STUDIES IN REACTIVE SEPARATIONS

A THESIS SUBMITTED TO THE

UNIVERSITY OF PUNE

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN THE FACULTY OF ENGINEERING

IN

CHEMICAL ENGINEERING

SUBMITTED BY

KIRAN DINKAR PATIL

UNDER THE GUIDANCE OF

DR. B.D. KULKARNI

PLACE OF RESEARCH
CHEMICAL ENGINEERING & PROCESS DEVELOPMENT DIVISION,
NATIONAL CHEMICAL LABORATORY,
PUNE 411 008, INDIA

NOVEMBER 2010

Dedicated to

My Parents, Wife and Son

CERTIFICATE

This is to certify that the work incorporated in the thesis titled, "Studies in Reactive Separations" submitted by Mr. Kiran D. Patil for the Degree of Doctor of Philosophy, in Chemical Engineering at University of Pune, was carried out by him under my supervision at Chemical Engineering and Process Development Division , National Chemical Laboratory, Pune-411 008, India. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

Dr. Bhaskar D.Kulkarni

(Research Guide)

DECLARATION

I herby declare that the thesis titled, "Studies in Reactive Separations" submitted by me for the Degree of Doctor of Philosophy is the record of work carried out by me at Chemical Engineering and Process Development Division of National Chemical Laboratory, Pune-411 008, India under the guidance of Dr. Bhaskar D. Kulkarni. The thesis has not formed the basis for the award of any Degree, Diploma, Associateship, and Fellowship, Titles in this or any other University or other institutions of Higher Learning. I further declare that the material obtained from other sources has been duly acknowledged in the thesis.

Date: November 2010   **Mr. Kiran D. Patil**

ACKNOWLEDGEMENTS

I also thank all my colleagues in the department for their co-operation and constructive suggestions during my research work. I would like to thank my friend, Jitendra, for his patience during the Aspen Plus simulation of this work. Without his expert assistance and advice, many extra valuable months would have been unnecessarily spent.

I am also grateful to department staff at MIT, Pune, India, especially, Shri Satish More, Shri Tushar Gandre, Shri Shantaram Bharekar and Shri Ashok Ghule for their help and support during my experimental work. Thanks are due to my student friends for their help and support in sample and data analysis during the experimental work.

Change is the pattern of life. With the submission of this thesis, I sever a long association with National Chemical Laboratory, Pune, India and it is with mixed feelings I do so. I spent my most of time during my Bachelor's, Master's and Doctorial level research work in the plush green surroundings of the NCL campus, which I guess resembles the paradise and where I shall be ever willing to come back.

Last, but not the least, I wish to express my gratitude to my parents, who have always been a major source of encouragement and support in all my academic pursuits. I wish to thank to my wife, Varsha and son, Aditya for their love, sacrifice, understanding, endless patience and encouragement when most needed.

November 2010   **Kiran Dinkar Patil**

Pune

CONTENTS

1 **INTRODUCTION**

2 **LITERATURE REVIEW**

3   MODELLING OF REACTIVE DISTILLATION PROCESSES

4   REACTION KINETICS AND PHASE EQUILIBRIUM STUDIES FOR SYNTHESIS OF ISO AMYL ACETATE

[A] Reaction Kinetics Studies

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE

Notations

a	interfacial area, m^2
B	bottoms flow, mol s^{-1}
c	number of components, dimensionless
C	molar conversion fraction of the reactant
CAO	initial concentration of acetic acid (kmol m^{-3})
D	distillate flow, mol s^{-1}
D_a	Damkohler number, dimensionless
E	energy flux, W m^{-2}
F^V	vapor feed stream, mol s^{-1}
F^L	liquid feed stream, mol s^{-1}
f	component feed stream, mol s^{-1}
h	heat transfer coefficient, W m^{-2} K^{-1}
H	molar enthalpy, J mol^{-1}
k_1	pseudo-first-order reaction rate constant, s^{-1}
K	vapor-liquid equilibrium constant, dimensionless
L	liquid flow rate, mol s^{-1}
M	molar holdup, mol
Q	heat duty, w
-r	reaction rate (mol g^{-1} min^{-1})
r	number of reactions, dimensionless
r_j	ratio of side stream flow to inter stage flow on stage j, dimensionless
$R_{m,j}$	reaction rate, mol m^{-3} s^{-1}
R_u	gas constant, m^3 atm $kmol^{-1}$ K^{-1}
R	reflux ratio
R	gas constant (kJ $mol^{-1}K^{-1}$)
t	time, s
T	temperature, K
v	reaction volume (liquid holdup)
v_o	volumetric flow rate entering the stage
V	vapor flow rate, mol s^{-1}
x	mole fraction in liquid phase, dimensionless
XA	conversion of acetic acid
y	mole fraction in vapor phase, dimensionless

Greek Letters

ş	accumulated sum of the reaction molar turnover flow rates until the nth stage from the top
τ	residence time, dimensionless
ρ	density, kg m^{-3}
γ	activity coefficient
ϕ	thiele modulus, dimensionless
Bi	Biot number, dimensionless
β	Prater number, dimensionless
γ	Arrhenius number, dimensionless

Subscripts

i	component index
I	referring to interface
j	stage index
t	total
B	bottom product
D	distillate
n	stage
k	base component (Acetic Acid)

Superscripts

F	referring to feed stream
L	referring to liquid phase
V	referring to vapor phase

List of Abbreviations

CPI	chemical process industry
EQ	equilibrium
EO	ethylene oxide
ETBE	ethyl tert-butyl ether
GL	gas to liquid
HOAC	acetic acid
HETP	height equivalent of theoretical plate
HTU	height of transfer unit
LAB	linear alkyl benzene
ISAMAC	iso amyl acetate
ISAMOH	iso amyl alcohol
MeOH	methanol
MeOAc	methyl acetate
MTBE	methyl *tert*-butyl ether
NEQ	non-equilibrium
NRTL	non random two liquid
NTSM	number of theoretical stages per meter
ODE	ordinary differential equation
RD	reactive distillation
SRS	minimum sum of residual squares resulting in the fitting procedure
TAME	tert-amyl-methyl ether
TLP	three-layers of porosity

Abstract

Reactive Separation Processes (RSP's) combine the unit operations of reaction and separation into a single, simultaneous operation. It provides an important synergistic effect and brings about several advantages. This fusion of reaction and separation into one combined operation brings simplicity and novelty to the process flow sheet. This technology has been proved to have conclusive advantages over conventional technologies in terms of their energy; capital cost reductions and increased reaction efficiency. RSP's are popular for the cost savings in investment and operation garnered on successful scale-up to commercial operations. These technologies are gaining importance due to economic opportunities which have caused the emergence of new industries using new separation and process technologies, to give better efficiencies of operation and quantification of product demanded by food, pharmaceuticals, polymer, and electronic industries. Due to changes in the availability and pricing of the key resources, and growing concern for protecting our environment, these technologies are also being seen as front-runner in the field of industrial separations.

Scope of reactive separations is thus very wide and vast, and for the purpose of this thesis after initial literature review, we have decided to focus and restrict our work on Reactive Distillation (RD). RD, also called catalytic distillation, can be considered as reaction and distillation combined into one new unit operation.

RD is an attractive and promising process, which has been established in a variety of successful commercial applications. Compared with the conventional process of carrying out reaction and separation sequentially, the *in-situ* removal of products formed in the reaction zone of a RD column can favorably influence conversion and selectivity, especially of equilibrium limited reactions. Together with a significantly reduced effort in the separation train, this can result in major energy as well as capital cost savings. However, there are feasibility constraints resulting both from thermodynamics and chemistry. In addition to this, the process intensification leads to

higher complexity. This holds especially true for the case of heterogeneously catalyzed RD with its complex interaction between vapor, liquid and immobilized solid catalyst.

This research work is focused to study reactive separation processes, with a special consideration on experimental work on laboratory RD column. The esterification of iso amyl alcohol with acetic acid to form iso amyl acetate and water, catalyzed by the ion exchange resin, TULSION MP T-63 (Thermax India Ltd) is chosen as a test system in this work. Iso amyl acetate synthesis is examined with experiments carried out in the laboratory, in combination with modeling, simulation and validation of the models through the simulation tools.

The experimental part includes experiments in laboratory scale RD column (diameter, 50 mm, approximately 3-m-tall), carefully evaluated data-base for describing chemical reaction and phase equilibria. The simulations are based on the equilibrium-stage approach. The bridge between experiments and simulation is a detailed analysis of transferability of reaction kinetics from its determination in a laboratory batch reactor to its application in a RD column. Reaction kinetics is the key in the simulation of RD process. In this context, rigorous kinetic experiments are performed in the batch reactor to generate the data to examine the effects of various operating parameters such as temperature, stirrer speed, mole ratio, catalyst loading etc. on conversion. Based on the experimental results; a Pseudohomogeneous reaction kinetics model is developed for the esterification reaction system. Despite its simplicity, this model gives better results and is recommended for further use.

Phase equilibrium data are the basic information of the system required for the design of equilibrium stages of vapor-liquid separation equipment like distillation. Hence Vapor-liquid equilibrium (VLE) data for the present system is obtained by carrying out several experiments in Othmer type apparatus in the laboratory. Further

the VLE data from the databank of Aspen Plus is also used to simulate the RD column separately to observe how the results vary with the experimental data and the Aspen Plus databank data.

A Laboratory RD column (diameter, 50 mm, height approximately 3 meter) is designed and operated for iso amyl acetate synthesis from esterification of iso amyl alcohol and acetic acid. The design of the RD column is based on extensive simulation studies with commercial available software such as Aspen Plus. (Aspen Tech, Inc., Version 7.0, 2007) The design, construction and commissioning of this experimental facility is the part of the current research work. The design of the experimental facility is focused on the selection of catalyst, catalyst support and column internals for RD. A total of 30 reactive distillation experiments in laboratory scale column are performed. All the relevant process parameters such as feed flow, feed location, reboiler duty, molar ratio of reactants etc, with their effect on conversion and purity are examined. The comparisons between simulations of different modeling depths and RD experiments are performed.

To carry out simulations of RD column, three equilibrium stage models of different complexity are developed. Rigorous simulation is performed using the RADFRAC model from the steady-state simulator, Aspen Plus to get the optimum design and operating conditions of these models. In these models liquid phase non-idealities are taken into account by the NRTL-model. The gas phase is assumed to be ideal and the vapor phase nonideality considered is the dimerization of acetic acid as described by the Hayden-O'Conell second virial coefficient model. The Aspen Plus built-in association parameters were employed to compute fugacity coefficients. Reaction rates for Pseudohomogenous model calculated by laboratory batch reactor were used for simulation to yield a steady state solution.

In Model # A: assumption of physical and chemical equilibrium shows that the additional assumption of chemical equilibrium on each stage is not valid. In Model #B (without decanter), taking the reaction kinetics into account yields better but still not satisfactory results. In Model # C, taking the reaction kinetics into account and incorporating decanter model, the simulation results of model agree experimental results quantitatively. This indicates that the modeling depth of the simpler equilibrium-stage model with decanter (Model # C) is sufficient.

In order to use the RADFRAC model from Aspen Plus for simulating a RD column with confidence, the reliability of the model is tested by comparing the simulation results obtained with the experimental data on laboratory scale RD column. Further the validated model is used to study the behavior of RD system for various operating parameters. The steady state simulation of RD column brings forth a number of important issues related to the optimal design techniques. Many of these issues are peculiar to RD and would not reasonably be anticipated without *a priori knowledge* of the phenomena involved.

It should be noted that the external mass transfer resistance at the solid–liquid interface is not considered here. An exhaustive rate based model is required to be solved to consider these effects, which is out of the scope of the present work. Nevertheless, the simplified model used here is able to explain the results over the conditions of interest. The temperature and composition profiles for this system from the Equilibrium Model # C are compared with experimental results under the same conditions. Reasonably good agreement between the experimental and simulation results was realized.

The experimental results obtained in this work clearly show that it is feasible to obtain high-purity iso amyl acetate in a RD column with almost-quantitative conversion. It is observed that as boil-up

increases, the amount of iso amyl alcohol, which is excess in the feed, increases in top product thereby improving the purity of the bottom product. As anticipated, the time required to attain the steady state was more for lower boil-up rate. It is also seen, though the conversion and purity levels were substantially high, better results were obtained at lower flow rates due to large residence time offered under this condition.

It is suggested that the best feed location for heavy reactant (iso amyl alcohol) was from the top of the reactive zone (Stage No.10) and light reactant (acetic acid) from bottom of the reactive zone. (Stage No.15) Thus provides countercurrent flow of liquid and vapor in RD column. For a typical run, conversion of 99.3% of acetic acid, with iso amyl acetate purities of 98.15 % was achieved. The optimum molar ratio, of acetic acid to iso amyl alcohol is determined as 0.5 for the adopted configuration and experiments are conducted at or very close to this molar ratio.

Key words: reactive separation processes, reactive distillation, esterification, phase equilibrium, reaction kinetics, experimental work, modeling and simulation, equilibrium mode
Aspen plus.

CHAPTER 1

INTRODUCTION

1.1 Background

The discipline of chemical engineering is undergoing a major transformation. A new paradigm of "*borderless chemical engineering science*" is emerging. The demands from the Society for `cleaner` technologies rather `clean-up` technologies, the emergence of `performance chemicals and materials` etc., is driving the profession towards achieving symbiotic relationship with other disciplines. The need for more efficient and environmentally *'cleaner'* processes has led to a growing interest in novel processes and hybrid process systems, which combine conventional and non-conventional processes. (Anastas et al, 2003)

A drive towards `*Process Intensification'* is leading to the search of novel reactor configurations, which will enhance selectivity as well as productivity. Combination of reaction and separation in a `*combo'* system is likely to bring large dividends. Enhancement in conversion, selectivity, energy utilization, reduction in equipment cost and separation of otherwise difficult to – separate mixtures are some of the motives behind its several applications. It has become an attractive technology not only for reaction engineers but also for separation technologists. (Santi Kulprathipanja, 2002)

Separations are the heart of chemical and process engineering. Since separation processes usually follow the reaction steps, adoption of an integral approach to reaction and separation may provide significant improvements in process design and/or operation. Increasing is being paid to *in situ* product removal within the reactor. The main reasons for considering *in situ* removal of product (s) from the reaction zone are: (i) to enhance conversion in equilibrium limited reactions by shifting the equilibrium towards the desired

product, (ii) to prevent further, undesirable, reaction of products and consequently improve selectivity, and (iii) as a remedy for product-inhibited reactions. (E.S.Perez Cisneros, 1997)

The ever-increasing globalization of the chemical process industries (CPI) is bringing an environmental awareness to various corners of the world at a pace never anticipated in the past. Numerous ecological calamities have made citizens realize that pollution prevention is necessary for humanity's survival. The CPI aims particularly at energy, capital expenditure and variable feedstock cost savings due to fierce global competition and requirements for sustainable development. Increasingly novel processes are used in the industry to achieve these aims.

It is important to have an efficient and sustainable technology for the separation/recovery and production of industrial chemicals. Green engineering principles have been described recently in the context of design, both for manufacturing molecules in chemical processes and for more general products and systems. (Malone and Doherty, 2000) Green engineering can also have a major impact on by-product formation as well as other factors identified in green engineering principles. (Anastas et al, 2003)

Reactive distillation (RD) is a combination of reaction and separation in a single vessel owing to which it enjoys a number of specific advantages over conventional sequential approach of reaction followed by distillation or other separation techniques. (Taylor and Krishna, 2000) RD processes have wide prospects to apply it to chemical engineering and other industry fields. Improved selectivity, increased conversion, better heat control, effective utilization of reaction heat, scope for difficult separations and the avoidance of azeotropes are a few of the advantages that RD offers. It brings compactness and cost-effectiveness to a chemical plant. However, not all reactions can be conveniently conducted in reactive distillation

units. Since reactive distillation involves interaction of reaction, distillation and mixing processes, its applicability for a particular reaction depends on the chemical and physical properties of the system and system components.

The fusion of unit operations is not new; it has been in limited use since the 1920s. The Eastman Kodak process for methyl acetate affords the most classical example of the benefits of in situ separation by RD where the reactor followed by several distillation columns was replaced with considerable economic advantages by one integral RD column. (DeGarmo et al, 1992, Doherty et al, 1992) The technique of RD is well known for carrying out esterification reactions (Keyes, 1932). But the crucial development in the late 1980s exposed previously untapped potential and led to a rejuvenation of this technology. The development was the means to support fine catalyst particles in such fashion, which allows both effective mass transfer and reaction on the surface of the catalyst.

However, this concept has gained considerable attention recently for carrying out catalyzed liquid-phase reactions, the catalyst in this case is usually incorporated in the form of a structured packing. (Towler et al, 2000).This advance permitted heterogeneous reactions to be considered for RD and introduced the possibility of using hybrid columns, which contains both reactive and non-reactive sections. The success of this hybrid RD technology has been found to be particularly advantageous for processes like synthesis of methyl-*tert* ether (MTBE), Ethyl *tert*-butyl ether (ETBE) etc. (Mahajani et al, 2001)

In situ product separation by distillation offers applications in esterification (e.g. for methyl acetate, ethyl acetate, amyl acetate, hexyl acetate etc.), tran-esterification (e.g. for butyl acetate, alkyl phenyl oxalate etc.), hydrolysis (e.g. for ethylene glycol, Isopropyl alcohol, Lactic acid etc.), metathesis (e.g. for methyl oleate, tetraethyl ethylene

etc.), etherification (e.g. for MTBE, ETBE, TAME etc.), alkylation reaction (e.g. for Cumene, p-xylene, ethyl benzene, LAB etc.)

An excellent review on industrial applications of RD was given by Sharma and Mahajani (2003) and Hiwale et al, (2004).

Due to increased worldwide competition, increased fuel prices and more stringent emission limits, the benefits of applying RD and process intensification will increase. Moreover, due to increased knowledge by industrial experience and by academic research, the barriers for implementing RD and process intensification will be further reduced. (Harmsen, 2007) The suitability of RD for a particular reaction depends on various factors such as volatilities of reactants and products, reaction and distillation temperatures etc. and hence, the use of RD for every reaction may not be feasible. (Malone and Doherty, 2000) Exploring the candidate reactions for RD, itself is an area that needs considerable attention to expand the domain of RD processes. (Mahajani et al, 2003). RD has been successfully used and investigated in the past for several reactions such as etherification, esterification, hydrogenation, hydrodesulfurisation and polymerization Various reviews have been published on this aspect (Doherty and Buzad, 1992; Podrebarac et al, 1997; Towler et al, 2000; Taylor and Krishna, 2000; Mahajani and Chopade, 2001; Sharma and Mahajani; 2003 and, Hiwale et al, 2004, Almedia-Riveria C.P et al, 2004; Harmsen, 2007).

With the remarkable progress during past decades has been seen on several other fronts, such as in the development of column hardware, modeling for design and simulation, control strategies, and so on, many more reactions and separations are yet to be evaluated.

The focus of future research should be planned to explore potential candidate reactions and separations for RD processes, which are of commercial importance. (Sharma and Mahajani, 2003) Column hardware can have significant influence on the conversion and

selectivity; the non-equilibrium (NEQ) cell model can properly describe such aspects. Though sophisticated NEQ stage models are available already, detailed information on thermodynamics and mass transfer parameters for various hardware configurations is woefully lacking in the open literature.

Paradoxically, such information has vital consequences for the conversion and selectivity of RD columns. (Taylor and Krishna, 2000) Besides, more research on other areas of this technology, there is need for more experimental work with the express purpose of model validation. In such process studies, parameters need to be measured along the height of RD columns.

Nevertheless , with the remarkable progress that has been seen on several other fronts, such as the development of column hardware, modeling for design and simulation, control strategies and so on, and considering the pace at which new applications are being explored, RD is destined to become one of most important tools for process integration and intensification. RD for many different processes has been rapidly implemented in more than 150 commercial operations of the petrochemical and chemical industry. These implementations show large capital and energy cost reductions, a lower environmental impact and safe and reliable operation. RD can also be seen as the front-runner in the field of process intensification. (Harmsen, 2007)

1.2   Motivation and Significance of the Work

1.2.1 Motivation of the Work

The increased interest in industrial and academic field in reactive distillation has led to increasing number of publications and patents on this subject in the last decade, many of which are dealt with the modelling aspects of reactive distillation processes. To improve the economics, flexibility, operability, and safety of column-

based separation processes, design that considers steady state as well as dynamic behaviour is desired.

The chemical and petroleum industries are experiencing fundamental changes. Rapid globalization of the industries, economic and political changes in the world order, environmentally driven governmental regulations and social pressures (e.g. decrease of consumption, increase of reuse and recycling), declining reserves of some raw materials, and increasing competition and overcapacity are the circumstances in which companies are fighting for their future existence. (Juha Tanskanen, 1999)

As a response, the chemical and petroleum industries are slowly realizing the significance of new technologies - compared to incremental improvements in the existing processes - as a means of producing products more competitively while simultaneously protecting the environment. The need for more efficient and environmentally 'cleaner' processes has led to a growing interest in novel processes and hybrid process systems, which combine conventional and non-conventional processes. Even though a notable risk has to be taken, the availability of modern, low-cost and continually more efficient computers together with the progress made in computational methods, modelling, process simulation, process control and experimental work facilitate investments in such technologies.

This study was motivated by dramatic example of the RD synthesis of methyl acetate by Eastman Chemicals and considered to be the textbook example of a task integration-based process synthesis (Stankiewicz and Moulijn, 2002; Stankiewicz, 2003; Li and Kraslawski, 2004) Using this example one can qualitatively assess the inherent value of this processing strategy. The process costs are substantially reduced (~ 80%) by the elimination of units and the possibility of heat integration. Using task integration-based synthesis

the conventional process, consisting of 11 different steps and involving 28 major pieces of equipment, is effectively replaced by a highly task-integrated RD unit.

This study was also motivated by several technical issues. RD is now an established unit operation in process technology and can be seen as the front-runner in the field of process intensification, there are still significant gaps in the current body of knowledge particurily concerning the rigorous experimental work for the purpose of validation of the model. With expertise available in the associated areas, the current work was an opportunity to direct effort towards this aspect of reactive distillation using a combining of simulation and experimentations.

1.2.2 Objectives of the Work:

A relatively wide focus was assumed for this research to permit significant contributions to be made in several areas. In particular, an improved understanding of the behavior of hybrid RD columns and associated design issues can help to reduce the technical risk in developing this technology (especially locally) and experimental work can provide the basis for further work which should clearly demonstrate that this technology is feasible and profitable.

This thesis was undertaken with the objective of making technical contributions to the body of knowledge associated with synthesis of iso amyl acetate in hybrid reactive distillation column in the following areas:

1. Development of effective modeling techniques for steady state equilibrium-stage (EQ) model of RD column
2. The understanding of obscure operating characteristics for RD.
3. Design strategy for hybrid RD
4. Development of simulation strategy using Aspen Plus and MATLAB

5. Generation of phase equilibrium and reaction kinetic data in the laboratory

6. Construction and testing of a lab-scale RD column for Batch/ continuous RD operations

7. Selection of catalyst, catalyst support and column internals for reactive distillation process

8. Examination of process parameters, including the operating temperatures, feeding positions, feed flow rate, molar ratio, reboiler duty, catalyst loading etc on separation and conversion in RD column.

9. Validation of models with experimental results

10. Present the summary and conclusions of the present investigations and discusses future directions of research work for suitability of applying RD techniques for issues related to design, feasibility and profitability.

1.3 Plan of Research

1. Literature search to assess the potential of RD technology to provide tools for design, synthesis and operational issues of these processes.

2. Literature review for various methodologies of process modeling, simulation, reaction kinetics and thermodynamics, phase equilibrium studies, hardware structure and design, conceptual design to evaluate feasibility, experimental work on laboratory cum pilot scale and understand their strengths and drawbacks.

3. Identification of the processes where these novel methodologies can be implemented to enhance better performance.

4. The development of EQ models of different depths for RD and generation of computer programs and source codes in MATLAB from the available algorithms for the novel

methodologies of process modeling. Development of simulation strategies using Aspen plus.

5. The design, construction and commissioning of the experimental facility for RD process.

6. The generation of VLE data in the laboratory and to calculate BIP'S using NRTL model. Performance of conceptual design studies to generate RCM and to understand the azeotropic behavior of the system.

7. The generation of rigorous experimental data in batch reactor to study the effects of various parameters (such as temperature, stirrer speed, mole ratio, catalyst loading etc.) and fit the kinetic model(s) for solid catalyst esterification reaction.

8. The experimental plans on Continuous Reactive Distillation (CRD) to study the influence of various operating parameters such as a feed flow rate, feed compositions, feed locations, molar ratio, reboiler duty etc. on the conversion and separation.

9. Analysis and comparison of results and judging the performance of the proposed methodologies.

1.4 Methodologies:

The aspect considered in the thesis is to develop a methodology for design, simulation and analysis of RD processes. There is a need for more rigorous experimental work with the express purpose of model validation. Hence our main aim is to develop experimental facilities to study esterification reactions via RD.

For the development RD technology needs enormous support from research on various aspects. The main focus is on study of:

a) Reaction Kinetics and Thermodynamics
b) Phase Equilibrium Studies
c) Hardware Structure and Design
d) Conceptual Design to evaluate Feasibility
e) Modeling and Simulation
f) Experimental work on Laboratory scale

Rigorous experimental data is obtained in batch reactor and the reaction kinetics is developed. VLE data are generated using Othmer type apparatus in the laboratory and the VLE data from the databank of Aspen Plus is also used to simulate the column separately to observe how the results vary with the experimental data and the Aspen Plus databank data. The RD experiments in laboratory scale includes carefully evaluated database for describing chemical reaction and phase equilibria.

The design of the experimental facility is focused on the selection of catalyst, catalyst support and column internals for RD. A detailed investigations has been made on the influence of various operating parameters (such as a feed flow rate, feed compositions, feed stage locations, reboiler duty, catalyst loading, molar ratio etc on conversion and separation) to examine the optimum performance of RD column for iso amyl acetate synthesis.

Three equilibrium stage (EQ) models of different complexity are developed. The simulation results are generated for equilibrium stage model of RD column using MATLAB and Aspen Plus. Experimental results are compared with simulation results obtained by commercial simulators such as Aspen Plus (Version 7.0, 2007, Aspen Tech, Inc.)

1.5   Thesis Outline

The thesis is sub divided into following major topics: the background, motivation, objectives and methodology of the research work (Chapter 1), Supplement to this core are the literature review

(Chapter 2), development of equilibrium stage models for steady state simulation of RD column along with solution strategies for modeling equations to study the influence of various operating variables, (Chapter 3); generation of phase equilibrium and reaction kinetics data in the laboratory (Chapter 4); and the experimental work on laboratory scale RD column, which has been constructed as part of this thesis. (Chapter 5), Comparison of experimental and simulation results (Chapter 6), the conclusions and scope for further work (Chapter 7).

Thesis is organized into a total of seven chapters. The chapter schemes and brief information are summarized as follows:

Chapter 1: This chapter presents the background, motivation, significance of current research work and highlights the main research objectives with methodologies adopted.

Chapter 2: This chapter provides a general overview of potential of RD technology; literature review on tools for design, synthesis and operational issues of these processes along with brief introduction to various methodologies as applied in the present research work.

Chapter 3: This chapter addresses the development of a satisfactory steady state model for RD, which requires attention considering the fundamental behavior of the system, including the reaction and phase behavior, together with the principles behind the equilibrium stage model for distillation operations. In this chapter, EQ model for RD processes is presented along with solution strategies for modeling equations. Simultaneous reaction and separation makes modeling complicated and hence knowledge of vapor-liquid equilibrium and reaction equilibrium constant/reaction kinetics is needed for modeling RD processes. The full RD column model is developed and then applied to simulation of iso amyl acetate column.

The model is validated with laboratory experimental data and then used to study the behavior of RD system for various operating parameters. The steady state simulation of RD column brings forth a number of important issues related to the optimal design techniques. Many of these issues are peculiar to RD and would not reasonably be anticipated without *a priori knowledge* of the phenomena involved. For example, the addition of theoretical equilibrium stages and an increase in the reflux ratio does not always have a directionally equivalent effect.

Chapter 4: This chapter deals with generation of experimental data for phase equilibrium and reaction kinetics in batch reactor for esterification reactions. This chapter is divided into two parts: (A) Phase Equilibrium studies, (B) Reaction Kinetics studies in batch reactor.

The experimental VLE data is obtained in the laboratory using Othmer type apparatus. The VLE results are put into the Aspen data regression simulation to find the required binary parameters for the six binary systems so as to put them together into the final RD column simulation. The phase equilibrium data are used to calculate BIP'S using NRTL model and for conceptual design studies of RD column such as residue curve mapping (RCM), understanding the azeotropic behavior etc. The use of RCM for the design of RD processes is investigated and shown to provide useful information regarding the feasibility of reaction-separations. Combined with simulation tools (Aspen Plus), these techniques form the basis of a proposed design strategy for hybrid RD. The VLE data from the databank of Aspen Plus is also used to simulate the column separately to examine how the results vary with the experimental data and the Aspen Plus databank data.

Rigorous experimental data are obtained in batch reactor to study the effects of various operating parameters such as temperature, stirrer speed, mole ratio, catalyst loading etc. These data are then used to fit Pseudohomogenous kinetic model for heterogeneous solid catalyst esterification reaction and evaluated rate constant and activation energy.

Chapter 5: This chapter describes the experimental apparatus for RD that is constructed in conjunction with the simulation studies. A Laboratory RD column (diameter, 50 mm; height approximately 3 m) is designed and operated for iso amyl acetate synthesis from iso amyl alcohol and acetic acid. The design of the RD column is based on simulation studies. The design, construction and commissioning of this experimental facility is the part of the current research work. The experimental part includes RD experiments in laboratory scale, carefully evaluated database for describing chemical reaction and phase equilibria. The design of the experimental facility is focused on the selection of catalyst, catalyst support and column internals for RD. Here influence of various operating parameters (such as a feed flow rate; molar ratio of reactants, feed stage locations, reboiler duty, etc.) on the conversion and separation is discussed.

Chapter 6: In this chapter discussions on results are presented. The simulation results are presented for three equilibrium stage model of different complexity (Model # A, Model # B and Model # C) for the RD column using MATLAB and Aspen Plus. The NRTL model is selected as the property method for this simulation. Rigorous simulation is performed using the RADFRAC model from the steady-state simulator, Aspen Plus to get the optimum design and operating conditions of these models. In Model # C, taking the reaction kinetics into account and incorporating decanter model, the simulation results of model agree experimental results quantitatively. This indicates that the modeling depth of the simpler equilibrium-stage model with decanter (Model # C) is sufficient.

Model predictions are compared with experimental results generated from the experimental facility as discussed in Chapter 5. This chapter also highlights the main findings for influence of various operating parameters such as a feed flow rate; feed compositions, feed stage locations, reboiler duty, catalyst loading, boil-up rate etc. on the conversion and separation in RD column. It is observed that the best feed location for heavy reactant (iso amyl alcohol) is from the top of the reactive zone (Plate No. 10) and light reactant (acetic acid) is from bottom of the reactive zone (Plate No.15). For a typical run, conversion of 99.5% of iso amyl acetate, with iso amyl acetate purities of 98.15 % is achieved. It is observed that as boil-up increases, the amount of iso amyl alcohol, which is excess in the feed, increases in top product thereby improving the purity of the bottom product. The optimum molar ratio, of acetic acid to iso amyl alcohol is determined as 0.5 for the adopted configuration and experiments are conducted at or very close to this molar ratio.

Chapter 7: This chapter concludes the thesis, highlighting the summary and conclusions of the present investigations and discusses future directions of research work for suitability of applying RD techniques for issues related to design, feasibility and profitability.

CHAPTER 2
LITERATURE REVIEW

2.1 Introduction to Reactive Separation Processes:

Reactive separation processes (RSP) are unique in that they combine the normally unit operations of reaction and separation into a single, simultaneous operation. This fusion of reaction and separation operations into one combined operation brings for the simplicity and novelty this approach brings to the process flow sheet. This technology has been proved to have conclusive advantages over conventional technologies in terms of their energy and capital cost reductions as well as in increased reaction efficiency. (Levenspiel, 1965 and Astarita, 1967) These reactive separations are also coveted for the investment and operation cost savings garnered on successful scale-up to commercial operations.

RSP's as a whole is not a new concept and numerous applications have been commercialized over the course of last decade. Numerous applications have been commercialized for traditional separation methods over the course of six decades. However, the academic and industrial communities have taken renewed interest in the development and commercialization of reactive separations in recent years in response to economic opportunities which have caused the emergence of new industries using new separation and process technologies, to give better efficiencies of operation and quantifying product demanded by food, pharmaceuticals, polymer, and electronic products. Due to changes in the availability and pricing of the key resources, and growing concern for protecting our environment, these technologies are also being seen as front-runner in the field of industrial separations. (Santi Kulprathipanja, 2002)

Combination of the chemical reaction with the physical process of reaction mass separation in one single integrated operation is an effective method for technological processes intensification. It has been established that the removal of reaction products in the process of their formation facilitates the increase in the rate of both reversible processes according to Le–Chatelier's principle and irreversible reactions due to the law of mass action (as the removal of reaction products results in the increase of reagents concentration in the reaction zone).
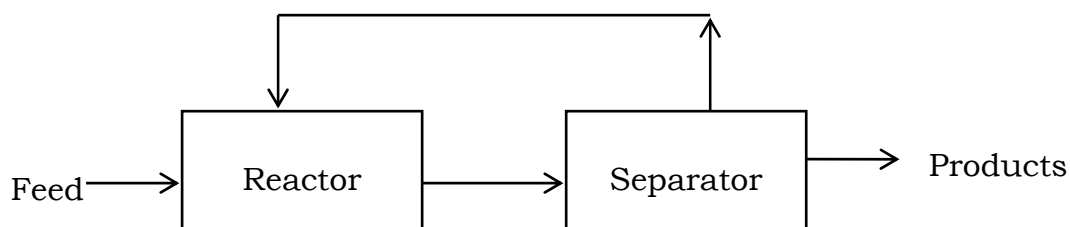
(a) Sequential reaction/separation Process
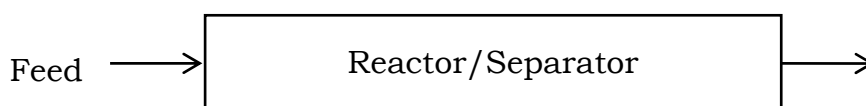
(b) Integrated reaction/separation Process

Figure 2.1 Principles of Combined Reaction and Separation System

The concept of the RSP is schematically presented in figure 2.1 (a) and the sequential reactor/separation process is shown in figure 2.1(b). (William Leet and Kulprathipanja, 2002) In traditional process design, (the sequential reactor/separation process a chemical reactor) is typically sequenced with a downstream separator. In this way, feed is first converted into valued products, which are then isolated and recovered in the separator. To optimize the product yield and purity, the operating conditions of the reactor and the separator are varied to achieve optimal economic performance subject to prevailing

constraints. In many cases, recycle streams are incorporated into the process to reprocess unreacted feed or intermediate products back through the reactor and separator to increase the overall process yields.

In contrast, the design of RSP focuses on integrating the reactor and separator operations into a single process operation with simultaneous reaction and separation. In combining sequential processing steps into an integrated processing approach, additional process benefits may be achieved. These benefits include the elimination of one or more recycle streams, which are associated with the optimizing performance of the original sequential process configuration. More excitingly, the integration may lead to the design of a separation process, which cannot be achieved with separate reactor and separator process flow elements.

The applications of RSP design are numerous and span a broad range of process operations. The developments and applications of reactive separations are not new. For example, reactive absorption has long been practiced for the removal of acid gases in petroleum production and refining industries, and acid /base extractions and reactive distillations have long been practiced in the purification of chemicals. However, mention the phrase "reactive separations" and chemists and engineers will likely point out to more recent commercialization of reactive distillation technologies for the esterification of acetic acid to methyl acetate and etherification of methanol with isobutylene to methyl tertiary butyl ether (MTBE) as classic examples of the art of reactive separation design.

The following section gives a brief summary of important reactive separation processes.

Important examples of Reactive Separations are **R**eactive **D**istillation (RD), [Another name is **C**atalytic **D**istillation (CD)], **R**eactive **A**bsorption (RA), **R**eactive **E**xtraction (RE), **R**eactive

Membrane **S**eparation (RMS), **R**eactive **E**xtractive **D**istillation (RED), **R**eactive **Des**orption (RDES), **R**eactive **Ads**orption (RADS), **R**eactive **Chr**omatography (RCHR), **P**ervaporation (P) and some other similar processes.

Various techniques may be considered for selective removal, for example:

Reactive Distillation (RD): In situ product separation by distillation offers applications in esterification (e.g. for methyl acetate, ethyl acetate, amyl acetate, hexyl acetate etc.), tranesterification (e.g. for butyl acetate, alkyl phenyl oxalate etc.), hydrolysis (e.g. for ethylene glycol, Isopropyl alcohol, Lactic acid etc.), metathesis (e.g. for methyl oleate, tetraethyl ethylene etc.), etherification (e.g. for MTBE, ETBE, TAME etc.), alkylation reaction (e.g. for Cumene, p-xylene, ethyl benzene, LAB etc.). The technique of RD is well known for carrying out esterification reactions (Keyes, 1932). However, this concept has gained considerable attention recently for carrying out catalyzed liquid-phase reactions, the catalyst in this case is usually incorporated in the form of a structured packing. The Eastman Kodak process for methyl acetate affords the most dramatic example of the benefit s of in situ separation by RD where the reactor followed by several distillation columns was replaced with considerable economic advantages by one integral RD column.

a) **Reactive Extraction:** By deliberate addition of a second liquid phase containing a selective solvent, we may extract the desired product from the reaction zone and prevent further side reactions. The extraction of furfural using a hydrocarbon solvent is an example. Sharma (1985) has reported several other examples of reactions, which would profit from introduction of additional phase.

b) **Chemical Adsorption:** A process where gases combine with particular solids such that the binding forces are comparable to

those characterizing chemical compound formation may be called as chemical adsorption or chemisorption. A novel reactor concept suggested by Swaaji and Zuiderweg (1972) involves the use of a solid adsorbent, in trickle phase through a packed catalytic reactor, for selective removal of a product. Also, this concept has been verified experimentally by Kuczynski (1986) for the synthesis of methanol, which involves an equilibrium-limited reaction.

c) **Supercritical Extraction:** In equilibrium-limited biocatalyzed reactions, removal of the desired products, which are often thermally labile, *in situ* by supercritical extraction with carbon dioxide or other non-condensable gases cal lead to substantial benefits. Adschiri et al, (1992), have applied supercritical extraction with carbon dioxide to the removal of products from a liquid-phase reaction system as a mean to enhance the selectivity.

d) **Membrane Reactors:** A permselective ceramic membrane-walled tabular catalytic reactor can be considered for carrying out dehydration reactions, the membrane serves to selectively remove hydrogen, thus shifting the equilibrium towards the desired product. An experimental study by Becker et al, (1993), has shown that using this concept for dehydration of ethyl benzene results in a 20% increase in conversion over conventional fixed bed operation.

Scope of reactive separations is thus very wide and vast, and for the purpose of this thesis after initial literature review, we have decided to focus and restrict our work on Reactive Distillation (RD). Reactive distillation, also called catalytic distillation, can be considered as reaction and distillation combined into one new unit operation.

Therefore, in this chapter a brief review of the state of the art in RD is presented.

2.2   State of the Art in Reactive Distillation:

The combined RSP can be successfully implemented even on the basis of conventional chemical technologies. A number of practical applications and industrial trials carried out in the production of organic and inorganic products have demonstrated the potential of the new approach as a universal method in technology intensification. Laboratory research and industrial trials have demonstrated that the reactive separation operation can be successfully implemented in a wide range of known chemical processes such as oxidation, esterification, condensation, hydration of olefins, dehydration, condensation processes, halogenations of hydrocarbons, etc.

Reactive Distillation (RD) is a combination of reaction and distillation in a single vessel owing to which it enjoys a number of specific advantages over conventional sequential approach of reaction followed by distillation or other separation techniques. It is also called as **C**atalytic **D**istillation (CD). Reactive distillation processes have wide prospects to apply it to Chemical Engineering and other industry fields. Improved selectivity, increased conversion, better heat control, effective utilization of reaction heat, scope for difficult separations and the avoidance of azeotropes are a few of the advantages that reactive distillation offers. (Taylor and Krishna, 2000) Completely, advantages of the combined reactive mass exchanges processes (Reactive Distillation) play special role at creation of low waste technologies for producing various organic substances. Special meaning, as was shown, has increase of selectivity and reagents conversion by one pass.

The introduction of an *in situ* separation in the reaction zone or vice versa leads to complex interactions between vapor–liquid equilibrium, mass transfer rates, diffusion and chemical kinetics,

which poses a great challenge for design and synthesis of these systems. (Taylor and Krishna, 2000) RD being a relatively new field, the research on various aspects such as modeling and simulation, process synthesis, column hardware, non-linear dynamics and control etc. is in progress. The suitability of RD for a particular reaction depends on various factors such as volatilities of reactants and products, reaction and distillation temperatures etc. and hence, the use of RD for every reaction may not be feasible. (Malone and Doherty, 2002) Exploring the candidate reactions for RD, itself is an area that needs considerable attention to expand the domain of RD processes. (Hiwale et al, 2003)

2.3   Industrial Applications of Reactive Distillation:

The concept of combining separation and reaction in single multifunctional reactor is used for enhancement of overall performance is not new to chemical engineering world. The recovery of ammonia in classical Solvay process for soda ash of the 1860s may be cited as probably the first commercial application of RD as shown in Figure 2.2. (Sharma and Mahajani, 2003) Many old processes have made use of this concept. The production of propylene oxide, ethylene dichloride, sodium methoxide, and various esters of carboxylic acids are some examples of processes in which RD has found a place in some form or other, without attracting attention as a different class of operation. RD process gained separate status as promising multifunctional reactor and separator when huge demand for MTBE (methyl tert-butyl ether) by refiners in 1980s. (Malone and Doherty, 2000)

In the classical Solvay process for ammonia recovery, reaction takes place close to boiling conditions. Design is based on concept of RD. This is shown in Figure 2.2. (Sharma and Mahajani, 2003)

Historic Example: **Ammonia Recovery in Solvay process (1869)**

Figure labels (top to bottom):
- NH_3+CO_2 for absorber
- Cooler
- Liquor preheater — Filter liquor
- Strippper — $(NH_4)_2CO_3= 2NH_3 + Co_2 + H_2O$
- Lime milk
- Prelimer
- $(NH_4)_2SO_4+ CaO = 2NH_3 + CaSO_4+H_2O$
- $2NH_4Cl + CaO = 2NH_3 + CaCl_2 + H_2O$
- Distillation Column
- Low Pressure Steam
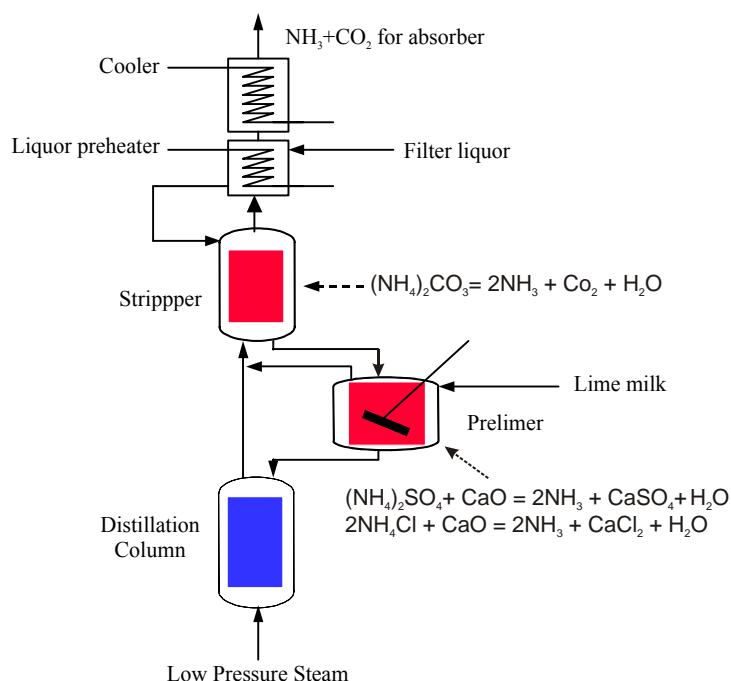
Figure 2.2 Ammonia Recovery in Solvay Process (1869)

The commercial success of RD for the production of MTBE was immediately followed by another remarkable achievement with the Eastman Kodak Process that condensed the whole chemical plant for methyl acetate in single RD unit that accepts reactants and delivers pure products. Since demonstrations of its ability to render cost effectiveness and compactness to chemical plant, RD has been explored as a potentially important process for several other chemicals and reactions such as esterification, etherification, acetalizations, hydrogenations, alkylation and hydrations have been explored.

An excellent review of industrial application of reactive distillation is given by Hiwale et al, (2004).

Figure 2.3 shows schematic representations of conventional and RD processes for production of chemicals on industrial scale.
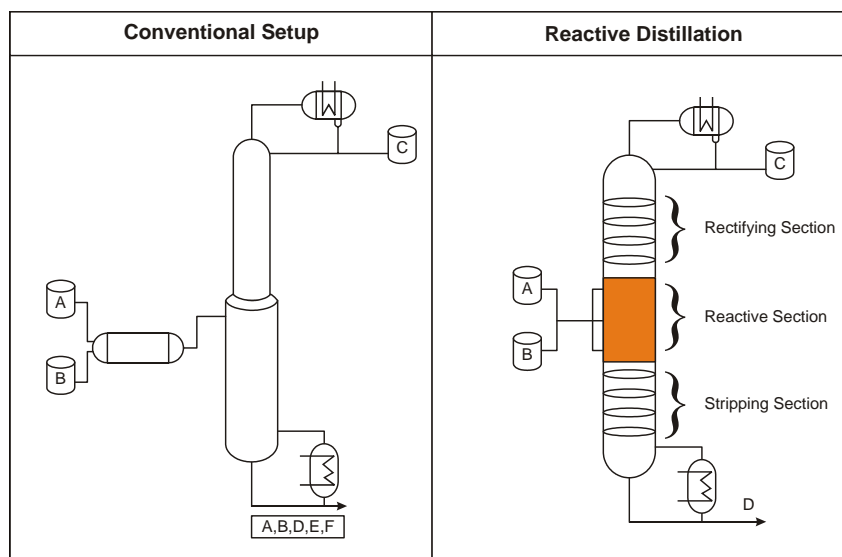
[Figure 2.3 Schematic Representations of Conventional and Reactive Distillation Processes

In this section, we consider some of successful industrial RD processes.

Let us begin by considering a reversible reaction scheme: $A + B \leftrightarrow C + D$ where the boiling points of the components follow the sequence A, C, D and B. The traditional flow sheet for this process consists of a reactor followed by a sequence of distillation columns; see Fig. 2.4(a).

The mixture of A and B is fed to the reactor, where the reaction takes place in the presence of a catalyst and reaches equilibrium. A distillation train is required to produce pure products C and D. The unreacted components, A and B, are recycled back to the reactor. In practice the distillation train could be much more co complex than the one portrayed in Fig. 2.4(a) if one or more azeotropes are formed in the mixture. The alternative configuration is shown in Fig. 2.4(b). The RD column consists of a reactive section in the middle with nonreactive rectifying and stripping sections at the top and bottom. The task of the rectifying section is to recover reactant B from the product stream C. In the stripping section, the reactant A is stripped from the product stream D. In the reactive section the products are separated in situ,

driving the equilibrium to the right and preventing any undesired side reactions between the reactants A (or B) with the product C (or D). For a properly designed RD column, virtually 100% conversion can be achieved.

(a)   (b)
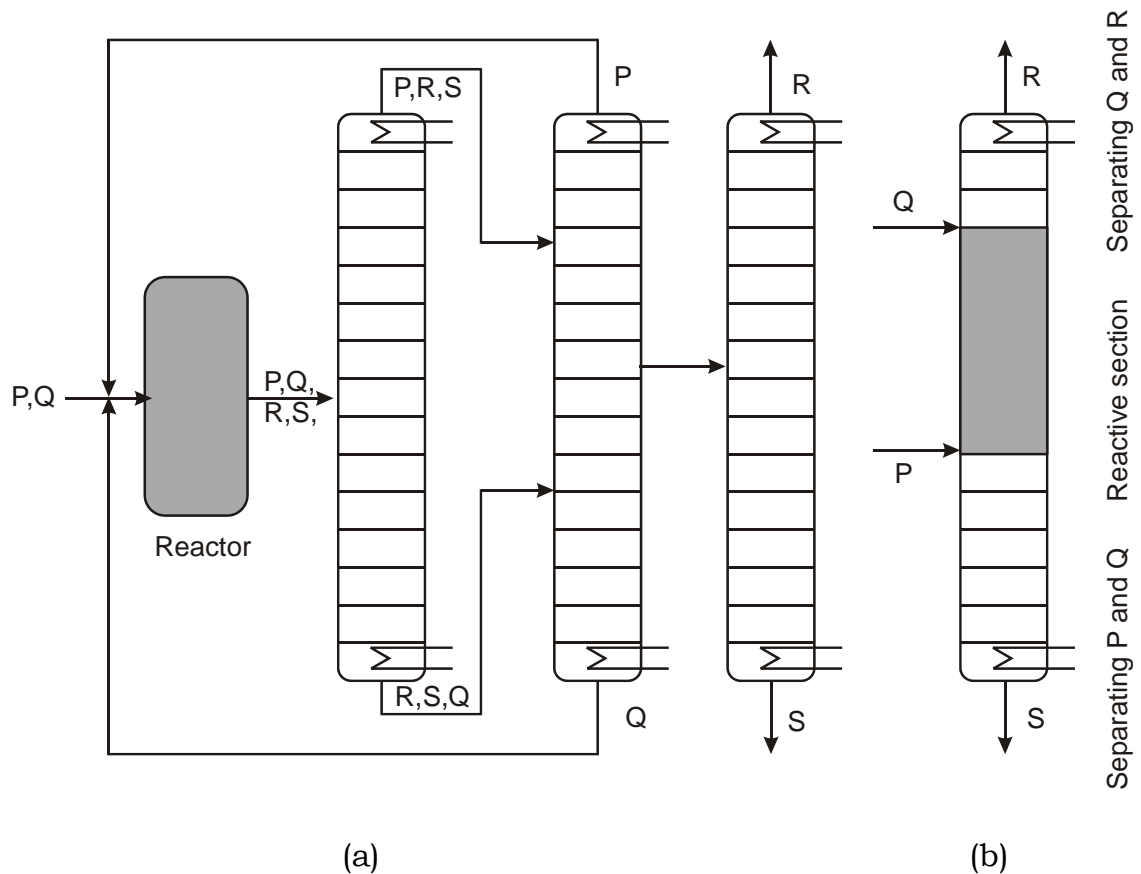
Figure 2.4. Processing Schemes for a Reaction Sequence $A + B \leftrightarrow C + D$
Where C and D are both desired products.
(Taylor and Krishna, 2000)

    (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.
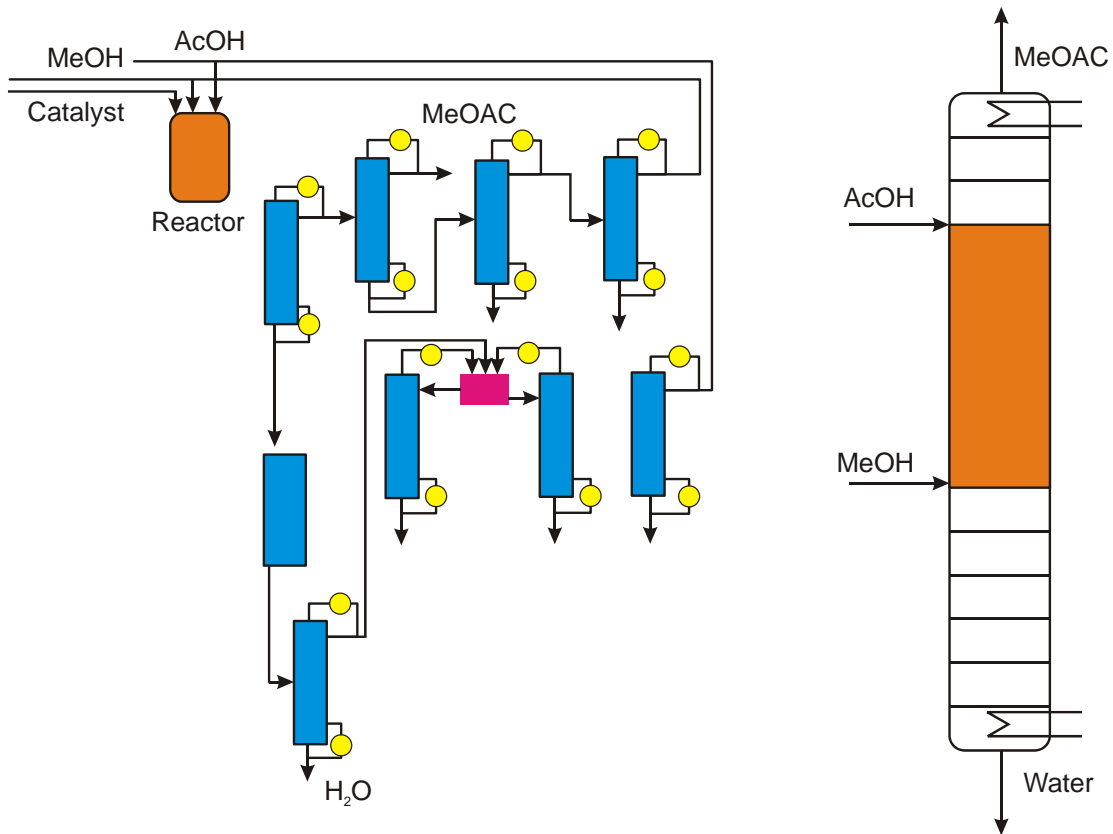
**Figure 2.5. Processing Schemes for the Esterification Reaction
MeOH+AcOHH ↔ MeOAc+ H2O.** (Siirola, 1995).

(c)   Conventional processing scheme consisting of one reactor followed by nine distillation columns.

(d)   The reactive distillation configuration.

The most spectacular example of the benefits of RD is in the production of methyl acetate. The acid catalyzed reaction MeOH+AcOHH ↔ MeOAc+ H2O was traditionally carried out using the processing scheme shown in Figure 2.5(a), which consists of one reactor and a train of nine distillation columns. In the RD implementation (see Figure 2.5(b)) only one column is required and nearly 100% conversion of the reactant is achieved. The capital and operating costs are significantly reduced (Siirola, 1995).

For the acid catalyzed reaction between *iso*-butane and methanol to form methyl *tert*-butyl ether: *iso*butene+MeOH ↔ MTBE, the traditional reactor-followed- by-distillation concept is particularly complex for this case because the reaction mixture leaving the reactor

forms three minimum boiling azeotropes. The RD implementation requires only one column to which the butenes feed (consisting of a mixture of *n*-butene, which is non-reactive, and *iso*-butene which is reactive) and methanol is fed near the bottom of the reactive section. The RD concept shown in Figure 2.5(a) is capable of achieving close to 100% conversion of *iso*-butene and methanol, along with suppression of the formation of the unwanted dimethyl ether (Sundmacher, 1995). Also, some of the azeotropes in the mixture are "reacted away" (Doherty and Buzad, 1992).

For the hydration of ethylene oxide to mono-ethylene glycol: EO+H2O→PEG, the RD concept, shown in Fig. 2.6(b) is advantageous for two reasons (Ciric and Gu, 1994). Firstly, the side reaction EO+EG→DEG is suppressed because the concentration of EO in the liquid phase is kept low because of its high volatility. Secondly, the high heat of reaction is utilized to vaporize the liquid-phase mixtures on the trays. To achieve the same selectivity to EG in a conventional liquid-phase plug flow reactor would require the use of 60% excess water (Ciric & Gu, 1994). Similar benefits are also realized for the hydration of *iso*-butene to *tert*-butanol (Velo, Puigjaner and Recasens, 1988)

Several alkylation reactions, aromatic+olefin ↔ alkyl aromatic, are best carried out using the RD concept not only because of the shift in the reaction equilibrium due to in situ separation but also due to the fact that the undesirable side reaction, alkyl aromatic+olefin↔dialkyl aromatic, is suppressed. The reaction of propene with benzene to form cumene, benzene+ propene↔Cumene (Shoemaker & Jones, 1987; see Figure 2.6(c), is advantageously carried out in a RD column because not only is the formation of the undesirable di-isopropylbenzene suppressed, but also the problems posed by high exothermicity of the reaction for operation in a conventional packed-bed reactor are avoided. The alkylation of *iso*-butane to *iso*-octane, *iso*-butane+n-butene↔*iso*-octane is another

reaction that benefits from a RD implementation because in situ separation of the product prevents further alkylation : *iso*-octane $+n$-butene $\leftrightarrow C_{12}H_{24}$ (Doherty and Buzad, 1992).
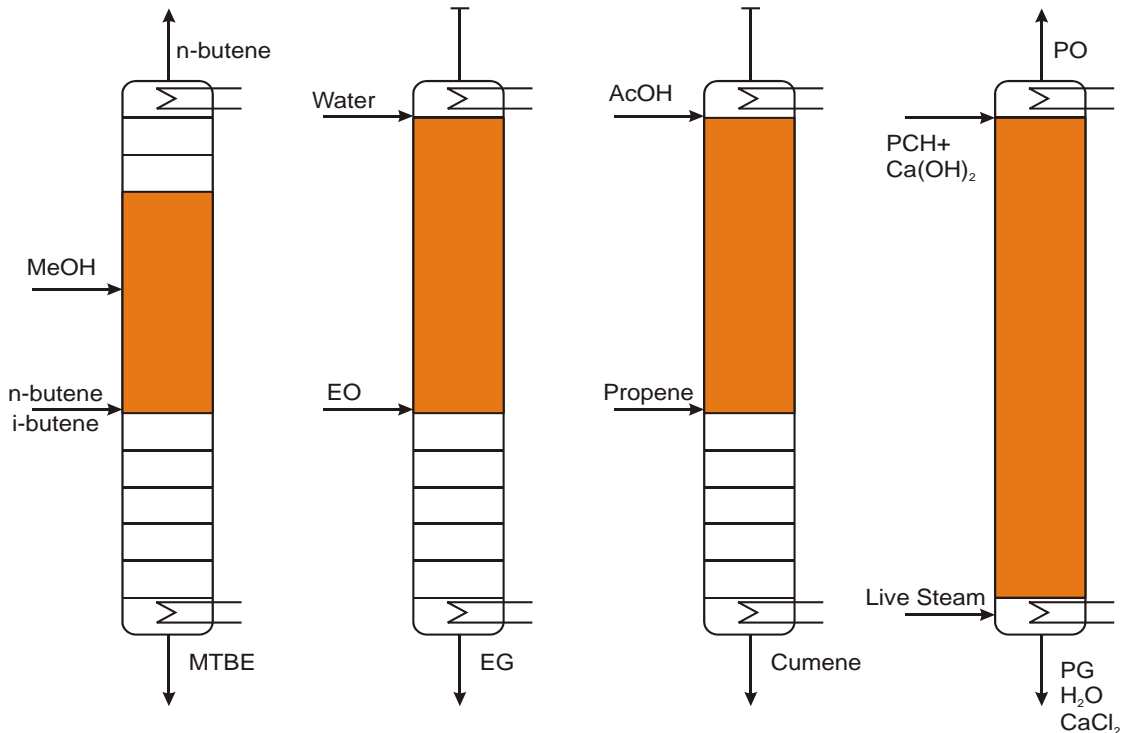
Figure 2.6 Reactive Distillation Concepts

(a) Reactive distillation concept for synthesis of MTBE from the acid-catalyzed reaction between MeOH and iso-butene. The butene feed is a mixture of reactive iso-butene and non-reactive n-butene.
(b) Reactive distillation concept for the hydration of ethylene oxide to ethylene glycol.
(c) Reactive distillation concept for reaction between benzene and propene to form Cumene. (d) Reactive distillation concept for reaction production of propylene oxide from propylene chlorohydrin and lime. Grid lines indicate the reactive sections.

The reaction between propylene chlorohydrin (PCH) and Ca(OH)$_2$ to produce propylene oxide (PO) is best implemented in an RD column, see Figure 2.6(d). Here the desired product PO is stripped from the liquid-phase by use of live steam, suppressing hydrolysis to propylene glycol (Bezzo, Bertucco, Forlin & Barolo, 1999).

From the foregoing examples, the benefits of RD can be summarized as follows: (Taylor and Krishna, 2000)

(a)   Simplification or elimination of the separation system can lead to significant capital savings.

(b)   Improved conversion of reactant approaching 100%. This increase in conversion gives a benefit in reduced recycle costs.

(c)   *Improved selectivity*: Removing one of the products from the reaction mixture or maintaining a low concentration of one of the reagents can lead to reduction of the rates of side reactions and hence improved selectivity for the desired products.

(d)   Significantly reduced catalyst requirement for the same degree of conversion.

(e)   *Avoidance of azeotropes:* RD is particularly advantageous when the reactor product is a mixture of species that can form several azeotropes with each other. RD conditions can allow the azeotropes to be "reacted away" in a single vessel.

(f)   Reduced by-product formation.

(g)   *Heat integration benefits:* If the reaction is exothermic, the heat of reaction can be used to provide the heat of vaporization and reduce the reboiler duty.

2.4   Constraints and Difficulties in RD Implementations

Some of the successes of RD are so dramatic that we might think of all the liquid-phase chemical processes should be based on simultaneous reactions and separations instead of more conventional separation sequence. This is not always possible since combining reaction and distillation is not always advantageous in some case, it may not feasible. (Sharma and Mahajani, 2003). There are several constraints and foreseen difficulties for RD processes (Towler and Frey, 2000):

(i)   *Volatility Constraints:* The reagents and products must have suitable volatility to maintain high concentration of the reactants and low concentrations of products in the reaction zone.

(ii)   *Residence time requirement:* If the residence time for the reaction is long, a large column size and large tray hold-ups will be needed and it may be more economical to use reactor-separator arrangements.

(iii) *Scale-up to large flows:* It is difficult to design RD processes for very large flow rates because of liquid distribution problems in packed RD columns.

(iv)   *Process conditions mismatch*: In some processes the optimum conditions of temperature and pressure for distillation may be far from optimal reaction or vice versa.

2.5 Classifications of the RD Literature

Due to its potential for improved process design and the success of its commercial applications, RD gained the interest of both academics and industry toward its use and application in commercial processes. Figure 2.7 shows schematic diagram for classifications of the reactive distillation literature. (E.S.P. Cisneros, 1997)
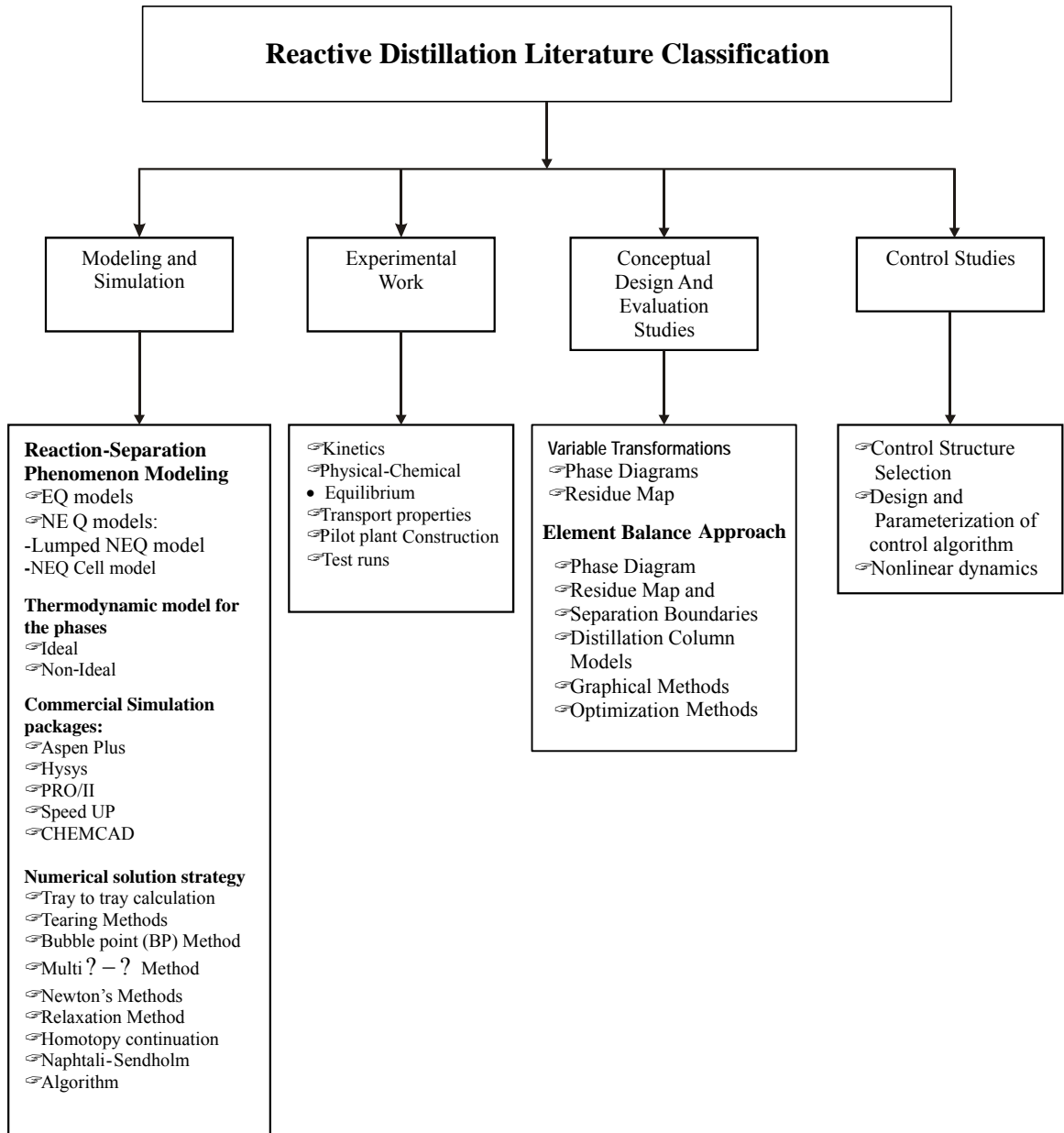
Figure 2.7: Schematic diagram for Classifications of the Reactive Distillation Literature (Modified from E.S.P.Cisneros, 1997)

Figure 2.8 shows RD technology and assessment and Figure 2.9 shows main stages for design of RD processes.

Reactive Distillation Technology

Classification

Homogeneous

Heterogeneous

Homogeneously Or Auto Catalyzed

Immobilization Of Catalyst Pellets

Auto-catalytic Structures

Trays

Random Or Structured Packing

Feasibility → No → Conventional

Yes

Hydrodynamic

Modeling

Kinetics

Plug Flow

Mixed Flow

Physical Separation

n^{th} order Reaction

Chemical Equilibrium

Equilibrium Stage Model

Non-equilibrium Stage Model

Optimization

Conventional Process

Laboratory Experiments

Yes

No

Pilot Plant Experiments

Scale-up

Figure 2.8 Reactive Distillation Technologies and Assessment

2.6 Main Stages for Design of RD Processes

The design of technologies including combined processes (Reactive Distillation) consists of several stages, as given below:

[I] **CHOICE OF SEPARATION PROCESSES**

1) Collection and processing of physicochemical information, needed for the choice or separation process and analysis or statics
2) Selection of separation process, raising product yield
3) Choice of operating conditions for the RD process (T, P, catalyst, additional substances. etc.)

[II] **ANALYSIS OF STATICS**

Definitions of RD Limiting steady states, ensuring maximal product yield.

Estimation of complexity for practical realization of maximal product yield	
Simulation	Experiment on laboratory column

Construction of basic technological flow sheet to produce the target product.

[III] **MATHEMATICAL MODELING**

1) Performance of experimental research in order to design the mathematical models.
2) Construction of mathematical models.

[IV] **DATA PREPARATION FOR DESIGNING**

1) Calculation of static operating parameters of technological flow sheet and operating parameters for separates devices.
2) Dynamic simulation for separate devices and technological flow sheet, allowed interval of external parameters variation, recommendations for starting and stopping modes
3) Preliminary economical estimation based in material energy balances
4) Selection of monitoring system and automatic control for the target product manufacturing
5) Study in depth or separate blocks technological flow sheet on laboratory and scaled- up industrial installations.

PROJECTING
INTRODUCTION TO INDUSTRY

Figure 2.9 Main Stages for Design of Reactive Distillation Processes

2.7 Challenges in Research for RD processes:

(a)   *Evaluations of many more reactions and separations:*
With the remarkable progress during past has been seen on several other fronts, such as in the development of column hardware, modeling for design and simulation, control strategies, and so on, many more reactions and separations are yet to be evaluated. The focus of future research should be planned to explore potential candidate reactions and separations for RD processes, which are of commercial importance. (Sharma & Mahajani, 2003)

(b)   *Scale- up of reaction columns:*
A major focus if research and development in future years should be the scale-up of reaction columns. Also the methods of choosing the best equipment (for homogenous and heterogeneous catalysis) will have to be improved. Work will have to be done to ensure that the benefit of combining reaction and distillation can be enjoyed to the full by employing the most suitable equipment. (Schoenmakers and Blessling, 2003)

(c)   *Deeper investigations on hydrodynamics, maldistribution, and/or mass transfer limitations:*
Hydrodynamics, maldistribution, and/or mass transfer limitations during scale-up studies are worthy of deeper investigations. Reliable scale-up solely on the basis of laboratory scale experiments does not appear to be possible yet (Frey, et al, 2003).

(d)   *Detailed study on thermodynamics and mass transfer parameters for various hardware configurations:*
Column hardware can have significant influence on the conversion and selectivity; the NEQ cell model can properly describe such aspects. Though sophisticated NEQ stage models are available already, detailed information on thermodynamics and mass transfer parameters for various hardware

configurations is woefully lacking in the open literature. Paradoxically, such information has vital consequences for the conversion and selectivity of RD columns. There is crying need for research in this area. (Taylor and Krishna, 2000)

(e) *Research focus on CFD studies:*

Detailed research focus should be given on modern tools of CFD (Computational fluid dynamics), which is valuable in developing better insights into hydrodynamics and mass transfer in RD column. (Van Baten and Krishna, 2000, Higler et al, 1999a, Higler and Taylor, 1999)

(f) *Rigorous experimental work:*

Besides, more research on hydrodynamics and mass transfer, there is need for more rigorous experimental work with the express purpose of model validation. (Taylor and Krishna, 2000)

(g) *Control studies for kinetic controlled processes:*

Control studies for kinetic controlled processes are missing to a large extent and further research is required to close this gap. (Kienle and Marqardt, 2003)

(h) *Development of methods for feasibility analysis:*

Feasibility analysis for RD has advanced to the point that useful engineering methods can be implemented relatively easily. However, attainable region methods are still relatively new and there remains significant potential for developing a framework to generate process alternatives with combined reaction and separation using this approach.

If these methods could be developed further, it should be possible to link attainable region models for feasibility methods to build a useful design tool (synthesis methodology) for generating and screening process alternatives for multifunctional reactor-separator devices. (Gadewar et al, 2003)

2.8   Feasibility and Alternatives Studies:

For conceptual design of RD, systematic methods are needed for deciding the feasibility of the process. The feasibility product compositions from RD are determined for a given feed column pressure, and Damkohler number (Da). This dimensionless number, Da, evaluates the effective rate of the chemical reaction in comparison to the fed flow rate.

Dimensionless parameter groups are an efficient tool for process evaluation and performance, which allow estimation of the relevance of certain transport resistances from experimental data. Sundmacher et al, (1994) has discussed classification of RD processes by dimensionless numbers. Here only most important qualitative results are given:

(i)   *Damkohler number (Da):* This dimensionless number, Da, evaluates the effective rate of the chemical reaction in comparison to the fed flow rate.

$$Da = \frac{k_f \, V_{cat}}{F} \, \alpha \, \frac{\text{Effective rate of reaction}}{\text{Feed flow rate}} \qquad (2.1)$$

Where,

k_f =   Effective reaction rate constant including internal transport resistances of the Catalyst packings

V_{cat} =   Catalyst volume installed in the column

F   =   Feed flow rate

If   Da << 1   corresponds to little or no extent of reaction

(The reaction is far from equilibrium)

If   Da >> 1   approaches to chemical reaction equilibrium.

(ii)   *Thiele Modulus (ϕ):* Internal mass transport inside the catalyst particles should be evaluated with the help of Thiele modulus.

$$\phi = \frac{1}{S_V} \sqrt{\frac{r}{c_L^t \, x i D_{eff,i}^s}} \qquad \alpha \qquad \frac{\text{Rate of chemical reaction}}{\text{Rate of intraparticle diffusion}} \qquad (2.2)$$

Where,

r = the intrinsic reaction rate at liquid bulk conditions

$D_{eff,i}^s$ = effective diffusion coefficient of selected reaction component inside the catalyst particle.

If $\phi \ll 1$ Intraparticle diffusion resistances will be negligible.

(iii) *Biot number (Bi):* The importance of external transport resistances at the outer surface of catalyst particles is estimated with Biot number.

$$B_{i,m}^{LS} = \frac{\left(\frac{1}{S_V}\right) k_i^{LS}}{D_{eff,i}^s} \qquad \alpha \qquad \frac{\text{Rate of liquid} - \text{solid mass transfer}}{\text{Rate of intraparticle diffusion}} \qquad (2.3)$$

Where, k_i^{LS} =Liquid-solid mass transfer coefficient of the key component, i which can be estimated from published correlations. (Goto, et al, 1997)

For most of RD processes the Biot number ranges from 10-100 and for this range we consider the external mass transport to be negligible. (Sundmacher and Qi, 2003)

(iv) *Prater number (β):* The heat of reaction may increase or decrease the reaction temperature inside the catalyst particle. The significance of this phenomenon is evaluated by means of Prater number (β):

$$\beta = \frac{\left(-\Delta_R H^o\right) C_t^L \, x i \, D_{eff,i}^s}{\lambda_{eff}^s \, T^L} \qquad \alpha \qquad \frac{\text{Rate of intraparticle diffusion}}{\text{Rate of intraparticle heat conduction}} \qquad (2.4)$$

It was found that for most RD processes, the Prater number has values less than 10^{-3}; the internal heat-transport effects can be neglected.

(v)   *Arrhenius number (γ):* Arrhenius number can determine the thermal sensitivity of the chemical reaction kinetics:

$$\gamma = \frac{E_A}{\left(RT^L\right)} \tag{2.5}$$

Where, E_A = activation energy

Feasibility analysis in RD must incorporate all the features for ideal and azeotropic mixtures, as well as new phenomena caused by the introduction of the chemical reaction. Results from feasibility studies are used to identify and organize alternative column sequences. With generally include fully nature column, non-reactive columns, and/or hybrid columns (both reactive and non-reactive sections in the same device)

2.8.1 Conceptual Design and Evaluation Studies:

Conceptual design methods estimate equipment sizes (number of reactive stages, number of non-reactive stages and column diameter), feed flows and locations, heating and cooling loads, catalyst concentrations and liquid hold- ups. This provides the basis for an economic evaluation and ranking of the process alternatives from stage 1.

2.8.2 Need of Conceptual Design:

McCabe –Thiele and Ponchon-Savarit methods are well known design methods for the conventional non-reactive RD columns. The later incorporates energy balance and hence, is slightly complicated and is not as popular as McCabe-Thiele method. These methods work very well for ideal systems. However for non-ideal systems, these methods cannot be very well extended to obtain information on the feasibility of the method. In addition, these methods cannot answer the questions like:

For the required output compositions, what is the minimum reflux ratio? Is the required output composition feasible with any value of reflux ratio or number of stages?

This is due to the VLE characteristics of the system of interest pose certain limitations on feasibility. The best example is the system in which azeotropes are formed. Azeotropes can be very well seen in the binary McCabe-Thiele x-y plot. However, for multicomponent systems, such azeotropes (which may be multiple in numbers) are not so easy to be located in the composition space unless one uses special graphical (or geometric) techniques. Residue Curve Map (RCM) is valuable tool that helps design engineer to identify azeotropes and similar fixed composition in the composition space. Depending on the properties of these fixed points and their behavior one can work out feasibility of the design, feasible alternatives (column sequences), minimum reflux ratio/stages, etc. For non-RD all one needs is the VLE data for a given system and for the reaction kinetics and thermodynamics. Once the feasibility evaluation is done, actual number of stages, column diameter, and column internals may be worked out with simultaneous studies. Such feasibility studies based on geometric methods that make use of minimum basic information of thermodynamics and kinetics form a conceptual design process of RD.

2.8.3 Review of Conceptual Design Methods:

Most conceptual design methods are based on the EQ stage model. However, some recent developments have open up the possibility of using NEQ models for RD design. Barbosa and Doherty (1988c) developed fixed-point method for the design of single feed RD column. These methods use material balances written around a stage in each section of the column (above and below feed stage) and corresponding end of the column. A number of extensions of the approach Barbosa and Doherty (1988c) have appeared in literature. Barbosa and Doherty (1988d) extended their own methodology to

double feed columns. Buzad and Doherty (1994, 1995) and Buzad and Doherty (1994) provide a further extension in order to handle kinetically controlled reactions in three components systems.

Ung and Doherty (1995e) considered RD processes involving multiple reactions. Okasinski and Doherty (1998) relax some of the assumptions underlying the methods of Barbosa, Bazad and Doherty. Mahajani and Kolah (1996) extended the methods of Doherty and co-workers for packed RD columns. An assumption in their methods is that liquid phase back mixing is totally absent. Mahajani (1999b) also addressed the design of RD processes for multicomponent kinetically controlled reactive system. Haun and co-workers (Haun, 1988, Haun and Lien, 1996, 1998, Haun, Westerberg and Lien, 2000b) developed a phenomena based method for the analysis and design of reactive separation processes.

2.9 Equipment Selection and Hardware Design:

2.9.1 Equipment Selection:

The ranking of alternatives in stage –2 is used to decide if more detailed studies of one, or perhaps a few, alternative(s) is warranted. The most fruitful approach combines high-fidelity models incorporating hydrodynamics and mass transfer with new hardware design and tests (Malone, 2000).For simple equilibrium reactions, two operating conditions can be distinguished (Schoenmakers and Bessling, 2003):

1) The range in which the conversion is influenced mainly by the concentration of the component to be separated, this range is called as *"Control by Distillation"*

2) The range in which the conversion is influenced mainly by residence time and reaction constant, this range is called as *"Controlled by Kinetics"*.

Industrial process design should aim at operating condition within these ranges: just sufficient residence time and only necessary expenditure for the distillation. In view of this an alternative configuration is considered: A reaction can be run within a column, that is normally understood as RD, but can also be run in an outside reactor with a pump recycle. Such a sequential arrangement exhibits the same conversion as the simultaneity of a reactor with pump recycle stream and a RD configuration is compared.

Different equipment may be chosen to combine reaction and distillation within the limiting condition of reaction velocity, relative volatility and catalytic mechanism. Equipment suitable for combining reaction and distillation (for homogeneous catalysis):

1)   Rectification column
2)   Column with larger volume in bottom
3)   Stirred vessel with rectifying column
4)   Stirred vessel with full column
5)   Vessel cascade with column
6)   Stirred vessel with evaporator
7)   Evaporator

Equipment suitable for combining reaction and distillation (for heterogeneous catalysis):

1)   Rectification column with catalytic packings
2)   Rectification column with catalytic internals in the down comers
3)   Rectification column with side stream reactors
4)   Column and reactor with pump around
5)   Evaporator and reactor with pump around

2.9.2 Column Hardware for RD:

The successful commercialization of RD technology requires special attention to the hardware design and standard methods used for conventional distillation may not work in this case. The column should beside favorable conditions for both reaction and distillation. The catalyst used in RD columns can be either homogenous or

heterogeneous. The well-known example of the Eastman Kodak process for production of methyl acetate uses homogenous H_2SO_4 as catalyst. However, heterogeneous catalyst such as, anion and cations exchanges are preferred over their homogenous counterparts. Before modeling aspects can be considered, careful attention needs to be paid to hardware design aspects. Towler and Frey (2000) have presented an excellent summary of hardware design aspects of RD columns. Some of the important issues are discussed below.

The Hatta number for most RD applications is expected to be smaller than about unity (Sundmacher, Rihko & Hoffmann, 1994) and the froth regime is usually to be preferred on the trays because of the desire to maintain high liquid hold-up on the trays. In the Eastman process for methyl acetate manufacture specially designed high liquid hold-up trays are used (Agreda, et al, 1990). Figure 2.10 shows counter-current vapor-liquid contacting in trayed columns.
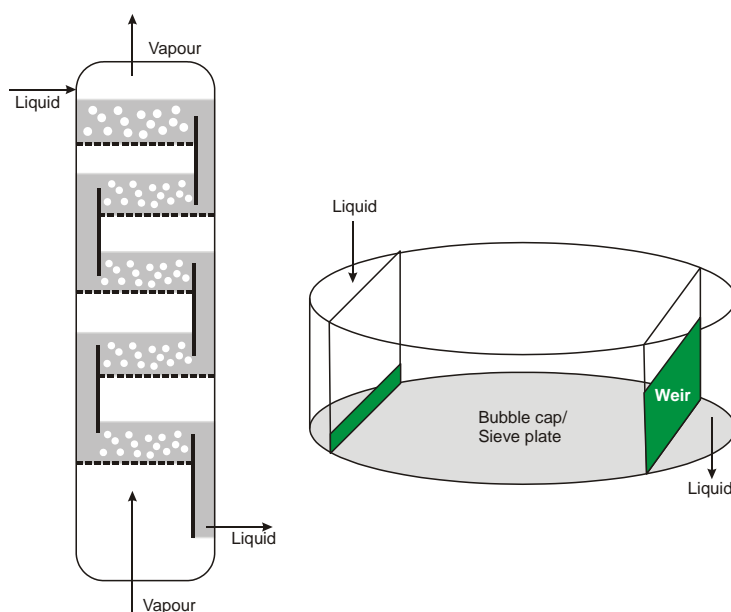
Figure 2.10. Counter-current Vapor-Liquid contacting in Trayed Columns

2.9.3 Hardware for Homogenous Reactions:

RD column, in which the reaction takes place in the liquid phase, can be operated counter-currently and sufficient degree of

staging can be achieved in a multitray column or in a column with random or structured packing. The packing in this case is inert and serves only to provide even liquid distribution in the column and suppress liquid phase back mixing. Packing column usually have much lower hold-up than tray columns, so for homogenous RD, tray column are preferred. The tray column can be operated in the spray, mixed froth or bubbly flow regimes. As the liquid hold-up and the residence time requirement is higher, the preferred regimes of operations is the bubbly flow regime, which can be achieved by operating the column at lower superficial vapor velocities. The higher weir height ensures liquid hold-up on the tray. CFD studies can provide better inside for the column performance based on liquid hold-up, pressure drop, residence time distribution and mass transfer aspects.

2.9.4 Hardware for Heterogeneous Reactions:

For heterogeneous catalyzed processes, hardware design poses considerable challenges. The catalyst size, hold-up in the column, low-pressure drop, good vapor-liquid and liquid-solid contact and mass transfer are the basic criteria for design. The catalyst particle sizes used in such operations are usually 1-3 mm range. Larger particle sizes lead to intra-particle diffusion limitations.

(a) Spherical baskets   (b) Cylindrical container   (c) Wire gauze envelopes
                                                             for catalyst particles
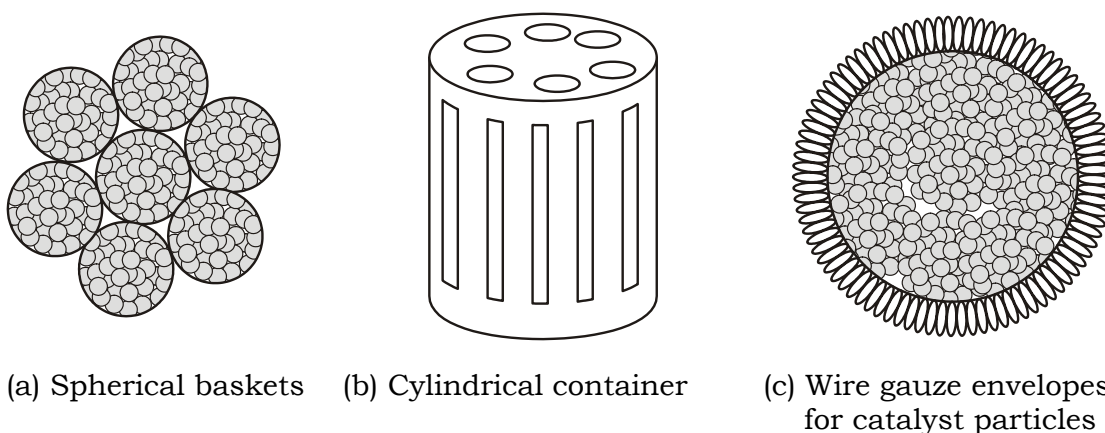
Figure 2.11 Various 'tea-bags' configuration for column internals. Catalyst particles need to be enveloped in wire gauze packings and placed inside RD columns.

Some basic shapes of packing are: (Refer Figure 2.11 and 2.12)

1) Porous shapes filled with catalyst inside them

2) Cylindrical shaped envelopes with catalyst inside them

3) Wire gauze envelopes with various shapes, spheres, tablets, doughnuts

4) Horizontally disposed wire-mesh, filled with catalyst

5) Horizontally disposed wire-mesh tubes containing catalysts.

(a)   (b)
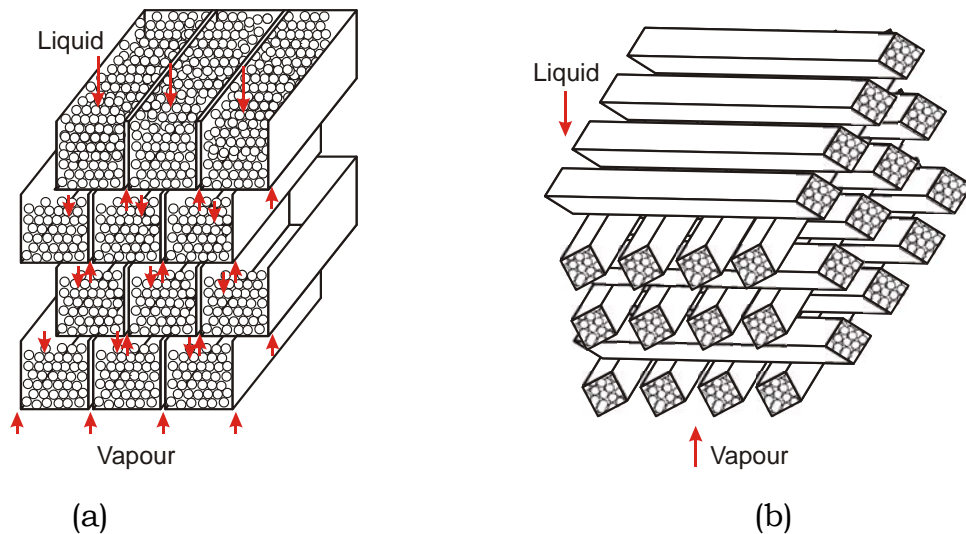
Figure 2.12 Horizontally Disposed Column Internals

(a) Wire gauze gutters and (b) wire gauze tubes containing catalyst.
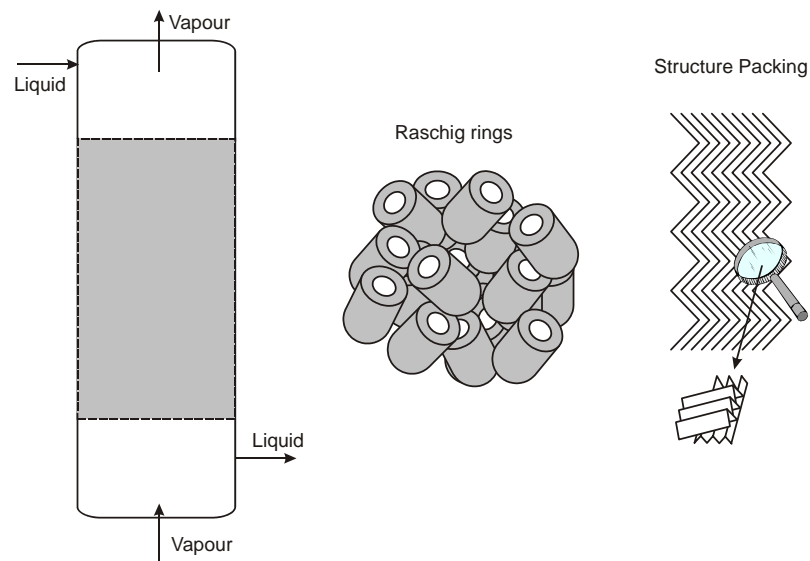
Figure 2.13.Counter-current Vapor-Liquid Contacting in Packed Columns.
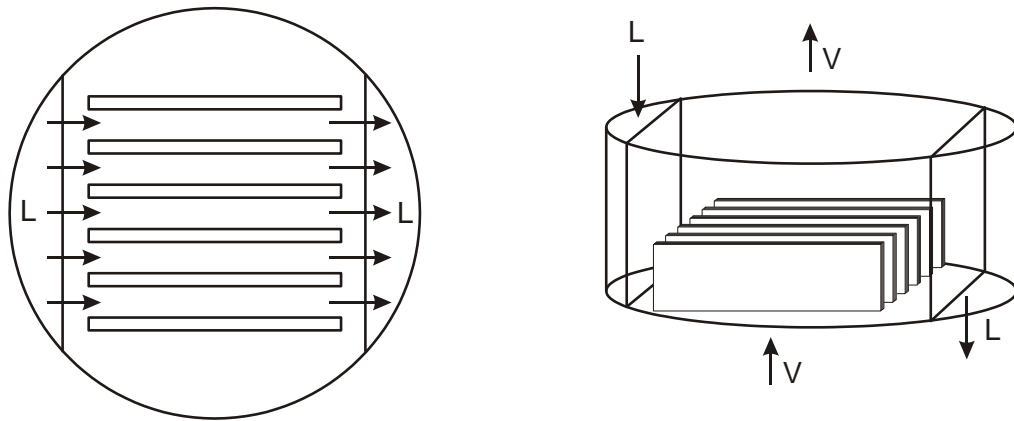
Figure 2.14 Catalyst Envelopes Placed along the Liquid Flow Path.

(a)   (b)   (c)
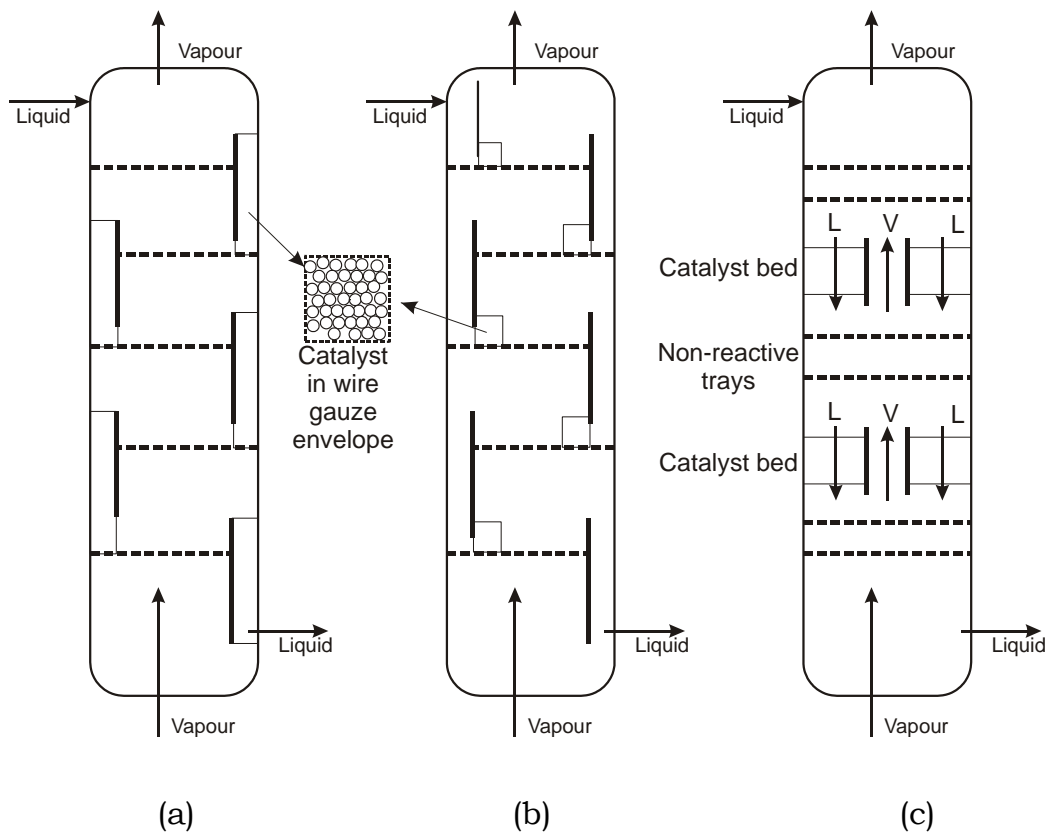
Figure 2.15 Counter-current Vapor-Liquid -Catalyst Contacting in Trayed Columns.

(a) Catalyst in envelopes inside down comers,
(b) Tray contacting with catalyst placed in wire gauze envelopes near the liquid exit from the down comers and
(c) Alternating packed layers of catalyst and trays.

The various catalysts and structure can be classified broadly in five different categories (Taylor and Krishna, 2000, 2003):

(i)   *Alternative reaction-distillation zones:* The column is provided with alternate spaces that offer different structures for reaction and distillation.

(ii)   *Catalyst coatings:* The catalyst may be specially prepared by coating a catalytically active material on a suitable support that is in the form of distillation column packings. The catalytic packing prepared in this way can be either random or structured.

(iii)   *Emulsion or Block Polymerization:* The polymeric catalysts are either prepared by conventional emulsion polymerization or molded with thermoplastic like polyethylene or it is prepared by block polymerization in molds.

(iv)   *Suspended (fluidized) catalytic distillation*: The catalyst particles can be used in the suspended (fluidized) form over a distillation tray or catalyst envelopes can be placed on a tray or in the down comers in RD column along the direction of the liquid flow path across a tray.

(v)   *Three-Levels of Porosity::*
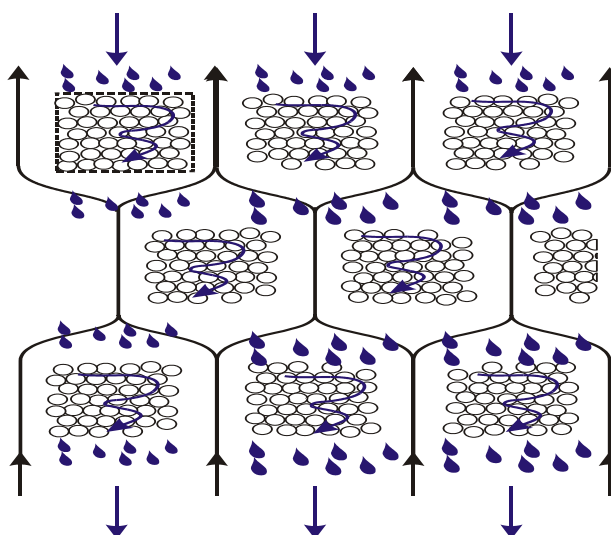
Figure 2.16 TLP concept

These structures provide continuous three-phase medium in which both reaction and distillation occur simultaneously. The different commercial catalytic packings from CDTech, Sulzer, and Koch Engineering are available. The packings are based on three-levels of porosity (TLP) concept. In these packings-

a)   Nanometer to micrometer size 'pores' inside the catalyst articles,

b)   Millimeter size 'pores' between catalyst particles packed in clusters.

c)   Centimeter size 'pores' between the various clusters.

Vapor flows through the centimeter pores whereas liquid through millimeter pores.

Common advantages of TLP packings:

1.   Embedded catalyst in the support structure does not entrain with the products

2.   Less wear and attrition of embedded catalyst.

3.   Increase in catalyst life and reduction of catalyst loss.

Some commercial available examples of catalytic packings based on TLP concept are Catalytic bales, structured packings like Katamax (developed by Koch Engineering company), Katapak –Katapak S and Katapak SP (Katapak SP are used when large mass transfer area is desired to improve the performance of systems involving fast reactions)

2.10 Thermodynamics and Kinetics of RD:

2.10.1 Thermodynamic Aspects:

Knowledge of thermodynamics is very important to understand and design the reactive separation systems. Basic thermodynamic information required for the analysis of reactive distillation is the vapor-liquid equilibrium behavior and the reaction equilibrium constant. In the case of relatively slow reactions the one should

know the reaction kinetics (rate equation) than the equilibrium constants. Thermodynamics also provides us model for determination of the properties of the reacting fluids along with basic relations such as, energy balance equations. Occurrence of both, reaction and separation makes modeling more complicated hence, challenging.

An introductory review of RD thermodynamics was provided by Frey and Stichlmair (1999a). The classical thermodynamic problem of determining the equilibrium conditions of multiple phases in equilibrium with each other is addressed in standard texts (Walas, 1985; Sandler, 1999). The equally important, and computationally more difficult, problem of finding the composition of a mixture in chemical equilibrium has also been well studied. The combined problem of determining the equilibrium points in a multiphase mixture in the presence of *equilibrium* chemical reactions has been the subject of a recent literature review by Seider and Widagdo (1996).

The effect that equilibrium chemical reactions have on two-phase systems has been considered at length by Doherty and coworkers (Barbosa & Doherty, 1987a, b, 1988a- d, 1990; Doherty, 1990; Ung & Doherty, 1995a-e). The first paper by Barbosa and Doherty (1987a) considers the influence of a single reversible chemical reaction on vapor-liquid equilibria. The second paper (Barbosa & Doherty, 1987b) introduces a set of transformed composition variables that are particularly useful in the construction of thermodynamic diagrams for reacting mixtures.

It is interesting to observe that reactive azeotropes can occur even for ideal mixtures (Barbosa and Doherty, 1987a, 1988a). Further, non-reactive azeotropes can disappear when chemical reactions occur. A reactive azeotrope has been found for the system isopropanol- isopropyl acetate-water-acetic acid (Song, et al, 1997). The influence the reaction equilibrium constant has on the existence

and location of reactive azeotropes was investigated for single reaction systems by Okasinski and Doherty (1997a, b).

Barbosa and Doherty (1988a) provide a method for the construction of phase diagrams for reactive mixtures. Doherty (1990) develops the topological constraints for such diagrams. Ung and Doherty (1995a-e) have extended the methods of Barbosa and Doherty to deal with mixtures with arbitrary numbers of components and reactions. The influence of homogeneous reaction kinetics on chemical phase equilibria and reactive azeotropy was discussed by Venimadhavan, et al, (1994) and Rev (1994).

Venimadhavan, Malone and Doherty (1999a) employed a bifurcation analysis to investigate in a systematic way the feasibility of RD for systems with multiple chemical reactions. Feasible separations are classified as a function of the Damkohler number. For the MTBE system, they showed that there is a critical value of the Damkohler number that leads to the disappearance of a distillation boundary. Frey and Stichlmair (1999b) describe a graphical method for the determination of reactive azeotropes in systems that do not reach equilibrium. Lee, Hauan and Westerberg (2000e) discussed circumventing reactive azeotropes.

Residue curve maps (RCM) and heterogeneous kinetics in methyl acetate synthesis were measured by Song, Venimadhavan, Manning, Malone and Doherty (1998). They found that the residue curves for the kinetically controlled cases are qualitatively similar to the curves for the equilibrium case. Thus, the production of methyl acetate by RD can be carried out in either regime. Open evaporation accompanied by liquid-phase chemical reactions has also been studied by Pisarenko et al, (1988b) and Solokhin, Blagov, Serafermov and Timofeev (1990a,b).

2.10.2 Kinetic Aspects

RD processes are often designed from equilibrium assumptions for chemical reactions. Most of the reactions carried out in RD columns are kinetically controlled and they can be strongly affected by inter and intraphase mass and energy transfer resistances. In the RD column the reaction can be carried out in a column sequence with an external recycling loop, a non-RD column on top of a reactive reboiler, or a full RD column. The kinetics of the chemical reactions carried out in a RD column play an important role on the performance of the process.

For the reliable design and operation of counter current columns, it is important to determine and analyze the kinetics of the reaction. Some guidelines to formulate the rate expressions, the transport resistance have to be accounted for describing the kinetics of reactions under the operating conditions of RD.

CHAPTER 3

MODELLING OF REACTIVE DISTILLATION PROCESSES

3.1 Models for Reactive Distillation Processes:

An effective way of decomposing the modeling aspects of reactive distillation involves the following classification of the models existing for distillation with reaction (Baur, 2000).

1. Steady-state equilibrium stage mode (EQ stage model), with either chemical equilibrium or n^{th} order kinetic reaction model, with or without stage efficiencies
2. Dynamic equilibrium stage model (Dynamic EQ stage model)
3. Steady State EQ stage model with stage efficiencies
4. Dynamic EQ stage model with stage efficiencies
5. Steady-state non-equilibrium (NEQ) stage model, where the interphase mass transfer is described by rigorous Maxwell-Stefan equations.
6. Dynamic non equilibrium stage model (Dynamic NEQ model)
7. Steady-state non-equilibrium cell model, developed by Higler (1999) that accounts for staging of the vapor and liquid phases during crosscurrent contacting on a distillation tray.

There are two modeling approach in use for reactive distillation
1. Equilibrium Stage Model
2. Rate based Model (Non-equilibrium Stage Model- NEQ Model)

An EQ stage model is simple and easy to use, and a NEQ stage model is rigorous but more realistic and involves additional effects due to mass transfer and heat transfer (Baur et al, 2002). An excellent review on modeling and simulation has been presented by Taylor and Krishna (2000).

In this section, brief information on Equilibrium stage and Non-equilibrium stage model are presented.

3.2 Equilibrium (EQ) Stage Models:

The development and application of the EQ stage model for conventional (i.e. non-reactive) distillation has been described in several textbooks (for example, Holland, 1963, 1981; Henley and Seader, 1981; Seader and Henley, 1998) and reviews (Wang and Wang, 1980; Seader, 1985; Taylor and Lucia, 1994). In this chapter, we are concerned with the extension of this standard model to distillation accompanied by chemical reaction(s).

EQ model assumes phase equilibrium with incoming and outgoing streams. Only limited amount of data is required to develop such models for RD processes, if both, phase and chemical equilibrium are assumed. NEQ models takes in account heat and mass transfer. The amount of information needed to develop reliable kinetic and mass transfer models greatly exceeds that for simple equilibrium stage models.
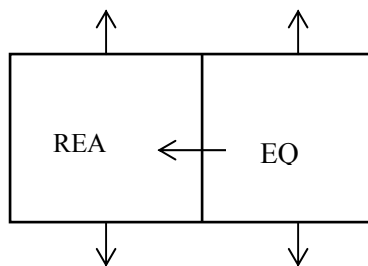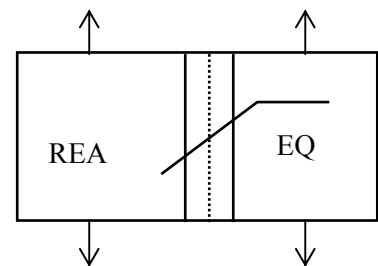
EQ Stage model   **Rate based (NEQ) model**

Model 1: Phase and chemical equilibrium

Model 2: Phase equilibrium and reaction kinetics

Model 3: Murphree efficiency and reaction kinetics

Model 4: Mass and Heat transport and reaction kinetics

Figure 3.1 Reactive Distillation Process Models

Model 1: The RD is modeled as a countercurrent multistage process with physical and chemical equilibrium on each stage.

Model 2: The assumption of chemical equilibrium is dropped and the reaction is described by a second order bulk reaction kinetics.

Model 3: It takes into account of residence time distribution of the liquid flow in the packing. Neither phase nor chemical equilibrium is achieved at these stages; Murphree efficiencies are used to give desired separation capacities.

Model 4: In rate-based approach (i.e. Model 4), heat and mass transfer are directly taken into account using two-film theory.

In this work, three equilibrium stage models of different complexity for the simulation of reactive distillation are used.

1)   Model # A (Phase Equilibrium+ Chemical equilibrium):

It assumes physical and chemical equilibrium are achieved at each stage. The reactive distillation is modeled as a countercurrent multistage process with physical and chemical equilibrium on each stage.

2)   Model # B (Phase Equilibrium+ Bulk Reaction Kinetics, without Decanter Model):

In this model the assumption of physical equilibrium is kept and the reaction kinetics at each stage is described by a second order reaction. No decanter model is employed.

3)   Model # C (Phase equilibrium+ Bulk Reaction Kinetics with Decanter Model):

In this model, the assumption of physical equilibrium is kept and the reaction kinetics at each stage is described by a second order reaction. Decanter model is used to account for phase splitting behavior at the top of RD column.

Rigorous process simulations are carried out to find the optimum design and operating conditions for the reactive distillation column

using these three models. The detailed discussions on simulation strategies, results obtained and their comparisons with experimental data by these models are discussed in Chapter 6.

3.3 Non-equilibrium (NEQ) Stage Models:

The NEQ stage model for RD follows the philosophy of rate-based models for conventional distillation (Krishnamurthy and Taylor, 1985; Taylor and Krishna, 1993; Taylor, Kooijman and Hung, 1994; Seader and Henley, 1998). The description of the interphase mass transfer, in either fluid phase, is almost invariably based on the rigorous Maxwell-Stefan theory for calculation of interphase heat and mass transfer rates (Bravo et al., 1993; Higler et al, 1998; 1999a, 1999b; Kerul et al, 1998, Lee and Dudukovic, 1998; Sawistowski and Pilavakis, 1979; Sundmacher, 1995 and Sundmacher and Hoffmann, 1996; Zheng and Xu, 1992a).

In the literature, there has been considerable attention to the phenomenon of multiple steady states. Using EQ stage model, steady state multiplicities have been reported for applications such as synthesis of MTBE (Guttinger and Morari, 1999; Jacobs and Krishna; 1993; Mohl et al, 1999; Nijhuis et al, 1993; Haun et al, 1995), synthesis of ETBE (Sundmacher, Unde and Hoffmann, 1999), Synthesis of TAME (Mohl et al, 1999; Rapmund et al, 1998) and for the production of ethylene glycol (Ciric and Miao, 1994; Kumar and Daoutidis, 1999) Schrans et al, (1996) and Kumar and Daoutidis (1999) have performed dynamic simulations using the EQ stage approach to show the rich dynamic features of RD columns. For example, it has been shown by Schrans et al, 1996 for MTBE synthesis, that a small perturbation of reactant feed to the column could trigger oscillations and could shift the column operation from one steady state with high conversion to another steady state, with a significantly reduced conversion.
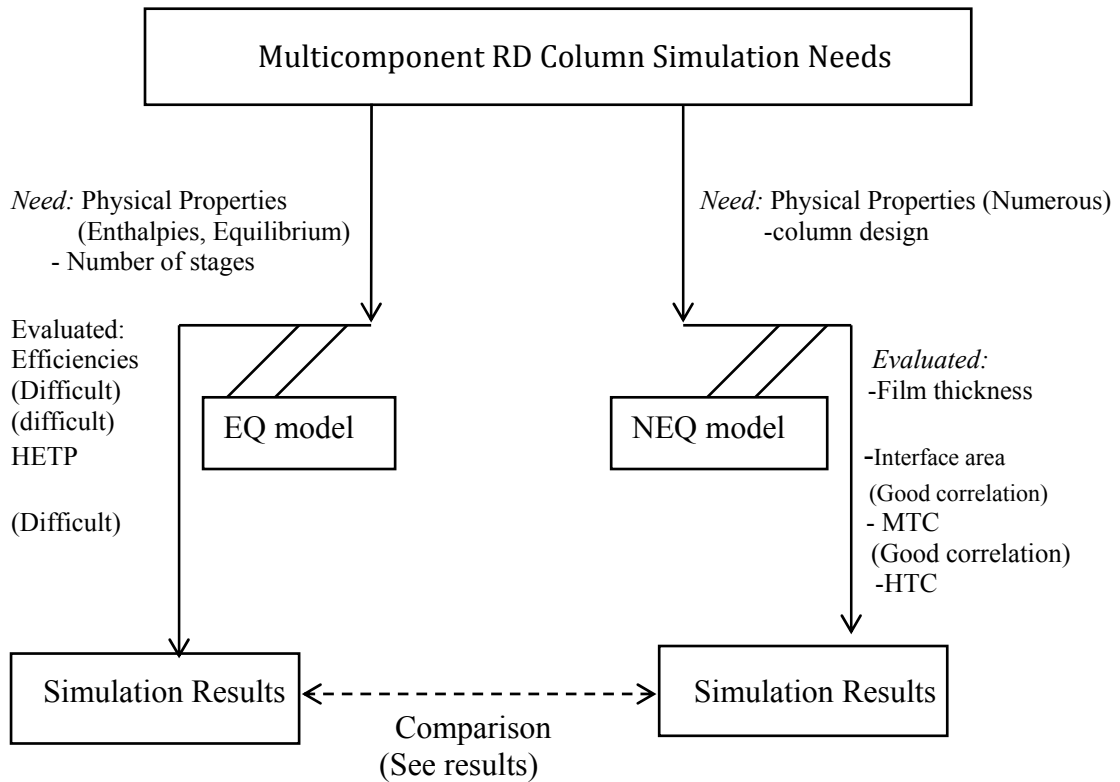
Figure 3.2 Model Requirements for EQ and NEQ Stage Model

3.4 Previous Modeling Studies:

Taylor and Krishna (2000) has given extensive review on modeling of reactive distillation. For the modeling of reactive distillation in packed columns, both equilibrium stage (EQ) and non-equilibrium stage (NEQ) approaches are used For esterification processes the simpler EQ models have shown good results in comparison with stationary experimental data (P. Moritz et al, 2002,)

Schmitt et al, (2004) reported comprehensive studies on the n-hexyl acetate synthesis by reactive distillation. They presented two different types of reactive distillation models, parameterized and compared in simulations in their work. Predictions from stage models of different complexity are compared to the results of their own experiments conducted in Laboratory scale as well as in pilot scale.

Popken et al, (2001) investigated synthesis and hydrolysis of methyl acetate by reactive distillation and developed an equilibrium-

stage model and showed that equilibrium-stage model is capable of describing the experiments in the packed column when the reaction kinetics, separation efficiency, and heat loss of the column are taken into account.

Singh et al, (2005) studied production of butyl acetate by catalytic distillation in laboratory scale column and developed dynamic equilibrium stage model and solved to predict the transient and steady-state results. All the simulations were performed using a steady-state simulator (Aspen Plus). The decanter model of Aspen Plus was used for the decanter simulation. In their work, they compared experimental data with simulation results and reported that an equilibrium stage model is capable of describing the column profiles quantitatively.

Further Sing et al, (2006) investigated recovery of acetic acid from aqueous solutions by reactive distillation in laboratory scale column and reported that the equilibrium stage model for reactive distillation predicts the performance well in agreement with the experimental results.

Bhatia et al, (2007) reported extensive theoretical and experimental studies on production of isopropyl palmitate in a catalytic distillation column. In their work, the experimental data were used to validate the theoretical predictions obtained from steady-state model and rate-based model.

Brehelin et al, (2006) reported experimental and simulation studies for production of propyl acetate by reactive distillation. Steady-state simulations based on EQ models were carried out using the commercial software ProSim Plus. They have shown that good agreement was observed between the experimental and calculated values of outputs (flow rates, concentrations and temperature) from simulation.

In this section, we present modeling equations for the Equilibrium stage dynamic model.

3.5 Development of Equilibrium Stage (EQ) Model:
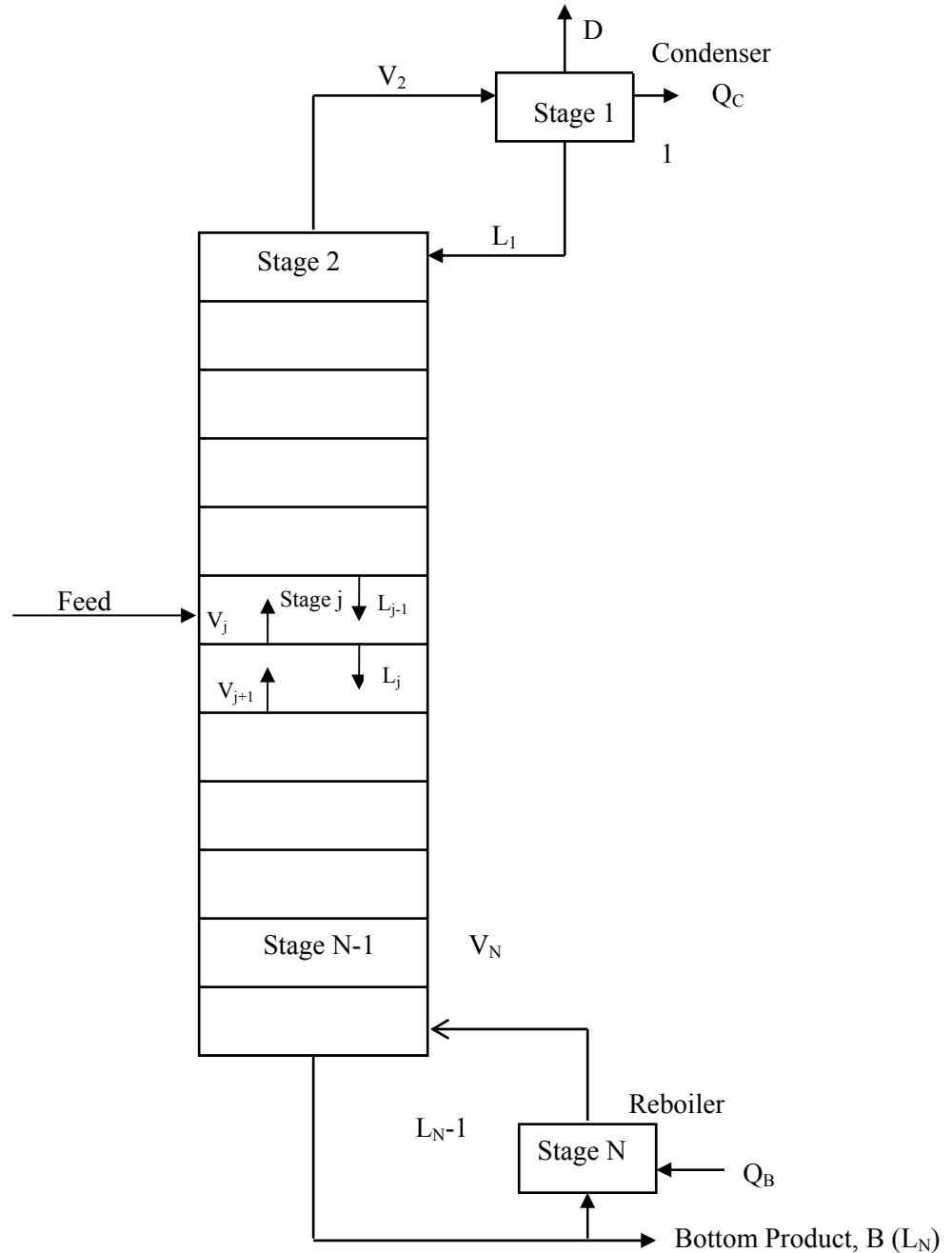
Figure 3.3 RD Column for Esterification of Acetic acid and iso amyl alcohol

The esterification of acetic acid with iso amyl alcohol is considered inside a RD column as shown in Figure 3.3. A single plate (j) in the column showing the corresponding streams is as shown in figure 3.4. The column has a total condenser and a reboiler. The total numbers of theoretical stages are 27 and numbered from top to bottom. Stage number 1 represent condenser and stage 27 represent the reboiler.
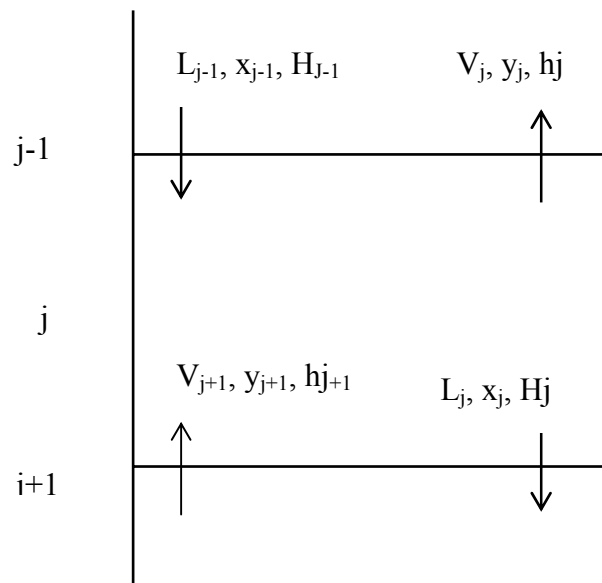
Figure 3.4 A single plate (j) in the column showing the corresponding streams

3.5.1 Model Assumptions:

The various assumptions made during the development of model were as follows:

1. The vapor and liquid on each plate and leaving on each plate are perfectly mixed. Moreover, the liquid on the plate has the same compositions as the liquid leaving the plate.
2. Constant molar liquid holdup is assumed for each stage.
3. Molar vapor holdup is negligible in comparison with the molar liquid holdup.

4. Simple or complex reaction(s) proceed only in the liquid phase and their rate can be described by an appropriate kinetic expression(s). (Preferably second order reaction kinetics)

5. The liquid phase is in equilibrium with the vapor phase leaving the plate.

6. Phase splitting is considered only in the decanter; liquid-liquid splitting inside the column is neglected.

7. The reactive zone is considered to be a multistage column with 6 theoretical stages per meter (NTSM) for reactive section catalyst packing.

8. The nonreactive zone is considered to be multistage column with 10 stages per meter for Hyflux packing for the present system.

9. The pressure decrease along the column height is assumed to be negligible.

The first assumption is reasonable for small and medium diameter columns in which the liquid on the plates is well mixed by the flowing vapor phase. However, this assumption is not valid, in case of large diameter columns and a more rigorous model of mixing on plates has to be applied. The third assumption about the vapor holdup is reasonable since the column works under atmospheric pressure. In such conditions, liquid density is much higher than vapor density.

The assumptions above lead to a model that consists of a set of ordinary differential and algebraic equations (DAE's). From the mass and energy dynamic balances on the jth plate according to Figure 3.3, the model is derived as follows:

3.5.2 Modeling Equations:

The equations that model equilibrium stages are known as MESH (**M**aterial balance, Phase **E**quilibrium relations, mole fraction **S**ummations, and **H**eat balance) equations.

[1] The <u>M</u>ass Balance of Component i around Plate j is given by:

$$\frac{d(x_{i,j}M_j)}{dt} = V_{j+1}y_{i,j+1} - L_jx_{i,j} + L_{j-1}x_{i,j-1} - V_jy_{i,j} + \Delta R_{i,j} \qquad (3.1)$$

M_j is the hold-up on stage j. With only few exceptions, M_j is considered to be hold-up only on the liquid phase. It is, however, important to include the hold-up of the vapor phase at higher pressures.

The component material balance (neglecting the vapor hold-up) is given by

$$\frac{dx_{i,j}}{dt} + M_j + \frac{dM_j}{dt}x_{i,j} = V_{j+1}y_{i,j+1} - L_jx_{i,j} + L_{j-1}x_{i,j-1} - V_jy_{i,j} + \Delta R_{i,j} \quad (3.2)$$

This is combined with overall mass balance around plate j:

$$\frac{dM_j}{dt} = V_{j+1} - L_j + L_{j-1} - V_j + \Delta R_j \qquad (3.3)$$

The subscripts i ranges in value from 1 to the number of components in the mixture. The subscripts j ranges in value from 1 to the number of plates, N. (In present system, N=27)

[2] The Phase <u>E</u>quilibrium Equation:

$$y_{i,j} = K_{i,j}x_{i,j} \qquad (3.4)$$

Where, K= equilibrium constant

giving,

$$\frac{d(x_{i,j})}{dt}M_j = V_{j+1}K_{i,j+1}x_{i,j+1} - L_jx_{i,j} + L_{j-1}x_{i,j-1} - V_jK_{i,j}x_{i,j} + \Delta R_{i,j} -$$
$$(V_{j+1} - L_j + L_{j-1} - V_j + \Delta R_j)x_{i,j}$$

$$(3.5)$$

[3] <u>S</u>ummation Equations:

The S equations are the mole fraction Summation equations

$$\sum_{i=1}^{c} x_{i,j} = 1 \; ; \; \sum_{i=1}^{c} y_{i,j} = 1 \tag{3.6}$$

[4] <u>H</u>eat Balance Equations:

The <u>H</u>eat balance equation around the plate j is given by:

$$\frac{d(H_{i,j} M_j)}{dt} = V_{j+1} h_{i,j+1} - L_j H_{i,j} + L_{j-1} H_{i,j-1} - V_j h_{i,j} \tag{3.7}$$

$$\frac{dH_{i,j}}{dt} M_j + \frac{dM_j}{dt} H_{i,j} = V_{j+1} h_{i,j+1} - L_j H_{i,j} + L_{j-1} H_{i,j-1} - V_j h_{i,j} \tag{3.8}$$

This is combined with overall energy balance around plate J:

$$\frac{dH_{i,j}}{dt} M_j = V_{j+1} h_{i,j+1} - L_j H_{i,j} + L_{j-1} H_{i,j-1} - V_j h_{i,j} - (V_{j+1} - L_j + L_{j-1} - V_j + \Delta R_j) + H_{i,j} \tag{3.9}$$

Under steady-state conditions all of the time derivatives in the above equations are equal to zero.

These equations are coupled with algebraic equations for reaction kinetics and vapor-liquid equilibrium. The model is presented for typical esterification reaction of acetic acid and iso amyl alcohol for the synthesis of iso amyl acetate.

3.5.3 Phase Equilibrium and Reaction Kinetics:

(1) Phase Equilibrium:

The reaction of iso amyl alcohol and acetic acid forms a highly liquid phase azeotropes have been observed experimentally in the iso amyl acetate system and other similar mixtures (Yeong-Tarng Tang et al, 2005) To account for nonideal vapor-liquid equilibrium (VLE) and

possible vapor-liquid-liquid equilibrium (VLLE) for these quaternary systems, the NRTL (non random two liquid) model is used for activity coefficients. The NRTL equation is an activity coefficient model that correlates the activity coefficients γ_i of a compound i with its mole fractions x_i in the concerning liquid phase. The NRTL model predicts the presence of these azeotropes and was found to be accurate in estimating their compositions.

It should be emphasized the quality of the model parameters (Table 3.1) is essential to generate correct process flow sheet. Two important steps to validate model parameters are: (1) good prediction of azeotropes, and (2) reasonable description of the liquid-liquid (LL) envelopes for VLLE systems. Correct description of the existence of azeotropes and the ranking of azeotropic temperatures will lead to generating correct residue curve map (RCM), and, consequently, placing separators in the right sections. (Chang et al, 2000)

A reasonable prediction of LL envelope can facilitate possible use of decanter which is often encountered in esterification reactive distillation systems. (Hanika et al, 1999, Gangadwala, et al, 2004, Huang et al, 2003) This is also the reason why the NRTL and UNIQUAC models are preferred for activity coefficients.

Since esterification reaction was carried out at atmospheric pressure, the vapor phase nonideality considered is the dimerization of acetic acid as described by the Hayden-O'Conell second virial coefficient model. (Hayden and O'Connell, 1975) The Aspen Plus built-in association parameters are used to compute fugacity coefficients.

The NRTL-model has been chosen for the description of the phase equilibrium data. Table 3.1 and 3.2 lists the model parameters for the present quaternary system where iso amyl acetate system is described by the NRTL model. (Chiang et al, 2002)

Table 3.1 Binary Parameters of the NRTL[a] Model for Acetic acid(1) + Iso amyl alcohol (2) + iso amyl acetate (3) +Water (4) Systems

(j,i))	$A_{ij}(K)$	$A_{ji}(K)$	α_{ij}
(1,2)	-316.8	178.3	0.17
(1,3)	-37.94	214.6	0.2
(1,4)	-110.6	424	0.299
(2,3)	-144.8	320.7	0.301
(2,4)	100.1	1448	0.298
(3,4)	254.5	2222	0.2

Table 3.2 Activity Coefficient Models Parameters for Iso amyl Acetate Esterification Systems

Comp.i	HOAC(1)	HOAC(1)	HOAC(1)	ISAMOH(2)	ISAMOH(2)	ISAMAC(3)
Comp.j	ISAMOH(2)	ISAMAC(3)	H2O(4)	ISAMC(3)	H2O(4)	H2O(4)
bij (K)	-316.8	-37.943	-110.57	-144.8	100.1	254.47
bji (K)	178.3	214.55	424.018	320.6521	1447.1	2221.5
cij	0.1695	0.2	0.2987	0.3009	0.298	0.2

[a] NRTL Model equations:

$$\ln Y_i = \frac{\sum_{j=1}^{nc} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{nc} G_{ki} x_k} + \sum_{j=1}^{nc} \frac{x_j G_{ij}}{\sum_{k=1}^{nc} G_{kj} x_k} \left[T_{ij} - \frac{\sum_{k=1}^{nc} x_k \tau_{ki} G_{kj}}{\sum_{k=1}^{nc} G_{kj} x_k} \right]$$

$$G_{ij} = \exp\left(- a_{ij} \tau_{ij} \right)$$

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T}$$

$$a_{ij} = C_{ij}$$

$$G_{ij} = 1$$

$$T_{ii} = 0$$

τ_{ij} and τ_{ji} are the dimensionless interaction parameters and the parameters α_{ji} and α_{jii} are the so-called non-randomness parameters

The Azeotrope data for iso amyl acetate esterification system is given in Table 3.3.

Table 3.3 Azeotrope Data for Iso amyl acetate Esterification System (Yeong-Tarng Tang et al, 2005)

ISAMOH/ISAMAC/H_2O

94.71°C

(0.0488, 0.1292, 0.822)

94.9°C

(0.046, 0.107, 0.847)

ISAMAC/H_2O

94.90°C

(0.1696, 0.8304)

95.2°C

(0.166, 0.834)

ISAMOH /H_2O

95.80°C

(0.1512, 0.8488)

95.8°C

(0.146, 0.854)

HOAC/ ISAMOH/ISAMAC

139.89°C

(0.2225, 0.6108, 0.1667)

HOAC / ISAMOH

140.07°C

(0.2585, 0.7415)

* Heteroazeotropes in boldface.

(2) Reaction Kinetics:

Modeling reactive distillation requires information on chemical equilibrium and in most cases on reaction kinetics. Reaction kinetic experiments were planned on the basis of preliminary reactive distillation simulations to determine the relevant temperature and concentration range. A total of 36 reaction kinetic experiments were carried out to study effect of various operating parameters on conversion. A pseudo-homogeneous model is fitted with kinetic data obtained from batch reactor and activation energy and rate expression for present esterification reaction is determined. This is discussed in Chapter 4.

The esterification of the acetic acid with iso amyl alcohol can be expressed in the following general form:

$$CH_3 - COOH + C_5H_{11} - OH \quad \xleftrightarrow{k} \quad C_5H_{11} - COO - CH_3 + H_2O$$
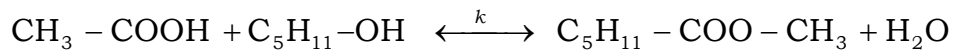
The solid catalysts used are acidic ion-exchange resin, such as Amberlyst 15 (Rohm and Hass) (Chiang et al, 2002) and Purolite CT179 (Purolite) (Saha et al, 2005) The solid catalyst can be either immobilized via structured packings such as Katapak-S (Sulzer Chemtech) or simply placed inside the tray with certain type of replacement mechanism (Davy Process Technology). The reaction rates are expresses in the Pseudohomogenous model, Eley-Rideal (ER) model or Langmuir-Hinshelwood and, generally, with the component represented in terms of activity. (Yeong-Tarng Tang et al, 2005)

The following section gives a brief literature for reaction kinetics of iso amyl acetate synthesis.

(a)   The reaction rate synthesis of iso amyl acetate can be expressed to a quasi-homogeneous model according to Chiang et al, (2002):

$$r = k_f \left[C_{CH_3OH} \cdot C_{C_5H_{11}OH} - \frac{C_{C_5H_{11}COOCH_3} \cdot C_{H_2O}}{K_{eq}} \right] \tag{3.10}$$

Where, $K_{eq} = \dfrac{K_f}{K_b} = 13.9 \, e^{-777/T}$, With $K_{eq} = 2$ for a temperature range of 100-150⁰C. (The reaction is slightly endothermic with an almost negligible heat effect)

(b) The best rate expression for the synthesis of amyl acetate over Amberlyst 15 is given by: (Lee et al, 2001)

$$-r_A = \frac{1.4934 \times 10^9 \exp\left(\dfrac{-6609}{T}\right)\left[a_{CH3COOH} \cdot a_{C5H11OH} - 1.7889 a_{C5H11COOCH3}\left(a_{H2O}\right)^4 \right]}{\left(1 + 0.792 \, a_{C5H11OH} + 27.136\left(a_{H2O}\right)^4\right)} \tag{3.11}$$

Where a = activity for species i.

(c) Saha et al, (2004) presented LHHW model for amyl acetate synthesis over Purolite- CT- 175 catalysts:

$$K_{eq} = \left(\frac{a_{C5H11COOCH3} \cdot a_{H2O}}{a_{CH3COOH} \cdot a_{C5H11OH}}\right)_{eq} = \left(\frac{x_{C5H11COOCH3} \cdot x_{H2O}}{x_{CH3COOH} \cdot x_{C5H11OH}}\right)_{eq} \times$$

$$\left(\frac{\gamma_{C5H11COOCH3} \cdot \gamma_{H2O}}{\gamma_{CH3COOH} \cdot \gamma_{C5H11OH}}\right)_{eq} \tag{3.12}$$

Where,

K_{eq} = equilibrium constant of the reaction

a = activity of the component

x = mole fraction of the component

γ = activity coefficient of the component

With following parameters:

Pre – expoential   factor (ko) $= 2.4 \times 10^{-5}\ (mol\,g^{-1}\,min^{-1})$

Activation   energy (E) $= 47.0\ (kJ\,mol^{-1})$

$K_{CH_3COOH}\ .^a{}_{CH_3COOH}$ $= 0.23$

$K_{C_5H_{11}OH}\ .^a{}_{C_5H_{11}OH}$ $= 2.12$

$K_{C_5H_{11}COOCH_3}\ .^a{}_{C_5H_{11}COOCH_3}$ $= 0.34$

$K_{H_2O}\ .^a{}_{H_2O}$ $= 2.21$

(d) Lee et al, (1999) reported the kinetic expressions for amyl acetate synthesis over Amberlyst 15:

$$r = m_{cat}(\ k_1\ C_{CH_3COOH} \cdot C_{C_5H_{11}OH} - k_{-1}\ C_{C_5H_{11}COOCH_3} \cdot C_{H_2O}\ )\quad (3.13)$$

$$k_1 = 31.1667\,exp\!\left(\frac{-51740}{RT}\right) \qquad\qquad (3.14)$$

$$k_{-1} = 2.2533\,exp\!\left(\frac{-45280}{RT}\right) \qquad\qquad (3.15)$$

$$k_1 = 1.13 \times 10^{-6}\left[\frac{m^6}{(kmol.kg.cat.s)}\right]\ (T = 363\,K) \qquad (3.16)$$

$$K_{eq} = 1.6\ (T = 363\,K) \qquad\qquad (3.17)$$

Where m = mass of catalyst (kg)

3.5.4 Solution of Model (MESH) Equations:

This section discusses different methods for steady state as well as dynamic simulation of RD problems. All the methods are more or less extension of the conventional simulation methods for distillation problems. Taylor and Krishna (2000) has given excellent review of steady-state algorithms and applications to solve these model equations.

3.5.4.1 Steady State Algorithms:

The steady state model of the RD process is obtained by setting all the time derivatives equal to zero, in model equations developed in earlier section. Different methods for steady state simulation for reactive distillation are:

(1)   Tray to tray calculations:

This is the simplest and most cumbersome method for the simulation of distillation problems. This involves a lot of computational efforts and is time consuming. It is possible code such algorithm, but ends with a large computer time and convergence problems.

To carry out simulation by this method, we need to know the vapor-liquid-equilibrium for the components involved, kinetic equation of the reaction, and relative rate of constants of reactions involved in the process.

Assumed values of feed and vapor compositions from top tray are checked by overall material balance. These guess values are changed if the material balance is not satisfied.

(2)   Tearing methods:

Tearing methods involves dividing model equations into groups to be solved separately. Following are the different algorithms for the simulation of the reactive distillation problems using tearing methods:

(a) Bubble Point (BP) method

To use this method, the derivation of the equation is changed to matrix notation, which has advantage that any interstate flow pattern is allowed. Here for the solution of the linearised material balance equations, tridiagonal matrix algorithm can be employed.

(b) $\theta - \eta$ method

This method is just extension of the multi-θ method of conventional distillation simulation to the reactive distillation problems. A correction factor η for the reaction rate is defined which is analogous θ for correcting molar flow rates. This method can be applied for steady state as well as dynamic simulation of the reactive distillation systems.

(3)   Relaxation Method:

Relaxation method involves writing MESH equation in unsteady state form and integrates them numerically until steady state solution has been found. This method is closely related to the dynamic simulation and also requires large computer time.

(4)   Homotopy Continuation method:

This method has its capability of forcing the desired solution by tracking a Homotopy curve regardless of the choice of the starting guess. This offers the good simulation tool for solving the complexity of reactive distillation systems, which arises due to non-idealities in the K-values and enthalpies or due to nature of column.

(5)   Minimization Method:

The error minimization can be carried out for the computation of the composition and temperature profiles. The method can provide good solution with higher convergence and also the solution independent of the estimates of the starting points. This method can be applied to the systems in which it is difficult to predict a priori approximate concentration and temperature profiles in the reactive distillation systems.

(6)   Naphtali and Sandholm Method:

This is most widely method and simultaneous correction technique. This method involves reducing the 2N number of equations from the set, rather than solving N (2C+3) equations simultaneously. This is done by writing the MESH equations in the form of individual molar flows.

(7)   Inside- Outside method:

The methods described above such as tearing methods and simultaneous correction methods, need the larger computational effort in calculating K-values, vapor and liquid phase enthalpies and their derivatives, particularly when rigorous thermodynamic models are utilized. This problem can be solved using inside-outside method. This employs two sets of thermodynamic property models:

(a)   A simple approximate empirical set frequently for converging inner loop

(b)   A rigorous and complex set used less frequently, is in the outer loop.

The MESH equations are solved in the inner loop with approximate set. The parameters in the empirical equation for approximate set are updated in the outer loop by rigorous equations, only at some intervals not at each iteration.

3.5.4.2 Computer-Based Methods:

In this section, computer-based simulation methods that have been developed for solving the EQ stage model equations are briefly discussed. Currently modeling studies are carried out using one or other commercial simulation package such as Aspen Plus, Pro/II, HYSYS, and SpeedUp which support the steady as well as dynamic simulation.

(a) MATLAB™ Simulation

The model equations developed in earlier section forms a mixed set of set of ordinary differential equations (ODE's) and algebraic equations. The equations for 27 stages and four-component system can be solved in MATLAB by ODE 15 S solver (which is an ordinary differential and algebraic equation (DAE) solver for stiff equations, variable order method)

(b) Aspen Plus Simulation:

Aspen Plus is a sequential modular simulation package, contains an extensive model library that allows most unit operations to be simulated easily and accurately. Despite the fact that a column equipped with structured packing, very good results were obtained using this model. Each unit operation block is solved in certain sequence. The process simulation capabilities of Aspen Plus enables us to predict the behavior of a process using basic engineering relationships such as mass and energy balances, phase and chemical equilibrium, and reaction kinetics. With reliable thermodynamic data, realistic operating conditions and the rigorous Aspen Plus equipment models, one can simulate actual plant behavior. Implementation of model equations and all simulations were carried out using the model RADFRAC from the steady-state simulator Aspen Plus, which is based on a rigorous equilibrium-stage model for solving the MESH equations.

The model is both rigorous enough to represent the process complexity and simple enough to ensure the feasibility of the process simulation.

Venkataraman, Chan and Boston (1990) describe the inside-out algorithm known as RADFRAC that is part of the commercial program Aspen Plus. Inside-out methods involve the introduction of new parameters into the model equations to be used as primary iteration variables. RADFRAC is able to handle both equilibrium reactions as well as kinetically limited reactions.

In built RADFRAC model for reactive distillation is used to simulate the equilibrium model in Aspen plus environment. The simulation is begun by putting together a basic flow sheet of a RADFRAC column with input streams of acetic acid and iso amyl alcohol and output streams on iso amyl acetate and water. The thermodynamic properties are calculated using the NRTL model The Hayden–O'Connell (Hayden and O'Connell, 1975) second virial coefficient model with association parameters was used to account for the dimerization of acetic acid in the vapor phase. The Aspen Plus built-in association parameters are employed to compute fugacity coefficients. Such deviations are mainly caused by the dimerization of the acetic acid. A reaction rate for Pseudohomogenous model calculated by laboratory batch reactor is used for simulation to yield a steady state solution.

3.5.5 Study of Effect of Operating Parameters on RD Column Performance:

An improved understanding of how different process conditions affect the performance of the overall behavior of RD column is helpful in the design of an optimal RD column. Typically following parameters are important to study its effect on RD column performance:

- Number of reactive and nonreactive stages
- Feed stage locations
- Reboiler heat duty
- Reflux ratio
- Feed flow rates
- Molar ratio

The key results of simulation, i.e. typical profiles of temperature, composition of liquid and vapor phases, molar flow rates of liquid and vapor phases are obtained for different operating conditions in RD column. Also it is useful to study temperature profile on each stage and concentration change during the process on specific stage.

The simulation results are generated for three equilibrium stage models of different depths of RD column using MATLAB and Aspen Plus. The detailed simulation results and discussions of effect of various operating parameters on RD column performance is presented in Chapter 6.

CHAPTER 4

REACTION KINETICS AND PHASE EQUILIBRIUM STUDIES FOR SYNTHESIS OF ISO AMYL ACETATE

This chapter is divided in to two sections : a) Reaction Kinetics Studies b) Phase Equilibrium Studies

[A] REACTION KINETICS STUDIES

4.1   Introduction:

Esterification reactions are ubiquitous reactions especially in pharmaceutical, perfumery and polymer industries, wherein; both heterogeneous and homogeneous catalysts have been widely used. The conventional esterification process employing sulfuric acid, methanesulfonic acid or *p*-toluenesulfonic, results in sulfur contamination of the final product, which is unacceptable. Other organic and inorganic acid catalysts also pose the same problem. (Yadav et al, 2008). Further, the use of homogeneous catalyst requires neutralization with an alkali, which leads to serious effluent problems on industrial scale. The concept of "Green Chemistry" has been pursued vigorously since early 1990's as a new approach for chemical industry to adopt rather than to continue with old traditional and polluting pathways.(Kumbhar et al, 1989) Catalytic processes such as acylation, alkylation, nitration, condensation, esterification, isomerization, oligomerization, which require acids, have been investigated with solid acid catalysts including zeolites, metal oxides, acid treated clays and their modified versions, and cation exchange resin, etc. (Yadav et al, 1994) The solid acid catalysts are non-corrosive, easy to separate from the reaction mixture and a variety of reactor types and configurations can be adopted on industrial scale.

They can also be used repeatedly over prolonged period of time without any difficulty in handling and storage.

The esterification of acetic acid with alcohols like *n*-butanol, ethanol, isobutyl alcohol, amyl alcohol and hexyl alcohol fall in a typical class of reacting systems. The alcohol is sparingly soluble in water and esters and water are almost immiscible. An additional feature is that the ester-water-alcohol forms a ternary heterogeneous azeotrope, which is minimum boiling. Hence, the vapors at the top of RD column condense to form two liquid phases of which aqueous phase is almost pure water. One can conveniently separate water and enhance the conversion. (Singh et al, 2005)

The low molecular weight organic esters have pleasant smell and are used in the food industry. Iso amyl acetate has been used in the industry as a solvent, and extractants, and polishing agent. It is used as artificial flavoring in banana-flavored bubble gums, as preservative in sodas and soft drinks as well as artificial scent for covering unpleasant odors (Teo and Saha, 2004). It is also used in large quantities in artificially pear- flavored food articles as additive in cigarettes, and as a solvent for tannins, nitrocellulose, lacquers, celluloid, and camphor. It is also used to manufacture celluloid cements, water proof varnishes, artificial silk, leather or pearls, photographic films, bronzing liquids and metallic paints, perfuming shoe polishes and dyeing and finishing textiles. (Saha et al, 2005)

4.2   Previous Studies:

Iso amyl acetate synthesis reaction was studied in the presence of various solid acid catalysts in the past. Lee et al, (1999) studied the kinetic behavior catalyzed by acidic cation exchange resin, Amberlyst 15. The kinetic data were correlated by a quasi-homogenous (QH) model with which the apparent rate constants at each reaction temperature were determined. They reported the activation energies of the forward and backward reactions as 51.74 kJ/mol and 45.28

kJ/mol respectively. Further Lee et al, (2000) investigated the kinetic behavior of the heterogeneous esterification of acetic acid with amyl alcohol over an acidic cation-exchange resin, Dowex 50Wx8-100. The experiments were conducted in a fixed-bed reactor at temperatures from 323 to 393 K and at molar ratios of feed (amyl alcohol to acetic acid) from 1 to 10. In their work, the kinetic data were correlated with the quasi-homogeneous, Langmuir-Hinshelwood, Eley-Rideal, and modified Langmuir-Hinshelwood models and shown the modified Langmuir-Hinshelwood model gave the best representation for the kinetic behavior of the reaction over wide ranges of temperature and feed composition.

Teo et al, (2004) presented kinetics of heterogeneous catalyzed esterification of acetic acid with iso amyl alcohol with a cation-exchange resin catalyst, Purolite CT-175, in a stirred batch reactor. Effects of various parameters such as speed of agitation, catalyst particle size, mole ratio of reactants, reaction temperature, catalyst loading, and reusability of the catalyst were studied to optimize the reaction condition. The kinetic data were correlated with the Langmuir–Hinshelwood–Hougen–Watson model.

Saha et al, (2005) studied the reaction kinetics with dilute acetic acid. The kinetic data were correlated with Langmuir-Hinshelwood-Hougen-Watson (LHHW) and Eley-Rideal (E-R) models. They presented detailed kinetic data and a reliable rate expression for the esterification of acetic acid with iso-amyl alcohol that would be useful for the simulation and design of an RDC for removing dilute acetic acid from aqueous streams.

Steinigeweg et al, (2002) reported the reaction kinetics for butyl acetate system using Amberlyst 15 as a catalyst and the kinetic constants for a Pseudohomogenous kinetic model are presented. Gangadwala et al, (2003) studied the esterification of acetic acid with n-butanol in the presence of ion-exchange resin catalysts such as

Amberlyst-15 to determine the intrinsic reaction kinetics. In their work, kinetic modeling was performed to obtain the parameters related to intrinsic kinetics. Pseudohomogenous, (PH), Eley-Rideal (ER), Langmuir-Hinshelwood-Hougen-Watson (LHHW), and modified LHHW models were presented.

Tang et al, (2005) presented an excellent review on the esterification of acetic acid with five different alcohols, ranging from C1 to C5 and presented data for reaction kinetics and phase equilibrium. Schmitt et al, (2006) presented reaction equilibrium and kinetics for n-hexyl acetate synthesis in batch reactor using Amberlyst CSP2 as a catalyst. Two kinetic models are tested, a pseudo-homogeneous and an adsorption-based model and shown that despite its simplicity, the pseudo-homogeneous model gives better results and was recommended for further use.

4.3   Esterification Reactions for Present Test System

A general esterification reaction can be expressed as
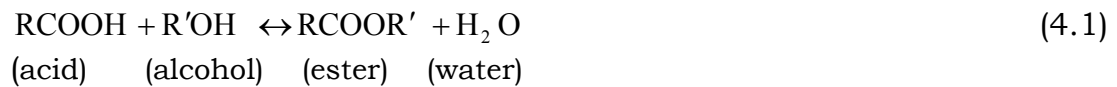
$$RCOOH + R'OH \leftrightarrow RCOOR' + H_2O \qquad\qquad (4.1)$$
(acid)   (alcohol)   (ester)   (water)

The synthesis of iso amyl acetate is done through esterification of acetic acid with iso amyl alcohol. The ester has wide application as a versatile solvent in chemical industry. It is a reversible reaction that takes place in the presence of acid catalyst. The catalyst used in the present experiment is a solid heterogeneous catalyst. Hence, reaction takes place on the surface of the catalyst. If the reaction is performed in a batch reactor, the conversion will increase and the reaction rate will drop with respect to time. Eventually it will attain equilibrium.

Iso amyl acetate is synthesized by esterification of acetic acid with iso amyl alcohol as per following reaction:

$$CH_3 - COOH + C_5H_{11} - OH \leftrightarrow C_5H_{11} - COO - CH_3 + H_2O \qquad (4.2)$$

(HOAC)   (ISAMOH)   (ISAMAC)   (Water)
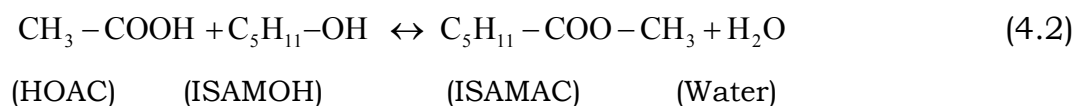
Since the self-catalyzed reaction is rather slow, reaction (4.2) is commonly catalyzed using strong inorganic acid, like sulfuric acid, p-toluene sulfuric acid and hydrochloric acid. However, they can cause some problems such as the formation of side reactions resulting in a corrosive environment by the discharge of acid containing waste (Teo and Saha, 2004). Heterogeneous catalysts such as zeolites, ion-exchange resins, and acidic clay catalysts are gaining importance of high purity of products, because they are easily removed from the reaction mixture and have lower corrosive effects (Y. Ma et al, 1996)

Most reactions catalyzed by ion-exchange resins can be classified as quasihomogenous or quasiheterogenous (Hasse et al, 2006). The kinetics of present model reaction catalyzed by Amberlyst or Dowex was described in previous investigations with both a quasihomogenous and quasiheterogenous. (Lee et al, 1999, 2001 and Saha et al, 2005) Cation exchange resins are excellent catalysts for esterification reactions, and do not get affected by the water of reaction and retain their activity (Chakrabati and Sharma 1993; Sharma 1995); therefore different cation exchange resins were used to assess their efficacy in this reaction.

In this chapter, the kinetics of the esterification reaction of iso amyl alcohol and acetic acid catalyzed by TULSION™ MP-T-63, T-62 and T-66, cation ion - exchange resin (Thermax India Ltd.) is presented.

Table 4.1 Properties Catalyst used (Thermax India Ltd.)

Catalyst	Particle size (μm)	Exchange capacity (meq/dry g)	Bulk density (kg/m^3)	Moisture content (%)	Porosity (%)	Temp stability (K)	Specific Sur.area (m^2/gm)	Pore Dia (A)	Cross linking (%)
T-62	300-1200	4.8	NA	<1	NA	403	35	NA	15
T-63	300-1200	4.9	NA	<1	40	408	35	400	15
T-66	300-1200	5.0	NA	<1	NA	403	NA	NA	NA

4.4 Kinetic Models

The kinetics of esterification reaction can be expressed using a simple Pseudohomogenous model or more complicated models based on the Langmuir-Hinshelwood Hougen-Watson (LHHW) mechanism or Eley-Rideal (ER) mechanism in the absence of any intraparticle diffusional limitations. Pseudohomogenous first and second order models are applicable to many ion-exchange resin catalyzed reactions and highly polar reaction medium. (Yadav et al, 2008)

In this section, brief description of various kinetic models is given.

4.4.1 Pseudohomogenous Model:

Among all the models, the simplest model is the Pseudohomogenous model.

Consider reaction given by equation (4.2). The rate expression for this reaction is

$$-r_{CH_3COOH} = k_1 \, C_{CH_3COOH} \cdot C_{C_5H_{11}OH} - k_2 \, C_{C_5H_{11}COOCH_3} \cdot C_{H_2O} \tag{4.3}$$

The reaction equilibrium constant is given by

$$K = \frac{k_1}{k_2} \tag{4.4}$$

The reaction equilibrium constant is calculated from

$$\ln \frac{K}{K^0} = \frac{\Delta H_R^{o(l)}}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \tag{4.5}$$

where, $K^0 = \exp \left[\dfrac{\Delta G_R^{o(l)}}{RT_0} \right]$ $\tag{4.6}$

Esterification reactions are known to be second order reversible reactions. Therefore, for the bimolecular type second order reactions,

$$A + B \leftrightarrow C + D \tag{4.7}$$

With restrictions that,

$C_{AO} = C_{BO}$ and $C_{CO} = C_{DO} = 0$

The rate expression can be written as,

$$-r_B = \frac{-d_{CB}}{dt} = C_{BO}\frac{dX_B}{dt} = k_1 C_A.C_B - k_2 C_C.C_D = k_1 C^2_{BO}\ (1-X_B)^2 - k_2\ (C_{BO}X_B)^2$$

... [4.8]

Where,

A= acetic acid

B= iso amyl alcohol

C= iso amyl acetate

D= water

At the equilibrium, $-r_B = 0$

Hence from the above equations, we determine the fractional conversion of B at the equilibrium condition by

$$K = \frac{C_{Ce},C_{De}}{C_{Ae}.C_{Be}} = \frac{X^2_{Be}}{(1-X_{Be})^2}$$ [4.9]

The equilibrium constant is given by equation [4.4] as,

$$K = \frac{k_1}{k_2}$$

Combining equation [4.4], [4.8] and [4.9] in terms the equilibrium conversion, we obtain,

$$\frac{-d_{XB}}{dt} = k_1 C_{BO}\left[(1-X_B)^2 - (1-\frac{X_{Be}}{X_{Be}}).\ X^2_B\right]$$ [4.10]

With conversions measured in terms of X_{Be}, this may be indicated as a pseudo second-order reversible reaction, which on integration gives,

$$\ln\left[\frac{X_{Be} - (2X_{Be}-1).X_B}{X_{Be} - X_B}\right] = 2k_1\left(\frac{1}{X_{Be}}-1\right)C_{BO}.t$$ [4.11]

Temperature and reaction rate:

We can examine the variation of the rate constant with temperature by Arrhenius law relationship,

$$k_1 = k_1^o exp\left[\frac{E_A}{RT}\right]$$ [4.12]

This is conveniently determined by plotting $\ln k_1$ versus $1/T$

4.4.2 Langmuir-Hinshelwood-Hougen-Watson (LHHW) Model:

The LHHW model is applicable whenever the rate-determining step is the surface reaction between adsorbed molecules. The rate expression for the LHHW model is

$$-r_A = \frac{A_f \left(\frac{-E_o}{RT}\right) \left(a_A \; a_B - \frac{A_r}{A_f} a_C \; a_D\right)}{(1 + K_B.a_B + K_D.a_D)^2} \qquad [4.13]$$

4.4.3 Eley-Rideal (ER) Model:

The ER model has been applied if in the rate-limiting step; surface reaction takes place between one adsorbed species and one nonadsorbed reactant from the bulk liquid phase. Moreover, because of the strong affinity of resins for water, the activity of water in the catalyst gel phase, where the reaction occurs, is distinctly different from that in the liquid phase. The rate expression for the ER model is

$$-r_A = \frac{A_f \left(\frac{-E_o}{RT}\right) \left(a_A \; a_B - \frac{A_r}{A_f} a_C \; a_D\right)}{(1 + K_B.a_B + K_D.a_D)} \qquad [4.14]$$

Where, where A_f and A_r are the Arrhenius pre exponential factors for the forward and reverse reactions, respectively, E_o is the activation energy of the reaction, R is the gas constant, and T is the temperature of the reaction. Parameters K_B and K_D are the adsorption equilibrium constants for amyl alcohol and water, respectively.

The adsorption equilibrium constant for species i, K_i can be defined as the ratio of the adsorption rate constant $K_{a,i}$ to the desorption rate constant, $K_{d,i}$:

$$K_A = \frac{K_{a,}A}{K_{d,}A} \qquad [4.15]$$

$$K_B = \frac{K_{a,}B}{K_{d,}B} \qquad [4.16]$$

$$K_C = \frac{K_{a,}C}{K_{d,}C} \qquad\qquad [4.17]$$

$$K_D = \frac{K_{a,}D}{K_{d,}D} \qquad\qquad [4.18]$$

A detailed description for the modeling aspects of homogenously acid-catalyzed reactions with LHHW model and the RE model was reported by Carberry (1976), Terjero (1996), Saha and Sharma (1996) and Teo and Saha (2004).

In order to account for non-ideal behavior of the bulk liquid phase, the activity of components was taken into account of the concentration of the components. (Saha et al, 2005) The UNIFAC group contribution method was used for the estimation of activity coefficients. (Poling et al, 2007)

Table 4.2 UNIFAC Activity Coefficient Parameters

Component	Liquid mole fraction, x	Activity coefficients, γ
Acetic acid	0.147	0.872
Iso amyl alcohol	0.476	1.060
Iso amyl acetate	0.189	1.836
Water	0.189	3.259

Reaction rates were calculated by the differential methods as proposed by Cunill et al, (2000). In the case of this heterogeneously catalyzed reaction, the equation:

$$(-r_A)V = N_{AO}\left(\frac{dX_A}{dt}\right) \quad \text{is used.} \qquad\qquad [4.19]$$

Where $-r_A$ is the reaction rate of acetic acid, V is the reacting mixture volume, N_{AO} is the initial number of moles of acetic acid, X_A is the conversion of acetic acid, and t is the time of the reaction.

The equilibrium constant was calculated from the component concentrations at equilibrium through the equation

$$K_{eq} = \left(\frac{a_C.a_D}{a_A.a_B}\right)_{eq} = \left(\frac{x_C.x_D}{x_A.x_D}\right)_{eq} \left(\frac{\gamma_C.\gamma_D}{\gamma_A..\gamma_B}\right)_{eq} \qquad [4.20]$$

Where K_{eq} is the equilibrium constant of the reaction, a is the activity of the component, x is the mole fraction of the component, and γ is the activity coefficient of the component. Subscripts A, B, C, and D denote acetic acid, iso amyl alcohol, iso amyl acetate, and water, respectively.

4.4.4 Selection of Model:

From a statistical stand point of view, the model with the least sum of squares and random residuals would be the most suitable. Moreover, it would be essential that the parameters of the model had a physicochemical meaning and the activation energy was positive.

The parameters for the different models were estimated by minimizing the sum of residual squares (SRS) between the experimental and calculated reaction rates using the equation of Sanz, (2002)

$$SRS = \sum_{samples} (r_{expt} - r_{cal.})^2 \qquad [4.21]$$

Where, SRS is minimum sum of residual squares resulting in the fitting procedure and r is the reaction rate. The subscripts expt and cal denotes experimental and calculated values, respectively.

4.5 Experimental Work:

4.5.1 Materials and Catalysts

Acetic acid (99.8%) and *iso*-amyl alcohol (99%) were purchased from Merck India Ltd., Mumbai. Iso *a*myl acetate (> 99% purity) was purchased from S.D. Fine Chemicals Ltd., Mumbai and distilled water was used for experimental work. TULSION™: T- 63, T-66 and T-62

MP, cation ion exchange resin (Thermax India Ltd., Pune) equivalent with Amberlyst-15 (ROHM HAAS, USA) was used as a solid catalyst for batch reaction kinetic studies.

4.5.2 Batch Reactor Reaction Kinetics Parameters:

1. Temperature: 90^0C to130^0C
2. Catalyst Loading: 3 gm to 10 gm
3. Mole ratio of reactants (ISAMOH/HOAC): 1:1, 2:1, 3:1 and 1:2
4. Stirrer Speed: 400 rpm, 600 rpm, 800 rpm, and 1000 rpm
5. Different catalyst: T-63, T-62 and T-66 (Thermax India Ltd)
6. Catalyst Reusability

The synthesis of iso amyl acetate is done through esterification of acetic acid with iso amyl alcohol. The ester has wide application as a versatile solvent in chemical industry. It is a reversible reaction that takes place in the presence of acid catalyst. The catalyst used in the present experiment is a solid heterogeneous catalyst. Hence, reaction takes place on the surface of the catalyst. If the reaction is performed in a batch reactor, the conversion will increase and the reaction rate will drop with respect to time. Eventually it will attain equilibrium.

Due to their prominence in separation from reaction mixture and purification of products, ion-exchange resins have been used as catalysts in some important chemical processes such as manufacture of methyl-*tert*-butyl ether (MTBE), *tert*-amyl methyl ether (TAME), etc. Cation exchange resins still hold an advantage as the preferred catalyst over other catalysts in the same class in industrial processes and they are thermally stable up to 135 ^{0}C. (Thermax Ltd., India)

4.5.3 Reactor Design for Reactive Distillation

Assume the Reactive Section to be a Packed Bed Reactor (PBR) with the following specifications:

The Catalyst used is TULSION MP-T–63 (Thermax India Ltd.), which is similar to Amberlyst- 15. (Roham and Hass, USA)

1.   Column diameter d = 50 mm
2.   Column Height h = 1 m
3.   Temperature range, T = 363 – 423 K
4.   P = 1 bar
5.   Conversion x_A = 0.90
6. V_o = 3 liter /hr = 3 x 10 $^{-3}$ m³ /hr = 8.333 x 10 $^{-7}$ m³/sec.
7. F_{AO} = 3 liter / hr = 3.15 kg / hr = 0.0525 kmol / hr
          = 1.458 x 10 $^{-5}$ kmol / sec

We have residence time,

$$\tau = \frac{V}{Vo} \qquad \qquad [4.29]$$

$$\tau = \frac{((\frac{\Pi}{4} \times d^2) \times h)}{V_O}$$

$$= \frac{[(\frac{\Pi}{4}) \times (0.05)^2 \times 1]}{3 \times 10^{-3}}$$

$$= 0.6544 \, \text{hrs} = 39.264 \, \text{min} = 2355.84 \, \text{sec} \qquad [4.30]$$

Now,

$$C_{AO} = \frac{\rho_A}{M_A}$$

$$= \frac{1050}{60} \qquad \qquad [4.31]$$

$$= 17.4 \, \text{kmol/m}^3$$

Since in reactive distillation, the products are continuously separated in the column, the forward reaction is favored most of the time. Hence we assume the overall reaction to be second order with respect to the reactants. (Fogler, 1995)

Thus,

$$(-r_A')_{obs} = k' \, C_A \, C_B \qquad \qquad [4.31]$$

Where,

$$k' = k_o\, e^{-E/RT} = 31.1667\, e^{\left(\frac{-51740}{363R}\right)} = 1.1173 \times 10^{-6} \qquad (m^3/kmol\, sec)$$

C_A = Molar concentration of acetic acid $(kmol/m^3)$

C_B = Molar concentration of iso amyl alcohol $(kmol/m^3)$

Since equimolar feed is passed,

$$\therefore \quad M = \frac{C_{BO}}{C_{AO}} = 1$$

$$C_A = C_{AO}\,(1 - x_A)$$

$$C_B = C_{AO}\left(M - \frac{b}{a}\, x_A\right) = C_{AO}\,(1 - x_A) \qquad \because \frac{b}{a} = 1 \quad \text{(by stoichiometry)}$$

$$\therefore \quad (-r_A')_{obs} = \underbrace{k'C_{AO}^2}_{3.2785 \times 10^{-4}}\,(1 - x_A)^2 \quad (kmol/m^3\, sec) \qquad [4.32]$$

But entire catalyst is not utilized in the reaction hence, assuming 80% efficiency we find actual rate as,

$$(-r_A') = \eta\,(-r_A')_{obs} = 0.8\,(-r_A')_{obs} \qquad [4.33]$$

Now the PBR design equation is,

$$\frac{W}{F_{AO}} = \int_0^{x_A} \frac{dx_A}{(-r_A')} \qquad [4.34]$$

Also,

$$\frac{W}{F_{AO}} = \int_0^{x_A} \frac{dx_A}{0.8\,(-r_A')_{obs}} \qquad [4.35]$$

The numerical solution of equation [4.35] is given in Table 4.3

Table 4.3 Numerical Integration of Equation [4.35]

Xa	$(-r_a')_{observed}$	$\dfrac{1}{(-r_a')_{obs}}$	$(-r_A')$	$\dfrac{1}{(-r_A')}$		
0	0.00032785	3050.17538	0.0002623	3812.719		
0.1	0.000265559	3765.64862	0.0002124	4707.061		
0.2	0.000209824	4765.89903	0.0001679	5957.374		
0.3	0.000160647	6224.84772	0.0001285	7781.06	For 80% efficiency	
0.4	0.000118026	8472.70940	9.442E-05	10590.89	W / (Fao), kg.sec/kmol)	18281.99
0.5	8.19625E-05	12200.7015	6.557E-05	15250.88	Wcat , (g)	265.0888
0.6	0.000052456	19063.5961	4.196E-05	23829.5		
0.7	2.95065E-05	33890.8376	2.361E-05	42363.55	For 100% efficiency	
0.8	0.000013114	76254.3846	1.049E-05	95317.98	W / (Fao), (kg.sec/kmol)	20725.94
0.9	3.2785E-06	305017.538	2.623E-06	381271.9	Wcat, (g)	300.5262
1.0	0		0			
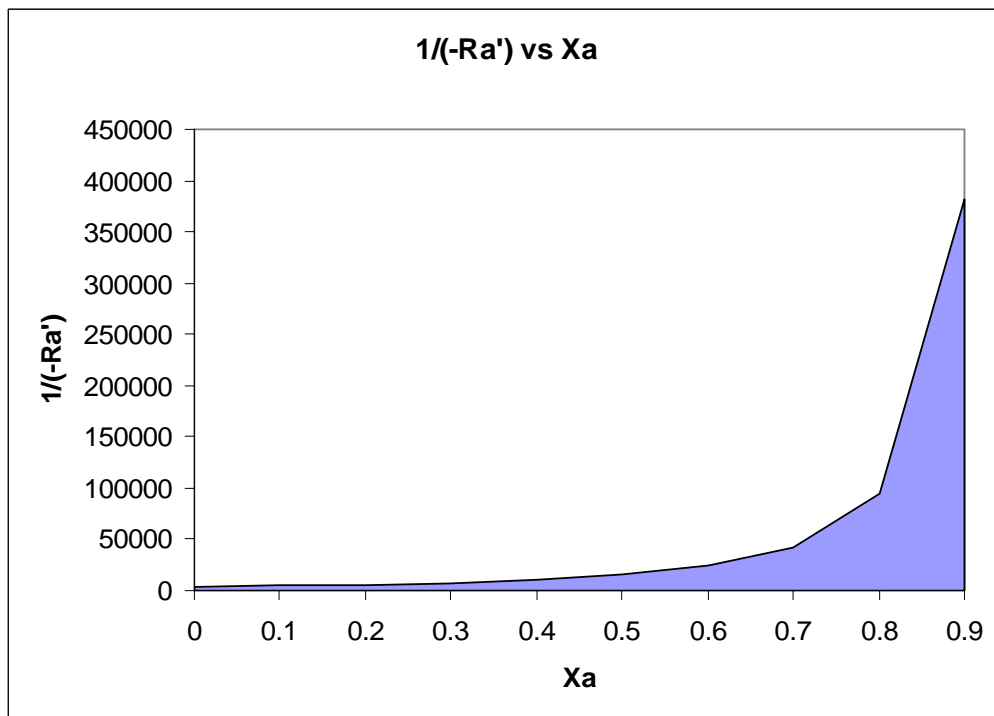
Figure 4.1 Graph of $\dfrac{1}{(-r_A')}$ **versus** Xa
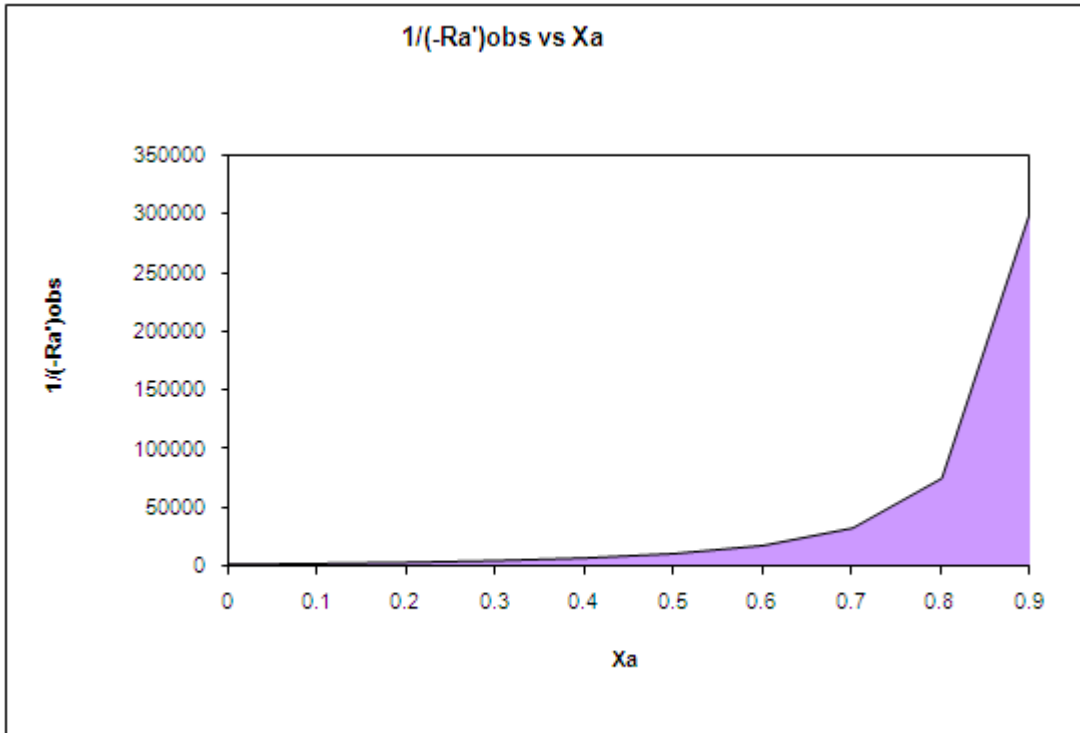
Figure 4.2 Graph of $\dfrac{1}{(-r_{A'})obs}$ **versus** X_a

Using Trapezoidal rule we get,

For 80% efficiency,

$$\frac{W}{F_{AO}} = 1.8281 \times 10^4$$

$$\therefore \quad W_{cat} = \underline{\underline{265.089 \text{ g}}}$$

For 100% efficiency,

$$\frac{W}{F_{AO}} = 2.0725 \times 10^4$$

$$\therefore \quad W_{cat} = \underline{\underline{300.52 \text{ g}}}$$

Based on this analysis, in reactive section, 350 gm of ion exchange resin as a catalyst is used in the reactive distillation packing for experimental work on reactive distillation column.

4.5.4 Experimental Set-up for Batch Reactor Reaction Kinetics:

The experimental set-up consists of heating chamber whose temperature can be set independently as shown in Figure 4.3. The reaction is performed in a 750 ml glass reactors equipped with stirrer and condenser and placed in heating chambers for the attainment of the required temperature. A motor drives the stirrer with a control over the speed of agitation. The speed can be measured using a non-contact type tachometer. Digital temperature indicator is provided to measure the temperature of the reaction mixture in the reactor.
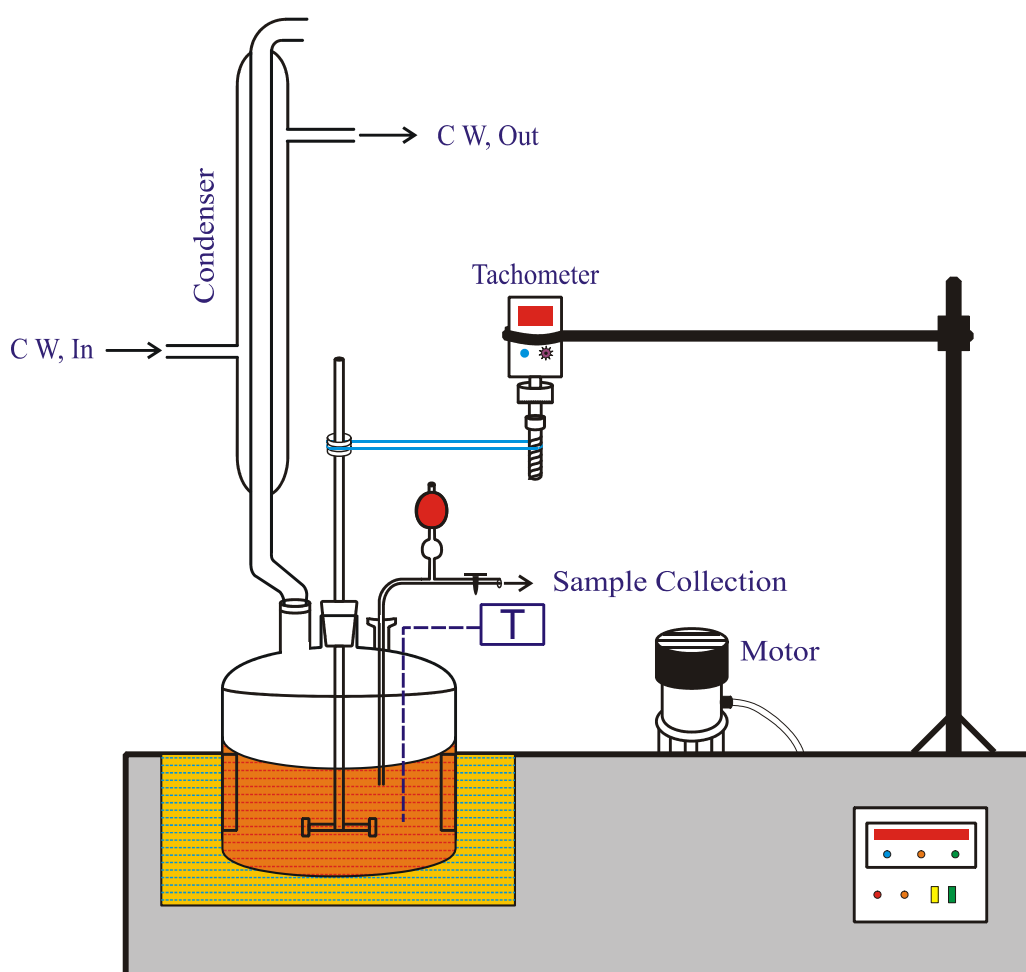
Figure 4.3 Schematic diagram of Batch Reactor for Kinetics Study of Esterification Reactions

4.5.5 Experimental Procedure

1.   Set the temperature of the heating chamber at the desired levels and start heating.

2.   Take measured quantities of acetic acid and iso amyl alcohol in the reactor.

3.   Place the reactor in the oil baths, start slow stirring and observe the reactor temperature.

4.   Once the desired temperature of the reaction mixture is attained, add the measured quantity of cation exchange resin (TULSION T-62, T-63 and T-66 MP) in the reactor. Consider this time as the zero reaction time. Increase the speed of agitation to desired value.

5.   Remove samples from all the reactors. Keep removing the samples as per the time intervals indicated in the tables.

6.   Take sample for GC Analysis and calculate conversions at every time interval.

4.5.6 Analysis:

Gas chromatography is used for the analysis of the different samples from the different locations of reactive distillation column.

Acetic acid, iso amyl alcohol, iso amyl acetate and water are analyzed using gas chromatograph (Model C-911, Mak Analytica India Ltd.) which is equipped with thermal conductivity detector (TCD). The samples are analyzed Porapak Q with hydrogen as carrier gas at a flow rate of 5×10^{-7} m^3/s. The injector and detector are maintained at a temperature of 493K and 423K respectively. The oven temperature is maintained isothermally at 513K to get the best resolution in less time.

The results obtained by GC are confirmed by independent titration using standard sodium hydroxide (NaOH) solution using phenolphthalein as indicator. The reliability of the titration method is confirmed with the help of analysis of standard samples containing iso amyl acetate to ensure the hydrolysis of ester does not takes place

during the course of titration. Acetic acid concentration is cross-checked by titrating the sample with dilute 0.1 N sodium hydroxide solution using phenolphthalein as indicator. The analytical relative uncertainty is <5%, which is good enough within the acceptable limits.

The typical chromatogram for this system and procedure for preparation for calibration charts for different components are discussed in Section 5.5.6 of Chapter 5.

4.5.7 Experimental Observation and Results:

Rigorous experiments are conducted in batch reactor to examine various operating parameters such as effect of temperature, stirrer speed, mole ratio variations, catalyst loading etc. on conversion. A total of 36 experimental runs are carried out in the laboratory. The results and discussions are discussed in following section.

4.5.7.1 Effect of Reaction Temperature:

The study on the effect of temperature is very important for a heterogeneously catalyzed reaction, as this information is useful in calculating the activation energy for this reaction.

Moreover, the intrinsic rate constants are strong functions of temperatures. Figure 4.4 presents the variation of conversion of acetic acid at different reaction temperatures in the range 363 K to 403 K at a feed mole ratio (alcohol to acid) of 1:1, at a stirrer speed of 600 rpm, and at 5 gm of catalyst loading. It shows that the higher temperature yields the greater conversion of acetic acid at a fixed contact time under otherwise identical conditions. Increasing the temperature is apparently favorable for the acceleration of the forward reaction. However, the equilibrium conversions were nearly equal (about 90%) the equilibrium conversion of acetic acid is independent of catalyst loading (after 3 hrs. of reaction).

Figure 4.5 and 4.6 shows effect of temperature on concentration of acetic acid and iso amyl acetate respectively.
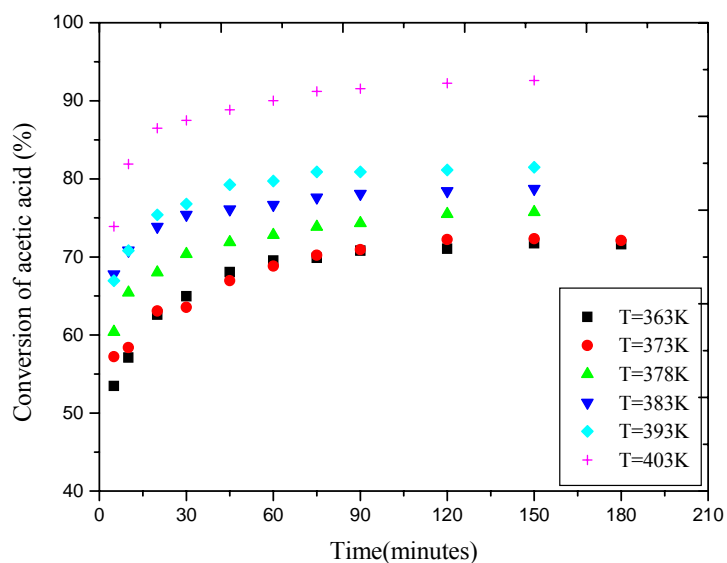
Figure 4.4 Effect of Temperature on Acetic acid Conversion

Catalyst loading: 5 gm, Mole ratio= 1:1, Stirrer Speed: 600 rpm,
Catalyst: TULSION MP T-63, Particle size= 0.3-1.2 mm
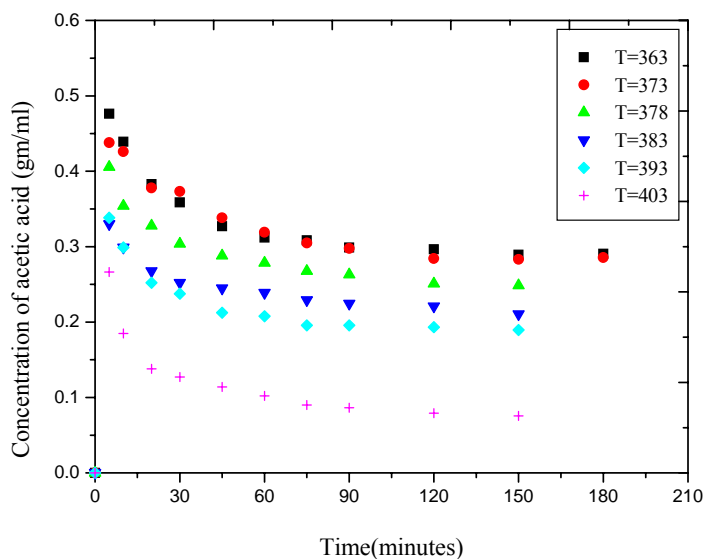
Figure 4.5 Effect of Temperature on Acetic acid Concentration

Catalyst loading: 5 gm, Mole ratio= 1:1, Stirrer Speed: 600 rpm,
Catalyst: TULSION MP T-63, Particle size= 0.3-1.2 mm
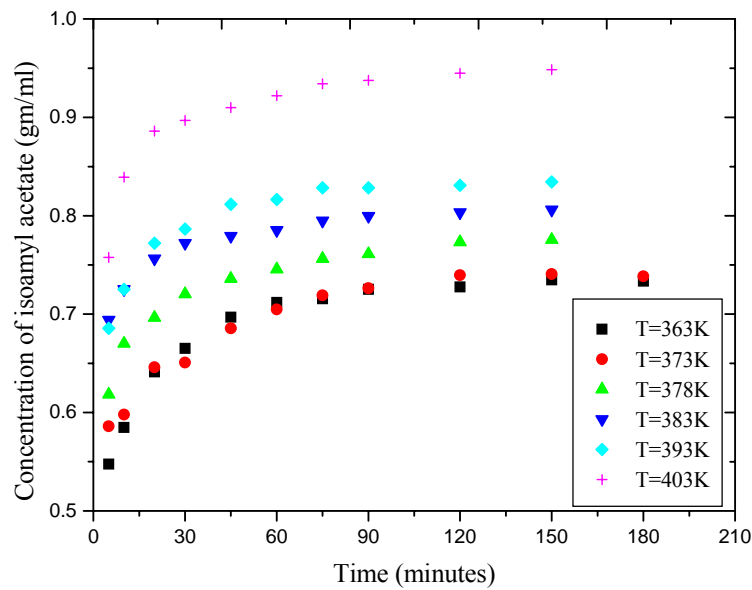
Figure 4.6 Effect of Temperature on iso amyl acetate Concentration

Catalyst loading: 5 gm, Mole ratio= 1:1, Stirrer Speed: 600 rpm,
Catalyst: TULSION MP T-63, Particle size= 0.3-1.2 mm

Determination of Heat of Reaction for Reactive Section

In this section, we determine the heat of reaction for reactive section.

Table 4.4 Determination of Heat of Reaction for Reactive Section

Components	Heat capacity coefficients					Heat of formation
	a (kJ/kmol)	b(1×10^3) (kJ/kmol)	c(1×10^5) (kJ/kmol)	d (1×10^8) (kJ/kmol)	e (1×10^{11}) (kJ/kmol)	ΔH_f (1×10^3) (kJ/ kmol)
Acetic acid	4.375	-2.397	6.757	-8.764	3.478	-432.25
Iso amyl alcohol	4.282	27.248	6.649	-10.683	4.474	-300
Iso amyl acetate	10.228	-14.943	13.033	-15.736	5.999	-511.2
Water	4.395	-4.186	1.405	-1.564	0.632	-241.81
Total	Δa 5.966	Δb -43.98	Δc 1.032	Δd 2.147	Δe -1.321	

Form of equation for the above data,

$$C \equiv a + bT^2 + cT^3 + dT^4 + eT^5$$ [4.36]

Where, C is Liquid Heat Capacity, kJ/ (kmol. K)

Heat of reaction at reference temperature (298 K),

$$\Delta H_R^0 \equiv \left(-241.81 - 511.2\right) - \left(-300 - 432.25\right)$$

$$\equiv -20.76 \times 10^3 \text{ kJ/kmol} \qquad\qquad [4.37]$$

Heat of Reaction at T, K,

$$\Delta H_{RT}^0 \equiv -20.76 \times 10^3 - \left[5.966 \times T\right] + \left[43.98 \times 10^3 \times \frac{(T)^2}{2}\right] - \left[1.032 \times 10^5 \times \frac{(T)^3}{3}\right]$$
$$- \left[2.147 \times 10^8 \times \frac{(T)^4}{4}\right] + \left[1.321 \times 10^{11} \times \frac{(T)^5}{5}\right]$$

$$[4.38]$$

Considering temperature at the top and bottom of Reactive Section (T = 406K),

$$\Delta H_{RT}^0 \equiv -20.76 \times 10^3 - \left[5.966 \times 406\right] + \left[43.98 \times 10^3 \times \frac{(406)^2}{2}\right] - \left[1.032 \times 10^5 \times \frac{(406)^3}{3}\right]$$
$$- \left[2.147 \times 10^8 \times \frac{(406)^4}{4}\right] + \left[1.321 \times 10^{11} \times \frac{(406)^5}{5}\right] = 2.914 \times 10^{23} \text{ kJ/kmol}$$

$$.....[4.39]$$

The positive sign indicates that the reaction is endothermic i.e. heat has to be supplied.

4.5.7.2 Effect of Reactant Molar Ratio

Esterification of acetic acid with iso amyl alcohol is an equilibrium-limited chemical reaction and because the position of equilibrium controls the amount of ester formed, the use of an excess of iso amyl alcohol increases the conversion of acetic acid. The initial molar ratio of iso amyl alcohol to acetic acid was varied from 1: 1 to 3:1 at a temperature of 383K, 5 gm of catalyst loading, and stirrer speed 600 rpm. The results are shown in Figure 4.7 to 4.9. As observed, the equilibrium conversion increases with the initial iso amyl alcohol-to-acetic acid mole ratio under otherwise identical conditions. The equilibrium conversion of acetic acid increased from about 78.71 % at a feed mole ratio (alcohol to acid) of 1:1 to 95.31 % at a

feed mole ratio (alcohol to acid) of 3:1. This is in accordance with the theory, as the increase in the concentrations of one of the reactants will enhance the forward reaction.

Figure 4.8 and 4.9 shows effect of reactant mole ratio on concentration of acetic acid and iso amyl acetate respectively.
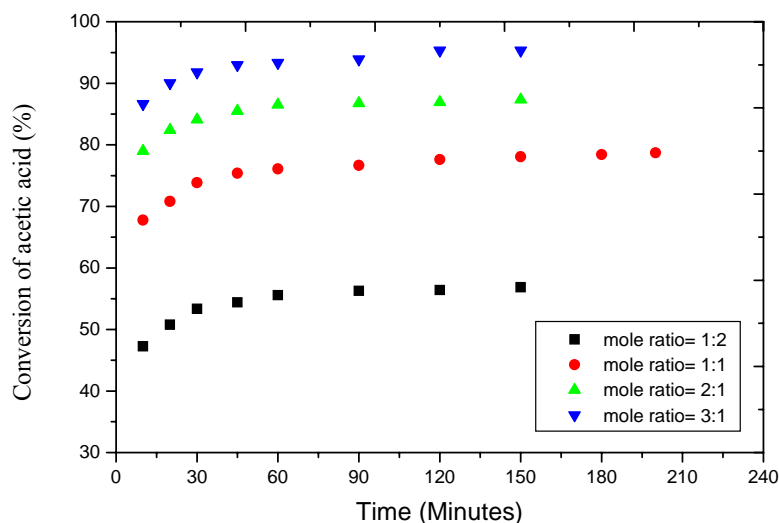
Figure 4.7 Effect of Mole Ratio on Acetic acid Conversion
Temperature =383K, Stirrer Speed: 600 rpm, Catalyst loading =5 gm,
Catalyst: TULSION MP T-63, Particle size= 0.2 mm-1.3mm
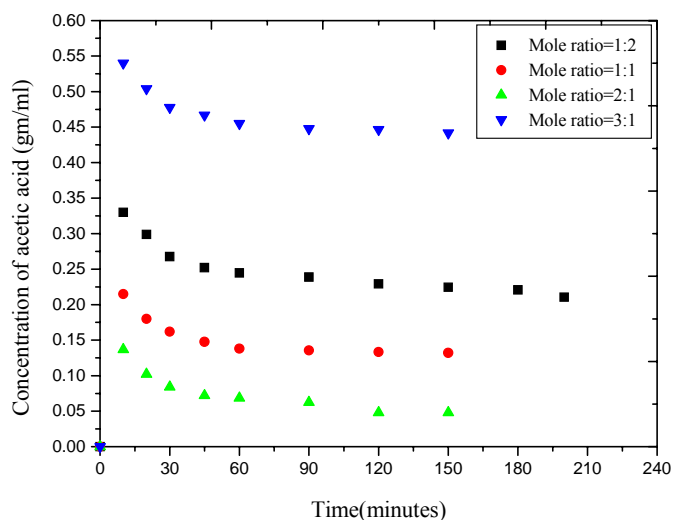
Figure 4.8 Effect of Mole Ratio on Acetic acid Concentration

Temperature =383K, Stirrer Speed: 600 rpm, Catalyst loading =5 gm,
Catalyst: TULSION MP T-63, Particle size= 0.2 mm-1.3mm
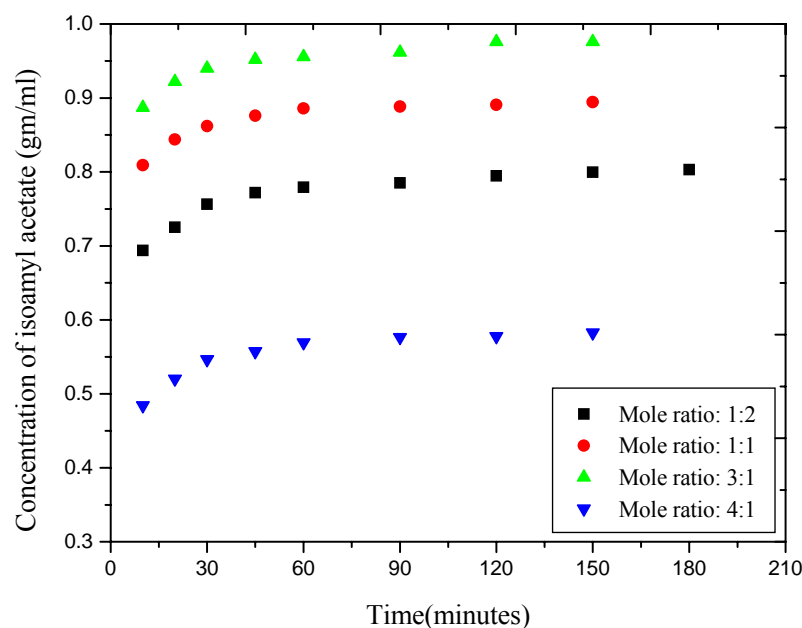
Figure 4.9 Effect of Mole Ratio on iso amyl acetate Concentration

Temperature =383K, Stirrer Speed: 600 rpm, Catalyst loading =5 gm,
Catalyst: TULSION MP T-63, Particle size= 0.2 mm-1.3mm

4.5.7.3 Effect of Stirrer Speed

In order to check the influence of external diffusion resistance, the experiments were conducted at different stirrer speeds, namely 400-1000 rpm at constant values of reaction temperature and catalyst loading. The results are shown in Figure 4.10- 4.12. In this range of stirrer speed, the experiments showed that there was very little effect of the speed of agitation, that is, no influence on external diffusion resistance from the bulk liquid to the surface of the catalyst was observed. Hence, all the further experiments were conducted at a stirrer speed of 1000 rpm.

Elimination of Mass Transfer Resistance:

In this reaction, there exist two types of mass transfer resistances, one across the solid–liquid interface and the other in the

intraparticle space. The effect of the speed of agitation is studied over a wide range of 400 to 1000 rpm to investigate the influence of an external mass transfer effect. Figure 4.10 shows the results obtained at different stirred speeds. It is clear from figure that the external mass-transfer resistance is negligible above 1000 rpm. Hence all the experiments are conducted at this speed of agitation.

Figure 4.11 and 4.12 shows effect of temperature on concentration of acetic acid and iso amyl acetate respectively.
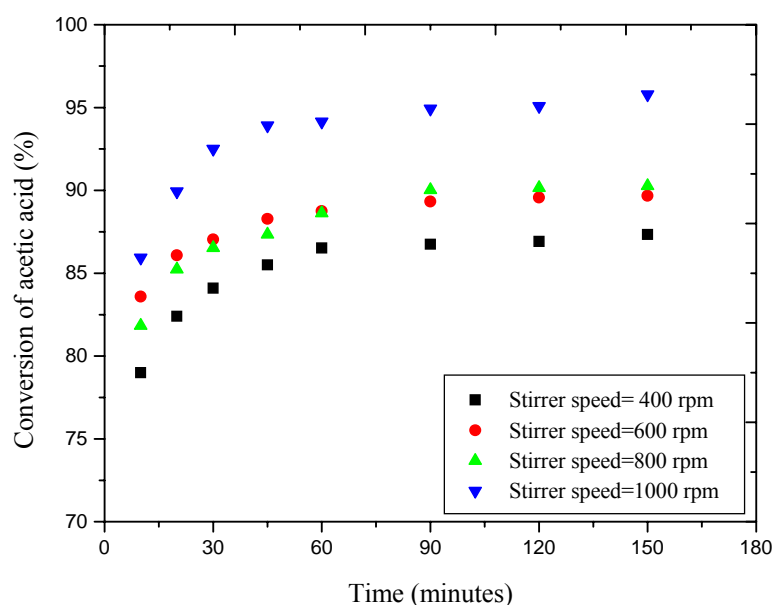
Figure 4.10 Effect of Stirrer Speed on Acetic acid conversion

Temperature =383K, mole ratio=2:1, Catalyst loading =5 gm,
Catalyst: TULSION MP T-63, Particle size= 0.2 mm-1.3mm
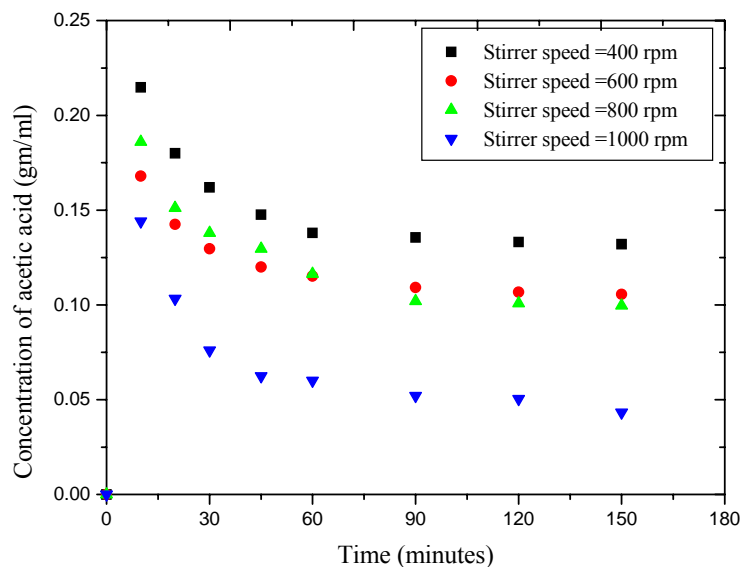
Figure 4.11 Effect of Stirrer Speed on Acetic acid Concentration

Temperature =383K, mole ratio=2:1, Catalyst loading =5 gm,
Catalyst: TULSION MP T-63, Particle size= 0.2 mm-1.3mm
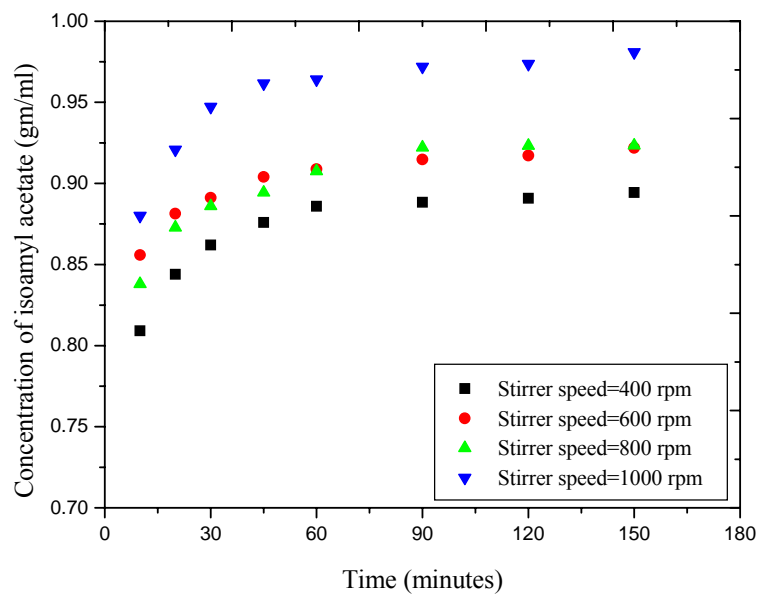
Figure 4.12 Effect of Stirrer Speed on iso amyl acetate Concentration

Temperature =383K, mole ratio=2:1, Catalyst loading =5 gm,
Catalyst: TULSION MP T-63, Particle size= 0.2 mm-1.3mm

4.5.7.4 Effect of Catalyst Loading

The catalyst loading was varied from 3 to 10 g dry-resin at a temperature of 383 K, feed mole ratio of 2:1, and stirrer speed of 1000 rpm. Figure 4.13 shows the plot of acetic acid conversion versus time at different catalyst loadings. It can be observed that the rate of reaction increases as the catalyst loading is increased.

Figure 4.14 and 4.15 shows effect of catalyst loading on concentration of acetic acid and iso amyl acetate respectively.
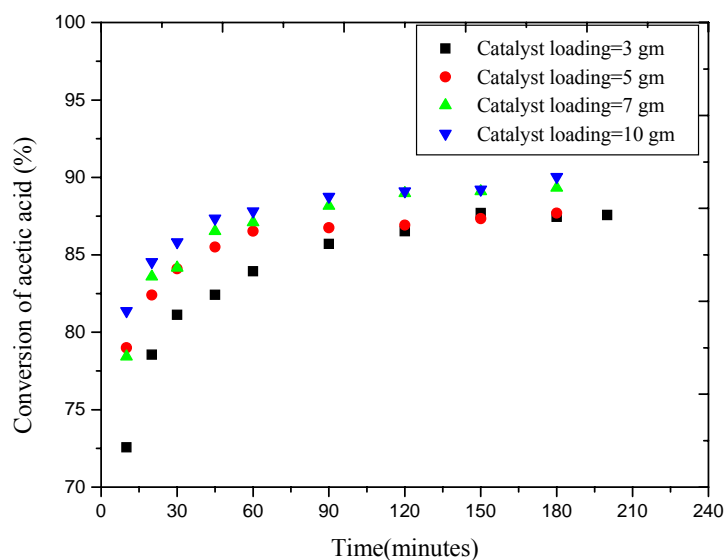
Figure 4.13 Effect of Catalyst Loading on Acetic acid Conversion

Temperature =383K, Mole ratio= 2:1, Stirrer Speed: 1000 rpm,
Catalyst: TULSION MP T-63, Particle size=0.2- 1.3 mm
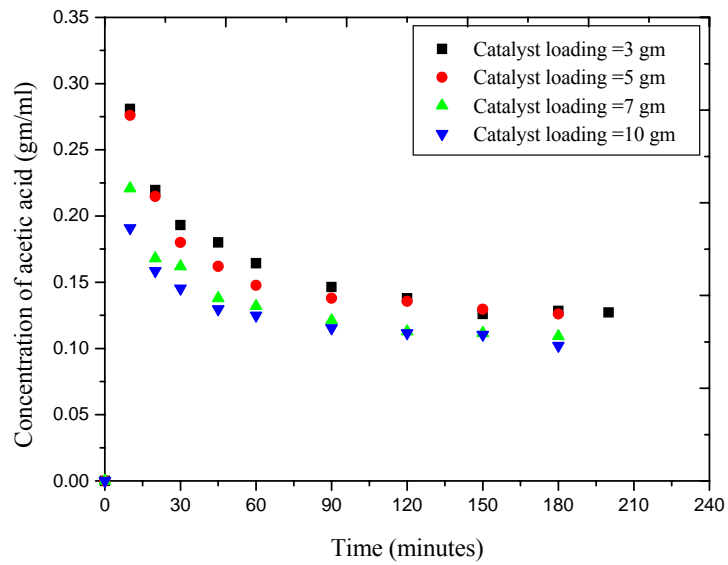
Figure 4.14 Effect of Catalyst Loading on Acetic acid Concentration
Temperature =383K, Mole ratio= 2:1, Stirrer Speed: 1000 rpm,
Catalyst: TULSION MP T-63, Particle size=0.2- 1.3 mm
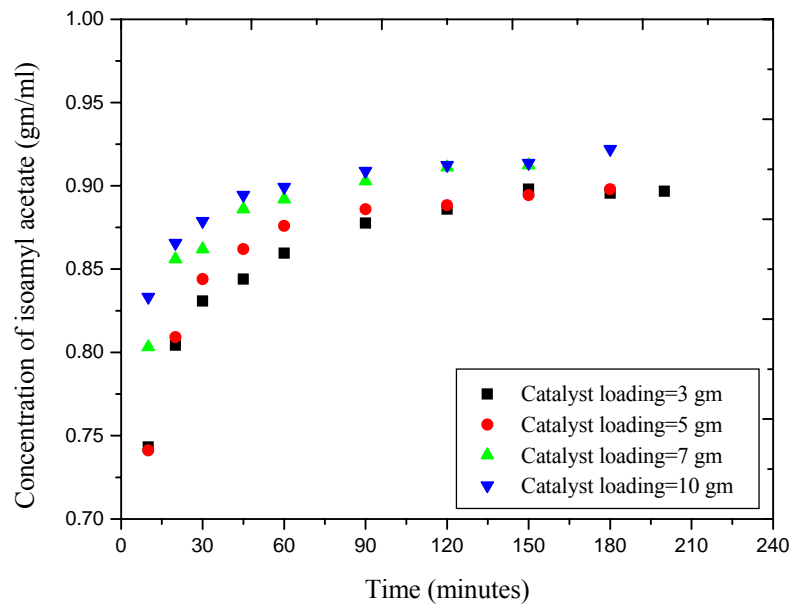
Figure 4.15 Effect of Catalyst loading on iso amyl acetate Concentration
Temperature =383K, Mole ratio= 2:1, Stirrer Speed: 1000 rpm,
Catalyst: TULSION MP T-63, Particle size=0.2- 1.3 mm

4.5.7.5 Effect of Catalyst Reusability

Reusability of TULSION MP-T-63 was tested by conducting two runs Figure 4.19 shows effect of catalyst reusability on conversion of acetic acid. After completion of the experiment, the catalyst was filtered, washed with of acetic acid and dried at 110^0C for 3h. It is observed that the there was only a marginal decrease in conversion. Thus the catalyst is reusable. Hence, we can say that catalyst thus can be used repeatedly for this reaction without sacrificing catalytic activity.

Figure 4.16 to 4.27 represents effect of catalyst reusability for T-62, T-63 and T-66 on conversion of acetic acid and concentration of acetic acid and iso amyl acetate respectively for diffrent operating parameters
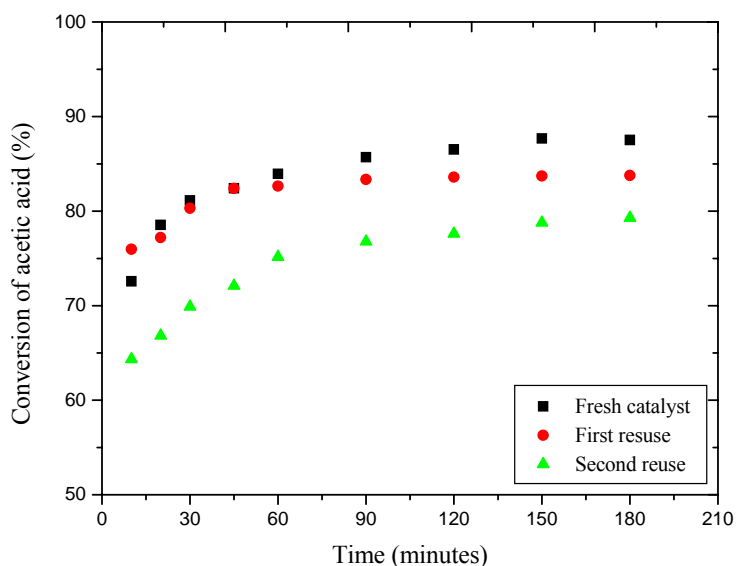
Figure 4.16 Effect of Catalyst Reusability on Conversion of Acetic acid

Stirrer Speed: 1000 rpm, Mole ratio= 2:1, Catalyst Loading: 3 gm,
Temperature: 383K
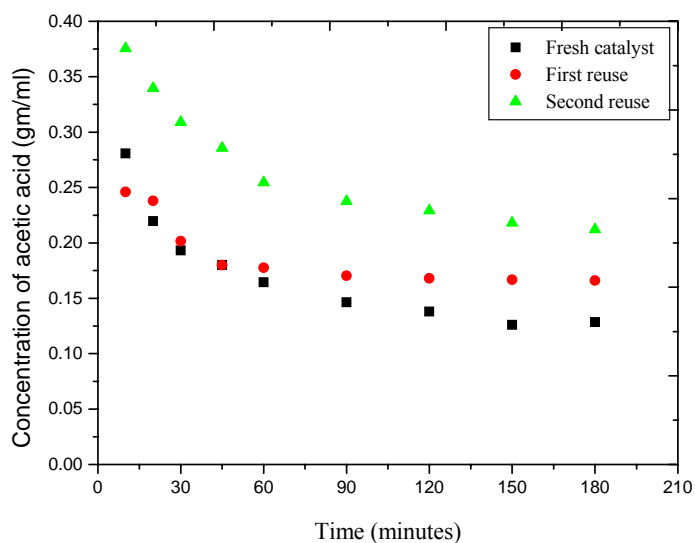
Figure 4.17 Effect of Catalyst Reusability on Concentration of Acetic acid

Stirrer Speed: 1000 rpm, Mole ratio= 2:1, Catalyst Loading: 3 gm, Temperature: 383K
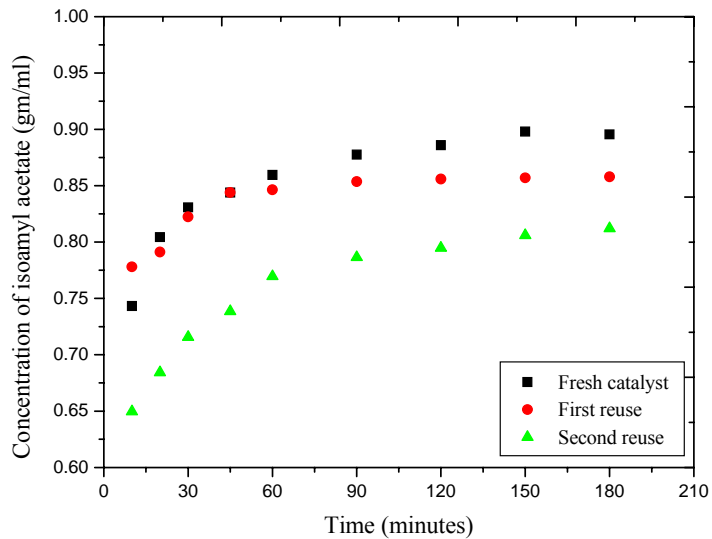
Figure 4.18 Effect of Catalyst Reusability on Concentration of iso amyl acetate

Stirrer Speed: 1000 rpm, Mole ratio= 2:1, Catalyst Loading: 3 gm, Temperature: 383K
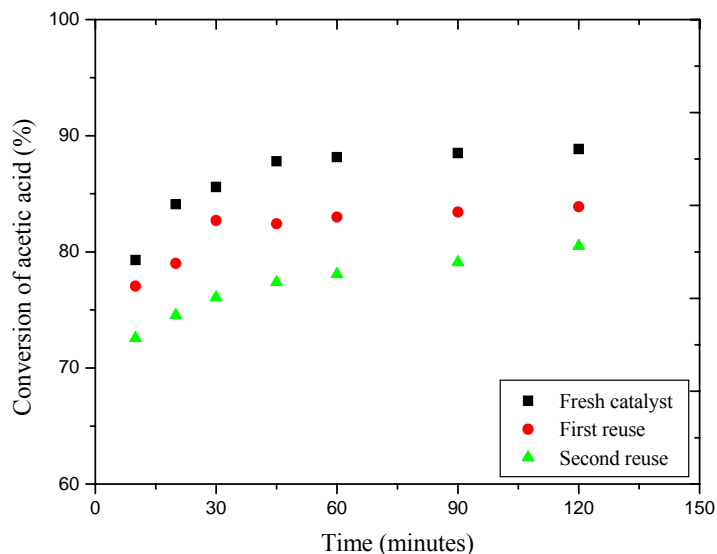
Figure 4.19 Effect of Catalyst Reusability on Conversion of Acetic acid

Stirrer Speed: 1000 rpm, Mole ratio= 2:1, Catalyst Loading: 5 gm,
Temperature: 383K
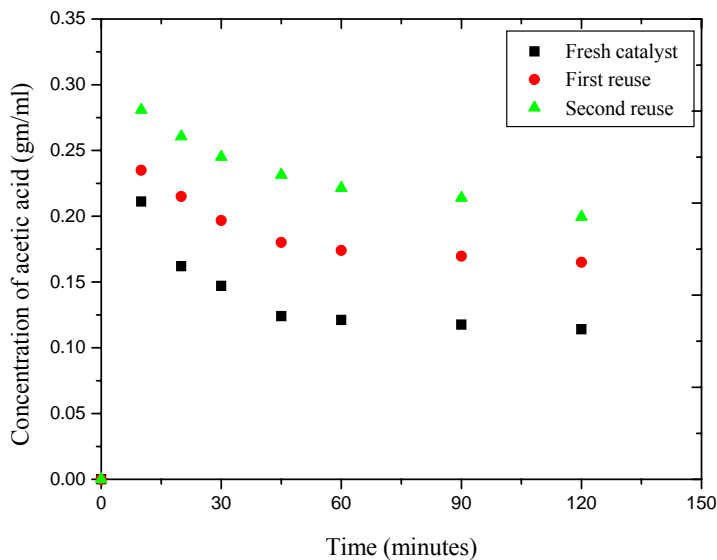
**Figure 4.20 Effect of Catalyst Reusability on Concentration of Acetic
acid**

Stirrer Speed: 1000 rpm, Mole ratio= 2:1, Catalyst Loading: 5 gm,
Temperature: 383K
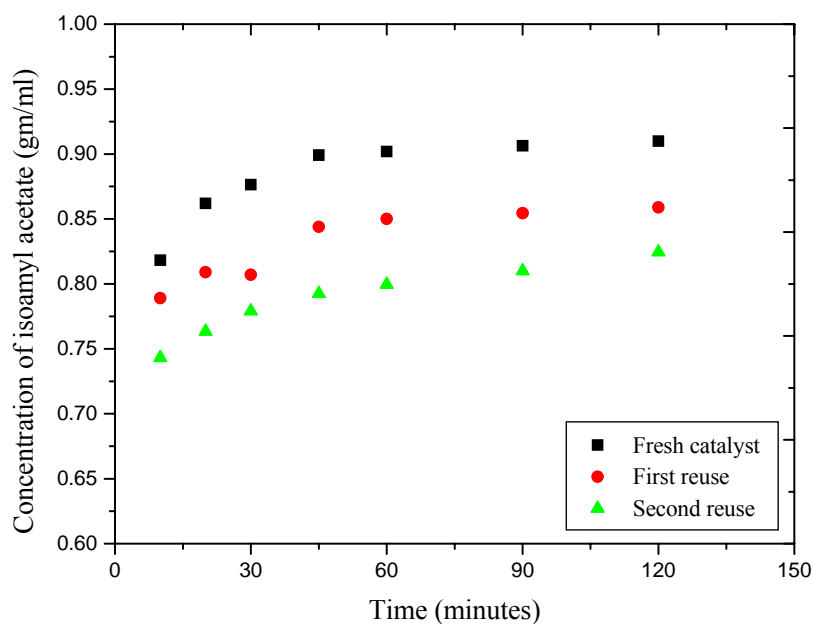
Figure 4.21 Effect of catalyst reusability on Concentration of iso amyl acetate

Stirrer Speed: 1000 rpm, Mole ratio= 2:1, Catalyst Loading: 5 gm, Temperature: 383K
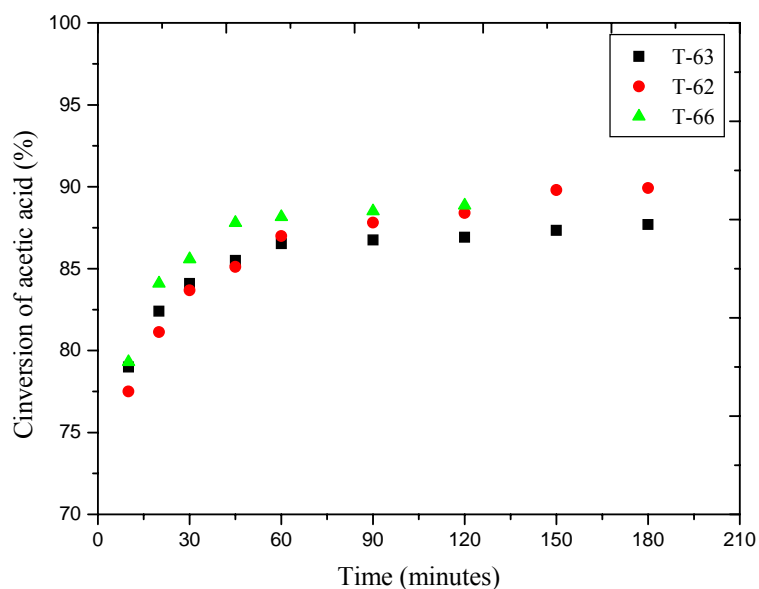
Figure 4.22 Effect of Different Catalyst on Acetic acid Conversion

Temperature =383K, Mole ratio= 2: 1, Stirrer Speed: 1000 rpm, Catalyst loading= 5 gm
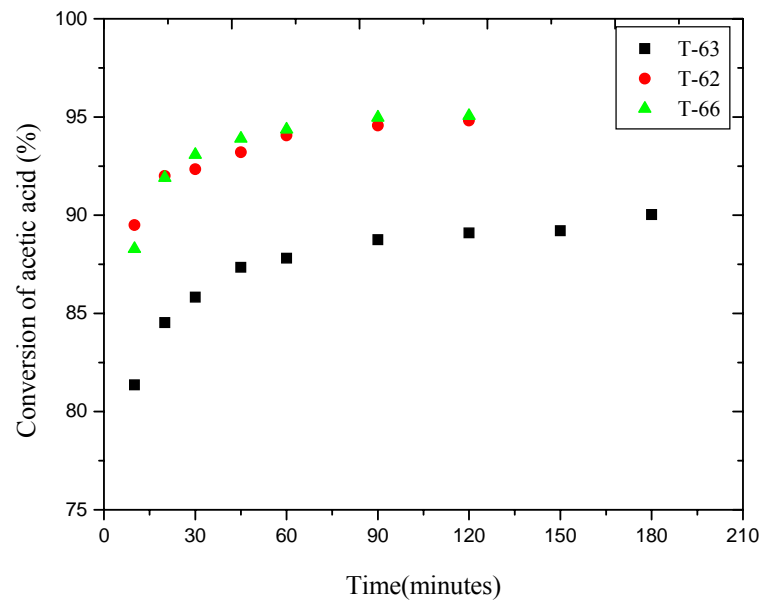
Figure 4.23 Effect of Different Catalyst on Acetic acid Conversion

Temperature =383K, Mole ratio= 2: 1, Stirrer Speed: 1000 rpm,
Catalyst loading= 10 gm
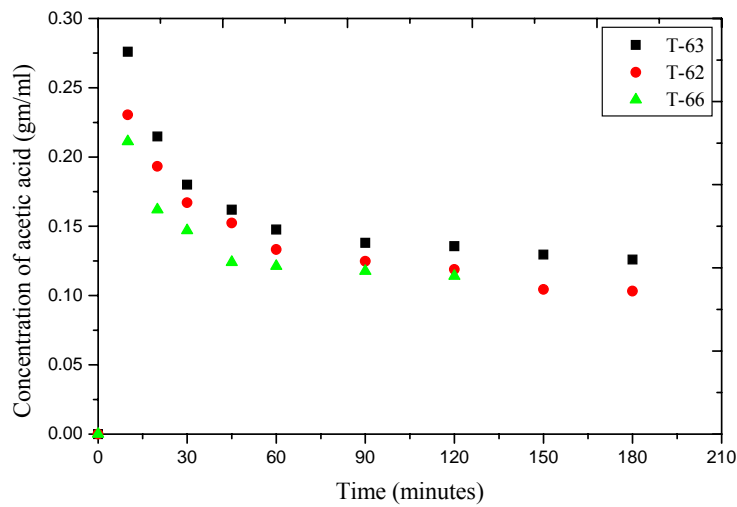
Figure 4.24 Effect of Different Catalyst on Acetic acid Concentration

Temperature =383K, Mole ratio= 2: 1, Stirrer Speed: 1000 rpm,
Catalyst loading= 5 gm
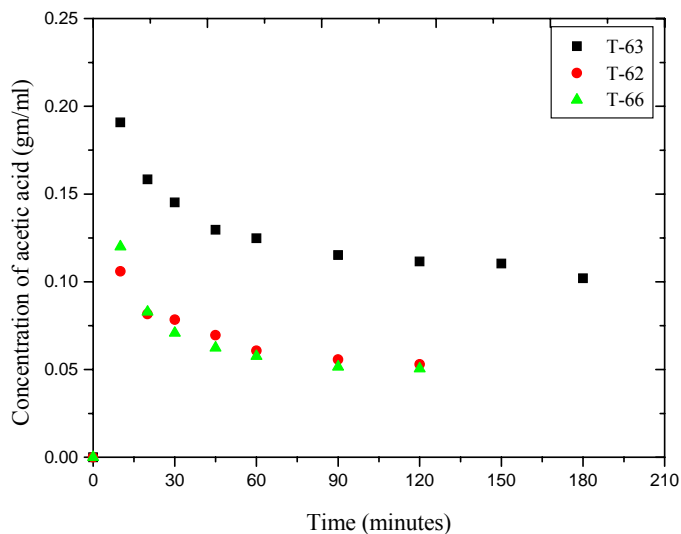
**Figure 4.25 Effect of different Catalyst on Acetic acid
Concentration**

Temperature =383K, Mole ratio= 2: 1, Stirrer Speed: 1000 rpm,
Catalyst loading= 10 gm
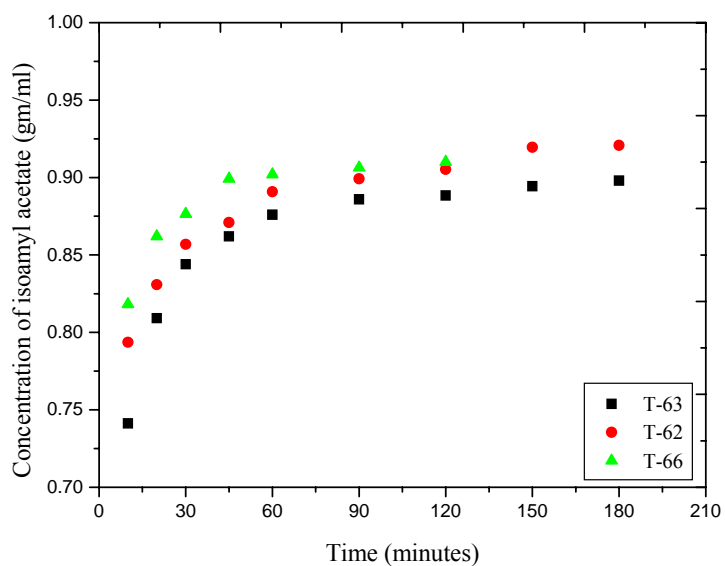
**Figure 4.26 Effect of different Catalyst on Iso amyl acetate
Concentration**

Temperature =383K, Mole ratio= 2: 1, Stirrer Speed: 1000 rpm,
Catalyst loading= 5 gm
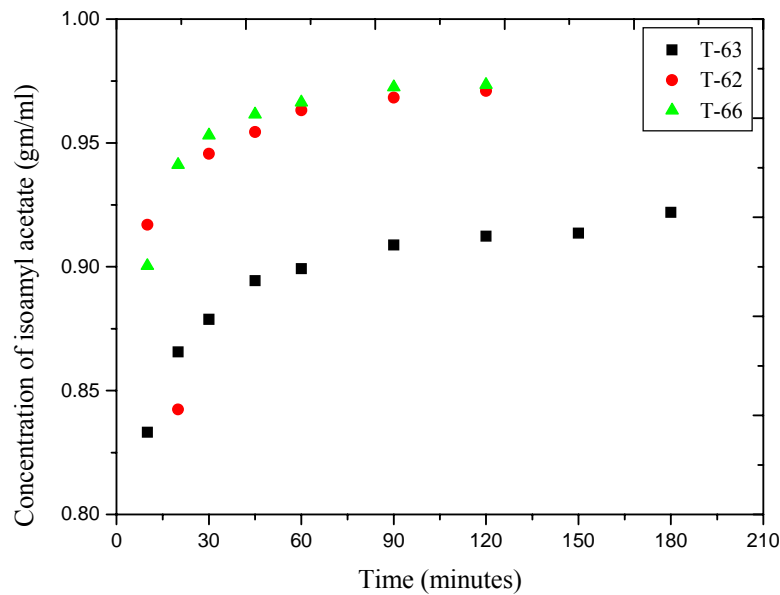
**Figure 4.27 Effect of Different Catalyst on iso amyl acetate
Concentration**

Temperature =383K, Mole ratio= 2: 1, Stirrer Speed: 1000 rpm,
Catalyst loading= 10 gm

4.5.9   Kinetic Model Fitting using Experimental Data:

The esterification reaction was kinetically controlled since the external mass transfer resistance and the intraparticle diffusion were absent. The catalyst used is a macro porous ion exchange resin. In macro porous resin, the reactants are able to diffuse into the pores without any resistance (Yadav and Thathagar, 2002). Therefore sorption effects can be neglected and Pseudohomogenous model should be sufficient for the present system.

The experimental data collected at temperatures 363 K to 403 K were used to plot $-\ln(1-X_A)$ versus time, which is shown in Figure 4.28.
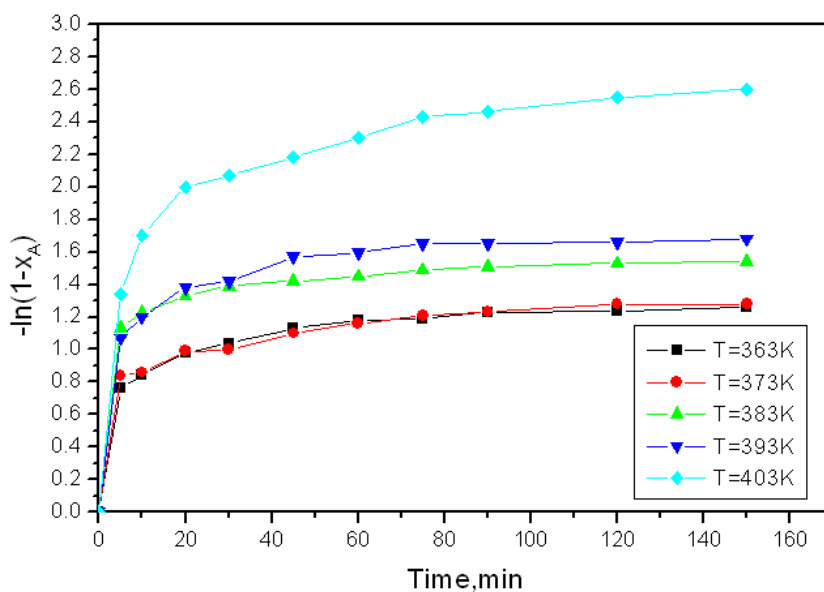
**Figure 4.28 Pseudo First Order Kinetic Plot of Esterification of Iso
amyl alcohol with Acetic acid**

The values of rate constants at different temperatures are
calculated. Arrhenius plot (Figure 4.29) is used to estimate the
frequency factor and energy of activation. The values of, -lnk is plotted
1/T as shown in Figure 4.29.
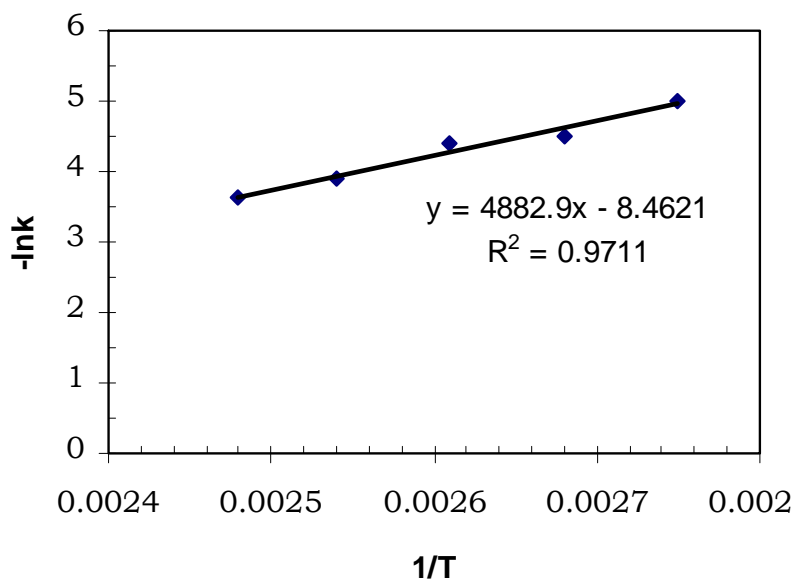
**Figure 4.29 Arrhenius plot for esterification of iso amyl alcohol with
acetic acid.**

The values of frequency factor and the activation energy are calculated as 3.54×10^3 moles/gm.min and 41.88 kJ/mol respectively.

The kinetic expression for iso amyl acetate synthesis over ion exchange resin (T-63) is given by:

$$k_1 = 3.54 \times 10^3 \exp\left(\frac{-41.88}{RT}\right)$$

This high value of activation energy also confirmed that the overall rate of reaction is not influenced by either external mass transfer or intraparticle diffusion resistance and it is an intrinsically kinetically controlled reaction on active sites.

Table 4.11 shows literature data for reaction kinetics for Amberlyst for different kinetic models.

Table 4.5 Reaction Kinetics Results
(Lee et al, 1999, 2003, Saha et al, 2005)

Model	Pre-exponential factor (mols/g.min)	Activation energy (kJ/mol)	K_{1a}	K_{2b}	K_{3c}	K_{4d}	SRS
LHHW	2.4×10^5	47	0.23	2.12	0.34	2.12	2.37×10^{-9}
E-R	3.65×10^5	46.7	0.99	6.10	2.41	8.97	4.35×10^{-9}
QH	3.39×10^3	40.3	-	-	-	-	8.30×10^{-9}

[B] PHASE EQUILIBRIUM STUDIES

4.6   Introduction

Vapor-Liquid Equilibrium (VLE) data are the basic information of the system required for the design of equilibrium stages of vapor-liquid separation equipment like distillation. Equilibrium data represents the composition of the mixture in the vapor phase (y) and that in the corresponding equilibrium liquid phase (x) at equilibrium. The compositions are presented in mole fractions of the more volatile component. Equilibrium compositions are functions of temperature and pressure. Therefore the VLE data are reported under isothermal or isobaric conditions. However, isobaric data are required more often because industrial separations are carried out at constant pressure.

Lee and Liang (1998) reported extensive data base for vapor-liquid equilibrium associating a reversible chemical reaction of the quaternary mixture, acetic acid-1-pentanol-water-n-amyl acetate using Othmer-type equilibrium still. The experimental VLE data were correlated by the models of UNIQUAC and NRTL with considerations of vapor molecule association of acetic acid.

Tan et al, (2005) reported experimental vapor–liquid equilibrium data of water/ethanol/1-butanol saturated with NaCl, KCl and NH_4Cl compared well with those predicted by Tan–Wilson and Tan–NRTL models for multicomponent solvent–solute mixture. The Wilson and NRTL solvent–solvent interaction parameters were obtained by the regression of the experimental vapor–liquid equilibrium data of the salt-free solvent mixture.

Campanella et al, (2003) examined the effect of the simultaneous chemical and phase equilibrium on the conceptual design of reactive distillation processes. Esterification of acetic acid with methanol, ethanol and butanol are examined. They calculated

azeotropic points, residue curve maps and distillation line diagrams using commercial software.

Lee et al (2000) determined the isothermal VLE data experimentally with a static-type apparatus for two binary systems of acetic acid + amyl alcohol and acetic acid + amyl acetate. Phase compositions were also measured for a quaternary system of amyl alcohol, acetic acid, amyl acetate, and water at simultaneous chemical and phase equilibria. These new binary data are applied to determine the binary parameters of the NRTL model for the corresponding systems that are needed for prediction of the multicomponent systems. By accounting the dimerization of acetic acid in the vapor phase, the reliability of the binary parameters obtained from different types of equilibrium data is evaluated by comparing the results of equilibrium calculations with the experimental phase compositions of the esterification system.

In this section, VLE data for six binary pairs, viz, Water + iso amyl alcohol, Water + Acetic acid, Water + iso amyl acetate, Acetic Acid + iso amyl alcohol, Acetic acid + iso amyl acetate and iso amyl alcohol + iso amyl acetate measured in Othmer type VLE apparatus. VLE data from the databank of Aspen Plus is also used to simulate the column separately to examine how the results vary with the experimental data and the Aspen Plus databank data.

4.7 Experimental Work

4.7.1 Experimental Setup for VLE measurements

The apparatus shown in Figure 4.30 is known as a vapor-liquid equilibrium still and has two essential parts: (1) Vaporizer, (2) Flash chamber or Equilibrium chamber. An electrical heating coil in the vaporizer at a slow rate vaporizes the binary liquid mixture. The vapor from this rises to the equilibrium chamber. Vapor and liquid equilibrium at the temperature and pressure of the chamber is

established. The thermometer records the temperature for the chamber, which extends well inside the equilibrium chamber.

C W, Out

Condenser

C W, In

PT 100 Bulb

Glass Packings

Drain Holes

Vacuum Jacket

Magnetic Stirrer

S2

Mixing Spiral

S1

Insulated Cottrell Pump

Vacuum Jacket

Heating Element

Capillary
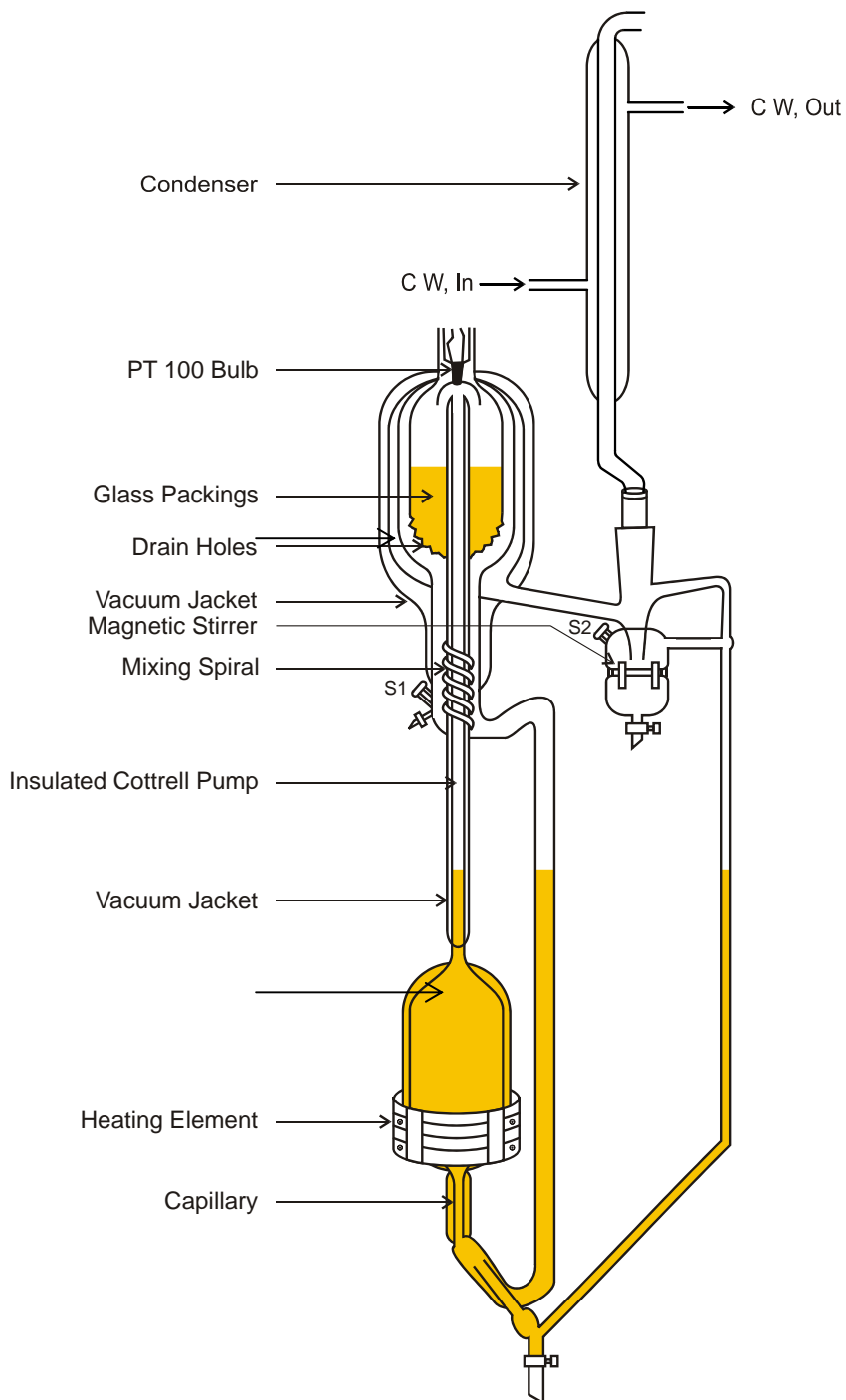
Figure 4.30 Schematic diagram of VLE Setup (Othmer Type Apparatus)

Connecting the vapor line to vacuum or pressure header may regulate the pressure of the chamber. The vapor and liquid phases separate from each other in the flash chamber. The liquid flows down

the liquid line through a water-cooled joint to the feeder line, through which the mixture again goes back to the vaporizer. The still may be drained through the feeder line and may be charged through either the vapor or the liquid line.

4.7.2 Experimental Procedure

1) Prepare a calibration chart of composition vs. refractive index (R.I.) or density, for the two pure components A and B and their mixtures with x_A varying from 0 to 1. Prepare the mixture of various compositions and determine the R.I. or density.

2) Prepare about 200 ml of mixture of A and B. The experiment should be started with the mixture richer in more volatile component (say 160 ml of A and 40 ml of B) so that in subsequent readings temperature increases. This mixture should be filled in the still through either of the limbs.

3) Switch on the power and slowly increase the power input in slow steps. Heating should be regulated so that there is no entrainment or foaming of the mixture from vaporizer to the flash chamber.

4) The circulation of the vapor and liquid will soon get established. Allow the system to approach equilibrium. This will be indicated by constant temperature of the thermometer at least for five minutes.

5) Take the liquid and vapor samples and determine the refractive index (or density) and determine the composition using GC. Also record the temperature and from R.I. (or density), determine x_A and y_A.

6) Drain out about 40 ml of mixture from the still and add about 40 ml of less volatile component. Repeat steps (1) to (5) and record the composition and temperature readings. Take at least six samples, covering whole range of compositions.

There are six binary pairs in the present test system are:

1.   Water + iso amyl alcohol
2.   Water + Acetic acid
3.   Water + iso amyl acetate
4.   Acetic Acid + iso amyl alcohol
5.   Acetic acid + iso amyl acetate
6.   Iso amyl alcohol + iso amyl acetate

4.7.3 Material:

Acetic acid (99.8%) and *iso*-amyl alcohol (99%) were purchased from Merck India Ltd., Mumbai, India, iso amyl acetate (> 99% purity) was purchased from S.D. Fine Chemicals Ltd., Mumbai, India and distilled water was used for experimental work.

4.7.4 Analysis:

Gas chromatography is used for the analysis of the different samples from the different locations of reactive distillation column.

Acetic acid, iso amyl alcohol, iso amyl acetate and water are analyzed using gas chromatograph (Model C-911, Mak Analytica India Ltd.) which is equipped with thermal conductivity detector (TCD). The samples are analyzed Porapak Q with hydrogen as carrier gas at a flow rate of 5×10^{-7} m^3/s. The injector and detector are maintained at a temperature of 493K and 423K respectively. The oven temperature is maintained isothermally at 513K to get the best resolution in less time.

The results obtained by GC are confirmed by independent titration using standard sodium hydroxide (NaOH) solution using phenolphthalein as indicator. The reliability of the titration method is confirmed with the help of analysis of standard samples containing iso amyl acetate to ensure the hydrolysis of ester does not takes place

during the course of titration. The analytical relative uncertainty is <5%, which is good enough within the acceptable limits.

The typical chromatogram for this system and procedure for preparation for calibration charts for different components is discussed in Section 5.5.6 of Chapter 5.

4.7.5 Observations and Results:

Table 4.6 VLE Results for Six Binary Systems

1.   Iso amyl Alcohol + Water

Temperature (^{0}C)	Vapor Mole fraction Iso amyl alcohol	Vapor Mole fraction Water	Liquid Mole fraction Iso amyl alcohol	Liquid Mole fraction Water
100	0	1	0	1
92	0.2587	0.7412	0.0500	0.9500
93	0.2268	0.7731	0.0750	0.9250
94	0.1540	0.8459	0.1500	0.8500
95	0.1277	0.8722	0.5500	0.4500
97	0.1485	0.8514	0.6250	0.3750
99	0.1683	0.8316	0.6750	0.3250
102	0.2114	0.7885	0.7500	0.2500
104	0.2311	0.7688	0.7750	0.2250
106	0.2547	0.7452	0.8000	0.2000
108	0.2833	0.7166	0.8250	0.1750
110	0.3185	0.6814	0.8500	0.1500
113	0.3628	0.6371	0.8750	0.1250
116	0.4199	0.5800	0.9000	0.1000
120	0.4959	0.5040	0.9250	0.0750
124	0.6013	0.3986	0.9500	0.0500
130	0.7556	0.2443	0.9750	0.0250
138	1	0	1	0

2. Acetic Acid + Water

Temperature (°C)	Vapor Mole fraction Acetic acid	Vapor Mole fraction Water	Liquid Mole fraction Acetic acid	Liquid Mole fraction Water
100	0	1	0	1
101	0.05832	0.9416	0.1000	0.9000
102	0.0894	0.9105	0.1500	0.8500
103	0.1389	0.8610	0.2250	0.7750
104	0.2108	0.7891	0.3250	0.6750
106	0.2903	0.7096	0.4250	0.5750
108	0.4028	0.5971	0.5500	0.4500
110	0.5054	0.4945	0.6500	0.3500
112	0.6221	0.3778	0.7500	0.2500
114	0.7561	0.2438	0.8500	0.1500
116	0.8706	0.1293	0.9250	0.0750
117	0.9550	0.04493	0.9750	0.0250
118	1	0	1	0

3. Iso amyl alcohol + Iso amyl Acetate

Temperature (°C)	Vapor Mole fraction Iso amyl alcohol	Vapor Mole fraction Iso amyl Acetate	Liquid Mole fraction Iso amyl alcohol	Liquid Mole fraction Iso amyl Acetate
148	0	1	0	1
146	0.09072	0.9092	0.0500	0.9500
144	0.2317	0.7682	0.1500	0.8500
142	0.3419	0.6580	0.2500	0.7500
140	0.5011	0.4988	0.4250	0.5750
139	0.8145	0.1854	0.8000	0.2000
138	1	0	1	0

4.   Acetic Acid + Iso amyl acetate

Temperature (°C)	Vapor Mole fraction Acetic acid	Vapor Mole fraction Iso amyl Acetate	Liquid Mole fraction Acetic acid	Liquid Mole fraction Iso amyl Acetate
148	0	1	0	1
144	0.1586	0.8413	0.0750	0.9250
140	0.3313	0.6686	0.1750	0.8250
138	0.4047	0.5952	0.2250	0.7750
136	0.4709	0.5290	0.2750	0.7250
134	0.5590	0.4409	0.3500	0.6500
132	0.6357	0.3642	0.4250	0.5750
130	0.6816	0.3183	0.4750	0.5250
128	0.7436	0.2563	0.5500	0.4500
125	0.8320	0.1679	0.6750	0.3250
122	0.9055	0.0944	0.8000	0.2000
120	0.9558	0.04415	0.9000	0.1000
118	1	0	1	0

5.   Water + Iso amyl acetate

Temperature (°C)	Vapor Mole fraction Water	Vapor Mole fraction Iso amyl Acetate	Liquid Mole fraction Water	Liquid Mole fraction Iso amyl Acetate
148	0	1	0	1
134	0.3332	0.6667	0.0250	0.9750
120	0.5705	0.4294	0.0500	0.9500
110	0.7083	0.2916	0.0750	0.9250
102	0.7843	0.2156	0.1000	0.9000
97	0.8557	0.1442	0.1500	0.8500
89	0.8738	0.1261	0.1750	0.8250
87	0.8863	0.1136	0.2000	0.8000

6.   Acetic acid + Iso amyl alcohol

Temperature (⁰ C)	Vapor Mole fraction Acetic acid	Vapor Mole fraction Iso amyl alcohol	Liquid Mole fraction Acetic acid	Liquid Mole fraction Iso amyl alcohol
138	0	1	0	1
136	0.1265	0.8734	0.0750	0.9250
134	0.2772	0.7227	0.1750	0.8250
132	0.3781	0.6218	0.2500	0.7500
130	0.4984	0.5015	0.3500	0.6500
128	0.6043	0.3956	0.4500	0.5500
126	0.6976	0.3023	0.5500	0.4500
124	0.7800	0.2199	0.6500	0.3500
122	0.8527	0.1472	0.7500	0.2500
120	0.9319	0.0680	0.8750	0.1250
118	1	0	1	0

4.8 Analysis of VLE data Using Aspen Plus Simulation

The simulation is begun by putting together a basic flow sheet of a RADFRAC column with input streams of acetic acid and iso amyl alcohol and output streams on iso amyl acetate and water as shown in Figure 4.31.
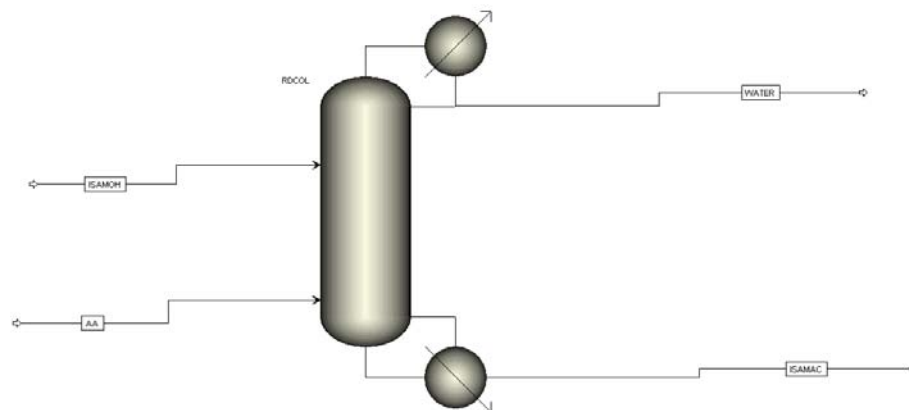
Figure 4.31 RADFRAC column for iso amyl acetate synthesis in Aspen Plus

Next, all the components that would be involved in the reactive distillation were chosen from the aspen plus component database. In this simulation, only four components are involved namely, acetic acid, isoamyl alcohol, isoamyl acetate and water. The NRTL model is selected as the property method for this simulation.

The VLE data from the above experimental data is first put into separate data regression worksheets in the aspen plus user interface. Once this was done, Aspen Plus calculated the temperature dependent binary parameters for each of the six binary systems.

Figure 4.32 is the T-XY profile for the acetic acid and iso amyl acetatae binary system. The solid lines show the established VLE profile from the Aspen Plus databank and the dots represent the results from the experimental setup.
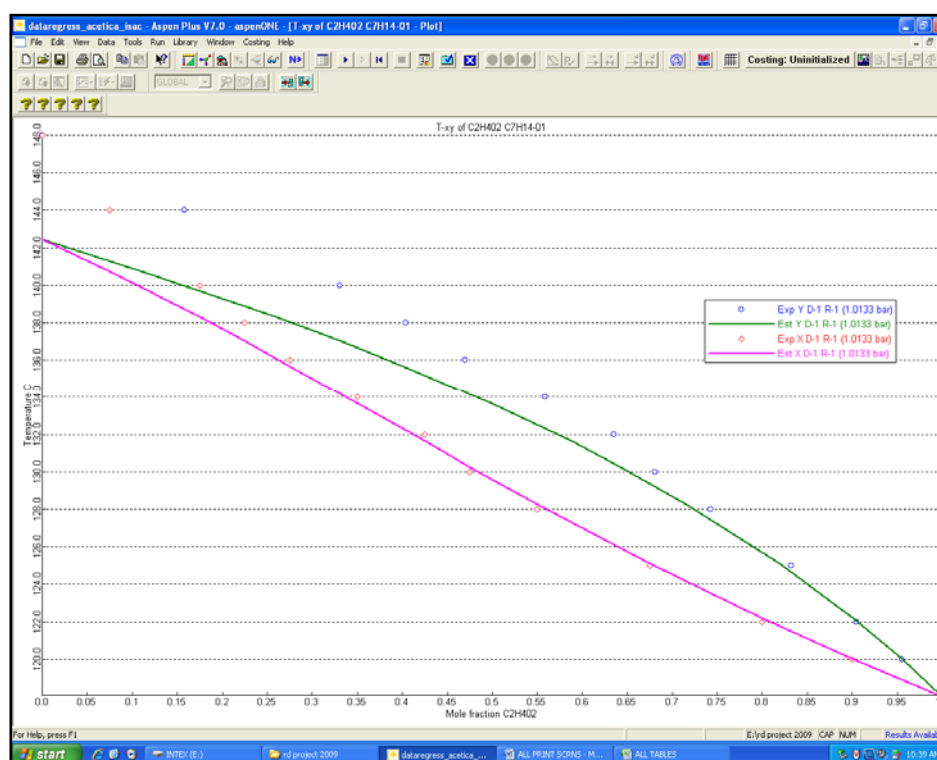
Figure 4.32 T x-y profile for acetic acid and iso amyl acetate

Figure 4.33 and 4.34 represents the T-XY profile for the acetic acid and water binary system and acetic acid and iso amyl alchol binary system respectively.
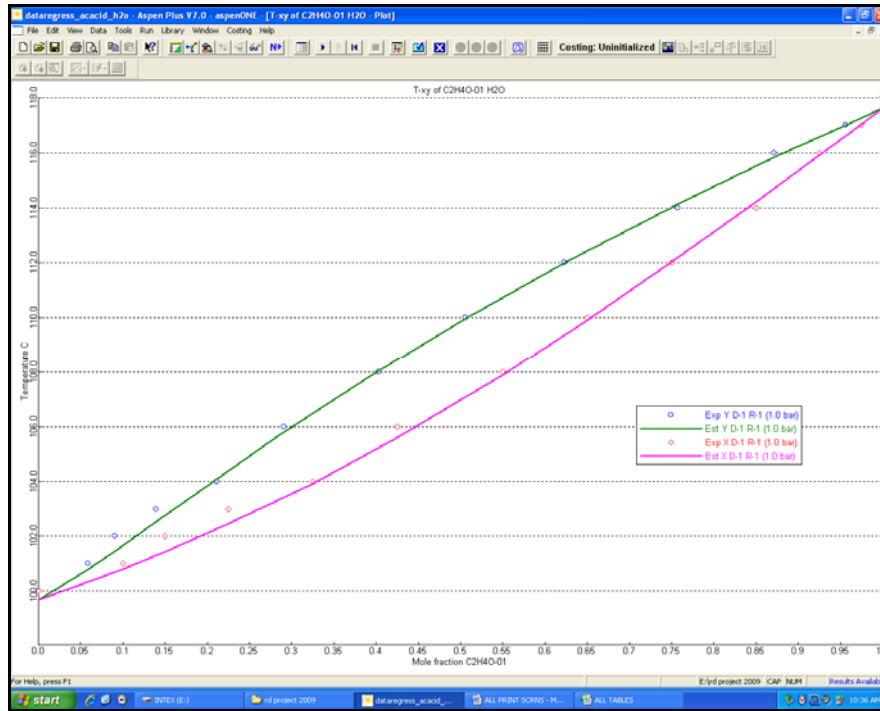
Figure 4.33 T x-y profile for acetic acid and water
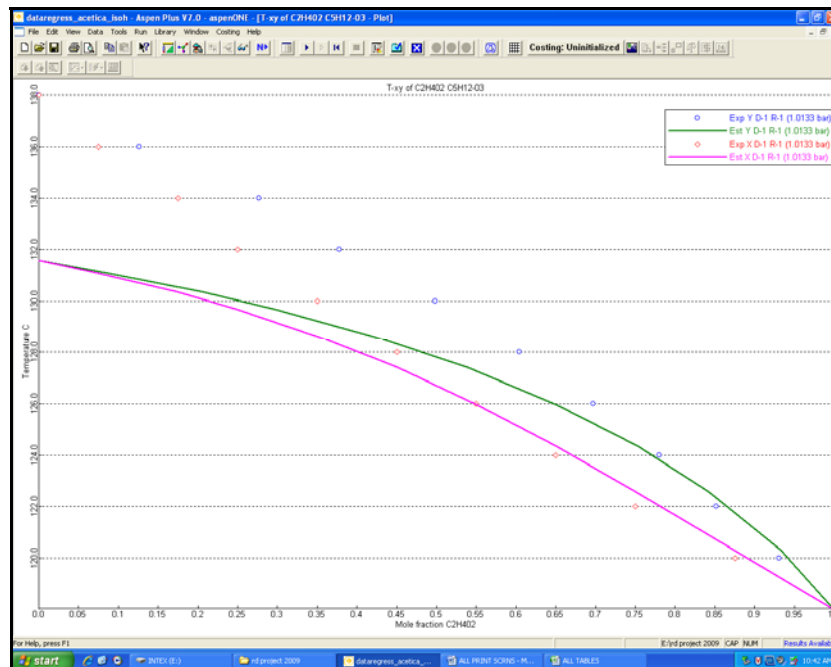
Figure 4.34 T x-y profile for acetic acid and iso amyl alcohol
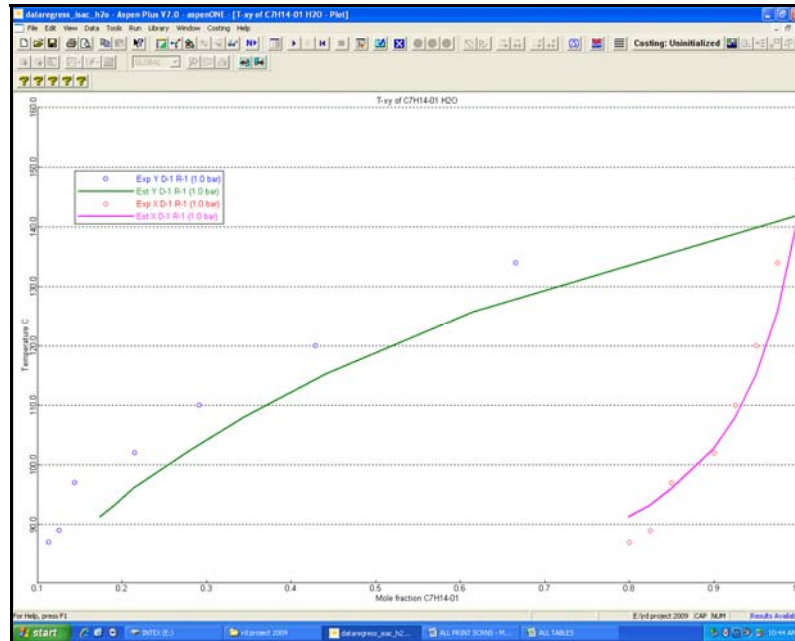
Figure 4.35 T x-y profile for iso amyl acetate and water

The Figure 4.35 and 4.36 shows the T-XY profile for the iso amyl acetae and water binary system and iso amyl alcohol and iso amyl acetate binary system respectively.
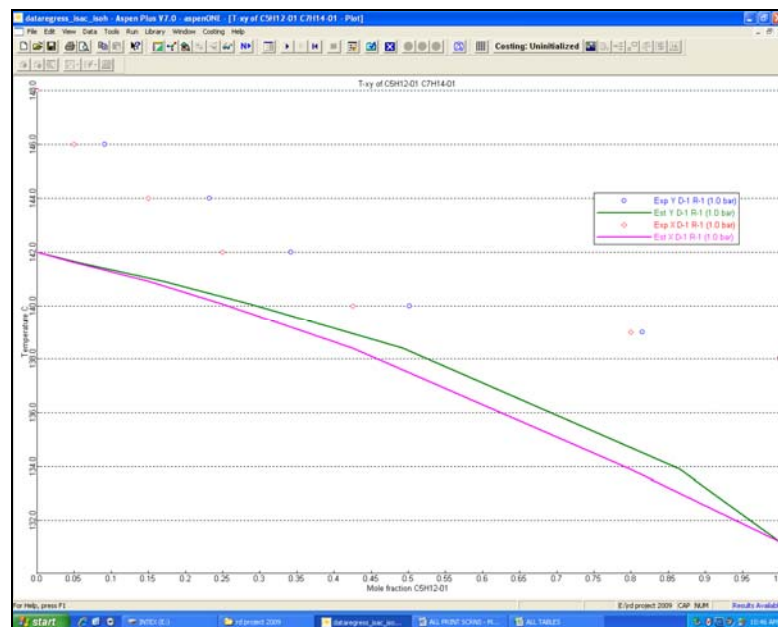
Figure 4.36 T x-y profile for iso amyl alcohol and iso amyl acetate
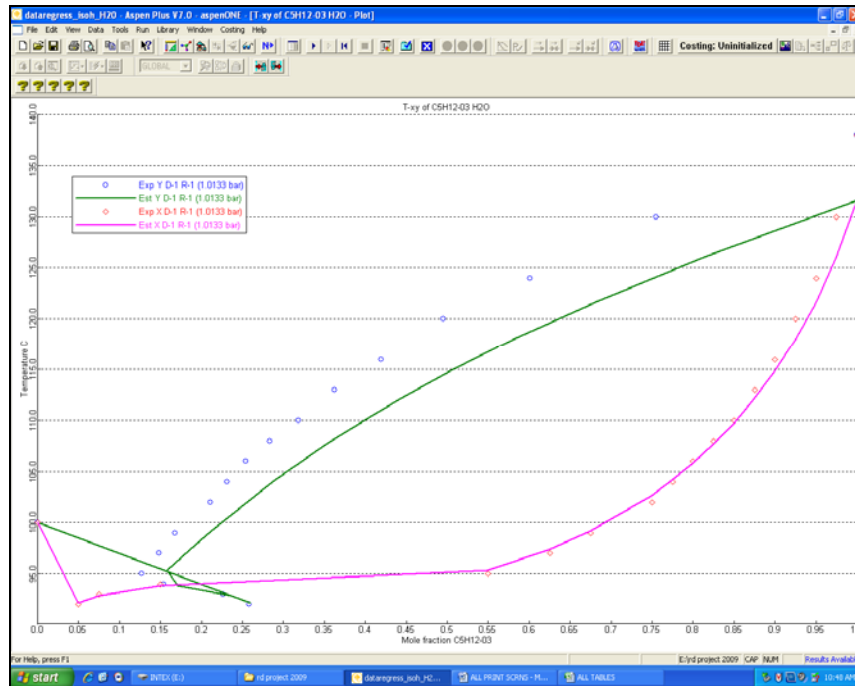
Figure 4.37 T x-y profile for iso amyl alcohol and water

The Figure 4.37 shows the T-XY profile for the iso amyl alcohol and water binary system. As can be seen in all the plots, there is a systematic error in the measurement of the temperature points, but as long as the same apparatus is used to find all the vapour pressure points, the systematic error cancels out.

We could have corrected the VLE problem by fitting the vapour pressure equation with the antoines constants. However since we only took measurements at 1 atm pressure, this could not be done. There may also be an error in the purity of the components.

The computation for each system are done separately. These temperature dependent binary parameters are input as user data into the NRTL Binary Interaction Parameters for each system.
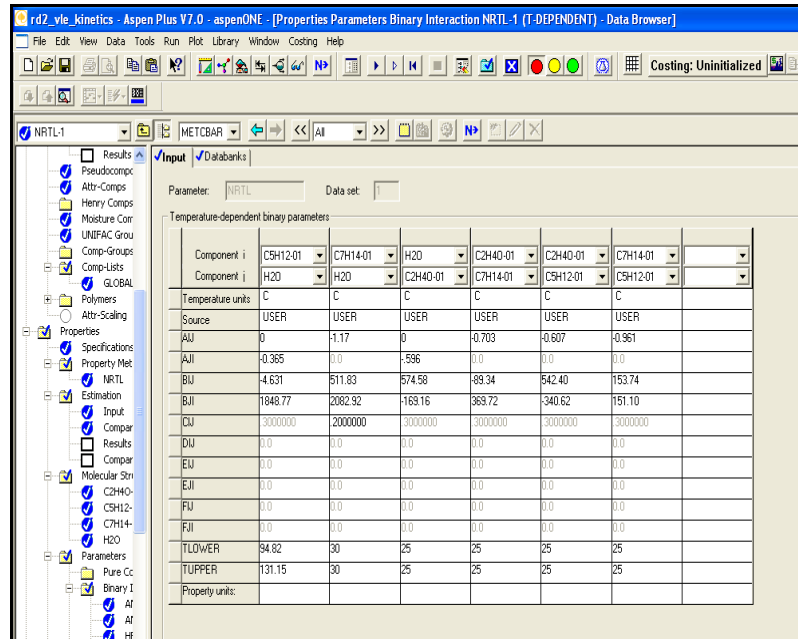
Figure 4.38 User Input Binary Parameters

Then for the input stream of acetic acid, a flowrate of 0.0525 kmol/hr is given. This was also the flowrate used in the actual column for conducting RD experiments.
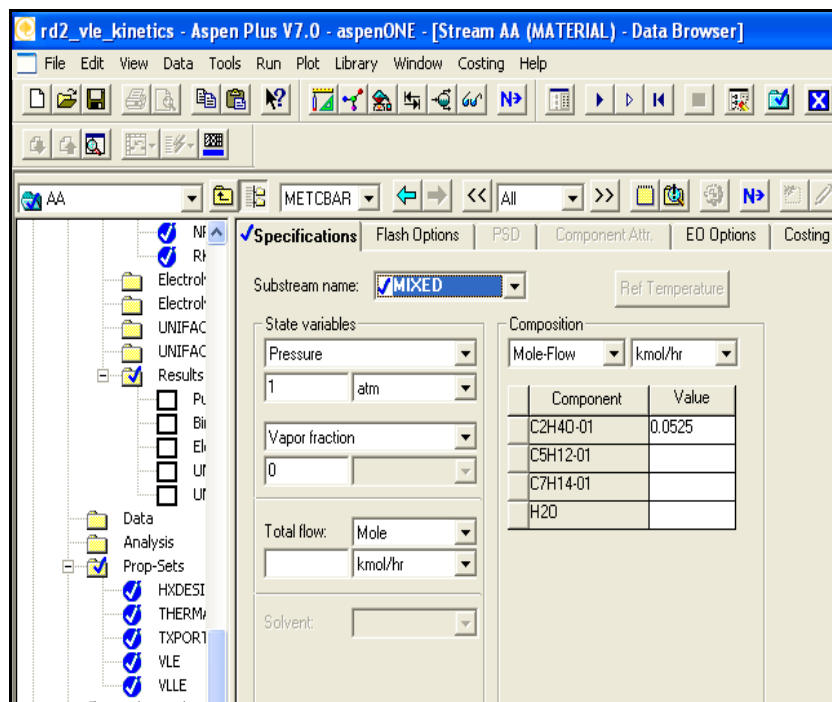
Figure 4.39 Data Input into Acetic acid Feed Stream

Similarly for the iso amyl alcohol, a mole flowrate of 0.0525 kmol/hr is specified with a vapour fraction of 0 and a pressure of 1 atm.
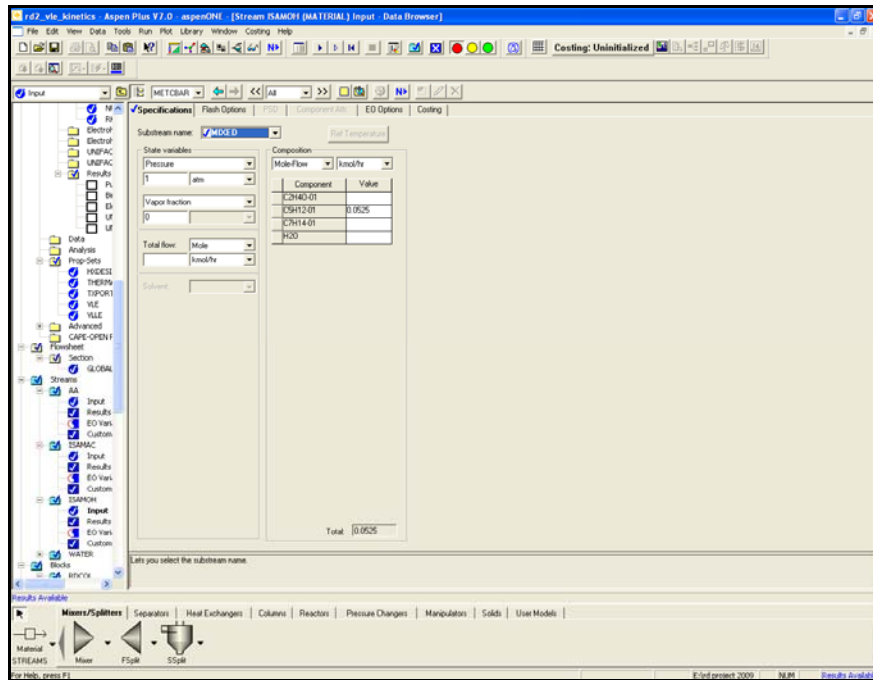
Figure 4.40 Data Input into iso amyl alcohol Feed Stream

Next the RADFRAC column had to be setup for equilibrium type calculations with an assumed 27 number of stages. A total condenser and a kettle reboiler are chosen. The reflux ratio is chosen as 2 and the boilup ratio as 4. After running the entire simulation, the number of stages, reflux ratio and the boil up ratio are changed using trial and error until the optimum value of each is found at which the required concentration of iso amyl acetate are being produced.
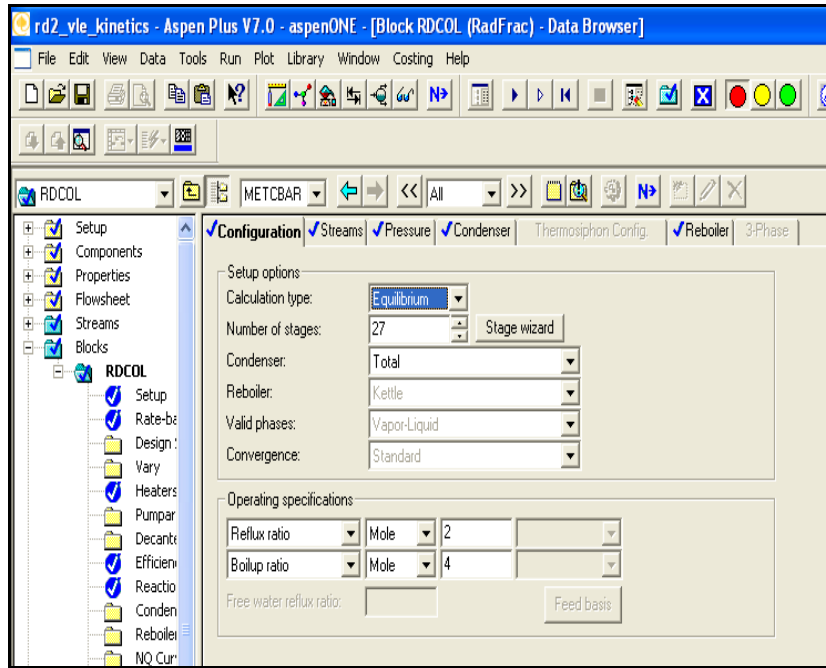
Figure 4.41 RADFRAC Column Setup

The feed location for isoamyl alcohol and acetic acid is kept at stages 10 and 15 respectively with iso amyl acetate being removed as product at the 27th stage and the water at the 1st stage. The operating pressure of the column and the condenser pressure is also set at 1 atm.
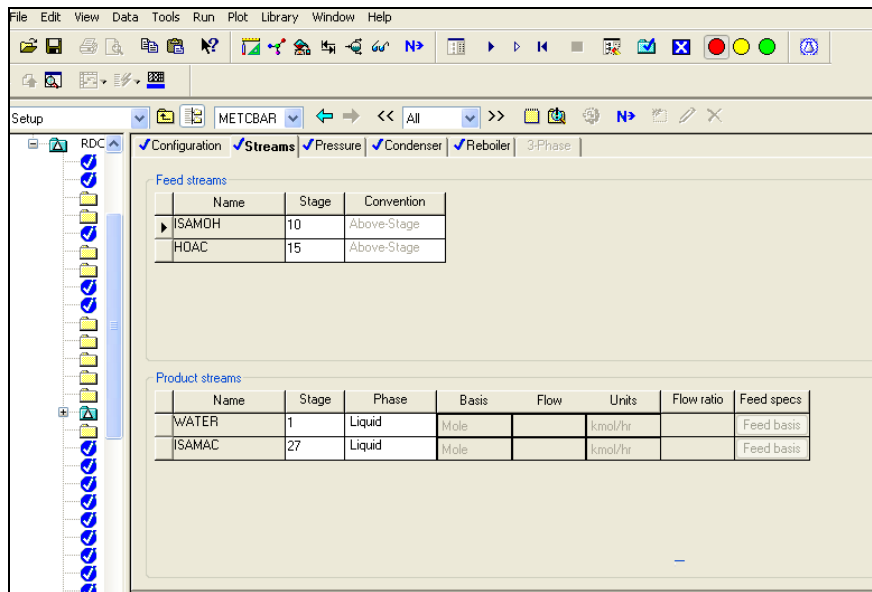
Figure 4.42 RADFRAC Column Feed and Product Stream Setup

Next the packed reactive zone is set between stages 10 and 15 with Mellapak type packing as is in the original column made by Sulzer with dimensions of 500X with a section packed height of 1 meter.
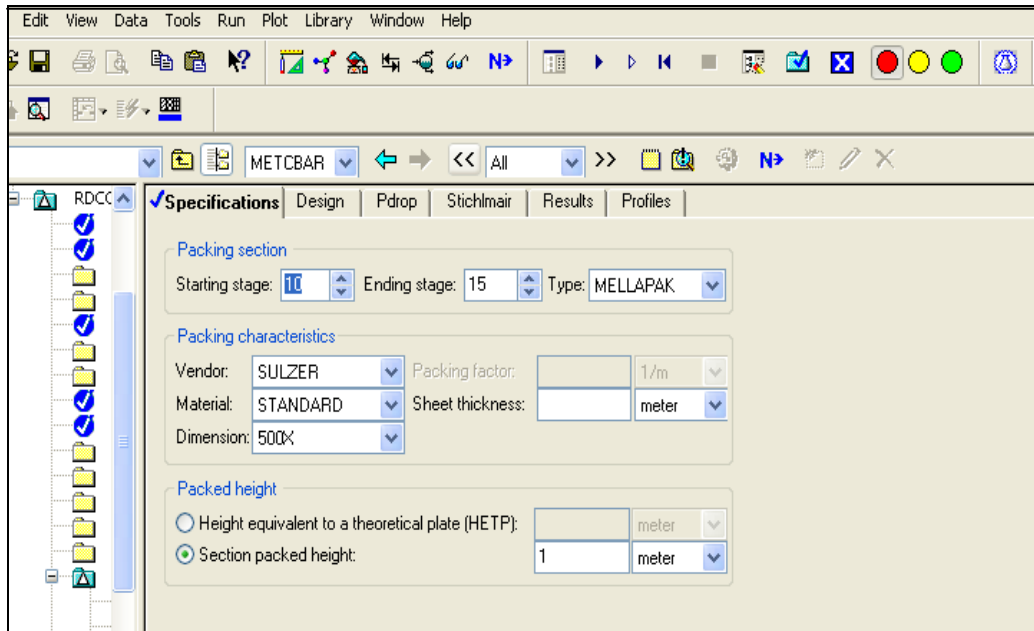
Figure 4.43 Pack Sizing Specifications for Reactive Section

Next the separtion sections from stage 2 to 9 and 16 to 26 are setup with mesh type packing with 50 mm diameter. Stages 2 to 9 are packed with section packed height of 0.75 m and stages 19 to 26 are packed with a height of 0.75 m.
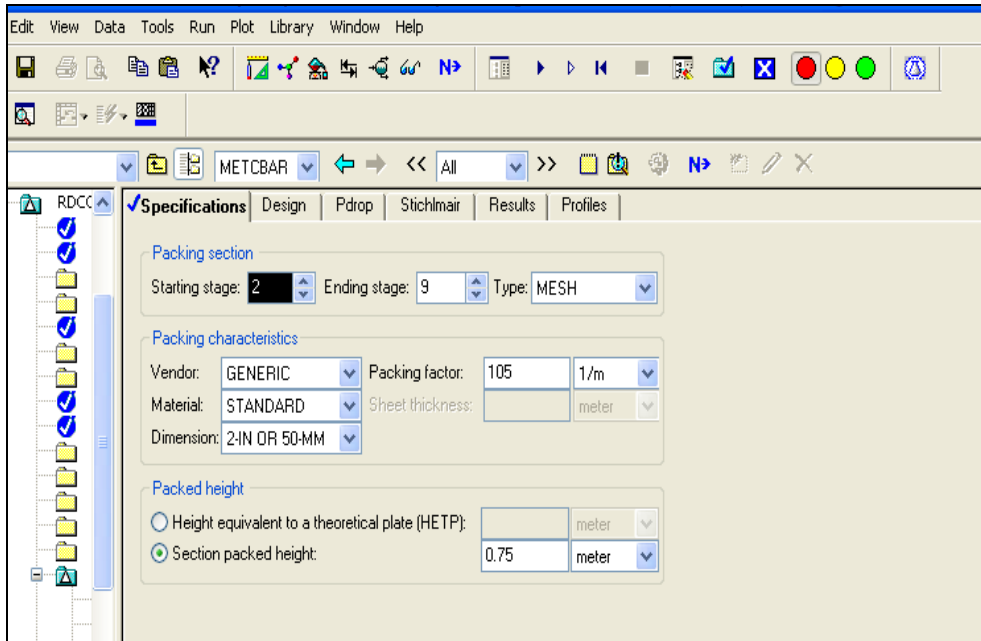
Figure 4.44 Pack Sizing Specifications for Rectification Section
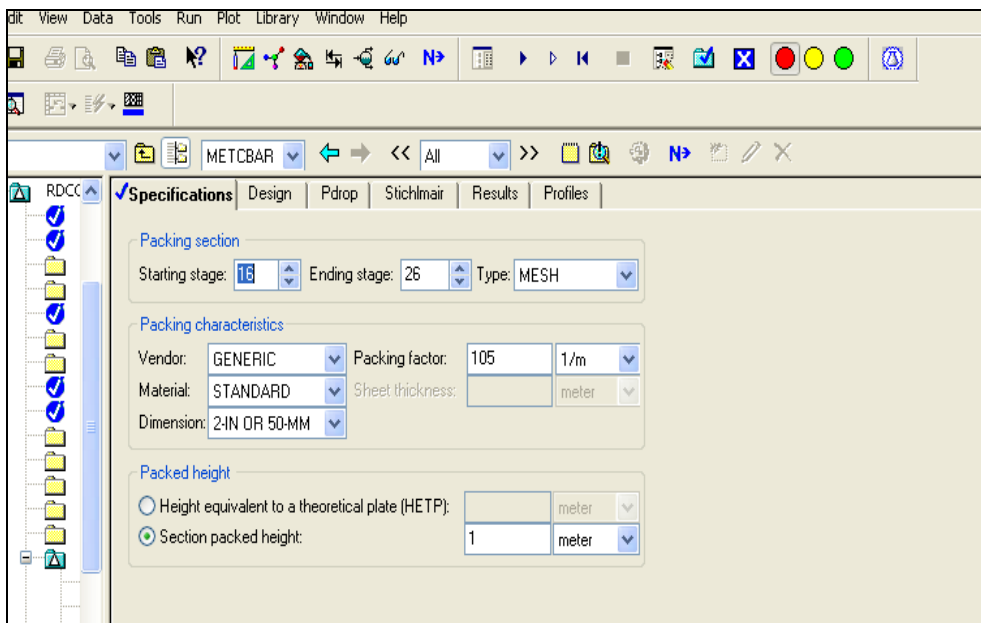
Figure 4.45 Pack Sizing Specifications for Stripping Section

The reaction kinetics are then entered into the reaction section for the reversible reaction given by the equation,

$$CH_3\text{-}COOH + C_5H_{11}\text{-}OH \xrightarrow{\ \ k\ \ } C_5H_{11}\text{-}COO\text{-}CH_3 + H_2O$$
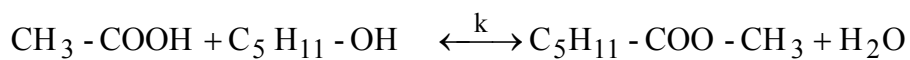
And the simulation is setup to compute the K_{eq} from the Gibbs energies.
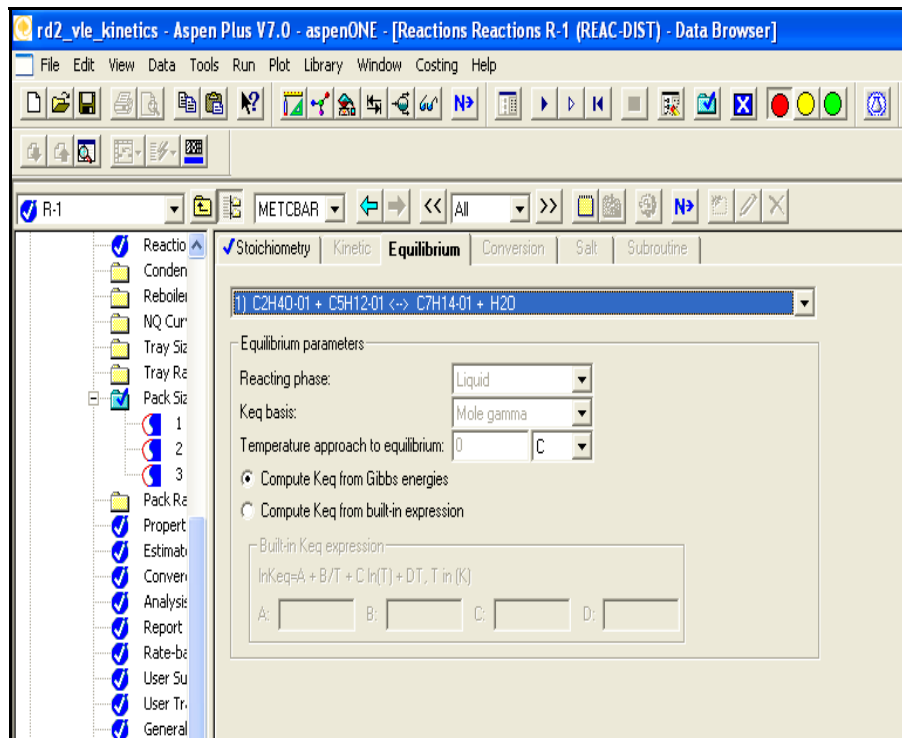
Figure 4.46 Equilibrium Reaction Parameters Input

The kinetic data for both the forward and the backward reaction is obtained from the Young-Tarang Tang et al, (2005) and it uses the same catalyst that has been used in the column and the kinetic setup as well.

The Figure 4.46 shows the forward reaction and its corresponding kinetic power law expression.

For Amberlyst 15 catalyst,

$$r = m_{cat} \left(k_1 \, C_{HAC} C_{AmOH} - k_{-1} \, C_{AmAc} C_{H_2O} \right)$$

$$k_1 = 31.1667 \exp(\frac{-51740}{RT})$$

$$k_{-1} = 2.2533 \exp(\frac{-45280}{RT})$$
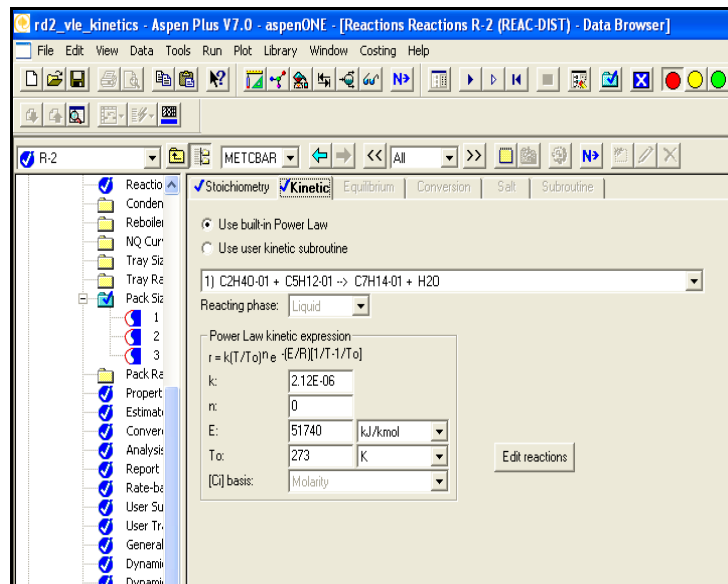
Figure 4.47 Data Input for Forward Reaction Kinetics

Obviously the amount of catalyst is different as is used in the setting up of the power law kinetic equations , so we adjusted m_{cat} until the acetic acid conversion calculated using the above parameters agreed with our experimental conversion. So to adjust mcat, the values of the pre exponential factor are reduced until they gave a favourable result. The figure 4.47 shows the backward reaction and the kinetic power law expression.
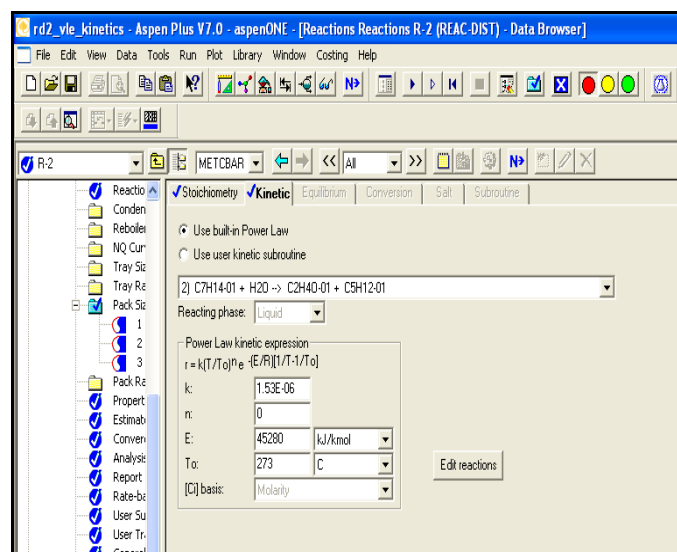
Figure 4.48 Data Input for Backward Reaction Kinetics

The VLE data from the databank of Aspen Plus is also used to simulate the column separately to see how the results vary with the experimental data and the aspen plus databank data. The result comparison and discussions has been shown in the Chapter 6.

Figure 4.49 Data set of Binary Parameters of Aspen plus Databank

4.9 Residue Curve Maps (RCM)

The quaternary system has two minimum-boiling binary azeotropes (iso amyl alcohol-water and amyl acetate water) and one maximum-boiling binary azeotrope (acetic acid-iso amyl alcohol). Whereas the azeotrope between acetic acid and iso amyl alcohol is homogeneous, the other two are heterogeneous azeotropes with rather high-purity water in the aqueous phase. There are two ternary azeotropes for acetic acid- iso amyl alcohol -amyl acetate and water-- iso amyl alcohol iso amyl acetate, and they are an unstable node and a saddle point, respectively, as shown Figure 4.50
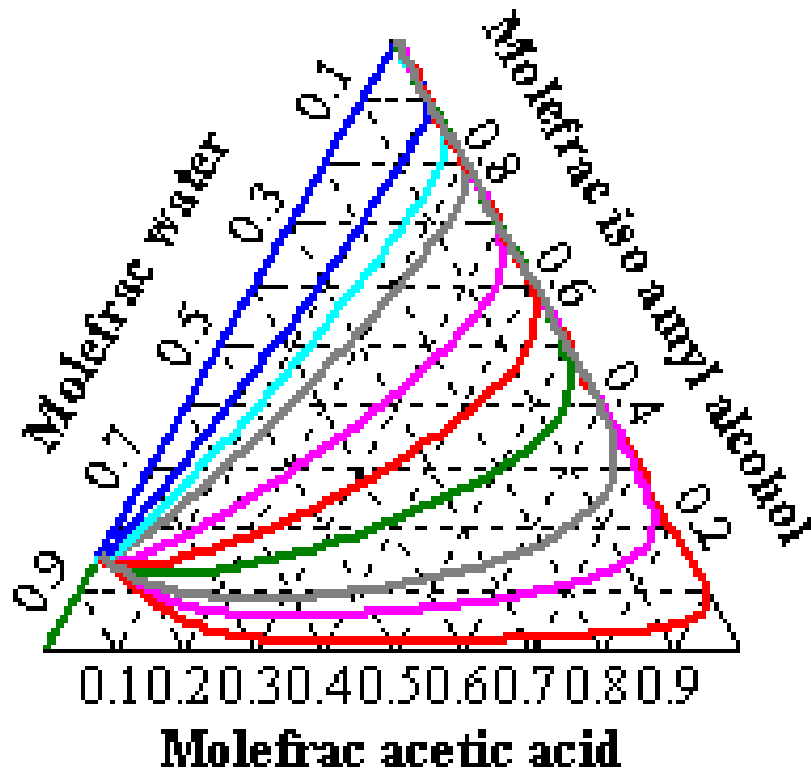
(a) Acetic Acid – iso amyl alcohol – water
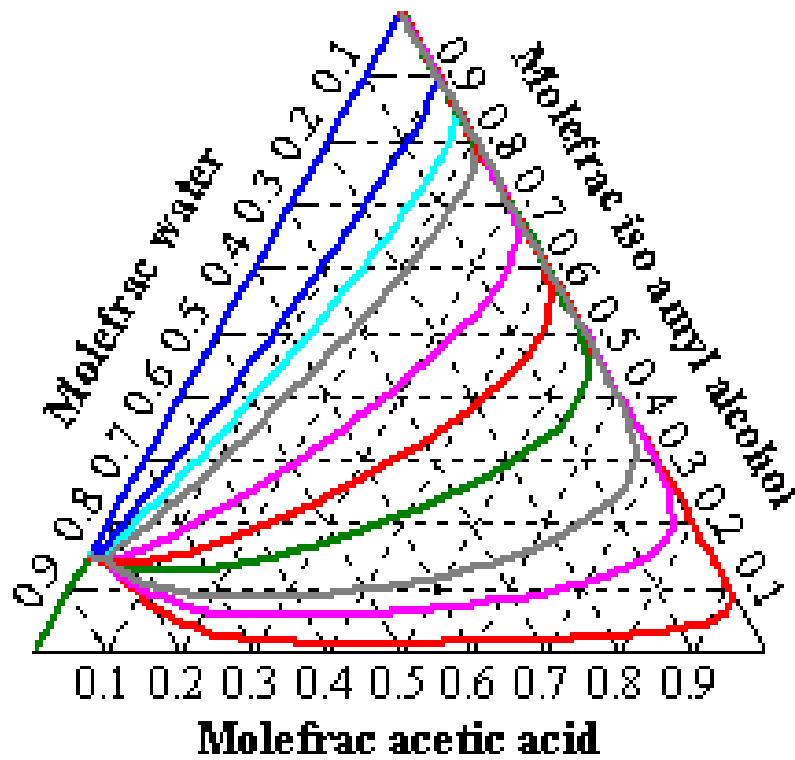
(b) Acetic Acid – iso amyl alcohol – iso amyl acetate
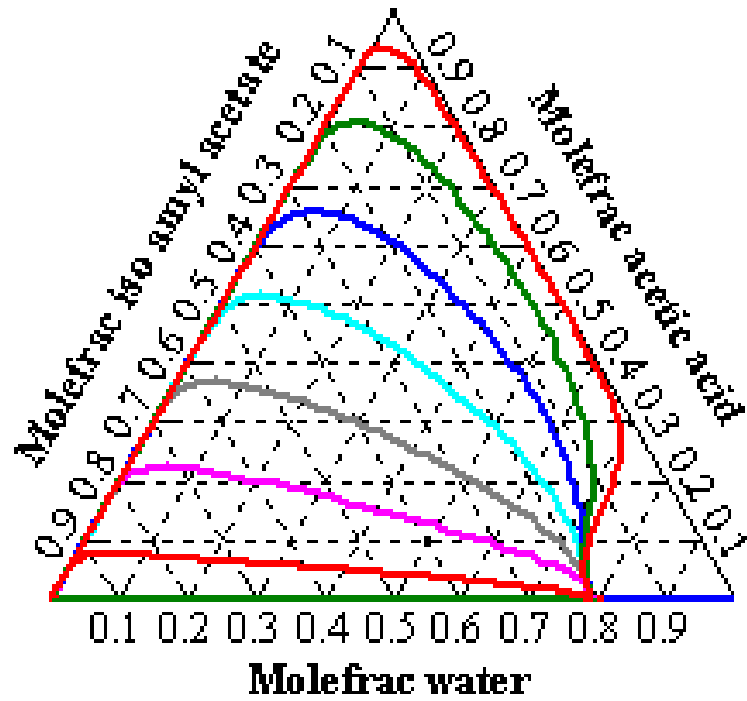
(c) iso amyl acetate – water - acetic acid
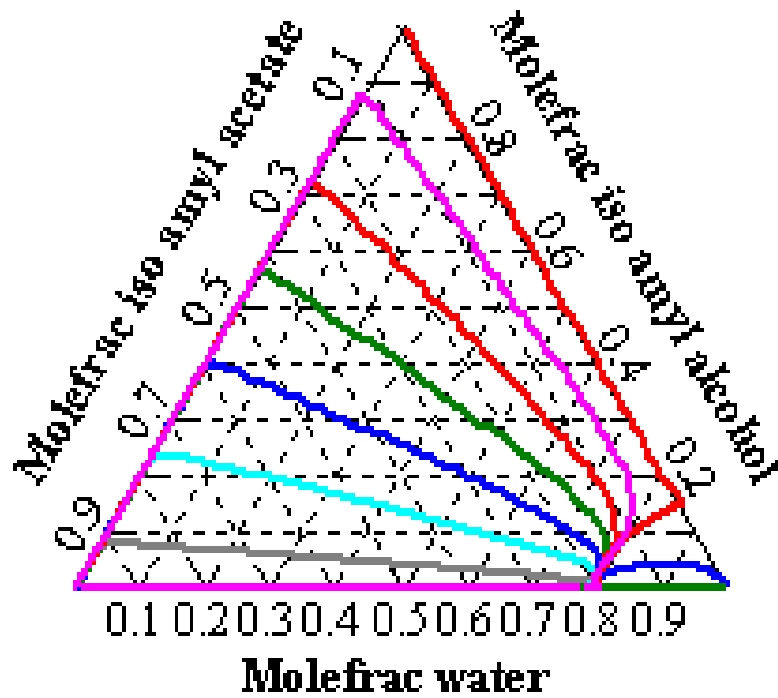
(d) iso amyl acetate – water – iso amyl alcohol

Figure No. 4.50 Residue Curve Maps for iso amyl acetate system

The water- iso amyl alcohol –iso-amyl acetate ternary azeotrope temperature is 95.2°C, which is in good agreement with the experimental result, 94°C. It is observed that a very large liquid-liquid (LL) envelope is observed for the water- iso amyl alcohol-iso amyl acetate system with one end of the tie lines connected to very high purity water.

The residue curves start from the minimum boiling ternary azeotrope (95.2 °C) and move toward three binary azeotropes (95.4, 96.0, and 140.5 °C) and two pure-component vortexes (100 and 148.8 °C), Two branches are of particular interest, one is the residue curves moving toward the amyl acetate vortex (148.8 °C) and the other is the residue curves converging to the maximum-boiling binary azeotrope (140.5 °C) near the iso amyl alcohol corner.

CHAPTER 5
REACTIVE DISTILLATION EXPERMENTS FOR SYNTHESIS OF ISO AMYL ACETATE

A laboratory reactive distillation experimental set up is designed and constructed to synthesize iso amyl acetate from iso amyl alcohol and acetic acid in order to support the simulation studies conducted via Aspen Plus. The motivation and objectives for experimental investigations are as follows:

1) Test the applicability of reactive distillation technology for iso amyl acetate synthesis ;
2) Validate steady state simulation results obtained from Aspen Plus (Version 7.0, 2007, Aspen Tech, Inc.);
3) Examine the effect of operating parameters (such as feed stage locations, feed flow rare, reboiler duty, molar ratio of the reactants etc.) on conversion and separation of reactive distillation column.

In the following section, brief review of literature for the present system is given.

5.1. Previous Studies:

The literature on this reaction in a RD column may be broadly classified in two categories. The first one, which deals with recovery of acetic acid from aqueous streams while the second category, which is directly related to the present work, aims at the production of iso amyl acetate from pure acetic acid and iso amyl alcohol.

The recovery of dilute acetic acid from wastewater streams is a major problem in the petrochemical and chemical industries (Saha et al, 2004).This includes the manufacture of cellulose esters, terphthalic acid, dimethyl terphthalate and reactions involving acetic anhydride. Among these processes, the process for the manufacture of

cellulose acetate from acetylation of cellulose by acetic acid, acetic anhydride and sulfuric acid, is typically associated with a 35% w/w aqueous solution of acetic acid as a waste stream. Terphthalic acid process involves the concentration even up to 65% w/w if acetic acid in water (Brunt, 1992). The wood distillation contains much lower concentrations (1-8 % w/w) of acetic acid. (Wagner et al, 1991).

Kuo et al, (1987) discussed the use of adsorbents for the recovery of acetic acid from aqueous solution. Yu et al, (2003) suggested the use of bipolar membrane electrodialysis for the recovery of acetic acid from dilute wastewater. Bianchi et al, (2003) reported the use of esterification to clean industrial water from acetic acid using n butanol and 2-ethyl 1-hexanol. Shi et al, (2005) proposed the use of SO_2 for recovery of acetic acid from an anaerobic fermentation broth.

RD is promising and cost-effective method of separation for the recovery of dilutes acetic acid from its aqueous streams. Moreover, a value added product in the form of iso amyl acetate is produced during recovery of acetic acid by esterification with iso-amyl alcohol. An additional column will be required for the complete separation of iso-amyl alcohol and iso-amyl acetate. The column would not involve water since it has the highest latent heat and hence the energy costs would be minimized. (Saha et al, 2005)

Iso amyl acetate synthesis in reactive distillation column was studied using dilute acetic acid by Lee et al (2005), Saha et al, (2005). Saha et al, (2000) have reported experimental results on the recovery of dilute acetic acid through esterification with higher alcohols such as n-butanol and iso amyl alcohol in a reactive distillation column using ion-exchange resin, Indion 130 as catalyst. The different column configurations were studied by changing the reflux location, length of catalytic zone, and length of total column height to get optimal results. The effect of various parameters for example, feed flow rate,

feed location, reflux ratio, molar ratio of reactant, and effect of recycle of water was studied experimentally. Singh et al (2006) showed RD is promising tool for recovery of acetic acid from aqueous solution by reactive distillation. However all the experimental studies in reactive distillation column were based on recovery of acetic acid using reactive distillation..

Chiang et al, (2002) presented comparison of coupled reactor/distillation column and reactive distillation for iso amyl acetate synthesis. In their work, they reported reactive distillation process is four times economical than coupled reactor/distillation based on Total Annual Cost (TAC). Singh et al, (2005) investigated theoretical and experimental aspects for production of butyl acetate by catalytic distillation. An equilibrium stage based dynamic model was developed and steady states as well as dynamic simulation results were compared with their experimental results in RD column.

Kloker et al, (2003) investigated the influence of operating conditions and column configuration on the performance of RD columns with liquid–liquid separators for two different esters, namely, ethyl acetate and hexyl acetate. The investigated column set-ups were equipped with liquid-liquid separators for the distillate to separate water from the organic components. For the modeling and simulation of the RD columns, the rate-based approach was applied.

Further Schmitt et al, (2004) presented comprehensive studies on the *n*-hexyl acetate synthesis by heterogeneously catalyzed reactive distillation. RD experiments were carried out both in laboratory and semi-industrial scale with different catalytic packings. Several variants of a basic column set-up and the influence of the most important process parameters were studied. Additionally, phase and chemical equilibria and reaction kinetics were measured. In their work, predictions from stage models of different complexity are compared to the results of experiments and shown that based on a

sound knowledge on reaction kinetics and thermodynamic properties, it is possible to successfully describe n-hexyl acetate synthesis in RD column.

It is realized that the experimental data on the present system, especially using pure acetic acid and iso amyl alcohol as feed to the column is limited and does not cover a wide range of operating parameters, such as reboiler duty, feed locations, feed flow rate, and molar ratio etc. Moreover, the column composition and temperature profiles, which helps to explain some important results, have not been reported in the previous studies.

Hence it is decided to conduct experimental runs on RD column using pure acetic acid and iso amyl alcohol as feed for the synthesis of iso amyl acetate and examine the performance of reactive distillation column for various operating parameters on conversion and purity of product.

5.2   Industrial Importance of Iso Amyl Acetate:

Iso amyl acetate has been used in the industry as a solvent, and extractants, and polishing agent. It is used as artificial flavoring in banana-flavored bubble gums, as preservative in sodas and soft drinks as well as artificial scent for covering unpleasant odors (Teo and Saha, 2004). It is also used in large quantities in artificially pear-flavored food articles as additive in cigarettes, and as a solvent for tannins, nitrocellulose, lacquers, celluloid, and camphor. It is also used to manufacture celluloid cements, water proof varnishes, artificial silk, leather or pearls, photographic films, bronzing liquids and metallic paints, perfuming shoe polishes and dyeing and finishing textiles. (Saha et al, 2005).

5.3   Why Reactive Distillation?

Esterification of iso amyl alcohol and acetic acid for the synthesis of iso amyl acetate has been the model reaction for the

present research studies in reactive distillation. The alcohol is sparingly soluble in water and esters and water are almost insoluble. An additional feature is that the ester-water-alcohol forms a ternary heterogeneous azeotrope, which is minimum boiling. Hence, in a typical RD column that consists of both reactive and nonreactive zones, the heterogeneous azeotrope or a composition close to azeotrope can be obtained as the distillate product. Moreover, the aqueous phase that forms after condensation of the vapor is almost pure water. (Singh et al, 2005) It can be easily withdrawn as a product, and the organic phase can be recycled back as reflux. The pure ester, which is the least-volatile component in the system, is realized as a bottom product. One can conveniently separate water and enhance the conversion.

The physical properties of the components in iso amyl acetate synthesis is given in Table 5.1.It can be synthesized from acetic acid and amyl alcohol via esterification reaction as follows:

$$CH_3\text{-}COOH + C_5H_{11}\text{-}OH \xleftrightarrow{\quad k \quad} C_5H_{11}\text{-}COO\text{-}CH_3 + H_2O \qquad (5.1)$$

(Acetic acid) (Iso amyl alcohol)   (Iso amyl acetate)   (Water)
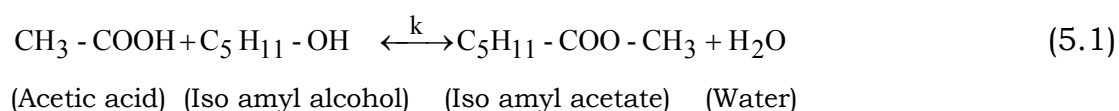
Since the self-catalyzed reaction is rather slow, reaction (5.1) is commonly catalyzed using strong inorganic acid, like sulfuric acid, or strongly acidic ion exchange resins. Most of previous researcher has used acidic cation exchange resin, for example Amberlyst 15 (Chiang et al, 2002), Purolite CT- 175 (Saha et al, 2005)

Table 5.1 Physical Properties of the components in Iso Amyl Acetate Synthesis

Comp.	CAS NO	MW	Chemical Formula	Density (gm/cc)	BP (^{o}C)	Vapor density (Air=1) (gm/cc)	Vapor pressure (mm of Hg)
Acetic Acid	64-19-7	60.05	CH_3COOH	1.05	118	2.1	11 mm Hg @ 20° C
Iso amyl alcohol	123-51-3	88.15	$C_5C_{11}OH$	0.813	132	3.04	2 mm Hg @ 20° C
Iso amyl acetate	123-92-2	130.1	$C_5H_{11}COOCH_3$	0.88	143	4.5	4 mm Hg @ 20° C
Water	7732-118-5	18	H_2O	1	100	-	17.5 mm Hg @ 20° C

The two reactants, acetic acid and iso amyl alcohol, are intermediate boilers, whereas the products, water and amyl acetate, are low and high boilers respectively. As iso-amyl acetate and water are the heaviest and lightest boiling substances respectively in the quaternary system, they can be continuously removed from the reaction zone in a RD column so that high conversions can be achieved, thus RD an attractive process for producing iso-amyl acetate. That's why reactions (5.1) are well suited for reactive distillation. However, the large boiling temperature difference between the reactants can be unfavorable from the reactions point of view.

5.4   Theory of Reactive Distillation:

Consider the reversible reaction given by equation (5.1).The law of mass action for this reacting system is given by

$$K = \frac{[C_5H_{11}COOCH_3][H_2O]}{[CH_3COOH][C_5H_{11}OH]} \tag{5.2}$$

If iso amyl acetate is desired product, Le-Chatelier's principle says that if water can be removed simultaneously during the course of the reaction, the reaction can be shifted in the forward direction and the conversion of iso amyl acetate can be enhanced.

The important limitation of the reactive distillation is that the volatilities of the components should be favorable. In the present system if we want to remove water, it should either have highest volatility or it should form a minimum boiling azeotrope (constant boiling mixture) with one or more than one component in the system. Table 5.2 shows boiling points of the components in the present system.

Table 5.2 Boiling points of the components

Components	Boiling points (ºC)
Acetic Acid	118
Iso amyl Alcohol	137.8
Iso amyl acetate	148.8
Water	100

If we want to increase the conversion towards iso amyl acetate, we have to remove water efficiently during the course of the reaction. Water forms ternary azeotrope with iso amyl alcohol and iso amyl acetate that boils at 93-95 ºC (Tang et al, 2005). Since this azeotrope is a minimum boiling azeotrope, instead of pure water one gets distillate compositions close to the ternary azeotrope.

The azeotrope can be either homogenous or heterogeneous. If on condensation of the vapors, the liquid forms two phases, the azeotrope is called as heterogeneous azeotrope. In the present system, the azeotrope is heterogeneous and forms two liquid phases on condensation. The aqueous phase is almost pure water and organic phase that consists of mainly iso amyl acetate and iso amyl alcohol can be recycled back to the column through reflux. Hence, ideally in a batch reactive distillation mode if one starts with stoichiometric mole ratio of iso amyl alcohol and acetic acid in the reactor, at the end of experiment experiment, the system should contains only iso amyl acetate in the reactor if the losses of iso amyl alcohol and other components with the overhead aqueous phase are negligible.(Singh et al, 2005)

5.5 Experimental Work:

5.5.1 Materials and Catalysts

Acetic acid (99.8%) and iso amyl alcohol (99%) were purchased from Merck India Ltd., Mumbai, India, iso amyl acetate (> 99% purity) was purchased from S.D. Fine Chemicals Ltd., Mumbai, India. In the reactive section of RD column, TULSION–T-63 MP,cation ion exchange

resin (courtesy Thermax India Ltd.), properties resemble with Amberlyst-15 (Rohm Haas, USA) is used as a catalyst. In reactive section, FX PA-DM™, structured packing; supplied by Fenix process Technologies, Pune, India for RD is used. Immobilization of the heterogeneous catalyst inside the reactive section of the column can be achieved by structured packings. This packing is made of corrugated wire-mesh sheets. Catalyst particles of 0.5 to about 1.3 mm can be fixed between the sheets of this packing.

In stripping and rectifying sections (non-catalytic sections), HYFLUX structured packings (High efficiency, low-pressure drop distillation packing) supplied by Evergreen Technologies, Mumbai, India is used.

5.5.2 Apparatus:

The simulation studies on the present test system is also conducted and indicated that this option can be promising than conducting the entire reaction in a reactive distillation column. The present work is aimed at performing an experimental investigation on a reactive distillation column operated in such a mode.

The experimental setup of a laboratory scale reactive distillation consists of 2.75-m-tall distillation column of inside diameter 50 mm that operates at atmospheric pressure is used is as shown in Figure 5.1.

The reboiler (capacity, 2 lit) is heated with the help of a heating mantle. (capacity, 2kW). The non-reactive rectifying and stripping sections are packed with wire mesh packing supplied by Evergreen Technologies, Mumbai, India. The number of theoretical stages per meter (NTSM) is 6 for reactive section and for nonreactive section 10 NTSM is used.

The middle reactive zone is packed with structured packing supplied by Fenix process Technology, Pune, India (FENIX DM

Structured Packing for RD) embedded with TULSION[R] –T- 63 MP, ion exchange resin (Thermax India Ltd) as a catalyst. The stripping section is 1 m tall, reactive section 1 m, and rectification section 0.75 m tall in height respectively. A proper insulation (with asbestos sheet and ropes) to minimize the heat losses to the surrounding. Two separate peristaltic pumps (0.1- 4 lph) are used to transfer the liquid from the two separate feed tanks to the different feed locations on the RD column.

In the condenser, two immiscible phases are formed, an aqueous phase i.e. almost pure water and an organic phase containing water, amyl alcohol and amyl acetate. The feed is preheated before introducing it to the column. Phase separator with the condenser is used to provide reflux to the column and to continuously withdraw water formed during the reaction. Thermometer wells are provided at different locations in the column to measure these temperatures (Position 3- Position 9, in Figure 5.1)

Figure 5.2 shows actual photograph of the experimental setup for continuous reactive distillation, which is functional in the Petrochemical Processes Lab, Department of Petrochemical and Petroleum Engineering at M.I.T., Pune, India. The design, construction and commissioning of this setup is the part of two research projects completed, funded by BCUD, University of Pune, India and All India Council for Technical Education, Research and Promotion Scheme, (AICTE,RPS Scheme), New Delhi, India.
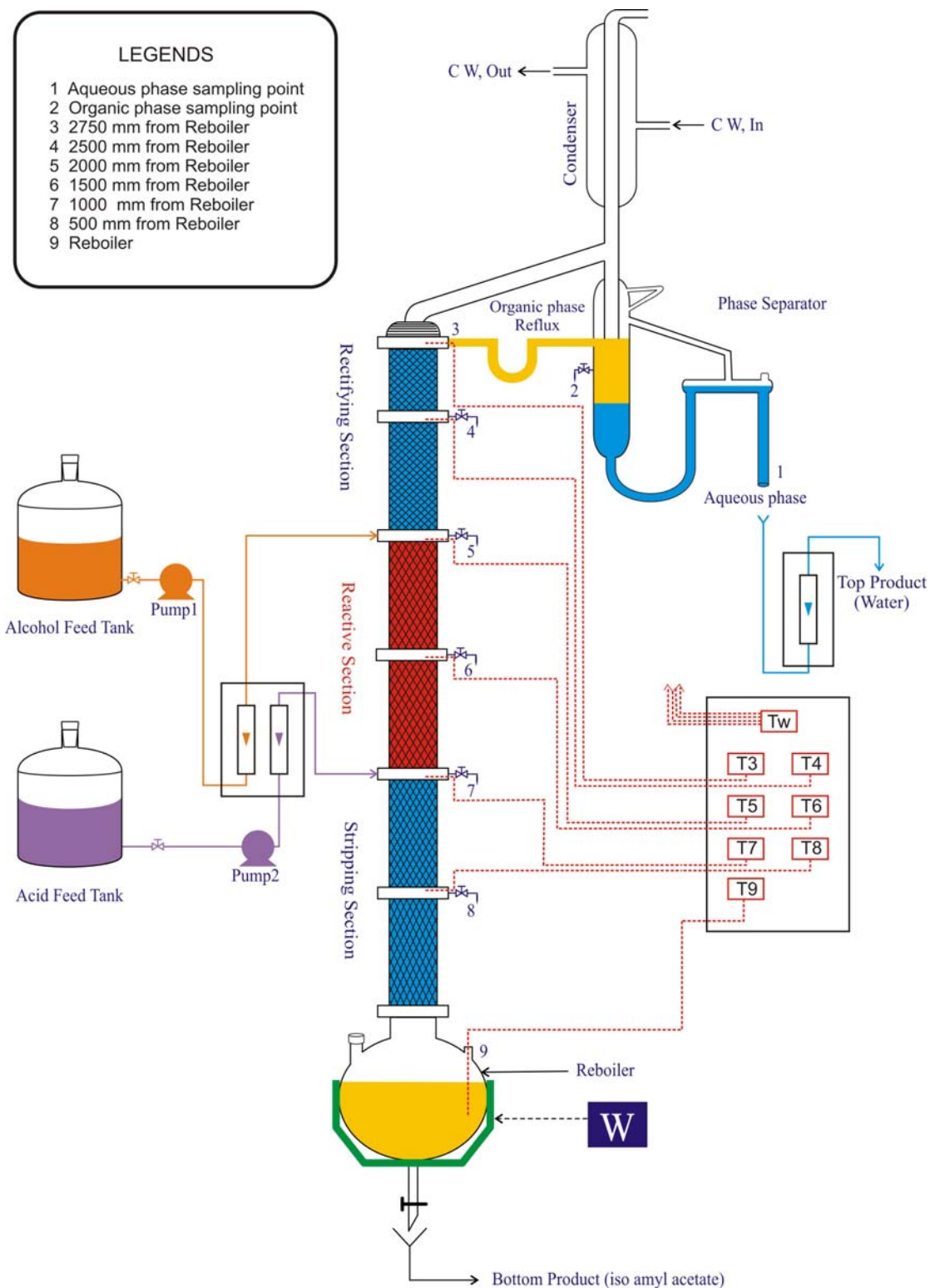
Figure 5.1 Experimental Setup for Continuous Reactive Distillation Column (Schematic View)

Figure 5.2 Photograph of Experimental Setup for Continuous Reactive Distillation Column, which is functional at Petrochemical Processes Lab. at MIT, Pune, India

The reactive distillation column for iso amyl acetate synthesis is consisting three distinct sections, which is discussed as below:

(1)   Reactive Section:

The reactive section is located between two non-reactive column sections that separate the reactants from the product. This configuration is shown in Figure 5.2. The function of the reactive section of RD column is simply to provide a location for the main reaction to proceed and, as such, there is no particular requirement for separation. This middle section packed with catalytic packing, which plays a dual role. It acts as catalyst and also provides sufficient interfacial area for G-L mass transfer. The reaction of acetic acid and iso amyl alcohol takes place in this section and products formed undergo distillation.

(2)   Non-reactive Rectifying Section:

The non-reactive sections of a hybrid reactive distillation column are imperative for achieving the desired process performance. In general, the rectification section of a reactive distillation column for iso amyl acetate synthesis should: (a) remove light reactant from the reaction zone;(b) prevent the loss of product in the distillate; and, (c) recycle unreacted reactants (acetic acid and iso amyl alcohol) to the reaction zone. This is a top section that separates the minimum boiling azeotrope of the ternary mixture of iso amyl alcohol, iso amyl acetate and water (boiling point 93-95 ^{0}C) from the other components.

(3)   Non-reactive Stripping Section:

This is a bottom section used for the separation of highest boiling iso amyl acetate from the other components. Preferably the stripping section should: (a) remove iso amyl acetate from the reaction zone to maintain favorable reaction conditions; (b) purify the iso amyl acetate product; (c) recycle unreacted reactants to the reactive section.

Following section gives information on various important parts of RD experimental setup.

(1)   Phase Separator Arrangement:

The typical arrangement for phase separator is as shown in Figure 5.3.
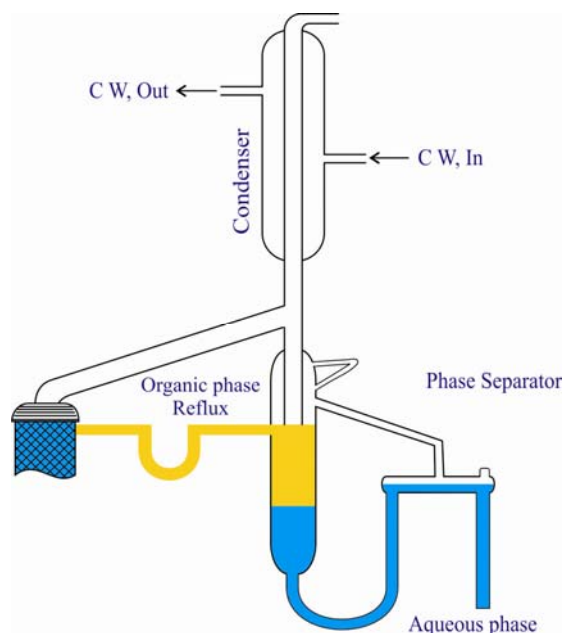
Figure 5.3 Phase Separator

The phase equilibria of the quaternary system revealed that a significant two-liquid region exists, and more importantly, that the tie lines are all pointed to high-purity water for the aqueous phase. It is evident that the liquid-liquid separation on the top of the column is beneficial for iso amyl acetate esterification processes. Therefore, a decanter was placed on top of the column, where high-purity water was withdrawn from the aqueous phase, and the organic phase was totally refluxed. Thus, a decanter constitutes an advantageous component of the reactive distillation column set-up.

In the conventional dean and stark's arrangement it is difficult to maintain constant level of aqueous phase. This affects the reflux rate to the column and also affects the top temperature. By using

phase separator arrangement, it was possible to maintain constant level of aqueous phase and constant reflux.

(2)   Flow Metering Pumps:

A peristaltic pump (capacity 4 lph) was used to introduce feed to the column. Two separate pumps were used for two feeds, namely acetic acid and iso amyl alcohol.

(3)   Condenser:

A double-coiled condenser was used and it has been ensured that the condensation is complete.

(3)   Heating Mantle:

The boil-up rate is an important parameter in reactive distillation processes. As the reflux ratio is fixed, the boil-up is the only operating parameter that can be efficiently changed to obtain the better performance. Hence it is possible to operate the column over a wide range of boil-up rates to study its effect. The capacity of heating mantle is 2 kW. A wattmeter was used to measure the wattage power supplied to the heating mantle.

5.5.3   Laboratory Scale RD Column Specifications:

1)   **Diameter of column** =ID: 50 mm, OD: 58 mm (Material of construction : Borosilicate glass)

2)   **Rectification Section:**

Height = 0.75 m, Type of packing = HYFLUX Packings (Evergreen Technologies, Mumbai, India) (Material of construction: SS 316, Size: 2 in. × 4 in., Pad density = 432 kg/m^3)

3)   Reactive Section:

Height, h = 1 m, Packings: FX PAK DM structured packing (Fenix Process Technologies, Pune, India), (Material of construction: SS 316L, Size: 2 in. × 4 in.)

4)   Stripping Section:

Height = 1 m, Type of packing = HYFLUX Packings (Evergreen Technologies, Mumbai, India) (Material of construction: SS 316, Size: 2 in. × 4 in., Pad density = 432 kg/m³)

5)   Catalyst Type: TULSION^R –T- 63 MP, Cation ion exchange resin, Thermax India Ltd.)

6)   Operating Pressure= Atmospheric

7)   Operating Temperature = 373-423 K

8)   Insulation: Glass wool with Asbestos rope, to a thickness approximately 1 inch. , was applied *in situ* to reduce the heat losses on the column performance.

9)   Digital Temperature Indicator: Total 8 points, Pt 100, Range: 0-300ºC, Accuracy: $\pm 0.1^O$C

Thermocouples are installed at 7 points of the column and at the condenser outlet. The thermocouples are connected to a switching unit and to a control panel mounted display to view all the temperatures at a time. This is shown in Figure 5.2.

10)   Peristaltic Pumps: 2 in numbers (Range: 0.1 to 4 lph)

11)   Feed Tanks: 2 in Nos, 10 liters,

Material of construction: Borosilicate glass

12)   Glass Rotameters: For Acid and Alkali (0.1 – 4 lph)

13) **Reboiler:** 2 Liter capacity with heating arrangement by Heating Mantle (2 KW)

14) **Heating Mantle**: 2 kW capacity

15) **Wattmeter:** Digital, Range 0-3 kW capacity

16) **Condenser:** Double surface with Phase Separator arrangement, Material of construction: Borosilicate glass

17) **Teflon Disc:** Total 6 in numbers fitted on RD column

18) **Sampling valves:** Total 6 in numbers mounted on RD column

5.5.4 Types of Packings used in Reactive Distillation Column:

In the following section brief discussion on type of packings used for both reactive and non-reactive sections of reactive distillation column is given.

(1) **Non-reactive Section Packings (Separation Section Packings):**

HYFLUX packings (High efficiency, low-pressure drop distillation packing) supplied by Evergreen Technologies, Mumbai, India is used for non-reactive section of reactive distillation column. HYFLUX is a family of structured tower packings, which are particularly useful when a moderate to large number of theoretical stages have to be accommodated in a limited height of the tower. The actual photograph of Hyflux packing is shown in Figure 5.4

Figure 5.4 Hyflux Packing for Non-reactive Section of RD Column

The open structure formed due to the proprietary lay of the filaments, the unique stitches employed and the special crimping and plying form tortuous channels for liquids which can continuously combine, divide and recombine for optimum mixing and contact with vapor. This results in intimate mixing between vapor passing upward through the controlled interconnecting passageways and the thin film of liquid flowing down the capillary wire network of the packing. The unique interaction results in high mass transfer rates (maximum separation efficiency) while maintaining low resistance to flow (low P/ theoretical stage).

**Table 5.3 Technical Data specifications for Hyflux Packings
(Evergreen Technologies Ltd., Mumbai, India)**

HETP	$\geq$ 100 to 200 mm in production columns $\geq$ 75 mm in pilot/laboratory stills
NTU/meter	$\leq$ 10 in production columns 13 in pilot/laboratory stills
P/ theoretical	0.05 - 0.75 mm Hg. plate
Vapor load	0.2 - 2.75 F factor m/s
Liquid load	$\leq$ 0.7 m 3 /m 2 h
Liquid holdup	3 to 8% w/w

Liquid Distribution

For better operation of HYFLUX packing it is necessary to have a good initial multipoint distributor. Because of the capillary action of multifilaments, the wall effects are nearly eliminated. However, for column heights larger than 3 meters intermediate redistributors would be recommended.

Materials of Construction

Stainless steel 304 and 316 grades and other higher alloys are used as materials of construction for these packings.

(2) Reactive Section Packings:

Simultaneous chemical reaction with distillation of the product (or one of the products), is highly desirable whenever it is feasible in the process technology. However, designing the column packing demands special treatment because the catalyst volume fraction is a variable parameter depending on the specific reaction and the process.

The catalyst was encapsulated vertically between layers of structured packing up to the designed height of packed bed placed within the distillation column.

Figure 5.5 (a) FX PAK-DM™: Packing for RD Catalyst Embedded Packing (Top view of packings)

FX PAK-DM™ structured packings for reactive distillation, supplied by Fenix Process Technologies, Pune, India is used and actual photographs are shown in Figure 5.5 (a) and (b). The catalyst packed column for reactive section is shown in Figure 5.6. These packings provide high separation efficiency and reaction capacity/rate with flexible design regarding catalyst element.

Figure 5.5 (b) FX PAK-DM™: Packing for RD Catalyst Embedded

Packing (Front view of packings)

Figure 5.6 Catalyst Packed Columns for Reactive Section

5.5.5 Operating Procedure:

The column reboiler is initially filled with feed mixture and heating is started with desired boil up rate. It takes about 20-25 minutes for vapors to reach to the top of RD column. Once the reflux to the column begins, the two feed streams are introduced

with feed preheater on. The feed temperature is typically in the range of 75-85⁰C. Every one hour temperatures from different locations (Position 3 to 9, in Figure 5.1) of RD column are recorded. Similarly every one hour, samples from reboiler are withdrawn for analysis. At steady state the samples from different locations are withdrawn and analyzed to get steady state composition profile. The temperature profile and outgoing stream compositions from top and bottom of RD column are measured and recorded. The time required to achieve the steady state in present experimental set up varies between 6 hrs to 9 hrs depending on the operating parameters used.

5.5.6 Analysis:

Gas chromatography is used for the analysis of the different samples from the different locations of reactive distillation column.

Acetic acid, iso amyl alcohol, iso amyl acetate and water are analyzed using gas chromatograph (Model C-911, Mak Analytica India Ltd.) which is equipped with thermal conductivity detector (TCD). The samples are analyzed Porapak Q with hydrogen as carrier gas at a flow rate of 5×10^{-7} m^3/s. The injector and detector were maintained at a temperature of 493K and 423K respectively. The oven temperature is maintained isothermally at 513K to get the best resolution in less time.

The results obtained by GC are confirmed by independent titration using standard sodium hydroxide (NaOH) solution using phenolphthalein as indicator. The reliability of the titration method is confirmed with the help of analysis of standard samples containing iso amyl acetate to ensure the hydrolysis of ester does not takes place during the course of titration. Acetic acid concentration is cross-checked by titrating the sample with dilute 0.1 N sodium hydroxide solution using phenolphthalein as indicator. The analytical relative uncertainty is <5%, which is good enough within the acceptable limits.

Figure 5.7 shows a typical chromatogram obtained for this system.
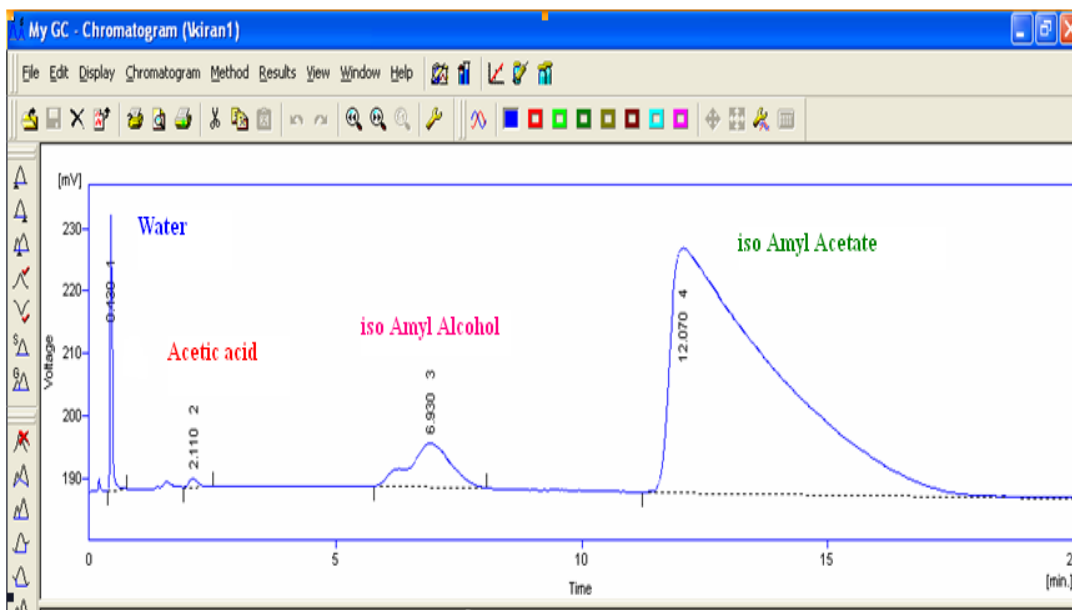
(a) Output using TCD
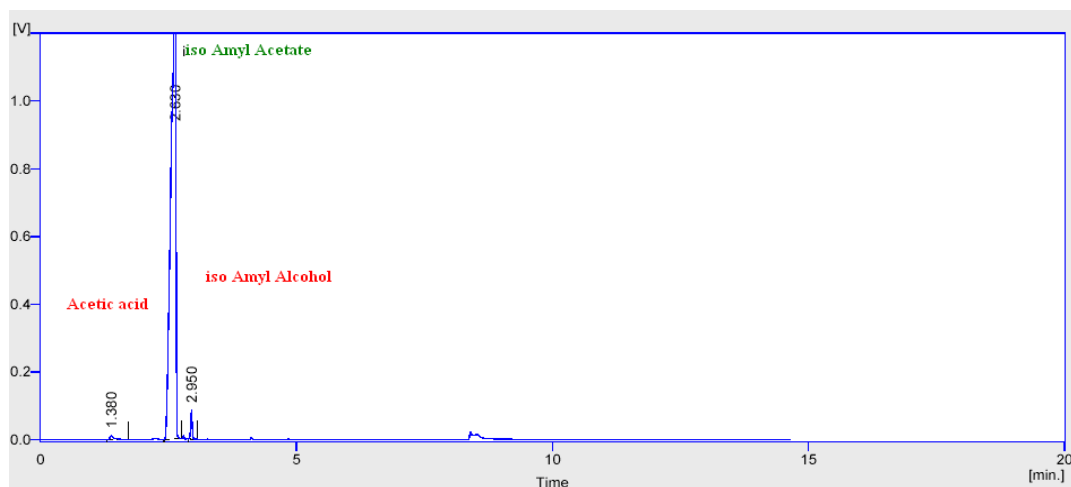
(b) Output using FID

Figure 5.7 Typical Chromatogram

5.5.7 Calibration Charts:

Results obtained from gas chromatogram indicated that area covered under each peak is related to their concentration in the

injected sample. For organic phase, to evaluate composition of sample, iso amyl acetate was regarded as internal standard. To prepare calibration chart for acetic acid and iso amyl acetate, their mixture in various weight ratios, defined as weight of acetic acid divided by weight of iso amyl acetate, are prepared and injected into the gas chromatography instrument. From the chromatogram obtained the ratio, defined as the area the area covered under the acetic acid peak divided by the area covered under the iso amyl acetate was determined. The graph of area ratio versus weight ratio indicated that this chart could be effectively utilized to evaluate the composition of sample obtained from the different streams at various times from reactive distillation column. By similar procedure, calibration chart for iso amyl alcohol and water was obtained.

Caliberation Acetic acid vs Iso amyl acetate

$y = 1.006x$
$R^2 = 0.9993$
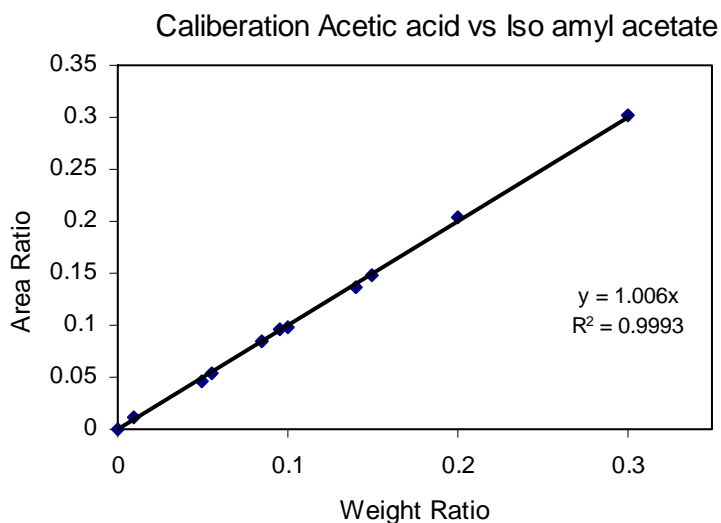
Figure 5.8 Calibration Chart for Acetic acid
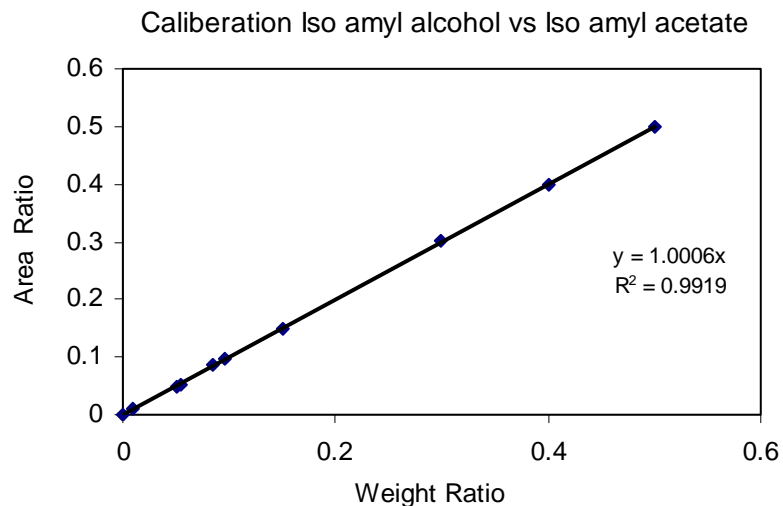
Figure 5.9 Calibration Chart for Iso Amyl Alcohol
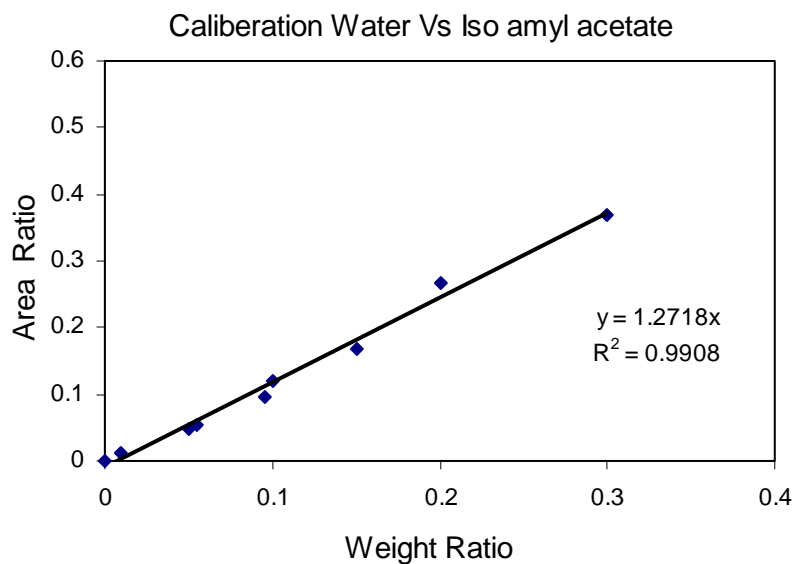
Figure 5.10 Calibration Chart for Water

5.5.8 Details of RD Experiments:

Table 5.4 Details of RD Experiment (Run No. # 10)

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.03200	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.03500	kmol/hr
3	Mole ratio, acid/alcohol	0.5384	-
4	Reboiler duty	1.12	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Reactive section on RD column	Position 5 to 7	
7	Conversions in terms of acetic acid	99.50	%
8	Bottom product Composition (mole fractions)	iso amyl acetate = 0.993	-
9	Top product compositions (mole fraction)	Water = 0.9845	-
10	Purity of bottom product	98.15	%

Table 5.7 shows the experimental results obtained under different operating conditions. The steady state experimental temperature and composition profiles for representative run (Run # 10) is as shown in Table 5.5 and 5.5 respectively.

Table 5.5 Steady State Temperature Profile in RD column (RUN No # 10)

Position/Section of RD Column	Column Temperature (°C) (Experimental)
1(Top)	94
2	128
3	129
4	130
5	131
6	132
7	133
8	146
9(Bottom)	147

Table 5.6 Steady State Composition Profile in RD column (Run No # 10)

Position on RD Column	Acetic acid	iso amyl alcohol	Water	iso amyl acetate
1	0.00	0.525	0.9845	0.164
2	0.000005	0.716	0.284	0.22
3	Two Phase	Two Phase	Two Phase	Two Phase
4	0.00005	0.605	0.029	0.35
5	0.00006	0.512	0.0285	0.459
6	0.1050	0.000007	0.0205	0.859
7	0.250	0.000002	0.000025	0.89
8	0.0355	0.00000025	0.000	0.975
9	0.00026	0.000002	0.000	0.993

The typical steady state experimental temperature and composition profile in RD column for Run No # 10 is as shown in Figure 5.11 and 5.12 respectively.
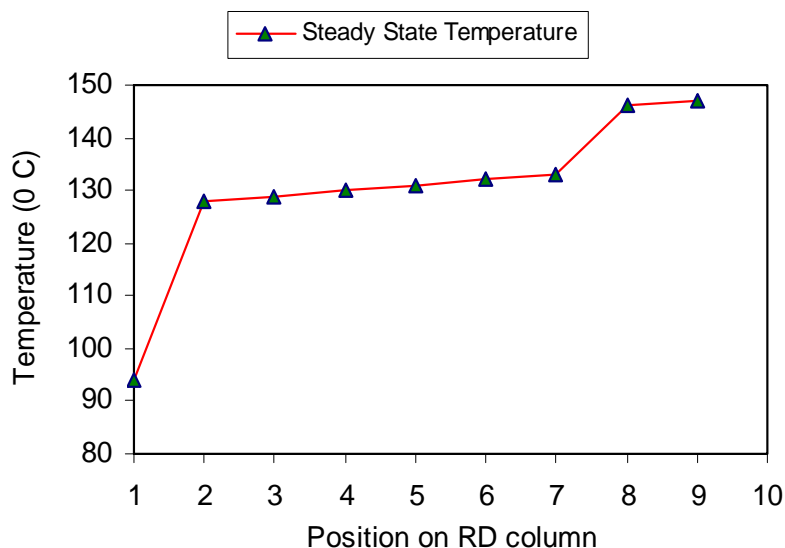
Figure 5.11 Steady State Temperature Profiles (Run No. # 10)

(Reactive Section, Position 5 to 7 on RD Column)
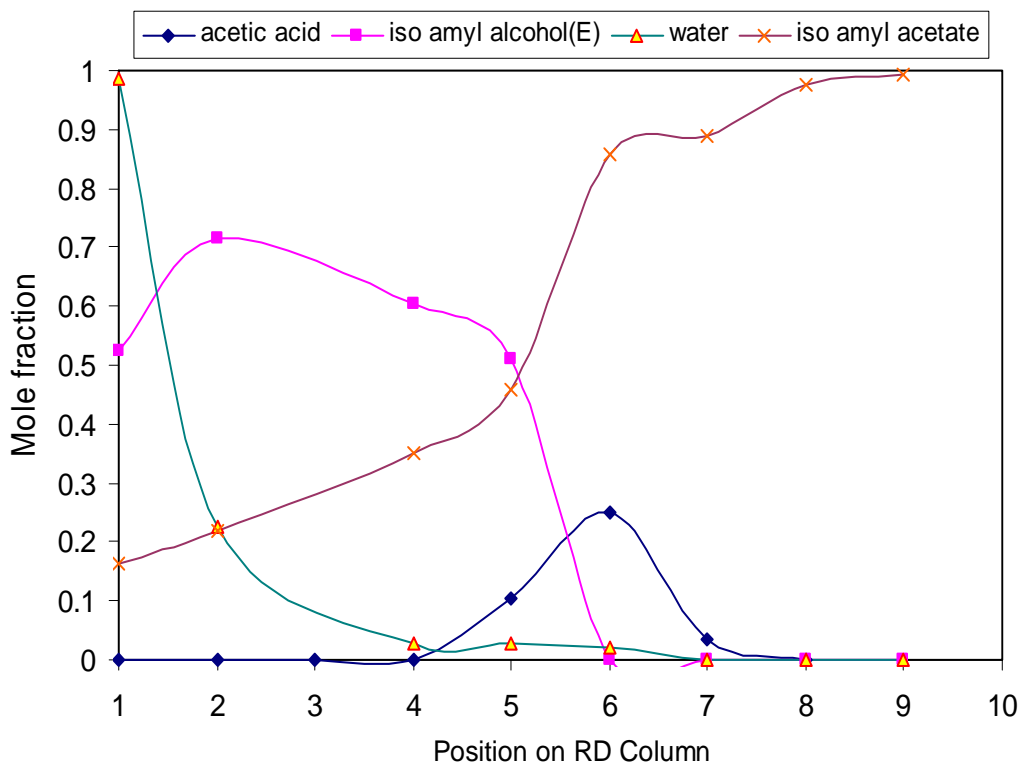
Figure 5.12 Steady State Composition Profiles (Run No. # 10)

(Reactive Section, Position 5 to 7 on RD Column)

Figure 5.11 shows the mole fractions of acetic acid, iso amyl alcohol, iso amyl acetate and water in the liquid phase. As seen from Figure 5.11, composition of 0.993 of iso amyl acetate at bottom and 0.9845 of water at top of RD column were achieved.

In this figure, position 5 to 7 represents the reactive stages on reactive distillation column. Position 5 is feed location for iso amyl alcohol and position 7 is feed location for acetic acid. In the reaction zone (Position 5 to 7), iso amyl alcohol is consumed, and as a result, its mole fraction decreases. The extremely low concentration of water in the reactive zone helps reaction to proceed near completion. Position 7 and 8 shows the transition between the reaction and stripping zones in the column. In the stripping zone, iso amyl acetate and iso amyl alcohol are being separated, resulting in the higher concentration of iso amyl acetate in the bottoms. High mole fractions of iso amyl acetate are obtained in the liquid phase.

The composition at position 3 is not shown here because of formation two phases, viz. organic and aqueous phase. The results of the runs conducted after reasonable gap, under otherwise similar conditions, are reproducible, indicating a minor loss in catalytic activity over the period of experimental runs on RD column.

The reaction zone is located at the middle of the column and is comprised of position 5 to 7 on the RD column. A smooth temperature profile is observed in the reactive zone where the catalyst is located. In this region, the temperature profile is extremely important because temperature extremes in this region can accelerate deactivation of the catalyst and thereby, decrease its performance.

In all the experimental runs, the temperature range in the reactive zone is 120-130 ^{0}C. Sufficiently high temperature ensures reaction to be at the chemical equilibrium and driven by distillation.

The temperature is below the limit set by the manufacture for the thermal stability of the catalyst (135 ^{0}C). The larger temperatures in the bottom are due to the presence of iso amyl acetate, which has a significantly higher molecular weight, and thus, a higher boiling temperature. (147 ^{0}C)

5.6 Experimental Observation and Results for Continuous Reactive Distillation Column:

The summary of experimental results obtained under different operating conditions is given in Table 5.7. The effect of different operating parameters such as feed flow rate, feed location, reboiler duty and molar ratio of acetic acid to iso amyl alcohol is examined.

The details of various RD experimental runs conducted on Laboratory RD column and different operating conditions along with comparison with simulation results are presented in Appendix 1.

Table5.7 Experimental Results obtained under Different Operating Conditions

Run No.	1	2	3	4	5	6	7	8	9	10	11
reboiler duty(kW)	0.80	0.75	0.75	1.0	0.85	1.0	1.0	1.0	1.12	1.12	1.15
feed flow of alcohol (kmol/hr)	0.02625	0.0200	0.0200	0.0300	0.0300	0.0320	0.0320	0.0340	0.0300	0.0350	0.0350
feed flow acid (kmol/hr)	0.0200	0.0185	0.0155	0.0255	0.0255	0.02625	0.0250	0.0300	0.02625	0.0320	0.0320
feed location for alcohol on position [a]	5	5	5	5	5	5	5	5	5	5	5
feed location for acetic acid on position [a]	7	7	7	7	7	7	7	7	7	7	7
acetic acid: alcohol ratio [b]	0.5384	0.5384	1.85	0.5384	0.5274	0.5394	0.5394	0.5384	0.5384	0.5384	0.5384
conversion [c]	99.50	99.70	65.40	99.49	98.90	99.10	98.75	99.20	99.05	99.50	98.45
Bottom Compositions (mole fractions)											
acetic acid	0.0004	0.0001	0.1400	0.00002	0.00004	0.0001	0.0001	0.0001	0.0007	0.0025	0.0003
iso amyl alcohol	0.1450	0.0028	0.0026	0.0001	0.00295	0.0478	0.0920	0.00157	0.0025	0.003	0.0025
iso amyl acetate	0.8545	0.9970	0.8572	0.9990	0.9970	0.9521	0.9079	0.9984	0.9900	0.993	0.9950
water	0.0001	0.0000	0.0001	0.00003	0.0000	0.000	0.0000	0.000	0.000	0.0014	0.0020
bottom flow (kmol/hr)	0.02319	0.0211	0.02030	0.0309	0.0303	0.0312	0.0315	0.0345	0.0313	0.0364	0.0363
Distillate Compositions (mole fractions)											
acetic acid	0.000	0.0001	0.0160	0.0002	0.0002	0.0001	0.0001	0.0002	0.0003	0.0004	0.0003
iso amyl alcohol	0.0166	0.0150	0.0002	0.0002	0.0003	0.0002	0.0002	0.0002	0.0002	0.0001	0.0005
iso amyl acetate	0.0170	0.0020	0.0010	0.0029	0.0190	0.0185	0.0177	0.0210	0.0200	0.0150	0.0180
water	0.9664	0.9829	0.9828	0.9967	0.9805	0.9812	0.9818	0.9786	0.9795	0.9845	0.9812
distillate flow (kmol/hr)	0.023055	0.01738	0.01468	0.02460	0.02582	0.02575	0.0245	0.0295	0.0249	0.0306	0.0306

[a] Position 5 denotes the top of catalyst zone; position 7 denotes the bottom of catalyst zone. [b] Molar ratio.
[c] in terms of acetic acid

Table5.7 Experimental Results obtained under Different Operating Conditions (Contd.)

Run No.	12	13	14	15	16	17	18	19	20	21	22
reboiler duty(kW)	1.25	1.10	1.0	1.25	1.35	1.30	1.40	1.50	1.60	0.80	1.20
feed flow of alcohol (kmol/hr)	0.0380	0.0380	0.0340	0.0350	0.0250	0.04375	0.0500	0.0520	0.0600	0.0262	0.0350
feed flow of acid (kmol/hr)	0.0350	0.0360	0.0310	0.0320	0.0200	0.0400	0.0400	0.0440	0.0450	0.0250	0.0300
feed location for alcohol on position [a]	5	5	5	5	5	5	5	5	5	5	5
feed location for acetic acid on position [a]	7	7	7	7	7	7	7	7	7	7	7
acetic acid: alcohol ratio [b]	0.5384	0.5384	0.5200	0.5200	1.00	0.5394	0.5394	0.5384	0.5384	0.5384	0.5367
conversion [c]	99.30	99.05	99.27	99.54	78.90	99.32	99.29	99.19	99.27	99.16	98.59
Bottom Compositions (mole fractions)											
acetic acid	0.000148	0.0001	0.00028	0.00021	0.0004	0.00287	0.0020	0.0001	0.0002	0.0009	0.0002
iso amyl alcohol	0.00085	0.0028	0.0022	0.0025	0.1300	0.0002	0.120	0.0760	0.1500	0.0003	0.0260
iso amyl acetate	0.999	0.9970	0.9972	0.9952	0.8695	0.9969	0.878	0.9219	0.8298	0.995	0.9738
water	0.000	0.0000	0.0003	0.0002	0.0001	0.000	0.000	0.002	0.0200	0.0001	0.000
bottom flow (kmol/hr)	0.0388	0.0398	0.0347	0.0364	0.0252	0.0447	0.0480	0.0490	0.05430	0.02714	0.0348
Distillate Compositions (mole fractions)											
acetic acid	0.000	0.0004	0.0001	0.0003	0.020	0.000	0.0002	0.0002	0.000	0.0002	0.0002
iso amyl alcohol	0.0140	0.0100	0.014	0.0110	0.0016	0.0140	0.0100	0.0150	0.0160	0.0090	0.0150
iso amyl acetate	0.0300	0.0020	0.030	0.0460	0.0189	0.0300	0.0160	0.0180	0.0145	0.0300	0.0200
water	0.9560	0.9876	0.9550	0.9427	0.9595	0.9560	0.9738	0.9668	0.9695	0.9608	0.9648
distillate flow (kmol/hr)	0.0342	0.0351	0.0302	0.0305	0.0198	0.0389	0.040	0.0455	0.0445	0.0240	0.0295

[a] Position 5 denotes the top of catalyst zone; position 7 denotes the bottom of catalyst zone. [b] Molar ratio.
[c] in terms of acetic acid

Table5.7 Experimental Results obtained under Different Operating Conditions (Contd.)

Run No.	23	24	25	26	27	28	29	30
reboiler duty(kW)	1.25	1.20	1.0	1.6	0.90	1.0	1.0	1.0
feed flow of alcohol (kmol/hr)	0.0500	0.0500	0.0320	0.0500	0.0195	0.0205	0.0205	0.0225
feed flow of acid (kmol/hr)	0.0350	0.0470	0.0350	0.0440	0.01789	0.0188	0.0188	0.0220
feed location for alcohol on position [a]	5	5	5	5	5	6	7	5
feed location for acetic acid on position [a]	7	7	7	7	7	5	5	7
acetic acid: alcohol ratio [b]	0.5367	0.5367	0.5367	0.5367	0.5200	0.5200	0.5200	0.6600
conversion [c]	98.67	92.96	97.90	97.94	99.37	90.45	65.45	84.80
Bottom Compositions (mole fractions)								
acetic acid	0.0006	0.0030	0.0005	0.00025	0.0002	0.0001	0.020	0.002
iso amyl alcohol	0.1900	0.020	0.010	0.0150	0.0098	0.01250	0.205	0.095
iso amyl acetate	0.7692	0.977	0.9890	0.9845	0.9900	0.8740	0.7734	0.9010
water	0.0002	0.000	0.000	0.0002	0.00	0.0000	0.0016	0.002
bottom flow (kmol/hr)	0.0490	0.0512	0.03614	0.0524	0.0220	0.0215	0.0220	0.0220
Distillate Compositions (mole fractions)								
acetic acid	0.020	0.0002	0.002	0.0002	0.0002	0.0002	0.0300	0.0350
iso amyl alcohol	0.0150	0.012	0.005	0.0050	0.00200	0.010	0.2200	0.0900
iso amyl acetate	0.0126	0.042	0.0480	0.0400	0.0100	0.1075	0.0145	0.0150
water	0.9524	0.9458	0.9450	0.9548	0.9878	0.8823	0.7354	0.8600
distillate flow (kmol/hr)	0.0345	0.0457	0.0308	0.0416	0.0158	0.0174	0.0170	0.0224

[a] Position 5 denotes the top of catalyst zone; position 7 denotes the bottom of catalyst zone. [b] Molar ratio.

[c] in terms of acetic acid[a]

In this section, effect of various operating parameters on conversion and separation is presented to assess the optimum performance of reactive distillation column.

5.6.1 Effect of Feed Flow Rate:

The residence time for the reactants inside the reactive zone is strongly influenced by the feed flow rate. The experiments are performed for different feed flow rates over the wide range of 0.0175 kmol/hr to 0.07 kmol/hr (1 lph to 4 lph). It is observed that better results are obtained at lower flow rates due to large residence time offered under this condition. Table 5.7 (Run Nos # 14 and 27) shows that, although the conversion and purity levels in each case are high, slightly better results are achieved at lower flow rates, due the sufficient residence time offered under this condition.

5.6.2 Effect of Reboiler Duty:
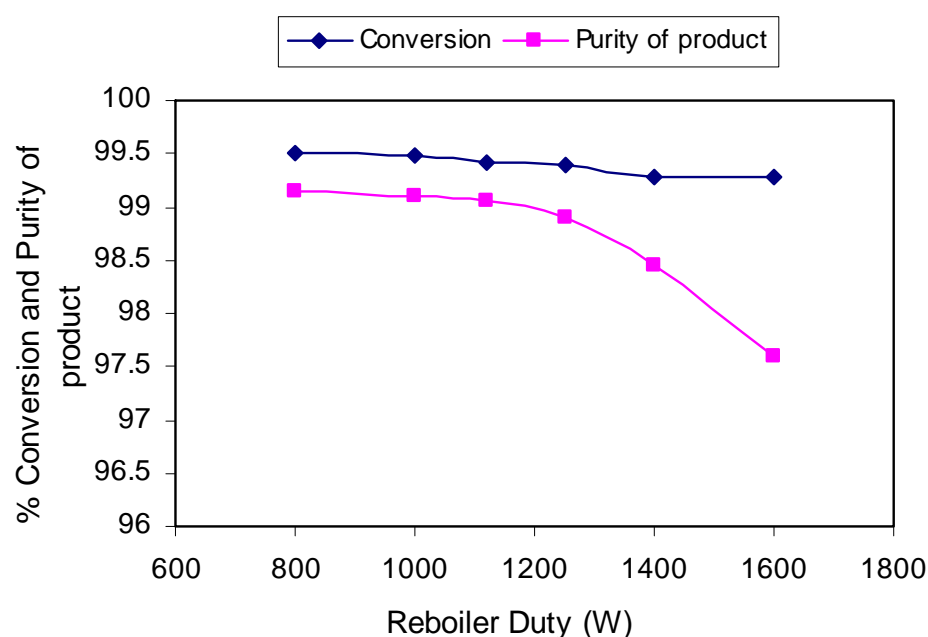
Figure 5.13 Effect of Reboiler Duty on Conversion of Acetic acid and Purity of Bottom Product

In the present system, the relative proportions of organic phase and aqueous phase in the top product decides the reflux ratio and it is

not a variable. The only operating variable that can make significant impact on the separation and reaction is the boil-up rate. Hence, it is decided to study the effect of boil-up rate on conversion over a wide range 0.8 –1.6 kW for excess alcohol in the feed. (Reboiler duty data taken from Table 5.7 for Run number 1, 4, 9, 12, 18 and 20)

Figure 5.13 shows effect of reboiler duty on conversion of acetic acid and purity of bottom product. As it can be seen from the figure that, there is no major effect of change in boil-up rate on the conversion of acetic acid and purity of the product and conversion is more than 99%. It is observed that as a boil-up increase, the amount of alcohol, which is excess in the feed, increases the conversion of top product. As anticipated, the time required to attain the steady state is more for lower boil-up rate.

5.6.3 Effect of Feed Location:

The present work is performed keeping in mind the evaluation of best choice for feed location. The experiments are performed with different feed locations on RD column, i.e. above the catalyst bed, middle of catalyst bed, and below the catalyst bed. (Position 5 to 7 is the reactive zone, See Figure 5.1)

Table 5.7 (Run Nos # 27, 28 and 29) confirms that for Run No # 27, if we introduce acetic acid on position 7 (below catalyst bed) and iso amyl alcohol on position 5 (above catalyst bed), conversion and purity of the product were substantially higher (99.37%), whereas for Run No # 28, conversion and purity decreased to 90.45% and 88.28 % respectively when acetic acid is introduced at position 5(above catalyst bed) and iso amyl alcohol at position 6. (middle of catalyst bed)

Also for Run No # 29, it is observed that, if we reverse the feed location for acetic acid and iso amyl alcohol with reference to Run No # 27, conversion and purity of product is realized only 65.45% and 70.28% respectively. Therefore it is suggested that heavy reactant (iso

amyl alcohol) is fed from the top of the reactive zone (Position 5) and light reactant (acetic acid) is fed from bottom (Position 7) of the reactive zone. Thus provides countercurrent flow of liquid and vapor in RD column.

5.6.4 Effect of Molar Ratio:

The experiments are carried out using different molar ratio of acetic acid to iso amyl alcohol. The molar ratio of acetic acid to iso amyl alcohol is varied from 0.33 to 1.85. For Run No # 3, for this molar ratio of 1.85, only 65.40% conversion of acetic acid is realized, where as for Run No # 16, (in Table 5.7), for molar ratio of 1, 78.90 % conversion of acetic acid is observed. It is observed that optimum molar ratio of acetic acid to iso amyl alcohol is found to be 0.5384 for higher conversion and purity of product.

In summary, the experimental results generated on laboratory reactive distillation column demonstrate that it is feasible to obtain high purity of iso amyl acetate via reactive distillation. It is suggested that one should use acetic acid as limiting reactant. However, it may be noted that large excess of iso amyl alcohol in the feed may also be undesired as one could get impure iso amyl acetate as the bottom product or loose iso amyl alcohol from the top of reactive distillation column through the aqueous phase. The best position for the introduction of the feed is at the top of reactive zone for iso amyl alcohol (Position 5) and below reactive zone for acetic acid (position 7).

5.7 Energy Balance Calculations for the Reactive Distillation Column:

Overall balance for the column is,

$$F = B + D \tag{5.3}$$

Overall enthalpy balance over the column is,

$$FH_F + Q_B = BH_B + DH_D + Q_C + Q_{Loss} \tag{5.4}$$

Where,

$$Q_{Loss} = Q_{Ln} + \overline{Q}_{Lm}$$

Now performing balance over the reboiler section we find the losses in the stripping section as

$$\overline{L}_m H_{Lm} + Q_B = BH_B + \overline{V}_{m+1} H_{Vm+1} \overline{Q}_{Lm} \tag{5.5}$$

Therefore,

$$\overline{Q}_{Lm} = \overline{L}_m H_{Lm} + Q_B - BH_B - \overline{V}_{m+1} H_{Vm+1} \tag{5.6}$$

Thus for our column the equation is,

$$\overline{Q}_{Lm} = \overline{L}_{19} H_{L19} + Q_B - BH_B - \overline{V}_{20} H_{V20} \tag{5.7}$$

Therefore, substituting simulation results from Aspen plus in Eq 5.7 we get,

$$\overline{Q}_{Lm} = 0.21968605 \times (-503682.96) + 5976 - 0.042 \times (-498437.9143) -$$
$$0.1780072 \times (-464157.81)$$

$$\overline{Q}_{Lm} = -1278.368 \, kJ/hr \tag{5.8}$$

To find Q_{Ln}, we do balance along the section from top stage to the end of reactive section as,

i.e. stage 2 to stage 18 and we get,

$$L_1 H_1 + F(H_{F1} + H_{F2}) + V_{19} H_{V19} = Q_{Ln} + V_2 H_{V2} + L_{18} H_{L18} \tag{5.9}$$

Therefore,

$$Q_{Ln} = L_1 H_1 + F(H_{F1} + H_{F2}) + V_{19} H_{V19} - V_2 H_{V2} - L_{18} H_{L18} \tag{5.10}$$

Therefore, substituting simulation results from Aspen Plus in Eq (5.10),

We get,

$$Q_{Ln} = 0.126642 \times (-320787.79) + 0.0525 \times (-797500.6628) + 0.18649843 \times (-457219.17)$$
$$- 0.18996343 \times (-280762.31) - 0.22817729 \times (-496540.85)$$

$$Q_{Ln} = -1130.82 \, kJ/hr \tag{5.11}$$

$$Q_{Loss} = Q_{Ln} + \overline{Q}_{Lm} \tag{5.12}$$

Thus,

$$Q_{Loss} = (-1130.82) + (-1278.368) = -2409.188 \, kJ/hr \tag{5.13}$$

Now using Eq.5.4 we find the condenser duty as,

$$Q_C = FH_F + Q_B - BH_B - DH_D - Q_{Loss} \tag{5.14}$$

Therefore,

$$Q_C = 0.0525 \text{ x } (-797500.6628) + 5976 - 0.042 \text{ x } (-498437.9143)$$
$$- 0.06332 \text{ x } (-330612.6406) - (-2409.188)$$

$$Q_C = 8385.187 \text{ kJ/hr} \tag{5.15}$$

Now, Reflux ratio can be obtained by balancing along the condenser section as,

$$V_2 = L_1 + D \tag{5.16}$$

The enthalpy balance across this section is,

$$V_2 H_{V2} = L_1 H_{L1} + DH_D + Q_C \tag{5.17}$$

Putting reflux term R and relating vapor and liquid streams as,

$$V_2 = (R+1)D \; ; L_1 = RD \tag{5.18}$$

Therefore final equation for reflux ratio becomes,

$$R = \left(\frac{(Q_C/D) + H_D - H_{V2}}{H_{V2} - H_{L1}} \right) \tag{5.19}$$

$$R = \left(\frac{(8385.187/0.06332) + (-330612.6406) - (-280762.31)}{(-280762.31) - (-320787.79)} \right) = 2.06 \tag{5.20}$$

5.8 Material Balance Calculations for the Reactive Distillation Column:

The material balance calculation for the RD column is done considering the feed streams to enter the reactive section only and the molar table with 90% conversion of reactants is calculated as:

The reaction-taking place is:

$$CH_3COOH + C_5H_{11}OH \Leftrightarrow H_2O + C_5H_{11}COOCH_3$$
$$\text{(HOAC)} \quad \text{(ISAMOH)} \quad \text{(WATER)} \quad \text{(ISAMAC)}$$
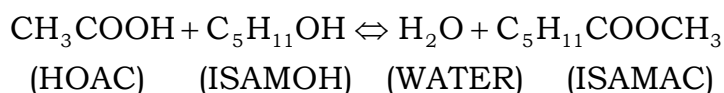
The reaction is in 1:1 stoichiometry. The mass balance calculation is done for each stream and the final mass conservation is done.

Feed stream HOAC:

Basis:

Total molar flow rate of feed = 0.0525 kmol/hr.

The feed contains pure acetic acid.

Therefore acetic acid flow rate = 0.0525 kmol/hr.

The feed stream HOAC table is given as

Table 5.8 Data for Feed Stream: HOAC

Component	Mole Fraction %	M.W.	Molar flow rate kmol/hr	Mass flow rate kg/hr
HOAC	1	60	0.0525	3.15
ISAMOH	0	88	0	0
WATER	0	18	0	0
ISAMAC	0	130	0	0
Total	1		0.0525	3.15

Feed stream ISAMOH:

Total molar flow rate of feed = 0.0525 kmol/hr.

The feed contains pure iso-amyl alcohol.

Therefore iso-amyl alcohol flow rate = 0.0525 kmol/hr.

The feed stream ISAMOH table is:

Table 5.9 Data Feed Stream: ISAMOH

Component	Mole Fraction %	M.W.	Molar flow rate kmol/hr	Mass flow rate kg/hr
HOAC	0	60	0	0
ISAMOH	1	88	0.0525	4.62
WATER	0	18	0	0
ISAMAC	0	130	0	0
Total	1		0.0525	4.62

Distillate stream WATER:

Total molar flow rate of distillate = 0.06332 kmol/hr.

The stream contains all the four components, with water as the major component.

Therefore water flow rate = (mole fraction of water x total flow rate).

Water flow rate = 0.731454 x 0.06332 = 0.046316 kmol/hr.

The distillate stream WATER table is:

Table 5.10 Data for Feed Stream: Water

Component	Mole Fraction %	M.W.	Molar flow rate kmol/hr	Mass flow rate kg/hr
HOAC	0.096209	60	0.006091954	0.365517233
ISAMOH	0.097653	88	0.006183388	0.54413814
WATER	0.731454	18	0.046315667	0.833682011
ISAMAC	0.074684	130	0.004728991	0.614768814
Total	1		0.06332	2.358106199

Bottom stream ISAMAC:

Total molar flow rate of bottom = 0.06332 kmol/hr.

The stream contains all the four components, with iso-amyl acetate as the major component.

Therefore iso-amyl acetate flow rate = (mole fraction of iso amyl acetate x total flow rate).

Iso-amyl acetate flow rate = 0.99780542 x 0.04167885 = 0.0415873 kmol/hr.

The bottom stream ISAMAC table is:

Table 5.11 Data for Feed Stream: ISAMAC

Component	Mole Fraction %	M.W.	Molar flow rate kmol/hr	Mass flow rate kg/hr
HOAC	0.00219452	60	9.14651E-05	0.005487904
ISAMOH	5.55E-08	88	2.31318E-09	2.0356E-07
WATER	4.11E-15	18	1.713E-16	3.0834E-15
ISAMAC	0.99780542	130	0.041587382	5.406359716
Total	0.999999996		0.04167885	5.411847824

Overall material balance:

Total feed In (kg/hr) = (Total HOAC mass flow rate) + (Total ISAMOH mass flow rate)

Total Feed In (kg/hr) = (3.5) + (4.62) = 7.77 kg/hr.

Total Feed Out (kg/hr) = (Total Water mass flow rate) +(Total ISAMAC mass flow rate)

Total Feed Out (kg/hr) = (2.3510) + (5.4118) = 7.769 kg/hr

Therefore,

Total feed In (kg/hr) $\equiv$ Total product Out (kg/hr).

CHAPTER 6

RESULTS AND DISCUSSIONS

6.1 Introduction

In this chapter discussion on results are presented. The experimental results obtained from continuous reactive distillation column (CRD), (as discussed in Chapter 5) are compared with simulation results predicted by three equilibrium stage models of different depths (Model #A, Model # B and Model #C) using Aspen Plus software.

Three types of equilibrium stage models with different complexity are developed, parameterized and compared in simulations in the present work. These models are based on the stage concept and use the assumption of vapor–liquid equilibrium on each stage. In Model # A, it is furthermore assumed that chemical equilibrium is reached on each stage, in Model# B, phase equilibrium and chemical reaction kinetics in the liquid phase is considered. In Model #C, in addition to considerations of phase equilibrium and chemical reaction kinetics in the liquid phase, decanter model is employed. In these models liquid phase non-idealities are taken into account by the NRTL-model and the gas phase is assumed to be ideal. Since esterification reaction is carried out at atmospheric pressure, the vapor phase nonideality considered is the dimerization of acetic acid as described by the Hayden-O'Conell second virial coefficient model. The Aspen Plus built-in association parameters are employed to compute fugacity coefficients. Reaction rates for Pseudohomogenous model calculated by laboratory batch reactor are used for simulation to yield a steady state solution.

For simulation work, we have used MATLAB and Aspen Plus software.

6.2   Simulation Work:

The procedure for the development of reactive distillation processes applied here can be divided into four steps. In the first step, the thermodynamic properties of the system are investigated to obtain a reliable description of liquid-phase nonideality that can be used for a preliminary feasibility analysis. Then, the reaction kinetics is investigated at conditions that are expected for the reactive distillation column. These results can be combined, and a simulation environment based on an equilibrium stage model can be employed. Experiments in a reactive distillation column on a laboratory scale are carried out subsequently to verify the simulation. Finally, simulation studies can be used to identify the role of important design parameters (e.g., numbers of reactive and nonreactive stages, number and location of feed positions, flow rate, reboiler duty) and to propose an optimal setup.

Therefore first results of simulations are presented and then simulation results obtained from Aspen Plus are used to validate three models developed viz Equilibrium stage Model # A, Model # B and Model # C with experimental results obtained in RD column.

This work considers the production of iso amyl acetate by reactive distillation. The research is focused on identifying suitable process conditions and limitations for the synthesis of iso amyl acetate. Simulation is used with equilibrium-stage model to identify optimum processing strategies. Adjustment of the design variables is performed to iteratively check the column performance.

In this chapter, the simulation results for reactive distillation of iso amyl alcohol and acetic acid to synthesize iso amyl acetate are presented and discussed in a systematic manner. A tiered approach is used in the modeling efforts. The feed flow rates employed for these simulations are ranges from 0.0175 kmol/hr to 0.07 kmol/hr (1 lph to 4 lph). The comparisons are based on the obtained temperature and

composition profiles. The system is first modeled considering physical and chemical equilibrium (Model #A). Physical equilibrium with a kinetically controlled reaction is incorporated in Model # B (without decanter) and Model # C. (with decanter). Finally the feasible design is obtained using the equilibrium stage model # C.

6.2.1 Assumptions regarding Column Configuration and Models

For reactive separation processes, modeling is required to describe and predict the reaction and separation that occur simultaneously. To study RD esterification for present system, reliable models are essential in order to reduce the development time and expensive experimental investigations. In this respect, traditional equilibrium-based models are used.

A number of assumptions concerning column configuration are used for the equilibrium model employed in this work. The distillation column is assumed to contain N stages/segments; the condenser is stage/segment 1 and the reboiler is stage/segment N. A total condenser is used. No reaction takes place in the condenser or in the reboiler. The chemical reaction is assumed to be a pseudo-homogeneous reaction that occurs in the liquid phase, with the reaction rate a function of temperature, composition and pressure.

The equilibrium model in this study consists of the conventional MESH equations (as discussed in Chapter 3) with implicit assumptions that are detailed here. Physical equilibrium is achieved on each stage. The liquid phase is well mixed. Pressure and temperature are assumed constant at each stage and are uniform throughout the liquid and vapor phases present. However, both pressure and temperature can vary from one stage to another stage.

In order to reduce the experimental work, reliable and accurate process simulation tools can be used for obtaining useful information needed for the design. In the present study, the simulation is carried

out using equilibrium stage model, RADFRAC available in Aspen Plus software package.(Version 7.0, 2007, Aspen Tech, Inc.) RADFRAC module in the steady-state simulator Aspen Plus (Version 2007) is based upon a rigorous equilibrium stage model for solving the mass balance, phase equilibrium, summation and energy balance (MESH) equations.

Physical and chemical properties for all species are taken from Aspen Plus component database. The reaction kinetics measured and evaluated in the laboratory kinetic studies is incorporated into the model. The modeling of the decanter is achieved by the Decanter model of Aspen Plus. The equilibrium constant is taken from Chiang et al, (2002).

The feed flow rate of both reactant, viz acetic acid and iso amyl alcohol is varied from 0.0175 kmol/hr to 0.07 kmol/hr and a feasible design is obtained. The reflux ratio is increased in order to reduce the catalyst volume required. The reboiler duty is also increased. The set conversion of iso amyl acetate (0.99) in the bottom is achieved with a reflux ratio of 2. Reflux has a twofold purpose in reactive distillation. Increasing reflux rate enhances separations and recycles unreacted reactants to the reaction zone and, thereby, increases conversion. As a result of the increasing reflux ratio several effects occurs in reactive distillation column: (i) the concentrations of reactants in the distillate are reduced; (ii) the reaction zone temperatures are reduced. It was observed that non-convergence of the simulation with higher value of reflux ratio.

When the catalyst volume is reduced, higher temperatures are found in the section closer to the condenser. Even though the reflux ratio and the condenser duty are increased with respect to the ideal design, the condenser did not cool the vapor leaving the top of the packing to ambient temperature. This is due to the smaller reaction volume as compared to the ideal case. Changing the number of stages

in either the reactive or non-reactive zones, did not result in an improved design when the total height of reaction and stripping zone were kept constant. An increase in the number of stages resulted in flat mole fraction profiles, which indicated that these regions are accomplishing little to no separation.

Another important consideration is to know the system behavior at the operating conditions: existence of azeotropes, VLE, properties and residue curve maps, distillation line diagrams, if available, and reliable thermodynamic and kinetic models. All these tools will give a description of the system and will help to predict its performance. Details for the physical properties and the phase equilibrium data of the iso amyl acetate system are presented in Chapter 4. For every system, the final objective is to find a reaction zone and feed location that accomplishes the purity specifications of the products and maximizes the rate by allowing a high concentration of reactants in the reaction zone. The definition of the feed and reaction zone location will depend on how well the system behavior is known, the volatilities of the reactants and products, the specifications of the distillate and bottoms, the characteristics of the reaction, and other considerations described in more detail in Subawalla and Fair (1999).

6.2.2 General Procedure for the Design of Reactive Distillation:

Unlike conventional distillation, detailed design of reactive distillation (minimum number of stages, minimum number of reactive stages, feed locations etc.) is less apparent. (Chiang et al, 2002) Sneesby et al, (1997) presented a design procedure for the ETBE reactive distillation system. Subawalla and Fair (1999) proposed a general design procedure for reactive distillation.

Chiang et al, (2002) outlined the general design procedure for reactive distillation, which is given in the following steps:

1) Fix the number of reactive trays ($N_{Rxn)}$ and guess the numbers of trays in the stripping and rectification sections (N_S and N_R, respectively).

2) Determine the minimum number of trays in the stripping and rectification section ($N_{S, min}$) from the short cut design with a desired specification of iso amyl acetate (99%) and set $N_S = 2$ $N_{S,min}$.

3) Increase the number of trays in the rectification section (N_R) until the top product specification (99% water) is met.

4) Repeat steps 2 and 3 until N_S converges (usually N_S does not change much for different N_R values)

5) Compute the total annual cost (TAC)

6) Change the minimum of reactive trays ($N_{Rxn) so}$ that the TAC is minimized.

6.2.3 Design Options- Reaction Zone

When iso amyl alcohol and acetic acid is fed to the reactive distillation unit, it contacts the catalyst and reacts selectively to form iso amyl acetate and water. Since water is the low boiling component and the lightest product, it will concentrate in the vapor phase and eventually leave the column as the major component of the distillate. In contrast, iso amyl acetate is the high boiling component and it will concentrate in the liquid phase, descending through the column to be removed as the bottom product from the reboiler.

At the beginning of this work, two designs were considered for reactive distillation in the system under study.

In the first design, a column with a total condenser is selected. Preliminary simulations are performed and convergence was feasible. However, the design is discarded since in the condenser, two immiscible phases are formed, an aqueous phase i.e. almost pure water and an organic phase containing water, amyl alcohol and amyl

acetate. When a total condenser is used, the overhead product is condensed, with a portion returned to column as reflux. It is difficult to maintain constant level of aqueous phase. This affects the reflux rate to the column and also affects the top temperature. General rules of thumb recommend the selection of a condenser pressure that allows ambient temperature water as the coolant.

In the second design, a reactive distillation column with a partial condenser is selected. In this design, the condenser with decanter (Phase separator) is used so as to allow condensation of the water from the vapor stream entering the condenser, and organic phase from decanter is recycled to the column as reflux. In this case the aim of the liquid-liquid separator is not product enrichment, but a withdrawal of the aqueous phase and a recycle of non-converted organic components to the column. The reaction zone is positioned as the middle section of the column. The positioning of the reaction zone within the column depends not only on the relative volatilities of the reactants and products, but also on the type of reaction.

The feed, consisting iso amyl alcohol and acetic acid is fed directly to the reaction zone in order to maximize its concentration in this region. Simulations are performed to examine the effect of feed location. For optimum conversion of iso amyl acetate the best feed location is identified as stage 10 for iso amyl alcohol (from top of the reactive zone) and stage 15 for acetic acid. (from bottom of the reactive zone)

Column diameter depends on the pressure drop, liquid and vapor loading and percentage of flooding allowed. The reactive distillation column diameter is set to 50 mm. Columns with variable diameters are rejected because the maximum divergences considering all column sections are about 8%. (Kister, 1992) For the non-reactive zone, initial estimates for the theoretical stripping stages and reflux ratio are taken from the short cut method simulations. The short cut

method for conventional distillation is employed with the Fenske equation for estimation of the minimum number of stages, the Underwood equation for minimum reflux estimation, the Gilliland correlation for the number of stages at finite reflux and the Fenske correlation for feed tray location.

An option to increase conversion in reactive distillation processes is to increase the column pressure and, thereby, to increase the temperature in the reactive section leading to an enhancement of the reaction rate. This is not possible using T-63, ion exchange resin as catalyst for this reaction because the increase in the column pressure would result in temperatures inside the reactive section of the column that are significantly above 408 K, which is the maximum operating temperature for the catalyst recommended by the manufacturer. Therefore column and condenser pressure is set at 1 atm.

6.2.4 Process Development and Simulation

Simulations with the equilibrium based model with bulk reaction kinetics in liquid phase (Model #C) are performed. For the reactive zone, the number of reactive stages is first specified as one, and the number of reactive stages is increased up to a maximum of 10. The initial estimate for the catalyst volume is obtained from reactor design for reactive distillation assuming reactive section to be a packed bed reactor (PBR). The detailed analysis is given in section 4.5.3 of Chapter 4. This represents the minimum catalyst volume required. This volume was split and distributed on the reactive stages. Since the conversion achieved was small, the catalyst volume was increased and the conversion increased to 0.99.

Figure 6.1 shows a basic process flow diagram and optimum design and operating parameters obtained for iso amyl acetate synthesis via reactive distillation.
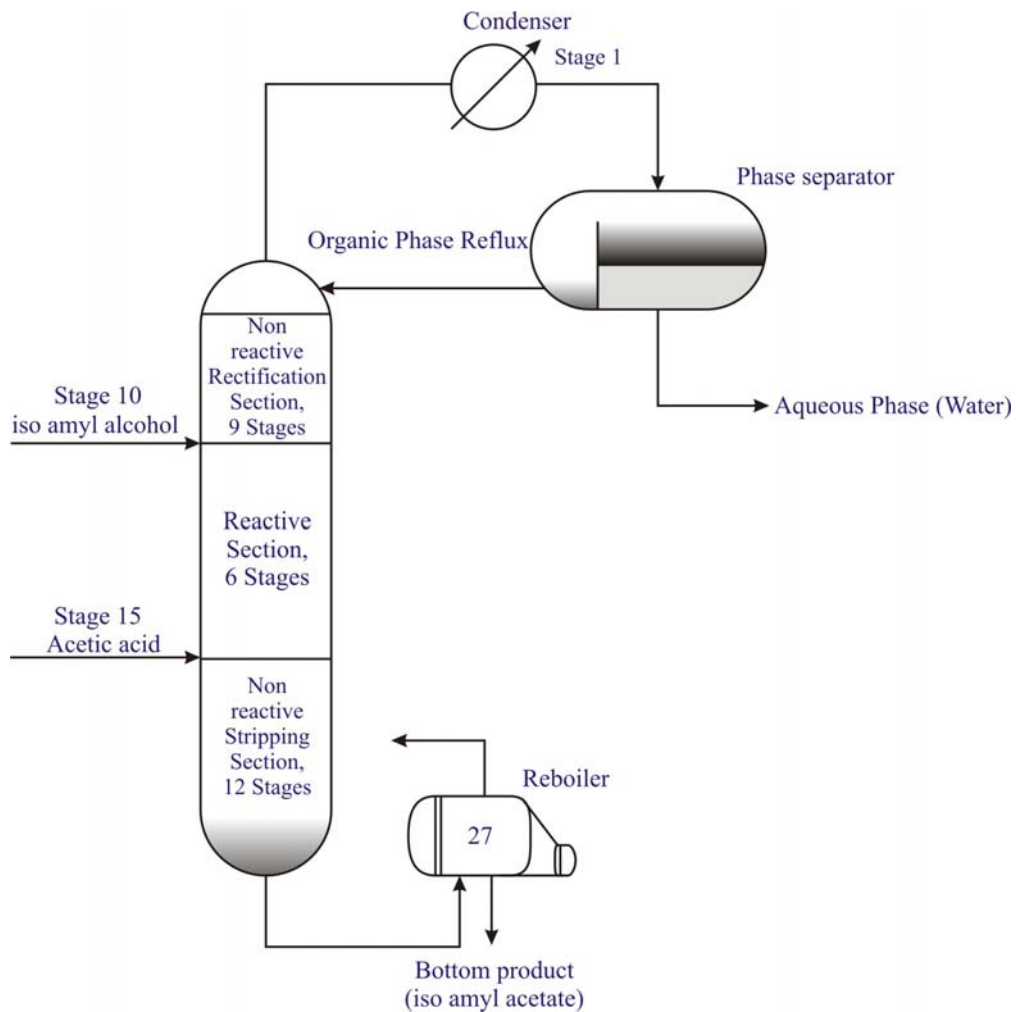
Figure 6.1 Reactive Distillation Process for synthesis of iso amyl acetate

Table 6.1 summarizes the feasible design obtained for the iso amyl acetate case under study.

Table 6.1 Design and Operating Parameters for the iso amyl acetate Reactive Distillation System.

Description	Equilibrium Stage Model # C
Total Number of Stages	27
Total packed height (m)	2.75 m
Number of Stages (reactive)	6
Number of Stages (stripping)	12
Number of Stages (rectification)	9
Reactive zone, height (m)	1 m
Stripping zone, height (m)	1 m
Rectification zone, height (m)	0.75 m
Column diameter (m)	0.05
Reflux ratio	2
Feed location for iso amyl alcohol (Top of reactive zone)	10
Feed location for acetic acid (bottom of reactive zone)	15
Reboiler duty (kw)	1.2
Mole fraction of iso amyl acetate (bottom)	0.99
Mole fraction of Water (top)	0.9915

6.3 Simulation Results:

In this section simulation results for Equilibrium stage model# A, model# B and Model # C are presented. For equilibrium model # B, we have simulated reactive distillation column without decanter and for Model # C with decanter. All the simulations are performed using steady state simulator.

6.4 MATLAB Results

The model equations (Model # B) form a mixed set of set of ordinary differential equations (ODE's) and algebraic equations. The equations for 27 stages and four-component system can be solved in

MATLAB by ODE 15 S solver (which is an ordinary differential and algebraic equation solver for stiff equations, variable order method)

The steady state composition profile obtained from MATLAB[TM] for four components, viz, acetic acid (HOAC), iso amyl alcohol (ISAMOH), iso-amyl acetate (ISAMAC) and Water (H$_2$O) are as shown in Figure 6.2.
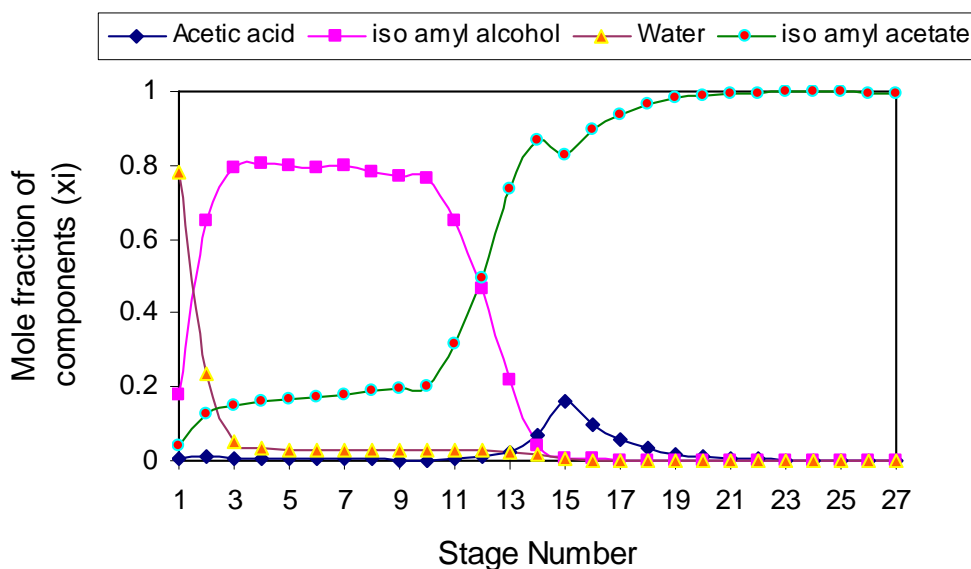
Figure 6.2 Steady state composition profiles by MATLAB (Model # B)

Figure 6.2 shows the mole fractions of acetic acid, iso amyl alcohol, iso amyl acetate and water in the liquid phase. In the reaction zone (stages 10 to 15), iso amyl alcohol is consumed, and as a result, its mole fraction decreases. Stages 15 and 16 show the transition between the reaction and stripping zones in the column. In the stripping zone, iso amyl acetate and iso amyl alcohol are being separated, resulting in the higher concentration of iso amyl acetate in the bottoms. High mole fractions of iso amyl acetate are obtained in the liquid phase. This is desirable since iso amyl acetate is the product of interest.

6.5 Aspen Plus Simulation:

6.5.1 Simulation Results for EQ stage Model # A:

The simulation was begun by putting together a basic flow sheet of a RADFRAC column with input streams of acetic acid and iso amyl alcohol and output streams on iso amyl acetate and water. The basic process flow sheet for iso-amyl acetate synthesis in Aspen Plus environment is as shown in Figure 6.3.
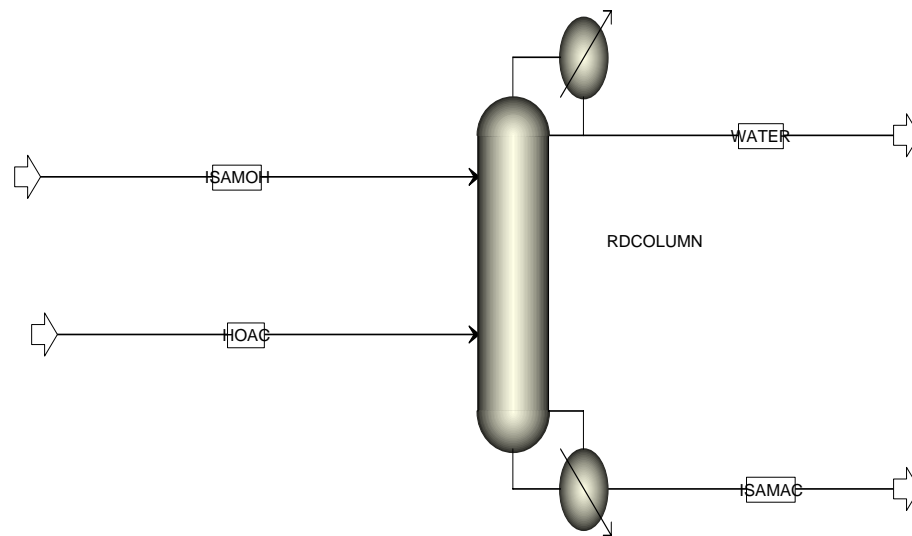
Figure 6. 3 RADFRAC model for iso-amyl acetate synthesis (Model # A)

All the components that would be involved in the reactive distillation are chosen from the Aspen Plus component database. The NRTL model is selected as the property method for this simulation.The VLE data obtained from experiments is first put into separate data regression worksheets in the Aspen Plus user interface. Once this is done, Aspen Plus calculates the temperature dependent binary parameters for each of the six binary systems. Reaction rates for Pseudohomogenous model calculated by laboratory batch reactor are used for simulation to yield a steady state solution. The feed location for iso amyl alcohol and acetic acid is kept at stages 10 and 15 respectively with isoamyl acetate being removed as bottom product at the 27th stage and the water as top product at the 1st stage. The operating pressure of the column and the condenser pressure is also set at 1 atm.

Base specification in Aspen Plus Simulation:

(Data Corresponding to Run No # 10, in Table 5.7 of Chapter 5)

Molar flow rates:

Feed 1 (Acetic acid)	:	0.03200 kmol/hr
Feed 2 (iso amyl alcohol)	:	0.03500 kmol/hr
Mole ratio (Acetic acid/ Alcohol)	:	0.5384
Reboiler Duty	:	1.12 kW
Pressure	:	1 atm
Number of stages	:	27
Reactive zone stages	:	10-15
Stripping section stages	:	16-26
Rectification section stages	:	2-9
Feed stage location:	:	
Feed 1 location (Acetic acid)	:	15 (below reactive zone)
Feed 2 location (iso amyl alcohol)	:	10 (above reactive zone)

It may be noted that all the base specifications given above is used for simulation of RD column for three different models, viz, Model # A, Model # B, Model # C in the following section.

The composition profile obtained from Aspen Plus simulation for four components, viz, acetic acid (HOAC), iso amyl alcohol (ISAMOH), iso-amyl acetate (ISAMAC) and Water (H_2O) are as shown in Figure 6.4.
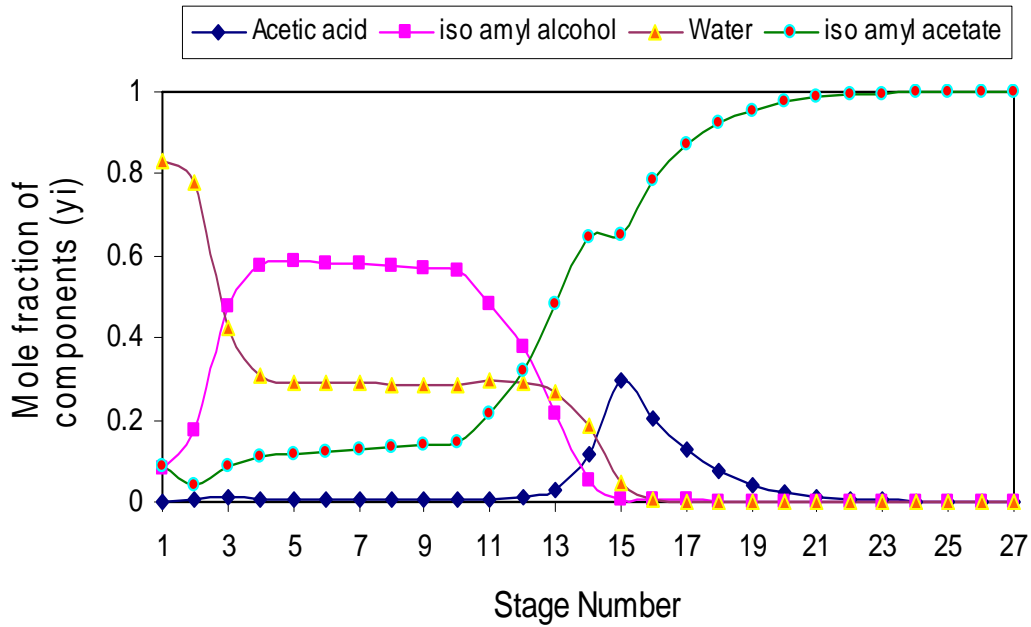
Figure 6.4. Steady State Composition Profile for Vapor Phase (Model # A)

Figure 6.4 shows the component mole fraction profile for the vapor phase. Acetic acid is observed to be the predominant component in the vapor phase in the reaction zone. A high mole fraction of acetic acid is achieved. This demonstrates that acetic acid can easily be separated in the partial condenser. The mole fraction of acetic acid reaches a maximum on stage 15. From this stage to either end of the distillation column, the mole fraction of acetic acid decreases, with minimum values in the condenser and the reboiler.

In contrast, the mole fraction of iso amyl acetate is opposite to that of acetic acid. Iso amyl acetate is mostly present in the stripping zone; its large mole fraction in the bottoms corresponds to the composition of the boil up from the reboiler.
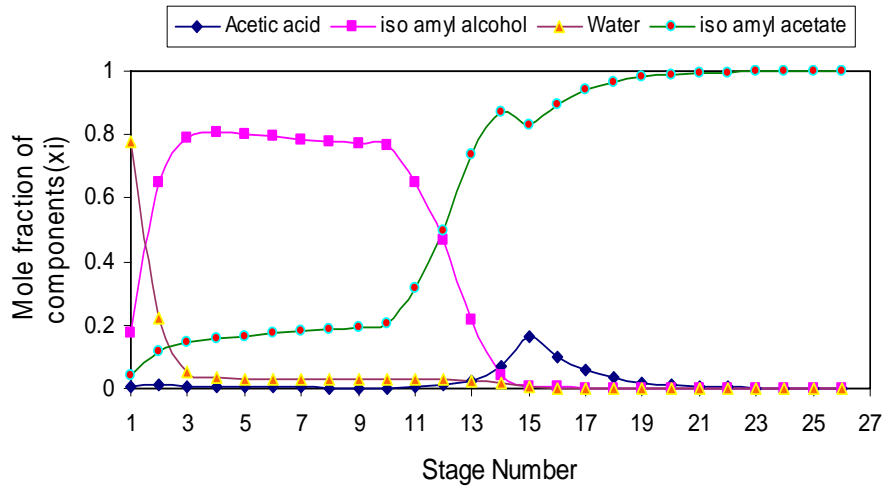
Figure 6.5 Steady State Composition Profile for Liquid Phase (Model #A)

Figure 6.5 shows the mole fractions of acetic acid, iso amyl alcohol, iso amyl acetate and water in the liquid phase. In the reaction zone (stages 10 to 15), iso amyl alcohol is consumed, and as a result, its mole fraction decreases. Stages 15 and 16 show the transition between the reaction and stripping zones in the column. In the stripping zone, iso amyl acetate and iso amyl alcohol are being separated, resulting in the higher concentration of iso amyl acetate in the bottoms. High mole fractions of iso amyl acetate are obtained in the liquid phase. This is desirable since iso amyl acetate is the product of interest.
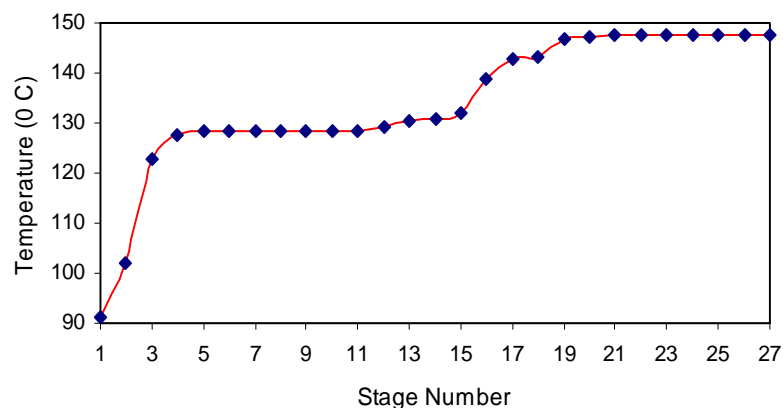
Figure 6.6 Steady State Temperatures Profile (Model # A)

Figure 6.6 shows the temperature profile obtained when the equilibrium model # A is employed. The reaction zone was located at the middle of the column and is comprised of stages 10 to 15. The remaining stages are pure separation stages. A smooth temperature profile is observed in the reactive zone where the catalyst is located. An important region is the reactive zone, where the catalyst is located.

In this region, the temperature profile is extremely important because temperature extremes in this region can accelerate deactivation of the catalyst and thereby, decrease its performance. It may be noted that the temperature range in the reactive zone is good enough for the thermal stability of catalyst. (135^0C). The larger temperatures in the bottom are due to the presence of iso amyl acetate, which has a significantly higher molecular weight, and thus, a higher boiling temperature. (147^0C)

6.5.2 Simulation Results for Model # B (Without Decanter)

In this model physical equilibrium is assumed on each stage and the reaction kinetics at each stage was described by a second order reaction. As discussed in Chapter 5, in the condenser, two immiscible phases are formed, an aqueous phase i.e. almost pure water and an organic phase containing water, amyl alcohol and amyl acetate. The organic phase is recycled back to column as reflux. However in this model does not account for decanter for separation of two immiscible phased that are formed in the condenser.

The simulation is begun by putting together a basic flow sheet of a RADFRAC column with input streams of acetic acid and iso amyl alcohol and output streams are iso amyl acetate and water. All the components that would be involved in the reactive distillation are chosen from the aspen plus component database. A Pseudohomogenous reaction kinetics model is used to describe the rate equation. The NRTL model is selected as the property method for this simulation. The basic process flow sheet for iso-amyl

acetate synthesis in Aspen Plus environment for this model is as shown in Figure 6.7. All the simulations are performed using steady state simulator (Aspen Plus)
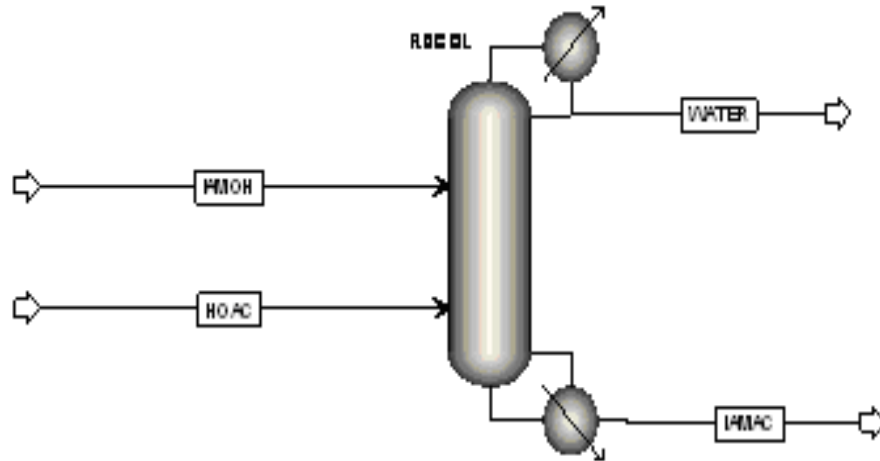
**Figure 6.7 RADFRAC Model for iso-amyl acetate Synthesis
(Model # B: Without Decanter)**

The steady state composition profile for vapor phase and liquid phase are as shown in Figures 6.8 and 6.9.
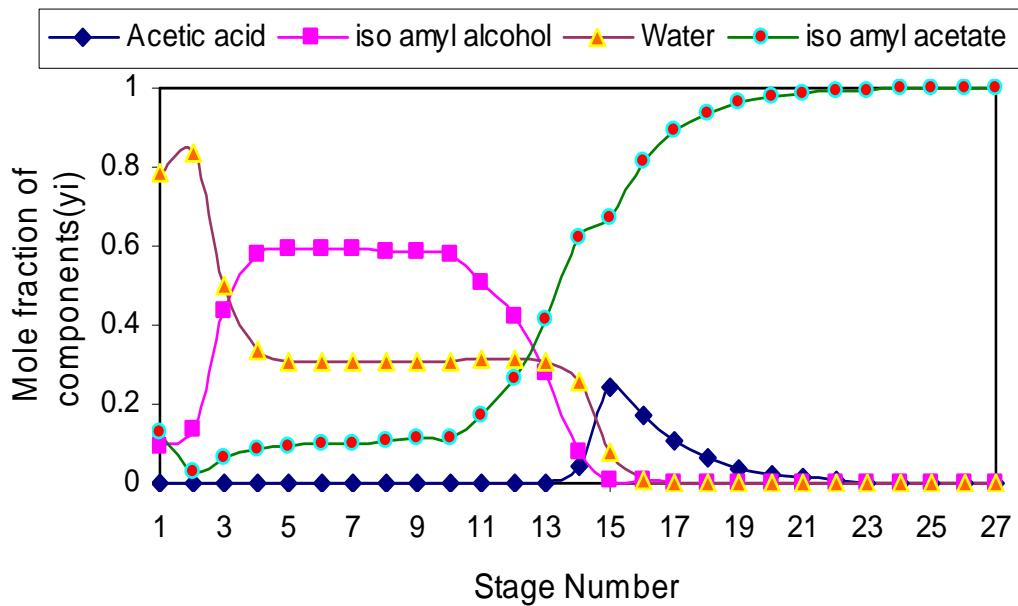
**Figure 6.8 Steady State Composition Profile for Vapor Phase
(Model # B: without Decanter)**
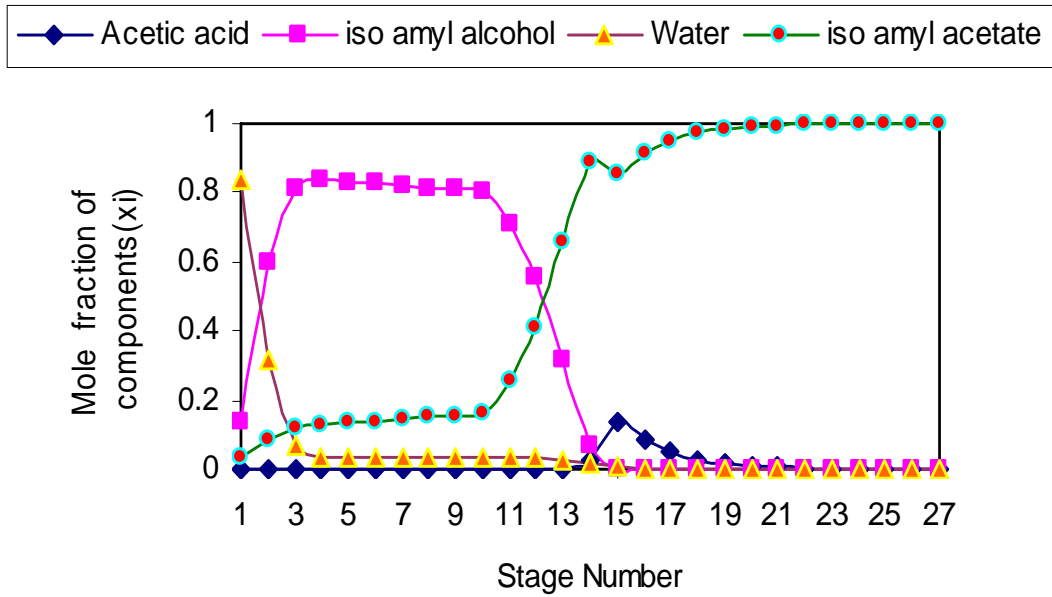
Figure 6.9 Steady State Composition Profile for Liquid Phase
(Model # B: without Decanter)

The steady state temperature profile is as shown in Figure 6.10
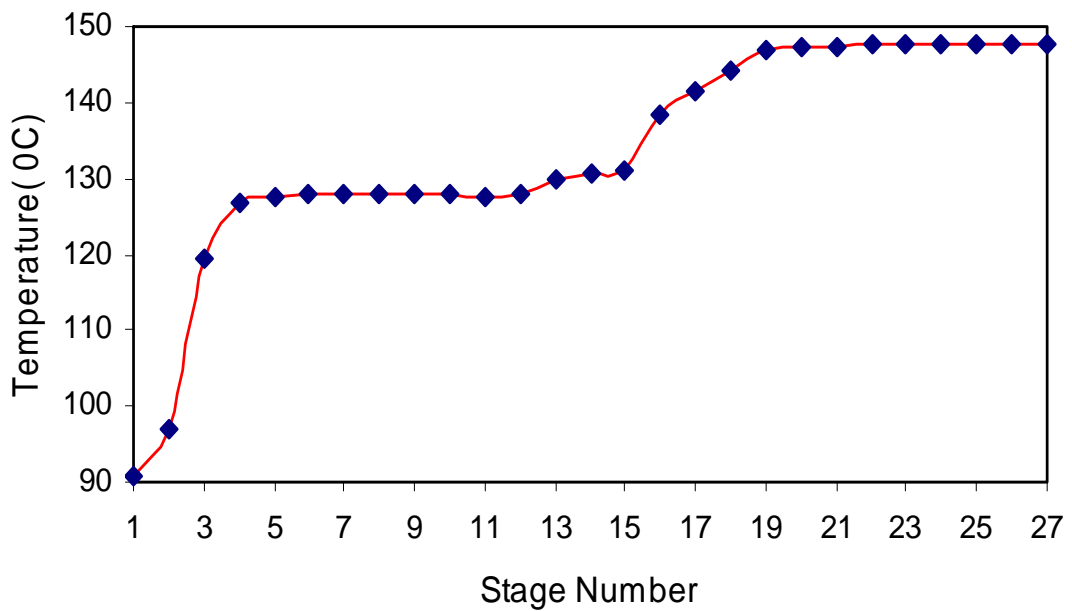
Figure 6. 10 Steady State Temperature Profile
(Model #B: without Decanter)

6.5.3 Simulation Results for Model # C (With Decanter):

In this model physical equilibrium is assumed on each stage and the reaction kinetics at each stage is described by a Pseudohomogenous reaction kinetic model. In this model, decanter is used for separation of two immiscible phased that are formed in the condenser. The basic process flow sheet for iso-amyl acetate synthesis in Aspen Plus environment for this model is as shown in Figure 6.11.
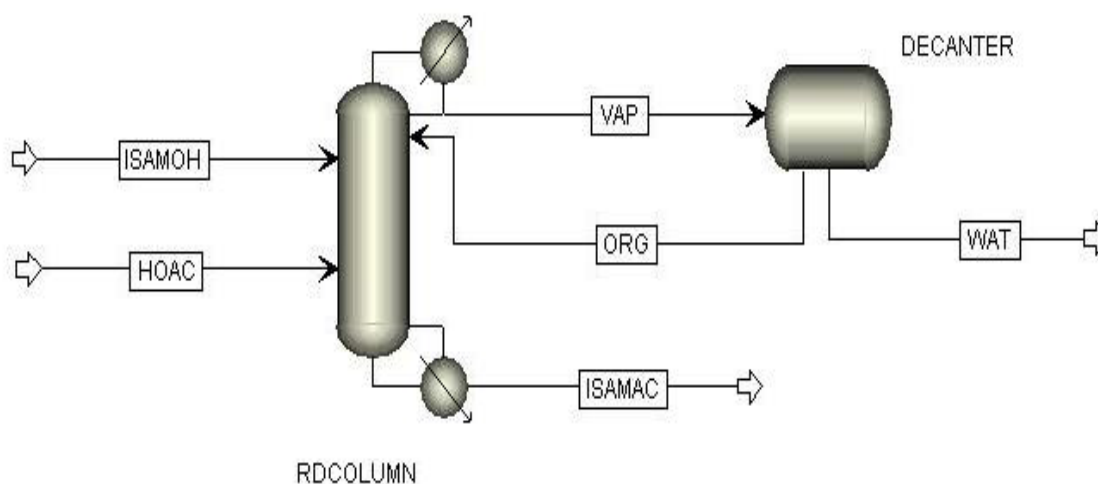
**Figure 6.11 RADFRAC Model for iso-amyl acetate Synthesis
(Model # C: With Decanter)**

The iso amyl acetate reactive distillation column is simulated using decanter. A Pseudohomogenous kinetics model is used to describe the rate equation. The decanter model of Aspen Plus is used for the decanter simulation. All the simulations are performed using steady state simulator.

The typical steady state composition profile for vapor and liquid phase are shown in Figure 6.12 and 6.13.
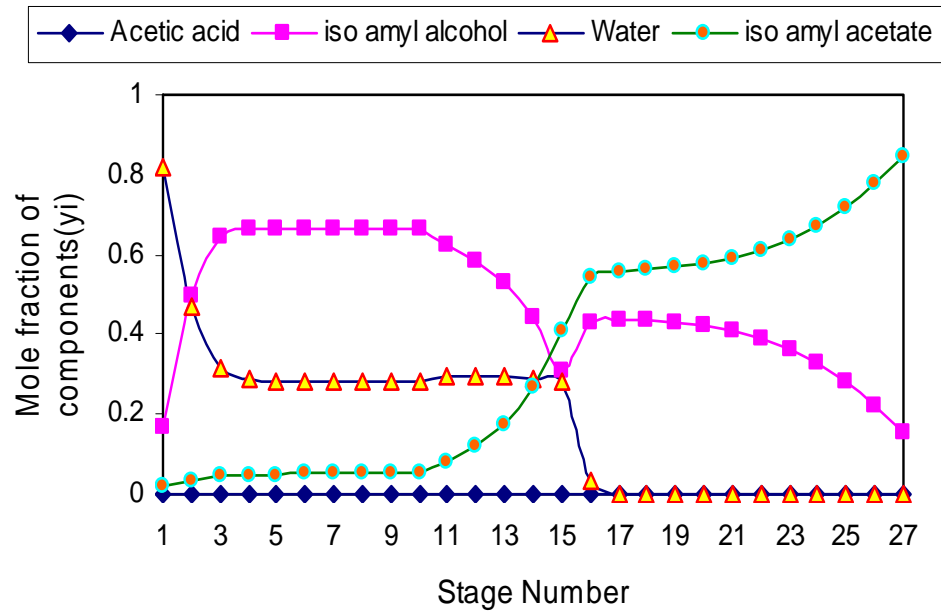
Figure 6.12 Steady State Composition Profile for Vapor Phase (Model # C)
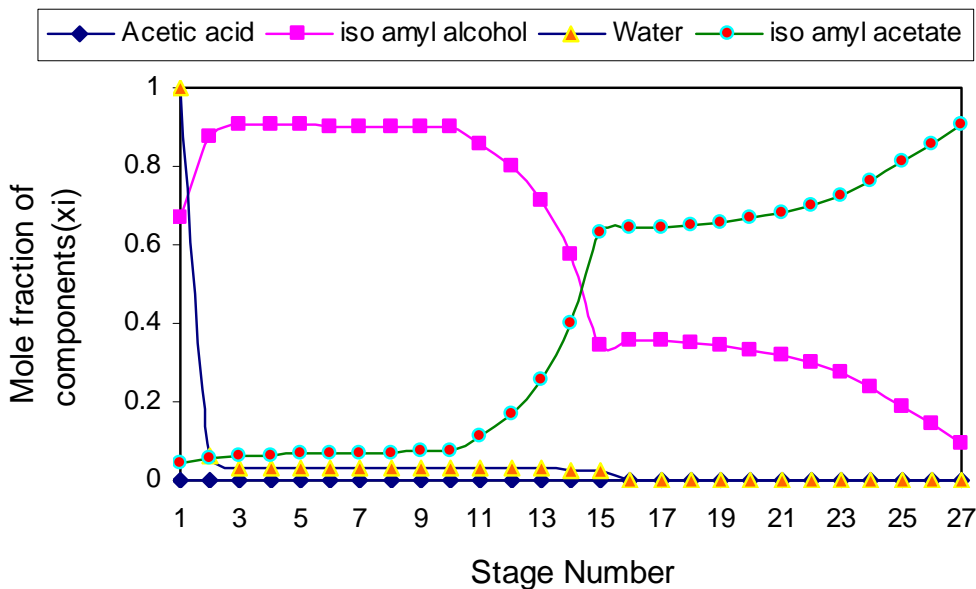
Figure 6.13 Steady State Composition Profile for Liquid Phase (Model # C)

The steady state temperature profile is as shown in Figure 6.14.
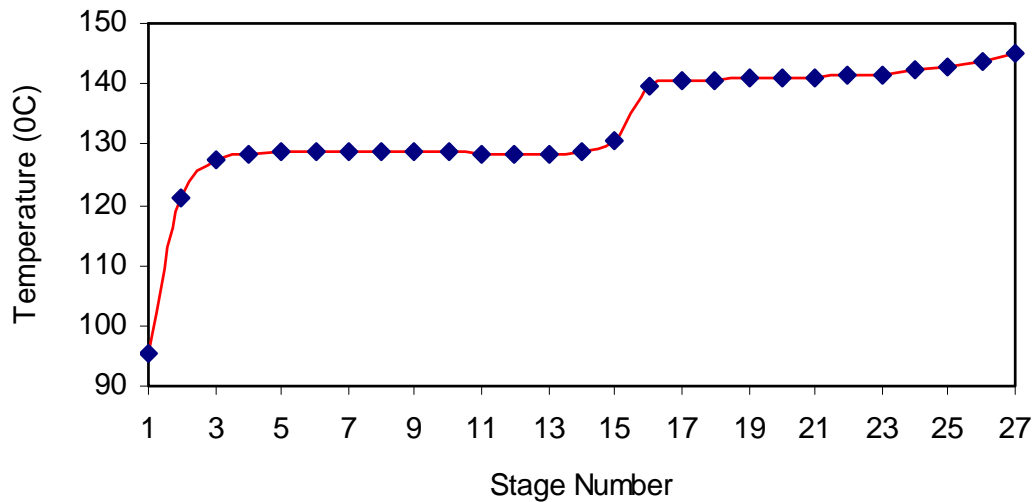
Figure 6.14 Steady State Temperature Profiles (Model # C)

6.6 Comparisons of Experimental Results with Model Predictions (RUN NO # 10)

Table 6.2 Details of the RD Experiment for Run No # 10

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.03200	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.03500	kmol/hr
3	Mole ratio, acid/alcohol	0.5384	-
4	Reboiler duty	1.12	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Reactive Stages on RD column	Position 5 to 7	
7	Conversions in terms of acetic acid	99.50	%
8	Bottom product composition (mole fractions)	iso amyl acetate = 0.993	-
9	Top product compositions (mole fraction)	Water = 0.9845	-
10	Purity of bottom product	98.15	%

The model predictions were compared with experimental results for a typical representative RD run (Run No #10), which is as shown in Figures 6.15 and 6.16.
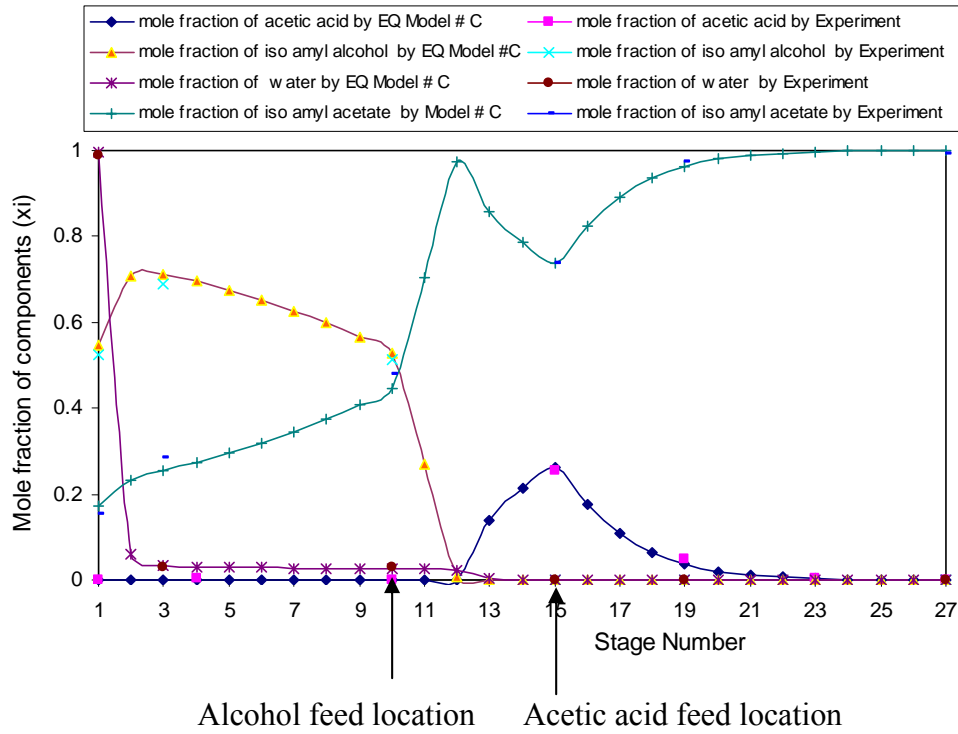
Figure 6.15 Comparisons of Aspen Plus Simulation and Experimental Results for Composition Profiles (Run#10) (Model #C)
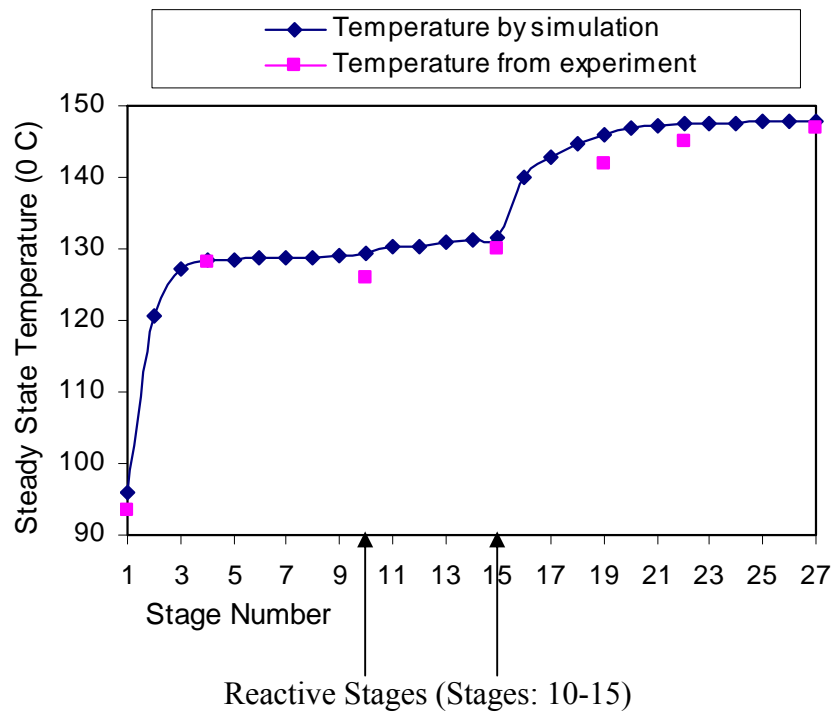
Figure 6.16 Comparisons of Aspen Plus Simulation and Experimental Results for Temperature Profile (Model # C) (Run#10)

The temperature and composition profiles for this system from the equilibrium model are compared with experimental data under the same conditions. Comparison of the experimental data with simulation results indicated that an equilibrium stage model is capable of describing the column profiles quantitatively. The same model (Model # C with decanter) and simulator are used further to predict the performance of the column.

6.6.1 Model Validation

In order to use the RADFRAC model from Aspen Plus for simulating a reactive distillation with confidence, the reliability of the model is tested by comparing the simulation results obtained with Model # C with the experimental data obtained on laboratory scale RD column. With the experimental results obtained under different operating conditions (see Table 5.7, as shown in Chapter 5) are compared with results of the simulation run and is presented in Appendix 1. It can be seen that the steady state composition profiles in the distillate and the bottom product and temperature profiles predicted by Aspen Plus, are in good agreement with the experimental data. The small difference may be due to the modified kinetic parameters that are based on the mole fraction rate expression.

Chiang et al, (2002) investigated the design alternatives for iso amyl acetate process with coupled reactor/ column and reactive distillation based on Total Annual Cost (TAC). Saha et al, (2005) have studied the performance of the present system in RD column with dilute acetic acid. It is realized that the experimental data on the system, pure acetic acid and iso amyl alcohol as feed to the column is limited and does not cover a wide range of operating parameters, such as reboiler duty, feed locations, feed flow rate, and molar ratio. Moreover, the column composition and temperature profiles, which helps to explain some important results, have not been reported in

their studies. Hence following section discusses all these issues for the present system.

6.7 Effect of Operating Parameters through Simulation Studies:

In this section, effect of various operating parameters on reactive column performance is discussed using simulation studies of equilibrium Model # C with decanter (phase separator), unless, otherwise mentioned.

It is challenging to cover a wide range of operating parameters in the experimental studies for reactive distillation in the laboratory. Therefore, it is decided to study this aspect with the help of validated model, through simulation work. The effect of various operating parameters such as the feed flow rate, feed stage location, reboiler duty, the number of reactive and nonreactive stages, molar ratio of reactants are studied with the help of simulation.

6.7.1. Effect of Feed Flow Rate:

In a catalytic RD process, the reaction occurred in the presence of a solid catalyst. The catalyst is placed in a packing to ensure high reaction rates while simultaneously allowing adequate flow of liquid and vapor in countercurrent mode. The aim was to optimize residence time of reactants in catalytic section of the column while minimizing pressure drop through the catalyst bed. In case of heterogeneous RD columns, the residence time of the RD column depends on the design of the column internal used, catalyst mass in the reactive zone and reflux ratio (Subawalla and Fair, 1999). The residence time for the reactants inside the reactive zone was strongly influenced by the flow rates of the acetic acid and iso amyl alcohol as feed.
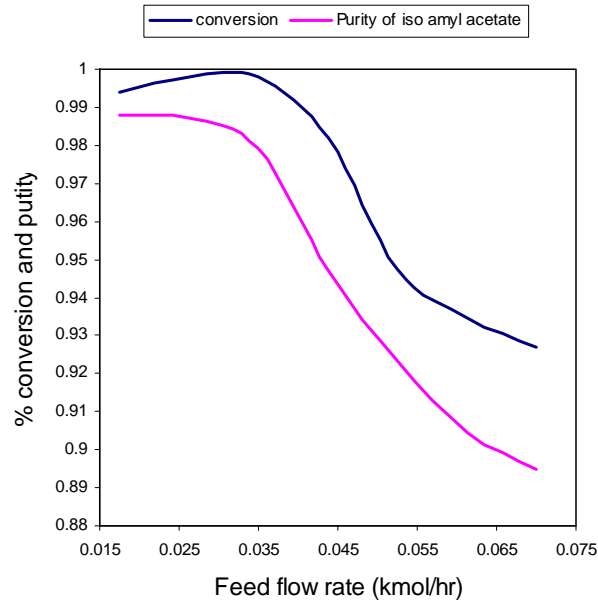
Figure 6.17 Effect of Feed Flow Rate on the Conversion of Acetic acid and Purity of iso amyl acetate

Figure 6.17 shows the effect of feed flow rate on conversion of acetic acid and purity over a wide range (molar ratio corresponds to Run No # 27, with reboiler duty of 1 kW). It is observed that large feed flow rates are not desirable since the residence time is not sufficient and column operates in kinetically controlled regime. This is observed in RD experiments as discussed in Section 5.6.1 of Chapter 5. Due to the limitation of the present experimental set up, the experiments could not be conducted at high feed flow rates.
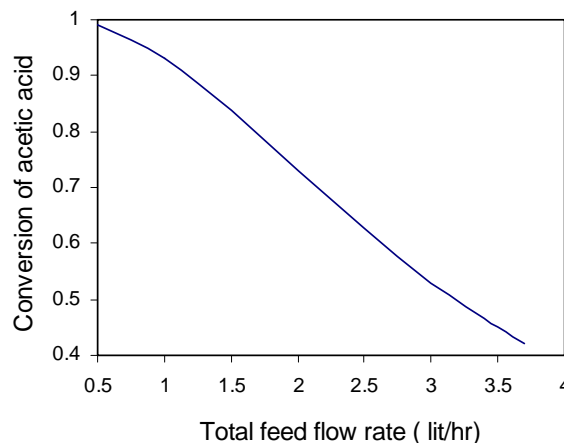
Figure 6.18 Effect of Total Feed Flow Rate on the Conversion of Acetic acid

Figure 6.18 shows effect of total feed flow rate on the conversion of acetic acid. The molar ratio of iso amyl alcohol to acetic acid is kept constant and both the feed streams flow rates are varied simultaneously. From figure 6.18, it is clear that conversion decreases as the flow rates increases implying that the system operates in the kinetically controlled regime. With a relatively very small flow rate, it may be feasible to obtain near 100 % conversions.

6.7.2. Effect of Reflux Ratio:

The reflux rate and reflux ratio are important parameters and affect both reaction and separation performance in a reactive distillation column. A high reflux rate increases the separation of products and reactants, thereby enhancing the conversion beyond the chemical equilibrium conversion following Le Chatelier's principle (Subawalla and Fair, 1999). Besides, the reflux ratio also significantly affects the reactive zone residence time for both equilibrium and non-equilibrium-limited systems. The excessive reflux leads to the operating problems and insufficient reaction holdup, thus causing incomplete conversion (Agreda et al, 1990). Therefore, the RD columns should be operated at an optimum reflux ratio to ensure the good separation performance and sufficient residence time in the column.

Reflux has a twofold purpose in reactive distillation. Increasing reflux rate enhances separations and recycles unreacted reactants to the reaction zone and, thereby, increases conversion. As a result of the increasing reflux ratio several effects occurs in reactive distillation column: (a) the concentrations of reactants in the distillate are reduced; (b) the reaction zone temperatures are reduced.

As mentioned in Chapter 5, in the present system of interest, reflux ratio is decided by the relative proportion of the organic and aqueous phase in the top product and it is not variable. Hence it was decided to study the effect of reflux ratio on conversion of iso amyl acetate through simulation.
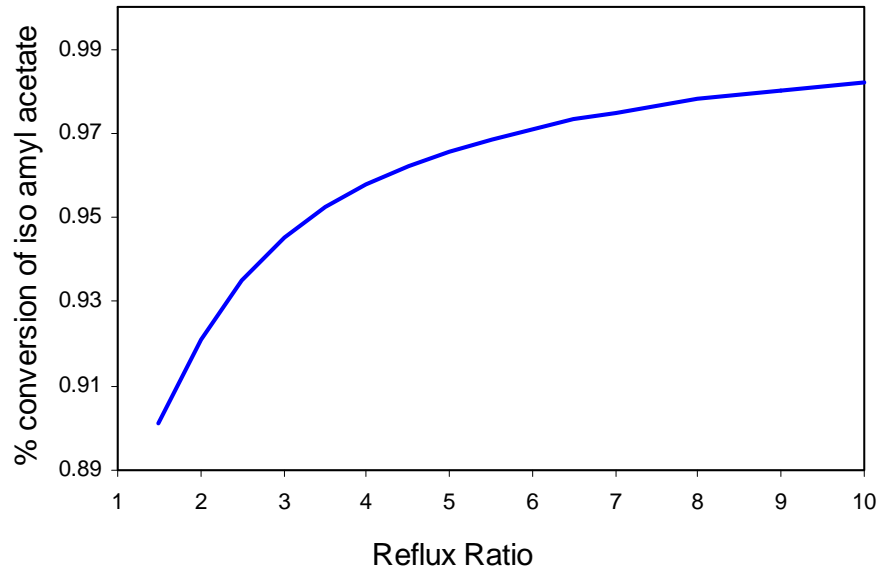
Figure 6.19 Effect of Reflux Ratio on the Bottom Product Mole Fraction (iso amyl acetate)

Figure 6.19 shows effect of reflux ratio on bottom product mole fraction. It is clear from the above that as reflux ratio increases; conversion of bottom product (iso amyl acetate) also increases.

To examine the effect of reflux ratio on conversion, the simulation studies are performed separately in Aspen Plus considering kinetics of both forward reaction as well as backward reaction. It is observed that the conversion increases at a higher reflux ratio due to increased concentration of iso amyl alcohol in the reactive zone.

6.7.3. Effect of Reboiler Duty:

The reboiler duty is one of the important parameter, which can affect on performance of reactive distillation column. In reactive distillation, the reboiler duty must be set to ensure sufficient recycle of unreacted, heavy reactant to the reaction zone without excluding the light reactant from the reaction zone. If the reboiler duty is too high or too low, conversion and subsequently product purity, is decreased.
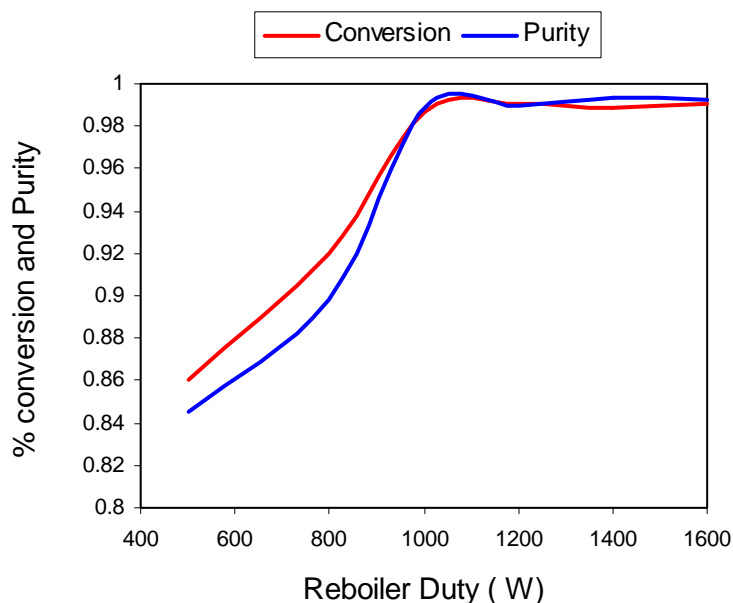
Figure 6.20 Effect of Reboiler Duty on the Conversion of Acetic acid and Purity of iso amyl acetate.

In present system, the reflux ratio is decided by the relative amount of organic phase and aqueous phase in the top product and it is not adjustable. Boil- up rate is only operating variable that can make significant influence on the separation and reaction. Therefore, it is decided to examine the effect of boil-up rate on conversion and purity over a wide range of reboiler duty.

Figure 6.20 indicates effect of reboiler duty on conversion of acetic acid and purity of iso amyl acetate in 27 stage iso amyl acetate reactive distillation column and clearly shows the presence of an optimum duty. The feed flow rate is chosen from 0.0175 kmol/hr to 0.07 kmol/hr. It is examined that, at lower reboiler duty, conversion is very low and as boil-up increases, the amount of iso amyl alcohol, which is excess in the feed, increases in the top product and thus improving purity of bottom product. As expected, for lower boil-up rates, the time required to reach steady state was more. The similar trend is observed on experimental investigation for effect of reboiler duty on conversion and purity, as discussed in Section 5.6.2 of Chapter 5.

6.7.4. Effect of Number of Reactive and Nonreactive Stages:

The key function of reactive section of reactive distillation column is simply to provide a position for the main reaction to proceed and, as such, there is no specific requirement for separation. This implies that, ideally. Only one equilibrium stage of a column needs to be packed with catalyst although the physical dimension of the stage could be relatively large to meet the catalyst requirement. However, simulations show that higher conversions are possible where more than one equilibrium stage is reactive.

Figure 6.21 shows the effect of varying the number of reactive stages in the six stage iso amyl acetate column. All other operating variables, including the number of separation stages, reflux ratio, reboiler duty and feed conditions are fixed.
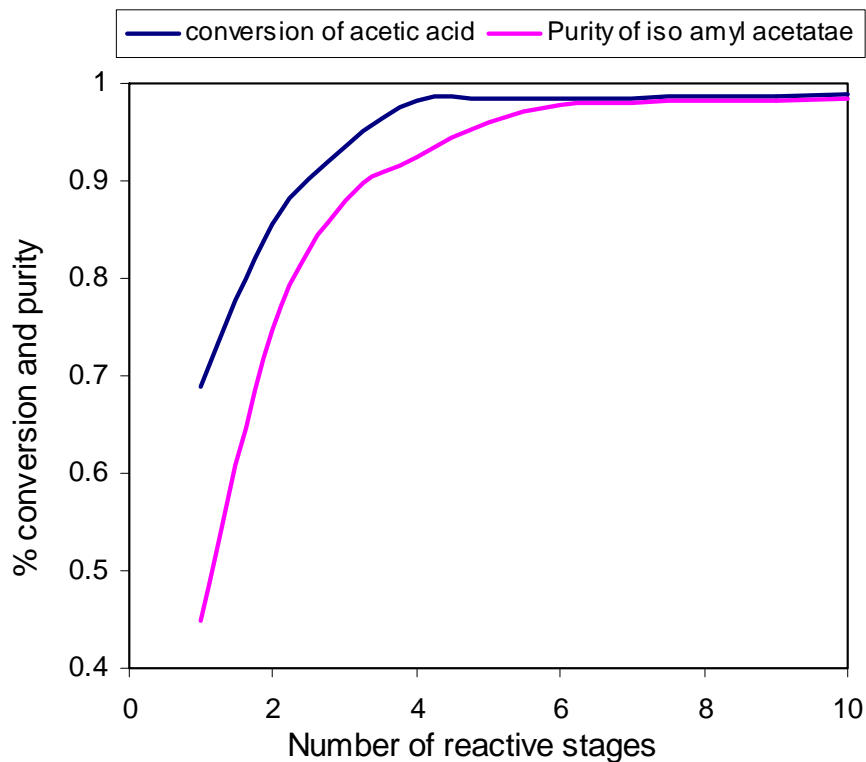
Figure 6.21 Effect of the Number of the Reactive Stages on the Conversion of Acetic acid and Purity of iso amyl acetate

The figure shows that 4-5 stages are sufficient to achieve the desired conversion and purity. It is observed that, further increase in

the number of reactive stages hardly influence the performance of the column. It is also observed that even with one reactive stage in the column can yield conversions on the order of 70%.

The improved conversion with an increased number of reactive stages results from the benefits of additional separation which are obtained. However most of conditions, assigning all the catalyst in a reactive distillation column to a single stage would have an insignificant effect on the overall conversion realized. Note that this is different to the data presented in Figure 6.20 as it shows an increase in the number of separation stages at the cost of reactive stages.

When high-purity iso amyl acetate is required, a higher number of nonreactive stages below the reactive section of the column is needed. It is also observed that 12 stages in nonreactive stripping section are sufficient to get higher conversion and purity. Only 9 stages on nonreactive rectification section are sufficient since the decanter ensures a sufficient separation of water from the organic compounds because of the low solubility's of iso amyl alcohol and iso amyl acetate in water.

6.7.5. Selection of Feed Stage Location:

A simulation has been carried out using Aspen Plus for reactive distillation column to choose best feed location for two reactants. Figure 6.22 and 6.23 shows the effect of feed stage locations on purity of bottom product for two reactants: Acetic acid and iso amyl alcohol. Experiments are also conducted on RD column for various positions to investigate best possible feed location for the two reactants, i.e. above the catalyst bed, middle of catalyst bed, and below the catalyst bed. (Position 5 to 7 is the reactive zone, See Figure 5.1)
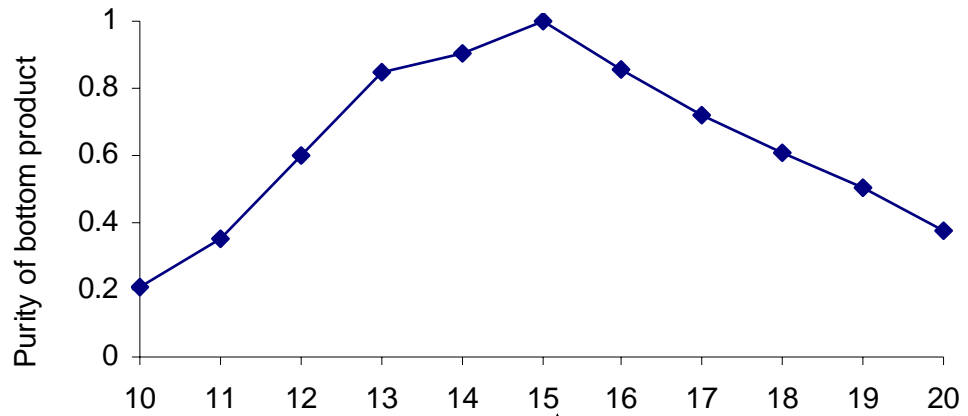
Best location for Acetic acid (Stage 15, from bottom of reactive zone)

Figure 6.22 Effect of Feed Stage Location (Acetic acid) on Purity
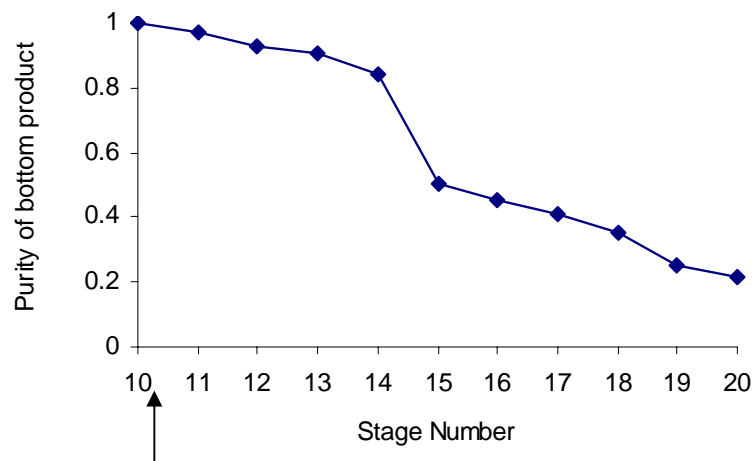
Best location for iso amyl alcohol (Stage 10, from top of reactive zone)

Figure 6.23 Effect of Feed Stage Location (iso amyl alcohol) on Purity

As mentioned previously in Chapter 5, the two reactants, acetic acid and iso amyl alcohol, are intermediate boilers, whereas the products, water and amyl acetate, are low and high boilers respectively. From the reaction kinetics point of view (keeping the reactant concentrations as high as possible) , the heavy reactant , iso amyl alcohol is fed to the column from the top of section of reactive zone, and the light reactant (acetic acid) comes in lower section of the reactive zone.

From Figure 6.22 and 6.23, it is observed that the best feed location for heavy reactant (iso amyl alcohol) is fed from the top of the reactive zone (Stage No.10) and light reactant (acetic acid) is fed from bottom of the reactive zone. (Stage No.15) Thus provides countercurrent flow of liquid and vapor in reactive distillation column.

6.7.6 Effect of Molar Ratio of Acetic acid to iso amyl alcohol:

The molar ratio of reactants significantly affects the reaction conversion and the loads on downstream product purification. If the reactant excess is too low, product conversion is unfavorably limited while if it is too high, product purity is decreased.

The feed molar ratio of the reactants plays a vital role in determining the conversion of acetic acid, distillate purity as well as the relative compositions of the top and bottom streams. Esterification reaction of acetic acid to iso amyl alcohol is equilibrium –limited reaction. The use of an excess of iso amyl alcohol increases the conversion of acetic acid as the position of equilibrium controls the amount of ester formed.
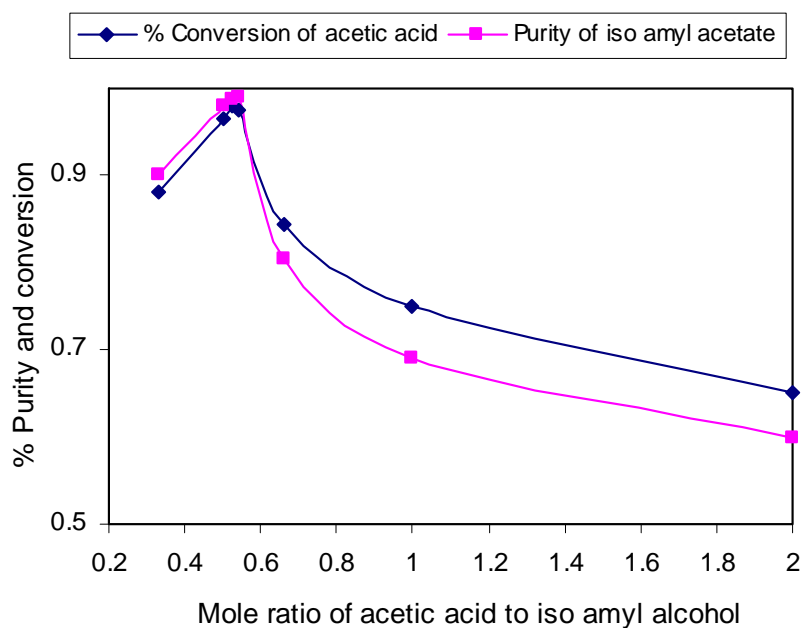
Figure 6.24 Effect of Molar Ratio of Acetic acid to iso amyl alcohol on Conversion of acetic acid and Purity of iso amyl acetate

Figure 6.24 shows the effect of molar ratio of acetic acid to iso amyl alcohol, on acetic acid conversion and purity of iso amyl acetate, predicted by simulation. The experiments are also performed using different mole ratio of acetic acid to iso amyl alcohol. The molar ratio of acetic acid to iso amyl alcohol is varied from 0.33 to 1.85 to examine the effect of mole ratio on conversion and purity. This is discussed in Section 5.6.4 of Chapter 5.

It has been already observed by experiments that (See Table 5.7, in Chapter 5), increasing molar ratio of iso amyl alcohol to acetic acid, results in an increase in conversion and decrease in purity. The feed molar ratio of acetic acid to iso amyl alcohol is investigated at 0.33, 0.5, 0.5405, 0.5363, 0.66, 1 and 2. There is an increase in conversion of acetic acid from 84.8% to 98 % when the molar ratio of acetic acid to *iso*-amyl alcohol is increased from 0.66 to 0.5263. When the feed mole ratio of acetic acid to iso amyl alcohol is 2, the conversion of acetic acid is dropped by 23% as compared to feed mole ratio 0.33 of acetic acid to iso amyl alcohol. This results shows that any further increase in feed mole ratio of acetic acid to iso amyl alcohol under those specific reacting conditions would not improve the conversion of acetic acid. In addition to this, at feed molar ratio of 0.66 and 0.33, traces of iso amyl alcohol were detected at the bottom product.

Since iso amyl alcohol forms a binary azeotrope with water at 95.4 ^{0}C and a ternary azeotrope with water and iso amyl acetate at 93.8^0 C, it is therefore expected that most of the iso amyl alcohol available will form azeotropes and move upwards of the column. This clarifies for the very low conversion of acetic acid with a feed molar ratio of 0.66; as the limited availability of iso amyl alcohol to react with acetic acid in reactive zone is further limited by the formation of azeotropes. These results further confirm that the feed mole ratio of 0.5 is optimal. As it meant that all the alcohol shifts up into the reactive zone to react with acetic acid and thus improve conversion.

Therefore it is concluded that acetic acid to iso amyl alcohol molar ratio of 0.5 is optimum for the adopted configuration and further experiments were conducted at or very close to this mole ratio.

Simulation Results for VLE User Data and Aspen Plus Data Bank:

As Mentioned in section 4.8 of Chapter 4, the VLE data from the databank of Aspen Plus is also used to simulate the RD column separately to observe how the results vary with the experimental data and the Aspen Plus databank data. The following table shows the stagewise profile summary of the reactive distillation column.

Table 6.3 Profile Summary

Stage	Temperature	Pressure	Heat duty	Liquid flow	Vapor flow
	C	Bar	Kw	kmol/hr	kmol/hr
1	89.4784291	1.01325	**-2.0910199**	0.12330343	0
2	95.9840899	1.01325	0	0.10792784	0.18495514
3	121.884023	1.01325	0	0.1197841	0.16957955
4	128.587714	1.01325	0	0.12523657	0.18143581
5	129.576209	1.01325	0	0.12619444	0.18688828
6	129.781654	1.01325	0	0.12644676	0.18784615
7	129.87492	1.01325	0	0.12658333	0.18809847
8	129.941525	1.01325	0	0.12668519	0.18823505
9	129.994584	1.01325	0	0.12676737	0.18833691
10	130.037814	1.01325	0	0.12683532	0.18841908
11	130.073286	1.01325	0	0.12689227	0.18848704
12	130.102504	1.01325	0	0.12694042	0.18854398
13	130.126635	1.01325	0	0.17368438	0.18859214
14	133.755294	1.01325	0	0.17767766	0.18283609
15	135.412818	1.01325	0	0.19213913	0.18682938
16	133.577146	1.01325	0	0.19811915	0.20129085
17	131.893821	1.01325	0	0.20244759	0.20727087
18	130.507326	1.01325	0	0.24544647	0.2115993
19	132.400317	1.01325	0	0.2392996	0.20209818
20	134.217863	1.01325	0	0.23391949	0.19595131
21	135.823612	1.01325	0	0.22943141	0.1905712
22	137.158714	1.01325	0	0.22577005	0.18608312
23	138.227785	1.01325	0	0.22279899	0.18242176
24	139.068282	1.01325	0	0.22037882	0.1794507
25	139.726244	1.01325	0	0.21839104	0.17703053
26	140.243829	1.01325	0	0.21674144	0.17504275
27	140.655209	1.01325	**1.72576927**	0.04334828	0.17339315

In Table 6.3 shows the heat duty of the condenser and the reboiler and also the stagewise temperature profile of the column. The figure also depicts the temperature profile of the column.
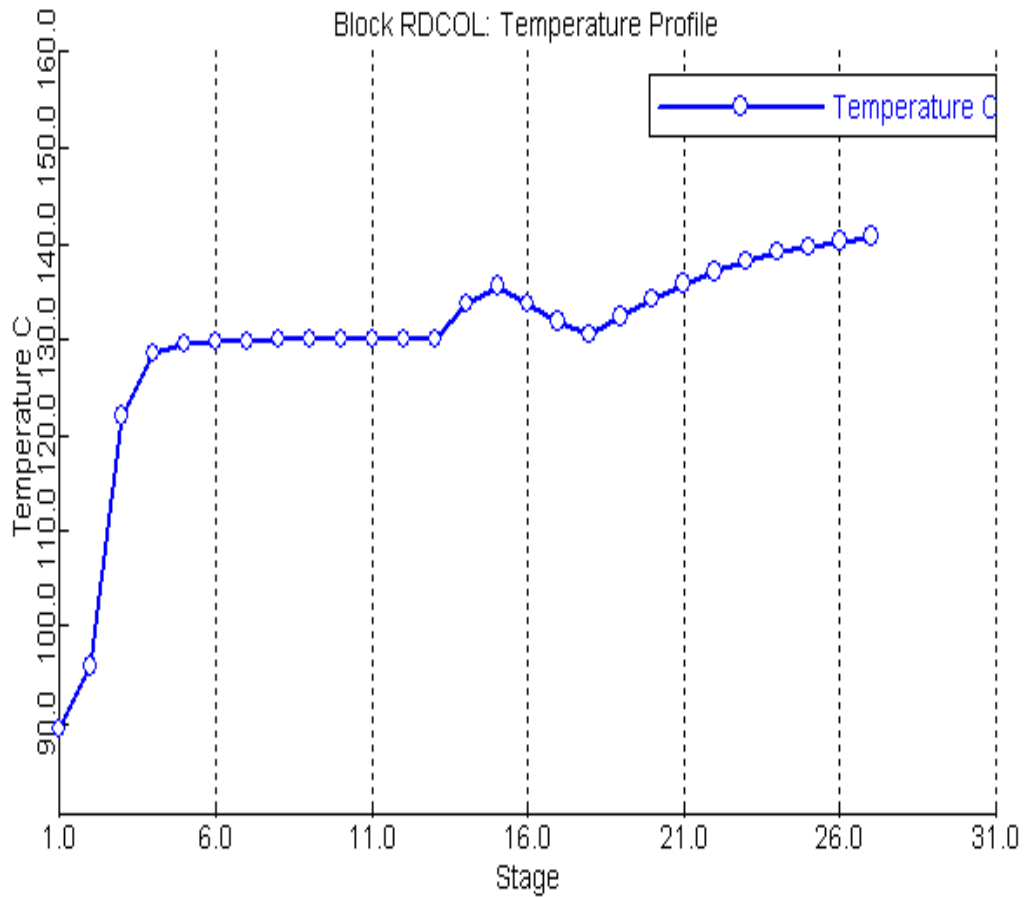
Figure 6.25 Stagewise Temperature Profile of the column

The Table 6.4 shows the stagewise liquid composition profile of the reactants and the products.

Table 6.4. Liquid Composition Profile

Stage	Acetic Acid	Iso amyl Alcohol	Iso amyl Acetate	Water
1	0.00493909	0.04462052	0.1435035	**0.80694**
2	0.0292378	0.21180869	0.52670409	0.232249
3	0.03256745	0.24690367	0.67863474	0.041894
4	0.02888947	0.23125054	0.71738426	0.022476
5	0.02521002	0.21429976	0.74063099	0.019859
6	0.02206795	0.19997046	0.75880631	0.019155
7	0.01944534	0.18810953	0.77369652	0.018749
8	0.01727477	0.17827944	0.78600817	0.018438
9	0.01548911	0.170106	0.79621829	0.018187
10	0.01402746	0.16329134	0.8046994	0.017982
11	0.01283604	0.15759782	0.811752	0.017814
12	0.01186825	0.15283388	0.81762128	0.017677
13	0.01108425	0.14884363	0.82250857	0.017564
14	0.11985005	0.00694276	0.86241856	0.010789
15	0.26112481	0.00028572	0.73700294	0.001587
16	0.34965967	2.07E-05	0.65010227	0.000217
17	0.4143149	2.05E-06	0.58564965	3.34E-05
18	0.46633677	2.51E-07	0.53365723	5.75E-06
19	0.39568074	2.92E-07	0.60431799	9.77E-07
20	0.32765417	3.41E-07	0.67234536	1.37E-07
21	0.266358	3.96E-07	0.73364159	1.60E-08
22	0.21358037	4.54E-07	0.78641917	1.59E-09
23	0.16934103	5.09E-07	0.83065847	1.38E-10
24	0.13271799	5.57E-07	0.86728145	1.06E-11
25	0.10247378	5.94E-07	0.89752562	7.47E-13
26	0.07739634	6.19E-07	0.92260304	4.83E-14
27	0.05643719	6.27E-07	**0.94356218**	2.89E-15

As can be seen, the mol fraction of the Iso amyl acetate is 0.943 and that of water is 0.806. The following plot illustrates the stagewise liquid composition profiles of the reactants and the products.
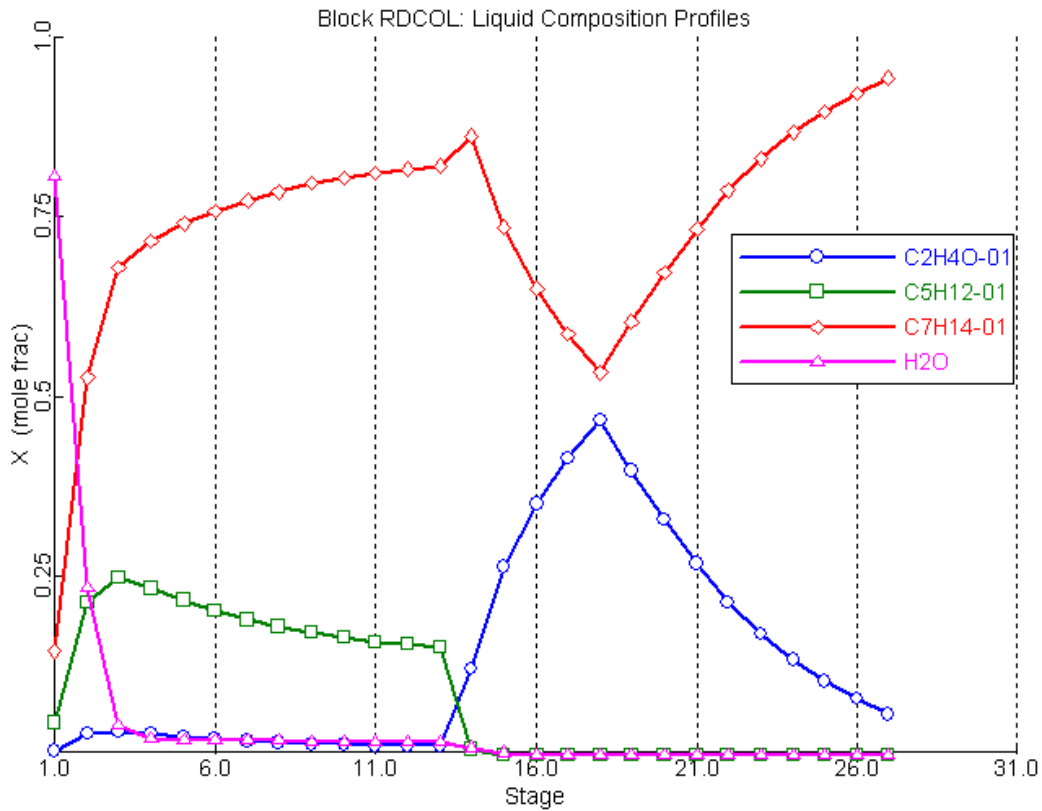
Figure 6.26 Stagewise Liquid Composition Profiles

The Table 6.5 shows the amount of Iso amyl acetate and water that is being generated and the amount of acetic acid and iso amyl alcohol being used up in the reaction zone from stages 10 to 15.

The Table 6.5 and 6.6   illustrates the comparison in results between user VLE input data and the aspen plus databank data.

Table 6.5. Simulation Results using User Data

RESULTS USING USER DATA				
Mole Fraction				
	Acetic Acid Stream	**Bottoms Stream**	**Iso amyl Alcohol Stream**	**Distillate Stream**
C2H4O-01	1	0.056437	0	0.004939
C5H12-01	0	6.27E-07	1	0.044621
C7H14-01	0	0.943562	0	0.143504
H2O	0	2.89E-15	0	0.806937

Table 6.6. Simulation Results using Aspen Plus Databank Data

	Acetic Acid Stream	Bottoms Stream	Iso amyl Alcohol Stream	Distillate Stream
RESULTS USING ASPEN PLUS DATABANK DATA				
Mole Fraction				
C2H4O-01	1	0.01859889	0	0.03010285
C5H12-01	0	1.2265e-08	1	0.04281249
C7H14-01	0	**0.9814011**	0	0.12821953
H2O	0	4.3805e-17	0	**0.79886512**

As can be seen from the result tables and plots of the previous chapter, the simulation of the reactive distillation column has shown many conclusive results.
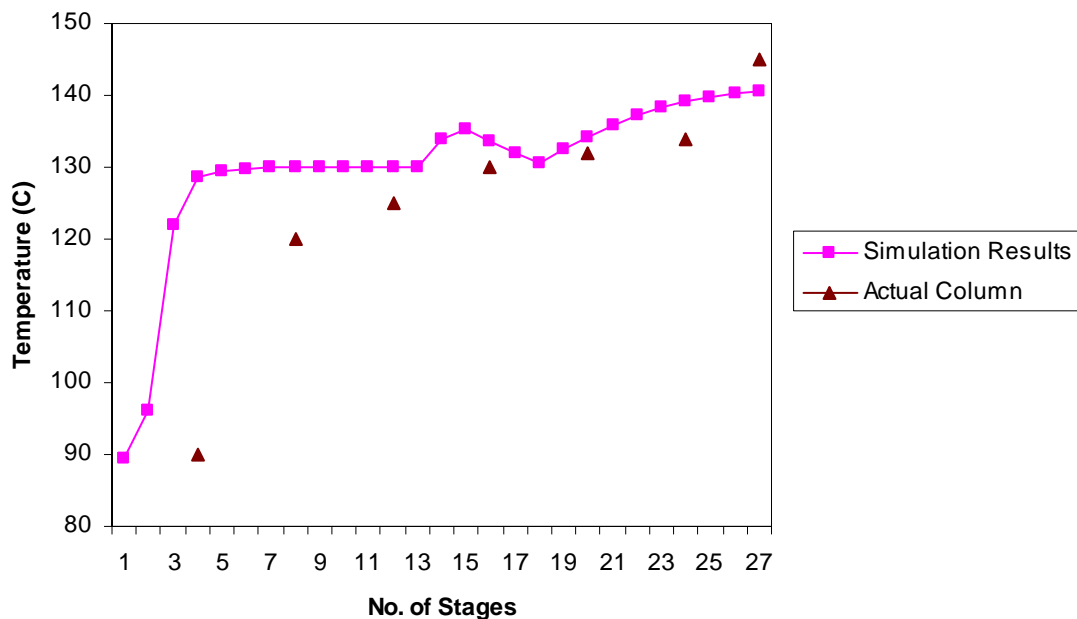
Figure 6.27. Temperature profile of actual column and Simulation Results

Also as can be seen from Figure 6.27 , the temperature profile of the simulated column and the actual column increase at the same rate thus giving almost same results for the mol fraction of isoamyl acetate in the bottoms and water in the overhead stream.

The mol fraction of isoamyl acetate in the bottoms stream using databank data was 98% as compared to 94% using the user data. The experimental kinetic data also gave good results.

There is a very good agreement between the results from the Aspen Plus Databank and the actual column.

Table 6.7. Final Result Comparisons

	Experimental Results	Simulation Results (Aspen Databank)	Simulation Results (User Data)
Internal Diameter of column	50 mm	51 mm	51 mm
Mole fraction of Iso Amyl acetate in Bottoms	0.983	0.9814011	0.943562
Mole Fraction of Water in Distillate	0.895	0.79886512	0.806937

6.8   Conclusion:

A steady-state equilibrium (EQ) model is developed for a packed reactive distillation column. The three steady state equilibrium models of different depths considered in this study are:

1)   Model # A: Physical and chemical equilibrium are achieved at each stage. The reactive distillation is modeled as a countercurrent multistage process with physical and chemical equilibrium on each stage.

2)   Model # B: the assumption of physical equilibrium is kept and the reaction kinetics at each stage is described by bulk reaction kinetics in liquid phase. This model does not use decanter model for separation of immiscible phases that are formed at top of RD column.

3)   Model # C: This model is same as Model # B. In addition to this, decanter model is employed to account for phase splitting behavior at the top of RD column.

Predictions from stage models of different complexity are compared to the results of experiments. The three models are compared for the iso amyl acetate system. In Model A, assumption of physical and chemical equilibrium shows that the additional assumption of chemical equilibrium on each stage is not valid. In Mode l# B (without decanter), taking the reaction kinetics into account yields better but still not satisfactory results. In Model # C, taking the reaction kinetics into account with decanter model, gives the simulation results of models agree with experimental results quantitatively. This indicates that the modeling depth of the simpler equilibrium-stage model with decanter (Model # C) is sufficient.

The model is validated with laboratory experimental data and then used to study the behavior of RD system for various operating parameters. The steady state simulation of RD column brings forth a number of important issues related to the optimal design techniques. Many of these issues are peculiar to RD and would not reasonably be anticipated without *a priori knowledge* of the phenomena involved. In summary, RADFRAC (equilibrium model) in Aspen Plus is used for simulations of the iso amyl acetate system using Model # C. A series of simulations are performed for the laboratory scale RD column, and a very good agreement between simulated and experimental data is obtained.

It should be noted that the external mass transfer resistance at the solid–liquid interface is not considered here. An exhaustive rate based model is required to be solved to consider these effects, which is out of the scope of the present work. Nevertheless the simplified model used here is able to explain the results over the conditions of interest. The temperature and composition profiles for this system from the

equilibrium model are compared with experimental results under the same conditions. Reasonably good agreement between the experimental and simulation results is realized.

The developed model (Model# C) is able to describe the process behavior in an entire range of operating conditions, improving understanding of the process. The investigations enable several important conclusions to be drawn. Better results are obtained at lower flow rates due to the sufficient residence time in the reactive zone. It is found that that, at lower reboiler duty, conversion is very low and as boil-up increases, the amount of iso amyl alcohol, which is excess in the feed, increases in the top product and thus improving purity of bottom product. As expected, for lower boil-up rates, the time required to reach steady state is more. The optimum molar ratio, of acetic acid to iso amyl alcohol is determined as 0.5 for the adopted configuration and experiments are conducted at or very close to this molar ratio.

The phase equilibria of the quaternary system revealed that a significant two-liquid region exists, and more importantly, that the tie lines are all pointed to high-purity water for the aqueous phase. It is evident that the liquid-liquid separation on the top of the column is beneficial for iso amyl acetate esterification processes. Therefore, a decanter is placed on top of the column, where high-purity water is withdrawn from the aqueous phase, and the organic phase is totally refluxed. Thus, a decanter constitutes an advantageous component of the reactive distillation column set-up.

The experimental results generated in this work clearly show that it is feasible to obtain high-purity iso amyl acetate in a reactive distillation column with almost-quantitative conversion. Experiments have shown that the best position for the introduction of the feed is at the top of the reactive zone, and, by increasing number of stages, conversion increases. It is suggested that the best feed location for

heavy reactant (iso amyl alcohol) is from the top of the reactive zone (Stage No.10) and light reactant (acetic acid) is from bottom of the reactive zone. (Stage No.15) Thus provides countercurrent flow of liquid and vapor in reactive distillation column.

The kinetic model development is crucial, and the Pseudohomogenous kinetic model is developed, on the basis of the data generated in the composition region of interest, predicts the experimental results of a laboratory continuous RD column successfully.

CHAPTER 7

CONCLUSIONS AND SCOPE FOR FUTURE WORK

7.1 Conclusions:

In this work, design aspects of hybrid reactive distillation for the synthesis of iso amyl acetate; have been studied via steady state simulation and experimentation on RD column. Processing strategies are identified through the extensive use of simulation tools (Aspen Plus) employing three equilibrium-stage models of different complexity: Model #A, Model # B and Model # C. An accurate and efficient simulation of the reactive distillation process is successfully developed for the steady state case using the equilibrium (EQ) stage models # A, # B and # C. Model # C is used to demonstrate the design of iso amyl acetate reactive distillation column and to investigate the effect of various operating variables such as feed stage location, reboiler duty, reflux ratio etc on conversion and purity of product.

From the comparisons of composition and temperature profiles for the model, in Model # A, assumption of physical and chemical equilibrium shows that the additional assumption of chemical equilibrium on each stage is not valid. In Model# B (without decanter), taking the reaction kinetics into account yields better but still not satisfactory results. In Model# C, taking the reaction kinetics into account with decanter model, gives the simulation results of models agree with experimental results quantitatively. This indicates that the modeling depth of the simpler equilibrium-stage model with decanter (Model# C) is sufficient for the present system.

Simulation results are used to design a laboratory reactive distillation column for the synthesis of iso amyl acetate from iso amyl alcohol and acetic acid. A laboratory reactive distillation column with novel structured and reactive packings (diameter,50 mm, height,

approximately, 3 m) is designed and operated for iso amyl acetate synthesis to examine it's feasibility of the present system. The design, construction and commissioning of this experimental facility is the part of the current research work. The experimental part includes reactive distillation experiments in laboratory scale, carefully evaluated database for describing chemical reaction and phase equilibria. The design of the experimental facility is focused on the selection of catalyst, catalyst support and column internals for reactive distillation process. It is observed that the best feed location for heavy reactant (iso amyl alcohol) is from the top of the reactive zone (Stage No.10) and light reactant (acetic acid) is from bottom of the reactive zone. (Stage No.15) Thus provides countercurrent flow of liquid and vapor in reactive distillation column.

The experimental results generated in this work clearly show that it is feasible to obtain high-purity iso amyl acetate in a reactive distillation column with almost-quantitative conversion. It is observed that as boil-up increases, the amount of iso amyl alcohol, which is excess in the feed, increases in top product thereby improving the purity of the bottom product. As anticipated, the time required to attain the steady state is more for lower boil-up rate. It is also seen, though the conversion and purity levels are substantially high, better results are obtained at lower flow rates due to large residence time offered under this condition.

In order to use the RADFRAC model from Aspen Plus for simulating a reactive distillation column with confidence, the reliability of the model is tested by comparing the simulated results obtained in this study with the experimental data generated on laboratory scale reactive distillation column. With the same experimental conditions (from Table 5.7 as shown in Chapter 5) are compared with results of the simulation run in and are presented in Appendix 1. It can be seen that the steady state composition profiles in the distillate and the bottom product, predicted by Aspen Plus, are

in good agreement with the experimental data. The small difference may be due to the modified kinetic parameters that are based on the mole fraction rate expression.

Vapor-liquid equilibrium data are the basic information of the system required for the design of equilibrium stages of vapor-liquid separation equipment like distillation. Hence experimental data for phase equilibrium is obtained in Othmer type apparatus in the laboratory. The experimental VLE results are put into the Aspen Plus data regression simulation to find the required binary parameters for the six binary systems so as to put them together into the final reactive distillation column simulation. The phase equilibrium data are used to calculate BIP'S using NRTL model and for conceptual design studies of reactive distillation column such as residue curve mapping (RCM), understanding the azeotropic behavior etc. The use of RCM for the design of reactive distillation processes is investigated and shown to provide useful information regarding the feasibility of reaction-separations. The VLE data from the databank of Aspen Plus is also used to simulate the column separately to examine how the results vary with the experimental data and the aspen plus databank data.

Reaction kinetics is the key in the simulation of RD column. Therefore rigorous kinetic experiments are performed in batch reactor to generate the data to study the effects of various operating parameters such as temperature, stirrer speed, mole ratio, catalyst loading etc. on conversion. The kinetic data generated from laboratory experiments is then used to fit the Pseudohomogenous kinetic model and evaluated the rate constant and activation energy of the esterification reaction between iso amyl alcohol and acetic acid. This model is satisfactory for iso amyl acetate synthesis in RD column.

It should be noted that the external mass transfer resistance at the solid–liquid interface is not considered here. An exhaustive rate

based model is required to be solved to consider these effects, which is out of the scope of the present work. Nevertheless the simplified model used here is able to explain the results over the conditions of interest. The temperature and composition profiles for this system from the equilibrium model are compared with experimental results under the same conditions. Reasonably good agreement between the experimental and simulation results is realized.

7.2 Scope for Future Work:

Reactive distillation is determined to be an attractive alternative to the conventional reaction/separation strategies for the synthesis of iso amyl acetate. In this work, the simulation and experimental studies for reactive distillation for iso amyl acetate is accomplished, but substantial technical challenges remain. One important challenge is the examination of the catalyst deactivation, which can never be avoided, but may possibly be attenuated through proper selection of operating conditions. The selection of packing is found to significantly influence both the conversion and selectivity.

At this point, a comprehensive economic evaluation is beyond the scope of present studies. This would be a necessary step in determining if the synthesis of iso amyl acetate by reactive distillation will be more economical than the conventional process. This can be established through an experimental effort.

An attempt has made here to fulfill the objectives outlined in Chapter 1. However, there is significant potential to continue the simulation and experimental aspects of this research, using the reactive distillation experimental facility created during this research work.

Here are the suggestions for future work in this context:

1)   The results obtained in this study may be explained with the help of more realistic non-equilibrium (NEQ) model. Once the model is validated, one can perform dynamic studies (through both experiments and simulation) and propose a proper control strategy for RD operation.

2)   In addition to this, optimization of the design by process optimization techniques, operability would be necessary.

REFERENCES

[1]   A. Higler, Modeling Reactive Distillation, PhD. Thesis, Clarkson University, New York, 1999

[2]   Agreda, V. H., Partin, L. R., & Heise, W. H., High-purity methyl acetate via reactive distillation. *Chemical Engineering Progress*, 86(2), 1990, pp 40-46.

[3]   Aiouache, F. and Goto, S., Reactive distillation-pervaporation hybrid column for *tert*-amyl alcohol etherification with ethanol, *Chemical Engineering Science*, 58, 2003,pp 2465- 2477

[4]   Ajay Singh, Anand Tiwari, Sanjay M. Mahajani and Ravindra D. Gudi, Recovery of Acetic Acid from Aqueous Solutions by Reactive Distillation, *Ind. Eng. Chem. Res.* 2006, *45,* pp 2017-2025

[5]   Ajay Singh, R. Hiwale, S. M. Mahajani, R. D. Gudi, Production of Butyl Acetate by Catalytic Distillation. Theoretical and Experimental Studies, *Ind. Eng. Chem. Res.,* 2005, *44, pp* 3042-3052

[6]   Almedia-Riveria C.P., Swinkels P., Grevink J, Designing distillation processes: present and future, *Computers and Chemical Engineering*, 28(10),2004,pp 1997-2020

[7]   Anastas, P.T., and Zimmerman, J.B., Design through the twelve principles of green engineering, *Env. Sci. and Tech.*, 37, 2003, pp 95 - 101.

[8]   Andrzej Stankiewicz, Jacob A. Moulijn, Process intensification, *Ind. Eng. Chem. Res.*, 41 (8), 2002**,** pp1920–1924

[9]   Andrzej Stankiewicz, Reactive separations for process intensification: an industrial perspective, *Chemical Engineering and Processing ,*Volume 42, Issue 3, 2003, pp 137-144

[10]   Aspen plus Version 7.0, 2007 User Guide, Aspen Technology, Inc. (http://www.aspentech.com)

[11]   Astarita, G., Mass transfer with chemical reaction, Elsevier Publishers, 1967

[12]   Barbosa, D., and Doherty, M. F., A new set of composition variables for the representation of reactive phase diagrams. *Proceedings of the Royal Society London A,* 1988b pp*413-*459

[13]   Bianchi, C. L., Ragaini, V., Pirola, C. and Carvoli, G., A new method to clean industrial water from acetic acid via esterification, *Applied Catalysis B: Environmental,* 40, 2003, pp 93-99

[14]   Bravo, J. L., Pyhalathi, A., & Jaervelin, H., Investigations in a catalytic distillation pilot plant: Vapor/ liquid equilibrium, kinetics and mass transfer issues. *Industrial and Engineering Chemistry Research,* *32,* 1993, pp 2220-2225.

[15]   Carberry, J., Chemical and catalytic reaction engineering", 2nd edition, McGraw-Hill, New York, 1976

[16]   Chakrabarti A, Sharma M, Cation exchange resins as catalysts, *React Polym,* 20, 1993, pp 1

[17]   Cheng-Ching Yu, Chien-Lin Kuo, and David S. H. Wong, Design alternative for the amyl acetate process: coupled reactor/ column and reactive distillation, *Ind. Eng. Chem. Res.*, 41, 2002, pp 3233-3246

[18]   Ciric, A. R., & Miao, P., Steady-state multiplicities in an ethylene glycol reactive distillation column, *Industrial and Engineering Chemistry Research,* *33,* 1994, pp 2738-2748.

[19]   DeGarmo, J.L., Parulekar, V. N., & Pinjala, V., Consider reactive distillation. *Chemical Engineering Progress,* 3, 1992, pp 43 – 50.

[20]   Dhale, A.D., Myrant, L. K., Chopade, S. P., Jackson, J. E. and Miller, D. J., Propylene glycol and ethylene glycol recovery from aqueous solution via reactive distillation, *Chemical Engineering Science ,*59, 2004,pp 2881-2890

[21]   Doherty, M. F., & Buzad, G., Reactive distillation by design. Chemical Engineering Research and Design, *Transactions of the Institution of Chemical Engineers,* Part A, 70, 1992, pp 448-458.

[22]   Doherty, M.F. and Malone, M.F., Conceptual design of distillation systems, McGraw-Hill, New York, 2001

[23]   E. A. Campanella and B. A. Mandagaran, Phase Equilibria for Quaternary Mixtures In Esterification Reaction Systems, *Latin American Applied Research* , 33 , 2003, pp 223-231

[24]   E.S.P. Cisneros, Modeling, Design and Analysis of Reactive Separation Processes, Ph.D. Thesis, The Technical University of Denmark, Bygning pp 229, 1997,DK-2800

[25]   Fogler, S. H., Elements of Chemical Reaction Engineering, New Delhi: Prentice-Hall, Second ed., 1995, pp 625–626.

[26]   Gangadwaga, J., Mankar, S. and Mahajani, S., Esterification of acetic acid with butanol in the presence of ion exchange resins as catalysts, *Industrial and Engineering Chemistry Research*, 42, 2003, pp 2146-2155

[27]   Gangadwala J, Kienle A, Stein E, Mahajani S., Production of butyl acetate by catalytic distillation: Process design studies. *Ind Eng Chem Res, 43*, 2004, pp 136-144.

[28]   Guttinger, T. E., & Morari, M., Predicting multiple steady states in distillation: Singularity analysis and reactive systems, *Computers and Chemical Engineering, 21*, 1997, pp S995-S1000.

[29]   Hanika J, Smejkal Q, Kolena J., Butyl acetate via reactive distillation modeling and experiment. *Chem Eng Sci.,* 54, 1999. pp 5205-5212

[30]   Harmsen, G. Jan**,** Reactive distillation: The front-runner of industrial process intensification. A full review of commercial applications, research, scale-up, design and operation , *Chemical Engineering and Processing,*46, 2007, pp 774 -780

[31]   Hauan, S., Hertzberg, T., & Lien, K. M., Why methyl-tertbutyl-ether production by reactive distillation may yield multiple solutions., *Industrial and Engineering Chemistry Research, 34,* 1995, pp 987-991.

[32]   Hayden JG, O'Connell JP., A generalized method for predicting second virial coefficients. *Ind Eng. Chem. Process Des. Dev.,* 14, 1975, pp 209-216

[33]   Henley, E. J., & Seader, J. D., Equilibrium-stage separation operations in chemical engineering. New York: Wiley, 1981

[34]   Henry Kister, Distillation Design, McGraw-Hill, 1992

[35]   Higler, A. P., Krishna, R., Ellenberger, J., & Taylor, R., Counter-current operation of a structured catalytically packed bed reactor: Liquid-phase mixing and mass transfer, Chemical *Engineering Science*, 1999a, *54*, pp 5145-5152.

[36]   Higler, A. P., Taylor, R., & Krishna, R., Modeling of a reactive separation process using a nonequilibrium stage model, *Computers and Chemical Engineering, 22*, 1998, pp S111-S118.

[37]   Higler, A. P., Taylor, R., & Krishna, R., Nonequilibrium Modeling of reactive distillation: Multiple steady states in MTBE synthesis, *Chemical Engineering Science*, 1999, *54*, pp 1389-1395.

[38]   Hiwale, R. S.; Bhate, N. V.; Mahajani, Y, S.; Mahajani, S. M. Industrial Applications of Reactive Distillation: Recent Trends. *International. Journal of Chemical Reactor Engineering, 2,* 2004, R1.

[39]   Holland, C. D, Multicomponent Distillation, Englewood Cliffs, NJ: Prentice-Hall, 1963.

[40]   Holland, C. D., Fundamentals of Multicomponent Distillation, New York: McGraw-Hill, 1981.

[41]   Huang SG, Yu CC., Sensitivity of thermodynamic parameter to the design of heterogeneous reactive distillation: Amyl acetate esterification *Chin Inst Chem Eng.* 34, 2003, pp 345-355

[42]   Jacobs, R., & Krishna, R., Multiple solutions in reactive distillation for methyl-tert-butyl ether synthesis, Industrial *and Engineering Chemistry Research, 32,* 1997, pp 1706-1709.

[43]   Juha P. Tanskanen, Phenomenon Driven process design; focus on multicomponent reactive and ordinary distillation, Ph.D Thesis, University of Oulu, Finland,1999

[44]   Keyes, D. B., Esterification processes and equipment. *Industrial and Engineering Chemistry, 24,* 1932, pp 1096-1103.

[45]   Kloker et al., On the development of new column internals for reactive separations via integration of CFD and process simulation, *Catalysis Today*, 79-80, 2003, pp 479-485

[46]   Kreul, L. U., Gorak, A., Dittrich, C., & Barton, P. I., Dynamic catalytic distillation: Advanced simulation and experimental validation, *Computers and Chemical Engineering, 22,* 1998, pp S371-S378.

[47]   Krishna, Reactive separations: more ways to skin a cat, *Chemical Engineering Science,* 57, 2002, pp 1491-1504

[48]   Kumar, A., & Daoutidis, P., Modeling, analysis and control of ethylene glycol reactive distillation column, *American Institute of Chemical Engineers Journal, 45,* 1999, pp 51-68.

[49] Kumbhar, P.S ,Yadav, G.D, Catalysis by sulfur promoted superacidic zirconia: condensation reactions of hydroquinone with aniline and substituted anilines, *Chem. Eng. Sci.*, 44, 1989, pp 2535-2544

[50] Lee, J. H., & Dudukovic, M. P., A comparison of the equilibrium and nonequilibrium models for a multicomponent reactive distillation column. *Computers and Chemical Engineering, 23*, 1998, pp 159-172.

[51] Lee, J. W., Hauan, S., Lien, K. M., & Westerberg, A. W., Graphical methods for designing reactive distillation columns. The Ponchon-Savarit Diagram, *Chemical Engineering Science, 55,* 2000a , pp 3140-3152

[52] Lee, J. W., Hauan, S., Lien, K. M., and Westerberg, A. W., Difference points in extractive and reactive cascades. II Generating design alternatives by the lever rule for reactive systems, *Chemical Engineering Science, 55,* 2000c, pp 3161-3176.

[53] Lee, M. J., Wu, H.T. and Lin, H-M, Kinetics of catalytic esterification of acetic acid and amyl alcohol over Dowex, *Industrial and Engineering Chemistry Research*, 39, 2000, pp 4094-4099.

[54] Lee, M. J.; Chen, S. L.; Kang, C. H.; Lin, H. M. Simultaneous Chemical and Phase Equilibria for Mixture of Acetic Acid, Amyl Alcohol, Amyl Acetate, and Water. *Ind. Eng. Chem. Res., 39,* 11, 2000, pp 4383-4391

[55] Lee, M. J.; Wu, H. T.; Kang, C. H.; Lin, H. M., kinetic behavior of amyl acetate synthesis catalyzed by acid cation exchange resin. *J. Chin. Inst. Chem. Eng.* 30, 1999, pp117-123

[56] Levenspiel , O., Chemical reaction engineering, Pergamon Press, Oxford, 1965

[57] Li et al., Kinetics of esterification of acetic acid with amyl alcohol over Amberlyst 15, *Journal of Chemical Engineering Japan*, 34, No.7, 2001, pp 960-963

[58] Liang-sun Lee A and Shen-Jang Kiang, Phase and reaction equilibria of acetic acid -1-pentanol –water-n-amyl acetate system at 760 mm Hg, *Fluid Phase Equilibria,* 149, 1998, pp 57-74.

[59]   M. Brehelin, D. Rouzineau, F. Forner, J.-U. Repke1, M. Meyer, G. Wozny, Production of Propyl Acetate by Reactive Distillation: From Experiments to Simulation, *SYMPOSIUM SERIES NO. 152, IChemE,* 2006

[60]   Mahajani S. M. and Chopade S. P., Reactive distillation: processes of commercial importance, In Encyclopedia of Separation Science, by Wilson I. D., Edlard T. R., Poole C. A. and Cooke M. (Eds.), Academic Press, London, UK, 2001, pp 4075-408

[61]   Mahajani S. M. and Chopade S. P., Reactive distillation: processes of commercial importance, In Encyclopedia of Separation Science by Wilson I. D., Edlard T. R., Poole C. A. and Cooke M. (Eds.), Academic Press, London, UK, (2001)

[62]   Malone, M.F., Doherty, M.F., Huss, R.S., Green chemical engineering aspects of reactive distillation, *Environ. Sci. & Technol,* 2000

[63]   Malone, M.F., Doherty, M.F., Reactive distillation, *Ind. Eng. Chem. Res.* 39, 2000, pp 3953-3957

[64]   Markus Kloker, Eugeny Y. Kenig, Markus Schmitt, Klaus Althaus, Hartmut Schoenmakers, Influence of operating conditions and column configurations on the development of RD columns with liquid- liquid separators, *The Canadian Journal of Chemical Engineering,* 81, 2003, pp 725-732

[65]   Markus Schmitt and Hans Hasse, Chemical equilibrium and reaction kinetics of heterogeneously catalyzed *n*-hexyl acetate esterification, *Ind. Eng. Chem. Res., 45,* 2006, pp 4123-4132

[66]   Markus Schmitt and Hans Hasse, Synthesis of n-hexyl acetate by reactive distillation, C*hemical Engineering Science,* 43, 2004, pp 397-409

[67]   Markus Schmitt, Claudia von Scala, Peter Moritz, Hans Hasse, Synthesis of n-hexyl acetate by reactive distillation, C*hemical Engineering Science,* 43, 2004, pp 397-409

[68]   Mohl, K. D., Kienle, A., Gilles, E. D., Rapmund, P., Sundmacher, K., &Hoffmann, U., Steady-state multiplicities in reactive distillation columns for the production of fuel ethers MTBE and TAME: Theoretical analysis and experimental verification, *Chemical Engineering Science, 54,* 1999, pp 1029-1043.

[69]   Moritz, Blagov, and Hasse, Heterogen katalysierte Reaktivdestillation: Design und Scale-up am Beispiel von Methylacetat, *Chem. Ing. Tech.,* 74, 2002, pp 1207–1218.

[70]   Ng F., and Rempel G., Catalytic Distillation, *Encyclopedia of Catalysis*, John Wiley and Sons, 2, 2003, pp 477-505

[71]   Nijhuis, S. A., Kerkhof, F. P. J. M., & Mak, A. N. S. , Multiple steady states during reactive distillation of methyl-tert-butyl ether, *Industrial and Engineering Chemistry Research, 32,*1997, pp 2767-2774.

[72]   Podrebarac G., Ng F., and Rempel G., More uses for Catalytic Distillation, *CHEMTECH,* 27, No.5, 1997, pp 37-45

[73]   R. Baur, A. Higler, R. Taylor, and R. Krishna, Comparison of Equilibrium Stage and Nonequilibrium Stage Models for Reactive Distillation, *Chem. Eng. J.*, 76, , 2000, pp 33-47

[74]   R. Baur, Modeling Reactive Distillation Dynamics, PhD. Thesis, Clarkson University, New York, 1999

[75]   R. Krishnamurthy, R. Taylor, A non equilibrium stage model of multicomponent separation processes. Part I: Model Description and Method of Solution, *AIChE J.*, 31, No.3, 1985, pp 449-456.

[76]   R. Krishnamurthy, R. Taylor, A non equilibrium stage model of multicomponent separation processes. Part III: the influence of unequal component efficiencies in process design problems, *AIChE J.*, 31, 1985, pp 1973-1985.

[77]   R. Krishnamurthy, R. Taylor, A non-equilibrium stage model of multicomponent separation processes. Part IV: A novel approach to packed column design, *AIChE J.*, 33, No.2, 1987, pp 325-327.

[78]   R. Taylor, R. Krishna, and H.A. Kooijman, real world modeling of distillation, *Chemical Engineering Progress*, 99,7, 2003, pp28-39

[79]   Rapmund, P., Sundmacher, K., & Hoffmann, U., Multiple steady states in a reactive distillation column for the production of the fuel ether TAME II experimental validation, *Chemical Engineering and Technology, 21*, 1999, pp 136-139.

[80]   S. Bhatia, A.L. Ahmad, A.R. Mohamed, S.Y. Chin, Production of isopropyl palmitate in a catalytic distillation column: Experimental studies, *Chemical Engineering Science,* 61, 2006, pp 7436– 7447

[81]   Saha, B, Teo, H, Production of Isoamyl acetate: Heterogeneous kinetics and techno feasibility evaluation for catalytic distillation, *International Journal of Chemical Reactor Engineering*, 3, 2005

[82]   Saha, B, Teo, H, Production of Isoamyl acetate: Heterogeneous kinetics and techno feasibility evaluation for catalytic distillation, *International Journal of Chemical Reactor Engineering*, 3, 2005

[83]   Saha, B. and Sharma, M. M., Reaction of dicylopentadiene with formic acid and chloroacetic acid with and without cation-exchange resins as catalysts, *React. Funct. Polym.*, 34, 1097, pp 161-173

[84]   Saha, B., Chopade, S. P. and Mahajani, S. M., "Recovery of dilute acetic acid through esterification in a reactive distillation column", *Catalysis Today,* 60, 2000, pp147-157

[85]   Santi Kulprathipanja (Ed), Reactive separation processes**,** Taylor and Francis Group, 2002

[86]   Sawistowski, H., & Pilavakis, P. A., Distillation with chemical reaction in a packed column. *Institute of Chemical Engineers Symposium Series, 56,* 1979, pp 49-63.

[87]   Schoenmakers, H. G. and Bessling, B., Reactive and catalytic distillation from an industrial perspective, *Chemical Engineering and Processing*, 42, No.3, 2003, pp145-155

[88]   Schrans, S., de Wolf, S., & Baur, R., Dynamic simulation of reactive distillation. An MTBE case study, Computers *and Chemical Engineering, 20,* 1996, pp S1619-S1624.

[89]   Seader, J. D., & Henley, E. J., Separation Process Principles. New York: Wiley, 1998.

[90]   Sharma MM, Some novel aspects of cation exchange resins as Catalysts, *React Polym*, 26, 1995, pp 3

[91]   Sharma, M. M.; Mahajani, S. M. Industrial application of reactive distillation (A review). In *Reactive Distillation-status and future trends*; Sundmacher, K., Kienle, A., Eds.; Wiley-VCH: New York, 2003; pp 1-29 (ISBN 3-527-30579-3.]

[92]   Sneesby, M. G., Tade, M. O., Datta, R., & Smith, T. N., ETBE synthesis via reactive distillation,1.Steady-state simulation and design aspects, *Industrial and Engineering Chemistry Research, 36,* 1997a, pp 1855-1869.

[93]   Steinigeweg and Gmehling, *n*-Butyl Acetate Synthesis via Reactive Distillation: Thermodynamic Aspects, Reaction Kinetics, Pilot-Plant Experiments, and Simulation Studies, *Ind. Eng. Chem. Res,*, *41,*2000, pp 5483-5490

[94]   Subawalla, H., & Fair, J. R. , Design guidelines for solid-catalyzed reactive distillation systems, *Industrial and Engineering Chemistry Research, 38,* 1999, pp 3696-3709

[95]   Sundmacher, K., & Hoffmann, U., Development of a new catalytic distillation process for fuel ethers via a detailed nonequilibrium model. *Chemical Engineering Science, 51,* 1996, pp 2359-2368.

[96]   Sundmacher, K., Kienle, A., (Eds), Reactive Distillation-Status and Future Trends, Wiley-VCH: New York, 2003.

[97]   Sundmacher, K., Rihko, L. K., and Hoffmann, U., Classification of reactive distillation processes by dimensionless numbers. *Chemical Engineering Communication,* 127, 1994, pp 151- 167.

[98]   Sundmacher, K., Zhang, R. -S., & Hoffmann, U., Mass transfer effects on kinetics of nonideal liquid phase ethyl tert-butyl ether formation., *Chemical Engineering and Technology, 18,* 1995, pp 269-277.

[99]   T. C. Tan and S. H. Gan, Vapor–Liquid Equilibrium of Water/Ethanol/1-Butanol/Salt Prediction and Experimental Verification, *Chemical Engineering Research and Design, 83,* 2005, pp 1361–1371

[100] Taylor, R, and Krishna, R, Multicomponent Mass Transfer, John Wiley, New York, 1993

[101] Taylor, R., & Lucia, A., Modeling and analysis of multicomponent separation processes. *A.I.Ch.E. Symposium Series No. 304*, vol. 91, 1994, pp. 9-18

[102] Taylor, R., Krishna, R, Modeling of homogenous and heterogeneous reactive distillation, Chapter 9, Reactive Distillation-Status and Future Trends, Book by Sundmacher, K., Kienle, A., (Eds) , Wiley-VCH: New York, 2003

[103] Taylor, R., Krishna, R., Kooijman, H., Real-world modeling of distillation, Chemical Engineering Progress, www.cepmagazine.org, July 2003

[104] Taylor, R.; Krishna, R., Modeling reactive distillation. *Chem. Eng. Sci., 55*, 2000, pp 5183-5229.

[105] Tejero, J., Cunill, F., Izquierdo, J. F., Iborra, M., Fite, C. and Parra, D., Scope and limitations of mechanistic inferences from kinetic studies on acidic macroporous resins. The MTBE liquid-phase synthesis case", *Applied Catalysis A: General,* 134, 1996, pp 21-36

[106] Teo, H. T. R. and Saha, B., Heterogeneously catalyzed esterification of acetic acid with *iso*-amyl alcohol: kinetic studies, *Journal of Catalysis*, 228, 2004, pp 174-182

[107] Teo, H. T. R., and B. Saha, Heterogeneously catalyzed esterification of acetic acid with Iso-amyl alcohol: kinetic studies, *Journal of Catalysis*, 228, 2004, pp 174-182.

[108] Thermax India Ltd, Product Catalogue, 2008

[109] Tim Popken, Sven Steinigeweg, and Jurgen Gmehling, Synthesis and Hydrolysis of Methyl Acetate by Reactive Distillation Using Structured Catalytic Packings: Experiments and Simulation, *Ind. Eng. Chem. Res.* 2001, *40,* pp 1566-1574

[110] Towler, G. P., & Frey, S. J., Reactive distillation, in S. Kulprathipanja, Reactive separation processes. Philadelphia: Taylor and Francis (Chapter 2), 2000.

[111] Towler, G.P., Frey, S.J, Reactive Distillation, Chapter 2, in Reactive separation Processes, (Ed. S.Kulpratipanja), Taylor and Francis, Philadelphia, 2000

[112] Ung, S., and Doherty, M. F., Calculation of residue curve maps for mixtures with multiple equilibrium chemical reactions. *Industrial and Engineering Chemistry Research,* No. *34,* 1995a, pp 3195-3202.

[113] Venkataraman, S., Chan, & Boston, Reactive distillation using ASPEN PLUS. *Chemical Engineering Progress, 86,* 8, 1990, pp 45-54.

[114] Wang, J. C., & Wang, Y. L., A review on the modeling and simulation of multi-stage separation processes, In W. D. Seider, & R. S. H. Mah, *Foundations of computer aided chemical process design,* vol. II, 1981, pp. 121-170.

[115] Wan-Jen Hung, I-Kuan Lai Yi-Wei Chen, Shih-Bo Hung, Hsiao-Ping Huang, Ming-Jer Lee, and Cheng-Ching Yu, Process chemistry and design alternatives for converting dilute acetic acid to esters in reactive distillation, *Ind. Eng. Chem. Res., 45,* 2006, pp 1722-1733

[116] Wan-Jen Hung, I-Kuan Lai, Shih-Bo Hung, Hsiao-Ping Huang, Ming-Jer Lee, and Cheng-Ching Yu, Control of Reactive Distillation Columns for Amyl Acetate Production Using Dilute Acetic Acid, *Journal of the Chinese Institute of Engineers,* 2006, 29, No. 2, pp 319-335

[117] Xiaoning Li and Andrzej Kraslawski, Conceptual process synthesis: past and current trends, Chemical Engineering and Processing ,Volume 43, Issue 5, 2004, pp 583-594

[118] Xu, Z. P. and Chuang, K. T., Kinetics of acetic acid esterification over ion exchange catalysts, *The Canadian Journal of Chemical Engineering,* ,74, 1996,pp 493-500

[119] Yadav G.D., Thathagar, M.B., Esterification of maleic acid with ethanol over cation exchange resin catalysts, *React Func Polym,,* 52, 2000, pp 99-110

[120] Yadav, G. D., Mehta, P.H., Heterogeneous catalysis in esterification reactions: preparation of Phenethyl acetate and cyclohexylactetate using variety of solid acid catalysts, Ind. Eng. Chem. Res., 33, 1994, pp 2198- 2208

[121] Yadav, G.D, Murkute, A.D, Kinetics of synthesis of perfumery grade p-tert-butylcyclohexyl acetate over ion exchange resin catalyst *International Journal of Chemical Reactor Engineering.* 1, S_5, 2003

[122] Young-Tarang Tang, Yi-Wei Cheng, Huang, Yu, Design of reactive distillation for acetic acid esterification, *AIChE Journal,* 51,No. 6, 2005,pp 1683-1699

[123] Zheng, Y., & Xu, X., Study on catalytic distillation processes, Part I: Mass transfer characteristics in catalyst bed within the column, *Chemical Engineering Research and Design, Transactions of the Institution of Chemical Engineers, Part A, 70,* 1992a, pp 459-546.

APPENDIX 1

COMPARISONS OF EXPERIMENTAL RESULTS OBTAINED ON CONTINUOUS REACTIVE DISTILLATION COLUMN (RDC) WITH SIMULATION RESULTS

This section gives the comparison of experimental data generated during the course of experimental runs on Continuous Reactive Distillation (CRD) and simulation results. The results given here are essentially in tabular form since it is convenient to correlate the experimental results with modeling and simulation studies results as discussed in Chapter 6 for RD column performance. Here steady state composition profiles of products (iso amyl acetate as bottom product and Water as top product) and temperature are given.

It may be noted that the composition at position 3 is not shown here, because of the formation of two liquid phases (viz, an organic and phase and an aqueous phase), which makes the analysis difficult. In all experimental runs, the temperature in the reactive zone (Position 5 to 7 on RD column, see Figure 5.1) was in the range of 120-130^{0}C, which is within limit set by the manufacturer for the thermal stability of the catalyst (135 ^{0}C)

RUN # 1

Table A-1 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.02000	kmol/hr
2	Feed Flow Rate(iso amyl alcohol)	0.02625	kmol/hr
3	Mole ratio, acid/alcohol	0.5384	-
4	Reboiler duty	0.8	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	99.50	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.8545	-
8	Top product compositions (mole fraction)	Water = 0.9664	-
9	Purity of bottom product	88.60	%

Table A-2 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, ^0C (Expt)	Temp, ^0C (Sim)
1(Top)	0.05208	0.0517	0.9664	0.9756	92	94.2241
2	0.06656	0.0678	0.2760	0.2873	127	129.3056
3	Two phase	Two Phase	Two phase	Two Phase	129	130.4054
4	0.083	0.0811	0.0226	0.0230	129	130.4278
5	0.0865	0.0874	0.0235	0.0229	130	130.4365
6	0.0243	0.2565	0.022	0.0226	131	130.4213
7	0.0556	0.5690	0.01860	0.0195	133	132.1569
8	0.6123	0.5876	0.0075	0.0008	141	140.0980
9(Bottom)	0.8545	0.8605	0.000	0.000	144	143.7720

RUN # 2

Table A-3 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.01850	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.02000	kmol/hr
3	Mole ratio, acid/alcohol	0.5384	-
4	Reboiler duty	0.75	kW
5	Feed Location: (position on RD distillation column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	99.70	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.9970	-
8	Top product compositions (mole fraction)	Water = 0.9829	-
9	Purity of bottom product	98.60	%

Table A-4 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, ºC (Expt)	Temp, ºC (Sim)
1(Top)	0.2389	0.24640	0.9829	0.9965	92	94.1054
2	0.3345	0.3436	0.265	0.2873	124	125.5759
3	Two phase	Two Phase	Two phase	Two Phase	125	126.6839
4	0.606	0.6080	0.0226	0.0225	125	126.7383
5	0.8067	0.8107	0.0235	0.0201	126	126.7964
6	0.789	0.7913	0.0001	0.00011	127	126.8655
7	0.7125	0.7260	0.00002	1.30E-06	128	128.3737
8	0.9765	0.9647	0.000	0	141	140.0621
9(Bottom)	0.997	0.9997	0.000	0	145	147.000

RUN # 3

Table A- 5 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.01550	kmol/hr
2	Feed Flow Rate(iso amyl alcohol)	0.0200	kmol/hr
3	Mole ratio, acid/alcohol	1.85	-
4	Reboiler duty	0.75	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	65.40	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.8572	-
8	Top product compositions (mole fraction)	Water = 0.9828	-
9	Purity of bottom product	98.60	%

Table A-6 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, ^{0}C (Expt)	Temp, ^{0}C (Sim)
1(Top)	0.05	0.05175	0.9828	0.9955	95	94.2241
2	0.066	0.06784	0.2670	0.2873	127	129.3056
3	Two Phase	Two Phase	Two Phase	Two Phase	129	130.4054
4	0.0843	0.08119	0.024	0.0230	130	130.4278
5	0.0887	0.08748	0.0225	0.02296	131	130.4365
6	0.234	0.2565	0.02213	0.02265	132	130.4214
7	0.5789	0.5690	0.0165	0.019585	133	132.1569
8	0.598	0.5876	2.50E-05	1.56E-06	142	140.098
9(Bottom)	0.8572	0.8711	0.000	0.000	144	143.7721

RUN # 4

Table A -7 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.02550	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.03000	kmol/hr
3	Mole ratio, acid/alcohol	0.5384	-
4	Reboiler duty	1.0	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	99.49	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.9990	-
8	Top product compositions (mole fraction)	Water = 0.9967	-
9	Purity of bottom product	98.75	%

Table A-8 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, ^0C (Expt)	Temp, ^0C (Sim)
1(Top)	0.07867	0.08081	0.9967	0.9980	96	98.6810
2	0.09675	0.1068	0.2697	0.2856	125	127.4339
3	Two Phase	Two Phase	Two Phase	Two Phase	126	128.5101
4	0.1234	0.1342	0.02867	0.02953	129	128.545
5	0.14323	0.1478	0.02978	0.02934	129	128.5719
6	0.5109	0.5419	0.02343	0.02590	130	129.6968
7	0.9236	0.9315	0.0150	0.01413	132	130.5517
8	0.9867	0.9946	5.50E-05	8.99E-07	143	147.4548
9(Bottom)	0.999	0.9999	0.000	0.0000	146	147.7123

RUN #5

Table A -9 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.02625	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.03000	kmol/hr
3	Mole ratio, acid/alcohol	0.5274	-
4	Reboiler duty	0.85	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	98.90	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.9970	-
8	Top product compositions (mole fraction)	Water = 0.9805	-
9	Purity of bottom product	99.55	%

Table A-10 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, ^{o}C (Expt)	Temp, ^{o}C (Sim)
1(Top)	0.05324	0.0492	0.9805	0.9976	96	94.27018
2	0.06545	0.0625	0.2950	0.287458	123	125.3877
3	Two Phase	Two Phase	Two Phase	Two Phase	124	126.5134
4	0.0712	0.0703	0.0367	0.038108	125	126.5389
5	0.07456	0.0730	0.039	0.038052	127	126.5426
6	0.269	0.2977	0.03767	0.03756	126	125.9923
7	0.8212	0.8059	0.025	0.027629	129	130.3563
8	0.9178	0.9186	6.70E-04	2.27E-06	142	145.1846
9(Bottom)	0.9970	0.9984	0.000	0.000	145	147.6048

RUN # 6

Table A -11 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.02625	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.03200	kmol/hr
3	Mole ratio, acid/alcohol	0.5394	-
4	Reboiler duty	1	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	99.10	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.9521	-
8	Top product compositions (mole fraction)	Water = 0.9812	-
9	Purity of bottom product	98.55	%

Table A-12 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, ^oC (Expt)	Temp, ^oC (Sim)
1(Top)	0.088	0.08727	0.9812	0.99	94	95.3022
2	0.01	0.1139	0.2650	0.285264	124	127.0704
3	Two Phase	Two Phase	Two Phase	Two Phase	126	128.1723
4	0.1456	0.1406	0.03345	0.032788	127	128.1958
5	0.167	0.1540	0.0334	0.032563	129	128.201
6	0.645	0.6224	0.0269	0.02758	130	127.8903
7	0.8675	0.8708	0.0050	0.006932	132	130.5244
8	0.985	0.9857	5.60E-05	5.46E-07	143	141.3644
9(Bottom)	0.9521	0.9998	0.00	0.000	146	146.1189

RUN # 7

Table A -13 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.0250=	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.03200	kmol/hr
3	Mole ratio, acid/alcohol	0.5394	-
4	Reboiler duty	1	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	98.75	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.9079	-
8	Top product compositions (mole fraction)	Water = 0.9818	-
9	Purity of bottom product	94.55	%

Table A-14 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, °C (Expt)	Temp, °C (Sim)
1(Top)	0.043	0.04536	0.9818	0.9975	94	95.3434
2	0.06	0.0589	0.2450	0.2876	125	127.5325
3	Two Phase	Two Phase	Two Phase	Two Phase	126	128.6266
4	0.073	0.0692	0.031	0.02968	127	128.6491
5	0.076	0.0732	0.032	0.02962	130	128.6543
6	0.275	0.2549	0.0326	0.02951	131	128.3642
7	0.6123	0.6324	0.0280	0.02421	132	130.6644
8	0.6656	0.6560	5.60E-05	2.15E-06	139	140.7716
9(Bottom)	0.907	0.9159	0.000	0.000	147	144.9161

RUN # 8

Table A -15 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.03000	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.03400	kmol/hr
3	Mole ratio, acid/alcohol	0.5384	-
4	Reboiler duty	1	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	99.20	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.9984	-
8	Top product compositions (mole fraction)	Water = 0.9786	-
9	Purity of bottom product	97.65	%

Table A-16 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, ^oC (Expt)	Temp, ^oC (Sim)
1(Top)	0.054	0.0541	0.9786	0.9956	96	95.17879
2	0.07	0.0688	0.2970	0.287176	125	125.6853
3	Two Phase	Two Phase	Two Phase	Two Phase	126	126.8216
4	0.0778	0.0778	0.034	0.036726	127	126.8476
5	0.081	0.0811	0.0367	0.03666	128	126.8524
6	0.3045	0.3206	0.0355	0.035696	129	126.4746
7	0.845	0.8381	0.0298	0.026194	131	131.3346
8	0.939	0.9487	5.00E-05	2.00E-06	143	146.0168
9(Bottom)	0.9984	0.9994	0.000	0.000	146	147.6577

RUN # 9

Table A -17 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.02625	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.03000	kmol/hr
3	Mole ratio, acid/alcohol	0.5384	-
4	Reboiler duty	1.12	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	99.05	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.9900	-
8	Top product compositions (mole fraction)	Water = 0.9795	-
9	Purity of bottom product	98.85	%

Table A-18 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, ^0C (Expt)	Temp, ^0C (Sim)
1(Top)	0.124	0.1358	0.9795	0.9975	97	96.65221
2	0.1809	0.1839	0.2460	0.282431	126	128.9037
3	Two Phase	Two Phase	Two Phase	Two Phase	129	130.033
4	0.259	0.2626	0.02345	0.023532	130	130.152
5	0.356	0.3238	0.02133	0.022868	131	130.3833
6	0.934	0.9545	0.01756	0.017435	133	132.6928
7	0.864	0.8372	0.00289	0.000322	134	133.4975
8	0.9867	0.9842	0.000	0.000	145	146.9569
9(Bottom)	0.999	0.9999	0.000	0.000	147	147.71

RUN # 10

Table A-19 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.03200	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.03500	kmol/hr
3	Mole ratio, acid/alcohol	0.5384	-
4	Reboiler duty	1.12	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	99.50	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.993	-
8	Top product compositions (mole fraction)	Water = 0.9845	-
9	Purity of bottom product	98.15	%

Table A-20 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, ^0C (Expt)	Temp, ^0C (Sim)
1(Top)	0.164	0.1722	0.9845	0.995	94	95.9664
2	0.22	0.2317	0.2245	0.2650	128	127.3063
3	Two Phase	Two Phase	Two Phase	Two Phase	129	128.5327
4	0.35	0.3448	0.029	0.0280	130	128.7532
5	0.459	0.4469	0.0285	0.0265	131	129.2832
6	0.859	0.8584	0.0205	0.00227	132	130.9619
7	0.89	0.9062	0.000025	2.33E-05	133	131.8457
8	0.975	0.9634	0.000	0.000	146	145.9797
9(Bottom)	0.993	0.9997	0.000	0.000	147	147.7015

RUN # 11

Table A- 21 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.03200	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.03500	kmol/hr
3	Mole ratio, acid/alcohol	0.5384	-
4	Reboiler duty	1.15	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	98.45	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.9950	-
8	Top product compositions (mole fraction)	Water = 0.9812	-
9	Purity of bottom product	99.05	%

Table A-22 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, ^{0}C (Expt)	Temp, ^{0}C (Sim)
1(Top)	0.1598	0.1662	0.9812	0.9976	97	96.0797
2	0.221	0.2224	0.2540	0.2806	124	126.8554
3	Two Phase	Two Phase	Two Phase	Two Phase	126	128.066
4	0.31	0.3230	0.0298	0.02969	128	128.2509
5	0.423	0.4099	0.02867	0.02834	127	128.6641
6	0.843	0.8602	0.043	0.0043	129	130.9882
7	0.7457	0.7245	0.00509	4.64E-05	130	131.4313
8	0.947	0.9590	0.000	0.000	143	145.7773
9(Bottom)	0.995	0.9996	0.000	0.000	147	147.6991

RUN # 12

Table A -23 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.03500	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.03800	kmol/hr
3	Mole ratio, acid/alcohol	0.5384	-
4	Reboiler duty	1.25	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	99.30	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.999	-
8	Top product compositions (mole fraction)	Water = 0.9560	-
9	Purity of bottom product	97.26	%

Table A-24 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, ^0C (Expt)	Temp, ^0C (Sim)
1(Top)	0.09878	0.1047	0.956	0.9970	99	97.2351
2	0.1276	0.1349	0.2645	0.2842	124	126.4486
3	Two Phase	Two Phase	Two Phase	Two Phase	126	127.6269
4	0.1645	0.1652	0.031	0.0325	128	127.6726
5	0.1987	0.1833	0.0324	0.0322	129	127.7153
6	0.705	0.7265	0.0269	0.0259	130	129.4748
7	0.8235	0.8395	0.0020	0.0018	132	131.0851
8	0.9889	0.9803	0.000	0.000	145	146.7723
9(Bottom)	0.999	0.9998	0.000	0.000	147	147.7067

RUN # 13

Table A- 25 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.03600	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.03800	kmol/hr
3	Mole ratio, acid/alcohol	0.5384	-
4	Reboiler duty	1.10	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	99.05	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.9970	-
8	Top product compositions (mole fraction)	Water = 0.9876	-
9	Purity of bottom product	99.54	%

Table A-26 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, ^{0}C (Expt)	Temp, ^{0}C (Sim)
1(Top)	0.1067	0.1120	0.9876	0.99	100	98.09624
2	0.1453	0.14300	0.2543	0.283819	122	124.8132
3	Two Phase	Two Phase	Two Phase	Two Phase	126	125.9877
4	0.1761	0.1725	0.0387	0.03872	127	126.0351
5	0.1866	0.1893	0.0398	0.038355	125	126.0758
6	0.856	0.8768	0.0293	0.028051	128	127.9114
7	0.7323	0.74489	0.0105	0.001134	130	130.8541
8	0.9456	0.9553	0.000	0.000	143	145.6066
9(Bottom)	0.997	0.9995	0.000	0.000	145	147.692

RUN # 14

Table A -27 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.03100	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.03400	kmol/hr
3	Mole ratio, acid/alcohol	0.5200	-
4	Reboiler duty	1.0	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	99.27	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.9972	-
8	Top product compositions (mole fraction)	Water = 0.9550	-
9	Purity of bottom product	95.74	%

Table A-28 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, ^{0}C (Expt)	Temp, ^{0}C (Sim)
1(Top)	0.098	0.1047	0.955	0.99	95	96.2345
2	0.1232	0.1344	0.0723	0.28425	124	125.4246
3	Two Phase	Two Phase	Two Phase	Two Phase	125	126.5836
4	0.1543	0.1634	0.0387	0.036518	127	126.6282
5	0.1754	0.1794	0.0376	0.0362	127	126.6654
6	0.769	0.7986	0.02876	0.027826	129	130.2049
7	0.7765	0.7869	0.002	0.001604	131	131.6108
8	0.9564	0.9680	0.000	0.000	144	146.1935
9(Bottom)	0.9972	0.9998	0.000	0.000	147	147.7

RUN # 15

Table A -29 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.03200	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.03500	kmol/hr
3	Mole ratio, acid/alcohol	0.5200	-
4	Reboiler duty	1.25	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	99.54	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.9952	-
8	Top product compositions (mole fraction)	Water = 0.9427	-
9	Purity of bottom product	98.14	%

Table A-30 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, °C (Expt)	Temp, °C (Sim)
1(Top)	0.1654	0.1776	0.9427	0.9790	97	96.8641
2	0.235	0.2403	0.22459	0.2799	126	127.7245
3	Two Phase	Two Phase	Two Phase	Two Phase	129	128.9671
4	0.356	0.3655	0.0256	0.0265	129	129.2258
5	0.4978	0.4825	0.0234	0.0249	130	129.885
6	0.8345	0.8569	0.00145	0.0016	131	132.8274
7	0.7612	0.7468	0.0004	1.62E-05	132	133.2214
8	0.9434	0.9670	0.000	0.000	145	146.1468
9(Bottom)	0.9952	0.9997	0.000	0.000	146	147.7035

RUN # 16

Table A -31 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.02000	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.02500	kmol/hr
3	Mole ratio, acid/alcohol	1.00	-
4	Reboiler duty	1.35	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	78.90	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.8695	-
8	Top product compositions (mole fraction)	Water = 0.9595	-
9	Purity of bottom product	82.14	%

Table A-32 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, ^{0}C (Expt)	Temp, ^{0}C (Sim)
1(Top)	0.05	0.048592	0.9505	0.9760	101	99.2830
2	0.06234	0.061569	0.2450	0.2799	126	127.4125
3	Two Phase	Two Phase	Two Phase	Two Phase	128	128.5931
4	0.0698	0.068322	0.0268	0.0298	129	128.6171
5	0.0712	0.070954	0.0275	0.0297	128	128.6206
6	0.224	0.243484	0.03	0.0297	129	128.3069
7	0.6345	0.61306	0.021	0.0245	131	130.4566
8	0.6453	0.630701	0.000	0.000	142	140.507
9(Bottom)	0.8695	0.8507	0.000	0.000	145	144.0304

RUN # 17

Table A -33 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.04000	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.04375	kmol/hr
3	Mole ratio, acid/alcohol	0.5394	-
4	Reboiler duty	1.30	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	99.32	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.9969	-
8	Top product compositions (mole fraction)	Water = 0.9560	-
9	Purity of bottom product	98.16	%

Table A-34 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, ^0C (Expt)	Temp, ^0C (Sim)
1(Top)	0.0998	0.1075	0.956	0.986	99	98.1816
2	0.1245	0.1382	0.2490	0.284085	124	125.5081
3	Two Phase	Two Phase	Two Phase	Two Phase	125	126.6717
4	0.1654	0.1689	0.03456	0.03611	127	126.7183
5	0.1854	0.1863	0.0341	0.035768	126	126.760
6	0.779	0.8176	0.0268	0.027255	130	130.6319
7	0.7654	0.78384	0.0011	0.001474	131	131.1358
8	0.9543	0.9676	0.000	0.000	144	146.1745
9(Bottom)	0.9969	0.9997	0.000	0.000	147	147.6999

RUN # 18

Table A -35 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.04000	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.05000	kmol/hr
3	Mole ratio, acid/alcohol	0.5394	-
4	Reboiler duty	1.40	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	99.29	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.878	-
8	Top product compositions (mole fraction)	Water = 0.9738	-
9	Purity of bottom product	88.12	%

Table A-36 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, ^{0}C (Expt)	Temp, ^{0}C (Sim)
1(Top)	0.0409	0.041593	0.9738	0.9808	100	99.4136
2	0.05129	0.052235	0.2610	0.0714	125	126.1611
3	Two Phase	Two Phase	Two Phase	Two Phase	126	127.335
4	0.05534	0.056891	0.03408	0.0349	128	127.3599
5	0.05998	0.05835	0.0342	0.0348	127	127.3619
6	0.2109	0.230811	0.0354	0.0354	128	126.7282
7	0.6453	0.639687	0.03	0.0281	130	129.1583
8	0.6453	0.657592	0.000	0.000	142	140.7882
9(Bottom)	0.878	0.89873	0.000	0.000	145	144.230

RUN # 19

Table A -37 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.04400	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.05200	kmol/hr
3	Mole ratio, acid/alcohol	0.5384	-
4	Reboiler duty	1.50	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	99.19	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.9219	-
8	Top product compositions (mole fraction)	Water = 0.9668	-
9	Purity of bottom product	90.12	%

Table A-38 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, ^oC (Expt)	Temp, ^oC (Sim)
1(Top)	0.04423	0.04572	0.9668	0.989	100	99.33657
2	0.05437	0.05709	0.2640	0.2876	126	125.8571
3	Two Phase	Two Phase	Two Phase	Two Phase	128	127.0464
4	0.0634	0.06153	0.03598	0.0360	128	127.0723
5	0.0643	0.0628	0.03654	0.0360	129	127.0743
6	0.2289	0.2445	0.03659	0.0363	130	126.4612
7	0.6654	0.67142	0.0276	0.0276	131	129.1805
8	0.7067	0.6966	0.000	0.000	140	141.2363
9(Bottom)	0.9219	0.9233	0.000	0.000	144	145.3096

RUN # 20

Table A- 39 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.04500	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.06000	kmol/hr
3	Mole ratio, acid/alcohol	0.5384	-
4	Reboiler duty	1.60	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	99.27	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.8298	-
8	Top product compositions (mole fraction)	Water = 0.9695	-
9	Purity of bottom product	90.12	%

Table A-40 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, ⁰C (Expt)	Temp, ⁰C (Sim)
1(Top)	0.03754	0.0366	0.9695	0.9770	98	99.5051
2	0.04708	0.0462	0.2456	0.2881	125	126.3526
3	Two Phase	Two Phase	Two Phase	Two Phase	127	127.5103
4	0.0512	0.0508	0.0345	0.0342	128	127.5344
5	0.0542	0.0522	0.0341	0.03426	128	127.5362
6	0.245	0.2147	0.03543	0.03519	129	126.8393
7	0.6122	0.6089	0.245	0.02824	130	129.0212
8	0.632	0.6228	0.000	0.000	142	140.4285
9(Bottom)	0.8298	0.8387	0.000	0.000	145	143.2192

RUN # 21

Table A -41 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.02500	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.026250	kmol/hr
3	Mole ratio, acid/alcohol	0.5384	-
4	Reboiler duty	0.80	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	99.16	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.995	-
8	Top product compositions (mole fraction)	Water = 0.9608	-
9	Purity of bottom product	99.02	%

Table A-42 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, ^{0}C (Expt)	Temp, ^{0}C (Sim)
1(Top)	0.2245	0.2363	0.9608	0.99	94	95.7520
2	0.3012	0.31939	0.2560	0.276433	125	126.0327
3	Two Phase	Two Phase	Two Phase	Two Phase	127	127.5198
4	0.532	0.5289	0.03012	0.030079	129	128.182
5	0.734	0.72604	0.02765	0.026761	130	129.4288
6	0.745	0.745	0.0002	0.000215	131	130.3519
7	0.6087	0.6006	0.0004	3.65E-06	132	131.4139
8	0.912	0.9070	0.000	0.000	143	143.4693
9(Bottom)	0.995	0.9990	0.000	0.000	147	147.6691

RUN # 22

Table A -43 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.03000	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.03500	kmol/hr
3	Mole ratio, acid/alcohol	0.5367	-
4	Reboiler duty	1.20	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	98.59	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.9738	-
8	Top product compositions (mole fraction)	Water = 0.9648	-
9	Purity of bottom product	95.10	%

Table A-44 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, ⁰C (Expt)	Temp, ⁰C (Sim)
1(Top)	0.05233	0.05468	0.9648	0.998	98	99.1693
2	0.0704	0.07048	0.2750	0.287147	126	127.4651
3	Two Phase	Two Phase	Two Phase	Two Phase	128	128.5972
4	0.08078	0.08188	0.03	0.029675	129	128.6289
5	0.08976	0.08676	0.031	0.029605	130	128.6289
6	0.305	0.2839	0.02867	0.029024	129	128.4803
7	0.6545	0.6789	0.0205	0.023561	132	131.1725
8	0.7453	0.737413	0.000	0.000	143	141.7636
9(Bottom)	0.9738	0.9839	0.000	0.000	145	146.8017

RUN # 23

Table A -45 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.03500	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.05000	kmol/hr
3	Mole ratio, acid/alcohol	0.5367	-
4	Reboiler duty	1.25	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	98.67	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.7692	-
8	Top product compositions (mole fraction)	Water = 0.9524	-
9	Purity of bottom product	75.10	%

Table A-46 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, ^{0}C (Expt)	Temp, ^{0}C (Sim)
1(Top)	0.03	0.0316	0.9524	0.9654	102	99.59901
2	0.04	0.0399	0.265	0.2884	126	126.404
3	Two Phase	Two Phase	Two Phase	Two Phase	128	127.5629
4	0.044	0.04351	0.033	0.03417	129	127.5867
5	0.046	0.0445	0.03456	0.0341	126	127.5881
6	0.186	0.1946	0.03675	0.0356	127	126.78
7	0.589	0.5756	0.0300	0.0288	130	128.7196
8	0.5908	0.5868	0.00001	3.71E-06	137	140.0903
9(Bottom)	0.7692	0.7992	0.0000	0.0000	145	142.2226

RUN # 24

Table A -47 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.04700	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.05000	kmol/hr
3	Mole ratio, acid/alcohol	0.5367	-
4	Reboiler duty	1.20	kW
5	Feed Location:] (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	92.96	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.977	-
8	Top product compositions (mole fraction)	Water = 0.9458	-
9	Purity of bottom product	94.26	%

Table A-48 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, ^oC (Expt)	Temp, ^oC (Sim)
1(Top)	0.132	0.1429	0.9458	0.986	96	97.5185
2	0.175	0.1805	0.2469	0.2884	121	122.7014
3	Two Phase	Two Phase	Two Phase	Two Phase	125	123.8828
4	0.206	0.2204	0.045	0.0463	124	123.9493
5	0.234	0.2451	0.0465	0.0456	125	124.0237
6	0.805	0.8269	0.0165	0.0160	126	127.5377
7	0.564	0.5608	0.00025	0.0002	129	128.1738
8	0.806	0.8277	0.000	0.000	141	140.2276
9(Bottom)	0.977	0.9968	0.000	0.000	146	147.5614

RUN # 25

Table A -49 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.03200	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.03500	kmol/hr
3	Mole ratio, acid/alcohol	0.5367	-
4	Reboiler duty	1.0	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	97.90	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.9890	-
8	Top product compositions (mole fraction)	Water = 0.9450	-
9	Purity of bottom product	96.35	%

Table A-50 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, ^{0}C (Expt)	Temp, ^{0}C (Sim)
1(Top)	0.154	0.1442	0.9450	0.969	95	97.49418
2	0.190	0.1887	0.2750	0.281936	122	125.2611
3	Two Phase	Two Phase	Two Phase	Two Phase	124	126.4293
4	0.258	0.2511	0.037	0.036032	125	126.5261
5	0.3006	0.2952	0.0359	0.035143	127	126.6805
6	0.854	0.8830	0.0143	0.014674	128	129.8822
7	0.69	0.6878	0.0094	0.00017	130	131.1568
8	0.913	0.9403	0.000	0.000	145	144.9265
9(Bottom)	0.989	0.9994	0.000	0.000	147	147.6856

RUN # 26

Table A -51 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.04400	kmol/hr
2	Feed Flow Rate(iso amyl alcohol)	0.05000	kmol/hr
3	Mole ratio, acid/alcohol	0.5367	-
4	Reboiler duty	1.6	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	97.94	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.9845	-
8	Top product compositions (mole fraction)	Water = 0.9548	-
9	Purity of bottom product	92.35	%

Table A-52 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, ^{0}C (Expt)	Temp, ^{0}C (Sim)
1(Top)	0.1300	0.1495	0.9548	0.986	99	97.39425
2	0.1878	0.2016	0.2659	0.281936	125	126.9852
3	Two Phase	Two Phase	Two Phase	Two Phase	129	128.1214
4	0.269	0.2875	0.031	0.029756	127	128.2593
5	0.3435	0.3515	0.026	0.028773	129	128.5221
6	0.886	0.8963	0.0112	0.010929	130	130.7915
7	0.732	0.7449	0.00014	0.000106	133	132.1279
8	0.9409	0.9645	0.0000	0.0000	144	146.0288
9(Bottom)	0.9845	0.9997	0.0000	0.0000	146	147.7016

RUN # 27

Table A -53 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.01789	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.01950	kmol/hr
3	Mole ratio, acid/alcohol	0.5200	-
4	Reboiler duty	0.90	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	99.37	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.9900	-
8	Top product compositions (mole fraction)	Water = 0.9878	-
9	Purity of bottom product	99.45	%

Table A-54 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, °C (Expt)	Temp, °C (Sim)
1(Top)	0.170	0.1598	0.9878	0.9890	91	93.1346
2	0.2209	0.2173	0.2769	0.0527	120	122.6931
3	Two Phase	Two Phase	Two Phase	Two Phase	121	123.8958
4	0.328	0.3289	0.020658	0.0206	122	124.1058
5	0.4506	0.4353	0.019677	0.0196	125	126.6398
6	0.578	0.6024	0.018186	0.0181	126	127.8744
7	0.943	0.9572	0.01193	0.0119	130	130.4027
8	0.886	0.8907	0.000	0.000	136	138.7768
9(Bottom)	0.990	0.9994	0.000	0.000	145	147.6862

RUN # 28

Table A -55 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.01880	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.02050	kmol/hr
3	Mole ratio, acid/alcohol	0.5200	-
4	Reboiler duty	1.0	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 6 (below reactive zone) acetic acid on position 5 (above reactive zone)	
6	Conversions in terms of acetic acid	90.45	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.8740	-
8	Top product compositions (mole fraction)	Water = 0.8823	-
9	Purity of bottom product	88.28	%

Table A-56 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, ^oC (Expt)	Temp, ^oC (Sim)
1(Top)	0.0986	0.1046	0.8823	0.9021	92	93.1346
2	0.249	0.2875	0.2670	0.281936	119	122.6931
3	Two Phase	Two Phase	Two Phase	Two Phase	122	123.8958
4	0.6645	0.6882	0.165	0.16756	123	124.1058
5	0.698	0.7017	0.159	0.167225	125	126.6398
6	0.512	0.5474	0.00032	0.000281	128	127.8744
7	0.359	0.3678	0.0003	1.18E-06	130	130.4027
8	0.4067	0.4105	0.000	0.000	139	138.7768
9(Bottom)	0.874	0.8942	0.000	0.000	146	147.6862

RUN # 29

Table A- 57 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.01880	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.02050	kmol/hr
3	Mole ratio, acid/alcohol	0.5200	-
4	Reboiler duty	1.0	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 7 (below reactive zone) acetic acid on position 5 (above reactive zone)	
6	Conversions in terms of acetic acid	65.45	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.7734	-
8	Top product compositions (mole fraction)	Water = 0.7354	-
9	Purity of bottom product	70.28	%

Table A-58 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, ^0C (Expt)	Temp, ^0C (Sim)
1(Top)	0.124	0.1329	0.7354	0.7756	90	93.1346
2	0.3245	0.3008	0.2570	0.2819	120	122.6931
3	Two Phase	Two Phase	Two Phase	Two Phase	124	123.8958
4	0.665	0.6778	0.287	0.2537	125	124.1058
5	0.701	0.6852	0.265	0.2538	125	126.6398
6	0.498	0.5147	0.0003	0.0003	129	127.8744
7	0.534	0.5161	0.00058	0.00064	132	130.4027
8	0.5409	0.5250	0.00101	0.0014	140	138.7768
9(Bottom)	0.7734	0.7980	0.0016	0.0012	144	147.6862

RUN # 30

Table A -59 Details of the RD Experiment

Sr. No.	Measurements	Value	Units
1	Feed Flow Rate (acetic acid)	0.02200	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.02250	kmol/hr
3	Mole ratio, acid/alcohol	0.6660	-
4	Reboiler duty	1.0	kW
5	Feed Location: (position on RD column)	iso amyl alcohol on position 5 (above reactive zone) acetic acid on position 7 (below reactive zone)	
6	Conversions in terms of acetic acid	84.80	%
7	Bottom product composition (mole fractions)	iso amyl acetate = 0.9010	-
8	Top product compositions (mole fraction)	Water =0.8600	-
9	Purity of bottom product	92.47	%

Table A-60 Comparison of Experimental and Simulation Results for Compositions of Top and Bottom Products and Temperature at Steady State

Position	X_{ISAMAC} (Expt)	X_{ISAMAC} (Sim)	X_{Water} (Expt)	X_{Water} (Sim)	Temp, ^{0}C (Expt)	Temp, ^{0}C (Sim)
1(Top)	0.1245	0.1598	0.86	0.9878	91	93.1346
2	0.234	0.2173	0.2790	0.2819	121	122.6931
3	Two Phase	Two Phase	Two Phase	Two Phase	124	123.8958
4	0.343	0.3289	0.02234	0.020658	126	124.1058
5	0.453	0.4353	0.01987	0.01967	127	126.6398
6	0.587	0.6024	0.0165	0.0181	129	127.8744
7	0.934	0.9572	0.01	0.0119	131	130.4027
8	0.886	0.8907	0.00003	0.00007	136	138.7768
9(Bottom)	0.901	0.9994	0.000	0.000	145	147.6862

APPENDIX 2

DETAILS OF RESEARCH PROJECTS COMPLETED DURING THE RESEARCH WORK

During this research work, I received following two research grants:

1) "Modeling, Simulation Synthesis and Analysis for Reactive Distillation Processes for Esterification Reaction", **BCUD, University of Pune, India,** (File No: BCUD/578, dated on 10th January 2007, 2 years), *Completed in February 2009,* pp 100.

2) "Studies in Reactive Separations", **All India Council for Technical Education (AICTE), New Delhi, India, under Research Promotion Scheme (RPS),** (File No: 8023/BOR/RPS/-11/2006-2007, dated on 26th February 2007, 2 years) *Completed in August 2009,* pp 120.

APPENDIX 3

LIST OF RESEARCH PUBLICATIONS

(a)   Conference / Workshop/ Symposium Oral / Poster Presentations (National/ International)

[1]   Furquan Momin, Rushi Bakotia, <u>Kiran Patil</u>, Simulation Studies on Esterification Reactions using Reactive Distillation, presented in *National Conference on Cleaner Technology and Environment*, NIT, Ahemadabad, (May 2007).

[2]   <u>Kiran Patil</u>, Furquan Momin, Reactive distillation for Esterification Reaction, Presented in *CHEMCON, 2007,* Kolkata, India. in CD ROM (Ref CT-1115) (December 2007)

[3]   <u>Kiran Patil</u>, Studies in Reactive Separations, Presented a Poster in *First Conference for Pune University Teachers*, BCUD, University of Pune**,** (November 2007)

[4]   <u>Kiran Patil</u>, Pradnya Baviskar, Puneet Karan, Process for the Continuous Production of Isoamyl acetate via Reactive Distillation, presented a Poster in *AVISHKAR 2008,*arranged by BCUD, University of Pune**,** (Sept.2008)

[5]   <u>Kiran Patil</u>, Furquan Momin, Modeling and Simulation for Synthesis of Isoamyl acetate by Reactive Distillation, Presented in *INNOVATION 2008*, arranged by BCUD, University of Pune, (November 2008)

[6]   <u>Kiran Patil</u>, Furquan Momin, Iso amyl acetate Synthesis via Reactive Distillation: Simulation Studies, presented in *National Conference, NUCONE 2008, NIT, Ahemadabad*, October 2008.

[7]   <u>Kiran Patil</u>, Bhaskar D. Kulkarni, Furquan Momin, Saloni Salvi, Process for the Continuous Production of Isoamyl Acetate via Reactive Distillation, Presented in *CHEMCON 2008, Indian Institute of Chemical Engineers, Chandigad, 2008,* available in CD ROM (Ref CT-106) (December 2008)

[8]   <u>Kiran Patil,</u> Bhaskar D. Kulkarni, Puneet Karan, "Production of fatty Acid Esters by Reactive Distillation: Experimental studies", presented at *CHEMCON – 2009,* held at Visakhapattanam in December 2009, [Ref No: TS 1598], (December 2009)

[9]   <u>Kiran Patil</u>, Pankaj Choudhary, Tanvi Bhatia, Distillation Operations: Methods, Operational and Design Issues, Presented in *National Conference on Advances in Heat and Mass Transfer*, FAMT, Ratnagiri, 30-31 (October 2009)

[10]   <u>Kiran Patil</u>, Kedar Vechalekar, Modeling and Control Aspects of Reactive Distillation, presented in *National Conference on Advances in Heat and Mass Transfer*, FAMT, Ratnagiri, (October 2009)

[11] <u>Kiran Patil</u>, Kedar Vechalekar, Priyanka Kadam, Distillation Operations: Modeling and Control Issues, Presented in *National Conference on Advances in Heat and Mass Transfer*, FAMT, Ratnagiri, (October 2009)

[12] <u>Kiran Patil</u>, Bhaskar D. Kulkarni, Puneet Karan, Purva Goel, Cleaner Technology for Recovery of Acetic Acid from Industrial Waste Water via Reactive Distillation, Presented in *Indo-Italian Conference on Emerging Trends in Waste Management Technologies (ETWMT – 2009), MAEER's, MIT, Pune (December 2009)*

[13] <u>Kiran Patil</u>, Bhaskar D. Kulkarni, Modeling and Simulation for Reactive Distillation Process using Aspen Plus, Presented in National Symposium on Reaction Engineering (NSRE-2010), at NIT**,** Raipur (January 2010)

[14] <u>Kiran Patil</u>, Bhaskar D. Kulkarni, Reactive Distillation Technology for Cleaner Production of Industrial Chemicals, Presented in *International Conference on Instrumentation (ICI-2010): "Automation for Future"* at Cummins College of Engineering, (January 2010)

(b) Publications in Referred Journals (National/ International)

[1] <u>Kiran Patil</u>, Bhaskar D. Kulkarni, Kinetics of the Esterification Reaction of Acetic acid with 1-Pentanol over Ion Exchange Resin as Catalysts, (*Communicated to International Journal of Chemical Reactor Engineering)*

[2] <u>Kiran Patil</u>, Bhaskar D. Kulkarni, Synthesis of iso amyl acetate Synthesis by Reactive Distillation: Simulation and Experimental Studies (*Communicated to Asia-Pacific Journal of Chemical Engineering)*

[3] <u>Kiran Patil</u>, Bhaskar D. Kulkarni, Catalytic Distillation Modeling and Simulation using Aspen Plus *(Under Preparations)*

Other Publications:

Publication of Books:

Published following Four textbooks for degree courses in *Chemical Engineering* <u>covering the syllabus of major Universities of India</u> from Nirali Publishers, Pune, India.

[1] Principles of Mass Transfer Operations, Volume I, Sixth Edition, 2010

[2] Principles of Mass Transfer and Separation Processes ,Volume II, Sixth Edition, 2010

[3] Mechanical Operations: Principles and Applications , Fourth Edition, 2009

[4] Chemical Engineering Economics and Costing , (In Press)