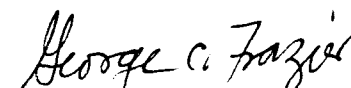
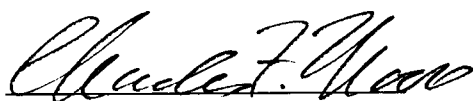


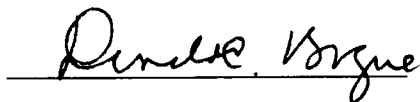
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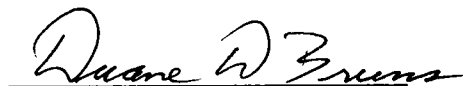
I am submitting herewith a dissertation written by Mohamed Ahmad Abdulla entitled "Reactive Distillation in Packed Columns." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemical Engineering.


George C. Frazier, Major Professor

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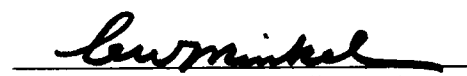








Accepted for the Council:


Associate Vice Chancellor and
Dean of The Graduate School

REACTIVE DISTILLATION IN PACKED COLUMNS

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee

Mohamed A. Abdulla

December 1997

DEDICATION

I dedicate this work to my wife, Dalal Abduli, for her support during my graduate study.

ACKNOWLEDGMENTS

I would like to thank many people who have helped me during my research: Doug Fielden and his crew at the machine shop, Frank Holliway, and Rick Bowers. Special thanks to the members of my committee, D. Bruns, D. Bogue, C. Moore, and D. Clark, for their generous aid. To my advisor, Dr. George Frazier, from whom I have learned more than from anyone else, for his support and the knowledge I gained, I am very grateful.

ABSTRACT

Reactive distillation is becoming a popular technique for chemical separation because it has many advantages over conventional distillation processes. The use of reactive distillation allows one to utilize the heat of reaction to enhance mass transfer, to influence the chemical equilibrium by removing the reaction products, and in some cases to overcome the restrictions of azeotropic mixtures.

Although the results of many studies have been published dealing with the simulation of reactive distillation in plate columns, few publications have dealt with the simulation of reactive distillation in packed columns. In this study, a mathematical model was developed to simulate reactive distillation processes in packed columns. In addition, the esterification reaction of methanol and acetic acid was studied experimentally to verify the model. Because of the corrosive nature of the system used, a packed column is more advantageous than a plate column since corrosion resistance packings are available and the columns are potentially less expensive.

To accurately represent the mass and heat transfer in packed columns, the model considered both the mass and heat balance equations and the vapor-liquid interfacial flux calculations for multicomponent systems. The concentration and temperature profiles were calculated along the column using a Runge-Kutta method to solve the set of differential equations representing the system.

An 84-inch-long laboratory packed column with a 1.5-inch i.d. was built and filled with 1/4-inch intalox saddle packing in order to perform the esterification reaction to compare

with the predictions of the model. Selected reflux ratios, methanol-to-acid ratios, and feed rates were used to study the effects of these variables on distillate purity and reactant conversion.

The concentration and temperature profiles predicted by the model showed good agreement with the experimental results. The maximum error was 20% in one run, and the minimum error was 0.56% in another run. The average error of all of the runs was about 10%, which is considered satisfactory since many variables and parameters affected both the experimental results and model predictions. The simulation showed that the results are relatively sensitive to the mass transfer coefficient for the vapor-liquid interface. It is therefore important that an accurate mass transfer correlation be available for the packing of interest for use in precise column design.

Reflux ratio affects both distillate purity and fractional conversion. At a constant boil-up rate, distillate purity increased with increase in reflux ratio, while the fractional conversion decreased. It therefore appears that an optimal value of the reflux ratio may exist which may be different from that obtained for conventional distillation.

At constant reflux ratio and boil-up rate, the increase in methanol to acid feed ratio increased the conversion but reduced the distillate purity. The conversion also increased when a low feed rate was used with small changes in the distillate purity.

Liquid hold-up is a particularly important factor in the reactive distillation of the methanol-acetic acid system. This study showed that if a packing were available capable of providing double the hold-up of the Intalox packing used in this study then the reactant conversion potentially could be increased from 86% to 95% in the laboratory column.

This study showed, further, that should the mass transfer model be simplified, the computational time can be reduced by as much as 20% in some cases, but with a little loss in accuracy. The simplified model can be used for preliminary, scoping calculations required for column optimization, but the complete model is recommended for finalizing the design.

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LIST OF SYMBOLS

A	Cross sectional area of the column, m^2
a	Interfacial area per unit volume, m^2/m^3
a_p	Specific packing area, m^2/m^3
B	Bottom flow rate, mol/s
C_p	Specific heat at constant pressure, J/mol K
C_t	Total molar density, mol/ m^3
D	Diffusivity, m^2/s , also distillate flow rate, mol/s
E	Heat transfer rate, W/ m^2 , also correction factor in Equation 3.3.48
F	Feed flow rate, mol/s
Fr	Froude number
g	Acceleration due to gravity, $9.81 m/s^2$
H	Molar enthalpy, J/mol
H_o	Liquid holdup, m^3/m^3
H_R	Heat of reaction, J/mol
h	Heat transfer coefficient, W/ $m^2 K$
J	Diffusive flux, mol/ $m^2 s$
K	Equilibrium constant
k	Mass transfer coefficient, m/s
k_r	Reaction rate constant, $m^3/mol s$
L	Liquid flow rate, mol/s

l	Component liquid flow rate, mol/s
M	Molecular weight, kg/mol
N	Diffusive flux, mol/m ² s
P	Total pressure, atm
P^s	Saturated vapor pressure, atm
Pr	Prandtl number
q	Heat flux, W/m ²
R	Universal gas constant
Re	Reynolds number
r	Reaction rate, mol/m ³ s
Sc	Schmidt number
T	Temperature, K
t	Temperature, C
V	Vapor flow rate, mol/s
v	Component vapor flow rate, mol/s
We	Weber number
x	Liquid mole fraction
y	Vapor mole fraction
Z	Position in distillation column, m

Subscripts

B	Referring to bottom conditions
-----	--------------------------------

- b Referring to boiling point
- c Referring to critical properties
- D Referring to distillate conditions
- F Referring to feed.
- i Component number
- j Component number
- k Component number.
- m Referring to mixture
- n Number of components
- t Referring to total

Superscripts

- I Referring to interface conditions.
- o For dilute solution
- L Referring to liquid phase
- V Referring to vapor phase
- Partial molar value

Greek Letters

- ε Defined by equation 3.2.25
- δ Weighing factor
- Φ Defined by Equation 3.3.51

ϕ	Volume fraction in equation 2.4.11
Γ	Thermodynamic factor from activity coefficient model
γ	Activity coefficient.
η	Dipole moment.
λ	Thermal conductivity, W/m.K
μ	Fluid viscosity, or chemical potential
ν	Stoichiometric coefficient for a component in a reaction
Θ	Defined by Equation 3.3.50
ρ	Density, kg/m ³ .
σ	Surface tension, dyne/cm.
ω	Acentric factor.

1. INTRODUCTION

The combined simultaneous performance of a chemical reaction and a multicomponent distillation is called reactive distillation. The technology was first applied in the 1920s to esterification processes using a homogeneous catalyst and was reviewed later by Keyes (1932). More recently, the technology was applied to several distillation and gas cleanup treatments. The most important advantage of reactive distillation is the reduction in capital cost. By conducting the reaction and distillation in one column, two process steps are combined in one, along with eliminating other associated pumps, piping, and instrumentation. Depending on the specific chemical reaction being performed, other advantages of using reactive distillation might include:

- (1) the utilization of the heat of the reaction for the evaporation of liquid phase,
- (2) the self regularity of the temperature of the reactor when exothermic reactions are conducted due to evaporative cooling.
- (3) the ability to influence the chemical equilibrium by fast product removal, and
- (4) the ability to separate azeotropic mixtures.

Many commercial reactive distillation processes have been developed. Some of these can be found in the process for the production of high purity methyl acetate patented by Agreda (1982); the process for the production of Nylon (Grosser et al, 1987); and the process for the production of methyl tert-butyl ether (MTBE) (Smith, 1981). Reactive distillation technology may also be applied to many chemical reactions such as isomerization, dimerization, esterification, and reactions involving the separation of closely

boiling point mixtures of the same nature such as m-xylene and p-xylene (Terril et al, 1985). Having a relative volatility of 1.02, m-xylene and p-xylene can be separated by reactive distillation using sodium p-xylene as a reactive entrainer. On the other hand, it requires many more plates and a higher reflux ratio to separate them by extractive or azeotropic distillation.

Most of the research done in modeling and simulating reactive distillation processes has been performed on plate column operations. One can refer to the work of Suzuki (1971); Saito (1971); Kumatso and Holland (1977); and Chang and Seader (1988). Little attention has been directed to performing such processes in packed columns. The only work that existed was that of Sawistowski and Pilavakis (1988), until Yuang and Xien (1992b) developed a model to simulate a catalytic distillation process based on the rate-based, or non-equilibrium, model of Krishnamurthy and Taylor (1985).

The use of packed columns for a wide variety of applications in industry is increasing. This is due to the evolution of higher capacity and higher efficiency mass transfer packings and improvements in distributors and support plates. Coker (1991) suggested that in gas plants, the trays that were previously used in fractionating columns can now be replaced by packings. Packings, such as plastic saddles and rings, can improve the capacity for absorption and heat transfer applications. Packed columns have also been found to be advantageous where corrosion resistance is essential. With improvements in the design of liquid distributors, packed columns of large diameters have been used increasingly for applications in the chemical industry.

For many reactive distillation systems, acids like acetic acid are the primary reactant with alcohols such as methanol or ethanol in esterification reactions. Both acetic acid and sulfuric acid, which is used as a catalyst in such reactions, can be harmful and corrosive to column interiors. In many cases, a special column design, which could increase the capital cost, would be necessary to prevent this problem (Agreda, 1990).

With such advantages of packed column uses in industry, a feasibility study is necessary for modeling and operating reactive distillation processes, taking into account existing models that have been developed for conventional packed column operations.

To describe the operation of a multicomponent reactive system in a packed column, the steady state mass balance, the energy balance, the reaction kinetics, and the interface mass and heat transfer must be solved along the column length. A suitable numerical method with a fast conversion time should be implemented to solve the set of differential equations.

Sawistowski and Pilavakis (1988) applied Gear's method to solve the set of differential equations. The model was based on a single constant value of mass transfer coefficient obtained from an experiment on a binary system. In many runs convergence was not attained and the model was not applicable to the multiple feed case.

The method described by Yuxiang and Xien (1992) was based on the non-equilibrium model described by Krishnamurthy and Taylor (1985), and thus consisted of a large number of non-linear equations, which they solved using Newton's method. The solution requires the evaluation of the partial derivatives of the thermodynamic properties with respect to temperature, pressure, and composition, which are the most awkward to

obtain and the ones that have the most influence on the rate of convergence, as suggested by Krishna (1993). Moreover, the pressure is considered an unknown variable in this model, and thus the derivatives of K values, with respect to the pressure, must be evaluated. Krishna suggested that neglect of these derivatives (even though they are often small) can lead to convergence difficulties.

It would be useful then if a model could be developed that utilizes the advantages of both previous models. This numerical model should provide reliable and fast convergence, incorporate all physical property calculations, and evaluate the interfacial flux by use of an appropriate but theoretically based models. Once developed, the model could be used to study the effect of various parameters on conversion and distillate composition as well as to develop a design for a packed column for a particular reactive distillation application.

1.1 OBJECTIVE

The objective of this work is to model a multicomponent reactive system in a packed distillation column. The output from the model for a specific reaction (such as the esterification reaction of methanol and acetic acid) will be verified with experimental data collected from a laboratory experimental column.

1.2 METHODOLOGY

The mathematical model consists of the solution of the steady state component material and energy balances at each increment of the packing. The balances incorporate

the solution of the mass and energy transfer along the interface in both phases, the kinetics of the chemical reaction, and the vapor-liquid equilibrium for the multicomponent system. The Runge-Kutta method subroutine provided by Matlab (1994) is used in the program developed to solve the model equations on a Unix workstation. Composition and temperature profiles in both phases are determined at each packing increment.

Experimental data are necessary to determine the validity of this model. Thus, a model reactive system will be used to validate the model, this system is the production of methyl acetate from methanol and acetic acid. The esterification reaction will be conducted in a laboratory packed tower using selected packings. The experimental results, particularly the product purity and reactant conversion, for a given packing height will be compared with results obtained by calculations from the model.

2. LITERATURE REVIEW

2.1 REACTIVE DISTILLATION IN GENERAL

The idea of reactive distillation goes back to the 1920s when it was applied to esterification reactions. The techniques applied to homogeneous reactions were reviewed by Keyes (1932). Esterification is considered one of the most important reactions in the chemical industry. More than 500 esters are produced by various manufacturers all over the world (McKetta, 1983). These esters cover a wide range of uses, including plasticizers, flavors and fragrances, pesticides, solvents, medicinals, surface-active agents, chemical intermediates, and monomers for resins and high molecular weight polymers. In 1979, 254 million pounds of carboxylic esters were produced in the US, totaling 133 million dollars in sales (McKetta, 1983).

Conversion limitations in esterification reactions were the main reason for the development of reactive distillation processes. Since esterification reactions are equilibrium limited, and reversible, it is difficult to achieve high conversion of reactants in a fixed bed or a stirred tank reactor. Immediate separation of the ester after its formation will increase the conversion. Another problem associated with the production of esters is the formation of azeotropes. In systems such as the production of methyl acetate from methanol and acetic acid, a difficult problem is the purification of methyl acetate from the minimum boiling azeotropes of methyl acetate with water (5 wt% water) and methyl acetate with methanol (18 wt% methanol).

Closely boiling point mixtures are usually difficult to separate in conventional distillation columns. The most effective method of separation is extractive distillation, where a third component (an entrainer) is added to increase the relative volatility between the two original components. This process is very effective if the two components are of different chemical nature. However, it cannot be effective if the two components are of the same chemical nature, such as isomers, since the entrainer will have almost the same effect on both components and, therefore, does not change their relative volatility.

Doherty et al (1985) explored the possibility of using fast, reversible, and selected reactions combined with distillation to separate close boilers. They showed that it is possible to separate m-xylene and p-xylene (relative volatility =1.02) by using sodium p-xylene as a reactive entrainer in a column with 11 theoretical plates. The idea is to introduce a third component in the column so that a reversible reaction occurs. The reactive entrainer should react with one of the isomers, for example the heavy one, and form a heavy component so that the light isomer goes to the distillate, while the heavy isomer, reaction entrainer, and reaction product go to the bottom. A second column will be needed to separate the heavy isomer from the entrainer. An overhead purity of 99.99% of p-xylene on a solvent-free basis was achieved in a column of 11 trays. A recent study by Grosser et al (1987) showed that for mixtures with a relative volatility less than 1.06, there is a large economic incentive to consider the use of a reactive entrainer in a distillation column.

The application of reactive distillation to reactions that rely on a solid heterogeneous catalyst has been described by Sennewald et al (1971). A promising area

for this application is the production of ethers. With the new regulations of the Clean Air Act, a large demand of ethers for gasoline reformulation is expected. Ethers, such as methyl tert-butyl ether (MTBE), tert-amyl methyl ether (TAME), and ethyl tert-butyl ether (ETBE), are expected to be in high demand in the next few years. In the production of MTBE from methanol and isobutylene, a conversion of 90-97% of isobutylene can be achieved in a single stage conventional process using two series-flow reactors followed by a separation and external recycle of excess methanol. Degarmo (1992) suggested that in a reactive distillation column, a conversion of isobutylene up to 99% or higher can be achieved. This increase in production should quickly defray the cost of implementing reactive distillation. A polymeric catalyst packing, which was shaped like rasching rings, was used by Sundmacher (1993) for the production of MTBE in a 104 cm laboratory packed column, and a 99% conversion of isobutene was achieved by Jacob et al (1993) using the same process.

The technology is even more promising for TAME, since the reaction between methanol and isoamylene is moderately limited by the reaction equilibrium. Degarmo et al (1992) suggested that it is possible to achieve a 60-70% conversion of isoamylene using a single stage conventional process, while in a reactive distillation process, the conversion can be boosted to 91% or higher.

Koch Engineering Company, Inc.; UOP, Inc.; and Huls AG have incorporated reactive distillation technology into the Huls MTBE process, and the resultant process, Ethermax (for the production of MTBE, TAME, or ETBE) is available for license by UOP.

Many other authors investigated the application of reactive distillation in the chemical industry. Grosser (1987) has investigated the application of reactive distillation to polycondensation reactions, such as in the production of Nylon 6,6. Dupart et al (1991) focused on the separation of 3-picoline and 4-picoline isomers through complexation by an organic acid. There are many candidate reactions that can be investigated to be implemented by reactive distillation, such as isomerization, dimerization, esterification, chlorination, hydration, polymerization, and methylation reactions.

In general, reactive distillation is a promising technique that can achieve higher conversion levels than conventional processes for selected chemical reactions. Other benefits include reduced capital cost, reduced plant operational costs, the utilization of the heat of the reaction for the evaporation of liquid phase, and the elimination of reactor hot spots.

As in many reactions involving acids and alcohols, corrosion plays a major role in equipment design and cost. In the Eastman plant (Agreda, 1990), a methanol recovery column was added to reduce the corrosion rate, and detailed corrosion studies were made to determine the best construction materials for the equipment needed in the commercial plant. Furthermore, the presence of acetic acid and the sulfuric acid catalyst in esterification reactions increases the tendency of corrosion in such systems. Keyes (1932) stated that it is necessary to have as intimate contact as possible between the vapor and the liquid. This means that the ordinary bubble-cap plate is appropriate in most cases. However, when corrosive vapors or liquids are present in the reaction, bubble-cap plates are not always feasible because the construction of these plates from corrosion-resistant

materials is very expensive. It becomes necessary in these cases to resort to the filled type of columns, usually made of stoneware and acid-resisting filler.

With many types of corrosion resistance packing available from many vendors, packed columns are considered much cheaper than plate columns, and with the new development in structured packing, larger diameters and longer columns have been constructed and operated in the chemical industry. In many gas purification plants, plate-type columns were reconstructed and filled with packings. In other columns, plates were replaced by newly invented structured packings.

A recent study by Fuchigami (1990) of the hydrolysis of methyl acetate in distillation columns used a packed column filled with ion-exchange resin tablets to avoid the use of an expensive anti-corrosive material for the column. Other studies by Neuman (1984) and Pilavakis (1988) have considered packed-type columns for the same reason.

From the previous discussion, it is clear that there are some operational and economical incentives for exploring the possibility of using packed columns instead of plate columns for some reactive distillation systems. Therefore, the theoretical modeling of such systems and a study of the possibility of achieving high conversion with packed columns compared to plate columns is very important.

2.2 THEORETICAL MODELS FOR REACTIVE DISTILLATION IN PLATE COLUMNS

The increased study of reactive distillation in plate columns was accompanied by the development of many algorithms to model these systems. Many simulation and design

models were developed and are currently available for modeling reactive distillation processes in plate towers. Since 1970, calculation procedures for rigorously solving the mass, equilibrium, and energy balances in a multicomponent, multistage reactive distillation have been reported. For a numerical calculation, the different methods can be divided into three categories: (1) the bubble-point method using tear variables; (2) the dynamic approach, or relaxation technique; and (3) models using the Newton-Raphson method.

The tearing method, considered first by Suzuki et al in 1971, was sufficiently fast when applied to steady state cases, and little computer storage was necessary since no derivative computing was needed. However, in certain cases, such as for highly non-ideal solutions, in solutions with complex reaction kinetics, or where large differences in the boiling points of the various reaction components exist, convergence is very difficult. For unsteady state cases, the relaxation method provided better stability but was slower than that for the steady state case (Komatsu, 1977). In this case, some special corrective techniques had to be used when considering simple methods for solving the set of unsteady cases equations representing the system. In many of these cases, Euler's method and the classical Runge-Kutta methods were used, and due to the large number of iterations required, the computing speed sharply decreased. Bogaki et al (1988) investigated all reported methods for both steady and unsteady state cases and proposed the Adams-Moulton method to solve the set of differential equations for the reacting system. The proposed method proved to be very fast and numerically stable. The obtained results from their simulation were consistent with the experimental data

presented by Komatsu (1977) for the esterification reaction of ethanol and acetic acid in a plate tower.

The Newton-Raphson method was first considered by Nelson (1971) and was implemented later by Komatsu and Holland (1977) and Izarraraz et al.(1980). In all of these works, convergence was achieved very quickly from a stable starting guess. This method has proven to be applicable to many cases. However, it requires large computer storage and the computation of complicated derivatives. Chang and Seader (1988) considered the Homotopy-continuation method to overcome the convergence problem encountered by the Newton-Raphson method because of the high degree of interaction among the iteration variables. Furthermore, Aljeski (1991) considered the mixing effect on the plates in modeling the reactive system. Ruiz (1995) reviewed all the models that have been developed for plate columns and concluded that all the models are not rigorous enough to include hydraulic variables such as pressure gradients, liquid holdup, and weeping and flooding. Without this capability, only instantaneous chemical reaction dynamic paths can be properly analyzed using the simultaneous chemical and physical equilibrium approach. Ruiz developed a robust and generalized model that consists of a set of ODEs obtained from mass and energy balances around each plate, condenser, and reboiler. In addition, he developed a set of algebraic equation correlations to predict physical properties, plate hydraulics, and mass and heat transfer, along with a set of optional procedures for considering the dynamics of the reflux drum, the reboiler, and the classical feedback control structure. Many different types of trays were considered, and

the program was implemented for personal computers in a package called READYS (REActive Distillation DYnamic Simulator).

From the previous discussion, it is clear that extensive work has been done in modeling reactive systems in plate distillation columns. Recently, Aspen Plus has come out with a new software package for modeling reactive distillation processes. On the other hand, little attention has been directed to reactions in packed distillation columns.

2.3 THEORETICAL MODELS FOR PACKED COLUMNS

2.3.1 Introduction

The use of packed columns for separation problems in distillation and absorption has been extended in recent years due to improvement in the design of packings and other arrangements used for the packings, especially liquid distributors which influence the mass transfer in the column (Wardle, 1994). In comparison with the design models for stage columns, packed columns received less attention in the literature, and the design of packed columns was usually based on the assumption of Height Equivalent to a Theoretical Plate (HETP). An inaccurate plate efficiency or an inaccurate HETP can result in large errors of the calculated product composition, even if the number of theoretical plates has been computed with sufficient accuracy. Most of the methods for calculating HETP do not consider the kinetics of multicomponent mass transfer and are based on the assumption of non-diffusional interactions between the components on mass transfer.

Two approaches have been proposed to describe the behavior of packed columns. The first divides the packed column into a large number of discrete mass transfer sections,

with each being considered equivalent to a theoretical stage in a tray column. Holland (1975) considered this approach. The second approach attempts to solve the differential equations derived from the use of the two-film theory of mass transfer. Rosenberg (1980), Treybal (1968), Srivastava (1983), and Gorak (1985) are examples of work found in the literature that considered various types of numerical methods to solve the differential equations associated with this approach.

2.3.2 Theoretical Models for Multicomponent Systems in Packed Columns

The objective of this section is to critically examine models used for simulating packed column separation processes. As mentioned in the previous section, early design models were based on the HETP or the equilibrium stage analogy proposed by Holland (1975), which contrasts with packed column operations where mass transfer must be accounted for explicitly. In the simple model for tray columns, only phase equilibrium relationships are required to determine the compositions of the liquid and vapor phases, while in continuous contact columns, the rate of mass transfer between the phases determines the phase compositions, which is a function of the mass transfer resistance, the interfacial area, and the vapor-liquid equilibrium. Even though this model is used in practice, there is no theoretical justification for this approach, and there are numerous difficulties in correlating the HETP versus design and operating conditions (Treybal, 1980).

The second approach is to solve directly the differential equations generated by applying the two-film concept of mass transfer. Stocker and Wilke (1977) solved the

absorption problem by considering the integration of the dynamic equations to steady state, thus avoiding iterations in the spatial direction. Feintuch and Treybal (1978) used the shooting method to solve the two-point boundary value problem. Kelly and Rousseau (1984) tested the Feintuch method for a multicomponent gas absorption problem and noticed many convergence problems, mathematical discontinuities, and large errors between the theoretical and experimental mole fractions of the sweet gas.

Table 2.3.1 shows a comparison between the calculated and experimental data of a 3-component system from the work of Feintuch and Treybal. The temperatures from the experimental data were much higher than the calculated ones. The calculated height of the column was just over half of the experimental value.

Feintuch (1973) stated that possible errors in the calculation of the physical properties, the inaccuracy of the correlations used for the interfacial area and mass transfer, and experimental errors may have caused the increase in the packing height.

Table 2.3.1 Calculated vs. experimental data for Acetone-Air-Water system (Feintuch, 1973)

Materials	Experimental data	Calculated data
Gas Temperature Inlet, °F	58.8	58.8
Gas Temperature Outlet, °F	72.0	55.6
Liquid Temperature Inlet, °F	54.5	54.5
Liquid Temperature Outlet, °F	69.3	62.9
Acetone Recovery, %	92.55	92.55
Packing Height, Ft	16.29	8.96

Von Rosenberg (1980) conducted a steady state simulation of multicomponent distillation using finite difference techniques. In his development, Von Rosenberg assumed constant vapor and liquid molal rates in each section of the column. Furthermore, all liquid and vapor streams were considered at their bubble and dew point temperatures. Consequently, no enthalpy balance was required, and only material balance was used. The overall mass transfer coefficient used was considered to be equal for all components. In addition, constant relative volatilities were assumed throughout the column. Due to many simplification assumptions, the Von Rosenberg model is limited in its application, and any modifications can increase the complexity and the dimensionality of the equations, thus increasing the difficulties in convergence and computer execution time.

Srivastava and Joseph (1984) applied the orthogonal collocation method to the dynamic model equations of a multicomponent packed separation column. This model is based on the two-film theory of heat and mass transfer and utilizes experimental correlations for the transfer coefficients. The method was found to converge rapidly with respect to the number of collocation points. The advantage of this method over the finite difference method is that fewer spatial discretization points are needed to achieve the same accuracy. Figure 2.3.1 shows the steady state profile of liquid composition by both Von Rosenberg and Srivastava. Whereas Von Rosenberg used 25 grid points for each section of the column, the collocation method only required 3 collocation points to achieve the same accuracy.

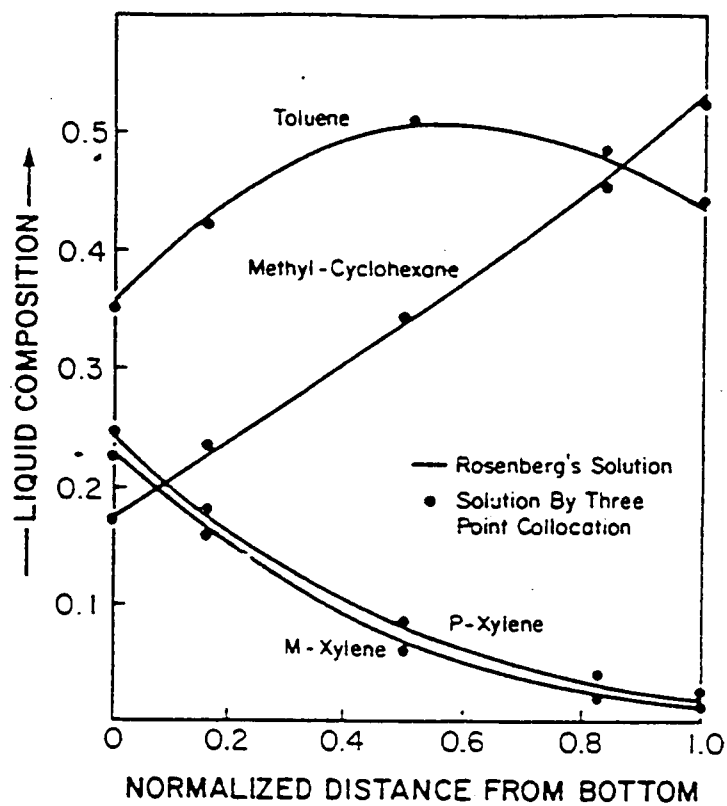


Figure 2.3.1 Steady state profile of liquid composition (Srivastava, 1984)

Srivastava's model considered the effective diffusivity model for the interphase mass transfer and was found to greatly effect the accuracy of the results and the actual description of the mass transfer calculation.

Billingsley and Chirachavala (1981) improved upon all previous works and developed a model for solving the packed column problem. To solve the non-equilibrium multicomponent two phase steady state problem, they used polynomial approximations along with the Newton-Raphson iteration to integrate the non-linear differential equation. The elements of the Jaccobian matrix were computed analytically, and the linear differential equations were solved by collocation using B-spline basis functions.

Billingsley and Chirachavala showed that the procedure was effective in obtaining solutions even when the equations were stiff. In four of the tests they ran, convergence was attained in just a few iterations; however, for stiff problems, more iterations were required to attain conversion. This model would be very attractive if the Jaccobian matrix could be easily calculated. Unfortunately, this is not the case. Moreover, this method considered the mass transfer coefficients, the thermal conductivity, and the effective diffusivities as constants, and it ignored the effects of concentration on the multicomponent diffusion coefficient.

Hitch et al (1986) developed an algorithm for the steady state simulation of multicomponent adiabatic absorption in packed columns. The differential equations that describe the physical absorption were reduced to algebraic equations by using a finite difference method. The algebraic equations were then solved by using a block-tridiagonal matrix decomposition procedure. Two advantages of this model over all of the models

described previously are that it is flexible enough to simulate more than one type of mass transfer process and it is capable of handling complex multicomponent systems in a rigorous fashion. The computer simulation, known as SIMCAL, was tested with experimental data obtained from a pilot plant, and its performance was compared with that of an algorithm previously developed by Kelley (1984). The results showed that SIMCAL more accurately simulated actual plant conditions.

Gorak and Vogelpohl (1985) considered the Runge-Kutta method to solve the set of differential and matrix equations describing the multicomponent distillation problem in a packed column. Although many simplifications were applied to this model, the model considered the exact solution of the multicomponent mass transfer equations developed by Krishna and Standard (1979). The main goal of his study was to test the Krishna/Standard model against experimental results from ternary distillation in a packed column.

Krishnamurthy and Taylor (1985) considered a rate-based, or a non-equilibrium, model that is quite different from all of the previously discussed models. Their model, which was called MERQ (Material balance, Energy balance, Rate eQuilibrium), did not attempt to model the column as a differential contactor, but instead used the non-equilibrium stage analysis. They established a set of equations consisting of the heat and mass transfer rate equations and the equilibrium relationships at the interphase. The model provided better descriptions and evaluations of the transport properties, such as the heat and mass transfer coefficients and the interfacial area. It also provided an effective solution of the highly non-ideal MERQ equations. Krishnamurthy and Taylor solved the MERQ equations simultaneously using Newton-related methods to overcome the non-

linearity. As previously mentioned, the solution requires the evaluation of the partial derivatives of the thermodynamic and transport properties with respect to temperature, composition, and in some cases, pressure, which are the greatest challenges to this model. According to Krishna (1993), the neglect of these derivatives (even though they are often small) can lead to convergence difficulties.

The major differences between the various methods summarized in Table 2.3.2 are in the boundary conditions required to specify the problem (absorption versus distillation) and in the numerical methods used to solve the differential-algebraic systems of equations. Gorak (1987) compared the sensitivity of the non-equilibrium stage method (NSM) and the differential technique (DT) with experimental data taken from a laboratory column of 0.1 m diameter containing SULZER CY packing (0.5 m packing height) at total reflux conditions. Both methods gave similar results and differed only in numerical efficiency.

Another major difference between the various methods summarized in Table 2.3.2 is the model used to describe the interphase mass transfer. For multicomponent systems, the rate of mass transport at the interphase can be modeled using the expression

$$N_i = C_i^L \dot{k}^L (X^I - X^L) + X^L N_i \quad (2.3.1)$$

$$N_i = C_i^V \dot{k}^V (Y - Y^I) + Y^I N_i \quad (2.3.2)$$

where $\dot{k}^L$ and $\dot{k}^V$ are the matrices of the effective mass transfer coefficient, and X^I and Y^I are the column vectors of the liquid and the vapor mole fractions at the interface. For a rigorous multicomponent system, both $\dot{k}^L$ and $\dot{k}^V$ should be evaluated using the Generalized Maxwell-Stefan equations. While in the effective method, both $\dot{k}^L$ and $\dot{k}^V$

Table 2.3.2 Models for Packed Column Separation Processes

Author	Process	Model	Solution methodology	Mass transfer model
Holland (1975)	Distillation	Equilibrium stage	Conventional methods for equilibrium stage process	---
Stocker/Wilke(1977)	Absorption	Differential techniques	Integration of dynamic equations to steady state	Effective diffusivity model
Feintuch & Treybal (1978)	“	“	Shooting method	“
Von Rosenberg & Hadi (1980)	Distillation	“	Finite difference	“
Billingsley&Chirachavala (1981)	Distillation & Absorption	“	Global Spline Collocation	“
Srivastava&Joseph (1984)	Distillation	“	Orthogonal collocation	“
Gorak&Vogelpohl (1985)	“	“	Range-Kutta method	Solution to the Generalized Maxwell-Steffan equations
Krishnamurthy & Taylor (1985)	Distillation & Absorption	Non-equilibrium stage analogy	Simultaneous solution of nonlinear equations	“
Hitch,Rousseau&Ferrel (1986)	Absorption	Differential contactor	Finite difference	Effective diffusivity model

are approximated as diagonal matrices of the effective transport coefficients and do not account for the multicomponent diffusion effect.

2.3.3 Modeling of Packed Column Reactive Distillation Processes

As mentioned in Section 2.2, the simulation of reactive distillation in plate columns has been extensively developed. Very little, however, has been done with regard to packed distillation columns. Sawistowski and Pilavakis (1979, 1988) were the first to develop an algorithm to solve such a problem. In their model, they considered the liquid phase reaction kinetics and the effect of the reaction on the interfacial transport fluxes. The set of differential-algebraic equations resulting from the mass and energy balance and the flux equations was solved using Gear's Method. The model did not account adequately for the interfacial fluxes in the multicomponent system but instead made use of a single constant mass transfer coefficient for each species obtained from binary experimental system. The model was also limited to the single feed case and convergence of the model was not achieved in many cases.

Yuxiang and Xien (1992b) were the first to consider a catalytic active packing reactive distillation process. In their model, they extended the non-equilibrium stage model of Krishnamurthy and Taylor (1985) to include chemical reaction effects, and they tested the model against experimental data for the production of MTBE in a reactive distillation process. Any inaccuracy in the calculation of the Jaccobian matrix in the non-equilibrium method could affect the convergence. Even though the model successfully used the Newton method for calculation efficiency, the proper formulation of the Jacobian

matrix is a big problem to be solved. More convergence problems are expected with the addition of chemical reactions terms.

It is clear from the previous discussion that the development of a practical model based on theoretical principles of packed column reactive distillation processes is incomplete. Therefore, further research in this area which explores the possibility of considering packed columns for processes involving highly corrosive environments would be useful. With the various numerical methods discussed in the previous section, it should be possible to choose one that could show a reasonable conversion incorporating the Generalized Maxwell-Stefan model for describing the mass transfer at the interface.

2.4 LIQUID PHASE MULTICOMPONENT DIFFUSION COEFFICIENT

2.4.1 Introduction

For process engineering calculations of the mass transfer coefficient, it is always required to know the value of the diffusion coefficient. In multicomponent systems, this value is quite complex and difficult to evaluate since it involves the dependency on the concentration of the different components, in addition to other factors such as temperature and pressure. In this section, we will discuss the application of the Generalized Maxwell-Stefan equation for calculating the multicomponent diffusion coefficient in the liquid phase.

2.4.2 Molecular Diffusion in Fluids

Mathematically, diffusion processes in binary mixtures can be described using Fick's Law

$$J_1 = -C_t D_{12} \nabla x_{12} \quad (2.4.1)$$

where J_1 is the diffusion flux of component 1, relative to the local molar average velocity of the fluid.

For multicomponent mixtures, Fick's Law can be extended for a system with n components to

$$J = -C_t [D] \nabla X \quad (2.4.2)$$

where $[D]$ is a $(n-1) \times (n-1)$ matrix of the multicomponent Fick's diffusion coefficient. In the multicomponent case, the Fick's diffusion coefficient is a strong composition dependent (Krishna and Taylor, 1993), and all attempts to correlate the multicomponent Fick's diffusion coefficient were unsuccessful. The Generalized Maxwell-Stefan (GMS) equation, which is based on the theory of irreversible thermodynamic, was used to correlate the multicomponent (GMS) diffusion coefficient (Krishna, 1993). The GMS can be expressed as

$$\frac{x_i}{RT} \nabla \mu_i = \sum_{j=1}^n \frac{(x_i J_j - x_j J_i)}{C_t D_{ij}} \quad (2.4.3)$$

where D_{ij} is the binary diffusion coefficient. Equation 2.4.3 can be expressed in the form

$$J = -C_t [B]^{-1} [\Gamma] \nabla X \quad (2.4.4)$$

where $[B]$ is an $(n-1) \times (n-1)$ matrix with elements

$$B_{ii} = \frac{x_i}{D_{in}} + \sum_{\substack{k=1 \\ i \neq k}}^n \frac{x_k}{D_{ik}} \quad (2.4.5)$$

$$B_{ij} = -x_i \left[\frac{1}{D_{ij}} - \frac{1}{D_{in}} \right]$$

and $[\Gamma]$ is an $(n-1) \times (n-1)$ matrix of thermodynamic factors with elements

$$\Gamma_{ij} = \delta_{ij} + x_i \left. \frac{\partial \ln \gamma_i}{\partial x_j} \right|_{T,P,k \neq j,n} \quad (2.4.6)$$

where δ_{ij} is a weighing factor

$$\delta_{ij} = 1 \quad \text{if } i = j$$

$$\delta_{ij} = 0 \quad \text{if } i \neq j$$

The value of Γ_{ij} for liquid mixtures can be estimated using activity coefficient models for multicomponent systems. For ideal mixtures, $[\Gamma]$ reduces to the identity matrix.

Evaluation of the $[B]$ matrix requires knowledge of the binary diffusion coefficient D_{ij} , which is a function of concentration. In the next section, we will discuss various equations in the literature that can be used to predict the diffusion coefficient in concentrated mixtures.

2.4.3 Diffusion Coefficient in Concentrated Liquid Mixtures

Most methods for predicting the GMS diffusion coefficients attempt to correlate the dilute coefficient D_{ij} as a function of composition.

Vignes (1966) suggested the composition dependence for a binary liquid mixture as

$$D_{ij} = (D_{ij}^o)^{x_j} (D_{ji}^o)^{x_i} \quad (2.4.8)$$

Krishna and Taylor (1993) judged that this equation is not always accurate as was shown earlier by Vignes and is not successful for mixtures containing an associated component such as methanol.

Leffler and Cullinan (1970) included the viscosity in the relation as

$$D_{12} = (D_{12}^o \mu_2)^{x_2} (D_{21}^o \mu_1)^{x_1} \quad (2.4.9)$$

A number of studies suggested the following expression

$$D = D^o \Gamma^m \quad (2.4.10)$$

where D^o is a function of the infinite dilution coefficient D_{21}^o and D_{12}^o and the composition of the mixture. Ruthbun and Babb (1966) found that $m=0.6$ for systems that exhibited positive deviation from Rault's Law and that $m=0.3$ for systems having negative deviation.

Siddiqi and Lucas (1986) investigated 43 mixtures of two polar components and found that Equation 2.4.10 can be correlated with $m=1$ and

$$D^o = \phi_2 D_{12}^o + \phi_1 D_{21}^o \quad (2.4.11)$$

where ϕ is the volume fraction.

Wesselingh and Krishna (1991) discussed the generalization of the Vignes equation to multicomponent mixtures in the form of

$$D_{ij} = \prod_{k=1}^n (D_{ij}, x_{k \rightarrow 1})^{x_k} \quad (2.4.12)$$

where the $D_{ij}, x_{k \rightarrow 1}$ are the limiting values of the Maxwell-Stefan diffusivities in a mixture where k is present in very large excess.

Wesselingh and Krishna (1990) suggested the following model for the limiting diffusivities:

$$D_{ij, x_{k \rightarrow 1}} = \left(D_{ij}^o + D_{ji}^o \right)^{\frac{1}{2}} \quad (2.4.13)$$

Combining Equations 2.4.12 and 2.4.13 yields the following expression for the binary Maxwell-Stefan diffusivity in a multicomponent system (Krishna, 1993):

$$D_{ij} = \left(D_{ij}^o \right)^{\frac{(1+x_j-x_i)}{2}} \left(D_{ji}^o \right)^{\frac{(1+x_i-x_j)}{2}} \quad (2.4.14)$$

In all these equations, the calculation of D_{ij} also requires the determination of the composition derivatives of the liquid phase activity coefficients to compute the elements of $[\Gamma]$ for non-ideal systems. It can be seen then that there is great uncertainty about generalizing these equations since they are very sensitive and dependent on the concentration of the components and on the activity coefficient models used to compute the composition derivatives. Because of the lack of experimental data for diffusion coefficients in multicomponent system, there is a need for further research in this area.

2.5 THE MANUFACTURE OF METHYL ACETATE

2.5.1 Background

The manufacture of methyl acetate via the reaction of methanol and acetic acid is difficult because of reaction equilibrium limitations and because of the formation of minimum boiling point azeotropes. Keyes (1932) discussed early attempts to develop a

continuous method for the production of methyl acetate. Two columns, a mixing tank, and three condensers were required to achieve a 70 mole percent ester in the distillate of the recovery column, whereas the first column was used as a reaction column. Keyes (1932) suggested adding a sulfuric acid catalyst to the reaction mixture in the mixing tank.

Sawistowski et al (1988) found that a second column was required to achieve high purity methyl acetate, but Agreda (1990) invented a process whereby a high purity methyl acetate of 99 wt% was produced in a single reactive distillation column in the presence of a sulfuric acid catalyst. The use of bubble cap trays in the reaction zone were required to achieve high liquid holdup. Residence time for the reaction mixture is crucial for high conversion and high product purity. For this reaction, high holdup times to attain the maximum residence time were achieved by using reverse flow trays with high weirs, high bubble cap risers, and large inlet and flow reversing zone sumps.

2.5.2 Concept and Reaction Kinetics

In a conventional methyl acetate process, liquid methanol is reacted with liquid acetic acid in the presence of an acidic catalyst to form methyl acetate and water according to Equation 2.5.1:



The rate of reaction is a function of the temperature, the catalyst concentration, and the concentration of the products and reactants. The reaction equilibrium constant is a weak temperature dependent (Smith, 1939). Therefore, the reaction product will contain all four reaction components, and a high conversion of one reactant can only be achieved

in the excess of the other reactant. However, if the reaction mixture is allowed to flash, there is a vapor composition that is related to the liquid composition by the activity coefficients and the vapor pressures of the components in the vapor. At vapor-liquid and reaction equilibrium, the ratio of product to reactants in the vapor phase is higher than in the liquid phase because of the higher volatility of methyl acetate relative to the other components. Thus, the overall extent of reaction achieved between the vapor and the liquid phases is greater than can be achieved in the liquid phase alone (Agreda et al, 1990).

Since the reaction is reversible, the rate of reaction is increased by removing the methyl acetate product from the reaction mixture. In addition, the counter-current flow of the reactants from the opposite ends of the column will ensure maximum contact and therefore high conversion of both reactants.

A difficult problem encountered by Sawistowski et al (1988) was the formation of the minimum boiling point mixture (azeotropes) of methyl acetate-methanol and methyl acetate-water. The distillate purity was always limited by the methyl acetate-methanol azeotrope (18 wt% methanol). To avoid the need for additional distillation columns and recycle streams, laboratory experiments performed at Eastman Chemical Company (Agreda, 1990) showed that acetic acid flowing from the top of the column works as an extractive agent, and the counter-current flow of acetic acid and methyl acetate and its azeotropes can be used to purify methyl acetate.

Figure 2.5.1 shows the basis of the counter-current reactive distillation column, where the reaction would take place in the middle section of the column. Methanol is fed

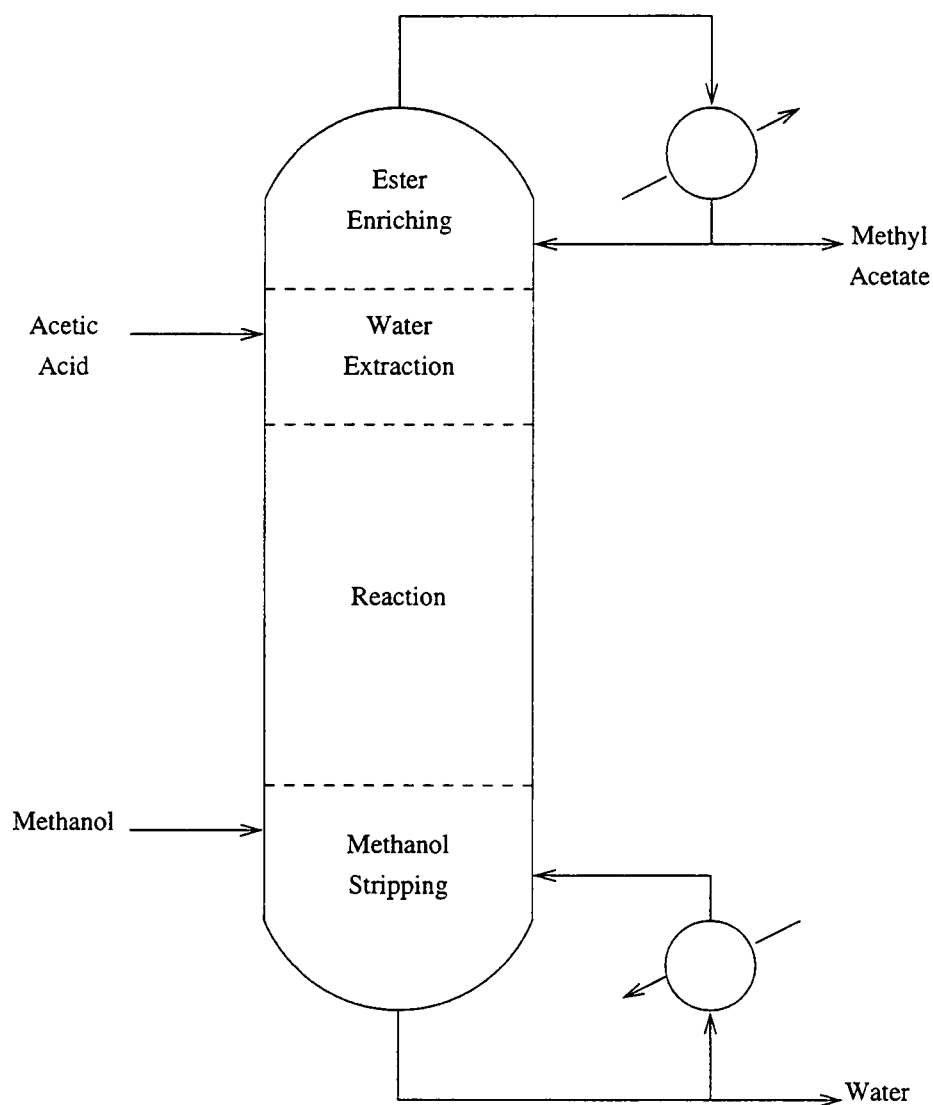


Figure 2.5.1 Conceptual diagram for the methyl acetate reactive distillation process (Agreda, 1990)

near the bottom of the column and acetic acid near the top of the column. Above the reaction section, water and methanol are extracted by acetic acid, while in the lower section, methanol is stripped from the by-product water. Methyl acetate should be the refined product at the distillate, and water should be the bottom product.

Early investigations of the use of a catalyst with this reaction were conducted using hydrochloric acid (Smith, 1939), sulfuric acid (Sawistowski et al, 1979), and an acidic organic polymer (Neuman, 1984) as catalysts. Agreda (1990) tested various types of catalysts and suggested that sulfuric acid is the most effective and economical for this reaction. Other catalysts that have been used successfully were phosphoric acid and Amberlite 200 acidic cation exchange resin. However, when phosphoric acid is used, a larger reactor is required, while the cation exchange resin requires a more complex reactor design. The catalyst can either be fed with the acetic acid feed or a few plates below that. The location of the catalyst feed is a major factor in the amount of water and/or methanol in the product, and only experimental testing will determine that location in the absence of a good predictive design model.

The rate of formation of the ester, r_E , per unit volume of liquid ($\text{gmol/m}^3 \cdot \text{s}$) was given by Smith (1939) as

$$r_E = \frac{k_r [H^+] C_t x_M x_A}{(x_M + K_e x_W)} \quad (2.5.2)$$

where K_e is the equilibrium constant and was found by Pilavakis (1974) to be

$$K_e = \frac{\rho_M}{M_M (0.11 + 0.0007043 t^{1.556})} \quad (2.5.3)$$

in which ρ_M is the density of methanol in gm/liters , and the term in parenthesis is in gmol/liters, and t is the temperature in °C.

The subscripts A, M, W refer to acetic acid, methanol and water, respectively. The value of k_r (m³/gmol.s) is given as

$$k_r = 1.2 \times 10^3 \exp\left(\frac{-10000}{RT}\right) \quad (2.5.4)$$

where the activation energy is in kcal/kmol, $R=1.987$ cal/mol. K , T is in K, and $[H^+]$ is the concentration of the catalyst.

Agreda et al (1990) developed an equation that covers the full range of compositions encountered in the column at various catalyst concentrations. Unfortunately, the values for the constants used in that equation were not provided.

2.5.3 Operating Conditions

There are many factors in reactive distillation that are expected to have a significant effect on the distillate purity and the conversion, as is the case for conventional distillation. The position and the ratio of the two feed components play a major role in the distillate purity and the conversion. Agreda (1990) suggested that the acetic acid and methanol feeds are to be fed in approximately stoichiometric quantities. However, an excess of methanol of the molar ratio 1.1-2 may be used to ensure the maximum conversion of acetic acid. Neuman (1984) showed that a ratio of 1.2 would be satisfactory for an adequate distillate purity and conversion.

Tests on feed position by both Agreda (1990) and Neuman (1984) showed that maximum conversion is attainable by feeding methanol closer to the reboiler and feeding the acetic acid near the top of the column.

The reflux ratio is expected to have a significant effect on the operation of the column. As the reflux ratio increases, the purity of the distillate increases, but the conversion decreases. This is probably due to the coupled effect of distillation and reaction. While purity increases, the reaction rate decreases because the column is near chemical equilibrium, and therefore the total conversion decreases. Agreda (1990) suggested that the optimum reflux ratio is about 1.5-1.7 and that the conversion decreases rapidly at a reflux ratio above 2.0.

The feed flow rate also has a large effect on the conversion and to a less extent on the distillate purity. Tests by Neuman (1984) in a chemorectification packed column showed that there are limits in the allowable flow rates because the reactor is also a distillation column. Table 2.5.1 shows that at low flow rates, the run was stopped because the feed rate was too low, and no reaction was taking place. At high flow rates, conversion declined very rapidly, and the column flooded.

The flow rate of the 95-98% sulfuric acid catalyst is expected to have little effect on the distillate purity, but the conversion may increase, as shown by Sawistowski et al (1988). Agreda (1990), however, suggested that when sulfuric acid is used, its flow rate is beneficial in a ratio of 1 kg sulfuric acid for 100 kg of acetic acid feed, and when higher catalyst concentration is employed, lower holdup times are required but give rise to an increased corrosion rate.

Table 2.5.1 Conversion and distillation purity as a function of feed rate. Neuman (1984)

Acetic acid mol/s	Methanol mol/s	Conv. %	Distillate wt %		
			<u>water</u>	<u>methanol</u>	<u>ester</u>
3.42×10^{-4}	4.12×10^{-4}	No Reaction			
4.46×10^{-4}	5.36×10^{-4}	84.1	2	8	90
5.94×10^{-4}	6.59×10^{-4}	72.1	2	8	90
6.86×10^{-4}	8.37×10^{-4}	66.2	1.5	5.5	93
7.73×10^{-4}	9.46×10^{-4}	60.3	2	8	90
8.26×10^{-4}	9.91×10^{-4}	The Column Flooded			

3. MATHEMATICAL MODELING

3.1 INTRODUCTION

Following the discussion in Chapter 2 of the models developed for reactive distillation in packed columns, the model presented here will consider the advantages of the Sawistowski et al method (1988) and Krishnamurthy's non-equilibrium method (1985) for packed column design.

The model will consider the simplification of the material balance to differential equations as described by Sawistowski et al (1988). The differential equations representing the energy balance will be derived and solved simultaneously with the material balance equations. The mass and heat fluxes across the interface will be calculated using the method described by Krishnamurthy and Taylor (1985). The calculation technique assumes the distillate rate and composition and then calculates the composition, the rate, and the temperature of both phases along the column. The convergence test is based on matching the bottom composition from the overall material balance and the equilibrium relation around the reboiler.

The Krishnamurthy model (1985) developed for steady state multicomponent packed distillation columns resulted in a large set of non-linear equations. The necessity of calculating the Jaccobian matrix and solving the large set of equations at each grid point increases the overall conversion time. Moreover, inaccuracies in the Jaccobian matrix could cause convergence problems. To overcome such problems, the need for Jaccobian matrix calculations was limited to the flux equations, while the material and heat balance

equations were solved as differential equations along the column. The following assumptions were made in the development of the model:

- 1) Mass and heat transfer occur only through the interface
- 2) The column is adiabatic
- 3) The two-film theory of mass transfer applies
- 4) The reaction takes place only in the liquid phase
- 5) The vapor phase is ideal
- 6) The pressure drop through the column is negligible

3.2 DESCRIPTION OF THE MODEL

A schematic illustration of a section of the packing located at position z , is shown in Figure 3.2.1 where the liquid from the section above comes into contact with the vapor from the section below. Mass and energy are exchanged across the interface between the phases. The total height of the column is equal to the total height of all the sections from top to bottom. For n chemical components, the following equations describe each section of the packing:

1-Total Material Balance

$$\frac{dL}{dZ} = -N_i^L aA + H_o A \sum_{i=1}^n v_i r_i \quad (3.2.1)$$

$$\frac{dV}{dZ} = -N_i^V aA \quad (3.2.2)$$

$$N_i^L = N_i^V \quad (3.2.3)$$

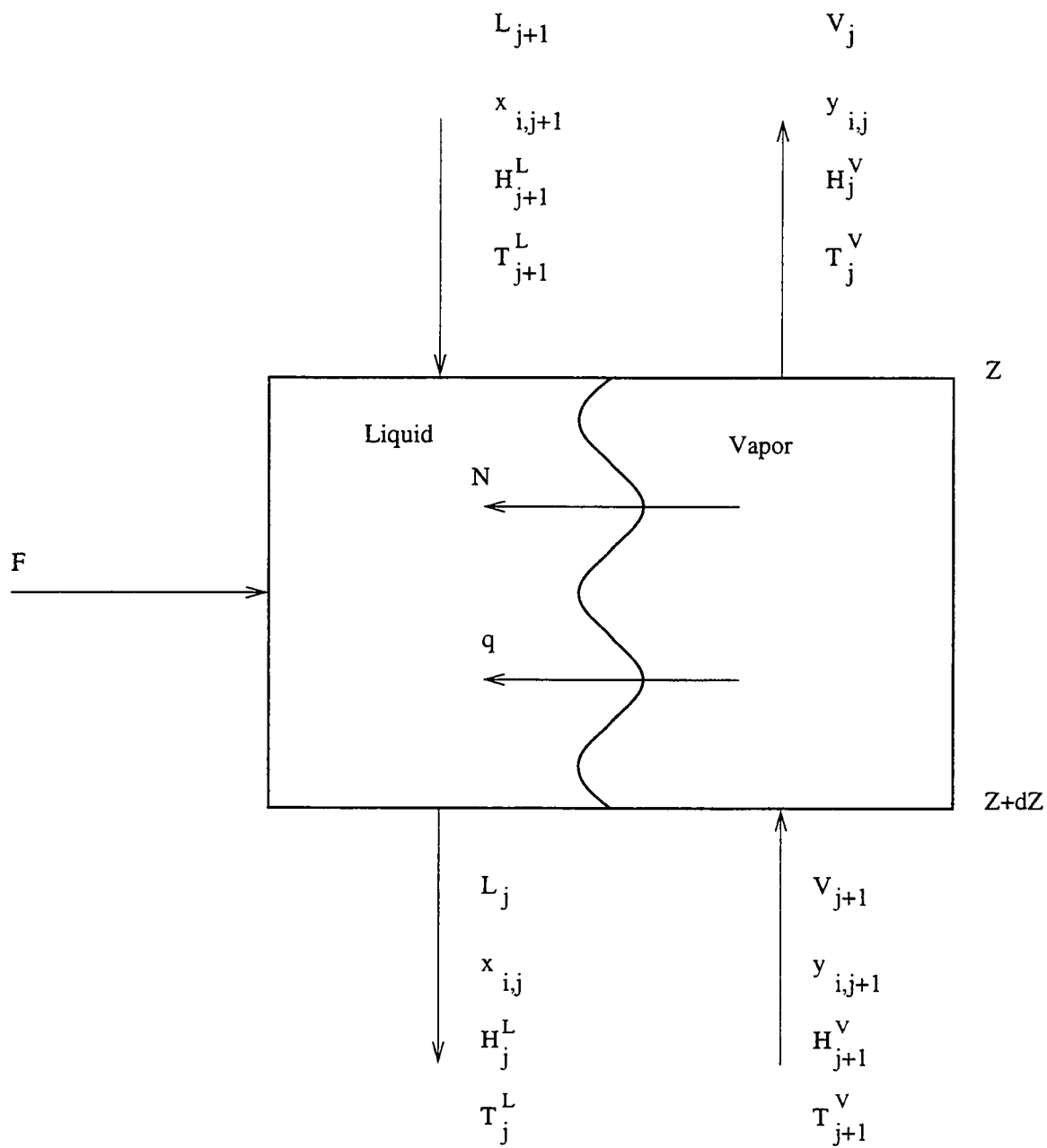


Figure 3.2.1 Schematic diagram of a section of a packing in a packed column

where N_i^L and N_i^V are the total fluxes of the liquid and the vapor phases in each segment of the packing. The fluxes are positive for the transfer from the vapor to the liquid phase and negative for the liquid to the vapor phase. a is the interfacial area for mass and heat transfer per unit volume.

2-Component Material Balances

$$\frac{dv_i}{dZ} = \frac{d(Vy_i)}{dZ} = -N_i^V aA \quad (3.2.4)$$

$$\frac{dl_i}{dZ} = \frac{d(Lx_i)}{dZ} = -N_i^L aA + r_i H_o A \quad (3.2.5)$$

The derivatives of the mole fractions can be calculated by substituting Equations 3.2.1 and 3.2.2 into Equations 3.2.4 and 3.2.5:

$$\frac{dy_i}{dZ} = \frac{1}{V} \left(-y_i \frac{dV}{dZ} - N_i^V aA \right) \quad (3.2.6)$$

$$\frac{dx_i}{dZ} = \frac{1}{L} \left(-x_i \frac{dL}{dZ} - N_i^L aA + r_i H_o A \right) \quad (3.2.7)$$

3-Heat Balance

The temperature profile of both liquid and vapor may not be the same along the column because of the reaction and surface evaporation. The temperature of both phases can be calculated by (1) assuming that the system operates under equilibrium conditions, that is, the liquid is at its bubble point and the vapor at its dew point or (2) by deriving the

heat balance equation to get the temperature derivative equations. For the second approach, the derivation is as follows:

$$\frac{d(VH^V)}{dZ} = \sum_{i=1}^n N_i^V \alpha A H_i^V + h^V \alpha A (T^V - T^I) \quad (3.2.8)$$

$$\frac{d(LH^L)}{dZ} = \sum_{i=1}^n N_i^L \alpha A H_i^L + h^L \alpha A (T^I - T^L) + H_o \alpha A H_R \sum_{i=1}^n v_i r_i \quad (3.2.9)$$

To express the heat balance equations in terms of T^V , T^L , and T^I , the left-hand side of Equation 3.2.8 can be expanded to

$$\frac{d(VH^V)}{dZ} = \frac{d}{dZ} \sum_{i=1}^n v_i H_i^V = \sum_{i=1}^n v_i \frac{dH_i^V}{dZ} + \sum_{i=1}^n H_i^V \frac{dv_i}{dZ} \quad (3.2.10)$$

The two parts of the right-hand side of Equation 3.2.10 can be expressed as follows:

For small changes in pressure with height (Z),

$$\frac{dH_i^V}{dZ} = \frac{dH_i^V}{dT^V} \frac{dT^V}{dZ} = C_{p_i}^V \frac{dT^V}{dZ} \quad (3.2.11)$$

The second part of Equation 3.2.10 can be expressed as

$$\sum_{i=1}^n H_i^V \frac{dv_i}{dZ} = \sum_{i=1}^n N_i^V \alpha A H_i^V \quad (3.2.12)$$

Substituting Equations 3.2.11 and 3.2.12 into Equation 3.2.10 yields

$$\frac{d(VH^V)}{dZ} = \sum_{i=1}^n v_i C_{p_i}^V \frac{dT^V}{dZ} + \sum_{i=1}^n N_i^V \alpha A H_i^V \quad (3.2.13)$$

Substituting Equation 3.2.13 into the left-hand side of Equation 3.2.8 yields

$$\sum_{i=1}^n v_i C_{p_i}^V \frac{dT^V}{dZ} + \sum_{i=1}^n N_i^V \alpha A H_i^V = \sum_{i=1}^n N_i^V \alpha A H_i^V + h^V \alpha A (T^V - T^I) \quad (3.2.14)$$

Rearranging Equation 3.2.14 gives the differential equation for the vapor temperature

$$\frac{dT^V}{dZ} = \frac{h^V a A (T^V - T^I)}{\sum_{i=1}^n v_i C p_i^V} \quad (3.2.15)$$

In the same manner and assuming that

- A small change in pressure with height

$$\bullet \quad H^L \sum_{i=1}^n v_i r_i = H_R \sum_{i=1}^n v_i r_i \quad (3.2.16)$$

the liquid phase temperature can be derived to give

$$\frac{dT^L}{dZ} = \frac{h^L a A (T^I - T^L)}{\sum_{i=1}^n l_i C p_i^L} \quad (3.2.17)$$

4-Equilibrium Relationship

$$y_i^I = \frac{\gamma_i P_i^S x_i^I}{P} \quad (3.2.18)$$

where x_i^I and y_i^I are the mole fractions of the liquid and vapor side of the interface, γ_i is the activity coefficient, P_i^S is the saturated vapor pressure of component i , and P is the total pressure in the segment. The bulk phases at the interface sum to unity.

$$\sum_{i=1}^n x_i^I = 1 \quad (3.2.19)$$

$$\sum_{i=1}^n y_i^I = 1 \quad (3.2.20)$$

5-Mass and Heat Transfer Rates

The mass transfer rates are calculated from the following equations:

$$N_i^L = \sum_{k=1}^{n-1} k_{i,k}^L (x_k^I - x_k) + x_i N_t^L \quad (3.2.21)$$

$$N_i^V = \sum_{k=1}^{n-1} k_{i,k}^V (y_k - x_k^I) + y_i N_t^V \quad (3.2.22)$$

where $k_{i,k}^L$ and $k_{i,k}^V$ are multicomponent mass transfer coefficients which are determined from binary mass transfer coefficients $k_{i,k}^{bL}$ and $k_{i,k}^{bV}$ (Krishna and Standart, 1976).

In the same way, the heat transfer rates are expressed as follows:

$$E^L = h^L (T^I - T^L) + \sum_{i=1}^n N_i^L \bar{H}_i^L \quad (3.2.23)$$

$$E^V = h^V \frac{\varepsilon^V}{e^{\varepsilon^V} - 1} (T^V - T^I) + \sum_{i=1}^n N_i^V \bar{H}_i^V \quad (3.2.24)$$

where h^L and h^V are the heat transfer coefficients in the liquid and the vapor phases, and the quantity ε^V in the right-hand side is a correction factor due to high flux (Bird et al, 1960) and is defined as follows:

$$\varepsilon^V = \sum_{i=1}^n \frac{N_i^V C p_i^V}{h^V} \quad (3.2.25)$$

The corresponding term for the liquid phase is close to unity and is omitted from Equation 3.2.23.

6- Balance around the Condenser

To start the integration from the top, it is necessary to know the top conditions, which are considered the initial conditions for the differential equations representing the

material and heat balances (Equations 3.2.4 to 3.2.7 and 3.2.15 to 3.2.17). In this algorithm, the distillate flow rate, D , and the reflux ratio, L/D , will be specified and fixed in advance. Thus, the vapor flow rate to the condenser, Figure 3.2.2, will be calculated from the material balance around the condenser (Equation 3.2.26).

The distillate composition is to be specified in this algorithm and is always adjusted by the convergence criteria at the bottom. Assuming total condenser operation, the liquid and vapor mole fractions, x_1 and y_2 , are calculated from Equation 3.2.27.

$$V=L+D \quad (3.2.26)$$

$$y_2=x_1=x_D \quad (3.2.27)$$

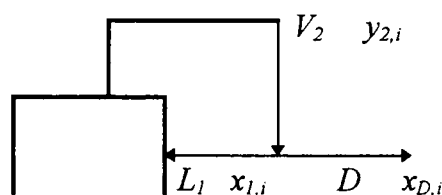


Figure 3.2.2 Schematic diagram of the reflux inlet

7-Feed Streams

When the liquid feed enters the packing segment, some evaporation or condensation might occur due to the differences in temperature between the feed stream and the column. For small differences in temperature, the amount of evaporation will be very small, as is the case with the acetic acid feed at the top. Methanol entering at the

bottom is expected to evaporate due to the large temperature difference. The flow rates and compositions of the stream leaving segment j , Figure 3.2.3, are calculated as follows:

$$L_j = L_{j-1} + F^L \quad (3.2.28)$$

$$V_{j+1} = V_j + F^V \quad (3.2.29)$$

$$x_{j,i} = \frac{L_{j-1}x_{j-1,i} + F^L x_{F,i}}{L_{j,i}} \quad (3.2.30)$$

$$y_{j+1,i} = \frac{V_j y_{j,i} + F^V y_{F,i}}{V_{j+1}} \quad (3.2.31)$$

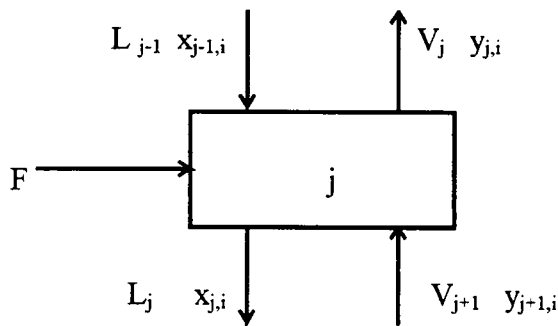


Figure 3.2.3 Schematic diagram of feed inlet to the column

8-Bottom Conditions

The stepwise integration continues until it reaches the bottom of the column where the material balance around the reboiler determines the bottom composition and checks the convergence imposed by assuming the distillate composition. The stepwise integration yields the following values, as shown in Figure 3.2.4, $(L_{k-1}, x_{k-1,i}, V_k, y_{k,i})$. The $n+1$

unknowns, representing the bottom flow rate and compositions, are calculated from the following $n+1$ equations:

$$L_{k-1} = V_k + B \quad (3.2.32)$$

$$L_{k-1}x_{k-1,i} + V_k r_{k,i} = Bx_{B,i} + V_k y_{k,i} \quad i = 1, 2, \dots, n \quad (3.2.33)$$

In order to check for the convergence at the bottom, the vapor mole fraction at the last segment, y_k , is compared with the one calculated from the equilibrium relationship relating the bottom liquid and the vapor rising from the reboiler:

$$y_{B,i} = \frac{\gamma_{B,i} P_{B,i}^s x_{B,i}}{P} \quad (3.2.34)$$

The convergence is achieved when the two values (y_k and y_B) are close within a certain tolerance. The distillate composition is adjusted based on a minimization routine that minimizes the difference between the two values of y at the bottom.

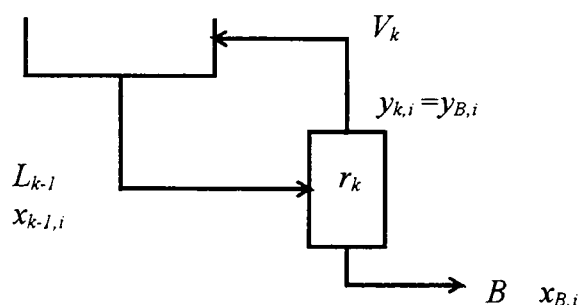


Figure 3.2.4 Schematic diagram of the bottom streams

3.3 ESTIMATION OF PHYSICAL PROPERTIES AND COLUMN CHARACTERISTICS

The following properties needed for the calculation of physical properties of each component were obtained from Reid et al (1987):

- the pure component boiling point, T_b
- the molecular weight, M
- the critical temperature, T_c
- the critical pressure, P_c
- the critical volume, V_c
- the acentric factor, ω
- the dipole moment, η

These properties are provided in Table 3.3.1.

Table 3.3.1 Physical properties of the system

Component	Mol. wt.	T_b , K	T_c , K	P_c , atm	V_c , cm ³ /mol	ω	η
Acetic acid	60	391.05	594.4	57.15	171	.4624	1.3
Methanol	32.04	337.85	513.2	79.86	118	.5656	1.7
Methyl acetate	74.04	330.09	506.8	46.3	228	.3253	1.7
Water	18	373	647.3	218.3	57.1	.3449	1.8

3.3.1 Estimation of Vapor Phase Properties

1-Density

Amagat's law of additive volumes for ideal gases is used to evaluate the mixture density.

$$\rho = \frac{PM}{RT} \quad (3.3.1)$$

$$\text{where } M = \sum_i^n y_i M_i \quad (3.3.2)$$

2-Viscosity

The vapor viscosities are calculated using the equation of Chung et al (1984).

$$\mu = 40.785 \times 10^{-7} \frac{F_c (MT)^5}{V_c^{3/2} \Omega_v} \quad (3.3.3)$$

$$\text{where } F_c = 1 - 2756\omega + 0.059035\mu_r^4 + \kappa \quad (3.3.4)$$

$$\Omega_v = 1.16145(T^*)^{-1.4874} + 0.52487 \exp(-0.7732T^*) + 2.16178 \exp(-2.43787T^*) \quad (3.3.5)$$

$$\text{and } T^* = 1.2593T_r \quad (3.3.6)$$

In Equation 3.3.4, ω is the acentric factor, and κ is a special correction for highly polar substances such as alcohols and acids. Values of κ for our system are provided in Table 3.3.2. The term η_r is a dimensionless dipole moment and is given by:

$$\eta_r = 131.3 \frac{\eta}{(V_c T_c)^5} \quad (3.3.7)$$

Reid et al (1987) stated that the average absolute error between Chung's method and the experimental values was approximately 1.9 percent.

Table 3.3.2 The Association Factor κ in Equation. 3.3.4

Compound	κ
Acetic Acid	.0916
Methanol	.215
Methyl Acetate	0
Water	.076

For the gas mixture, the Wilke method (1950) was used:

$$\mu_m = \frac{\sum_{i=1}^n y_i \mu_i}{\sum_{j=1}^n y_j \phi_{ij}} \quad (3.3.8)$$

where

$$\phi_{ij} = \frac{\left[1 + \left(\mu_i / \mu_j \right)^{.5} \left(M_j / M_i \right)^{.25} \right]^2}{\left[8 \left(1 + M_i / M_j \right) \right]^{.5}} \quad (3.3.9)$$

and

$$\phi_{ji} = \frac{\mu_j}{\mu_i} \frac{M_i}{M_j} \phi_{ij} \quad (3.3.10)$$

The average error in Equation 3.3.8 is reported by Wilke (1950) to be 3.2 percent.

3-Specific Heat

The specific heat was taken from Sinnott (1993), with the constants given in Table

3.3.3

$$C_p = a + bT + cT^2 + dT^3 \quad (3.3.11)$$

Table 3.3.3 Constants for Equation 3.3.11

Component	a	b x 10 ²	c x 10 ⁴	d x 10 ⁹
Acetic Acid	4.84	25.485	-1.753	49.488
Methanol	21.15	7.092	.2587	-28.52
Methyl Acetate	16.55	22.454	-.4342	29.144
Water	32.243	.19555	.10555	-3.59

The specific heat of the mixture is estimated by

$$C_{p_m} = \sum_{i=1}^n y_i C_{p_i} \quad (3.3.12)$$

4-Diffusion Coefficient

The equation of Fuller et al (1969) is used to calculate the binary diffusion coefficients. Reid et al (1987) found that this equation gave smaller errors when compared with other equations.

$$D_{ij} = \frac{1 \times 10^{-7} T^{1.75} \left[(1/M_i) + (1/M_j) \right]^5}{P \left[\sqrt[3]{V_i} + \sqrt[3]{V_j} \right]^2} \quad (3.3.13)$$

The molecular diffusion volumes, V , are found by summing the atomic contributions in Table 3.3.4.

Table 3.3.4 Diffusion volumes in Fuller's equation (Fuller et al, 1969)

C	15.9	F	14.7
H	2.31	Cl	21
O	6.11	Br	21.9
N	4.54	I	29.8
S	22.9	H₂O	13.1

5-Thermal Conductivity

The thermal conductivity of methanol and water was taken from Reid et al (1987) in the polynomial form as follows:

Methanol :

$$\lambda = -7.793 \times 10^{-3} + 4.167 \times 10^{-5} T + 1.214 \times 10^{-7} T^2 - 5.184 \times 10^{-11} T^3 \quad (3.3.14)$$

Water:

$$\lambda = 7.341 \times 10^{-3} - 1.013 \times 10^{-5} T + 1.801 \times 10^{-7} T^2 - 9.1 \times 10^{-11} T^3 \quad (3.3.15)$$

For acetic acid and methyl acetate, the following equations are taken from Daubert et al (1989):

Acetic acid:

$$\lambda = \frac{1.691 \times 10^{-6} T^{1.6692}}{1 + \frac{6.58 \times 10^2}{T} + \frac{-9.54 \times 10^4}{T^2}} \quad (3.3.16)$$

Methyl acetate:

$$\lambda = \frac{5.593 \times 10^{-4} T^{.8932}}{1 + \frac{1.966 \times 10^3}{T}} \quad (3.3.17)$$

The mixture conductivity is calculated using the Wilke method (1950)

$$\lambda_m = \frac{\sum_{i=1}^n \frac{y_i \lambda_i}{\sum_{j=1}^n y_j \phi_{ij}}}{\sum_{j=1}^n y_j \phi_{ij}} \quad (3.3.18)$$

where ϕ_{ij} is calculated from Equations 3.3.9-10, and the average error is expected to be between 2-5 percent (Perry, 1985).

3.3.2 Estimation of Liquid Phase Properties

1-Density

The pure component liquid density is calculated from the data given by Daubert et al (1989) using the following equation:

$$\rho = \frac{aM}{b^{(1+(1-\frac{T}{c})^d)}} \quad (3.319)$$

The constants in the equation are provided in Table 3.3.5.

Table 3.3.5 Constants for the liquid-phase density equation (Daubert,1989)

Component	a	b	c	d
Acetic acid	1.5791	.26954	592.71	.26843
Methanol	2.308	.27192	512.58	.2331
Methyl acetate	1.21	.25855	506.8	.2745
Water :				
T < 333 K	5.459	.30542	647.13	.081
333 < T < 403	4.9669	.27788	647.13	.1874

The mixture density is calculated from the additive relation:

$$\rho_m = \frac{\sum_{i=1}^n x_i M_i}{\sum_{i=1}^n x_i \frac{M_i}{\rho_i}} \quad (3.3.19)$$

2-Viscosity

The viscosities of the pure components are calculated from equations provided in Reid et al (1987) as follows:

Acetic acid : $\mu = \exp\left(-4.519 + \frac{1384}{T}\right)$ (3.3.20)

Methanol: $\mu = \exp\left(-39.35 + \frac{4826}{T} + 1.091T - 1.127 \times 10^{-4} T^2\right)$ (3.3.21)

Methyl Acetate: $\mu = \exp\left(-4.2 + \frac{940.9}{T}\right)$ (3.3.22)

Water: $\mu = \exp\left(-24.71 + \frac{4209}{T} + 4.527 \times 10^{-2} T - 3.376 \times 10^{-5} T^2\right)$ (3.3.23)

From the discussion presented in Reid et al (1987) about liquid mixture viscosity, it seems that there is no accurate or reliable method for aqueous liquid mixtures. The two equations presented by Reid et al (1987) are the Gransberg and Nissan method and the Teja and Rice method. The first one is not applicable for aqueous mixtures, while the second one requires experimental parameters that are not available in our case. For this reason, the following approximation is used (Perry, 1985):

$$\mu_m^{1/3} = \sum_{i=1}^n x_i \mu_i^{1/3} \quad (3.3.24)$$

3-Specific Heat

The liquid specific heats are taken from Daubert et al (1989) with the constants given in Table 3.3.6.

$$C_p = a + bT + cT^2 + dT^3 + eT^4 \quad (3.3.25)$$

The mixture specific heat is calculated as a mole fraction average from Equation 3.3.12.

Table 3.3.6 Consants for the liquid specific heat

Component	$a \times 10^{-5}$	$b \times 10^{-2}$	c	d	e
Acetic acid	.501	2.456	0	0	0
Methanol	1.076	-3.806	.979	0	0
Methyl acetate	1.9157	-6.363	1.575	0	0
Water	2.7637	-20.901	8.125	-1.4116×10^{-2}	3.701×10^{-7}

4-Diffusion Coefficient

The method of Wilke-Chang (1955) is used to calculate the diffusion coefficient in a dilute liquid mixture as follows:

$$D_{12}^o = 7.4 \times 10^{-15} \frac{(\phi_2 M_2)^5 T}{\mu_2 V_1^6} \quad (3.3.26)$$

where species 1 is the solute, which is present in infinitely low concentrations in the solvent. V is the molar volume of the solute at its normal boiling point, and ϕ is an associate factor for the solvent. The values of V and ϕ are given in Table 3.3.7. The associate factor for methyl acetate was considered the same as that for ethyl acetate, as

calculated by Wilke and Chang (1955); and the error in their equation is estimated to be 6%.

Table 3.3.7 Molar volumes and associate factors for the Wilke-Chang equation

Component	$V \text{ cm}^3/\text{mol}$	ϕ
Acetic acid	64.1	1
Methanol	42.5	1.9
Methyl acetate	84.32	1.37
Water	18.7	2.26

As discussed in Section 2.4.3 , the diffusion coefficient needs to be corrected for concentrated liquid mixtures. The following Vignes equation (1966) is used to calculate the binary diffusivities in multicomponent systems:

$$D_{ij} = \left(D_{ij}^o\right)^{\frac{(1+x_j-x_i)}{2}} \left(D_{ji}^o\right)^{\frac{(1+x_i-x_j)}{2}} \quad (3.3.27)$$

5-Thermal Conductivity

The liquid thermal conductivities of the pure components are taken from Daubert et al (1989) in the polynomial form

$$\lambda = a + bT + cT^2 + dT^3 \quad (3.3.28)$$

The values of the constants in Equation 3.2.28 are given in Table 3.3.8.

Table 3.3.8 Constants for the liquid-phase thermal conductivity

Component	$a \times 10^1$	$b \times 10^4$	$c \times 10^6$	$d \times 10^9$
Acetic acid	2.123	-1.82	0	0
Methanol	2.837	-2.81	0	0
Methyl acetate	2.777	-4.17	0	0
Water	-4.267	56.903	-8.0065	1.815

For liquid mixtures, the method of Li (1976) is used with an expected error of 5%. Li proposed the following equations:

$$\lambda_m = \sum_{i=1}^n \sum_{j=1}^n \phi_i \phi_j \lambda_{ij} \quad (3.3.29)$$

with $\lambda_{ij} = 2(\lambda_i^{-1} + \lambda_j^{-1})^{-1} \quad (3.3.30)$

$$\phi_i = \frac{x_i V_i}{\sum_{j=1}^n x_j V_j} \quad (3.3.31)$$

Li (1976) stated that the harmonic mean approximation for λ_{ij} was chosen over a geometric mean after extensive testing and comparison of the calculated and experimental values of λ_m .

6-Surface Tension

The surface tension of the pure components is calculated from the following equation (Reid et al, 1987), and the constants are given in Table 3.3.9:

$$\sigma = 1 \times 10^{-3}(a - bt) \quad (3.3.32)$$

Table 3.3.9 Constants for the liquid surface tension equation

Component	a	b
Acetic acid	29.58	.0994
Methanol	24	.0733
Methyl acetate	27.95	.1289
Water	75.83	.1477

Again, there is no reliable equation to determine the surface tension of aqueous solutions. For our case, the water concentration throughout the column does not exceed 20 mole%. Thus, an equation for nonaqueous mixtures will be applied. The following equation for nonaqueous mixtures is considered to give an average error of 5% for hydrocarbon mixtures (Reid et al,1985):

$$\sigma_m^{1/4} = \frac{\rho_m}{M_m} \sum_{i=1}^n \frac{x_i \sigma_i^{1/4}}{\rho_i / M_i} \quad (3.3.33)$$

7-Vapor Pressure

The Antoine's Equation is provided from the work of Perry (1985), and the constants are given in Table 3.3.10.

$$\log P^s = a - \frac{b}{(t + c)} \quad (3.3.34)$$

Table 3.3.10 Constants for the vapor pressure equation

Component	a	b	c
Acetic acid	15.6699	10821.1	698.09
Methanol	7.78763	1473.11	230
Methyl acetate	7.20211	1232.83	228
Water	7.96681	1668.1	228

3.3.3 Vapor-Liquid Equilibrium

The vapor phase is considered ideal, and the activity coefficient is calculated to account for the non-ideal liquid phase. The phase equilibrium equation can be written as

$$y_i = \frac{x_i \gamma_i P^s}{P} \quad (3.3.35)$$

The simplicity of the Wilson method, which requires only binary interaction parameters, makes it one of the most useful methods for multicomponent systems. Walas (1985) recommended this method as giving more accurate results than other methods for multicomponent systems.

The activity coefficient of a component in a multicomponent system is calculated from the following relation:

$$\ln \gamma_i = 1 - \ln \left(\sum_{j=1}^n x_j \Lambda_{ij} \right) + \sum_{k=1}^n \frac{x_k \Lambda_{ki}}{\sum_{j=1}^n x_j \Lambda_{kj}} \quad (3.3.36)$$

$$\text{where } \Lambda_{ij} = \left(V_j / V_i \right) \exp \left(\frac{-\lambda_{ij}}{RT} \right) \quad (3.3.37)$$

The binary interaction parameters, λ_{ij} , for the system considered here is taken from Gmehling (1977) and given in Table 3.3.11.

Table 3.3.11 Binary interaction parameters for the Wilson equation

Binary system	λ_{12}	λ_{21}
(1)Acetic acid - (2)Methanol	-67.5078	-93.6183
(1)Acetic acid - (2)Methyl acetate	269.7074	-208.93
(1)Acetic acid - (2)Water	111.6579	705.5876
(1)Methanol - (2)Methyl acetate	776.5663	9.1172
(1)Methanol - (2)Water	243.9486	435.1416
(1)Methyl acetate - (2)Water	645.7225	1918.232

3.3.4 Transfer Coefficients and Liquid Hold-up

1-Mass Transfer Coefficient

The correlation developed by Onda et al (1968) is used to estimate the binary mass transfer coefficients in both the liquid and vapor phases. The selection of this correlation is based on the wide range of packing sizes, including the laboratory-size packings, the correlation can be applied to. The binary vapor-phase mass transfer coefficient is obtained from the following equation:

$$\frac{k^{bV}}{a_p D^V} = A Re_V^{0.7} Sc_V^{0.333} (a_p d_p)^{-2} \quad (3.3.38)$$

where d_p is the nominal packing size, and a_p is the specific packing area (m^2/m^3 of the packing). The constant A has the value 2.0 if the packing size is less than 0.012 m and the value 5.23 if the packing size is greater than (or equal to) 0.012 m. Re_V is the vapor-phase Reynolds number

$$Re_V = \frac{\rho_t^V u_V}{\mu^V a_p} \quad (3.3.39)$$

where u_V is the superficial velocity of the vapor. The vapor-phase Schmidt number is

$$Sc_V = \frac{\mu^V}{\rho_t^V D^V} \quad (3.3.40)$$

The binary liquid-phase mass transfer coefficient is obtained from the following equation:

$$k^{bL} \left(\frac{\rho_t^L}{\mu^L g} \right)^{0.333} = 0.0051 (Re'_L)^{0.667} Sc_L^{-0.5} (a_p d_p)^{0.4} \quad (3.3.41)$$

where Sc_L is the Schmidt number for the liquid phase

$$Sc_L = \frac{\mu^L}{\rho_t^L D^L} \quad (3.3.42)$$

and Re'_L is the liquid-phase Reynolds number based on the interfacial area

$$Re'_L = \frac{\rho_t^L u_L}{\mu^L a} \quad (3.3.43)$$

The interfacial area a (m^2/m^3 packing) is obtained from Onda's correlation

$$a = a_p \left(1 - \exp \left\{ -14.5 (\sigma_c / \sigma)^{0.75} Re_L^{0.1} Fr_L^{-0.05} We_L^{0.2} \right\} \right) \quad (3.3.44)$$

where σ is the surface tension of the liquid, and σ_c is the critical surface tension of the packing material. The liquid-phase Reynolds number based on the specific surface area is

$$\text{Re}_L = \frac{\rho_i^L u_L}{\mu^L a_p} \quad (3.3.45)$$

The liquid-phase Froude (Fr_L) number is

$$Fr_L = \frac{a_p u_L^2}{g} \quad (3.3.46)$$

The Weber (We_L) number is

$$We_L = \frac{\rho_i^L u_L^2}{a_p \sigma} \quad (3.3.47)$$

The matrices of the mass transfer coefficients in both phases are expressed as

$$\dot{k}^V = k^V E^V = k^V \Phi \exp \Phi (\exp \Phi - 1)^{-1} \quad (3.3.48)$$

$$\dot{k}^L = k^L E^L = k^L \Theta (\exp \Theta - 1)^{-1} \quad (3.3.49)$$

where

$$\Theta = \Gamma^{-1} \Phi \quad (3.3.50)$$

The elements of the matrix Γ are defined by Equations 2.4.6 and 2.4.7. The elements of matrix Φ are defined as

$$\begin{aligned} \Phi_{ii} &= \frac{N_i}{k_{in}^{bV}} + \sum_{\substack{j=1 \\ j \neq i}}^n \frac{N_j}{k_{ij}^{bV}} & i, j = 1, 2, \dots, n-1 \\ \Phi_{ij} &= -N_i \left(\frac{1}{k_{ij}^{bV}} - \frac{1}{k_{in}^{bV}} \right) \end{aligned} \quad (3.3.51)$$

The matrix of mass transfer coefficient k^V in the vapor phase is the inverse of matrix B^V :

$$B_{ii}^V = \frac{y_i}{k_{in}^{bV}} + \sum_{\substack{j=1 \\ j \neq i}}^n \frac{y_j}{k_{ij}^{bV}} \quad i, j = 1, 2, \dots, n-1$$

$$B_{ij}^V = -y_i \left(\frac{1}{k_{ij}^{bV}} - \frac{1}{k_{in}^{bV}} \right) \quad (3.3.52)$$

The matrix of mass transfer coefficients in the liquid phase, k^L , is the product of the equation

$$k^L = B^L \Gamma^{-1} \quad (3.3.53)$$

The matrices ϕ^L and B^L are obtained from the same equations as the vapor phase by replacing the vapor mole fractions and the mass transfer coefficients in the gas phase with the corresponding values in the liquid phase.

2-Heat Transfer Coefficients

Heat transfer coefficients are based on the Chilton-Colburn analogy. With $j_H = j_D$, the average value of the mass transfer coefficient is used to estimate the heat transfer coefficient using the above analogy with respect to the Onda correlations for mass transfer coefficients. For the liquid phase, the heat transfer coefficient is

$$h^L \left(\frac{\rho^L}{\mu^L g} \right)^{0.333} = 0.0051 (\text{Re}')^{0.667} \text{Pr}^{-0.5} (\alpha_p d_p)^{0.4} (\rho^L C p_m) \quad (3.3.53)$$

The corresponding equation for the vapor phase is

$$h^V = 2 \alpha_p \lambda \text{Re}^{0.7} \text{Pr}^{0.333} (\alpha_p d_p)^{-2} \quad (3.3.54)$$

where

$$Pr = \frac{Cp\mu}{\lambda} \quad (3.3.55)$$

3-Liquid Holdup

Liquid holdup is calculated from the correlations of Shulman et al (Treybal, 1968). The equations provided below are for 1/4-inch Ceramic Intalox Saddles, which are used in the experimental column. The diameter of a sphere of the same surface as a single packing particle, d_s , is taken from the work of Kelley (1984) and estimated to be 0.0087 m. The equations provided below are for Berl saddle packings and are also applicable to Intalox saddles, as suggested by Kelley(1984).

The total holdup, H_t , consists of two parts:

$$H_t = H_o + H_s \quad (3.3.56)$$

The static holdup, H_s , is calculated from the following equation:

$$H_s = \frac{4.23 \times 10^{-3} \mu^{0.4} \sigma^{0.55}}{d_s^{1.56} \rho^{0.37}} \quad (3.3.57)$$

The operating (or moving) holdup, H_o , is calculated from the following set of equations:

$$\beta = 1.508 d_s^{0.376} \quad (3.3.58)$$

$$H_{sw} = 5.0114 \times 10^{-5} d_s^{1.56} \quad (3.3.59)$$

$$H_{tw} = \frac{2.32 \times 10^{-6} (737.5L')^\beta}{d_s^2} \quad (3.3.60)$$

$$H_{ow} = H_{tw} - H_{sw} \quad (3.3.61)$$

$$\Psi = \frac{2830 L'^{0.57} \mu^{0.31}}{\rho^{0.84} (3.24 L'^{.413} - 1)} \left(\frac{\sigma}{0.073} \right)^{0.28177 - 0.262 \log L'} \quad (3.3.62)$$

$$H_o = H_{ow} \Psi \quad (3.3.63)$$

3.4 CALCULATION PROCEDURE

The calculational procedure is divided into two parts: the first describes the computation of the fluxes and interface conditions, and the second describes the modifications applied to the method developed by Sawistowski et al (1988) and the application of the method to our problem.

3.4.1 Computation of the Fluxes

To solve the differential equations representing each packing segment, one needs to evaluate the molar fluxes across the interface or the rate of mass transfer across the interface for each component. For this purpose, we may rewrite the equations representing the mass and heat transfer rates in the following way (Krishna, 1993):

- $n-1$ mass transfer rate equations in the liquid phase

$$(R^L) = C_i^L [k_L] (x^I - x^L) + N_i(x^L) - (N) = (0) \quad (3.4.1)$$

- $n-1$ mass transfer rate equations in the vapor phase

$$(R^V) = C_i^V [k_V] (y^V - y^I) + N_i(y^L) - (N) = (0) \quad (3.4.2)$$

- n interfacial equilibrium equations

$$Q^I = K_i x_i^I - y_i^I = 0 \quad (3.4.3)$$

- One energy continuity equation ($E^V - E^L = 0$)

$$E^I = q^V - q^L + \sum_{i=1}^n N_i \Delta H_{vapi} \quad (3.4.4)$$

where

$$q^V = h^V (T^V - T^I) \quad (3.4.5)$$

$$q^L = h^L (T^I - T^L) \quad (3.4.6)$$

- *Two* mole fraction equations that sum to unity

$$S^L = \sum_{i=1}^n x_i^I - 1 = 0 \quad (3.4.7)$$

$$S^V = \sum_{i=1}^n y_i^I - 1 = 0 \quad (3.4.8)$$

The $3n+1$ equations have the following $3n+1$ variables that need to be determined.

- $2n$ interfacial mole fractions, x_i^I and y_i^I .
- n molar fluxes N_i .
- *One* interface temperature T^I .

Krishna (1993) described various ways to solve this set of equations and suggested that using Newton's Method (App. A), which is known to be very fast in matrix manipulation, is the best way to reduce the number of iterations and minimize the need for the evaluation of the thermodynamics properties and mass transfer coefficient.

Before applying Newton's Method, the bulk conditions, x^L, y^V, T^L , and T^V , will be determined from the material and energy balance equations, as described in Section 3.4.1. The thermodynamic properties and the mass and heat transfer coefficients will be determined from the appropriate models and equations, as described in Section 3.3.

To apply Newton's Method, the set of $3n+1$ equations are arranged in the vector function of the form.

$$(F)^T = (R_1^L, R_2^L, \dots, R_{n-1}^L, E^I, R_1^V, R_2^V, \dots, R_{n-1}^V, Q_1^I, Q_2^I, \dots, Q_{n-1}^I, Q_n^I, S^L, S^V) \quad (3.4.9)$$

And the unknown variables are arranged in the vector form

$$(\chi)^T = (N_1, N_2, \dots, N_{n-1}, N_n, x_1^I, x_2^I, \dots, x_n^I, y_1^I, y_2^I, \dots, y_n^I, T^I) \quad (3.4.10)$$

The convergence is achieved when (χ) causes $F(\chi)=0$ using Newton's Method, as described in Appendix A. The calculation procedure for the flux is shown in Figure 3.4.1.

3.4.2 The Differential Technique Calculation Procedure

The method developed by Sawistowski et al (1988) is modified to enhance the calculational procedure, to improve the calculation speed, and to generalize the method to various column configurations. The modifications that were applied to the method include the following:

- Calculating the flux using the method described by Krishna (1993), which includes representing the multicomponent mass transfer coefficients, incorporating thermal conditions, and applying Newton's method to easily solve the nonlinear behavior of the system of equations representing the interface conditions.
- Adding the heat balance equation in the stepwise calculation to calculate the temperature profile along the column.
- Adding the heat transfer equation to the interface conditions.

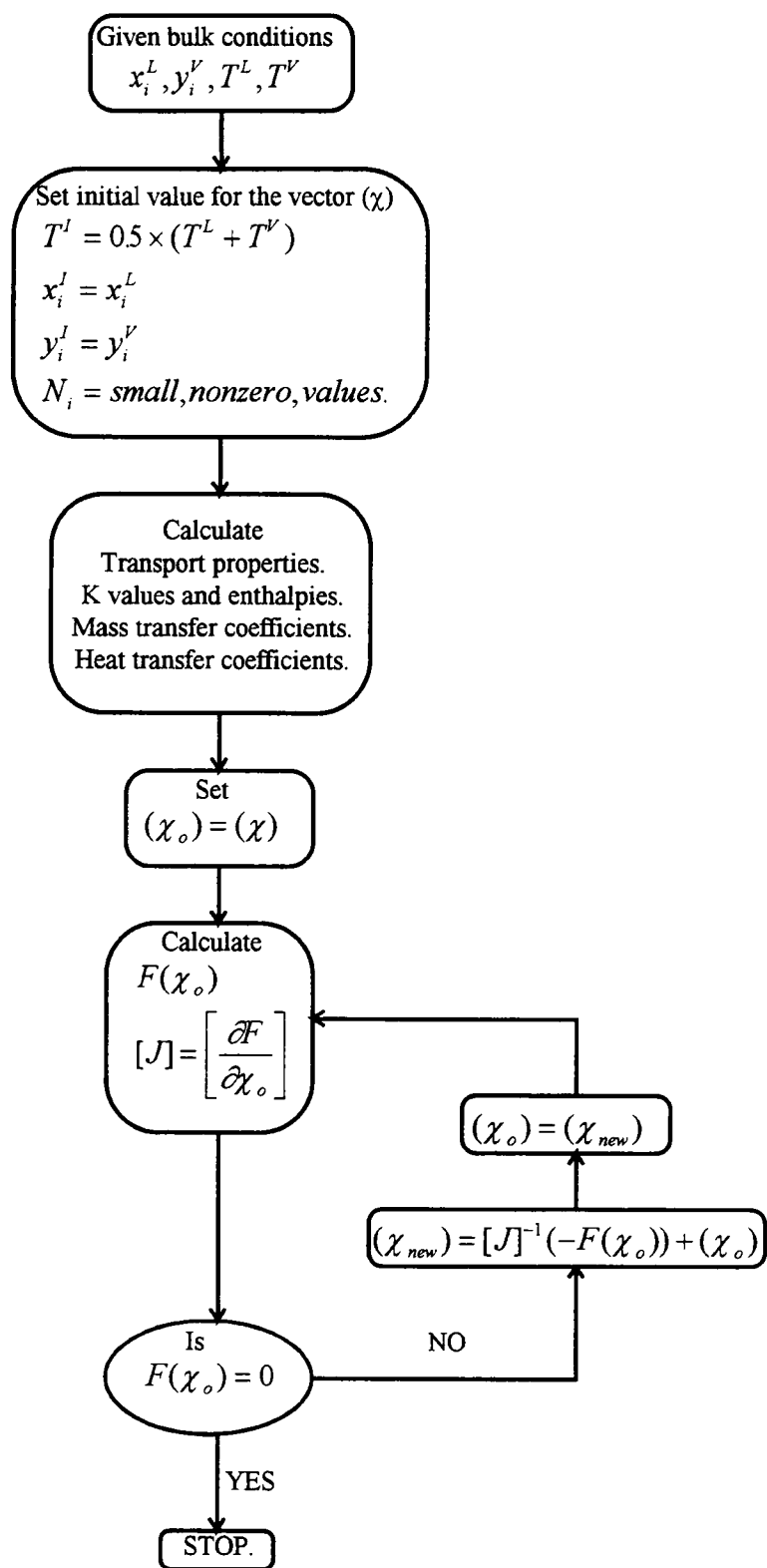


Figure 3.4.1 Flow chart for the computation of the fluxes

- Applying the method to multiple feed ports, which Sawistowski et al (1988) failed to do.
- Utilizing many Matlab (1994) routines, such as matrix manipulation routines, minimization routines, and differential equation solvers, to facilitate the calculation.

With such modifications, the calculational procedure, as described first by Sawistowski et al (1988) and modified here, is shown in Figure 3.4.2 and described below:

- 1) Input all physical parameters and constants needed for the calculations of physical properties and column characteristics.
- 2) Set the flow rates of the feeds (methanol, acetic acid, and catalyst).
- 3) Set the molar flow rate of the distillate and the reflux ratio.
- 4) Assume the distillate composition.
- 5) Calculate the flow rates and the compositions of the reflux and vapor flowing to the condenser using Equation (3.2.27).
- 6) Calculate the temperature of the reflux and the vapor flowing to the condenser using the bubble point calculation.
- 7) Start the integration procedure using the initial conditions, L_1 , $x_{1,i}$, V_2 , $y_{2,i}$, and the temperature of the condenser.
- 8) Calculate the physical properties, column characteristics, mass and heat transfer coefficients, and fluxes using the routine described in Section 3.4.1
- 9) Calculate the reaction rate, according to Equation (2.5.2).

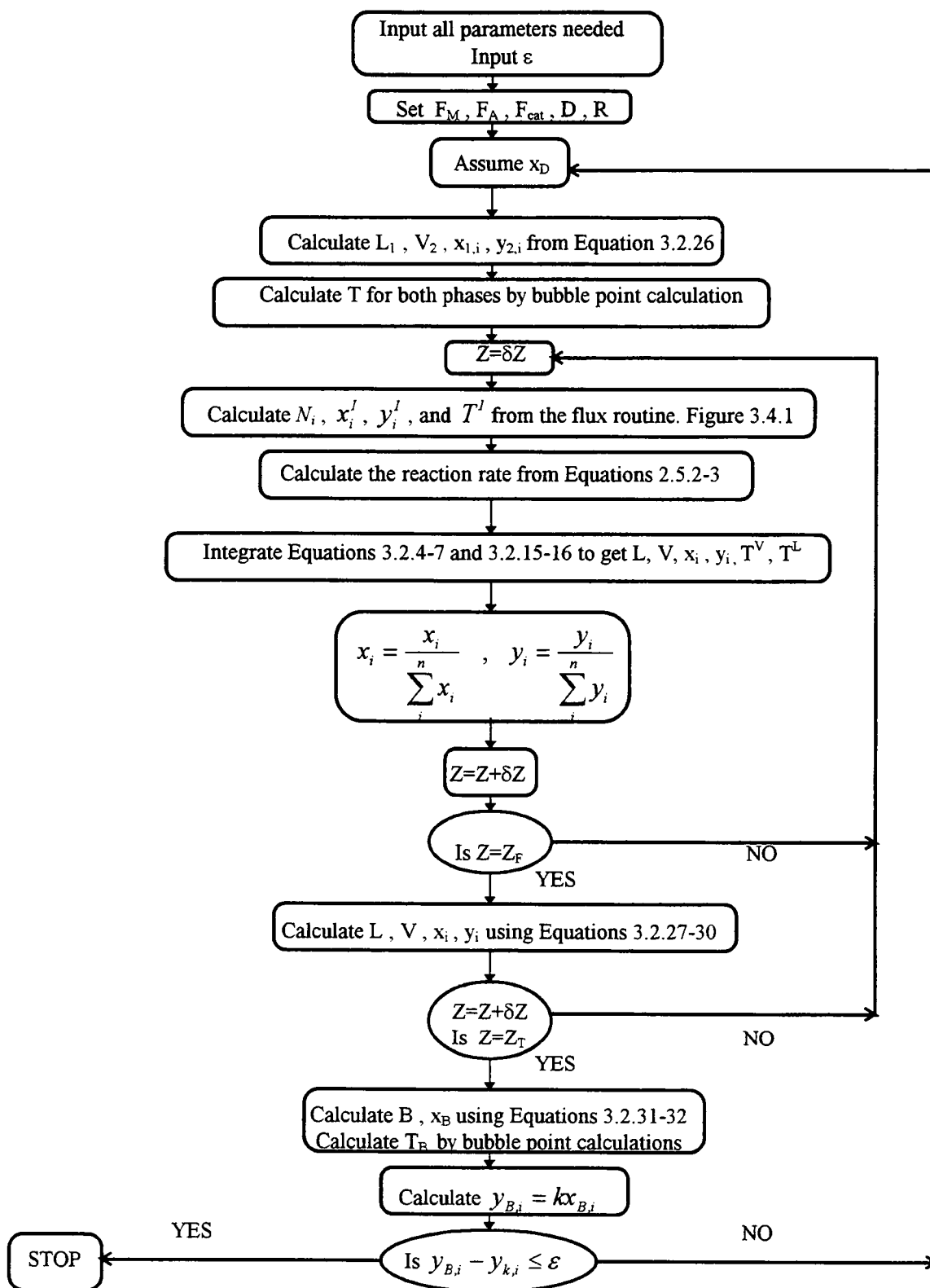


Figure 3.4.2 Flow chart for the differential technique calculation procedure

- 1) Integrate Equations 3.2.4 to 3.2.7 , 3.2.15 and 3.2.17 using the Runge-Kutta routine to obtain the flow rates, the mole fractions, and the temperatures of both phases for the next packing segment.
- 2) Normalize the mole fractions in both phases, such that

$$x_i = \frac{x_i}{\sum_i^n x_i} \quad (3.4.10)$$

$$y_i = \frac{y_i}{\sum_i^n y_i}$$

- 3) Repeat steps 7-11 until the next feed point is reached.
- 4) Calculate the conditions below the feed using Equations 3.2.28 to 3.2.31
- 5) Repeat steps 7-13 until the bottom of the column is reached.
- 6) Calculate the flow rate and composition of the segment below the feed using Equations 3.2.32; Equation 3.2.33; and the flow rates, composition, and temperature of the last segment before the feed (L_{k-1} , $x_{k-1,i}$, V_k , y_k).
- 7) Calculate the temperature of the bottom using the bubble point calculation.
- 8) Calculate the composition of the vapor leaving the reboiler using the equilibrium relationship with the liquid leaving the reboiler.
- 9) Calculate the difference ($y_B - y_k$).

- 10) Terminate the calculation if the difference is within 1%. Otherwise, assume a new estimate of the top composition based on the minimization routine used in the bottom. Then, return to Step 4, and redo the calculations.

4. EXPERIMENTAL METHODS

The experimental effort focused on building a laboratory packed column that can be used to determine the conversion of the esterification reaction and the distillate purity under various operating conditions. These data are needed to verify the model described in chapter 3. This chapter contains a detailed description of how the column was built, how the runs were made, how the samples were analyzed, what experimental difficulties were faced, and how these difficulties were overcome.

4.1 LITERATURE REVIEW

The literature shows that Corrigan and Ferris (1969) were the first to conduct an esterification reaction of methanol and acetic acid in one column. They developed a batch experiment in a plate distillation column. The system consisted of a ten-gallon, glass-lined, jacketed reactor with three sections of Oldshue sieve trays and a 2-inch glass pipe running from the reactor to the bottom of the column. Various experimental runs were made to achieve a high concentration of methyl acetate. By recycling some of the product to the reactor, a distillate was achieved containing 92.5 mol% methyl acetate. In the continuous run, 88% methyl acetate was achieved in the distillate when the sulfuric acid catalyst was added during the run. A distillate containing 90.4 mole% methyl acetate was achieved when the sulfuric acid was added from the beginning of the run.

Sawistowski and Pilavakis (1979) were the first to conduct such a reaction in a packed column using sulfuric acid as a catalyst. A 3-inch i.d. glass column filled with 8-

mm glass rasching rings was tested with a mixed feed of methanol and acetic acid and with separate feeds. Experimental results were poor compared to the work of Corrigan and Ferris, and the distillate composition was always close to the azeotropic composition (35% methanol). The bottom product was also rich in the unreacted acetic acid and methanol. It was concluded that a proper alcohol-acid ratio and feed location are essential for achieving higher conversion and distillate purity.

In a heterogeneous system, Neumann and Sasson (1984) tested the recovery of dilute acetic acid by esterification in a packed chemorectification column using an ion exchange resin as a catalyst. Their main purpose was to achieve a high conversion of acetic acid to methyl acetate since aqueous acetic acid is a waste product of reactions using acetic anhydride as a reagent. The experiment was performed in a 1-inch i.d., 80 cm-long, packed column filled with a combination of rasching rings and 150 grams of Dowex 50W8 10-15 mesh resin beads in acidic form. Several experimental runs were made under various reflux, feed ratio, and feed rate conditions. Neumann and Sasson achieved a higher conversion and distillate purity than Sawistowski, possibly because of the use of a heterogeneous catalyst and the establishment of better operating conditions.

The aforementioned works show that a high conversion of reactants can be achieved by determining the optimal feed ratios, feed locations, and reflux ratios. In our experiments, we will try to determine those optimal operating conditions, and the results will be compared with the theoretical findings determined by solution of the model equations presented in Chapter 3.

4.2 COLUMN DESIGN AND DESCRIPTION

The experimental distillation column consisted of five sections of Pyrex pipes, each with an internal diameter of 1.5 inches. The total packing height of the distillation column was 84 inches, as shown in Figure 4.2.1. Based on previous works ((Pilavakis,1979) and Nueman, 1984)) and on theoretical findings from the model on feed locations and the effect on conversion and product purity; the column sections were designed to provide maximum contacts between the reactants and to provide maximum separation between the products and by-products. The top section above the acetic acid feed was designed to be 12 inches long to provide enough height to enrich the ester and to separate any acetic acid from the ester. The acetic acid feed also extract any rising methanol and water vapor from the ester. The middle section, where most of the reaction is expected to occur, was 48 inches long and considered to be enough to increase the conversion and provide a maximum contact between the reactants. The lowest section below the methanol feed was 24 inches. In this section, the reaction is expected to continue and methanol and any ester formed are stripped from the by-product water . The column was filled with a 1/4-inch ceramic intalox saddle packing. At the top of the column, a Martin-Monsanto compact reflux dividing head with a 40-mm i.d. was used to collect the distillate and to provide a precise reflux count. This device provides low heat loss below the reflux divider section. The condensate formed in the condenser collects in a ring-shaped tray, where it drains to a PTFE ball valve take-off at the center of the divider. The valve is controlled by a magnet energized from a repeating cycle timer. A thermocouple is supplied to determine the distillate temperature.

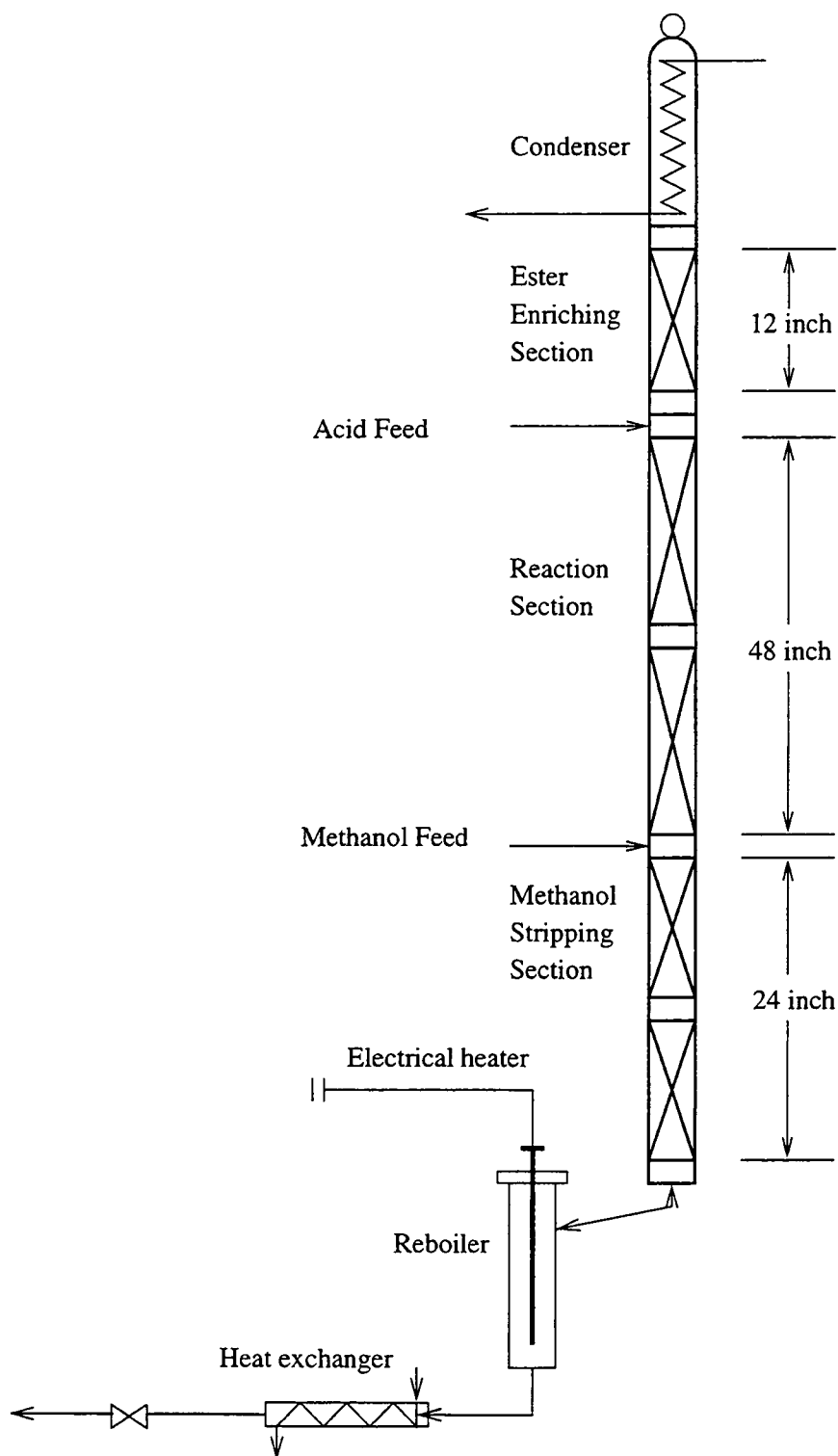


Figure 4.2.1 Length of packing for the three sections of the column

A 14-inch long, 1.5-inch i.d., Pyrex pipe was used as a reboiler at the bottom of the column. Heat was supplied by an 18-inch long, 3/4-inch o.d., Vycor glass rod heater with a 7.5-inch heating length. The heater supplies the heat by infrared radiation, conduction, and convection. A variable transformer controls the output voltage and the power supplied to the reboiler. The bottom product from the reboiler is cooled with an ice bath before being neutralized with a dilute caustic soda solution, and the bottom flow rate is controlled by a valve.

Three sampling spacers were designed for liquid and vapor sampling. Two were located just above the methanol and the acid feed spacers, and the other was located in the middle of the reaction zone, as shown in Figure 4.2.2. The sampling spacers, Figure 4.2.3, were made from PVC and were designed to provide easy sampling of both the liquid and the vapor. A small tray connected to the spacer provided the liquid reservoir for sampling. In addition, a port was made for measuring the temperature with a pocket thermometer.

The acetic acid feed spacer was mounted below the first sampling spacer, and a similar spacer was used for the methanol feed 24 inches from the bottom.

A piston pump was used to feed the methanol from the storage tank to the elevated feed tank where methanol flowed by gravity through a valve to the column. Acetic acid was fed from the storage tank and was pumped by nitrogen pressure up to the feed port. The tank was supplied with a vent valve to release vapor pressure in the tank and in the nitrogen flow stream when the system is not in use. The sulfuric acid catalyst was mixed with the acetic acid in the required proportion and was fed along with the acetic acid to the column.

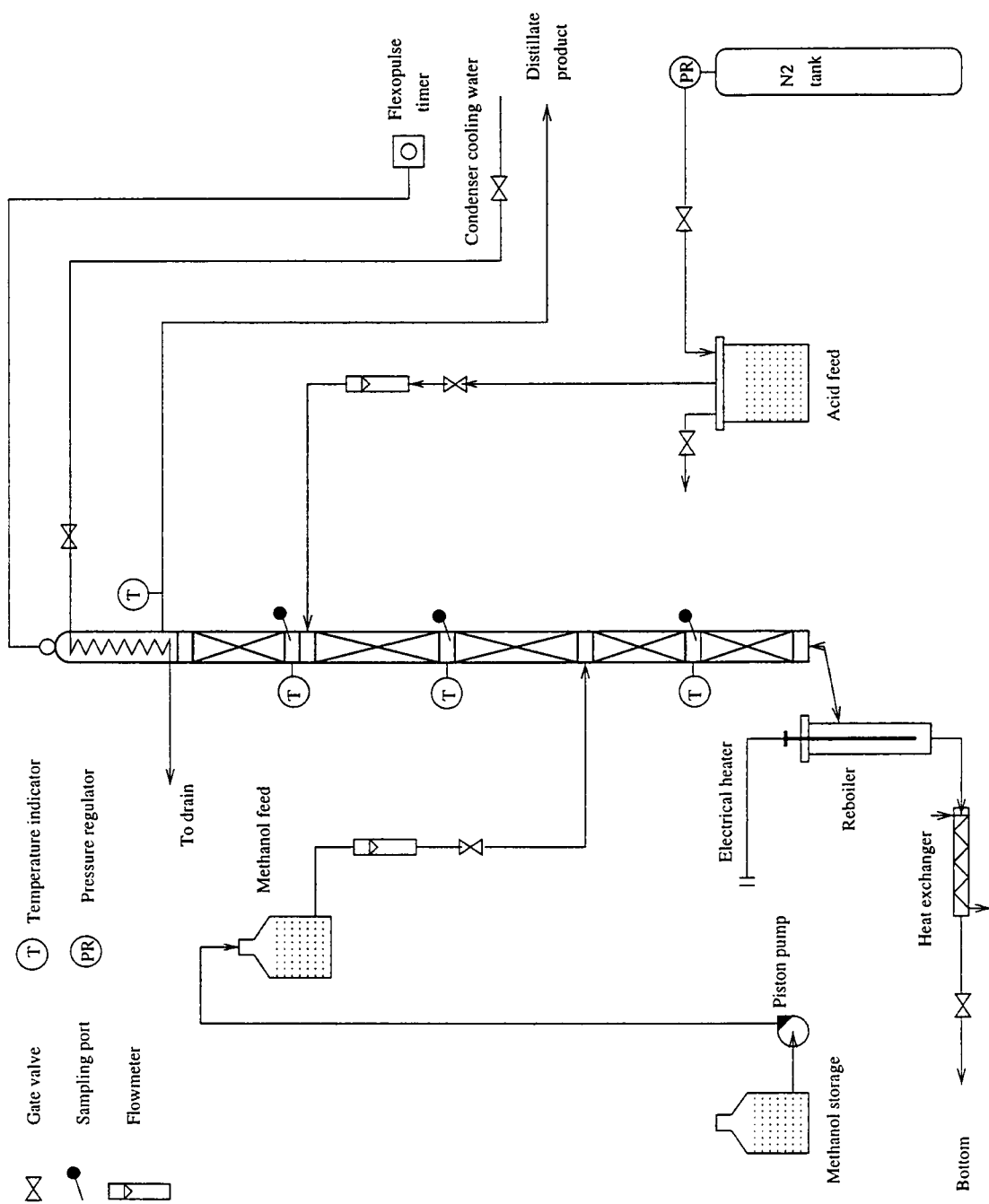


Figure 4.2.2 Laboratory experimental packed distillation column

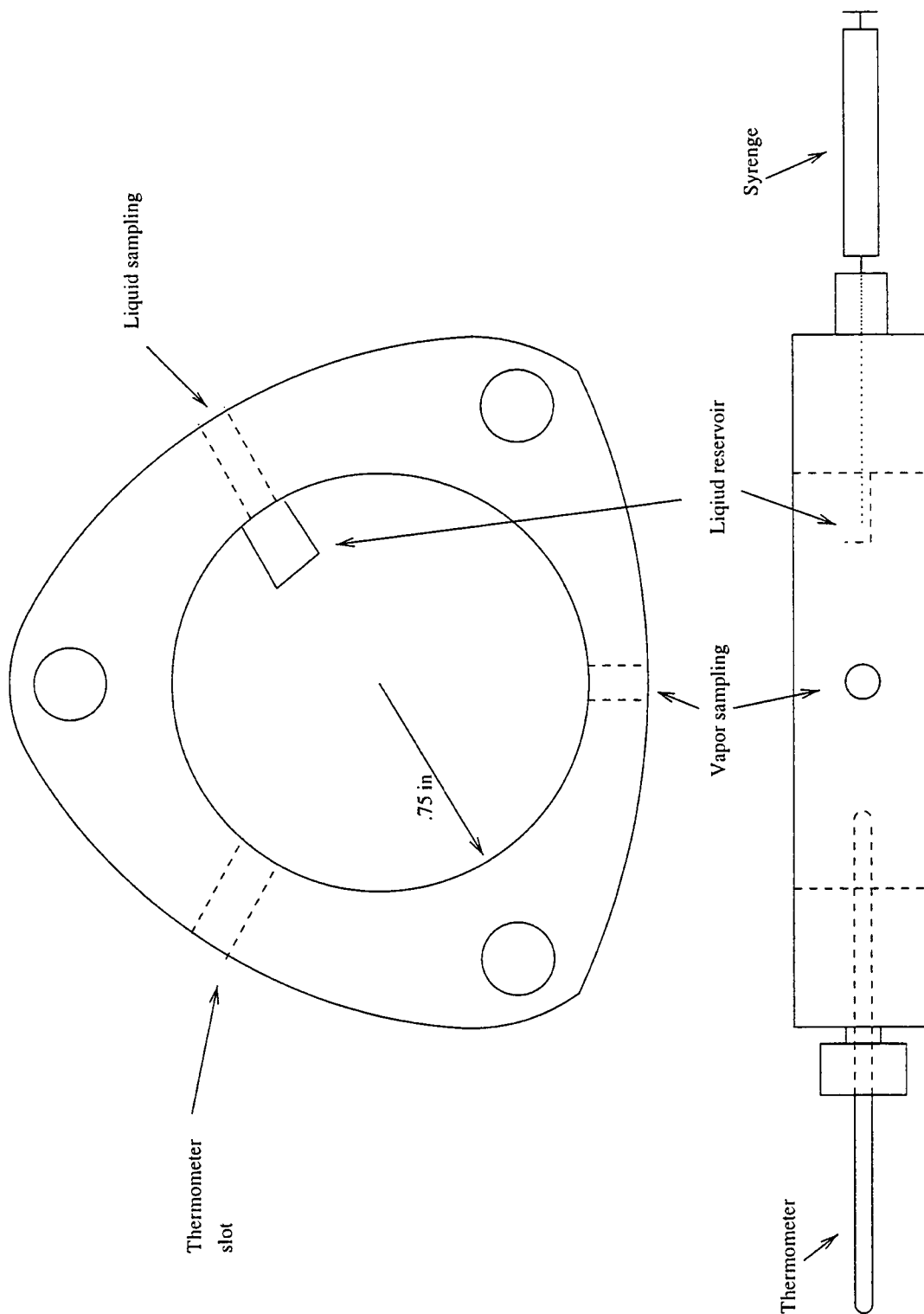


Figure 4.2.3 Sampling spacer

In order to reduce the heat loss, the two lower sections of the packing were wrapped with heating tape, and the entire column was then insulated with fiber glass, one-inch thick.

The interior of the column, the storage and feed tanks, and the valves were expected to come into contact with the acetic acid and the sulfuric acid catalyst. For this reason, all feed and sampling spacers and all packing supports were made of PVC, and a stainless steel valve was used to regulate the bottom flow. A picture of the whole system is shown in Figure 4.2.4.

4.3 EXPERIMENTAL PROCEDURE

4.3.1 Materials

An HPLC methanol feed contained a small percentage of water (0.1%) supplied by Fisher Ltd. was used; however, even a slightly higher percentage of water should not affect the conversion or the reaction (Agreda, 1990).

Glacial acetic acid of 99.9% purity supplied by Fisher Ltd., which contained minor impurities such as acetic anhydrides and chlorides, was also used as a reactant.

A 96% sulfuric acid solution was used as a catalyst and was mixed with the acetic acid in a proportion of 1 Kg. sulfuric acid per 100 Kg. acetic acid. The proportion was increased in some runs to determine the effect of the catalyst concentration on the conversion.

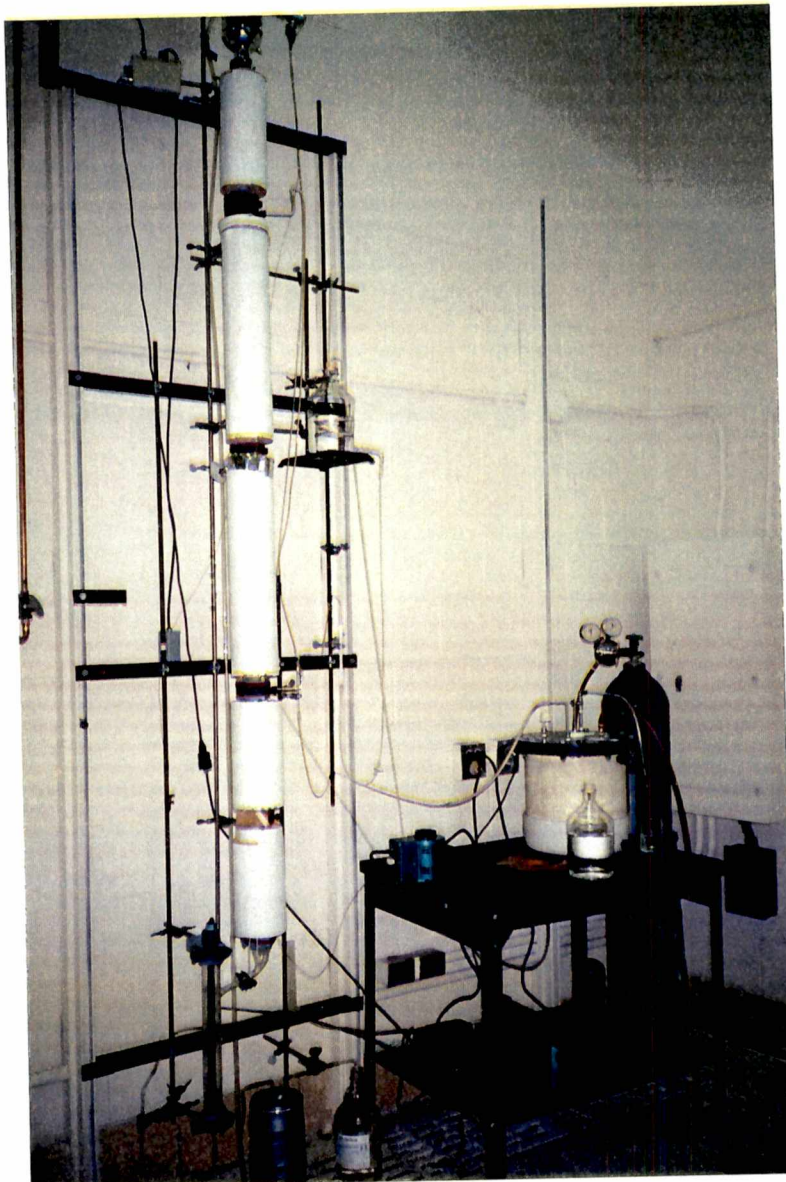


Figure 4.2.4 Photograph of the experimental column

Tap water was supplied to the condenser to cool the distillate to room temperature, and an ice bath was used to cool the bottom product before it was neutralized with a dilute sodium hydroxide solution.

4.3.2 Experimental Testing and Runs

Before performing any experimental runs of the reactive system, the column operation was tested with a methanol-water system. Various runs were made to test the reflux head operation, to detect any leakage, to establish the amount of heat required in the heating tape, and to examine the separation efficiency of the column. The reflux head proved to be excellent in its operation and separation efficiency. The test also showed the necessity of using insulation to reduce heat loss and, thus, to reduce the heat supplied to the reboiler. It was noticed also that the liquid level in the reboiler needs to be monitored and adjusted throughout the run to avoid any overflow of or drainage from the reboiler.

The experimental run starts by opening the methanol and acetic acid feed valves at the desired flow rates, while keeping the bottom flow valve closed until the liquid in the reboiler reaches the desired level. At this point, heat is supplied to the liquid in the reboiler, and the bottom flow valve is opened to maintain the liquid at the desired level and to avoid an overflow. Initially, extra heat was supplied to shorten the time required to heat the column. However, when the vapor reached the condenser, the heat was gradually reduced. Once the vapor started to rise from the reboiler, additional heat was supplied from the heating tape to the lower section of the column below the methanol feed.

Depending on the flow rates, the column required 30-60 minutes to heat up and for the vapor to reach the condenser. The column continued to operate at total reflux for approximately one hour before reaching the steady state. Before taking any distillate product from the column, the feed flow meters were checked to make sure that the flow was stable. The temperatures were also checked throughout the one-hour period, and the distillate valve was not opened until the temperature at each location in the column became steady.

Once the steady state was achieved, the distillate valve was opened to the desired reflux ratio, and the column was allowed to operate for 3-4 hours. During this period, the distillate and bottom flow rates were measured, and samples from the distillate, the bottom, and the three intermediate sampling ports were taken and analyzed hourly.

In order to maintain the required flow rate, it was necessary to increase the nitrogen pressure in the acetic acid tank since the acid level in the tank tends to decrease. In addition, because the liquid level in the reboiler fluctuated, it was necessary to adjust the bottom flow rate to maintain the required liquid level. In general, the column operated efficiently with no major problems during the experiments.

4.3.3 Experimental Techniques

One of the goals of the experiments was to discover the optimal operating conditions for achieving distillate purity and maximum reactant conversion. Since the feed positions were fixed in advance based on the literature review (Agreda, 1990), the experimental work focused on finding the best reflux ratio, feed ratio (methanol to acetic

acid), feed rate, and catalyst concentration. The experiments were started with a selected feed ratio, feed rate, boil-up rate, and catalyst concentration, and then the operation was tested using various reflux ratios. In three additional tests, the feed ratio, the feed rate, and the catalyst concentration were each used as variables.

4.4 SAMPLE ANALYSIS

Two major problems had to be faced before considering the best way to analyze the samples. The first problem was the presence of the sulfuric acid catalyst in the samples, and the second problem was the unavailability of a way to detect the amount of water in the samples.

4.4.1 Sulfuric Acid Removal

Sulfuric acid is corrosive and at high temperatures is expected to react with and degrade the stationary phase of the packed column used in gas chromatography (GC). Thus, a considerable amount of time was spent testing two methods to see if they were feasible before deciding which method to use. One approach was to neutralize the sulfuric acid in the sample with a base before injecting the sample into the GC. The major problems in this approach were (1) the concentration of the sulfuric acid in the sample was not known, and (2) there was a possibility that the added base would neutralize some of the acetic acid in the sample. Moreover, this technique requires that the operation be conducted under closed conditions and at very low temperatures. Otherwise, the reaction of methanol and acetic acid at room temperature might continue; and, under open

conditions, the acetic acid or methanol vapors might rise from the sample. Ultimately, this approach proved to be unsuitable for our system, and a search for a better alternative was conducted.

The other approach that was considered was the use of Raman Spectroscopy, a technique in which a laser ray is passed through the sample, and the intensity of the various components in the sample are related to their concentration in the sample. Even though a linear relation between the concentration and the intensity was achieved, the same linear relation was not achievable after each experiment. Some factors that might affect the reproducibility of the linear relation are the following (Grasselli et al, 1991):

- Variations in the intensity of the exciting light from one scan to the next,
- Variations in the sample, including changes in refractive index and optical attenuation,
- Variations in the orientation of different samples in the optical path.

Since Raman Spectroscopy requires an appreciable volume contained in a relatively wide container for the laser to pass through, it was impossible to collect the required volume of samples needed for analysis from the intermediate sampling ports.

Ultimately, it was more accurate and less time consuming to use gas chromatography even though the sulfuric acid could potentially destroy or degrade the packed column. After discussing this issue with the manufacturer, we were assured that the column would last until all experimental work was completed (about 200 injections) since the sulfuric acid concentration was not expected to be higher than 1 wt%.

4.4.2 Water Detection

The gas chromatography available in the lab (Vista 6000) has only a flame ionization detector (FID), which does not detect water. Thus, the amount of water in the sample was determined by a volume balance around the sample, which was injected into the GC. The following steps were followed to assure accuracy in this technique:

1. Several GC packings were tested to determine the one that provides the best separation of the three components in the sample (methanol, acetic acid, and methyl acetate). The packed column "stainless steel 15% FFAP on chromosorb" which is a high polarity general purpose column recommended for free acids and phenols was the best available column for separating the three components at various temperatures. In order to separate the components, the helium flow rate was maintained at 4 ml/min., and the column was initially heated to 85 °C for 2 minutes. Following this, the temperature was raised 20 °C/min. until the column temperature reached 195 °C. The injection temperature was 220 °C, and the detection temperature was 270 °C. The retention time was 2.7 minutes for methyl acetate, 3.2 minutes for methanol, and 9.5 minutes for acetic acid.
2. Calibration curves were drawn for each of the three components relating the injected volume versus the area of the peak.
3. Tests were conducted to detect the effect of mixing on volume change since for non-ideal systems it was expected that a little change in volume would occur upon mixing. Known volumes of the three components were mixed, and a sample was injected into the GC. Then, the volume of each component was calculated using the calibration

curves. The test showed that the change in the volume was less than 4%, and, thus, no correction was made for volume change upon mixing.

4. Known volumes of the three components and water were mixed, and 1 μl of the mixed sample was injected into the GC. The volume of the three components was then calculated from the corresponding calibration curves, and the volume of the water was calculated by subtracting the total volume of the three components from the volume that was injected into the GC. The tests showed that the volume of water was close to the mixed volume within a 6% error.

5. The mole fractions were calculated from the known volumes of the components.

4.5 EXPERIMENTAL DIFFICULTIES

The following difficulties were encountered during the experimental runs and analysis:

- The liquid level in the reboiler was fluctuating due to relatively violent boiling action, and a routine watch and adjustment of the bottom flow rate was necessary to maintain the required liquid level. Samples taken at various time intervals showed approximately a 10% variation in the sample concentrations.
- The flow rate of the acetic acid feed decreased as the acid level in the tank decreased. Therefore, a routine check of the acetic acid feed was required to insure a stable flow rate. An increase in the nitrogen pressure in the tank maintained the required flow rate.

- In many cases, liquid samples taken by syringe from the intermediate sections of the column were mixed with gas bubbles. Therefore, extra care was required when taking samples to prevent vapor from getting into the syringe and to insure the real representation of the liquid samples.
- Some of these difficulties might have appreciably affected the sample concentration and might have given an inaccurate representation of the real state in the column.

5. RESULTS AND DISCUSSION

Experimental runs were performed under various operating conditions and then compared with theoretical predictions from the model. The model predictions including the model convergence and the speed of calculations, are also discussed and analyzed. The experimental findings were then compared with that of previous works in both packed and plate columns. The model and the experimental findings were analyzed to study the effect of the operating parameters on conversion and distillate purity. At the end, a reduced, simplified form of the model was tested.

5.1 EXPERIMENTAL RESULTS

The experimental runs at different operation conditions showed that a high distillate purity can be achieved when operating under optimal flow conditions. By varying reflux ratio, methanol to acid ratio, and feed rates, a 95.1 mole% distillate purity of methyl acetate was achieved at a reflux ratio of 2.5 and methanol/acetic acid feed ratio of 1.2. A higher concentration of the ester could have been achieved at higher reflux but the rate of increase was expected to be small and have a negative effect on conversion and thus to be economically insufficient. A maximum conversion of acetic acid of 95.9% was achieved when the reflux ratio was decreased to 1.5. Further decrease of the reflux ratio may increase the conversion but decreases the distillate purity. The following paragraphs provide a summary of the experimental runs showing feed rates, and temperatures and

different variables under which the experimental runs were performed. In all the runs the acetic acid and methanol feed temperatures were kept at 25 °C.

Acetic acid was the limiting reactant in all the experimental runs. The fractional conversion, X , was therefore calculated, based on the acid, as follows:

$$X = \frac{\text{moles acid reacted}}{\text{moles acid fed}} = \frac{Dx_{De} + Bx_{Be}}{F_{acid}} \quad (5.1.1)$$

where x_{De} , and x_{Be} are the mole fraction of the ester in the distillate and the bottom respectively. Equation (5.1.1) follows from the reaction stoichiometry, in which one mole of ester is produced for each mole of acid converted.

5.1.1 Operation at Selected Reflux Ratios

Under constant boil-up rate, the operation of the column was tested under various reflux ratios while keeping the feed rates constant and keeping the methanol to acid ratio constant at 1.2. The results of these runs are shown in tables 5.1.1 to 5.1.4.

Experimental Input

- Acid rate= 2.058×10^{-3} gmol/s.
- Catalyst (H_2SO_4) rate= 1.26×10^{-5} gmol/s.
- Methanol to acid ratio=1.2.

Run No. 1

Reflux ratio=1.5

Distillate rate= 1.75×10^{-3} gmol/s.

Table 5.1.1 Experimental results for Run no. 1

Distance down the column, m	Mole fraction				Temperature , °C
	<u>Acid</u>	<u>Methanol</u>	<u>Ester</u>	<u>Water</u>	
Distillate, (0)	0	0.081	0.87	0.049	55.4
Above acid feed, (.32)	0.009	0.171	0.801	0.019	55.8
Reaction section, (1)	0.391	0.073	0.436	0.1	69
Stripping section, (2.08)	0.163	0.399	0.281	0.157	63.5
Bottom, (2.7)	0.145	0.273	0.181	0.401	

Run No. 2

Reflux ratio=2

Distillate rate= 1.4×10^{-3} gmol/s

Table 5.1.2 Experimental results for Run no. 2

Distance down the column, m	Mole fraction				Temperature , °C
	<u>Acid</u>	<u>Methanol</u>	<u>Ester</u>	<u>Water</u>	
Distillate, (0)	0	0.0415	0.9245	0.034	55.4
Above acid feed, (.32)	0.007	0.092	0.85	0.051	55.8
Reaction section, (1)	0.4082	0.0351	0.4419	0.1147	69.5
Stripping section, (2.08)	0.1861	0.4	0.261	0.1528	64
Bottom, (2.7)	0.1725	0.254	0.1868	0.3809	

Run No. 3

Reflux ratio=2.5

Distillate rate= 0.92×10^{-3} gmol/s**Table 5.1.3 Experimental results for Run no. 3**

Distance down the column, m	Mole fraction				Temperature , °C
	<u>Acid</u>	<u>Methanol</u>	<u>Ester</u>	<u>Water</u>	
Distillate, (0)	0	0.035	0.951	0.014	55.6
Above acid feed, (.32)	0.0092	0.0972	0.8541	0.0395	56
Reaction section, (1)	0.349	0.089	0.453	0.109	68.3
Stripping section, (2.08)	0.126	0.4831	0.2697	0.1212	64.5
Bottom, (2.7)	0.091	0.431	0.183	0.295	

Table 5.1.4 Distillate purity and fractional conversion at different reflux ratios

Run No.	Reflux Ratio	Distillate Purity %	Fractional Conversion %
1	1.5	87	95.91
2	2	92.45	90.93
3	2.5	95.1	79.39

As shown in Figure 5.1.1, the distillate purity tends to increase as the reflux ratio increased. As it is the case in conventional distillation, there are operational and economical factors that limits the use of high reflux ratio. But in this case, conversion is the factor that limits the increase in the reflux ratio as shown in Figure 5.1.2.

As the reflux ratio increases, the conversion decreases. This can be explained that as the reflux ratio increases, the liquid flow rate down the column increases and the concentration of the unreacted reactants increase in the bottom product. The column in this case behaves as a distillation column more than as a reactor. So for reactive distillation, the choice of the operational reflux ratio should be based on the desired distillate purity, overall conversion and economical factors. Although not determined here, there is clearly an optimal reflux value for this reflux ratio.

5.1.2 Operation with Selected (Methanol/Acid) Feed Ratios

The column operation was also tested with selected methanol to acid feed ratios, at a given reflux ratio of 2 and constant boil-up rate. Since the acid is the limiting reactant, more acid is expected to react as the ratio increases. However, distillate purity may decrease due to the increase of this ratio. The following set of experiments were expected to show the effect of variable feed ratio on distillate purity and overall conversion. The results of these runs are shown in tables 5.1.5 to 5.1.6.

Experimental Input

- Acid Flow rate = 2.058×10^{-3} gmol/s.
- Catalyst flow rate = 1.26×10^{-5} gmol/s.
- Reflux ratio = 2.

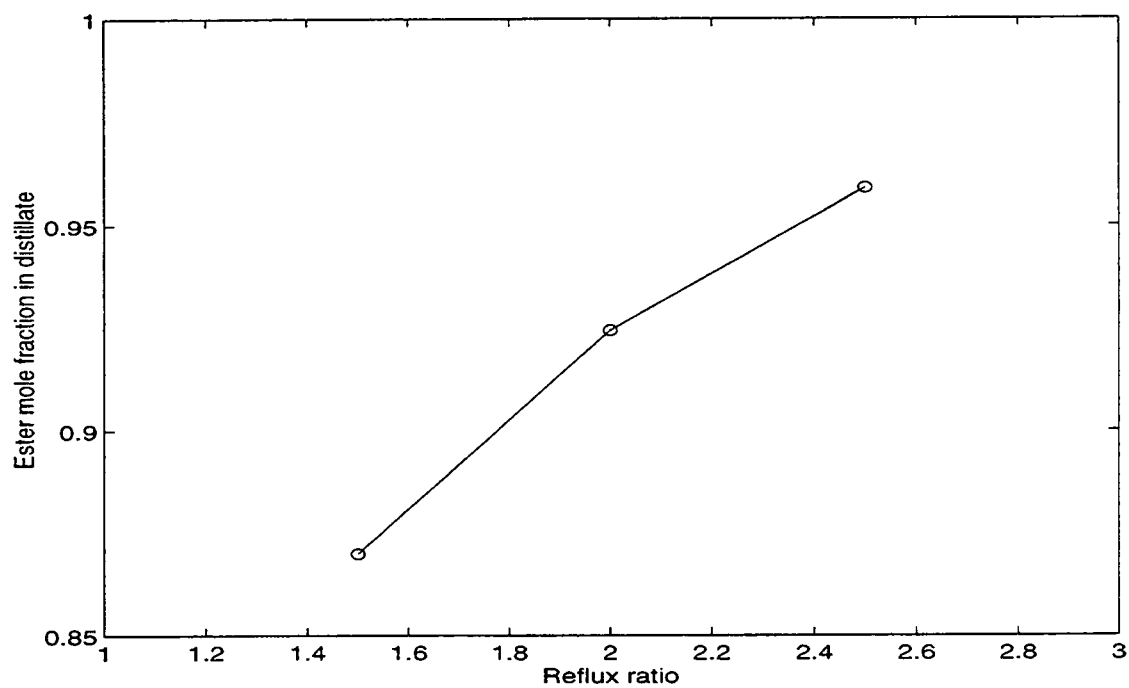


Figure 5.1.1 Effect of reflux ratio on the distillate purity

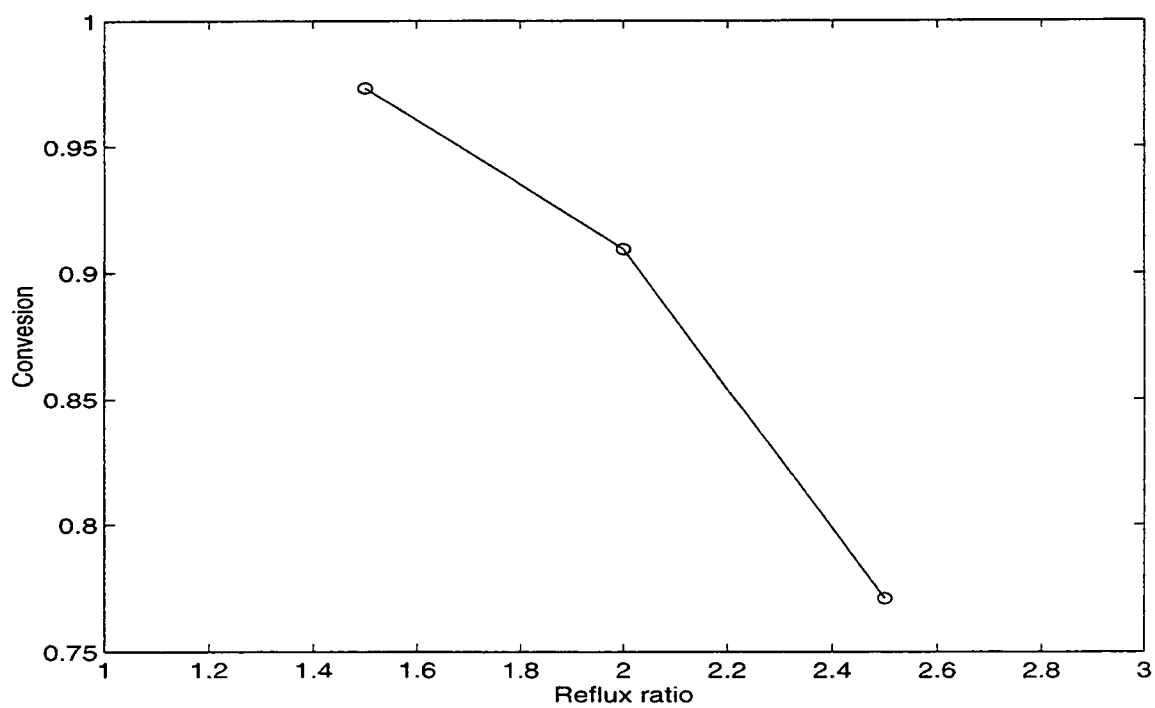


Figure 5.1.2 Effect of reflux ratio on the conversion

Run No. 4

Methanol to acid ratio=1.1

Distillate rate= 1.28×10^{-3} gmol/s.

Table 5.1.5 Experimental results for Run no. 4

Distance down the column, m	Mole fraction				Temperature, °C
	<u>Acid</u>	<u>Methanol</u>	<u>Ester</u>	<u>Water</u>	
Distillate, (0)	0	0.038	0.931	0.031	55.4
Above acid feed, (.32)	0.0029	0.118	0.84	0.0391	55.8
Reaction section, (1)	0.422	0.0253	0.431	0.1217	71
Stripping section, (2.08)	0.201	0.342	0.281	0.176	65
Bottom, (2.7)	0.153	0.321	0.177	0.349	

Run No. 5

Methanol to acid ratio=1

Distillate rate= 1.25×10^{-3} gmol/s.

Table 5.1.6 Experimental results for Run no. 5

Distance down the column, m	Mole fraction				Temperature, °C
	<u>Acid</u>	<u>Methanol</u>	<u>Ester</u>	<u>Water</u>	
Distillate, (0)	0	0.031	0.943	0.026	55.6
Above acid feed, (.32)	0.0039	0.129	0.8437	0.0235	55.8
Reaction section, (1)	0.465	0.041	0.408	0.086	67
Stripping section, (2.08)	0.183	0.365	0.291	0.161	63.5
Bottom, (2.7)	0.202	0.241	0.153	0.404	

Figure 5.1.3 shows that the increase in the feed ratio produced a decrease in the distillate purity since the amount of the methanol used in excess of the acid increased in the column and thus increased the amount of methanol vapor raising to the top of the tower. In contrast to that, the conversion of acetic acid increased by the increase in the methanol ratio since more acid is reacted with the excess methanol used as shown in Figure 5.1.4.

5.1.3 Operation with Selected Feed Rates

Tables 5.1.7 and 5.1.8 show the result of the effect of the feed flow rates on the conversion and distillate purity. The flow of both reactants were varied than that of run 2. This series of runs were conducted at constant boil-up rate, constant feed ratio of 1.2, and constant reflux ratio of 2.

Experimental Input

- Methanol to acid ratio=1.2.
- Reflux ratio=2.

Run No. 6

Acid rate= 4.116×10^{-3} gmol/s.

Catalyst rate= 2.52×10^{-5} gmol/s.

Distillate rate= 2.5×10^{-3} gmol/s.

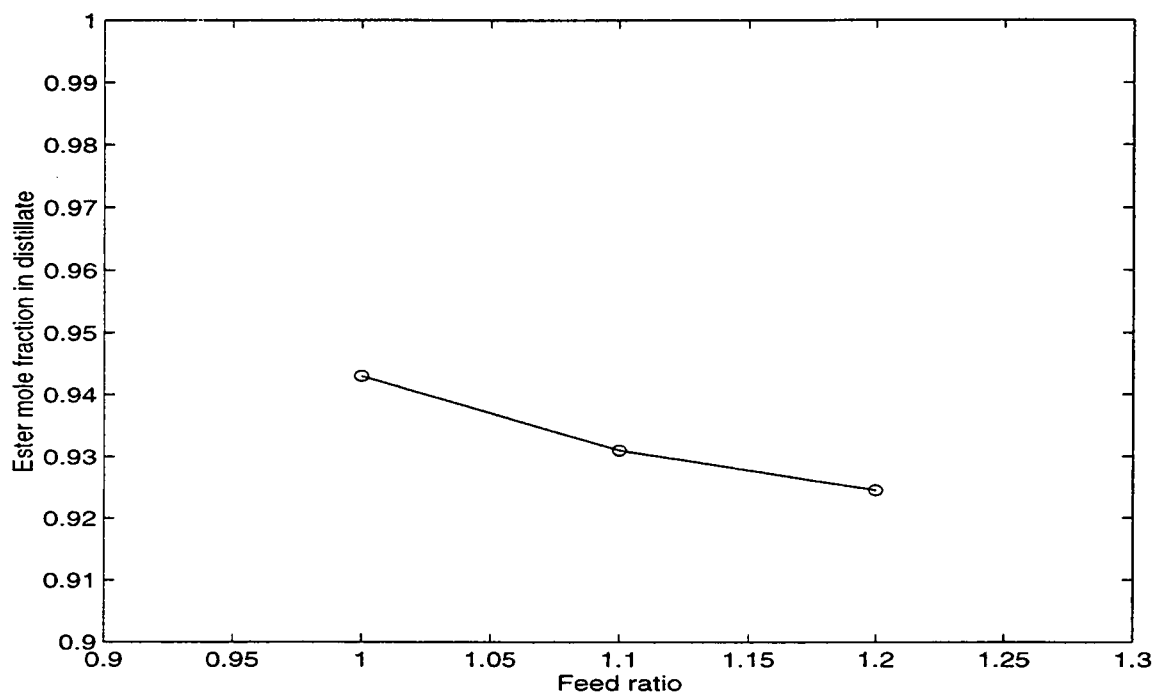


Figure 5.1.3 Effect of feed ratio on the distillate purity, for a constant Reflux Ratio of 2.

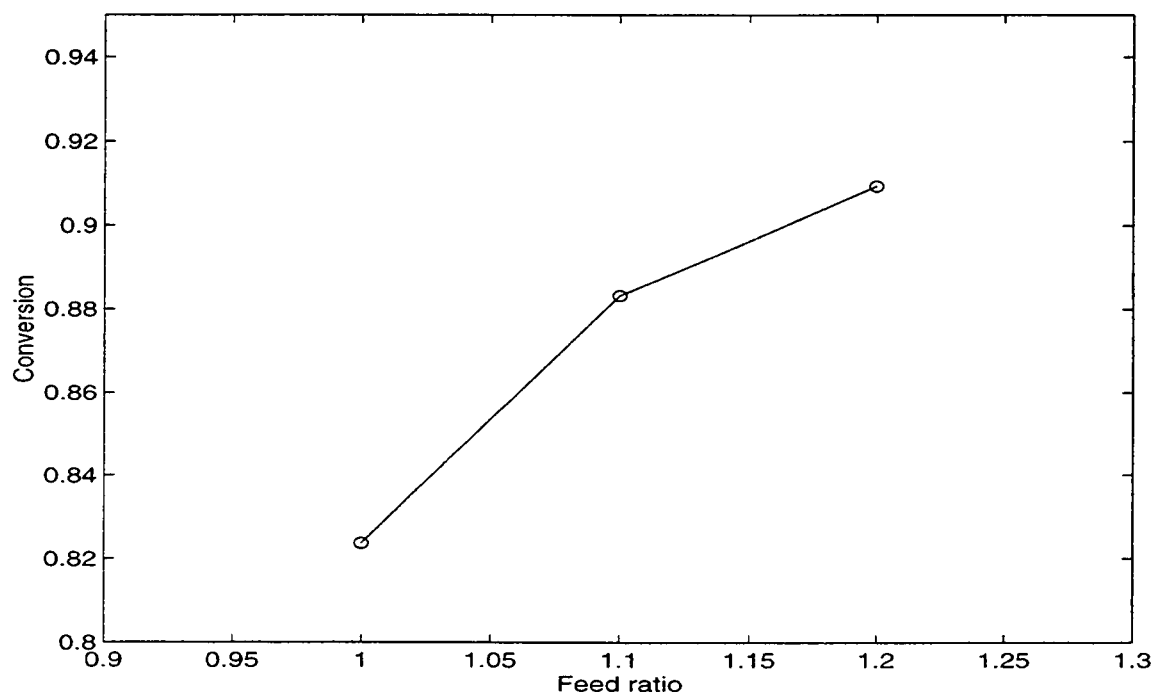


Figure 5.1.4 Effect of feed ratio on the conversion for a constant reflux ratio of 2

Table 5.1.7 Experimental results for Run no. 6

Distance down the column, m	Mole fraction				Temperature , °C
	<u>Acid</u>	<u>Methanol</u>	<u>Ester</u>	<u>Water</u>	
Distillate, (0)	0	0.049	0.919	0.032	55.4
Above acid feed, (.32)	0.005	0.149	0.807	0.039	56.3
Reaction section, (1)	0.42	0.065	0.442	0.073	79.5
Stripping section, (2.08)	0.219	0.362	0.298	0.121	69
Bottom, (2.7)	0.275	0.241	0.188	0.296	

Run No. 7

Acid rate= 1.029×10^{-3} gmol/s.

Catalyst rate= 0.63×10^{-5} gmol/s.

Distillate rate= 0.935×10^{-3} gmol/s.

Table 5.1.8 Experimental results for Run no. 7

Distance down the column, m	Mole fraction				Temperature , °C
	<u>Acid</u>	<u>Methanol</u>	<u>Ester</u>	<u>Water</u>	
Distillate, (0)	0	0.041	0.93	0.029	55.5
Above acid feed, (.32)	0.005	0.131	0.821	0.043	55.8
Reaction section, (1)	0.317	0.051	0.495	0.137	60
Stripping section, (2.08)	0.1075	0.3733	0.3173	0.2019	61.5
Bottom, (2.7)	0.071	0.3021	0.1339	0.493	

Figure 5.1.5 shows that a large increase in the acid flow rate did not produce a large decrease in the distillate purity. Doubling the flow rate of the acid produced a 0.55 % decrease in the distillate purity, whereas the conversion decreased sharply from 90.9 % to 86.8 % as shown in Figure 5.1.6. The effect of flow rate on conversion is bounded by the fact that at higher flow rates the column will flood and no distillation will take place, while at very low flow rate the conversion might decrease again as the flow rate becomes very low for the reaction to take place.

5.2 COMPARISON OF EXPERIMENTAL AND THEORETICAL RESULTS

5.2.1 Model Calculations

The model developed in chapter 3 was programmed and solved using Matlab mathematical software on a Unix workstation(Appendix C). The main program and the subroutines for physical properties and the flux calculations required 56 KB of storage memory and 8 MB of Ram memory . The fourth-order Runge-Kutta method supplied by Matlab was used to solve the differential equations representing the system, using the reflux flow rate, vapor rate to the condenser, and the liquid and vapor mole fractions at the top as the initial values. Many other matrix manipulating functions such as the inverse and the pseudo inverse functions were also used to perform the flux calculations.

Due to the non-linearity of the differential equations, the calculation was slow in some regions especially below the acid feed. In general, the calculation was fast, especially when the tolerance for the Runge-Kutta ODE solver in Matlab was increased from 10^{-6} to 10^{-4} . In addition, reducing the tolerance for the interface temperature calculation in the

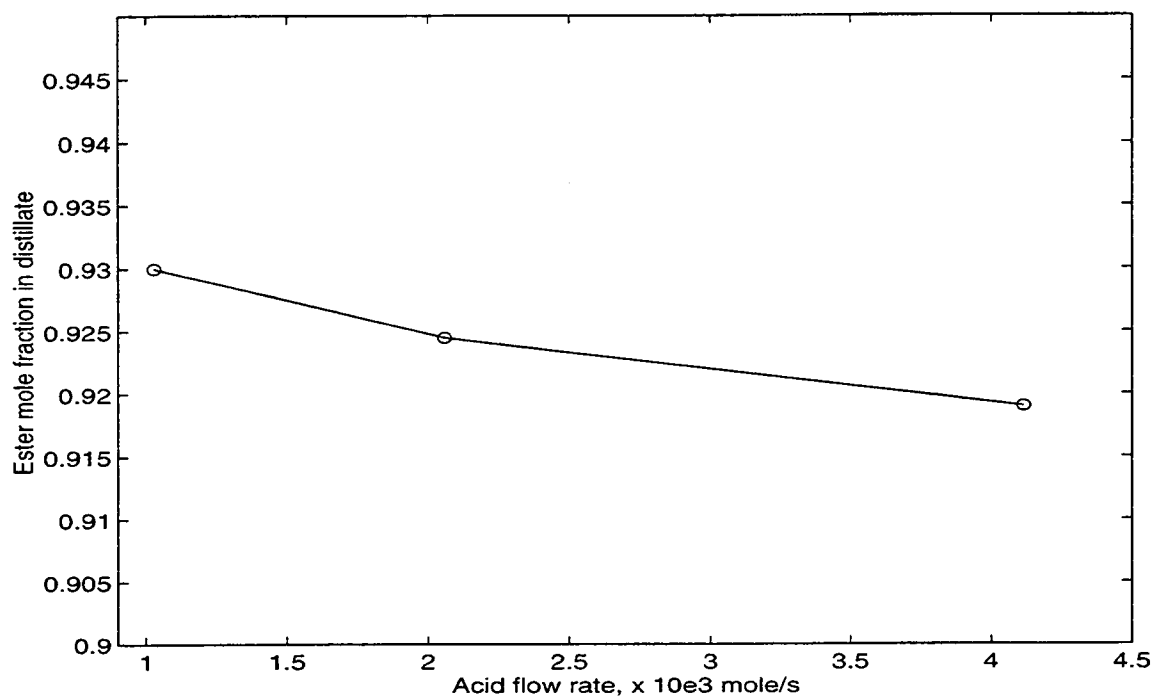


Figure 5.1.5 Effect of flow rate on the distillate purity for a constant reflux ratio of 2.

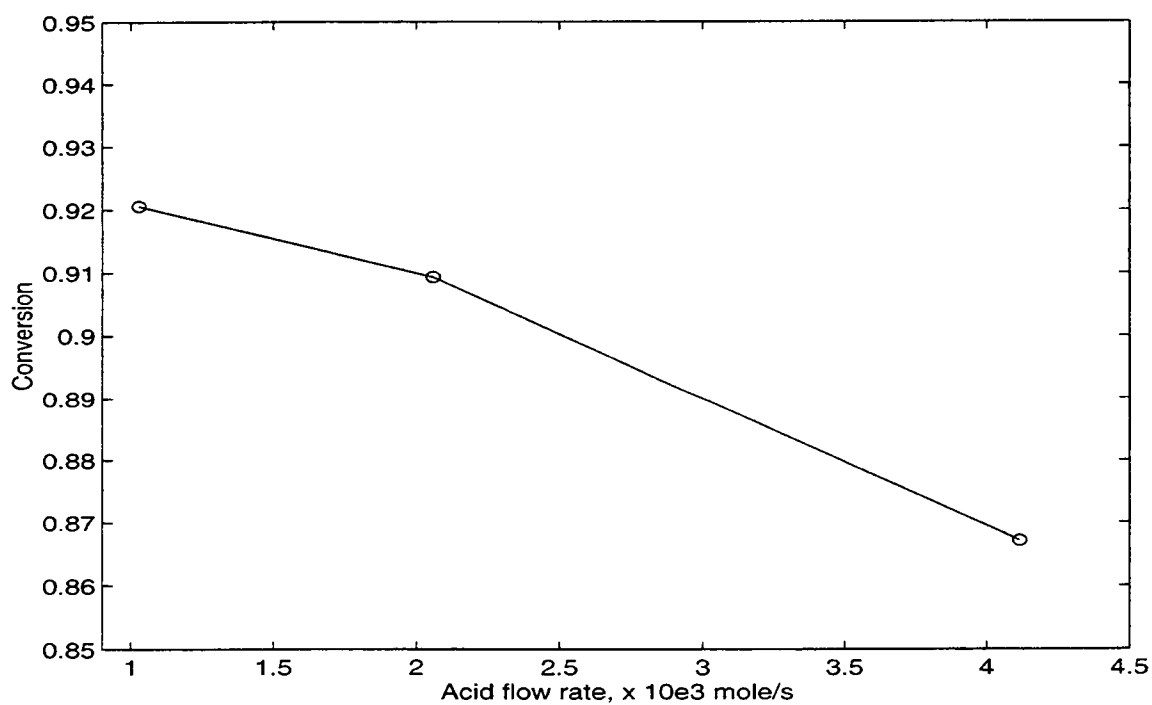


Figure 5.1.6 Effect of flow rate on the conversion for a constant reflux ratio of 2.

flux calculation routine helped increase the speed of the calculation. The calculational time varied from one run to another with a minimum of 16 minutes for run 2 to 35 minutes for run 5.

The Newton's-Method used to calculate the interfacial flux showed fast and stable conversion. In all the runs, the routine required between 3 and 4 iterations to converge and yield the fluxes and the interface temperature and concentration in both phases.

Convergence time for the overall calculation was effected by the non-linearity of the differential equations while little time was taken to calculate the physical properties and column parameters.

The model calculates the concentration and temperature profile along the column. In addition reaction rate was calculated and plotted to show the locations of high rate of reactions.

5.2.2 Comparison of Experimental and Theoretical Results

As shown in Figures 5.2.1 to 5.2.4 , the experimental results are very close to the model predictions and the differences are considered satisfactory taking into account many factors that may have an effect on both the experimental and theoretical concentration profiles . Some of these factors are :

- It is expected that the reaction continued during the sampling and injection of the sample into the GC.
- Due to the liquid level fluctuation in the reboiler, caused by violent bubbling, the increase or the decrease of the bottom flow rate may had an effect on the concentration profile in the column. Analysis of the samples of the intermediate

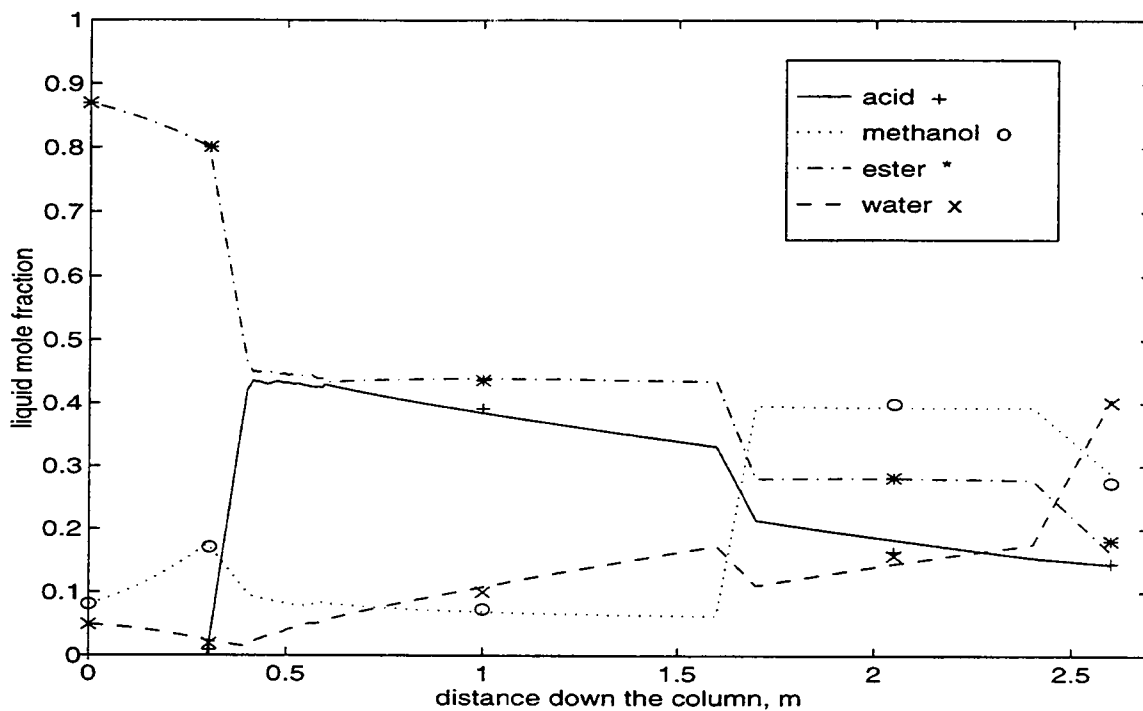


Figure 5.2.1 Theoretical and Experimental liquid mole fraction profiles for Run 1. Acid flow = 2.058×10^{-3} gmol/s, methanol/acid ratio=1.2, and reflux ratio=1.5.

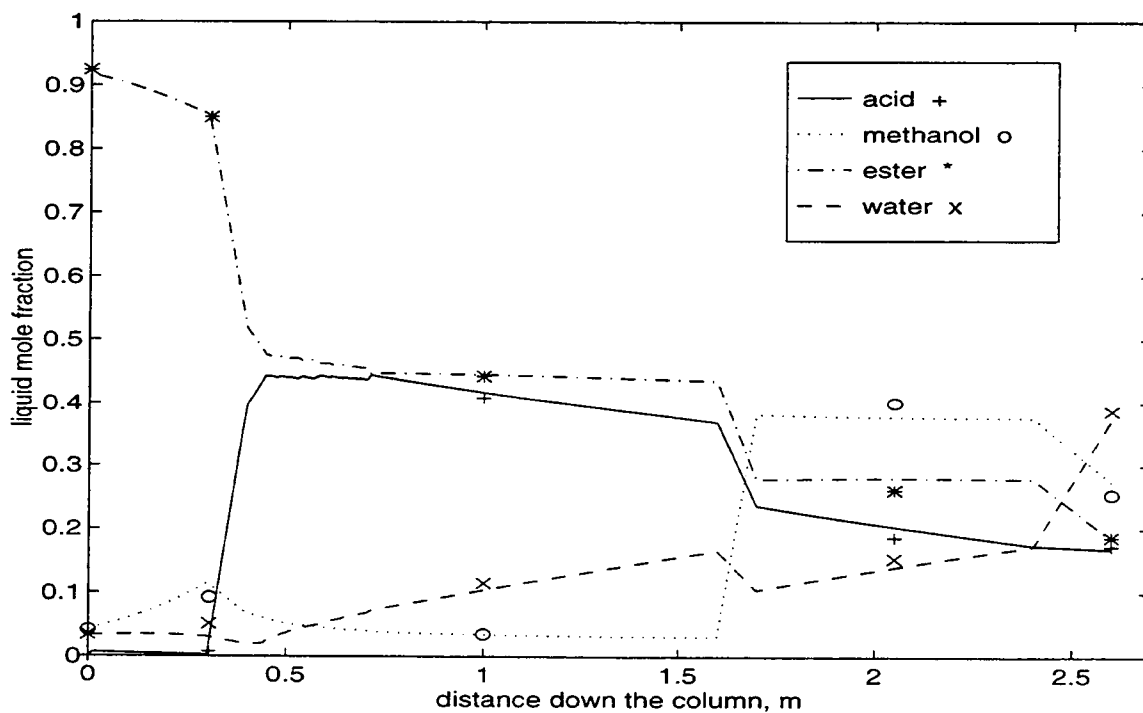


Figure 5.2.2 Theoretical and Experimental liquid mole fraction profiles for Run 2. Acid flow = 2.058×10^{-3} gmol/s, methanol/acid ratio=1.2, and reflux ratio=2.

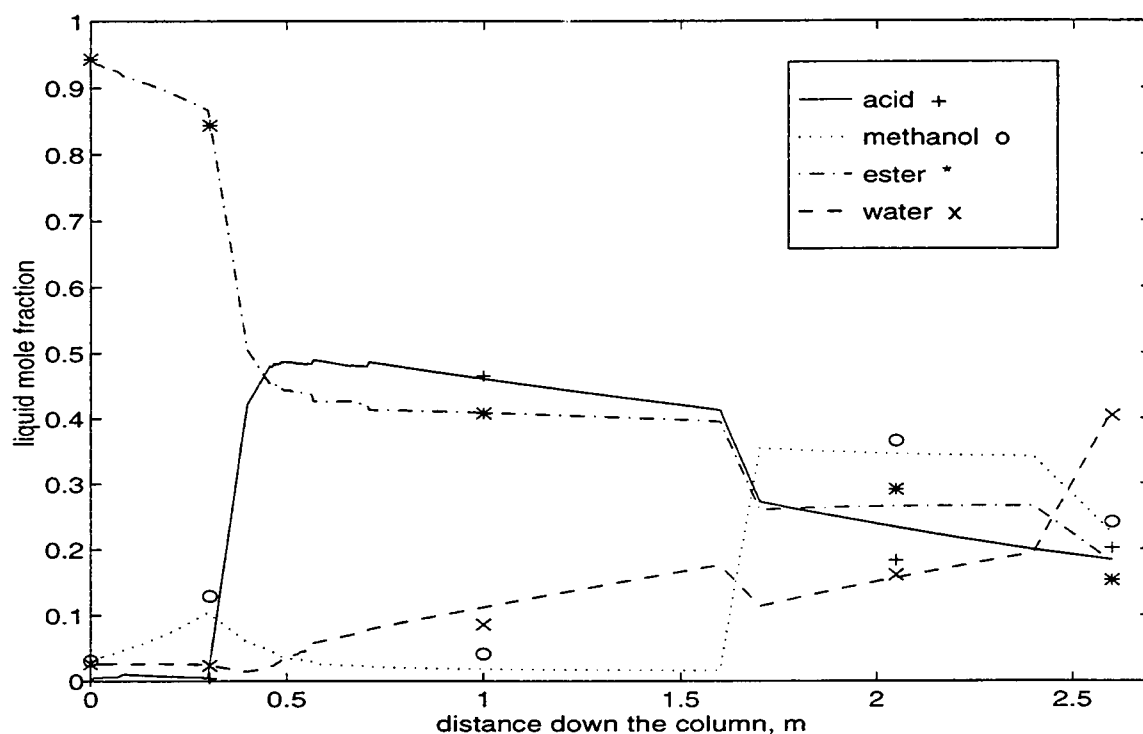


Figure 5.2.3 Theoretical and Experimental liquid mole fraction profiles for Run 5.
Acid flow= 2.058×10^{-3} gmol/s, reflux ratio=2, methanol/acid ratio=1.

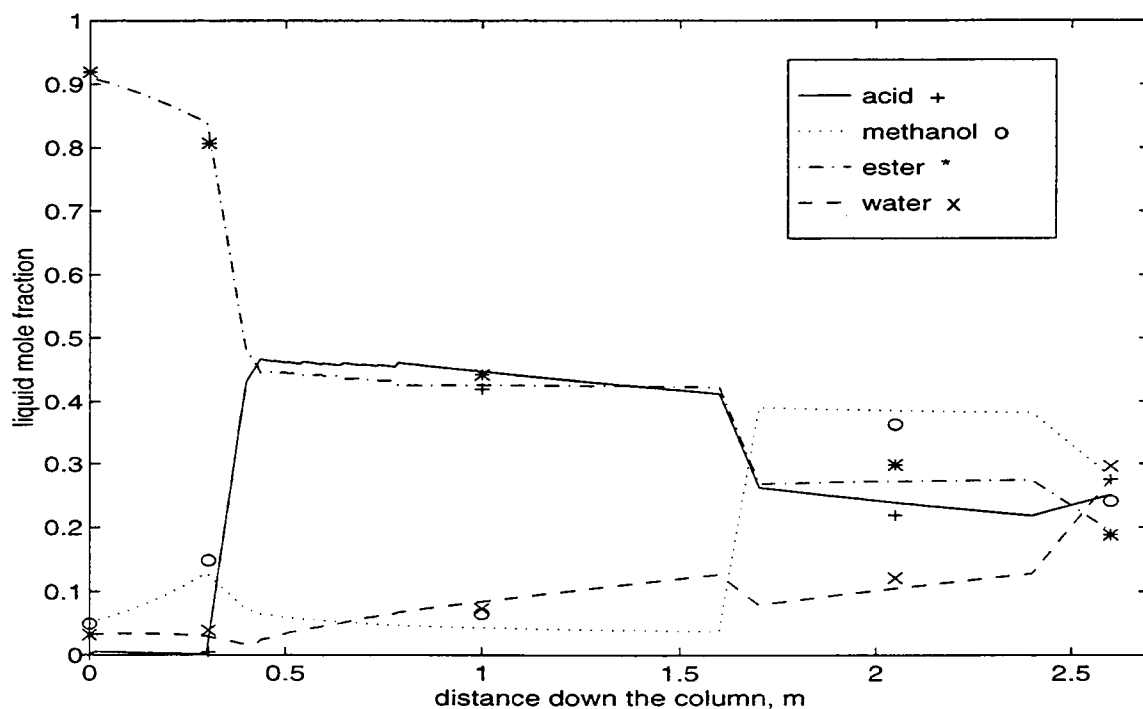


Figure 5.2.4 Theoretical and Experimental liquid mole fraction profiles for Run 6.
Acid flow= 4.116×10^{-3} gmol/s, reflux ratio=2, methanol/acid ratio=1.2.

section of the column showed some difference in the results at different sampling times.

- Theoretical findings are also affected by the various correlations used in the model. Up to 10% error was expected in many physical properties correlations such as the liquid mixture surface tension and liquid mixture viscosity. In addition, mass transfer coefficient correlation is considered to have an appreciable effect on any model predictions and thus is the case here as will be shown in section 5.4.

Figure 5.2.1 shows the concentration profile for Run 1 and one can see that the experimental concentrations of methyl acetate in particular are very close to the theoretical predictions. The maximum difference between the experimental and the predicted values is 3% at the bottom while a minimum difference of 0.5% occurred at distance of 1 meter from the top. At a distance of 2.05 meters, the acetic acid concentration showed the maximum difference of 7%. The maximum disagreement between experimental and theoretical findings was encountered in the bottom product, and may be due to sampling difficulties and high rate of reaction at the bottom which required a fast sampling and injection into the GC, a process which was not always accomplished easily. Figure 5.2.3 shows that the error between experimental and theoretical concentrations of the ester is about 20%, while the acetic acid concentration exhibited a 9% error in the same run.

The maximum error in all the runs was encountered in Run 5 and is shown in Figure 5.2.3. At 2.08 meters from the top, the acetic acid model result showed a 26% error while methanol and ester showed an error of 8% and 10% respectively.

Except for Run 5, the error was in the range of 0.5-13%, with an average of 10% and thus the comparison is considered satisfactory, and repeated experimental runs at the same conditions showed a little improvement in the result.

5.2.3 Description of the Concentration and Temperature Profiles

As was shown in Figure 5.2.1 to 5.2.4 the ester concentration decreases down the column as it is the lowest boiling point component. In the first section above the acid feed, the concentration of the ester decreases sharply while the concentration of methanol, water, and acid increases in general as heavier components than the ester.

Below the acid feed, the ester concentration decreases at a smaller rate because of the high rate of reaction and the formation of the ester. Methanol concentration decreases sharply as it is consumed by the reaction. The acid concentration also decreases in this region as it is also consumed by the reaction. Water as a product of the reaction increases down the column in all regions.

In the third section below the methanol feed, the ester concentration decreases but in a much smaller rate due to the dual operations of the formation by reaction and by evaporation. In this region the ester continues to form by reaction due to the high ratio of methanol to acid and the higher holdup, while methanol concentration decreases in a very small rate. The acid concentration decreases down the column as it's consumed by the reaction. Water concentration increases down the column as produced by the reaction and little evaporation of it takes place.

Because of the high liquid volume in the reboiler, approximately 0.3 liter, the bottom product showed a high concentration of water as a result of high rate of reaction.

Water concentration varied from a minimum of 28% in run 6 to about 50% in run 7, with all other runs in the 40% range. Methanol concentration in the bottom varied based on the conversion and methanol to acid ratio. In cases where this ratio increased the methanol showed a higher concentration in the bottom. In general the concentration of water and acetic acid increased while the concentration of the lighter components methanol and ester decreased in the bottom product.

As shown in Figures 5.2.5 to 5.2.8, the reaction rate and the temperature are higher in the reaction zone specially where the acid is fed, and decrease as the concentration of methanol decreases by reaction. Below the methanol feed, where the concentration of methanol is high, the reaction rate and the temperature increase again since methanol react with the remaining acetic acid.

The predicted temperature profile for Run 2 and Run 5 are shown in Figures 5.2.5 and 5.2.7 which also demonstrate a good agreement with experimental values measured using thermometers mounted at selected heights in the column. The temperature profile in reactive distillation is quite different than that in non-reactive distillation where the temperature increases monotonically down the column as the concentration of the high boilers increases. In reactive systems the temperature depends on the feed locations the rate of the reaction.

For our system, Figure 5.2.5 shows that the temperature of the distillate is close to the boiling point of methyl acetate (b.p 56.9 °C) since the distillate contains more than 90% ester. The temperature below the acid feed increases to a maximum then slightly decreases down the column, this can be attributed to the high concentration of acetic acid

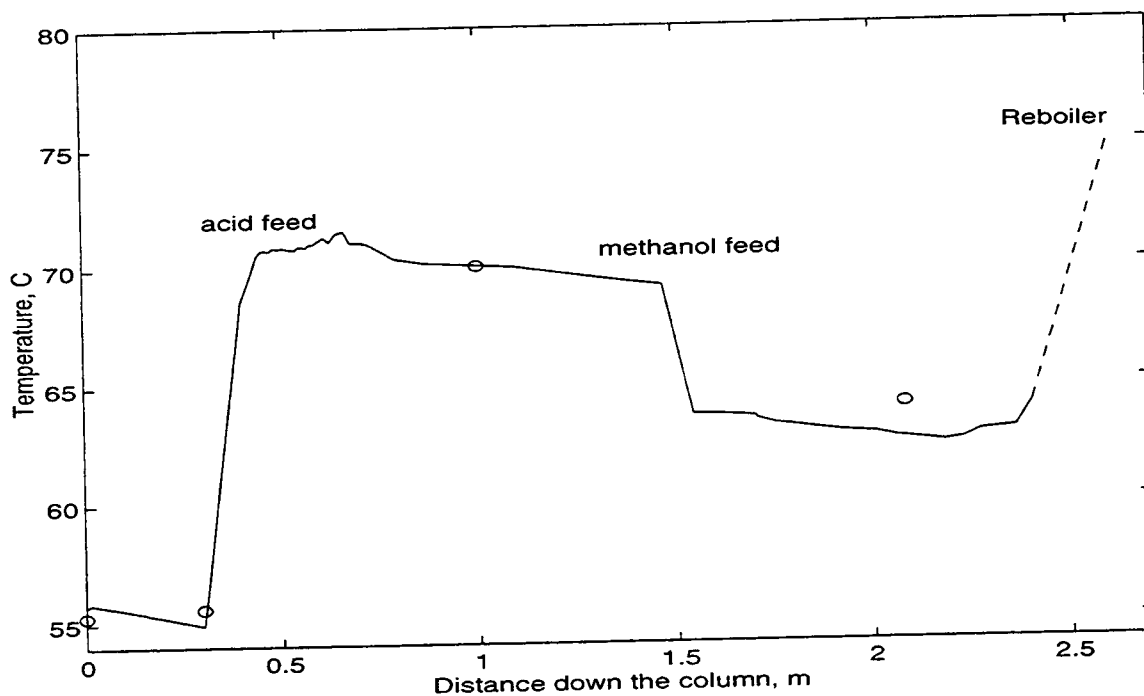


Figure 5.2.5 Theoretical and experimental temperature profiles for Run2.
 Acid flow= 2.058×10^{-3} gmol/s, reflux ratio=2, methanol/acid ratio=1.2
 'o' experimental values, '___' theoretical prediction

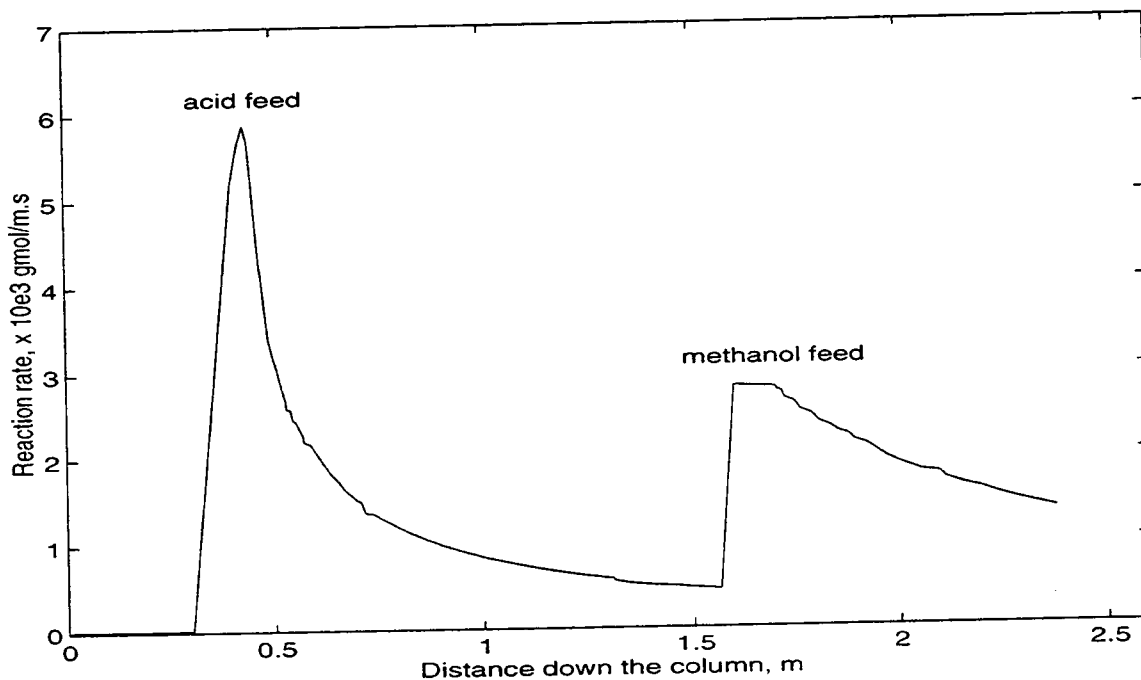


Figure 5.2.6 Calculated reaction rate profile for Run 2
 Acid flow= 2.058×10^{-3} gmol/s, reflux ratio=2, methanol/acid ratio=1.2

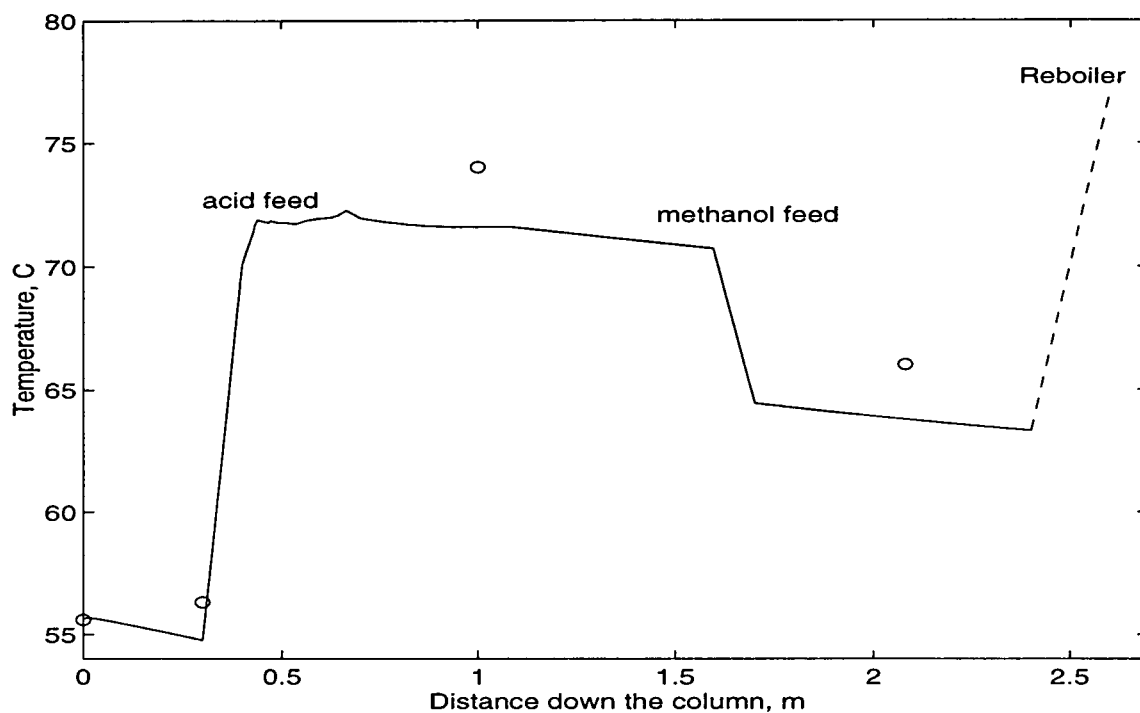


Figure 5.2.7 Theoretical and experimental temperature profiles for Run 6.

Acid flow= 4.116×10^{-3} gmol/s, reflux ratio=2, methanol/acid ratio=1.2.

'o' experimental values, '___' theoretical prediction

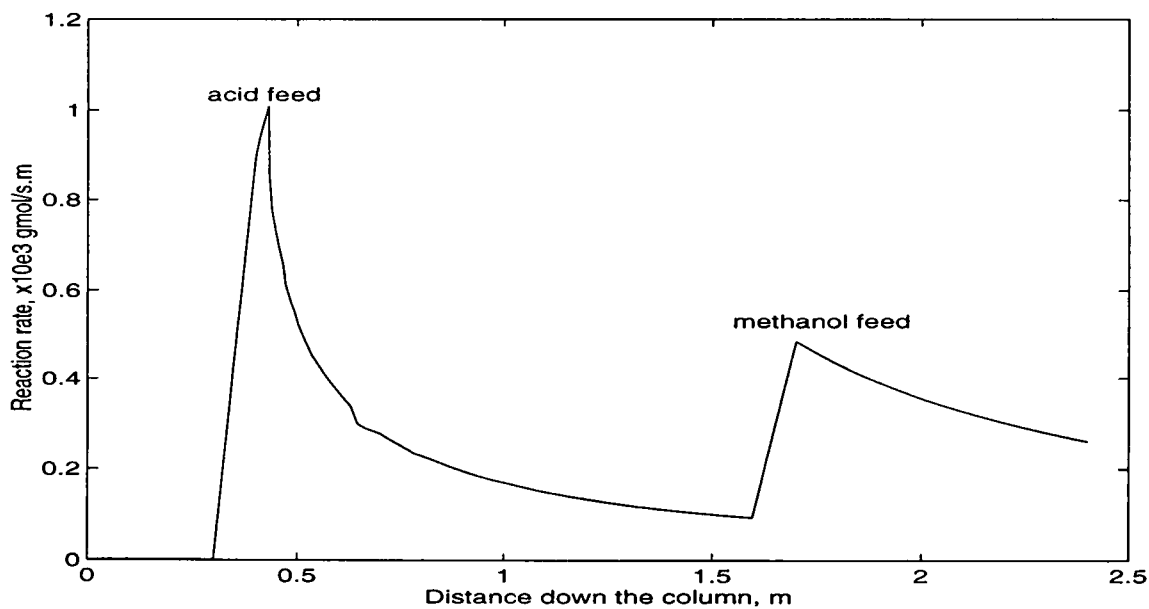


Figure 5.2.8 Calculated reaction rate profile for Run 6

Acid flow= 4.116×10^{-3} gmol/s, reflux ratio=2, methanol/acid ratio=1.2.

and the heat of reaction as the rate of reaction reaches its maximum as shown in Figure 5.2.6. As the reaction rate continues down the column, the concentration of the ester increases while the concentration of the high boilers acid and methanol decreases by consumption by the reaction. As a result, the temperature tends to decrease a few degrees. Below the methanol feed, where a cold methanol is fed (25 °C), the methanol concentration is high while the acid concentration decreases as it is diluted and then consumed by the reaction. In addition, the reaction rate is higher in this section because of the high concentration of methanol which produces more ester and reduces the temperature. The slight decrease of the temperature in this section is attributed to the evaporative cooling happens due to the evaporation of the ester formed due to reaction. Since the liquid holdup in the reboiler is much greater than that in the column, an appreciable fraction of the conversion of acetic acid to ester takes place in the reboiler (about 20% in Run 2). As a result, the temperature in the reboiler goes up again as more water is produced by reaction.

The temperature profile of all the runs are approximately the same with a maximum difference of 2.5 °C as shown in Figure 5.2.7 for run 6. The reboiler showed higher temperature when the concentration of the high boiler water increased from one experiment to another. For all the runs, the column operated in the temperature range of 55-75 °C while the reboiler temperature reached a maximum of 87 °C.

The interesting temperature profile raises the question of the temperature decrease down the column as opposite to what happens in conventional distillation. Figure 5.2.9 shows the temperature profile of the same esterification reaction in a plate column from

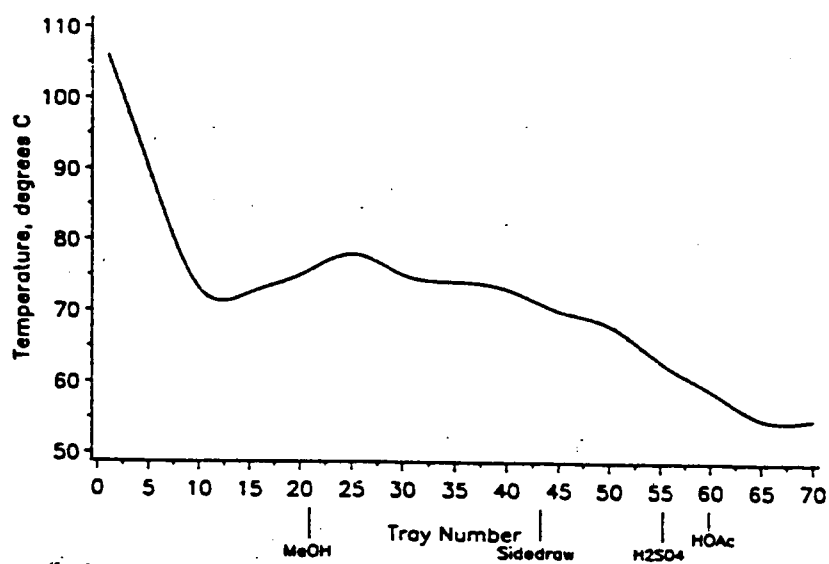


Figure 5.2.9 Temperature profile for the esterification reaction of methanol and acetic acid in a plate column (Agreda, 1990).

the Eastman plant(Agreda, 1990). The profile shows an increase in the temperature down the column as the reaction takes place. Below the methanol feed, the temperature decreases as the concentration of methanol increases before increasing again to the boiling point of water as the bottom contains more than 98% water.

5.3 EFFECT OF CHANGING SELECTED PARAMETERS ON THE CONCENTRATION PROFILE AND CONVERSION

Several parameters are changed in the model calculations in this section to show their predicted effects on conversion and concentration profiles. Since liquid hold-up is an important parameter for the rate of reaction, the effect of increase in liquid hold-up on conversion is studied. Mass transfer coefficient calculated from the equation of Onda et al (1971) is also multiplied by a selected factor to show the sensitivity of the model results to the value of the interfacial mass transfer coefficient.

As mentioned in section 2.4.2, the exact solution to the Maxwell-Stefan equations presented by Krishna and Standart (1976) was adopted in the calculation of the mass transfer coefficient and the fluxes for the multicomponent system, which in turn, involves a lot of matrix calculations for parameters required to allow for the effect of the non-ideality of the system, the finite mass transfer, and the cross effects.

In this section also, certain simplifications of the model on the agreement between experimental and theoretical will be tested. Such simplification, are expected to ease some mathematical difficulties such as singular matrices encountered in the flux calculation, and also to reduce the calculation time.

5.3.1 Effect of Liquid Hold-up

The overall acetic acid conversion can be increased in principal by higher liquid holdup in the column. The discussion in Section 2.5 showed that a special hold-up tank was designed in addition to the high weir plates in order to increase the conversion in the Eastman plant (Agreda, 1990). In our experimental column, we were limited to use the intalox saddle packing since other types of high hold-up packings were not available in the size suitable for the experimental work. We assume here a hypothetical packing that has a higher hold-up and use it to study the effect on the conversion. Figure 5.3.1 shows that the model predicts that doubling the hold-up could increase the conversion from 0.863 to 0.959 for Run 6. Decreasing the hold-up to half of its original value lowered the conversion to 0.826. This study reveals the suitability of the packed column for reactive distillation if high hold-up packings were available.

5.3.2 Effect of Mass Transfer Coefficients

The Onda equations (3.3.38 and 3.3.41) (Onda, 1968) used to calculate mass transfer coefficients is based on experimental work on packings other than the intalox saddle used here. In addition, Onda allowed for an error of 20% in the value of mass transfer coefficients from his model. In this study we varied the value of the mass transfer coefficients calculated from the model by 25% to show the effect on the concentration profile and the agreement with experimental results.

Figure 5.3.2 shows the effect of varying the mass transfer coefficients on the concentration profile for Run 6. When increasing the values by 25%, the concentration profile showed to be in a good agreement with experimental values especially in the case

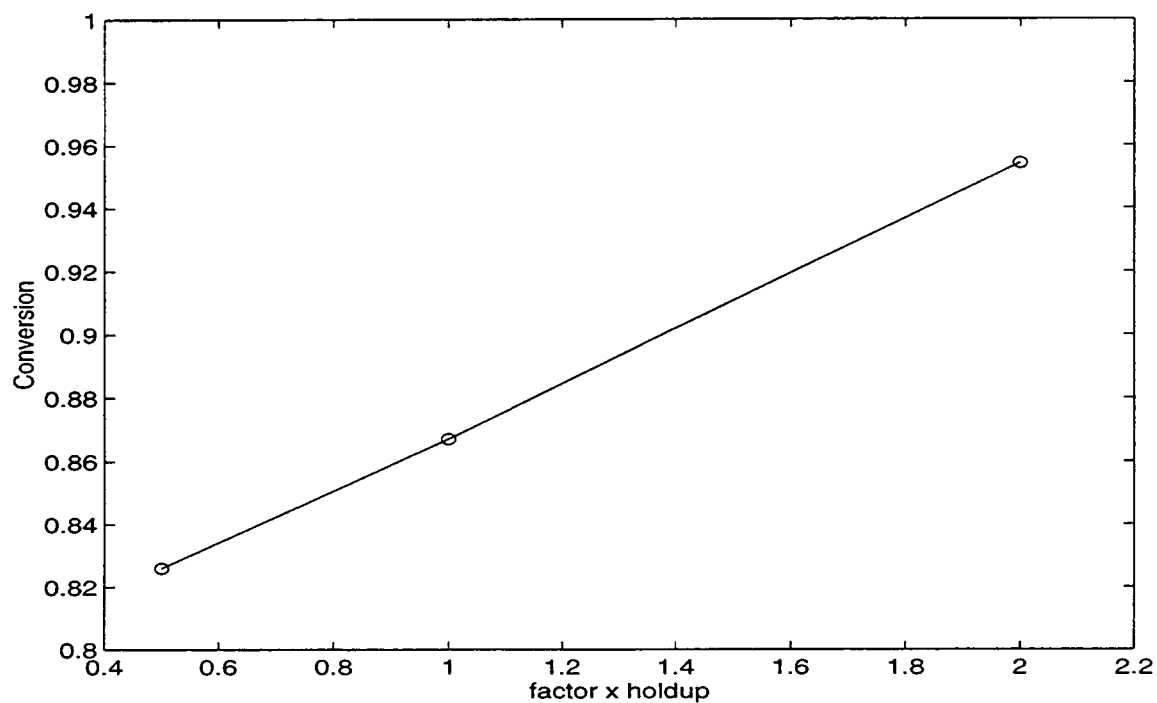


Figure 5.3.1 The predicted effect of liquid hold-up on conversion for Run 6.
Acid flow= 4.116×10^{-3} gmol/s, reflux ratio=2, methanol/acid ratio=1.2.

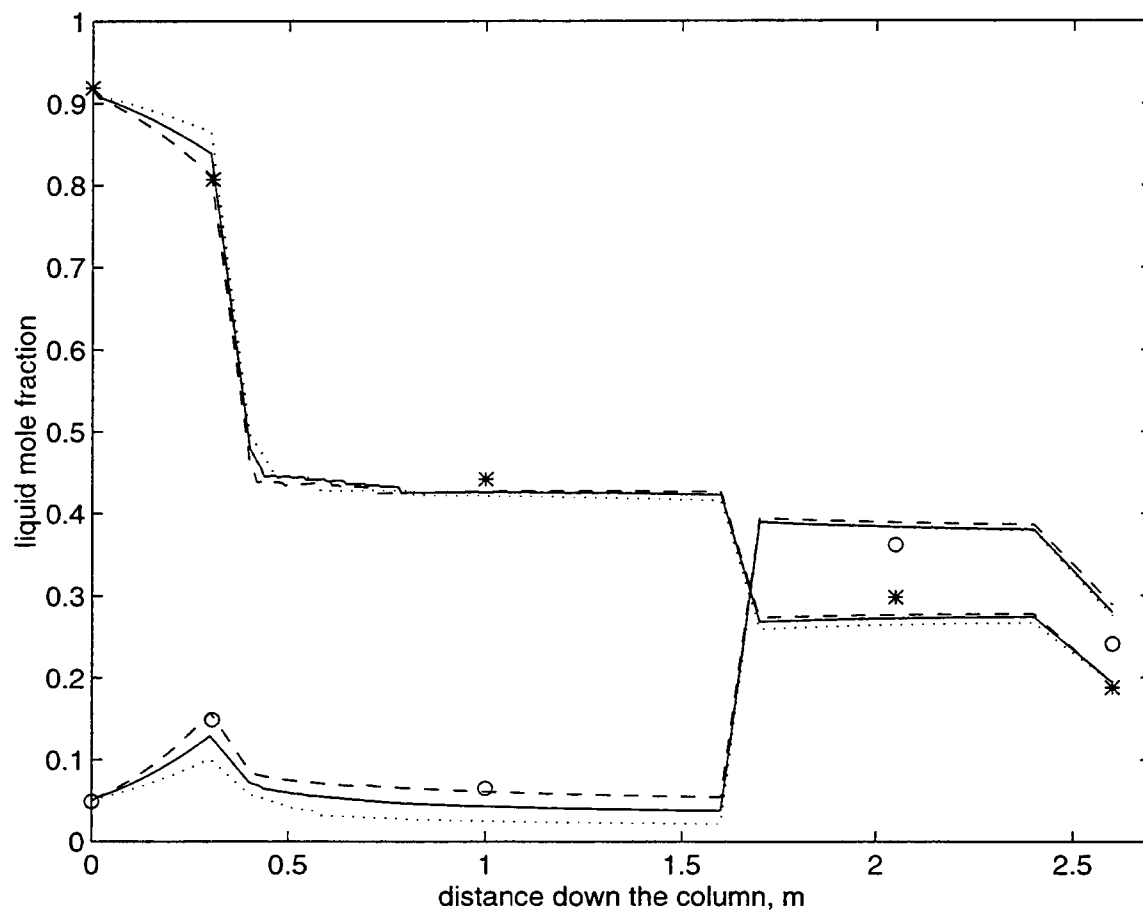


Figure 5.3.2 The effect of the correction of the mass transfer coefficients on the concentration profiles of methanol and ester for Run 6.

Acid flow= 4.116×10^{-3} gmol/s, reflux ratio=2, methanol/acid ratio=1.2.

"- - - -" +25% , '.....' -25%

of methanol. For the ester, the profile showed a little improvement than the original concentration profile. When decreasing the value of mass transfer coefficients by 25% , the concentration profile of methanol showed a very large error with experimental values especially for methanol at a distance of 1 meter as shown in Figure 5.3.2. The study reveals that the accuracy of the mass transfer coefficients model is crucial in giving an actual representation of the behavior of the packed column and the necessity to develop new correlational mass transfer models that give better results.

5.3.3 The Effect of the Γ Matrix

The exact solution to the GMS equation introduced by Krishna and Standart(1976) allows for the nonideality of the liquid phase through the introduction of the matrix Γ (Equation 2.4.4) . For an ideal liquid phase, the matrix Γ equals the identity matrix. The calculation was performed using the actual value of the matrix Γ calculated from the Wilson method for activity coefficients, and then the calculation was repeated considering the matrix equals the identity matrix.

Figure 5.3.3 shows a little larger error between the experimental values and the theoretical predictions when the Γ matrix is taken as the identity matrix. Table 5.3.1 shows the percent errors between theoretical and experimental values of the mole fraction with the Γ simplification. The simplification in the Γ matrix did not produce a large error in the model predictions but reduced the calculation time by 18%. The results reveals that the non-ideality of the system does not have much effect on the mass transfer model since

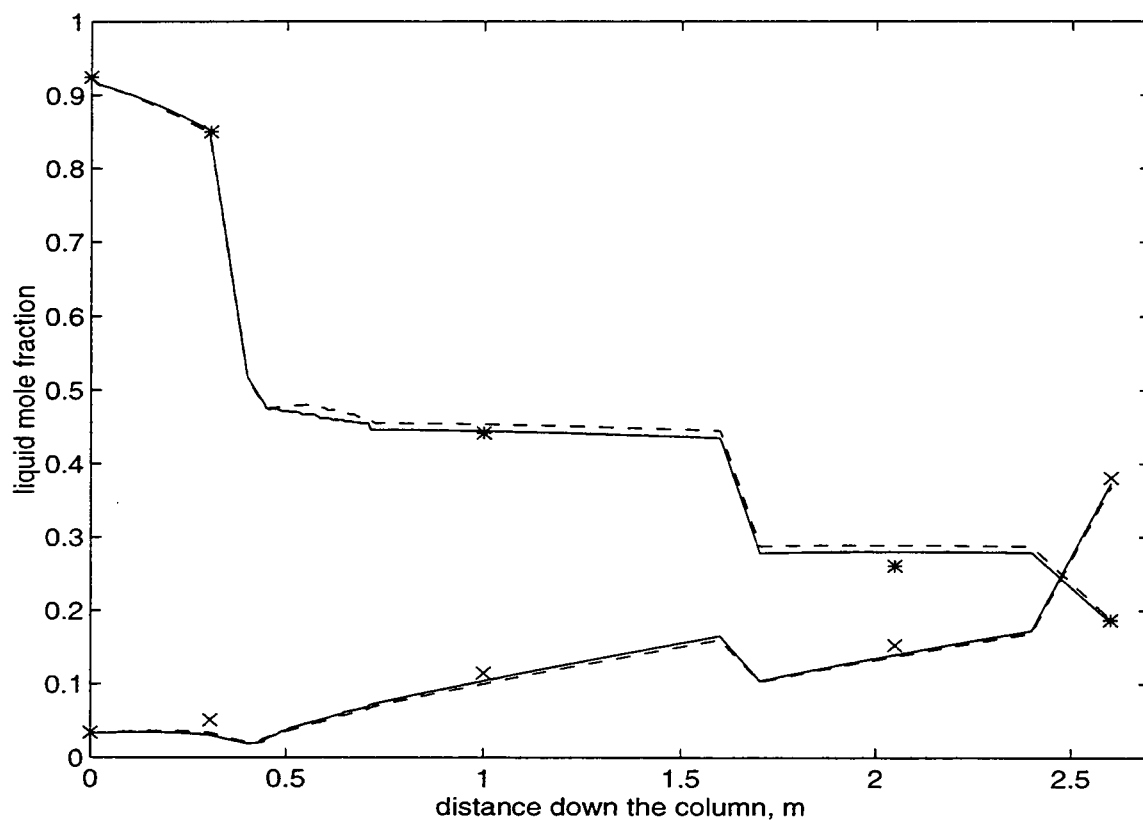


Figure 5.3.3 The effect of the correction factor matrix Γ on the mole fraction profile of methyl acetate '*', and water 'x' for Run 2.

Acid flow= 2.058×10^{-3} gmol/s, reflux ratio=2, methanol/acid ratio=1.2.

'-' with the Γ matrix, '--' without the Γ matrix

the effect of the nonideality of the system contributes more to the value of the vapor-liquid equilibrium constant.

When examining the value of the matrix Γ at different heights in the column from the model, the diagonal values of the matrix were very close to unity, while the non-diagonal values were close to zero, and thus were expected to have a little effect on the concentration profile.

Table 5.3.1 The percent error in the model predictions with the simplification of the Γ matrix

Height, m	Experimental mole fraction		The percent error in the model with Γ calculated		The percent error in the model with $\Gamma = I$	
	ester	water	Ester	water	ester	water
1	.4419	.1147	.56	-7.6	4.5	-12.8
2.08	.261	.1529	7.3	-5.4	13	-6.9

5.3.4 The Effect of Finite Mass and Heat Transfer

In situation where the mass transfer rate is large, or when more than one component diffuses, the mass and heat transfer coefficients should be corrected to account for the finite mass and heat transfer. The correction factor matrix E was introduced in Equations 3.3.48 and 3.3.49 to account for the finite mass transfer, while the correction factor ϵ , was introduced in Equation 3.2.23 to account for the finite heat transfer.

The model was tested under the condition of low mass and heat fluxes ($E=I$, and $\epsilon=1$), and under high mass and heat fluxes (both E and ϵ are calculated from the corresponding equations in the model). It follows from Figure 5.3.4 that the concentration profile was largely effected by the correction factors especially in the case of the ester, and

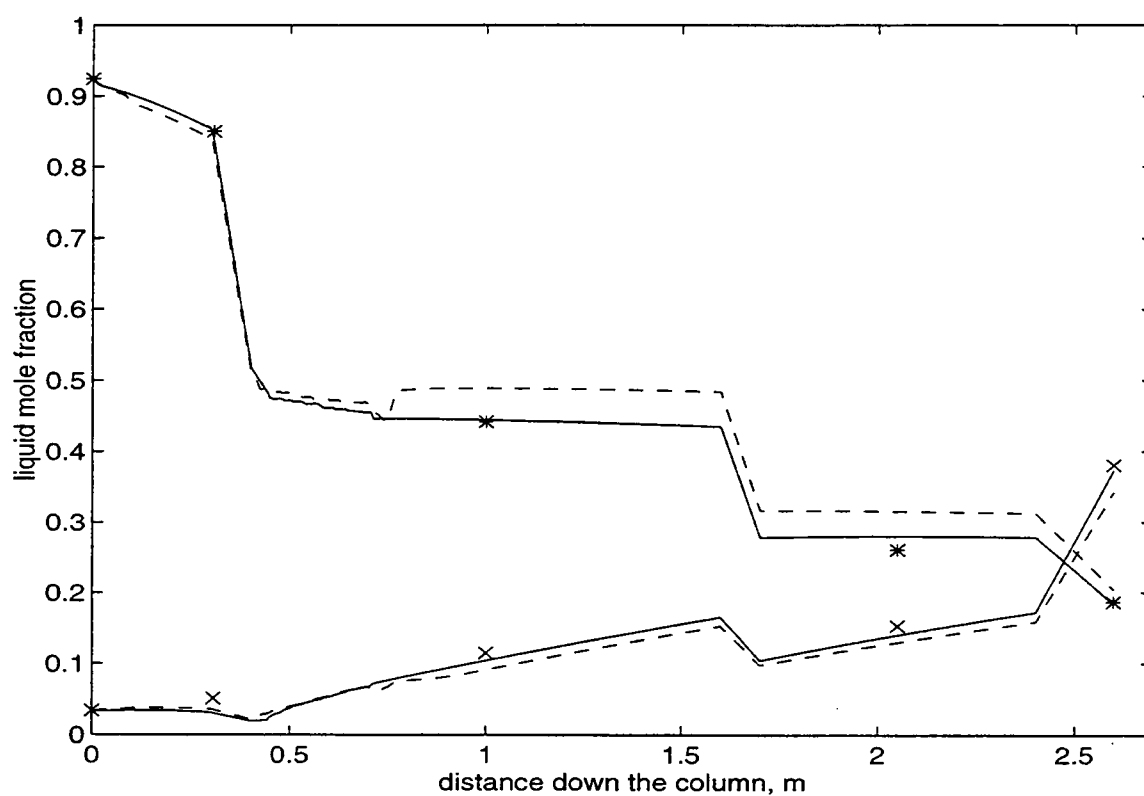


Figure 5.3.4 The effect of the finite mass and heat transfer correction factors on the mole fraction profile of methyl acetate '*', and water 'x'. for Run 2.

Acid flow= 2.058×10^{-3} gmol/s, reflux ratio=2, methanol/acid ratio=1.2

'-' with the correction, '--' without the correction

as shown in Table 5.3.2 the error in the ester concentration at height 2.08 meters rose from 7.3% to 22.6% when the correction factors were not considered in the calculation.

Even though the reduction in calculation time was 20%, the inclusion of the correction factors in the calculation seems to be important.

When examining the values of the correction factors in both phases at the heights presented in Table 5.3.2, we noticed that the values in the liquid phase are close to unity or the identity matrix, while they were less than that by about 10% in the vapor phase, which implies that the finite mass and heat transfer were more encountered in the vapor phase than in the liquid phase as shown in table 5.3.3.

Table 5.3.2 The percent error in the model predictions without the correction factors

Height, m	Experimental mole fraction		The percent error in the model with E and ε calculated		The percent error in the model with E = I, and $\varepsilon=1$	
	ester	water	Ester	water	ester	water
1	.4419	.1147	.56	7.6	10.9	-21.5
2.08	.261	.1529	7.3	-5.4	22.6	-9

Table 5.3.3 The correction factors for finite mass and heat transfer at a height of 2.08 m

Correction Factor	Liquid Phase			Vapor Phase		
Heat transfer, ε	.9963			.897		
Mass transfer, E	$\begin{bmatrix} .9852 & .0005 & .0005 \\ -.0005 & .9876 & -.0048 \\ .0083 & .0036 & .9752 \end{bmatrix}$			$\begin{bmatrix} .8543 & -.0123 & -.024 \\ -.014 & .8764 & -.0164 \\ -.0237 & -.014 & .8442 \end{bmatrix}$		

5.3.5 The influence of Cross Effects

The diffusion coefficient of a component in a multicomponent system is a function of the mole fractions of all the components in the mixture, which in turns makes the mass transfer coefficient and the component flux dependent on the mass transfer and the fluxes of other components present in the mixture, due to molecular interactions between molecules. Based on Equations (3.4.1) and (3.4.2) for the fluxes calculations, the component total flux is a function of the matrix $\vec{k}$, which contains the binary mass transfer coefficients of the component with all the components in the mixture, such that the total component flux is dependent on the diffusional interactions between the molecules in the mixture. In order to neglect the diffusional cross effects in the calculations, the matrix $\vec{k}$, becomes diagonal, and the individual component flux is a function of its own driving force.

Table 5.3.4 shows that the neglect of the cross effect produced a larger error in the concentration profile than when the cross effects were taken into account. However, as shown in Figure 5.3.5, the error is not that worse due to the little differences of the binary diffusion coefficients and thus the binary mass transfer, and also due to the small off-diagonal values of the matrix $\vec{k}$ (Table 5.3.5).

Table 5.3.4 The percent error in the model prediction without the cross effects

Height, m	Experimental mole fraction		The percent error in the model with cross effects		The percent error in the model without cross effects	
	ester	water	Ester	water	ester	water
1	.4419	.1147	.56	-7.6	4	-8.2
2.08	.261	.1529	7.3	-5.4	10	-6.1

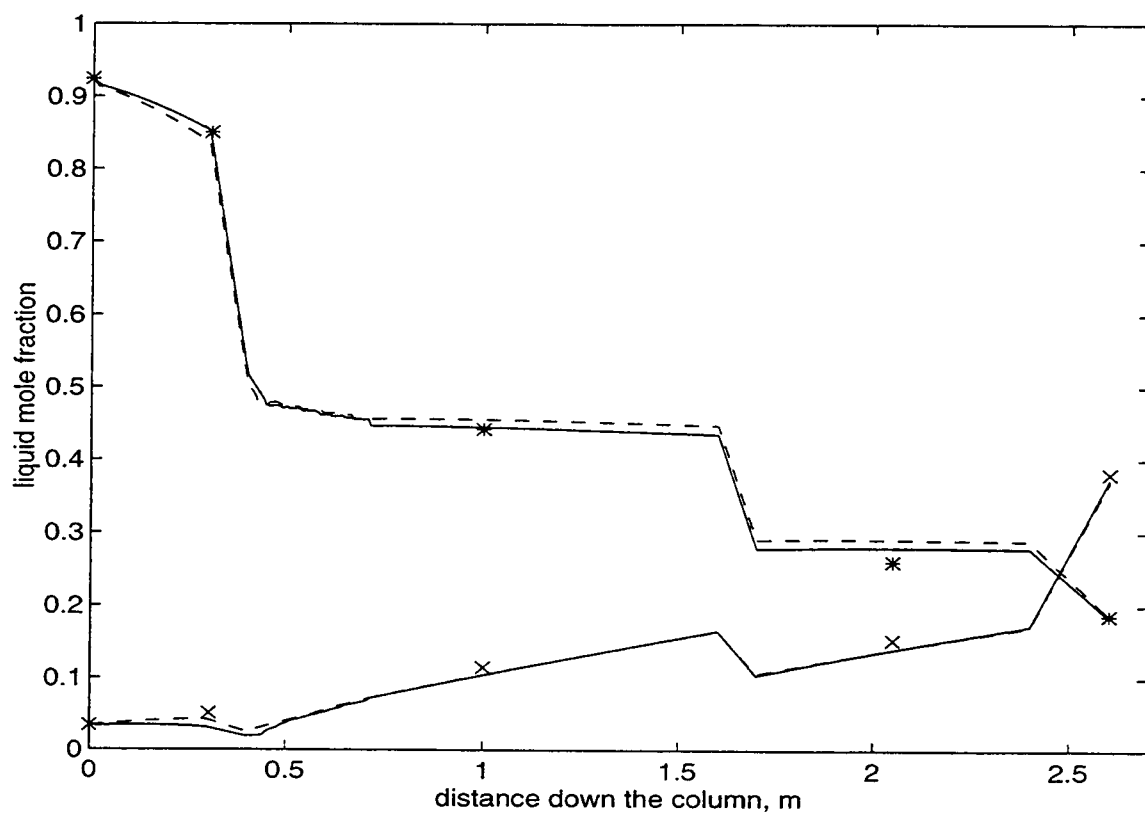


Figure 5.3.5 The influence of cross effects on the mole fraction profiles of methyl acetate '*', and water 'x'. for Run 2.

Acid flow= 2.058×10^{-3} gmol/s, reflux ratio=2, methanol/acid ratio=1.2

'——' with cross effects, '-----' without cross effects.

Table 5.3.5 The values of mass transfer coefficients with cross effects

Height, m	$\dot{k}_L \times 10^5, \text{ m/s}$	$\dot{k}_V \times 10^3, \text{ m/s}$
1	$\begin{bmatrix} 3.666 & .061 & .44 \\ .04 & 3.321 & .155 \\ -.678 & -.234 & 2.064 \end{bmatrix}$	$\begin{bmatrix} 2.6 & -.09 & -.1 \\ .1 & 3.4 & .1 \\ 1.4 & .8 & 3.9 \end{bmatrix}$
2.08	$\begin{bmatrix} 3.65 & -.13 & -.148 \\ .355 & 3.867 & .944 \\ -.863 & .324 & 1.974 \end{bmatrix}$	$\begin{bmatrix} 2.2 & -.09 & -.1 \\ .1 & 2.9 & .1 \\ 1 & .6 & 3.1 \end{bmatrix}$

5.4 COMPARISON OF RESULTS WITH LITERATURE RESULTS

When comparing the results of this work with previous works in packed or plate column, one can see that the results are impressive and suggests that a scale up and improvement in the design of some of the column components could enhance the conversion of acetic acid and the distillate purity of methyl acetate. Table 5.4.1 shows the large difference between the results of the present work and that of Sawistowski et al (1979). Their results were poor mainly because of the improper feed positioning of methanol and acetic acid. For the 3 in diameter and 92 cm high column they used, the acetic acid feed was mounted at a 23 cm from the top while methanol was fed at a distance of 46 cm from the top, which left only a small portion of the column for the reaction zone. Most of the reaction is expected to take place in the middle section between the two feeds, and the reduction of this section height might have had a diverse effect on conversion. Furthermore, acetic acid works as an extractive agent which extract any

methanol vapor rising above the acid feed and thus minimizing the concentration of methanol in the distillate product.

The results of Sawistowski et al (1977) showed a distillate composition of methyl acetate close to the minimum azeotropic mixture (35 mole% methanol) which suggests that the extraction process did not take place possibly because of the high flow of methanol vapor and low conversion. In the present work, the distillate purity was always close to or higher than 90 mole%.

Even though the comparison with the Eastman pilot plant is not valid here, we present the comparison to show that their results can be approached in a packed column if the modifications applied to the plate column were applied to a larger scale packed column. In their design, Eastman company used 45.4 kg/hr methyl acetate production capacity column with 8 in diameter in the stripping and reacting zone and 6 in diameter in the extraction and rectification zone with a height of 30.5 m. The reaction zone has a high

Table 5.4.1 Comparison of the present results with previous works at a reflux ratio of 2.

Subject	Present work (1.5 in- 2.14 m long) Packed with .25 in intallox saddle	Sawistowski et al (3 in - 0.92 m long) Packed with .25 in rasching rings	Eastman Pilot Plant (8 in- 30.5 m long) Plate column
Distillate Purity, mol%	95.1	70.8	98
Conversion %	95.9	87.3	99
Best combination of Distillate Purity, mol%	92.45	68.4	98
Conversion %	90.93	69.9	99

hold-up reverse flow bubble cap trays which provided the necessary high hold-up for the reaction to go to completion and to achieve maximum conversion of the acetic acid. In addition, a separate hold-up tank was used to increase the conversion in the reaction zone by feeding a portion of the reaction mixture from the reaction zone to the reaction tank which has a large hold-up. Moreover, two intermediate sidedraw systems consist of two distillation column was used to remove any impurities and recycle any methyl acetate and any unreacted acetic acid from the rectification zone to the reaction zone. The Eastman plant showed that proper positioning of the feed, high hold-up, and recycling of any unreacted acid to the reaction zone are necessary to boost the conversion. For packed columns, higher conversion than achieved by our work should be achieved by using high hold-up packings and the implementation of a recycling system similar to the Eastman company design.

6. SUMMARY AND CONCLUSIONS

6.1 SUMMARY

Reactive distillation in a packed column was studied both experimentally and theoretically. A 2.14 meters long and 1.5 inch diameter column was designed and filled with a ¼ inch intalox saddle packing. The esterification reaction of methanol and acetic acid was the system used in this study. While keeping the boil-up rate constant, several quantities were varied to study their effects on both the conversion and the distillate purity. In one set of experiments, the reflux ratio was varied from 1.5 to 2.5 at a constant acid feed rate of 2.06×10^{-3} gmol/s, and methanol/acid feed ratio of 1.2. In another set of experiments, the acid feed rate was varied from 1.03×10^{-3} to 4.12×10^{-3} gmol/s., while keeping the reflux ratio constant at 2, and the methanol/acid feed ratio constant at 1.2. In the last set of experiments, the methanol/acid feed ratio was varied from 1 to 1.2, while keeping the reflux ratio constant at 2, and the acid flow rate constant at 2.06×10^{-3} .

A mathematical model representing the multicomponet reactive system in a packed column was developed. The resulting system of differential equations was solved using a Runge-Kutta method and programmed using Matlab software on a Unix workstation. The model calculates the concentration and temperature profiles in both phases. In addition, the interfacial mass fluxes, liquid and vapor mole fractions are calculated using the Newton method to solve the system of non-linear equations representing the mass and heat transfer between the two phases.

Comparisons between the experimental and theoretical results were made. In addition, the effect of liquid hold-up on conversion and the effect of the mass transfer coefficients on the agreement between theoretical and experimental results was studied theoretically. Several simplifications were made to the model in order to save some calculational time, and the effect of these simplifications on the concentration profile was studied.

6.2 CONCLUSIONS

Several conclusions can be made about both the experimental and theoretical results. In addition, the comparison of the results with previous works in the literature showed the significance of the results of this work. The experimental results in each series of runs were achieved while maintaining a constant boil-up rate. The conclusions are:

1. Experimental runs under variable reflux ratios showed that at higher reflux ratios higher distillate purity can be achieved while the conversion of the limiting reactant decreases. At a reflux ratio of 2.5 the ester purity achieved was 95.1% , while the conversion was 79.4%. On the other hand, at a reflux ratio of 1.5 ester purity in the distillate was 87% while the conversion increased to 95.9%.
2. Experimental runs under variable methanol/acid feed ratio showed that the increase in methanol to acid ratio from 1 to 1.2 increased the conversion from 82% to 91%, while the distillate purity decreased slightly, from 94.5% to 92.5%.
3. Experimental runs under variable feed rates showed that at a low acetic acid feed rate of 1.03×10^{-3} gmol/s., the conversion achieved was 92%, and that the conversion decreased to 86.8 % when the feed was increased by a factor of 4. For the same flow

rates, a little change was noticed on the distillate purity. The flow rates are governed by the boundary of flooding at high flow rates, and the boundary of little reaction occurring at low flow rates.

4. Comparing to the experimental work of Sawistowski and Pilavakis (1979), a better result in terms of distillate purity and conversion was achieved in this work. This is mainly attributed to the better design of the distillation column, the use of a longer column, the proper positioning of the feeds, and use of a precise and effective reflux head helped increase the distillate purity and the conversion.
5. The mathematical model predictions agreed with the experimental results with an average error of 10% . The minimum error was 0.5% in Run 2 and the maximum error was 23% in Run 5. The discrepancy between experimental and theoretical results is due to the experimental difficulties and the inaccuracy of the physical properties and column characteristics correlations, particularly the hold-up and mass transfer correlations.
6. The model developed here exhibited little mathematical difficulties and gave a reasonable convergence time, since the need to calculate the Jaccobian matrix was limited to the flux calculations routine. This is the major time consuming calculation that the non-equilibrium model suffered from.
7. Experimental results and theoretical predictions showed that for the corrosive system studied here, packed columns might be more suitable for reactive distillation than plate columns if high hold-up packings are used to increase the conversion. The amount of hold-up in the column using the intallox saddles packings did not exceed 10% of the packed volume at any height. A postulated theoretical increase in the liquid hold-up showed a sharp increase in overall conversion, and thus showed the necessity to use higher hold-up packings.
8. The study showed the agreement between experimental and theoretical results can be improved if the mass transfer coefficients were multiplied by a factor of 1.25. This shows the need to improve mass transfer coefficient correlations.
9. Theoretical predictions showed about 4% increase in the percentage error with experimental results when the correction factor for the non-ideallity of the system was

ignored in the Generalized Maxwell-Stefan (GMS) solution for mass transfer in multicomponent systems. On the other hand, computational time decreased by 18%.

10. Theoretical predictions showed a 14% increase in the percentage error with experimental results when the correction factors for finite mass and heat transfer rates was ignored in the calculation. On the other hand, the computational time decreased by 20%.

11. Theoretical predictions showed a 3% increase in the percentage error with experimental results when the diffusional cross effects were ignored in the calculations. This simplification reduced the computational time by 9%.

12. Very few experimental works have been reported in the literature to validate several methods used to describe multicomponent mass transfer. The study here indirectly verified experimentally the exact solution to the Maxwell-Stefan equation for the mass transfer in a multicomponent system.

7. RECOMMENDATIONS

1. The model developed here was used to study the esterification reaction of methanol and acetic acid. After showing good agreement between the model predictions and experimental results, other esterification reactions, which are equilibrium limited reactions, such as the production of ethyl acetate and propyl acetate, can be studied theoretically in the same manner.
2. The model can also be used to study other reactions such as closely boiling point mixtures which are difficult to separate even with extractive or azeotropic distillation.
3. The experimental results could be enhanced by using high hold-up packings to increase the conversion. The scale up of the results here, should not be generalized without further study on larger sizes of columns and packings.
4. The mathematical model describing the system could be solved using a different numerical method other than the Runge-Kutta method used here. A comparison of the results could give a better understanding of the best method in terms of mathematical difficulties and calculational time.
5. There is a need to develop new models for mass transfer in packed columns that covers a wide range of packings, since existing models are applicable for few types of packings.
6. Due to the nature of the temperature profile in the column, new strategies may be required for the control of the column for a specified steady state. The development of such strategies should be considered.

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APPENDICES

Appendix A

Newton's Method
For the solution of systems of nonlinear equations

Newton's Method

The equation to be solved is in the form

$$(F((x))) = (0) \quad (A.1)$$

where (F) is a vector consisting of all the equations to be solved and (x) is the vector of variables. A Taylor series expansion of the function vector around the point (x_o) at which the functions are evaluated gives

$$(F((x))) = (F((x_o))) + [J]((x) - (x_o)) + O(|(x) - (x_o)|^2) \quad (A.2)$$

where $[J]$ is the Jaccobian matrix of partial derivatives of (F) with respect to (x) .

$$J_{ij} = \partial F_i / \partial x_j \quad (A.3)$$

If (x) is the is the actual solution to the system of equations, then $(F((x))) = (0)$. And if $O(|(x) - (x_o)|^2)$ term is neglected then equation A.2 can be rearranged to give

$$[J]((x) - (x_o)) = -(F((x_o))) \quad (A.4)$$

And the only unknown is (x) , and can be calculated by solving the linear system of equation A.4.

Algorithm To solve equation A.4

- 1- Set iteration counter to zero. Estimate $(x)_o$.
- 2- Compute $(F(x))_k$ and $[J]$.
- 3- Solve Equation A.4 for $(x)_{k+1}$.
- 4- Check for convergence; if not achieved, increment k and return to step 2.

Appendix B

Estimation of the Thermodynamic Factor

Wilson Model For Multicomponent Systems

Dimensionless Gibbs excess energy

$$S_i = \sum_{j=1}^n x_j \Lambda_{ij} \quad (\text{B.1})$$

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp\left(-\frac{A_{ij}}{RT}\right) \quad (\text{B.2})$$

Unconstrained first composition derivatives

$$Q_i = -\ln(S_i) - \sum_{k=1}^n \frac{x_k \Lambda_{ki}}{S_k} \quad (\text{B.3})$$

Unconstrained second composition derivatives

$$Q_{ij} = -\frac{\Lambda_{ij}}{S_i} - \frac{\Lambda_{ji}}{S_j} + \sum_{k=1}^n \frac{x_k \Lambda_{ki} \Lambda_{kj}}{S_k^2} \quad (\text{B.4})$$

Activity coefficients

$$\ln \gamma_i = 1 + Q_i \quad (\text{B.5})$$

Thermodynamic factor

$$\Gamma_{ij} = \delta_{ij} + x_i (Q_{ij} - Q_{in}) \quad (\text{B.6})$$

Appendix C.
Computer Program

```

% Program recdstl.m
% Program for the initial conditions and input data

clear
global xmw Tc nc Pc cat OUT
global Ln Vn B xn yn Xcat Tln Vol Tgn
xmw=[60;32.04;74.08;18];
Tc=[592.7;512.6;506.8;647.3];
Pc=[57.15;79.86;46.3;218.6];
nc=4;

% Given: Feed flow rate, composition, and temperature for the acetic acid and
%          methanol feed

Acfed=2.058e-3;      % gmol/sec
xA=[1;0;0;0];

Mefed=1*Acfed;      % gmol/sec
xM=[0;1;0;0];

cat=1.26e-5;        % gmol/sec
tol=1e-4;

% Given: Distillate rate and assuming the reflux and composition

Dist=1.25e-3;      %g mol/sec
Reflux=2;
xd=[0;.031;.943;.026];

[Td,yd]=bbpoint(xd);

% Flow rates and composition of the streams below the reflux, mol/sec

xl=xd;
yv=xd;
L0=Reflux*Dist;
V0=L0+Dist;

% Call it u0

% the flow rate of the vapor to the condenser, gmol/sec
% the composition of the vapor to the condenser

u0(1)=L0;
u0(2)=V0;

for i=1:4
    u0(i+2)=xl(i);
end

% the flow rate of liquid from the condenser, gmol/sec
% and the composition

```

```

for i=1:4
u0(i+6)=yv(i);
end

```

% length of the first section (from top to the acid feed inlet), tf; m

```

t0=0;
tf=.3;

```

% Starting the integration using Runge-Kutta method

```

[t,u]=ode45('main1',t0,tf,u0,tol);
m=length(u);
t1=t;
u1=u;

```

% Results of the first packing section

```

OUT1=OUT

```

% Introducing the acid feed, Acfed, mol/sec

```

L1=OUT1(2)+Acfed
V1=OUT1(3)

```

% Calculating the composition of the next increment

```

for i=1:4
y1(i)=OUT1(i+7);
x1(i)=(Acfed*xfA(i)+OUT1(2)*OUT1(i+3))/L1;
end

```

% The flow rates and the temperature of the liquid and the vapor below the feed

```

u0(1)=L1;
u0(2)=V1;

```

```

for i=1:4
u0(i+2)=x1(i);
u0(i+6)=y1(i);
end

```

```

[Tl1,y11]=bbpoint(x1);
[Tv1,ze]=dewpoint(y1);

```

% The length of packing between the acid and the methanol feed, tf=1.22 m

```

t0=.4;
tf=1.6;

```

% Start the integration up to the methanol feed

```

[t,u]=ode45('main1',t0,tf,u0,tol);
t2=t;
u2=u;

% Results from the second packing section

OUT2=OUT

% Introducing the methanol feed, Mefed, mol/sec

L2=OUT2(2)+Mefed
V2=OUT2(3)

% Calculating the composition of the next increment

for i=1:4
y2(i)=OUT2(i+7);
x2(i)=(Mefed*xfM(i)+OUT2(2)*OUT2(i+3))/L2;
end

% The flow rates and the temperature of the liquid and the vapor below the feed

u0(1)=L2;
u0(2)=V2;

for i=1:4
u0(i+2)=x2(i);
u0(i+6)=y2(i);
end

Tl2,y22]=bbpoint(x2);
[Tv2,ze]=dewpoint(y2);

% The length of packing between the methanol feed and the reboiler, tf=.61 m

t0=1.7;
tf=2.4;

% Start the integration up to the reboiler

[t,u]=ode45('main1',t0,tf,u0,tol);
m=length(u);
t3=t;
u3=u;

% Results from the second packing section

OUT3=OUT

t=[t1;t2];
t=[t;t3];

```

```

u=[u1;u2];
u=[u;u3];

% Calculate the Bottom flow rate and composition

Ln=OUT(2);
Vn=OUT(3);
B=OUT(2)-OUT(3);

    for i=1:4
        xn(i)=OUT(i+3);
        yn(i)=OUT(i+7);
    end

Tgn=OUT(13);
Tln=OUT(12);
Vol=.000285;          % m3
Xcat=cat/B;

z0=[.2 .1 .1 .3];
z=least('fun',z0)
t=[t;2.6];

zz=[Ln Vn z yn];
u=[u;zz];

m=length(u);
for j=1:m
    for i=3:6
        if u(j,i)<=0
            u(j,i)=.0001;
        else
            u(j,i)=u(j,i);
        end
    end
end

for j=1:m
    ut(j)=u(j,3)+u(j,4)+u(j,5)+u(j,6);
end

for j=1:m
    for i=3:6
        u(j,i)=u(j,i)/ut(j);
    end
end

% Experimental results

tt=[0;.305;1;2.05;2.6];

```

```

ac=[0;.005;.42;.219;.275];
me=[.049;.149;.065;.362;.241];
es=[.919;.807;.442;.298;.188];
wr=[.032;.039;.073;.121;.296];

figure(1)
plot (t,u(:,3),'y-',t,u(:,4),'m:',t,u(:,5),'c-',t,u(:,6),'g--');hold on
axis([0 2.7 0 1]);
xlabel('distance down the column, m'); ylabel('liquid mole fraction');
plot(tt,ac,'w+',tt,me,'wo',tt,es,'w*',tt,wr,'wx');hold on
legend('acid '+' ','methanol o','ester *','water x');

```

% To check the value of yn by equilibrium calculation

```

convtn=(xd(3)*Dist+z(3)*B)/Acfed
[TB,yz]=bbpoint(z);
yz;

```

```

sum=0;
for i=1:4
diff(i)=(yn(i)-yz(i))^2;
sum=sum+diff(i);
end
sum

```

```

for j=1:m
xx(1)=u(j,3);
xx(2)=u(j,4);
xx(3)=u(j,5);
xx(4)=u(j,6);
[Tbb,ybb]=bbpoint(xx);
S(j,1)=Tbb;
end
S;
for j=1:m
ot(1,j)=t(j);
ot1(1,j)=u(j,3);
ot2(1,j)=u(j,4);
ot3(1,j)=u(j,5);
ot4(1,j)=u(j,6);
ot5(1,j)=S(j,1);
end
Lp=[ot;ot1;ot2;ot3;ot4;ot5];

```

% Printing the results

```

fid=fopen('Rn5.outp','w');
fprintf(fid,' Output for Run no.5\n');
fprintf(fid,' \n');
fprintf(fid,' Acid feed rate = ');
fprintf(fid,'%4.3e',Acfed);
fprintf(fid,' gmol/s\n');

```

```

fprintf(fid,' methanol feed rate = ');
fprintf(fid,'%4.3e',Mefed);
fprintf(fid,' gmol/s\n');
fprintf(fid,' Catalyst feed rate= ');
fprintf(fid,'%4.3e',cat);
fprintf(fid,' gmol/s\n');
fprintf(fid,' Reflux ratio = ');
fprintf(fid,'%3.2f',Reflux);
fprintf(fid,' \n');
fprintf(fid,' \n');
fprintf(fid,' Distillate rate = ');
fprintf(fid,'%4.3e',Dist);
fprintf(fid,' gmol/s\n');
fprintf(fid,' Conversion = ');
fprintf(fid,'%4.3f',convtn);
fprintf(fid,' \n');
fprintf(fid,' \n');
fprintf(fid,'      Mole fraction and Temperature profile\n');
fprintf(fid,'      ~~~~~~\n');
fprintf(fid,' Z,m   Xac   Xm    Xes   Xw    Tl,C\n');
fprintf(fid,' %6.3f %6.4f %6.4f %6.4f %6.4f %5.2f\n',Lp);
fclose(fid);

```

```
% Program main.m
% Program to calculate the flow rates and the temperature of the
% liquid and the vapor streams through the columns
```

```
function [out1,out2]=main1(t,u)
global xmw Tc nc Pc cat OUT
```

```
xmw=[60;32.04;74.08;18];
Tc=[594.4;512.6;506.8;647.3];
Pc=[57.15;79.86;46.3;218.6];
R=1.987;
P=1;
```

```
area=.00114; %m2
```

```
% >>>>>>>>> Flow rates, and mole fractions
```

```
for i=1:10
if u(i)<=0
u(i)=0.001;
else
u(i)=u(i);
end
end
```

```
for i=1:4
x(I)=u(I+2);
y(i)=u(i+6);
end
```

```
sumx=0;
sumy=0;
for i=1:4
sumx=sumx+x(i);
sumy=sumy+y(i);
end
```

```
for i=1:4
x(i)=x(i)/sumx;
y(i)=y(i)/sumy;
end
```

```
Lf=u(1); %g mol/sec
Gf=u(2);
```

```
L=Lf/area;
G=Gf/area; % gmol/m2.sec
xcat=cat/(Lf+cat);
```

```
% >>>>>>>>> Bubble point, C
```

```
[Tl,ytl]=bbpoint(x);
```



```

    RN(i)=DM(i)/Nt;
end

% average mole fraction

for i=1:4
    Xav(i)=(x(i)+DM(i+8))/2;
    Yav(i)=(y(i)+DM(i+4))/2;
end

% ----- Correction for non-ideal liquid

Tii=DM(13)-273;
[kv,ML]=kval(Tii,Xav);

% ----- Calculate the diffusivity (m2/sec)

[Dc,diff]=dfusvty(Tii,Tii,P,viscl,xmul,Xav,Yav,dens);

% ----- Calculate the heat of vaporization; joule/mole

[vap]=htvap(Ti);

% ----- Mass transfer coefficient, (m/sec)
% ----- Heat transfer coeff., (W/m2.k)
% ----- Interfacial area, (m2/m3)

[KL,KG,af,htg,htl]=mtrnsfr(viscg,viscl,densg,densl,MWL,MWG,G,L...
    ,dens,sigm,condcg,condcl,cplm,cpgm,Nt,Ct,Ti,N,cpl,cpg,Xav,Yav...
    ,Dc,diff,ML);

% >>>>>>>>>> Calculate interface Parameters (N,x,y,T)

[X]=flux(DM,KL,KG,htg,htl,Ti,Ti,Xav,Yav,vap,Ct);
DT=abs(X(13)-DM(13));
DM=X;
end
X;

% >>>>>>>>>> Total flux, mol/m2.sec

sumN=0;
for i=1:4
    sumN=sumN+X(i);
end

% >>>>>>>>>> Liquid Holdup; m3/m3

[holdup]=holdp(G,L,densg,densl,MWL,MWG,viscl,sigm);

% >>>>>>>>>> Constants in Reaction and Flux equations; m2

```



```

% Program Bbpoint.m
% Bubble point temperature

function [Tl,y]= bbpoint(xd)

aa=[8.021;8.08097;7.06524;8.07131];
bb=[1936.1;1582.271;1157.63;1730.63];
cc=[258.45;239.726;219.726;233.426];
v=[57.54;40.73;79.84;18.07];
cap=[0 -67.5078 269.7074 111.6579;-93.6183 0 776.5663 243.9483;
-208.93 9.1172 0 645.7225;705.5876 435.1416 1918.232 0];

Pt=760;
R=1.987;
nc=4;
Temp=100;
ft=1;

while abs(ft) > .001
    tempk=Temp+273;
    for i=1:nc
        for j=1:nc
            A(i,j)=(v(j)/v(i))*exp(-cap(i,j)/(R*tempk));
        end;
    end

    for k=1:nc
        Q1=0;
        for j=1:nc
            Q1=Q1+xd(j)*A(k,j);
        end
        Q2=0;
        for i=1:n
            Q3=0;
            for j=1:nc
                Q3=Q3+xd(j)*A(i,j);
            end
            Q2=Q2+(xd(i)*A(i,k))/Q3;
        end
        G(k)=exp(1-log(Q1)-Q2);
    end

    for i=1:nc
        ps(i)=exp(2.302*aa(i)-2.302*bb(i)/(Temp+cc(i)));
        dp(i)=2.302*bb(i)/((Temp+cc(i))^2);
        XK(i)=ps(i)*G(i)/Pt;
    end

    ft=0;
    ftt=0;

    for i=1:nc
        y(i)=XK(i)*xd(i);
    end

```

```
    ft=ft+y(i);  
    ftt=ftt+y(i)*dp(i);  
end
```

```
ft=ft-1;  
Temp=Temp-(ft/ftt);  
end
```

```
Tl=Temp;  
y=[y];
```

```
% Program Dewpoint.m
% Dew point temperature
```

```
function [Tg,x]= dewpoint(y)

aa=[8.021;8.08097;7.06524;8.07131];
bb=[1936.1;1582.271;1157.63;1730.63];
cc=[258.45;239.726;219.726;233.426];
v=[57.54;40.73;79.84;18.07];
cap=[0 -67.5078 269.7074 111.6579;-93.6183 0 776.5663 243.9483;
-208.93 9.1172 0 645.7225;705.5876 435.1416 1918.232 0];

Pt=760;
R=1.987;
nc=4;
Temp=40;
ft=1;

for i=1:n
    G(i)=1;
end

while abs(ft) > .001

    tempk=Temp+273;

    for i=1:nc
        ps(i)=exp(2.302*aa(i)-2.302*bb(i)/(Temp+cc(i)));
        dp(i)=2.302*bb(i)/((Temp+cc(i))^2);
        XK(i)=ps(i)/Pt;
    end

    Xt=0;
    for i=1:nc
        x(i)=y(i)/(XK(i)*G(i));
        Xt=Xt+x(i);
    end

    eps=.1;
    while abs(eps) > .0001

        for i=1:nc
            x(i)=x(i)/Xt;
        end

        for i=1:nc
            for j=1:nc
                A(i,j)=(v(j)/v(i))*exp(-cap(i,j)/(R*tempk));
            end
        end

        for k=1:nc
            Q1=0;
```

```

for j=1:nc
    Q1=Q1+x(j)*A(k,j);
end
Q2=0;
for i=1:nc
    Q3=0;
    for j=1:nc
        Q3=Q3+x(j)*A(i,j);
    end
    Q2=Q2+(x(i)*A(i,k))/Q3;
end
G(k)=exp(1-log(Q1)-Q2);
end

Xn=0;
for i=1:nc
    x(i)=y(i)/(XK(i)*G(i));
    Xn=Xn+x(i);
end

eps=Xn-Xt;
Xt=Xn;
end

for i=1:nc
    ps(i)=exp(2.302*aa(i)-2.302*bb(i)/(Temp+cc(i)));
    dp(i)=2.302*bb(i)/((Temp+cc(i))^2);
    XK(i)=ps(i)/Pt;
end

ft=0;
ftt=0;

for i=1:nc
    x(i)=y(i)/(XK(i)*G(i));
    ft=ft+x(i);
    ftt=ftt-y(i)*dp(i)/((G(i)*XK(i)));
end

ft=ft-1;
Temp=Temp-(ft/ftt);

end

Tg=Temp;

```

```
% Program spheat.m
% Program to calculate the specific heat single and multicomponent system
```

```
function [cpg,cpl,cpgm,cplm]= spheat(Tg,Tl,x,y)
Tg=Tg+273;
Tl=Tl+273;
```

```
global xmw Tc
```

```
% cpg in J/mol.K then cpgm in J/kg.K from Coulson "chemical Eng."
% cpl in J/mol.K then cplm in J/kg.K from Ried & Prausnitz "the prop. of
% Gases & Liquids" using the method of Rowlinson-Bondi State method.
% Liquid heat capacity from the data in
```

```
nc=4;
R=8.314;
```

```
% Gas heat capacity constants
```

```
cpa=[4.84;21.15;16.55;32.243];
cpb=[25.485e-2;7.092e-2;22.454e-2;19.238e-4];
cpc=[-1.753e-4;2.587e-5;-4.342e-5;10.555e-6];
cpd=[49.488e-9;-2.852e-8;29.144e-9;-3.59e-9];
```

```
% Liquid heat capacity constants
```

```
A=[5.01e4;1.076e5;1.9157e5;2.7637e5];
B=[2.456e2;-3.806e2;-6.363e2;-2.0901e3];
C=[0;9.79e-1;1.575;8.125];
D=[0;0;0;-1.4116e-2];
E=[0;0;0;9.3701e-6];
```

```
cpgm=0;
cplm=0;
```

```
for i=1:nc
    cpg(i)=cpa(i)+cpb(i)*Tg+cpc(i)*Tg2+cpd(i)*Tg3;
    cpl(i)=A(i)+B(i)*Tl+C(i)*Tl2+D(i)*Tl3+E(i)*Tl4;
    cpl(i)=cpl(i)/1000;
end
```

```
for i=1:nc
    cpgm=cpgm+y(i)*1000*cpg(i)/xmw(i);
    cplm=cplm+x(i)*1000*cpl(i)/xmw(i);
end
```

```

% Program MWT.m
% Program to calculate the molecular weights of the liquid and vapor mixtures

function [MWL,MWG]=mwt(xcomp,ycomp)
global x

nc=4;
xl=0;
yl=0;
for i=1:nc
    sl=xcomp(i)*xmw(i);
    sg=ycomp(i)*xmw(i);
    xl=sl+xl;
    yl=sg+yl;
end
MWL=xl;
MWG=yl

```

```
% Prog dnsty.m
% Program to calculate the density of the gas and the liquid

% The density of gas is calculated using ideal gas law, kg/m3
% The density of the liquid mixture is calculated assuming additive volumes
% densl=kg/m3
```

```
function [densg,densl,dens,Mdens]=dnsty(Tg,Tl,P,MWG,MWL,L,x)
global xmw Tc Pc
```

```
nc=4;
Zra=[.2225;.2334;.2552;.2338];
R=82.056;
Tg=Tg+273;
Tl=Tl+273;
Area=.00114; % m2
A=[1.5791;2.308;1.121;5.459];
B=[.26954;.27192;.25855;.30542];
C=[592.71;512.58;506.8;647.13];
D=[.26843;.2331;.2745;.081];
```

```
% Gas Density
```

```
densg= 1e3*MWG*P/(R*Tg);
```

```
% Liquid Density
```

```
for i=1:nc
    if Tl > 333.15
        A(4)=4.9669;
        B(4)=.27788;
        C(4)=647.13;
        D(4)=.1874;
    end
    Mdens(i)=A(i)/(B(i)^(1+(1-(Tl/C(i)))^D(i)));
    dens(i)=Mdens(i)*xmw(i);
end
```

```
% Liquid mixture; method of additive volumes
```

```
ww=0;
wro=0;
L=L/1000; % kmol/m2.sec
for i=1:4
    w(i)=x(i)*L*MWL*Area;
    ww=ww+w(i);
    wro=wro+(w(i)/dens(i));
end

densl=ww/wro;
```

% Program vscsty.m

% Program to calculate the viscosity of both liquid and gas.

% Viscosity of the gas is calculated using the equation of Chung et al.. (see Properties of gases and %
liquids P.396)

% Gas viscosity in mP, then $\times 10^{-7} = \text{kg/m.s}$, $T=\text{K}$, $P=\text{atm}$

```
function [viscg,viscl,xmul,xmu]= vscsty(Tg,Tl,x,y)
global xmw Tc Pc
```

```
Tl=Tl+273;
```

```
Tg=Tg+273;
```

```
Vc=[171;118;228;57.1];
```

```
omega=[.447;.556;.326;.344];
```

```
k=[.0916;.215;.14;.076];
```

```
diplm=[1.3;1.7;1.7;1.8];
```

% Gas viscosity; mP

```
for i=1:4
```

```
    Mur(i)=131.3*diplm(i)/(Vc(i)*Tc(i))^-.5;
```

```
    Fc(i)=1-.2756*omega(i)+.059035*Mur(i)^4+k(i);
```

```
    Ts(i)=1.2593*Tg/Tc(i);
```

```
    Yv(i)=(1.16145*Ts(i)^(-.14874))+.52487*exp(-.7732*Ts(i))...
```

```
    +2.16178*exp(-2.43787*Ts(i));
```

```
    xmu(i)=40.785*Fc(i)*((xmw(i)*Tg)^.5)/(Yv(i)*Vc(i)^.667);
```

```
end
```

% Gas mixture viscosity; Kg/m.sec

% the method of Wilke (Ried. Prop. of gases and liquids; p.407)

```
up=0;
```

```
for i=1:4
```

```
    down=0;
```

```
    for j=1:4
```

```
        fy(i,j)=(1+((xmu(i)/xmu(j))^.5)*((xmw(i)/xmw(j))^.25))^2;
```

```
        fy(i,j)=fy(i,j)/((8*(1+(xmw(i)/xmw(j))))^.5);
```

```
        down=down+y(j)*fy(i,j);
```

```
    end
```

```
    up=up+y(i)*xmu(i)/down;
```

```
end
```

```
viscg=1e-7*up;
```

% Liquid viscosity is calculated using the equations in (Ried & Prausnitz the prop. of Gases and Liquids
% pp.441) $\text{visc}=\text{Kg/m.s}$

% For Acid;methanol;water;ester , $\text{xmul}=\text{cp}$, $T=\text{K}$

```
xmul(1)=exp(-4.519+(1.384e3/Tl));
```

```

xmul(2)=exp(-39.35+(4826/Tl)+(.1091*Tl)-(1.127e-4*Tl^2));
xmul(3)=exp(-4.2+(9.409e2/Tl));
xmul(4)=exp(-24.71+(4.209e3/Tl)+(4.527e-2*Tl)+(-3.376e-5*Tl^2));

```

% For liquid mixture, the following approximation is used Mixture viscosity, in Kg/m.s

```

viscl=0;
for i=1:4
    viscl=viscl+x(i)*xmul(i)^.334;
end
viscl=.001*viscl^3;

```

```
% Program sftnsn.m
% Program to calculate the surface tension of liquid mixture
% sigm= N/m
```

```
function [sigm]=sftnsn(Tl,x,dens,densl,MWL)
```

```
global xmw
```

```
a=[29.58;24;27.95;75.83];
b=[.0994;.0733;.1289;.1477];
```

```
sig=0;
for i=1:4
    sgm(i)=a(i)-b(i)*Tl;
    sig=sig+(x(i)*xmw(i)*sgm(i)^.25)/dens(i);
end
sigm=.001*(densl*sig/MWL)^4;
```

% Program cndctv.m

% Program to calculate the thermal conductivities of both gas and liquid

```
function [condcg,condcl]= cndctv (P,Tg,Tl,MWG,MWL,cpg,cpl,x,y,xmu)
global xmw Tc Pc
```

```
Tl=Tl+273;
```

```
Tg=Tg+273;
```

```
nc=4;
```

```
Zra=[.2225;.2334;.2552;.2338];
```

```
R=82.056;
```

% Constants for thermal cond. of gases

```
a=[1.691e-6;0;5.593e-4;0];
```

```
b=[1.6692;0;8.932e-1;0];
```

```
c=[6.58e2;0;1.966e3;0];
```

```
d=[-9.54e4;0;0;0];
```

% Thermal conductivity of gases was calculated using correlations presented

% by Ried "Properties of gases and liquids" =W/m.K

```
tcondg(1)=(a(1)*Tg^b(1))/(1+(c(1)/Tg)+(d(1)/Tg^2));
```

```
tcondg(2)=-7.797e-3+4.167e-5*Tg+1.214e-7*Tg^2-5.184e-11*Tg^3;
```

```
tcondg(3)=(a(3)*Tg^b(3))/(1+(c(3)/Tg)+(d(3)/Tg^2));
```

```
tcondg(4)=7.341e-3-1.013e-5*Tg+1.801e-7*Tg^2-9.1e-11*Tg^3;
```

% Liquid thermal conductivity is calculated with different methods, W/m.K

% Ref. " Prop. of gases and Liquids" p.546

% For Acetic acid, and the ester, the Sato method p.550

```
tbp(1)=390;
```

```
tbp(3)=329.7;
```

```
for i=1:2:3,
```

```
tr(i)=Tl/Tc(i);
```

```
Tbr(i)=tbp(i)/Tc(i);
```

```
up(i)=(1.11/(xmw(i)^.5))*(3+20*(1-tr(i))^.667);
```

```
down(i)=3+20*(1-Tbr(i))^.667;
```

```
tcondl(i)=up(i)/down(i);
```

```
end
```

% for water: table 10-5 p.546

```
tcondl(4)=-.3838+5.245e-3*Tl-6.369e-6*Tl^2;
```

% for methanol table (10-5) p.547

```
tcondl(2)=3.225e-1-4.785e-4*Tl+1.168e-7*Tl^2;
```

% Gas mixture

```

up=0;
for i=1:4
    down=0;
    for j=1:4
        fy(i,j)=(1+((xmu(i)/xmu(j))^.5)*((xmw(i)/xmw(j))^2.5))^2;
        fy(i,j)=fy(i,j)/((8*(1+(xmw(i)/xmw(j))))^.5);
        down=down+y(j)*fy(i,j);
    end
    up=up+y(i)*tcondg(i)/down;
end
condcg=up;

```

% Liquid mixture conductivity using Li-method P. 565
 % molar volume using the Racket techniques p.67; cm³/mol

```

vmix=0;
for i=1:nc
    tr(i)=Tl/Tc(i);
    vm(i)=(R*Tc(i)*Zra(i)^(1+(1-tr(i)).28571))/Pc(i);
    vmix=vmix+x(i)*vm(i);
end

for i=1:nc
    fy(i)=x(i)*vm(i)/vmix;
end

for i=1:nc
    for j=1:nc
        ww(i,j)=2*((1/tcondl(i))+(1/tcondl(j)))^(-1);
    end
end

cndm=0;
for i=1:nc
    for j=1:nc
        cndm=cndm+fy(i)*fy(j)*ww(i,j);
    end
end
condcl=cndm;

```

```
% Program kval.m
% Program to calculate k-values using the wilson equation for activity coefficient
```

```
function [kv,ML]= kval(Tx,xc)

Tx=Tx+273;
R=1.987;
nc=4;
pt=760;

aa=[8.021;8.08097;7.06524;8.07131];
bb=[1936.1;1582.271;1157.63;1730.63];
cc=[258.45;239.726;219.726;233.426];
v=[57.54;40.73;79.84;18.07];
cap=[0 -67.5078 269.7074 111.6579;-93.6183 0 776.5663 243.9483;
-208.93 9.1172 0 645.7225;705.5876 435.1416 1918.232 0];

for i=1:nc
    for j=1:nc
        A(i,j)=(v(j)/v(i))*exp(-cap(i,j)/(R*Tx));
    end
end

for i=1:nc
    Q1=0;
    for j=1:nc
        Q1=Q1+xc(j)*A(i,j);
    end
    S(i)=Q1;
end

for i=1:nc
    Q2=0;
    for j=1:nc
        Q2=Q2+xc(j)*A(j,i)/S(j);
    end
    Q(i)=-log(S(i))-Q2;
end

for i=1:nc
    for j=1:nc
        Q3=0;
        for k=1:nc
            Q3=Q3+xc(k)*A(k,i)*A(k,j)/S(k)^2;
        end
        QQ(i,j)=-(A(i,j)/S(i))-(A(j,i)/S(j))+Q3;
    end
end

for i=1:nc
    G(i)=exp(1+Q(i));
end
```

```

for i=1:nc-1
    for j=1:nc-1
        if i==j
            delt=1;
        else
            delt=0;
        end
        Ml(i,j)=delt+xc(i)*(QQ(i,j)-QQ(i,nc));
    end
end
ML=Ml;

for i=1:nc
    ps(i)=exp(2.302*aa(i)-2.302*bb(i)/(Tx+cc(i)-273));
    dp(i)=2.302*bb(i)/((Tx+cc(i)-273)^2);
    kv(i)=ps(i)*G(i)/pt;
    y(i)=kv(i)*xc(i);
end

```

```
% Program Dfusvty.m
% Diffusion coefficient of single and multicomponents in the liquid and vapor phase
```

```
% Diffusivity of the gas (Ref Mass Transfer, Hines & Maddox)
% Diff= m2/s. T=K, P=atm,
```

```
function [Dc,diff]=dfusvty(Tg,Tl,P,viscl,xmul,x,y,dens)
global xmw Tc Pc
```

```
Tl=Tl+273;
Tg=Tg+273;
nc=4;
v=[51.88;29.9;72.34;12.7]; % atomic volume
xmul=.001*xmul;
```

```
for i=1:nc
    for j=1:nc
        if j==i
            diff(i,j)=0;
        else
            xx= ((1/xmw(j))+(1/xmw(i)))^1.5;
            diff(i,j)=1e-7*Tg^1.75*xx;
            diff(i,j)=diff(i,j)/(P*(v(i)^.334+v(j)^.334)^2);
        end
    end
end
```

```
% Diffusivity of the liquid
```

```
% The method of Wilke-Chang for liquid mixture is used
% Ref: (the prop. of gases and liquids, pp.618)
% Dlm=m2/s , T=K, Vm=cm3/mol, viscl=cp
```

```
fy=[1;1.9;1.37;2.26];
Temp=Tl-273;
```

```
% Molar volume in cm3/mol
```

```
for i=1:nc
    Vm(i)=1000*xmw(i)/dens(i);
end

for i=1:nc
    for j=1:nc
        if i==j
            Dlb(i,j)=0;
        else
            Dlb(i,j)=7.4e-15*(fy(j)*xmw(j))^1.5*Tl/(xmul(j)*Vm(i)^.6);
        end
    end
end
```

% Diffusion coeff. in concentrated liquid mixtures
% the maxwell-stefan diffusivity is computed using the vignes equation

```
for i=1:nc
    for j=1:nc
        if i==j
            Dc(i,j)=0;
        else
            Dc(i,j)=(Dlb(i,j)^((1+x(j)-x(i))/2))*Dlb(j,i)^((1+x(i)-x(j))/2);
        end
    end
end
```

```
% Program htvap.m
% Program to calculate Heat of Vaporization; joule/mole
```

```
function[vap]=htvap(Tg)
global xmw Tc

Tg=Tg+273;

for i=1:4
    Tr(i)=Tg/Tc(i);
end

Tr1=390.9/Tc(1);
Tr2=337.6/Tc(2);
Tr4=373/Tc(4);
Tr3=329.9/Tc(3);

vap(1)=23697*((1-Tr(1))/(1-Tr1)).38;
vap(2)=35278*((1-Tr(2))/(1-Tr2)).38;
vap(4)=40683*((1-Tr(4))/(1-Tr4)).38;
vap(3)=30145*((1-Tr(3))/(1-Tr3)).38;
```

```

% Program mtrnsfr.m
% Program to calculate the mass and heat transfer coeff. using Onda's correlations

function [KL,KG,af,htg,htl]=mtrnsfr(viscg,viscl,densg,densl,MWL,MWG,G,L...
,dens,sgm,condcg,condcl,cplm,cpgm,Nt,Ct,Tg,N,cpl,cpg,x,y,Dc,diff,ML)
global xmw Tc nc

% Parameters for the 8 mm packing

ap=984; % m2/m3
sgmc=.061; % N/m
dp=.006; % m
g=9.81;
G=G/1000; %kmol/m2.s
L=L/1000; %kmol/m2.s
Tg=Tg+273;
Ct=Ct*1000; % mol/m3
Cv=1e6/(82.05*Tg);

% The vapor and the liquid velocities; m/s

VG=G*MWL/densg;
VL=L*MWG/densl;

% The liquid and the vapor Reynolds numbers are

Rev=densg*VG/(viscg*ap);
Rel=densl*VL/(viscl*ap);

% The liquid-phase Froude number

Fr=(ap*VL^2)/g;

% The liquid-phase Weber number

We=(densl*VL^2)/(ap*sgm);

% The interfacial area; m2/m3

af=ap*(1-exp(-1.45*((sgmc/sgm)^.75)*(Rel^.1)*(Fr^(-.05))*(We^.2)));

% The liquid-phase Reynolds number based on the interfacial area

Rela=densl*VL/(viscl*af);

% The low flux mass transfer coefficients are calculated from the Onda correlation m/sec
% Calculate the rate factor, fl, and fv

for i=1:nc
    for j=1:nc
        if j==i
            Scg(i,j)=0;

```

```

    Scl(i,j)=0;
    kl(i,j)=0;
    kg(i,j)=0;
    else
    Scg(i,j)=viscg/(densg*diff(i,j));
    Scl(i,j)=viscl/(densl*Dc(i,j));
    kl(i,j)=.0051*Rela^.667*(ap*dp)^.4*Scl(i,j)^(-.5)*(((g*viscl/densl)^(.333));
    kg(i,j)=2*Rev^.7*Scg(i,j)^.333*(ap*diff(i,j))*((ap*dp)^(-2));
    end
    end
end

for i=1:nc-1
    for j=1:nc-1
        if i==j
            kv(i,j)=0;
            kL(i,j)=0;
        else
            kv(i,j)=-y(i)*((1/kg(i,j))-(1/kg(i,nc)));
            kL(i,j)=-x(i)*((1/kl(i,j))-(1/kl(i,nc)));

            fv(i,j)=-N(i)*((1/(Cv*kg(i,j)))-(1/(Cv*kg(i,nc))));
            fl(i,j)=-N(i)*((1/(Ct*kl(i,j)))-(1/(Ct*kl(i,nc))));
        end
    end
end

kv(1,1)=(y(1)/kg(1,nc))+(y(2)/kg(1,2))+(y(3)/kg(1,3))+(y(4)/kg(1,4));
kv(2,2)=(y(2)/kg(2,nc))+(y(1)/kg(2,1))+(y(3)/kg(2,3))+(y(4)/kg(2,4));
kv(3,3)=(y(3)/kg(3,nc))+(y(1)/kg(3,1))+(y(2)/kg(3,2))+(y(4)/kg(3,4));

fv(1,1)=(N(1)/(Cv*kg(1,nc)))+(N(2)/(Cv*kg(1,2)))+(N(3)/(Cv*kg(1,3)))+(N(4)/(Cv*kg(1,4)));
fv(2,2)=(N(2)/(Cv*kg(2,nc)))+(N(1)/(Cv*kg(2,1)))+(N(3)/(Cv*kg(2,3)))+(N(4)/(Cv*kg(2,4)));
fv(3,3)=(N(3)/(Cv*kg(3,nc)))+(N(1)/(Cv*kg(3,1)))+(N(2)/(Cv*kg(3,2)))+(N(4)/(Cv*kg(3,4)));

fl(1,1)=(N(1)/(Ct*kl(1,nc)))+(N(2)/(Ct*kl(1,2)))+(N(3)/(Ct*kl(1,3)))+(N(4)/(Ct*kl(1,4)));
fl(2,2)=(N(2)/(Ct*kl(2,nc)))+(N(1)/(Ct*kl(2,1)))+(N(3)/(Ct*kl(2,3)))+(N(4)/(Ct*kl(2,4)));
fl(3,3)=(N(3)/(Ct*kl(3,nc)))+(N(1)/(Ct*kl(3,1)))+(N(2)/(Ct*kl(3,2)))+(N(4)/(Ct*kl(3,4)));

kL(1,1)=(x(1)/kl(1,nc))+(x(2)/kl(1,2))+(x(3)/kl(1,3))+(x(4)/kl(1,4));
kL(2,2)=(x(2)/kl(2,nc))+(x(1)/kl(2,1))+(x(3)/kl(2,3))+(x(4)/kl(2,4));
kL(3,3)=(x(3)/kl(3,nc))+(x(1)/kl(3,1))+(x(2)/kl(3,2))+(x(4)/kl(3,4));

```

% Calculate the matrix of correction factor

```

fl=inv(ML)*fl;
El=fl*inv((exp(fl)-eye));
Ev=fv*inv(exp(fv)-eye);

```

% The matrix of high flux mass transfer coeff.; m/sec

```

KG=inv(kv)*Ev;

```

```

KL=inv(kL)*ML*EI;

% Calculating the heat transfer coeff. using the analogy of mass and heat with the
% Onda correlation, W/m2.k

% Prandtl Number

Prl=cplm*viscl/condcl;
Prg=cpgm*viscg/condcg;

htg=2*condcg*ap*Rev^.7*Prg^.333*((ap*dp)^(-2));
htl=.0051*cplm*densl*Rela^.667*Prl^(-.5)*((ap*dp)^.4)/(((densl/(viscl*g)))^.333);

% Heat transfer rate factor

Hv=0;
Hl=0;
for i=1:4
    Hv=Hv+N(i)*cpg(i);
    Hl=Hl+N(i)*cpl(i);
end
Hv=Hv/htg;
Hl=Hl/htl;

% High flux heat transfer coefficients

EEv=Hv/(exp(Hv)-1);
EEl=Hl/(exp(Hl)-1);
htg=htg*EEv;
htl=htl*EEl;

```

```

% Program flux.m
% Program to calculate the flux

% DM is the vector of the unknown variables

function [X]= flux(DM,KL,KG,htg,htl,Tg,Tl,x,y,vap,Ct)

% constants used in the equations

Ct=Ct*1000; % mol/m3
Cv=1e6/(82.05*Tg); % mol/m3
pt=760;
nc=4;
R=1.987;

aa=[8.021;8.08097;7.06524;8.07131];
bb=[1936.1;1582.271;1157.63;1730.63];
cc=[258.45;239.726;219.726;233.426];
v=[57.54;40.73;79.84;18.07];
cap=[0 -67.5078 269.7074 111.6579;-93.6183 0 776.5663 243.9483;
-208.93 9.1172 0 645.7225;705.5876 435.1416 1918.232 0];

% calculation of the activity coeff. & K-values

xc(1)=DM(9);
xc(2)=DM(10);
xc(3)=DM(11);
xc(4)=DM(12);

for i=1:nc
    for j=1:nc
        A(i,j)=(v(j)/v(i))*exp(-cap(i,j)/(R*(DM(13))));
    end
end

for k=1:nc
    Q1=0;
    for j=1:nc
        Q1=Q1+xc(j)*A(k,j);
    end
    Q2=0;
    for i=1:nc
        Q3=0;
        for j=1:nc
            Q3=Q3+xc(j)*A(i,j);
        end
        Q2=Q2+(xc(i)*A(i,k))/Q3;
    end
    G(k)=exp(1-log(Q1)-Q2);
end

for i=1:nc

```

```

ps(i)=exp(2.303*aa(i)-2.303*bb(i)/(DM(13)+cc(i)-273));
dp(i)=2.303*bb(i)/((DM(13)+cc(i)-273)^2);
XK(i)=ps(i)*G(i)/pt;
end

```

% derivatives with respect to x & T

```

for i=1:nc
    Q4=0;
    for j=1:nc
        Q4=Q4+xc(j)*A(i,j);
    end
    S(i)=Q4;
end

for i=1:nc
    for j=1:nc
        Q5=0;
        for k=1:nc
            Q5=Q5+xc(k)*A(k,i)*A(k,j)/(S(k)^2);
        end
        Q(i,j)=-(A(i,j)/S(i))-(A(j,i)/S(j))+Q5;
        dGX(i,j)=1+Q(i,j);
    end
end

```

% Constructing the diffusion flux vectors

```

DY=[y(1)-DM(5);y(2)-DM(6);y(3)-DM(7)];
DX=[DM(9)-x(1);DM(10)-x(2);DM(11)-x(3)];

Jl=Ct*KL*DX;
Jv=Cv*KG*DY;

```

% constructing the matrix F (independent equations)

```

F(1)=Jv(1)+y(1)*(DM(1)+DM(2)+DM(3)+DM(4))-DM(1);
F(2)=Jv(2)+y(2)*(DM(1)+DM(2)+DM(3)+DM(4))-DM(2);
F(3)=Jv(3)+y(3)*(DM(1)+DM(2)+DM(3)+DM(4))-DM(3);
F(4)=vap(1)*DM(1)+vap(2)*DM(2)+vap(3)*DM(3)...
+vap(4)*DM(4)+htg*(Tg-DM(13))-htl*(DM(13)-Tl);
F(5)=Jl(1)+x(1)*(DM(1)+DM(2)+DM(3)+DM(4))-DM(1);
F(6)=Jl(2)+x(2)*(DM(1)+DM(2)+DM(3)+DM(4))-DM(2);
F(7)=Jl(3)+x(3)*(DM(1)+DM(2)+DM(3)+DM(4))-DM(3);
F(8)=XK(1)*DM(9)-DM(5);
F(9)=XK(2)*DM(10)-DM(6);
F(10)=XK(3)*DM(11)-DM(7);
F(11)=XK(4)*DM(12)-DM(8);
F(12)=DM(5)+DM(6)+DM(7)+DM(8)-1;
F(13)=DM(9)+DM(10)+DM(11)+DM(12)-1;

F=F(:);

```

% constructing the jacobian matrix

```
J(1,1)=y(1)-1;
J(1,2)=y(1);
J(1,3)=y(1);
J(1,4)=y(1);
J(1,5)=-Cv*KG(1,1);
J(1,6)=-Cv*KG(1,2);
J(1,7)=-Cv*KG(1,3);
```

```
J(2,1)=y(2);
J(2,2)=y(2)-1;
J(2,3)=y(2);
J(2,4)=y(2);
J(2,5)=-Cv*KG(2,1);
J(2,6)=-Cv*KG(2,2);
J(2,7)=-Cv*KG(2,3);
```

```
J(3,1)=y(3);
J(3,2)=y(3);
J(3,3)=y(3)-1;
J(3,4)=y(3);
J(3,5)=-Cv*KG(3,1);
J(3,6)=-Cv*KG(3,2);
J(3,7)=-Cv*KG(3,3);
```

```
J(4,1)=vap(1);
J(4,2)=vap(2);
J(4,3)=vap(3);
J(4,4)=vap(4);
J(4,13)=-htg-htl;
```

```
J(5,1)=x(1)-1;
J(5,2)=x(1);
J(5,3)=x(1);
J(5,4)=x(1);
J(5,9)=Ct*KL(1,1);
J(5,10)=Ct*KL(1,2);
J(5,11)=Ct*KL(1,3);
```

```
J(6,1)=x(2);
J(6,2)=x(2)-1;
J(6,3)=x(2);
J(6,4)=x(2);
J(6,9)=Ct*KL(2,1);
J(6,10)=Ct*KL(2,2);
J(6,11)=Ct*KL(2,3);
```

```
J(7,1)=x(3);
J(7,2)=x(3);
J(7,3)=x(3)-1;
J(7,4)=x(3);
```

$J(7,9)=Ct*KL(3,1);$
 $J(7,10)=Ct*KL(3,2);$
 $J(7,11)=Ct*KL(3,3);$

$J(8,5)=-1;$
 $J(8,9)=DM(9)*XK(1)*dGX(1,1)+XK(1);$
 $J(8,10)=DM(9)*XK(1)*dGX(1,2);$
 $J(8,11)=DM(9)*XK(1)*dGX(1,3);$
 $J(8,12)=DM(9)*XK(1)*dGX(1,4);$
 $J(8,13)=DM(9)*XK(1)*dp(1);$

$J(9,6)=-1;$
 $J(9,9)=DM(10)*XK(2)*dGX(2,1);$
 $J(9,10)=DM(10)*XK(2)*dGX(2,2)+XK(2);$
 $J(9,11)=DM(10)*XK(2)*dGX(2,3);$
 $J(9,12)=DM(10)*XK(2)*dGX(2,4);$
 $J(9,13)=DM(10)*XK(2)*dp(2);$

$J(10,7)=-1;$
 $J(10,9)=DM(11)*XK(3)*dGX(3,1);$
 $J(10,10)=DM(11)*XK(3)*dGX(3,2);$
 $J(10,11)=DM(11)*XK(3)*dGX(3,3)+XK(3);$
 $J(10,12)=DM(11)*XK(3)*dGX(3,4);$
 $J(10,13)=DM(11)*XK(3)*dp(3);$

$J(11,8)=-1;$
 $J(11,9)=DM(12)*XK(4)*dGX(4,1);$
 $J(11,10)=DM(12)*XK(4)*dGX(4,2);$
 $J(11,11)=DM(12)*XK(4)*dGX(4,3);$
 $J(11,12)=DM(12)*XK(4)*dGX(4,4)+XK(4);$
 $J(11,13)=DM(12)*XK(4)*dp(4);$

$J(12,5)=1;$
 $J(12,6)=1;$
 $J(12,7)=1;$
 $J(12,8)=1;$

$J(13,9)=1;$
 $J(13,10)=1;$
 $J(13,11)=1;$
 $J(13,12)=1;$

$J=pinv(J);$
 $JF=J*(-F);$
 $X=JF+DM;$

```

% Program Holdup.m
% Program to calculate the holdup in the column (m3/m3)
% using the equations of Shulman (Treybal P.206)
% packing : Ceramic Intalox Saddle (.25 inch)

function [holdup]= holdp(G,L,densg,densl,MWL,MWG,viscl,sigm)

ds=.0078;    % m
eps=.75;

LL=L*MWL/1000; % kg/m2.sec
GG=G*MWG/1000;

B=1.508*(ds^.376);

% The static liquid hold-up

Pls=(4.23e-3*(viscl^.04)*(sigm^.55))/((ds^1.56)*(densl^.37));

% The total liquid hold-up for water

Pltw=(2.32e-6*(737.5*LL)^B)/(ds^2);

% H, the multiplier considering non-aqueous liquids in contact

h=(sigm/.073)^(.2817-.262*log10(LL));
H=(1404*(LL^.57)*(viscl^.13)*h)/((densl^.84)*(3.24*(LL^.413)-1));

% The static liquid hold-up for water

Plsw=5.014e-5/(ds^(1.56));

% The operating liquid hold-up for water

Plow=Pltw-Plsw;

% The operating liquid hold-up for the liquid mixture

Plo=Plow*H;

% The total liquid hold-up for the liquid mixture

Plt=Plow+Pls;
holdup=Plt;

```

```

% Program reaction.m
% Program to calculate the reaction rate
% Reaction rate in mol/m3.sec

function [rj]=reaction(Tl,x,Xcat,Ct,Cm)

% Equilibrium constant K

rt=.11+.0007043*(Tl^1.556)
K=Cm/rt;
R=1.987;
Ct=Ct*1000;    %mol/m3

% Reaction Constant m3/mol.sec

Krate=1.2e3*exp(-10200/(R*(Tl+273)));

% Reaction term mol/m3.sec

rj=Krate*Ct^2*Xcat*x(1)*x(2)/(x(2)+K*x(4));

```

```
% Program molvol.m
% Program to calculate the molar volume of components
% RHO in gm/cm3, Temp in C, molar volume in cm3/mol.
```

```
function [Vm]=molvol(Temp)
```

```
global xmw
```

```
RHO(1)=1.0724-.0011229*Temp+5.8e-9*Temp^2-2.0e-9*Temp^3;
RHO(2)=.80999-.925e-3*Temp-4.1e-6*Temp^2;
RHO(3)=.95932-1.271e-3*Temp-.405e-6*Temp^2-6.09e-9*Temp^3;
```

```
if Temp <= 55
RHO(4)=1;
elseif Temp > 55
RHO(4)=1.0147-.0005263*Temp;
elseif Temp > 75
RHO(4)=1.0254-.000667*Temp;
elseif Temp > 100
RHO(4)=1.044-.00085*Temp;
end
```

```
for i=1:4
Vm(i)=xmw(i)/RHO(i);
end
```

```
% Program fun.m
% Program to calculate the bottom composition based on a minimization routine.
```

```
function f=fun(z)
```

```
global xmw
global Ln Vn B xn yn Xcat Tln Vol Tgn
```

```
area=.00114;
L=Ln/area;
P=1;
[TB,yz]=bbpoint(z);
```

```
% Calculate the Molecular Weight
```

```
Tgn=TB;
Tln=TB;
[MWL,MWG]=mwt(z,yz);
```

```
% Calculate the Density, Kg/m3
```

```
BB=B/area;
[densg,densl,dens]=dnsty(Tgn,Tln,P,MWG,MWL,BB,z);
```

```
% Molar density; kmol/m3
```

```
Ct=densl/MWL;
Cm=dens(2)/xmw(2);

[rj]=reaction(Tln,z,Xcat,Ct,Cm);
rj=rj*Vol;
```

```
f(1)=xn(1)*Ln-yz(1)*Vn-z(1)*B-rj;
f(2)=xn(2)*Ln-yz(2)*Vn-z(2)*B-rj;
f(3)=xn(3)*Ln-yz(3)*Vn-z(3)*B+rj;
f(4)=xn(4)*Ln-yz(4)*Vn-z(4)*B+rj;
```

Appendix D1.

Computer Output for Run No. 1

Output for Run no.1

Acid feed rate = 2.058e-03 gmol/s
methanol feed rate = 2.470e-03 gmol/s
Catalyst feed rate= 1.260e-05 gmol/s
Reflux ratio = 1.50

Distillate rate = 1.750e-03 gmol/s
Conversion = 0.959

Mole fraction and Temperature profile

Z,m	Xac	Xm	Xes	Xw	Tl,C
0.000	0.0001	0.0810	0.8699	0.0490	55.24
0.002	0.0001	0.0814	0.8695	0.0489	55.24
0.021	0.0001	0.0851	0.8666	0.0482	55.19
0.040	0.0001	0.0891	0.8634	0.0474	55.15
0.059	0.0001	0.0933	0.8601	0.0465	55.11
0.077	0.0001	0.0978	0.8566	0.0454	55.06
0.096	0.0001	0.1026	0.8530	0.0443	55.01
0.115	0.0001	0.1077	0.8491	0.0430	54.96
0.134	0.0001	0.1132	0.8451	0.0416	54.90
0.152	0.0001	0.1189	0.8409	0.0401	54.84
0.171	0.0001	0.1250	0.8365	0.0384	54.78
0.190	0.0001	0.1314	0.8319	0.0366	54.72
0.209	0.0001	0.1381	0.8271	0.0347	54.66
0.227	0.0001	0.1452	0.8221	0.0326	54.59
0.246	0.0001	0.1527	0.8168	0.0304	54.53
0.265	0.0001	0.1605	0.8114	0.0281	54.46
0.284	0.0001	0.1686	0.8057	0.0256	54.39
0.300	0.0001	0.1760	0.8005	0.0234	54.33
0.400	0.4204	0.0999	0.4656	0.0142	69.39
0.407	0.4266	0.0978	0.4608	0.0149	69.69
0.411	0.4324	0.0951	0.4538	0.0188	70.01
0.415	0.4360	0.0934	0.4494	0.0212	70.22
0.418	0.4353	0.0929	0.4498	0.0220	70.20
0.423	0.4340	0.0921	0.4506	0.0234	70.16
0.427	0.4351	0.0912	0.4489	0.0247	70.23
0.429	0.4345	0.0908	0.4493	0.0254	70.21
0.446	0.4311	0.0887	0.4510	0.0291	70.10
0.450	0.4303	0.0882	0.4515	0.0300	70.08
0.452	0.4300	0.0881	0.4516	0.0303	70.07
0.457	0.4314	0.0876	0.4502	0.0307	70.14
0.460	0.4324	0.0871	0.4493	0.0312	70.19
0.462	0.4323	0.0869	0.4491	0.0316	70.20
0.463	0.4322	0.0868	0.4492	0.0319	70.19
0.467	0.4333	0.0862	0.4481	0.0324	70.26
0.471	0.4343	0.0857	0.4472	0.0329	70.31
0.472	0.4342	0.0855	0.4470	0.0333	70.31
0.473	0.4341	0.0854	0.4471	0.0335	70.31
0.475	0.4353	0.0853	0.4454	0.0341	70.37
0.477	0.4349	0.0851	0.4456	0.0344	70.36
0.492	0.4323	0.0837	0.4467	0.0373	70.28

0.497	0.4315	0.0832	0.4470	0.0382	70.25
0.500	0.4329	0.0820	0.4446	0.0404	70.35
0.502	0.4325	0.0818	0.4448	0.0409	70.34
0.519	0.4299	0.0805	0.4458	0.0438	70.25
0.526	0.4316	0.0801	0.4432	0.0451	70.35
0.531	0.4308	0.0797	0.4435	0.0460	70.33
0.546	0.4286	0.0787	0.4442	0.0485	70.26
0.558	0.4269	0.0779	0.4448	0.0504	70.20
0.562	0.4263	0.0777	0.4449	0.0511	70.18
0.564	0.4257	0.0785	0.4448	0.0509	70.15
0.566	0.4261	0.0795	0.4435	0.0509	70.16
0.567	0.4255	0.0803	0.4434	0.0507	70.13
0.569	0.4260	0.0813	0.4421	0.0507	70.15
0.571	0.4259	0.0823	0.4414	0.0504	70.13
0.572	0.4253	0.0835	0.4412	0.0501	70.10
0.573	0.4260	0.0834	0.4404	0.0503	70.13
0.574	0.4258	0.0833	0.4404	0.0505	70.13
0.577	0.4248	0.0847	0.4402	0.0503	70.07
0.578	0.4262	0.0845	0.4385	0.0507	70.15
0.580	0.4260	0.0844	0.4386	0.0510	70.14
0.587	0.4251	0.0840	0.4389	0.0521	70.11
0.591	0.4245	0.0838	0.4391	0.0527	70.09
0.596	0.4296	0.0823	0.4330	0.0551	70.37
0.600	0.4290	0.0820	0.4332	0.0558	70.36
0.675	0.4192	0.0781	0.4356	0.0670	70.05
0.750	0.4104	0.0752	0.4371	0.0773	69.77
0.825	0.4021	0.0728	0.4381	0.0870	69.52
0.900	0.3943	0.0708	0.4386	0.0963	69.28
0.975	0.3868	0.0692	0.4388	0.1052	69.05
1.050	0.3796	0.0678	0.4388	0.1139	68.84
1.125	0.3725	0.0666	0.4385	0.1223	68.63
1.200	0.3656	0.0656	0.4381	0.1306	68.43
1.275	0.3589	0.0648	0.4376	0.1387	68.24
1.350	0.3523	0.0640	0.4369	0.1468	68.05
1.425	0.3458	0.0634	0.4361	0.1547	67.87
1.500	0.3393	0.0629	0.4353	0.1625	67.69
1.575	0.3330	0.0624	0.4344	0.1703	67.51
1.600	0.3309	0.0622	0.4341	0.1728	67.45
1.700	0.2138	0.3959	0.2798	0.1105	62.88
1.705	0.2133	0.3958	0.2798	0.1111	62.87
1.749	0.2092	0.3953	0.2800	0.1155	62.77
1.793	0.2052	0.3948	0.2802	0.1199	62.68
1.837	0.2012	0.3944	0.2802	0.1242	62.59
1.880	0.1972	0.3941	0.2803	0.1284	62.50
1.924	0.1934	0.3938	0.2803	0.1326	62.41
1.968	0.1896	0.3935	0.2802	0.1367	62.32
2.012	0.1858	0.3934	0.2801	0.1408	62.24
2.055	0.1821	0.3932	0.2799	0.1448	62.16
2.099	0.1784	0.3931	0.2797	0.1488	62.08
2.143	0.1748	0.3930	0.2795	0.1527	62.00
2.187	0.1712	0.3930	0.2792	0.1566	61.92

2.230	0.1676	0.3930	0.2789	0.1605	61.84
2.274	0.1641	0.3930	0.2786	0.1643	61.77
2.318	0.1606	0.3930	0.2783	0.1681	61.69
2.362	0.1571	0.3931	0.2779	0.1719	61.62
2.400	0.1541	0.3932	0.2775	0.1751	61.55
2.600	0.1435	0.2877	0.1625	0.4064	65.96

Appendix D2.

Computer Output for Run No. 2

Output for Run no.2

Acid feed rate = 2.058e-03 gmol/s
methanol feed rate = 2.470e-03 gmol/s
Catalyst feed rate= 1.260e-05 gmol/s
Reflux ratio = 2.00

Distillate rate = 1.400e-03 gmol/s
Conversion = 0.909

Mole fraction and Temperature profile

Z,m	Xac	Xm	Xes	Xw	Tl,C
0.000	0.0001	0.0415	0.9244	0.0340	55.74
0.002	0.0015	0.0420	0.9227	0.0338	55.77
0.008	0.0046	0.0434	0.9186	0.0334	55.83
0.014	0.0065	0.0450	0.9155	0.0330	55.86
0.020	0.0064	0.0458	0.9147	0.0331	55.84
0.038	0.0060	0.0487	0.9118	0.0335	55.79
0.057	0.0056	0.0519	0.9087	0.0338	55.73
0.076	0.0053	0.0552	0.9055	0.0341	55.67
0.095	0.0049	0.0588	0.9020	0.0343	55.62
0.113	0.0046	0.0626	0.8984	0.0344	55.56
0.132	0.0043	0.0666	0.8946	0.0344	55.50
0.151	0.0041	0.0709	0.8906	0.0344	55.43
0.170	0.0038	0.0754	0.8864	0.0343	55.37
0.188	0.0036	0.0802	0.8821	0.0341	55.31
0.207	0.0033	0.0853	0.8775	0.0339	55.24
0.226	0.0031	0.0906	0.8728	0.0335	55.18
0.245	0.0030	0.0962	0.8678	0.0330	55.11
0.263	0.0028	0.1021	0.8627	0.0324	55.04
0.282	0.0026	0.1082	0.8574	0.0317	54.97
0.300	0.0025	0.1143	0.8522	0.0310	54.91
0.400	0.3966	0.0673	0.5171	0.0190	68.62
0.409	0.4056	0.0660	0.5092	0.0191	69.02
0.425	0.4208	0.0636	0.4959	0.0196	69.72
0.442	0.4374	0.0606	0.4815	0.0205	70.50
0.445	0.4407	0.0593	0.4773	0.0227	70.68
0.447	0.4424	0.0583	0.4748	0.0245	70.78
0.448	0.4421	0.0582	0.4750	0.0248	70.77
0.452	0.4414	0.0578	0.4753	0.0256	70.75
0.454	0.4426	0.0570	0.4733	0.0270	70.83
0.456	0.4423	0.0569	0.4734	0.0274	70.82
0.467	0.4405	0.0560	0.4741	0.0294	70.76
0.474	0.4394	0.0554	0.4745	0.0306	70.72
0.481	0.4405	0.0536	0.4732	0.0326	70.80
0.482	0.4406	0.0535	0.4730	0.0329	70.81
0.483	0.4405	0.0534	0.4730	0.0330	70.81
0.486	0.4416	0.0526	0.4712	0.0346	70.88
0.488	0.4413	0.0524	0.4713	0.0350	70.87
0.497	0.4400	0.0519	0.4716	0.0364	70.83
0.503	0.4392	0.0515	0.4719	0.0374	70.80
0.507	0.4404	0.0506	0.4698	0.0392	70.88

0.509	0.4400	0.0505	0.4699	0.0396	70.86
0.521	0.4385	0.0499	0.4702	0.0414	70.81
0.528	0.4377	0.0495	0.4704	0.0424	70.79
0.533	0.4393	0.0491	0.4688	0.0429	70.87
0.534	0.4394	0.0489	0.4685	0.0431	70.88
0.535	0.4393	0.0489	0.4685	0.0432	70.88
0.538	0.4412	0.0482	0.4666	0.0441	70.98
0.541	0.4408	0.0480	0.4667	0.0445	70.97
0.553	0.4394	0.0475	0.4670	0.0462	70.92
0.565	0.4380	0.0470	0.4672	0.0478	70.87
0.569	0.4375	0.0468	0.4673	0.0484	70.85
0.575	0.4393	0.0463	0.4655	0.0489	70.95
0.579	0.4408	0.0459	0.4639	0.0493	71.02
0.580	0.4409	0.0458	0.4637	0.0496	71.03
0.581	0.4409	0.0458	0.4637	0.0497	71.03
0.584	0.4425	0.0454	0.4613	0.0509	71.13
0.587	0.4422	0.0452	0.4613	0.0512	71.12
0.598	0.4409	0.0448	0.4615	0.0528	71.07
0.610	0.4396	0.0444	0.4617	0.0543	71.03
0.614	0.4413	0.0438	0.4594	0.0555	71.13
0.616	0.4410	0.0437	0.4594	0.0559	71.12
0.627	0.4398	0.0434	0.4595	0.0573	71.08
0.642	0.4382	0.0429	0.4597	0.0592	71.02
0.645	0.4396	0.0420	0.4574	0.0611	71.11
0.647	0.4393	0.0419	0.4574	0.0614	71.10
0.664	0.4375	0.0414	0.4575	0.0635	71.05
0.667	0.4385	0.0416	0.4563	0.0635	71.09
0.669	0.4383	0.0415	0.4564	0.0638	71.08
0.680	0.4372	0.0412	0.4564	0.0652	71.05
0.683	0.4369	0.0412	0.4564	0.0655	71.04
0.686	0.4379	0.0412	0.4550	0.0659	71.09
0.688	0.4376	0.0412	0.4550	0.0662	71.08
0.696	0.4368	0.0410	0.4550	0.0671	71.05
0.701	0.4364	0.0409	0.4551	0.0677	71.04
0.703	0.4363	0.0403	0.4552	0.0681	71.05
0.705	0.4362	0.0403	0.4552	0.0683	71.04
0.706	0.4361	0.0403	0.4552	0.0685	71.04
0.712	0.4434	0.0388	0.4462	0.0716	71.43
0.718	0.4429	0.0387	0.4462	0.0722	71.42
0.793	0.4357	0.0372	0.4462	0.0810	71.18
0.868	0.4287	0.0360	0.4458	0.0895	70.96
0.943	0.4221	0.0350	0.4452	0.0978	70.74
1.018	0.4155	0.0341	0.4444	0.1059	70.54
1.093	0.4092	0.0335	0.4435	0.1139	70.34
1.168	0.4029	0.0329	0.4424	0.1218	70.15
1.243	0.3967	0.0324	0.4413	0.1295	69.96
1.318	0.3906	0.0321	0.4401	0.1372	69.78
1.393	0.3846	0.0317	0.4389	0.1448	69.60
1.468	0.3786	0.0315	0.4376	0.1524	69.42
1.543	0.3726	0.0313	0.4362	0.1599	69.25
1.600	0.3681	0.0311	0.4351	0.1656	69.12
1.700	0.2366	0.3811	0.2783	0.1040	63.64
1.705	0.2361	0.3810	0.2784	0.1046	63.63

1.749	0.2316	0.3802	0.2789	0.1093	63.52
1.793	0.2273	0.3794	0.2792	0.1140	63.41
1.837	0.2231	0.3788	0.2795	0.1186	63.31
1.880	0.2189	0.3782	0.2797	0.1231	63.21
1.924	0.2148	0.3777	0.2799	0.1275	63.12
1.968	0.2108	0.3773	0.2800	0.1319	63.02
2.012	0.2069	0.3769	0.2800	0.1362	62.93
2.055	0.2030	0.3765	0.2800	0.1405	62.84
2.099	0.1991	0.3763	0.2800	0.1447	62.75
2.143	0.1953	0.3760	0.2799	0.1488	62.67
2.187	0.1915	0.3758	0.2797	0.1529	62.58
2.230	0.1878	0.3757	0.2796	0.1570	62.50
2.274	0.1841	0.3755	0.2793	0.1610	62.42
2.318	0.1805	0.3754	0.2791	0.1650	62.34
2.362	0.1769	0.3754	0.2788	0.1689	62.26
2.400	0.1738	0.3754	0.2785	0.1723	62.19
2.600	0.1682	0.2741	0.1842	0.3735	66.02

Appendix D3.

Computer Output for Run No. 5

Output for Run no.5

Acid feed rate = 2.058e-03 gmol/s
 methanol feed rate = 2.058e-03 gmol/s
 Catalyst feed rate= 1.260e-05 gmol/s
 Reflux ratio = 2.00

Distillate rate = 1.250e-03 gmol/s
 Conversion = 0.824

Mole fraction and Temperature profile

Z,m	Xac	Xm	Xes	Xw	Tl,C
0.000	0.0001	0.0310	0.9429	0.0260	55.94
0.002	0.0017	0.0314	0.9413	0.0256	55.98
0.008	0.0051	0.0326	0.9376	0.0248	56.06
0.014	0.0044	0.0337	0.9367	0.0252	56.02
0.019	0.0039	0.0347	0.9359	0.0255	55.98
0.023	0.0054	0.0355	0.9339	0.0252	56.01
0.027	0.0042	0.0364	0.9336	0.0258	55.96
0.031	0.0057	0.0373	0.9316	0.0255	55.99
0.036	0.0062	0.0381	0.9303	0.0255	55.99
0.040	0.0061	0.0387	0.9296	0.0256	55.97
0.059	0.0057	0.0415	0.9265	0.0263	55.91
0.068	0.0055	0.0430	0.9248	0.0266	55.88
0.082	0.0104	0.0466	0.9175	0.0255	55.96
0.094	0.0100	0.0487	0.9156	0.0257	55.91
0.113	0.0094	0.0524	0.9123	0.0259	55.84
0.132	0.0088	0.0564	0.9087	0.0261	55.76
0.150	0.0082	0.0606	0.9049	0.0262	55.69
0.169	0.0077	0.0651	0.9009	0.0262	55.61
0.188	0.0072	0.0699	0.8966	0.0262	55.53
0.207	0.0068	0.0750	0.8921	0.0261	55.45
0.225	0.0064	0.0803	0.8873	0.0259	55.37
0.244	0.0060	0.0860	0.8824	0.0257	55.29
0.263	0.0056	0.0919	0.8771	0.0253	55.21
0.282	0.0053	0.0982	0.8717	0.0249	55.13
0.300	0.0050	0.1045	0.8662	0.0244	55.05
0.400	0.4218	0.0589	0.5050	0.0143	69.77
0.409	0.4313	0.0572	0.4965	0.0150	70.21
0.448	0.4711	0.0492	0.4607	0.0190	72.17
0.454	0.4779	0.0476	0.4546	0.0198	72.52
0.457	0.4804	0.0471	0.4523	0.0201	72.65
0.461	0.4782	0.0444	0.4542	0.0231	72.59
0.463	0.4799	0.0443	0.4530	0.0228	72.67
0.464	0.4814	0.0439	0.4516	0.0230	72.75
0.467	0.4838	0.0434	0.4495	0.0232	72.87
0.471	0.4818	0.0410	0.4512	0.0260	72.82
0.473	0.4836	0.0407	0.4496	0.0262	72.91
0.477	0.4826	0.0392	0.4502	0.0279	72.89
0.478	0.4843	0.0389	0.4488	0.0281	72.98
0.483	0.4838	0.0381	0.4489	0.0293	72.97

0.484	0.4866	0.0368	0.4451	0.0315	73.14
0.486	0.4863	0.0366	0.4452	0.0318	73.13
0.491	0.4860	0.0366	0.4451	0.0322	73.12
0.492	0.4873	0.0358	0.4431	0.0339	73.21
0.493	0.4871	0.0357	0.4431	0.0340	73.20
0.501	0.4859	0.0352	0.4435	0.0354	73.16
0.504	0.4854	0.0349	0.4436	0.0361	73.14
0.509	0.4852	0.0351	0.4433	0.0363	73.13
0.510	0.4865	0.0343	0.4412	0.0380	73.22
0.511	0.4864	0.0342	0.4413	0.0382	73.22
0.519	0.4853	0.0337	0.4415	0.0395	73.18
0.523	0.4848	0.0335	0.4417	0.0400	73.16
0.528	0.4831	0.0335	0.4426	0.0408	73.08
0.530	0.4849	0.0324	0.4395	0.0432	73.21
0.532	0.4847	0.0323	0.4396	0.0435	73.20
0.540	0.4837	0.0319	0.4397	0.0447	73.17
0.545	0.4831	0.0317	0.4399	0.0454	73.14
0.550	0.4831	0.0321	0.4393	0.0455	73.14
0.551	0.4843	0.0313	0.4373	0.0471	73.23
0.552	0.4842	0.0312	0.4373	0.0472	73.22
0.559	0.4833	0.0309	0.4374	0.0483	73.19
0.562	0.4830	0.0308	0.4375	0.0486	73.18
0.567	0.4900	0.0261	0.4261	0.0578	73.67
0.571	0.4895	0.0259	0.4262	0.0584	73.66
0.646	0.4817	0.0240	0.4262	0.0681	73.39
0.653	0.4810	0.0238	0.4262	0.0690	73.36
0.661	0.4802	0.0236	0.4261	0.0700	73.34
0.664	0.4814	0.0237	0.4245	0.0704	73.40
0.667	0.4812	0.0237	0.4245	0.0707	73.39
0.678	0.4801	0.0235	0.4244	0.0720	73.36
0.681	0.4798	0.0234	0.4244	0.0724	73.35
0.684	0.4810	0.0235	0.4227	0.0728	73.41
0.687	0.4807	0.0235	0.4227	0.0731	73.40
0.698	0.4796	0.0232	0.4227	0.0745	73.37
0.703	0.4791	0.0231	0.4226	0.0752	73.35
0.709	0.4864	0.0216	0.4132	0.0788	73.79
0.714	0.4860	0.0215	0.4131	0.0794	73.77
0.789	0.4791	0.0204	0.4123	0.0883	73.54
0.864	0.4724	0.0195	0.4112	0.0969	73.32
0.939	0.4659	0.0187	0.4100	0.1054	73.12
1.014	0.4595	0.0182	0.4086	0.1137	72.91
1.089	0.4533	0.0177	0.4071	0.1219	72.72
1.164	0.4471	0.0173	0.4055	0.1301	72.53
1.239	0.4410	0.0170	0.4039	0.1381	72.35
1.314	0.4350	0.0168	0.4021	0.1461	72.17
1.389	0.4290	0.0166	0.4004	0.1540	72.00
1.464	0.4230	0.0164	0.3986	0.1619	71.83
1.539	0.4171	0.0163	0.3968	0.1698	71.66
1.600	0.4123	0.0163	0.3952	0.1762	71.52
1.700	0.2723	0.3542	0.2600	0.1136	65.37
1.705	0.2716	0.3540	0.2601	0.1143	65.35
1.749	0.2663	0.3525	0.2612	0.1201	65.21

1.793	0.2611	0.3511	0.2620	0.1257	65.07
1.837	0.2561	0.3498	0.2628	0.1312	64.94
1.880	0.2512	0.3487	0.2635	0.1366	64.81
1.924	0.2464	0.3477	0.2640	0.1419	64.69
1.968	0.2418	0.3467	0.2645	0.1470	64.57
2.012	0.2372	0.3459	0.2649	0.1521	64.45
2.055	0.2326	0.3451	0.2652	0.1571	64.34
2.099	0.2282	0.3444	0.2654	0.1620	64.23
2.143	0.2238	0.3437	0.2656	0.1668	64.12
2.187	0.2195	0.3432	0.2657	0.1716	64.02
2.230	0.2153	0.3426	0.2657	0.1763	63.92
2.274	0.2111	0.3422	0.2658	0.1810	63.82
2.318	0.2070	0.3417	0.2657	0.1856	63.72
2.362	0.2029	0.3414	0.2656	0.1901	63.62
2.400	0.1994	0.3411	0.2655	0.1940	63.54
2.600	0.1838	0.2240	0.1802	0.4120	67.28

VITA

Mohamed A. Abdulla was born in Sharjah, United Arab Emirates, in 1966 and raised in the city of Dubai. He obtained his Bachelor of Science in Chemical and Petroleum Engineering from The United Arab Emirates University in May 1989. He worked six months with Dubai Aluminum Company (DUBAL). In January 1990 he joined the UAE University as a teaching assistance from which he was sent to the United States for graduate study. He obtained his Master of Science in Chemical Engineering from Washington University at St. Louis in August 1992. He is married to Dalal Abduli and has one daughter, Hend, and two sons, Ahmad and Abdulrahman.