature namely Volterra series, neural networks, ARMAX and block-oriented nonlinear model. Block-oriented nonlinear models combine both linear dynamic element and static nonlinear element in their structure. The main advantage of block-oriented nonlinear modeling approach is the simplicity in its structure and does not require high costs in identification tests and computation. The important models of this block-oriented model class are Wiener and Hammerstein models (Zhu, 2001). Hence, this research aims to attempt the Wiener and Hammerstein models for the modeling of reactive distillation column.

1.5 Research Objectives

The objectives of the research are

- i) To develop a suitable fundamental model based on first principles and to develop an algorithm in MATLAB environment to solve model equations
- ii) To validate the first principle model through plant data and to conduct open loop simulation studies under steady-state condition
- iii) To apply different block-oriented nonlinear models using the data obtained from validated first principle model and choose the best block-oriented nonlinear model
- iv) To perform model analysis in order to prove the suitability and stability of the best selected model based on model validation results in modeling the dynamics of reactive distillation column.

1.6 Scope of Work

The main focus of the research is to develop suitable nonlinear dynamic models which can be used in model based control strategies.

A first principle mathematical model based on total mass balance, component balance, enthalpy balance and reaction kinetics was developed. The calculation of activity coefficient was included in the model in order to account for the liquid phase non-ideality of the system. Simulation studies under steady-state and unsteady-state conditions were carried out to validate the mathematical model using real plant data. The Murphree tray efficiency used in the first principle model was approximated using steady-state plant data in order to increase the model accuracy. The data generated from the validated first principle model was used for the development of nonlinear black-box block-oriented nonlinear models.

Wiener and Hammerstein models are the important models of block-oriented nonlinear model class. Wiener model consists of a linear dynamic block followed by a nonlinear static block. On the other hand, Hammerstein model is the reverse of Wiener

model in which the nonlinear static block precedes the linear dynamic block. Two multiple-input-single-output (MISO) models were developed in this research to model the dynamics of the reactive distillation column. The first MISO model used reflux flow rate and reboiler heat load as inputs and bottom product composition as output, while the second MISO model used reflux flow rate and reboiler heat load as inputs and top product composition as output. In this research, wavelet based Wiener, wavelet based Hammerstein and sigmoidnet based Wiener models were compared in modeling of the reactive distillation column. In wavelet based Wiener and Hammerstein models, wavelet based nonlinear function was used to describe the nonlinear static block and Output Error (OE) model was used to describe the linear dynamic block. Conversely, in sigmoidnet based Wiener model, sigmoidnet based nonlinear function was used to describe the nonlinear static block and Output Error (OE) model was used to describe the linear dynamic block. The research also points out the effect of different input sequence designs namely random Gaussian and random uniform input sequence on the identification of each model and the results were compared. The parameters of the sigmoidnet based Wiener model were estimated using iterative prediction-error minimization method. Nonlinear model parameters estimation, model validation and analysis were carried out using system identification toolbox in MATLAB and the capability of the models to capture the dynamics of the reactive distillation column was verified with validated first principle model results.

1.7 Organization of thesis

The thesis is divided into five chapters. Chapter 1 outlines the background of the research on reactive distillation column. In addition, this chapter also describes the problem statement, objectives, scopes of research and organization of thesis.

Chapter 2 describes the dynamics in reactive distillation column. This chapter also discusses the types of nonlinear models applied for reactive distillation column which can be classified into three categories namely fundamental models, empirical models and hybrid models.

Chapter 3 outlines the methodology of this work. This chapter is divided into two important sections in which the first section describes the first principle modeling and simulation strategy while the second section describes the block-oriented nonlinear models development.

Chapter 4 discusses the important findings and results of the research. This chapter includes the steady-state and dynamic validation of first principle model with plant data. Nonlinearity study using steady-state analysis is also discussed in this chapter. Next, different block-oriented nonlinear models are compared and the suitable block-oriented models are chosen which can be used to represent the dynamics of the reactive distillation column. Finally, model analysis of block-oriented models is presented.

Chapter 5 presents the conclusion of the research. The recommendations are made based on the present work for future research directions.

CHAPTER 2

LITERATURE REVIEW

2.1 Dynamics in Reactive Distillation Column

Nonlinear behaviors such as multiple steady states, sustained oscillation and internal state multiplicities are observed in reactive distillation processes due to complex processing configurations which involve the interaction of the reaction kinetics and distillation of vapor-liquid (Katariya *et al.*, 2006). There are two types of multiple steady states occur in reactive distillation column namely input multiplicities and output multiplicities. Input multiplicities occur when different sets of input variables produce the same set of output variables. Output multiplicities occur when a set of inputs produce different values of output variables.

Ciric and Miao (1994) carried out homotopic continuation studies to explore the steady state multiplicities in a reactive distillation column producing ethylene glycol from ethylene oxide and water. Their investigation resulted in three-branch multiplicity at large values of holdup volume and a complex switchbacking multiplicity at small value of holdup volume. Their drawback indicated that the multiplicities observed were mainly due to coupling between the bilinear reaction rate and the large volatility differences. Feed or holdup volume distribution, temperature dependency of reaction rate and the exothermic heat of reactions were not the factors causing multiplicities in the reactive distillation column.

Eldarsi and Douglas (1998) investigated the multiple steady states in MTBE catalytic distillation column. Their findings revealed that methanol flow rate was a critical feed flow rate to determine whether single steady state or multiple steady state

solutions exist in reactive distillation processes. Their simulation studies also revealed that the steady state solution only exist when above or below the critical value of molar feed ratio (methanol/butylenes) take place.

Sneesby *et al.* (1998) investigated the multiplicity and pseudo-multiplicity in Methyl Tert Butyl Ether (MTBE) and Ethyl Tert Butyl Ether (ETBE) reactive distillation. Their investigation resulted in input multiplicities of bottom temperature, isobutylene conversion and ETBE product purity when the reboiler duty varies at fixed reflux flow rate. They concluded that the input multiplicities occurred due to the need to optimize the heat input to the column at desired isobutylene conversion and ETBE product purity. Output multiplicities were observed for either one of the conditions applies : condition (1) $dD/dL > 0$ or condition (2) $dB/dQ > 0$, where D, L, B and Q refer to distillate flow rate, reflux flow rate, bottom flow rate and reboiler duty respectively. On the other hand, pseudo-multiplicity occurred when molar inputs were used rather than mass inputs due to the parallel between output transformation and the input transformation as explained by Jacobsen and Skogestad (1991). Thus, it was necessary to conduct simulation studies in term of mass inputs only.

Wang and Wong (2006) reported that output multiplicities occur at high isopropanol purity when all the unreacted propylene was refluxed at the top of reactive distillation. The design was extremely sensitive to stoichiometric balance in the production of high purity isopropanol. A slight decrease in water feed resulted in large increase in reboiler feed while a slight increase in water feed resulted in significant purity decrease of isopropanol. An alternative design proposed which employ a small reflux ratio and recycle some excess propylene using a recycled feed eliminate the output multiplicity although input multiplicity remains to be found. This design results in less sensitivity to variation in stoichiometric balance.

Katariya *et al.* (2006) revealed that Damkohler number, Da was an important parameter that resulted in nonlinear effect in reactive distillation column for the synthesis of Tert Amyl Methyl Ether (TAME). A step change in the 2-methyl-1-butene (2M1B) concentration in the feed was implemented to investigate the dynamic response of the column reboiler temperature and TAME purity in bottoms. The analysis was

carried out by using two different Damkohler number ($Da = 1$ and 2). Their findings revealed a nonlinear behavior of sustained oscillation in the open loop simulation for Damkohler number ($Da = 2$). On the other hand, the first order response was indicated in the simulation studies for Damkohler number ($Da = 1$). An increase in the size of step change resulted in an increase in amplitude of the sustained oscillation. They also observed an internal state multiplicity which was an unusual behavior occurs in reactive distillation. For the same conversion of amylene and TAME purity in bottoms, composition and temperature profiles near the feed stage was different. Internal state multiplicity occurred when there were two or more steady-state compositions and temperature profiles realized for same input with identical top product composition, x_D and bottom product composition, x_B .

Kumar and Kaistha (2008) investigated the effect of reboiler duty on the temperature and conversion variation in the reactive tray for both fixed reflux rate and reflux ratio. At fixed reflux flow rate, the reactive tray temperature exhibited output multiplicities with respect to reboiler duty which may render the reactive distillation column to drift from the desired high conversion steady-state to low conversion steady state despite the steam valve position was kept constant. On the other hand, output multiplicities were not shown in the reactive tray temperature with respect to reboiler duty when the reflux ratio was fixed, thus preventing the reactive distillation to deviate from desired conversion steady state. Instead of adjusting the reflux flow rate to be in ratio with the distillate, it was better to adjust the reflux ratio in order to maintain desired temperature in the reactive tray of reactive distillation column. This phenomenon may occur due to upstream fluctuations in the reflux flow rate when the reflux flow rate is fixed.

Kumar and Kaistha (2008) also investigated the input effects of reboiler duty, acetic acid flow rate and methanol flow rate on the temperature variations on reactive tray and stripping tray of reactive distillation column. Input multiplicities were not shown in the stripping tray temperature with respect to any these three inputs. However, the reactive tray temperature exhibited input multiplicities to all the three inputs. They explained that this phenomenon occurs when the acetic acid is fed in large excess relative to methanol or if the reboiler duty is lowered sufficiently.

The observation of nonlinearity behaviors in reactive distillation column namely multiple steady states, sustained oscillation and internal state multiplicities motivates the exploration of suitable nonlinear models to be used in reactive distillation column.

2.2 Nonlinear Process Models

There are three types of nonlinear models available for the implementation of nonlinear model based control strategies namely fundamental models, empirical models and hybrid models.

2.2.1 Fundamental Models

Fundamental models or first principle models are derived by applying mass, energy and momentum balances to the process. In the absence of spatial variations, the resulting models have the general form

$$\dot{x} = f(x, u) \quad (2.1)$$

$$0 = g(x, u) \quad (2.2)$$

$$y = h(x, u) \quad (2.3)$$

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 (2.1) and algebraic equations (2.2) are derived from conservation laws and various constitutive relations, while the output equations (2.3) are chosen by the control system designer.

Fundamental modeling approach practically demonstrates the true process of a reactive distillation by means of rigorous mass balance, energy balance, non-ideality of liquid-vapor in the model. Fundamental models are highly constrained with respect to their structure and parameters. Thus, less process data is required to develop these models. In addition, model parameters may be estimated from laboratory experiments and routine operating data which can avoid time-consuming plant tests. The fundamental model can be extrapolated over a wide range of operating regions as long

as the underlying assumptions are valid. The main disadvantage of fundamental modeling approach is that the dynamic model obtained may be too complex to be applied for control purposes. Fundamental model often involves 10^2 - 10^3 differential equations and a comparable number of algebraic relations for a realistic complexity of processes (Pearson, 2003). Thus, simplification of the model is needed with significantly fewer equations but still constrained by the underlying physics of the process. Validation of the fundamental model with plant data is needed prior to be applied in the control application (Henson, 1998). There are two types of fundamental model of reactive distillation column namely equilibrium model and non-equilibrium model.

2.2.1.1 Equilibrium Models

The equilibrium model assumes vapor-liquid equilibrium at every stage of reactive distillation column. The departure from equilibrium of reactive distillation column is applied by incorporating Murphree efficiency in tray columns or the height equivalent of a theoretical plate (HETP) for packed columns. The equations that incorporated in the equilibrium model are known as the MESH equations (Material balance, Equilibrium relationship, Summation balance and Heat balance) (Taylor and Krishna, 2000). Reduction or simplification method is significant to derive a suitable fundamental model which can be implemented in nonlinear model-based control strategies.

Espinosa *et al.* (1994) developed a simple and effective nonlinear model for synthesis and control of reaction distillation systems. Their assumptions in the development of simplified dynamic model included neglect of vapor holdups, heat losses to the environment and heat of reactions. Equimolar overflow and chemical and physical equilibrium were assumed. A suitable transformation of variable was proposed to define a new set of state variables which resulted in identical balance equations with conventional distillation. A reduction method using orthogonal polynomials was used to approximate the transformed composition and flow profiles of the reactive distillation column in order to further reduce the computational time. They concluded that the reduced model was in good agreement with rigorous model for ideal quaternary system.