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Date : 13th June 2007

Signature :

Supervisor : Associate Professor Dr. M. Ibrahim b. A. Mutalib

Date : 13 - JUNE - 07

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Simulation Study on Operations Aspects of a Reactive Distillation Column for Production of Ethyl Acetate Using ASPEN PLUS™ and ASPEN DYNAMIC™

By

©Ir. Yee Sew Ping

A THESIS

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Simulation Study on Operations Aspects of a Reactive Distillation Column for Production of Ethyl Acetate using ASPEN PLUS^{TM} and ASPEN DYNAMIC^{TM}

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Ir. Yee Sew Ping
13th June 2007

DEDICATION

This thesis is dedicated to my parents and family, who have provided the much needed encouragement and support to me in my endeavor to complete the research. This work is also especially dedicated to my husband, Tuck Leong, who has provided much encouragement, guidance and being source of inspiration throughout my studies.

Ir. Yee Sew Ping
13th June 2007

ABSTRACT

Ethyl acetate is a widely used organic compound in manufacturing of printing inks, paints, coatings, perfume, film, food additives, pharmaceutical and others due to its low boiling point. There were numerous research carried out in different areas related with ethyl acetate production. In recent years, due to the increasing trend in ethyl acetate demand, reactive distillation that combined reaction process and distillation process technique has been used for ethyl acetate production studies. However, most of the researchers focus on column configuration and control of the column. There are limited studies being carried out on starting up a reactive distillation column in dynamic simulation.

The present research looked into using the replicated reactive distillation model for ethyl acetate production to study the reactive distillation column behaviors and suitability of conventional method for start-up operations. The model replicated is used to determine the best controller pairing and tuning is carried out for the controller determined.

The steady state reactive distillation column is modeled using commercial simulator, ASPEN PLUS^{TM}, and validated against results published by researchers. The validated model is used in studying the start-up operations using conventional method. The dynamic state study is carried out using ASPEN DYNAMIC^{TM}. Two best controllers are determined by RGA method. Tuning of the controllers is carried out using Ziegler Nichols (ZN) method.

The reactive distillation model for ethyl acetate production has been successfully replicated and validated in the present research. Starting up the reactive distillation column involving reaction with conventional method is very challenging. At such, three different start-up strategies were studied. The best strategy was selected and optimized in order to achieve the shortest start-up time and stable operations.

ABSTRAK

Etil asetat adalah komponen organik yang luas kegunaannya dalam pembuatan dakwat, cat, penyalutan, pewangi, filem, mangkin makanan, industri ubat-ubatan dan lain-lain disebabkan oleh takat didihnya yang rendah. Beberapa kajian telah diterbitkan dalam pelbagai aspek berkenaan dengan pembuatan etil asetat. Kebelakangan ini, memandangkan kepada permintaan etil asetat yang telah meningkat, kajian telah digunakan keatas penyulingan bertindak balas yang mengabungkan teknik-tenik proses tindak-balas dan proses penyulingan bagi penghasilan etil asetat. Walaubagaimanapun, kebanyakan kajian hanya menumpukan kepada susuncara turus dan kawalan turus. Kajian berkenanan dengan operasi permulaan turus dalam keadaan dinamik adalah terhad.

Penyelidikan ini tertumpu kepada penggunaan model penyulingan bertindak balas direkabentuk untuk kajian operasi permulaan turus dan kesesuaian kaedah lazim untuk permulaan turus. Model itu telah digunakan untuk menentukan pasangan kawalan turus yang terbaik dan penalaan ke atas sistem kawalan telah dilaksanakan bagi pasangan kawalan turus yang ditentukan.

Model keadaan stabil itu direkabentuk dengan menggunakan perisian simulasi komersil, ASPEN PLUS^{TM} dan dibandingkan dengan keputusan-keputusan yang telah diterbitkan oleh kajian-kajian lepas. Model yang sama digunakan untuk mengkaji operasi permulaan turus dengan cara lazim. Pengajian keadaan dinamik adalah dijalankan dengan menggunakan ASPEN DYNAMIC^{TM}. Dua pasangan kawalan yang terbaik ditentukan dengan menggunakan kaedah RGA. Kawalan-kawalan telah ditala-haluskan dengan menggunakan kaedah Ziegler Nichols (ZN).

Model penyulingan bertindak balas bagi pembuatan etil asetat telah berjaya direkabentuk and dibandingkan dalam penyelidikan ini. Operasi permulaan penyulingan bertindak balas yang melibatkan tindak balas adalah amat mencabar. Oleh itu, tiga jenis operasi permulaan yang berlainan telah dikaji. Operasi permulaan yang terbaik dipilih dan diperbaiki untuk mencapai masa permulaan yang tersingkat and operasi yang agak stabil.

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LIST OF SYMBOLS AND ABBREVIATION

ε	Packing voidage or reaction volume
λ	Relative gain
Λ	Relative gain array
τ_D	Derivative time
α_i	Exponent of i^{th} component
τ_I	Integral time
ρ_L	Liquid density
ΔP	Pressure drop across the section
$\Delta\bar{u}$	Input variable
$\Delta\bar{y}$	Output variable
ϕL	Volumetric liquid holdup
∇N^{f}_{Gi}	Vapor phase file mass transport
∇N^{f}_{Li}	Liquid phase file mass transport
Π	Product operator
a	Specific surface area of the packing
Ac	Acetic acid
A_{da}	Minimum area under the downcomer apron
BOTTOM	Material stream for Bottom stream in ASPEN PLUS^{TM}
C	Controlled variables
C_i	Concentration of the i^{th} component
C_k	Percent volume fraction of acid catalyst
D	Derivative time
E	Activation energy
EQ	Equilibrium
EA	Ethyl acetate
ETBE	Ethyl-tert-butyl-ether
Eth	Ethanol
FEED, FEED 1	Material streams for feeds in ASPEN PLUS^{TM}
FORTRAN	The IBM Mathematical Formula Translating System
g	Acceleration due to gravity

H_2O	Water
h_{Crest}	Height of the liquid crest over the weir
H_2SO_4	Sulphuric acid
HETP	Height equivalent to a theoretical plate
I	Integral time
IOL	Input-output linearizing
K	Vapor-liquid equilibrium ratio or Proportional gain or Close/Open loop gain
K_1	Denominator of pre-exponential factor of k_1
k, k_1,k_2	Pre-exponential factor
K_{BL}	A dimensionless constant, equal to 0.555
K_c	Ultimate gain
K_{dc}	A constant
K_{Pack}	Packing constant
K_{Weir}	Weir constant
L	Liquid
l_{fV}	Liquid volume fraction in the packed section
LMTD	Log mean temperature difference
L_{Weir}	Total weir length
M	Manipulated variables
MA	Methyl acetate
Matlab	Matrix laboratory
MESH	Material balance, vapor liquid equilibrium equations, mole fraction summations and heat balance
MIMO	Multiple inputs-multiple output
MTBE	Methyl-tert-butyl-ether
n	Temperature exponent
N	Number of components
NRTL	Non-Random-Two-Liquids
P	Proportional gain
PI	Proportional-integral
PID	Proportional-Integral-Derivative

PPC	Pattern-based predictive control
P_u	Ultimate period
Q_L	Volumetric liquid flow rate from the stage
Q_L	Volumetric flow rate of liquid from the tray for that pass
r	Rate of reaction
r_j	Ratio of sidestream flow to interstage flow
R	Gas law constant
$R_{m,j}$	Rate of reaction m on stage j
RD	Reactive distillation
RGA	Relative Gain Array
SC	Simultaneous convergence
SISO	Single input-single output
T	Absolute temperature
TAME	Tert-amyl methyl ether
T_o	Reference temperature
TOP	Material stream for distillate stream in ASPEN PLUS™
u	Input
U_j	Hold up on stage j
U_L	Liquid velocity in the packed section
u_L	Superficial liquid velocity
UNIFAC	Universal functional activity coefficient
UNIQUAC	Universal quasi-chemical activity coefficient
V	Vapor
VAP	Material stream for Vapor stream in ASPEN PLUS™
v_{im}	Stoichiometric coefficient of component in reaction m
x	Mole fraction of component in the liquid phase
y	Mole fraction of component in the vapor phase or output
Z	Height of packing in the section
ZN	Ziegler Nichols

1.0 INTRODUCTION

The production of ethyl acetate is typically done through esterification process and this has presented an opportunity for the application of reactive distillation. Reactive distillation involved combining the reaction and distillation process in a single equipment or unit operation and thus able to lower the capital and operating costs significantly in comparison to the conventional technology of having a reactor and a separate distillation column.

1.1 Ethyl Acetate

Esters, the organic compound that contains two parts, namely first the 'alcohol part' and secondly the 'acid part'. It is formed by esterification process typically esterification of alcohol, carboxylic acid, dicarboxylic acid and even glucose. Carboxylic acid esters are the most pleasant-smelling organic compounds. It is used as the flavors and fragrances of fruits, flowers and others. It is an excellent solvent and reaction intermediates. Typically, esters are prepared by the reaction of an alcohol (R-OH) or phenol () with acid or acid derivatives (Morrison & Boyd, 1992).

Ethyl acetate is one of the carboxylic acid esters. Appendix A gives the typical ethyl acetate properties. Other names for ethyl acetate are Acetic acid ethyl ester, Acetic ether, Acetoxyethane, Ethyl acetic ester and Ethyl ethanoate. It is used in manufacturing of printing inks, paints, coatings, artificial fruits, perfume, film, food additives, laminates, pharmaceuticals and others. Ethyl acetate is also used in formulation of adhesives and lacquers and as favorable solvent for vitamin E production. Due to its low boiling point, it is suitable for the production of high-grade defatting detergent.

Ethyl acetate, used as solvent in paints, has contributed to at least 10% of the total ethyl acetate usage demand. In pharmaceuticals, it usage constitutes some 35% of the total ethyl acetate usage demand. It is mainly used to manufacture amoxylcillin and sulpha drugs. The expected demand for ethyl acetate in the pharmaceutical industry presently is estimated at 35,000 ton per annum. World wide, its demand is expected to grow at 8-

10% per annum, due to the high demand in packaging sector and pharmaceuticals sector. The current global capacity for ethyl acetate is 1.2 Million Tonnes (India Infoline, 2002).

There are several ethyl acetate manufacturing plants around the world, and it is produced through different components and methods such as esterification of acetic acid with ethanol, liquid-phase oxidation reaction of n-butane with ethyl acetate produced as a byproduct and condensation of acetaldehyde. The world largest ethyl acetate plant is located at Saltend, Hull, United Kingdom (UK), which belongs to BP. It was commissioned in June 2001 and is designed for 220,000 tonnes/yr. Others producers include Celanese in Pampa, Eastman in Kingsport, and Eastman in Longview with the capacities of 130 million lb/yr, 59 million lb/yr and 51 million lb/yr respectively. The demand is expected to reach 180 million pounds in the year 2006 with a forecast of 3.4 percent growth for period through the year 2006. (The Innovation group, 2003)

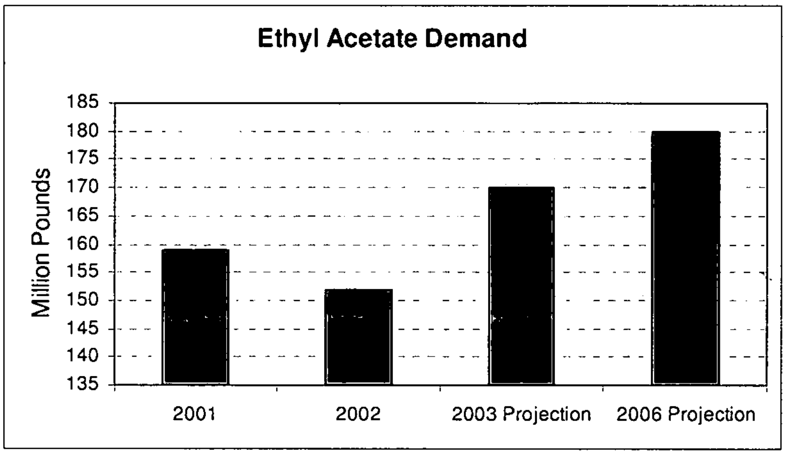


Figure 1: Ethyl Acetate Demand (The innovation Group, 9-Sept-03)

1.2 Reactive Distillation

Reactive or catalytic distillation (RD) technique is the combination of reaction process and distillation process within the same unit operations. The concept is to distill away the reacted products soon after its formation in order to shift the chemical equilibrium towards higher conversion. Patents of reactive distillation dated back to the 1920's. Due to the complexity of the distillation column, a lot of studies have been carried out and has taken a long time prior to its application by industry.

Apart from the benefit of pushing the reaction equilibrium close to the product side, reactive distillation is also able to save the equipment cost since it managed to combine the reactor and the separate column in one device. It has been reported in a methyl acetate production in Kingsport, Tennessee, only one fifth of the conventional capital investment cost and energy usage is expended as a result of adopting this technology (Doherty and Malone, 2001). The improvement was attributed, among others, to the fact that it is also able to eliminate the complicated product recovery processes as the reactants are almost fully converted in the column. The unconverted reactants are recycled back to the column through the reflux flow and the boilup flow. This helps to further reduce recycle cost and catalyst usage.

In some cases, the formation of azeotropes could be avoided using reactive distillation technology. This is because of the conditions in the reactive distillation column allowing for the reactants and products to be "reacted away" from the azeotropic state. Another benefit is from the heat integration, where heat generated from the exothermic reaction can be used directly as heat of vaporization thus able to reduce the reboiler duty.

Another interesting point is reactive distillation column could potentially avoid hot spots and reaction runaways using liquid vaporization as the thermal flywheel. Runaway reaction may occur during intentional chemical conversion process, self-heating and thermal instability or incompatibility of materials during storage, transport or unit operations

MTBE(methyl-tert-butyl-ether) was the first well known commercial examples of reactive distillation being applied in the industrial scale. There were other productions where the reactive distillation technology were reported to be used such as ETBE (ethyl-tert-butyl-ether), methyl acetate and TAME (tert-amyl methyl ether). Appendix B provides some of the typical reactive distillation processes (Okur and Bayramoglu, 2001).

In addition, reactive distillation technology could be potentially utilized for the hydration processes for producing Ethylene Glycol, Propylene Glycol, aromatic alkylation (Cumene and Akly Benzenes), nitritation (Nylon) and oligomerization (1-Butene) reactions.

1.3 Problem Statement

Due to the increasing trend in the demand of ethyl acetate, there is a need to improve its production by expanding the capacity of existing plant or new plant through the used of new technology.

Although reactive distillation has been identified as the promising new technology to help achieve the above, there were still insufficient understanding developed in the past especially in its design and operations, which tend to be more complex as a result of the integration between reaction and separation in a single unit operations. Often studies were made based on specific system rather than looking at overall perspective in view of the variation reported for different systems especially when dealing with the operational aspects.

On the operations of the reactive distillation involving ethyl acetate production, previous researchers have been focusing more on the steady state condition using mainly simulation. Studies covering the dynamic state are very limited and often focused only on control. There were limited researches carried out on the start-up behavior of the reactive distillation column available in the literature.

The combination of reaction and separation in one column increases the complexity of the process. Therefore, starting up a reactive distillation column is very different from starting up a conventional distillation column, in which only separation process takes place. In view of the criticality in developing better understanding on the behaviors of the reactive distillation column applied to the ethyl acetate production, especially during start-up and control operations, the study was commissioned to cover these aspects. The outcome is aimed at developing better control strategies using conventional controllers and better understanding of the start-up behaviors of the column.

1.4 Research Objectives

Overall, this research focused on studying the operational aspects of a reactive distillation column for the production of ethyl acetate. Simulation model i.e., steady state and dynamic state, for the reactive distillation process is replicated using commercial simulators namely ASPEN PLUS ^{TM} and ASPEN DYNAMIC^{TM}. The study involves looking at the operational behavior of the simulated system, followed with determination of the best controller pairings based on the available controlled and manipulated parameters using Ziegler Nichols method, and lastly, the start-up behaviors for the system using conventional method.

The research endeavors to address the following objectives:

i. To model a reactive distillation column steady state and dynamic state model using commercial simulator namely ASPEN PLUS^{TM} and ASPEN DYNAMIC^{TM} for the production of ethyl acetate for the purpose of undertaking the study.

ii. To determine the best possible control strategies for the column operations using ASPEN DYNAMIC^{TM}.

iii. To study and understand the start-up dynamic of the reactive distillation column behaviors from cold start-up and suitability of conventional method for start-up operations. The work is limited to the use of conventional controllers in view of its wide scale application across industry.

iv. To propose an optimized strategy in starting up a reactive distillation column based on the understanding of start-up operations.

1.5 Research Scope

In addressing the research objectives, the following scopes have been defined for the purpose of executing the research.

The esterification of acetic acid and ethanol using sulphuric acid as the catalyst to produce ethyl acetate is chosen for the research work.

There are two reaction rate equations used in the ethyl acetate production whereby one of the reaction rate equations is not in power law expression as required by ASPEN PLUS^{TM}. At such, the reaction rate equation is converted into power law expression and validated against the original equation using t-test and correlation coefficient methods.

A simulation model of the reactive distillation producing ethyl acetate is replicated using a commercial simulator namely the ASPEN PLUS ^{TM}. The model is validated with experimental data and simulated data under steady state condition obtained from literature and then converted to a dynamic simulation for the purpose of studying the operations and control of the system.

The best controller strategies for the system are determined using Relative Gain Array (RGA) method. Reflux rate, condenser duty, reboiler duty and bottom rate are used as the manipulated variables while the top stream composition of ethyl acetate and the bottom stream composition of water are used as the controlled variables. Ziegler Nichols method is used to tune the controller in order to achieve satisfactory operations.

In considering the complexity of the reactive distillation operations, a start-up study is also conducted using dynamic simulator namely ASPEN DYANMIC^{TM} with the aim of understanding the behaviors of the column during start-up and to propose a better operations sequence for starting up.

1.6 Research Contribution

Upon understanding the reactive distillation column behaviors during start-up using commercial simulators, i.e. ASPEN PLUS™ and ASPEN DYNAMIC™, it could be utilized in ethyl acetate production plant, which would be able to minimize the loss of material and time involved to stabilize the column at the initial stage. The proposed optimized reactive distillation column start-up strategy is able to reduce the start-up timing and dampen the fluctuation of pressure and temperature. Furthermore, the best control strategy determined would allow the column to handle any disturbances without upsetting the plant and producing off specification product.

2.0 LITERATURE REVIEW

Conventionally, ethyl acetate can be produced through batch or continuous esterification process using different equipment configurations and catalysts. In order to minimize the capital cost and operating cost, reactive distillation of ethyl acetate production is considered as an excellent alternative to the conventional design. The number of literature involving ethyl acetate has grown in recent years due to more researches focusing in getting higher purity products. Operations and control of reactive distillation studies are looked into in order to have a better understanding on reactive distillation in steady state and dynamic state. The limitations of these literatures are described and will be addressed in this research.

2.1 Ethyl Acetate Production

There are three main conventional processes in the production of ethyl acetate namely the Tishchenko Reaction, the Continuous Esterification process and the Batch Esterification process.

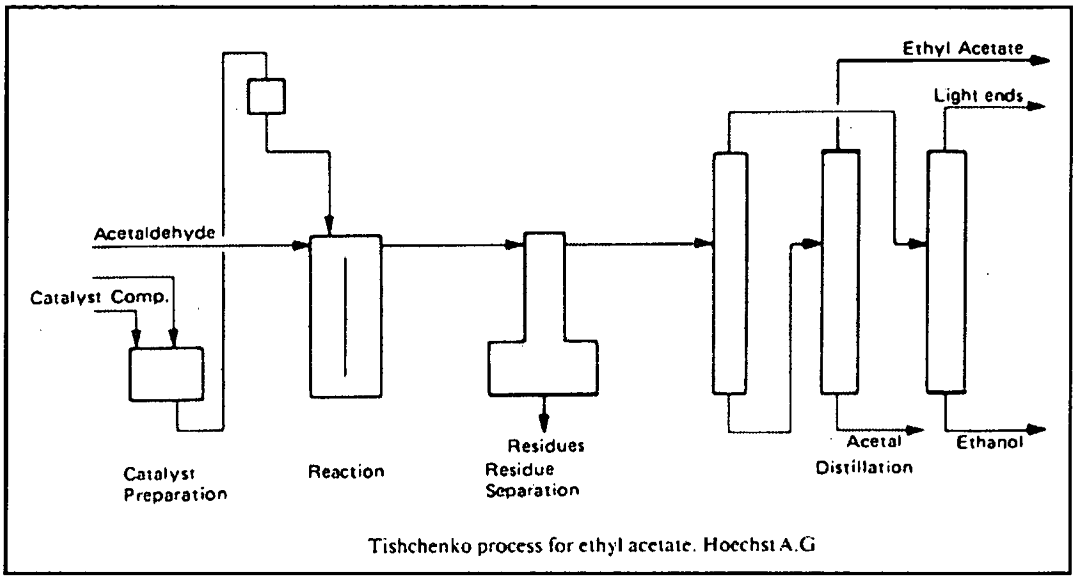
i. The Tishchenko Reaction (Mcketta & Cunningham, 1984).

The process is able to deliver a 61% yield with the presence of aluminum ethoxide as catalyst. The manufacturing plants were mostly developed in Europe.

Reaction Equation:

$$2CH_3CHO \rightarrow CH_3COOCH_2CH_3 \qquad \textbf{Equation 1}$$

The catalyst, aluminum ethoxide is mixed with acetaldehyde and the reaction takes place at 0°C for about 1hour. After the reaction stage, the mixture is separated to produce the final product, ethyl acetate and non-converted acetaldehyde. The process is summarized in Figure 2.



Tishchenko process for ethyl acetate. Hoechst A.G

Figure 2: The Tishchenko Reaction (Mcketta & Cunningham, 1984)

ii. The Continuous Esterification Process (Kroschwitz & Grant, 1996)

Esterification of ethanol and acetic acid is another alternative to produce ethyl acetate. Acetic acid, excess ethyl alcohol and concentrated sulfuric acid are mixed in a reactor. The mixture is pumped through a reaction column, a separator and two recovery columns in order to obtain high purity ethyl acetate. Ethyl acetate is sent to the reaction column operating at 80°C; the top product stream is transferred to the first recovery column to produce 83% ester, 9% alcohol and 8% water at 70°C. After passing through a separator and another recovery column, the overhead column contains 95-100% ethyl acetate. Figure 3 shows the continuous esterification process.

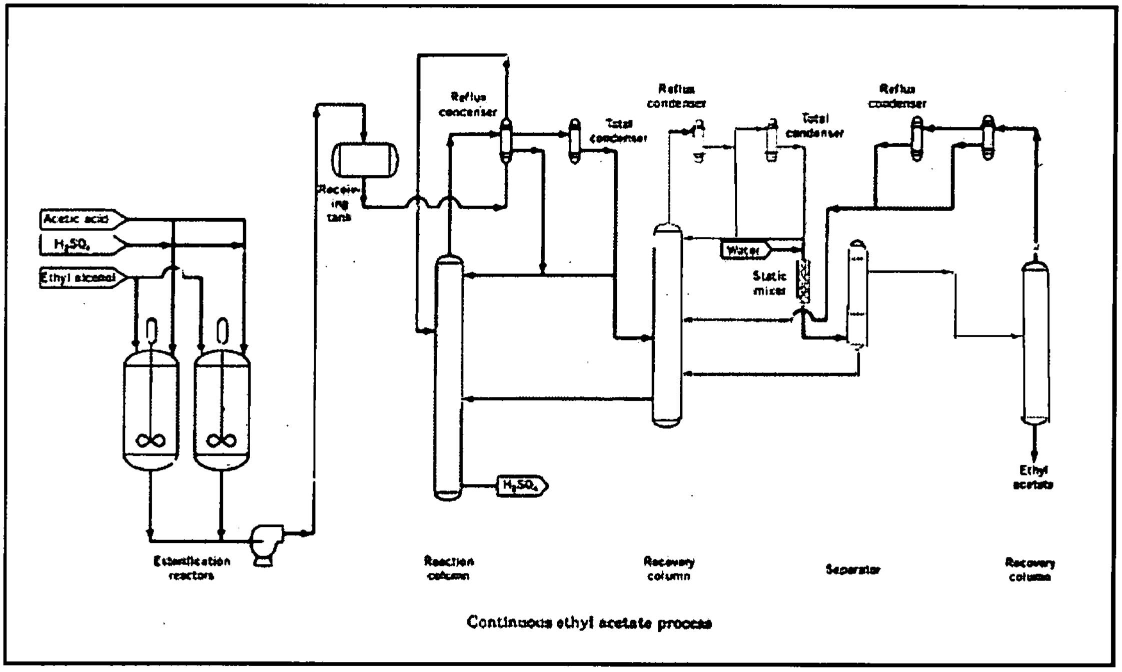


Figure 3: The Esterification Process (Continuous process) (Kroschwitz & Grant, 1996)

iii. The Batch Esterification Process (Kroschwitz & Grant, 1996)

In the batch esterification process, acetic acid, ethanol and concentrated sulfuric acid are added in a reactor. The reactor is heated using a closed coil steam pipe. A fractionating column is used and maintained at 70°C in order to give a ternary azeotropic mixture of 83% ethyl acetate, 9% alcohol and 8% water. Low boiling point of overhead product relative to water is vaporized to fractionating column from the reactor. The vapor from the fractionating column is condensed, part of it is returned to the top of the column as reflux, and the remaining to the storage. The reactants in the storage are recovered through a recovery column. Figure 4 shows the esterification batch process.

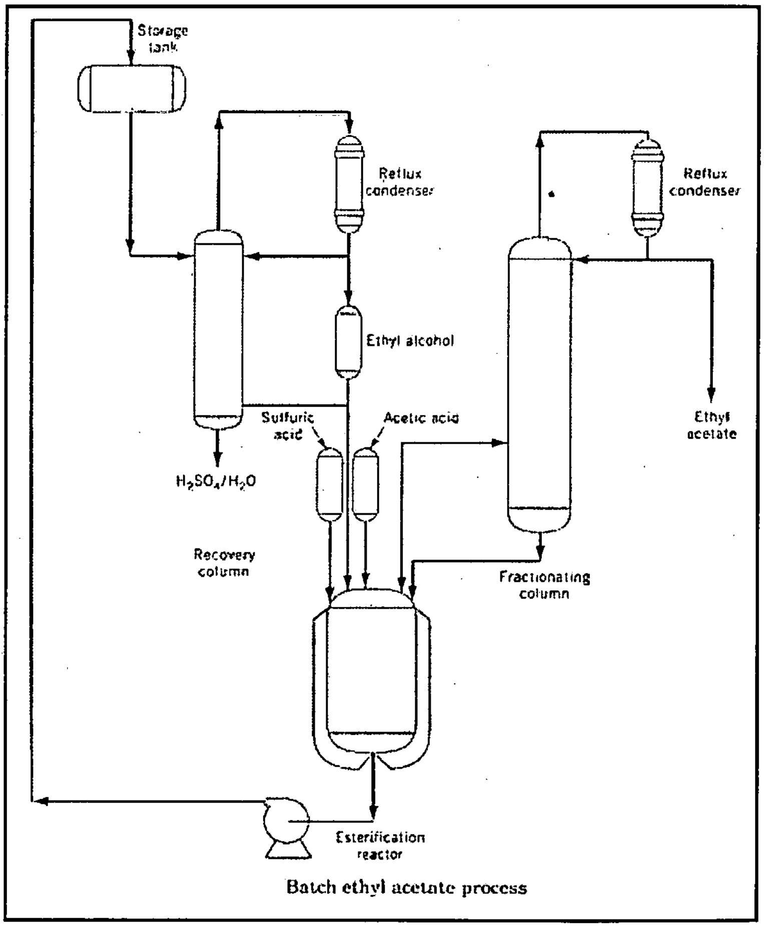


Figure 4: The Esterification Process (Batch process)

(Kroschwitz & Grant, 1996)

2.2 Reactive Distillation for Ethyl Acetate Production

According to Taylor & Krishna (2000), the first reactive distillation patent dated back to the 1920s. They listed some of the early journal articles published by Keyes (1932), Leyers and Othmer (1945a,b), Schniep et al. (1945), Berman et al. (1948b) and Merman et al. (1948a). Most of these early publications mainly deal with the use of homogeneous self-catalyzed reactions.

In 1988, a robust numerical procedure for simulating reactive distillation using homotopy-continuation method was developed by Chang and Seader, (1988). Acetic acid (1), ethanol (2), water (3) and ethyl acetate (4) were the four components used in their work. These authors highlighted that due to the non-ideal nature of the liquid phase mixture caused by the presence of polar molecules, it is important to select the correct thermodynamic property for computing the vapor-liquid equilibrium because acetic acid tends to form a dimmer and a trimer in the vapor phase. For mixtures of ethyl acetate-water, acetic acid-water, and ethyl acetate-acetic acid-water, the presence of azeotropes were detected. They concluded that the application of reactive distillation for the esterification of ethanol with acetic acid is technically unfavorable using a single two-product distillation column for the conditions imposed in the study. Reason being is the K-value (vapor-liquid equilibrium ratio) of ethyl acetate was too close to ethanol and water, making the separation of ethyl acetate from ethanol and water in these stages very difficult.

A study on the effect of liquid-phase activity model on the simulation of reactive distillation for production of ethyl acetate was conducted by Okur and Bayramoglu (2001). The catalyzed reaction equations are as following:

$CH_3COOH\ (1) + C_2H_5OH\ (2) \rightleftharpoons H_2O\ (3) + CH_3COOC_2H_5\ (4)$ **Equation 2**

$$r_1 = k_1 C_1 C_2 - \frac{k_1}{K_1} C_3 C_4 \quad (mol/s\ m^3)$$ **Equation 3**

$k_1 = (4.195C_k + 0.08815)\ \exp(-6500.1/T)\ (m^3/mol\ s)$ **Equation 4**

$K_1 = 7.558 - 0.012T$ **Equation 5**

C_k is the percent volume fraction of acid catalyst = 0.4

Matlab (ver 5.0)^{TM} was used by them to set up and solve the simulation model. The simultaneous convergence (SC) method based on the multivariable Newton-Raphson algorithm was used. Different physical properties were tested using various reflux ratio and the results were compared. Among the physical properties used consist of UNIQUAC (universal quasi-chemical activity coefficient), Modified UNIFAC (universal functional activity coefficient) by Dortmund (Okur and Bayramoglu, 2001), Modified UNIFAC model by Lynbgy (Okur and Bayramoglu, 2001) and Empirical model by Suzuki (Okur and Bayramoglu, 2001). The results indicate that highest conversion was obtained using UNIQUAC but with higher reflux ratio.

A study conducted later to investigate ethyl acetate reactive distillation process was carried out by Kenig et al. (2001), to determine the feasibility of a proposed reactive distillation for a limiting case of simultaneous phase equilibrium and chemical equilibrium. The same four components studied by Chang and Seader, (1988) were used. A rate-based simulator involving a variety of FORTRAN^{TM} subroutine was used by Kenig et al. (2001) to predict the column concentrations, temperatures and other important variables for their study. In addition, reactive distillation experiments for homogeneously catalyzed esterification of acetic acid and ethanol to produce ethyl acetate and water were performed for validation. Sulphuric acid (H_2SO_4) was chosen as the catalyst. In the simulation, NRTL (non-random-two-liquids activity coefficient) model was selected for the thermodynamic property. Both set of results were compared and found to be in good agreement. Appendix C provides the information on the normal boiling points of the pure components and the azeotropes compositions. From the study, it was suggested that in order to obtain high conversion of ethyl acetate in the distillate and water in the bottom, it is preferably to use two separate feed points. The higher boiling temperature acetic acid is to be fed above the ethanol feed location. If reaction took place in all stages in the column, acetic acid would be found in distillate stream. In order to eliminate the above, it was recommended to limit the reaction zone within the center section of the column, leaving the section above and below it to be non-reactive.

Chang and Seader, (1988), Okur and Bayramoglu (2001) and Kenig et al. (2001) studied ethyl acetate production using esterification of acetic acid and ethanol. They were using robust numerical procedure, Matlab (ver 5.0)^{TM} and process simulators.

2.3 Operations and Control of Reactive Distillation Column

The first dynamic simulation study on reactive distillation was performed by Alejski and Duprat (1996). A 20-stage reactive distillation column was chosen to simulate the esterification process of ethanol and acetic acid. Comparison was made between published experimental data and the results obtained from their simulation. Their findings indicated that there was strong influence of various parameters on the process resulting from complex interactions between vapor-liquid equilibrium, reaction kinetics and hydraulics of the column, leading to complicated dynamic behaviors. The following three models were used in their study:

Table 1: Three Models used by Alejski and Duprat (1996)

Parameters	Model I	Model II	Model III
Plates Holdup	Determined by Francis Weir	Constant	Constant
Pressure Drop	Calculated on each plate	Constant	Constant
Flows of Phase	Determined by energy balance	Determined by mass and energy balance	Constant

Model I took into account of both hydraulic and thermodynamics phenomena that considered the plate holdup in the column. While model II and III only account for the thermodynamics, thus leaving the hydraulic aside. Based on the comparison made between the published experimental results and the simulation models, Model I was found to be the best to match the experimental data though with some deviations still observed. According to Alejski and Duprat (1996), the differences could be due to the simplifications made on the mathematical model. The conclusion from their study was that hydraulics should be considered for any dynamic simulation of the reactive distillation system.

Another study done by Vora and Daoutidis (2001) focused on dynamics and control of an ethyl acetate reactive distillation column. A column configuration producing higher conversion and purity at steady state was proposed. Analysis of the dynamic simulation and control study was carried out for different control configurations. The column was simulated in steady state to find the best configuration. It was observed that higher ethyl acetate conversion could be obtained when feeding the reactants into two different trays compared with single feeding. This finding was in agreement with Kenig et al. (2001) observation. Earlier research on reactive distillation for ethyl acetate production showed the attainable conversion for ethyl acetate was only at 30% with 50% purity for single feed column configuration. It was lower than equilibrium conversion (66%) and azeotropic composition (54% for binary ethanol-ethyl acetate azeotrope). With the multiple-feed configuration, the ethyl acetate conversion could achieve 76.8% with 65% purity. The multiple-feed configuration was used by Vora and Daoutidis (2001) for conducting control study. In the control configuration the following manipulated variables and controlled variables were used:

Table 2: Controller Configuration in Vora and Daoutidis (2001) study

Controller	Manipulated Variable	Controlled Variable
1	Distillate flow rate	Condenser holdup
2	Reflux flow rate	Distillate stream product purity
3	Condenser heat duty	Condenser Pressure
4	Bottom flow rate	Reboiler holdup

The controllers were tested for different incremental changes in the set point for the product purity. The performances of the controllers were observed. The model based on linear and nonlinear feedback controllers, along with conventional SISO PI controllers, were designed. The nonlinear controller is based on the nonlinear dynamic model that comprised of a standard nonlinear input-output linearizing (IOL) state feedback controller together with a linear error feedback with integral action. From the observations, the nonlinear controller was able to enforce the desired response in a smooth fashion. The linear controller also achieved the desired set-point but with a slight degradation in the output responses and some oscillations in the input responses. They concluded that nonlinear controller was able to eliminate the disturbance whereas the PI controllers demonstrated larger settling times and substantial overshoot.

Loperena et al. (2000) conducted a study on PI control for a high-purity ethylene glycol reactive distillation column. The controlled variable is ethylene glycol purity and the manipulated variable is boilup ratio, which is directly related with reboiler heat input. They have proposed new idea in the control study. New idea was proposed based on the analysis of the underlying input/output bifurcation diagram and modeling error compensation techniques. The result is found to be satisfactory as it was shown to be equivalent to a standard PI controller with antireset windup structure.

Al-Arfaj and Luyben (2002) conducted a design and control study on olefin metathesis production. Three different design cases were considered i.e. low conversion/low pressure, low conversion/high pressure and high conversion/high pressure. Effects of the selected design parameters, such as number of trays, operating pressure, holdup per tray and reflux ratio, were investigated to obtain a better understanding of the process on the steady state design. The findings are high conversion could be achieved using higher number of trays, higher hold up per tray, lower operating pressure and higher reflux ratio. Higher reflux ratio and number of trays would probably make the case uneconomical. Therefore, optimization on number of trays and reflux ratio was performed. The outcomes of the optimization study are low conversion/high pressure design is more economical but recovery system may be needed to increase the product purity, which may incur more overall cost. The high conversion/high pressure is not economical but no further processing is required to increase the product purity. Different control structures were also studied for the low conversion/low pressure design. From the finding, they have examined the composition temperature cascade control structure and found out that it is able to provide the most effective control.

In the same year, Al-Arfaj and Luyben (2002) studied the control of methyl acetate (MA) reactive distillation for high-conversion design and low-conversion design with different operating conditions. Three control structures were proposed and studied for both column designs. They found that it was easier to control the column with low-conversion design.

Engell and Fernholz (2003) studied the control of semibatch reactive separation process using methyl acetate as example. In their study, single input-single output control (SISO), multiple inputs-multiple outputs control (MIMO) and nonlinear predictive control were studied using pilot plant and neural net plant model. They concluded that there is strong interactions and process nonlinearity that make the control problem difficult and the deviation from the optimal operations resulted losses in efficiency. From their comparison, better results can be obtained by nonlinear predictive control.

Tian et al. (2003) studied the control of ethyl tert-butyl ether (ETBE) reactive distillation process by developing a pattern-based predictive control (PPC) scheme incorporating conventional proportional-integral (PI) controller. Pattern-based predictive control is a method that does not reply on exact process models while providing improved control performance. Cases studies were carried out with a pilot-scale reactive distillation column at laboratory for ETBE. They concluded that PPC could provide improved control performance for set-point tracking and disturbance rejection cases.

Alejski and Duprat (1996) and Vora and Daoutidis (2001) have conducted the studies on dynamic control for ethyl acetate production with different configurations. Loperena et al. (2000), Al-Arfaj and Luyben (2002), Engell and Fernholz (2003) and Tian et al. (2003) studied the different column control methods with different productions. Kenig et al. (2001) have conducted their studies using 82 stages reactive distillation column while Vora and Daoutidis (2001) used a 13 stages reactive distillation column. Kenig et al. (2001) could have piloted the reactive distillation column based on the real plant information obtained from their sponsor. Vora and Daoutidis (2001) mainly focused on dynamics and control of a reactive distillation column, thus, a 13 stages reactive distillation column model was used in their studies. The research done was focus on the outcome of the controllers. The outcomes were compared with mathematical model and pilot plant modeling. However, proper tuning of the controller has not been performed appropriately for this integrated reaction and separation column for the paring determined.

2.4 Reactive Distillation Start-up

Starting up of a reactive distillation column is expected to be complex due to the additional features in comparison to the conventional distillation column. There are many factors that can impact the performance of start-up operations in a distillation column. Different start-up strategies can produce different outcomes. Sequence in starting up a column is one of the main factors that could determine its performance. There are several known start-up strategies for conventional distillation. The most recommended strategy is the total reflux operations.

Reepmeyer et al. (2004) proposed four different strategies for starting up distillation column namely;

i. Conventional: Set all control variables to steady-state values and wait.
ii. Total Reflux: Column is run in loop operations, no distillate removal.
iii. Total Distillate Removal: Exact opposite of total reflux strategy, column is run without reflux.
iv. Time Optimized (developed for heat-integrated columns): heating duty and reflux are set to 1.3 their steady-state values.

Schneider et al. (2001) carried out a dynamic study on methyl acetate process. For model validation, several experiments have been carried out using pilot plant column. A comparison on the simulation results, experimental data and numerical investigation for the determination of the most sensitive parameters were presented. They concluded that the simulation results generally are in agreement with the experimental data. It has been shown that in the numerical investigation, the reaction kinetics and the model of the column periphery has the most significant influence on the simulation results especially in the case of dynamic processes like reactive batch distillation.

A rigorous process model was developed by Reepmeyer et al. (2004) to simulate the start-up of a cold and empty reactive distillation (RD) column and validated with a transesterification process. Strategies for time optimal start-up of an RD column were presented. They concluded that the mostly used strategy for conventional distillation i.e.

total reflux, is only recommendable with limitations when applied to RD column. They have tried two alternatives to improve the start-up time, i.e. a) recycle of bottom product and b) initial charge of product. The following table shows the 3 different schemes for recycle of bottom product and 4 different schemes for initial charge of product chosen by them.

Table 3: Strategies chosen by Reepmeyer et al. (2004)

Recycle of Bottom Product Session:	
1	No recycle is the base case.
2	Split factor = recycle stream/bottom stream = 1 (for duration 5000s and 10000s)
3	Split factor = 10
Initial Charge of Product:	
1	Initial charge with feed.
2	Initial charge with high boiling liquid feed component in excess
3	Initial charge with low boiling liquid d feed component in excess.
4	Initial charge with liquid resembling the steady state bottom product
5	Initial charge with liquid resembling the steady state top product

They have also conducted the study on two examples, i.e. a) transesterification of a fatty methylester and b) esterification of ethyl acetate. The simulation matched with the experimental results for transesterfication of a fatty methylester. The new strategies did not provide significant improvement on the start-up period for transesterification of a fatty methylester process. In the study, there was no experimental data available for esterification of ethyl acetate with single feed operations. However, based on the simulation, the start-up time was reduced from 6.24 hours to 1.07 hours for initial charge of the top product to the column strategy. Therefore, it is useful to keep the top product from the last charge to prefeed the column before the next start-up.

Two mathematical models were proposed by Elgue et al. (2004) for the simulation of the dynamic behaviors during start-up operations from an empty cold state. The models were validated through experiments carried out on a batch distillation pilot plan, with perforated trays, supplied by a water methanol mixture. Two critical points to consider were the column behavior and the thermosiphon (heating equipment for the column) performance. At the beginning of the start-up conducted on the experiment, an oscillatory behavior was observed. This behavior is directly related to the thermosiphon technology. The liquid heated by the thermosiphon only flows to the vessel when its temperature is high enough. Therefore, the heat internal reflux inside the vessel shows an oscillatory behavior, decreasing until the vessel mixture reached bubble point. Bottom plates appear to heat up from the beginning of the start-up. In fact, even before temperature reaches bubble point, a slight vapor flow, due to the thermosiphon heat, escapes from the vessel and begins to heat bottom plates.

As a summary of this section, some works have been carried out on column start-up and dynamic behaviors lately. Schneider et al. (2001) conducted a start-up operations on methyl acetate production. Elgue et al. (2004) carried out a study on water methanol mixture. Reepmeyer et al. (2004) carried out a study on reactive distillation column start-up on ethyl acetate production. Nevertheless, those studies were using proprietary process simulator and mathematical models for comparison with laboratory results and literature data. There may be lack of thermodynamic and hydraulic consideration in the integrated reaction and separation column as compared to the commercial simulator.

2.5 Limitations of the Previous Research Works

There were numerous research carried out related to ethyl acetate production. Apart from RD column steady state studies, the researchers also looked into column control as well. Based on the outcomes of the studies, multiple feeds column configuration was recommended for obtaining the highest product purities possible. Several control models were suggested by researchers for column control. However, there were limited studies being carried out on reaction distillation column start-up using dynamic state simulation. At present, there have been no research carried out using commercial simulator.

As commented by Chang and Seader (1988), the application of reactive distillation to the esterification of ethanol with acetic acid is not technically favorable in a two-product distillation column because of very close K-value for the components. Numerical method may not be sufficient in handling this complex reactive distillation column for acetic acid and ethanol esterification process. It is believed that commercial simulation software, like ASPEN PLUS^{TM} should be able to present better results as compared to proprietary programming. ASPEN PLUS^{TM} program considers the thermodynamic package and suitable for strong liquid phase non-ideality system.

Alejski and Duprat (1996) concluded that hydraulics should be considered in dynamic simulation. They did mention that hydraulic is characterized by a relatively small time constant while thermodynamic processes are associated with a large time constants. Nevertheless, using commercial simulator, it is able to incorporate more details hydraulic model and provide a more accurate and precise results.

Vora and Daoutidis (2001) studied the controllers' performance for linear and non-linear control and other researchers studied for different controls. Conversely, tuning of the controller has not been appropriately performed for this integrated reaction and separation column for the paring determined. Widely used tuning method, Ziegler Nichols method in close-loop, is able to fine tune the controller to ensure fast response to disturbance during steady state operations.

Reepmeyer et al. (2004) mainly looked at optimizing the start-up for ethyl acetate simulation, without details study on the dynamic. More details studies may be required for reactive distillation for better understanding. It is very critical to understand the behaviors of the column before field installation.

This research aims to address the shortcoming from the previous research works as mentioned above.

3.0 THEORY

Reactive distillation reacts following the Le Chatlier's Principle, where a reversible reaction will react toward the equilibrium for any external stress introduced. Reactive distillation can be categories into hybrid column and non-hybrid column based on the different reaction zone. There are two types of mathematic modeling for reactive distillation, i.e. Equilibrium stage model and Non-equilibrium stage model.

Relative gain array method is one of the methods in determining the best controller pair. Tuning of controller is required to achieve satisfactory desired control outcome. Among the popular tuning methods are Trial and Error method, Cohen-Coon method and Ziegler Nichols method.

3.1 Reversible Reaction

Reversible reaction is a chemical reaction where the products have the tendency to convert back to reactants. For example, consider the following chemical reaction, where A and B are reactants and C and D are products.

$$\mathbf{A + B \rightleftharpoons C + D} \qquad \textbf{Equation 6}$$

For most of the reaction, the equilibrium point is found to lie towards the left hand side and therefore producing little products (C and D) as shown below.

$$\underleftarrow{\mathbf{A + B \rightleftharpoons C + D}}$$

If one or more reaction products are removed from the reaction system, it is expected that more products will be formed. Thus, adding more reactants will cause the product conversion to increase and vice versa due to the Le Chatlier's Principle. According to the principle, if external stress is introduced to the system at equilibrium, the system will adjust itself to minimize the stress and move towards establishing a new equilibrium. As shown in the equation below, if one of the products, say D is removed continuously, more products are formed when the chemical reaction moved towards to a new equilibrium.

$$\underrightarrow{\mathbf{A + B \rightleftharpoons C +}}\cancel{\mathbf{D}}$$

3.2 Reactive Distillation

Reactive distillation is typically used with reversible reaction. The conventional process consists of a reactor followed by a distillation column. Conversions of reactants only occur in reactor and are limited by the equilibrium conditions. On the other hand, the application of reactive distillation column clearly enables the separation of product during the reaction stage and thus capable of pushing the reaction equilibrium close to the product side. According to Institute Fur Automatic (2002), there are fundamentally two types of reactive distillation column, i.e. Non-hybrid column and Hybrid column. For a Non-hybrid column, reaction takes place in all trays including condenser and reboiler. For a Hybrid column, the reaction zone is limited to certain section in the column (rectifying and/or stripping sections) as shown in Figure 5. Normally, non-hybrid column is used for homogeneous (liquid) catalyst design while hybrid column is used for heterogeneous (solids) catalyst.

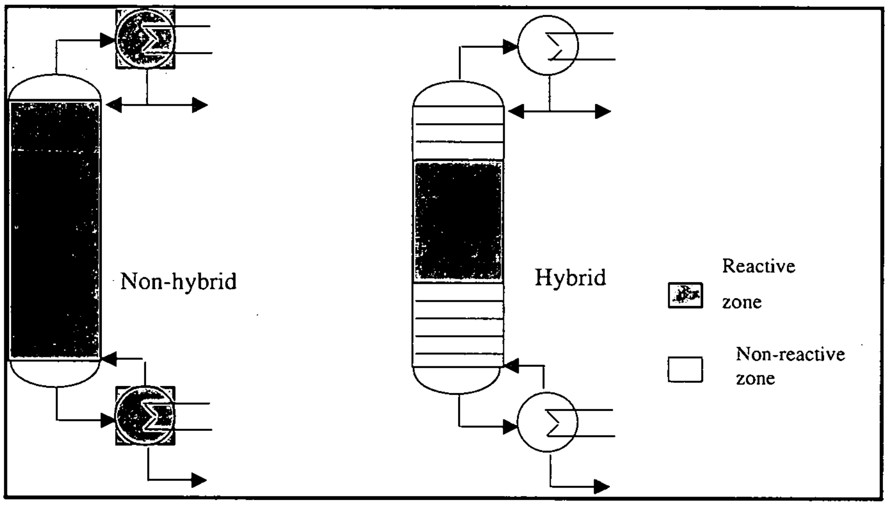


Figure 5: Type of Reactive Distillation Column (Institute Fur Automatic, 2002)

3.3 Model of Reactive Distillation Column

a) Steady State Model

There are two types of mathematic modelings used for reactive distillation namely, the equilibrium stage model and the rate based stage model or also known as the Non-equilibrium stage model. Most of the researchers preferred the equilibrium stage model due to the reactive distillation column complexity.

i. Equilibrium (EQ) Stage Models (Taylor & Krishna, 2000)

It is a simplified model based on vapor-liquid physical equilibrium. Following is the schematic diagram of equilibrium stage.

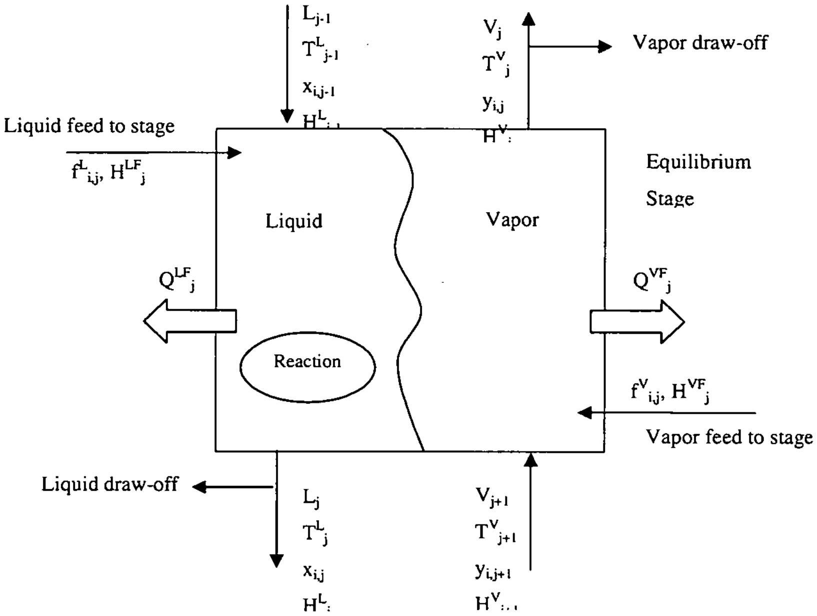


Figure 6: Equilibrium Stage Schematic Diagram

Vapor from the stage below and liquid from the stage below is in contact. The vapor and liquid streams leaving the stage are assumed to be in equilibrium with each other. The equations that model equilibrium stages are **MESH** (material balance, vapor liquid equilibrium equations, mole fraction summations and heat balance) equations. The reaction equation(s) is incorporated into the equilibrium stage model to represent the reaction(s) taking place at each stage.

The **M** equations represented the material balance equation.

$$\frac{dU_j}{dt} = V_{j+1} + L_{j-1} + F_j - (1+r_j^V)V_j - (1+r_j^L)L_j + \sum_{m=1}^{r}\sum_{i=1}^{c} v_{i,m}R_{m,j}\varepsilon_j. \qquad \textbf{Equation 7}$$

U_j is the hold up on stage j and can be considered to be only liquid phase hold-up in very few exceptions. It is important to include the hold-up of the vapor phase at higher pressures. $R_{m,j}$ is the rate of reaction m on stage j.

The equation taking consideration of the vapor hold-up is

$$\frac{dU_j x_{i,j}}{dt} = V_{j+1}y_{i,j+1} + L_{j-1}x_{i,j-1} + F_j z_{i,j} - (1+r_j^V)V_j y_{i,j} - (1+r_j^L)L_j x_{i,j} + \sum_{m=1}^{r} v_{i,m}R_{m,j}\varepsilon_j \qquad \textbf{Equation 8}$$

where, r_j is the ratio of sidestream flow to interstage flow:

$$rV_j = SV_j / V_j \qquad \textbf{Equation 9}$$

$$rL_j = SL_j / L_j \qquad \textbf{Equation 10}$$

$v_{i,m}$ is the stoichiometric coefficient of component i in reaction m and ε_j is the reaction volume.

The **E** equations are the phase equilibrium relation. In many early papers, chemical reaction equilibrium is not considered because it is more difficult to model.

$$y_{i,j} = K_{i,j}x_{i,j} \qquad \textbf{Equation 11}$$

The **S** equations are the summation equations

$$\sum_{i=1}^{c} x_{i,j} = 1 \qquad \sum_{i=1}^{c} y_{i,j} = 1 \qquad \textbf{Equation 12}$$

The enthalpy balance equation is

$$\frac{dU_jH_j}{dt} = V_{j+1}H_{j+1}^V + L_{j-1}H_{j-1}^L + F_jH_j^F - (1+r_j^V)VjH_j^V - (1+r_j^L)LjH_j^L - Q_j \qquad \textbf{Equation 13}$$

The superscripted **H**'s are the enthalpies of the appropriate phase. Normally, this is referring to liquid phase enthalpy.

Under steady-state conditions, the deviation of all the above equations are equal to zero.

ii. Rate-based Stage Model/ Non-equilibrium stage model (Kenig et. al., 2001)
This model considered the actual rates of multicomponent mass transport, heat transport and chemical reactions directly. Mass transfer rate at vapor-liquid interface is described based on the two-film model. The model requires thermodynamic properties, not only for calculating the phase equilibrium but also for calculating the driving force for mass transfer and in reactive distillation the thermodynamics properties is useful for taking into account the effect of non-ideal component behaviour in the calculation of reaction rates and chemical equilibrium constants. (Taylor and Krishna, 2000).

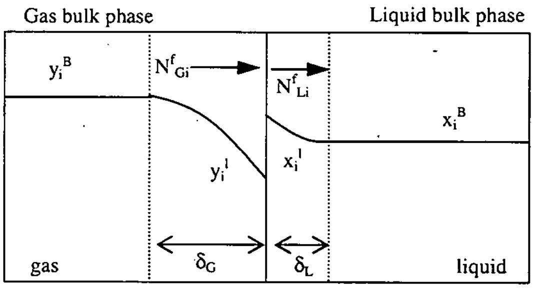


Figure 7: Rate-based Stage Model Schematic Diagram

Maxwell-Stefan equations are used for multicomponent diffusion in the films. In order to descript the real case for gases and liquids, Maxwell-Stefan equations have been modified for the usage.

$$\frac{x_i}{RT}\frac{d\mu_i}{dz}=\sum_{j=1}^{n}\frac{x_i N_j - x_j N_i}{cD_{ij}} \qquad i=1,\ldots,n.$$ **Equation 14**

Therefore, to model vapor-liquid mass transfer, the film model and the Maxwell-Stefan diffusion model have to be combined. In the rate-based stage model, the equilibrium state only appears at the interface.

The mass balance equations for rate-based models are written separately for each phase. As in the reactive distillation chemical reactions take place in the liquid phase only.

$$0 = -\frac{d}{dl}(Lx_i^B) + (N_{Li}^B a' + R_L^B \phi_L)A_c \qquad i = 1,\ldots,n. \qquad \textbf{Equation 15}$$

$$0 = \frac{d}{dl}(Gy_i^B) - N_{Gi}^B a' A_C \qquad i = 1,\ldots,n. \qquad \textbf{Equation 16}$$

where, ϕL is the volumetric liquid holdup. It depends on the vapor and liquid flows and is calculated from empirical correlations.

The bulk phase balances is given by the summation of the equations for the liquid and vapor bulk mole.

$$\sum_{i=1}^{n} x_i^B = 1, \qquad \sum_{i=1}^{n} y_i^B = 1 \qquad \textbf{Equation 17}$$

The vapor-phase film mass transport is described as following

$$\nabla N_{Gi}^f = 0 \qquad i = 1,\ldots,n. \qquad \textbf{Equation 18}$$

The liquid phase is considered as an additional region where reaction and mass transfer occur simultaneously.

$$\nabla N_{Li}^f - R_{Li}^f = 0 \qquad i = 1,\ldots,n. \qquad \textbf{Equation 19}$$

At the vapor-liquid interface, the thermodynamic equilibrium between the two phases is assumed:

$$y_i^I = K_i x_i^I \qquad i = 1,\ldots,n. \qquad \textbf{Equation 20}$$

The reboiler and condenser of the column are modeled as equilibrium stages.

iii. Model to be used in ASPEN PLUS^{TM}

In this study, equilibrium model is used in view of the complexity of the reactive distillation and most commonly used by the researchers. Radfrac column in ASPEN PLUS^{TM} 12.1 Model Library is an equilibrium state model for simulating all types of multistage vapor-liquid fractionation operations. Therefore, Radfrac column is selected for this study. Depending on the thermodynamic package selected, this model is suitable for systems exhibiting strong liquid phase non-ideality. In addition, the column can model chemical reactions. (Aspen Tech, 2003)

iv. Assumption in the simulation

The following assumptions are made to outline the scope of work for the research.

1) Vapor and liquid phase are in thermodynamic equilibrium, when both phases exist.
2) Ideal vapor phase since the vapor phase non-ideality is known to be less significant in esterification process as the column pressure is moderate.
3) The reaction only in the liquid phase.
4) The molar vapor holdup is negligible compared to the molar liquid holdup.
5) Adiabatic operations and no heat losses to surrounding.
6) Heat of mixing at each stage considered negligible.

b) Kinetic Power Law Expression

All chemical reactions can be expressed in some form of reaction equations, which have functions for rates of reactions. These constants depend on the type of reactions e.g. equilibrium, reversible or irreversible. The rate of reaction is expressed in kinetic power law expression as shown in Equation 21 below.

$$r = k\left(\frac{T}{T_o}\right)^n e^{-\left(\frac{E}{R}\right)\left(\frac{1}{T}-\frac{1}{T_o}\right)} \prod_{i=1}^{N} C_i^{\alpha_i}$$

Equation 21

Where:

r =Rate of reaction
k =Pre-exponential factor
T =Absolute temperature
T_o =Reference temperature
n =Temperature exponent
E =Activation energy
R =Gas law constant
Π =Product operator
N =Number of components
C_i =Concentration of the i^{th} component
α_i =Exponent of i^{th} component

The rate equations with H_2SO_4 catalyst that were used by most of the researchers for catalyzed ethyl acetate production are shown below (Equation 22 and Equation 23). (Okur and Bayramoglu, 2001) The same rate equations are used in this research.

$$k_1 = 1.76615 \exp(-6500.1/T) \ (\text{m}^3/\text{mol s})$$

Equation 22

$$k_2 = \frac{1.76615}{(7.558 - 0.012T)} \exp(-6500.1/T) \ (\text{m}^3/\text{mol s})$$

Equation 23

In view of the different format obtained for Equation 23, the equation is converted to power law expression format, Equation 24. This is to ensure the same rate equations to be used in replicating the model in ASPEN PLUS^{TM} without additional software required. The details are elaborated in Chapter 4 and Chapter 5.

$$k_2 = \left(0.0002459T^{1.3066059}\right)e^{\left(-\frac{6500.1}{T}\right)} (\text{m}^3/\text{mol s})$$

Equation 24

c) Dynamic State Model

There are additional information and equations required for dynamic state model simulation. The proper dimensions for the reactive distillation column are required which includes hydraulic model, condenser and reboiler. The information is important to simulate the hydraulic holdup for the column.

i. Dynamic State Model Equations

Under dynamic state conditions, the time derivations in the steady state equilibrium stage model equations are not equal to zero. The equilibrium stage model equations have been discussed in part (a) section (i). In summary, the following equations are used.

The material balance equation as shown by Equation 7.

$$\frac{dU_j}{dt} = V_{j+1} + L_{j-1} + F_j - (1 + r_j^V)V_j - (1 + r_j^L)L_j + \sum_{m=1}^{r}\sum_{i=1}^{c} v_{i,m} R_{m,j} \varepsilon_j . \qquad \textbf{Equation 25}$$

The equation taking into account of the vapor hold-up is,

$$\frac{dU_j x_{i,j}}{dt} = V_{j+1} y_{i,j+1} + L_{j-1} x_{i,j-1} + F_j z_{i,j} - (1 - r_j^V) V_j y_{i,j} - (1 + r_j^L) L_j x_{i,j} + \sum_{m=1}^{r} v_{i,m} R_{m,j} \varepsilon_j \qquad \textbf{Equation 26}$$

The equation for the vapor liquid equilibrium,

$$y_{i,j} = K_{i,j} x_{i,j} \qquad \textbf{Equation 27}$$

The summation equations as shown by Equation 12.

$$\sum_{i=1}^{c} x_{i,j} = 1 \qquad \sum_{i=1}^{c} y_{i,j} = 1 \qquad \textbf{Equation 28}$$

The enthalpy balance equation as shown below,

$$\frac{dU_j H_j}{dt} = V_{j+1} H_{j+1}^V + L_{j-1} H_{j-1}^L + F_j H_j^F - (1 + r_j^V) V j H_j^V - (1 + r_j^L) L j H_j^L - Q_j \qquad \textbf{Equation 29}$$

ii. Distillation Column Hydraulic

Besides the dynamic state equations, the information for the column hydraulic is required. There are several column hydraulic models that can be used for dynamic simulation, i.e. a) simple tray, b) rigorous tray, c) simple packing and d) rigorous packing.

The information required for the simulation included height equivalent to a theoretical plate (HETP), diameter of packed/tray section, weir height, spacing between trays, tray/packing rating and tray/packing sizing pending on the model selected for the simulation. For simple tray hydraulic equation, Francis weir is used for single pass tray.

$$Q_L = K_{Weir} L_{Weir} h_{Crest}^{1.5}$$ **Equation 30**

Where:

Q_L = Volumetric liquid flow rate from the stage

K_{Weir} = Weir constant

L_{Weir} = Total weir length

h_{Crest} = Height of the liquid crest over the weir

The rigorous tray modeling is based on the Francis weir equation with downcomer holdup (h_{dc}) taken into consideration and the equation used for accounting liquid head loss in the downcomer, h_{dc} is:

$$h_{dc} = K_{dc}\left(\frac{Q_L}{A_{da}}\right)^2$$ **Equation 31**

Where:

K_{dc} = A constant

Q_L = Volumetric flow rate of liquid from the tray for that pass

A_{da} = Minimum area under the downcomer apron

For the simple packing hydraulic equation, the model involved the liquid flow rate from a packed section and the amount of the liquid. It can be expressed in the following equation.

$$l_{fV} = K_{Pack} U_L$$

Equation 32

Where:

l_{fV} = Liquid volume fraction in the packed section

U_L = Liquid velocity in the packed section

K_{Pack} = Packing constant

In rigorous packing calculation, the fractional volumetric holdup in a packed section is considered. The following equation expressed the rigorous packing calculation.

$$\frac{V_L}{V} = K_{BL}\left(\frac{u_L^2 a}{g\varepsilon^{4.65}}\right)^{\frac{1}{3}}\left[1+20\left(\frac{\Delta P}{Z\rho_L g}\right)\right]$$

Equation 33

Where:

K_{BL} = A dimensionless constant, equal to 0.555

u_L = Superficial liquid velocity

a = Specific surface area of the packing

g = Acceleration due to gravity

ε = Packing voidage

ΔP = Pressure drop across the section

Z = Height of packing in the section

ρ_L = Liquid density

The tray pressure drop (ΔP) is calculated based on the following formula.

$$\Delta P = 9.81 \times 10^{-3}(h_d + (h_w + h_{ow}) + h_r)\rho_L \qquad \textbf{Equation 34}$$

Where:

h_d = Dry tray pressure drop, $51\left[\frac{u_h}{C_0}\right]^2 \frac{\rho_v}{\rho_L}$

C_0 = Orifice coefficient

u_h = Velocity through the holes, m/s

ρ_v = Vapor density

ρ_L = Liquid density

$h_w + h_{wo}$ = Head of clear liquid on the tray

h_r = Residual head, $\frac{12.5x10^3}{\rho_L}$

3.4 Development of Control Strategy

The process controller's job is to maintain the process variable at set point, regardless of whether the set point is constant or has just been changed. For a distillation column, obviously, it is desirable to maximize the purity of the top and bottom products. Controller(s) is used in distillation column to automatic control manipulated parameter to meet the set products purities. Choosing the control strategy is very important to maintain stable operations. There are several methods that can be used in pairing the input variable(s) and output variables(s) for column controller(s). Relative Gain Array (RGA) is one of the methods that used in this research. Controller tuning is carried out using Ziegler Nichols method which the controller parameters can be calculated according to a formula.

a) Steady State Gain

Relative gain analysis is a widely used technique in the design of control systems for multivariable plants. The analysis is based on a "relative gain array" (RGA), which is a matrix of interaction measures for all possible single-input single-output (SISO) pairings of the variables considered. The RGA thus indicates the preferable variable pairing in decentralized (multiloop SISO) control systems based on interaction considerations. The RGA was originally proposed for steady state only, based on the interpretation as a ratio between two gains. (Kurt, 1995)

In order to use RGA method, the steady state gain for each input and output selected are determined. Steady state gain is the ratio of the change in the steady state value of the output divided by the magnitude of the step change made in the input. In a nut shell, it is the ratio of steady state change in the output variable ($\Delta \bar{y}$) to the steady state step change in the input variable ($\Delta \bar{u}$).

$$K = \left(\frac{y - \bar{y}}{u - \bar{u}} \right)_{(t \to \infty)} = \frac{\Delta \bar{y}}{\Delta \bar{u}} \qquad \textbf{Equation 35}$$

b) Relative Gain Array (RGA)

The relative gain array was developed by Bristol (1966). The Relative Gain Array (RGA) is used to match up variables that have the biggest effect on another, without having undesirable effects on the others. Inaccurate pairing could result in poor control performance and reduced stability margins. RGA is a matrix of number, the ijth element in the array is called relative gain, λ_{ij}. It is the ratio of the open loop gain divided by the close loop gain. The open loop gain is the steady state gain between the ith controlled variable (output) and the jth manipulated variable (input) when all other manipulated variable (input) are constant. The closed loop gain is the steady state gain between the same two variables when all other controlled variables (output) are constant.

$$\lambda_{ij} = \frac{\text{Open loop gain between } y_i \ \& \ u_j}{\text{Closed loop gain between } y_i \ \& \ u_j} = \frac{\delta_{yi} / \delta_{uj}\big|_u}{\delta_{yi} / \delta_{uj}\big|_y}$$

Equation 36

Equation 37 is the RGA matrix with the relative gains.

$$\text{RGA}, \ \Lambda = \begin{bmatrix} \lambda_{11} & \lambda_{12} & \dots & \lambda_{1n} \\ \lambda_{21} & \lambda_{22} & \dots & \lambda_{2n} \\ \dots & \dots & \dots & \dots \\ \lambda_{n1} & \lambda_{n2} & \dots & \lambda_{nn} \end{bmatrix}$$

Equation 37

The rule of the loop pairing is to select the control loop by paring the controlled output with the manipulated variable in such a way that the relative gain, λ are positive and as close as possible to unity. The relative gain λ is interpreted using Table 4.

Table 4: RGA Interpretation Table (The University of Edinburgh, 2004)

If λ is	Pairing Effect
1	The best pairing because both gains have the same effect.
>1	Require higher controller gain in closed loop. If other loops are open, the system could easily become unstable. This pairing should not be used.
<0	Closed loop has an opposite affect. This can cause the system to be unstable if operated in open loop.
0<λ<1	The pairing should only be used if between 0.5 and 1.0.

The RGA can be used for multiple inputs and multiple outputs (MIMO) system. However, for a 2x2 RGA system, there is an alternative way to calculate by using the formula given below (Equation 38):

$$\lambda_{11} = \frac{1}{1 - \dfrac{K_{12}K_{21}}{K_{11}K_{22}}}$$ **Equation 38**

The equation is derived from a linearized steady state model

$$y_1 = K_{11}u_1 + K_{12}u_2$$

$$y_2 = K_{21}u_1 + K_{22}u_2$$

Open loop gain for u_2 is constant is:

$$\left[\frac{y_1}{u_1}\right]_{\overline{m}_2} = K_{11}$$

For closed loop gain solve model for $y_2 = 0$:

$$y_1 = K_{11}u_1 - (K_{12}K_{21}/K_{22})u_1$$

Therefore, closed loop gain:

$$\left[\frac{y_1}{u_1}\right]_{\overline{y}_2} = K_{11} - (K_{12}K_{21}/K_{22})$$ **Equation 39**

Dividing the open loop gain by closed loop gain generated Equation 38.

In the 2X2 case, this is the only element that has to be calculated because the sum for row and column is 1.

The best pairing controllers can be fine tuned using different methods in order to satisfy the desired outcomes within the shortest possible time.

c) Proportional, Integral and Derivative (PID) Controller Tuning

Tuning is the adjustment made on the controller parameters to achieve satisfactory desired control outcome. Controller tuning is critical to ensure that the measurable process parameters reach the set point in the shortest possible time with less transient. The time consumed and the effort to stabilize the unit operations can be minimized. There are three types of controllers depending on the model of the process to be controlled, i.e. Proportional (P) controller, Proportional-Integral (PI) controller, Proportional-Integral-Derivative (PID) controller. The commonly used control algorithm is PID control.

The PID controller can be modeled by the function, where proportional gain (K_c), integral time (τ_I) and derivative time (τ_D) are the parameters to be tuned in the controller. Equation 40 shows the relation among the PID controller parameters.

$$p(t) = \bar{p} + K_c\left[e(t) + \frac{1}{\tau_I}\int_0^t e(t)dt - \tau_D\frac{de(t)}{dt}\right] \qquad \textbf{Equation 40}$$

Among the popular methods for PID tuning are Trial and Error method, Cohen-Coon method, Ziegler Nichols method and others.

i. The Trial and Error Method (Shaw, 2004)

This method is also called " by-guess-and by-golly" method or on-line trial tuning. Referred to Appendix D for the details of the tuning method. The main disadvantage of using the trial and error method is that it is time consumed because of the large number of trials required. This is made worse when the process dynamics are slow. Furthermore, the testing can be expensive due to the loss productivity or poor product quality. (Seborg et al. 1989)

iii. Cohen-Coon Method

This is an open-loop method proposed by Cohen and Coon in 1953 and it was used as the alternative to the Ziegler Nichols method. (Coughanowr, 1991). Referred to Appendix E for the details of the tuning method.

Although Cohen Coon method is the alternative to Ziegler Nichols method, there are advantages and disadvantages of the method. This method requires only a single experiment and does not require operating at stability limits hence, it is more favorable compared to Ziegler Nichols. However, the disadvantages are more.

Cohen Coon method is an open-loop controller, where the controller is controlled in manual mode. In view of the manual control, there is no automatic corrective action that will be taken by the controller when a significant set point changes occurred. The results obtained may be easily distorted in the test. Therefore, it may be difficult to determine the slope at the inflection point accurately, especially if the measurement is noisy and a small recorder chart is used. (Seborg et al. 1989). The method is not recommended for processes that have oscillatory open-loop responses since the process model will be inaccurate.

iv. Ziegler Nichols method

Ziegler Nichols method is considered as closed-loop method because the controller remains in the loop as an active controller in automatic mode. This method was first proposed by Ziegler and Nichols (1942), who were engineers for a major control hardware company in the United States (Taylor Instrument Companies of Rochester, NY.). The big advantage of this method is the controller parameters can be calculated according to a formula. (ATCGMB, 2004)

The current work uses the Ziegler Nichols method to tune the PID controller of the reactive distillation column in dynamic state, modeled above. The major steps involved are shown in Figure 8.

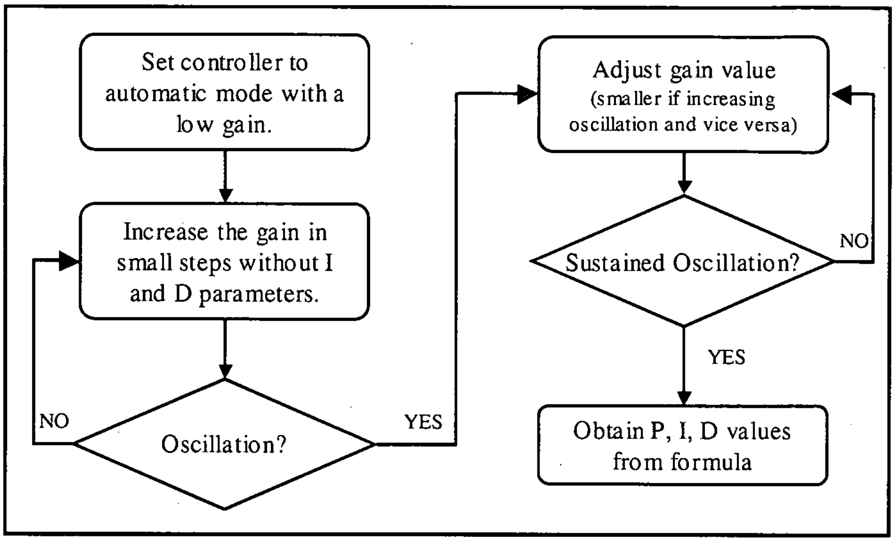


Figure 8: Ziegler Nichols Tuning Steps

The controller I and D parameters are turned off and set the controller gain with a low gain. The controller gain, P is increased slowly until oscillation trend is observed. The P parameter is adjusted on the smaller step to obtain a sustainable oscillation. The sustainable controller gain, P is the ultimate gain, K_c. The ultimate period is measured from the period of oscillation, P_u. Using the K_c and P_u values, the control parameters for the controllers can be calculated based on formulas in Table 5 below.

Table 5: Ziegler Nichols Design Relations

Controller	**Controller Parameters**		
	K_c	τ_I	τ_D
Proportional, P	$0.5\ K_{cu}$	--	--
Proportional and Integral, PI	$0.45\ K_{cu}$	$P_u/1.2$	--
Proportional, Integral and Derivative, PID	$0.6\ K_{cu}$	$P_u/2$	$P_u/8$

d) Evaluation of Controller Performance

The selected controllers are evaluated. There are several methods to evaluate the controller performance, one of the evaluation methods is introducing feed disturbance by changing the feed flow rate and observed the controller response to the disturbance. The controllers' performances are evaluated based on the time taken for control parameters to reach set point and steady state when one of the feeds disturbances is introduced. A good controller is able to adjust the manipulated parameter in order to direct the controlled parameter to reach steady state.

3.5 Evaluation of Reactive Distillation Column Start-up

An important area for control of chemical processes is to have an adequate control system for start-up operations of reactive distillation column. During start-up from cold column, the chemical process is far from its normal operating conditions, and may display very different behavior.

It is crucial to study and understand reactive distillation column start-up behavior in order to minimize the start-up time required, wastage of products and energy consumption. The impact is very significant if the start-up operations is very frequent for some chemical processes.

There are four main start-up strategies, i.e. conventional, total reflux, total distillate and time optimized. Total reflux start-up strategy is used in this work. Three different initial component(s) at reboiler stage in reactive distillation column are studied for ethyl acetate production.

4.0 METHODOLOGY

In this chapter, the steps of converting the reaction rate equation and replicating the model is discussed in detail. The converted reaction rate equation and replicated model are validated against laboratory results and simulation results, provided by previous researchers, as earlier described in Chapter 2. Figure 9 is the summarized methodology adopted in this research work.

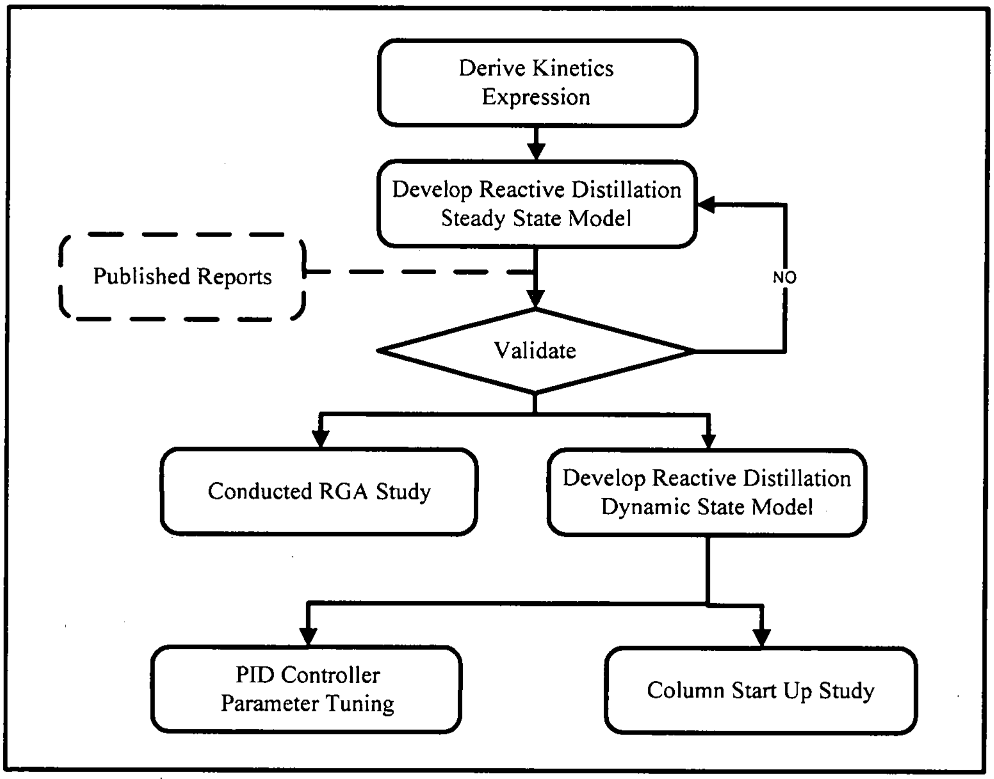


Figure 9: Methodology adopted in this research work

The reactive distillation steady state model is replicated using the derived kinetics expression. The model is validated with experimental data published in literatures. Upon validation, the model is used to conduct RGA study in order to determine the best pairing. Fine tuning is carried out for the best controller pair determined. The same model is used for reactive distillation column start-up study as well.

4.1 Modeling of Reactive Distillation Model in Steady State

a) Steady State Model

Figure 10 shows the configuration of the reactive distillation model in ASPEN PLUS^{TM}.

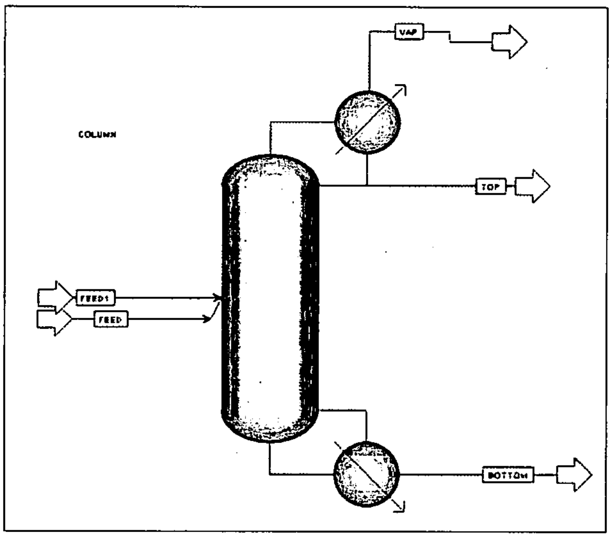


Figure 10: ASPEN PLUS^{TM} Model

The material streams for feeds and products are connected and labeled as FEED, FEED1, TOP, BOTTOM and VAP. FEED and FEED 1 are the feed streams, TOP is the distillate stream, BOTTOM is the bottom stream and VAP is the vapor stream. The operating conditions and distillation column specifications are specified in the Blocks Column Setup worksheet in ASPEN PLUS^{TM} simulator. There are four different ways of introducing the feed into the column namely above stage, on stage, vapor and liquid in ASPEN PLUS^{TM}. Above stage means the feed is introduced between stages, on stage means the feed is introduced on the designated stage, vapor means the vapor phase feed is introduced on the designated stage and liquid means the liquid phase feed is introduced on the designated stage.

The components are specified under Component worksheet and each feed operating conditions are input to the Streams worksheet in the program. The property model is selected from the Properties Specification worksheet.

The reaction information is filled in the Reaction worksheet while the reaction zone and hold up are specified under the Block Column Reaction worksheet.

The major steps to create an ASPEN PLUS^{TM} steady state model are illustrated in Figure 11. All the print screens in the ASPEN PLUS^{TM} simulation are available in Appendix G.

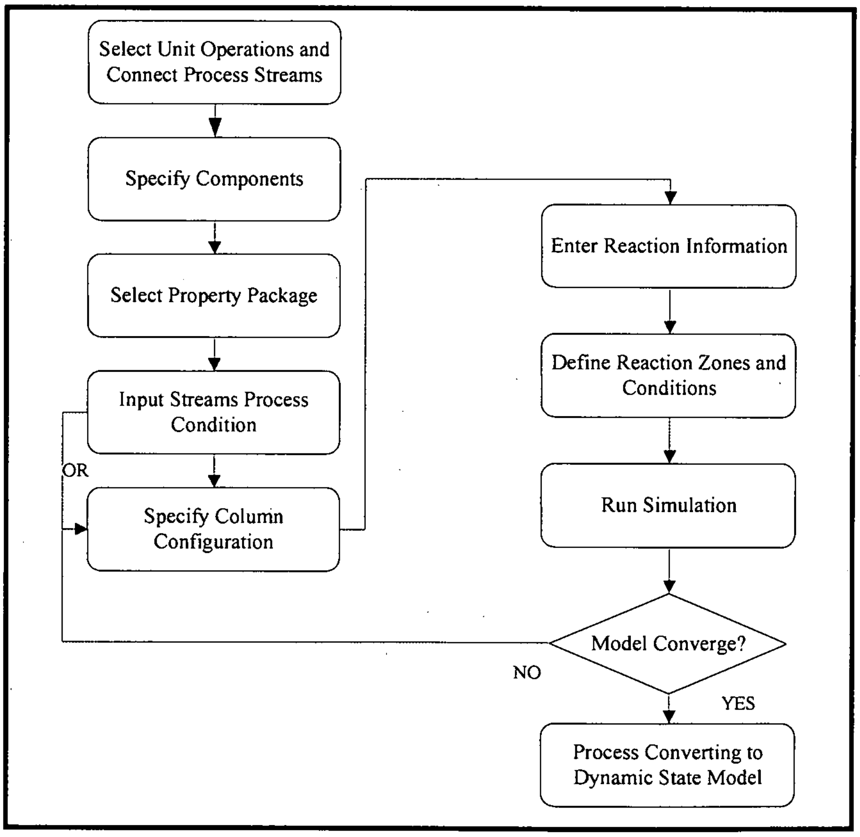


Figure 11: Major Steps To Replicate Steady State Model in ASPEN PLUS^{TM}

The equilibrium stage model, Radfrac column is selected from the ASPEN PLUS^{TM} model library. Components involved in the reaction are specified and selected from the components list. The components are acetic acid, ethanol, ethyl acetate and water. All the properties for the reactants and products are pre-set for the simulation. UNIQUAC property package is chosen for the model based on Okur and Bayramoglu (2001) recommendation. In this work, both Kenig et al. (2001) 82 stages reactive distillation column and Vora and Daoutidis (2001) 13 stages reactive distillation column are modeled based on the information available in the papers published by Kenig et al. (2001) and Vora and Daoutidis (2001).

The rates of equations are entered following Power Law form dictated by the simulator. Print screens from ASPEN PLUS^{TM} showing the details of this step are attached in Appendix G.

The model is then completed and ready to be executed. The converged results are compared with experimental data and simulated data from journals to validate the model.

i. T-Test Validation

T-test is a statistical method to assess whether the means of two groups are statistically different from each other. Both sample groups must have the same number of data points. Rejection criteria used is $t_0 > 2.807$ at confidence level of 95%. This means that for 95% of the time, the data sets do not deviate from each other. (Montgomery, et al. (1998)) The t_0 for data set is calculated using built-in function in Excel.

ii. Correlation Coefficient

The correlation coefficient is a measure of how well the trends in the predicted values follow the trends in the actual values provided. Correlation coefficients can range from 0 to 1. For a good fit, the correlation coefficient will be close to 1. Correlation coefficients are also determined by built-in function in Excel.

b) Kinetic Power Law Expression

In view of the presence of H_2SO_4 catalyst in the reaction, the rate of reactions for reverse chemical reaction is different from the forward chemical reaction. The new rate of reaction, k_2 (Equation 42) is being introduced.

$$r_1 = k_1 C_{ethanol} C_{HAc} - k_2 C_{Water} C_{EthA}$$ **Equation 41**

$$k_2 = \frac{k_1}{K_1}$$ **Equation 42**

$$K_1 = 7.558 - 0.012T$$ **Equation 5**

$$k_1 = 1.76615 \exp(-6500.1/T) \ (m^3/mol\ s)$$ **Equation 22**

$$k_2 = \frac{1.76615}{(7.558 - 0.012T)} \exp(-6500.1/T) \quad (m^3/mol\ s)$$ **Equation 23**

As shown in Equation 22, k_1 is already in Power Law expression. The objective is to convert k_2 into similar form in order to simulate the reaction in ASPEN PLUS^{TM} without additional software required. The k_2 values for temperature ranging from 100K to 450K is generated using Equation 23. Curve Expert 1.3^{TM} software was used to derive the power law expression by correlations functions. The new correlation is shown in Equation 24.

$$k_2 = \left(0.0002459T^{1.3066059}\right) e^{\left(-\frac{6500.1}{T}\right)}$$ **Equation 24**

c) Reactive Distillation in Dynamic State

Using the converged steady state model replicated in Sections 4.1, the simulation is transferred to dynamic mode following the steps summarized in Figure 12.

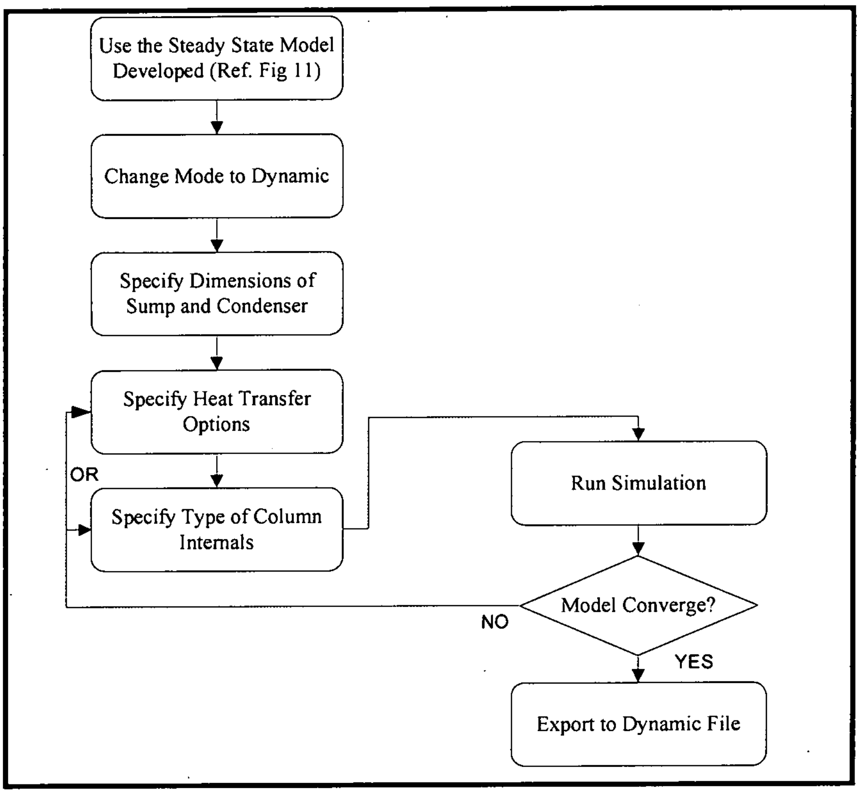


Figure 12 : Major Steps In Dynamic Simulation

In order to export the steady state model into dynamic model; the simulation mode is converted to Dynamic mode in Setup worksheet. The condenser and reboiler (sump) specifications are captured under Blocks Column Dynamic worksheet. After that, reflux drum dimension and type are specified. The vessel type selected is horizontal and head type is elliptical with length of 10cm and diameter of 10cm. Total liquid volume fraction is 0.5. Sump dimension and type are specified. The head type selected is elliptical with height of 8cm and diameter 10cm. The equipment dimensions are referred to paper published by Kenig et al. (2001) in order to replicate the same model for validation. Heat transfer for condenser and reboiler can be calculated by ASPEN based on constant duty, constant temperature or the Log Mean Temperature Difference (LMTD). For this research, LMTD is selected for condenser and constant temperature for reboiler in order to study the start-up condition. Under hydraulic section, simple packing is selected with 5cm diameter for stage 2 to stage 81. The same information is used in modeling 13 stages reactive distillation column for current research since equipment dimensions are not available in paper published by Vora and Daoutidis (2001).

When the dynamic simulation converges with the appropriate values for the parameters described above, the file can be exported to dynamic simulation file by changing to "Flow Driven Dynamic Simulation".

4.2 Development of Control Strategy

a) Steady State Gain

The following manipulated variables and controlled variables are selected by referring to Vora and Daoutidis (2001) research in order to determine the best pairing. The component composition is controlled using mass flow rate.

Table 6: Manipulated variables and Controller Variable for RGA calculation

	Manipulated Variable	Controlled Variable
Set 1	Bottom rate (M1) Reboiler Duty (M2)	Top Stream ethyl acetate composition (C1) Bottom Stream water composition (C2)
Set 2	Bottom rate (M1) Reflux rate (M3)	Top Stream ethyl acetate composition (C1) Bottom Stream water composition (C2)
Set 3	Bottom rate (M1) Condenser Duty (M4)	Top ethyl acetate composition (C1) Bottom Stream water composition (C2)
Set 4	Bottom rate (M1) Reflux ratio (M5)	Top ethyl acetate composition (C1) Bottom Stream water composition (C2)

Using the model validated, the steady state gain is calculated for each input and output selected to determine the open loop gain and close loop gain in establishing the relative gain array (RGA). The step change is varied by several increments of 0.1%, 0.5% and 1% to the initial value. Similar method is repeated for the rest of the configuration.

b) Relative Gain Array (RGA) Calculation

Based on the relative gain calculated using Equation 38, an RGA matrix is developed and interpreted using Table 4 in Chapter 3.

$$\lambda_{11} = \frac{1}{1 - \frac{K_{12}K_{21}}{K_{11}K_{22}}}$$

Equation 38

The best pairing is when relative gain calculated equal to 1, where both open loop and close loop gains have the same effect. However, relative gain between 0.5 to 1 is considerably good to be used. (Willis, 1999)

c) Ziegler Nichols Close Loop Fine Tuning

Two set of controllers are determined through RGA method, fine tuning is carried out using Ziegler Nichols method. Each controller is tuned separately in the dynamic simulation. The Integral (I) and Derivative (D) modes are turned off and only turned on the Proportional (P) mode for the controller.

The proportional gain is increased in small steps until response first exhibits a sustained oscillation. The proportional gain is adjusted accordingly to obtain the sustainable oscillation. The ultimate gain (Kc) and ultimate period (Pu) is determined from the oscillation trend obtained. The controller parameters for PID controller are calculated based on Table 5.

d) Evaluation of Controllers Performance

The two set of tuned controllers are used in the model replicated to simulate in the column's dynamic state. The controllers' performances are evaluated based on the time taken for control parameters to reach set point and steady state when one of the feeds disturbances is introduced. The feed is increased by 10% respectively.

4.3 Evaluation of Reactive Distillation Column Start-up

The replicated model in steady state is used to simulate the different start-up conditions for two different models, i.e. Kenig et al. (2001) 82 stages reactive distillation column model and Vora and Daoutidis (2001) 13 stages reactive distillation column model. The start-up conditions proposed are i) fill up reboiler with ethanol and acetic acid at the same ratio, ii) fill up reboiler with ethanol only and iii) fill up reboiler with acetic acid only.

The steps involved in each strategy are discussed in Table 7. Each strategy is applied into different models.

Table 7: Reactive Distillation Column Start-up Strategies

Strategy	Description
Strategy 1	• Step 1 : Fill up the reboiler with equal mole of ethanol and acetic acid. • Step 2 : Heat up the reboiler to reach 79°C in 0.05hrs, maintain for 1 hrs before feed in ethanol and acetic acid. • Step 3 : Extract the top product when condenser pot level reaches 0.7m.
Strategy 2	• Step 1 : Fill up the reboiler with ethanol at the same reboiler level as strategy 1. • Step 2 : Heat up the reboiler to reach 79°C in 0.05hrs, maintain for 1 hrs before feed in acetic acid. • Step 3 : After 0.5hrs, feed in ethanol. • Step 4 : Extract the top product when condenser pot level reaches 0.7m.
Strategy 3	• Step 1 : Fill up the reboiler with acetic acid at the same reboiler level as strategy 1. • Step 2 : Heat up the reboiler to reach 79°C in 0.05hrs, maintain for 1 hrs before feed in ethanol. • Step 3 : After 0.5hrs, feed in acetic acid. • Step 4 : Extract the top product when condenser pot level reaches 0.7m.

The pressure, temperature and liquid components mole fraction for top stream, top tray, condenser, reboiler, acetic acid feed tray, ethanol feed tray, feed tray between acetic acid feed and ethanol feed are evaluated.

5.0 RESULTS AND DISCUSSIONS

In this chapter, analyses of best controller pair tuning and reactive distillation column start-up are discussed in addition to presenting the validation of the reaction rate equation, k_2 and reactive distillation column. The reaction rate equation, k_2 is validated with the original equation and used in the reactive distillation column modeling. To ensure the reactive distillation column is accurately replicated, the model is validated with experimental data from Vora and Daoutidis (2001) and Kenig et al. (2001) researches.

The validated reactive distillation column is then used to determine the best controller pair using RGA method, whilst fine tuning is carried out using Ziegler Nichols close loop method. The performance of the tuned best controller pair is deliberated in this chapter.

Distillation column start-up study is conducted using the same reactive distillation column model. There are three different strategies being considered and the best strategy is further optimized in order to achieve the criteria identified in section 5.7(b).

5.1 Validation of reaction rate equation, k_2

Reaction rate equation in ASPEN PLUS^{TM} is in Power Law expression. One of the reaction rate equations, k_2 is in different term as shown in Equation 24. Additional programming, i.e. FORTRAN^{TM} is required using Equation 24 in ASPEN PLUS^{TM}, therefore, the reaction rate equation, k_2, is derived into Power Law expression using Curve Expert 1.3^{TM} software. Two set of data are generated using the derived k_2, and original equation.

$$k_2 = \frac{1.76615}{(7.558 - 0.012T)} \exp(-6500.1/T)$$ **Equation 23**

$$k_2 = \left(0.0002459T^{1.3066059}\right) e^{\left(-\frac{6500.1}{T}\right)}$$ **Equation 24**

The derived k_2 is compared with the original equation and validated using t- test and correlation coefficient.

The calculated t_0 is 8.24E-08; hence the data is well between acceptable ranges. The correlation coefficient for these data series is 1.00.

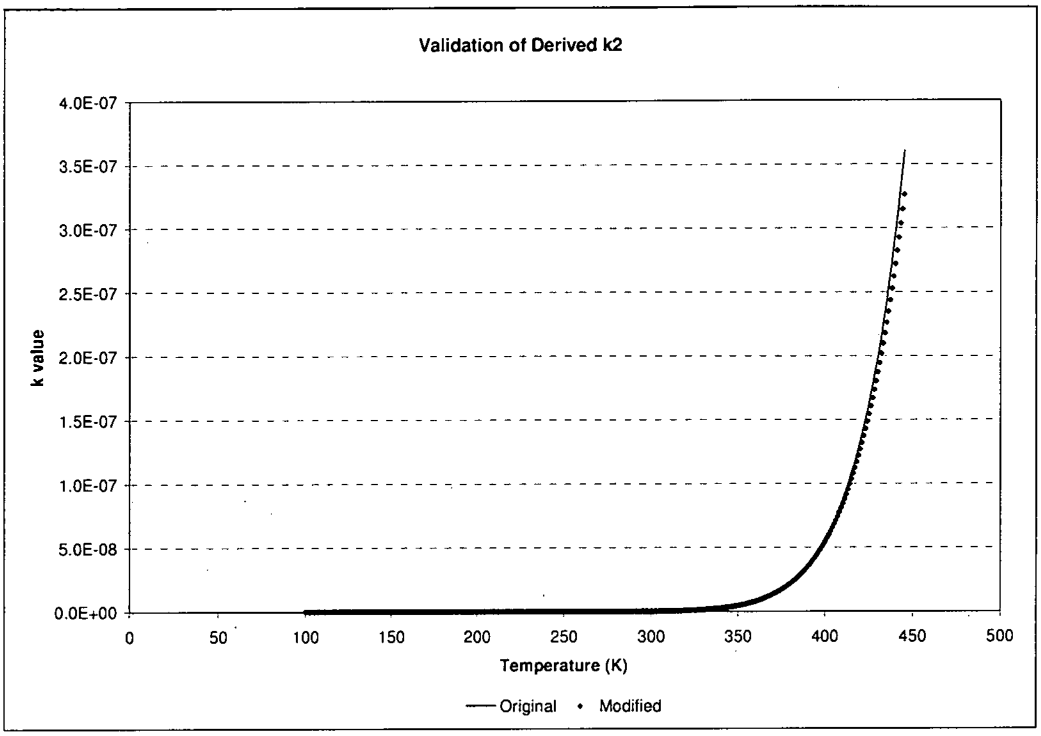


Figure 13: Validation of Derived k_2

5.2 Validation of Reactive Distillation Column

The reactive distillation column modeled in Steady State using ASPEN PLUS^{TM} is validated against the results published by Vora and Daoutidis (2001), which is based on simulation and experimental results by Kenig et al. (2001).

Based on the reactive distillation configured by Vora and Daoutidis (2001) in their simulation, the following set up and results are obtained.

Table 8: Distillation Column Configuration and Specifications For Double Feeds Catalytic Ethyl Acetate Synthesis (Vora and Daoutidis (2001))

Items	**Units**	**Specifications**	
Feed Details			
Feed No.		Feed 1	Feed 2
Flow rate	mol min^{-1}	414	411.9
Pressure	Atm	1	1
Feed stage		4	11
Composition		Acetic Acid	Ethanol
Column Details			
Number of Stages		13	
Column Pressure	Atm	1	
Condenser Liquid Holdup	mol	4.4108×10^4	
Re-boiler Liquid Holdup	Mol	1.4703×10^5	
Reflux Rate	mol min^{-1}	810.6	
Bottom Flow, B	mol min^{-1}	425.1	

Table 9: Simulation Results (Vora and Daoutidis (2001))

Items	**Units**	**Specifications**	
Composition			
	Mole Fraction	Top	Bottom
Acetic Acid (Ac)		0.003	0.21
Ethanol (Eth)		0.08	0.14
Ethyl Acetate (EA)		0.65	0.13
Water (H_2O)		0.24	0.52
Product Flow	mol min^{-1}	400.8	425.1
Ethanol Conversion (Eth)	Mole %	76.8	
Ethyl Acetate Purity (EA)	Mole %	65	

The ASPEN PLUS™ 13 stages reactive distillation column model replicated based on Vora and Daoutidis (2001) 13 stages model configuration is validated. The following table is the comparison between the results obtained from Vora and Daoutidis (2001) and ASPEN PLUS™ model.

Table 10: Comparison between Vora and Daoutidis (2001) and ASPEN PLUS™ model.

Items	**Units**	**Specifications**			
Composition		Vora and Daoutidis (2001)		ASPEN PLUS™ Model modeled in this research	
	Mole Fraction	Top	Bottom	Top	Bottom
Ac		0.00	0.21	0.00	0.25
Eth		0.08	0.14	0.16	0.10
EA		0.65	0.13	0.60	0.16
H_2O		0.24	0.52	0.24	0.50
Product Flow	mol min^{-1}	400.8	425.1	400.8	425.1
Eth Conversion	mole %	76.8		75	
EA Purity	mole %	65		60	

The results from ASPEN PLUS™ model is in good agreement with Vora and Daoutidis (2001) simulation results except for few parameters. This can be attributed to the fact that different process simulators and thermodynamic property package were used by Vora and

Daoutidis (2001) as compared to the current work. The thermodynamic property package used by Vora and Daoutidis (2001) was not specified in their work.

In order to further validate the ASPEN PLUS^{TM} model, experimental data from Kenig et al. (2001) is used for comparison. A 82 stages reactive distillation column is modeled based on Kenig et al. (2001) 82 stages reactive distillation column configuration. The parameters validated against Kenig et al. (2001) 82 stages reactive distillation column configuration are temperature and each component profiles.

The validation is done using the correlation coefficient method. The T- test method is not suitable for validation as the number of data in the two sets are not equal.

a) Validation of Temperature Profile

The data is generated from ASPEN PLUS^{TM} steady state. The experimental temperature profile is almost matching with the simulation results with correlation coefficient of 0.92.

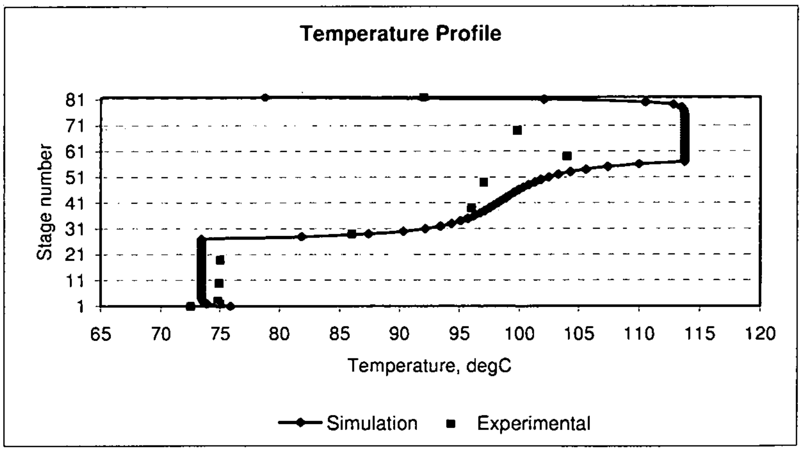


Figure 14: Validation of Temperature Profile

b) Validation of Concentration Profiles

The data is generated from ASPEN PLUS^{TM} steady state. Each component liquid phase profile is compared with the experimental data.

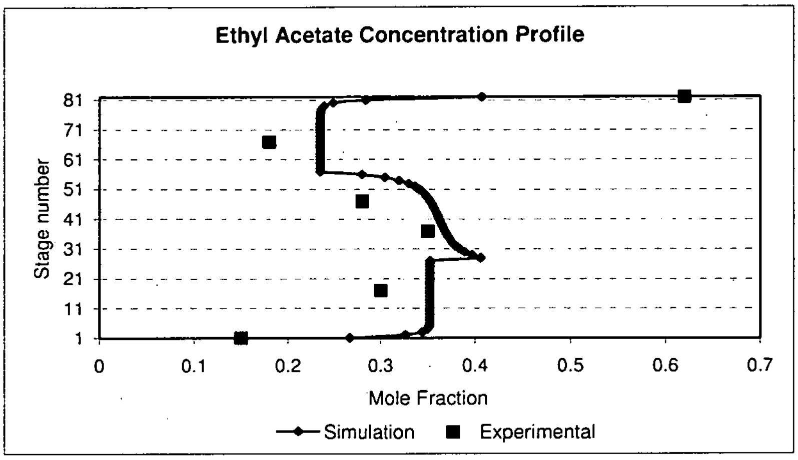


Figure 15: Validation of Ethyl Acetate Concentration Profile

The calculated correlation coefficient is 0.85 for the matching between the simulated and experimental data for ethyl acetate production.

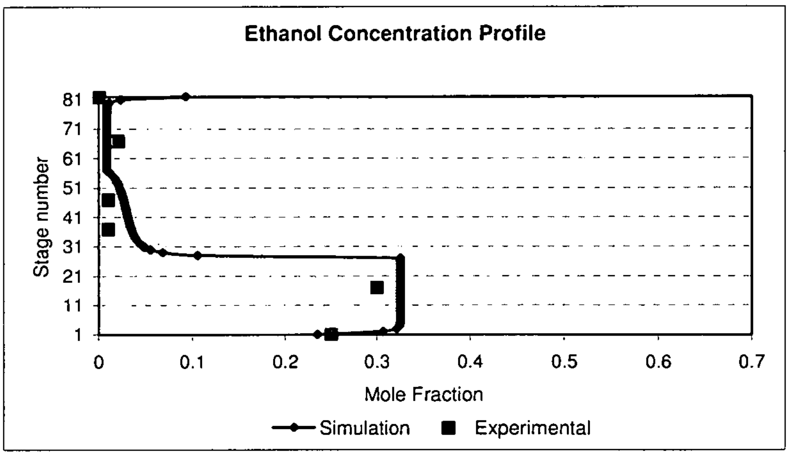


Figure 16: Validation of Ethanol Concentration Profile

The calculated correlation coefficient is 0.96 for the matching between the simulated and experimental data for ethanol component.

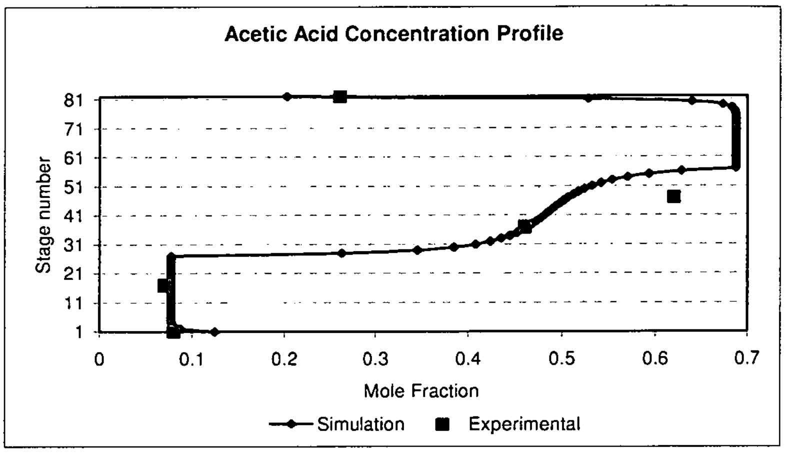


Figure 17: Validation of Acetic Acid Concentration Profile

For acetic acid component, the calculated correlation coefficient is 0.99 for the matching between the simulated and experimental data.

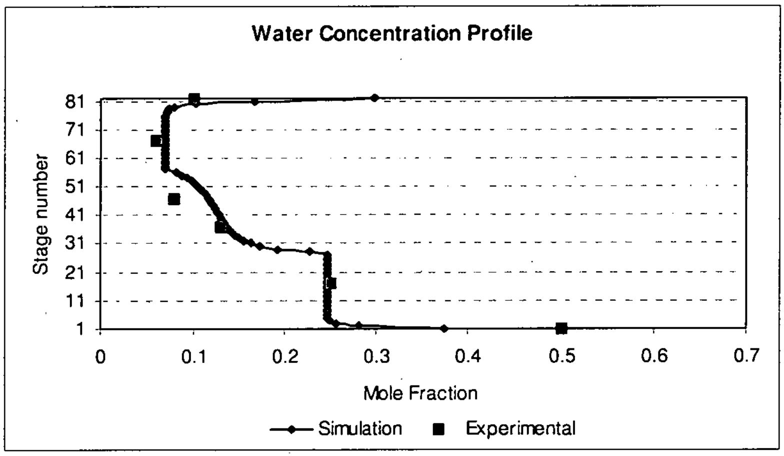


Figure 18: Validation of Water Concentration Profile

The calculated correlation coefficient is 0.79 for the matching between the simulated and experimental data for water production.

Through the validation discussed above, the simulated result is in reasonably good agreement with the experimental data by Kenig et al. (2001). Therefore, it is concluded that the modeled reactive distillation column can be used for further study in this research.

5.3 Steady State Gain

Table 6 is the manipulated variables and controller variables determined in this study. There are 4 sets of controller pairing. Relative gain is calculated based on the steady state gain and the results are showed in . Reader is referred to Appendix H for the individual set results obtained from the simulation.

Set 4			
K_{11}	-0.00541	K_{15}	0.54069
K_{12}	0.00012	K_{25}	0.03511
RGA, Λ = 0.260			

Table 6: Manipulated variables and Controller Variable for RGA calculation

	Manipulated Variable	**Controlled Variable**
Set 1	Bottom rate (M1) Reboiler Duty (M2)	Top Stream ethyl acetate composition (C1) Bottom Stream water composition (C2)
Set 2	Bottom rate (M1) Reflux rate (M3)	Top Stream ethyl acetate composition (C1) Bottom Stream water composition (C2)
Set 3	Bottom rate (M1) Condenser Duty (M4)	Top ethyl acetate composition (C1) Bottom Stream water composition (C2)
Set 4	Bottom rate (M1) Reflux ratio (M5)	Top ethyl acetate composition (C1) Bottom Stream water composition (C2)

Table 11: Relative Gain for the 3 sets of Controller Pairing

Calculated Gain			
Set 1			
K_{11}	-0.32502	K_{21}	0.08308
K_{12}	0.00225	K_{22}	0.00015
RGA, Λ = 0.208			
Set 2			
K_{11}	-0.58272	K_{13}	0.05847
K_{12}	0.44972	K_{23}	0.02900
RGA, Λ = 0.391			
Set 3			
K_{11}	-0.32943	K_{14}	0.07860
K_{12}	-0.00183	K_{24}	-0.00013
RGA, Λ = 0.226			

Set 4			
K_{11}	-0.00541	K_{15}	0.54069
K_{12}	0.00012	K_{25}	0.03511
RGA, Λ = 0.260			

5.4 Relative Gain Array Results

The RGA for the selected manipulated variables and controlled variables are calculated and tabulated. RGA is defined for all the configurations using Equation 38 and Equation 39 .

$$\lambda_{11} = \frac{1}{1 - \frac{K_{12}K_{21}}{K_{11}K_{22}}}$$ **Equation 38**

Close loop gain = $K_{11} - (K_{12}K_{21}/K_{22})$ **Equation 39**

i. For Set 1, the RGA is, $\Lambda_1 = \begin{bmatrix} 0.21 & 0.79 \\ 0.79 & 0.21 \end{bmatrix}$, which meant that the pairing for Set 1 should be bottom rate to control Bottom stream water composition and reboiler duty to control Top stream ethyl acetate composition.

ii. For Set 2, the RGA is, $\Lambda_2 = \begin{bmatrix} 0.39 & 0.64 \\ 0.64 & 0.39 \end{bmatrix}$, which meant that the pairing for Set 2 should be bottom rate to control Bottom stream water composition and reflux rate to control Top stream ethyl acetate composition.

iii. For Set 3, the RGA is, $\Lambda_3 = \begin{bmatrix} 0.23 & 0.77 \\ 0.77 & 0.23 \end{bmatrix}$, which meant that the pairing for Set 3 should be bottom rate to control Bottom stream water composition and condenser duty to control Top stream ethyl acetate composition.

iv. For Set 4, the RGA is, $\Lambda_4 = \begin{bmatrix} 0.26 & 0.74 \\ 0.74 & 0.26 \end{bmatrix}$, which meant that the pairing for Set 4 should be bottom rate to control Bottom stream water composition and reflux ratio to control Top stream ethyl acetate composition.

Based on the RGA calculated, the best configuration is Set 1 with RGA closer to unity, 1. Therefore, the Set 1 configuration, which is opposite from the original pairing, would be considered for controlling purpose.

5.5 Controller Tuning Results

Tuning is carried out for the two controllers selected based on the RGA study which are a) reboiler duty to control Top stream ethyl acetate composition (Controller 1) and b) bottom rate to control Bottom stream water composition (Controller 2). To achieve the best parameters, numerous trials are carried out. Refer to Appendix I for the tuning results with different gain.

a) Controller 1 Tuning

For the Controller 1, the controller Gain is increased slowly starting from 1.00%/%. The oscillation trend is observed. Hence, the controller gain is increased to 3.00%/% to observe the trending. For the 3.00%/% gain, there is some minor oscillation trend at the initial stage but it is not sustainable. The controller gain is increased to 5%/% to observe the trending.

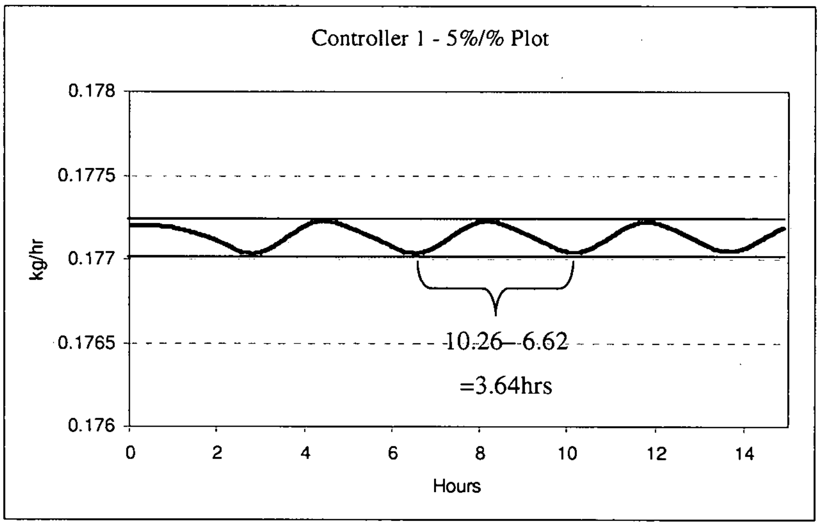


Figure 19: Oscillation Trend for Controller 1 with 5%/% Gain

From the results, it shows that controller gain of 5%/% produce a sustained oscillation, which is the "Ultimate Gain". The "Ultimate Period" measured is 3.64hrs based on the trending.

b) Controller 2 Tuning

For the Controller 2, the controller gain is increased slowly starting from 1.00%/%. There is no sustainable oscillation observed with controller gain of 1.00%/%. Therefore, the gain is increased to 2%/%. The oscillation was found to be out of the normal control range. The controller gain step change is reduced from 1%/% to 0.2%/%. However, there is no sustainable oscillation observed for controller gain of 1.2%/%. The controller gain step change is further reduced to 0.05%/% in order to determine the ultimate gain. Sustainable oscillation is noticed for controller gain of 1.05%% after running for more than 10 hours.

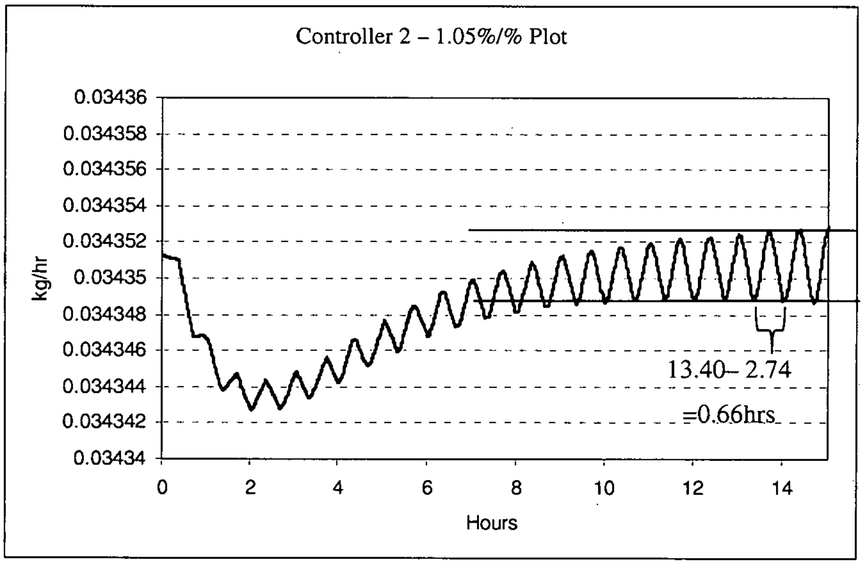


Figure 20: Oscillation Trend for Controller 2 with 1.05%/% Gain

Thus, 1.05%/% is the "Ultimate Gain" for The "Ultimate Period" measured is calculated, 0.66hrs based on the oscillation trend.

c) Controller Parameters

As discussed in Chapter 3, the controller parameters are calculated based on Ziegler Nichols design relations, which are shown in Table 5.

Table 5: Ziegler Nichols Design Relation

Controller	**Controller Parameters**		
	K_c	τ_I	τ_D
Proportional, P	0.5 K_c	--	--
Proportional and Integral, PI	0.45 K_c	P_u /1.2	--
Proportional, Integral and Derivative, PID	0.6 K_c	P_u /2	P_u /8

For the Controller 1, the PID controller parameters calculated are 3%/%, 1.82hrs and 0.455hrs respectively. The PID controller parameters for Controller 2 are 0.63%/%, 0.33hrs and 0.0825hrs respectively.

The calculated PID controller parameters are used in the best pairing controller and the result is evaluated.

5.6 Controllers Performance Evaluation

The best controller pair determined by RGA method, as shown in Figure 21, consists of two controllers. In the Controller 1, the reboiler duty controls Top stream ethyl acetate composition. In the Controller 2, the bottom rate controls Bottom stream water composition. Both controllers are evaluated and the findings are shown in Figure 22 and Figure 23. The disturbance introduced is increased the feed flow rates by 10%. The Controller 1 tried to reach steady state after running for 7 hours. However, the Controller 2 is not able to control the bottom stream water composition and fluctuate after running for 7 hours. The simulation is discontinued due to the erratic performance of Controller 2.

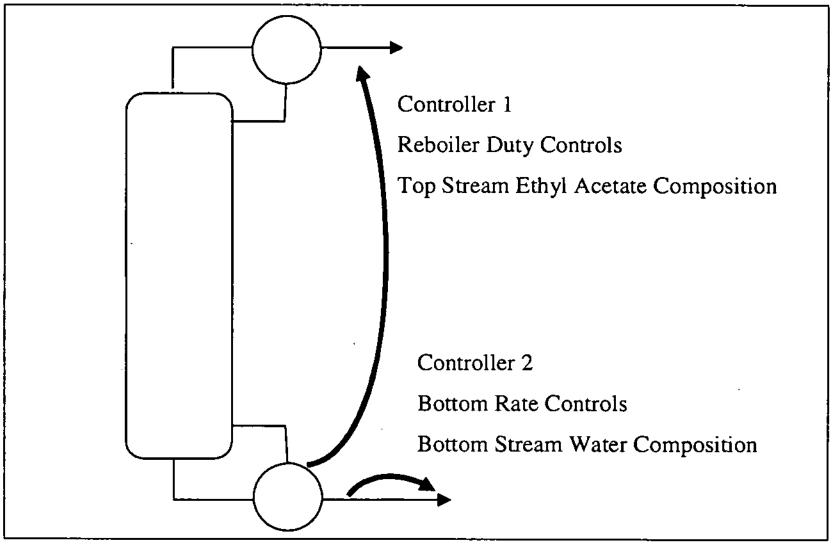


Figure 21: The Best Controller Pair Determined by RGA Method

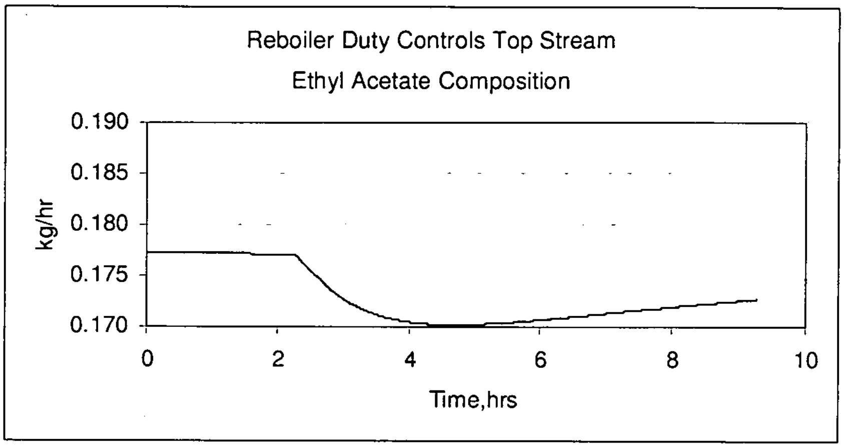


Figure 22: Controller 1 Performance (Reboiler Duty Controls Top Stream Ethyl Acetate Composition)

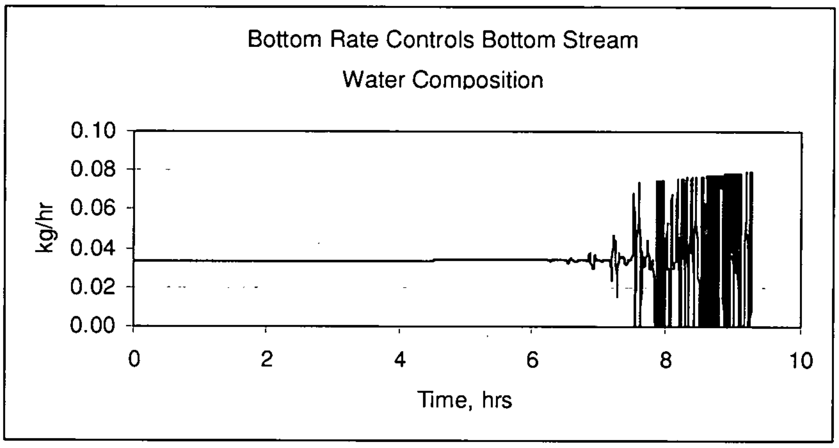


Figure 23: Controller 2 Performance (Bottom Rate Controls Bottom Stream Water Composition)

The results from the evaluation showed that the two controllers would not be able to operate in steady state even though they are the best pair from RGA study. This could be attributed to the following factors.

a) Best pairing is determined based on steady state

The control pair is determined in steady state model whilst the evaluation is done in dynamic state model.

b) Controller 1 is physically far apart

The Controller 1 whereby reboiler duty controls the top stream ethyl acetate component is physically far apart. It could have affected the overall controller pair performance. Based on the controller performances shown in Figure 22 and Figure 23, only Controller 1 performance is acceptable.

c) Tuning of the controllers

Tuning of the controllers were carried out individually hence discounting the effects of interactions. When tuning the specified controller, the other controller is not able to put on close loop because it is not fine tuned and could affect the tuning results.

To support the factor of physical impact to controller pairing, a different pair of controller was selected and both controllers are physically closer as shown in Figure 24. The new controller pair selected is reflux ratio to control top stream ethyl acetate component and bottom rate to control bottom stream water component, which is Set 4 controller pairing. The tuning is carried out based on Ziegler Nichols method. The PID calculated for reflux ratio controller is 0.036%/% (Proportional gain), 40.8mins (Integral time) and 10.2mins (Derivative time). The PID calculated for bottom rate controller is 0.035%/% (Proportional gain), 42mins (Integral time) and 21mins (Derivative time).

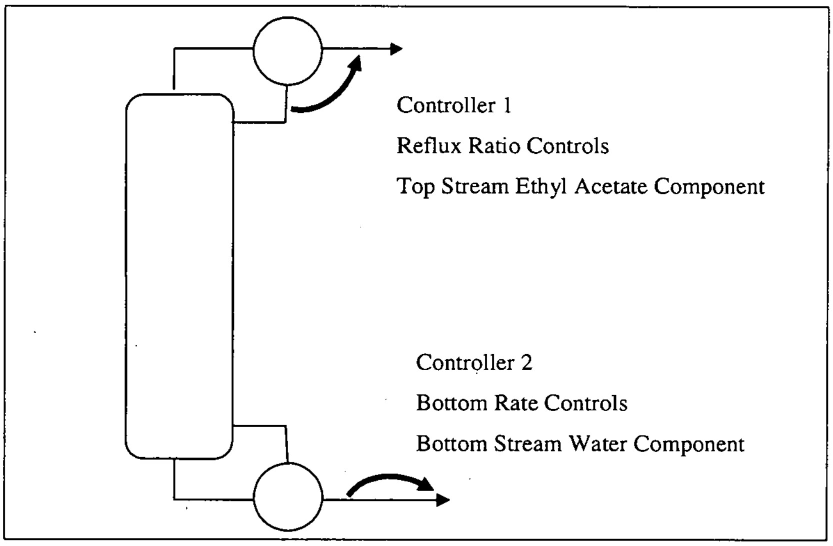


Figure 24: The New Controller Pair

Figure 25 and Figure 26 show the performances of the controllers selected and tuned. The control parameters reached steady state at about 9.5hrs without fluctuation for the same disturbance introduced, i.e. increased the feed flow rates by 10%.

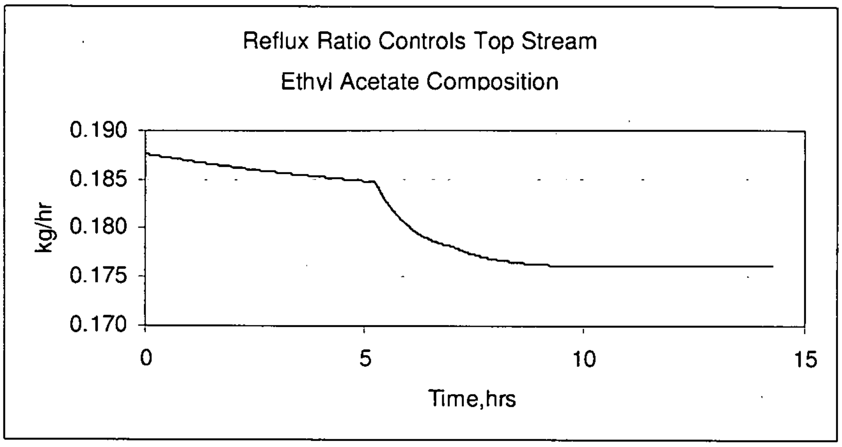


Figure 25: Performance for Reflux Ratio Controls Top Stream Ethyl Acetate Composition

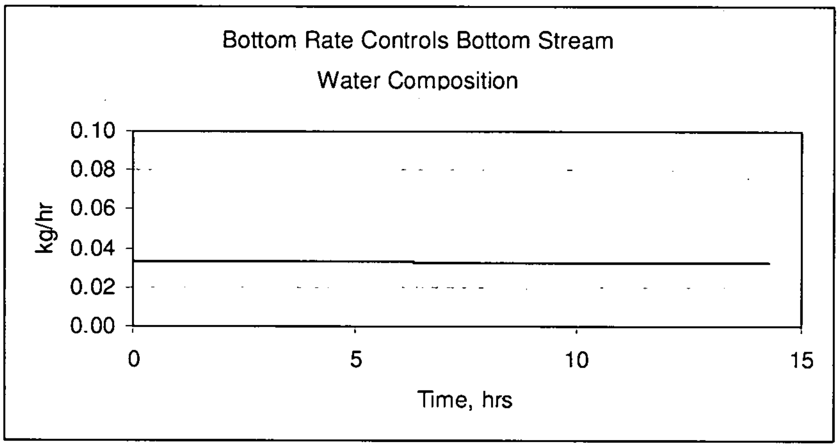


Figure 26: Performance for Bottom Rate Controls Bottom Stream Water Composition

5.7 Reactive Distillation Column Start-up Results

The most commonly used conventional distillation start-up procedure is total reflux. The same procedure is adopted for starting up the reactive distillation column. The intention of this study is to evaluate if the conventional method i.e. total reflux start-up, can be used in ethyl acetate reactive distillation column startup. Three proposed total reflux start-up strategies are compared and the best strategy is optimized to achieve the shortest time taken in reaching steady state.

a) Start-up Strategy

The three reactive distillation column start-up strategies discussed in Chapter 4 are studied in this research. The steps involved in each strategy are discussed in Table 7. Each strategy is applied into different models, i.e. Kenig et al. (2001) 82 stages reactive distillation column model and Vora and Daoutidis (2001) 13 stages reactive distillation column model.

Table 7: Reactive Distillation Column Start-up Strategies

Strategy	**Description**
Strategy 1	• Step 1 : Fill up the reboiler with equal mole of ethanol and acetic acid. • Step 2 : Heat up the reboiler to reach 79°C in 0.05hrs, maintain for 1 hrs before feed in ethanol and acetic acid. • Step 3 : Extract the top product when condenser pot level reaches 0.7m.
Strategy 2	• Step 1 : Fill up the reboiler with ethanol at the same reboiler level as strategy 1. • Step 2 : Heat up the reboiler to reach 79°C in 0.05hrs, maintain for 1 hrs before feed in acetic acid. • Step 3 : After 0.5hrs, feed in ethanol. • Step 4 : Extract the top product when condenser pot level reaches 0.7m.
Strategy 3	• Step 1 : Fill up the reboiler with acetic acid at the same reboiler level as strategy 1. • Step 2 : Heat up the reboiler to reach 79°C in 0.05hrs, maintain for 1 hrs before feed in ethanol. • Step 3 : After 0.5hrs, feed in acetic acid. • Step 4 : Extract the top product when condenser pot level reaches 0.7m.

The reboiler heating up time taken is 0.05hrs and assumed to be the same for all three strategies in this simulation. This is because the simulation work scope is focused mainly on the start-up conditions after reactants are fed in. In view of the boiling point for ethanol is 78°C, 79°C is chosen for reboiler heating temperature. The reboiler is maintained at 79°C for 1 hour in order to ensure steady state of reboiler heating is obtained prior to feeding in reactants.

The strategies are ranked against several criteria in order to select a strategy that will be used in optimization study of the start-up procedures. Optimized start-up is able to reduce the capital, operations cost and improved reactant conversion.

b) Start-up Strategy Selection Criteria

The criteria for the selection are:

i. Duration taken to achieve steady state

Time taken to achieve steady state after start-up is an important factor as it determines the duration of the start-up phase of the reactive distillation column. The shorter duration taken to reach steady state operations, the faster product will be produced and the faster the process will be placed on automatic control. This will improve process efficiency and safety.

Duration to achieve steady state operations is defined as the time taken from initialization to time when all key parameters stop behaving in transient manner.

ii. Pressure fluctuation

Pressure fluctuation is defined as the difference between the highest and lowest recorded pressure during the start-up phase. A start-up strategy that has lower pressure fluctuation is desired.

The maximum pressure of the column will determine the material to be used for fabrication, wall thickness of the distillation column and pressure safety device sizing. If the pressure fluctuates, a thicker column with different type of material is required. The pressure safety device is required to protect the distillation column from over pressure due to unforeseen situation such as blocked outlet.

Changes in pressure also indicate the occurrence of weeping and flooding in the trays of the reactive distillation column. These occurrences lower the efficiency of the column.

iii. Temperature fluctuation

Similar to pressure indication, temperature is another critical factor for distillation column design. The temperature fluctuation range during start-up should be considered in column sizing, column interlock selection and temperature transmitter selection.

Both pressure and temperature are the main monitoring parameters for distillation column.

iv. Time taken for top product stream to be available for withdrawer based on condenser pot level

This factor is considered because it is related to the time taken to produce product from the reactive distillation column. The top stream will start to draw out based on condenser pot level. Time taken for condensate to reach the set level is based on the amount of light components formed in the column and condensed at condenser pot.

Based on the criteria above, the best strategy is determined by comparing the pressure, temperature and time taken to reach steady state. Each criteria is ranked from 1-3, where 3 is the best.

c) Kenig et al. (2001) 82 Stages Reactive Distillation Model

The three start-up strategies are applied to Kenig et al. (2001) 82 stages reactive distillation model that has been validated. From the results obtained, the reactive distillation column took a very long time (>80 hours) to reach steady state for all the three strategies. This could be due to high number of stages for the distillation column used by previous research for steady state laboratory study purpose and it is not suitable for dynamic study.

i. Top Stream Result for Strategy 1

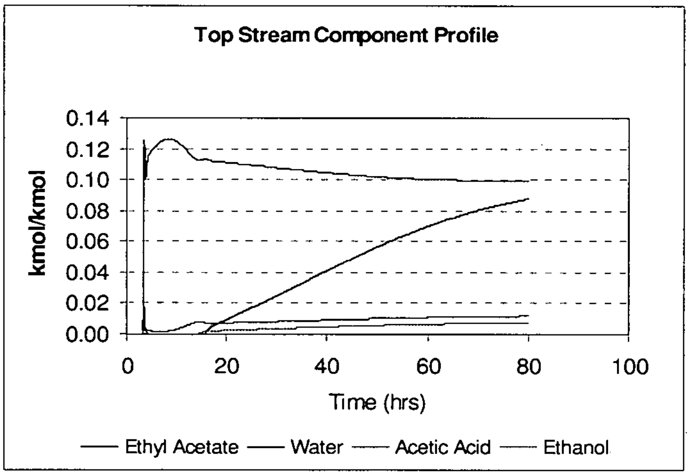


Figure 27: 82 Stages Model Top Stream Result for Strategy 1

Ethyl acetate product is obtained after 13 hours and it has not reach steady state after running for 80 hours.

ii. Top Stream Result for Strategy 2

The same observation noticed as compared with Strategy 1.

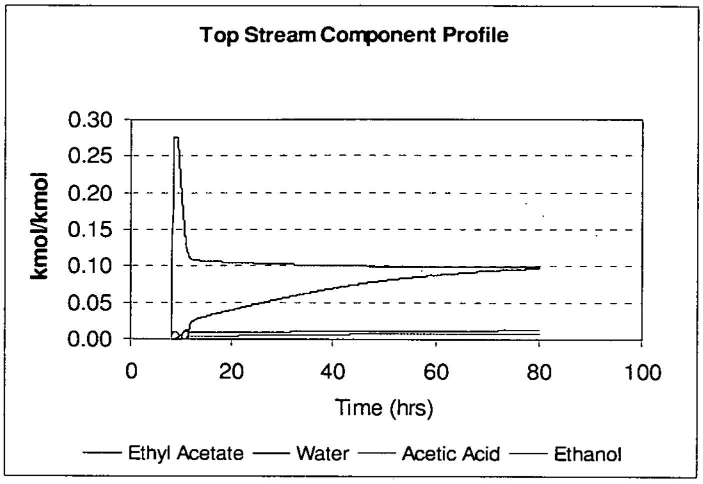


Figure 28: 82 Stages Model Top Stream Result for Strategy 2

iii. Top Stream for Strategy 3

The same observation noticed as compared with Strategy 1 and 2. The time taken to product ethyl acetate product is longer as compared with Strategy 1 and Strategy 2.

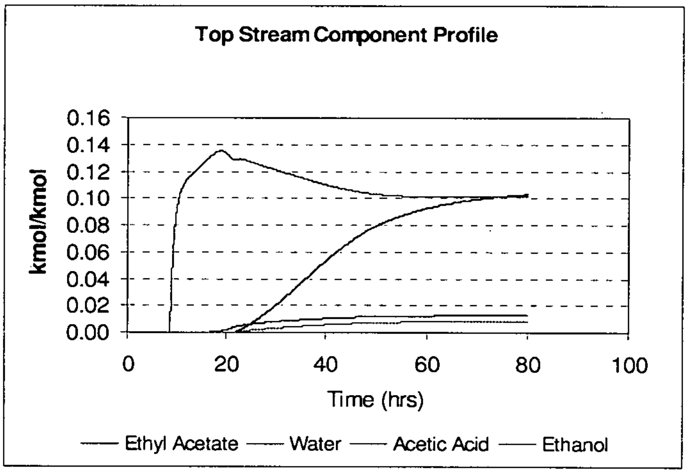


Figure 29: 82 Stages Model Top Streams Result for Strategy 3

In view of the long duration to reach steady state, this model is not used for reactive distillation column start-up study.

d) Vora and Daoutidis (2001) 13 Stages Reactive Distillation Model

The three start-up strategies are applied to Vora and Daoutidis (2001) 13 stages reactive distillation model that has been validated. From the results obtained, the column took approximately 3-4 hours to reach steady state for all the three strategies. At such, this model is used for comparing the three different start-up strategies. The following stages are considered in comparison as they represent the whole reactive distillation column, i.e. condenser stage, tray 7 (tray between acetic acid feed tray and ethanol feed tray), reboiler stage and top stream.

i. Condenser

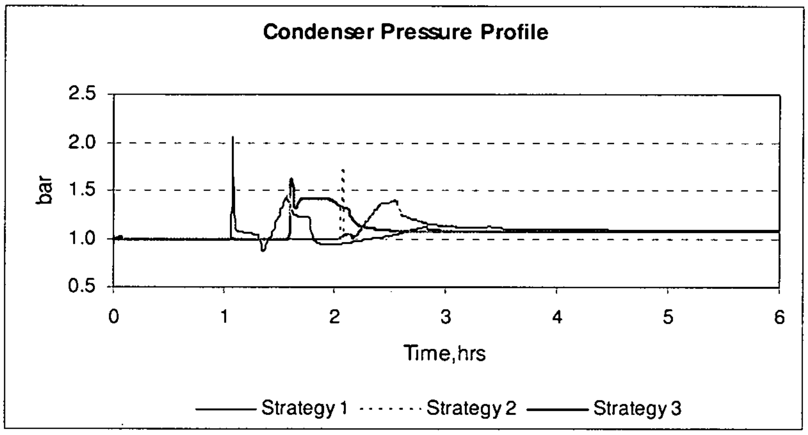


Figure 30: Condenser Pressure Profile for Three Strategies

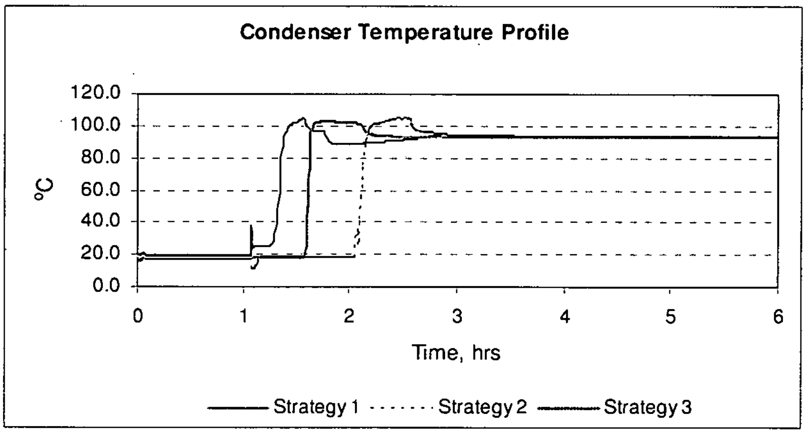


Figure 31: Condenser Temperature Profile for Three Strategies

Based on the temperature and pressure trends, Strategy 1 took the shortest time to reach steady state followed by Strategy 3 and Strategy 2. However, the range of pressure swing for Strategy 1 is greater than the other two strategies. Strategy 1 has pressure fluctuation of 1.17 bar while Strategy 2 and Strategy 3 are 0.73bar and 0.63bar respectively. The temperature difference between maximum and minimum for Strategy 1 is 85.7°C, Strategy 2 is 93.82°C and Strategy 3 is 86.62°C.

The ranking for condenser based on the results is shown as below (Table 12).

Table 12: Ranking of condenser for Three Strategies

Criteria	Strategy 1	Strategy 2	Strategy 3
Shortest time to reach steady state	3	1	2
Less pressure fluctuation	1	2	3
Less temperature fluctuation	3	1	2
Total	7	4	7

ii. Tray 7

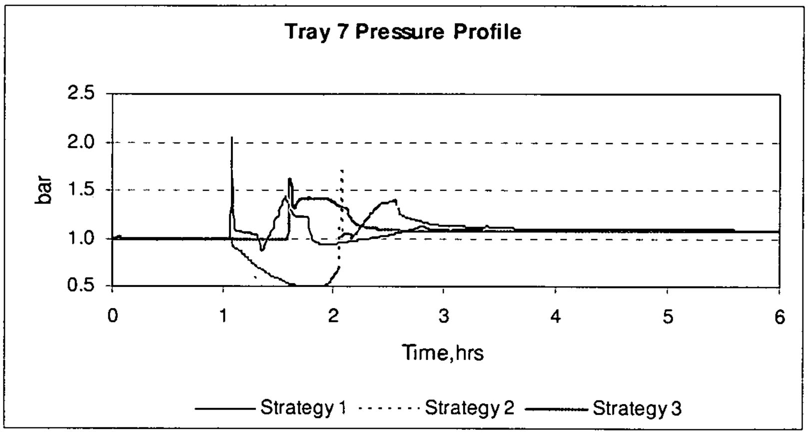


Figure 32: Tray 7 Pressure Profile for Three Strategies

For Tray 7, which is the tray located between acetic acid and ethanol feed trays; Strategy 1 took the shortest time to reach steady state. The pressure difference between maximum and minimum for Strategy 1 is 1.17bar, Strategy

2 is 1.23bar and Strategy 3 is 0.63bar. As shown in Figure 33, the temperature fluctuation is greater for Strategy 1 (151.5°C) as compared to Strategy 2 (143.9°C) and Strategy 3 (97.5°C).

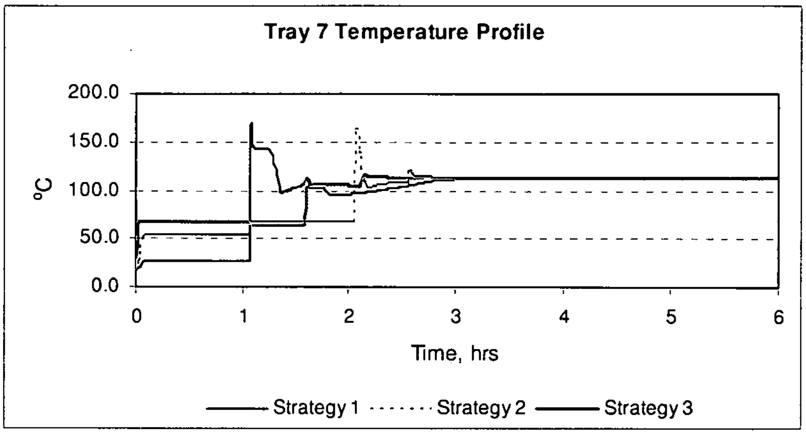


Figure 33: Tray 7 Temperature Profile for Three Strategies

The ranking for Tray 7 based on the results is shown as in Table 13.

Table 13: Ranking of Tray 7 for Three Strategies

Criteria	Strategy 1	Strategy 2	Strategy 3
Shortest time to reach steady state	3	1	2
Less pressure fluctuation	2	1	3
Less temperature fluctuation	1	2	3
Total	6	4	8

iii. Reboiler

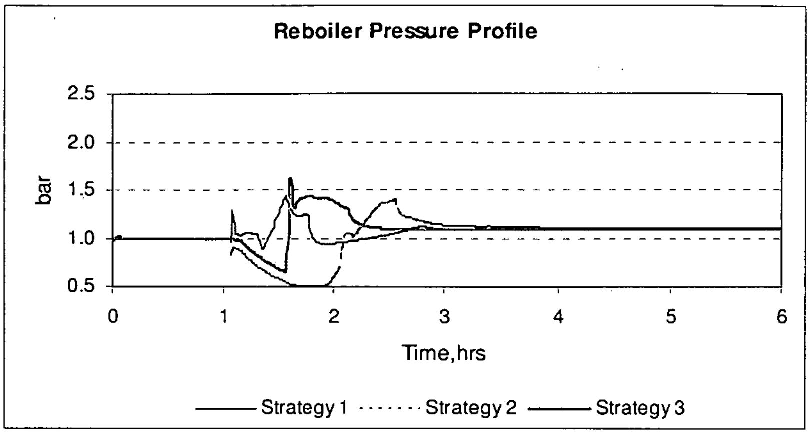


Figure 34: Reboiler Pressure Profile for Three Strategies

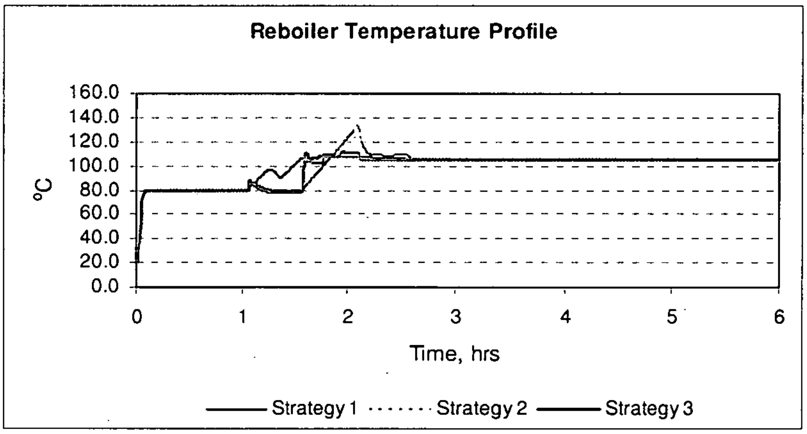


Figure 35: Reboiler Temperature Profile for Three Strategies

Similar to Condenser and Tray 7, Strategy 1 for reboiler took the shortest time to reach steady state. The range of pressure swing for Strategy 1 is smaller than the other two strategies. Strategy 1 has pressure fluctuation of 0.56bar while Strategy 2 and Strategy 3 are 0.92bar and 0.97bar respectively. The temperature fluctuation is greater for Strategy 2 (112.2°C) as compared to Strategy 1 (88.3°C) and Strategy 3 (90.4°C).

The ranking for reboiler based on the results is shown as in Table 14.

Table 14: Ranking of Reboiler for Three Strategies

Criteria	Strategy 1	Strategy 2	Strategy 3
Shortest time to reach steady state	3	1	2
Less pressure fluctuation	3	2	1
Less temperature fluctuation	3	1	2
Total	9	4	5

iv. Top Stream

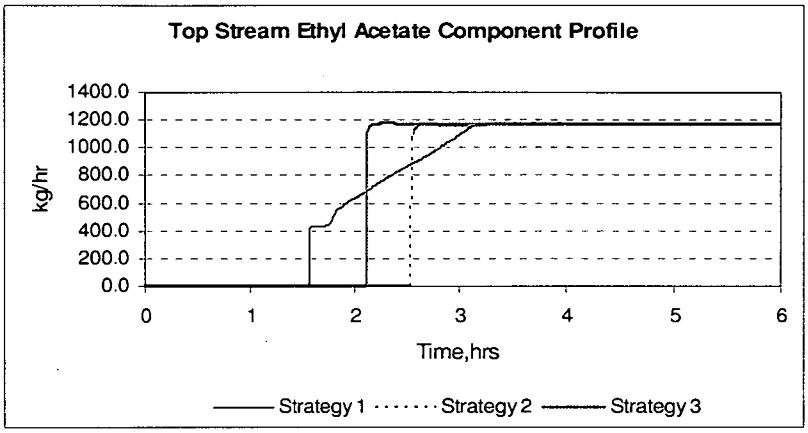


Figure 36: Top Stream Pressure Profile for Three Strategies

As shown in the trend above, Strategy 1 took the shortest time to produce ethyl acetate at top stream. The time taken is 1.57hrs as compared to Strategy 2, 2.56hrs and Strategy 3, 2.12hrs.

The ranking for the 4th criteria is shown as below (Table 15).

Table 15: Ranking of Top Stream for Three Strategies

Criteria	Strategy 1	Strategy 2	Strategy 3
Shortest time to produce product	3	1	2

Based on the overall ranking, it is concluded that Strategy 1 is the best strategy to be further optimized for start-up study with the highest scoring.

Table 16: Summary of Selection Matrix

Criteria	**Strategy 1**	**Strategy 2**	**Strategy 3**
Shortest time to reach steady state	9	3	6
Less pressure fluctuation	6	5	7
Less temperature fluctuation	7	4	7
Shortest time to produce product	3	1	2
Total	25	13	22

e) Strategy 1 Start-up Evaluation Prior to Optimization

The start-up evaluation is conducted using 8 stages i.e. the condenser stage, top tray, top stream, acetic acid feed tray (tray 4), tray between acetic acid feed and ethanol feed (tray 7), ethanol feed tray (tray 11), tray between ethanol feed and reboiler (tray 12) and reboiler stage. These stages are representative of the entire reactive distillation column.

For Strategy 1, the reboiler stage is filled up with ethanol and acetic acid at equal-mole prior to starting-up. The reactive distillation column configuration is shown in Figure 37. Acetic acid and ethanol are introduced simultaneously into reactive distillation column at hour 1.0.

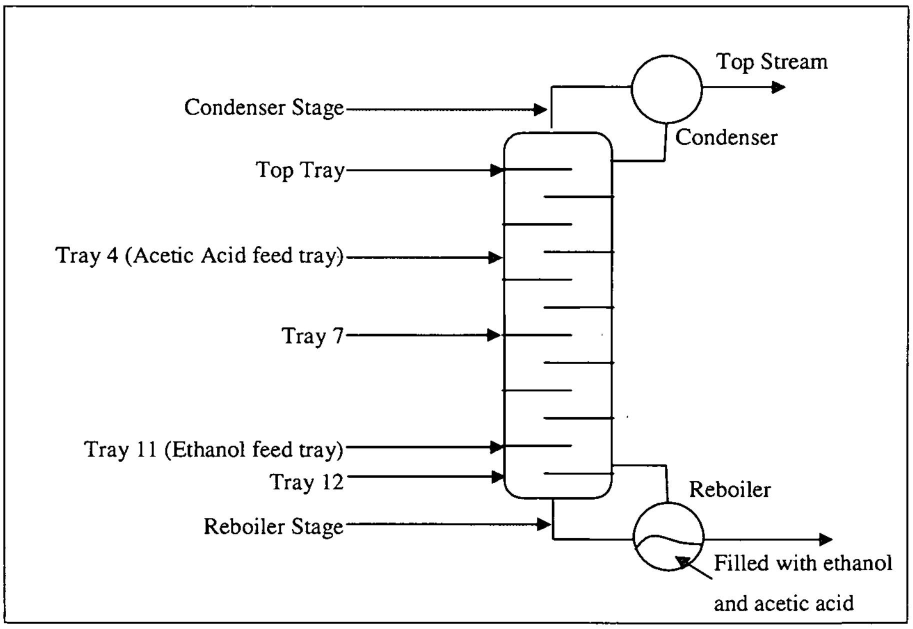


Figure 37: Strategy 1 Reactive Distillation Column Configuration

Pressure, temperature and components profiles are studied for each stage and presented in the following sections.

i. Pressure Profiles

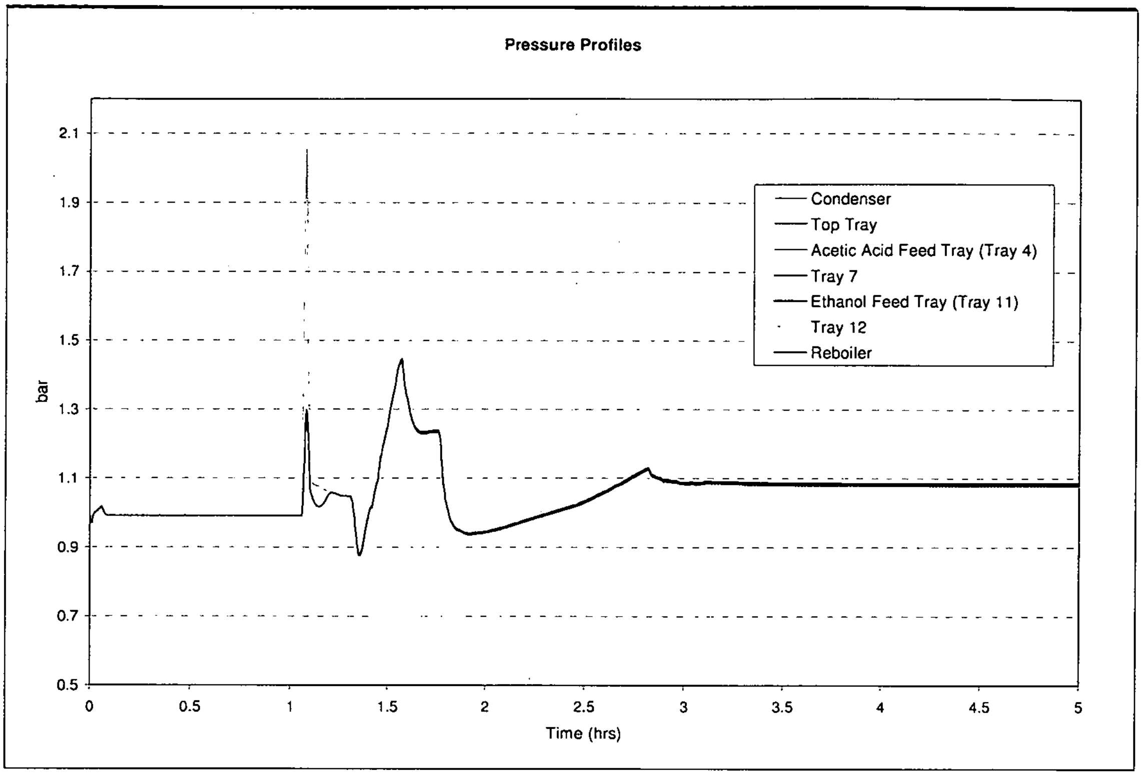


Figure 38: Pressure Profiles for Strategy 1

As shown in the graph Figure 38, the pressure profile is similar for all the trays in the reactive distillation column except for reboiler stage. Lower pressure fluctuation is observed in the reboiler as the reboiler is liquid filled. All the trays pressure spiked to as high as 2.05 bars after 1 hour, when both ethanol and acetic acid are introduced into the reactive distillation column. It is believed to be a result of the exothermic reaction between acetic acid and ethanol. The fluctuation in pressure profile is observed from hour 1 to 2 and slowly stabilized by the third hour. Pressure fluctuation is due to dynamics on the column trays during the initial phase of reaction more liquid is formed between tray 4 and tray 11 as shown in Figure 39 where reaction is expected to occur. The liquid level profile is retrieved from the ASPEN DYANMIC^{TM}

simulator. This can be further explained through tray pressure drop formula as shown below.

$$\Delta P = 9.81 \times 10^{-3}(h_d + (h_w + h_{ow}) + h_r)\rho_L$$ **Equation 34**

One of the factors is liquid level on the tray, where the tray pressure drop is proportional to liquid level on the tray. Therefore, high pressure is observed when more liquid is formed.

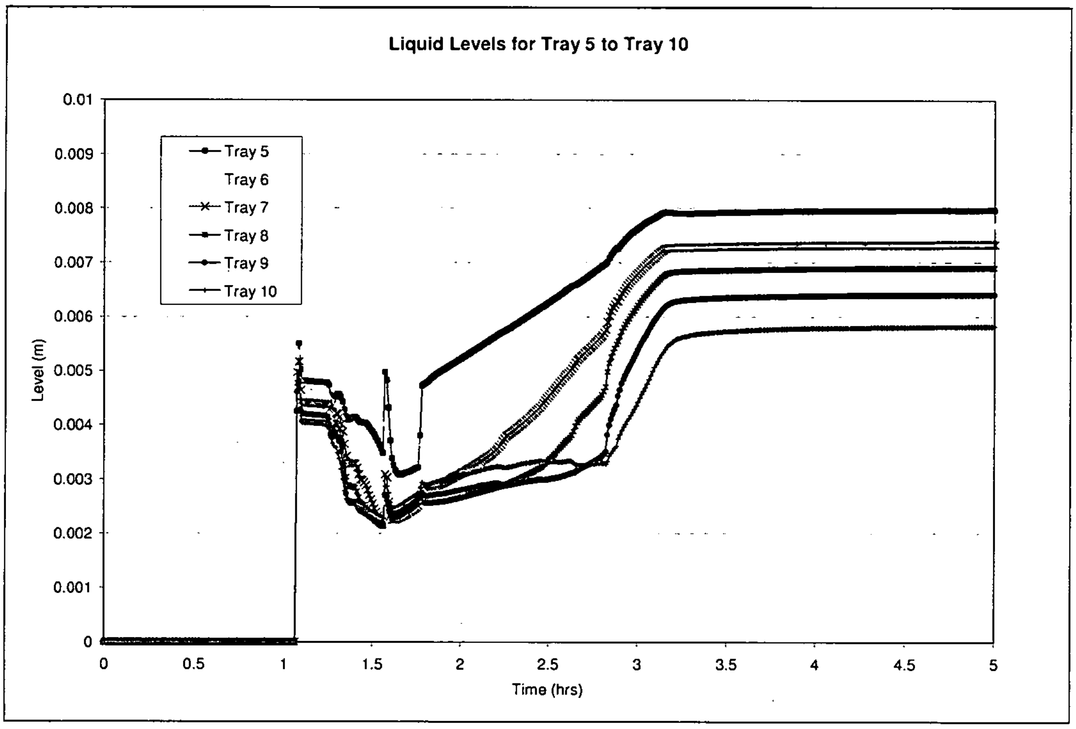


Figure 39: Liquid Level for Tray 5 to Tray 10 for Strategy 1

From hour 3 onwards the pressure became stable as the reaction approaches equilibrium condition.

ii. Temperature Profiles

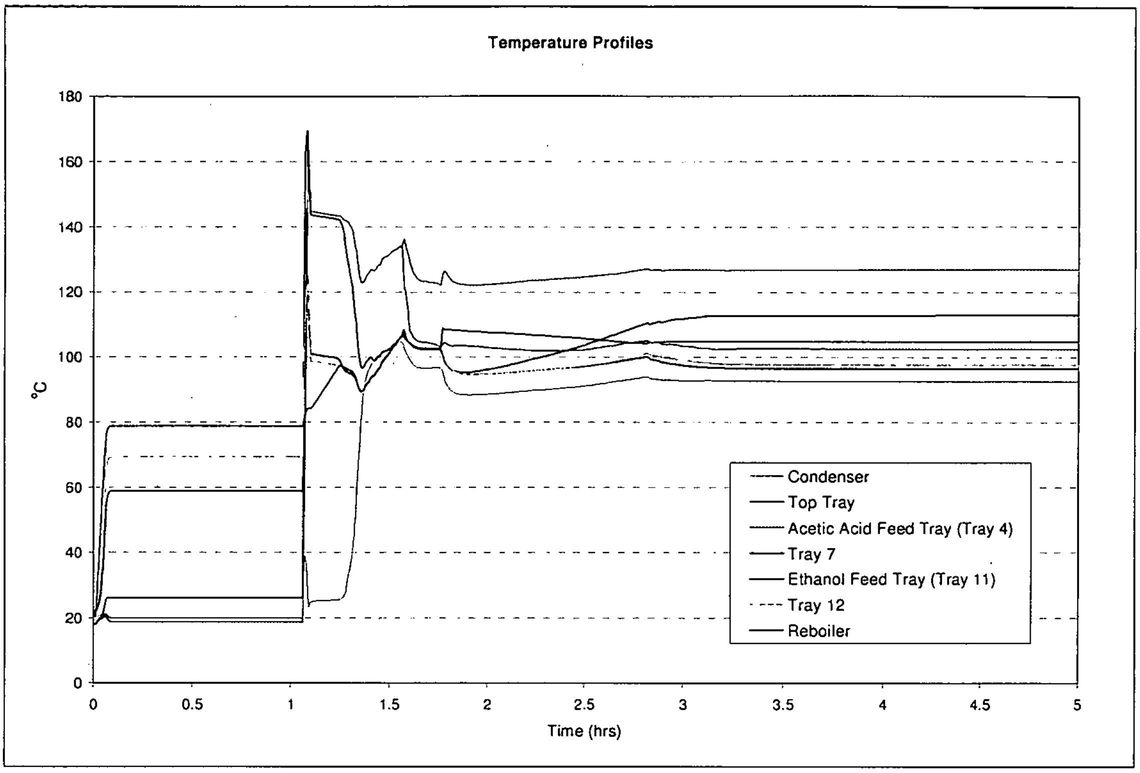


Figure 40: Temperature Profiles for Strategy 1

Figure 40 shows that the temperature profile in the reactive distillation column. As the reboiler is heated up at time 0, temperature of the lower trays increases accordingly. The higher tray i.e. "top tray", "condenser", "Tray 7" showed little effect as they are physically higher. This temperature profile maintained constant until acetic acid and ethanol are introduced into the reactive distillation column at hour 1.

The temperature fluctuation from hour 1 to 2 is mainly due to the initial phases of the reaction. Exothermic reaction between acetic acid and ethanol takes place, thereby increasing the temperature to about 170°C. Calculated heat of formation of ethyl acetate and water is -18.08kJ/mol based on the reboiler heating temperature at 79°C. From observations in Figure 40, tray 7 and acetic acid feed tray (tray 4) show highest temperature. It is likely that the reaction first occurs between these trays as ethanol vapor (from tray 11) comes into contact with acetic acid.

Tray 7 temperature increases from hour 2 to 3 and then stabilized. This shows that more products are being produced in Tray 7 as time goes by. This is in congruence with increase of ethyl acetate (product) concentration in this tray shown in Figure 41.

As the reaction reaches equilibrium by hour 3, the fluctuation dampens. Acetic acid tray still has the highest temperature due to exothermic reaction. The top most tray has slightly lower temperature as the reflux flow from condenser, which is cooler, enters this stage.

The condenser stage has the lowest temperature as vapor product is being condensed to liquid and thereby rejecting heat.

iii. Ethyl Acetate Liquid Mole Fraction Profiles

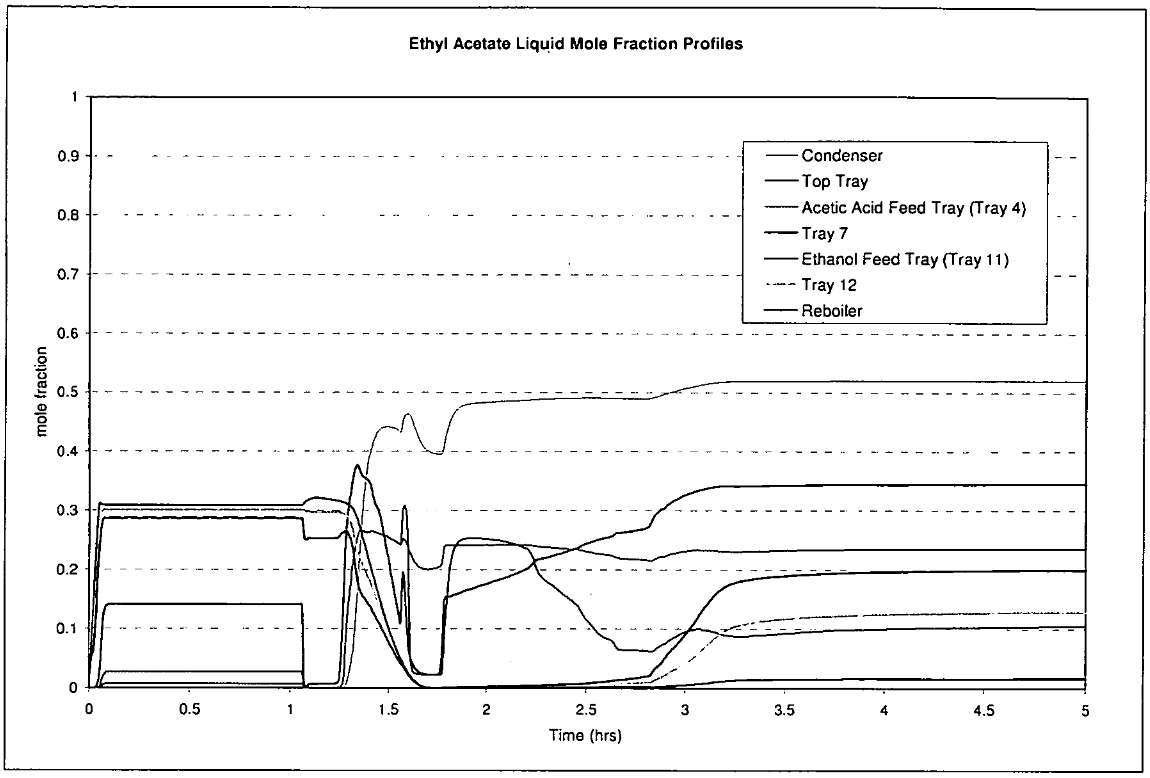


Figure 41: Ethyl Acetate Liquid Mole Fraction Profiles for Strategy 1

Ethanol and acetic acid can react to form ethyl acetic and water under normal conditions. In view of the presence of ethanol and acetic acid in reboiler stage whilst reboiler is heating up, ethyl acetate is found in each lower column trays at the beginning of the simulation run.

As shown in the graph, the concentration of ethyl acetate is lower at the higher stages because ethyl acetate is initially formed at reboiler stage before acetic acid and ethanol fed in. The ethyl acetate concentration maintained whilst reboiler temperature maintained at 79°C. While acetic acid and ethanol are fed into the column simultaneously, the reaction starts (concentration of ethyl acetate increases) to occur at Tray 4 and Tray 7 while concentration of ethyl acetate reduces in ethanol feed tray (Tray 11) signally reduction of reaction.

This phenomenon can be explained by the fact that reboiler temperature of 79°C would have vaporized the ethanol fed into the column. Ethanol vapor travels upwards until it gets in contact with acetic acid which flows downward from its feed tray (Tray 4). This is confirmed by the increased of product (ethyl acetate) concentration in Tray 7. Higher concentration of product is expected in Tray 4 due to higher amount of acetic acid present there.

As the reaction proceeds pass hour 2.5, it is observed that higher concentration of ethyl acetate is found at Tray 7 compared to Tray 4. This shows that the reaction zone is more effectively located between the two reactants feed trays.

As this startup strategy adopts a total reflux approach, product (ethyl acetate and water) is being channeled back into the column from the condenser. When the liquid product flow reaches the lower trays by hour 3, some amount of ethyl acetate can be observed in these trays. As the column reaches steady state by hour 3, vapor and liquid flows in the column are stabilized hence resulting in constant concentration of products in all the stages. This is further supported by other observations i.e. pressure and temperature in this section of the discussion.

iv. Water Liquid Mole Fraction Profiles

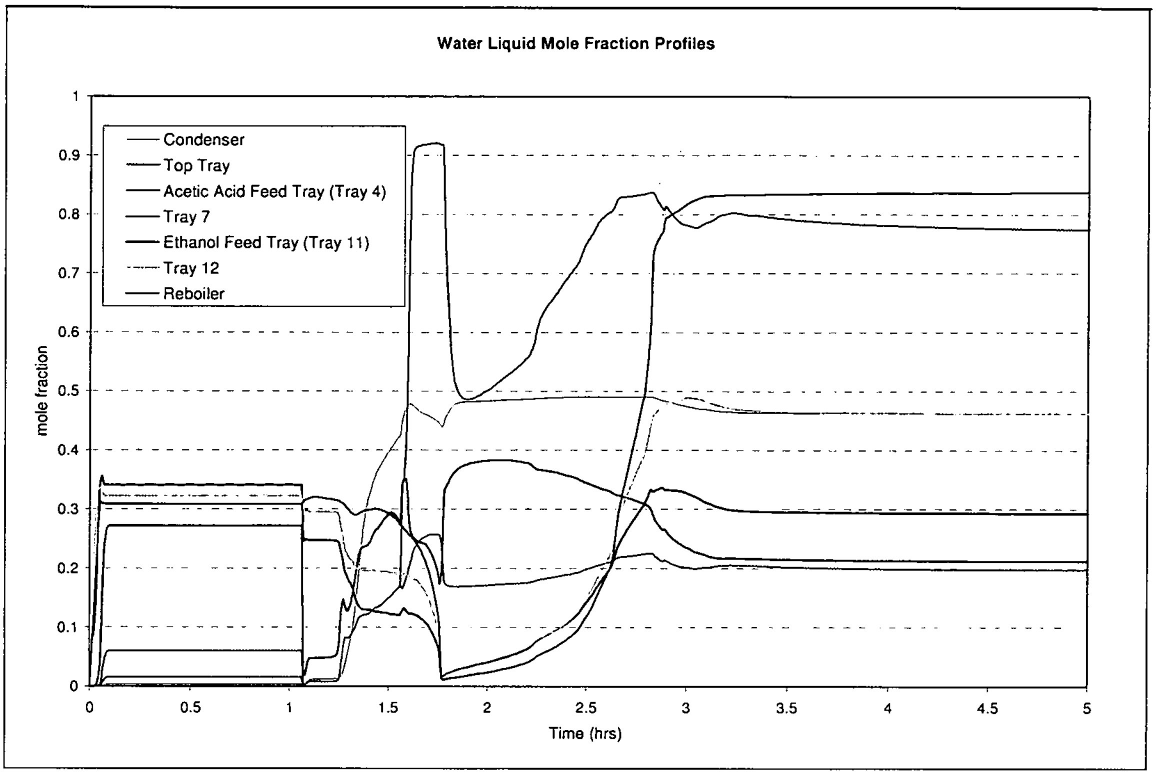


Figure 42: Water Liquid Mole Fraction Profiles for Strategy 1

Generally the trend of water concentration is similar to that of ethyl acetate as water is a by-product of the reaction between acetic acid and ethanol. Since water has comparatively higher boiling point, high concentration of water is noted at the lower trays.

However, it is noticed that top tray has high water concentration as well. This could be due to total reflux operations, where cooling effect may have cooled down the water vapor component. Equilibrium is reached at about 3.0 hours, where water concentration is constant at all trays.

v. Acetic Acid Liquid Mole Fraction Profiles

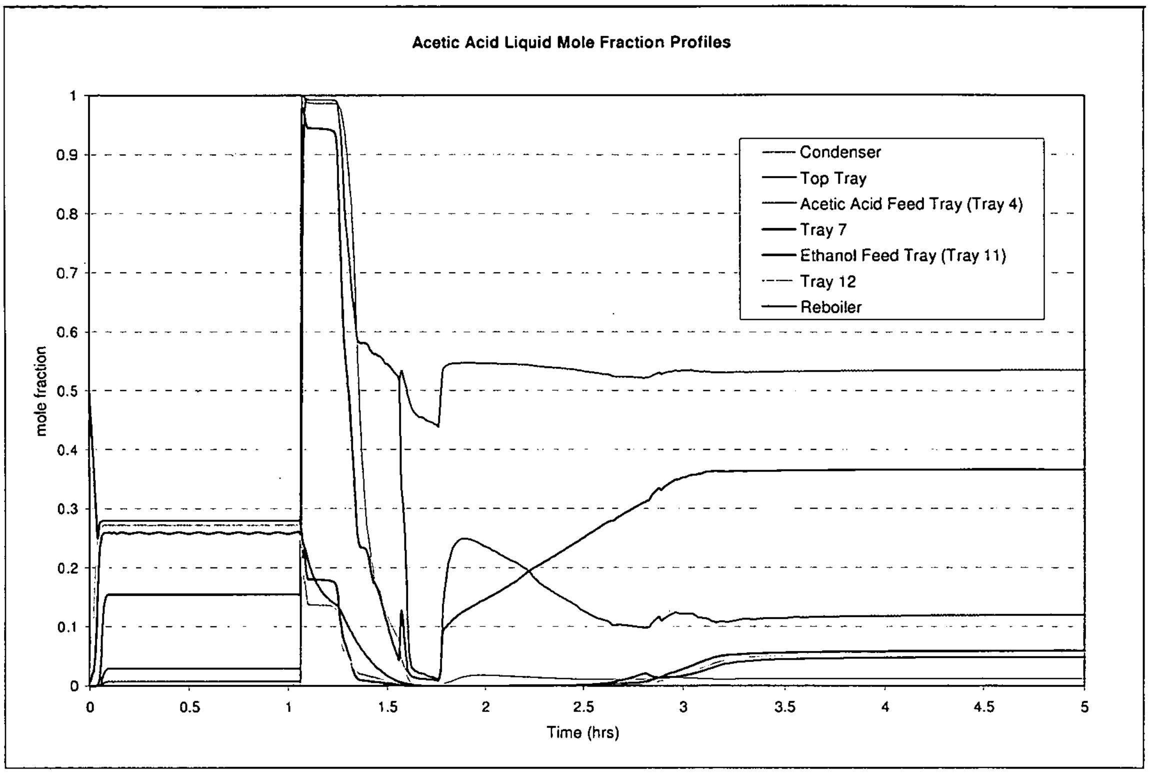


Figure 43: Acetic Acid Liquid Mole Fraction Profiles for Strategy 1

Acetic acid is one of the two reactants in an equal-molar reaction with ethanol. During start up, there is 0.5 mole fraction of acetic acid in reboiler stage; therefore, acetic acid can be found in all column trays. The acetic acid could be brought to tray above reboiler stage by means of entrainment in ethanol vapor.

At hour 1, acetic acid is introduced into the reactive distillation column at Tray 4, hence almost 1mole fraction concentration. As the top tray and Tray 7 is located close by acetic acid can also be found at high concentrations at the tray. At the same time ethanol is being introduced at Tray 11 (bottom of the column).

Concentration of acetic acid reduces as reaction takes place. This trend is in agreement with the ethyl acetate concentration illustrated in Figure 41. The mole fraction of acetic acid is displaced by the ethyl acetate concentration.

As the reaction reaches equilibrium, there will be constant amount of unreacted acetic acid. This is confirmed by presence of a constant amount of this feed at Tray 4 and 7. Small amount of acetic acid is observed to be present in all stages of the column. Acetic acid flows to the bottom tray with the reflux and liquid flow while some amount can be entrained to upper trays by rising vapor of the distillation process.

vi. Ethanol Liquid Mole Fraction Profiles

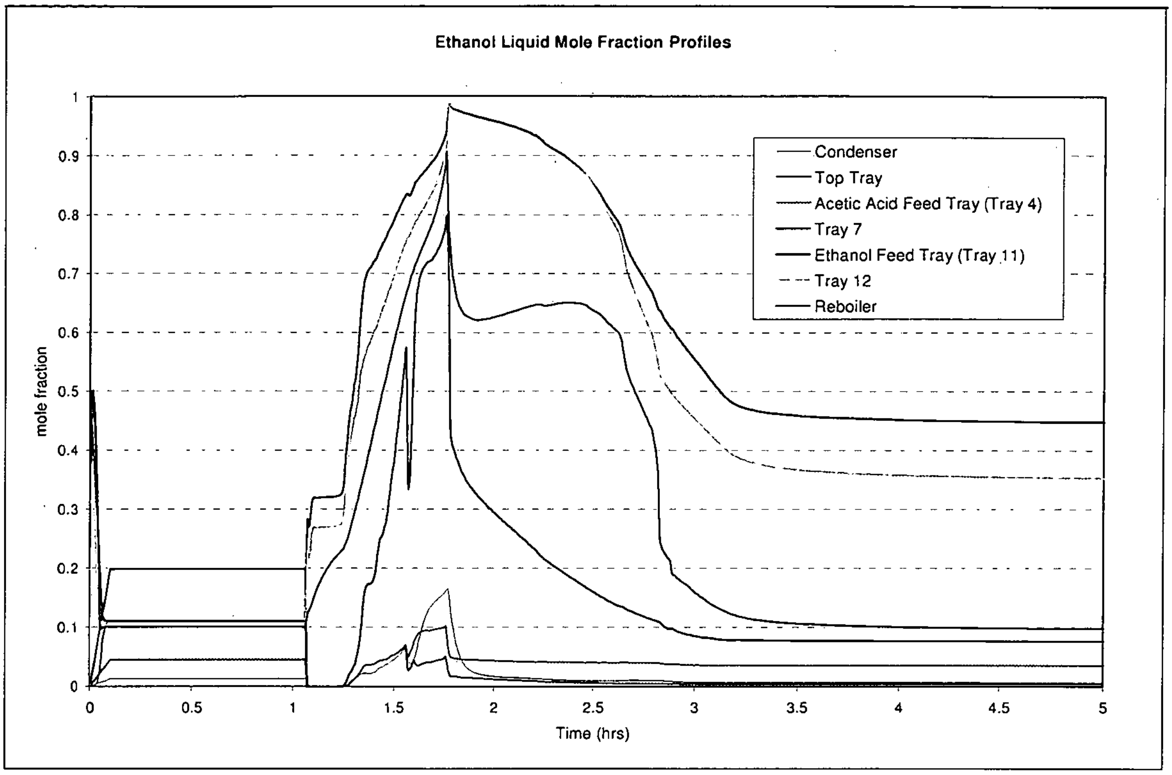


Figure 44: Ethanol Liquid Mole Fraction Profiles for Strategy 1

Ethanol can be found in all trays as the vapor fills the whole column from the amount in reboiler prior to startup owing to its low boiling point. As ethanol is introduced at hour 1, the ethanol composition dropped because of aggressive forward reaction occurring. This is supported by ethyl acetate and water components formation as shown in Figure 41 and Figure 42.

The increment of ethanol component is believed to be related to high products components pushing the reaction to move in the reverse direction and converting back to ethanol and acetic acid.

When the reaction reached equilibrium, it is noticed that most of the ethanol component is found at the bottom trays, which is very close to the ethanol feed

i. Pressure Profiles

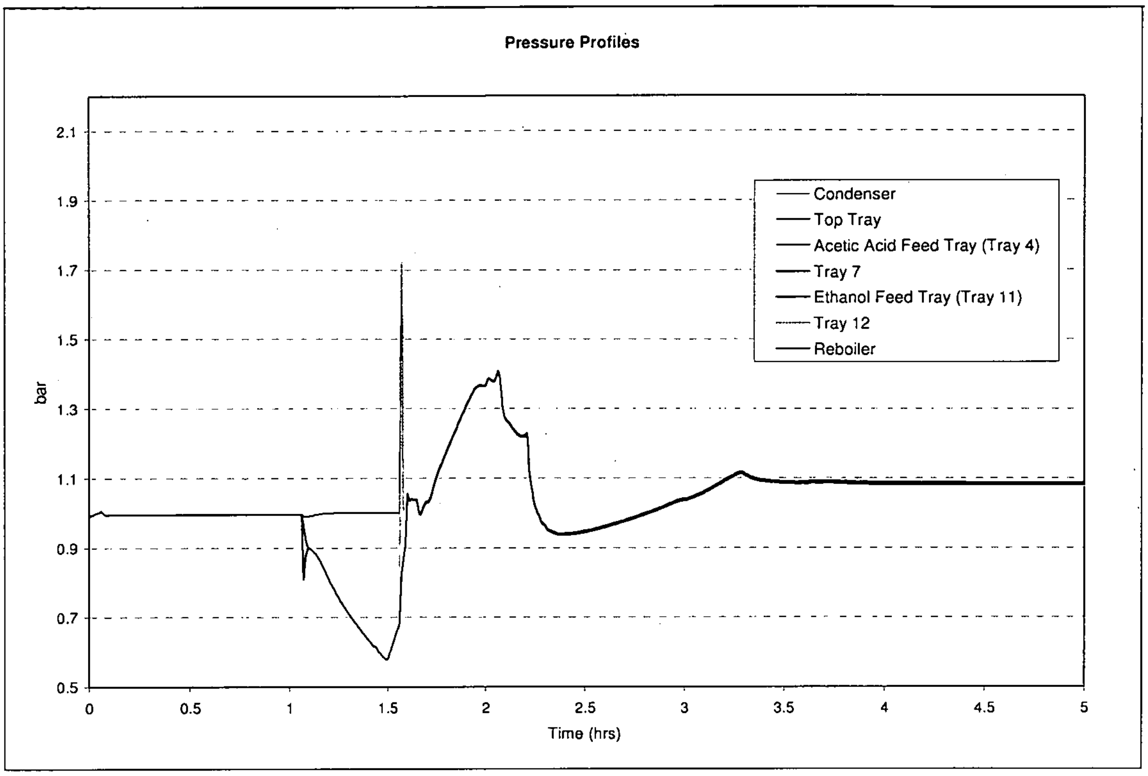


Figure 46: Pressure Profiles for Strategy 2

As shown in the Figure 46, the pressure profile is similar for all the trays in the reactive distillation column except for top tray and condenser stage. All the trays pressure is at 1 bar prior to introduction of acetic acid into the reactive distillation column. Acetic acid is introduced into reactive distillation column at hour 1 for 0.5 hours. It is observed that pressure for all the trays dropped to 0.5 bars except for top tray and condenser stage during that period of time. This could be due to the impact of acetic acid liquid on the already evaporated ethanol in reactive distillation column. It is supported by Figure 47 where no liquid level is observed prior to the introduction of acetic acid. The pressure spiked to as high as 1.72 bars after 1.5 hours, when ethanol is introduced into the reactive distillation column. It is believed to be a result of the exothermic reaction between acetic acid and ethanol. The fluctuation in pressure profile is observed from hour 1.5 to 3.5 and slowly stabilized by the fourth hour as the reaction approaches equilibrium condition. Pressure fluctuation is due to dynamics on the column trays during the initial phase of reaction when more liquid is formed between tray 4 and tray 11 as shown in Figure 47 where reaction is expected to occur. The liquid level profile is retrieved from the ASPEN DYANMIC^{TM} simulator. This can be further explained through tray pressure drop formula as shown in .

$$\Delta P = 9.81 \times 10^{-3}(h_d + (h_w + h_{ow}) + h_r)\rho_L \qquad \textbf{Equation 34}$$

One of the factors is liquid level on the tray, where the tray pressure drop is proportional to liquid level on the tray. Therefore, high pressure is observed when more liquid is formed.

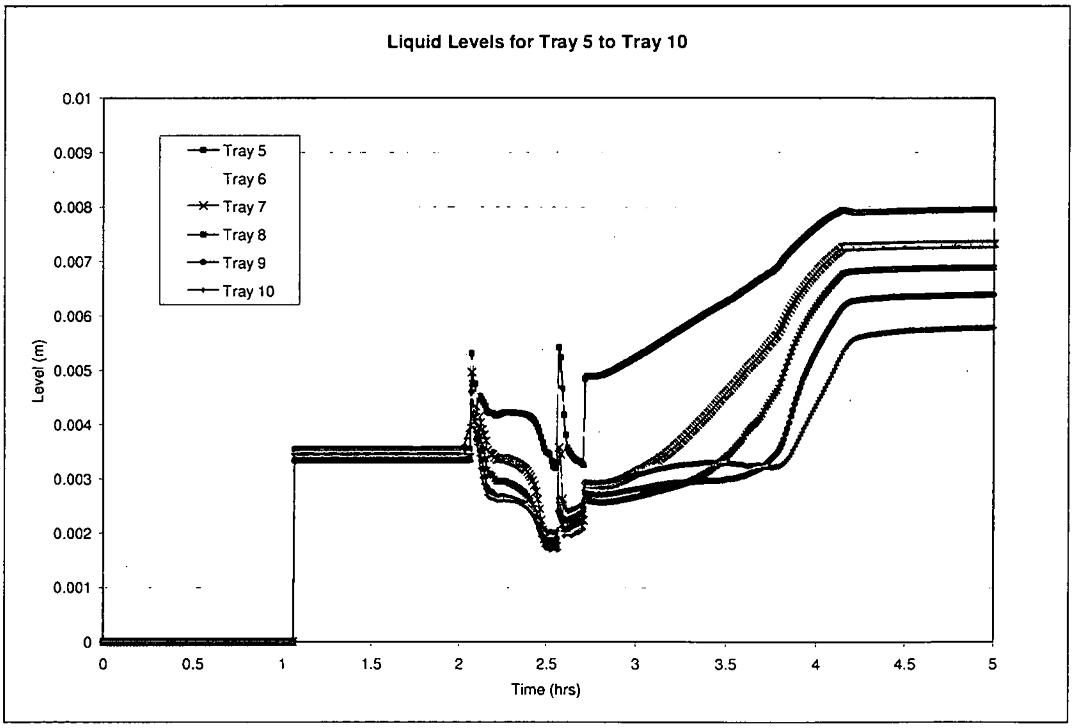


Figure 47: Liquid Level for Tray 5 to Tray 10 for Strategy 2

ii. Temperature Profiles

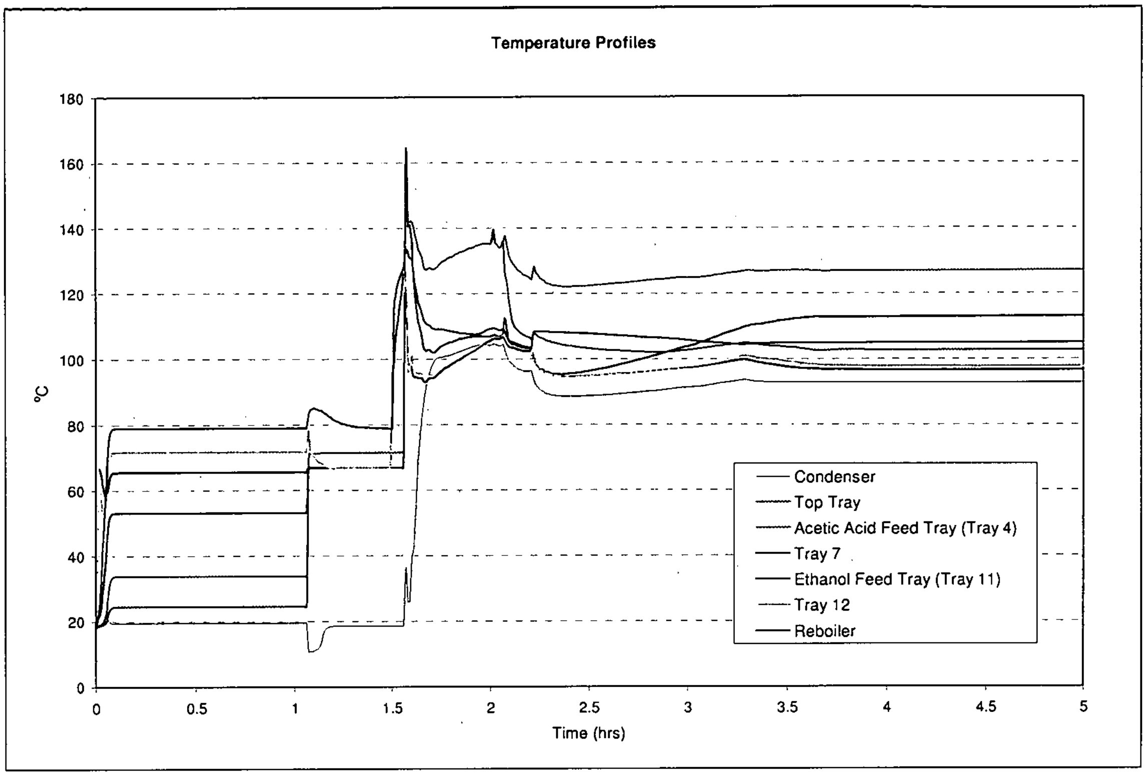


Figure 48: Temperature Profiles for Strategy 2

Figure 48 shows that the temperature profile in the reactive distillation column. As the reboiler is heated up at time 0, temperature of the lower trays increases accordingly. The higher tray i.e. "top tray", "condenser", "Tray 7" showed little effect as they are physically higher. This temperature profile maintained constant until acetic acid is introduced into the reactive distillation column at hour 1.

The temperature fluctuation from hour 1.5 to 2.5 is mainly due to the initial phases of the reaction. Exothermic reaction between acetic acid and ethanol takes place, thereby increasing the temperature to about 165°C. Calculated heat of formation of ethyl acetate and water is -18.08kJ/mol based on the reboiler heating temperature at 79°C. From observations in Figure 48, tray 7 and acetic acid feed tray (tray 4) show highest temperature. It is likely that the reaction first occurs between these trays as ethanol vapor (from tray 11) comes into contact with acetic acid.

Tray 7 temperature increases from hour 2.5 to 3.5 and then stabilized. This shows that more products are being produced in Tray 7 as time goes by. This is in congruence with increase of ethyl acetate (product) concentration in this tray shown in Figure 49.

As the reaction reaches equilibrium by hour 4.0, the fluctuation dampens. Acetic acid tray still has the highest temperature due to exothermic reaction. The top most tray has slightly lower temperature as the reflux flow from condenser, which is cooler, enters this stage.

The condenser stage has the lowest temperature as vapor product is being condensed to liquid and thereby rejecting heat.

iii. Ethyl Acetate Liquid Mole Fraction Profiles

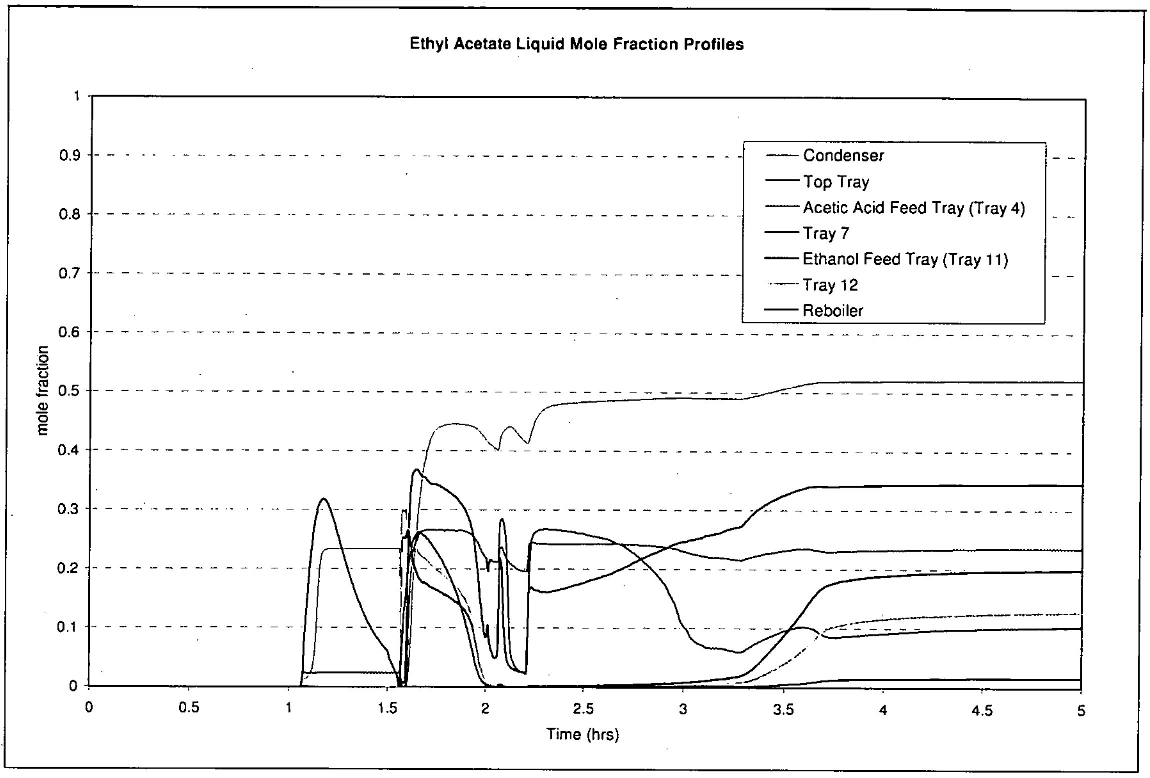


Figure 49: Ethyl Acetate Liquid Mole Fraction Profiles for Strategy 2

Ethanol and acetic acid can react to form ethyl acetic and water under normal conditions. In view of the presence of ethanol alone whilst reboiler is heating up, there is no ethyl acetate found in reactive distillation column. Ethyl acetate is only observed after acetic acid is introduced into the reactive distillation column at hour 1.0.

While acetic acid is fed into the column, the reaction starts (concentration of ethyl acetate increases) and the concentration is constant at condenser stage and top tray. This could be due to the fact that ethanol vapor travels upward and brings acetic acid liquid up to condenser stage and top tray for reaction. Ethanol is introduced at hour 1.5, hence ethyl acetate is formed at all trays at that period of time. Concentration of ethyl acetate reduces in most of the trays after hour 2.0. This phenomenon can be explained by the fact that reboiler temperature of 79°C would have vaporized the ethanol fed into the column. Ethanol vapor travels upwards until it gets in contact with acetic acid which flows downward from its feed tray (Tray 4). This is confirmed by the increased of product (ethyl acetate) concentration in Tray 7.

As the reaction proceeds pass hour 3.0, it is observed that higher concentration of ethyl acetate is found at Tray 7 compared to Tray 4. This shows that the reaction zone is more effectively located between the two reactants feed trays.

As this startup strategy adopts a total reflux approach, product (ethyl acetate and water) is being channeled back into the column from the condenser. When the liquid product flow reaches the lower trays by hour 3.5, some amount of ethyl acetate can be observed in these trays. As the column reaches steady state by hour 3.5, vapor and liquid flows in the column are stabilized hence resulting in constant concentration of products in all the stages. This is further supported by other observations i.e. pressure and temperature in this section of the discussion.

iv. Water Liquid Mole Fraction Profiles

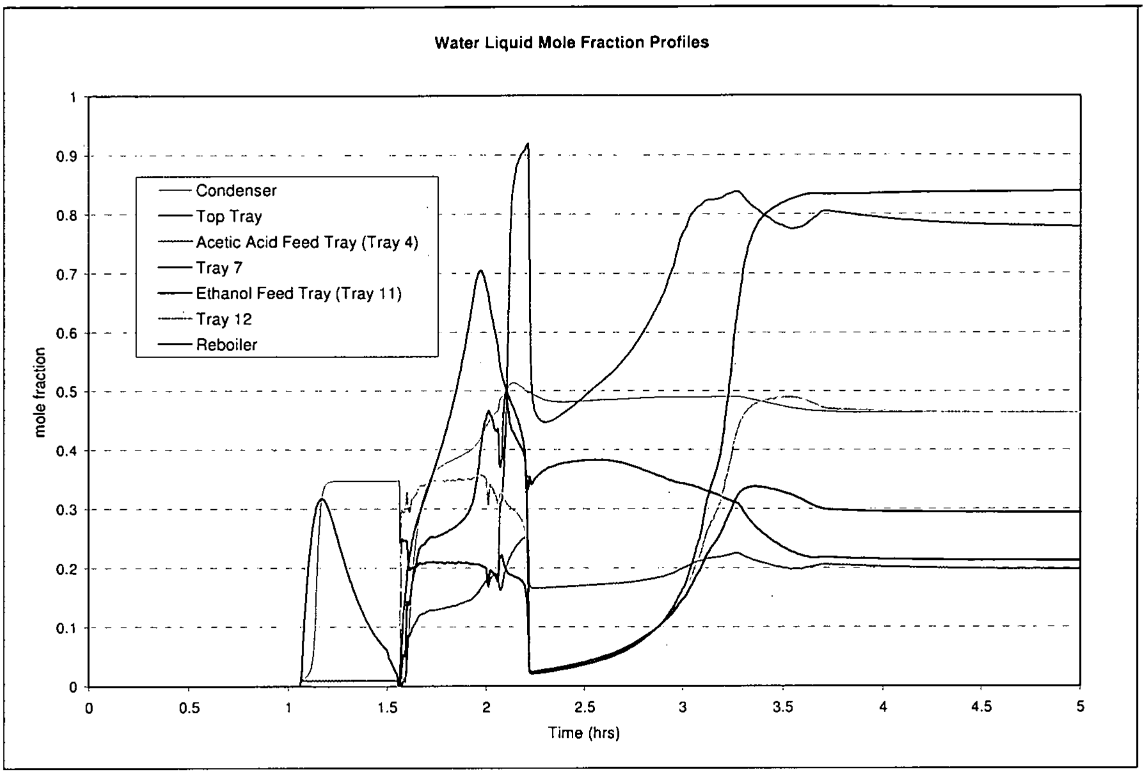


Figure 50: Water Liquid Mole Fraction Profiles for Strategy 2

Similar to ethyl acetate trend, water concentration trending is almost the same as water is a by-product of the reaction between acetic acid and ethanol. Since water has comparatively higher boiling point, high concentration of water is noted at the lower trays.

However, it is noticed that top tray has high water concentration as well. This could be due to total reflux operations, where cooling effect may have cooled down the water vapor component. Water concentration is constant at all trays when equilibrium is reached at about 4.0 hours.

v. Acetic Acid Liquid Mole Fraction Profiles

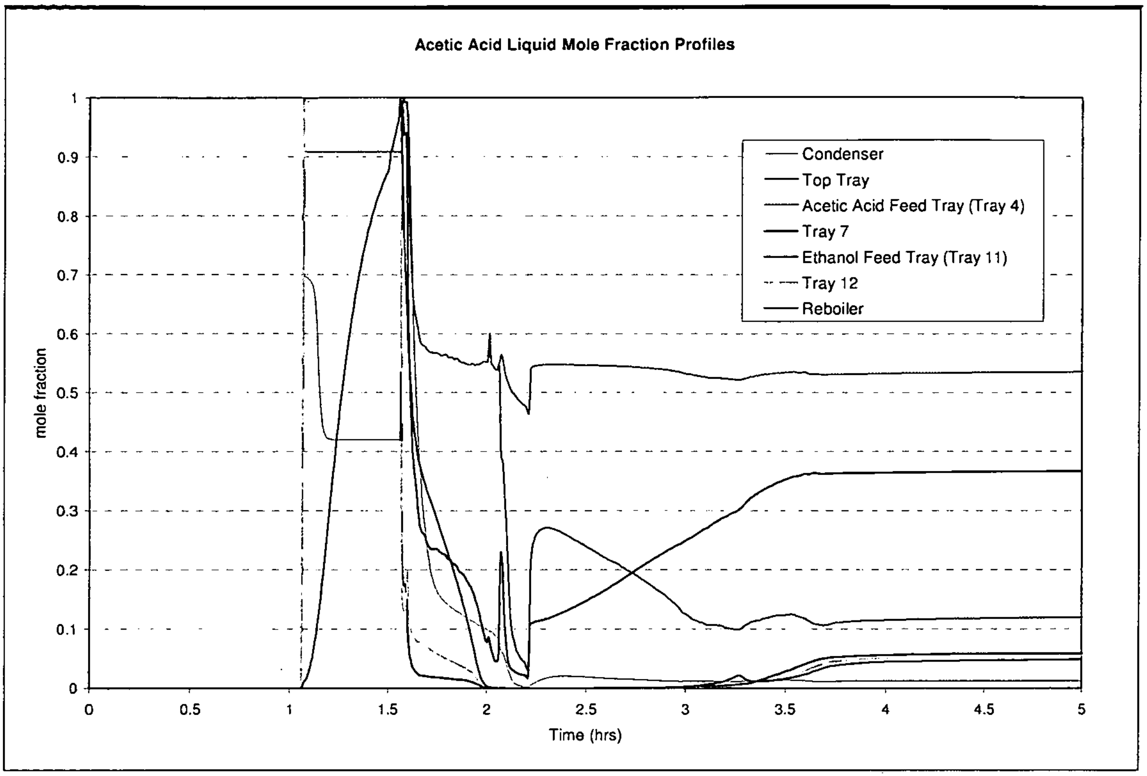


Figure 51: Acetic Acid Liquid Mole Fraction Profiles for Strategy 2

For Strategy 2, ethanol is the only reactant presented at reboiler stage, therefore, during startup, there is no acetic acid in reboiler stage. Acetic acid is introduced at hour 1.0 after reactive distillation column start-up. High acetic acid concentration is observed after feed in at all trays. It is believed that the acetic acid could be brought to tray above reboiler stage by means of entrainment in ethanol vapor.

Concentration of acetic acid reduces as reaction takes place when ethanol is introduced in reactive distillation column at hour 1.5. This trend is in agreement with the ethyl acetate concentration illustrated in Figure 49. The mole fraction of acetic acid is displaced by the ethyl acetate concentration.

As the reaction reaches equilibrium, there will be constant amount of unreacted acetic acid. This is confirmed by presence of a constant amount of this feed at Tray 4 and 7. Small amount of acetic acid is observed to be present in all stages of the column. Acetic acid flows to the bottom tray with the reflux and liquid flow while some amount can be entrained to upper trays by rising vapor of the distillation process.

vi. Ethanol Liquid Mole Fraction Profiles

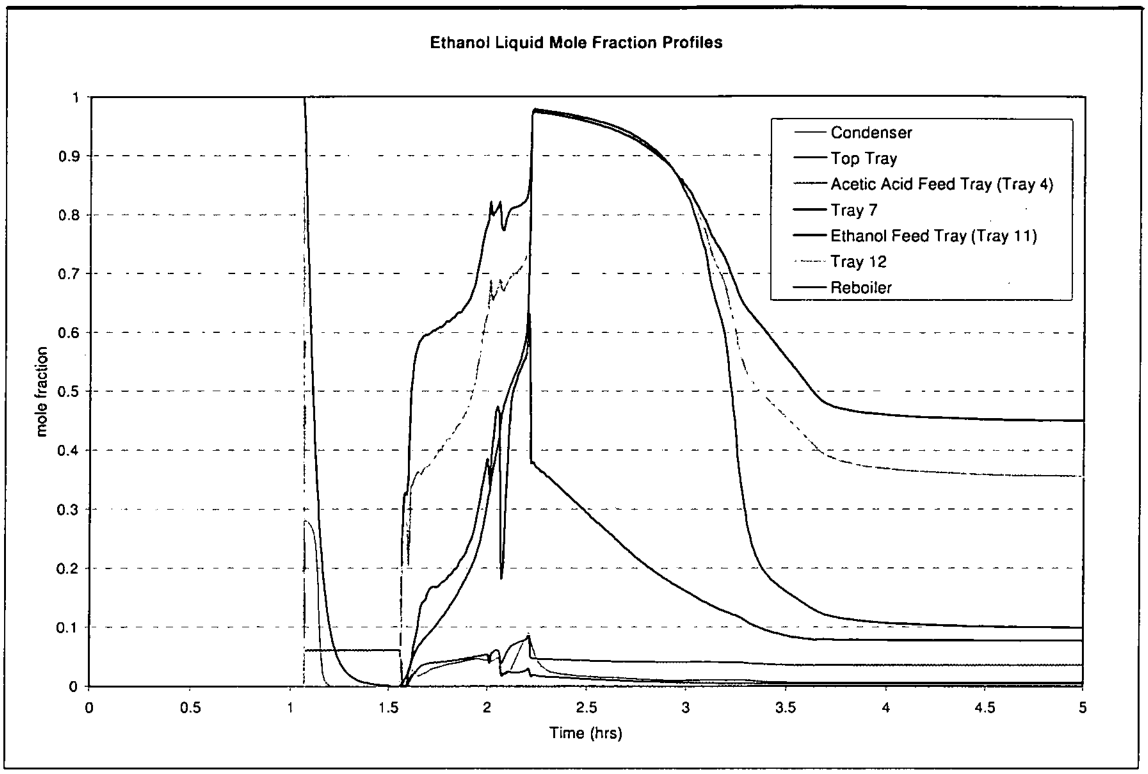


Figure 52: Ethanol Liquid Mole Fraction Profiles for Strategy 2

Only ethanol is found in all trays during start-up since ethanol is the single reactant presented at reboiler stage. As acetic acid is introduced at hour 1, the ethanol composition dropped due to aggressive forward reaction occurring. This is supported by ethyl acetate and water components formation as shown in Figure 49 and Figure 50.

Ethanol concentration increased at hour 1.5 when ethanol is introduced into reactive distillation column. The increment of ethanol component at hour 2.0 to 2.5 is believed to be related to high products components pushing the reaction to move in the reverse direction and converting back to ethanol and acetic acid.

When the reaction reached equilibrium, it is noticed that most of the ethanol component is found at the bottom trays, which is very close to the ethanol feed tray (Tray 11). It could be due to the reaction between acetic acid feed tray and ethanol tray has restricted the ethanol from flowing upwards. The similar phenomenon is noted for acetic acid component as most of the acetic acid presented at top trays instead of bottoms trays.

g) Strategy 3 Start-up Evaluation Prior to Optimization

The start-up evaluation is conducted using the same 8 stages i.e. the condenser stage, top tray, top stream, acetic acid feed tray (tray 4), tray between acetic acid feed and ethanol feed (tray 7), ethanol feed tray (tray 11), tray between ethanol feed and reboiler (tray 12) and reboiler stage. These stages are representative of the entire reactive distillation column.

For Strategy 3, the reboiler stage is filled up with acetic acid prior to starting-up. The reactive distillation column configuration is shown in Figure 53. Ethanol is introduced into reactive distillation column at hour 1.0 followed by acetic acid at hour 1.5.

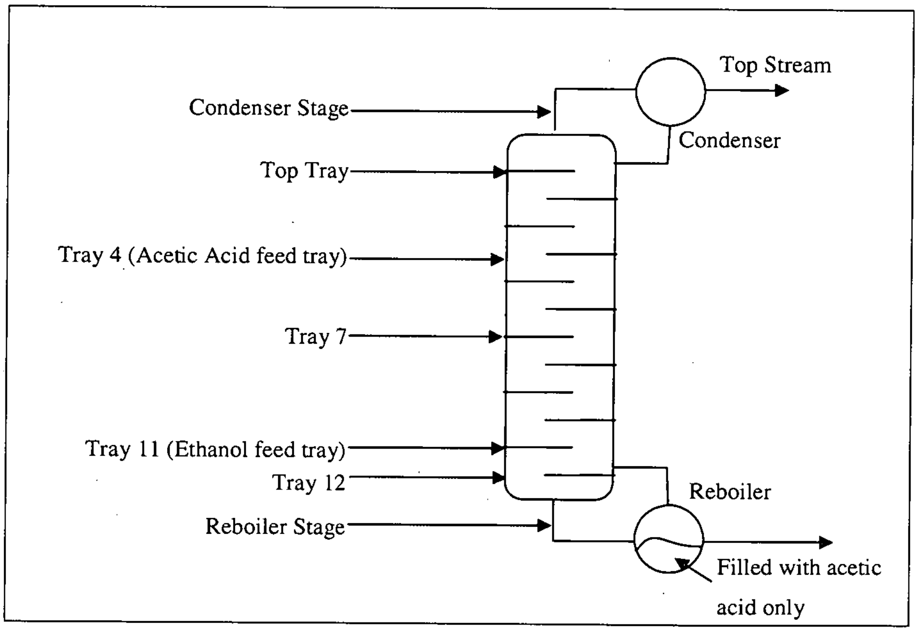


Figure 53: Strategy 3 Reactive Distillation Column Configuration

Pressure, temperature and components profiles are studied for each stage and presented in the following sections.

i. Pressure Profiles

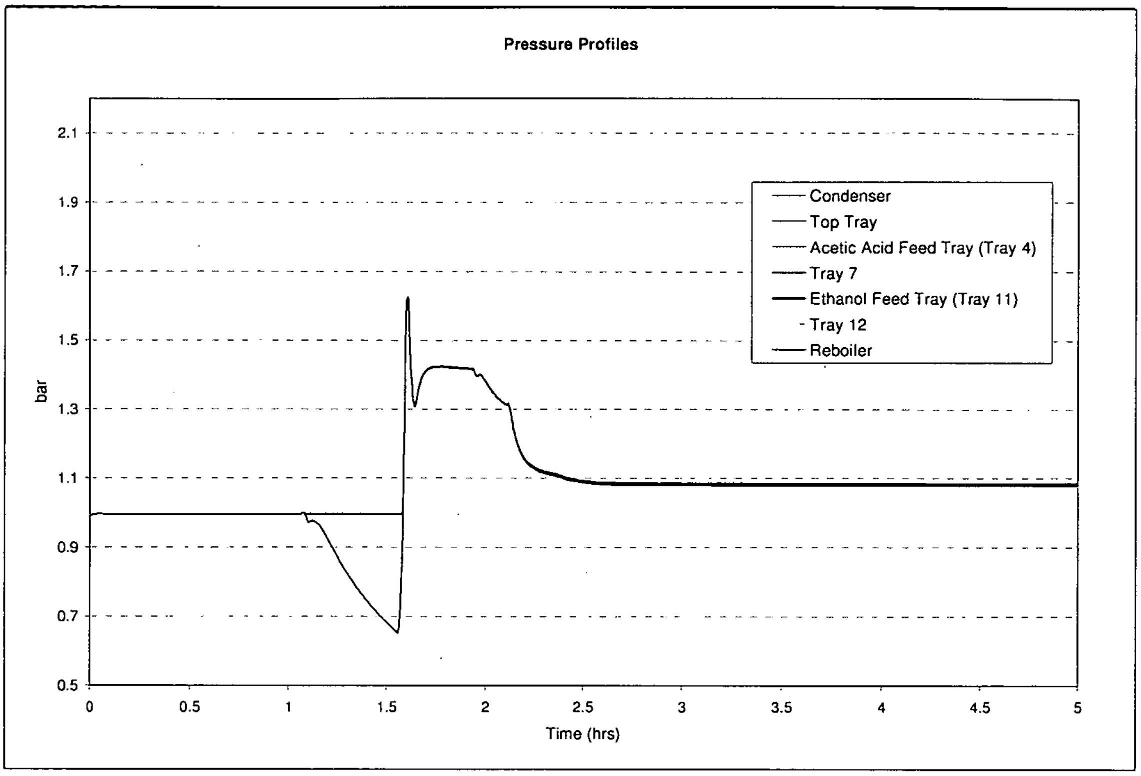


Figure 54: Pressure Profiles for Strategy 3

As shown in the graph Figure 54, the pressure profile is similar for all the trays in the reactive distillation column for trays located underneath ethanol feed tray (Tray 11) and ethanol feed tray itself. All the trays pressure is at 1 bar prior to introduction of ethanol. Ethanol is introduced into reactive distillation column at hour 1.0 for 0.5 hours. Pressure for all the trays dropped to 0.5 bars during that period of time except for top tray and condenser stage. This could be due to the impact of ethanol liquid on the "empty" reactive distillation column. It is supported Figure 55 where no liquid level is observed prior to ethanol is introduced. The pressure spiked to as high as 1.61 bars after 1.5 hours, when acetic acid is introduced into the reactive distillation column. It is believed to be a result of the exothermic reaction between acetic acid and ethanol. The fluctuation in pressure profile is observed from hour 1.5 to 2.5

and slowly stabilized by the third hour as the reaction approaches equilibrium condition. Pressure fluctuation is due to dynamics on the column trays during the initial phase of reaction more liquid is formed between tray 4 and tray 11 as shown in Figure 55 where reaction is expected to occur. The liquid level profile is retrieved from the ASPEN DYANMIC^{TM} simulator. This can be further explained through tray pressure drop formula as shown below.

$$\Delta P = 9.81 \times 10^{-3}(h_d + (h_w + h_{ow}) + h_r)\rho_L$$ **Equation 34**

One of the factors is liquid level on the tray, where the tray pressure drop is proportional to liquid level on the tray. Therefore, high pressure is observed when more liquid is present.

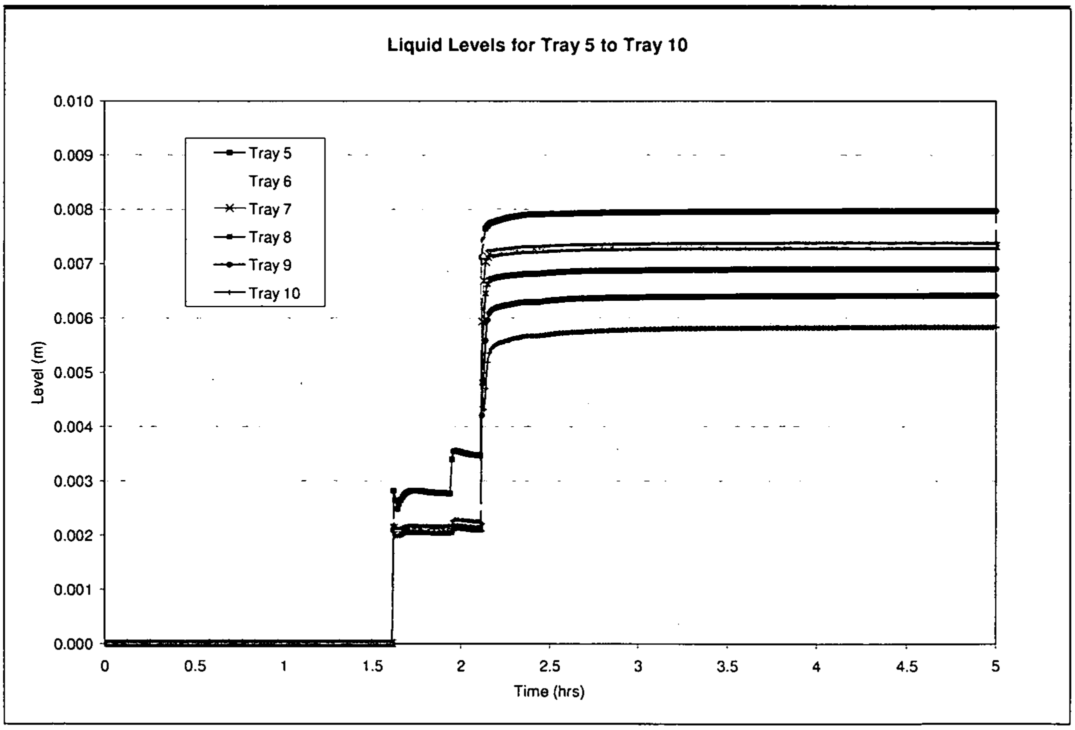


Figure 55: Liquid Level for Tray 5 to Tray 10 for Strategy 3

ii. Temperature Profiles

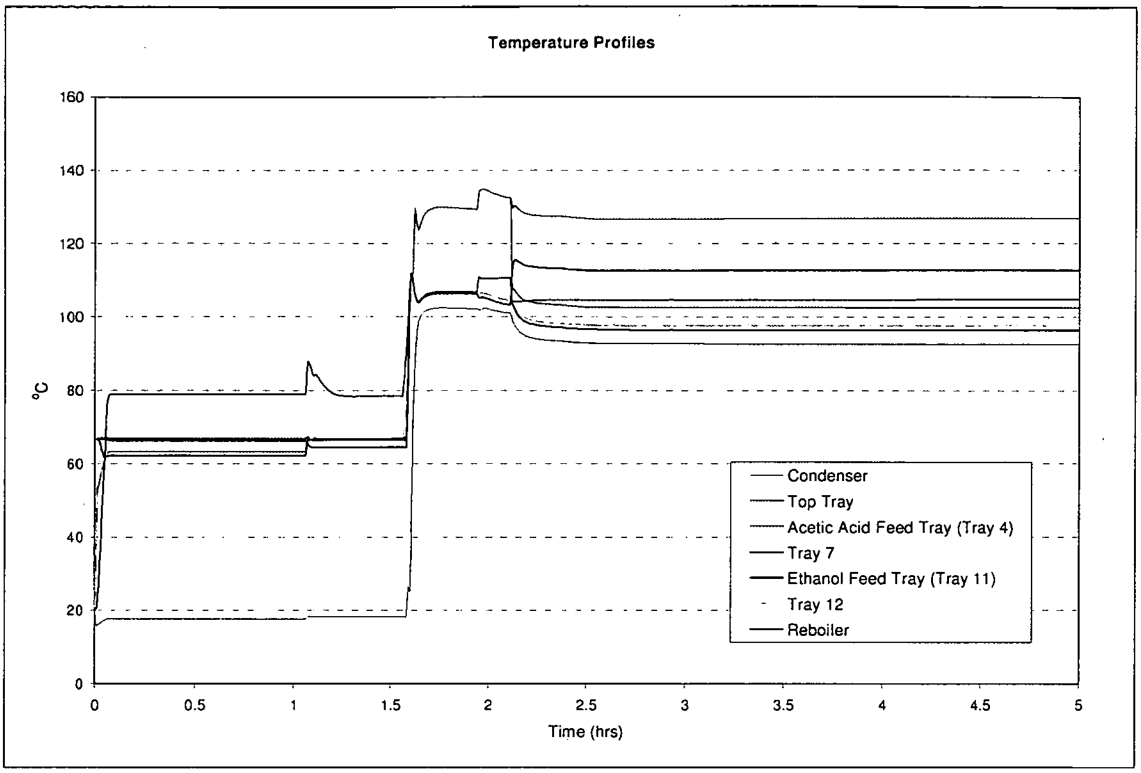


Figure 56: Temperature Profiles for Strategy 3

Figure 56 shows that the temperature profile in the reactive distillation column. As the reboiler is heated up at time 0, temperature of the lower trays increases accordingly. The higher tray i.e. "top tray", "condenser", "Tray 7" showed little effect as they are physically higher. This temperature profile maintained constant until acetic acid is introduced into the reactive distillation column at hour 1.5.

The temperature fluctuation from hour 1.5 to 2.0 is mainly due to the initial phases of the reaction. Exothermic reaction between acetic acid and ethanol takes place, thereby increasing the temperature to about 134°C. Calculated heat of formation of ethyl acetate and water is -18.08kJ/mol based on the reboiler heating temperature at 79°C.

Tray 7 temperature increases drastically at hour 2.1 and then stabilized. This shows that more products are being produced in Tray 7 at that time. This is in congruence with increase of ethyl acetate (product) concentration in this tray shown in Figure 57.

As the reaction reaches equilibrium by hour 3.0, the fluctuation dampens. Acetic acid tray still has the highest temperature due to exothermic reaction. The top most tray has slightly lower temperature as the reflux flow from condenser, which is cooler enters this stage.

The condenser stage has the lowest temperature as vapor product is being condensed to liquid and thereby rejecting heat.

iii. Ethyl Acetate Liquid Mole Fraction Profiles

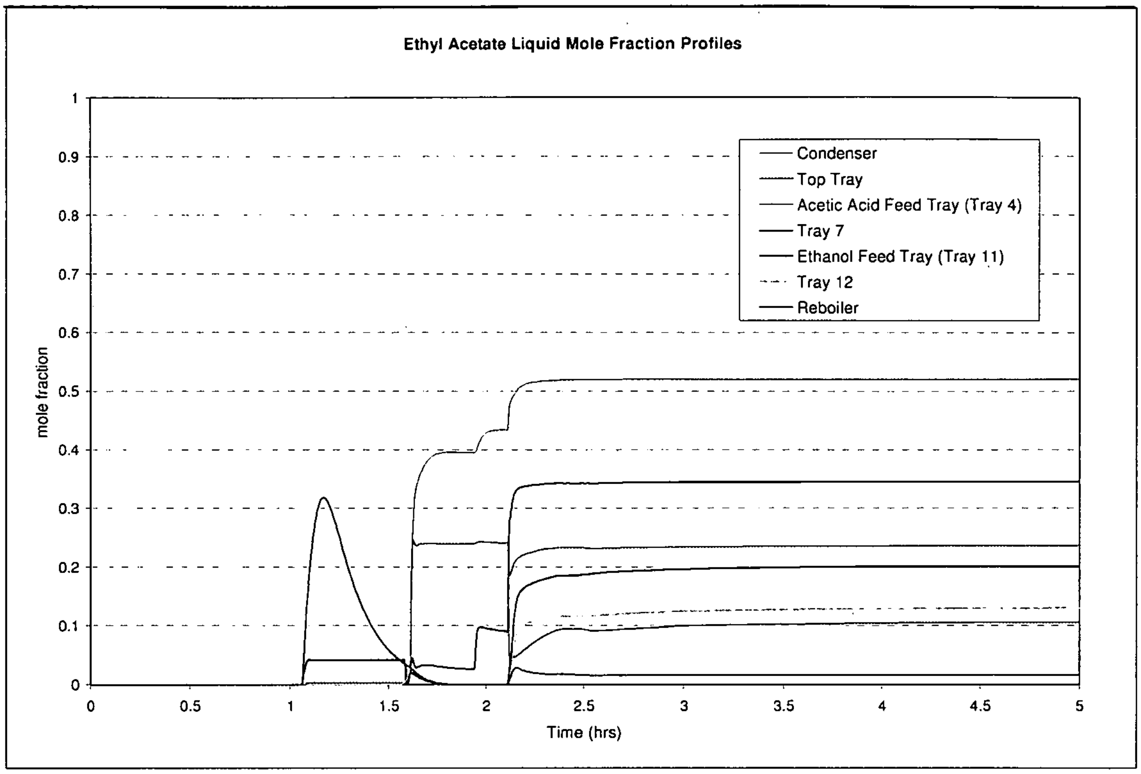


Figure 57: Ethyl Acetate Liquid Mole Fraction Profiles for Strategy 3

Ethanol and acetic acid can react to form ethyl acetic and water under normal conditions. In view of the presence of acetic acid alone whilst reboiler is heating up, there is no ethyl acetate is found in reactive distillation column. Ethyl acetate is only observed after ethanol is introduced into the reactive distillation column at hour 1.0.

While ethanol is fed into the column, the reaction starts (concentration of ethyl acetate increases) and ethyl acetate is mainly found at reboiler stage where this stage is filled up with acetic acid. Acetic acid is introduced at hour 1.5, hence ethyl acetate is formed at all trays at that period of time. Ethanol vapor travels upwards until it gets in contact with acetic acid which flows downward from its feed tray (Tray 4).

As the reaction proceeds pass hour 2.5, it is observed that higher concentration of ethyl acetate is found at Tray 7 compared to Tray 4. This shows that the reaction zone is more effectively located between the two reactants feed trays.

As this startup strategy adopts a total reflux approach, product (ethyl acetate and water) is being channeled back into the column from the condenser. When the liquid product flow reaches the lower trays by hour 2.5, some amount of ethyl acetate can be observed in these trays. As the column reaches steady state by hour 2.5, vapor and liquid flows in the column are stabilized hence resulting in constant concentration of products in all the stages. This is further supported by other observations i.e. pressure and temperature in this section of the discussion.

iv. Water Liquid Mole Fraction Profiles

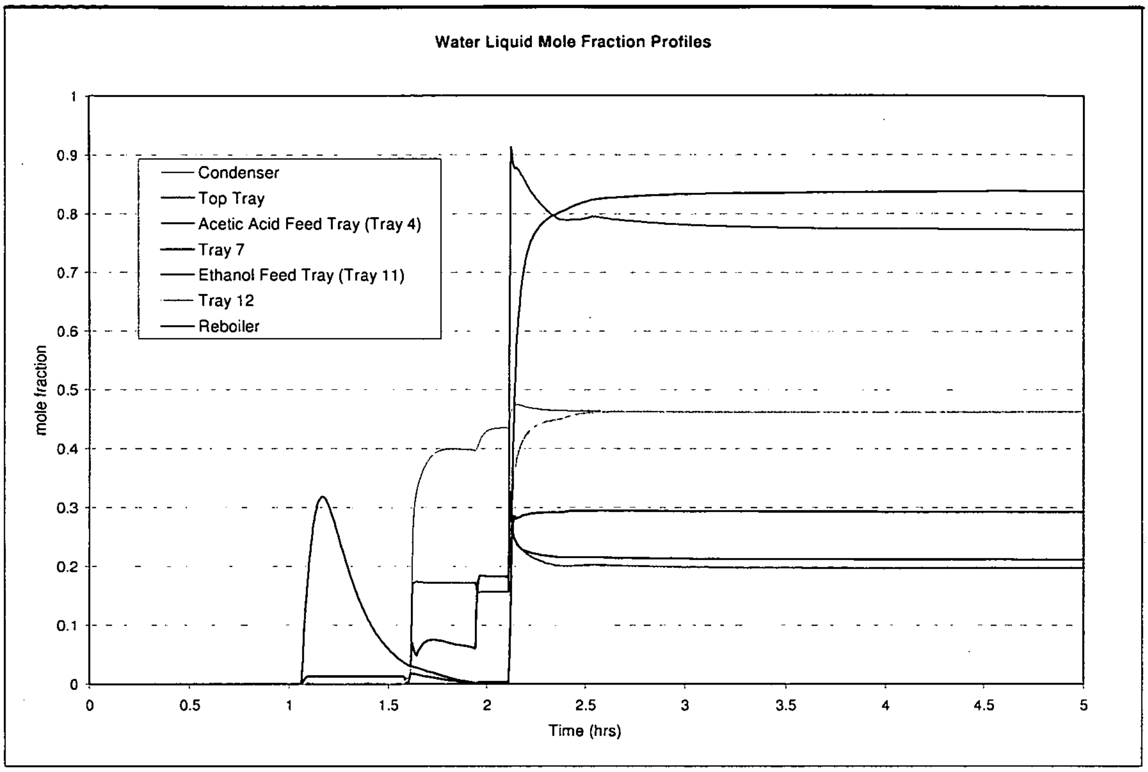


Figure 58: Water Liquid Mole Fraction Profiles for Strategy 3

Generally the trend of water concentration is similar to that of ethyl acetate as water is a by-product of the reaction between acetic acid and ethanol. High concentration of water is noted at lower trays because water has comparatively higher boiling point.

However, it is noticed that top tray has high water concentration as well. Cooling effect due to total reflux operations may have cooled down the water vapor component. Equilibrium is reached at about 2.5 hours, where water concentration is constant at all trays.

v. Acetic Acid Liquid Mole Fraction Profiles

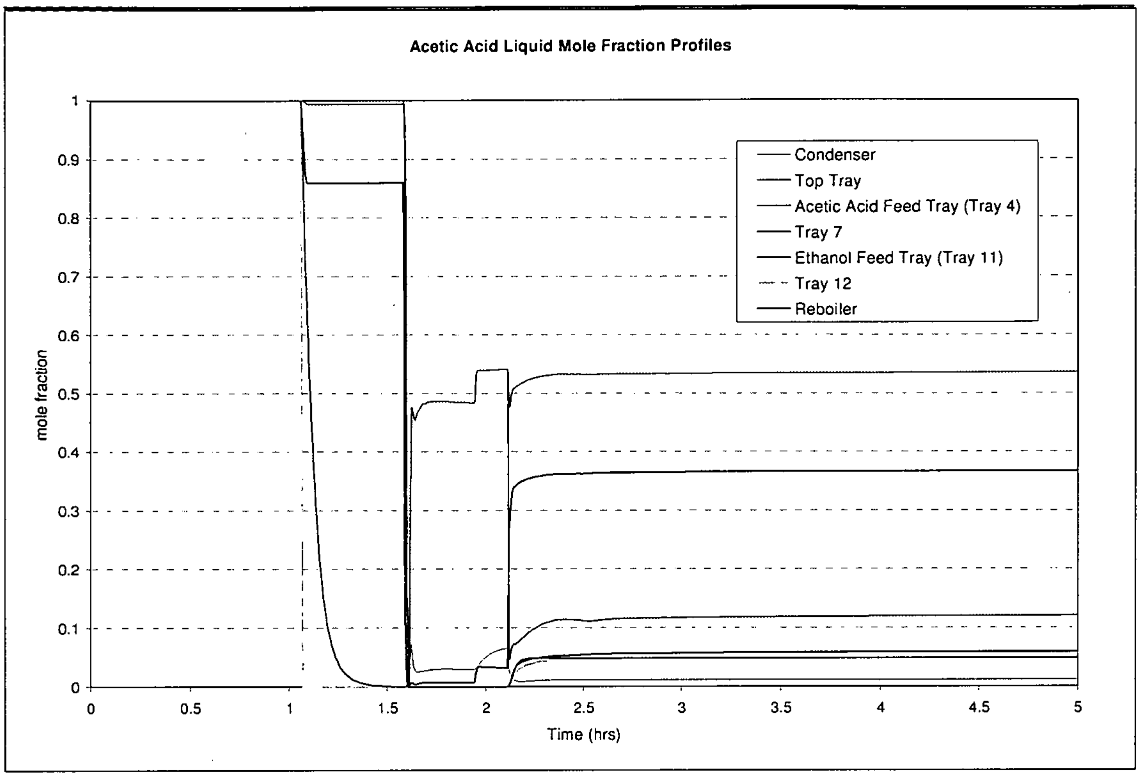


Figure 59: Acetic Acid Liquid Mole Fraction Profiles for Strategy 3

For Strategy 3, acetic acid is the only reactant presented at reboiler stage, therefore, during startup, there is only acetic acid in reboiler stage. Ethanol is introduced at hour 1.0 after reactive distillation column start-up. High acetic acid concentration is observed after feed in at all trays. It is believed that the acetic acid could be brought to tray above reboiler stage by means of entrainment in ethanol vapor. This is supported by the reduction of acetic acid at reboiler stage.

Concentration of acetic acid reduces significantly as reaction takes place when acetic acid is introduced in reactive distillation column at hour 1.5. This trend is in agreement with the ethyl acetate concentration illustrated in Figure 57. The mole fraction of acetic acid is displaced by the ethyl acetate concentration.

As the reaction reaches equilibrium, there will be constant amount of unreacted acetic acid. This is confirmed by presence of a constant amount of this feed at Tray 4 and 7. Small amount of acetic acid is observed to be present in all stages of the column. Acetic acid flows to the bottom tray with the reflux and liquid flow while some amount can be entrained to upper trays by rising vapor of the distillation process.

vi. Ethanol Liquid Mole Fraction Profiles

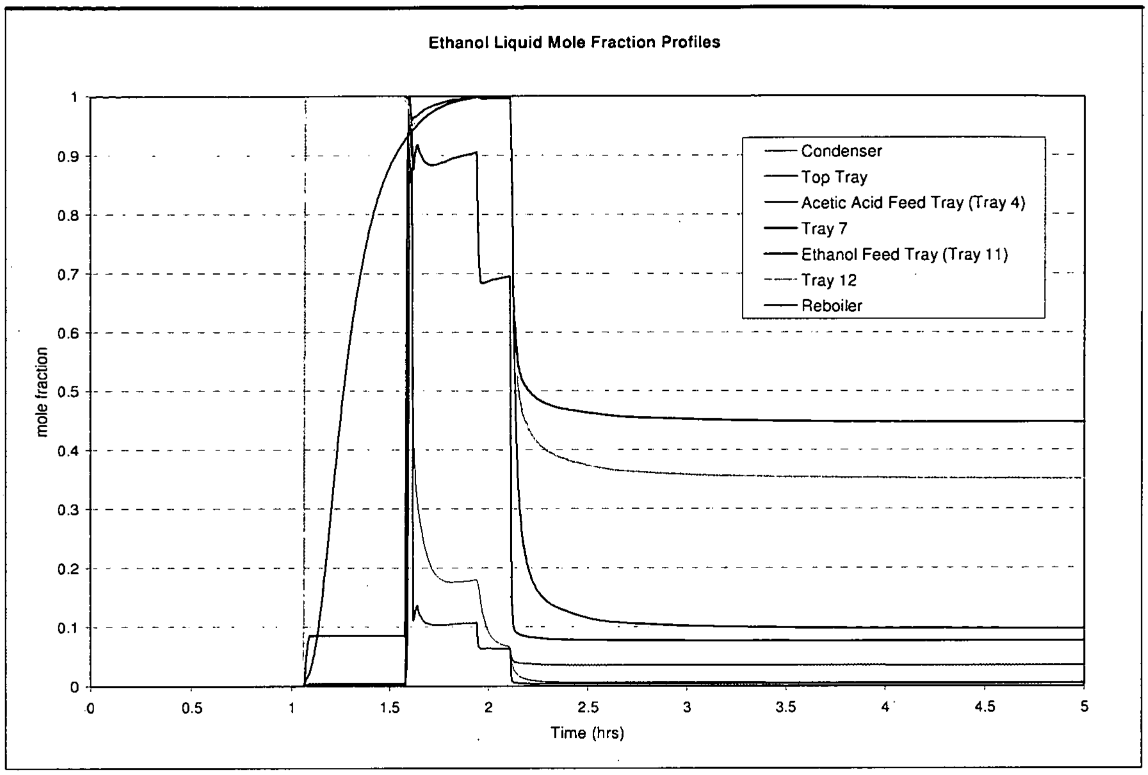


Figure 60: Ethanol Liquid Mole Fraction Profiles for Strategy 3

Ethanol is introduced into the reactive distillation column at hour 1.0, therefore, ethanol is found in the distillation column after hour 1.0. Tray 11 and Tray 12 have the highest ethanol concentration at about hour 1.0 because ethanol is fed in at Tray 11. As acetic acid is introduced at hour 1.5, the ethanol composition dropped because of aggressive forward reaction occurring.

Ethanol concentration at reboiler stage is in the increasing trend from hour 1.0 to hour 2.0 and dropped to a constant level after 2.5 hours. It is believed that ethanol liquid flows downwards to reboiler stage from ethanol feed tray (Tray 11) when ethanol is feeding in and started to form products after contacting with acetic acid.

When the reaction reached equilibrium, it is noticed that most of the ethanol component is found at the bottom trays, which is very close to the ethanol feed tray (Tray 11). It could be due to the reaction between acetic acid feed tray and ethanol tray has restricted the ethanol from flowing upwards. The similar phenomenon is noted for acetic acid component as most of the acetic acid presented at top trays instead of bottoms trays.

h) Strategy 1 Start-up after Optimization

From previous section Strategy 1 is selected as the strategy to be optimized in the study. Strategy 1 is optimized in order to reduce the start-up timing and dampen the fluctuation of pressure and temperature.

There are several attempts carried out in order to achieve the optimization. Pressure, temperature and each component profiles are looked into and compared. The appropriate steps that resulted in the least pressure fluctuation and the fastest in reaching steady state are adapted.

Based on the outcome of Strategy 1, it is noticed that maintaining reboiler temperature at 79°C for 1hour is not required in view of the constant profiles obtained in all the parameters. Hence, it is proposed to reduce from 1hour to 0.5hours. In order to speed up the reactants evaporation rate, the reboiler heating temperature is increased from 79°C to 90°C. It is not advisable to go beyond 90°C because one of the products i.e. water has a boiling temperature of 100°C.

Based on the comparison carried out for the three different strategies in section c, it is clearly shown that strategy 3 has the less pressure and temperature fluctuation. Therefore, start up sequence for strategy 3 is adapted for strategy 1 improvement. The difference observed for strategy 3 is ethanol is fed into the column followed by acetic acid. The same sequence is adapted for strategy 1 optimization, where acetic acid is fed 0.1hours after ethanol. Top product is extracted when reboiler level reaches 0.3m instead of 0.7m in the initial start up procedure. This is able to reduce the start up time required.

The best performance is observed using the following steps.

- Step 1: Fill up the reboiler with equal mole of ethanol and acetic acid.
- Step 2: Heat up the reboiler to reach 90°C in 0.05hrs, maintain for 0.5hrs before feed in reactants.
- Step 3: Feed in ethanol and maintain for 0.1hours at 30kg/hr feed rate.
- Step 4: Feed in acetic acid at 30kg/hr feed rate.
- Step 5: Extract the top product when condenser pot level reaches 0.3m.

The column reaches steady state running for approximately 1 hour later after extracting the top product.

i. Top Stream

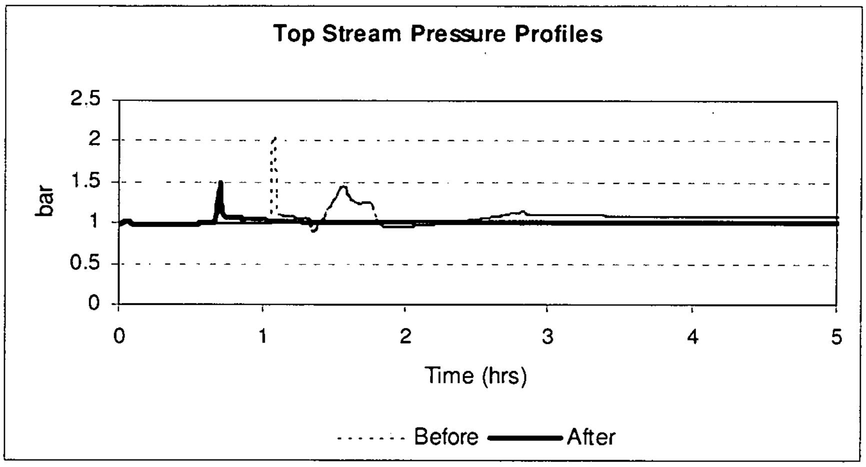


Figure 61: Top Stream Pressure Profiles Before and After Optimization

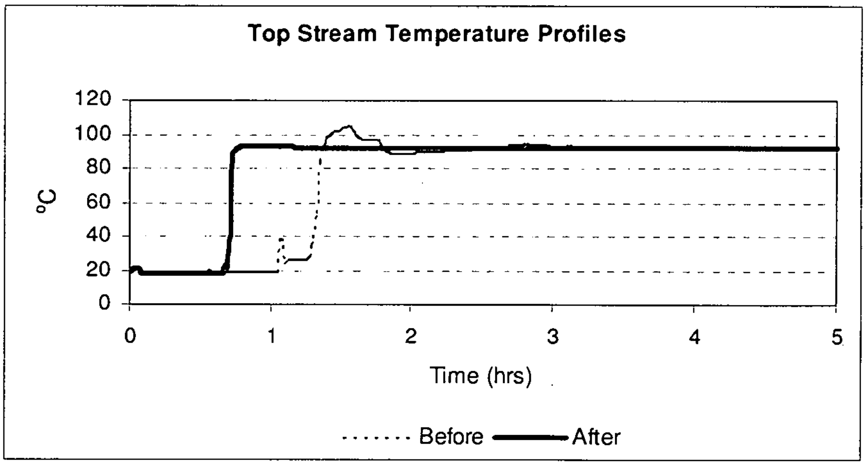


Figure 62: Top Stream Temperature Profiles Before and After Optimization

In view of reduction of 0.5hours in maintaining reboiler temperature, both pressure and temperature profiles are shifted 0.5hours to the front. Therefore, pressure spike is observed at 0.5hours. A more stable pressure and temperature profile are obtained after optimization. Pressure spike due to reaction is dampened from 2bar to 1.5bar with the optimized strategy. Both pressure and temperature achieved stead state profiles at time 1.5 for optimized strategy.

Less pressure and temperature fluctuation could be due to more stable liquid level available at trays as shown in Figure 63 during products formation as compared with initial Strategy 1. Reasons being are reboiler heating temperature is increased to 90°C and most of ethanol component evaporated. More liquid could have been extracted from the reactive distillation column, where top stream is extracted 0.72 hours as compared to 1.60 hours for Strategy 1.

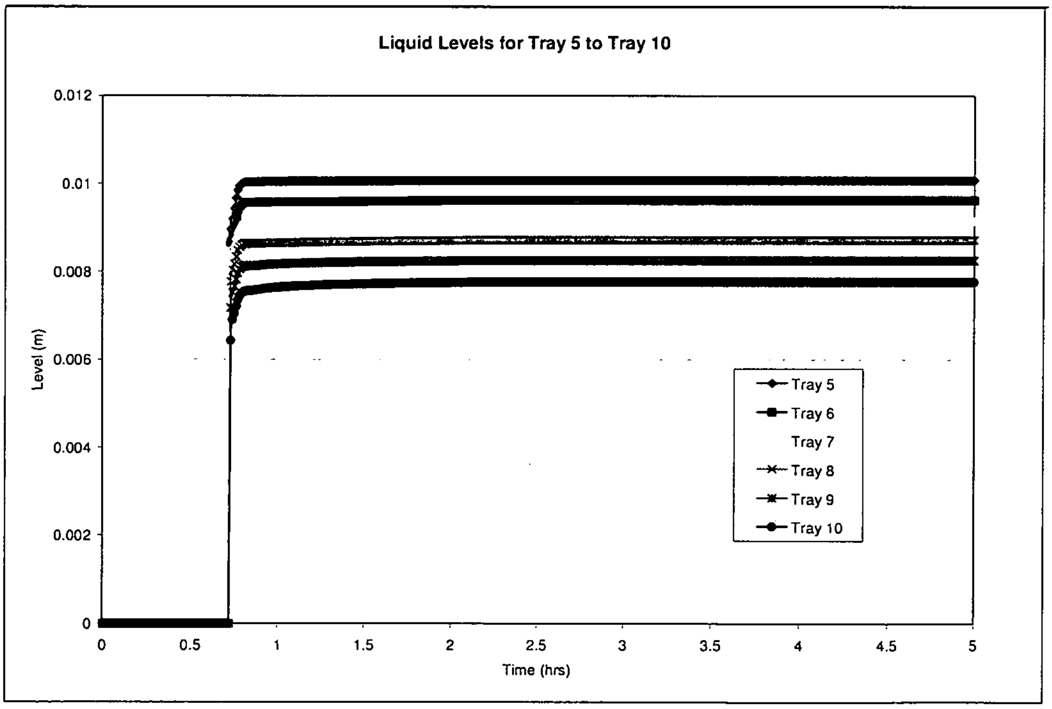
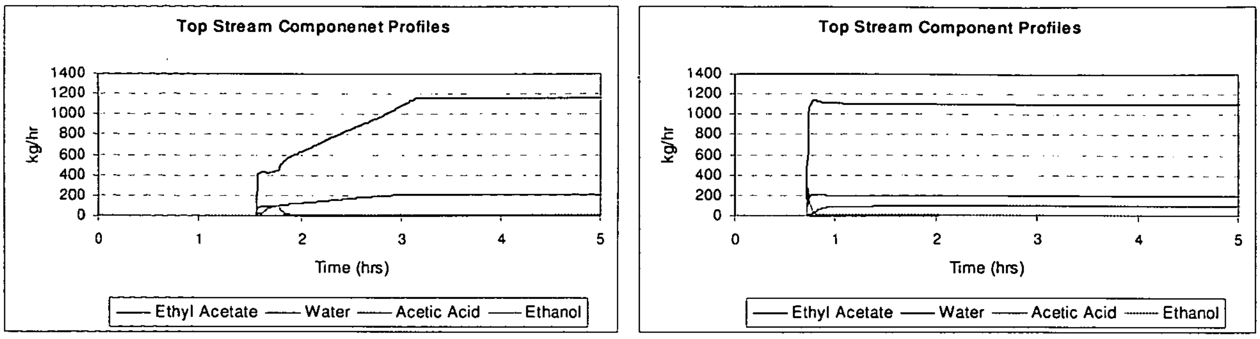


Figure 63: Liquid Level for Tray 5 to Tray 10 for Optimized Strategy



Before Optimization After Optimization

Figure 64: Top Stream Component Profiles Before and After Optimization

Ethyl acetate for top stream reached steady state within 1.0 hour for optimized strategy as compared with original Strategy 1 that required 3.0 hours. However, the total ethyl acetate produced for optimized strategy is slightly lower (1164kg/hr vs. 1106kg/hr). This could be due to lower retention time for reaction to take place when the reboiler level is reduced from 0.7m to 0.3m before top stream is extracted.

Acetic acid is found at top stream for optimized strategy. This could be due to the closer location to acetic acid feed tray and acetic acid is "brought up" by high ethanol evaporation rate in view of higher initial reboiler heating temperature.

ii. Tray 7

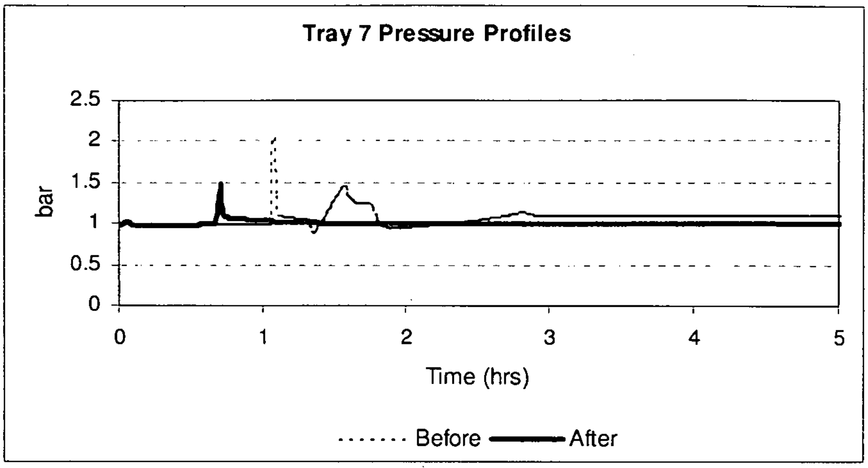


Figure 65: Tray 7 Pressure Profiles Before and After Optimization

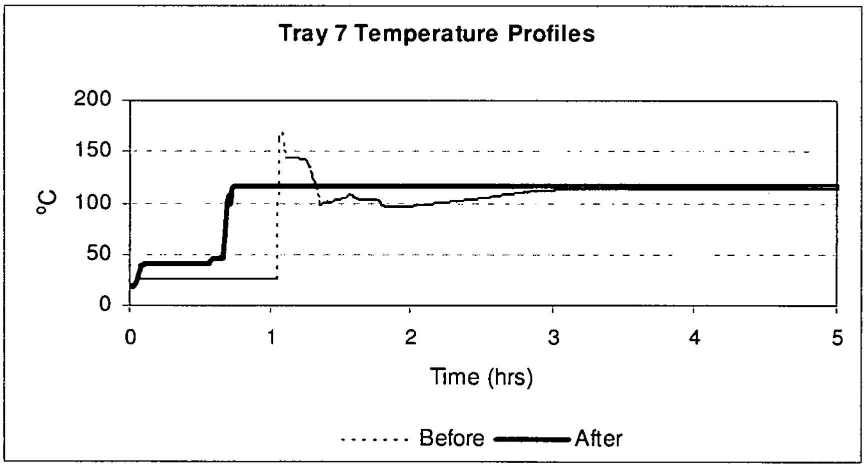
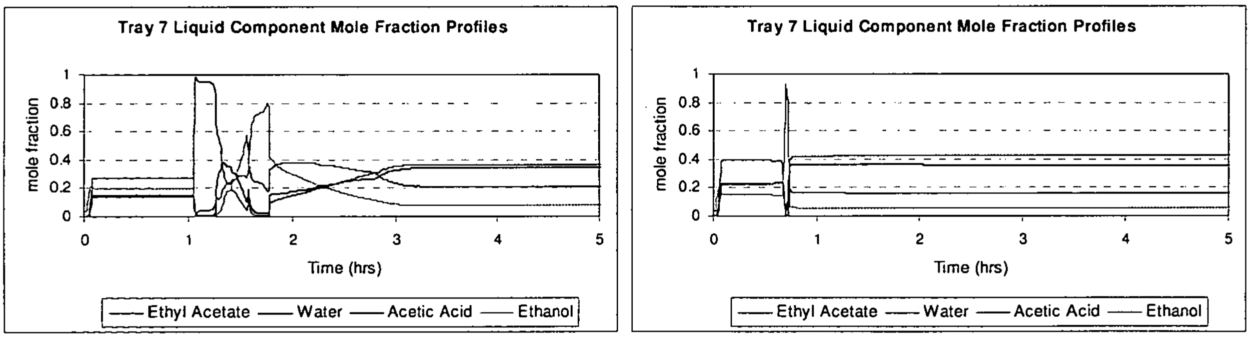


Figure 66: Tray 7 Temperature Profiles Before and After Optimization

In view of all the trays in the column have the same profile for pressure and temperature after optimization, Tray 7 that is located in between acetic acid feed tray and ethanol feed tray is selected for this optimized strategy discussion.

As shown in the pressure and temperature profiles above, the pressure fluctuation and temperature fluctuation have improved and the maximum pressure amplitude has reduced from 2bar to 1.5bar. The pressure spike is caused by the reaction between acetic acid and ethanol. Similar to top stream explanation, pressure is dampened by less liquid level formed at each tray due to higher reboiler heating temperature and more liquid have been removed from top stream.

The temperature profile for optimized strategy is more stable as compared with initial Strategy 1. This could be contributed by less pressure fluctuation. Both temperature increased from reboiler heating temperature after reactants are introduced, where reaction between ethanol and acetic acid take place. Reduction of 0.5hours for reboiler heating period has brought both the pressure and temperature profiles forward by 0.5hours. This is part of optimization effort to reduce the start-up time. Steady state is achieved for both temperature and pressure at approximately hour 1.



Before Optimization

After Optimization

Figure 67: Tray 7 Liquid Component Profiles Before and After Optimization

In general, all the components concentration reached the same concentration for both Strategy 1 and optimized strategy during steady state. The major differences for both strategies are the time taken to reach steady state and initial component profiles prior to steady state. It is noticed that optimized strategy has more stable component profiles during start-up and took shorter time to achieve steady state.

For initial Strategy 1, reaction is trying to reach equilibrium state from hour 1.0 to 2.0, while optimized strategy reaction fluctuation is less than 0.5 hours. As shown in Figure 67, the reaction fluctuation for optimized strategy only observed from hour 0.60 to 0.80. The time taken for optimized strategy to reach steady state is 2 hours lesser than strategy 1 (1 hour vs. 3 hours).

In optimized strategy, ethanol is fed into the column prior to acetic acid, thus, ethanol concentration is high when feeding into the column as compared with initial Strategy 1 where acetic acid is fed prior to ethanol. Less water fluctuation observed in optimized strategy could be due to more stable temperature profile, thereby, water component evaporated and condensed in trays is more stable. Similar to top stream acetic acid observation, more acetic acid is found at Tray 7 for optimized strategy. This can be attributed to the fact that closer location of Tray 7 to acetic acid feed tray and acetic acid liquid with high density will tend to flow downwards in the reactive distillation column.

6.0 CONCLUSION

The present work has successfully replicated the reactive distillation model in steady state simulation, ASPEN PLUS^{TM} and dynamic state simulation, ASPEN DYNAMIC^{TM}. The model can be used to study the steady state process performance and operability issues in parallel. The model is replicated for ethyl acetate production using acetic acid and ethanol feeds.

Without requiring additional program such as FOTRAN^{TM} in ASPEN PLUS^{TM}, the second reaction rate is derived into Power Law Coefficient format. The derived reaction rate is validated using t-test and correlation coefficient. The calculated t_0 is 8.24E-08 (between acceptable ranges) and correlation coefficient is 1.00. The model with the derived second reaction rate is validated with laboratory results (82 stages reactive distillation column) and simulated results (13 stages reactive distillation column) obtained from journals and the results are found to be satisfactory. The parameters validated for 82 stages reactive distillation column are temperature and each component (ethyl acetate, water, ethanol and acetic acid) profiles. The parameters validated for 13 stages reactive distillation column are each component and product flow rate for top stream and bottom stream as well as the ethanol conversion and top stream ethyl acetate purity.

The RGA method is used for choosing the best paring in selected manipulated variables and controlled variables by using the model in ASPEN PLUS^{TM}. The best pairing from the selected configurations is reboiler duty to control top ethyl acetate composition and bottom rate to control bottom water composition. The tuning of the controllers is carried out in ASPEN DYNAMIC^{TM} using Ziegler Nichols method. However, the best controller pair determined by RGA performed erratically when they are put into dynamic simulation. The situation is addressed by choosing a controller pair that is located physically nearer as compared to the pair determined by RGA method.

Three different start-up strategies are studied using ASPEN DYNAMIC^{TM} and the results are compared. The best strategy obtained is Strategy 1 where reboiler is filled with acetic acid and ethanol during start-up. This strategy is further optimized by adapting reactants introduction sequence from another strategy, i.e. Strategy 3. The outcome of the optimized strategy showed that less pressure and temperature fluctuation and shorter time taken to achieve steady state.

7.0 RECOMMENDATIONS

This research focused on modeling a reactive distillation column in ASPEN PLUS^{TM} platform. The replicated model is exported to ASPEN DYNAMIC^{TM}. The best pairing for selected manipulated variables and controlled variables is determined. Column start-up condition is studied. The steady state performance and operability issues are analyzed.

The following are the recommendations for future development:

i. To build a scaled up pilot plant using the results obtained from the model replicated in order to be one step closer to commercial plant development.

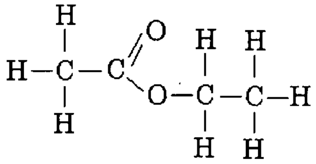
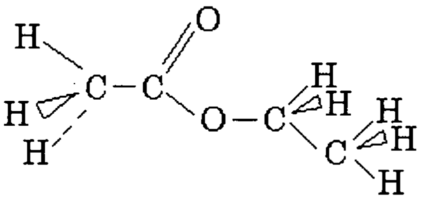
ii. To further study the effect of catalyst, temperature and pH changes for ethyl acetate reactive distillation column.

iii. To develop a model predictive control (MPC), which is already widely used in the process industries. MPC for the model is able to predict the constraints for any input and provide an optimal solution for the controller on line.

iv. To conduct the similar study using other type of reactions if ASPEN PLUS^{TM} and ASPEN DYNAMIC^{TM} simulators are available. One type of reactions is Ethyl-Tert-Butyl-Ether (ETBE), which is a high-performance fuel additive. By having the model, the performance of the distillation column can be observed and predicted in order to study the yield of ETBE and further optimization.

8.0 APPENDICES

Appendix A: Typical Ethyl Acetate Properties

Properties	
Appearance	*Clear, Colorless*
Odor	*Like pineapple*
Melting Point	*-84°C*
Boiling point	*77°C*
Solubility	*Freely soluble in alcohol and acetone.* *Moderate soluble in water (9g/100mL)*
Vapor Density	*3.0 (air=1.0)*
Vapor Pressure	*76 mmHg at 20°C* *100 mmHg at 27°C*
Flash Point	*-4°C*
Relative Density at 27°C	*0.895 – 0.898*
Auto ignition Temperature	*427°C*
Structure Formula	$C_4H_8O_2$ 
3-D Structure	

Appendix B: Some Typical Reactive Distillation Processes (Okur and Bayramoglu, 2001).

Reactants	Products
Adipic acid + hexamethylenediamine	Salt
Butadiene + sulfur dioxide	Butadiene sulfone
Ethylene oxide + water	Ethylene glycol
Isobutene + methanol	Methyl tert-butyl ether
Isobutylene + ethanol	ETBE
Isobutylene + methanol	MTBE
Benzene + Xylene	Toluene
Acetic anhydride + water	Acetic acid
Acetic acid + ethanol	Ethyl acetate + water
Acetic acid + methanol	Methyl acetate + water
Acrylic acid + ethanol	Ethyl acrylate + water
Butanol + ethyl acetate	Ethanol + butyl acetate
Formic acid + ethanol	Ethyl formate + water
Meta-xylene + tert-butyl benzene	Tert-butylmeta-xylene + benzene
Meta-xylene + di-tert-butyl benzene	Ter-butyl benzene + ter-butyl meta-xylene
Meta-xylene + sodium para-xylene	Sodium meta-xylene + para-xylene
Ethylene oxide + water	Ethylene glycol + diethylebe glycol
Dimethyl teraphthalate + ethylene glycol	Diglycol teraphthalate + methanol

Appendix C: Normal Boiling Point of the Pure Component and Azeotropic Compositions.

Normal Boiling Point	Mol% of Composition			
	EtAc	EtOH	H_2O	AcOH
70.1	58.7	15.9	25.4	
70.6	69.0		31.0	
71.8	55.4	44.0		
77.1	100.0			
78.2		90.8	9.2	
78.4		100.0		
100.0			100.0	
117.9				100.0

Appendix D: The Trial and Error Tuning Method

The steps involved are summarized below:

i. Eliminate the integral and derivative action by setting τ_D to 0 and τ_I to as large a value as possible.

ii. Set K_c at a low value and put the controller on automatic.

iii. Increase the controller gain K_c by small increments until continuous cycling occurs after a small set point or load change. The term "continuous cycling" refers to a sustained oscillation with constant amplitude.

iv. Reduce K_c by a factor of 2.

v. Decrease τ_I in small increments (this increases integral control) until continuous cycling occurs again. Set τ_I to 3 times this value.

vi. Increase τ_D until continuous cycling occurs. Set τ_D equal to one third this value.

Appendix E: Cohen and Coon Controller Tuning Method

The steps involved are:

i. After the process reaches steady state, switch the controller to manual mode. Introduce a small step change in the controller output and record the transient, which is the process reaction curve,

ii. Figure 68.

iii. Draw a straight line tangent to the curve at the setpoint of inflection. The intersection of the tangent line with the time axis is the apparent transport lag (τ), the apparent first-order time constant (θ). The steady state gain, Kp is the ΔT/ΔP.

iv. The values of Kp, τ and θ are used for the controller setting in Appendix F.

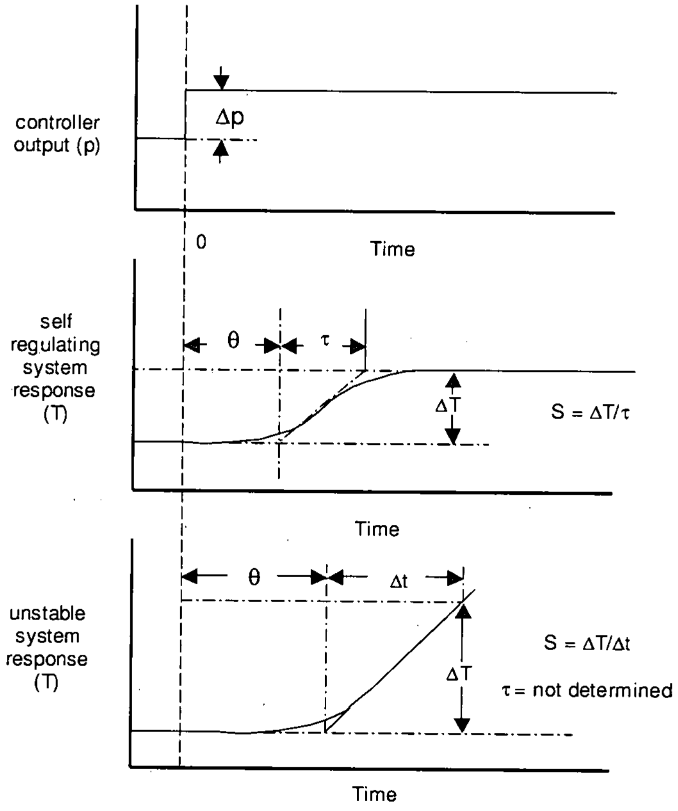
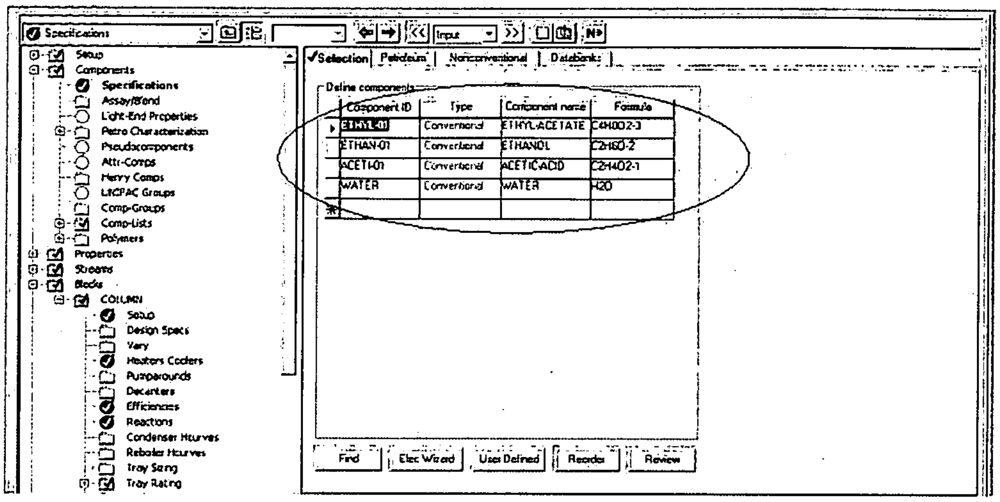


Figure 68: Process Reaction Curve

Appendix F: Cohen and Coon Controller Design Relations (Quantum, 2004)

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

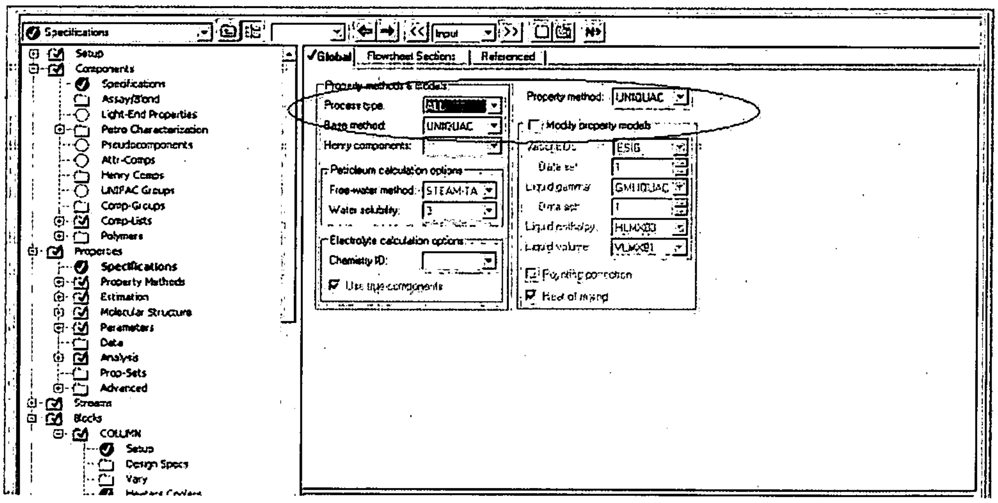
Appendix G: Print Screens of ASPEN PLUSTM Simulation (Section 4.2)



Define components

Component ID	Type	Component name	Formula
ETHYL-01	Conventional	ETHYL-ACETATE	C4H8O2-3
ETHAN-01	Conventional	ETHANOL	C2H6O-2
ACETI-01	Conventional	ACETIC-ACID	C2H4O2-1
WATER	Conventional	WATER	H2O

Figure 69: Selection of Reactants and Products



Property methods & models

Process type: ALL

Base method: UNIQUAC

Henry components:

Petroleum calculation options

Free-water method: STEAM-TA

Water solubility: 3

Electrolyte calculation options

Chemistry ID:

☑ Use true components

Property method: UNIQUAC

☐ Modify property models

Vapor EOS: ESIG

Data set: 1

Liquid gamma: GMUQUAC

Data set: 1

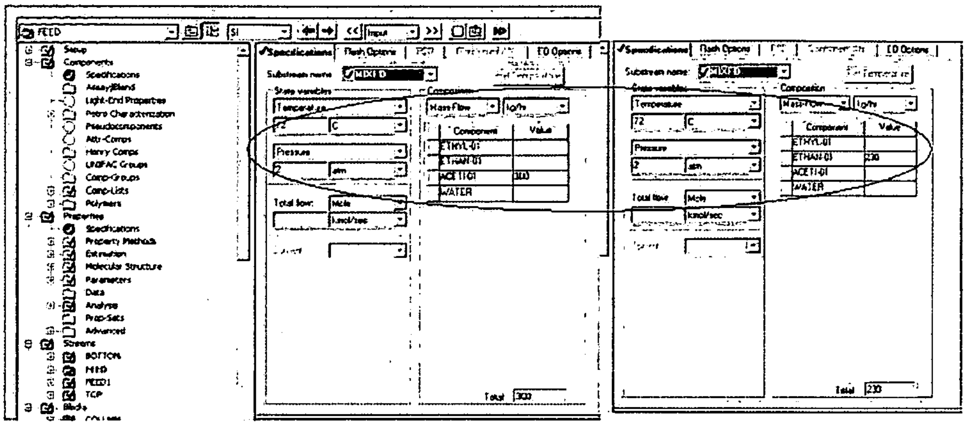
Liquid enthalpy: HLMX00

Liquid volume: VLMX01

☑ Poynting correction

☑ Heat of mixing

Figure 70: Selection of Property Package



Specifications

Substream name: MIXED

State variables

Temperature: 72 C

Pressure: 2 atm

Total flow: Mole kmol/sec

Composition: Mass-Flow kg/hr

Component	Value
ETHYL-01	
ETHAN-01	
ACETI-01	300
WATER	

Total 300

Specifications

Substream name: MIXED

State variables

Temperature: 72 C

Pressure: 2 atm

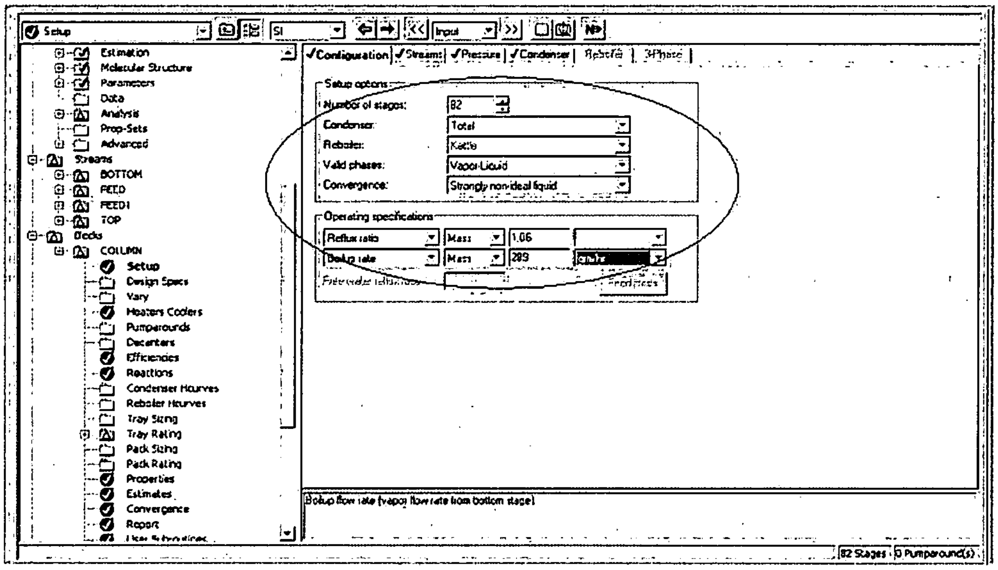
Total flow: Mole kmol/sec

Composition: Mass-Flow kg/hr

Component	Value
ETHYL-01	
ETHAN-01	230
ACETI-01	
WATER	

Total 230

Figure 71: Feed Streams Information



Configuration

Setup options

Number of stages: 82

Condenser: Total

Reboiler: Kettle

Valid phases: Vapor-Liquid

Convergence: Strongly non-ideal liquid

Operating specifications

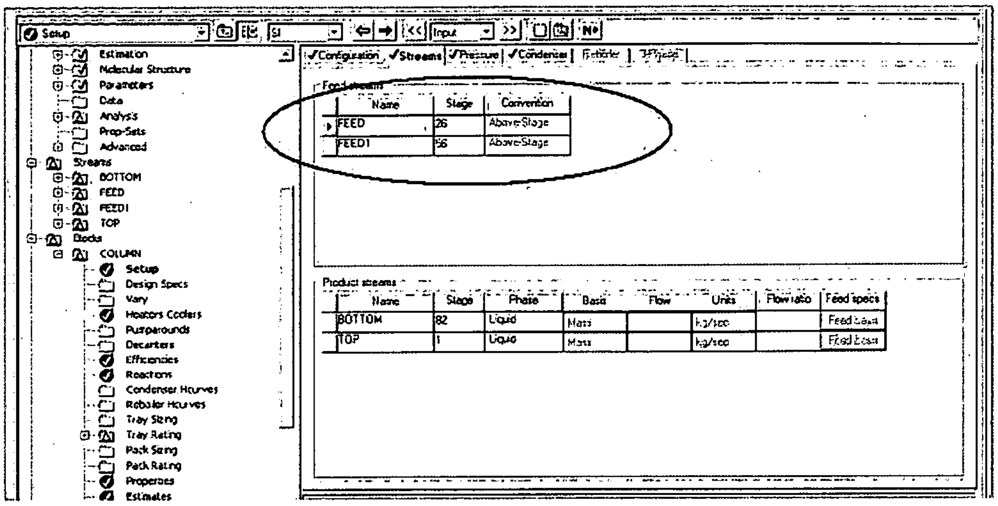
Reflux ratio: Mass 1.06

Boilup rate: Mass 289

Boilup flow rate (vapor flow rate from bottom stage)

82 Stages 0 Pumparound(s)

Figure 72: Column Configuration



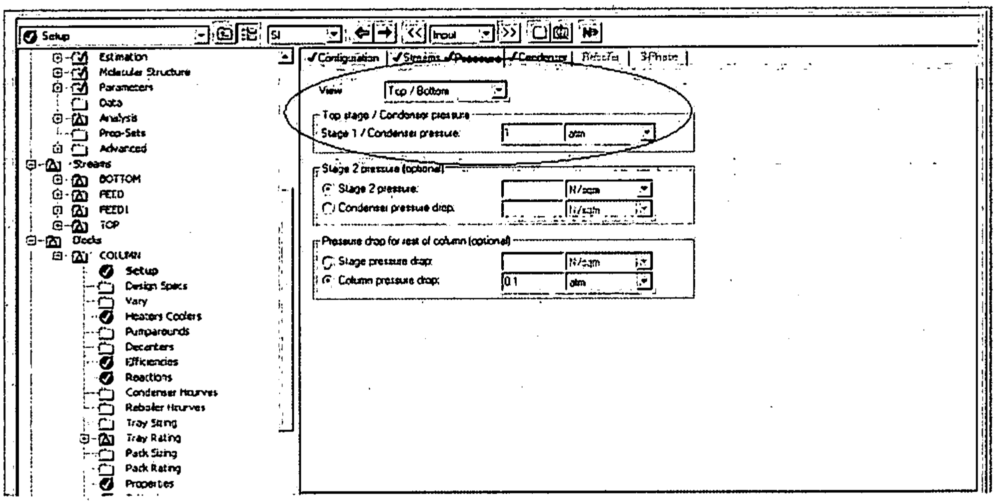
Feed streams

Name	Stage	Convention
FEED	26	Above-Stage
FEED1	56	Above-Stage

Product streams

Name	Stage	Phase	Basis	Flow	Units	Flow ratio	Feed specs
BOTTOM	82	Liquid	Mass		kg/sec		Feed basis
TOP	1	Liquid	Mass		kg/sec		Feed basis

Figure 73: Feeds Tray Information



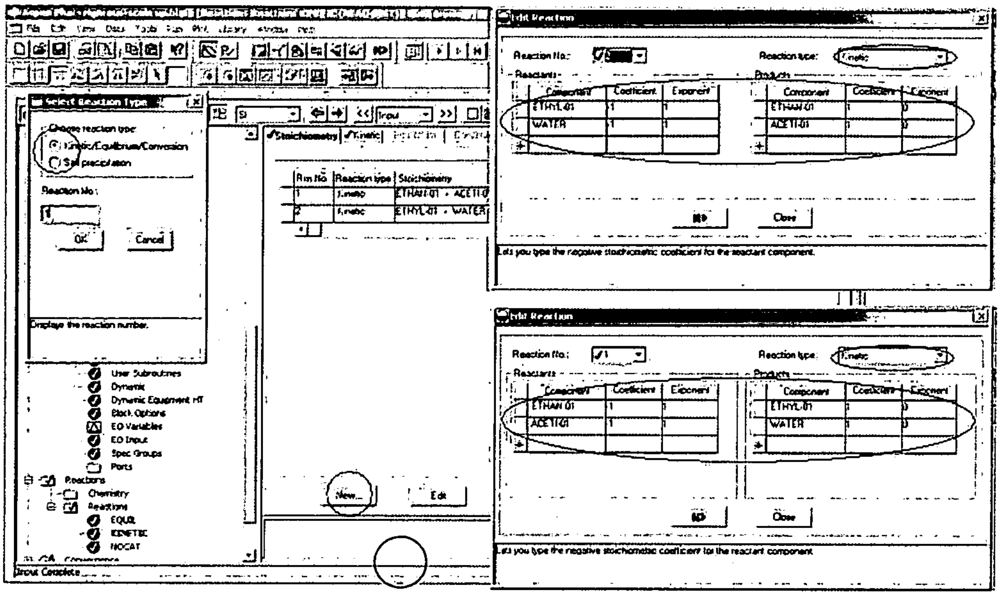
View: Top / Bottom

Top stage / Condenser pressure
Stage 1 / Condenser pressure: 1 atm

Stage 2 pressure (optional)
● Stage 2 pressure: N/sqm
○ Condenser pressure drop: N/sqm

Pressure drop for rest of column (optional)
○ Stage pressure drop: N/sqm
● Column pressure drop: 0.1 atm

Figure 74: Condenser Pressure Information



Select Reaction Type

Choose reaction type:
● Kinetic/Equilibrium/Conversion
○ Salt precipitation

Reaction No.: 1

Displays the reaction number.

Rxn No.	Reaction type	Stoichiometry
1	Kinetic	ETHAN-01 + ACETI-0
2	Kinetic	ETHYL-01 + WATER

Edit Reaction

Reaction No.: 2 Reaction type: Kinetic

Reactants

Component	Coefficient	Exponent
ETHYL-01	1	1
WATER	1	1

Products

Component	Coefficient	Exponent
ETHAN-01	1	0
ACETI-01	1	0

Lets you type the negative stoichiometric coefficient for the reactant component.

Edit Reaction

Reaction No.: 1 Reaction type: Kinetic

Reactants

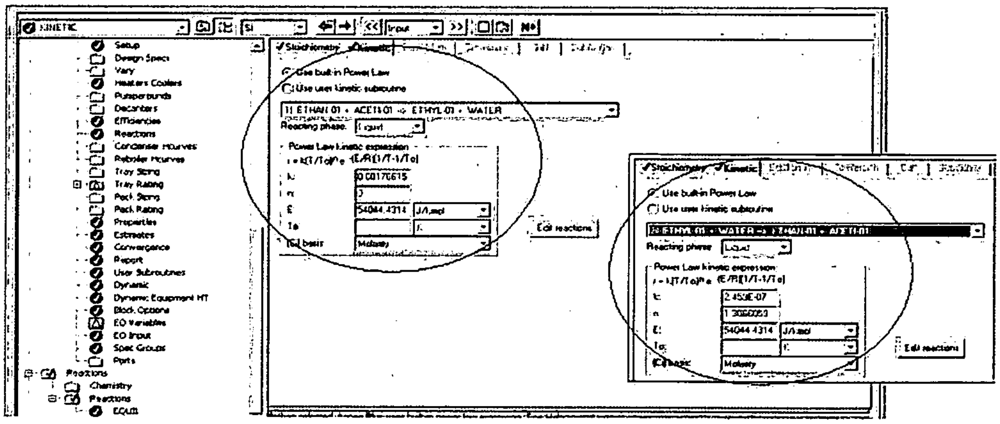
Component	Coefficient	Exponent
ETHAN-01	1	1
ACETI-01	1	1

Products

Component	Coefficient	Exponent
ETHYL-01	1	0
WATER	1	0

Lets you type the negative stoichiometric coefficient for the reactant component.

Figure 75: Kinetic Reactions Information



● Use built-in Power Law
○ Use user kinetic subroutine

1) ETHAN-01 + ACETI-01 --> ETHYL-01 + WATER

Reacting phase: Liquid

Power Law kinetic expression
r = k(T/To)^n e -(E/R)[1/T-1/To]

k: 0.00176615
n: 0
E: 54044.4314 J/kmol
To: K
[Ci] basis: Molarity

● Use built-in Power Law
○ Use user kinetic subroutine

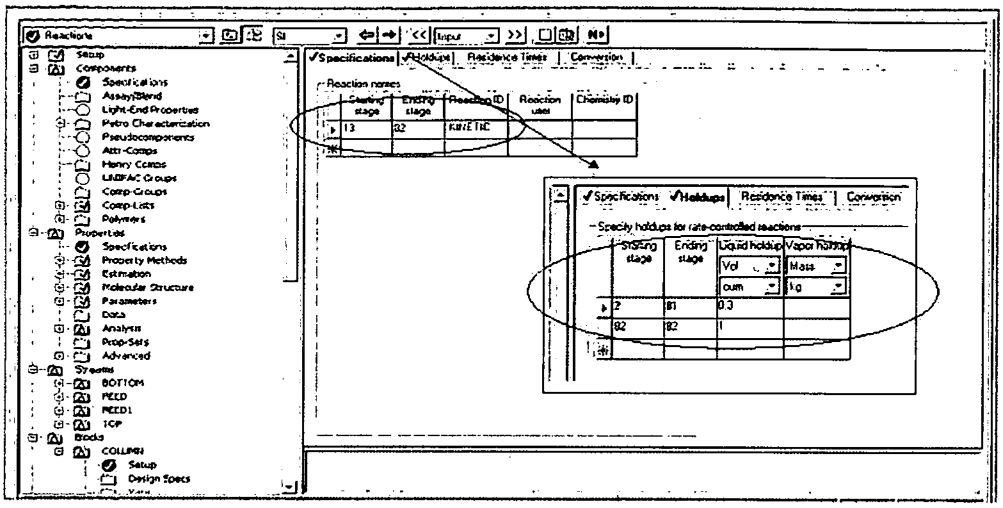
2) ETHYL-01 + WATER --> ETHAN-01 + ACETI-01

Reacting phase: Liquid

Power Law kinetic expression
r = k(T/To)^n e -(E/R)[1/T-1/To]

k: 2.453E-07
n: 1.3066053
E: 54044.4314 J/kmol
To: K
[Ci] basis: Molarity

Figure 76: Rate of Reaction Equation Information



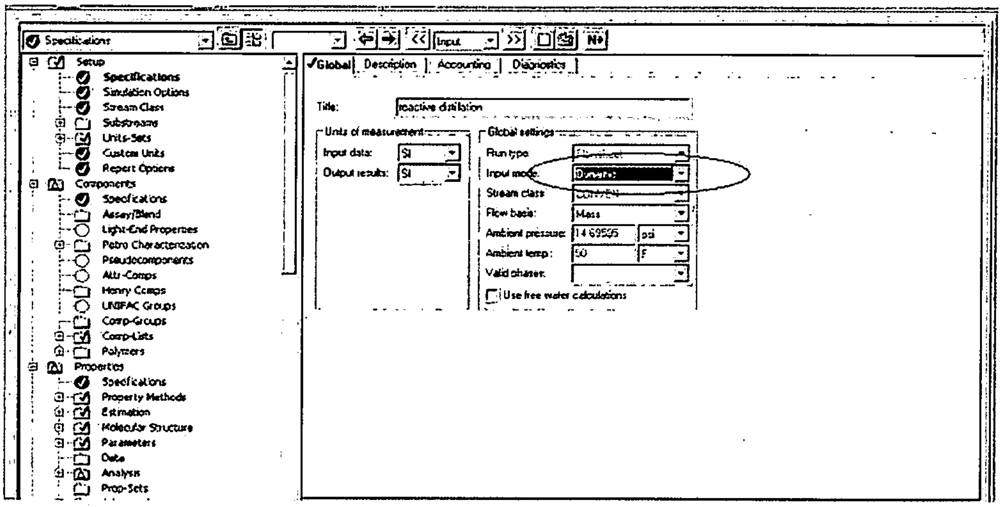
Reaction names

Starting stage	Ending stage	Reaction ID	Reaction user	Chemistry ID
13	82	KINETIC		

Specify holdups for rate-controlled reactions

Starting stage	Ending stage	Liquid holdup Vol cum	Vapor holdup Mass kg
2	81	0.3	
82	82	1	

Figure 77: Reaction Zone and Holdup Information

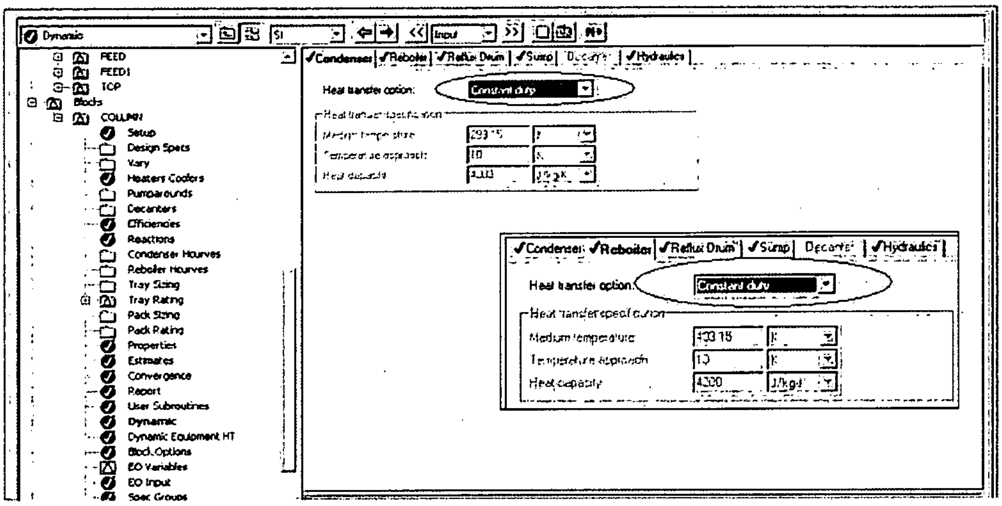


Title: reactive distillation

Units of measurement
Input data: SI
Output results: SI

Global settings
Run type: Flowsheet
Input mode: Dynamic
Stream class: CONVEN
Flow basis: Mass
Ambient pressure: 14.69595 psi
Ambient temp.: 50 F
Valid phases:
☐ Use free water calculations

Figure 78: Change the input mode



Condenser:

Heat transfer option: Constant duty

Heat transfer specification

Medium temperature: 293.15 K

Temperature approach: 10 K

Heat capacity: 4200 J/kg-K

Reboiler:

Heat transfer option: Constant duty

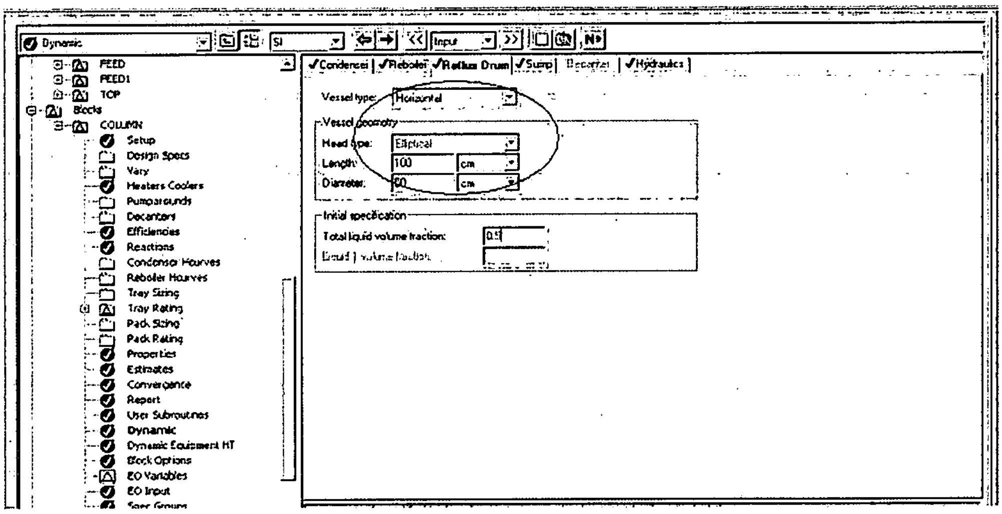
Heat transfer specification

Medium temperature: 433.15 K

Temperature approach: 10 K

Heat capacity: 4200 J/kg-K

Figure 79: Heat Transfer Option Information



Vessel type: Horizontal

Vessel geometry

Head type: Elliptical

Length: 100 cm

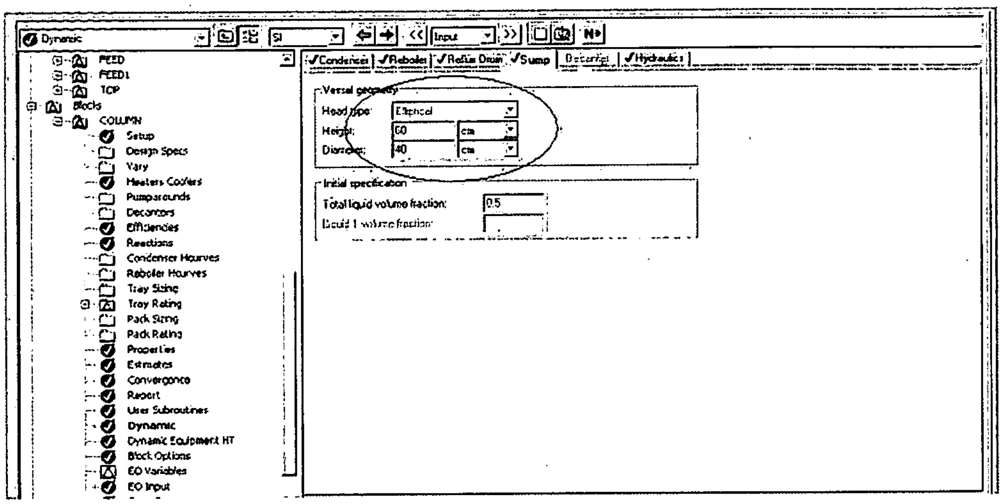
Diameter: 60 cm

Initial specification

Total liquid volume fraction: 0.5

Liquid 1 volume fraction:

Figure 80: Reflux Drum Information



Vessel geometry

Head type: Elliptical

Height: 60 cm

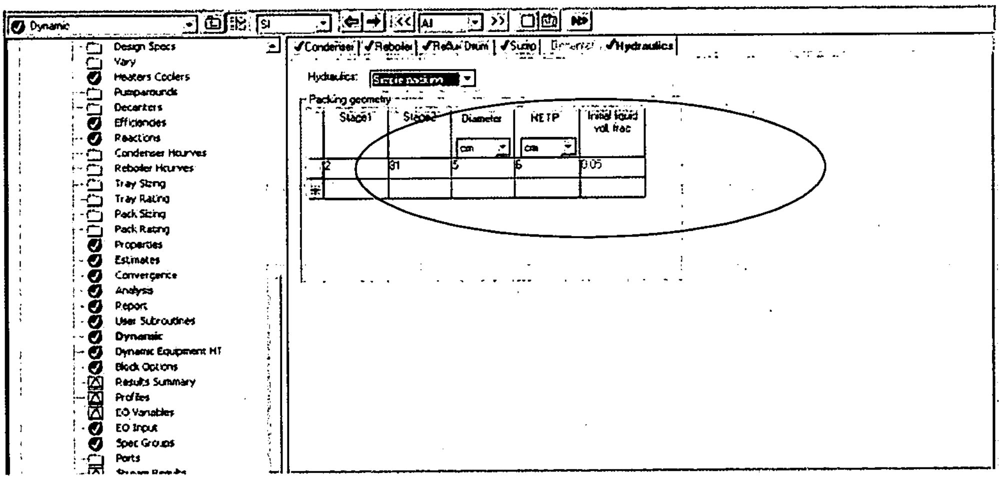
Diameter: 40 cm

Initial specification

Total liquid volume fraction: 0.5

Liquid 1 volume fraction:

Figure 81: Sump Information

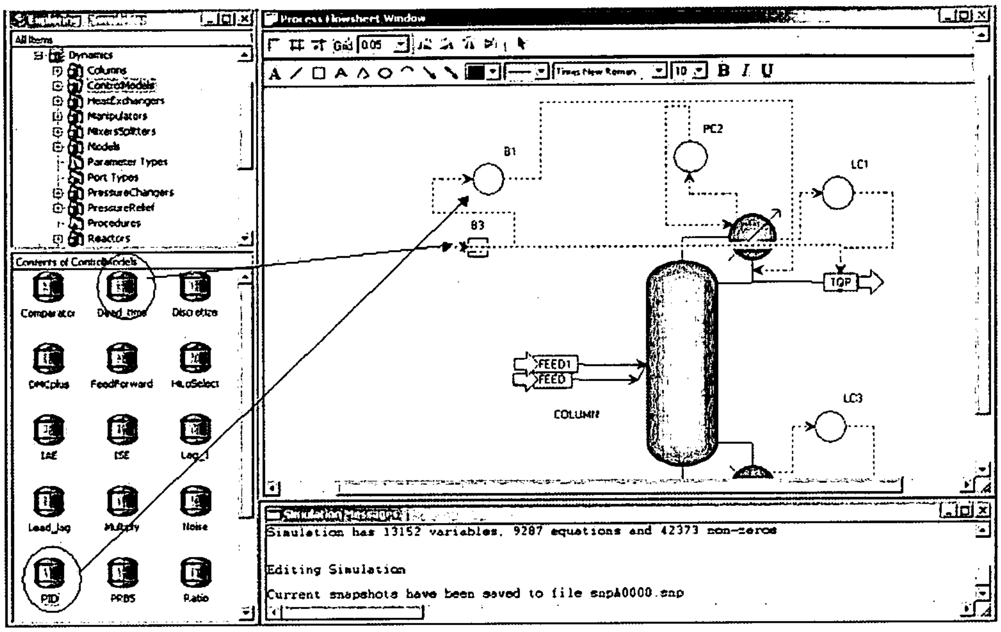


Hydraulics: Simple packing

Packing geometry

	Stage1	Stage2	Diameter cm	HETP cm	Initial liquid vol. frac
	2	31	5	6	0.05
*					

Figure 82: Hydraulic Information



```
Simulation has 13152 variables, 9287 equations and 42373 non-zeros

Editing Simulation

Current snapshots have been saved to file snpA0000.snp
```

Figure 83: Insert Dead Time and PID Controller

Appendix H: Simulation Data for RGA Calculation

Manipulated Variable (kg/hr)		Controlled Variable (kg/hr)	
		C1	**C2**
Initial Information			
M1	0.24	0.1771	0.03349
M2	78.27		
M3	0.30634		
M4	-102.98		
Set 1			
Constant M2	M1 + 0.1%	0.1771	0.03351
	M1 + 0.5%	0.1767	0.03358
	M1 + 1.0%	0.1762	0.03367
Constant M1	M2 + 0.1%	0.1773	0.03350
	M2 + 0.5%	0.1780	0.03355
	M2 + 1.0%	0.1787	0.03360
Set 2			
Constant M3	M1 + 0.1%	0.1770	0.03351
	M1 + 0.5%	0.1764	0.03356
	M1 + 1.0%	0.1755	0.03362
Constant M1	M3 + 0.1%	0.1773	0.03350
	M3 + 0.5%	0.1778	0.03353
	M3 + 1.0%	0.1783	0.03357
Set 3			
Constant M4	M1 + 0.1%	0.1771	0.03351
	M1 + 0.5%	0.1766	0.03358
	M1 + 1.0%	0.1761	0.03366
Constant M1	M4 + 0.1%	0.1774	0.03350
	M4 + 0.5%	0.1780	0.03355
	M4 + 1.0%	0.1789	0.03361
Set 4			
Constant M1	M1 + 0.1%	0.1773	0.03350
	M1 + 0.5%	0.1783	0.03357
	M1 + 1.0%	0.1829	0.03386
Constant M5	M4 + 0.1%	0.1769	0.03350
	M4 + 0.5%	0.1746	0.03355
	M4 + 1.0%	0.1641	0.03379

Appendix I: Tuning Results for Controllers

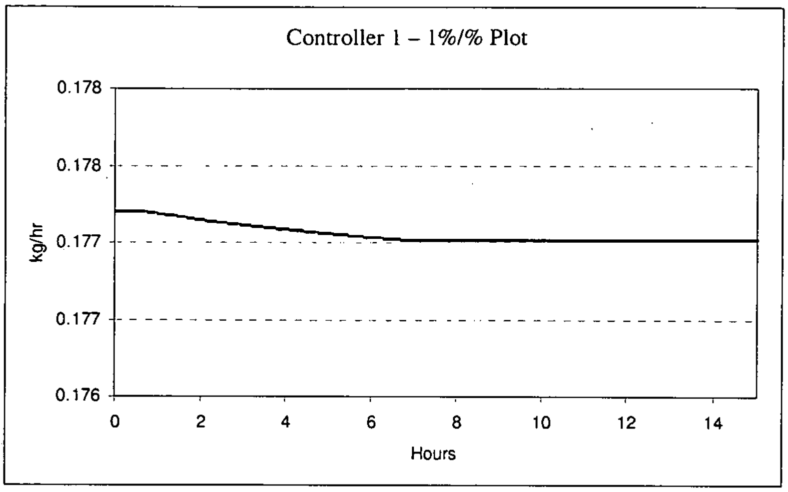


Figure 84: Oscillation Trend for Controller 1 with 1.00%/% Gain

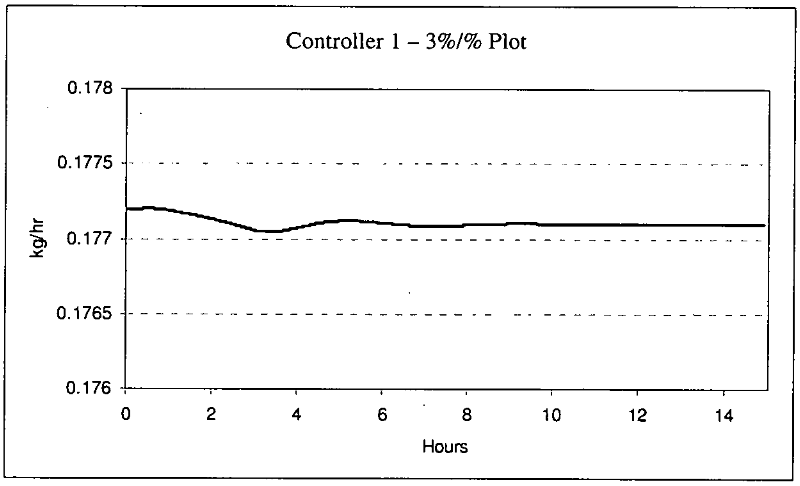


Figure 85: Oscillation Trend for Controller 1 with 3.00%/% gain

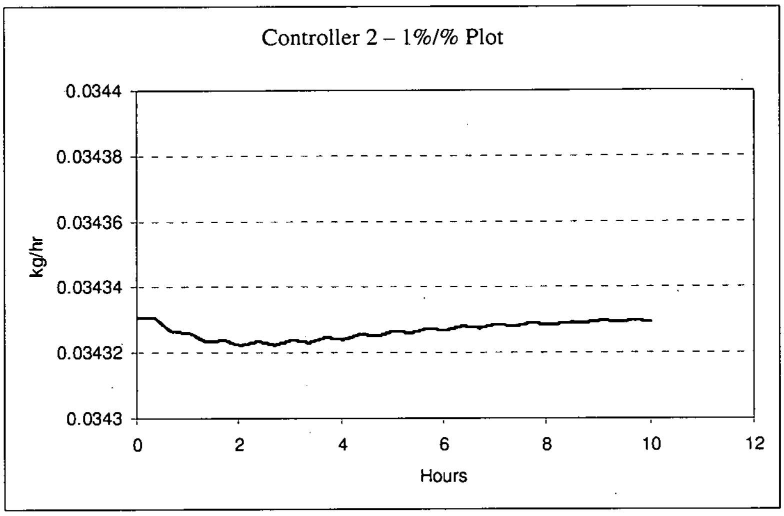


Figure 86: Oscillation Trend for Controller 2 with 1.00%/% gain

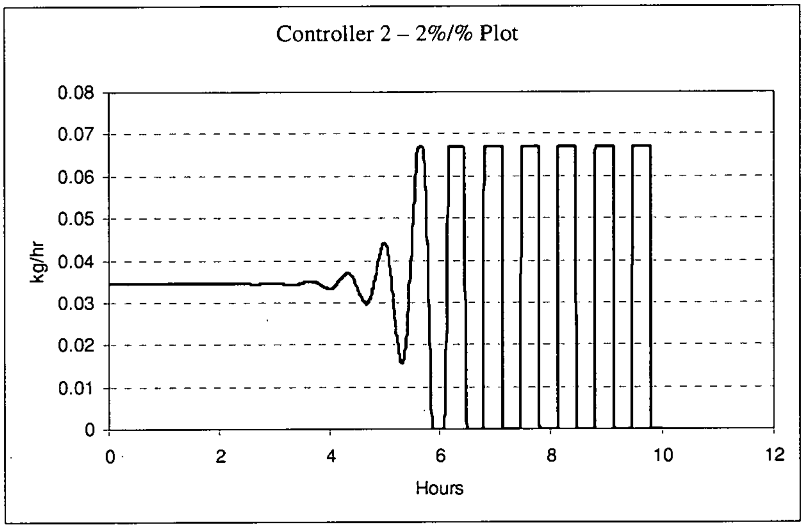


Figure 87: Oscillation Trend for Controller 2 with 2.00%/% gain

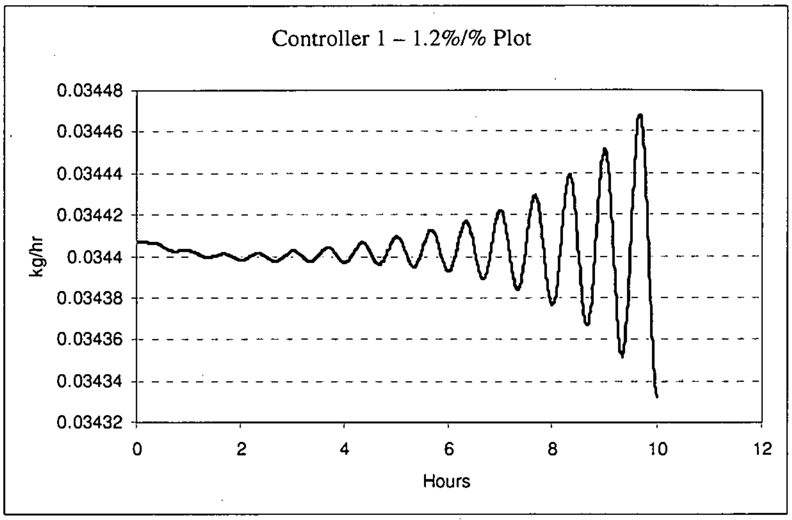


Figure 88: Oscillation Trend for Controller 2 with 1.2%/% gain

Appendix J: Fine Tuning of Dynamic Simulation Runs

Run No.	Feeding time, hrs	Condensate Level, m	Steady State after Running for
1	0.04	0.005	Error
2	0.05	0.005	3 hours
3	0.2	0.005	8 hours
4	0.5	0.005	9 hours
5	0.05	0.01	No stable after 6 hours
6	0.05	0.001	3 hours

i. Feeding time of 0.05hrs is selected because of the faster timing taken to reach steady state.

ii. Condensate level of 0.005m is selected based on the following reasons:
   a. The same timing taken to reach steady state as compared to lower condensate level (0.001m).
   b. Middle point between 0.01m and 0.001m.
   c. It is more practical from measurement point of view.

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