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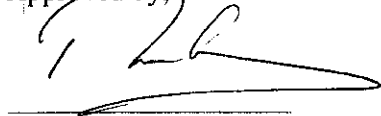
Control of Reactive Distillation Column

By

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Approved by,

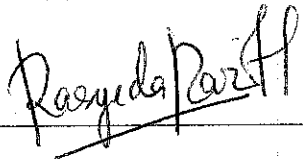


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CERTIFICATION OF ORIGINALITY

This is certify that I am responsible for the work submitted in this project, that the original work I as my own except as specified in the references and acknowledgements, and that original work contained herein have not been undertaken or done by unspecified sources or persons.



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ABSTRACT

Reactive distillation is a process of simultaneous reaction and distillation in a single unit in which the reactant and products are continuously separated from the liquid reaction phase into nonreactive vapor phase. In this project, a developed steady-state model of reactive distillation is simulated and modified into dynamic-state model. The dynamic-state model can be used to study the behavior of the column. The reaction involved in this study is a reversible reaction, i.e., esterification of acetic acid and ethanol into ethyl acetate and water. One of the reactants is fed in excess to shift the reaction equilibrium to the right. The open loop step change was performed to study the dynamic effects of changing column parameters towards the compositions profile for distillate and bottom. The result obtained was used to determine the initial controller settings which then can be further optimized. Feedback controller is applied to the column using proportional and integral action to counter the disturbance.

In the course of applying the feedback controllers, interaction between the possible control loops was studied to identify the best control strategy. From the simulation performed, the control strategy applied seems to provide stable response. From the examination of complete simulation, the model works within the reactive distillation process basis principles. The approach and results from this project is essential for further study involving more complex and rigorous model of reactive distillation process.

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Faculty and FYP Committee in Chemical Engineering Program of University Technology PETRONAS, for allocating this project title for me. With this opportunity, I am able to explore and deeper my understanding, both in theory and practical. I learn to appreciate the importance of computer programming in enhancing chemical processes.

Indeed, the production of this book has touched and drawn upon all those close to me. Thanks to my family and friends for their enthusiasm encouraged me to persevere.

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ABBREVIATIONS

ETBE	ethyl-tert-butyl-ether
MTBE	methyl-tert-butyl-ether
ODE	ordinary differential equation
RD	reactive distillation
RGA	relative gain array
CV	controlled variable
PID	Proportional, Integral and Derivative

Subscript

i	component
n	stage number
sp	set point

NOMENCLATURE

A	acetic acid
B	ethanol
C	ethyl acetate
D	water
x_a	acetic acid mol fraction (liquid phase)
x_b	ethanol mol fraction
x_c	ethyl acetate mol fraction
x_d	water mol fraction
α	relative volatility
M	total mass balance
γ	Liquid phase activity coefficient

CHAPTER 1

INTRODUCTION

1. INTRODUCTION

1.1 Background of Study

Reactive distillation is a process where the synthesis of a chemical compound and separation from reactant and by-products is realized within a single equipment unit. It applied concept of the conventional distillation with reactor which is performed in a single equipment unit called reactive distillation column. The reactants are converted to the product in a reaction zone located within a distillation column, simultaneous separation of the product in a separation zone and recycling of the unreacted reactants back to the reaction zone. Reactive distillation is a relatively new concept in industrial practice yet a high promising chemical process technology. It was patented for methyl-tert-butyl-ether (MTBE) synthesis in 1980 (Smith, 1980) and was commercialized two years later (Smith and Huddleston, 1982).

The concept applied is an essential in process design since it is economically favorable in many cases. Much attention, research and study have concentrated on conventional distillation, which is reliable, simple and nevertheless gives a lower cost-efficient approach to reaction and separation. In reactive distillation, the reaction and separation step are combine into a single reactive distillation step. Since its introduction into the industry in 1980s, reactive distillation has become very popular and considered panacea for reaction and separation problems (Sethi and Singh, 2000). For esterification reactions, it has been first pronounced by Backhaus in 1921, however only a small number of experimentally validated model for reactive distillation columns have been published.

One general application of reactive distillation, described by Terrill, Sylvestre, and Doherty, is the separation of a close-boiling or azeotropic mixture of two components, where a reactive entrainer is introduced into the distillation. One of the reactant reacts with the reactive entrainer and separates from the azeotropic mixture thus azeotropic problem is reduce. Other application of reactive distillation can be seen in industrial for

reaction of formaldehyde and methanol to produce methylal and water, using a solid acid catalyst, as described by Masamoto and Matsuzuki. Commercial industrial application of reactive distillation includes reaction of isobutene with methanol to produce methyl-tert-butyl ether (MTBE), using a solid, strong-acid ion-exchange resin catalyst, as patented by Smith and further developed by DeGarmo, Parulekar and Pinjala (J.D Seader, 1998). One of the applications is used in esterification of acetic acid with methanol to produce methyl acetate and water, using sulfuric acid catalyst, as patented by Agreda and Partine, and described by Agreda, Partin and Heise which attracts point of interest in this research project.

In general, the potential advantages of reactive distillation in comparison to the conventional one are significant. The capital cost resulting from the merging of the two units separately into a single item of equipment is much reduced. For reactions with high heat of reaction, the need for inter-stage heat transfer equipment is eliminated. All heat transfer takes place at the reboiler and condenser. The reactant conversion can be increased by continuously recycling reactant to the reaction zone and removing the products from reaction zone to improve the reaction stoichiometry. Furthermore, with excess of one of the reactant help the reaction equilibrium to favor on the right side. The principle of increasing conversion by continuous removal of product from reacting mixture and feed excess of one reactant is in accordance with the Le Chatlier's principle.

For reactive distillation, at any point near the catalyst the heat of reaction causes additional mass transfer due to vaporization and condensation compare to distillation alone. Therefore, heat of reaction will not affect the temperature and hence does not affect the equilibrium. In other words, energy efficiency is increased through direct utilization of the heat of reaction for separation. However, the drawback is that the advantages can be eliminated by kinetics: equilibrium and mass transfer issues, catalyst placement, and the compatibility of separation and reaction condition for a given system.

1.2 Problem statement

1.2.1 Problem Identification

A growing application of reactive or catalytic distillation is the combined operation of chemical reaction and distillation in one vessel. To be effective, it must be possible to carry out the reaction and phase separation at the same pressure and range of temperature, with reactant and product favoring different phases so that an equilibrium-limited reaction can go to completion.

The main task in this project is to simulate a reactive distillation column by implementing the steady-state model which had been developed previously for further study and to improve the effectiveness in controlling the reactive distillation. Therefore, this project needs to validate available the models that have been developed previously on MATLAB program with literature data and evaluate several control strategy possible for the reactive distillation column. The models will be further studied in steady-state and dynamic simulation. The MATLAB program was important tool used in this research and is applied to design and perform the simulation of the selected control strategy for the reactive distillation column. Through simulation, the effective pairing of controlled and manipulated variables is identified specifically by applying the Relative Gain Array (RGA). Therefore, the dynamic model is able to resemble an ideal quaternary reactive distillation column. The approach and result s from this project is essential for study involving other reaction especially involving multicomponents in the reactive distillation process and as the starting point for more complex or rigorous model of reactive distillation process.

In this project, the study was done specifically based on the synthesis reaction of ethanol and acid acetic to form ethyl acetate and water. Research done previously had specified 13 equilibrium stages for the reactive distillation which include the overhead receiver stage, the rectifying section, the reactive section consist of 6 stages, the feed stage, the stripping section consist of 4 stages and the reboiler. Every stage performs different composition for four respective components in achieving equilibrium state.

1.2.2 Significant of Project

Reactive distillation is relatively new, thus limited number of experimentally validated models were available. In most studies, experimental validation was focused on the steady state behavior of the reactive distillation columns. By conducting control strategy on the simulation model, a better understanding could be developed leading to better controller design to handle the system. At the completion of this project, useful knowledge in various scopes could be gathered, some leaving for further study. The project also acts as a basic reference to future the researchers particularly in reaction and separation process field to expose them to the importance of applying reactive distillation column in the industry.

The importance of mathematical models for equipment design cannot be denied, including the reactive distillation column. By simulating the developed models into MATLAB, several operation parameters and variation of probable parameters will be studied from the process response result. The parameters that will be studied for the reactive distillation processes are the feed flowrate, feed composition, distillate withdrawal rate, reflux ratio, number of stages and pressure of condenser and reboiler. For expansion of study in this area, the column will be taken into account with the hydraulics and pressure drop inside the column since extreme in either vapor or liquid flowrate will cause undesired vapor traffic. It is also necessary to have the design tower specification before operating any processes such as size of reaction zone, catalyst requirements, column diameter and feed location.

1.3 Objectives and Scope of Study

The main objective of this research project is to design and simulate appropriate control strategy for the specific reactive distillation column. The simulation was done using MATLAB program. The model is to be validated with available literature data. Previously model developed on steady state was extended to incorporate dynamic behavior which is then used for control study. By observing the steady-state and dynamic response of the system, the characteristic and performance of the column can be revealed.

Towards developing and designing possible control strategy for the reactive distillation, this project provides an opportunity to understand the features and common used in MATLAB software.

For this project, four main stages in obtaining and optimizing the control strategy were identified as below:

1. Simulation of a steady state reactive distillation column.
2. Simulation of a dynamic state reactive distillation column.
3. Identification of Process Interaction.
4. Optimization of controller settings.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2. LITERATURE REVIEW AND THEORY

2.1 Literature Review

Reactive Distillation is a unit operation that is gaining acceptance in chemical process and petroleum plants. The combination of reaction and separation has significant advantages in many chemical systems. However, there are only limited experimentally validated models for reactive distillation column published up to now. More researchers are getting involved in experimental studies or modeling and simulation work to further explore more possible application of reactive distillation process in industry.

Commercial application of reactive distillation in industry is one of literature resource that is easily available for study purposes in this field. One of the early literatures is transalkylation process of close-boiling meta and para xylenes by formation of tert-butyl meta-xylene by Saito et al (1971). Some of the latest works on reactive distillation are discussed below.

2.1.1 MTBE production from synthesis reaction between Isobutylene and Methanol

The Methyl Tertiary Butyl Ether (MTBE) and Polypropylene plants are both Malaysia refineries which uses reactive distillation column in their production. It produces MTBE through the synthesis reaction between methanol and isobutylene in liquid phase. The reaction is an exothermic reaction which uses selected resin as the reaction catalyst. Reaction takes place at its reaction temperature 300-400⁰C and pressure in the range of 700 – 800 kPa (operating manual of Methyl Tertiary Butyl Ether (MTBE) Malaysia). The reactive distillation column, namely the Finishing Reactor Section, is where the distillation and reaction occurs simultaneously achieving the final conversion of isobutylene to MTBE product. The fractionation tower yields finished MTBE product from the bottom with C₄ raffinate with methanol entrained by the azeotrope at the top.

For optimization of operation, excess of methanol must be maintained in the center portion containing the ion exchange resin catalyst. Heat integration had been thoroughly utilized throughout the process.

2.1.2 Ethyl Glycol Reactive Distillation Column

A related by Kumar and Daoutidis (1999) is published on the modeling, analysis and control of ethyl glycol reactive distillation. The study is done on steady-state variation of the product purity with respect to the reboiler heat duty with a conventional model that assumes negligible vapor hold-up. The mathematical model presented consist of a set of differential and algebraic equation for each stage, where the differential equations include the total component mole balances in the liquid and vapor phase and overall enthalpy balance. Meanwhile the algebraic equations include the phase equilibrium relation, the ideal gas equation, the pressure drop correlation (Eckert and Kubicek, 1994) and Francis weir formula. Similar to this project, the ideal phase equilibrium relations (Raoult's Law), the saturation vapor pressures of the components are evaluated by the standard Antoine's equation.

2.1.3 Detrimental Influence of Excessive Fractionation on Reactive Distillation

this research by Sneesby et al (1998), is on designing several reactive distillation columns for various feed compositions and design philosophies using the production of ETBE as an example. Four different design philosophies are considered:

1. Base-case design (30 ideal design)
2. Maximum isobutylene conversion design
3. High ETBE purity design
4. Reduce fractionation design
5. Reduce fractionation and increased reflux design

The column designs are completed using simulation with Pro/II (Simulation Science, 1994).

The results from the simulation show that the ETBE purity was increased significantly and the overall column performance was enhanced for both types of feed when the number of theoretical stages was reduced. Moreover, reducing fractionation will cause higher ethanol concentration in the distillate. This is potentially harmful if there is no ethanol recovery equipment downstream process. They concluded that the best design of reactive distillation is one cooperated with high reflux ratios and a restricted number of theoretical stages as increasing the number of theoretical stages could actually be detrimental to process performance.

2.1.2 Design insights for reactive distillation

A research by studied on the design of reactive distillation. He studied the effect on reaction that occurred in the column with different reflux ratios. From the work, he found that the degree of conversion decreases as the reflux ratio increases. The result show that, the maximize conversion will be obtained when reflux ratio between lies between 1.5 and 2. He also observed that as the mixtures travel down the column, the separation tend to be more difficult compared to the upper section of the column. This was proven also using the McCabe-Thiele diagram.

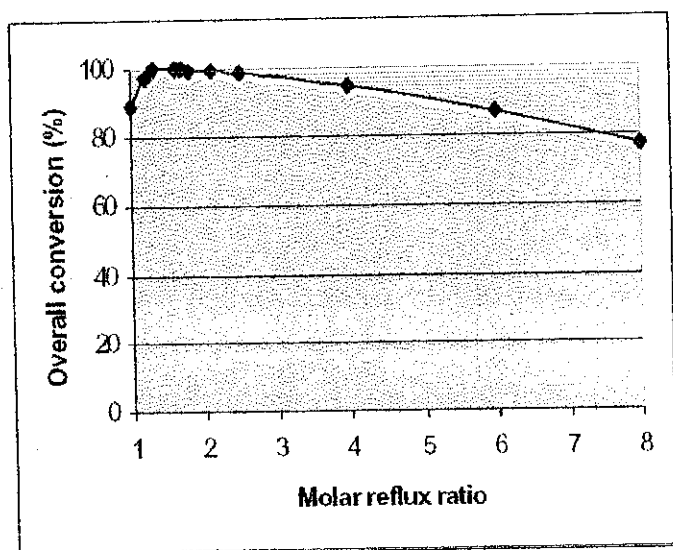


Figure 2.1: Effect of Molar reflux ratio to the overall conversion.

2.1.3 Recent Advances in Reactive Distillation - Effect of Reflux Ratio and Pressure

A related literature by M. F. Doherty and M. F. Malone, (Dallas Paper 203c, November 3, 1999) discussed and studied the effect of reflux ratio toward number of trays needed to obtain high product purity. The result from the study shows that, number of trays for separation is at minimum when reflux ratio is between 1.5 and 2.1. As the reflux ratio exceeding 2.1 and below 1.5, the column will be operated at higher number of trays. Upon all, the optimize reflux ratio is needed for process efficiency. In his research, he also study the behavior of the process at varies operating pressure. It is to study effect of operating pressure towards number of trays needed for the separation at a specific reflux ratio.

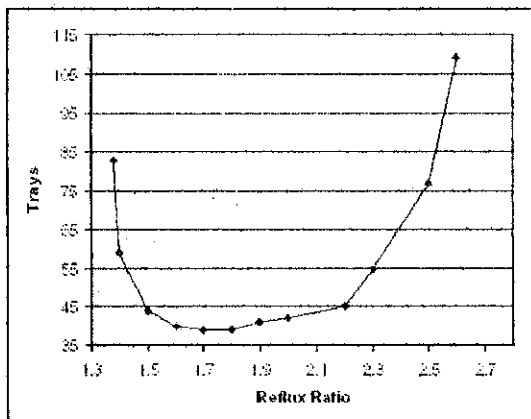


Figure 2.2

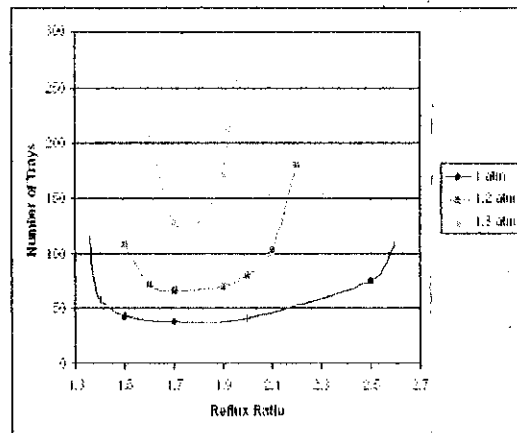


Figure 2.3

Figure 2.2: Effect of Reflux Ratio on number of stages requires.

Figure 2.3: Effect of Reflux Ratio and pressure on number of stages requires.

2.2 Control of Chemical Process

2.2.1 General Concept

For any process behavior with no controllers in the system it is called open loop response. The dynamic behavior with feedback controllers include within the process is called the closed loop response. There are three type of variables involves in every process or system, which are controlled variables, manipulated variables and load/ disturbance variables.

For a reactive distillation column the controlled, manipulated and load variables are identified as below:

1. Controlled Variables

Controlled variables for reactive distillation column are distillate product and bottom compositions. The component to be controlled is the ethyl acetate composition in bot streams.

2. Manipulated Variables

For a reactive distillation column, the manipulated variables are the reflux and distillate flow or the reflux ratio, the coolant flow (condenser duty), the steam flow (reboiler duty) and bottom withdrawal. For this project, the effect of reflux ratio and reboiler duty towards the process output response will be monitored

3. Load/ Disturbance

Load or disturbance for this process are changes of the feed flow rates and feed composition.

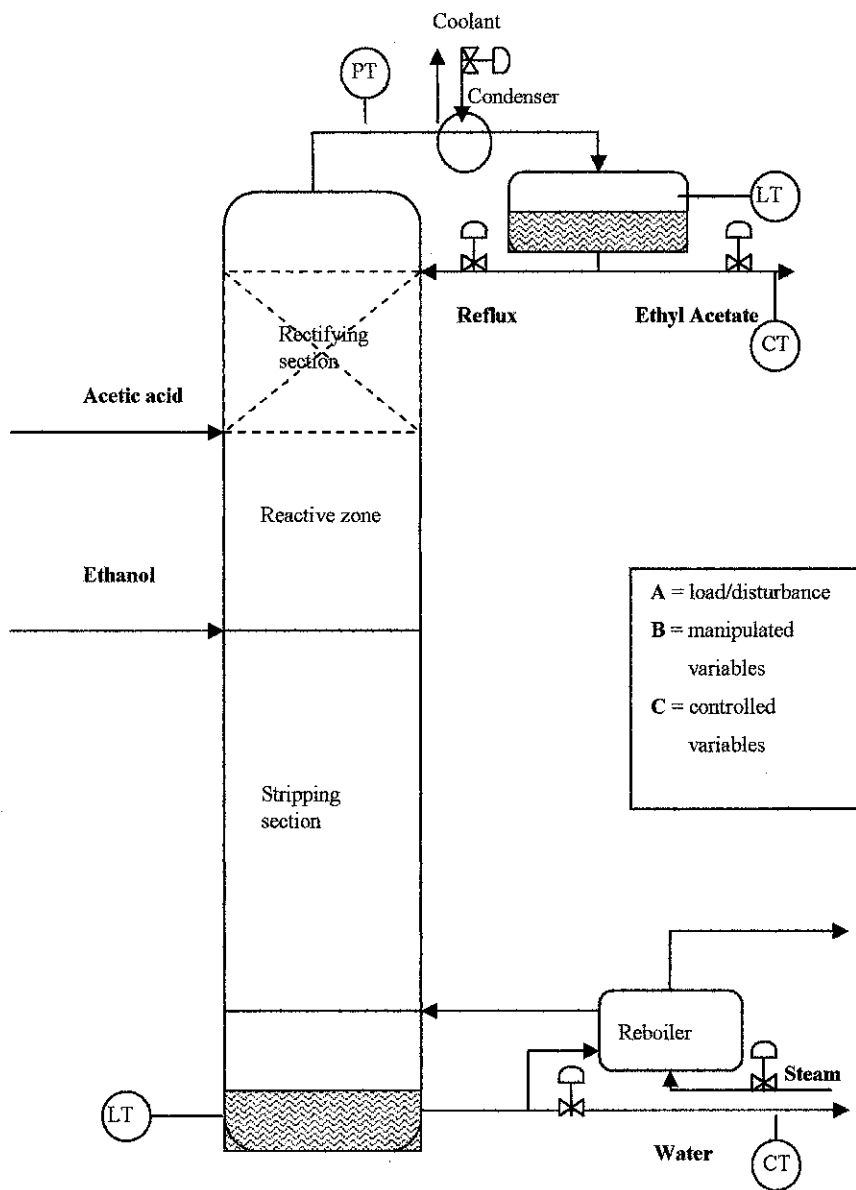


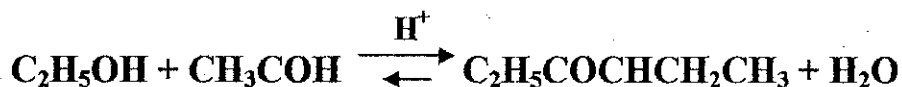
Figure 2.4 Schematic Diagram of a Distillate Column with Column Variables

2.3 THEORY

2.3.1 Reaction and Separation

Reactive distillation process involves reversible reaction of singular or bimolecular reactants forming product and byproduct in certain process. To simplify analysis done on the process, the reaction can be assumed to be an elementary reaction which the order of reaction of each species is identical with the stoichiometric coefficient of that species.

The elementary reaction for the esterification process which been studied in this research project can be written as bellow:



Esterification is a process where acid catalyzed condensation of an alcohol reacts with a carboxylic acid yields and ester and water. $\text{C}_2\text{H}_5\text{OH}$ (ethanol) is less volatile component than CH_3COH (acetic acid) and are denoted as component A and B throughout this project. In this project, it is identified that component A will be fed at different stage from component B where A will enter the column at higher column stage above the feed stage of component B. The reason is, this will increase the effectiveness for contacting mode between reactants. More volatile product, $\text{C}_2\text{H}_5\text{COCHCH}_2\text{CH}_3$ (ethyl acetate) denoted as component C will be constantly removed as the distillate product, thus the rate of reverse reaction will be very small and the reaction continue to proceed towards completion in the forward reaction.

2.3.1.1 Rate Law

To illustrate the effects of a reactive distillation, let's take the equation:



Taking the reaction to be elementary, the rate law is:

$$r_r = k \left(C_A C_B - \frac{C_C C_D}{K} \right)$$

In reactive distillation, one of the products is continually removed causing the concentration of the removed product to be kept at low value. As a result the forward reaction will always have higher reaction rate rather than the reverse reaction thus providing more product.

$$r_A = k \left(C_A C_B - \frac{C_C C_D}{K} \right)$$

Further, the removal of byproduct can also be done by introducing a reactive entrainer, for example benzene, which reacts with water to form azeotropic component and separates from the desirable product.

2.3.1.2 Rate Equation

$$r_{Cn} = k_1 C_{nA} C_{nB} - k_2 C_{nC} C_{nD} \quad (2.1)$$

$$k_1 = 29000 e^{-7150/T} \quad (2.2)$$

$$k_2 = 7380 e^{-7150/T} \quad (2.3)$$

2.3.1.3 Vapor Liquid Equilibrium (VLE) Model

The equilibrium relation between vapor and liquid phase is;

$$y_i = \gamma_i k x_i \quad (i=\text{component A,B,C}) \quad (2.4)$$

γ = Liquid phase activity coefficient

Where $\sum y_i = 1$

The nonideality in liquid phase is represented by liquid phase coefficient. If we assume that $\gamma=1$ the equation above reduces to the familiar relation known as Raoult's Law for ideal solution and the phase equilibrium calculation would be considerably simple.

However such an approximation would not represent the real condition occurs in the process.

2.3.1.4 Volatility

The volatility of the component will determine the main product in the distillate and bottom. The distillate will be rich with light products and bottom will be rich with heavy products.

2.3.1.5 Mathematical Modeling

The reaction occurs in all trays, thus the material and component balance for tray n is:

i) *Material balance for tray n*

$$\frac{dM}{dt} = L_{n-1} + V_{n+1} - L_n - V_n + \sum r_i \quad (2.5)$$

ii) *Component balance for component i at tray n*

$$\frac{d(x_i)}{dt} = \frac{1}{M} [L_{n-1}x_{n+1,i} + V_{n+1}y_{n+1,i} - L_nx_{n,i} - V_ny_{n,i}] + (-k_1x_{n,A}x_{n,B} + kx_{n,C}x_{n,D}) \quad (2.6)$$

2.4 Process Control

2.4.1 Mc Cabe Thiele - Stage Method for Trayed Towers

General distillation operation consists of a column containing the equivalent of N theoretical stages; a total condenser in which the overhead vapor leaving the top stage is totally condensed to give a liquid distillate product and liquid reflux that is returned to the stage; a partial reboiler in which liquid from the bottom stage is partially vaporized to give a liquid bottom product and vapor boilup that is returned to the bottom stage and an intermediate feed stage. By means of multiple, countercurrent contacting stages arranged in a two-section cascade with reflux and boilup, it is possible to achieve a sharp separation between the components, unless an azeotrope (J.D. Seader, 1998).

For one or two stage feed configuration, the feed which contains a more volatile (light) component and a less volatile (heavy) component enters the column at feed stage/s. At the feed-stage pressure, the feed may be a liquid vapor or mixture of liquid and vapor.

The goal of distillation is to produce from the feed a distillate rich in the light key (i.e., $x_{C_{Dist}}$ approaching 1) and bottoms product rich in the heavy key (i.e., $x_{C_{Boil}}$ approaching 0.0). The ease or difficulty with which the separation can be achieved depends on the relative volatility, α , of the components (heavier key as the base for α) where

$$\alpha_{1,2} = K_1/K_2$$

If the two components form ideal solution form ideal solutions and follow the ideal gas law in the vapor phase, Raoult's law applies to give

$$K_1 = P_1^s / P \quad \text{and} \quad K_2 = P_2^s / P$$

Thus, the relative volatility is given simply by the ratio of vapor pressure, $\alpha_{1,2} = P_1^s / P_2^s$ and thus is a function only of temperature as given in Antoine's equation,

$$\log_{10} p^* = A - \frac{B}{T+C}$$

As the temperature (and therefore the pressure) increases, $\alpha_{1,2}$ decreases. At the convergence pressure of the mixture, $\alpha_{1,2} = 1.0$ and separation cannot be achieved at this or any higher pressure.

2.4.2 Interaction between Variables

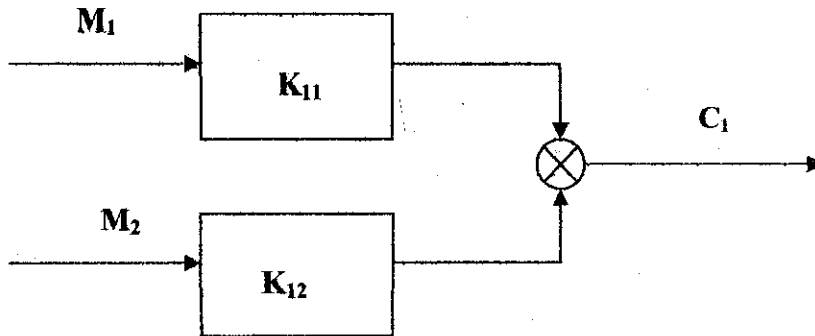
A typical distillation column has five controlled variables and five manipulated variables. The controlled variables are product composition (top and bottom), column pressure, and the liquid level in the reflux drum and column base. The five manipulated variables are product flows, distillate and bottom, reflux flow and the heat duties for both condenser and reboiler. For the reactive distillation developed using the program, it only take into consideration the respond towards top and bottom product purity. In this project, for simplicity of the dynamic modeling, it is assumes that the liquid hold up at each tray is maintain constant and similarly the liquid level in the reboiler and reflux drum.

Basically, the process is described by the Transfer Function below;

$$C_1 = K_{11}M_1 + K_{12}M_2$$

$$C_2 = K_{21}M_1 + K_{22}M_2$$

where K_{ij} denotes the steady state gain between C_i and M_j . M_1 is the perturbation for the manipulated variable which is the reflux flowrate when sustaining a load disturbance while M_2 is also the perturbation for boil-up vapor when one of the feed property changes.



According to Bristol's relative Gain Array method, his approach is based on the concept of a relative gain, λ_{ij} between a controlled variables and manipulated variable which is defined to be between the dimensionless ratio of two steady-state gains:

$$\lambda_{ij} = \frac{(\delta C_i / \delta M_j)_M}{(\delta C_i / \delta M_j)_C} = \frac{\text{open loop gain}}{\text{closed-loop gain}}$$

for $i = 1, 2, 3 \dots n$ and $j = 1, 2, 3 \dots n$

$(\delta C_i / \delta M_j)_M$, denotes a partial derivative that is evaluated with all of the manipulated variables except M_j held constant. Thus $(\delta C_i / \delta M_j)_C$ can be interpreted as a closed-loop gain that indices the effect of M_j on C_i when all of the other feedback control loop are closed. It is convenient to arrange the relative gains in a relative gain array (RGA) denoted by Λ :

$$\Lambda = \begin{matrix} & \begin{matrix} M_1 & M_2 & \dots & M_n \end{matrix} \\ \begin{matrix} C_1 \\ C_2 \\ \dots \\ C_n \end{matrix} & \begin{pmatrix} \lambda_{11} & \lambda_{12} & \dots & \lambda_{1n} \\ \lambda_{21} & \lambda_{22} & \dots & \lambda_{2n} \\ \dots & \dots & \dots & \dots \\ \lambda_{n1} & \lambda_{n2} & \dots & \lambda_{nn} \end{pmatrix} \end{matrix}$$

To determine the recommended controller pair, the positive relative gains that are closest to one in each row and column is selected. The relative gain is used to pair the manipulated variable to the most suitable controlled variable in any system.

2.4.3 Feedback Control Strategy

The three-mode controller with proportional, integral and derivative (PID) feedback control action had become commercially available since 1930s (Seborg, 1989). A feedback controller compares the measured value to the set point and takes the appropriate correction by sending signal to control element for adjustment of the manipulated variable in order to compensate the error.

The P, PI, and PID controller action is described in the equations given below;

$$\text{Proportional (P)} \quad p(t) = \bar{p} + K_c [e(t)]$$

$$\text{Proportional and Integral (PI)} \quad p(t) = \bar{p} + K_c \left[e(t) + \frac{1}{\tau_I} \int e(t^*) dt^* + \tau_D \frac{de}{dt} \right]$$

$$\text{Proportional, Integral and Derivative (PID)} \quad p(t) = \bar{p} + K_c \left[e(t) + \frac{1}{\tau_I} \int e(t^*) dt^* + \tau_D \frac{de}{dt} \right]$$

For P controller action only, increasing the controller gain tends to make the controller response faster. However too large of a value for K_c could lead to the response exhibiting undesirable degree of oscillation or even become unstable.

For PI controller, with constant K_c , increasing the time integral makes controller response slower and more sluggish. Theoretically, offset will be eliminated for all value of τ_I between 0 and infinity. But, for extremely large value of τ_I , the controlled variables will return to the set point very slowly after a load upset or set point change occurs.

For PID controller, with constant K_c and τ_I , increasing τ_D tends to improve the response by reducing the maximum deviation, response time and degree of oscillation. However, if it is too large, measurement noise tends to be amplified and the response may become

very oscillatory or even become unstable. Thus, a suitable value has to be determined. The derivative action was seldom used for flow controller due to the fast response and noisy measurement which could easily destabilize the controller.

2.4.5 PID Controller Tuning

For feedback controller, the controller setting must be adjusted for a system performance to be satisfactory. Good control performance can be achieved with a proper choice of tuning constant values, but poor performance and even instability can result from a poor choice of values (E. Marlin, 2000). Many methods can be used to determine the tuning constant values. Controller tuning methods based on dynamic performance have been used for many decades (Lopez et al., 1969), such as Cohan and Coon Open-loop method and Ziegler Nichols Closed-loop method. These methods can be used if a process model or frequency response data are available.

Table 2.1 shows the formula for determining the settings of the respective Proportional (P), Proportional and Integral (PI), and Proportional, Integral and Derivative (PID) controller based on the open loop response curve. The curve obtained for the changes of control variable subject to the manipulated variable.

Table 2.1 : Cohan and Coon Design Relation

Controller	Settings	Cohen-Coon
P	K_c	$\frac{1}{k} \frac{\tau}{\theta} [1 + \theta/3\tau]$
PI	K_c	$\frac{1}{k} \frac{\tau}{\theta} [0.9 + \theta/12\tau]$
	τ_i	$\frac{\theta [30 + 3(\theta/\tau)]}{9 + 20(\theta/\tau)}$
PID	K_c	$\frac{1}{k} \frac{\tau}{\theta} \left[\frac{16\tau + 3\theta}{12\tau} \right]$
	τ_i	$\frac{\theta [32 + 6(\theta/\tau)]}{13 + 8(\theta/\tau)}$
	τ_d	$\frac{4\theta}{11 + 2(\theta/\tau)}$

2.4.6 Control of Reactive Distillation Column

With correct and suitable controller setting, the controller action command used in MATLAB program to control the distillate composition by adjusting the reflux ratio is described as below;

$$RR(t) = RRi + K_c \left[e(t) + \frac{1}{\tau_I} \int e(t) dt \right]$$

Where

$RR(t)$ = new reflux ratio value in time domain

RRi = steady state reflux ratio

$e(t)$ = set point (i.e., 0.8118) – $xc(1)$

where $xc(1)$ represents the composition of ethyl acetate at stage one.

For controlling the bottom section, the controller action adjusts the reboiler duty to compensate the error and bring back the bottom product composition to its set point. The command used in MATLAB is described as below;

$$Qr(t) = Qri - K_c \left[e(t) + \frac{1}{\tau_I} \int e(t) dt \right]$$

Where

$Qr(t)$ = new reflux ratio value in time domain

Qri = steady state reflux ratio

$e(t)$ = set point (0.13) – $xc(13)$

Where $xc(13)$ represents the composition of ethyl acetate at stage thirteen.

2.4.7 Feedforward Control Strategy

A feedforward controller strategy detects and calculates disturbances as they enter the process. The corrective action is then calculated and made concurrently to the manipulated variables with the aim to keep the output variables close to the desired value. Thus, the corrective action is implemented as soon as the disturbance enters the system

For feedforward controller, the feedforward function to anticipate the load change has to be determined first. It is calculated by taking the ratio of the load/disturbance transfer function to manipulated transfer function.

$$G_{F(s)} = \left(\frac{M}{L} \right)_{(s)} = \left(\frac{\text{manipulated variable}}{\text{disturbance}} \right)_{Y_{\text{constant}}}$$

To design a feedforward controller, that is, to find $G_F(s)$, both $G_L(s)$ and $G_M(s)$ transfer function must be determined which can be obtained by open loop step change. The objective is to hold the controlled variable constant at its steady-state value, therefore, the change or perturbation of controlled variable, $Y(s)$, should be zero. The output $Y(s)$ is given by the equation,

$$Y(s) = G_{L(s)}L(s) + G_{M(s)}M(s) \dots\dots\dots (a)$$

The left term of the equation is set to zero and solving for the relation between $M(s)$ and $L(s)$ give the feedforward controller transfer function.

$$\left(\frac{M(s)}{L(s)} \right)_{(Y=0)} = G_{F(s)} = \left(\frac{-G_L}{G_M} \right)_{(s)}$$

Where

$$G_L = \frac{K_L}{\tau s + 1} \quad \text{and} \quad G_M = \frac{K_M}{\tau s + 1}$$

K_L is the load gain while K_M is the manipulated gain. Both gains are obtained from the process step change and the above transfer functions only obtained if it is a first order process.

CHAPTER 3

METHODOLOGY/PROJECT WORK

3. METHODOLOGY

3.1 Procedure Identification

In order to achieve the objectives of the project within allocate time, planning and strategy for progress of work are important. The strategy to completion of project is divided into several steps. The summary of the strategy can be referred to Figure 3.1.

Research on the related topic is done through out the first two weeks. Several literature reviews are referred in carrying out this project either on the theory side or the computational side. The MATLAB programming is used in this work for modeling and simulation purposes. The kinetic reaction of reaction involves which is the esterification is studied and the rate law and rate of reaction is identified. With the obtained rate law and all the kinetics involve shown in Equation 2.1 to Equation 2.6, the overall balance including the component balance is derived.

3.1.1 Familiarization of MATLAB

With the completed equations which will be used in the modeling, study on MATLAB program is done. It is important in order to translate the mathematical modeling into commands that can be read and run by the program. Familiarization of MATLAB is done by understanding the command codes and function used by referring to the previous study. This step can be called as the 'heart' of the project since it controls the flexibility of this project from the beginning until it is complete. After deep understanding on the program, the mathematical model will be translated into command codes and function so that simulation on the model can be done. Both the dynamic and steady state model will be simulated in the developed functions and codes.

3.1.2 Run of Steady- State Simulation

At steady-state, any change of component with respect to time is ignored in which the component settles at one constant value throughout the study period. For steady state model, the overall balance derived from equation 2.5 will be used to calculate the final components composition and monitor the response profile. It is simulated in MATLAB program using several initial conditions. The impact of number of input parameters to output parameters is observed through the simulation. For steady state model, the components profile is monitored at each stage rather than changes of components composition with respect to time. The variation of ethanol, acetic acid, ethyl acetate and water with respect to stages are shown in the composition (reactant/product) versus number of stages plot, obtained from the MATLAB simulation. Besides, the temperature profile with respect to stages and reaction rate profile for double feed configuration are also monitored from the simulation. In order to calculate the temperature profile, the energy balance equation of the feed, mixture and the product formed.

3.1.3 Dynamic State Simulation

Dynamic state is defined as a condition where changes in a parameter with respect to time are taken into consideration. The composition profile is observed through the time span and the trend obtained will be studied for deeper explanation in the next section. For dynamic state model, Equation 2.5 will be used to measure the components at each tray which change with respect to time. The model is developed by applying the first order differential equation (ODE1) to calculate the component composition change.

The changes on the output parameters can be observed clearly after variation of parameters changes are applied to the column. The variation of parameters is done by changing the reflux ratio and reboiler duty from -5% to 5% of its initial condition for the manipulated variables. For load/ disturbance, the changes on the feed flowrates are carried out by increasing the first feed rate with 20mol/s while the second feed rate is remain constant followed by changing the second feed rate with first feed rate is constant

with the same amount of increment. The steps were followed by increasing both feed rates and then reducing both feed rate with 20 mol/s.

Open loop step change is carried out in order to calculate the transfers functions involve in this process. Step change is done by changing the reboiler duty with +0.0366 and reflux ratio with +0.2 from its initial value. The feed rate will be decreased with 30mol/s and 35 mol/s for the first and second feed rate respectively.

The concentration profiles obtained are used to develop the transfer function for the process and the load/disturbance. The profiles obtained from the simulation are first order response which fitted in model transfer function below:

$$G(s) = \frac{Ke^{-\theta s}}{s + 1}$$

The process gain K for the model is found by calculating the ratio of the change in the steady state value of output parameters to the size of the input parameters.

$$K = \frac{\Delta output}{\Delta input}$$

Time constant for the transfer function can be calculated by drawing a tangent line at the point of inflection of the step response; the intersection of the tangent line and the time axis is the time delay. It also can be found by calculating the time response for 63.2% completion of the response profile. The time delay can be calculated by subtracting the response time when its start to change from the steady state with the time when the input is applied to the column. The above steps are applied to all the composition change from the step change.

3.1.4 Development of Closed-loop Controller

Feedback Controller

After introducing the step change to the column it is found out that process interaction involves between the controlled variables. In order to reduce this interaction, Bristol's Relative Gain Array (RGA) method is applied. The process gain K for the manipulated variables is used to determine the element of the RGA. The calculation involves for this method was also been developed using MATLAB. From the RGA result, the effective pairing for better control strategy was selected for further expansion of work.

The Cohen and Coon Open-loop method is applied in this project to find the best controller tuning. The equation by Cohen and Coon involves calculation to find the controller parameters, for the selected controller action which is the Proportional and Integral action. The controller tuning is done until satisfactory controller response was obtained from the dynamic simulation. The feedback controller is used to manipulate the reboiler duty and reflux ratio in order for it to compensate the error detected from the controlled variables (distillate and bottom). With correct controller setting, the controller able to bring the controller variables back to its set point after load/ disturbance is introduced to the column.

3.1.5 Simulation on Complete Control Strategy

Finally, the simulation on complete control strategy is done using the program. The completed process control includes the feedback controller for both distillate composition control and bottom composition is run repeatedly.

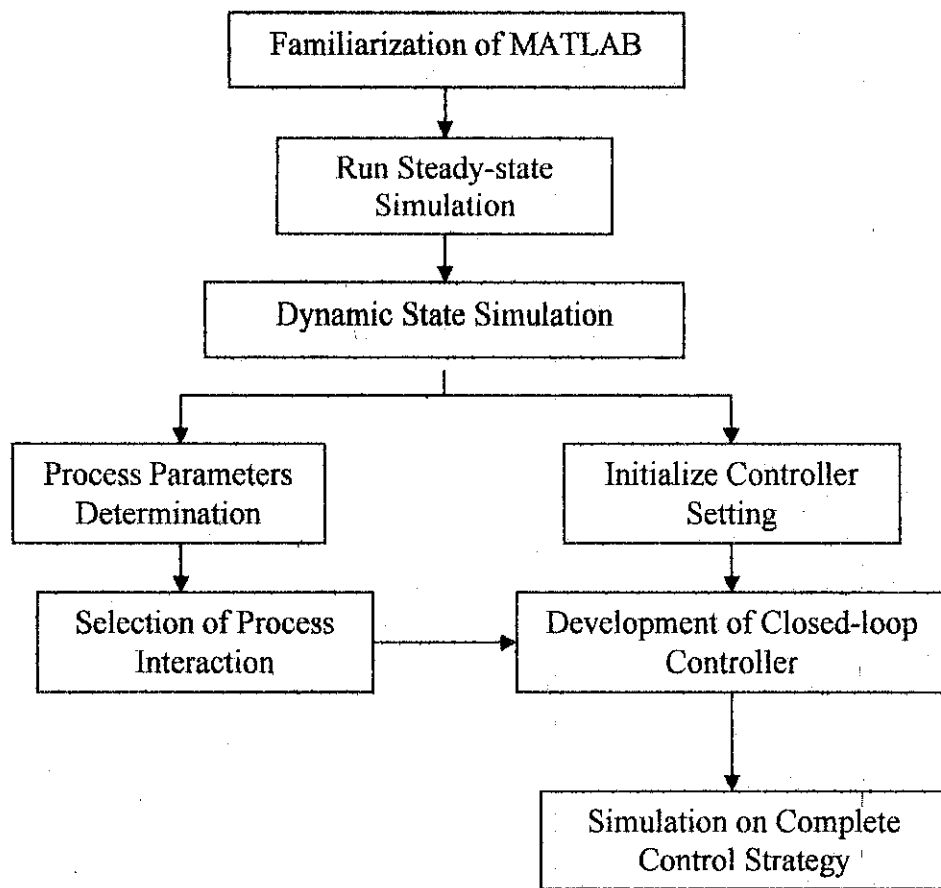


Figure 3.1: Strategy of Control of Reactive Distillation

CHAPTER 4

RESULT AND DISCUSSION

4. RESULT AND DISCUSSION

4.1 Overview

The modeling of the reactive distillation was successfully done for both steady-state and dynamic state. Simulation study was then performed on the steady-state and dynamic state model to observe the effect of column parameters on the composition profile of components in the reactive distillation column especially the distillate and bottom product.

A step change is introduced to the column parameter to study its effect toward the distillate and bottom product. Only one parameter would be applied with a step change at one time as the column load or disturbance. The step change is applied based on Cohan and Coon open loop method of tuning. Tuning of controller settings is done from the step change results.

4.2 Simulation Result

4.2.1 Steady State Model

A process is a steady state when the state variables do not change with time. The rate of accumulation is zero throughout the time.

The study is generally taken based on the production of ethyl acetate and water from reaction between ethanol and acetic acid with present of acid sulfuric to boost up the reaction kinetics. The study on steady-state model is done by evaluating the model developed by the previous study. For simulation purposes, an initial operating condition is assumed with reasonable value for practices.

For this study, the reactant and product are assigned with certain variables as follows:

Table 4.0 Assignment of Variables

Acetic Acid	xa
Ethanol	xb,
Ethyl Acetate	xc (more volatile, removed as distillate product, undesirable for bottom product),
water	xd (boiled off as bottom product),
Feed1 purity	A = za1, B = zb1
Feed2 purity	A = z2a, B = z2b.

Table 4.1: Initial Condition for Steady-State Reactive Distillation Model.

Parameters	Initial Condition	unit
feed1 flowrate	410	Mol/s
feed2 flowrate	415	Mol/s
Reflux Ratio	1.98	-
Reboiler duty	4.00e6	Watt
Feed1 A purity	1	-
Feed1 B purity	0	-
Feed2 A purity	0	-
Feed2 B purity	1	-
Column Pressure	14.7	Psia
Number of trays	13	Stages
Feed1 tray	4	-
Feed2 tray	9	-
Sulfuric Acid feed tray	4	-

Basically, a simulation on the steady state model is done and the composition profile by applying the initial condition is obtained as shown in Figure 4.1. From the figure, the

composition of ethyl acetate increases as it approached to the top of the column. The distillate composition obtained at the top tray is approximately 0.81 while the composition of ethyl acetate observed in the bottom product stream is 0.13. The major component of bottom product is water since it is the least volatile component in the stream. The highest peak of acetic acid is observed at stage 4 where it is being fed in liquid form into the column. Ethanol is fed into the column at stage 9 where the highest concentration of ethanol is identified. Between stage 4 and 9, both reactants contact each other, in countercurrent mode, where ethyl acetate and water are formed. In the reactive distillation column, continuous reaction and separation is realized based on the result obtained. This can be described as in the reactive zone (stage 4 to stage 9), the formation of ethyl acetate from conversion of ethanol and acetic acid is noticed but the degree of separation is relatively low. As the vaporized products flow upward to the rectification zone, the separation between components is improved as the relative volatility of the components increases. Besides, the desired degree of separation of the products and reactant is achieved with a given amount of reflux ratio. Therefore, the reactive distillation process can be said to provide a mechanism for overcoming both the limitation on conversion due to chemical equilibrium as well as the difficulties in purification imposed by the water-ethyl acetate and ethanol-ethyl acetate azeotropes (Agreda et al., 1990) as observed in the composition profile. Furthermore, the temperature and reaction rate profile are also being monitored from the simulation as shown in Figure 4.2 and 4.3.

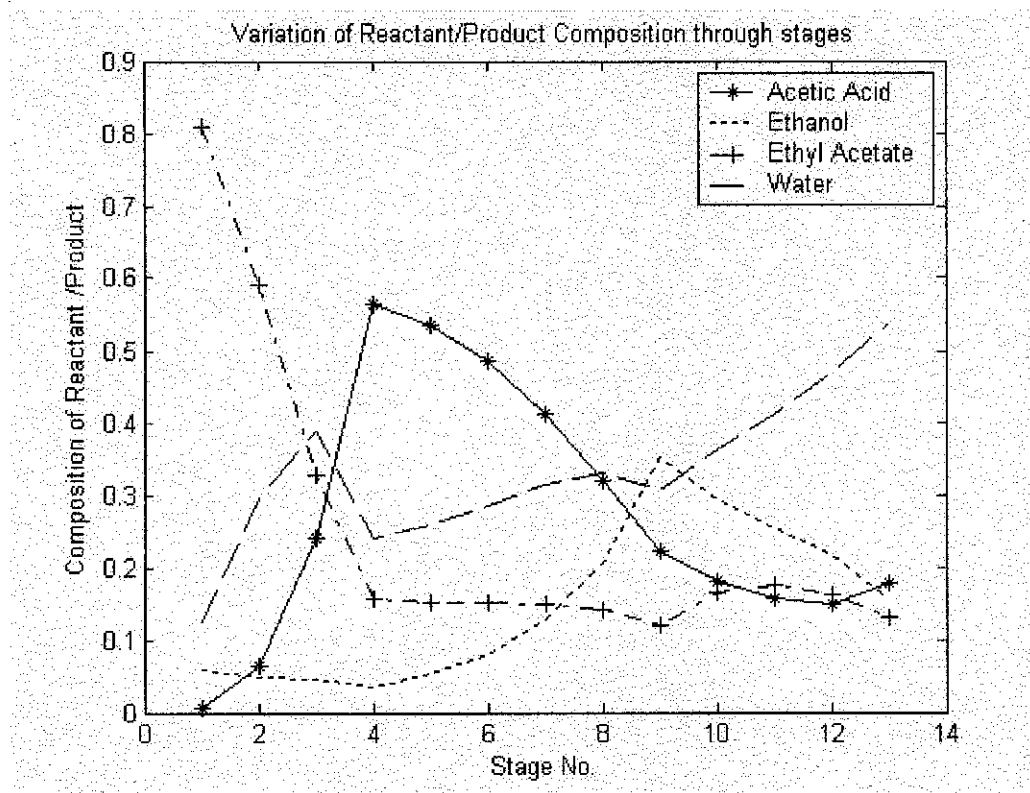


Figure 4.1: Variation of Component A, B, C, and D through Stages

As mention above, acetic acid is being introduced into the column at stage 4 along with acid sulfuric. The trays located above this stage, act as the rectification section or know as purification section which eliminates components other than ethyl acetate. The second feed (ethanol) is fed at stage 9. Due to ethanol having a relatively low boiling point, it will vaporize upon entering the column and flows upward since it is more volatile compare to the first feed (acetic acid) which flows downward. The respective stages where the two reactants contact and react (Stage 4 to stage 9), are the extractive and reactive section in which the esterification process takes place. The reaction of reactant and separation of product occurs simultaneously and continuously throughout the column resulted in different composition at each stage.

Stage 9 and below form the stripping section where the composition of ethyl acetate, ethanol and acetic acid decrease as they approach stage 13. Although the recovery of ethyl acetate at top column is still high, yet there is a slight loss of desired product (ethyl acetate) and the unconverted reactant (methanol and acetic acid) in the bottom stream.

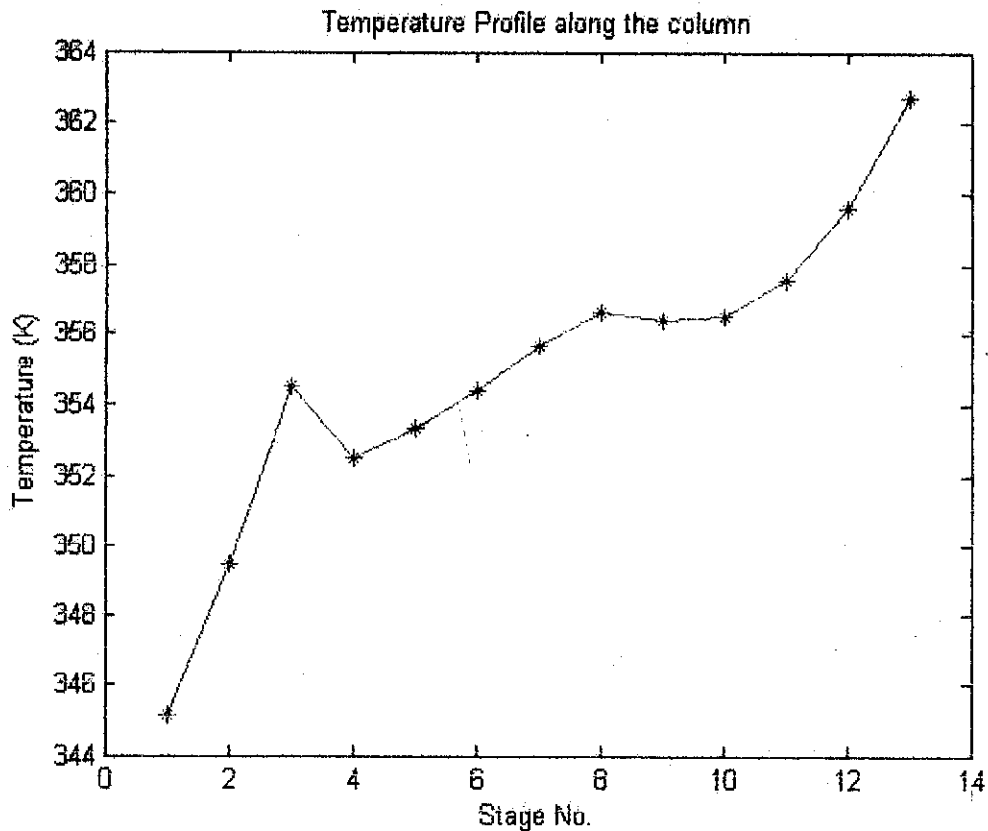


Figure 4.2: Temperature Profile through Stages

Figure 4.2 above indicates the temperature profile in the reactive distillation column. The temperature profile at each tray can be determined by solving Antoine's equation for each component at each stage. The temperature profile of each tray shows that at stage where the feed is fed, the temperature will experience slight decrement. This is due to the feed condition which is subcooled. The temperature increases from top condenser section to the bottom reboiler section. The temperature in this figure represents the boiling point for the separation to occur for a certain product or reactant at the respective tray. Low boiling point component (more volatile), ethyl acetate, will exist mainly at the top of the column while the highest boiling point component (low volatility), water, will be concentrated at the bottom section. The ease or difficulty with which the separation can be achieved depends on the relative volatility of the components.

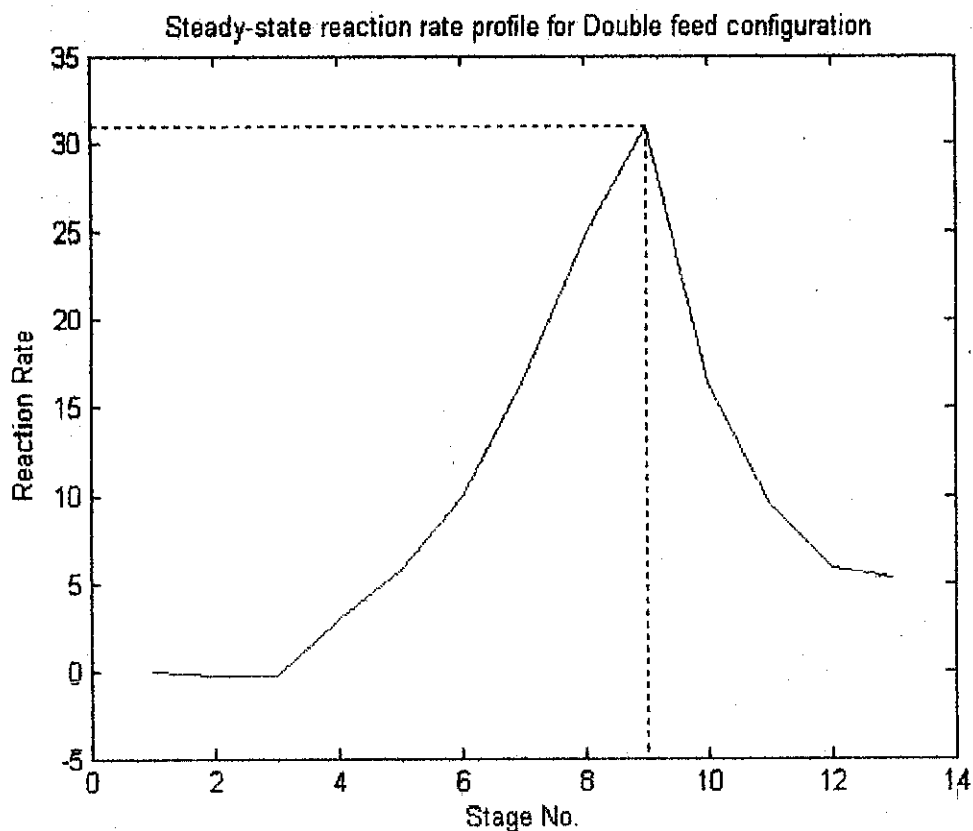


Figure 4.3: Reaction Rate Profile through Stages

The Figure 4.3 shows the reaction rate profile for the process at every stage. The reaction rate in this process is presented by measuring the reversible reaction of forward and backward reaction rate for the esterification process. For esterification of ethanol and acetic acid in order to produce ethyl acetate and water, the forward reaction rate is the rate of consumption of the limiting reactant (ethanol) to form ethyl acetate and water, while the backward reaction rate is the rate of converting the products (water and ethyl acetate) back to the reactant. Rapid reaction rate occurs at stage 9 where the ethanol enters. Beyond this stage, the esterification takes place, and reaction rate start to vary with respect to the reactant and product concentration at each tray. It is observed that the concentration of reactants at each tray decreased when moving up the column. The reaction rate of this esterification process is a function of reactant and product concentration. Thus as the concentration decreases as moving from tray 9 to 1, the reaction rate also decrease. From the figure, it is observed that the reaction rate is at its

highest rate at stage 9 and decreases at bottom section. This bottom section does not promote any reaction process, but it tends to strip all the light keys (i.e., ethyl acetate) to produce a bottom product that reaches in heavy key (by product, i.e., water).

4.2.2 Dynamic State Model

The dynamic state model is used to study and evaluate the effect of column parameters, such as manipulated and disturbance variables towards the production of ethyl acetate and water from esterification of ethanol and acetate acid. In this work, the disturbances are introduced to the column to study the dynamic response of the model. The disturbances represent the input variables to the column. The aim of dynamic study is to observe the response or dynamic behavior of a reactive distillation column to possible disturbances in certain process parameters. The disturbance will be introduced by changing the input parameters one at a time and in sequence in order to investigate its impact on the output parameters.

The disturbances introduced are as follows:

- a) A step change in reflux ratio.
- b) A step change in reboiler steam flowrate.
- c) A step change in feed flowrate A and B.
- d) A step change in feed composition A and B.

Set 0: No Disturbance

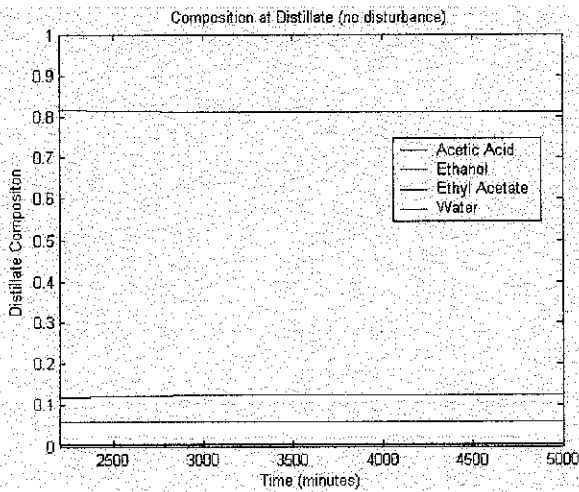


Figure 4.4

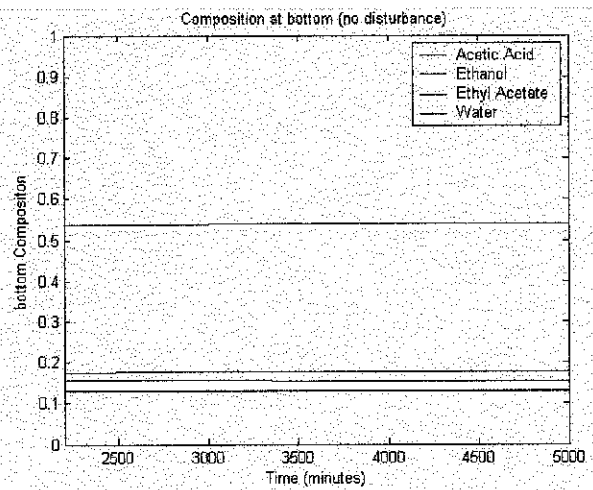


Figure 4.5

Figure 4.4 and Figure 4.5: Composition profile when no step disturbance introduced at distillate and bottom respectively.

Figure 4.4 shows the dynamic behavior of ethyl acetate (red line) composition at distillate when no disturbance is introduced on the column parameter. The composition of ethyl acetate at the specific initial operating parameter as refer to Table 4.1 is 0.81 for the distillate product and remain constant throughout time when no disturbance is applied. Figure 4.5 shows the composition of ethyl acetate in bottom product at steady state. The bottom composition of ethyl acetate is 0.13. The changes in the composition profile of the products when there is disturbance will be discussed next.

4.2.3 Variation of Parameter

(i) Variation in Reflux Ratio

Table 4.2 Variation of Parameters; Reflux Ratio

Variation of Parameters	Effect Toward Distillate Composition	Effect Toward Bottom Composition	Effect Toward Conversion
Reflux Ratio • $\pm 1\%$	a) + 1% • Increased by 0.148%. b) - 1% • Decreased by 0.468%.	a) + 1% • No effect. b) - 1% • No effect.	• No changes.
• $\pm 2\%$	a) + 2% • Increased by 0.458%. b) - 2% • Decreased by 0.739%.	a) + 2% • Increased by 0.220%. b) - 2% • Decreased by 0.220%.	• No changes.
• $\pm 3\%$	a) + 3% • Increased by 0.702%. b) - 3% • Decreased by 1.084%.	a) + 3% • Increased by 0.497%. b) - 3% • Decreased by 0.497%.	• No changes.
• $\pm 4\%$	a) + 4% • Increments by 1.01%. b) - 4% • Decreased by 1.355%.	a) + 4% • Increased by 0.692%. b) - 4% • Decreased by 0.692%.	• No changes.
• $\pm 5\%$	a) + 5% • Increased by 1.256%. b) - 5% • Decreased by 1.70%.	a) + 5% • Increased by 0.770%. b) - 5% • Decreased by 0.770%.	• No changes.

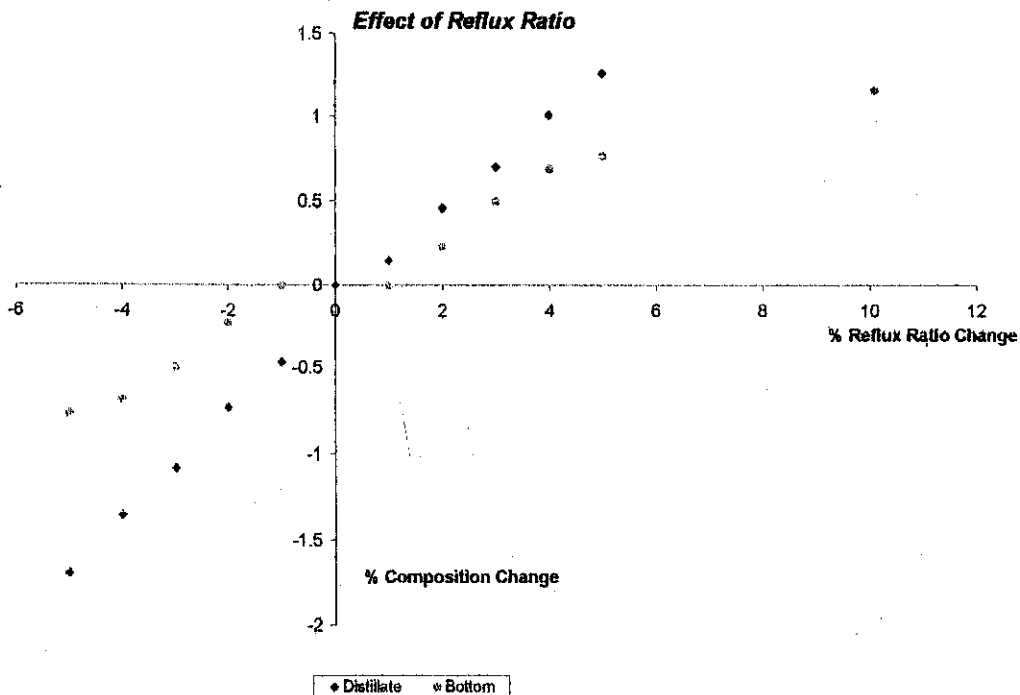


Figure 4.6: Effect of Reflux Ratio to Controlled Variables.

The result obtained by varying the reflux ratio from $\pm 1\%$ to $\pm 5\%$, is plotted into a graph of percentage composition changes versus percentage reflux ratio changes. The composition in this study represents the ethyl acetate composition. From the graph, it is observed that the effect of adjusting the reflux ratio towards the distillate composition does not produce a smooth straight line relation.

As the reflux ratio is changed, the bottom composition will also be affected but the change is rather randomly fluctuates. For distillate and bottom product, change in composition with respect to the reflux ratio change can be described as a nonlinear process.

From the result, it is observed that as the reflux ratio increases, the composition of ethyl acetate also increased. Higher reflux ratio helps the process to achieve the desired degree of separation. The ease or difficulty with which the separation can be achieved depends on the relative volatility of the components. If the temperature (and therefore the

	(0.345%). b) - 4% • No effect.	(2.692%). b) - 4% • 0.0039 increments; (3.0%).	
• $\pm 5\%$	a) + 5% • 0.0029 decrements; (0.357%). b) - 5% • No effect.	a) + 5% • 0.004 decrements; (3.077%). b) - 5% 0.0048 increments; (3.692%).	• No changes.

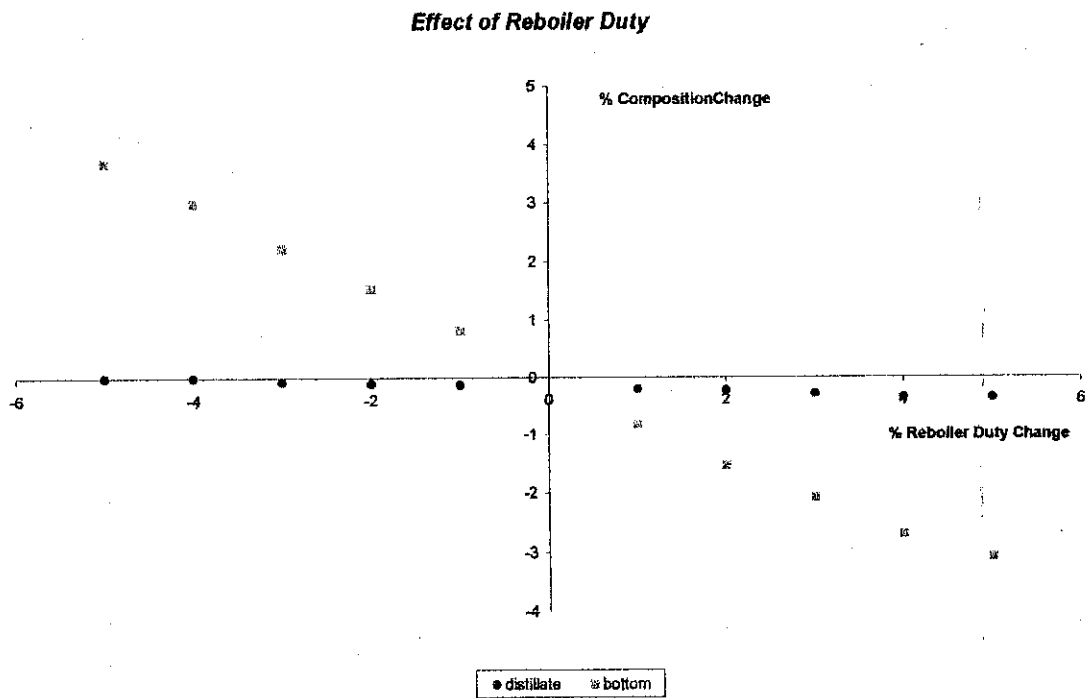


Figure 4.7 Effect of Reboiler Duty to Controlled Variables

As the reboiler duty is change from $\pm 1\%$ to $\pm 5\%$, the result shows an interesting finding. For the distillate line, it obtained a slope with small magnitude that is 0.0377 while bottom line's slope is relatively steep with value of 0.7031. The results explained that a large change in the bottom composition is observed as the reboiler duty change. This can be seen from the graph, as the reboiler duty increases, the composition of ethyl acetate in

bottom product decreases. Likewise, the distillate product shows the same trend but the slope is rather small, which mean low only small change in ethyl acetate composition is observed as the reboiler duty changed.

From the graph, it is found that the bottom column section shows slightly nonlinear relation between the bottom composition and reboiler duty. It is observed that, change in both reflux ratio and reboiler duty effect the purity of distillate and bottom product.

(iii) Variation of Feed Flowrates

Table 4.4 Variation of Parameters; Feed Flowrates

Variation of Parameters	Effect Toward Distillate Composition	Effect Toward Bottom Composition	Effect Toward Conversion
Feed Flowrate			
1) feed1 (+20mol/s) (acetic acid)	<ul style="list-style-type: none"> Remain constant 	<ul style="list-style-type: none"> Increased by 1.923% 	<ul style="list-style-type: none"> Increased by 2.32%
2) feed1 (-20mol/s)	<ul style="list-style-type: none"> Decreased by 0.407% 	<ul style="list-style-type: none"> Decreased by 0.308% 	<ul style="list-style-type: none"> Decreased by 2.338%
3) feed2 (+20mol/s) (ethanol)	<ul style="list-style-type: none"> Decreased by 0.591% 	<ul style="list-style-type: none"> Increased by 1.538% 	<ul style="list-style-type: none"> Increased by 1.818%
4) feed2 (-20mol/s)	<ul style="list-style-type: none"> Increase by 0.246% 	<ul style="list-style-type: none"> Decreased by 1.923% 	<ul style="list-style-type: none"> Decreased by 2.564%
5) both feeds increased by 20mol/s	<ul style="list-style-type: none"> Decreased by 0.468% 	<ul style="list-style-type: none"> Increased by 3.846% 	<ul style="list-style-type: none"> No changes.
6) both feeds decreased by 20mol/s	<ul style="list-style-type: none"> Slight change but settled at initial steady-state value 	<ul style="list-style-type: none"> Decreased by 3.846% 	<ul style="list-style-type: none"> No changes.

As the step change for feed flowrate is applied to the column, besides the distillate and bottom product, the conversion of reactant are also observed. It is observed that, change in feed flowrate either on first or second stage may affects the conversion of acetic acid

(limiting reactant) into ethyl acetate. Meanwhile, as both feeds are changed on the same magnitude, the amount of conversion of ethanol and acetic acid was not being affected by this change. In this work, the conversion is obtained by subtracting moles of limiting reactant that remain in the top and bottom streams with moles of limiting reactant at feed stage. When a reaction involves reversible reaction, in order to favor the reaction equilibrium to the right, one of the reactant is used in excess. More unconverted reactant is available, thus pushing the reaction equilibrium to the product side, following the Le Chatlier's principle.

From Table 4.5, as acetic acid flowrate is increased from 410 to 430mol/s, no change was observed in the distillate composition. However, there is an increase in the bottom composition but decrease in conversion. As the temperature drops due to increase amount of cold feed (i.e., from storage tank), reaction rate will drops since the reaction kinetics and the equilibrium constant depend on the temperature condition. With the reboiler duty remain the same, liquid (non volatile) tends to flow downward and contaminated bottom composition.

As the feed flow of acetic acid decreases, the composition at distillate and bottom will also decreases. However the conversion increases. The heat generated from the reboiler is said to be in excess after reduction of feed rate. This will increased the bottom section temperature which will be able to remove the amount of ethyl acetate left in the bottom stream.

As both feed were increased at 20mol/s, the distillate composition was found to decrease and the bottom composition increased while the conversion remains the same. This is due to insufficient amount of reflux flow and reboiler duty for separation to maintain at their initial compositions value respectively as more feed is fed. When both feed rate is reduced, the reboiler duty and reflux ratio are said to exceed the column duty for the reduced amount of feed. Therefore, the distillate product stream tends to increase with ethyl acetate component and bottom composition of ethyl acetate decreased.

4.2.4 Step Change

Table 4.5 Step Change on Column Parameters

Set no	Column parameter	Step change	Distillate			Bottom		
			kp	Time constant	time delay	kp	Time constant	time dela
1	Reflux ratio	+0.2	0.1035	400	0	0.00754	250	0
2	Reboiler duty	+0.0366	-0.0546	480	0	-0.0656	400	0
3	Feed1	-30	1.433e-4	520	0	1.33e-4	495	0
4	Feed2	-35	-1.2e-4	400	130	1.343e-4	530	0

An open-loop step change is introduced to the process on reflux ratio, reboiler duty, first feed flow (acetic acid) and second feed flow (ethanol). From the result, the process parameters, which are the process gain, time constant and time delay, was calculated based on a first order model. The results shows that the process is related to several column parameters, thus yield several input and output relations for the process.

A block diagram summarizing the type of parameter change made and the output variables is shown in Figure 4.8.

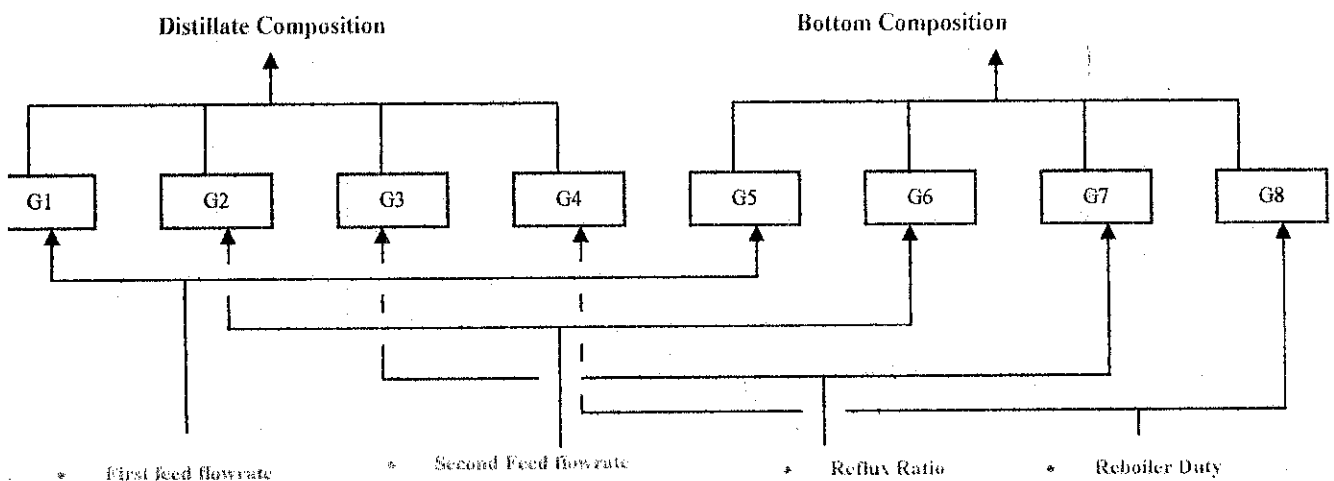
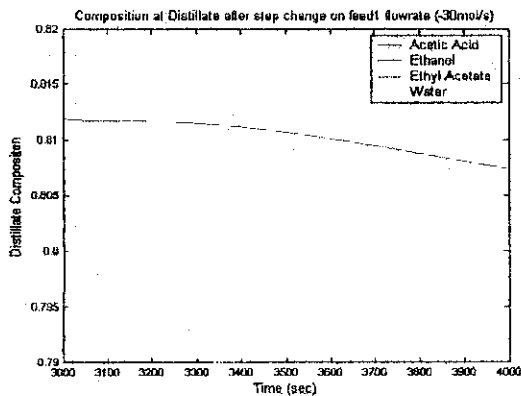


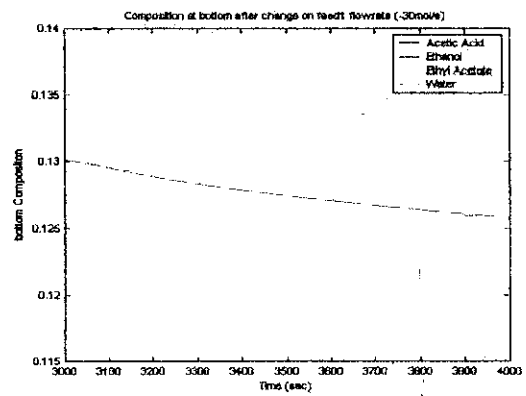
Figure 4.8 Block diagram of reactive distillation process.

The dynamic behavior of this process can be determined based on the relationship between the output variables with the manipulated variables or with the load disturbances. The manipulated variables for this process are the reboiler duty and reflux ratio, while the load disturbances are recognized as the first and second feed flow rate. Bristol's Relative Gains Array method is applied to determine the best pairing concerning only the controlled variables and manipulated variables.

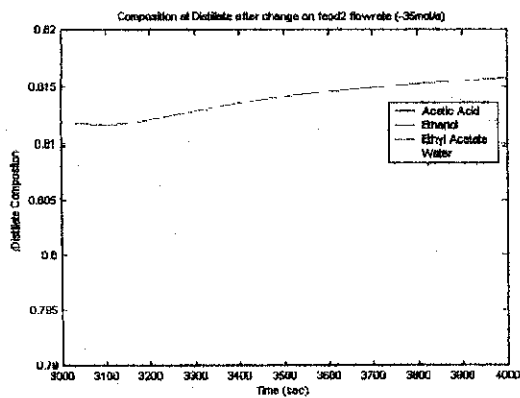
The load disturbance into the process from step change method on first and second feed is shown in Figure a and b and Figure c and d respectively.



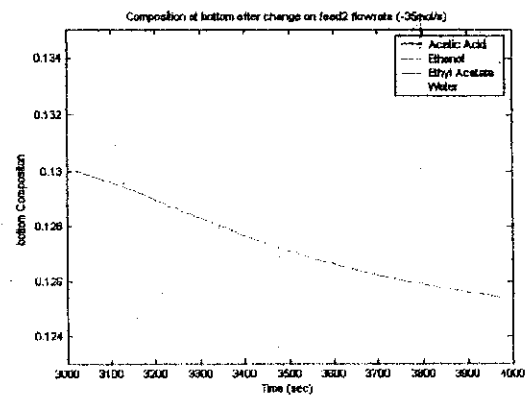
(a)



(b)



(c)



(d)

Figure 4.9 Process dynamic response of reactive distillation after load change

The process dynamic response can be modeled as transfer functions described in Table 4.6.

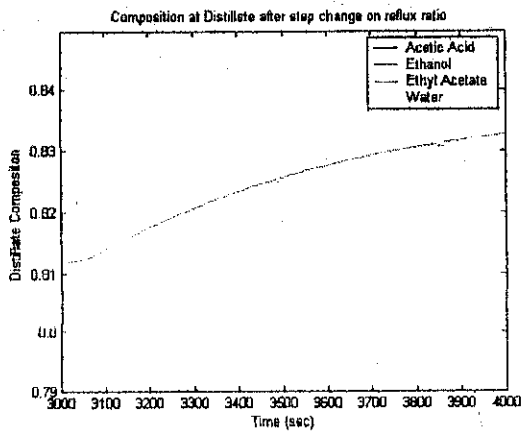
Table 4.6 Process Dynamic Response after Load Change

No	Figure 4.9	Transfer Function
1	(a)	$G1 = G_{L11} = \frac{1.433e^{-4}}{520s + 1}$
2	(b)	$G5 = G_{L12} = \frac{1.33e^{-4}}{595s + 1}$
3	(c)	$G2 = G_{L21} = \frac{1.2e^{-4}}{400s + 1}$
4	(d)	$G6 = G_{L22} = \frac{1.343e^{-4}}{530s + 1}$

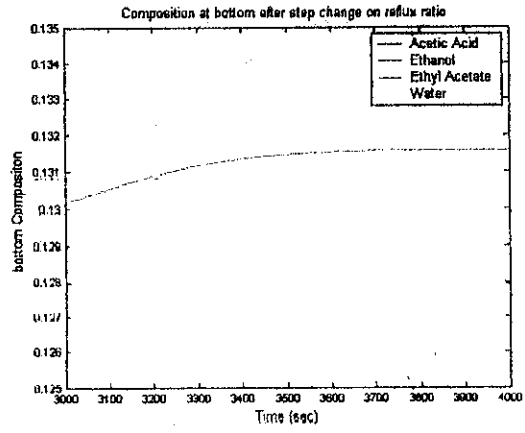
Table 4.7 Result Obtained from Bristol's Relative Gain Array Method.

	Reflux ratio	Reboiler Duty
Distillate	1.0645	-0.0645
Bottom	-0.0645	1.0645

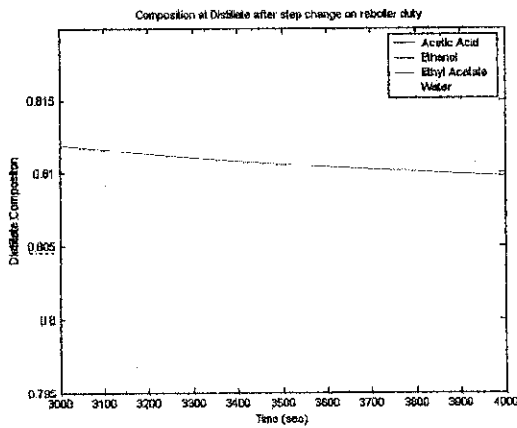
From the result obtained from the RGA analysis, it is recommended that the distillate composition is paired with reflux ratio while bottom product composition is paired with the reboiler duty. This is because the pairing with other manipulated variable corresponds to a negative relative gain which is undesirable. An incorrect pairing can result in poor control system performance and reduced stability margins. The result from open loop test on the reflux ratio and reboiler duty is shown in Figure 4.10.



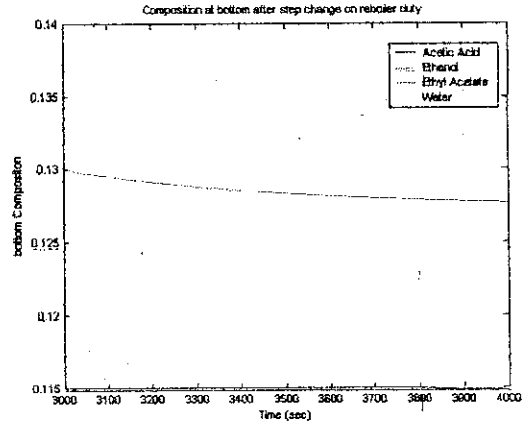
(a)



(b)



(c)



(d)

Figure 4.10 Process Dynamic Response of Reactive Distillation after Reflux Ratio and Reboiler Duty change.

From the RGA analysis, only dynamic response shows on Figure 4.10 (a) and (b) will be used further study in this project. The developed transfer functions adapted from the selected open loop response is defined as below:

1) Process Transfer Function for Figure 4.10 (a)

$$G3 = G_{p11} = \frac{0.1035}{400s + 1}$$

2) Process Transfer Function For Figure 4.10 (b)

$$G8 = G_{P22} = \frac{0.0656}{400s + 1}$$

The process transfer function and the process variables obtained above is then used for determining the controller setting.

4.2.5 Feedback Controller

After introducing the step change to the column and the process interaction is measured, the process parameters as well as the process transfer function can be calculated. The process transfer functions, denoted by the term G_{P11} and G_{P22} are the two input output relations used.

The Cohen and Coon Open-loop method is applied to find the best controller tuning. The equation used to calculate the controller parameters are as show in Table 2.1. In this study only Proportional and Integral controller action is used for maintaining the controlled variable at its set point. When using Cohan and Coon method, it was observed that the controller gain, K_c obtained is very large since the process gain, K_p is very small. This lead to instable controller response when tested on the model. Thus, the method of tuning using Cohen-Coon method was used to provide the initial value.

The tuning method is then change to trial and error method. This method is not suitable in certain operation since it is quite time consuming if a large number of trials is required to obtain satisfactory K_c , τ_i , and τ_D or if the process dynamics are quite slow.

After several adjustments by varying K_c value using the trial and error method, the acceptable value of K_c and τ_i for distillate control strategy is obtained at 35 second and 47 second respectively. The controller works by adjusting the reflux ratio to compensate the error signal sent to the controller. When the distillate composition is reduced as disturbance is introduced, the reflux ratio will be adjusted by the PI controller action by increasing the reflux ratio.

This step is carried out in several sets of K_c and τ_I value. In the first part, τ_I remains constant as the value of K_c keeps increasing until continuous oscillation obtained. This refers to oscillation with constant amplitude. When continuous oscillation is obtained at the specific K_c value, the τ_I will be reduced until continuous oscillation occurs once again. As the time integral is at 15.5 s, continuous oscillation is observed. The actual value of time integral is equal to three times this value (D.E. Seborg, 1989). Thus, the value of time integral is approximately 47 seconds.

Figure 4.11 (a) and (b) below represent the result obtained after applying Proportional and Integral controller action to adjust the reflux ratio toward the distillate and bottom product of ethyl acetate respectively.

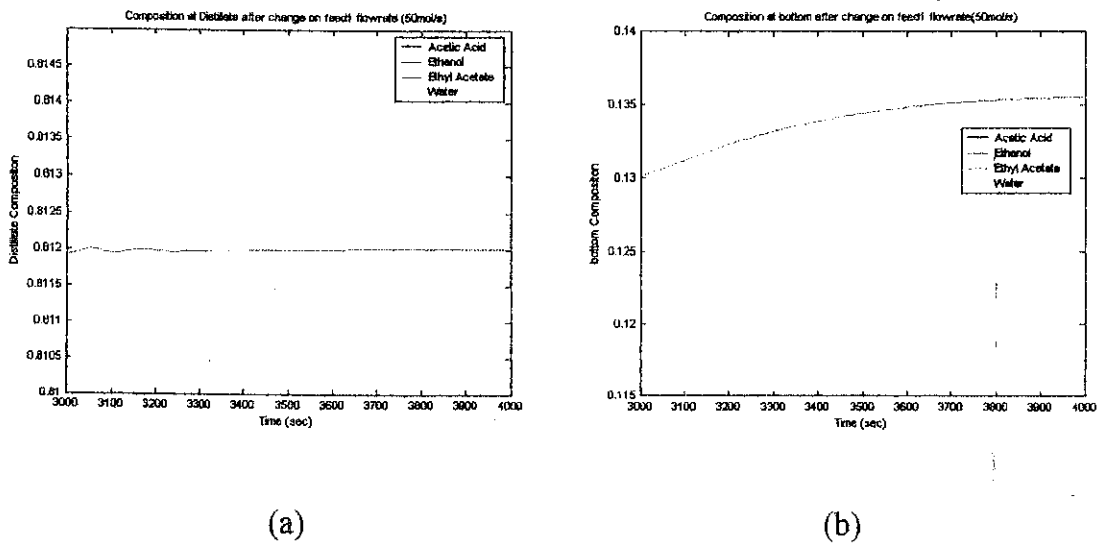


Figure 4.11(a) and (b) Ethyl Acetate composition profile at distillate and bottom after adjusting the reflux ratio by PI controller action respectively.

As discussed in previous section, the action taken by the controller toward the reflux ratio gives significant affect to distillate as its bring the ethyl acetate composition back to its set point after load change is introduced. The controller settings are able to eliminate offset with fast response time to achieve the set point. Figure 4.11(b) shows that the action taken by the controller is not able to eliminate the offset occur after the load change.

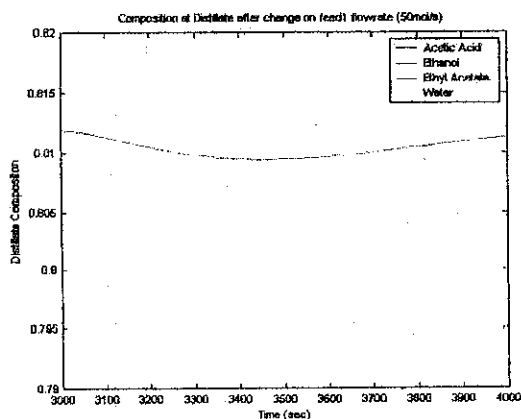
Where,

$$G_{C1} = 35 \left(1 + \frac{1}{47s} \right), \quad G_{P11} = \frac{0.1035}{400s + 1}$$

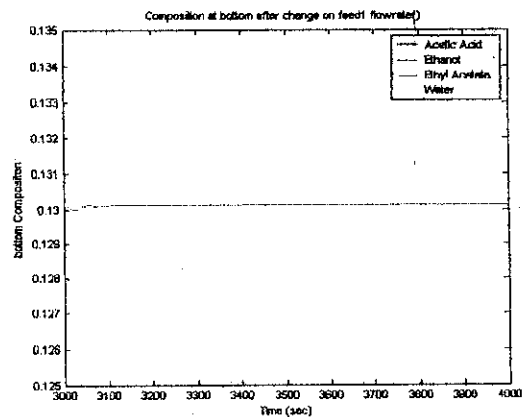
$$G_{L11} = \frac{1.433e^{-4}}{520s + 1}, \quad G_{L21} = \frac{1.2e^{-4}}{400s + 1}$$

Similar steps for bottom section are done in determining the control strategy for controlling the bottom product composition. The result shows that, for bottom product composition, it is observed the satisfactory value of K_c and τ_i for the controller is -30.5 and 70.5 second respectively. Negative controller gain means, as bottom product composition is increased, the reboiler duty will be reduced, to produce less vapor product and lowered the temperature so that only component with high volatility will be vaporized. Thus, less ethyl acetate left in the bottom stream.

Figure 4.15 (a) and (b) below represent the result obtained after applying Proportional and Integral controller action to adjust the reboiler duty towards the distillate and bottom product of ethyl acetate respectively.



(a)



(b)

Figure 4.15 (a) and (b) Ethyl Acetate composition profile at distillate and bottom after adjusting the reboiler duty by PI controller action respectively.

Upon installing this controller action with optimize controller setting the result before and after the installation is observed and shown in Figure 4.16 and 4.17.

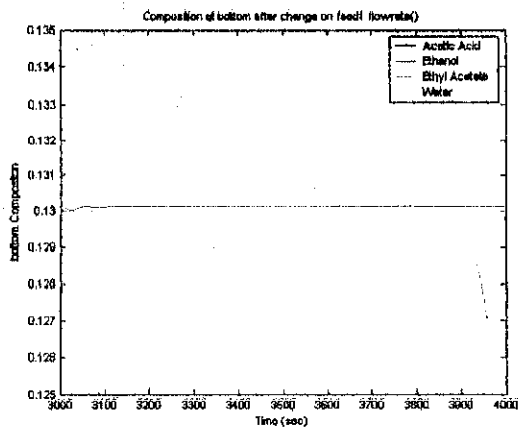


Figure 4.16

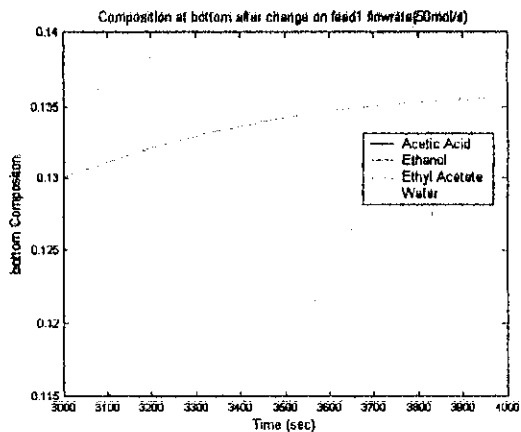


Figure 4.17

Figure 4.16: Effect of applying optimize controller gain and integral time on distillate closed-loop response to a unit step change in first feed flowrate.

Figure 4.17: Effect on distillation composition as the first feed flowrate change without feedback controller mode.

The selected control strategy is applied to control the distillate composition. The simplified diagram for both strategies is described as following diagram:

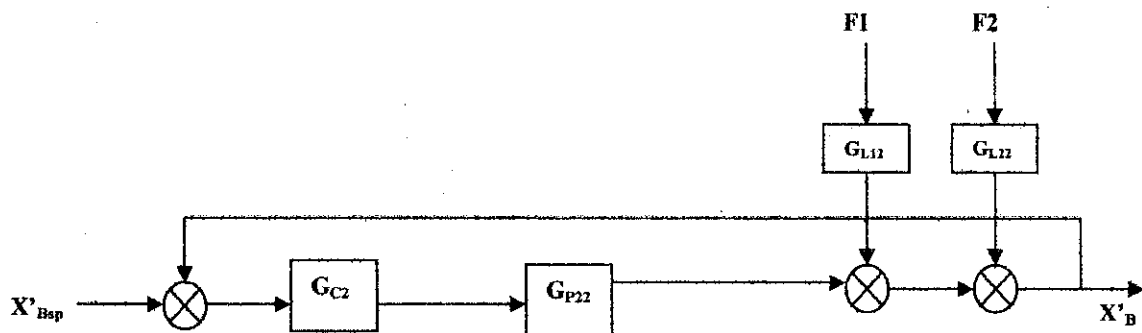


Figure 4.18: Block diagram developed for the bottom control system.

The block diagram indicates the following relations:

Where,

$$G_{C2} = 30.5 \left(1 + \frac{1}{50s} \right), \quad G_{P22} = \frac{0.0656}{400s + 1}$$
$$G_{L22} = \frac{1.343e^{-4}}{530s + 1}, \quad G_{L12} = \frac{1.33e^{-4}}{595s + 1}$$

4.2.6 Multivariable Controller

Process interaction exists in this study as discussed in Section 4.1.3 from the variation of parameters. A suitable method is needed to overcome this problem. Furthermore, from both results as refer to Table 4.2 and 4.3, it can be concluded that, change in distillate composition is a lot more affected by the reflux ratio while change in reboiler duty gives significant affect to the bottom composition. This study helps to find the relation between control variables and manipulated variables in order to obtain an effective control scheme for the reactive distillation process.

From the variation of parameters step, it is observed that, as the reflux ratio is being adjusted, both bottom and distillate composition will be affected as well as when the reboiler duty is changed. Therefore, the result shows that, there is interaction between both controlled variables with both manipulated variables. In order to anticipate this problem, a multivariable control strategy is applied in the next step. This control strategy is also known as the decoupler. The decoupler works by calculating the correct value for each control loop to take action so that by adjusting either the reflux ratio or reboiler duty in order to control one controlled variables will not disturb other controlled variable which is at its steady state. This control strategy is still incomplete due to time constrain.

The summary of developed control strategy is briefly described in the Figure 4.19.

Table 4.8: List of Transfer Function Involved In the Decoupling System.

Nomenclature	Transfer Function
G_{P12}	$\frac{-0.082}{1000s+1}$
G_{P21}	$\frac{0.0129}{450s+1}$
D_{21}	$\frac{G_{P21}}{G_{P12}}$
D_{12}	$\frac{G_{P12}}{G_{P21}}$
G_{P11}	$\frac{0.104}{800s+1}$
G_{P22}	$\frac{-0.0638}{500s+1}$

By applying this control strategy, the process interaction is expected to be reduced.

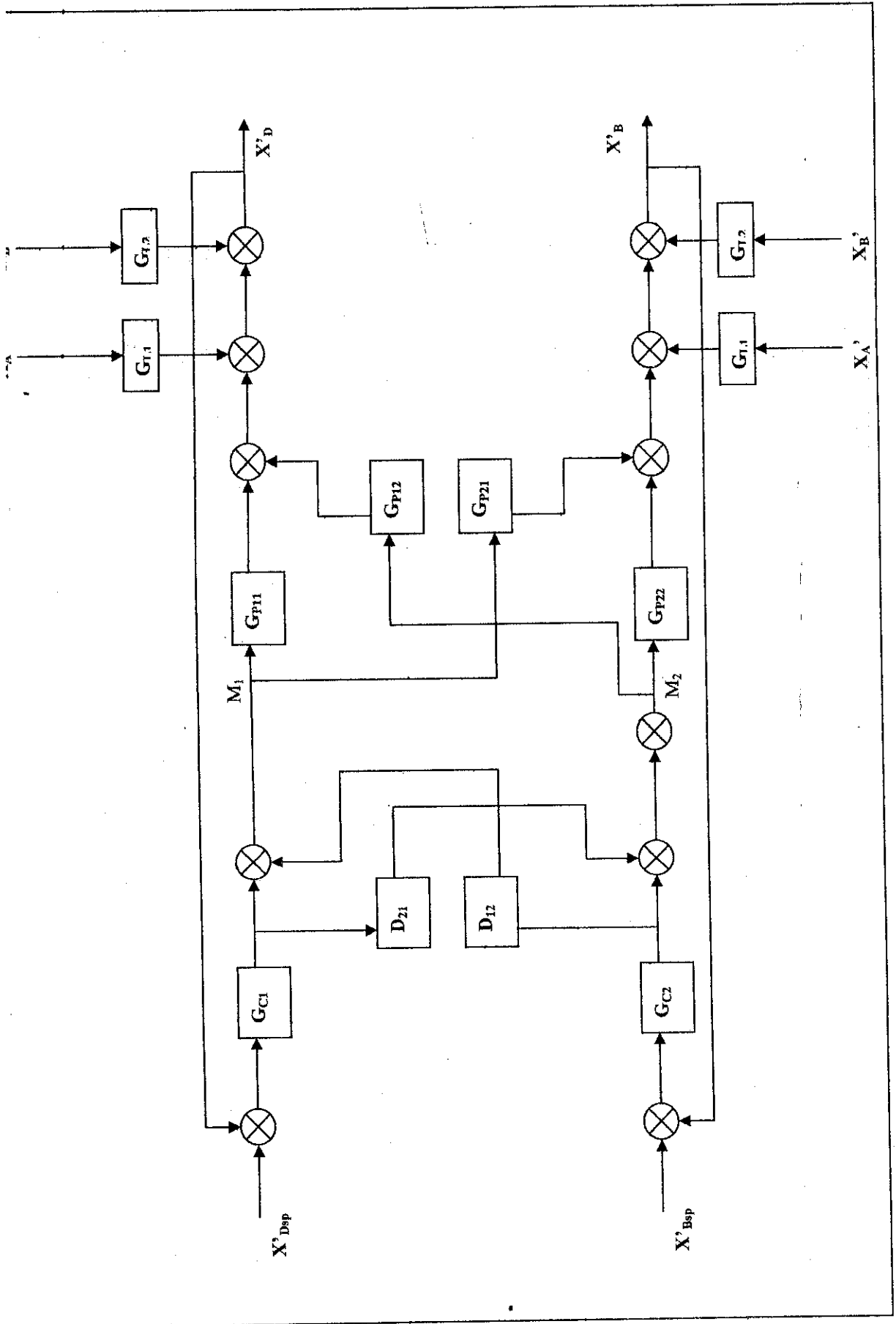


Figure 4.19: A decoupling control system for reactive distillation column

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5. CONCLUSION AND REMOMMENDATION

5.1 Conclusion

In this study, the steady state and dynamic simulation of the reactive distillation column based on the production of ethyl acetate from ethanol and acetic acid has been successfully conducted.

The work explains the impact of several operational parameters i.e., reflux ratio and reboiler duty, on the product composition at distillate and bottom. Also the impact on reaction rate and conversion was observed. While most of the impacts show similar trend as what would be expected from conventional distillation column, there are few interesting behavior that should be noted especially on the conversion and reaction rate in the column.

Using open loop response curve, the tuning of the controller was determined using g open loop method i.e., Cohen and Coon. However due to small value obtained for the process gain, the setting for K_c was found to be very large nad when tested has caused the controller to be instable. Therefore, further tuning was adopted in order to achieve stable control.

Through the interaction study using Bristol's RGA, the suitable pairing was to pair the distillate composition with reflux ratio and bottom distillate with reboiler duty.

A simulation to both the control loop has indeed demonstrated a stable response.

5.2 Recommendation

The process model for this project is carried out without considering changes in the tray holdup as a result of hydrodynamic changes of the column. Liquid holdup is assumed constant and variation of pressure drop is ignored for model simplification. Heat losses were also assumed to be negligible.

In order to improve the present model, several recommendations can be implemented for further expansion and continuation of the work from the similar area.

The Francis Weir tray hydraulics can be used to study the variation of vapor and liquid holdup in the column. Francis weir relation is used to relate the liquid holdup on tray M_n to the liquid flow rate leaving the tray L_n .

$$F_L = 3.33L_w (h_{ow})^{1.5}$$

F_L = liquid flow rate over weir

L_w = length of weir

h_{ow} = height of weir

All the properties of many mixtures in this project whether vapor or liquid is estimated using ideal gas and liquid theories. However, when the chemical natures of the components are dissimilar, nonideality must be taken into account instead. This step can be done differently depending on the conditions: for gas mixture at low to moderate pressures, correlations are used for fugacity coefficient, f . For liquid at these pressures, correlations are used for 'activity coefficient, γ ' (Jack Winnick, 1997). For mixture at high pressure, the equation of state is valid for both phases.

Due to time constrain, the effect of feed composition towards the controlled variables and conversion of reactants is not simulated in the MATLAB program. Any changes in feed composition is expected to affect the degree conversion since the rate of reaction of this process dependent on the concentration of the reactant given by equation 2.1.

Process interactions involve in this process where changes on reboiler duty or reflux ratio change the controlled variables, distillate and bottom composition, simultaneously. This condition makes the control strategy to be more complex. Therefore, a multivariable control is applied. This controller measures and compare both signals transmit from the present value of bottom and distillate composition and calculates the corrective action to be taken to both controlled variables. The transfer functions involve in the multivariable control have been developed yet not being simulated. This control strategy would be highly recommended to be studied as the field is still a newcomer in chemical processes especially when dealing with process control. It also help to reduce complex interaction within the process.

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APPENDIX

Dynamic Model

File Name Etbess7.m

```
global T xa xb xc xd Dist_par r l v RRi RR distillate v l hac het hetac hw  
global hac het hetac hw Hac Het Hetac Hw v H_b h_b feed2 feed1  
global k rga d Kp QC Conversion Qm delQC distillate t
```

```
tt=cputime;  
%Dist_par(1) = input('feed1 flowrate:');  
%Dist_par(2) = input('feed2 flowrate:');  
%Dist_par(3) = input('Reflux Ratio:');  
%Dist_par(4) = input('Reboiler duty:');  
%Dist_par(5) = input('za1:');  
%Dist_par(6) = input('zb1:');  
%Dist_par(7) = input('zc1:');  
%Dist_par(8) = input('zd1:');  
%Dist_par(9) = input('za2:');  
%Dist_par(10) = input('zb2:');  
%Dist_par(11) = input('zc2:');  
%Dist_par(12) = input('zd2:');  
%Dist_par(13) = input('Pressure:');  
%Dist_par(14) = input('number of trays:');  
%Dist_par(15) = input('feed1 tray:');  
%Dist_par(16) = input('feed2 tray:');  
%Dist_par(17) = input('acid sulphuric feed:');
```

```
Dist_par(1) = 410;%input('feed1 flowrate:');  
Dist_par(2) = 415;%input('feed2 flowrate:');  
Dist_par(3) = 1.98;%input('Reflux Ratio:');  
Dist_par(4) = 4.000e6;%input('Reboiler duty:');  
Dist_par(5) = 1;%input('za1:');  
Dist_par(6) = 0;%input('zb1:');  
Dist_par(7) = 0;%input('zc1:');  
Dist_par(8) = 0;%input('zd1:');  
Dist_par(9) = 0.0;%input('za2:');  
Dist_par(10) = 1;%input('zb2:');  
Dist_par(11) = 0;%input('zc2:');  
Dist_par(12) = 0;%input('zd2:');  
Dist_par(13) = 14.7;%input('Pressure:');  
Dist_par(14) = 13;%input('number of trays:');  
Dist_par(15) = 4;%input('feed1 tray:');  
Dist_par(16) = 9;%input('feed2 tray:');  
Dist_par(17) = 4;%input('acid sulphuric feed:');
```

```
nt = Dist_par(14);  
nf2 = Dist_par(16);  
zb2i = Dist_par(10);  
feed2i = Dist_par(2);  
RRi = Dist_par(3);  
Qri = Dist_par(4);  
feed1i = Dist_par(1);
```

```
disp('introduce disturbance/step change to the column');
```

```

Dist_par(18)= input('magnitud step in reflux ratio:');
Dist_par(19)= input('time of reflux ratio step change:');
Dist_par(20)= input('magnitud step in vapor:');
Dist_par(21)= input('time of vapor step change:');
Dist_par(22)= input('magnitud of feed A comp.change:');
Dist_par(23)= input('time of feed A comp.change:');
Dist_par(24)= input('magnitud of feed A flow change:');
Dist_par(25)= input('time of feed A flow change:');
Dist_par(26)= input('magnitud of feed B comp.change:');
Dist_par(27)= input('time of feed B comp.change:');
Dist_par(28)= input('magnitud of feed B flow change:');
Dist_par(29)= input('time of feed B flow change:');

```

```

stepr = Dist_par(18);
tstepr= Dist_par(19);
stepv = Dist_par(20);
tstepv= Dist_par(21);
stepzfA=Dist_par(22);
tstepzfA = Dist_par(23);
stepfA= Dist_par(24);
tstepfA = Dist_par(25);
stepzfB= Dist_par(26);
tstepzfB = Dist_par(27);
stepfB= Dist_par(28);
tstepfB = Dist_par(29);

```

```

if t<tstepfB;
    feed2=feed2i;
else
    feed2=feed2i+stepfB;
end

```

```

if t<tstepfA;
    feed1=feed1i;
else
    feed1=feed1i+stepfA;
end

```

```

%initial conditions
for i =1:nt,
    xa(i)=0.5;
end

```

```

for i =1:nt,
    xb(i)=0.5;
end

```

```

for i =1:nt,
    xc(i)=0.0;
end

```

```

for i =1:nt,
    xd(i)=0.0;
end

for i =1:nt,
    T(i) = 365;
end

j=0;
for i=1:nt;
    c0(i+j)=xa(i);
    j=j+3;
end

j=1;
for i=1:nt;
    c0(i+j)=xb(i);
    j=j+3;
end

j=2;
for i=1:nt;
    c0(i+j)=xc(i);
    j=j+3;
end

j=3;
for i=1:nt;
    c0(i+j)=xd(i);
    j=j+3;
end

[t,c] = ode15s('Rex8',[0:5:5000],c0,[]);

time=cputime-tt

fprintf('xa=%f\n',c(end,1:4:nt*4-3))
fprintf('xb=%f\n',c(end,2:4:nt*4-2))
fprintf('xc=%f\n',c(end,3:4:nt*4-1))
fprintf('xd=%f\n',c(end,4:4:nt*4))

fprintf('r=%f\n',r(end,:))

fprintf('T=%f\n',T(end,:))
fprintf('l=%f\n',l(end,:))
fprintf('v=%f\n',v(end,:))

t=[0:5:5000];

plot(t,c(:,1),'k',t,c(:,2),'b',t,c(:,3),'r',t,c(:,4),'g'),...
title('Composition at Distillate after change on feed1 flowrate ()'),...
xlabel('Time (sec)'),...
ylabel('Distillate Compositon'),...
legend('Acetic Acid', 'Ethanol', 'Ethyl Acetate', 'Water'),...
axis([3000 4000 0.79 0.82]);

```

pause

```
plot(t,c(:,1),'k',t,c(:,2),'b',t,c(:,3),'r',t,c(:,4),'g'),...
title('Composition at Distillate after change on feed1 flowrate ()'),...
xlabel('Time (sec)'),...
ylabel('Distillate Compositon'),...
legend('Acetic Acid', 'Ethanol', 'Ethyl Acetate', 'Water'),...
axis([3000 4000 0.0 0.85]);
```

pause

```
plot(t,c(:,49),'k',t,c(:,50),'b',t,c(:,51),'r',t,c(:,52),'g'),...
title('Composition at bottom after change on feed1 flowrate(')'),...
xlabel('Time (sec)'),...
ylabel('bottom Compositon'),...
legend('Acetic Acid', 'Ethanol', 'Ethyl Acetate', 'Water'),...
axis([3000 4000 0.115 0.14]);
```

pause

```
plot(t,c(:,49),'k',t,c(:,50),'b',t,c(:,51),'r',t,c(:,52),'g'),...
title('Composition at bottom after change on feed1 flowrate(')'),...
xlabel('Time (sec)'),...
ylabel('bottom Compositon'),...
legend('Acetic Acid', 'Ethanol', 'Ethyl Acetate', 'Water'),...
axis([3000 4000 0.1 0.55]);
```

pause

```
plot(t,1-(c(:,1)*v(1)+c(:,49)*l(nt))/feed1),...
title('conversion of etyl acetate'),...
xlabel('Time (sec)'),...
ylabel('distillate (ethyl acetate)'),...
axis([3000 4000 0.7 0.9]);
```

pause

z=[1:1:nt]';

```
plot(z,c(end,1:4:nt*4-3),'*-',z,c(end,2:4:nt*4-2),'o-',z,c(end,3:4:nt*4-1),'+-',z,c(end,4:4:nt*4),'-.-'),...
title('Variation of Reactant/Product Composition through stages'),...
xlabel('Stage No.'),...
ylabel('Composition of Reactant /Product'),...
legend('Acetic Acid', 'Ethanol', 'Ethyl Acetate', 'Water'),...
```

pause

```
z=[1:1:nt]';
plot(z,T(end,:),'*-',)
title('Temperature Profile along the column'),...
xlabel('Stage No. '), ylabel ('Temperature (K) ')
```

pause

```
z=[1:1:nt]';
plot(z,r(end,:))
title('Steady-state reaction rate profile for Double feed configuration'),...
xlabel('Stage No. '), ylabel ('Reaction Rate ')
```

Feedback Controller

File Name: Rexfb.m

```
function f = Rex(t,c)
%-----
% Ethyl Acetate reactive distillation column
%-----
global T xa xb xc xd iT r Dist_par l v P Tf Tf2 za1 zb1 zc1 zd1 za2 zb2 zc2 zd2 dist distillate delQC Qm
QC
global H_b h_b hac_b Hac_b het_b hetac_b hw_b Het_b Hetac_b Hw_b ya_b yb_b yc_b yd_b pm E RR
E1

    feed1i = Dist_par(1);% 414
    feed2i = Dist_par(2);% 411.9

    RRi      = Dist_par(3);%2.023
    Qri      = Dist_par(4);% 6.868e6

    zal1     = Dist_par(5);%1.0;
    zbl1     = Dist_par(6);%0;
    zcl1     = Dist_par(7);%0;
    zdl1     = Dist_par(8);%0;

    za2i     = Dist_par(9); %0;
    zb2i     = Dist_par(10);%1.0;
    zc2i     = Dist_par(11);%0;
    zd2i     = Dist_par(12);%0;
    Pi       = Dist_par(13);%14.696
    nt       = Dist_par(14);% 13
    nf1      = Dist_par(15);%4
    nf2      = Dist_par(16);%11
    hs4      = Dist_par(17); %4;

    stepr = Dist_par(18);
    tstepr = Dist_par(19);
    stepv = Dist_par(20);
    tstepv = Dist_par(21);
    stepzfA = Dist_par(22);
    tstepzfA = Dist_par(23);
    stepfA = Dist_par(24);
    tstepfA = Dist_par(25);
    stepzfB = Dist_par(26);
    tstepzfB = Dist_par(27);
    stepfB = Dist_par(28);
    tstepfB = Dist_par(29);

    P = Pi;

    if t < tstepfA;
        feed1 = feed1i;
    else
        feed1 = feed1i + stepfA;
    end

    if t < tstepzfB;
```

```

zb2=zb2i;

zb2=zb2i + stepzfB;
end

if t<tstepfB;
    feed2=feed2i;
else
    feed2=feed2i+stepfB;
end

j=0;
for i=1:nt;
    xa(i)=c(i+j);
    j=j+3;
end

j=1;
for i=1:nt;
    xb(i)=c(i+j);
    j=j+3;
end

j=2;
for i=1:nt;
    xc(i)=c(i+j);
    j=j+3;
end

j=3;
for i=1:nt;
    xd(i)=c(i+j);
    j=j+3;
end

RR = RRi;

sp1 = 0.130038;
if t>tstepfA;
for t=tstepfA:5000;
    E1 = sp1 - c(51)
    Qr = -130.5*(E1 + E1*(t-tstepfA)/(70.5))*2732e3+ Qri;
end
else
    Qr = Qri;
end

%vle calculation
for i = 1:nt;
    iT=i;

    T(i) = fzero('vleEtac',T(i));

    ya(iT) = 10^((-0.554296*xb(iT)^2)+(-0.103685*xc(iT)^2)+(-0.324357*xd(iT)^2) + (-
2.013350*xb(iT)*xc(iT)) + (-0.705445*xb(iT)*xd(iT)) + (-2.25362*xc(iT)*xd(iT)) +
(0.837926*xa(iT)*xb(iT)^2) + (0.434061*xa(iT)*xc(iT)^2) + (0.523760*xa(iT)*xd(iT)^2) +

```



```
(3.354000*xa(iT)*xb(iT)*xc(iT)) + (-3.25231*xb(iT)*xc(iT)*xd(iT)) + (5.90329*xc(iT)*xd(iT)*xa(iT)) +
(-0.534056*xd(iT)*xa(iT)*xb(iT)) + (-0.452660*xb(iT)*xc(iT)^2) + (0.197296*xb(iT)*xd(iT)^2) +
(0.014715*xc(iT)*xd(iT)^2))*....
```

```
((2.718^(7.203594 - (7376.157 / (1.8*T(i) + 410.1814 - 459.7))))*839.1/P)*xa(iT);
```

```
yb(iT) = 10^((0.581778*xc(iT)^2)+(-0.257329*xd(iT)^2)+ (0.209245*xa(iT)^2) + (-
0.314853*xc(iT)*xd(iT)) + (-0.562636*xc(iT)*xa(iT)) + (0.451732*xd(iT)*xa(iT)) + (-
0.115411*xb(iT)*xc(iT)^2) + (0.074053*xb(iT)*xd(iT)^2) + (0.069531*xb(iT)*xa(iT)^2) + (-
0.409472*xb(iT)*xc(iT)*xd(iT)) + (-0.369985*xc(iT)*xd(iT)*xa(iT)) + (-0.082339*xd(iT)*xa(iT)*xb(iT))
+ (0.187010*xa(iT)*xb(iT)*xc(iT)) + (0.192416*xc(iT)*xd(iT)^2) + (1.092470*xc(iT)*xa(iT)^2) + (-
0.172565*xd(iT)*xa(iT)^2))*....
```

```
((2.718^(7.43437 - (6162.36 / (1.8*T(i) + 359.382 - 459.7))))*925.3/P)*xb(iT);
```

```
yd(iT) = 10^((-0.0601361*xd(iT)^2)+(1.865750*xa(iT)^2)+(0.229575*xb(iT)^2) +
(0.468416*xd(iT)*xa(iT)) + (0.355191*xd(iT)*xb(iT)) + (1.5110*xa(iT)*xb(iT)) + (-
0.0599682*xc(iT)*xd(iT)^2) + (-3.159970*xc(iT)*xa(iT)^2) + (0.067399*xc(iT)*xb(iT)^2) +
(1.037910*xc(iT)*xd(iT)*xa(iT)) + (-1.92225*xd(iT)*xa(iT)*xb(iT)) + (-0.755731*xa(iT)*xb(iT)*xc(iT))
+ (0.941858*xb(iT)*xc(iT)*xd(iT)) + (-1.365870*xd(iT)*xa(iT)^2) + (0.365254*xd(iT)*xb(iT)^2) + (-
2.13818*xa(iT)*xb(iT)^2))*....
```

```
((2.718^(6.53247 - (7173.79 / (1.8*T(i) + 389.4747 - 459.7))))*3206.7/P)*xd(iT);
```

```
yc(iT) = 10^((0.688636*xa(iT)^2)+(0.375534*xb(iT)^2)+ (0.024303*xc(iT)^2) +
(1.778630*xa(iT)*xb(iT)) + (1.275480*xa(iT)*xc(iT)) + (0.696279*xb(iT)*xc(iT)) +
(0.936722*xd(iT)*xa(iT)^2) + (0.717779*xd(iT)*xb(iT)^2) + (0.449357*xd(iT)*xc(iT)^2) +
(1.129140*xd(iT)*xa(iT)*xb(iT)) + (-2.11099*xa(iT)*xb(iT)*xc(iT)) + (0.746905*xb(iT)*xc(iT)*xd(iT))
+ (1.449790*xc(iT)*xd(iT)*xa(iT)) + (-1.642680*xa(iT)*xb(iT)^2) + (0.120436*xa(iT)*xb(iT)^2) +
(0.330018*xb(iT)*xc(iT)^2))*....
```

```
((2.718^(6.3307 - (5440.049 / (1.8*T(i) + 373.48 - 459.7))))*556/P)*xc(iT);
```

```
sumy=ya(i)+yb(i)+yd(i)+yc(i);
```

```
end
```

```
%molar holdup on condenser and trays
```

```
for i=1:nt-1,
```

```
  hp(i) = 4.4108e4;
```

```
end
```

```
%molar holdup on reboiler
```

```
hp(nt) = 1.47025e5 ;
```

```
%moles of reactant and products formed on each stage
```

```
for i = 1:hs4-1,
```

```
  Rac(i)=
```

```
(hp(i)*((1/(xa(i)/feval('vac',T(i))+xb(i)/feval('vet',T(i))+xc(i)/feval('vetac',T(i))+xd(i)/feval('vw',T(i))))*(fe
val('rconun',T(i))*xa(i)*xb(i)-feval('rcon2un',T(i))*xc(i)*xd(i)));
```

```
end
```

```
for i = hs4:nt,
```

```
  Rac(i)=
```

```
(hp(i)*((1/(xa(i)/feval('vac',T(i))+xb(i)/feval('vet',T(i))+xc(i)/feval('vetac',T(i))+xd(i)/feval('vw',T(i))))*(fe
val('rcon',T(i))*xa(i)*xb(i)-feval('rcon2',T(i))*xc(i)*xd(i)));
```

```
end
```

```
for i = 1:hs4-1,
```

```

Ret(i)=-
(hp(i)*((1/(xa(i)/feval('vac',T(i))+xb(i)/feval('vet',T(i))+xc(i)/feval('vetac',T(i))+xd(i)/feval('vw',T(i)))))*(feval('rconun',T(i))*xa(i)*xb(i)-feval('rcon2un',T(i))*xc(i)*xd(i)));
end

for i = hs4:nt,
    Ret(i)=-
    (hp(i)*((1/(xa(i)/feval('vac',T(i))+xb(i)/feval('vet',T(i))+xc(i)/feval('vetac',T(i))+xd(i)/feval('vw',T(i)))))*(feval('rcon',T(i))*xa(i)*xb(i)-feval('rcon2',T(i))*xc(i)*xd(i)));
end

for i = 1:hs4-1,
    Retac(i)=
    (hp(i)*((1/(xa(i)/feval('vac',T(i))+xb(i)/feval('vet',T(i))+xc(i)/feval('vetac',T(i))+xd(i)/feval('vw',T(i)))))*(feval('rconun',T(i))*xa(i)*xb(i)-feval('rcon2un',T(i))*xc(i)*xd(i)));
end

for i = hs4:nt,
    Retac(i)=
    hp(i)*((1/(xa(i)/feval('vac',T(i))+xb(i)/feval('vet',T(i))+xc(i)/feval('vetac',T(i))+xd(i)/feval('vw',T(i)))))*(feval('rcon',T(i))*xa(i)*xb(i)-feval('rcon2',T(i))*xc(i)*xd(i)));
end

for i = 1:hs4-1,
    Rw(i)=
    (hp(i)*((1/(xa(i)/feval('vac',T(i))+xb(i)/feval('vet',T(i))+xc(i)/feval('vetac',T(i))+xd(i)/feval('vw',T(i)))))*(feval('rconun',T(i))*xa(i)*xb(i)-feval('rcon2un',T(i))*xc(i)*xd(i)));
end

for i = hs4:nt,
    Rw(i)=
    hp(i)*((1/(xa(i)/feval('vac',T(i))+xb(i)/feval('vet',T(i))+xc(i)/feval('vetac',T(i))+xd(i)/feval('vw',T(i)))))*(feval('rcon',T(i))*xa(i)*xb(i)-feval('rcon2',T(i))*xc(i)*xd(i)));
end

%Reaction rate
for i = 1:hs4-1,
    r(i)=
    ((1/(xa(i)/feval('vac',T(i))+xb(i)/feval('vet',T(i))+xc(i)/feval('vetac',T(i))+xd(i)/feval('vw',T(i))))^2*(feval('rconun',T(i))*xa(i)*xb(i)-feval('rcon2un',T(i))*xc(i)*xd(i)));
end

for i = hs4:nt,
    r(i)=
    ((1/(xa(i)/feval('vac',T(i))+xb(i)/feval('vet',T(i))+xc(i)/feval('vetac',T(i))+xd(i)/feval('vw',T(i))))^2*(feval('rcon',T(i))*xa(i)*xb(i)-feval('rcon2',T(i))*xc(i)*xd(i)));
end

%enthalpy of feed 1
Tf = 391.7;
Tf = fzero('fbpc',Tf);

Hacf = (14.6392*(Tf*1.8-459.7) + (0.2299E-1/2)*(Tf*1.8-459.7)^2 - (0.1022E-4/3)*(Tf*1.8-459.7)^3 + (0.2589E-8/4)*(Tf*1.8-459.7)^4);
Hetf = (14.0485*(Tf*1.8-459.7) + (0.21531E-1/2)*(Tf*1.8-459.7)^2 - (0.2153E-5/3)*(Tf*1.8-459.7)^3 - (0.4607E-8/4)*(Tf*1.8-459.7)^4);

```

Hetacf = (24.9082*(Tf*1.8-459.7) + (0.3330E-1/2)*(Tf*1.8-459.7)^2 + (0.7317E-6/3)*(Tf*1.8-459.7)^3 - (0.1247E-7/4)*(Tf*1.8-459.7)^4);
Hwf = (7.9857*(Tf*1.8-459.7) + (0.4633E-3/2)*(Tf*1.8-459.7)^2 + (0.1403E-5/3)*(Tf*1.8-459.7)^3 - (0.6578E-9/4)*(Tf*1.8-459.7)^4);

hacf=Hacf-((7376.157*1.987*(Tf*1.8)^2)/((Tf*1.8-459.7+410.1814)^2));
hetf=Hetf-((6162.36*1.987*(Tf*1.8)^2)/((Tf*1.8-459.7+359.382)^2));
hetacf=Hetacf-((5440.049*1.987*(Tf*1.8)^2)/((Tf*1.8-459.7+373.48)^2));
hwf=Hwf-((7173.79*1.987*(Tf*1.8)^2)/((Tf*1.8-459.7+389.4747)^2));

hf1 = (za1*hacf+zb1*hetf+zc1*hetacf+zd1*hwf)*0.23901/9.486e-4/453.6;%liquid Enthalpy of the feed mixture(ideal mixing rules)

%enthalpy of feed 2
Tf2 = 351.5;

Tf2 = fzero('fbpci',Tf2);

Hacf2 = (14.6392*(Tf2*1.8-459.7) + (0.2299E-1/2)*(Tf2*1.8-459.7)^2 - (0.1022E-4/3)*(Tf2*1.8-459.7)^3 + (0.2589E-8/4)*(Tf2*1.8-459.7)^4)*0.23901/9.486e-4/453.6;
Hetf2 = ((14.0485*(Tf2*1.8-459.7) + (0.21531E-1/2)*(Tf2*1.8-459.7)^2 - (0.2153E-5/3)*(Tf2*1.8-459.7)^3 - (0.4607E-8/4)*(Tf2*1.8-459.7)^4)*0.23901/9.486e-4/453.6);
Hetacf2 = (24.9082*(Tf2*1.8-459.7) + (0.3330E-1/2)*(Tf2*1.8-459.7)^2 + (0.7317E-6/3)*(Tf2*1.8-459.7)^3 - (0.1247E-7/4)*(Tf2*1.8-459.7)^4)*0.23901/9.486e-4/453.6;
Hwf2 = (7.9857*(Tf2*1.8-459.7) + (0.4633E-3/2)*(Tf2*1.8-459.7)^2 + (0.1403E-5/3)*(Tf2*1.8-459.7)^3 - (0.6578E-9/4)*(Tf2*1.8-459.7)^4)*0.23901/9.486e-4/453.6;

hf2=za2*Hacf2+zb2*Hetf2+zc2*Hetacf2+zd2*Hwf2;%liquid Enthalpy of the feed mixture(ideal mixing rules)

%enthalpy of mixture on each stage
for i=1:nt,

T1(i)=1.8*T(i)-459.7;

Hac(i) = (14.6392*T1(i) + (0.2299E-1/2)*T1(i)^2 - (0.1022E-4/3)*T1(i)^3 + (0.2589E-8/4)*T1(i)^4);
Het(i) = (14.0485*T1(i) + (0.21531E-1/2)*T1(i)^2 - (0.2153E-5/3)*T1(i)^3 - (0.4607E-8/4)*T1(i)^4);
Hetac(i) = (24.9082*T1(i) + (0.3330E-1/2)*T1(i)^2 + (0.7317E-6/3)*T1(i)^3 - (0.1247E-7/4)*T1(i)^4);
Hw(i) = (7.9857*T1(i) + (0.4633E-3/2)*T1(i)^2 + (0.1403E-5/3)*T1(i)^3 - (0.6578E-9/4)*T1(i)^4);

H(i)=(ya(i)*Hac(i)+yb(i)*Het(i)+yc(i)*Hetac(i)+yd(i)*Hw(i))*0.23901/9.486e-4/453.6; %Vapor Enthalpy of the mixture(ideal mixing rules)

hac(i)=Hac(i)-((7376.157*1.987*(T1(i)+459.7)^2)/((T1(i)+410.1814)^2));
het(i)=Het(i)-((6162.36*1.987*(T1(i)+459.7)^2)/((T1(i)+359.382)^2));
hetac(i)=Hetac(i)-((5440.049*1.987*(T1(i)+459.7)^2)/((T1(i)+373.48)^2));
hw(i)=Hw(i)-((7173.79*1.987*(T1(i)+459.7)^2)/((T1(i)+389.4747)^2));

h(i)=(xa(i)*hac(i)+xb(i)*het(i)+xc(i)*hetac(i)+xd(i)*hw(i))*0.23901/9.486e-4/453.6;%liquid Enthalpy of the mixture(ideal mixing rules)

end

%enthalpy balance

```

coef=zeros(nt*2);
right_hand=zeros(nt*2,1);

coef(1,1)=1;
coef(1,2)=-RR;

coef(2,1)=-1;
coef(2,2)=-1;
coef(2,4)=1;

j=1;
for i=3:2:nt*2-3,
    coef(i,i-2)=h(j);
    j=j+1;
end

j=2;
for i=3:2:nt*2-3,
    coef(i,i)=-h(j);
    j=j+1;
end

j=2;
for i=3:2:nt*2-3,
    coef(i,i+1)=-H(j);
    j=j+1;
end

j=3;
for i=3:2:nt*2-3,
    coef(i,i+3)=H(j);
    j=j+1;
end

for i=4:2:nt*2-2,
    coef(i,i-3)=1;
end

for i=4:2:nt*2-2,
    coef(i,i-1)=-1;
end

for i=4:2:nt*2-2,
    coef(i,i)=-1;
end

for i=4:2:nt*2-2,
    coef(i,i+2)=1;
end

coef(nt*2-1,nt*2-3)=h(nt-1);
coef(nt*2-1,nt*2-1)=-h(nt);
coef(nt*2-1,nt*2)=-H(nt);

coef(nt*2,nt*2-3)=1;
coef(nt*2,nt*2-1)=-1;

```

```

coef(nt*2,nt*2)=-1;

right_hand(nf1*2-1)=-feed1*hf1;
right_hand(nf1*2)=-feed1;

right_hand(nf2*2-1)=-feed2*hf2;
right_hand(nf2*2)=-feed2;

L=coef\right_hand;

j=0;
for i=1:nt,
    l(i)=L(i+j);
    j=j+1;
end

j=1;
for i=1:nt,
    v(i)=L(i+j);
    j=j+1;
end

reflux = RR*l(1)/(RR+1)
distillate = l(1)/(RR+1)

% Condenser Duty
for i=1;
QC          = -((v(i)+l(i))*h(i)) + v(1+i)*H(1+i)
end

% Overall heat balance
overall = feed1*hf1 + feed2*hf2 + Qr - v(1)*h(1) - QC - l(nt)*h(nt)

%Total Conversion
Conversion= ((feed2)-(v(1)*xb(1)+l(nt)*xb(nt)))/(feed2)

j=0;
for i=1:nt,
    R(i+j)=Rac(i);
    j=j+3;
end

j=1;
for i=1:nt,
    R(i+j)=Ret(i);
    j=j+3;
end

j=2;
for i=1:nt,
    R(i+j)=Retac(i);
    j=j+3;
end

j=3;

```

```

for i=1:nt,
    R(i+j)=Rw(i);
    j=j+3;
end

j=0;
for i=1:nt,
    y(i+j)=ya(i);
    j=j+3;
end

j=1;
for i=1:nt,
    y(i+j)=yb(i);
    j=j+3;
end

j=2;
for i=1:nt,
    y(i+j)=yc(i);
    j=j+3;
end

j=3;
for i=1:nt,
    y(i+j)=yd(i);
    j=j+3;
end

for i=1:nt*4,
    z(i)=0;
end

z(nf1*4-3)=za1;z(nf1*4-2)=zb1;z(nf1*4-1)=zc1;z(nf1*4)=zd1;% acetic acid

z(nf2*4-3)=za2;z(nf2*4-2)=zb2;z(nf2*4-1)=zc2;z(nf2*4)=zd2;% ethanol

% overhead receiver
for i=1:4,
    f(i) = (v(2)*y(i+4)-(v(1)+l(1))*c(i)+R(i))/hp(1);%condenser(1st stage)
end

for i=5:20,
    if i<=8
        j=1;
        elseif i>=9 & i<=12
            j=2;
        elseif i>=13 & i<=16
            j=3;
        elseif i>=17 & i<=20
            j=4;
        end
    f(i) = (l(j)*c(i-4)+v(j+2)*y(i+4)-l(j+1)*c(i)-v(j+1)*y(i)+feed1*z(i)+R(i))/hp(j+1);
end

```

```

for i=21:48,
  if i<=24
    j=5;
    elseif i>=25 & i<=28
      j=6;
    elseif i>=29 & i<=32
      j=7;
    elseif i>=33 & i<=36
      j=8;
    elseif i>=37 & i<=40
      j=9;
    elseif i>=41 & i<=44
      j=10;
    elseif i>=45 & i<=48
      j=11;

  end
  f(i)= (l(j)*c(i-4)+v(j+2)*y(i+4)-l(j+1)*c(i)-v(j+1)*y(i)+feed2*z(i)+R(i))/hp(j+1);
end

for i=nt*4-3:nt*4,
  f(i)= ((l(nt-1)*c(i-4)-l(nt)*c(i)-v(nt)*y(i))+R(i))/hp(nt);
end

% reboiler
f=f(i);
%-----

```