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Modeling and Simulation of Ethyl Acetate Reactive Distillation Column

By

Vjaya Kumar Murgan

A THESIS
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ABSTRACT

Reactive distillation (RD) is an attractive way of improving process economics by combining distillation and reaction, especially for equilibrium limited reactions such as esterification. Two of the most studied esterification reactions via RD in the literature are methyl acetate synthesis and ethyl acetate synthesis. The ideal performance of the RD column would be to achieve almost complete conversion of both reactants while at the same time producing pure esters as distillate. From literature it was found that unlike other RD systems such as MTBE and ETBE, it is impossible to achieve ideal performance with normal double feed configuration, though the achieve conversion and purity of these systems are higher than the conventional method of reaction followed by separation. This is due to the formation of azeotropes between reaction products and reactant, which in turn hinders the achievement of complete conversion and producing pure esters as distillate.

Researchers had successfully exploit the mixture properties of methyl acetate system and device a RD configuration known as reactive-extractive distillation (RED) column that ultimately overcomes the azeotropic conditions in a single column and hence able to achieve ideal performance for this system. However, the conditions in ethyl acetate RD column do not allow us to exploit the mixture properties and furthermore the presence of four azeotropes as compared to two azeotropes in methyl acetate system complicates the separation process in ethyl acetate RD column.

Thus in this study attention were given to improve the ethyl acetate RD column performance. Initially, simulation model for esterification of acetic acid by ethanol in a RD column was developed and verified against equivalent experimental work and published simulation results. Upon confirming the applicability of the simulation model, the effects of changing various operating and design parameters on the column performance were studied in order to explore the possibility of improving the column performance. Through this analysis it is evident that the column performance could not be enhanced significantly due to formation of azeotropes between reaction products and reactant for nearly equal product split at both end of the column.

Finally a new configuration that involves the introduction of extractive zones below ethanol feed point and above acetic acid feed point with extraneous component as an extractive agent in the system in order to break one of the azeotropes between product and reactant, thus allowing the attainment of higher conversion and purity was proposed. With this configuration the column performance was significantly improved.

ABSTRAK

Penyulingan bertindakbalas berperingkat merupakan suatu penyelesaian atraktif untuk meningkatkan ekonomi process dengan menggabungkan penyuligan and tindak balas kimia dalam satu unit operasi, terutamanya bagi tindak balas kimia yang mempunyai keseimbangan terhad seperti untuk penghasilan ester. Tindak balas ester yang di beri tumpuan menerusi penyulingan bertindak balas ialah penghasilan metil acetat dan etil acetat. Performasi ideal turus penyulingan bertindak balas adalah untuk mencapai penukaran sepenuh bahan mentah tindak balas dan penghasilan produk yang mempunyai kepekatan tinggi. Dari hasil kajian lain, di dapati tidak seperti turus penyuling seperti MTBE dan ETBE, adalah sukar untuk mencapai performasi ideal dengan menggunakan konfugarsi normal, walaupun penukaran bahan mentah dan kepekatan produk adalah tinggi berbanding dengan cara penghasilan konvensi iaitu tindak balas kimia di ikuti penyulingan berperingkat. Ini adalah di sebabkan formasi "azeotropes" di antara produk dan bahan mentah tindak balas yang akhirnya menghalang pencapaian penukaran sepenuhnya dan penhasilan pruduk dengan kepekatan tinngi.

Para pengkaji telah berjaya mengeksplotasi ciri-ciri campuran system metil acetat dan menghasilkan konfigurasi turus penyulingan tindak balas berperingkat yang di kenali sebagai turus penyulingan bertindak balas dan ekstrak yang mampu mengatasi keadaan "azeotrope" dan seterusnya dapat mencapai performasi ideal. Walau bagaimanapun, ciri – ciri campuran system etil acetat tidak mengizinkan kerana kehadiran empat "azeotropes" berbanding dua "azeotropes" dalam system etil acetat menyukarkan proses penyulingan dalam turus penyulingan bertindak bals berperingkat.

Dengan itu dalam kajian ini keutamaan di berikan untuk memajukan performasi penyulingan tindak balas berperingkat etil acetat. Langkah pertama ialah dengan membangunkan modal simulasi untul proses esterifikasi acetic asid dengan etanol dalam turus penyulingan bertindak balas berperingkat dan di bandingkan dengan kerja eksperimen dan keputusan – keputusan simulasi yang standingnya. Selepas memastikan kebolehgunaan modal simulasi yang di bangunkan, kesan penukaran parameter – parameter proses and design terhadap perfromasi turus di lakukan untuk mengkaji samada perfomasi turus dapat di tingkatkan. Melalui analisis, adalah terbukti bahawa adalah sukar untuk meningkatkan performasi turus secara mendadak kerana formasi "azeotropes" di antara produk tindak balas dan bahan mentah tindak balas menyekat peformasi turus.

Akhirnya, konfigurasi baru yang melibatkan pengenalan zon ekstraktasi di bawah suapan ethanol dan di atas suapan acetic asid dengan pengenalan komponen lain sebagai agen extraktasi untuk memecahkan "azeotropes", dan seterusnya membenarkan pencapaian penukaran dan kepekatan tinggi di cadangkan. Dengan konfigurasi ini, performasi turus penyulingan bertindakbals berperingkat dapat di tingkatkan.

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Vjaya Kumar Murgan

To my beloved parents,
Murgan and Mariyayee
and my wife, Vani.
for their relentless support

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C	concentration of reactant/product	(mol/m^3)
r	rate of reaction	(mol/sec m^3)
C_k	Catalyst Concentration	(vol%)
T	Temperature	(K)
Kc	constant of reaction equilibrium	
k_1	forward reaction rate constant	(m^3/(mol sec))
k_2	reverse reaction rate constant	(m^3/(mol sec))
F_j	Feed flowrate into stage j	
V_{j+1}	Vapor flowrate from stage j+1	
V_{j-1}	Vapor flowrate from stage j-1	
V_j	Vapor flowrate from stage j	
V_1	Distillate flowrate	
V_N	Re-boiler vapor flowrate	
V_2	Vapor flowrate from column top	
L_j	Liquid flowrate from stage j	
L_{j-1}	Liquid flowrate from stage j-1	
L_{j+1}	Liquid flowrate from stage j+1	
L_1	Reflux flowrate	
L_2	Liquid flowrate from stage 2	
L_N	Bottom flowrate	
Q	Heat Lost from stage j	
hp_j	Liquid hold up on stage j	
$R_{j,I}$	number of moles generated or disappear through reaction for component i on stage j	
$x_{i,j}$,	mole fraction of component i in liquid flow L_j,	
$y_{i,j}$	mole fraction of component i in vapor flow V_j	
$z_{i,j}$	mole fraction of component i in feed flow F_j	
$v_{r,i}$	stoichiometric coefficient of component i for reaction r	

dhp_j/dt	Rate of total material (molar) change on stage j	(mol/min)
$dhp_{i,j,}/dt$	Rate of total material (molar) change of component i on stage j	(mol/min)
ΣR_{il}	net rate of change in the number of moles in the mixture due to participation in chemical reaction	
RR	Reflux Ratio	
S	Re-boil Ratio	
ρ_j	Molar density of the liquid phase on stage j	(mol/m^3)
M_j	volumetric holdup on stage j	(m^3)
H_T^R	total reactive liquid holdup in the column	(mol)
$k_{f,ref}$	reference forward rate constant for homogeneous pseudo-first order system	(s^{-1})
hpt	Total liquid phase hold up in the system	(mol)
ρ_r	Liquid phase molar density of the lowest boiling pure component in the system at reference temperature	(mol/m^3)
$H^L{}_j$	molar enthalpy of liquid phase on stage j	(cal/mol)
$H^v{}_j$	molar enthalpy of vapor phase on stage j	(cal mol)
$H_{z,j}$	molar enthalpy of feed introduced into stage j	(cal/mol)
Q_c	Condenser hear duty	(cal)
Q_R	Reboiler heat duty	(cal)
$h_{i,j}{}^o{}_v$	Vapor phase partial molar enthalpy of component i on stage j	(cal/mol)
c_{pv}	Vapor phase heat capacity at constant pressure	(cal/mol.K)
c1, c2, c3, c4	Heat capacity coefficients	
$\lambda_{i,j}$	heat of vaporization of component i on stage j	(cal/mol)
R	gas constant	(cal/mol.K)
B_i and C_i	Constants used in Antoine equations	
γ_i	Liquid phase activity coefficient of component i	
φ_i	Vapor phase fugacity coefficient of component i	
P	Total pressure of the system	(psia)
P_i^o	Saturated vapor pressure of component i	(psia)

$P_{c,i}$	Critical pressure of component i,	(psia)
v_{ki}	count of the *k*th group in component *I*	
R_k	Measure of Van der Waals volume ratio for group *k*	
Q_k	Measure of Van der Waals area ratio for group *k*	
V_{wk}	Van der Waals group volume	
A_{wk}	UNIFAC surface area	
Γ_k	Activity coefficient for group *k* in the mixture	
$\Gamma_{k,i}$	Activity coefficient for group *k* in pure component *i*	
F_R	Feed ratio	
X_i^s	stripping section transformed liquid composition variable of component *i*	
Y_i^s	stripping section transformed vapor composition variable of component *i*	
X_B^s	transformed bottoms composition	
h^s	stripping section continuous plate number	
s^*	modified reboil ratio for plate n	
c	number of components	
k	reference component	
X_i^r	rectifying section transformed liquid composition variable of component *i*	
Y_i^r	rectifying section transformed vapor composition variable of component *i*	
X_D^r	transformed distillate composition	
h^r	reactifying section continuous plate number	
r^*	modified reflux ratio for plate n	

List of Abbreviations

MEK	Methyl Ethyl Ketone
MIBK	Methyl Isobutyl Ketone
MTBE	Methyl Tertiary Butyl Ether
ETBE	Ethyl Tertiary Butyl Ether
TAME	Tertiary Amyl Methyl Ether
Ac	Acetic Acid
Et	Ethanol
Ea	Ethyl Acetate
W	Water
NEQ	Non Equilibrium Stage Model
MESH	material balance, vapor liquid equilibrium equations, mole fraction summations and heat balance
UNIQUAC	Universal Quasi-Chemical
UNIFAC	UNIQUAC Functional-Group Activity Coefficient
VLE	Vapor Liquid Equilibrium
CSTR	Continuous Stirred Tank Reactor
Da	Damkohler Number
DAE	Differential Algebraic Equations
RD	Reactive Distillation
RED	Reactive Extractive Distillation

CHAPTER 1

INTRODUCTION

Reactive distillation is a combination of reaction and separation in a single unit operation. It has captured the imagination of many researchers due to the demonstrated potential over the conventional method of processing. There are two major benefits of the reactive distillation operation. First, the in-situ removal of product from the reaction zone causes equilibrium-limited reactions to be shifted forward by LeChatelier's principle, thus allowing higher conversion. Second the improved selectivity due to removal of products from the reaction zone.

The advantage of reactive distillation method over conventional method of a reactor followed by a distillation column is best explained as follows:
Consider a reversible reaction scheme:

$$A + B \longleftrightarrow C + D$$

Where the volatility of the components follow the sequence A, C, D and B. To obtain the products of reaction, traditional method of processing involves a reactor followed by a sequence of distillation column (as shown in Figure 1.1(a)). The mixture of A and B is fed to the reactor, where the reaction takes place in the presence of catalyst and reaches equilibrium. A distillation train is required to separate products C and D. The unreacted components, A and B, are recycled back to the reactor. The separation process would be much more complex if one or more azetropes present in the mixture that leaves reactor.

The alternative configuration, reactive distillation is shown in Figure 1.1(b). It consists of reactive section in the middle with non-reactive rectifying and stripping sections at the top and bottom respectively. Liquid rich in A is fed to a stage between the top and middle section of the column. Vapor rich in B is fed to a stage between the middle and the bottom section of the column. In reactive section, reactant B is absorbed into the liquid phase where the reaction takes place with reactant A.

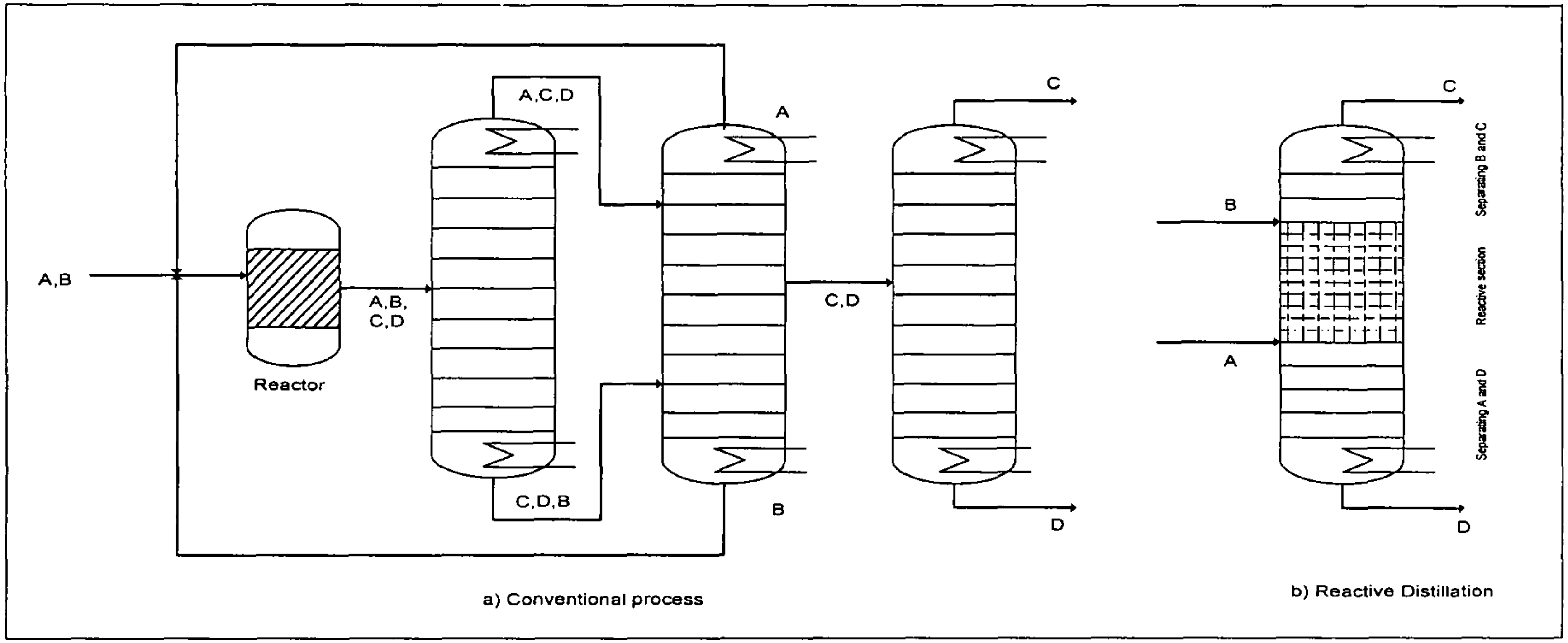

Figure 1.1: Processing schemes for a reaction sequence $A + B \leftrightarrow C + D$ where C and D are both desired products. (a) Typical configuration of a conventional process consisting of a reactor followed by a distillation train. (b) The reactive distillation configuration. The components A, C, D and B have increasing boiling points. Grid lines indicate the reactive sections. Adapted from Stichlmair and Frey (1999).

Products are separated in situ, driving the equilibrium to the right and preventing undesired side reactions between the reactants and the product. The task of rectifying section is to recover reactant A from the product stream C. In the stripping section, the reactant B is stripped from the product stream D. In a way, reactant A and B are recycled back to the reaction section.

For a properly designed reactive distillation column, virtually 100 % conversion can be achieved (Taylor and Krishna, 2000). There have been a number of systems that has met commercial success with reactive distillation technology such as synthesis of methyl acetate, methyl ethyl tertiary ether, ethyl tertiary butyl ether and ethylene glycol. For the systems mentioned nearly 100 % conversion of the reactant could be achieved in a single column. Since 1921, ethyl acetate system has been considered to be suitable for reactive distillation process and significant publications focusing on simulation, control, design and experimental work have been reported. However up to date there is no reported commercial application of reactive distillation technology for ethyl acetate system. It also should be noted that non-of the published results reported high conversion and purity of both reactants in a single column.

Apart from increased conversion and selectivity the following benefits could also be realized (Tuchlenski et. al.,2001; Taylor and Krishna, 2000) :

1. Simplification or elimination of the separation system that can lead to significant capital savings.
2. Significant reduction on catalyst requirement for the same degree conversion.
3. Reactive distillation can avoid the formation of azeotropes. The condition in the column could allow the azeotropes to be 'reacted away' in a single column.
4. Reduction in by-product formation by eliminating side reactions through instantaneous separation of products of reaction.
5. In the case of exothermic reaction, the heat of reaction can be utilized to provide heat of vaporization and reduce the re-boiler duty. Thus this provides heat integration benefits in reactive distillation process.

6. A simple and reliable temperature control can be achieved, since the maximum temperature in the reaction zone is limited to the boiling point of the reaction mixture. This avoids the formation of hot spot formation on the catalyst and the temperature control is relatively simple as compare to conventional reactor systems.

In order to apply reactive distillation technology in industrial scale, there are a number of constraints have to be fulfilled (Tuchlenski et. al.,2001; Taylor and Krishna, 2000):

1. The reagents and products must have suitable volatility to maintain high concentration of reactants and low concentrations of products in the reaction zone.
2. Chemical reaction has to take place entirely in the liquid phase, as wet catalysts pellets are available in liquid phase only.
3. Residence time for the reaction should not be too long. If the residence time too long, a large column size and large hold-ups will be needed. Thus it is more economic to use reactor-separator scheme.
4. Process condition for reaction and separation must be close in order to realize reactive distillation process. In some processes the optimum conditions of temperature and pressure for distillation may be far from optimal for reaction and vice versa.

In spite of the constraints, the advantages gained by utilizing reactive distillation have motivated a renewed interest in the use of it for the production of important chemicals (Agreda et al., 1990). Amount of publications and patents on this technology was reported to have increased rapidly since 1971 (Doherty, 2000). However, the interactions between the simultaneous reaction and distillation introduces a much more complex behavior compared to the use of conventional reactors and ordinary distillation columns, leading to challenging problems in the design, operation and control of reactive distillation column.

The selected system for reactive distillation process in this research is ethyl acetate synthesis. Ethyl acetate is an industrially important bulk chemical used primarily as a solvent in the paints, coating and inks industry. Consumption of ethyl acetate as an industrial solvent has increased in recent years, due in the main to it being preferred to Hazardous Atmospheric Pollutants such as methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK). The following table shows historical data on the demand of ethyl acetate from 1997 through 2003.

Table 1.1: Data on Demand of Ethyl Acetate from 1997 to 2003

Year	**Demand (Millions of pounds per year, ethyl acetate)**	**Price (USD) (Cent per pound)**
1997	200	59
1998	186	59
1999	157	62
2000	176	62
2001	159	62
2002	152	62
2003	170	62

As shown in table 1.1, the demand has fallen during the first five years, averaging a decline of five percent per year. However, in the last two years the demand for ethyl acetate has risen again due to the reason mentioned above. In addition, recent increase in the usage of ethyl acetate in coating industry is contributed by increasing

price of methyl ethyl ketone (MEK). Price per kg of methyl ethyl ketone (MEK) is RM 5.05/kg as compared to the price of ethyl acetate, which is RM 3.60/kg. Since ethyl acetate possesses the same function as methyl ethyl ketone it is being preferred over methyl ethyl ketone in the coating industry. Therefore, for the forecast period through 2006, demand is estimated to be 3.4 percent per year.

1.2 OBJECTIVES of RESEARCH

The main objective of this research project is to develop a validated mathematical model capable of describing ethyl acetate reactive distillation process. The research is aimed at fulfilling the following objectives:

1. To develop a simulation model for ethyl acetate reactive distillation column
2. To verify and validate the proposed simulation model
3. To analyze the impact of changing various process and design parameters on the column performance.
4. To introduce a new configuration that could significantly improve the column performance.

1.3 SCOPE of RESEARCH

The scope of research focuses on systematic approach to develop a reliable mathematical model that could represent ethyl acetate reactive distillation column. Suitable algorithm is proposed in order to solve the resulting mathematical model and then the simulation results are compared against equivalent experimental work and established simulation results available in literature. Upon validating the model, parametric analysis is carried out to determine the optimum input conditions that could give the best column performance. Two criteria are used to measure the column performance, namely conversion and ethyl acetate product purity. Finally attempt is made to further enhance the performance of the column by exploring different type of column configuration.

1.4 PROBLEM STATEMENT

Though ethyl acetate system is suitable for reactive distillation process; it is not attractive for commercialization due to its failure to operate at or near its ideal condition. Most of the modeling works on ethyl acetate reactive distillation column available in the literature emphasis on model development followed by simulation by using various solution strategies in order to determine the validity of the model (Alejski et al. 1988; Simandl J. and Svrcek, 1991; Bogacki et al., 1989). Apart from that interest also was shown in the control of ethyl acetate reactive distillation column (Nishith and Daoutidis, 2001). While, Huseyin and Mahmut, 2001 studied the effects of liquid phase activity model on the simulation of ethyl acetate reactive distillation column.

From the past work it is evident that there was not many attempt made to systematically analyze the factors that hinder the performance of ethyl acetate reactive distillation column. In the present study, parametric study is carried out to understand the behavior of the system under various operating and design parameters. Some of the parameters studied are:

- Reflux ratio at constant overhead
- Feed tray location
- Number of stages
- Damkohler number
- Pressure

Through parametric analysis, the system limitations are understood well and optimum conditions for maximum performance is obtained. Based on this analysis attempt can be made to device a new configuration that could ultimately improve the column performance.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The early used of reactive distillation could be traced back since the 1920s'. The earliest literatures in the area consist of several patents registered to Backhaus in 1921, 1922 and 1923a,b based on esterification processes using homogenous catalysts. Meanwhile, among the earliest journal articles on the subject was published by Keyes (1932), Leyes and Othmer (1945 a, b), Schniep et al. (1945) and Berman et al. (1948). These publications too, deal mainly with homogeneous self-catalyzed reactions such as esterifications, trans-esterifications and hydrolysis processes with the main objectives of obtaining steady state numerical solutions.

Despite of the various demonstrated potential of reactive distillation, research on this area ceased for quite a long time until a breakthrough was made in the field of combined process mathematical model simulation and design in the early 1970s' and the wide usage of computers among process designers. These have led to a renewed interest in the subjects (Doherty and Malone, 2001).

Following the development, the study has expanded to cover more systems and these were reported in journal papers and patents. The most classic success story for the application of reactive distillation is the Eastman Chemical Company's process for producing methyl acetate. The process was a radical departure from the traditional technology that had earlier been a genuine economic success for over 15 years. A hybrid reactive distillation device was able to replace an entire flow-sheet consisting of 11 major units plus all the heat exchangers, control systems, pumps, intermediate storage tanks and others (Doherty and Malone 2000). Besides synthesis of Methyl acetate, the synthesis of methyl ethyl tertiary butyl (MTBE), ethyl tertiary butyl ether (ETBE) and tertiary amyl methyl ether (TAME) have also met with commercial success.

The study of process modeling for reactive distillation is normally carried out in one of the two different approaches (Buzad & Doherty, 1994) i.e., simulation and design. In simulation the input and operating variables of a process are specified and the task is to solve for the resulting outputs. In design the input and selected output variables are specified and the task is to determine the optimal process configuration and the optimal design parameters that achieve the given product specification.

In the present study, simulation approach was employed to model ethyl acetate reactive distillation column and ethyl acetate reactive-extractive distillation column. Detailed simulation model was derived and verified against published simulation results and experimental work. Upon validating the model, parametric analysis was carried out to determine optimal column performance and also to analyse factors that impede the performance of the column. Based on the analysis, several improvements are proposed for enhancing the performance of ethyl acetate reactive distillation column.

2.2 Synthesis of Ethyl Acetate

There are various synthesis routes to produce ethyl acetate as depicted in Figure 2.1. However, most commercial production uses the esterification route of acetic acid with ethanol and this is the selected route chosen for the present work. This is also in view of it presenting the opportunity for the application of reactive distillation process. The reagents and products in this reaction have suitable volatilities in the reaction zone and the process condition, namely temperature and pressure, of this route suited well for the application of reactive distillation process.

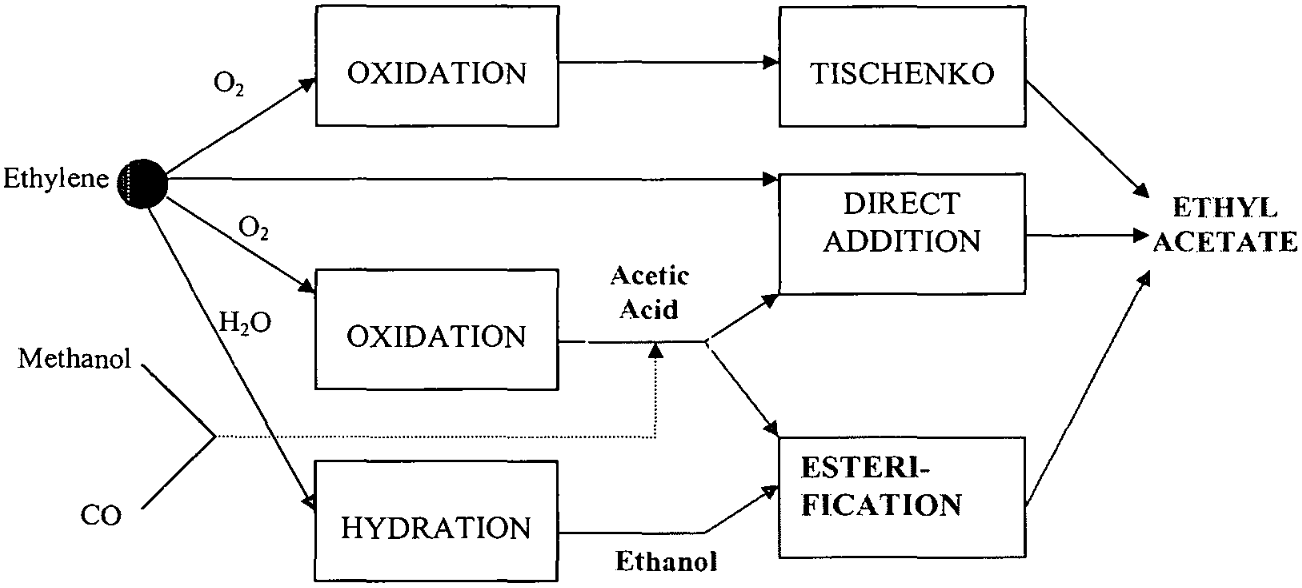

Figure 2.1: Routes To Ethyl Acetate Production (Red Lines Indicate The Selected Route In This Research Project).

Synthesis of ethyl acetate via reactive distillation is carried out by reacting acetic acid with ethanol. The above esterification reaction can be carried out with or without the presence of catalyst. Suzuki et al. (1971), Komatsu (1977), Izarraraz et al. (1980), Chang and Seader (1988), Alejski et al. (1988), Bogacki et al, (1989) and Simandl & Svrcek, (1991) discussed in detail the ethyl acetate synthesis using reactive distillation without the use of catalyst. While Chang and Seader (1988) present a good discussion on the features and the disadvantages of the above system.

Significant improvements in terms of conversion and product purity can be attained when the esterification reaction in the column is carried out with the presence of homogeneous sulfuric acid catalyst (Nishith and Daoutidis, 2001; Huseiyn & Mahmut, 2001). Features of homogenous catalytic ethyl acetate system are discussed by referring to the work of Nishith and Daotidis, (2001) and Yeong et al. (2003) in the following section.

2.2.1 Non-Catalytic Synthesis of Ethyl Acetate via Reactive Distillation

Alejski et al. (1988) theoretically studied the esterification of acetic acid with ethanol to produce ethyl acetate and water using un-catalytic second order reversible reaction kinetics. The column specifications and input condition used in their study is shown in the Figure 2.2. There are 8 theoretical stages, all at 1 atmosphere, inclusive re-boiler and condenser. The feed rate is 0.2584 mol/min, with a liquid distillate of 0.0425 mol/min, giving a bottom of 0.2159 mol/min. The feed is preheated to its bubble point at feed tray pressure and the reflux ratio used is 2.1. The feed is fed to sixth stage from the top and has the following mol fraction composition: acetic acid (z_1)= 0.2559, ethanol (z_2) = 0.6159, ethyl acetate (z_3) = 0.0539 and water (z_4) = 0.0743. Holdup volumes are 0.6 and 0.4 dm3, respectively, for re-boiler and in each of the stages (1 to 7). The simulation result obtained for the column is shown in Table 2.1.

Table 2.1: Simulation Results For Un-Catalytic Ethyl Acetate Reactive Distillation Column By Alejski Et Al., (1988)

		Alejski (1988)	
Quantity	Units	Top	Bottom
Composition			
Acetic acid (Ac)		0.001	0.1450
Ethanol (Et)		0.5430	0.4710
Ethyl Acetate (Ea)		0.4130	0.1440
Water (W)		0.0430	0.2400
Temperature	K	345.6	351.2
Product flow	mol /min	0.0425	0.2159
Et conversion	mole %	20.13	
Ac conversion	mole %	47.95	
Ea purity	mole %	41.29	
Reflux flow	mol/min	0.0893	

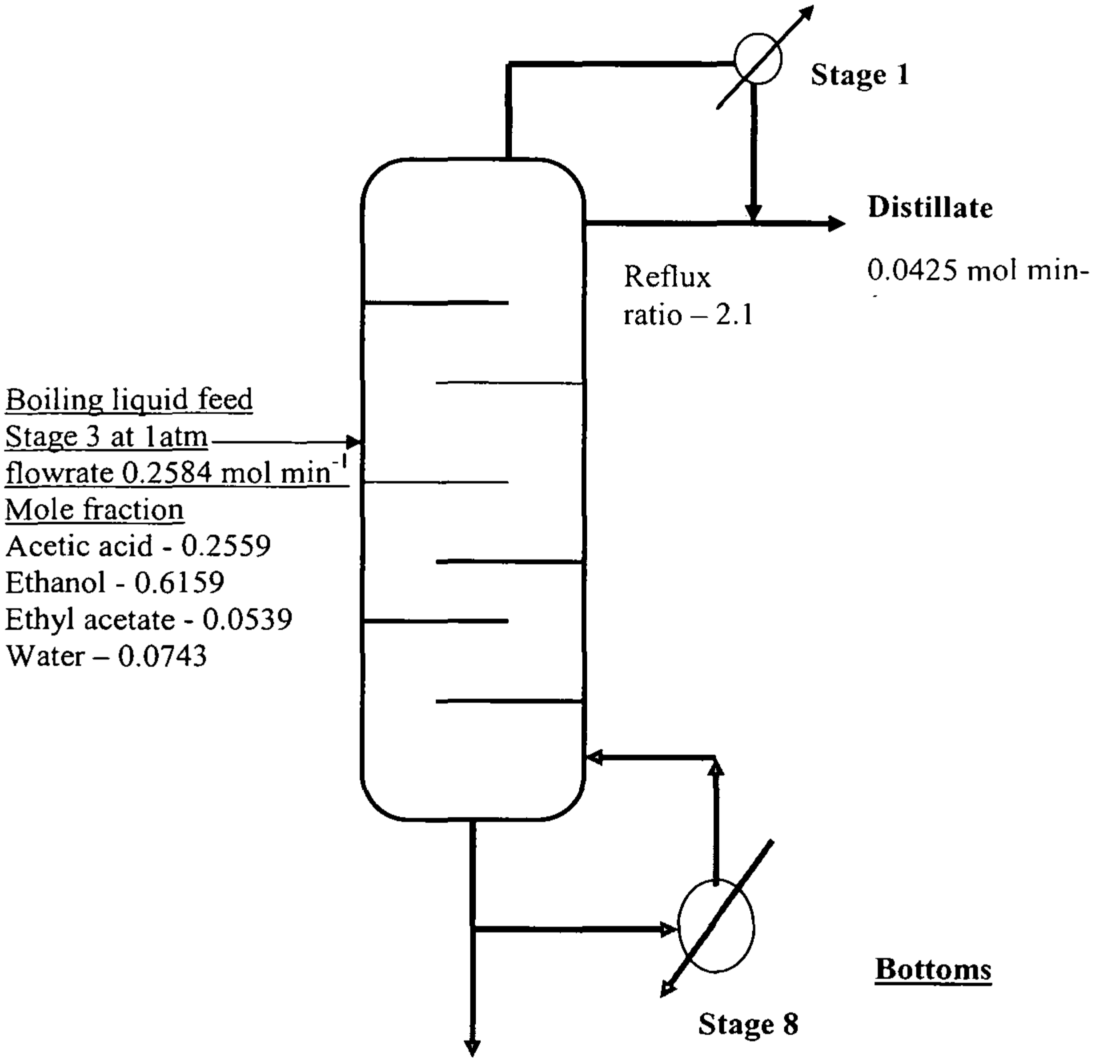

Figure 2.2: Typical Reactive Distillation Column Configuration And Specifications For Single Feed Un-Catalytic Ethyl Acetate Synthesis (Komatsu 1977)

The un-catalytic ethyl acetate reactive distillation column proposed by Alejski et al. (1988) has its limitations. Firstly, the achieved conversion of the column is 47.95 percent with respect to the limiting reactant i.e., acetic acid, which is found to be considerably lower than the equilibrium conversion i.e., 66 percent. Secondly, the achieved purity of ethyl acetate in the distillate is 41.30 percent and this is considered very low. The purity is even lower than the lighter binary azeotrope composition i.e., 54 % for ethanol-ethyl acetate azeotrope, which is supposed to be the purity limit for the top product composition of the column.

The main contributing factor for the poor performance of the column was mainly argued on the absence of catalyst to speed up the reaction in the column, which in turn severely limits the conversion. Even using an excess of ethanol by a ratio of 2.4, failed to drive the limiting reactant i.e., acetic acid, towards complete conversion. Unfortunately, the authors did not explore other configurations or alternatives that could possibly boost the performance of the column in terms of the achieved conversion and the ethyl acetate purity. Attention was given only on the numerical solution method for the mathematical model developed for the column shown in Figure 2.1. In addition the author did not mentioned or analysed the factor that limits the performance of this column.

2.2.2 Catalytic Synthesis of Ethyl Acetate via Reactive Distillation

Nishith and Daotidis, (2001) proposed a configuration, which feeds the two reactants i.e., ethanol and acetic acid, at two different feed locations i.e., above and below the reaction section and using sulfuric acid as the catalyst for the esterification reaction. They reported a higher conversion for the reaction and higher ethyl acetate purity were attained, as a result of doing so. From the comparison made on the two rate equations used for the non-catalytic and catalytic reaction as shown below, it is clearly evident that the catalytic reaction has a significantly higher rate of reaction and this has contributed to the superior performance attained by the configuration.

Rate equation for the catalytic reaction (Alejski & Duprat, 1996):

$r = k_l C_A C_B \quad - \quad k_l/K_c C_C C_D \quad (\text{mol/sec m}^3)$

where

$k_l = (4.195C_k + 0.08815) \exp(-6500.1/T) \quad (\text{m}^3 \text{/mol sec})$ and

$Kc = 7.558 - 0.012T$

k_l = reaction rate constant ($\text{m}^3/(\text{mol sec})$)

C = concentration of reactant/product

R = rate of reaction (mol/sec m^3)

C_k = Catalyst Concentration

T = Temperature (K)

Kc = constant of reaction equilibrium

Rate equation for the non-catalytic reaction (Arnikar et al., 1970):

On stages without catalyst a simpler rate equation is used:

$r = k_1C_AC_B - k_2C_CC_D$ (mol/sec m^3)

where

$k_1 = 0.485 \exp(-7186/T)$ (m^3 /mol sec) and

$k_2 = 0.123 \exp(-7186/T)$ (m^3 /mol sec)

k_1 = forward reaction rate constant (m^3/(mol sec))

k_2 = reverse reaction rate constant (m^3/(mol sec))

Figure 2.3 depicts the double feed catalytic ethyl acetate reactive distillation configuration as used by Nishith and Daoutidis, (2001) in their study. The column consists of 13 stages inclusive of the condenser and re-boiler. Acetic acid in saturated liquid form is fed into the column at stage 4, with a flow-rate of 414-mol minl^{-1}, while ethanol is fed at stage 11 in saturated vapor form with a flow-rate of 411.9-mol minl^{-1}. The column pressure is maintained at 1 atm and the reflux ratio used is 2.023. The liquid holdup in the condenser and the trays is 4.4108 x 10^4 mol, whilst the holdup in the re-boiler is 1.4703 x 10^5 mol.

Table 2.2 display the results obtained from the simulation study conducted. Based on the results, it can be easily concluded that the configuration proposed by them is attractive. Not only the conversion attained is higher than the equilibrium conversion of any conventional reactor, the ethyl acetate purity produced was found to be higher than the azeotropic composition, which normally present the limit of purity that could be achieved under conventional distillation. An interesting feature of the proposed configuration which was highlighted as the reason that had led to the superior performance is the fact that it has the ability to distribute the reaction throughout all the stages in the column, which is characteristically different from the single feed column, in which most of the reaction occurs in the re-boiler.

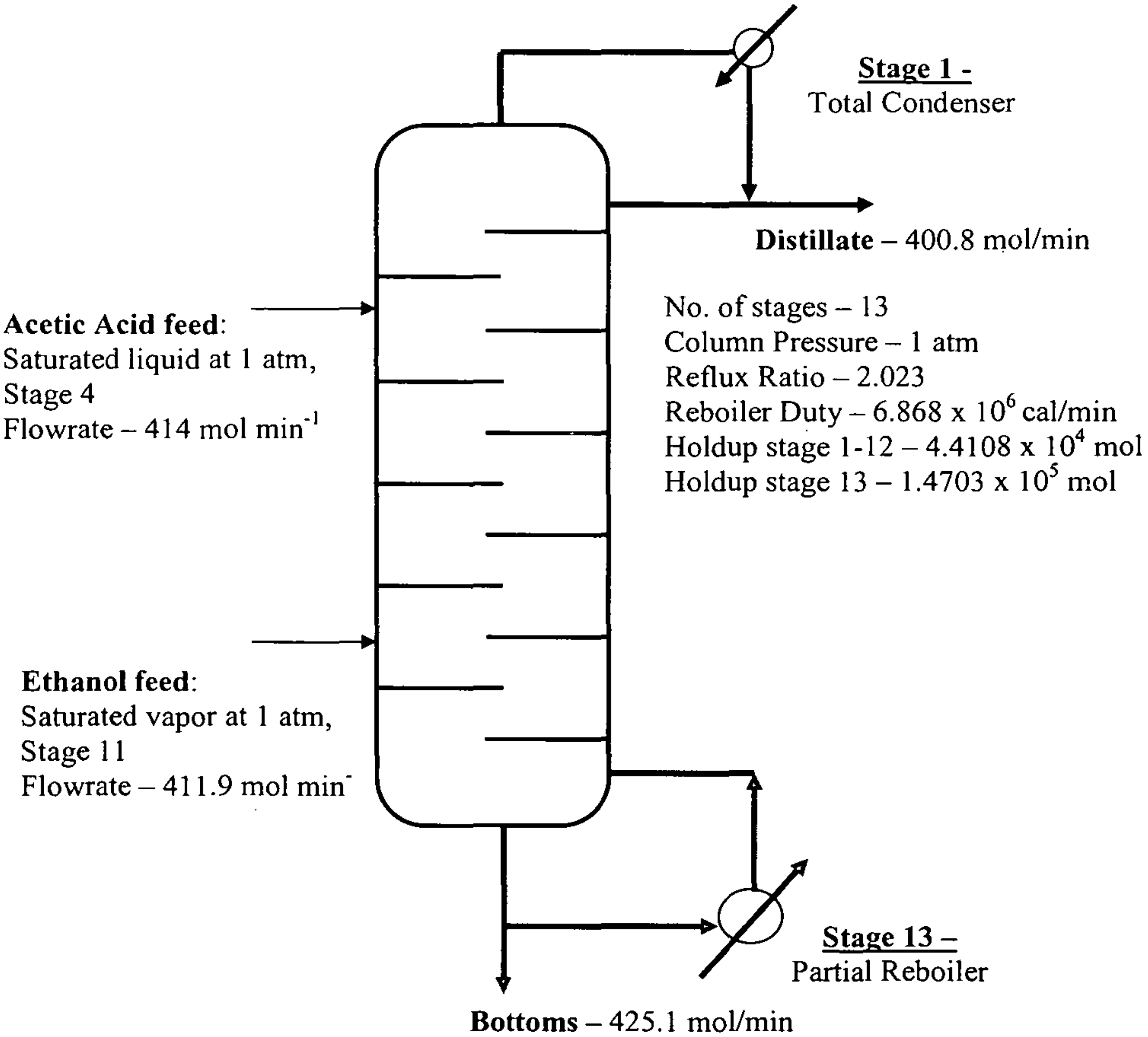

Figure 2.3: Typical Reactive Distillation Column Configuration And Specifications For Double Feed Catalytic Ethyl Acetate Synthesis (Nishith & Daoutidis 2001)

Table 2.2: Simulation Results For Catalytic Ethyl Acetate Reactive Distillation Column By Nishith And Daotidis, (2001).

Quantity	Units	Nishith & Daoutidis (2001) Top	 Bottom
Composition			
Acetic acid (Ac)		0.003	0.2100
Ethanol (Et)		0.080	0.1400
Ethyl Acetate (Ea)		0.650	0.1300
Water (W)		0.240	0.5200
Temperature	K	-	-
Product flow	mol /min	400.8	425.1
Et conversion	mole %	76.8	
Ea purity	mole %	65.0	
Reflux flow	mol/min	810.6	

Despite the promising outcome from the study, they have overlooked several operational facts. Firstly the introduction of catalyst throughout the column promotes reverse reaction in the zone located above the acetic acid feed point. This is expected due to low concentration of reactants causes reverse reaction to dominate. This has impeded the potential of increasing the column performance further. A parametric analysis, which could have been useful in order to gain some insight, was not conducted.

Though the achieved conversion and purity obtained were above the equilibrium conversion and azeotropic compositions respectively, it is still considered to be far from the performance that would be considered as attractive for the application of the technology.

2.2.3 Production of High Purity Ethyl Acetate

Yeong et al. (2003) published a paper, which concentrates on enhancing the performance of catalytic ethyl acetate reactive distillation column proposed by Nishith and Daotidis (2001). Their focal argument on Nishith and Daotidis (2001) work was that the configuration failed to produce high purity ethyl acetate in distillate (only 65 mol%), which requires further purification and bottom product stream consists of all four components in the system, thus, it will be very difficult for further treatment of this stream.

The conceptual design of the configuration proposed by Yeong et al. (2003) is depicted in Figure 2.4 below and Table 2.3 shows the design and operating conditions of the proposed design. The column consists of 29 stages inclusive condenser and re-boiler. Acetic acid (fresh and recycled) is fed into the column at stage 10, while fresh ethanol is fed into the column at stage 28. Reflux ratio is 2.613 and re-boiler duty is 1643.5 kW. As compared to the work of Nishith and Daotidis (2001), additionally this column consists of decanter and bottoms recycle stream, which is directed towards fresh acetic acid feed. Therefore undoubtedly this recycle stream is rich in acetic acid. As in this study the input flow-rates and kinetic model for the chemical reaction is taken from the work of Alejski and Duprat (1996), which also used by Nishith and Daotidis (2001). The four components system of Figure 2.4 was rigorously simulated using the Aspen Plus® process simulation package.

A decanter is included in the design because it is desired to have liquid phase splitting in the decanter into an organic phase and an aqueous phase. The entire aqueous phase stream is drawn from the system for further waste water treatment. A part of organic phase is refluxed back to the column as an entrainer to keep acetic acid down the column. The rest of the organic phase is taken out as ethyl acetate product stream. Unlike other paper in literature, which did not consider the treatment of bottom stream, the bottom stream in this proposed design is recycled and mixed with fresh acetic acid feed.

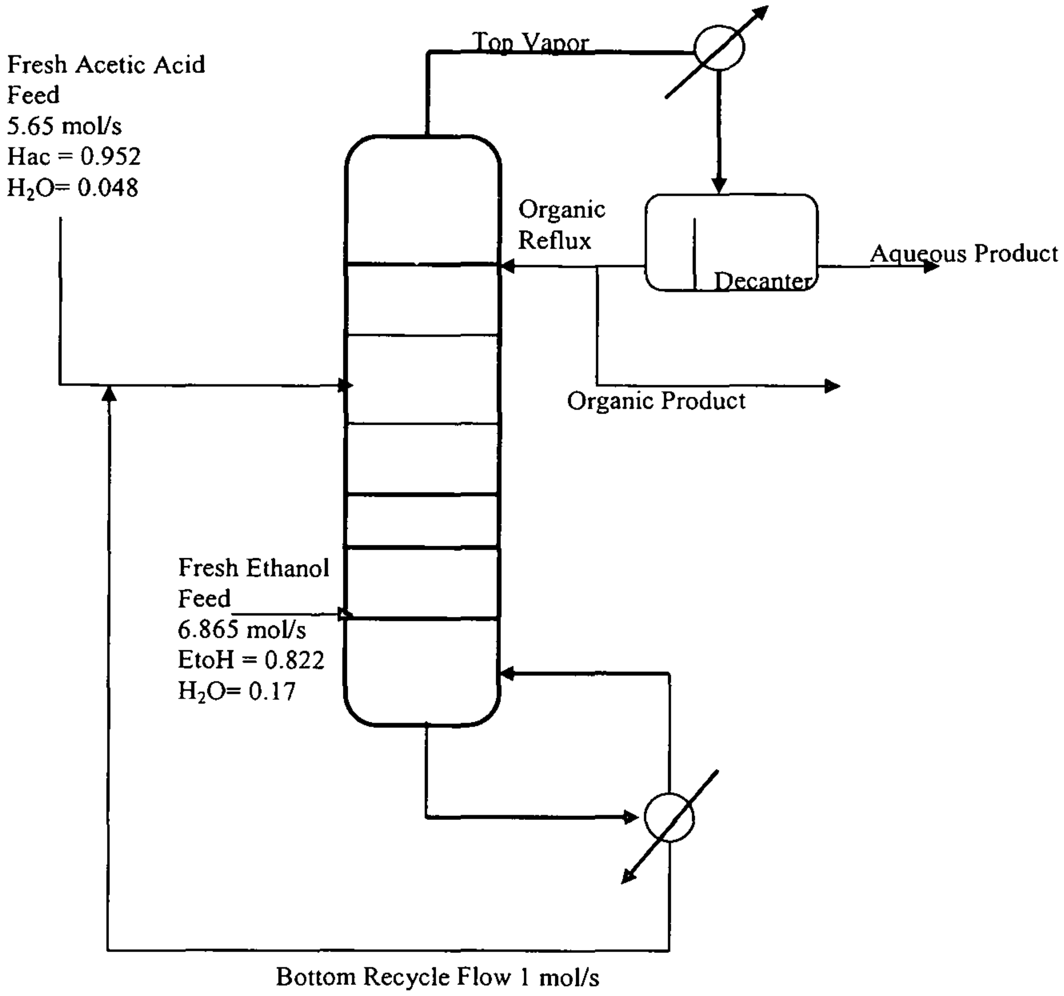

Figure 2.4: Conceptual Design Of Ethyl Acetate Reactive Distillation Column Proposed By Yeong Et Al. 2003.

Table 2.3: Reactive Distillation Column Design and Operating Condition (Yeong et. al.)

Ethyl Acetate Reactive Distillation	Specifications
Total Number of Stages	29
Number of stages in rectifying section	9
Number of stages in reactive section	20
Fresh acetic acid feed flow-rate (mol/s)	5.65
Recycle acetic acid feed flow-rate (mol/s)	6.65
Fresh ethanol feed flow rate (mol/s)	6.865
Bottoms recycle flow-rate (mol/s)	1
Organic reflux flow-rate (mol/s)	32.71
Acetic acid feed location	10
Fresh ethanol feed location	28
Re-boiler duty (kW)	1643.5

Figure 2.5 below summarizes the simulation results of the proposed configuration by Yeong et. al. (2003).

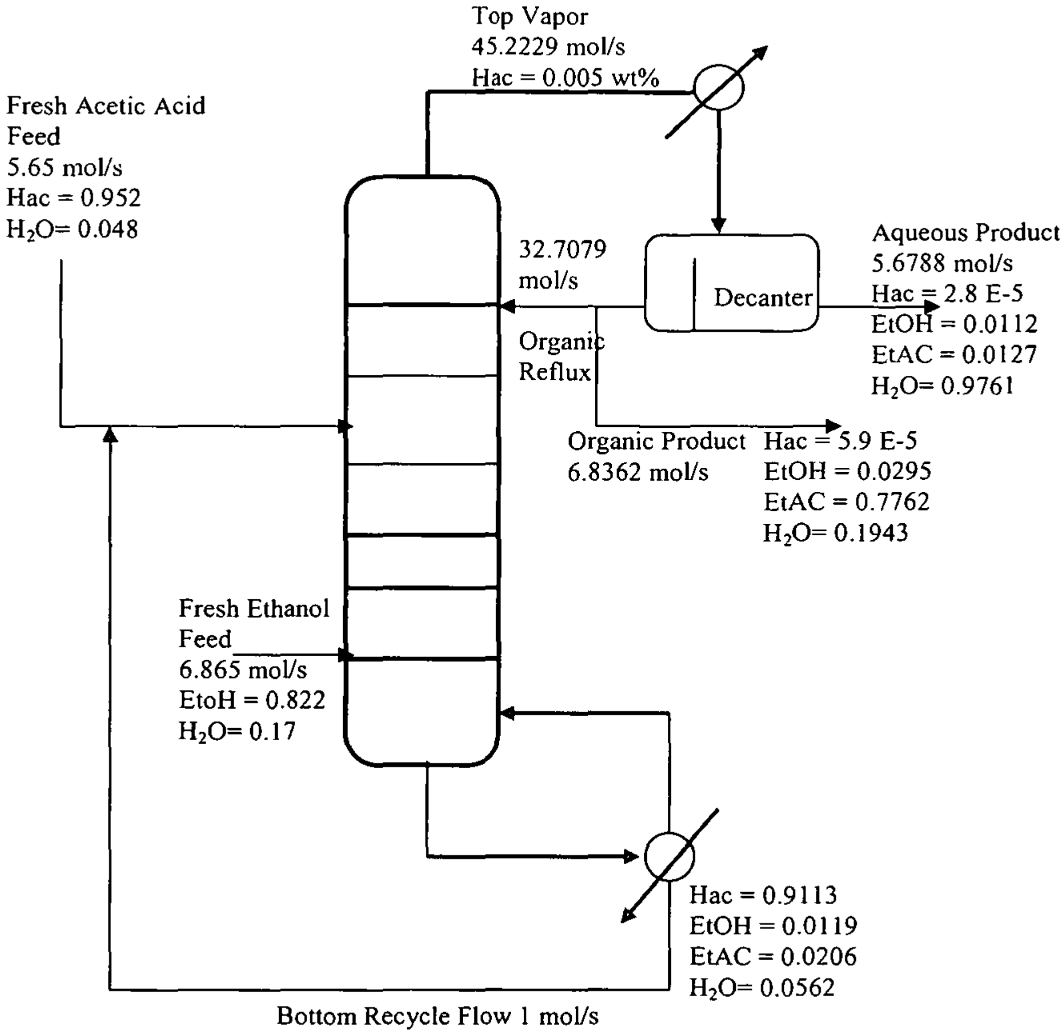

Figure 2.5: Simulation Results Of Ethyl Acetate Reactive Distillation Column Proposed By Yeong Et Al. 2003

The ethyl acetate product purity achieved via this configuration is 77.62 mol% that is only marginally improved as compared to configuration proposed by Nishith and Daotidis (2001), which gives ethyl acetate purity of 65 mol%. Meanwhile the achieved conversion with respect to acetic acid is 83%, which is higher than conversion achieved in configuration proposed by Nishith and Daotidis (2001) (76.8%). An interesting feature of this column is the recycle of bottom stream, which is rich in acetic acid thus eliminating the need for further separation of the bottom stream to recover reactant acetic acid. The column is design in such a way that the bottoms stream is reach in acetic acid. This is achieved in this study by manipulating the product distribution ratio (distillate/bottom). The author maintain high product take off at distillate, thus forcing lighter components (ethyl acetate, ethanol and water) to concentrate in the overhead leaving heavier component acetic acid which has highest relative volatility amongst the components in the system as bottom. Since the product take off favors at distillate the re-boiler duty expectedly higher as compared to configuration proposed by Nishith and Daotidis (2001). Despite the advantage of recovering valuable reactant from the bottom stream, this configuration suffers lost of product ethyl acetate via aqueous stream from the decanter, relatively higher re-boiler duty needed to perform the separation and ethyl acetate product purity is still not good enough for industrial specification.

Unlike other literatures on this topic, the authors have conducted detailed parametric analysis for the proposed configuration in order to gain some insight and to explore the potential of improving the performance of the proposed design. The parameters studied are:

1. Effect of fresh acetic acid feed and the total number of stages
2. Effect of the locations of acetic acid and ethanol feed stages
3. Effect of the bottom recycle flow-rate
4. Effect of organic reflux flow-rate
5. Effect of tray efficiency
6. Effect of water flow rate in the overall system

From the analysis carried out, the authors concluded that it is impossible to improve performance of the process in a single reactive distillation column. Finally, the authors proposed a new configuration with additional stripping column and two recycle streams. The stripping column's function is to further purify ethyl acetate product of the organic distillate stream. Though this configuration could give better results in terms of ethyl acetate product purity, it has failed to achieve reactive distillation process objectives, which is to produce high purity product and conversion in a single column. Therefore, this study will attempt to achieve these process objectives.

2.3 Modeling and Simulation of Ethyl Acetate Reactive Distillation Column

There were two approaches reported in literature, used to model reactive distillation column. Firstly, the equilibrium stage model, which was introduced by Grosser et al. (1987), Alejski and Duprat (1996) and Basualdo and Scenna (1995). Later, a more rigorous approach known as the none-equilibrium stage model (NEQ), was introduced by Kreul et al. (1998). The none-equilibrium stage model has some advantages over the equilibrium model, which is more commonly used. However, due to its complexity, many researchers have preferred the equilibrium stage model to be used for their study. In this section, the work done by Chang and Seader (1988) using the equilibrium stage model approach for ethyl acetate reactive distillation is reviewed. This is then followed by a review on the works using the none-equilibrium stage model.

2.3.1 Equilibrium Stage Modeling

Chang and Seader, (1988) described ethyl acetate reactive distillation column based on equilibrium stage model. In this method the vapor and liquid streams leaving the stage are assumed to be in equilibrium with each other. Each stage is described using the well established MESH (material balance, vapor liquid equilibrium equations, mole fraction summations and heat balance) equations for distillation. In addition, the reaction equation(s) is incorporated and integrated to the equilibrium stage model to represent the reaction(s) taking place at each stage. A complete separation process is modeled as a sequence of these equilibrium stages. In order to reduce the complexity of the model used, several assumptions were made and these among others consist of:

1. The process is treated as in physical equilibrium (vapor and liquid leaving any stage are in equilibrium) with kinetically controlled reaction,
2. Constant enthalpy per(at each) stage which allows enthalpy (derivatives or terms) to be excluded from the model,
3. Constant liquid holdup on the trays, which allows molar derivative, to be excluded from the model,
4. Ideal vapor phase system since the vapor phase non-ideality is less significance in esterification process due to modest operating pressure,

5. The reaction occurs only in the liquid phase and the liquid at each stage is perfectly mixed,
6. Vapor molar holdup and vapor phase chemical reactions are neglected,
7. Adiabatic operation and no heat lost to the surrounding,
8. Heat of mixing on each of the stage is negligible.

One of the major advantages of this approach lies in its' simplicity in the modeling part. It is an extension of conventional distillation modeling and anyone with a priori knowledge in conventional distillation could model the reactive distillation process easily. Though the modeling is quite straightforward, it has been proven that the approach is capable of representing experimental data closely for an ethyl acetate reactive distillation system (Chang and Seader, 1988). Other works on ethyl acetate reactive distillation were also carried out based on equilibrium stage modeling and the results obtained were favorable in terms of model validity (Simandl and Syrcek, 1991; Bogacki et al., 1989; Alejski et al., 1988; Alejski and Duprat, 1996). Thus it can be concluded that the equilibrium stage model is a very good pragmatic approach suitable particularly in the early stage of distillation process development.

On the contrary, the shortcomings of equilibrium stage models are:

- Deeper insight into reactive distillation process would not be possible as column properties such as hardware design information are not included in the modeling equations.
- For some cases such as ethylene glycol system it has been proven that equilibrium stage model is less sensitive to disturbance as compared to none-equilibrium model (Baur et al., 2001). This may cause problem if the model is used for control studies.

2.3.2 None Equilibrium (NEQ) Stage Modeling

The none-equilibrium stage model for reactive distillation uses the rate-based approach in developing the equations for representing distillation process (Taylor and Krishna, 2000). Deriving and solving the sets of equations using the none-equilibrium stage model is not as straightforward as using the equilibrium stage model. In NEQ model, hardware design information must be specified so that mass transfer coefficients, interfacial areas, liquid holdup, hydrodynamics of trays and energy holdup could be calculated. The NEQ 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. In addition, physical properties such as surface tension, diffusion coefficients and viscosity for calculating the mass and heat transfer coefficients and interfacial areas are required. Thus, separate modeling strategies need to be employed for reactive distillation using homogeneous and heterogeneous catalyst (Taylor and Krishna, 2000).

The main advantage of none equilibrium modeling lies in its ability to consider all factors involved in the model development process. This, in turn, allows for more accurate representation of the reactive distillation system. Such close representation to real system would be beneficial especially in control studies.

Nevertheless, the none-equilibrium stage model has significant shortcomings, which have deterred its application. This is mainly due to the absence of single general approach to derive the NEQ model for reactive distillation. There have been various approach and assumptions reported in the literature, thus creating a dilemma in terms of which approach to be used.

2.4 Thermodynamics of Ethyl Acetate System

In reactive distillation, as in conventional distillation, knowledge of the vapor liquid equilibrium is vital. When this equilibrium is superimposed on a chemical reaction, the concentration curve in a distillation column is appreciably influenced (Tuchlenski et al., 2001). Since reaction in reactive distillation process is assumed to occur in liquid phase only, detail treatment of liquid phase non-ideality is important. This is accounted in thermodynamics using the liquid phase activity coefficient. There are various thermodynamic models available for calculating the liquid phase activity coefficients.

Huseyin and Mahmut, (2001) made a comparison study on the effect of the liquid phase activity model on the simulation of ethyl acetate production by reactive distillation. In their study, detail equilibrium stage model representing the 25 stages double feed catalytic ethyl acetate reactive distillation was firstly developed. The model was then simulated using four different liquid phase activity models namely; UNIQUAC, modified UNIFAC Dortmund, modified UNIFAC Lynbgy and an empirical method developed by Komatsu et. al., 1977. The effects of reflux ratio on these models were also studied. It was found that at low reflux ratios, the discrepancies between the results from the various models were as high as 10 percent, whereas at high reflux ratios and with low conversion, the results became increasingly closer. The highest conversion was obtained from the UNIQUAC model with the other models estimations being more or less similar. On the other hand, the temperature profiles in the column were almost similar for the two versions of the UNIFAC models but the empirical model gave a significantly different temperature profile. They concluded that the empirical method is the more reliable for predicting activity coefficients, as it is determined through experimental method. But they did mention that only comparing experimental and simulation results could select the most suitable method. Their studies are continuing for this purpose

In summary, the work has highlighted the importance of selecting suitable liquid phase activity coefficient model for the simulation of ethyl acetate reactive distillation column. The effects on important performance parameters such as conversion, product purity and product distribution ratios were clearly shown with the purpose of cautioning future research work on the careful attention needed for the selection of liquid phase activity model. Nevertheless, the main lacking factor in this work is the failure of the author to compare the simulation results against any experimental work for validation. Also, the attempt on parametric study only focuses on reflux ratio, while leaving the other parameters of equally importance not studied.

2.5 Computer Simulation of Reactive Distillation Column.

Since the advent of digital computers, study on reactive distillation focused mainly on mathematical model development and its solution. In most of the solution procedures, the mathematics involved solving simultaneously sets of non-linear algebraic equations. Numerical methods were used as it was almost impossible to obtain the analytical solutions. Various algorithms suitable for implementation on digital computers for rigorously solving the mass and energy balance and the equilibrium state for multistage reactive distillation process have been reported (Jelinek and Hlavacek, 1976 ; Komatsu and Holland, 1977 ; Chang and Seader, 1988, Alejski et al., 1988 ; Bogacki et al., 1989; Simandl and Svrcek, 1991). Column of realistic complexity can be simulated, which among others include the effects of tray hydraulics and the mass transfer between liquid and vapor and between fluid and solid catalyst (Taylor and Krishna, 2000). Several commercial process modeling packages that includes all these effects for simulating steady state reactive distillation column have been introduced such as DESIGNER and RADFRAC (Juhaini et. al, 1999; Taylor and Krishna, 2000).

Typically, a simulation of reactive distillation column would requires specification to be given on the feed composition and quality, the column pressure, the reflux and reboil ratios, the total number of stages, the feed plate location and the liquid-phase holdups on each stage. The resulting composition profiles could then be determined using the simulation model. In the following sections, discussion is made on the various solution algorithm reported in literature for solving reactive distillation modeling equations.

2.5.1 Equation Tearing Procedures

Equation tearing procedures involve dividing the model equations into groups to be solved separately (Taylor and Krishna, 2000). Two such equation-tearing procedures are the bubble point method (BP) and the multi-theta method. Suzuki et al. (1971) applied BP method to solve modeling equations for ethyl acetate synthesis, and compared their results against experimental work. Komatsu and Holland (1977), on the other hand, used the multi-theta method on a case study involving esterification of acetic acid using reactive distillation.

The methods that fell under this category seemed to be quite straightforward, but it will fail to converge under the circumstances where the boiling points between the components are too large or when the kinetics are too complex, and the liquid solution are highly non-ideal.

2.5.2 Relaxation Method

Most of the methods proposed in this section are very sensitive to initial estimations. In the case where the starting data are estimated with great errors, there will be serious problems with the convergence of these methods. To overcome the drawback, relaxation method was proposed. This method involves writing the MESH equations in unsteady state form and integrating them numerically until a steady state solution is achieved (Henley and Seader, 1981). In a way, the approach resembles closely to the dynamic model. Bogacki et al., (1989) used this method for simulating esterification of acetic acid and compared their results against the numerical results obtained by Komatsu (1977). They used Adams-Moulton numerical integration method to integrate a simplified dynamic model, neglecting the enthalpy balance, until a steady state solution was obtained. Yang et al., (2001) too applied this method to obtain a steady state solution for an ETBE reactive distillation column. The obtained simulation results were found to be in good agreement with an experimental work.

Although this method seems to be attractive, the major disadvantage is mainly due to its slow convergence in arriving to the solution, which at times can be extremely time demanding.

2.5.3 Minimization Method

The method involves minimizing the sum squares of non-linear functions without calculating the derivatives (Powell, 1965). Similar to the relaxation method, it is useful for systems where it is difficult to predict the initial guest values for component compositions and temperature profile at the beginning stage of the simulation. Alejski et al. (1988) used this method for ethyl acetate synthesis and compared their results against the experimental work of Komatsu (1977). They claimed that this algorithm was able to produce more precise results than the earlier algorithms discussed in this work.

Similar to the relaxation method, the major disadvantage of this method is the lengthy time required to arrive at the solution. Therefore, applying it to a complex system may not be suitable.

2.5.4 Homotopy Continuation Method

The method is employed most oftenly for solving problems that are considered to be extremely difficult to solve with other methods such as Newton's method which requires solving large and complex partial differential system and due to its sensitivity to initial assumptions. For a detailed discussion on the method, reference could be made to the article written by Wayburn and Seader (1987). Chang and Seader (1988) employed this method successfully for reactive distillation process involving the esterification of acetic acid with ethanol to produce ethyl acetate. An important feature worth highlighting for the method is its ability to detect the presence of multiple steady states in reactive distillation system (Pisarenko et. al., 1993). Other application in reactive distillation system reported involves the use of the method for parametric sensitivity study (Sneesby et. al., 1997).

2.6 Designs and Analysis of Ethyl Acetate Reactive Distillation Column

Simulation and process design of reactive distillation operations involves two different types of calculation approach. In the case of process design, parameters such as the number of stages, the operational reflux ratio, the size of reaction section integrated within the distillation column which reflects the residence time for reaction, the temperature and pressure of the operation and the feed location(s) are among the critical parameters that need to be determined. While, simulation would normally takes place after the specifications for the above parameters have been made to the mathematical model used to represent the process. Due to the complexity encountered as a result of the integration between distillation and reactor design, a single comprehensive and globally accepted design method for reactive distillation is yet to be developed. On the contrary, the works related simulation, were published more widely based on several systems and using various modeling approaches.

While most reactive distillation process model was derived based on the EQ stage model, recent developments have opened up the possibility of using NEQ model for design and simulation of reactive distillation (Taylor and Krishna, 2000). Since this research work focused mainly on modeling and simulation of reactive distillation column, comprehensive review on the topic of process design will not be covered here. Instead, attempt is made to cover the subject with direct reference to the ethyl acetate system, which is used as the system in this research. This will provide good initial picture on the limitations and feasible separation modes for the system studied in this research project.

There have been reasonable amount of publications made on the design and analysis of ethyl acetate reactive distillation with most of them focusing on the various process alternatives for ethyl acetate synthesis and the feasibility of using reactive distillation column. Before developing design models for reactive distillation, Barbosa and Doherty (1988) studied the influence of chemical reactions on vapor liquid equilibria. According to them, the understanding of the above fundamental is essential for satisfactory design and synthesis of reactive distillation columns. They analysed the effects of chemical reaction on vapor liquid equilibria by observing the reactive phase diagrams representing the system under study. They presented a general algorithm for developing these phase diagrams for ideal and non-ideal systems. In developing the algorithm, they have assumed the components relative volatility within the system to be constant and the reactions have reached its equilibrium. Using a quaternary non-ideal system i.e., acetic acid-ethanol-ethyl acetate-water, they showed through their calculation that reactive azeotropes do not exist for this mixture. They also stressed the importance of getting the right thermochemical data for predicting correctly the behavior of the system as otherwise it will affects not only the type of distillation sequence that is needed in order to meet the product specifications, but it also gives rise to completely different physical situation such as existence of reactive azeotropes.

One important finding discovered from their research is that for constant volatility systems, they were able to show the conditions under which the reactive azeotropes could form. According to them, the reactive azeotropes could only occur if the volatility of both reactants is either higher or lower than the volatility of the products. However, it was proven later that the observation does not hold for non-constant volatility systems (Song et. al 1995).

To effectively visualise phase behavior, Barbosa and Doherty (1988), later introduced the use of residue curves maps. They defined a new set of transformed composition variables, which ultimately ease the representation and calculation of phase behavior. These residue curve maps explicitly show the existence of distillation boundaries, a concept that is important not only for the synthesis of distillation columns but also for the design of simple reactive distillation columns; since these distillation boundaries limit the range for feasible product specifications as a result of separating the mixture system. However, allowing the components in the mixture to react could modify the distillation boundaries to an extent that it either could eliminate the existing boundaries or create new ones. An interesting feature of this phenomenon is that through proper maneuvering by introducing reaction into the system could avoid the formation of azeotropes, which have been known to limit separation ability of any distillation process. According to them, for any binary and ternary mixtures undergoing instantaneous chemical reaction, non-reactive azeotropes do not present as products of the distillation since the components always reacted away from the azeotropes' composition.

Using MTBE system as an example, they demonstrated the outcome above. They calculated the residue curve map for both reactive and non-reactive mixture of isobutene-methanol-MTBE and the diagrams obtained for the non-reactive system are shown in Figure 2.6 below. It clearly shows the existence of a distillation boundary, which extends from the binary azeotropes of isobutene-methanol to the binary azeotropes of methanol-MTBE. In contrast, the reactive system as represented in Figure 2.7, shows that the non-reactive azeotropes have been eliminated. Since the reaction is in chemical equilibrium, binary azeotropes of isobutene-methanol react instantly to form MTBE. Meanwhile, binary azeotrpes of MTBE-methanol is impossible to form, as MTBE react to isobutene and methanol. Therefore we cannot have a binary mixture of isobutene-methanol and MTBE-methanol.

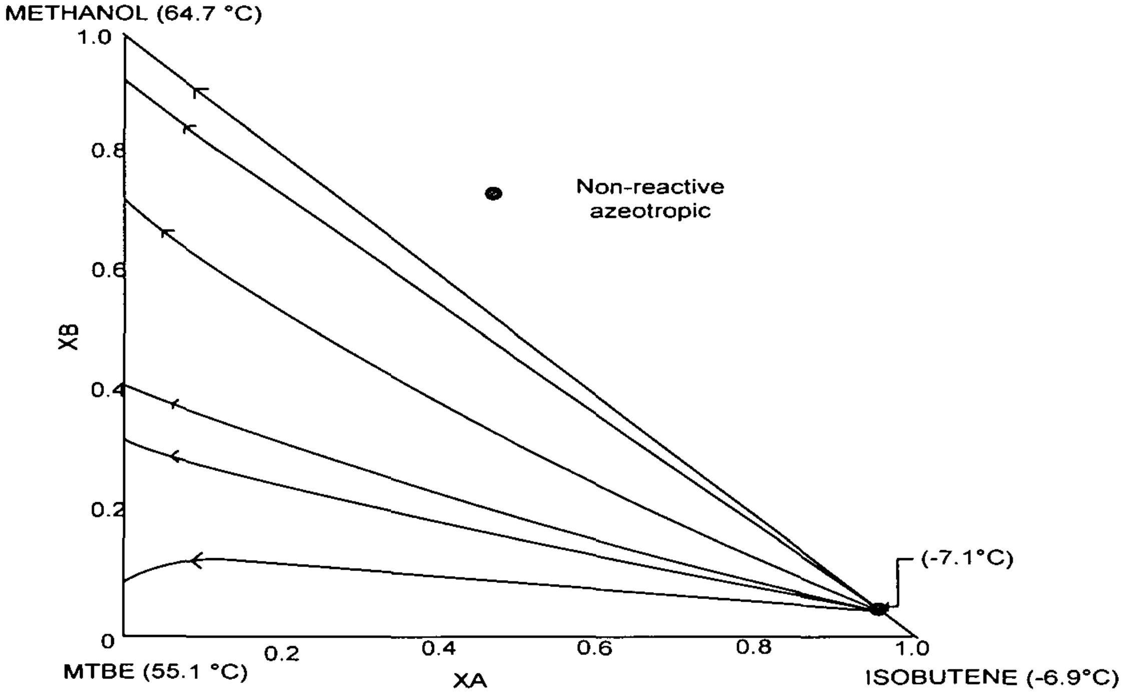

Figure 2.6: Residue Curve For The Non-Reactive System Isobutene-Methanol-MTBE

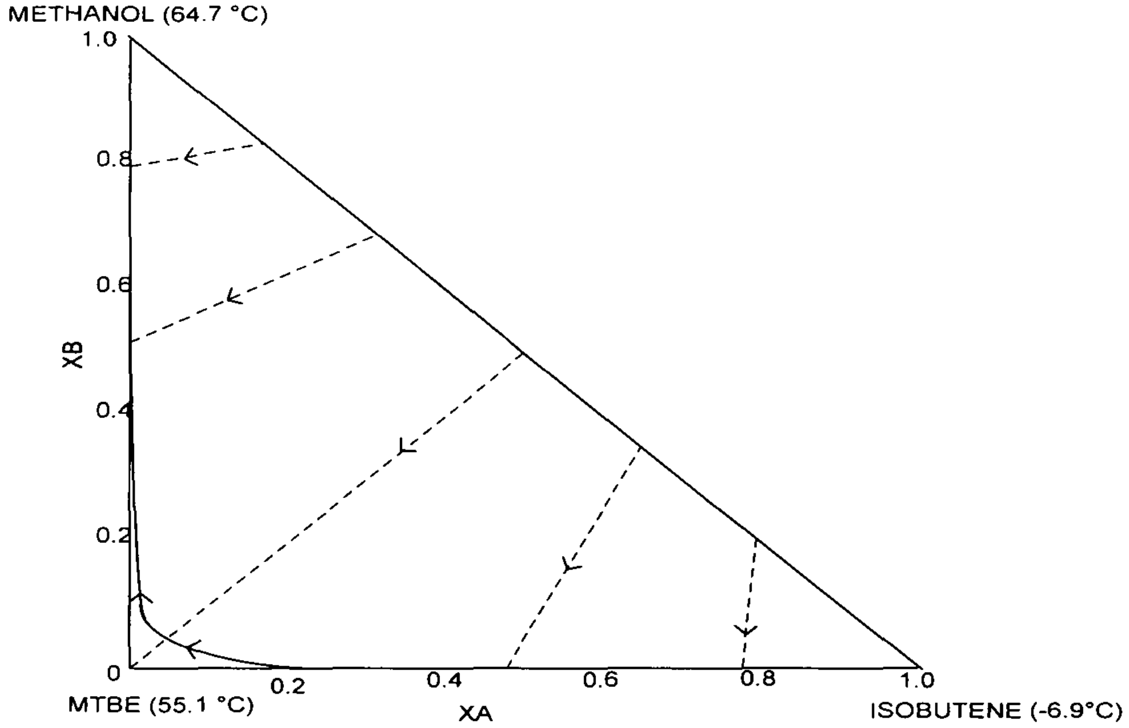

Figure 2.7: Residue Curve For The Reactive System Isobutene-Methanol-MTBE

Analysis made by them on four-component reactive mixtures, showed that for some system, the presence of reaction does not necessarily eliminates all the non-reactive azeotropes. They studied the mixture of ethyl acetate-ethanol-water-acetic acid system that undergoes liquid phase reaction. Under the non-reactive mixture, four azeotropes were known to be present. It was observed that the presence of reactions only eliminate two of the non-reactive azeotropes i.e., a ternary azeotropes of ethyl acetate-ethanol-water and a binary azeotropes of ethyl acetate-water. While the binary azeotropes of ethanol-water and ethanol-ethyl acetate still exist in the system. This could be explained from the fact that the mixture of ethanol-water or ethanol-ethyl acetate does not react with each other even in the presence of catalyst. Therefore, these azeotropes could still be obtained as the products of the reactive distillation. Thus, the use of residue curve maps during synthesis and design of reactive distillation process could predict its potential advantages if any, in comparison to the conventional arrangement consisting of reactor followed by distillation.

In an accompanying paper, Barbosa and Doherty (1988c) used the set of transformed composition variables to derive design equations for a single feed column for calculating minimum reflux ratios for reactive distillation column. They showed that the equations developed were relatively similar to the corresponding equations for conventional distillation with additionally reaction term was introduced in the equations. The design equation for stripping section of single feed reactive distillation column derived by Barbosa and Doherty (1988c) given by:

$$\frac{dX_i^s}{dh^s} = \frac{s^*}{s^*+1}(Y_i^s - X_i^s) + \frac{1}{s^*+1}X_B^s$$

i = *1,……., c-1*

i ? k

where

X_i^s = stripping section transformed liquid composition variable of component *i*

Y_i^s = stripping section transformed vapor composition variable of component *i*

X_B^s = transformed bottoms composition

h^s = stripping section continuous plate number

s^* = modified reboil ratio for plate n

c = number of components

k = reference component

The design equation for rectifying section of single feed reactive distillation column proposed by Barbosa and Doherty (1988c) given by:

$$\frac{dX_i^r}{dh^r} = X_i^r \frac{r^*+1}{r^*}Y_i^r + \frac{1}{r^*}Y_D$$

i = *1,……., c-1*

i ? k

where

X_i^r = rectifying section transformed liquid composition variable of component *i*

Y_i^r = rectifying section transformed vapor composition variable of component *i*

X_D^r = transformed distillate composition

h^r = reactifying section continuous plate number

r^* = modified reflux ratio for plate n

c = number of components

k = reference component

Initial condition for integration of set of differential equations for stripping section is taken as bottoms composition while initial composition for set of differential equations for rectifying section is taken as distillate composition.

Defining equation for transformed liquid and vapor phase composition, modified reboil ratio and reflux ratio can be referred to paper published by Barbosa and Doherty (1988c). Based on the above equations for stripping section and rectifying section which are functions of reboil ratio and reflux ratio respectively, they determined a feasible design by integrating numerically the equations beginning from the desired product composition. To illustrate their design procedure, an ideal quaternary system was selected, which undergo an equilibrium reaction type: -

$$A + B \longleftrightarrow C + D$$

The order of the components relative volatility by decreasing volatility is C > A > B > D. They concluded that if the resulting rectifying and stripping trajectories for the specified reflux ratio from the integration of above equations intersect, as shown in Figure 2.8 (a), then the proposed column is feasible. However, if the rectifying and stripping trajectories for the specified reflux ratio did not intersect as shown in Figure 2.8(b), then the proposed column will not be able to produce the desired products. For a special case where rectifying and stripping trajectories for specified reflux ratio just touch each other as shown in Figure 2.8(c), an infinite number of trays are required to realize the separation. Thus it represents minimum reflux condition.

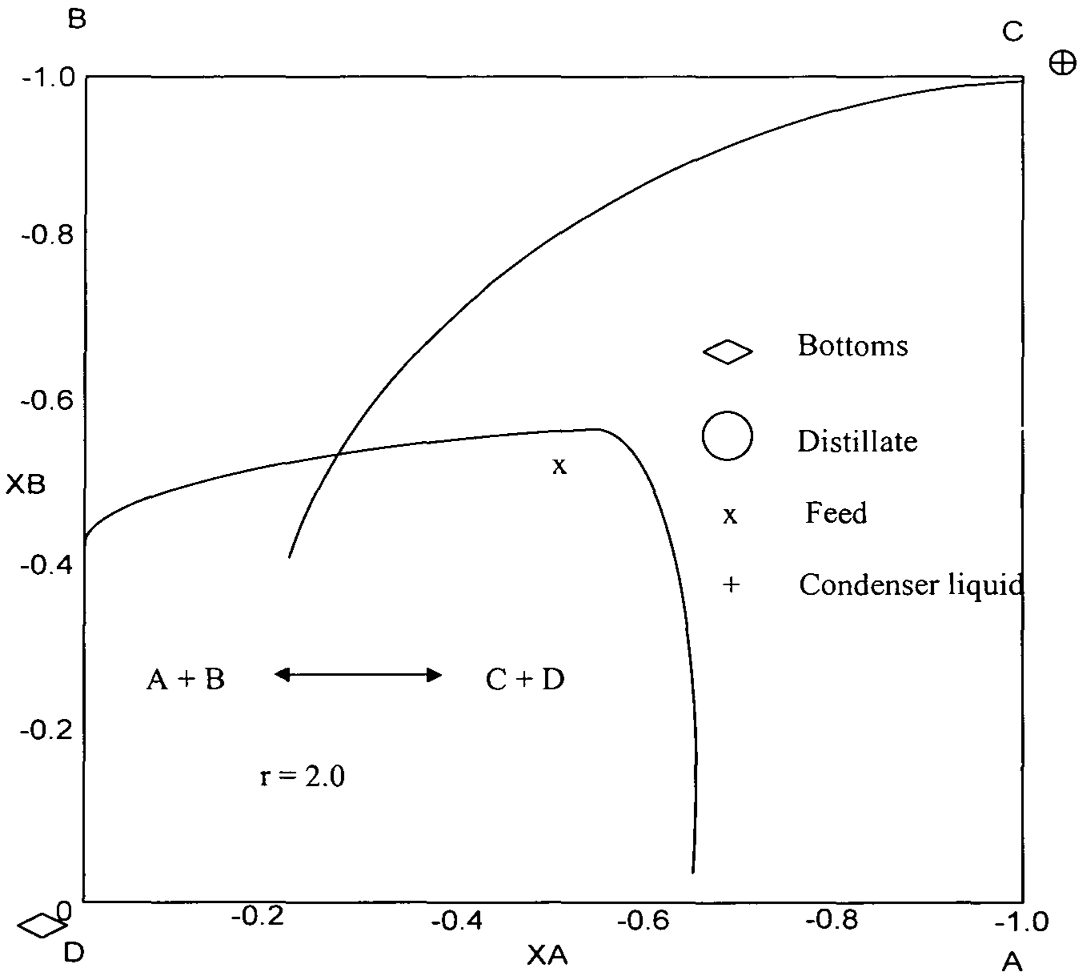

Figure 2.8(a): Feasible Separation Composition Profiles For The Reactive Distillation Of A Four Component Ideal System As A Function Of The Reflux Ratio (Barbosa & Doherty, 1988c).

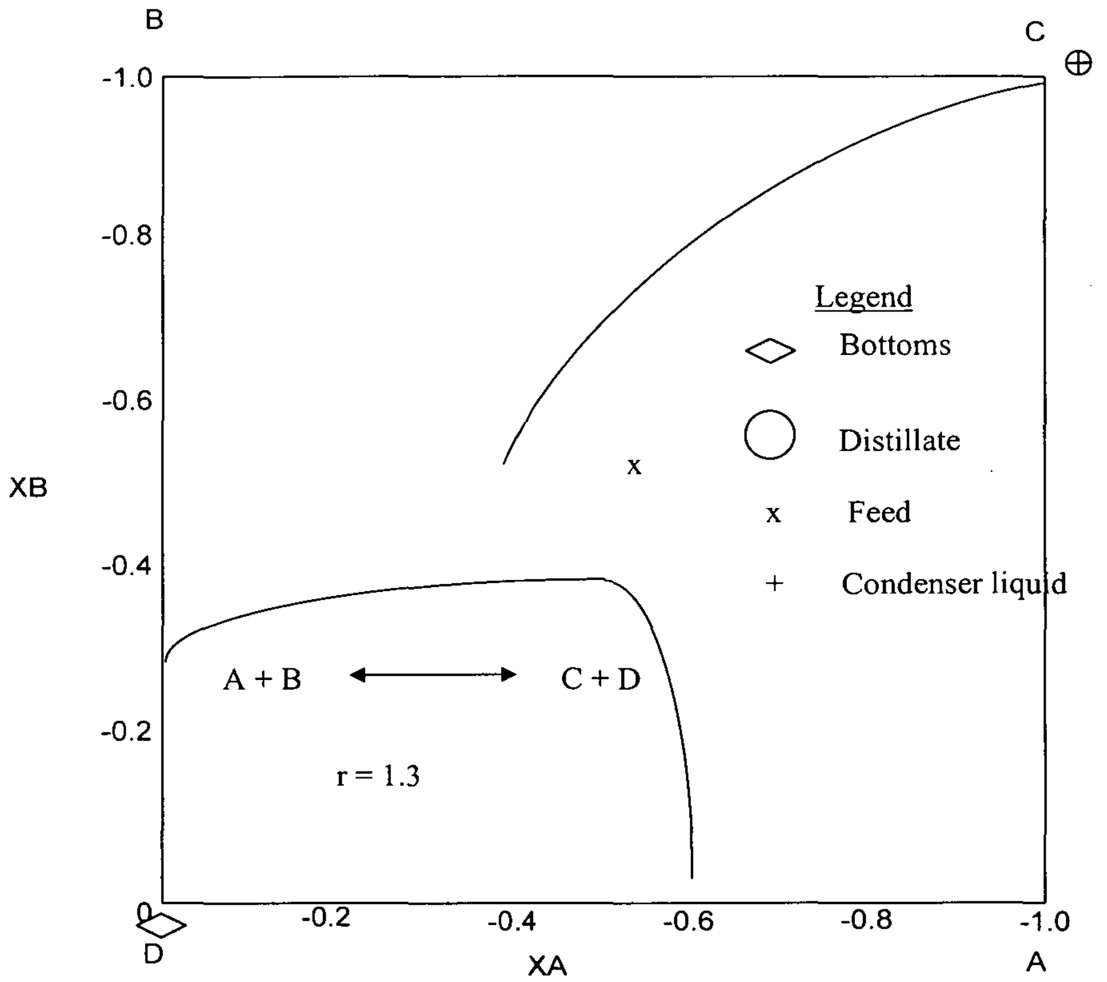

Figure 2.8(b): Unfeasible Separation Composition Profiles For The Reactive Distillation Of A Four Component Ideal System As A Function Of Reflux Ratio (Barbosa & Doherty, 1988c).

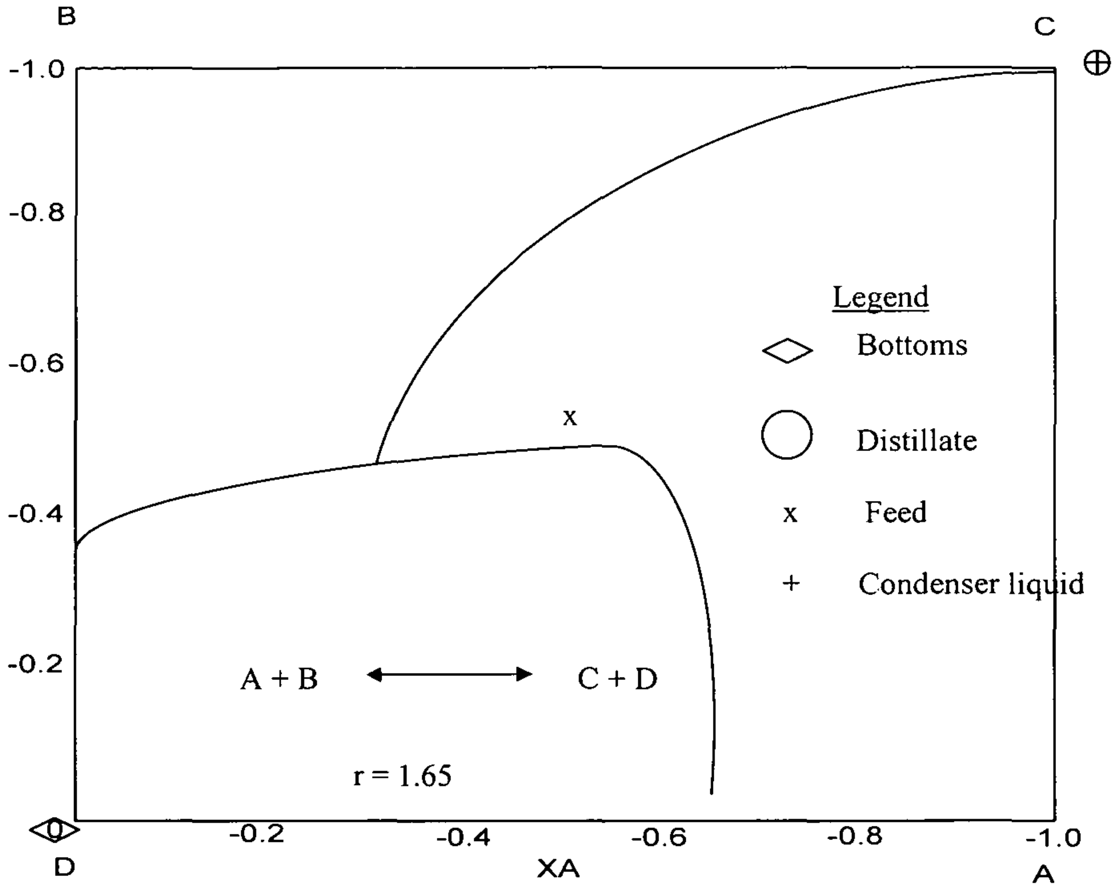

Figure 2.8(c): Minimum Reflux Composition Profiles For The Reactive Distillation Of A Four Component Ideal System As A Function Of Reflux Ratio (Barbosa & Doherty, 1988c).

In the accompanying paper Barbosa and Doherty (1988d) extended the methodology of single feed column as described above to double feed columns to study the column feasibility and to calculate the minimum reflux ratio. They illustrated the procedure using esterification processes. Production of methyl acetate was first considered followed then by the production of ethyl acetate. Ideally, the production of these esters using reactive distillation would consists of a single column to which acetic acid and alcohol feeds, enter at the upper and lower sections of the reaction zone respectively with a feed ratio of near unity. The products obtained from the column then should ideally be the ester as the distillate and water as the bottom product. However, their analysis on the systems showed that the column would be feasible only if the combinations of the feed ratios (F_R) are well above unity. For the esterification of methanol and acetic acid to produce methyl acetate, the F_R must be at least above 3 whereas for the esterification of ethanol and acetic acid to produce ethyl acetate, the F_R must be at least 7. From such finding, they suggested that one of the ways to do with single reactive distillation column is to isolate only one of the products from the esterification reaction i.e., the esters as one of the distillation product, leaving a binary mixture of the other product together with one of the reactants i.e., the acetic acid, as the other distillation product. Their design calculation shows that for methyl acetate system, to obtain the desired separation (pure methyl acetate as distillate and binary mixture of water and acetic acid), approximately 18 trays were needed for the stripping section, 31 trays for the middle section located between the subsequent feeds and 8 trays for the rectifying section. On the other hand, for ethyl acetate system, in order to obtain pure ethyl acetate as distillate and binary mixture of water and acetic acid as bottoms, approximately 20 trays were needed for the stripping section, 101 trays in the middle section and 5 trays in the rectifying section. It could easily be seen that enormous number of trays was needed to facilitate the reaction and separation for the ethyl acetate system. They have not provided any explanation for this difference though. However, the present study will attempt to explain this phenomenon. The authors also proposed two other process configurations as alternatives for the esterification processes but unfortunately did not present the results.

2.7 Overall Comment

There are various routes to produce ethyl acetate. However, the most suitable route for the application of reactive distillation process is by esterification reaction of acetic acid with ethanol. The catalytic ethyl acetate reactive distillation seems to be more promising in terms of performance (Nishith and Daotidis, 2001) as compared the non-catalytic ethyl acetate reactive distillation column (Komatsu, 1977). However the drawbacks of the design proposed by Nishith and Daotidis (2001) are 1) the top product purity is not high enough (only 65mol%) which requires further purification and 2) the bottom product stream consists all for components in the system, thus, it will be very difficult for further treatment of this stream.

Yeong et. al., (2003), alleviate this condition by introducing a new configuration, which involves recycle of bottom stream that is reach in acetic acid as a make up for fresh acetic acid introduced into the column. But this configuration also failed to improve the ethyl acetate product purity significantly. Finally, they had to introduce additional stripping column and recycle stream in order to achieve high ethyl acetate product purity. Initial idea of producing high purity product and conversion in a single column was not be able to achieve by these authors. Past research work failed to consider the possibilities of incorporating extractive section in the ethyl acetate reactive distillation column in order to overcome the limitation that exist in the column. However in this research work this is considered heavily in order to achieve superior performance in a single column. From the author's point of view previous work have failed to consider this as an alternative due to lack of parametric studies conducted on ethyl acetate reactive distillation column which is important to identify improvements.

Modeling of the reactive distillation column is better described using the equilibrium stage (EQ) method due its simplicity in comparison to the non-equilibrium (NEQ) method which requires significant amount of information which at times may not be available due to lack of fundamental studies to determine some of the required data. In addition, the accuracy obtained using the equilibrium stage (EQ) method was found to be acceptable. The use of proper liquid phase activity coefficients in the reactive distillation model are important in order to account for non-ideality in the liquid phase which existed in most of the system encountered. Of all the methods available for determining activity coefficient, empirical method was found to be the best method as the coefficients were determined based on experiment.

Upon various computer simulation method proposed in the literature, relaxation method was found to be less sensitive to the initial estimation required. Thus it is most suitable method for initial stage of process development. Simulation and design calculations are different types of calculations. Simulation study could give more insight on the behavior of the system in study as compared to design approach as via simulation the output response can be obtained immediately and analysis can be done.

THEORY

3.1 Introduction

This chapter begins with a brief introduction, which then moves into the concept of modeling process applied in Process Systems Engineering. Based on this modeling concept, the mathematical model for ethyl acetate reactive distillation column is developed.

In the process of building a model, real world problems are translated into equivalent mathematical formulations from which it is solved and then attempt is made to interpret the results, which provides the insight into the behavior of the real system. A model should resemble certain characteristics of the actual system. Those actual characteristics could include:

- correct response direction of the outputs as the inputs change;
- valid structure which correctly represents the connection between the inputs, outputs and internal variables;
- correct short and long term behavior of the model.

This overall process is represented schematically in Figure 3.1, which shows the four key steps in the overall modeling process (Law Averill M., 2000).

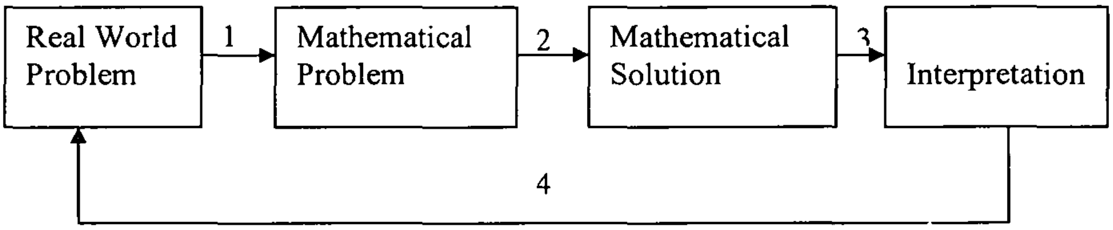

Figure 3.1: Real World Modeling Process

Each of the steps in Figure 3.1 has a very important role in the model building process. In step 1, the real world problem is translated into mathematical terms. Once the mathematical description of the real world system has been generated, it is then necessary to solve it for the unknown value of the variables representing the system (step 2). Step 3 of the process involves testing or validating the model to check whether it has been correctly implemented and to ensure that the model imitates the real world problem at a sufficient accuracy required. Once the model is verified and validated, the model can then be used for the intended purpose (step 4).

Model application areas in Process Systems Engineering are wide and the list of application is almost endless. However, it can be categorized into several well-defined areas. These are outlined in Table 3.1, which sets out the typical application area and the aims of the modeling.

Table 3.1: Typical Application Area And The Aim Of The Modeling (Law Averill M., 2000)

Application Area	Model use and aim
Process Design	Feasibility analysis of novel design Technical, economic, environmental assessment Effects of process parameter changes on process performance Optimization using structural and parametric changes Analysis process interactions Waste minimization in design
Process Control	Examining regulatory and control strategies Analyzing dynamics for set point changes and disturbances Optimal control strategies for batch operations Optimal control for multi-product operations Optimal start-up and shutdown policies
Trouble-shooting	Identifying likely causes for quality problems Identifying likely causes for process deviations
Process safety	Detection of hazardous operating regimes Estimation of accidental release events Estimation of effects from release scenario
Operator training	Start up and shut down for normal operations Emergency response training Routine operations training
Environmental impact	Quantifying emission rates for a specific design Dispersion predictions for air and water releases Characterizing social and economic impact Estimating acute accident effects (fire, explosion)

Table above clearly shows the wide range of applications of model and hence the importance of process modeling on the modern design, optimization and operation of the process systems. For this research project, developed model is utilized for process design study with the aim of analyzing the effects of changing process parameters on the column performance.

3.2 Modeling

In this section, mathematical model will be developed specifically for homogeneously catalyst ethyl acetate reactive distillation column. Figure 3.3 shows the schematic representation of reactive distillation column used as the basis for model development in this study. In deriving the mathematical model, several assumptions were made. Although the assumptions could slightly affect the accuracy of the model, the decision was consciously made in order to make the model more effective for simulation. The set of assumptions made are as follows:

1. The process is treated as in physical equilibrium (vapor and liquid leaving any stage are in equilibrium) with kinetically controlled reaction.
2. Constant enthalpy per stage which allows enthalpy derivatives to be excluded in the model
3. Constant liquid holdup on the trays, which allows molar derivative, excluded in the model.
4. Ideal vapor phase since the vapor phase non-ideality is known to be less significant in esterification process as the column pressure is moderate (1 – 4 atm).
5. The reaction occurs only in the liquid phase, with each stage acting as a perfectly mixed CSTR reactor.
6. Vapor molar holdup and vapor phase chemical reactions were neglected.
7. Adiabatic operation and no heat losses to surrounding.
8. Heat of mixing at each stage considered negligible.

3.2.1 Equilibrium Stage Modeling

A schematic diagram of an equilibrium stage is shown in Figure 3.2.

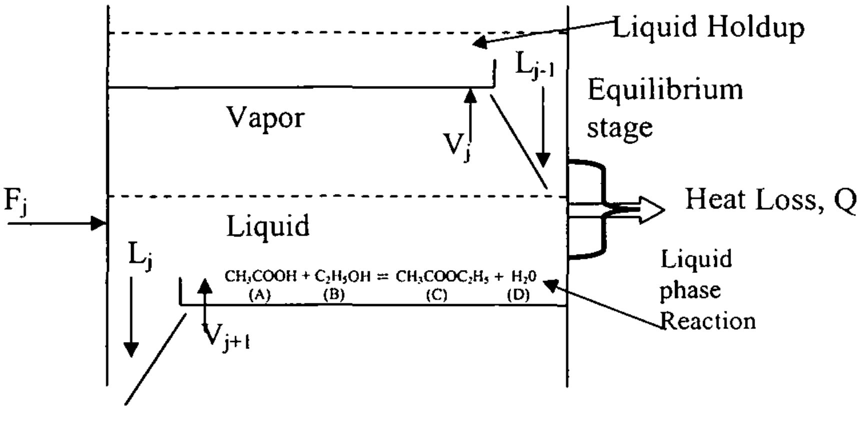

Figure 3.2: Vapor And Liquid Flow In Equilibrium Stage, J

As depicted in the figure above, vapor from the stage below and liquid from the stage above are brought into contact on the stage together with any fresh or recycled feeds. The vapor and liquid leaving the stage are assumed to be in equilibrium with each other. A complete separation process is modeled as a consequence of N of these equilibrium stages, as shown in Figure 3.3. The equations used to model these equilibrium stages are known as the **MESH** equations (**M**aterial balance, **E**quilibrium relationship, **S**ummation (constraint equation) and **H**eat (energy) balance). Additionally, the molar change in number of moles of component due to the proceeding reaction is considered in material balance equations.

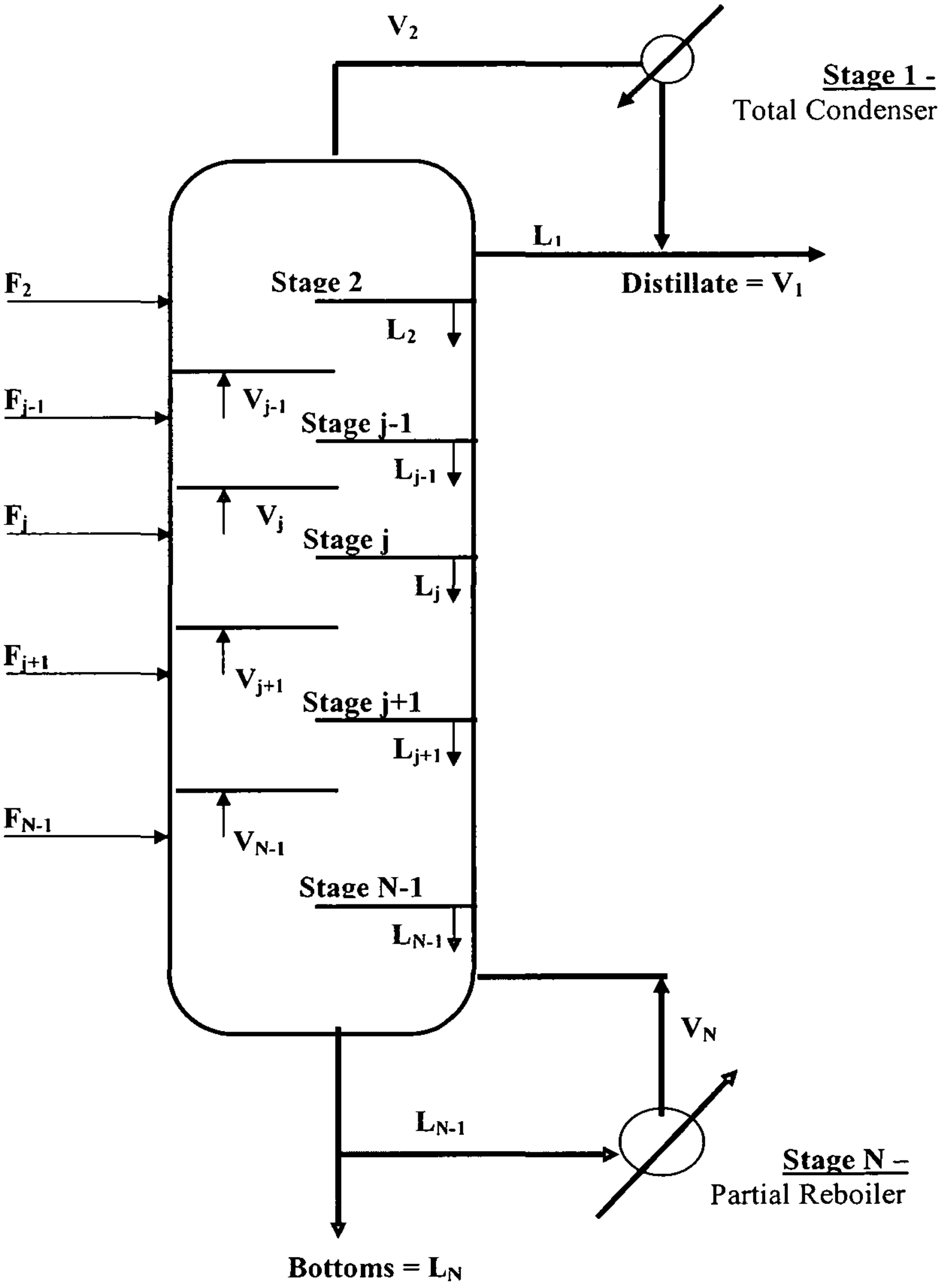

Figure 3.3: Schematic Representation of Multi-Stage Reactive Distillation Column

The solution of these sets of equations formed the basis of the rigorous model for the analysis of staged separation processes (Sinnott, 1998).

3.2.2 The MESH Equations

Steady state solution for reactive distillation modeling can be obtained by solving the modified MESH equations for distillation taking into account of the reaction in each of the individual stages. In the proposed modeling work, the modified MESH equations which, includes the equations that represent chemical reaction, are written in the unsteady state format. By integrating these equations numerically, steady state solutions were obtained. This method of solution is known as the relaxation method, which is normally used for dynamic model.

Figure 3.4 illustrates the flowchart of systematic modeling procedure for the simulation of the reactive distillation column. The flowchart below can be divided into two main stages. Stage one involves the model derivation whereby mathematical model for each of the individual component using MESH equation is developed. Meanwhile stage 2 involves simulation and solution of the mathematical model. In this stage attempt is made to solve the resulting model equations using appropriate solution technique and consequently the results are analyse by comparing it with an equivalent experimental work.

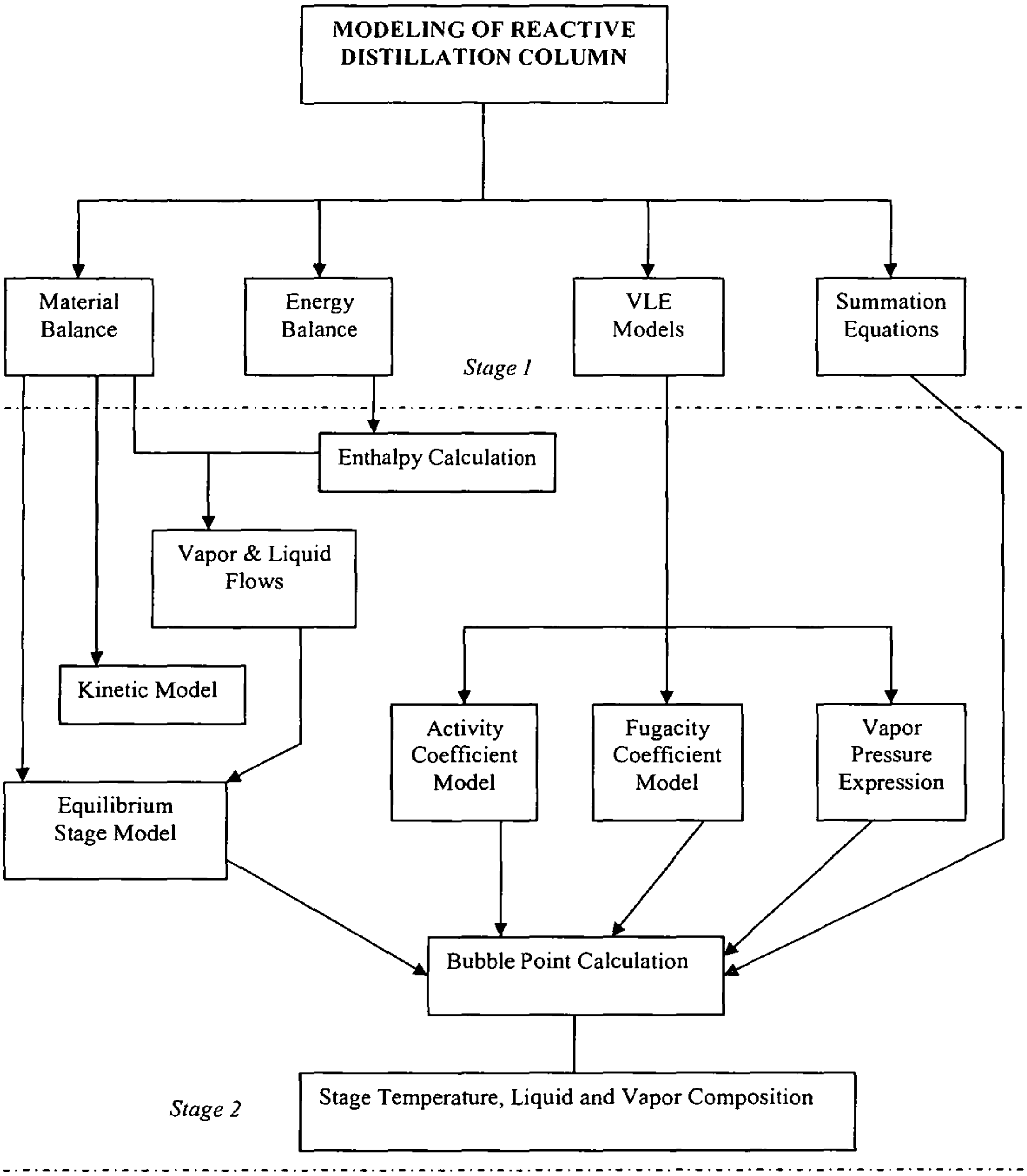

Figure 3.4: Modeling Flowchart for Reactive Distillation Column Simulation

3.3 Material Balance

In this section, the material balance for all the equilibrium stages including condenser and re-boiler is presented. The terms accounting for the reaction are incorporated to the mass balance equations for all stages in the ethyl acetate reactive distillation column in view of the possibility of reaction taking place outside the center section containing catalyst. To solve the material balance equation across the condenser, re-boiler and all the stages, the corresponding liquid, vapor and feed flow within the individual stages are required. These flows can be determined by solving the energy balance and the overall material balance equations simultaneously. The derivation of the energy balance equations is shown in the next section.

In deriving the material balance equations, the following definitions are useful in understanding and clarifying the derivation:

- Liquid hold up on stage j, hp_j is defined as the molar quantity of liquid mixture held at a specified constant value on stage j.
- $R_{j,I}$ is the number of moles generated or disappear through reaction for component i on stage j.
- Symbols $x_{i,j}$, $y_{i,j}$ and $z_{i,j}$ are the mole fraction of component i in liquid flow L_j, vapor flow V_j and feed flow F_j respectively.
- The $v_{r,i}$ term is the stoichiometric coefficient of component i for reaction r.
- The equilibrium stages are numbered downwards from the top of the column i.e., the total condenser is assigned as stage 1 while the re-boiler is assigned as stage N.

All the material balance equations i.e., overall and component balances, are derived from the basic equations shown below for overall mass balance and component mass balance respectively. Since the method for solution used is relaxation method, the equations are developed in the unsteady state form and where necessary the derivatives term are reduced to zero depending on the assumption made earlier in this section.

The unsteady state overall mass balance on a typical stage j with specific reaction R_j and liquid holdup hp_j is written as follows:

dhp_j/dt = Rate of total material (molar) change on stage j [mol/min]

= [Total molar flowrate change] + [Rate of moles change by reaction]

= (Flow in) – (Flow out) + $\sum \nu_{ir} R_{ij}$

The unsteady state component i material balance on a typical stage j with specific reaction R_j and liquid holdup hp_j is given by:

dhp_j/dt = Rate of total material (molar) change of component i on stage j [mol/min]

= $[\text{Molar flowrate change}]_{i,j}$ + $[\text{Rate of moles change by reaction}]_{i,j}$

= $(\text{Flow in})_{i,j} - (\text{Flow out})_{i,j}$ + $\nu_{ir} R_{ij}$

3.3.1 Material Balance across Condenser

The overall and component material balances across the condenser (total condenser) are derived based on Figure 3.5 below:

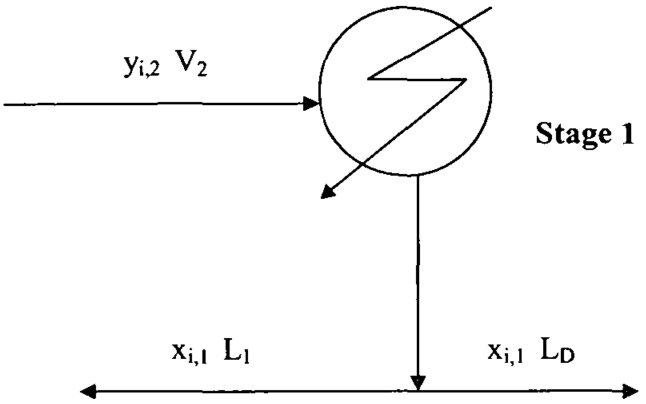

Figure 3.5: Schematic Representation of Stage 1 (Total Condenser)

The overall material balance across the total condenser is given as

$$dhp_1/dt = V_2 - L_1 - L_D + \Sigma R_{i1} \tag{3.1}$$

Due to the constant molar holdup assumption, equation 3.1 reduces to:

$$0 = V_2 - L_1 - L_D + \Sigma R_{i1} \tag{3.2}$$

where

V_2 = Vapor flow into condenser from stage 2

L_1 = Reflux flow rate

L_D = Distillate flow rate

ΣR_{i1} = net rate of change in the number of moles in the mixture due to participation in chemical reaction

Reflux Ratio

Reflux ratio is defined as the ratio of the reflux L_1 to the distillate L_D. Reflux is the liquid being returned to the column from condenser.

$$L_1 = RR\ L_D \tag{3.3}$$

where

RR = Reflux Ratio

Introducing equation 3.3 into equation 3.2 will produce

$$0 = V_2 - L_D(RR + 1) + \Sigma R_{i1} \tag{3.4}$$

The component material balance across the condenser is expressed as follows:

$$d(hp_1 x_i)/dt = V_2\, y_{i,2} - L_D\,(RR + 1)x_{i,1} + R_{i1} \tag{3.5}$$

where

R_{i1} = change in the number of moles of component i on stage j in the mixture due to participation in chemical reaction

Due to constant molar holdup assumption, equation 3.5 could be reduced to

$$(hp_1)d(x_i)/dt = V_2\, y_{i,2} - L_D\,(RR + 1)x_{i,1} + R_{i1} \tag{3.6}$$

3.3.2 Material Balance across Re-boiler

The overall and component material balance across the re-boiler (partial re-boiler) are derived based on Figure 3.6 below:

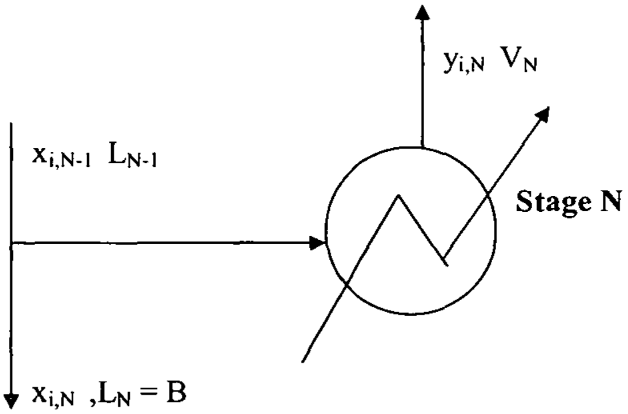

Figure 3.6: Schematic Representation of Stage N (partial Re-boiler)

Overall material balance across the re-boiler could be expressed as:

$$dhp_N/dt = L_{N-1} - L_N - V_N + \sum R_{iN} \tag{3.7}$$

$$0 = L_{N-1} - L_N - V_N + \sum R_{iN} \tag{3.8}$$

Re-boil ratio

From the definition of the re-boil ratio:

$$S = \frac{V_N}{B} \tag{3.9}$$

Using the definition shown in equation 3.9, the equation 3.8 can be simplify as follows:

$$0 = L_{N-1} - B\,(1 + S) + \Sigma R_{iN} \tag{3.10}$$

where

B = Bottoms flow-rate

S = Re-boil ratio

Based on the overall material balance, the component material balance is derived as follows:

$$d(hp_N x_i)/dt = L_{N-1}\, x_{i,N-1} - L_N\, x_{i,N} - V_N y_{i,N} + R_{i1} \tag{3.11}$$

$$hp_N d(x_i)/dt = L_{N-1}\, x_{i,N-1} - L_N\, x_{i,N} - V_N y_{i,N} + R_{i1} \tag{3.12}$$

3.3.3 Material Balance on each of the Equilibrium Stage

Material balance across the total condenser and the partial re-boiler has been derived in the preceding sections. In this section, the material balance across each of the individual equilibrium stage (tray) in the reactive distillation column is treated. Figure 3.7 below shows the schematic diagram representing the individual stages in the reactive distillation column.

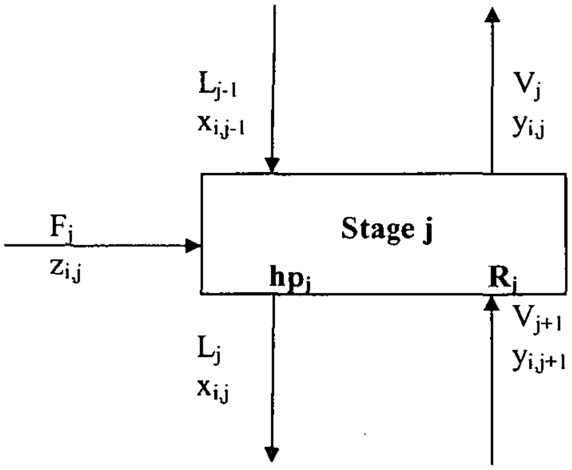

Figure 3.7: Schematic Representation of an Equilibrium Stage

The overall material balance for the equilibrium stage j is;

$$dhp_j/dt = F_j + L_{j-1} + V_{j+1} - L_j - V_j + \Sigma R_{i,j} \qquad (3.13)$$

Due to constant molar holdup assumption, Equation 3.13 reduces to:

$$0 = F_j + L_{j-1} + V_{j+1} - L_j - V_j + \Sigma R_{i,j} \qquad (3.14)$$

where

F_j = Total feed flow rate to stage j

The component material balance for the equilibrium stage j is given by:

$$d(hpj)xi_j/dt = F_j + L_{j-1} + V_{j+1} - L_j - V_j + R_{i,j} \qquad (3.15)$$

$$(hpj)dxi_j/dt = F_j + L_{j-1} + V_{j+1} - L_j - V_j + R_{i,j} \qquad (3.16)$$

In the stages where no feed is introduced, the term F_j reduces to zero.

3.3.4 Kinetic Model Formulation

Generally there are two types of catalytic reactions that can be carried out in the reactive distillation column, namely the homogenous catalyst reaction and the heterogeneous catalyst reaction. In the homogenous catalyst reaction, liquid catalyst is added to the system. While in the heterogeneous catalyst reaction, packed solid catalyst is placed in the center section of the column. In the study, attention is given to the homogeneous catalysed reaction due to the unavailability of sufficient reaction kinetics data for heterogeneously catalysed reaction. In the preceding section, the reactive distillation model is derived based on homogeneous catalysed reaction. The kinetic model and the rate expression for homogenously catalysed ethyl acetate reaction are described next.

The esterification of acetic acid and ethanol could be represented by the following stoichiometric equation:

$$\underset{(A)}{CH_3COOH} + \underset{(B)}{C_2H_5OH} \rightleftarrows \underset{(C)}{CH_3COOC_2H_5} + \underset{(D)}{H_20}$$

A = Acetic Acid
B = Ethanol
C = Ethyl Acetate
D = Water

The products of the reaction are ethyl acetate and water. Since this is a reversible reaction, under allowable condition, the ethyl acetate can react with water to reproduce acetic acid and ethanol. Using sulfuric acid as the homogenous catalyst, the rate of reaction can be significantly increased. Two different kinetic equations are used in the computations for each of the equilibrium stage i.e., with and without the catalyst.

For the system with sulfuric acid as the catalyst, the rate of reaction can be expressed as follows:

$$r = k_l C_A C_B - k_l/K_c\, C_C C_D \quad (\text{mol/sec m}^3) \tag{3.17}$$

where

$$k_l = (4.195C_k + 0.08815) \exp(-6500.1/T) \quad (\text{m}^3\text{/mol sec}) \tag{3.18}$$

and

$$Kc = 7.558 - 0.012T \tag{3.19}$$

where

k_1 = reaction rate constant (m^3/(mol sec))

C = concentration of reactant/product

R = rate of reaction (mol/sec m^3)

C_k = Catalyst concentration (vol%)

T = Temperature (K)

Kc = constant of reaction equilibrium

The catalyst concentration in equation 3.18 is assumed to be 0.4 vol%, the same as that in Nishith and Daotidis (2001), Alejski and Duprat, 1996, Huseyin okur and Mahmut Bayramoglu, 2001 and Yong et al., 2003. For the purpose of standardization with other work this value is fixed throughout this study. Since this catalyst concentration is quite low, it can be neglected in the calculation of vapor liquid equilibrium and assumed to be withdrawn from the column bottoms.

However, without the catalyst, simpler rate equations are used:

$$r = k_1 C_A C_B \quad - \quad k_2 C_C C_D \qquad (\text{mol/sec m}^3) \tag{3.20}$$

where

$$k_1 = 0.485 \exp(-7186/T) \qquad (\text{m}^3\ /\text{mol sec}) \tag{3.21}$$

$$k_2 = 0.123 \exp(-7186/T) \qquad (\text{m}^3\ /\text{mol sec}) \tag{3.22}$$

k_1 = forward reaction rate constant (m^3/(mol sec))

k_2 = reverse reaction rate constant (m^3/(mol sec))

All the constants for the above equations were obtained from the derived experimental data. For the catalysed reaction, the data were obtained form the work of Alejski et al. (1989), while for the un-catalysed reaction the data were obtained from the experimental work of Arnikar et al. (1970).

The concentrations in equation 3.17 and 3.20 can be expressed in terms of liquid compositions as follows:

$$C_{ji} = \rho_j x_{ji} \qquad (3.23)$$

where

C_{ji} = Concentration of component i on stage j (mol/m^3)

ρ_j = Molar density of the liquid phase on stage j

x_{ji} = liquid phase composition of component i on stage j

By combining equations 3.17 and 3.23, the following equation is obtained

$$r = (\rho_j)^2[k_1 x_A x_B \ - \ k_1/K_c\, x_C x_D] \qquad (\text{mol/sec m}^3) \qquad (3.24)$$

Similarly, combining equations 3.20 and 3.23 led to the equation below;

$$r = (\rho_j)^2[k_1 x_A x_B \ - \ k_2 x_C x_D] \quad (\text{mol/sec m}^3) \qquad (3.25)$$

The amount of reactant disappeared or product generated (in moles) for each component as a result of the reaction is given by the following equation;

$$R_{ji} = M_j\, .\nu_{r,i}.\, r_{ji} \quad (i = \text{ component } 1,2,3,\ldots) \qquad (3.26)$$

where

R_{ji} = volume of component i generated or disappeared due to the reaction on stage j (m^3)

r = rate of reaction as calculated from the two respective rate equations (moles/ sec.m^3)

M_j = volumetric holdup (m^3) on stage j

$\nu_{r,i}$ = stoichiometric coefficient of component i for the reaction. ($-\nu$ for reactant and $+\nu$ for product)

The principal reaction in the system is given below;

$$\underset{(A)}{CH_3COOH} + \underset{(B)}{C_2H_5OH} \rightleftarrows \underset{(C)}{CH_3COOC_2H_5} + \underset{(D)}{H_20}$$

Component stoichiometric coefficients ν_{ri} are:

$\nu_{r,a} = -1$	[forward reaction with respect to acetic acid (A)]
$\nu_{r,b} = -1$	[forward reaction with respect to ethanol (B)]
$\nu_{r,a} = 1$	[reverse reaction reaction with respect to ethyl acetate (C)]
$\nu_{r,d} = -1$	[reverse reaction with respect to water (D)]

Thus $\nu_{r,T} = \sum \nu_{r,i} = (-1) + (-1) + 1 + 1 = 0$

The above equation indicates that the net rate of change in the total number of moles in the mixture is zero. Therefore, the total number of moles on each of the equilibrium stage is constant. The term $\sum R_{ij}$ (net rate of change in number of moles) in total mass balance equation is equal to zero.

Substituting Equation 3.24 into Equation 3.26 gives the number of moles generated or disappeared on each stage for the catalysed reaction.

$$R_{ji} = M_j . \nu_{r,i} (\rho_j)^2 [k_1 x_A x_B - k_1/K_c \, x_C x_D] \quad \text{mol/m}^3 \qquad (3.27)$$

Similarly, substituting Equation 3.25 into Equation 3.26 gives the number of moles generated or disappeared on each stage for the uncatalysed reaction.

$$R_{ji} = M_j . \nu_{r,i} (\rho_j)^2 [k_1 x_A x_B - k_2 \, x_C x_D] \quad \text{mol/m}^3 \qquad (3.28)$$

Equations 3.27 and 3.28 are the two equations used in the simulation model to account for chemical reaction on each of the stage.

3.3.5 Damkohler Number for Homogenous Reaction

For a continuous flow reactor, the general definition of Damkohler number (Da) given by Fogler (1992), with reactant A taken as reference for the reaction, is;

$$\mathrm{Da} = \frac{\text{Rate of consumption of A by reaction}}{\text{Rate of transport of A by convection}}$$

Damkohler number provide quick estimation on the degree of conversion that can be achieved in a continuous flow reactor e.g. in continuous stirred tank reactor (CSTR). For a first order reaction, the Damkohler number become dimensionless. However, for second and higher order reaction, the Damkohler number will have an appropriate unit as could be shown from it's definition. The significance of the Damkohler number is that it provides a quick indication on the conversion of a reaction in any continuous reactor. It is vital to know the values of the respective Damkohler number that reflects high or low conversion. Normally a value of Da = 0.1 or less will give less than 10 % conversion and a value of Da = 10.0 or greater will usually give conversion more than 90 %.

For homogenously catalysed reactive distillation process, the Damkohler number is defined as a parameter that represents the measure of the rate of reaction relative to the product removal. According to Chen et al. (2000) and Venimadhavan et al. (1994), the Damkohler Number is defined as a dimensionless ratio of a characteristic liquid residence time (H_T^R / F) to the characteristic reaction time ($1/k_{f,ref}$) as shown in the equation below;

$$\mathrm{Da} = (H_T^R / F) / (1/k_{f,ref}) = H_T^R k_{f,ref} / F \qquad (3.29)$$

where H_T^R is the total reactive liquid holdup (mol) in the column, F is the total feed to the system and $k_{f,ref}$ (s^{-1}) is the reference forward rate constant for homogeneous pseudo-first order system. The reference forward rate constant $k_{f,ref}$ has the units of sec^{-1} or hr^{-1} regardless of the order of the reaction thus giving an advantage to the use of simple universal definition for the dimensionless Damkohler number for all reaction orders (Chen et. al., 2000; Venimadhavan et. al., 1994). $k_{f,ref}$ is evaluated at a reference temperature, e.g. the boiling point of the most volatile components in the system. In the case considered for the study performed, ethyl acetate is taken as the reference.

For homogeneously catalysed reactive distillation, a small value of Damkohler number implies one or more of the following conditions; a slow forward rate, a small liquid stage holdup, or a large feed flow-rate. According to Venimadhavan et al. (1994) and Chen et al. (2000), the reference rate constant is calculated as a fixed value. Therefore, changes in the Damkohler number imply changes in the liquid holdup on each of the reactive stage, assuming that the feed flow-rate is kept fixed throughout the operation. In general, when Damkohler number is smaller than 1, the process behaves as a non-reactive or normal distillation i.e., theoretically negligible amount of liquid holdup and no liquid phase reaction occurs. On the contrary, when the Damkohler number is much greater than 1, the process is said to have reached the equilibrium reactive limit for the reaction.

It should be noted that there is an optimum value for the Damkohler number for any specific reactive distillation system. As mentioned earlier, a large value of the Damkohler number implies large amount of liquid holdup on each stages. Therefore, the Damkohler number needs to be varied within such limit that represent a realistic liquid holdup, which according to Chen et al. (2000) is approximately in the range of 0.5 to 2 m^3. The optimum Damkohler number is not the same for all reactive distillation systems because it also depends on the value of the reference rate constant (calculated by equation 3.29) for any specified system.

In view of the fixed reference rate constant and the feed flow-rate used for the operation of the reactive distillation, the changes in the Damkohler number is only subjected to the variation made in the liquid holdup at each of the stages. For the case of ethyl acetate system, H_T^R (shown in Equation 3.29) represent the total holdup in the system, as reaction occurs throughout the column. Equation 3.29 can be rearranged as follows:

$$\text{hpt} = \text{Da} \,.\, F \,/\, k_{f,ref} \qquad (3.30)$$

where

hpt = Total liquid phase hold up in the system

F = Total feed rate into the system

$$k_{f,ref} = k_1 \,.\, \rho_r = [(4.195C_k + 0.08815)\exp(-6500.1/T)] \,.\, \rho_r \quad (\text{sec}^{-1}) \qquad (3.31)$$

where

ρ_r = Liquid phase molar density of the lowest boiling pure component in the system at reference temperature

The lowest boiling point component in the system studied is ethyl acetate. Therefore, the reference value used for T in Equation 3.30 refers to the boiling point of ethyl acetate, 350.25K. The reference molar density used is 1.6907×10^4, which is molar density of the reference component ethyl acetate. Replacing these values into equation 3.30 gives:

$$k_{f,ref} = [1.7662 \exp(-6500.1/T)] \,.\, 1.6907 \times 10^4 = 2.6018 \times 10^{-4} \quad (\text{sec}^{-1}) \qquad (3.32)$$

and replacing equation 3.32 into 3.30 gives

$$\text{hpt} = 3843.5(\text{Da} \,.\, F) \qquad (3.33)$$

In the simulation model used for the present study, equation 3.33 is used to calculate the total holdup in the system by specifying the Damkohler number (input variable). By treating Damkohler number as one of the input variable, it would be easier to study the impact of varying Damkohler number on the performance of the ethyl acetate reactive distillation column.

3.4 Energy Balance

The energy balance equations are derived in this section for each of the equilibrium stage in the column. The combinations of energy balance and overall material balance equations are then used in the developed simulation model to calculate liquid and vapor flow-rates throughout the column. Figure 3.8 illustrates the schematic diagram used for the derivation of the energy balance. It should be noted that the heat of reaction is not included in the energy balance equation because the enthalpies used in the equations to be derived, referred to the component's elemental state. Therefore the heat of reaction is accounted for automatically and no separate term is needed.

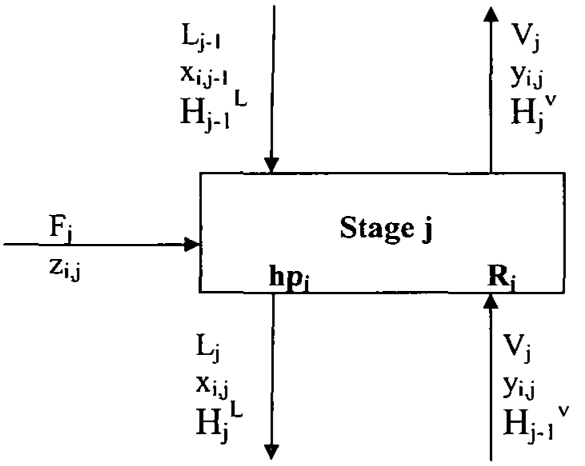

Figure 3.8: Schematic Representation of an Equilibrium Stage for Deriving Energy Balance Equation

The enthalpy balance across stage j on figure 3.8 is given by;

$$d(hp_jH_j)/dt = L_{j-1}H^L{}_{j-1} + V_{j+1}\,H^v{}_{j+1} + F_iH_{z,j} - L_j\,H^L{}_j - V_j\,H^v{}_j \quad \mathbf{(j=2,3,\ldots,N-1)} \tag{3.34}$$

where

$H^L{}_j$ = molar enthalpy of liquid phase on stage j (cal/mol)

$H^v{}_j$ = molar enthalpy of vapor phase on stage j (cal mol)

$H_{z,j}$ = molar enthalpy of feed introduced into stage j (cal/mol)

The equation is applicable only from stage 2 to stage N-1, excluding the condenser and reboiler. For stages without feed stream, the equation reduces to:

$$d(hp_jH_j)/dt = L_{j-1}H^L_{j-1} + V_{j+1}\,H^v_{j+1} \;+ - L_j\,H^L_j - V_j\,H^v_j \qquad (3.35)$$

For condenser (j=1) and re-boiler (j=N) the following expressions are used for representing the energy balance on these stages:

Energy Balance across condenser (stage1):

$$d(hp_1H_1)/dt = V_2\,H_2^v \;- (L_1 + L_D)\,H_1^L + Q_c \qquad (3.36)$$

where

Q_c = Condenser hear duty (cal)

Energy Balance across reboiler (stage1):

$$d(hp_NH_N)/dt = L_{j-1}\,H_{j-1}^L \;- L_N\,H_N^L - V_N\,H_N^v + Q_R \qquad (3.37)$$

where

Q_R = Reboiler heat duty (cal) (3.38)

Due to the assumptions of constant enthalpy and constant liquid hold-up, all the derivatives terms in the equations above are reduced to zero. The molar enthalpies for the liquid and vapor phase are calculated based on methods described next.

3.4.1 Enthalpy Calculation

The enthalpy of vapor phase for a component at ideal gas state is given by

$$h_{i,j}{}^{o}{}_{v} = ?^{T}_{0}\, c_{pv}{}^{o}\, dt \text{ (cal/mol)} \qquad (3.39)$$

where

$h_{i,j}{}^{o}{}_{v}$ = Vapor phase partial molar enthalpy of component i on stage j

c_{pv} = Vapor phase heat capacity at constant pressure (cal/mol.K)

T = Temperature (K)

As shown in the equation, the enthalpy of the component is calculated based on zero enthalpy as the reference state. This justifies the exclusion of enthalpy of reaction in the energy balance equation derived earlier.

Integrating equation 3.39 lead to the molar enthalpy equation below;

$$h_{ij}{}^{o}{}_{v}=c1_{i}*T+c2_{i}/2*T\hat{}2+c3_{i}/3*T\hat{}3+c4_{i}/4*T\hat{}4 \quad \text{(i = comp a,b,c,...)} \qquad (3.40)$$

where

c1, c2, c3, c4 = Heat capacity coefficients

The respective heat capacity coefficients for all the components are given in Table 3.2 below.

Table 3.2: Coefficients For Molar Enthalpy Equation.

Component	c1	c2	c3	C4
Acetic acid	14.6392	0.2299e-1	-0.1022e-4	0.2589e-8
Ethanol	14.0485	0.2153e-1	-0.4607e-5	-0.4607e-8
Ethyl acetate	24.9082	0.3329e-1	0.7317e-6	-0.1247e-7
Water	7.9857	0.4633e-3	0.1403e-5	-0.6578e-9

With the assumptions of ideal gas law vapor enthalpy of the mixture of four components becomes:

$$H_j^V = \sum (y_{i,j} h_{i,j}{}^o{}_v) \quad (3.41)$$

where

H_j^V = Molar enthalpy of vapor stream leaving stage j

$y_{i,j}$ = vapor composition of component i on stage j

The liquid phase enthalpy is given by the following equation:

$$H_j^L = \sum x_{i,j} \; [h_{i,j}{}^o{}_v - \lambda_{ij}] \quad (3.42)$$

where

$\lambda_{i,j}$ = heat of vaporization of component i on stage j

H_j^L = Molar enthalpy of liquid stream leaving stage j

$x_{i,j}$ = liquid phase composition of component i on stage j

The heat of vaporization is calculated using the following relationship:

$$\lambda_{i,j} = B_i R T_j\text{^}2 \,/\, (T_j + Ci)\text{^}2 \quad (i = \text{ component a,b,c,...}) \quad (3.43)$$

where

R = gas constant, (1.987 cal/mol.K)

T_j = Stage j temperature, (K)

B_i and C_i = Constants used in Antoine equations (refer to Table 3.3)

Table 3.3: Constants for Antoine Equation

Component	A_i	B_i	C_i	P_c (psia)
Acetic acid	7.20359	7376.157	410.1814	839.1
Ethanol	7.43437	6162.36	359.3826	925.3
Ethyl acetate	6.3307	5440.049	373.48	556
Water	6.53247	7173.79	389.4747	3206.7

3.5 Vapor Liquid Equilibrium

Mixture of ethyl acetate-ethanol-water-acetic acid is considered to be highly non-ideal in the liquid phase, due to the presence of polar molecules. Therefore, it is necessary to give a careful attention to the thermodynamics correlation selected to compute the vapor liquid equilibrium of the system. Figure 3.9 below represents the state of vapor and liquid in equilibrium as a function of physical properties of vapor and liquid respectively.

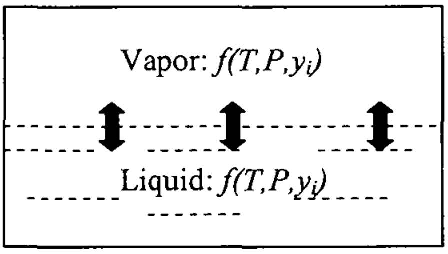

Figure 3.9: Schematic Representation of State of Vapor Liquid Equilibrium

To account for non-ideal behaviour, the phase equilibrium is described using activity coefficients for liquid phase and fugacity coefficients for the vapor phase. Vapor liquid equilibrium relationship is given by the equation;

$$y_i \varphi_i P = x_i \gamma_i P_i^o \qquad (i = \text{component } 1,2,3,\ldots) \qquad (3.44)$$

where

y_i = Vapor phase composition of component i

x_i = Liquid phase composition of component i

γ_i = Liquid phase activity coefficient of component i

φ_i = Vapor phase fugacity coefficient of component i

P = Total pressure of the system

P_i^o = Saturated vapor pressure of component i

Since the ethyl acetate reactive distillation column operates at modest pressure, the vapor phase non-ideality can be neglected. Therefore, vapor phase fugacity coefficient in Equation 3.44 is equal to 1 and equation 3.44 reduces to:

$$y_i P = x_i \gamma_i P_i^o \qquad (i = \text{component } 1,2,3,\ldots) \qquad (3.45)$$

If we assume that $\gamma = 1$, equation 3.45 reduces to the familiar relation known as Raoult's law for ideal solution and the phase equilibrium calculation would be considerably simpler. However such an approximation would not represent the real condition and will affect the simulation results.

3.5.1 Vapor Pressure Calculation

The saturated vapor pressure of the components in a system that are required for calculating the vapor liquid equilibrium (VLE) can be determined from the Antoine's equation. In the equation, the component-saturated vapor pressure is a function of temperature only. The Antoine equation used for calculation of saturation pressure P_i^o at given temperature T is given by

$$\ln P_i^o / P_c = A_i - B_i / (T_i + C_i) \qquad (3.46)$$

where

P_i^o = vapor pressure, psia

$P_{c,i}$ = Critical pressure of component i, psia

T_i = Temperature, °F

A_i , B_i and C_i are the Antoine equation constants for component i. The constants for each of the component in the system is tabulated below:

Table 3.4: Constants for Antoine Equation

Component	A_i	B_i	C_i	P_c (psia)
Acetic acid	7.20359	7376.157	410.1814	839.1
Ethanol	7.43437	6162.36	359.3826	925.3
Ethyl acetate	6.3307	5440.049	373.48	556
Water	6.53247	7173.79	389.4747	3206.7

3.5.2 Activity coefficient Model

Accurate prediction of liquid phase activity is vital as non-ideality in the liquid phase is relatively more significant even at low pressure. There were various models to predict liquid phase activity coefficient and they include empirical and semi-theoretical model such as Margules, Van Laar, Wilson, NRTL, UNIQUAC and UNIFAC. However, the most reliable method for predicting liquid phase activity coefficient is the empirical model derived based on experimental data.

For the mixture of ethyl acetate-ethanol-water-acetic acid used in the simulation of the reactive distillation in study, the empirical model developed by Suzuki et al. (1977) to determine the liquid activity coefficients is used. For the process improvement purposes later in the study, a different method is used to predict the liquid activity coefficient model, namely UNIFAC model as this method is deem to be suitable for the configuration to be proposed. In the proceeding sections, the model development for the empirical and UNIFAC model is described.

3.5.2.1 Empirical Model – Suzuki et al.(1977)

Empirical model to determine liquid phase activity coefficient for the mixture of ethyl acetate-ethanol-water-acetic acid is given below.

The activity coefficients are given by the equation;

$$\begin{aligned}\log_{10}\gamma_a = {} & ((a1*x_b(iT){}^\wedge 2)+(a2*x_c(iT){}^\wedge 2)+(a3*x_d(iT){}^\wedge 2) + \\ & a4*x_b(iT)*x_c(iT)) + (a5*x_b(iT)*x_d(iT)) + \\ & (a6*x_c(iT)*x_d(iT)) + (a7*x_a(iT)*x_b(iT){}^\wedge 2) + \\ & (a8*x_a(iT)*x_c(iT){}^\wedge 2) + (a9*x_a(iT)*x_d(iT){}^\wedge 2) + \\ & (a10*x_a(iT)*x_b(iT)*x_c(iT)) + (a11*x_b(iT)*x_c(iT)*x_d(iT)) \\ & + (a12*x_c(iT)*x_d(iT)*x_a(iT)) + (a13*x_d(iT)*x_a(iT)*x_b(iT)) \\ & + (a14*x_b(iT)*x_c(iT){}^\wedge 2) + (a15*x_b(iT)*x_d(iT){}^\wedge 2) + \\ & (a16*x_c(iT)*x_d(iT){}^\wedge 2))\end{aligned} \tag{3.48}$$

** Remaining activity are obtained by rotating the subscripts on the x's as follows:

$$a \longrightarrow b \longrightarrow d \longrightarrow c$$

a1, a2, a3, ..., a16 are constants which are given in the table below:

Table 3.5:Empirical Model (Suzuki) Model Constants Values

	Acetic Acid (a)	**Ethanol (b)**	**Ethyl Acetate (c)**	**Water (d)**
a1	-0.554296	0.581778	0.688636	-0.060136
a2	-0.103685	-0.257329	0.375534	1.865750
a3	-0.324357	0.209245	0.024303	0.229575
a4	-2.013350	-0.314853	1.778630	0.468416
a5	-0.705455	-0.562636	1.275480	0.355191
a6	-2.253620	0.451732	0.696279	1.511000
a7	0.837926	-0.115411	0.936722	-0.059968
a8	0.434061	0.074053	0.717779	-3.159970
a9	0.523760	0.069531	0.449357	0.067399
a10	3.354000	-0.409472	1.129140	1.037910
a11	-3.253310	-0.369985	-2.110990	-1.922250
a12	5.903290	-0.082339	0.746905	-0.755731
a13	-0.534056	0.187010	1.449790	0.941858
a14	-0.452660	0.192416	-1.642680	-1.365870
a15	0.197296	1.092470	0.120436	0.365254
a16	0.014715	-0.172565	0.330018	-2.1381180

3.5.2.2 Activity Coefficient Model – The UNIFAC Method

In the absence of reliable vapour liquid equilibrium experimental data or model, the liquid phase activity coefficients could be estimated by treating the solution as a mixture of functional groups instead of molecules, particularly in the presence of polar components. The UNIFAC (UNIQUAC Functional-group Activity Coefficients) group-contribution method, introduced by Fredenslund et al. (1977) is used in the study. The UNIFAC method is known to have several advantages over the other group contribution methods in the sense that (i) the parameters are essentially independent of temperature; (ii) the size and binary interaction parameters are available for a wide range of functional groups types; (iii) the predictions is reliable over a temperature range of 275 K to 425 K and for a pressure range of up to several atmosphere; and (iv) the extensive comparisons with experimental data are available.

The UNIFAC method, develop by Fredenslund et al. (1977) is similar in concept to the ASOG method, but it is based on the UNIQUAC equation

$$\ln\gamma_i = \ln\gamma_i^c + \ln\gamma_i^R \qquad (3.49)$$

where the superscript *C* refers to the combinatorial part of the activity coefficient and the superscript *R* refers to the residual part of the activity coefficient.

The combinatorial part of the activity coefficient is computed using the following expression

$$\ln\gamma_i^c = \ln\frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln\frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i}\Sigma_j x_j l_j \qquad (3.50)$$

where

$$l_i = (z/2)(r_i - q_i) - (r_i - 1) \qquad (3.51)$$

$$qi = ?\,_k \nu_{ki} Q_k \qquad (3.52)$$

$$r_i = ?\,_k \nu_{ki} R_k \qquad (3.53)$$

$$?_i = x_i q_i / ?_j x_j q_j \qquad (3.54)$$

$$F_i = x_i r_i / ?_j x_j r_j \qquad (3.55)$$

x_i = mole fraction of component i in the mixture

v_{ki} = count of the kth group in component I

R_k = a measure of Van der Waals volume ratio for group k

Q_k = a measure of Van der Waals area ratio for group k

Group parameters R_k and Q_k are obtained from Van der Waals group volume V_{wk} and surface area A_{wk} given by Bondi (1968)

$$R_k = \frac{v_{wk}}{15.17} \qquad (3.56)$$

$$Qk = \frac{A_{wk}}{2.5 \times 10^9} \qquad (3.57)$$

The number 15.17 and 2.5×10^9 are normalization factors recommended by Abrams and Prausnitz.(1975). Values of Rk and Qk are given in the appendix 1. The residual part of the activity coefficient is computed as follows

$$\ln \gamma_i^R = \Sigma_k v_{ki} (\ln \Gamma_k - \ln \Gamma_{k,i}) \qquad (3.58)$$

where the summation are over all groups, and

Γ_k = activity coefficient for group k in the mixture

$\Gamma_{k,i}$ = activity coefficient for group k in pure component i

The activity coefficient Γ_k is computed as follows

$$\ln\Gamma_k = Q_k[1-\ln(\sum_m \Theta_m \psi_{mk}) - \sum_m(\frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}})] \qquad (3.59)$$

where the summation are over all groups, and

$T_m = X_m Q_m / ?_n X_n Q_n$, area fraction of group *m* (3.60)

$X_m = ?_j x_j v_{mj} / ?_n ?_j x_j v_{nj}$, mole fraction of group m in the mixture (3.61)

$?_{mn} = \exp(-a_{mn}/T)$ (3.62)

$\{a_{mn}\}$ = set of group interaction parameters, a_{mn} ? a_{nm}

The activity coefficient ln G_{ki} is computed as follows

$$\ln\Gamma_{ki} = Q_k[1-\ln(\sum_m \Theta_{mi} \psi_{mk}) - \sum_m(\frac{\Theta_{mi} \psi_{km}}{\sum_n \Theta_{ni} \psi_{nm}}) \qquad (3.63)$$

where the summation are all groups in component *i*, and

$T_{mi} = X_{mi} Q_m / ?_n X_{ni} Q_n$, area fraction of group *m* in component *i* (3.64)

$X_{mi} = v_{mj} / ?_n v_{ni}$, mole fraction of group m in component *i* (3.65)

Values for the group-interaction parameters a_{mn} must be evaluated from experimental phase-equilibrium data. Sets of values *of* a_{nm} and a_{mn} taken from the work of Fredenslund et al. (1977) and are presented in appendix 1.

3.6 Summation Equations

In each stage of the reactive distillation column, the component liquid and vapor compositions must sum up to unity. These constraints are included in the stage-to-stage calculation so that the stage vapor and liquid compositions are validated and can be confidently used by other associated model equations. Equations for these summation equations are explained below.

The summation equation for liquid composition i on stage j is given as:

$$\sum_{i=1}^{c} x_{i,j} = 1.0 \qquad (3.50)$$

While the summation equation for vapor composition i on stage j is given as:

$$\sum_{i=1}^{c} y_{i,j} = 1.0 \qquad (3.51)$$

where c is the total number of components.

3.7 Simulation and Solution Strategy

In simulation, the input and operating variables of a process are specified and the task is to solve for the resulting outputs. The obtained results are then compared to experimental or established data published, in order to measure how well the model compliment with the real world situation. On the contrary, in design, the input and selected output variables are specified and the task is to determine the optimal process configuration and the optimal design parameters that could deliver the given product specifications. Figure 3.10 shows the summary flowchart of the steps or procedures taken in simulation of ethyl acetate reactive distillation column simulation.

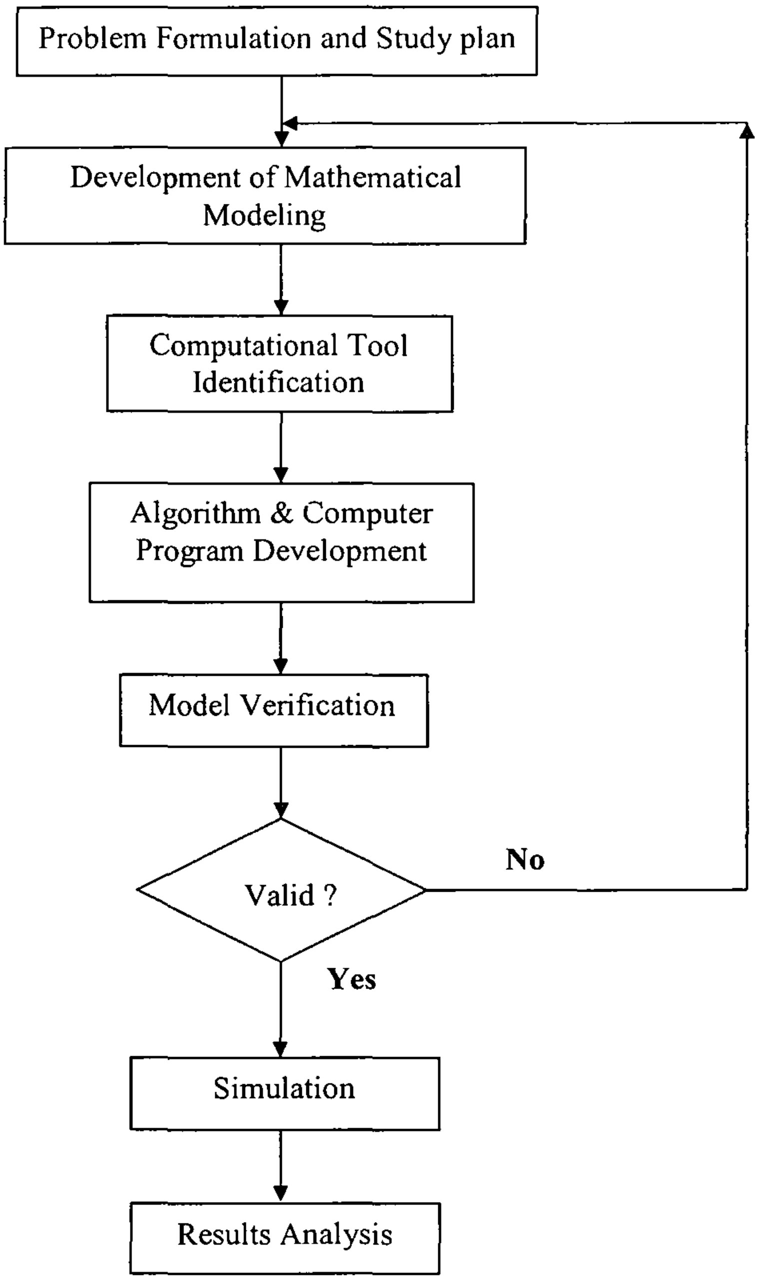

Figure 3.10: Procedure for Reactive Distillation Process Simulation

3.7.1 Simulation Procedures

Step 1: Data Collection

This is the initial step employed in the simulation of ethyl acetate reactive distillation column. All the necessary information regarding modeling and simulation are gathered from reliable sources. Important information includes kinetic model, vapor liquid equilibrium (VLE) model, equilibrium stage model, and the associated MESH equations. Once the necessary models have been determined, data related to these models such as parameters for VLE models, Antoine constants, components physical properties, components critical properties, components thermodynamics data properties and enthalpy data are gathered. In addition, column specifications such as configuration, feed specifications and input conditions are also determined in this step. Typical data and column configuration used in this study is shown in Figure 3.11. It should be noted that the same configuration shown in Figure 3.11 was used in the experimental work of Komatsu et al. (1977).

Step 2: Mathematical Model Development

Following to the above step, the mathematical model based on MESH equations are then developed. In deriving the model equations, all the assumptions involved for modeling and simulation are taken into account. In addition the strategy for solving the reactive distillation modeling equations is also identified. The resulting modeling equations in this study contain sets of differential-algebraic equations (DAE). Several numerical integration methods such as classical 4th order Runge-Kutta method, Adams method and Stiff Adams method and Stiff method based on backward differentiation formula (Gear, 2002) are available to solve differential-algebraic equations.

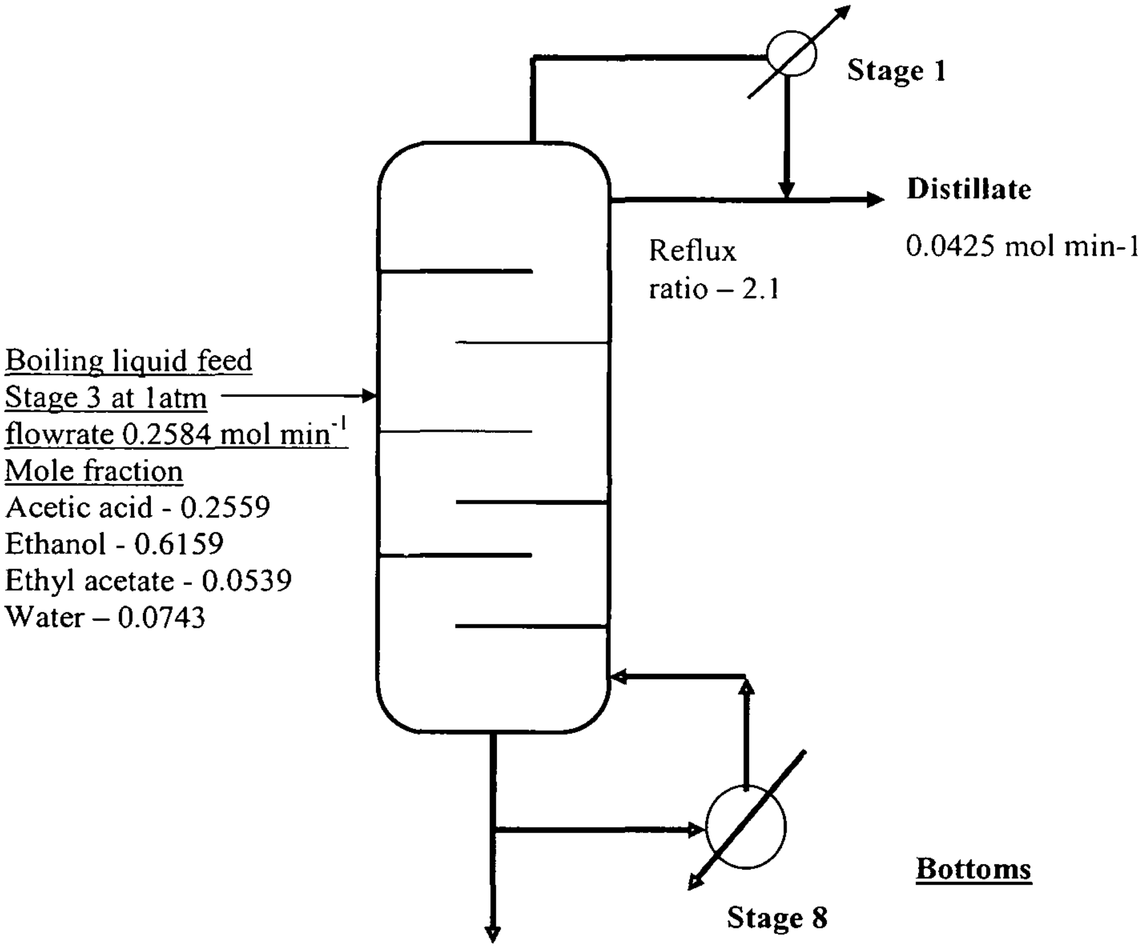

Figure 3.11: Typical Reactive Distillation Column Configuration And Specifications For Single Feed Un-Catalytic Ethyl Acetate Synthesis (Komatsu 1977)

Step 3: Computational Tool Identification

As the modeling equations involve sets of highly nonlinear differential and algebraic equations (DAE), the solution requires high-speed digital computer simulation. The solver can be a developed computer program or suitable available commercial software. In this study computer program is preferred over commercial software due to its flexibility and the developed computer source code can be extended for dynamics and control studies.

The simulation model was developed using MATLAB^{TM} which requires programming to be done for the mathematical model developed. MATLAB^{TM} is the main software used throughout this study to model and simulate ethyl acetate reactive distillation column. MATLAB^{TM} integrates computation, visualization and programming in an easy-to-use environment. MATLAB^{TM} is distinguished by its ability to perform all the simulation calculations in matrix form, its large library for built in functions, its strong structural language and its rich graphical visualization tools (Constantinides, 1999). For this study, the built in functions such as ODE and non-linear algebraic equations solvers were able to reduce the programming effort significantly.

Step 4: Algorithm and Program Development

Prior to the development of solution algorithm, suitable methods need to be identified in order to solve the steady state equilibrium stage model. Some of the approaches are:

- Bubble point method
- Modified newton's method
- Relaxation method
- Minimization method
- Inside-out method
- Homotopy continuation method

In this study, relaxation method was employed to obtain the steady state solution. As most of the methods listed above are very sensitive to initial estimations, relaxation method was chosen. Convergence has been the main problem with the other methods especially when the starting data was estimated with great errors. In addition, the method could be used also to study the dynamic behavior of the system.

Relaxation method involves writing the MESH equations in the unsteady-state form and integrating them numerically until a stable solution which represents the steady state solution is found (Komatsu, 1977; Jelinek and Hlavacek, 1976). In this method, the time derivatives in the modeling equations need not be set to zero. Thereby the modeling equations consists of large combination of complex nonlinear differential and algebraic equations (DAEs) that necessitates a numerical solution in order to obtain the steady state solution.

The algorithm for solving sets of differential and algebraic equations (DAEs) for the proposed reactive distillation column is shown in Figure 3.12. Based on the algorithm, the programming code for the system has been developed successfully. The developed main programming and subroutines were carefully tested and debugged in order to correct logic error. Continuous modifications were then made on the programming code to improve the smoothness of the program.

The sets of differential and algebraic equations (DAEs) used for the model have resulted in stiff equations. The suitable method for solving such system of stiff differential and algebraic equations (DAEs) was found to be the implicit, multi-step of varying order method. The MATLAB^{TM} built in function i.e., ODE15, was chosen in view of its capability of solving large systems of stiff differential and algebraic equations (DAEs). The MATLAB^{TM} ordinary differential equations (ODE) solver solves the sets of differential and algebraic equations (DAEs) described in the MATLAB^{TM} function file, which gives the modeling equations in MATLAB^{TM} language from time T_o to T_{final} from the given initial conditions.

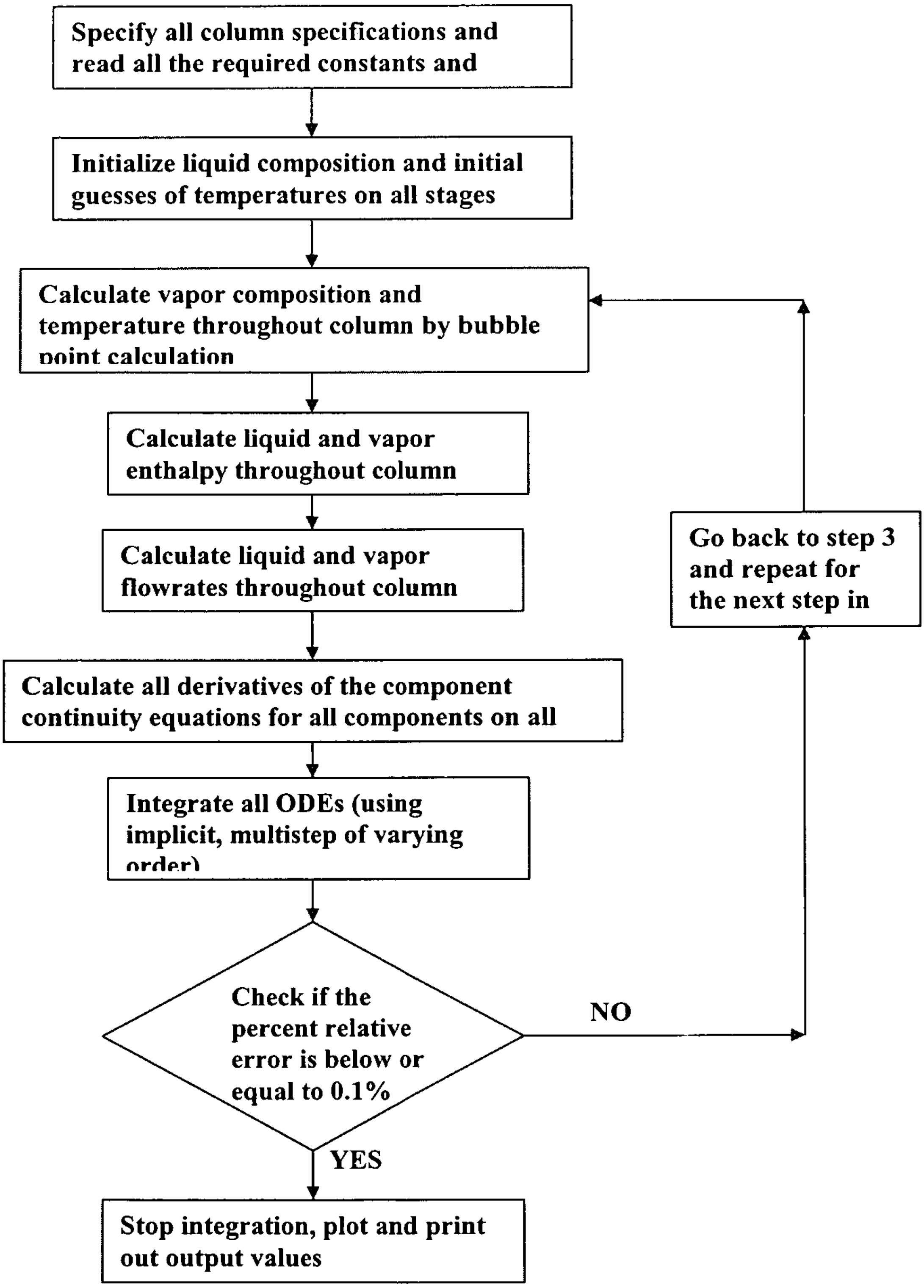

Figure 3.12: Algorithm For Solving Differential And Algebraic Equations From The Proposed Reactive Distillation Mathematical Model.

The following give the algorithm for solving sets of differential and algebraic equations (DAEs) (Chen et al., 2000), which is thoroughly translated into the programming codes for the reactive distillation simulation:

1. Specify all the specifications for the reactive distillation column in consideration and read all the constants and parameters related to model equations.
2. Initialize liquid compositions $x_{i,j}$ for the column or use last converged simulation results.
3. Calculate vapor compositions $y_{i,j}$ and temperature T_j on stage j through bubble point flash calculation.
4. Calculate liquid enthalpy and vapor enthalpy on stage j.
5. Calculate liquid and vapor rates throughout the column.
6. Calculate all the mass balance derivatives, and then calculate the residual from average of the absolute value of all derivatives.
7. Check if the residual is less than the specified error tolerance (e.g. 1.0×10^{-4}). If yes, converged steady state solution is obtained, then go to next step. If no, predict next $x_{i,j}$ by calling the integration routine, then got to step 3.
8. Stop integration, plot and print the output values such as liquid and vapor phase composition values, temperature profiles of the column and etc.

Step 5: Simulation study and model validation

After satisfactorily generating the MATLAB™ programming codes, the reactive distillation model is simulated by executing the codes in MATLAB™ environment. Initially the simulation model was verified with published experimental work using similar operating environment. This is followed with further verification against other published simulations results. Upon satisfactory results, the simulation model is then experimented with various conditions to obtain the behaviour of the system. If for some reasons the results are not found to be satisfactory, the mathematical model developed in Step 2 is revised and the following steps in Figure 3.12 need to be repeated.

Step 6: Result analysis

Finally, the results obtained from the simulation using different operating conditions are analyzed by means of plotting graphs and compared with other established results available in the literature. In this study, separate chapter is allocated to study the behavior of the system at various sets of input conditions and the impact on the performance of the column.

3.7.2 Column Initialisation

Before starting the simulation, the model equations describing the reactive distillation process must be first initialised, otherwise the simulation will fail to converge. The initial values that have to be specified to the simulation program consist of the liquid compositions and the temperatures for all the stages inside the column. With these values, the corresponding vapor compositions and stage temperature can be calculated through bubble point calculation. In addition, with these initial values, all the associated models equations can be initialised prior to starting the iteration.

In the present work, column initialization is relatively simple as the solution method employed in the simulation is capable of handling even wild initial guesses. However, it should be noted that the penalty associated with inappropriate guess is longer computing time required for convergence. Therefore, it is advisable to set realistic initial guess for simulation purpose. Initial guess for compositions on all stages are set equivalent to the feed compositions introduced to the system and the temperatures are set equivalent to the feed temperature.

Besides good initial estimation, the chosen numerical method based on backward differentiation formula is very efficient and greatly help the convergence and reduce the simulation time.

3.7.3 Bubble Point Calculation

In the reactive distillation simulation, bubble point calculation is vital as it provides the temperatures and the liquid and vapor phase compositions throughout the column. With the given system pressure and the initial liquid compositions, the temperature and vapor compositions is calculated through the bubble point calculation. The temperature and vapor compositions obtained are then used in the material and energy balance calculation. The vapor and liquid flows are determined by solving the total material balance and the energy balance simultaneously. The kinetic model included in the material balance will further update the liquid composition until steady state is achieved. The vapor liquid equilibrium model accounting for the non-ideality in liquid phase and the vapor pressure calculation are made with reference to the stage temperature and are included in the bubble point calculation. All the calculations are performed within the constraint of the summations equations.

In simulation, the stage-wise bubble point calculations were performed as describe above to obtain the temperature and composition profiles. The algorithm below is employed for performing the stage-wise bubble point calculation (Doherty and Malone, 2001):

1. Specify P and $x_{i,j}$.
2. Guess T.
3. Calculate P_j^o (T) from the Antoine equation (3.46).
4. Calculate $\gamma_{i,j}$ (T,x), from the empirical activity model equation (3.48) or UNIFAC equation.
5. Calculate $y_{i,j}$ from equation (3.45).
6. If $\sum_{i=1}^{c} y_{i,j} = 1.0$ is sufficiently close to unity, then stop iteration. Otherwise, adjust the T and return to step 3.

This is an iterative procedure whereby MATLAB^{TM} built in function, *FZERO* was used and has significantly ease the calculation procedure.

MODEL VALIDATION

4.1 Introduction

The developed simulation model described in the previous chapter is implemented in MATLAB^{TM} environment to obtain a steady state solution. The results obtained are compared against equivalent experimental and simulation works in order to determine how far the model reconciles with published results. The established experimental work reported by Komatsu (1977) was used as one of the reference. The result of his experimental work is shown in Table 4.1 for a single feed un-catalytic reactive distillation column. A reported simulation work by Alejski et al. (1988) was used as another source of reference whereby they have also used similar configuration as proposed by Komatsu (1977).

To further confirm the validity of the developed simulation model, comparison was then made against a more complex model developed by Nishith and Daoutidis (2001) in which they proposed a double feed catalytic reactive distillation column. The simulation result of their study is shown in Table 4.2. There were some distinct differences between their configuration as opposed to those proposed by Komatsu (1977) and these distinctions will be elaborated in the following sections.

Table 4.1: Experimental And Simulation Results Of Single Feed Un-Catalytic Ethyl Acetate Reactive Distillation Column (Komatsu, 1977).

Quantity	Units	Simulation Model Alejski, 1988		Experimental Work (Komatsu, 1977)	
		Top	Bottom	Top	Bottom
Composition					
Acetic acid (Ac)		0.001	0.1450	0.001	0.22
Ethanol (Et)		0.5430	0.4710	0.65	0.38
Ethyl Acetate (Ea)		0.4130	0.1440	0.29	0.04
Water (W)		0.0430	0.2400	0.059	0.36
Temperature	K	345.6	351.2	-	-
Product flow	mol /min	0.0425	0.2159	-	-
Et conversion	mole %	20.13		-	
Ac conversion	mole %	47.95		-	
Ea purity	mole %	41.29		-	
Reflux flow	mol/min	0.0893			

Table 4.2: Simulation Results Of Double Feed Catalytic Ethyl Acetate Reactive Distillation Column (Nishith And Daoutidis, 2001).

Quantity	Units	Nishith & Daoutidis (2001)	
		Top	Bottom
Composition			
Acetic acid (Ac)		0.003	0.2100
Ethanol (Et)		0.080	0.1400
Ethyl Acetate (Ea)		0.650	0.1300
Water (W)		0.240	0.5200
Temperature	K	-	-
Product flow	mol /min	400.8	425.1
Et conversion	mole %	76.8	
Ea purity	mole %	65.0	
Reflux flow	mol/min	810.6	

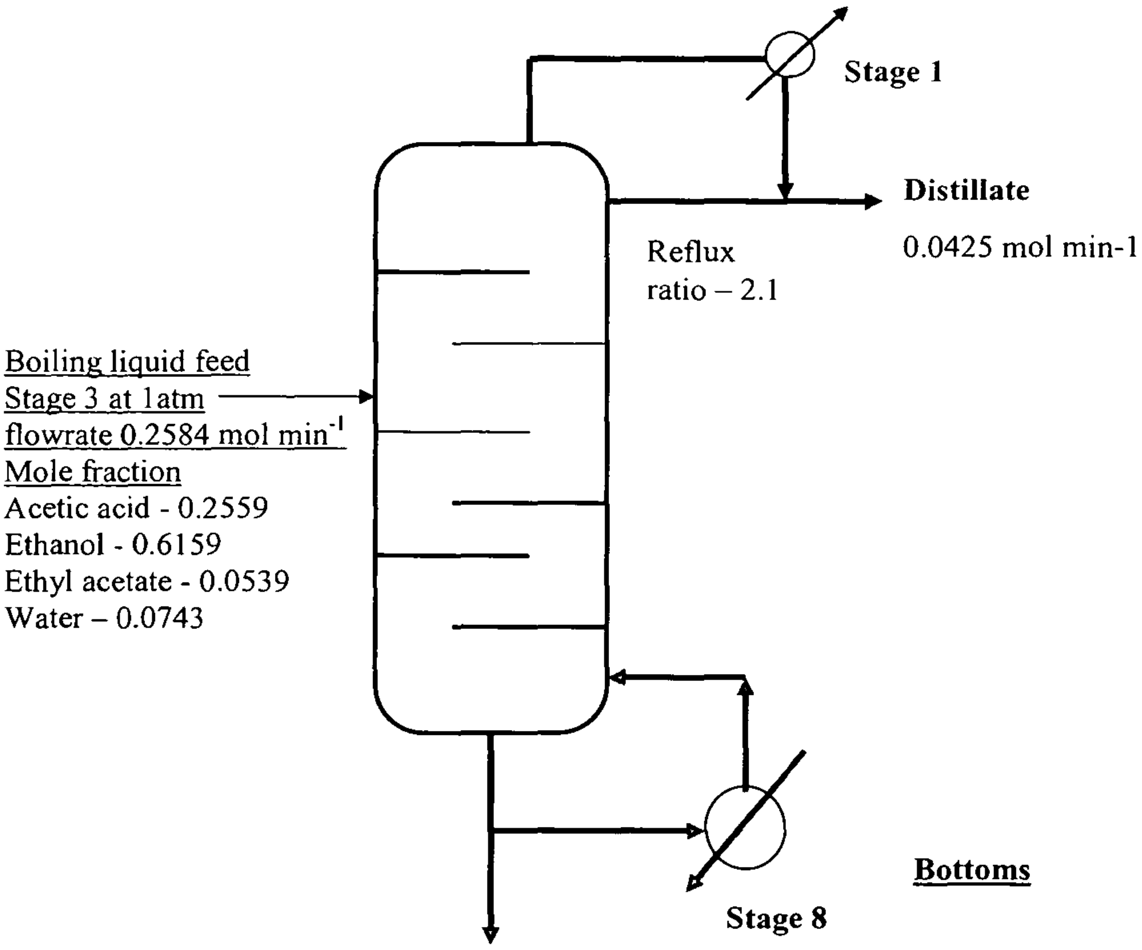

Figure 4.1: Typical Reactive Distillation Column Configuration And Specifications For Single Feed Un-Catalytic Ethyl Acetate Synthesis (Komatsu 1977).

4.2 Simulation of Single Feed Un-catalytic Reactive Distillation (Configuration 1)

Figure 4.1 above depicts a single feed un-catalytic ethyl acetate reactive distillation column configuration used by Komatsu in his experimental work. The column consists of 8 stages inclusive of condenser and re-boiler. Saturated liquid is fed into the column at tray 3, with a flow-rate of 0.2584-mol minl^{-1}. Stoichiometric excess of ethanol is used in the feed stream with a ratio of 2.41 ethanol to acetic acid.

The column pressure is 1 atm and the reflux ratio is set at 2.1. Liquid holdup in the condenser and trays is 0.4 liters whereas holdup in the re-boiler is 0.6 liters. Table 4.3 below summarises the first simulation basis used for the un-catalytic ethyl acetate reactive distillation column.

Table 4.3: Feed Specifications, Column Configuration and Operating Conditions used as Simulation Basis 1

Quantity	Units	Specifications
Feed Flowrate	**mol min^{-1}**	0.2584
Feed Phase		Saturated Liquid
Feed Temperature	**K**	355.29
Feed Pressure	**atm**	1.00
Feed Stage		3
Feed Composition		
Acetic acid (Ac)		0.2559
Ethanol (Et)		0.6159
Ethyl Acetate (Ea)		0.0539
Water (W)		0.0743
Number of Stages, N		8
Column Pressure, P	**atm**	1.00
Liquid Holdup		
Condenser, Tray	**liter**	0.4
Re-boiler	**liter**	0.6
Reflux Ratio, r		2.1
Re-boiler Ratio, r_b		0.5891
Bottom Flow, B	**mol min^{-1}**	0.2159

4.2.1 Results and Comparison

Table 4.4 summarises the steady state simulation results of the proposed model for un-catalytic ethyl acetate reactive distillation column in comparison to the published experimental data by Komatsu (1977) and the simulation work by Alejski (1988).

Table 4.4: Simulation Results For Un-Catalytic Ethyl Acetate Reactive Distillation Column.

Quantity	Units	Proposed Model		Simulation Model (Alejski, 1988)		Experimental Work (Komatsu, 1977)	
		Top	Bottom	Top	Bottom	Top	Bottom
Composition							
Acetic acid (Ac)		0.0022	0.1686	0.001	0.1450	0.001	0.22
Ethanol (Et)		0.5359	0.4949	0.5430	0.4710	0.65	0.38
Ethyl Acetate (Ea)		0.4257	0.1183	0.4130	0.1440	0.30	0.04
Water (W)		0.0361	0.2182	0.0430	0.2400	0.059	0.36
Temperature	K	339.23	354.17	345.7	351.2	-	-
Product flow	mol /min	0.0420	0.2164	0.0425	0.2159	-	-
Et conversion	mole %	18.56		20.13		-	
Ac conversion	mole %	44.67		47.95			
Ea purity	mole %	42.57		41.29		-	
Reflux flow	mol/min	0.0881		0.0893		-	

It should be noted that the reaction in the column for the above result is for un-catalysed reaction. The reaction rate model as proposed by Komatsu (1977) for un-catalysed reaction in liquid phase was used in the simulation developed. Figure 4.2 and 4.3 shows comparison of the concentration and temperature profiles along the column against the work of Alejski et al. (1988) using minimization method respectively.

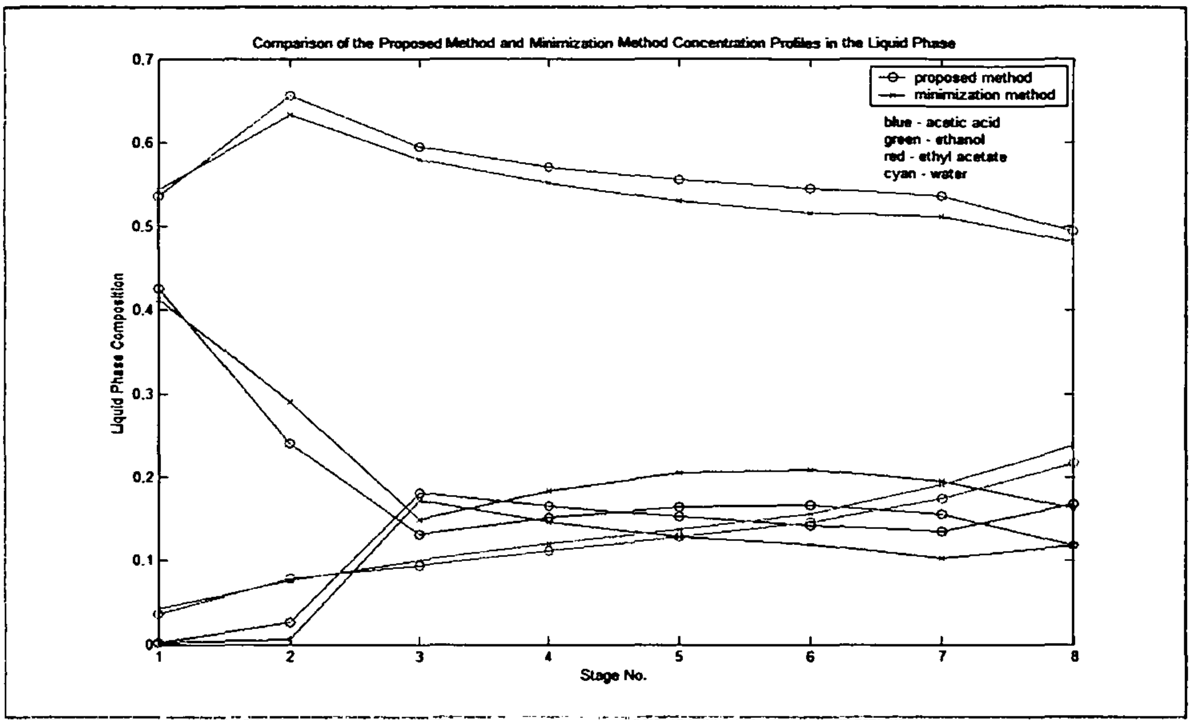

Figure 4.2: Comparison of the Proposed Method and Minimization Method Concentration Profiles in the Liquid Phase

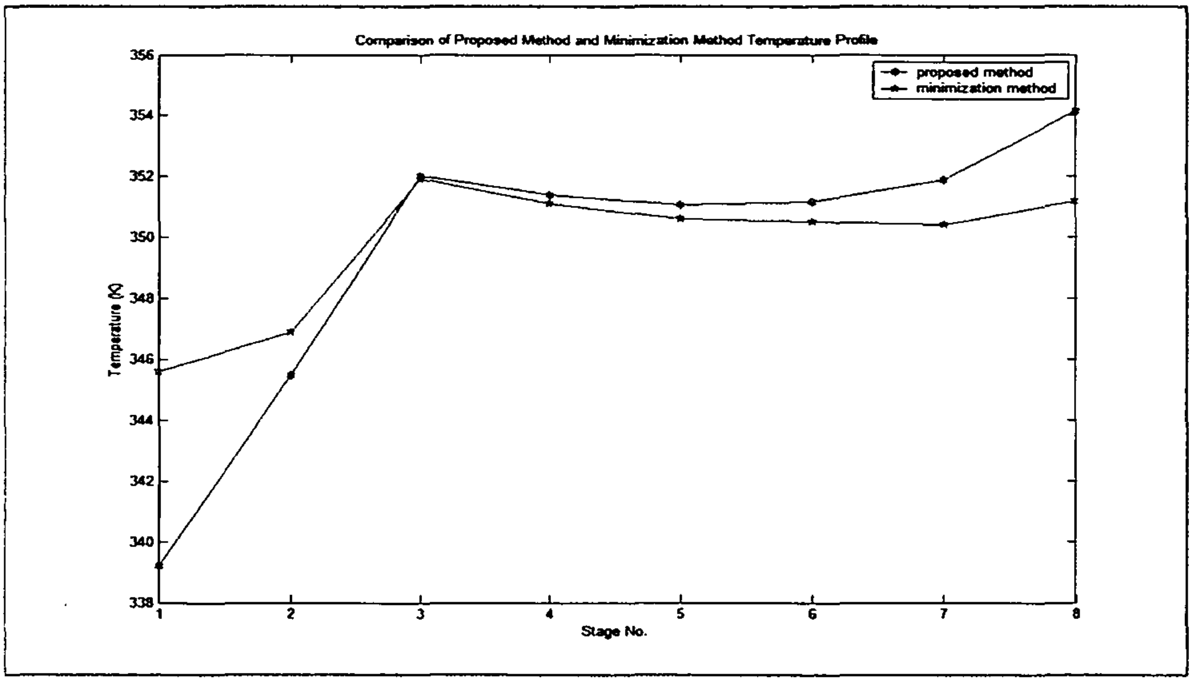

Figure 4.3: Comparison of the Proposed Method and Minimization Method Temperature Profile

As presented in the Table 4.4, Figure 4.2 and 4.3, comparison with the results obtained from the minimization method used by Alejski et al. (1988) against the simulation results from the study demonstrates a good agreement, which proves the validity of the proposed model and method. Alejski et al. (1988) did not include heat balance in his modeling work though, whereas in this study heat balance was included in the modeling process. This difference in the modeling has caused some slight deviations between these two studies. However, some slight significant deviations were observed between the simulated results and the experimental result of Komatsu (1977) though the profile was found to be almost similar. This could be caused by the inadequacy in the vapor liquid equilibrium model and the kinetic data used for the multi-component system. In addition, the model simplifications, which among others neglected the column hydraulics and the plate efficiencies, could further caused the model to deviate.

Overall, in view of the reasonably good agreement obtained between all the results, it was concluded that the developed simulation model in the study could be used for further analysis. A point to note is that the consistency showed by the two simulation results and the experimental result, indicating low achieved conversion and product purity obtained for the above un-catalysed reactive distillation configuration. Based on careful observation it was found that the main reasons for this deficiency are: 1) both reactants were introduced in liquid phase at same feed point, thus, countercurrent contact between reactants acetic acid and ethanol is reduced as ethanol which is lighter than acetic acid bound to evaporate from the feed point to stages above that has lower concentration of acetic acid, 2) catalysts were not presents in the column, 3) formation of azeotropes between reactants and products. In the lower portion of the column ethanol formed an azeotrope with water and washed out from the bottoms stream and above the feed point formation of azetrope between ethyl acetate-ethanol-water results in reactant, ethanol washed out in distillate stream as well and 4) insufficient number of trays for reaction and separation purposes causes the conversion and achieved purity to be much lower than those attained using the conventional reactor and distillation arrangement.

Table 4.5: Simulation Results for Configuration 1

No.	**xAc**	**Xet**	**Xetac**	**Xw**	**Tj (K)**	**ηAc (mol min-1)**	**yAc**	**yet**	**yetac**	**yw**	**Vj mol min-1**	**Lj Mol min-1**
1	0.0022	0.5362	0.4254	0.0362	339.24	0.000144	0.0000	0.3959	0.5925	0.0115	0.04175	0.08769
2	0.0260	0.6557	0.2393	0.0790	345.48	-0.000482	0.0011	0.5341	0.4275	0.0373	0.12945	0.08482
3	0.1810	0.5942	0.1303	0.0945	352.02	-0.005558	0.0208	0.6180	0.2989	0.0623	0.12658	0.34441
4	0.1660	0.5708	0.1517	0.1114	351.38	-0.004757	0.0172	0.5763	0.3362	0.0703	0.12776	0.34497
5	0.1532	0.5545	0,1645	0.1278	351.07	-0.004176	0.0147	0.5505	0.3560	0.0788	0.12833	0.34525
6	0.1421	0.5443	0.1669	0.1467	351.16	-0.003786	0.0131	0.5390	0.3574	0.0905	0.12861	0.34512
7	0.1437	0.5356	0.1552	0.1745	351.89	-0.003644	0.0125	0.5410	0.3348	0.1117	0.12847	0.34427
8	0.1685	0.4949	0.1186	0.2180	354.16	-0.007279	0.0201	0.5461	0.2756	0.1582	0.12762	0.21664

Although the conversion and product purity were found to be unattractive for reactive distillation to be employed for such production, the early intention is to make comparison between the result of the simulation model developed against published work for validation purposes and only such results were found available in literature. Such exercise provides the confidence for further study to be conducted using the developed simulation model especially in varying the various designs and operating parameters to investigate potential improvements that could be introduced. These present the next part of the research work.

4.3 Simulation of Double Feed Catalytic Reactive Distillation (Configuration 2)

Nishith and Daoutidis, (2001) proposed a double feed catalytic ethyl acetate reactive distillation configuration. The reported advantage of this configuration is that the performance of the column in terms of conversion and product purity was found to more superior than the earlier configuration. Basically, they proposed a configuration that involves feeding the two reactants in countercurrent direction and using homogeneous catalyst to aid the reaction that finally allows the attainment of higher conversion and purity.

Using the model developed, changes were made to the earlier configuration in order to simulate a reactive distillation configuration similar to those proposed by Nishith and Daoutidis, (2001), in view of its promising potential for undertaking further study for the ethyl acetate reactive distillation column. In addition, the results published by them are used to further confirm the validity of the developed simulation model for the present study.

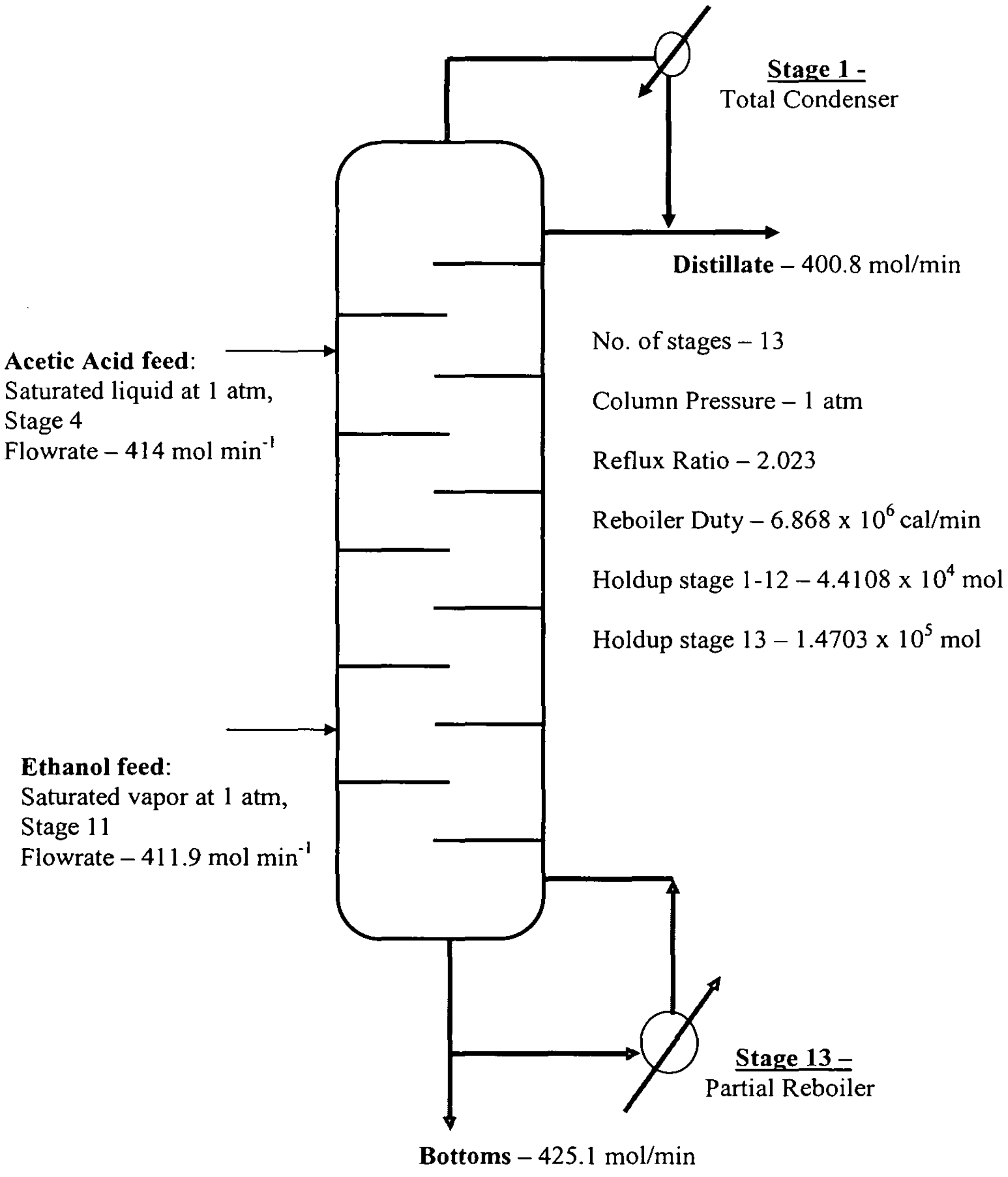

Figure 4.4: Typical Reactive Distillation Column Configuration And Specifications For Double Feed Catalytic Ethyl Acetate Synthesis (Nishith & Daoutidis 2001)

Figure 4.4 above depicts the double feed catalytic ethyl acetate reactive distillation column configuration used by Nishith and Daoutidis, (2001) in their simulation work. The column consists of 13 stages inclusive of the condenser and re-boiler. Acetic acid in saturated liquid form is fed into the column at tray 4, with a flow-rate of 414 mol minl^{-1}, while ethanol is fed at tray 11 in saturated vapor form with a flow-rate of 411.9 mol minl^{-1}. The column pressure is 1 atm and the reflux ratio is set at 2.023. Liquid holdup in the condenser and trays is 4.4108 x 10^4 mol, whereas holdup in the re- boiler is 1.4703 x 10^5 mol. Table 4.6 summarises the simulation basis for the double feed catalytic ethyl acetate reactive distillation column.

4.3.1 Simulation Results and Comparison

Table 4.6 summarizes the steady state simulation results obtained from the simulation model for the double feed catalytic ethyl acetate reactive distillation column. For the purpose of comparison, the published simulation results from Nishith and Daoutidis (2001) are also presented in Table 4.7.

Table 4.6: Feed Specifications, Column Configuration and Operating Conditions used as Simulation Basis 2

Quantity	**Units**	**Specifications**
Feed 1 Flowrate	**mol min^{-1}**	414
Feed 1 Phase		Saturated Liquid
Feed 2 Flowrate	**mol min^{-1}**	411.9
Feed 2 Phase		Saturated Vapor
Feed 1 Temperature	**K**	391.8
Feed 1 Pressure	**atm**	1.00
Feed 1 Stage		4
Feed 2 Temperature	**K**	351.4
Feed 2 Pressure	**atm**	1.00
Feed 2 Stage		11
Feed 1 Composition		
Acetic acid (Ac)		1
Ethanol (Et)		0
Ethyl Acetate (Ea)		0
Water (W)		0
Feed 2 Composition		
Acetic acid (Ac)		0
Ethanol (Et)		1
Ethyl Acetate (Ea)		0
Water (W)		0
Number of Stages, N		13
Column Pressure, P	**atm**	1.00
Liquid Holdup		
Condenser, Tray	**mol**	4.4108×10^4
Re-boiler	**mol**	1.4703×10^5
Reflux Ratio, r		2.023
Re-boiler Heat Duty, r_b		6.868×10^6 cal/min
Bottom Flow, B	**mol min^{-1}**	425.1

Table 4.7: Simulation Results For Catalytic Double Feed Ethyl Acetate Reactive Distillation Column.

		Proposed Model		Nishith & Daoutidis (2001)	
Quantity	Units	Top	Bottom	Top	Bottom
Composition					
Acetic acid (Ac)		0.019	0.2231	0.003	0.2100
Ethanol (Et)		0.1318	0.1123	0.080	0.1400
Ethyl Acetate (Ea)		0.6820	0.0896	0.650	0.1300
Water (W)		0.1672	0.5749	0.240	0.5200
Temperature	K	343.73	364.92	-	-
Product flow	mol /min	400.8	425.1	400.8	425.1
Et conversion	mole %	75.6		76.8	
Ea purity	mole %	68.2		65.0	
Reflux flow	mol/min	810.7		810.6	

Table 4.8 shows the detailed simulation results obtained from the steady state simulation of the catalytic double feed ethyl acetate reactive distillation column.

Table 4.8: Simulation Results for Configuration 2 – Double Feed Catalytic Ethyl Acetate Reactive Distillation Column

No.	XAc	xet	Xetac	Xw	Tj (K)	ηAc (molmin-1)	yAc	Yet	yetac	yw	Vj mol min-1	Lj Mol min-1
1	0.0190	0.1317	0.6820	0.1672	343.73	10.448	0.0009	0.1575	0.7855	0.0561	400.8	810.76
2	0.1171	0.1170	0.4190	0.3470	351.54	19.914	0.0104	0.1231	0.6907	0.1759	1211.5	773.73
3	0.2739	0.0773	0.2347	0.4142	357.27	9.1181	0.0578	0.0962	0.5345	0.3115	1174.4	766.59
4	0.5302	0.0449	0.1356	0.2894	354.69	-11.545	0.1525	0.0622	0.4221	0.3632	1167.4	1132.6
5	0.5106	0.0483	0.1327	0.3085	355.43	-12.521	0.1484	0.0676	0.4063	0.3776	1119.3	1131.8
6	0.4821	0.0584	0.1311	0.3284	356.22	-16.304	0.1395	0.0823	0.3924	0.3858	1118.5	1131.0
7	0.4419	0.0760	0.1299	0.3523	357.17	-22.646	0.1251	0.1072	0.3764	0.3914	1117.8	1130.6
8	0.3891	0.1032	0.1281	0.3797	358.27	-31.483	0.1045	0.1452	0.3550	0.3954	1117.4	1130.8
9	0.3258	0.1444	0.1239	0.4059	359.27	-42.395	0.0793	0.2009	0.3249	0.3950	1117.6	1132.0
10	0.2571	0.2069	0.1146	0.4213	359.76	-53.813	0.0535	0.2803	0.2826	0.3854	1118.8	1134.0
11	0.1905	0.3025	0.0964	0.4106	359.28	-62.681	0.0325	0.3914	0.2249	0.3512	1120.8	1135.0
12	0.1764	0.2052	0.1070	0.5114	362.01	-33.031	0.0335	0.2791	0.2379	0.4495	709.58	1136.9
13	0.2234	0.1122	0.0896	0.5749	364.91	-64.468	0.0577	0.1702	0.2080	0.5641	711.75	425.1

Table 4.9: Vapor-liquid equilibrium data for the proposed study

	K-values			
Stage	Acetic Acid	Ethanol	Ethyl Acetate	Water
1	0.048313	1.195684	1.151670	0.335364
2	0.088531	1.052101	1.648838	0.506798
3	0.210947	1.244717	2.278016	0.752055
4	0.287712	1.385242	3.113254	1.255298
5	0.290717	1.400551	3.062816	1.224250
6	0.289440	1.407955	2.993719	1.174836
7	0.283002	1.410681	2.897600	1.111174
8	0.268556	1.407253	2.771802	1.041183
9	0.243261	1.391395	2.622625	0.972985
10	0.208130	1.354754	2.465888	0.910324
11	0.170599	1.293897	2.333150	0.855357
12	0.189961	1.360280	2.222783	0.878951
13	0.258250	1.516900	2.322724	0.981316

Considering the column involves multiple feeds, the zones are defined as follows: The column section located below the lower feed is termed as the stripping section, whilst that located above the upper feed is termed as the rectifying section. The column section located between the upper and the lower feeds is termed as the reaction active zone.

For an ideal column performance, it is expected that a near complete conversion from the reaction is achieved and the two product that emerge from the distillation column consist of only the products from the reaction i.e. pure ethyl acetate at the top of the column and pure water at the bottom of the column. However in practice, such condition is not achievable due to the presence of substantial amount of water in the upper half of the column and the non-ideal behavior of the mixture, which hinders the achievement of complete conversion by enhancing the reverse reaction.

The achieved conversion in the simulation conducted is 75.60%, which is found to be higher than equilibrium conversion for the conventional arrangement of reactor followed by a separator. While the product purity achieved is 68.2% and this is higher than the azeotropic composition. The order of volatility for the components involved in the system in the decreasing sequence is ethyl acetate, ethanol, water and acetic acid. K value's of each component is given in Table 4.9. Considering these data and the result obtained from the simulation, it can be deduced that most of the reaction took place in the middle section of the column. Acetic acid is the least volatile component in the system, with K values much smaller than other components. Therefore it tends to flow down the column from the feed point with little vapourisation taking place, and thus hardly present in the rectifying zone. On the other hand, ethanol as reactant, which has significantly higher K value, is distributed more evenly along the column. Therefore, it can be observed that the production rate of ethyl acetate is positive in the middle and stripping section of the column while the deficiency of the reactant acetic acid in the rectifying section results in negative production rate of ethyl acetate.

Figure 4.5 shows the respective maximum concentration values for the reactants at the respective feed points. Acetic acid concentration depletes as it moves down the column whereas ethanol concentration depletes as it moves up the column. This is expected as much of the reactants were consumed as the reaction proceeds. Ethanol feed moves up the column mainly in the vapor phase. It is absorbed by the down-coming liquid phase, which is rich in acetic acid, and consequently reaction takes place. As the products are formed, ethyl acetate is stripped from the liquid phase and travel with the vapour phase to the top of the column. Water moves along with acetic acid in the liquid phase down the column. As shown in the same graph, the concentration of acetic acid is much higher when compared to ethanol in the middle section of the column. This tends to limit the reaction achieved in the zone. This suggests loading of excess ethanol would be favorable. This aspect will be further explored in a parametric analysis conducted later in the study.

The temperature profile along the column is shown in Figure 4.6. The temperature profile of the column is far from linear, with one temperature jump at feed point between stage 3 and 4 and temperature drop at ethanol feed point between stage 10 and 11. As expected, the temperature increases in the descending direction of the column, which in turn helps to increase the rate of reaction down the column.

Figure 4.7 shows the steady state reaction rate profile for the configuration. As shown in the graph in the first 3 stages from the top of the column, the reaction rates are negative as reverse reaction is prevalent in this zone. Low concentration of both the reactants, ethanol and acetic acid, couple with high concentration of products in these stages has led to the situation. This significantly affects the performance of the column in terms of conversion and product purity.

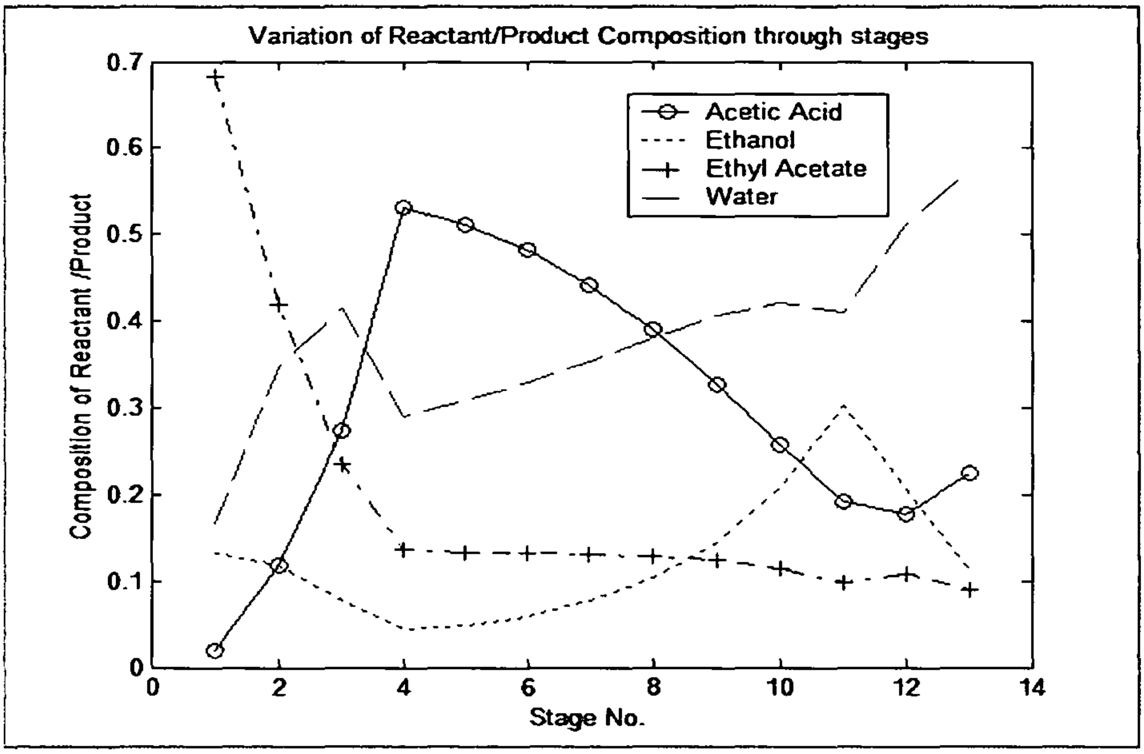

Figure 4.5: Steady State Liquid Phase Concentration Profile

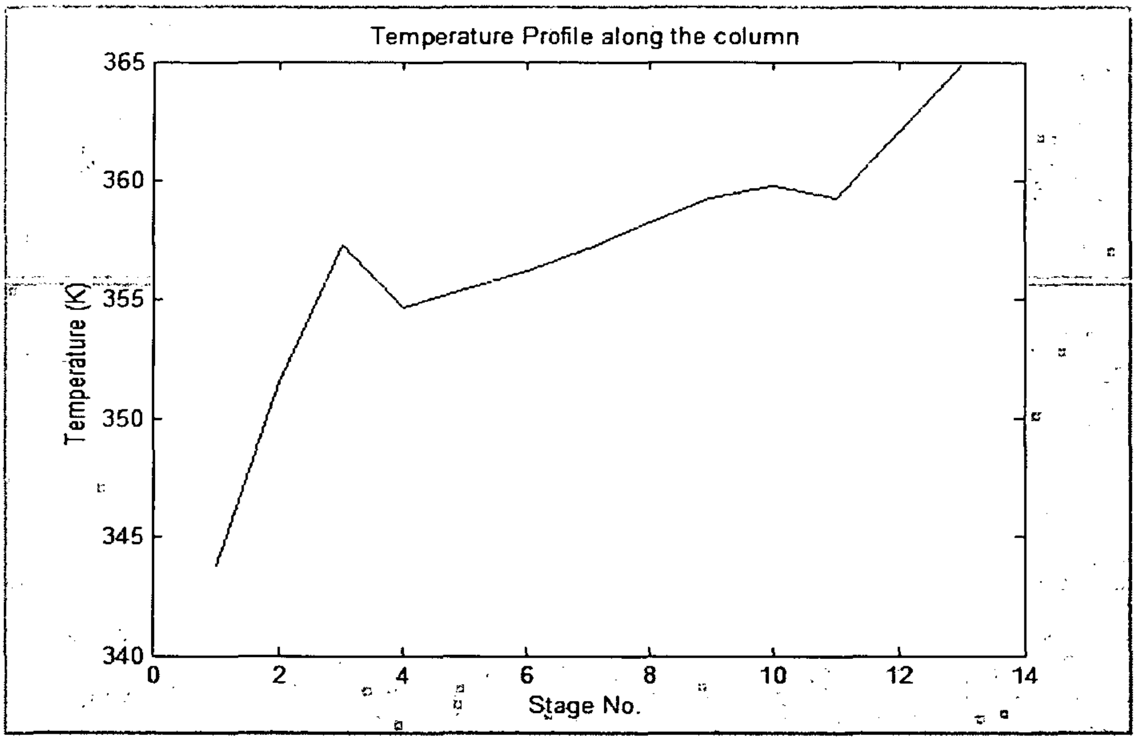

Figure 4.6: Steady State Temperature Profile Along The Column

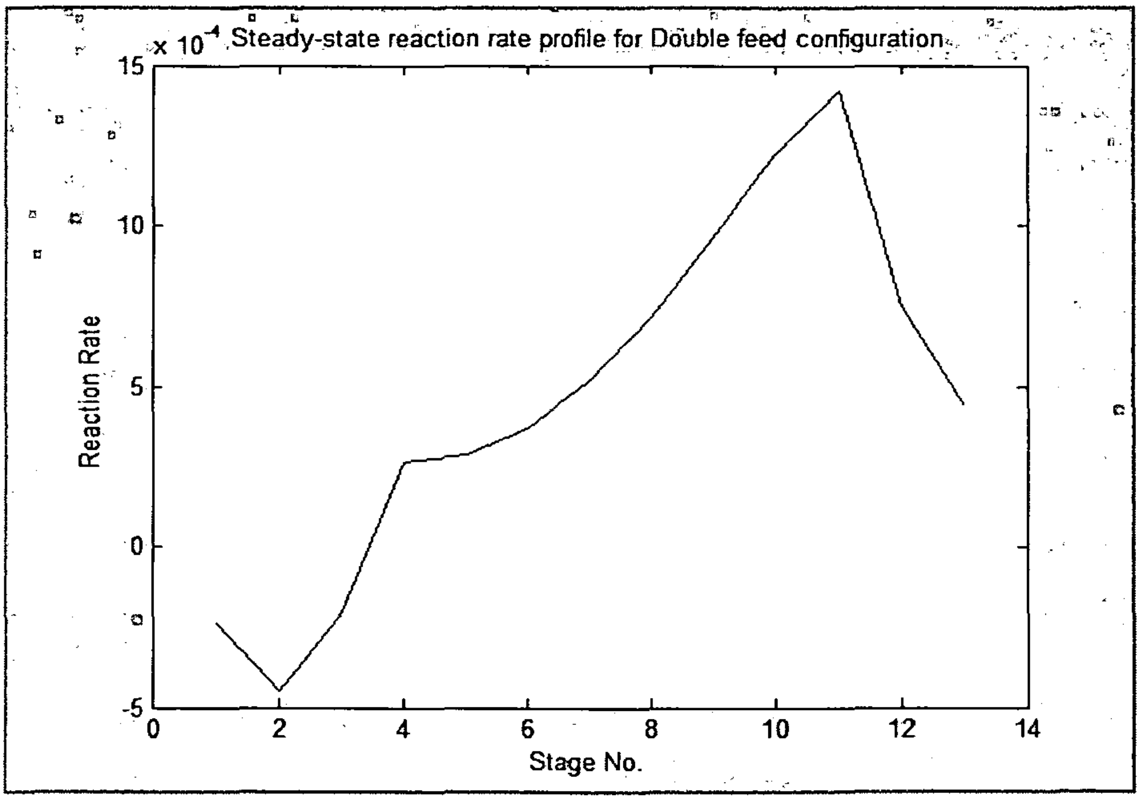

Figure 4.7: Steady State Reaction Rate Profile

Comparison on the developed simulation model against the simulation work of Nishith and Daoutidis, (2001) was made based on focal output variables from the simulation. The comparison is presented in Table 4.7. As indicated, the simulation results of this study are consistent with the simulation results from Nishith & Daoutidis (2001).

4.4 Overall Conclusion.

The validity of the developed mathematical model has been proven in this section for configuration 1 and configuration 2, by comparing the results obtained against experimental and complex simulation results published in the literature. The agreement between them was found to be reasonably well. Though there were slight deviations, it was justifiable. Amongst others that could course this observation are due to model simplifications, choice of physiochemical properties and reaction kinetic data. However, the consistency showed by the simulation results of this study for both configurations as compared to published results gives confidence to utilize this model for further studies, especially in the area of parametric analysis, control and safety. For the current study, the developed model is used for parametric analysis only, which will be discussed in the proceeding chapters.

While attempting to explain the behavior of the process, impeding factors that retard the column performance to operate at or near its ideal condition have been outlined. This could be useful for the process enhancement study, which will be conducted later in this research work. The following are the main contributing factors for under performance of ethyl acetate reactive distillation column in general:

- Lack of reactant acetic acid above the feed point promotes reverse reaction
- Formation of azeotropes between ethyl acetate-ethanol-water in the section above acetic acid feed point results in reactant ethanol being washed out from the column via distillate
- Formation of azeotropes between ethanol-water in the stripping section of the column results in reactant ethanol being washed out from the bottoms stream

In the following chapter, parametric analysis will be conducted in order to explore the possibilities to alleviate the above-mentioned limitations.

CHAPTER 5

PARAMETRIC ANALYSIS

5.1 Introduction

Reactive distillation column behaves significantly different from the conventional distillation columns due to the simultaneous interaction between the chemical reactions and the vapor liquid equilibria. The effects of key design and operating variables are discussed with reference to the double feed catalytic ethyl acetate reactive distillation column described earlier. The results are compared against a stipulated base case as shown in Figure 5.1, in order to understand the behavior of the system under various operating condition. The selected parameters used for the column's performance measurement are conversion and the overhead ethyl acetate product purity. Conversion is selected in view of the ability to indicate the extent of reactants consumption in producing specified amount of product whilst the product purity is selected due to the ability to indicate the degree of separation efficiency for the column.

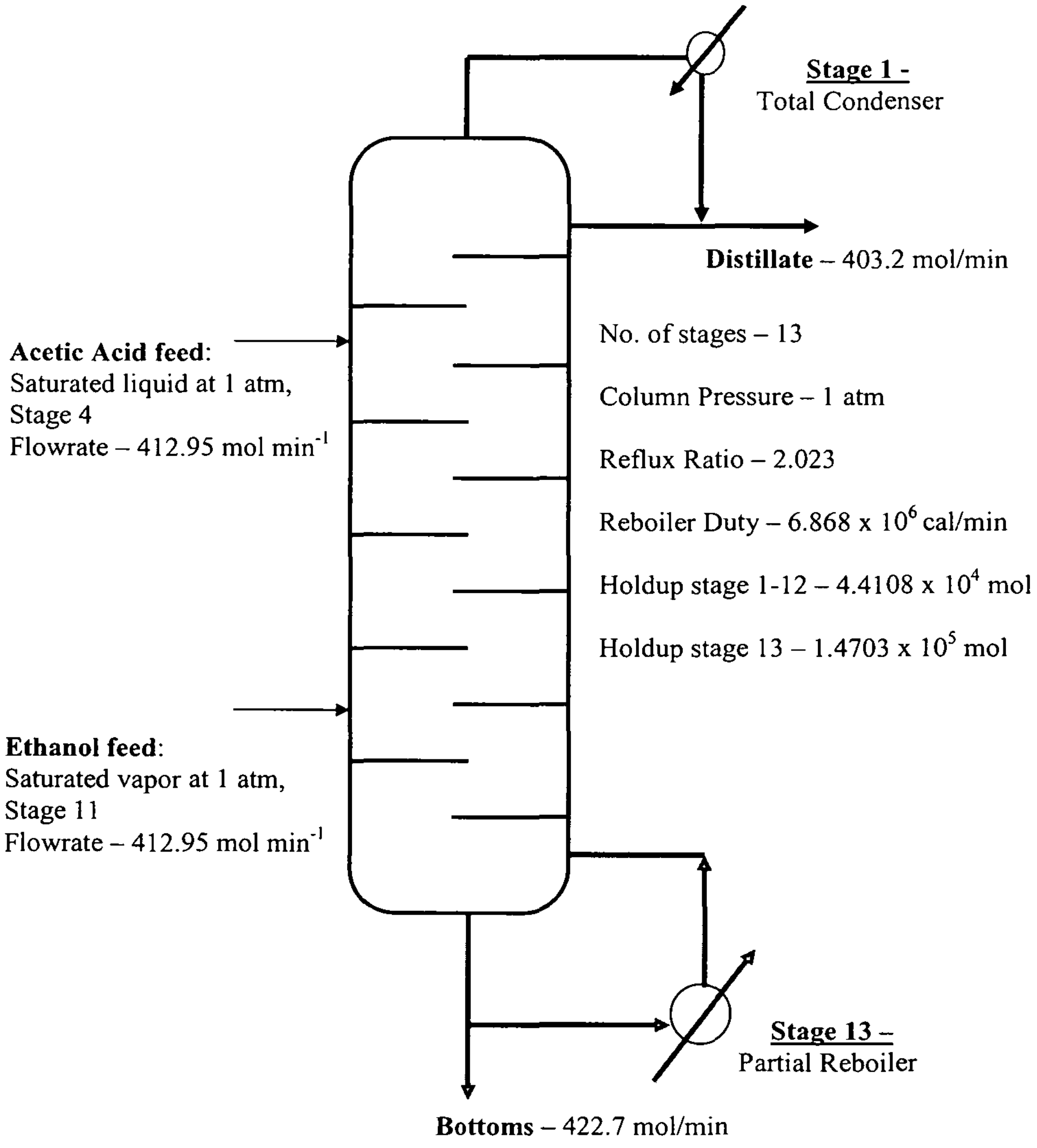

Figure 5.1: Base Case Reactive Distillation Column Configuration And Specifications For Double Feed Catalytic Ethyl Acetate Synthesis.

5.2 Base Case Configuration

Figure 5.1 depicts the configuration and the operating parameters used for the base case simulation. The column consists of 13 stages inclusive of condenser and re-boiler. Acetic acid in saturated liquid form is fed into the column at tray 4, with a flow-rate of 412.95mol minl^{-1}, while ethanol is fed at tray 11 in saturated vapor form with a flow-rate of 412.95mol minl^{-1}. The column pressure is 1 atm and the reflux ratio is 2.023. Liquid holdup in the condenser and trays is 4.4108×10^4 mol, whereas holdup in the re- boiler is 1.4703×10^5 mol. In this configuration, a homogenous catalyst i.e., sulfuric acid is used and it is introduced into the column at stage 4 together with acetic acid feed. Sulfuric acid is a non-volatile component thus will flow down the column from the feed point to the reboiler. Thus its presence on the first three stages located above the feed point could be assumed to be negligible. As a consequence, it is reasonable to assume that the reaction within the three top stages proceed without catalyst aid thus having significantly slower rate of reaction.

5.2.1 Simulation Results of Base Case

Two of the important output variables are used for comparison study in the parametric analysis. They are overall conversion and overhead ethyl acetate purity, which signify the overall performance of the column. Basically, in parametric analysis, variation is made on selected input variables, one at a time, with changes ranged within a certain specified limit from the base case value. The simulation results for the achieved conversion and the top ethyl acetate purity are then compared against the base case values in order to measure changes in the performance of the column. This will provide an indication whether such changes in the input variable would favour a better performance or vice versa. In the following section the effects of key design variables on the performance of ethyl acetate reactive distillation column is discussed. Table 5.1 summarizes the simulation results of base case configuration.

Table 5.1: Simulation Results Of Base Case Configuration.

		Configuration 3	
Quantity	Units	Top	Bottom
Composition			
Acetic acid (Ac)		0.006	0.1924
Ethanol (Et)		0.0719	0.1293
Ethyl Acetate (Ea)		0.7229	0.0895
Water (W)		0.1995	0.5887
Temperature	K	346.46	365.05
Product flow	mol /min	403.2	422.7
Overall conversion	mole %	79.7	
Ea purity	mole %	72.3	
Reflux flow	mol/min	815.6	

5.3 Effects of changes in Number of Stages

The ethyl acetate reactive distillation column is divided into three distinct zones as shown in Figure 5.1. The effects of varying the number of stages in each zone to the column performance are considered. For the analysis, the Damkohler number for the system is fixed at the base case value in order to study the effect of the number of stages alone on the column performance.

5.3.1 Variation in Number of Stages for the Rectifying Zone

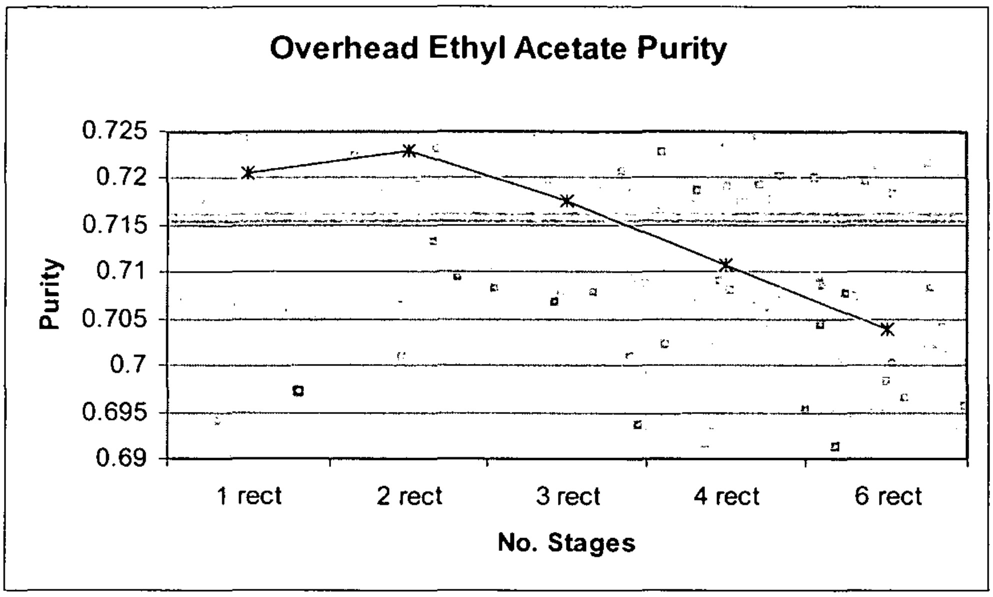

Figure 5.2a: Effects Of Variation In Number Of Rectifying Stages On Product Purity Of Ethyl Acetate Reactive Distillation Column.

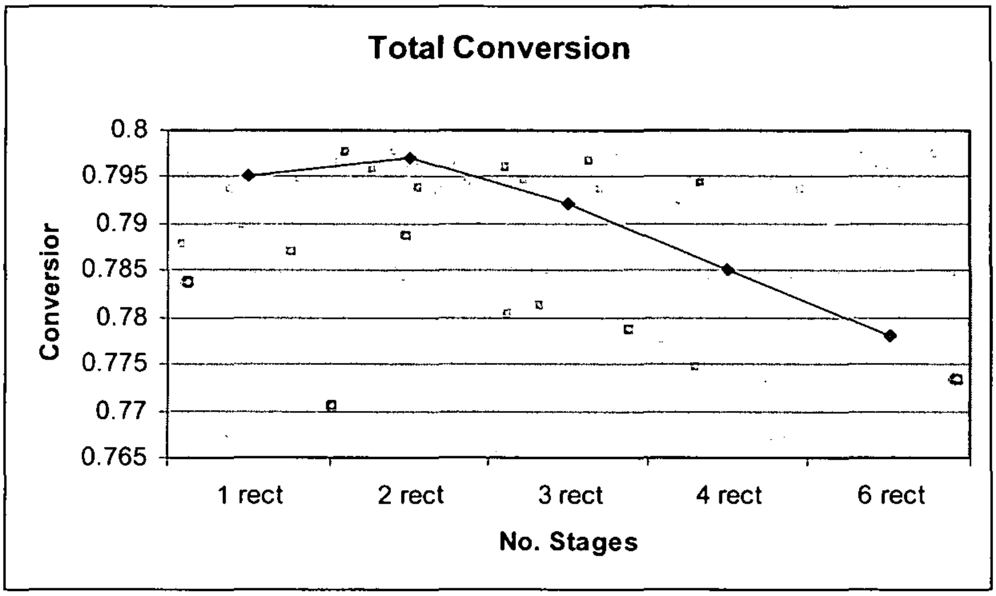

Figure 5.2b: Effects Of Variation In Number Of Rectifying Stages On Conversion Of Ethyl Acetate Reactive Distillation Column.

In this case, the number of stages in rectifying zone is varied while the other input parameters are kept fixed at the base case value. Ideally, the rectifying zone of the ethyl acetate reactive distillation column is expected to remove the heavy components from the rising vapor stream to give pure ethyl acetate distillate, to recycle the heavier un-reacted reactants back to the main reaction zone and to remove ethyl acetate from the reaction zone to maintain favorable reaction conditions. However, in practice, this is almost impossible to achieve mainly because the esterification reaction still takes place in the rectifying zone. Since the acetic acid has a low relative volatility compared to the other components in the system, it will have the tendency to flow down the column from its feed point. Thus only small amount is expected to be in the rectifying zone. Given the high concentration of ethyl acetate present in the rectifying zone, it then encourages the reverse reaction, which in turn reproduces the acetic acid reactant. This negative production rate of ethyl acetate increases as the number of stages is increased in the zone, thus lowering the column conversion and affecting the product purity. Another undesirable effect of increasing the number of rectifying stages is the lost of ethanol reactant in the distillate, which also affects the conversion achieved to a certain extent and the ethyl acetate purity.

5.3.2Variation in the Number of Stages in the Reaction Zone

Figure 5.3 shows the simulation results for the ethyl acetate column where the number of reactive stages was varied. As shown in the figure, the conversion and the ethyl acetate distillate purity was found to improve with increasing number of stages in the reaction zone.

The function of reactive zone is simply to provide a site for main reaction to proceed. In this case, all other variables including the number of separation stages in the rectifying and stripping zone, the reflux ratio, the reboiler duty and the feed conditions were fixed at the base case values. By adding stages in the reaction zone provides more sites for the esterification reaction to take place and in turn improves the conversion and the purity of the ethyl acetate distillate. Besides that, with increasing number of stages in the reaction zone, the separations of the reaction products become sharper as a consequence of the additional stages available for separation in the system. However, it should be noted that increasing the number of stages beyond a certain limit i.e., twenty for the system studied, would only lead to diminishing improvement in the column performance.

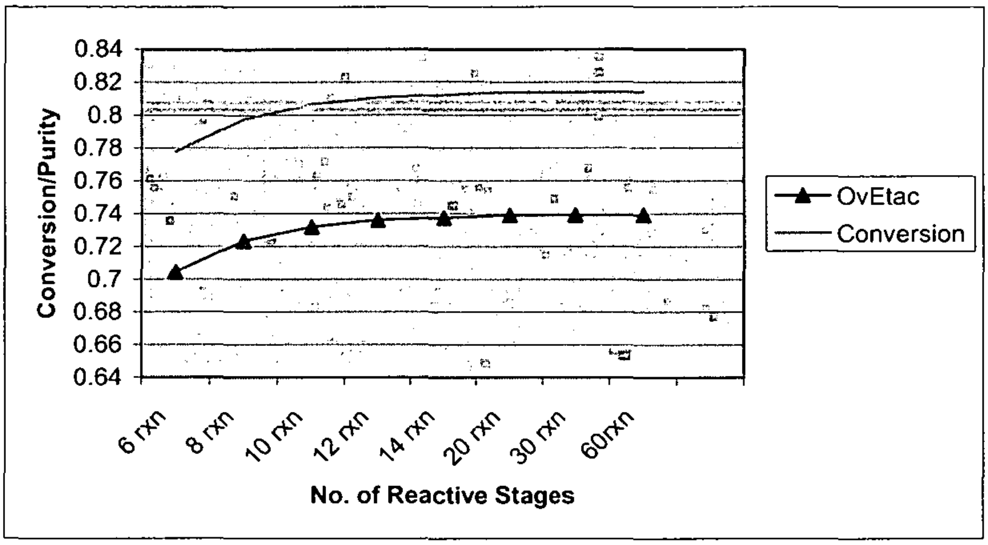

Figure 5.3: Effects Of Changes In Number Of Reactive Stages On Ethyl Acetate Reactive Distillation Column Performance.

5.3.3 Variation in the Number of Stages in Stripping Zone

In this case, the number of stages in the stripping zone was manipulated while keeping the number of stages in the other zones constant. The outcome on the important variables as a result of the changes made in the number of stages in the stripping zone is shown in Figure 5.4. As shown in the figure, the conversion and the ethyl acetate overhead purity increase as a result of increasing the number of stages in the stripping zone.

Theoretically, the stripping zone in the ethyl acetate reactive distillation column has the following functions: 1) Removal of the heavy reaction product from the reaction zone to maintain favorable reaction conditions, 2) Prevent losses of ethanol to the bottom product by vaporizing and recycling it back to the reaction zone, 3) Prevent loses of ethyl acetate to the bottom product, 4) Provides a medium for forward reaction to proceed. As a result, increasing the number of stages in the stripping zone leads to favorable effect on the column performance. The separation becomes sharper and the conversion increases. Hence the ethyl acetate distillate purity also increases. However, it was noted that an increase in number of stages in the stripping zone beyond a certain limit i.e., above 14 stages for this case, would only lead to diminishing improvement in the column performance. This is to be expected because increase in stripping stages results in more acetic acid, which is heaviest component in the system being discarded from the column via bottom stream. As a consequence, the column suffers lost of reactant acetic acid which in turn reduces the conversion of the column.

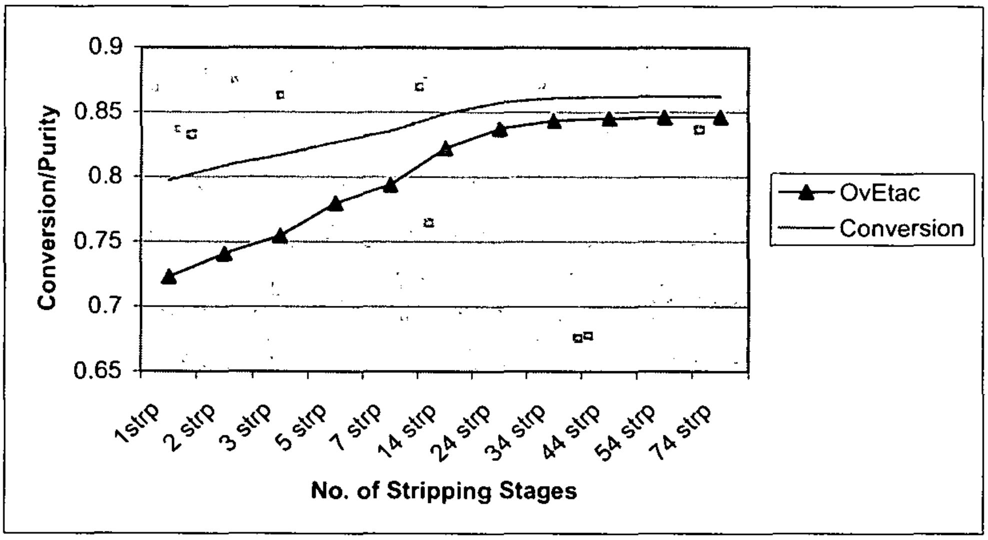

Figure 5.4: Effects of changes in number of stripping stages on Ethyl Acetate Reactive Distillation Column performance.

5.4 Effects of Changes in Pressure

In conventional distillation, the operating pressure of a column is normally set through an economic rationalization of heat transfer costs and the value of improved separation (via increasing relative volatility with reducing pressure) (Kister, 1992). However in reactive distillation the choice of operating pressure is made complicated by the indirect effects of pressure on the reaction equilibrium constant and the rate constant for kinetically controlled reaction via changing phase equilibrium temperatures. Increasing the pressure raises the boiling point temperatures along the column and these results in increase in forward reaction constant and decrease in reaction equilibrium constant (for exothermic reaction) and vice versa for decrease in pressure. In both cases one gives a favorable effect on conversion while the other produces an unfavorable effect on conversion. As a result of this interaction between the two parameters (forward reaction constant and reaction equilibrium constant), it is expected that there will be an optimal pressure for the system. This is clearly depicted in Figure 5.5, which indicates the presence of an optimum pressure with respect to ethyl acetate purity and the conversion when the parametric analysis was conducted on column pressure. The optimal pressure was found to be at 1 atmosphere. Any value that is higher or lower than this pressure results in decline in the ethyl acetate distillate purity and the conversion of the reactants.

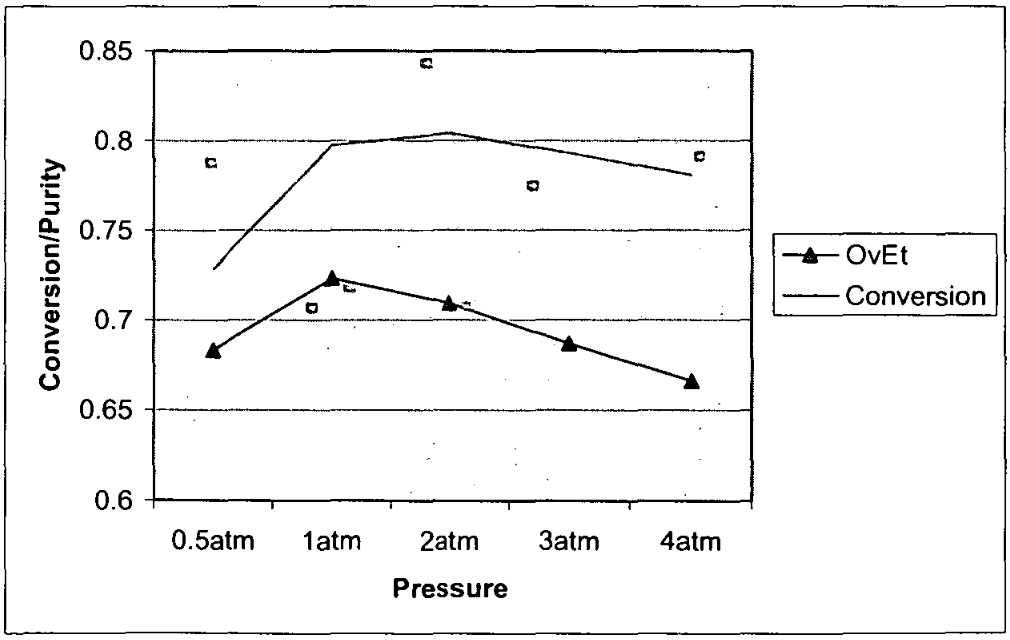

Figure 5.5: Effects of changes in Column Operating Pressure on Ethyl Acetate Reactive Distillation Column performance.

5.5 Effect of Changes in Damkohler Number

In this part, the effect of Damkohler Number (Da) on the performance of the ethyl acetate reactive distillation column is analyzed. As explained in chapter 3, for a homogeneous reactive distillation column, the Damkohler number is defined as a parameter that represents the measure of the rate of reaction relative to the product removal. The kinetic effect in the system is analyzed using the parameter. In principal, small value of Da corresponds to a state where little or no reaction takes place and the system is controlled by the phase equilibrium. On the contrary, a large value corresponds to a state where the reaction is closely approaching the reaction equilibrium. In the developed simulation model, Da number is taken as an input variable and it determines the extent of liquid holdup on each stage. Therefore, Da is varied at the cost of liquid stage holdup. As the Da increases, the liquid holdup on each stage increases as well. It should be noted that the Da could also vary at the cost of greater catalyst concentration or higher temperature but for the purpose of the study the two are kept constant.

As depicted in Figure 5.6, at small Da value, the conversion and the ethyl acetate purity are low. Insufficient liquid holdup on each stage results in low conversion of reactants towards products and hence the achieved purity is low as well. As the Da value increases, the conversion and the ethyl acetate distillate purity also increase due to larger holdup on the stages which promotes higher conversion and hence, increasing the ethyl acetate distillate purity. Nevertheless, it is observed that the conversion and the ethyl acetate product purity reach a plateau at Da value above 40. Therefore, it could be said that the reactive system has reached its reaction equilibrium limit.

Further increase in Da would not lead to any significant effect on the column performance. Operating the column above its optimum Da (Da=40) would not be economical, as it requires larger holdup with no significant effect on the column performance.

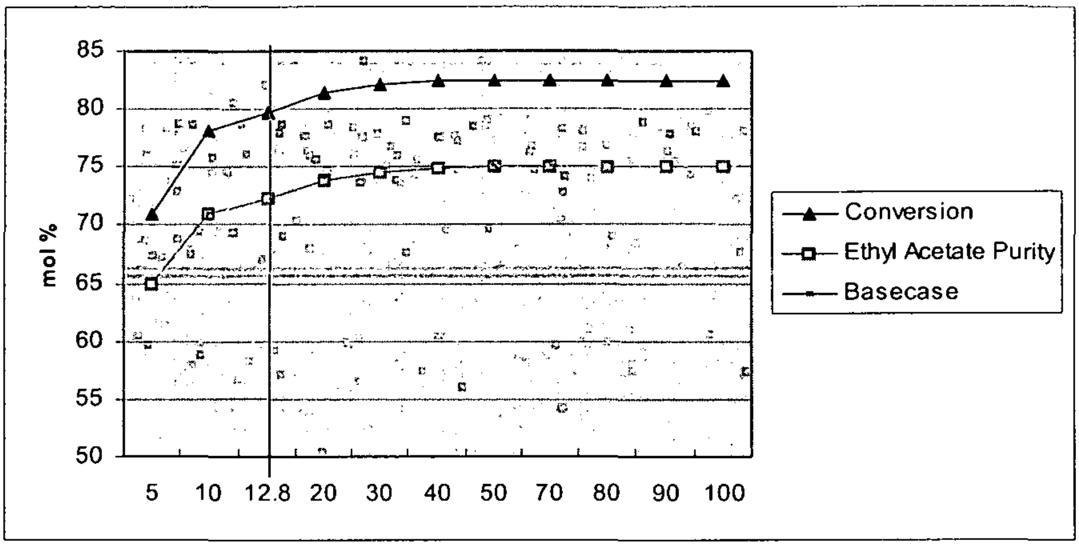

Figure 5.6: Effects of variation in Damkohler number on Ethyl Acetate Reactive Distillation Column performance.

5.6 Effect of Changes in Reflux Ratio at Constant Product Take Off

In this part of the work, the overhead product rate is fixed while the changes of the important column variables are investigated as a function of reflux ratio. Changing the reflux ratio will directly affect the internal liquid and vapour circulation inside the column. Changes in the reflux ratio are made accordingly i.e., –10%, -5%, +5% and +10% from the base case value. With the product rates fixed, the degree of separation is determined by the reflux ratio. Among the important variables looked at for evaluating the column performance as a result of changing the reflux ratio are the ethyl acetate purity, the reboiler duty, the conversion and, the condenser and reboiler temperature.

Figure 5.7 shows the plots of conversion and ethyl acetate purity against the reflux ratio at constant overhead product rate. The condenser and reboiler duties vary considerably as expected due to the variation of condensation and boil-up rates as the reflux ratio changes. Higher reflux ratio lead to increases in the energy requirement but at the same time increases the internal liquid and vapor rates throughout the column, which causes better separation and higher product purity. Nevertheless, for the case studied, the product compositions were found not to vary greatly at the distillate and bottoms when the changes in reflux ratio were made beyond the base case value. Accordingly the temperatures at the condenser and reboiler only vary slightly.

The total reaction rate and hence conversion were found to decrease with increasing reflux ratio. This phenomenon is due to high recycle rate of reaction products back into the column, which favours the reverse reaction and in turn reducing the total conversion of the system. As expected, the observation was reversed when decreasing the reflux ratio.

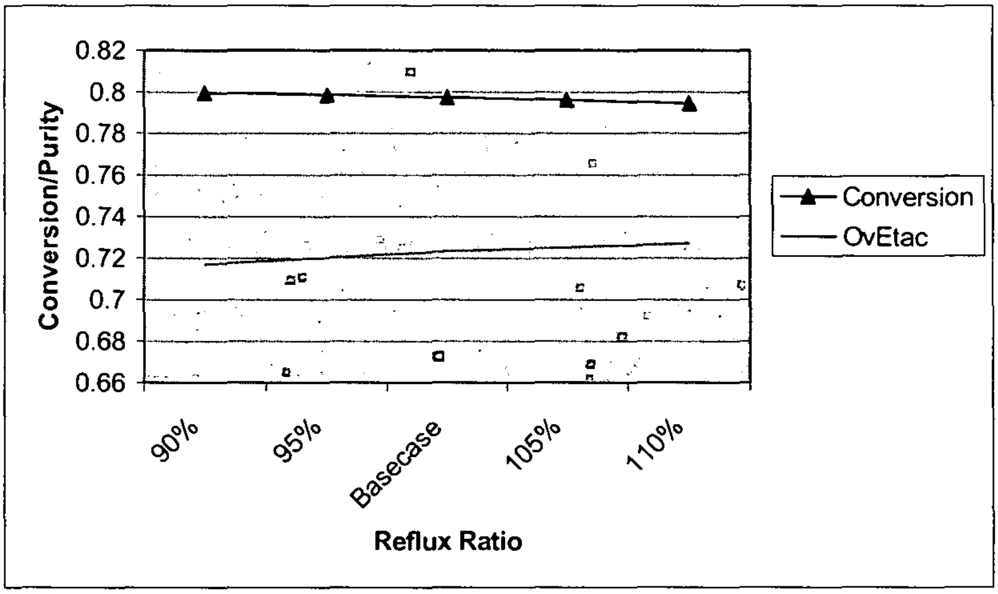

Figure 5.7: Effects of changes in Reflux ratio at constant product take off on Ethyl Acetate Reactive Distillation Column performance.

5.7 Effect of Excess Ethanol Feed.

As discussed in the earlier chapter, one of the possible factor that limits the achieved conversion and purity of the base case configuration is the lack of ethanol presence in the internal liquid flow, which in turn limits the reaction rate along the column and hence the product purity and conversion. Initially as shown in 5.8, as the percentage excess of ethanol is increased, the changes on the conversion and the ethyl acetate product purity are found to be rather small until the percentage excess of the ethanol feed reached 50%, at which the changes magnitude suddenly become more significant.

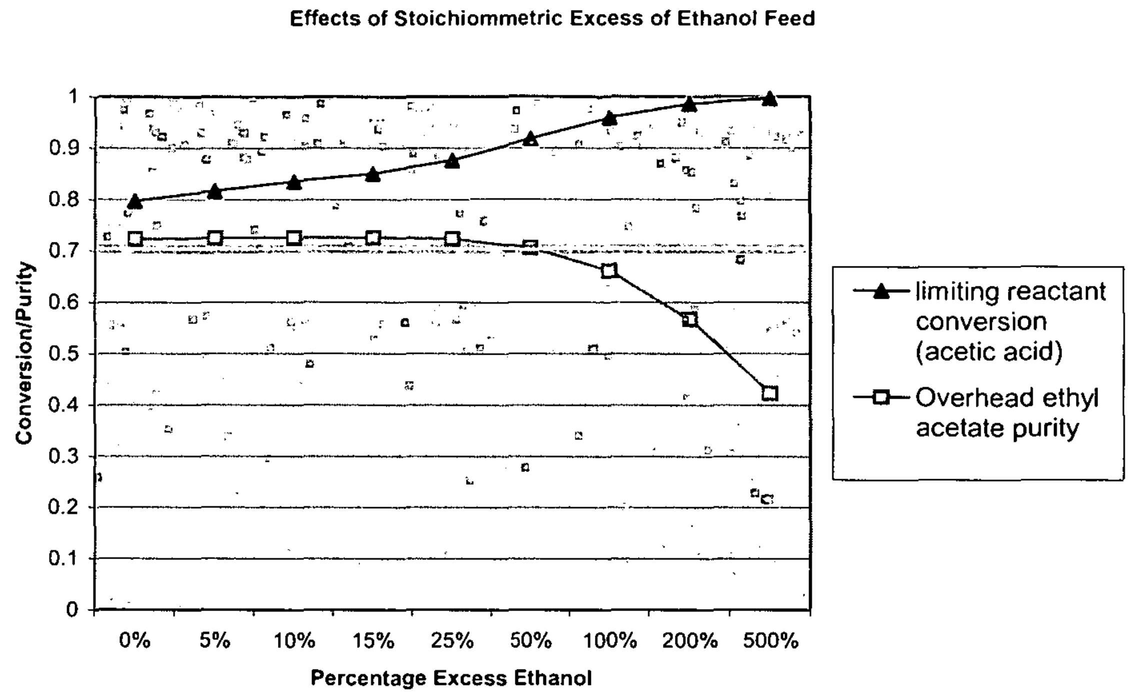

Figure 5.8: Effects of Stoichiometric excess of ethanol on Ethyl Acetate Reactive Distillation Column performance.

Excess of ethanol increases the concentration of ethanol in the liquid phase, which in turn results in higher reaction rate along the column, thus converting more reactants into products. By feeding excess ethanol into the column it is possible to completely exhaust acetic acid in the column and this would ease downstream separation of products from the reactants. However as shown in the graph, extremely large excess of ethanol is needed to achieve this condition. Increasing percent excess of ethanol above the optimum, results in gradual deterioration of product quality at distillate. This is to be expected, as the extra ethanol buildup in the rectifying zone tends to dilute the ethyl acetate in the distillate.

5.8 Effects of Excess Acetic Acid

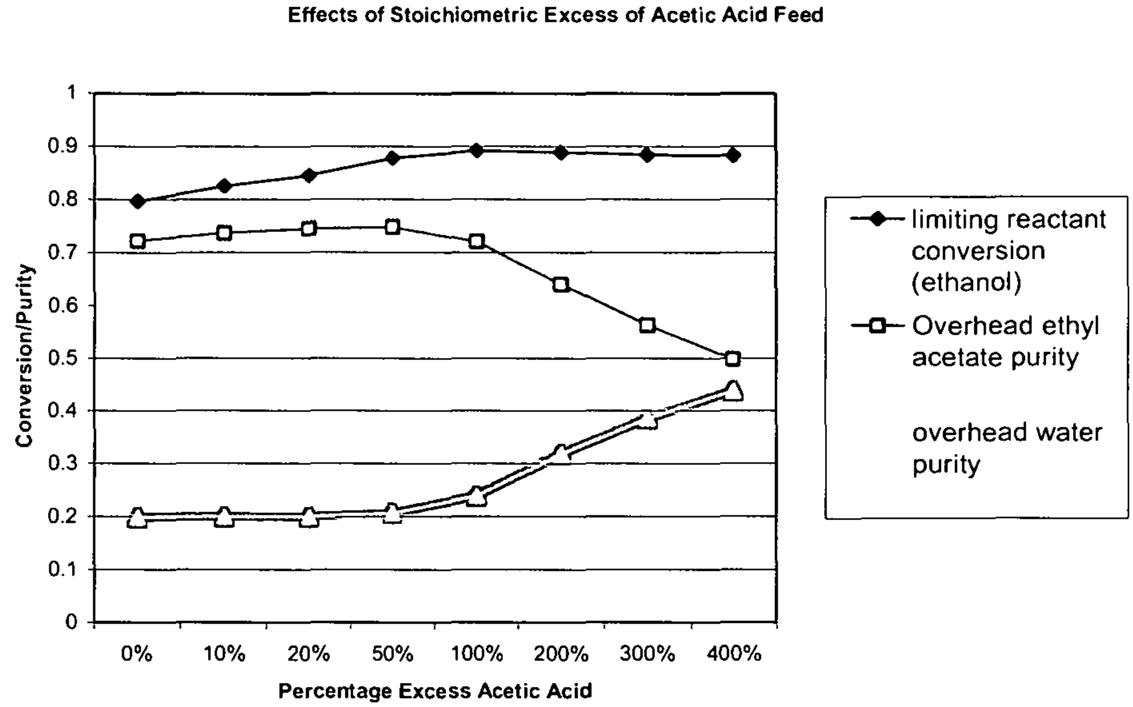

Figure 5.9: Effects of Stoichiometric excess of acetic acid on Ethyl Acetate Reactive Distillation Column performance.

Figure 5.9 shows the effect of increasing the percent excess of acetic acid on the ethanol conversion and the ethyl acetate distillate purity. The changes in the ethyl acetate purity is observed to initially increase in relatively small value until the percent excess of acetic acid feed approach 20 percent. Above this point, the ethyl acetate purity started to decline significantly due to the dilution of ethyl acetate distillate product by water produced from the reaction. Thus feeding the column with excess acetic acid resulted in high accumulation of water in the top portion of the column, as the acetic acid, which is the heaviest component in the system, tends to move downwards causing the operation temperature at the lower part of the column to increase. Subsequently, water is forced to move upward, being a lighter component, and fill up the upper section of the column thus causing the operating temperature at the upper section to also increase. Consequently, this reduces the product purity in the distillate.

5.9 Effect of Changing Feed Location

The column configuration used in the study is a multiple feed column. In the base case, the acetic acid in the form of saturated liquid is fed at stage 4 while ethanol in the form of saturated vapor, is fed at stage 11. The column section located below the lower feed is termed as the stripping section and that above the upper feed is termed as the rectifying section. The column section between the feeds is termed as the reaction zone. The countercurrent flow of the reactants causes the contact between them and thus leading to reaction on these stages. In addition, the zone also serves as a separation zone in view of the vapour-liquid contact that took place leading to separation of the components. The two feeds should be located in sufficient distance in order to enable sufficient contact to take place.

In the following analysis, feed locations are varied in order to study the impact on the column performance. It should be noted that the total number of stages are maintain as in the base case for this analysis. Initially, the distance between the feeds is moved closer to tray 5 and 10 (case study 1). Next, the distance is then move further to tray 3 and tray 12 (case study 2). Later, the feed points are moved one stage above to stage 3 and stage 10 (case study 3) before finally, the feed points are moved one stage below to stage 5 and stage 12 (case study 4) respectively. The simulation results for each of the case considered are discussed in the following sections.

5.9.1 Case Study 1

In this case study, the acetic acid and ethanol feeds locations are moved one stage closer to stage 5 and stage 10 respectively. As a result the distance for the countercurrent flow become shorter, which in turn reduces the reaction active zone. The results are shown in Figure 5.10. Both the conversion and the ethyl acetate distillate purity decline as compared to the base case results. Since the mole fraction of reactants in the rectifying section is low, the reaction rate in the rectifying section as depicted in Figure 5.11, is found to be negative which indicates that the reverse reaction is favoured. While, low concentration of ethanol in the stripping zone reduces the reaction rate (Figure 5.11) in this portion of column as compared to base case values. Therefore the total production rate of ethyl acetate decreases. This is indicated by the value of overall conversion, which is lower than initial specifications. Since the feeds are brought closer, the rectifying and stripping trays become more which results in better separation of light and heavy components in the system. Most of the light components, ethanol and ethyl acetate are concentrated in the distillate with less heavy components compared to initial specification. Meanwhile most of the acetic acid and water, which are heavy components, concentrate in the bottoms. Though the separation is enhanced the product purity is lower compared to the base case as a result of the decline in the conversion of reactants.

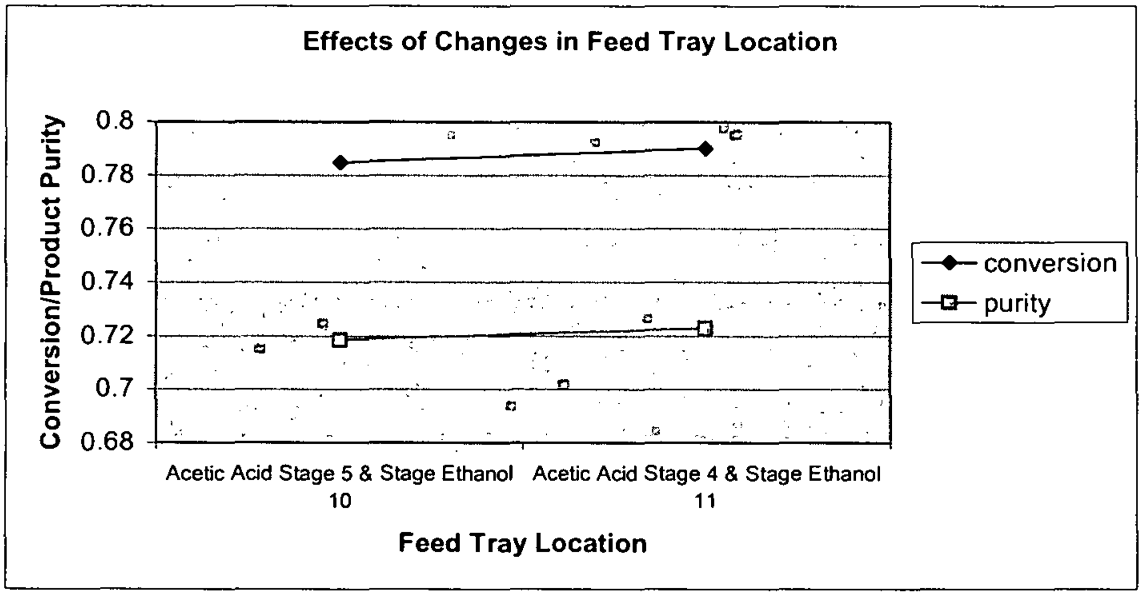

Figure 5.10: Effects of Feed Tray Location on Ethyl Acetate Reactive Distillation Column performance.

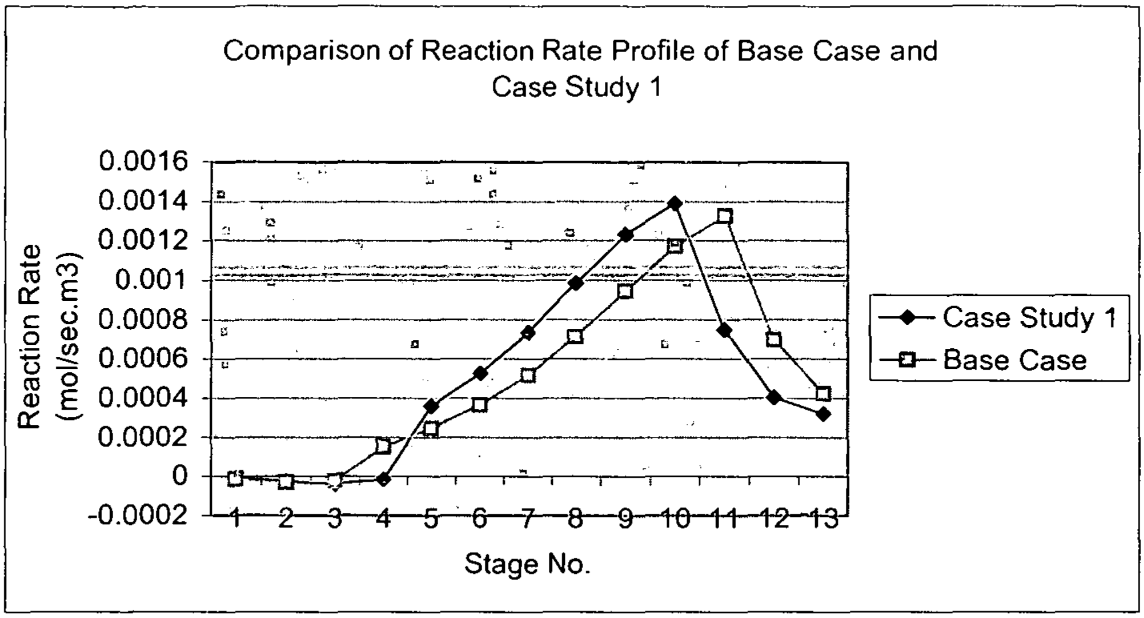

Figure 5.11: Comparison of Reaction Rate Profile along the Column of Base Case and Case Study 1

5.9.2 Case Study 2

In the second case, acetic acid is fed at stage 3 while ethanol is fed at stage 12. This resulted in the increase of reaction active zone from 8 stages to 10 stages. As indicated in Figure 5.12, both conversion and product purity reduce as a result of the change made to the two feed locations. Acetic acid as expected flow downwards as it is the heaviest component in the system thus appearing more in the lower section of the column. Once the acetic acid feed stage is move upwards to stage 3, the mole fractions of the acetic acid in the upper portion increases as compared to the base case, thus causing the forward reaction of the esterification reaction to increase in rectifying section as depicted in Figure 5.13. However as depicted in Figure 5.14 deficiency in ethanol composition in the middle section of the column results in low reaction throughout the reactive section (Figure 5.13). Whereas at stripping section of the column due to inefficiency in stripping process results in high concentration of ethanol (figure 5.14) and this in turn increase the reaction rate at stripping section of the column (Figure 5.13). In overall the conversion of the reactant is lower compared to base case due to decline in reaction rate at reaction zone (Figure 5.13). As depicted in Figure 5.14 ethyl acetate product purity also declined due to shorter rectifying and stripping zone as compared to base case, which results in inefficient separation process.

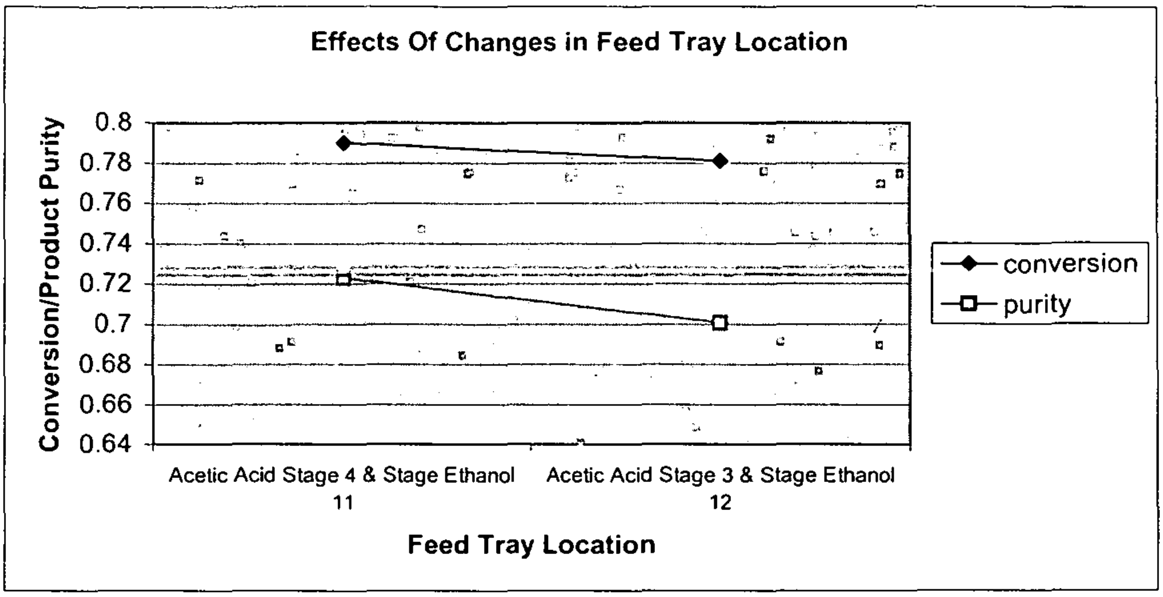

Figure 5.12: Effects of Feed Tray Location on Ethyl Acetate Reactive Distillation Column performance.

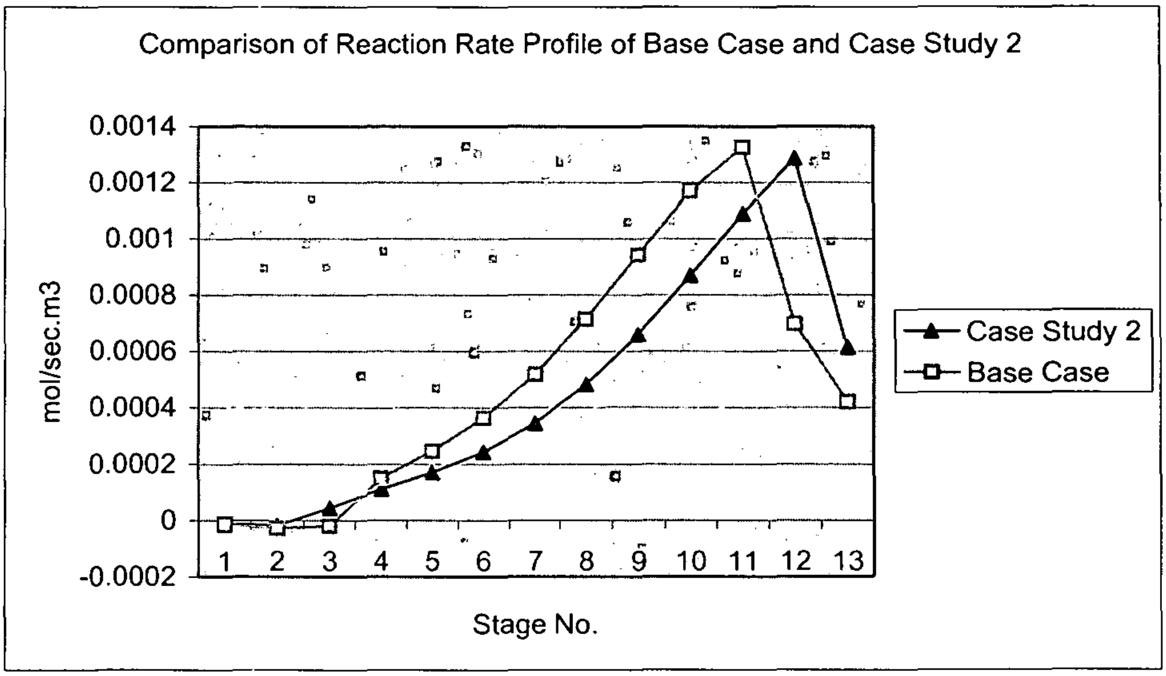

Figure 5.13: Comparison of Reaction Rate Profile along the Column of Base Case and Case Study 2

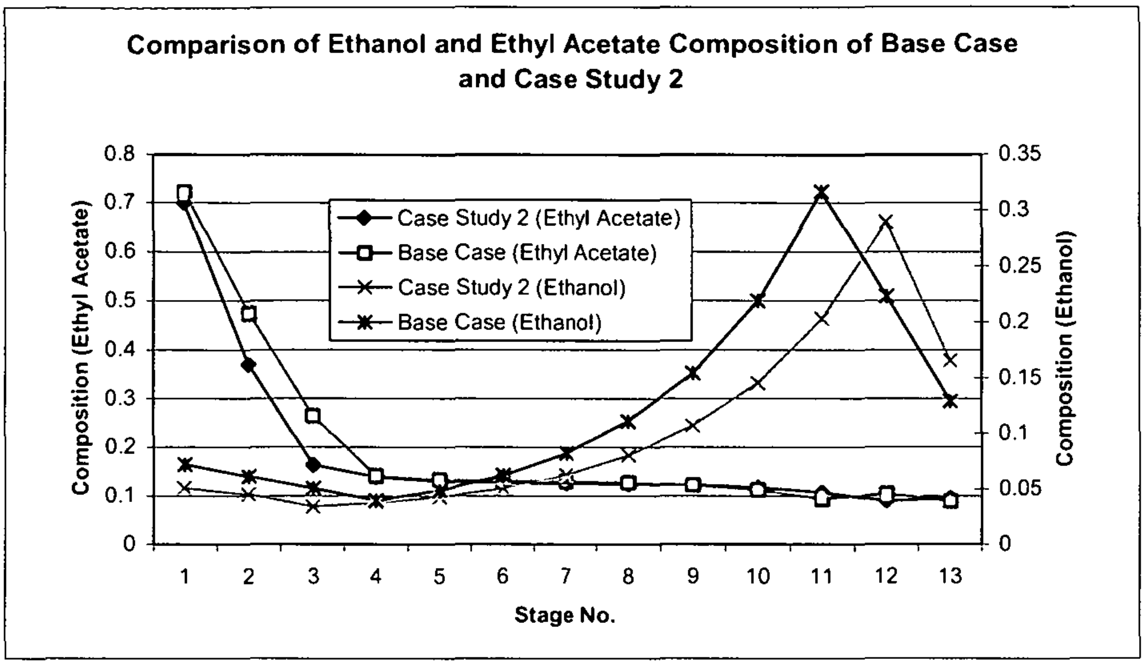

Figure 5.14: Comparison of Ethanol and Ethyl Acetate Composition along the Column of Base Case and Case Study 2

5.9.3 Case Study 3

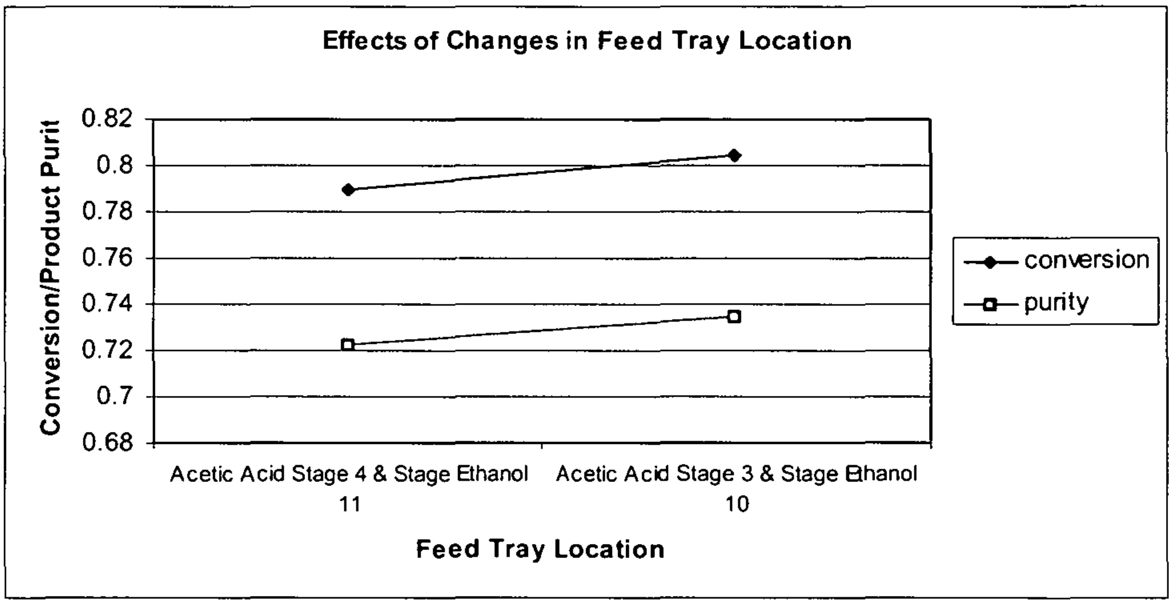

Figure 5.15: Effects of Feed Tray Location on Ethyl Acetate Reactive Distillation Column performance.

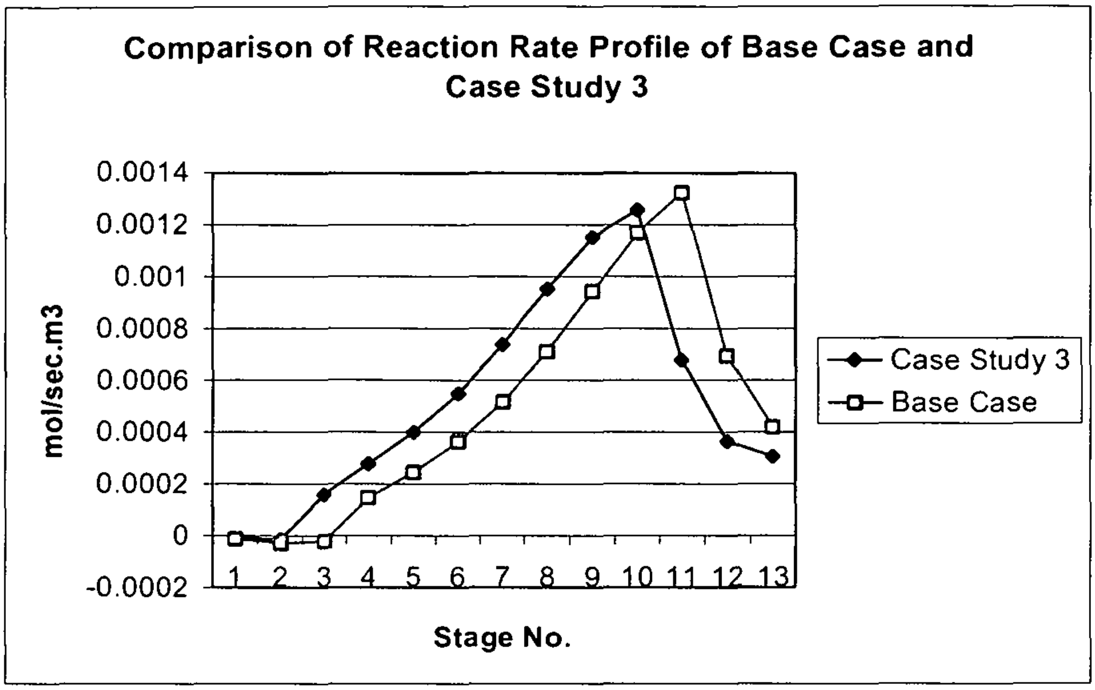

Figure 5.16: Comparison of Reaction Rate Profile along the Column of Base Case and Case Study 3

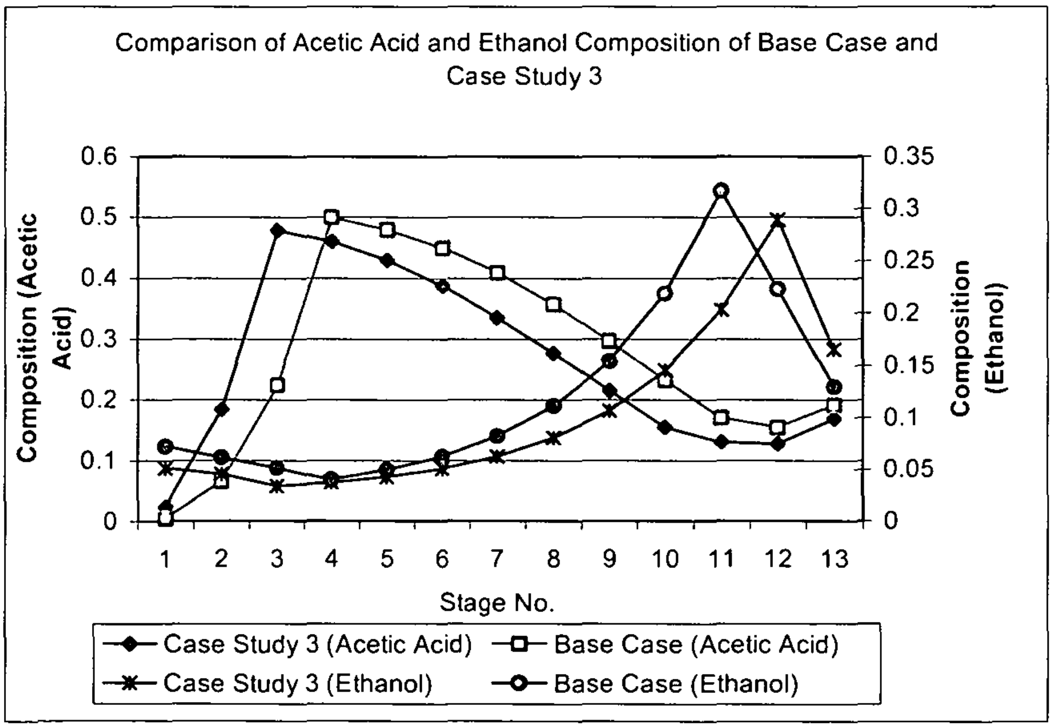

Figure 5.17: Comparison of Acetic Acid and Ethanol Composition along the Column of Base Case and Case Study 3

In case study 3 the feed point of acetic acid and ethanol are moved one stage above to tray 3 and tray 10 respectively. Total reactive stages are maintained with this configuration while rectifying zone become shorter and stripping zone is longer. As depicted in the Figure 5.15 the conversion of the system is improved by 4 percent. The product purity also increases with this configuration. As acetic acid feed point moved upwards the concentration of this reactant increases compared to base case whereby deficiency in acetic acid (Figure 5.17) in rectifying section of base case cause negative production rate of ethyl acetate, whereas, for this setup high concentration of acetic acid in rectifying section (Figure 5.17) enhance forward reaction rate to produce ethyl acetate. Comparison of reaction rate profile along the column is depicted in figure 5.16. Besides that, as ethanol distributed evenly throughout the column (5.17) and the tendency of acetic acid to flow down the column due to its low K value, results in better reaction rate throughout the column. The temperature of reboiler is at maximum compared to other case due to improvement in stripping process as a result of increase in stripping stages. Inefficiency in rectifying section leaves more unreacted acetic acid in the distillate but it is not significant. In overall the column performance of this configuration is more favorable compared to other configurations.

5.9.4 Case Study 4

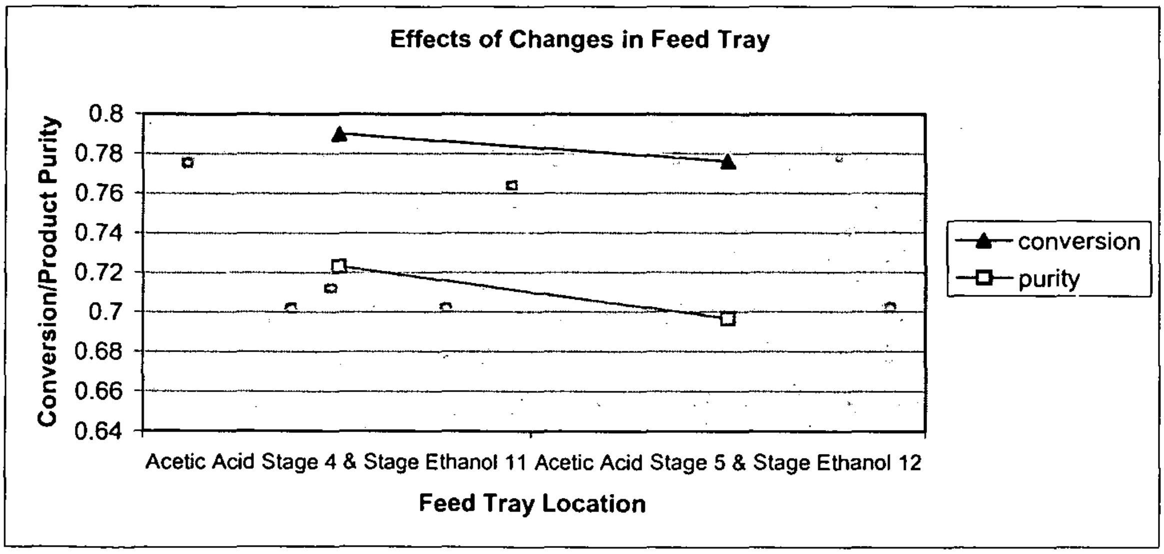

Figure 5.18: Effects of Feed Tray Location on Ethyl Acetate Reactive Distillation Column performance.

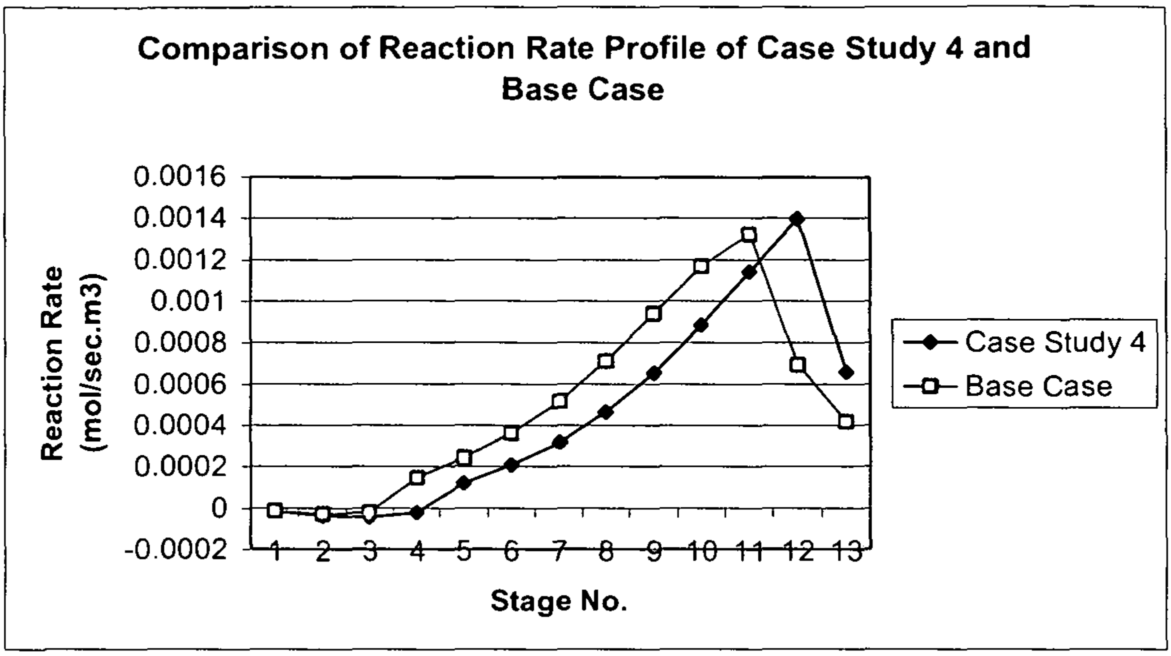

Figure 5.19: Comparison of Reaction Rate Profile along the Column of Base Case and Case Study 4

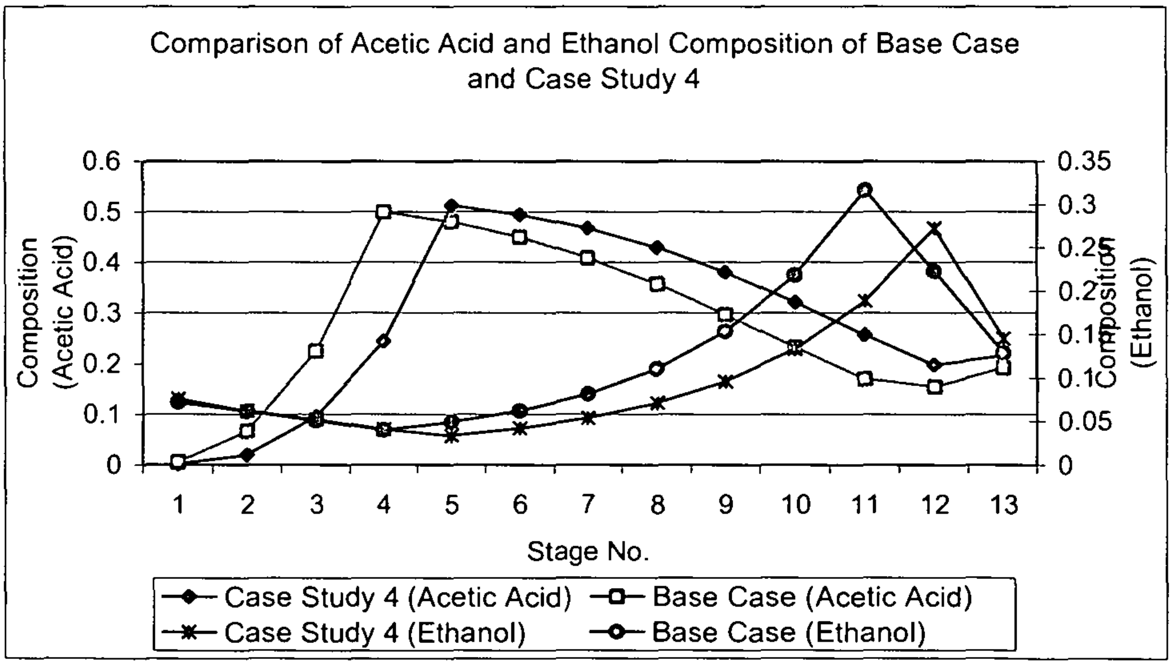

Figure 5.20: Comparison of Acetic Acid and Ethanol Composition along the Column of Base Case and Case Study 4

For case study 4 the feed points of acetic acid and ethanol are moved one stage below respectively. As shown in figure 5.18, the conversion and ethyl acetate product purity of the system decline as compared to base case values. The separation become sharper in rectifying section as the number of tray increase and the concentration of acetic acid are low compared to base case (Figure 5.20). Though ethanol concentration is higher in this zone it does not compensate for the deficiency in acetic acid and in turn reduces reaction rate in rectifying section as depicted in Figure 5.19. As shown in figure 5.20, from the acetic acid feed point to the bottom of the column the concentration of acetic acid is high, while reactant ethanol is low in concentration in the middle portion of the column due to inefficient stripping process. This contributes in low reaction rate in reaction zone (Figure 5.19). High concentration of ethanol and acetic acid in stripping zone increases production rate of ethyl acetate, however in overall the conversion of reactants are very low compared to base case.

5.10 Concluding Remarks

The effects of key operating and design variables on the column performance have been analysed in this chapter. The selected column performance indicators are overall conversion and overhead ethyl acetate product purity. The design and operating variables considered in parametric analysis are:

- Effects of changes in number of rectifying stages
- Effects of changes in number of reactive stages
- Effects of changes in number of stripping stages
- Effects of changes in pressure
- Effects of changes in Damkohler Number
- Effects of changes in reflux ratio at constant product take off
- Effects of excess ethanol feed
- Effect of excess acetic acid feed
- Effect of changing feed location

Simultaneous optimization of all variables is considered in order to gain deeper insight on the impact of independent changes of each of the variables on the column performance. Through this study insignificant variables can be screened out easily and significant variables can be identified for overall optimization. However overall optimization was not considered as it is beyond the scope of this research work.

Furthermore optimization study could only give best set of parameters to operate the column but it would not be able to alleviate the limitations (i.e. existence of azeotropes) exist in the system under consideration.

Table 5.2: Optimal Condition for Independent Changes in Number of Stages

	Base Case	Rectifying Optimal Value	Reactive Optimal Value	Stripping Optimal Value
Total rectifying stages	2	2		
Total reactive stages	8		20	
Total stripping stages	1			14
Overall Conversion	79.7	79.7	80.2	81.8
Distillate Ethyl Acetate Purity	72.3	72.3	72.4	77.7

Table 5.3: Result summary for feed location changes of double feed catalytic ethyl acetate reactive distillation column

	Base Case	Case Study 1	Case Study 2	Case Study 3	Case Study 4
Total rectifying stages	2	3	1	1	3
Total reactive stages	8	6	10	8	8
Total stripping stages	1	2	0	2	0
Overall Conversion (%)	79.7	78.5	78.1	80.4	77.6
Distillate Ethyl Acetate Purity (%)	72.3	71.9	70.1	73.5	69.7

Table 5.2 presents the optimal condition and performance indicator values for independent changes in number of three distinctive stages of double feed catalytic ethyl acetate reactive distillation column. As shown in Table 5.2, independent changes in number of stages do not result in significant improvement in the column performance. Meanwhile Table 5.3 presents summary of results for changes in feed location of the column. There is improvement in column performance when the acetic acid and ethanol feed points are located at stage 3 and stage 10 respectively. However, as for the case of changes in number of stages, only marginal improvement was noticed for changes in feed location. For changes in pressure, Damkohler Number, reflux ratio, ethanol flow-rate and acetic acid flow-rate the results obtained are not attractive as well. The improvement in terms of product purity and conversion are only marginal for these cases.

From this analysis the behavior and limitations of double feed catalytic ethyl acetate reactive distillation column is well understood. This analysis could be a good platform for process enhancement study that will be considered in the next chapter.

CHAPTER 6

PROCESS ENHANCEMENT

6.1 Introduction

In the previous chapter, parametric analysis was carried out in order to study the effect of design and operating variables on the ethyl acetate reactive distillation system. Through the analysis, it is evident that it is not possible to enhance the process performance significantly in order to produce high conversion and high purity separation. The main constrains that have led to the failure of the system consists of the followings;

1.) Close relative volatility of ethanol and water in the stripping zone results in reactant ethanol being washed away into the bottom stream. Therefore not all of the ethanol could react with the acetic acid to produce ethyl acetate product.
2.) Close relative volatilities of ethyl acetate, ethanol and water and due to the formation of azeotropes in the rectifying zone causing difficult separation in order to obtain high purity ethyl acetate at distillate.

In the parametric analysis, one of the main alternatives considered is to completely exhaust one of the reactants i.e., acetic acid by feeding excess ethanol. In doing so, the need for separation of acetic acid from water could be avoided. However, the system will still have to deal with the excess ethanol, which appears in the distillate thus affecting the purity of ethyl acetate. The above principal is used in conventional method of producing ethyl acetate where excess ethanol is used to push the conversion of the limiting reactant i.e., acetic acid, fully.

A more favorable case would be to achieve full conversion for both reactants, though it may not be possible, in order to completely avoid the need to separate the reactants from the products. Therefore, in this chapter, a modified configuration known as reactive extractive distillation is introduced which could potentially make the breakthrough needed to deliver higher conversion and at the same time producing higher ethyl acetate purity.

6.2 Reactive Extractive Distillation

In this section, the discussion is focused on the development of a modified configuration for esterification reaction of acetic acid with ethanol to produce ethyl acetate via reactive distillation process. The major goal for the development of this configuration is to improve the conversion of both reactants i.e., acetic acid and ethanol, for a single pass through the column while at the same time, achieving significantly higher product purity.

As mentioned in the introduction section of this chapter one of the major contributing factor for low conversion in the normal reactive distillation column is due to the close relative volatility between ethanol and water which results in reactant ethanol being washed out with water in the bottoms stream and hence lowering the overall conversion of the system. This suggests, lifting up more ethanol in the vapor form, would enhance overall conversion in the system, as the availability of reactant ethanol in the reactive zone can be increased. In the development of a new configuration, this factor is heavily considered. In addition, the ethanol-water mixture coming out through the bottom stream of the column would pose a difficult separation problem given that they formed an azeotrope. Conventional distillation scheme uses either pressure manipulation to vary the boiling points and composition of the azeotrope, or extractive agents to remove the water from ethanol by extractive distillation process. The two options, however, require additional distillation columns and recycle streams.

Using the conventional reactive distillation, it was also discovered earlier that producing a pure ethyl acetate distillate was not possible. Close relative volatility between ethyl acetate, ethanol and water in the zone above the acetic acid feed couple with low concentration of reactant in rectifying zone, which promotes reverse reaction, limits the separation efficiency and achieved conversion of this column respectively. Hence obtaining pure ethyl acetate distillate is not possible. Distillate that consists of ethyl acetate, ethanol and water requires additional complex separation scheme to obtain pure ethyl acetate. One of the possibilities is by utilising extractive distillation process to separate mixture of ethyl acetate-ethanol-water, which in turn will lead to increase in capital and operating cost.

A possibility to avoid the use of additional separation column to cater for the separation needed between ethanol and water is by combining the reactive and extractive distillation in a single column. In doing so, it is expected that higher conversion and distillate purity could be achieved. The modified configuration introduced here is termed as the reactive-extractive distillation column.

One of the classic success stories of the use of reactive-extractive distillation process is the synthesis of Methyl Acetate (Agreda & Partin, 1990). Using the new configuration, a better conversion and separation performance was achieved as compared to conventional reactive distillation column. In the system that consists of methyl acetate-methanol-water-acetic acid, the extractive action was used to break the azeotropes between methanol-methyl acetate and methyl acetate-water and in turn results in the achievement of higher purity methyl acetate distillate in a single column. The authors were able to achieve this by utilizing one of the remarkable aspect of the system i.e., using the acetic acid reactant as the entrainer, which breaks the two azeotropes, which are methyl acetate-methanol, and methyl acetate-water that was formed in the system. Figure 6.1 below illustrates the methyl acetate reactive extractive distillation column as proposed by Agreda & Partin (1990).

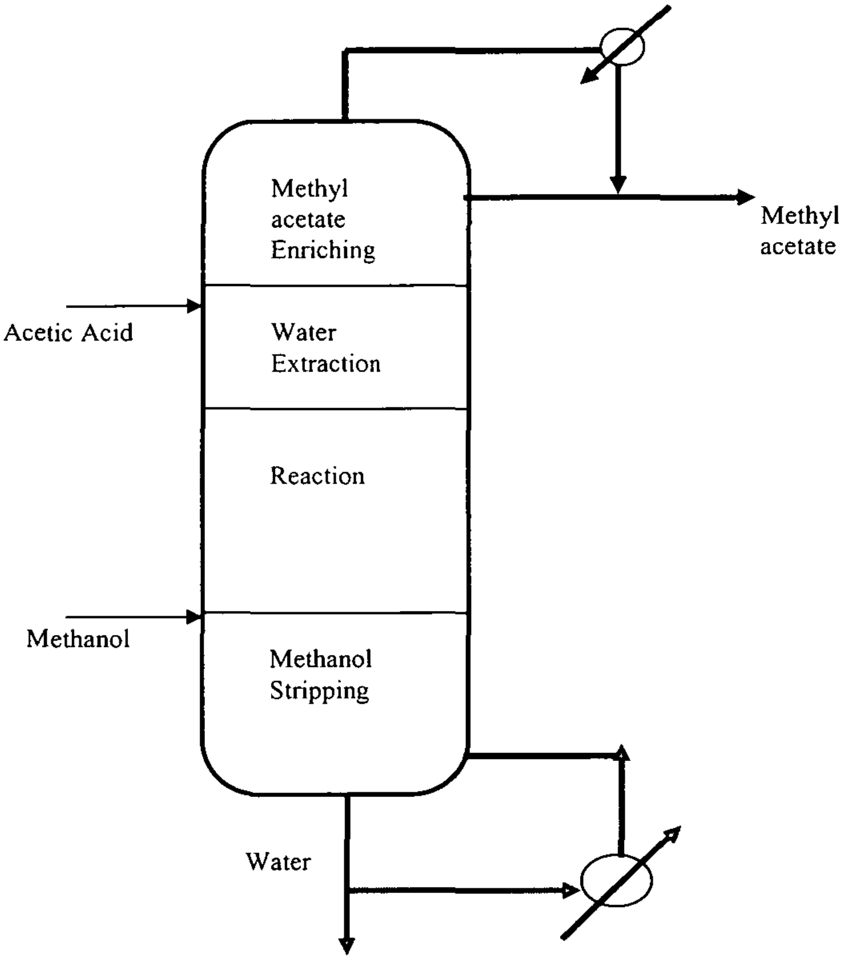

Figure 6.1: The Methyl Acetate Reactive Extractive Distillation Column

Agreda & Partin (1990) showed that using the configuration; complete reaction of the reactants was achieved while at the same time able to separate the products of the reaction i.e., methyl acetate and water, completely in a single column. The presence of the extraction zone in the column has drastically improved the column performance without which such ideal performance would be impossible to achieve.

In the configuration, acetic acid is fed few trays above the reaction zone to allow for it to come in contact with the azeotropes formed i.e., methyl acetate-methanol and methyl acetate-water, and thus breaking them. This section is termed as the extraction zone. In the reaction zone, the reaction is aided by a heterogeneous catalyst, which significantly enhances the reaction rate between acetic acid and methanol. In the rectifying zone, methanol and water is further separated from methyl acetate to produce pure methyl acetate distillate whilst in the stripping zone, the methyl acetate and methanol are stripped from the liquid phase thus leaving water to be produced as the bottom stream.

The reactive-extractive distillation configuration as shown in Figure 6.1 for methyl acetate system would not be suitable for the ethyl acetate system investigated in the study. The main reason is because the ethyl acetate system is found to be more complex as compared to the methyl acetate system due to the presence of four azeotropes. Thus a single extractive zone located at the top portion of the column will not be sufficient to break the azeotropes. In addition, one of the azeotropes i.e., ethanol-water, actually forms in the bottom section of the column. Another shortcoming is that none of the components in the ethyl acetate system could be utilised as the extractive agent to break all the azeotropes formed in the system. Therefore a completely different reactive-extractive-distillation configuration is needed if the use of such configuration is to be considered for the synthesis of ethyl acetate reactive distillation column.

6.2.1 Proposed Ethyl Acetate Reactive Extractive Distillation Column

In developing the alternative reactive-extractive distillation for ethyl acetate synthesis, the following have to be considered:

- extractive zone above acetic acid feed,
- extractive zone below ethanol feed and,
- suitable extractive agent.

Considering the above factors, the configuration as shown in Figure 6.2 is proposed. There are four distinctive zones in this configuration, namely; 1) rectifying zone, 2) extractive zone 1, 3) reaction active zone and 4) extractive zone 2. Out of many potential extractive agents for the ethanol-water, ethyl acetate-ethanol-water, ethyl acetate-water and ethyl acetate-ethanol separation, ethylene glycol was selected for the study in view of it, 1) being suitable extractive agent to break different types of azeotropes exist in the system (ethylene glycol suitable to break azeotropes of ethanol and also ethyl acetate), thus requiring only one common extractive agent to break different types of azeotropes exist in the system and 2) only requiring relatively simple distillation for recovery of the extractive agent.

As a result of applying the proposed configuration, it is expected that pure ethyl acetate could be produced as the overhead product of the column while water and ethylene glycol are produced as the bottom product of the column.

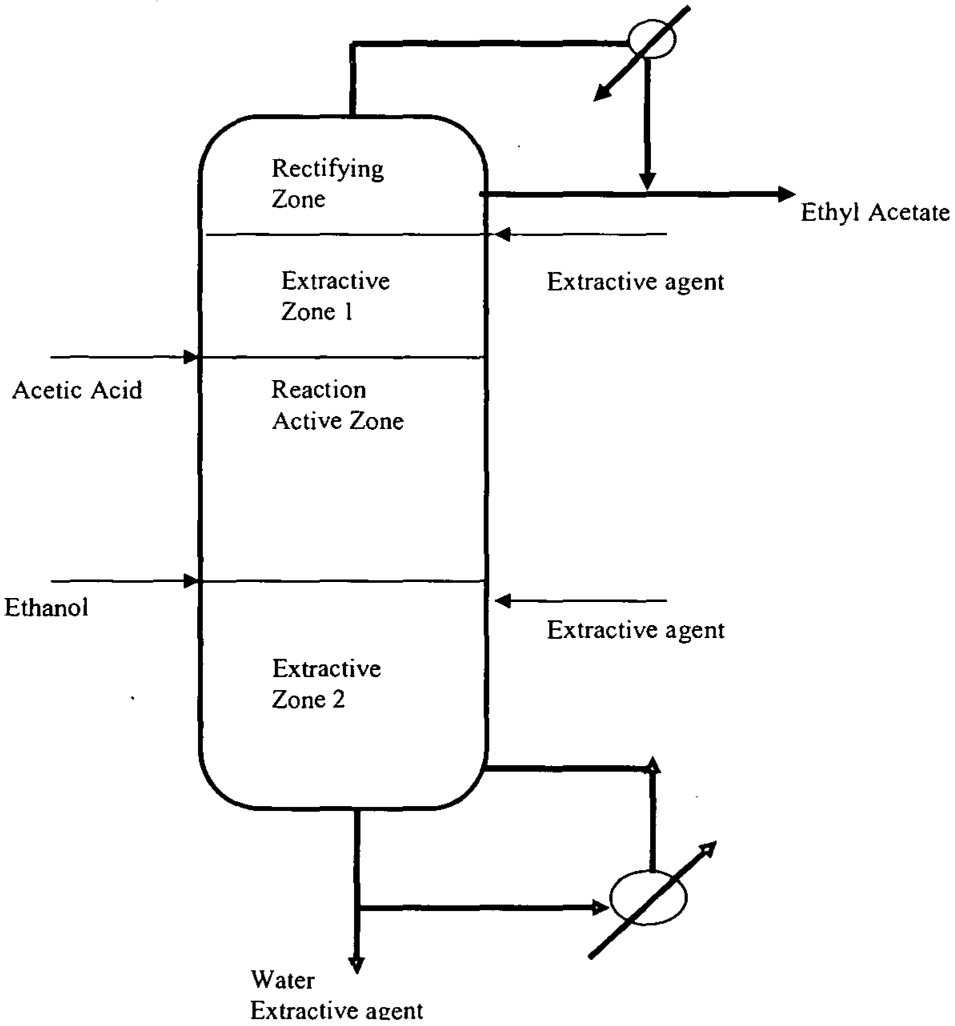

Figure 6.2: Conceptual Diagram Of The Ethyl Acetate Countercurrent Reactive Extractive Distillation Column

As depicted in Figure 6.2, the main objectives of proposing the column configuration is to ultimately achieve as close as possible to 100 % conversion of both reactants in a single column and at the same time producing high purity distillate. Simulation study on the above configuration for ethyl acetate reactive-extractive distillation column is carried out in the following sections in order to determine how far this configuration could achieve the set objectives.

6.3 Simulation Study

The simulation model developed for the conventional reactive distillation column in chapter 3 and chapter 4 was modified to suite the new reactive-extractive distillation configuration. The major differences of this configuration as compared to the conventional double feed reactive distillation column are;

1) additional component, ethylene glycol is incorporated as an extractive agent for the system,
2) additional feed streams namely the extractive agent introduced to the column is added.

The said changes require a number of modifications to be made to the simulation model. One of the major changes made in the simulation model is the Vapour-Liquid-Equilibrium (VLE) relation used as the system now involves five-component mixture. UNIFAC model was used for the VLE relations, as it is the most reliable model to predict VLE behavior of uncommon system. Discussion on the UNIFAC VLE model has been covered in Chapter 3.

Prior to simulate proposed ethyl acetate reactive extractive distillation column shown in Figure 6.2, base case configuration simulation, conventional ethyl acetate reactive distillation column is established first. This configuration would be a platform for comparison of simulation results of ethyl acetate reactive extractive distillation column.

6.3.1 Base Case Configuration – Ethyl Acetate Reactive Distillation Column

A simulation on the conventional reactive distillation column using empirical and UNIFAC vapor liquid equilibrium model was conducted. The configuration is simulated with two different vapor liquid equilibrium models in order to show closeness of simulation results when different vapor liquid equilibrium models are used. Once the results imminence between UNIFAC and empirical model is proven, UNIFAC model can be confidently used for new configuration that will be introduced in the later part of this chapter. Results description of this simulation is based on UNIFAC model, as this is used as base case or comparison purpose for new configuration that is introduced to enhance the ethyl acetate reactive distillation performance.

The conventional configuration and operating parameters of ethyl acetate reactive distillation column is shown in Figure 6.3. The column consists of 50 stages inclusive of one total condenser and one partial re-boiler. Reflux ratio and re-boiler duty are 3.0 and 8.3 x 10^6 cal/min respectively. Damkohler number is set at 80 with holdup in the individual stages is set at 5.7461 x 10^4 mol. Flow-rate of reactants ethanol and acetic acid are 351 mol/min^{-1} respectively. Reactant, acetic acid fed into the column in saturated liquid form at stage 4, whereas ethanol fed into the column in saturated vapor form at stage 40. Column operating pressure is 1 atmosphere and reactants introduced to the column at same pressure. Product take off are set to be equal at both distillate and bottom. It should be noted that there are vast changes in the column design specification as compared to configuration used in parametric analysis (chapter 5) in order to observe the performance of the column in more favorable condition (more number of stages and higher liquid holdup), towards conversion and purity. The Damkohler number as mentioned earlier is set at 80, which implies higher total liquid holdup on the stages. This modification was made deliberately in order to provide higher residence time for reaction and hence to obtain better conversion. If the number of stages were maintained as in previous chapter (figure 5.1), the liquid holdup on each of the stage would be very high.

However, practically it is not realistic to have too large liquid holdup on the stages (realistic liquid holdup on the stages between 0.5 to 2.0 m^3), as this will impose design and operating problem (Chen et al, 2000). Therefore to maintain realistic holdup, number of stages were increased as such the holdup on each of the trays are around $1.75m^3$. As a result of this distribution, total number stages increased to 50 stages for Damkohler number of 80.

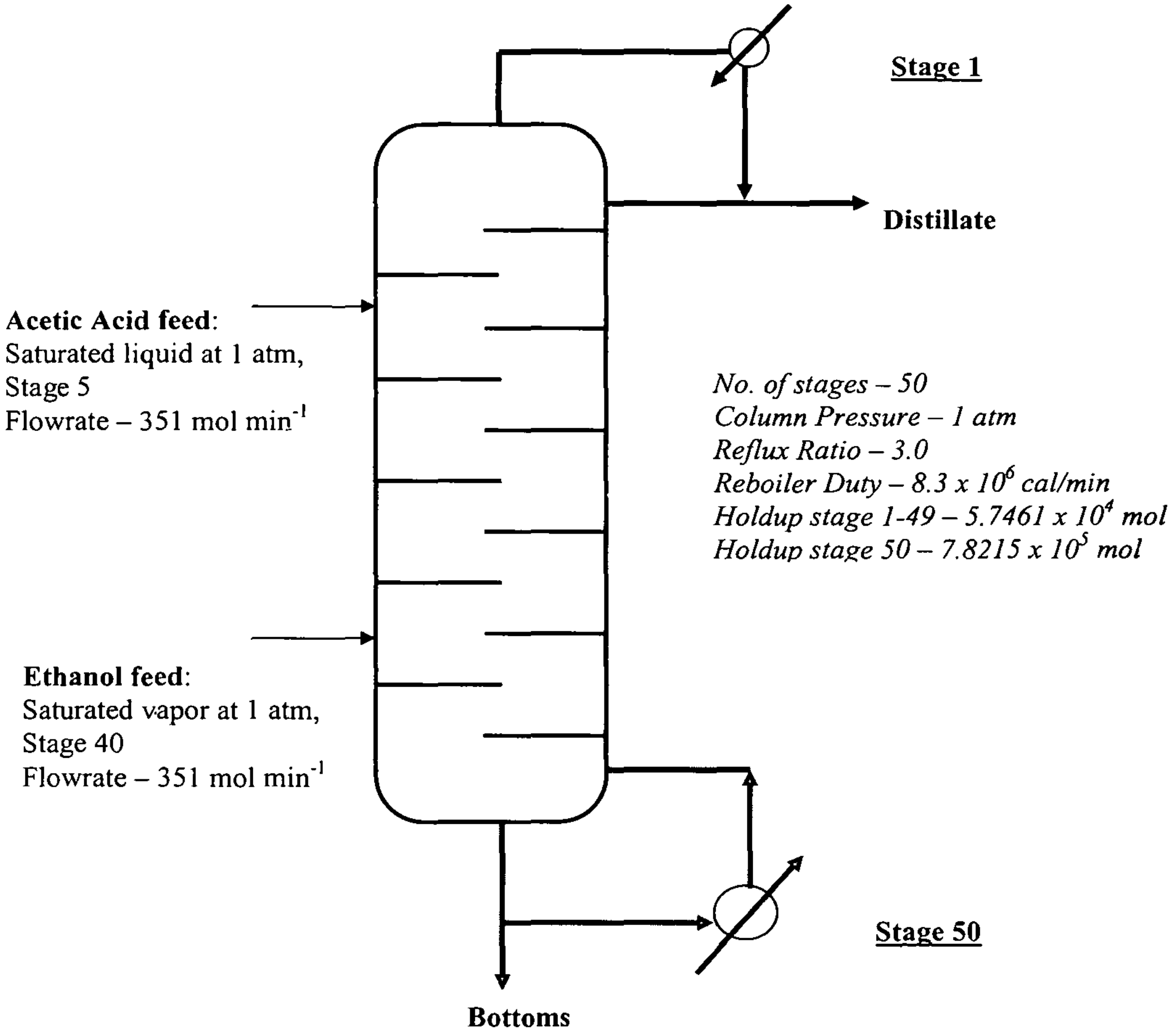

Figure 6.3: The Double Feed Reactive Distillation Column Configuration And Specifications For Ethyl Acetate Synthesis

6.3.1.1 Simulation Results

Table 6.1 compares the steady state simulation results of the base case configuration (catalytic double feed ethyl acetate reactive distillation column) shown in figure 6.3 using UNIFAC and empirical model.

Table 6.1: Simulation Results Of Base Case Configuration (Catalytic Double Feed Ethyl Acetate Reactive Distillation Column).

Quantity	**Units**	**Distillate**		**Bottom**	
		UNIFAC VLE Model	**Empirical VLE Model**	**UNIFAC VLE Model**	**Emperical VLE Model**
Composition					
Acetic acid (Ac)		**0.0055**	**0.0004**	**0.1592**	**0.1349**
Ethanol (Et)		**0.0632**	**0.0858**	**0.1114**	**0.0547**
Ethyl Acetate (Ea)		**0.7752**	**0.8567**	**0.0753**	**0.0284**
Water (W)		**0.1561**	**0.0572**	**0.6540**	**0.7819**
Temperature	**K**	**345.17**	**342.49**	**353.18**	**371.51**
Product flow	**mol /min**	**335.85**	**340.66**	**366.16**	**361.36**
Et conversion	**mole %**	**82.3**	**86**	**-**	**-**
Ea purity	**mole %**	**77.52**	**85.67**	**7.53**	**2.84**
Reflux flow	**mol/min**	**1010**	**1022**	**-**	**-**

As shown in the Table 6.1, the results of both models UNIFAC and empirical are in good agreement. The deviations between both results are less than 10%. Thus, UNIFAC model can be confidently used for simulation ethyl acetate reactive distillation column.

Figure 6.4, 6.5 and 6.6 show the liquid phase concentration profile, the temperature profile and the reaction rate profile along the column respectively for the steady state simulation using UNIFAC vapor liquid equilibrium model of the configuration shown in Figure 6.3.

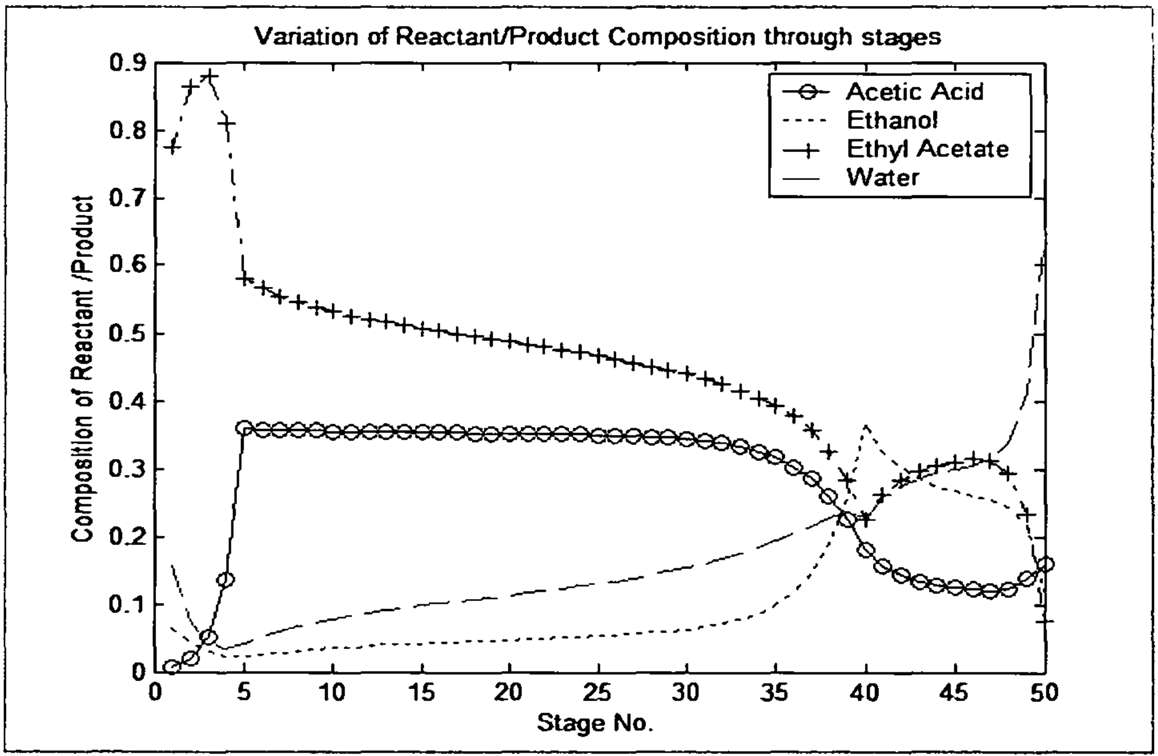

Figure 6.4: Steady State Liquid Phase Concentration Profile

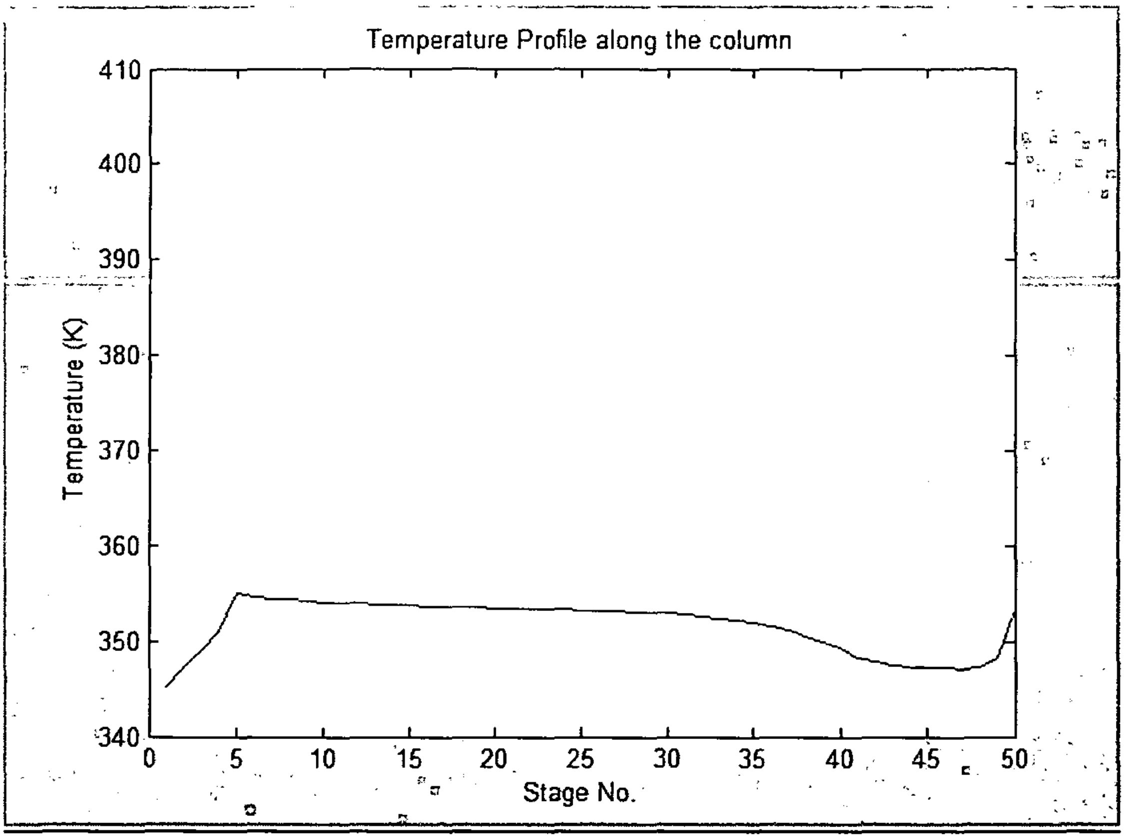

Figure 6.5: Steady State Temperature Profile Along The Column

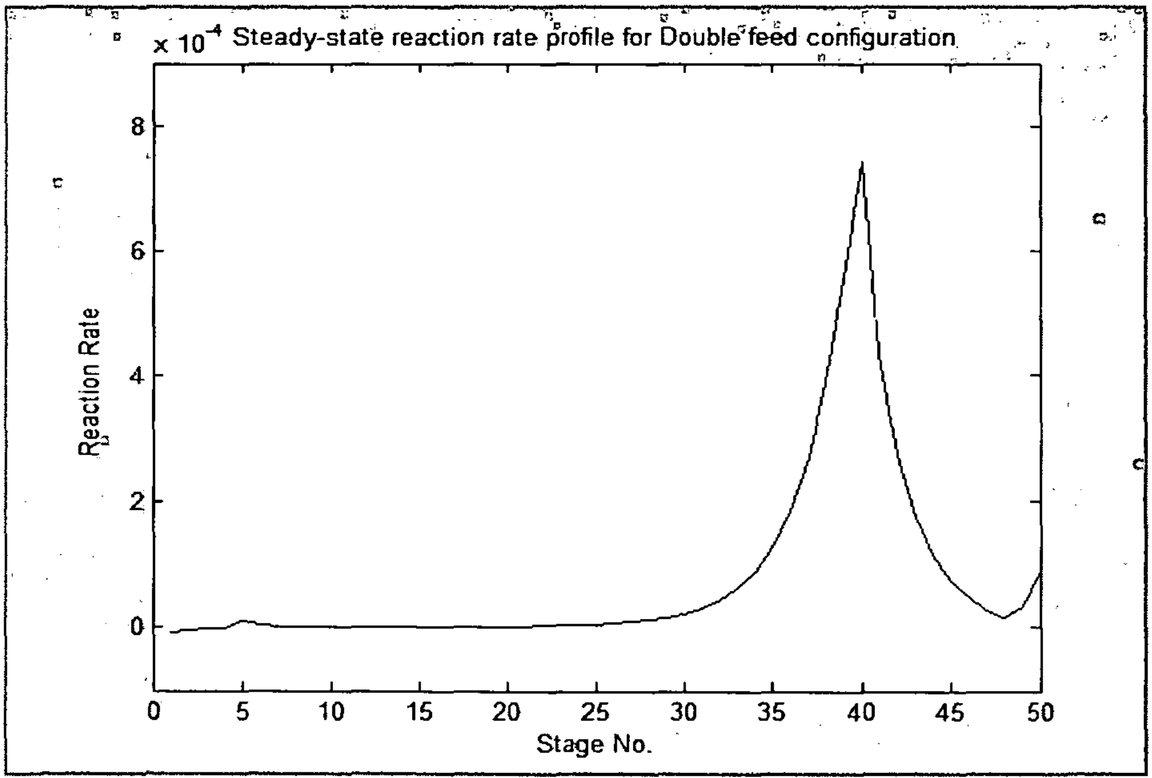

Figure 6.6: Steady State Reaction Rate Profile

As depicted in Table 6.1, the achieved conversion of the system is 82.3 % and the product purity (ethyl acetate) in the distillate is 77.52% when the product take off rate is set to be nearly equal at distillate and bottoms. (Though the achieved conversion and product purity improved as compared to the configuration used in parametric analysis (Figure 5.1), this configuration failed to achieved process objectives of reactive distillation column, which is almost complete conversion of reactants and pure ethyl acetate in the distillate. The limitations of the system as discussed earlier in this chapter, prevail given that there are vast modification in the specifications and design parameters introduced for the base case configuration.

Figure 6.4 shows that the ethanol fed into the system at stage 40, being washed away by water through the bottom stream in view of its close relative volatility to water. This hinders the performance of the column by limiting the achieved conversion of the system as lesser amount of ethanol could make their way up the column to the reaction active zone. In the region above the acetic acid feed, the formation of three binary and a ternary azeotropes between ethyl acetate, ethanol and water, limits the achieved ethyl acetate distillate purity. Therefore, the conventional reactive distillation would not be able to separate these components to obtain pure ethyl acetate in the distillate. Steady state temperature profile in Figure 6.5 shows sudden drop in temperature at ethanol feed point. This is due to the introduction of low boiling reactants in large quantity into the column couple with the high concentration of low boiling component i.e., ethanol. At this point also, it is noted that the reaction rate is at maximum due to high concentration of ethanol in liquid phase at this point driving the reaction positively. It is noted that the reaction rate declines above and below the feed point of ethanol. Insufficient ethanol in the liquid phase is the direct cause of this trend. While there is sudden increase in temperature in acetic acid feed point due to introduction of high boiler acetic acid in large quantity at saturated liquid condition into the column. Acute drop in reaction rate at acetic acid feed point is due to high concentration reaction products and lack of ethanol in this region of the column. On top of that, catalytic reaction starts from here, high concentration of product enhance negative reaction rate in this region of the column. Slight jump in reaction rate is observed in re-boiler due to high acetic acid this part of the column.

In overall, it would not be possible to achieve ideal performance using any normal reactive distillation configuration. The impeding factors highlighted above for the conventional reactive distillation configuration clearly limits the performance of the column even with larger column. Other alternatives need to be considered in order to enhance the performance of the column.

6.3.2 Simulation of Ethyl Acetate Reactive-Extractive Distillation Column

As discussed earlier, ideal performance of reactive distillation column would be to achieve high conversion of reactants and at the same time, producing high product purity. In the case of ethyl acetate synthesis studied in this work, the performance is measured by looking at the ethyl acetate distillate purity and the conversion of reactants acetic acid and ethanol. If the objectives of achieving almost complete conversion of both reactants (>95%) while at the same time producing high ethyl acetate distillate purity (>95%) are achieved, complex downstream separation could be avoided. The only separation to be considered is the separation of the bottoms product, which would be water and the extractive agent i.e., ethylene glycol, for recycling purposes. This separation is relatively simple and straightforward using ordinary distillation. Based on the proposed configuration, simulation study is carried out in the following sections and the applicability of the developed model in simulation environment is analysed. This is then followed by comparison of the results obtained with the conventional reactive distillation column, simulated earlier. Figure 6.7 below, schematically presents the double feed ethyl acetate reactive-extractive distillation configuration and simulation specifications.

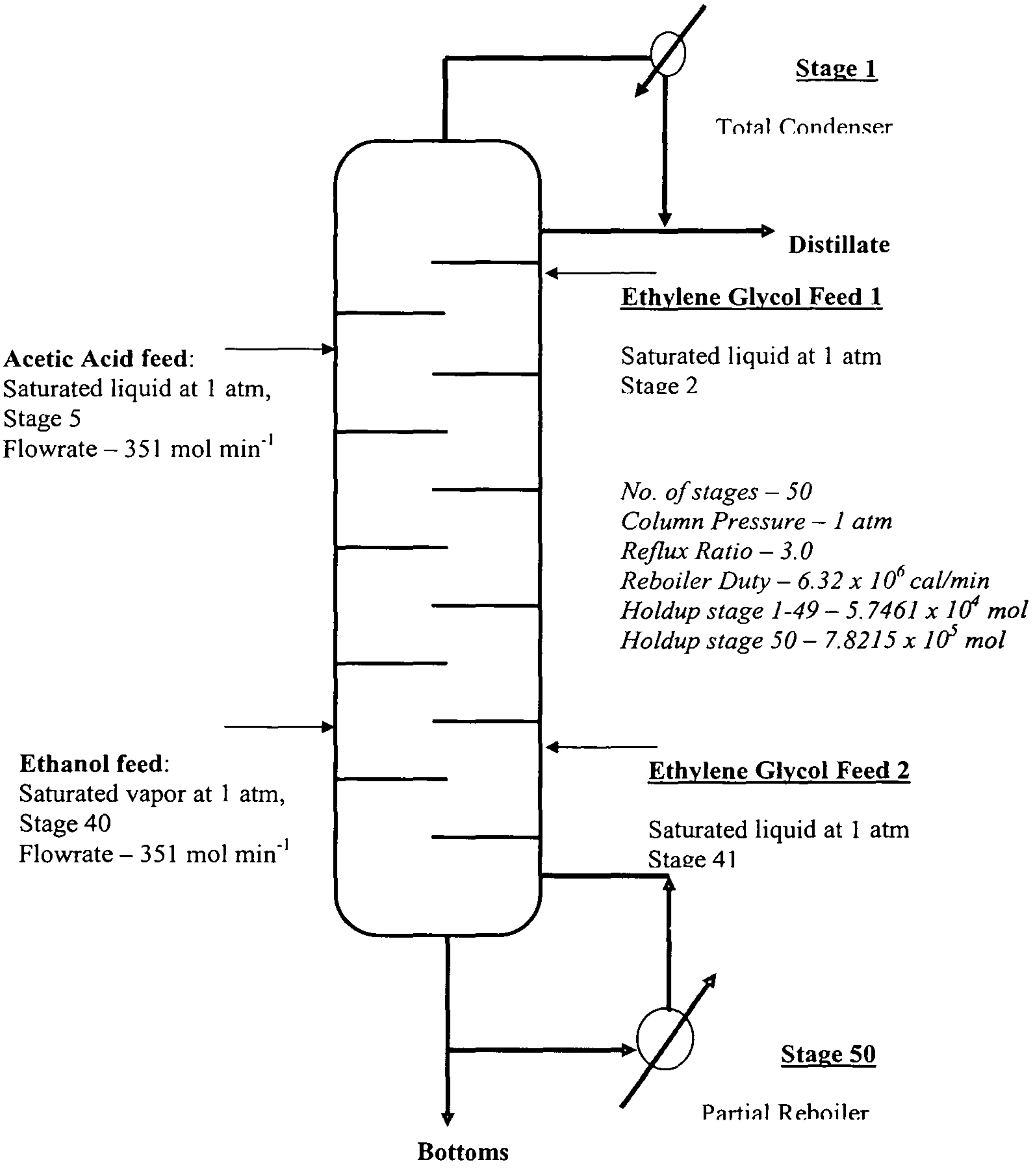

Figure 6.7: The Double Feed Reactive Extractive Distillation Column Configuration And Specifications For Ethyl Acetate Synthesis.

The column configuration above is exactly same as conventional reactive distillation configuration proposed earlier in this chapter (figure 6.3), with additional two extractive agent feed points for this configuration. The main objective of this section is to study the behaviour of the column with the addition of extractive agent in the system. As depicted in figure 6.7, extractive agent is fed into the column at stage 2 and stage 41. The feed location is determined based on simulation trial and error procedure in which these locations give better results as compared to other locations.

6.3.2.1 Simulation Results of Ethyl Acetate Reactive Extractive Distillation Column

Table 6.2 summarises the steady state simulation results of the proposed configuration i.e., the catalytic double feed ethyl acetate reactive extractive distillation column.

Table 6.2: Simulation Results For Catalytic Double Feed Ethyl Acetate Reactive Extractive Distillation Column.

Quantity	**Units**	**Distillate**	**Bottom**
Composition			
Acetic acid (Ac)		**0.0006**	**0.0052**
Ethanol (Et)		**0.0083**	**0.0030**
Ethyl Acetate (Ea)		**0.9815**	**0.0002**
Water (W)		**0.0096**	**0.2724**
Ethylene Glycol (Eg)		**0.0000**	**0.7192**
Temperature	**K**	**350.71**	**405.33**
Product flow	**mol /min**	**350.52**	**1251.5**
Et conversion	**mole %**	**98.07**	**98.07**
Ea purity	**mole %**	**98.15**	**0.02**
Reflux flow	**mol/min**	**1051.6**	

Figure 6.8, 6.9 and 6.10 display the liquid phase concentration profile, the temperature profile and the reaction rate profile along the column respectively.

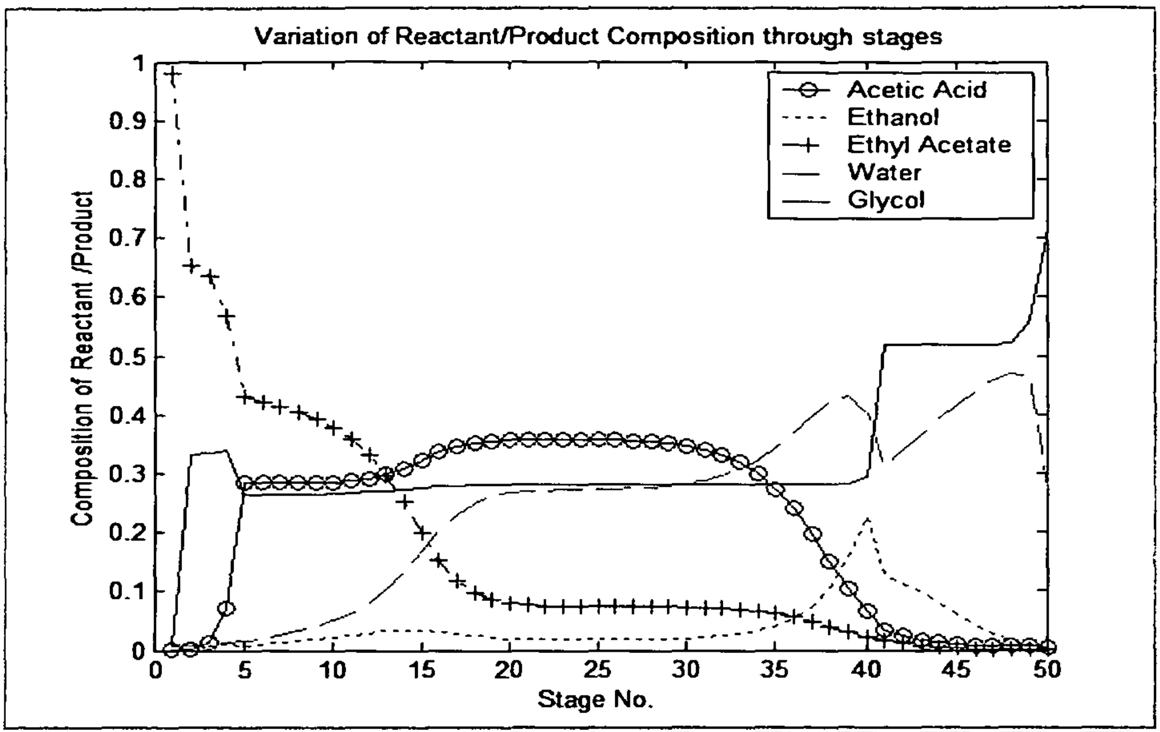

Figure 6.8: Steady State Liquid Phase Concentration Profile

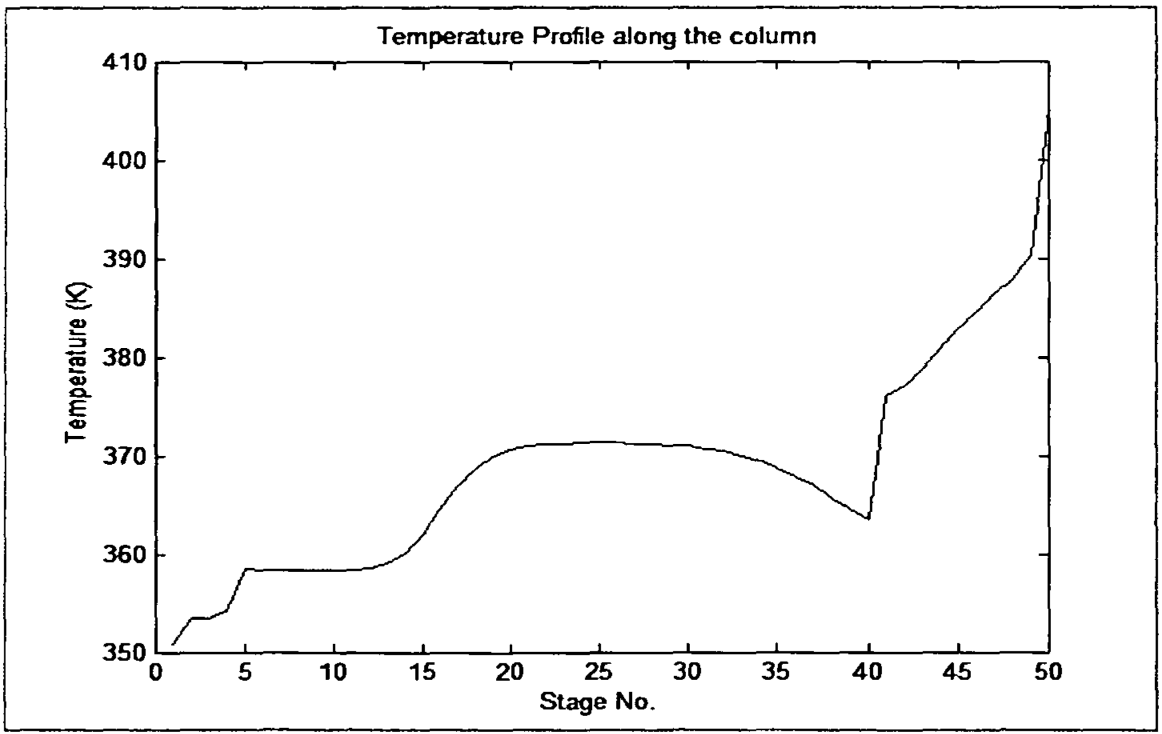

Figure 6.9: Steady State Temperature Profile Along The Column

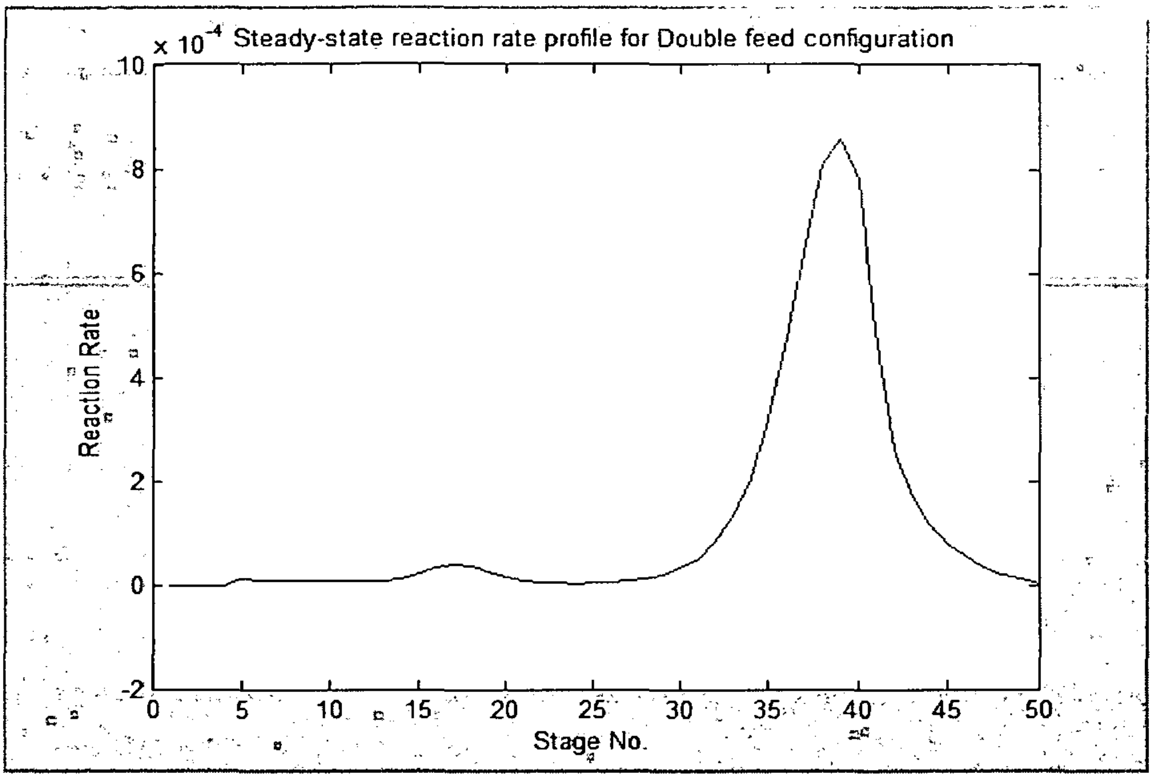

Figure 6.10: Steady State Reaction Rate Profile

As depicted in Table 6.2 and Figures 6.8, 6.9 and 6.10, synthesis of ethyl acetate in reactive extractive distillation configuration as proposed above gives favorable results in terms of both process objectives i.e., conversion and product purity. By utilising the proposed configuration, the achieved product purity is 98 %, which is significantly higher compared to the purity that can be achieved using conventional reactive distillation configuration. The achieved conversion of equi-molar reactants fed to the system is 98 % as well, which is impossible to achieve in conventional ethyl acetate reactive distillation system. Ethylene glycol, which is fed at two locations in the column, plays an important role to boost the overall performance of the column. Extractive agent, ethylene glycol fed to the column at stage 2 creates a favorable condition for the separation of close boiling components. Ethyl acetate, which is the lightest amongst the components in the system, is separated from the ethanol and water. Ethyl acetate goes overhead by the presence of ethylene glycol, whereas ethanol and water descend down the column with the extractive agent, ethylene glycol. In the rectification zone, ethylene glycol and to a lesser extent, ethanol, water and acetic acid is separated from ethyl acetate.

The temperature profile along column is depicted in figure 6.9. There are two-temperature jump at upper half of the column, namely extractive agent feed point 1 and acetic acid feed point. Understandably, this is due to introduction of high boiling components, acetic acid and ethylene glycol into the system. High concentration of acetic acid, ethylene glycol and water in the reaction active zone results in increasing temperature trend in this part of the column. However sudden drop in temperature was noted at ethanol feed point due to introduction of low boiling point component, ethanol into the system. At extractive agent feed point 2, again drastic temperature change was noted due to introduction of ethylene glycol in the system. From this point onwards, steep temperature profile is noted due to high concentration of high boiling component ethylene glycol in this zone.

In the reaction active zone from acetic acid and sulfuric acid feed point to ethanol feed point most of the reaction takes place here. Descending acetic acid and ascending ethanol from the respective feed points, creates a favorable condition in this portion of the column for reaction to take place. Active reaction rate in this zone exhaust most of the reactants in this zone itself. Since catalyst present in the bottom half of the column (feed point 2 and below) as well, reaction is still active in this zone. However it declines as it moves down the column as most of the reactants exhausted in the reactive zone. But presence of reaction in this zone supports the conversion in the column as it converts un-reacted reactants from the reaction active zone.

Extractive zone 2, located below reaction active zone, plays the same role as extractive zone 1. Extractive agent, ethylene glycol is added one tray below the ethanol feed. Presence of ethylene glycol prevents the formation of azeotropes between ethanol and water in the bottom half of the column as encountered in the conventional reactive distillation column, which significantly limits the performance of the column. By introducing ethylene glycol, more ethanol could be lifted up to participate in the reaction within the reaction active zone and hence increasing the overall conversion of the system. The product take off rate is set to be equally between distillate and bottoms. It should be noted that the re-boiler heat requirement for base case configuration is higher as compared to reactive extractive distillation configuration. Additional feed stream, ethylene glycol fed in the bottom portion reduces the L/V ratio in the column thus lower amount of re-boiler duty is required to achieved nearly the same product take off as conventional column.

Half of the formed reaction product is available in distillate (98 % ethyl acetate) and the remaining half is available in the bottoms (98 % water formed goes to the bottoms). This shows that the separation efficiency of the system is good. The extractive agent i.e., ethylene glycol, fed to the system is taken off together with the other components in the bottom stream as it is the heaviest component in the system. Significant improvements have been achieved by using reactive extractive distillation configuration for the synthesis of ethyl acetate as compared to the conventional reactive distillation configuration. In the following section comparison between these two configurations is made.

6.4 Comparison between Conventional Reactive Distillation Column and Reactive Extractive Distillation Column

1) Comparison of Column Operating Parameters

Table 6.3: Feed Specifications, Column Configuration and Operating Conditions used for Conventional Reactive Distillation Column and Extractive Distillation Column.

Quantity	Units	Specifications Conventional Reactive Distillation Column	Specifications Reactive Extractive Distillation Column
Feed Flowrate 1	mol min^{-1}	**351**	**351**
Feed Flowrate 2	mol min^{-1}	**351**	**351**
Ex. Agent 1 Flow rate	mol min^{-1}	-	**400**
Ex. Agent 2 Flow rate	mol min^{-1}	-	**500**
Feed 1 Stage		**5**	**5**
Feed 2 Stage		**40**	**40**
Ex. Agent 1 Feed Stage		-	**2**
Ex. Agent 2 Feed Stage		-	**41**
<u>Feed 1 Composition</u>			
Acetic acid (Ac)		**1**	**1**
Ethanol (Et)		**0**	**0**
Ethyl Acetate (Ea)		**0**	**0**
Water (W)		**0**	**0**
<u>Feed 2 Composition</u>			
Acetic acid (Ac)		**0**	**0**
Ethanol (Et)		**1**	**1**
Ethyl Acetate (Ea)		**0**	**0**
Water (W)		**0**	**0**

Number of Stages, N		**50**	**50**
Column Pressure, P	atm	**1**	**1**
<u>Liquid Holdup</u>			
Condenser, Tray	liter	*5.7461 x 10^4 mol*	*5.7461 x 10^4 mol*
Re-boiler	liter	*7.8215 x 10^5 mol*	*7.8215 x 10^5 mol*
Reflux Ratio, r		*3.0*	*3.0*
Re-boiler Duty, Qr_b	cal/min	*8.3 x 10^6 cal/min*	*6.32 x 10^6 cal/min*
Bottom Flow, B	mol min^{-1}		

2) Comparison of Results

Table 6.4: Comparison Of Steady State Simulation Results Of Conventional Reactive Distillation Column And Reactive Extractive Distillation Column

Quantity	**Units**	**Distillate**		**Bottom**	
		Conventional Reactive Distillation	**Reactive extractive Distillation**	**Conventional Reactive Distillation**	**Reactive extractive Distillation**
<u>Composition</u>					
Acetic acid (Ac)		**0.0055**	**0.0006**	**0.1592**	**0.0052**
Ethanol (Et)		**0.0632**	**0.0083**	**0.1114**	**0.0030**
Ethyl Acetate (Ea)		**0.7752**	**0.9815**	**0.0753**	**0.0002**
Water (W)		**0.1561**	**0.0096**	**0.6540**	**0.2724**
Ethylene Glycol (Eg)		**-**	**0.0000**	**-**	**0.7192**
Temperature	**K**	**345.17**	**350.71**	**353.18**	**405.33**
Product flow	**mol /min**	**335.85**	**350.52**	**366.16**	**1251.5**

Et conversion mole %	**82.3**	**98.07**	**-**	**98.07**
Ea purity mole %	**77.52**	**98.15**	**7.53**	**0.02**
Reflux flow mol/min	**1010**	**1051.6**	**-**	**-**

As shown in Table 6.3, the column specifications and the input parameters are exactly the same for both configurations except for the 2 additional input streams for the extractive agent in the reactive extractive distillation configuration.

Table 6.4 compares the steady state simulation results of conventional ethyl acetate reactive distillation column and ethyl acetate reactive extractive distillation column proposed in this study. It is evident that there are significant improvements in terms of conversion and product (ethyl acetate) purity with new configuration (reactive extractive distillation column) proposed in this study.

Conventional reactive distillation configuration (figure 6.3) failed to separate the reactants and products of reaction efficiently in the column especially in the zone identified as susceptible for azeotrope formation (i.e. above acetic acid feed point and below ethanol feed point). Due to inefficient separation most of the reactants are washed away in distillate and bottoms of the column, thus the achieved conversion of the system is low even with more number of stages and higher residence time for reaction. On the other hand, reactive extractive distillation configuration (figure 6.7) proposed in this study was able to perform better in terms of achieved conversion and purity in a single column due to introduction of two extractive sections in the column. Presence of ethylene glycol in these zones prevents formation of azeotropes through extractive action, which ensures more of the valuable reactant being pushed to reactive active zone and avoid lost of reactants with product of reaction through distillate and bottoms stream. In addition, extractive action above acetic acid feed point ensures high ethyl acetate product purity obtained from the distillate by breaking the azeotropes formed in this section of the column.

In overall by the introduction of extractive action in the column more favorable results were obtained as compared to equivalent conventional ethyl acetate reactive distillation configuration.

CHAPTER 7

CONCLUSION

7.1 Conclusions

Ethyl Acetate is an important industrial solvent, which requires relatively complicated processing particularly the separation process in order to produce it. There are various routes to produce ethyl acetate, but the most preferred route is via the esterification reaction of acetic acid and ethanol. The reaction system involved is found to be suitable for the application of reactive distillation process. However, it is not commercially attractive in view of the low conversion and ethyl acetate purity attainable using the option.

Previous work by other authors on ethyl acetate reactive distillation scheme has been the motivating factor for this research study. Un-catalytic ethyl acetate reactive distillation column proposed by Komatsu, (1977) and Alejski, (1988), has failed to push the conversion beyond its normal equilibrium limit and to produce ethyl acetate with a purity over the azeotropic composition limit. Meanwhile, the double feed catalytic ethyl acetate reactive distillation column as proposed by Nishith and Daotidis, (2001) managed to improve the performance of the column significantly but the scheme fails to produce high purity ethyl acetate as a product and completely convenrt all the reactants introduced to the system which would ideal case of reactive distillation column. This research study has explored the possibilities to improve the performance of the ethyl acetate reactive distillation column.

A steady state simulation model for ethyl acetate reactive distillation column was developed at the earlier part of the research work. Appropriate kinetic and vapor liquid equilibrium model were incorporated into the proposed model taking into account the non-idealities, particularly in the liquid phase. The simulation model developed was based on equilibrium stage model where liquid and vapor phases were assumed to be in phase equilibrium.

The resulting simulation model consists of large combination of complex nonlinear differential and algebraic equations (DAEs) that necessitates a numerical solution in order to obtain steady state solution. The suitable method for solving system of stiff differential and algebraic equations (DAEs) is found to be implicit, multi-step of varying order based on relaxation method. Matlab built in function ODE15s was used to solve these stiff differential and algebraic equations. The solution strategy employed was found to be efficient and robust for arbitrary initialisation though the convergence was considered slow especially when approaching the solution. The simulation results of this study were found to be comparable with other equivalent simulation work and experimental work.

In order to study the impact of important input parameters on the column performance, parametric analysis was carried out. The performance of the column was measured by
looking at overall conversion and ethyl acetate purity at distillate. Through parametric analysis, it was learned that the performance of the column could not be enhance significantly and thus requiring a completely different configuration.

A new configuration was proposed for the synthesis of ethyl acetate via reactive distillation. The scheme is called reactive-extractive distillation in view of the use of extractive agent for the purpose of breaking the azeotropes formed by the components in the system and thus aiding the separation to produce pure ethyl acetate. Two extractive sections couple with extraneous extractive agent were added in the existing conventional reactive distillation column. Through this configuration, performance of the column was enhanced significantly as compared to the conventional reactive distillation configuration. The achieved ethyl acetate purity at distillate was 98 percent and the total conversion for equi-molar feed was 98 percent as well.

It is hoped that this research study has open up a possibility for commercialisation of ethyl acetate reactive distillation process as the product purity and conversion achieved through the configuration proposed is considered attractive. In addition, by utilising the proposed configuration, significant cost saving can be achieved as the three unit operations required in the conventional process could be combined into a single unit. Meanwhile parametric analysis carried out earlier in this research work has been able to explain some of the factors that limit the performance of conventional reactive distillation column for synthesis of ethyl acetate.

7.2 Future Work

This research work has open up several opportunities for further study. The following issues are proposed for future work in modeling and simulation of ethyl acetate reactive distillation column.

7.2.1 Simulation of heterogeneous ethyl acetate reactive distillation column

Synthesis of ethyl acetate via reactive distillation process can be carried out with heterogeneous catalyst as well. The advantages of using heterogeneous catalyst in reactive distillation process is that reactive zone can be localize and hence unwanted reverse reaction can be avoided. Besides, the homogeneous catalysed reactions also are less favored owing to the operational problems of the separation and reuse of the catalyst. Reaction kinetics data are available for the esterification of ethanol and acetic acid to produce ethyl acetate and water (Geert Hangx, 2001). The suitable catalyst for this process is the cation exchange resins Purolite CT179. Simulation model used in the current work can be modified to account for heterogeneous reaction and comparison can be made on the effects of heterogeneous and homogenous catalyst on the performance of the reactive distillation column.

7.2.2 Experiments to compliment the simulation results

The best way to answer a simulation design is to do an experiment. Reactive extractive distillation column for the synthesis of ethyl acetate proposed in this research work does not have any other sources for comparison purposes, as this is the first of its kind. Therefore to compliment the simulation results obtained in this study, experiment work need to be carried out on this configuration.

7.2.3 Implementation of side reaction in kinetic model

The kinetic model used in the modeling equations can be expanded to account side reaction in order to obtain greater accuracy of the simulation results. The main side reaction for the synthesis of ethyl acetate is the dimerisation of acetic acid in the vapor phase. Appropriate kinetic equations need to be found for this reaction and can be included in the existing simulation model of this study.

7.2.4 Development of non-equilibrium stage model

The equilibrium stage model used in this research work is a very good pragmatic approach suitable particularly in the early stage process development such as the case of ethyl acetate reactive extractive distillation column simulation design. In the advance stage of development of this process, researchers can use the non-equilibrium stage model, which accounts for interaction phenomena (e.g. diffusional and direct reaction mass transfer interaction) and also hydraulic aspects of the column (e.g. description of residence time distribution and mixing). Through this model, detail column behavior can be understood.

7.2.5 Design and operating parameters optimization of reactive distillation column

In the parametric analysis carried out in chapter 5, it was noted that not all of the column operating and design parameters have significant impact on the column performance. Insignificant design and operating parameters can be screened out and future research work can consider of overall design and operating parameters optimization. This is to ensure that the basic configuration of the reactive distillation column is optimized in the first place before control study is to be performed.

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Appendix

UNIFAC Model Parameters Values

		-CH$_3$	-CH$_2$	-COOH	-OH	-COOCH$_3$	H$_2$O
R		0.9011	0.6744	1.3013	1.0000	1.9031	0.9200
Q		0.8480	0.5400	1.2240	1.2000	1.7280	1.4000
a_{mk}	-CH$_3$	0	0	986.5	1313	232.1	663.5
	-CH$_2$	0	0	986.5	1313	232.1	663.5
	-COOH	156.4	156.4	0	353.5	101.1	199.0
	-OH	300.0	300.0	-299.1	0	72.87	-14.09
	-COOCH$_3$	114.8	114.8	245.4	200.8	0	660.2
	H$_2$O	315.3	315.3	-151.0	-66.17	-256.30	0