SIMULATION OF MULTICOMPONENT DISTILLATION COLUMN

A DISSERTATION

submitted in partial fulfilment of the
requirements for the award of the degree
of
MASTER OF ENGINEERING
in
CHEMICAL ENGINEERING
(With Specialization in Advanced Transfer Process)

By

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MARCH, 1999

CANDIDATE'S DECLARATION

I hereby certify that the work presented in this dissertation entitled '**SIMULATION OF MULTICOMPONENT DISTILLATION COLUMN**' in partial fulfilment of the requirements for the award of the degree of **MASTER OF ENGINEERING in CHEMICAL ENGINEERING** with specialisation in ADVANCED TRANSFER PROCESS of the University of Roorkee, Roorkee, is an authentic record of my own work carried out during the period from July 1998 to March 1999 under the guidance of Dr. S. C. Gupta, Professor, Department of Chemical Engineering, University of Roorkee, Roorkee.

The matter presented in this dissertation has not been submitted by me for the award of any other degree of this or any other University.

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This is to certify that above statement made by the candidate is correct to the best of my knowledge.

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ACKNOWLEDGEMENTS

I am highly thankful to my guide **Dr. S.C. Gupta**, Professor, Department of Chemical Engineering, University of Roorkee, Roorkee, whose unfailing support, co-operation and supervision despite his own inconveniences helped me accomplish this work.

I would also like to thank, Dr. V.K. Agarwal, Assistant Professor, for his talented advice during all the phases of the present study.

Thanks are due to Dr. Surendra Kumar, Professor and Head, Department of Chemical Engineering, University of Roorkee, Roorkee, for providing all facilities and help during this dissertation.

I would like to thank Mr. Anuj Jain and Mr. B. B. Gulyani, research scholars, for their support and advice.

I am thankful to Mr. Suresh Sharma, Mr. Rajkumar, and Mr. Puran Singh, members of technical staff of HTRL for their help.

I am also indebted to my friends for their enthusiastic support and encouragement during the preparation of this report.

Pankaj Arora

ABSTRACT

This thesis presents an investigation on simulation studies of multicomponent reactive distillation column. Using the basic equations of material balance, enthalpy balance, phase equilibria and rate equation, a mathematical model has been developed. It has been solved by application of equation tearing method, which includes transforming the equations into tridiagonal matrix and using an iterative solution procedure. The model developed has been examined for ethanol-acetic acid multicomponent reactive system in a distillation column having 13 number of equilibrium stages and other specified geometrical and operating parameters. It has predicted the profiles for temperature, liquid and vapor compositions, liquid and vapor molar flow rates and extent of reaction at each equilibrium stage. Computed profiles have been compared with the reported data due to Suzuki et al., 1971. The acceptable accuracy of the ethanol-acetic acid simulations demonstrates the adequacy of the modeling process and validates its extension to other multicomponent reactive distillation columns.

The model has been further updated with inclusion of activity coefficient by UNIQUAC equation in combination with Marek's equation for association in vapor phase. It takes into account the nonideal behaviour of the system. Analysis of methanol-acetic acid multicomponent reactive system has been carried out by using the above model and profiles for temperature, vapor and liquid compositions, liquid and vapor molar flow rates, extent of chemical reaction at each stage and percent conversion with respect to acetic acid have been determined.

Effect of various parameters namely stage hold up, number of equilibrium stages, reflux ratio, feed composition, feed flow rate and column pressure on percent conversion and top ester (methyl acetate) mole fraction have been determined keeping other parameters constant. Analysis has shown that increase in stage hold up, number of equilibrium stages, reflux ratio, feed composition and column pressure favours higher product yield but increase in feed flow rate displays reverse trend.

The system has also been investigated when two feeds have been introduced at two different stages of the column. In fact, when methanol was introduced at the eleventh *stage and acetic acid on second stage in a column of 13 equilibrium stages including a reboiler and a condenser, a maximum yield of methyl acetate was obtained.*

Minimum value of reflux ratio has been computed by solving differential equation for rectification and stripping column simultaneously along with the appropriate condition for minimum reflux ratio and the value so obtained has been compared with reported data due to Doherty and Barbosa, 1988.

Using HYSYS software package ethanol-acetic acid multicomponent reactive distillation column has been simulated and the profiles for temperature, liquid and vapor compositions and molar flow rates have been obtained.

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NOMENCLATURE

B	Bottom molar flow rate (mol/min)
C	Number of components
D	Distillate molar flow rate (mol/min)
F	Feed molar flow rate (mol/min)
G	Vapour side stream from stage j
h_j	Enthalpy of liquid stream, L_j (cal/mol)
H_j	Enthalpy of vapour stream, V_j (cal/mol)
i	Component number
j	Stage number
K	Phase equilibrium constant
K_R	Reaction rate constant (dm^3/mol.min)
$k_{i,j}$	Dimerization equilibrium constant for associating component A at stage j
L	Liquid molar flow rate (mol/min)
N	Total number of stages in the column
r	Reflux ratio
$\Delta R_{i,j}$	Production rate of i-th component by chemical reaction rate on stage j
r_m^*	Modified reflux ratio
P_i^*	Vapour pressure of component i (atm)
P	Total pressure (atm)
Q_B	Heat duty of the reboiler (cal/mol)
Q_D	Heat duty of the condenser (cal/mol)
S	Reboil ratio
S_m^*	Modified reboil ratio
T	Absolute temperature (K)
U	Liquid side stream molar flowrate (mol/min)
V	Vapour molar flowrate (mol/min)
X_i	Transformed composition variable
$x_{i,j}$	Mole fraction of i^{th} component in liquid phase leaving j^{th} stage

Y_i	Transformed composition variable
$y_{i,j}$	Mole fraction of ith component in vapor phase leaving jth stage
$z_{i,j}$	Mole fraction of ith component in feed stream supplied to jth stage
Z_{ij}	Correction factor for nonideality of vapour phase
ΔH	Latent heat (cal/mol)

Greek letters

$\gamma_{i,j}$	Liquid phase activity coefficient of component i at stage j
ε	Convergence criteria
ν_i	Stoichiometric coefficient of component i
μ_j	Chemical potential of component i
ϕ_j	Hold up at stage j
ρ_{ij}	molar volume of component i at stage j (ml/mole)
α	Relative volatility

Subscript

ext	External
min	Minimum
k	Reference components

Superscript

l	Liquid phase
v	Vapour phase
•	Modified value

Abbreviations

EtOH	Ethanol
MeOH	Methanol
AcOH	Acetic acid
MeOAc	Methyl acetate
EtOAc	Ethyl acetate
DELR	Extent of reaction at a stage

CHAPTER 1

INTRODUCTION

Distillation is probably the most widely used separation process in chemical and allied industries; its applications ranging from the rectification of alcohol which has been practised since antiquity to the fractionation for crude oil. Basically, it is carried out by the production of a vapour by boiling the liquid mixture to be separated, condensing the resultant vapour and returning a part of the condensate to the still in such a way that the returned liquid is in intimate contact with the vapour on way to condenser. This process is capital and energy-intensive and also highly complicated. In fact, it has a large number of variables and a small change in the value of variables affects the separation process and its economics considerably. Therefore, analysis and simulation of distillation process is essential as it will lead to the determination of optimum values of variables for economic and quality conscious production of chemicals.

Perhaps, the first systematic analysis of distillation process was made in 1893 by Sorel who described it by a set of mathematical equation (total and component material balance, and energy balance). He applied graphs for phase-equilibrium data instead of equation. Because of the complexity, it was not widely applied until 1921 when Ponchon and later Savarit used an enthalpy-concentration diagram for this purpose. Later McCabe and Thiele developed a much simpler but less rigorous graphical technique for binary systems by assuming constant vapour and liquid molal flow rates from equilibrium stage to stage except across feed or side stream withdrawal stages. This method is widely applied even today as it provides valuable insight into changes in phase compositions from stage to stage. Still there are some other methods like Smokers equation, which are also used for the solution of binary systems. Prior to 1960, Thiele-Geddes and Lewis-Metheson method were the only two methods for the analysis and simulation of single feed multicomponent distillation systems.

Attempts in the late 1950s to adapt the Thiele-Geddes and Lewis-Matheson methods to computations with a digital computer had limited success. The real breakthrough in computerisation of equilibrium-stage calculations occurred when

Amundson and co-workers, starting in 1958, applied techniques of matrix algebra. This led to a number of successful computer-aided methods, based on sparse-matrix algebra, for Sorel's equilibrium-based model. Today, computer-aided design and simulation programs abound for the rigorous, iterative numerical solution of Sorel's equilibrium-based model for a wide variety of column configurations and specifications. Although the iterative computations sometimes fail to converge, the methods are widely applied and have become more flexible and robust with each passing year.

With the advancement in technology, there are some liquid mixtures which can not be separated into their components economically by ordinary distillation process, such situation especially arise when the difference in boiling point of components is less or they form an azeotrope. In such cases, special distillation techniques like extractive distillation, salt distillation, pressure swing distillation, homogeneous and heterogeneous azeotropic distillation are explored. The salient features of them are given below:

1. Extractive Distillation: A method that uses a large amount of a relatively high-boiling solvent to alter the liquid-phase activity of the mixture, so that the relative volatility of the key components becomes more favourable.
2. Salt Distillation: A variation of extractive distillation in which the relative volatility of the key components is altered by dissolving a soluble, ionic salt in the top reflux. Because the salt is non-volatile, it stays in the liquid phase as it passes down the column.
3. Pressure-swing Distillation: A method for separating a pressure-sensitive azeotrope that utilises two columns operated in sequence at two different pressures.
4. Homogeneous Azeotropic Distillation: A method of separating a mixture by adding an entrainer that forms a homogeneous minimum- or maximum-boiling azeotrope with one or more feed components.
5. Heterogeneous Azeotropic Distillation: A more useful azeotropic distillation in which a minimum-boiling heterogeneous azeotrope is formed by the entrainer. The azeotrope splits into two liquid phases in the overhead condensing system. One liquid phase is sent back to the column as reflux, while the other liquid phase is sent to another separation step or is a product.

In recent years, **multicomponent reactive distillation** is an emerging technology that has great potential as a process alternative for carrying out liquid phase chemical reactions. It combine chemical reaction and distillation in a single vessel and are becoming industrially more prominent. Such an operation can offer several advantages such as:

- It can reduce capital and production costs by combining two units into one.
- reaction conversion can be increased by overcoming chemical equilibrium limitations through the removal of reaction products,
- heat duty can be reduced by utilising the heat of reaction,
- limitations of azeotropic mixture can be overcome by reaction,
- recycle costs for excess reactant, which is necessary for a conventional reactor to prevent side reactions and chemical equilibrium limitation, can be reduced.

Application of multicomponent reactive distillation leads to a substantial cost savings compared to a conventional process. These savings result from:

- Lower capital costs due to reduction in number of equipments. Reaction and separation are carried out in the same column, thus eliminating one process step with associated major equipment, pumps, piping and instrumentation. For reactions with high heat of reaction, the need for inter-stage heat transfer equipment is eliminated. All heat transfer takes place at the reboiler and condenser.
- Lower operating costs due to higher conversion per pass. This leads to a higher rate of production, plus the unconverted reactant concentration may be low enough to eliminate recycling. The cost per unit mass of product is less. If the reaction is exothermic, the heat of reaction is utilised for the distillation and results in energy savings.

Although some investigators have studied various facets of multicomponent reactive distillation using various systems such as esterification of ethanol, MTBE, TAME, cumene, tetra butyl alcohol, tertiary amyl alcohol etc. But still there are certain ramifications, which have still not being fully understood. Therefore, there is a need to carry out detailed study on the simulation of a reactive distillation so that the same may be applied to real situations.

The present work has been planned with the following objectives:

1. To formulate a mathematical model of the multicomponent reactive distillation column and to develop a computer program for it.

   And to examine its validity against the data available in literature for the esterification of ethanol-acetic acid.

2. To carry out reactive distillation operation for the production of methyl acetate from methanol and acetic acid, using as a single feed and multiple feed column and by incorporating nonideal behaviour of the system.
3. To determine effect of operating parameters namely hold up on each stage, feed flow rate, number of equilibrium stages, reflux ratio, feed composition and column pressure on product yield.

CHAPTER 2

LITERATURE REVIEW

Distillation column can be used advantageously as a reactor for systems in which chemical reactions occur at temperatures and pressure suitable to the distillation of components. By continuous separation of products from reactants while the reaction is in progress, the reaction can proceed to a much higher level of conversion than without separation. According to Leyes and Othmer (1945), who discussed butyl acetate and dibutyl phthalate synthesis in a distillation column, the earliest literature references in this area are for patents registered to Backhaus in the 1920s to esterification processes using homogeneous catalysts. Further research, both of an experimental and theoretical nature, was conducted during later years.

Belck (1955) performed calculations with respect to reactive distillation of two and three component mixtures. He assumed a plate efficiency of 100% and adiabatic operation of the column. He also assumed that the heat of reaction as well as the influence of differences in temperature between various plates of the column on density, heat of vaporisation and reaction rate was negligible.

Marek (1956) examined a rectification column when a chemical reaction occurs among the components of the mixture. He derived a design procedure for a plate column based on material and enthalpy balances, including the effect of reaction.

Geelen and Wijffels (1965) investigated the reaction of vinyl acetate with stearic acid in both plate type and packed distillation column.

The calculations of multistage separation processes become more complex with increasing number of components; therefore the need for computer aided methods arises. Corrigan and Miller (1968) modelled the reactive distillation of the ethylene oxide-water-ethylene-glycol system with a digital computer, using the classical method of calculation from plate to plate.

Suzuki et al., (1971) describe a generally applicable plate to plate calculation for the esterification of ethanol with acetic acid. They employed tridiagonal matrix for solving material balances and modified muller's method for temperature convergence.

Pilavakis (1974) studied the esterification of methanol by acetic acid in a single stage packed reaction-distillation column. He conducted the experiments in a reaction distillation column and compared the results with theoretical model, developed for packed column.

Senthilnathan et. al., (1988) applied the method of Suzuki (1971) for system involving ionization equilibrium. They used the Muller's method of convergence to obtain the temperature profile in the column.

Holland (1980) extended the use of improved Thiele-Geddes procedure called the theta method which is one of the fast methods for solving distillation problems, for cases when one or more chemical reactions occur on each stage of a distillation column. The method was recommended for any type of distillation column in which mixtures behaviour do not deviate too widely from ideal solutions.

Sawistowski and Pilavakis (1987) carried out esterification of acetic acid by methanol in reaction distillation column. They predicted the effect of changing various operating parameters in order to maximize the overall conversion. Nelson (1971) used the Newton-Raphson method, Zamaitis (1980) used the Jacobian matrix method for solving the material balance equation.

The reactive distillation has been used to manufacture cumene by catalytic distillation (Shoemaker et. al., 1987), Methyl tert-butyl ether (Smith, 1990), tert-alkyl ether (Nocca et al., 1989 and Quang et al., 1989). Fuchigami (1990) employed reactive packing of ion-exchange resin to carry out the hydrolysis of methyl acetate in distillation column. Duprat and Gau (1991) carried out reactive distillation of pyridine mixtures with an organic acid and studied the parameter sensitivity and optimised the process.

Employing reactive distillation for reactions that rely on a solid heterogeneous catalyst is a more recent development. The technique of reactive distillation offers a particularly promising option for equilibrium limited reactions using solid catalyst. De Garmo et al., (1992) discussed the effects of catalyst and the catalysed production of ethers.

Barbosa, D. and Doherty, M.F. (1987) derived the equations describing the simple distillation of homogeneous reactive mixtures and computed residue curve maps for ideal and non-ideal systems. These maps show that, by allowing the components of a liquid mixture to react, we can either create or eliminate distillation boundaries. It is also shown that not all non-reactive azeotropes appear as product of the distillation process. Knowledge of these features is fundamental for the design and synthesis of sequences of reactive distillation columns.

Simandl, J.(1990) derived the equations describing the steady state operation of distillation towers with chemical reactions and solved them by two algorithms : (1)simultaneous solution after linearization ; and (2) the inside -outside method ,a tearing algorithm. The two algorithms were compared using a 13-tray ethyl acetate producing column.

Barbosa, D. and Doherty, M.F. (1987) introduced a new set of transformed composition variables to simplify the design equations for single and double-feed, multicomponent reactive distillation columns. These new equations are used to develop general method of calculating minimum reflux ratios for reactive distillation columns. Th application of these equations to the design of reactive distillation columns for esterficatio processes is discussed.

Alejski k. (1990) proposed a new method of solving reactive distillation columns using a transient model of the column and the diffusion model approximated by the cascade of stirred-cells for description of mixing on the plates. The accuracy of the algorithm considered was tested for the industrial acetic anhydride rectification column.

Abufares A.A. and Douglas P.L.(1995) developed a dynamic mathematical model for an MTBE catalytic distillation process. The model incorporates experimental kinetic rate data, rigorous thermodynamics, vapour-liquid non-idealities, and tray hydraulics. Both steady state and dynamic simulations were made. *SPEEDUP*, an equation oriented simulation package was used to solve the steady state and dynamic equations describing the system behaviour. *ASPENPLUS*, a steady state sequential modular simulation package was used to compare the steady state results from *SPEEDUP*.

Isla M.A. and Irazoqui H.A.(1996) analyzed all the steps needed to build a reactive column simulator for the MTBE synthesis. The column is modelled as a sequence of stages at partial equilibrium. The physical model adopted is discussed in depth as well as the resulting mathematical model. The solution algorithm, based on a Napthali-Sandholm type method, is simple, robust, and time efficient. The simulation module is used to perform sensitivity analysis to structural and operating variables like total catalyst load, catalyst distribution, operating pressure, and reflux ratio, among others. The analysed eleven component case study corresponds to a situation of practical interest.

Espinosa J. et al. (1995) presented a method to determine the product composition regions of single-feed reactive distillation columns. A new set of transformed compositions is introduced, and the resulting residue curve maps are studied for two reacting mixtures containing inert. Due to the geometrical properties of the new composition variables, by using the residue curves it is possible to determine the feasibility of a desired separation from the extreme limiting operating conditions. An interesting behaviour is observed for the highly nonideal reacting mixture isobutene-methanol-MTBE-butane. The minimum reflux ratio, for certain splits, corresponds to a finite number of trays in both column sections. The conditions for the occurrence of such a case are given.

Schrans S. and Sjoerd D. W.(1996) performed a dynamic simulations of a 15 stage MTBE reactive distillation column with the *SPEEDUP* flowsheeter. The simulations confirm that the column configuration with fixed bottom outflow rate can display steady-state multiplicity. Changes in the column operation (feed flow rate or composition) can cause a jump from one steady state to another or trigger oscillations. The observed steady-state multiplicity remains when the reboiler temperature is fixed rather than the bottom flow rate.

Sneesby M.G et al (1997) had performed column simulations using both *PRO/II* and *SPEEDUP*, which show excellent, agreement with previously published experimental data for a MTBE system and also agree well with each other for both MTBE and ETBE systems. A homotopy analysis was performed on the tuned simulation models to determine the effects of key design and operating variables on column performance and, subsequently, to develop a design method for reactive distillation columns.

Sneesby M.G.(1997) developed a dynamic simulation, based on the MESH equations with supplementary equations to model the main chemical reaction using *SPEEDUP*. The simulations were then utilised for the study of transient open-loop responses and for control system design. The control of a reactive distillation column present several difficulties not normally associated with distillation and dynamic simulation proved to be the ideal tool for the study and solution of these problems. Some general recommendations for the control of reactive ETBE columns are made, including the need to address control issues early in the design process to recognise implications on process equipment design.

Yuxiang Z. Xien X.(1992) modified the rate-based model for the design and simulation of separation processes so as to be suitable for the catalytic distillation process where the column consists of three parts : a rectifying and a stripping section with trays and a packed reactive section with a specially arranged structure. In order to accelerate the convergence, a better method for obtaining the initial values of iteration variables, that particularly suit this complicated problem, was advanced for the rate-based model. Using the kinetic model by Wang et al., the catalytic distillation process for the manufacture of MTBE was simulated.

Bessling B. et al (1997) developed the concept of reactive distillation lines on the basis of the transformation of concentration co-ordinates. It is applied to study the feasibility of a reactive distillation with an equilibrium reaction on all trays of a distillation column. Depending on the characterisation of the reactive distillation line diagrams, it can be decided whether a column with two feed states is required. On the basis of the reaction space concept, a procedure for the identification of reactive distillation processes is developed, in which the reactive distillation column has to be divided into reactive and non-reactive sections. This can be necessary to overcome the limitations in separation, which result from the chemical equilibrium. The concentration profile of this combined reactive/nonreactive distillation column is obtained using distillation lines.

Based on all the above literature cited and studied, the problem of "Simulation of multicomponent distillation column" can be summarised in the following manner:

1. systems studied so far,
2. degrees of freedom and specifications,
3. mathematical solution techniques used for solving of non linear algebraic equations.

2.1 SYSTEMS FOR MULTICOMPONENT REACTIVE DISTILLATION

A large number of reactions favourably performed by multicomponent reactive distillation are described in the literature. Table 2.1 lists few of them.

TABLE 2.1: Systems for multicomponent reactive distillation

Methyl acetate from methanol and acetic acid	Agreda et al., 1990
Ethyl acetate from ethanol and acetic acid	Komatsu, 1977
Butyl acetate from butanol and acetic acid	Hartig, Regner, 1971
MTBE from methanol and i-butene	Flato, Holfmann, 1992 Smith, 1990
ETBE from ethanol and isobutene	Thiel et al., 1997
TAME from methanol and 2-methyl-2-butene	Bravo, Pyhalahti, 1992 Thiel et al., 1997
TAME from methanol and 2-methyl-1-butene	Bravo, Pyhalahti, 1992
Ethyleneglycol from ethylene oxide and water	Gu, Ciric, 1992
Isooctane from isobutene and 1-butene	Huss, Kennedy, 1990
Ethylene benzene from benzene and ethylene	Smith et al., 1991
Cumene from benzene and propylene	Shoemaker, Jones, 1987
Tert-butyl-alcohol from isobutene and water	Velo et al., 1988
Nylon 6,6 prepolymer from adipic acid and hexamethylenediamine	Jaswal, Pugi, 1975
Tert-amyl alcohol from isoamylene and water	Gonzales, Fair, 1997

2.2 DEGREES OF FREEDOM AND SPECIFICATIONS

The solution to a multicomponent, multiphase, multistage separation problem is found in the simultaneous or iterative solution of the material balance, energy balance, and phase equilibria equations. This implies that a sufficient number of design variables is specified so that the number of remaining unknown (output) variables exactly equals the number of independent equations. When this is done, a separation process is said to be specified.

In our case, in addition of separation taking place in the distillation column, reaction is also considered. The reactions A + B $\leftrightarrow$ C+ D, where A and B are intermediate in volatility to C and D, and C has the highest volatility. In this case, the feed enters an ordinary distillation column somewhere near the middle, with C withdrawn as distillate and D withdrawn as bottoms. If B is less volatile than A, then B may enter the column separately and at a higher level than A.

An intuitively simple, but operationally complex, method of finding N_D, the number of independent design variables, degrees of freedom, or variance in the process, is to enumerate all pertinent variables, N_V, and to subtract from these the total number of independent equations or relationships, N_E, relating the variables:

$$N_D = N_V - N_E$$

Typically, the variables in a separation process are intensive variables such as composition, temperature, or pressure: extensive variables such as flow rate or heat transferred: and equipment parameters such as the number of equilibrium stages. Physicals such as enthalpy or K-values are not counted because they are functions of the intensive variables. The variables are relatively easy to enumerate, but to achieve an unambiguous count of N_E it is necessary to carefully seek out all independent relationships due to material and energy conservation's, phase equilirbia restrictions, process specifications, and equipment configurations.

Variable Specification	**Number of Variables**
1. Pressure at each stage (including partial reboiler)	N
2. Pressure at reflux divider outlet	1
3. Pressure at total condenser outlet	1
4. Heat transfer rate for each stage (excluding partial reboiler)	(N-1)
5. Heat transfer rate for divider	1
6. Feed mole fractions and total feed rate	C
7. Feed temperature	1
8. Feed Pressure	1
9. Condensate temperature (e.g., saturated liquid)	1

10.Total number of stages, N	1
11.Feed stage location	1
12.Sidestream stage location	1
13.Sidestream total flow rate, S	1
14.Total distillate flow rate, D or D/F	1
15.Reflux flow rate, L_R, or reflux ratio, L_r/D	1
	$N_D = (2N + C + 11)$

In most separation operations, variables related to feed conditions, stage heat transfer rates, and stage pressure are known or set. Remaining specifications have proxies, provided that the variables are mathematically independent of each other and of those already known. Thus, in the above list, the first 9 entries are almost always known or specified. Variables 10 to 15, however, have surrogates. Some of these are

16. Condenser heat duty, Q_C
17. Reboiler heat duty, Q_B
18. Recovery or mole fraction of one component in bottoms
19. Recovery or mole fraction of one component in distillate

2.3 MATHEMATICAL SOLUTION TECHNIQUES

A wide variety of iterative solution procedures for solving non-linear algebraic equations have appeared in the literature. In general, these procedures make use of equation partitioning in conjunction with equation tearing and/or linearization by Newton-Raphson techniques.

Early attempts to solve these equations resulted in the classical *stage-by-stage, equation-by-equation* calculational procedures of Lewis-Matheson in 1932 and Thiele-Geddes in 1933 based on equation tearing by solving simple fractionators with one feed and two products. Composition independent K-values and component enthalpies were generally employed. The Thiele-Geddes method was formulated to handle the case wherein the number of equilibrium stages above and below the feed, there reflux ratio, and the distillate flow rate are specified, and stage temperatures and interstage vapor (or liquid) flow rates are the iteration(tear) variables. Although widely used for hand calculations in the years immediately following its appearance in the literature, the Thiele-Geddes method was found often to be numerically unstable when attempts were made to program it for a digital computer. However, Holland and co-workers developed an improved Thiele-Geddes procedure called the *theta method*, which in various versions has been applied with considerable success.

The Lewis-Matheson method is also an equation-tearing procedure. It was formulated to determine stage requirements for specifications of the separation of two key components, a reflux ratio and a feed-stage location criterion. Both outer and inner iterations are required. The outer loop tear variables are the mole fractions or flow rates of nonkey components in the products. The inner loop tear variables are the interstage vapor (or liquid) flow rates. The Lewis-Matheson method was widely used for hand calculations, but it also proved often to be numerically unstable when implemented on a digital computer.

Rather than using an equation-by-equation solution procedure, Amundson and Pontinen in a significant development in 1958, showed that MESH equations could be combined and solved component-by-component from simultaneous linear equation sets for all N stages by an equation-tearing procedure using the same tear variables as the Thiele-Geddes method. Although too tedious for hand calculations, such equation sets are readily solved with a digital computer.

In a classic study in 1964, Friday and Smith systematically analysed a number of tearing techniques for solving the MESH equations. They carefully considered the choice of output variable for each equation. They showed that no one technique could solve all types of problems. Current practice is based mainly on the BP, SR, Newton-Raphson, and inside-out methods.

Based upon above study, in this thesis, simulation of steady state multicomponent reactive distillation column will be developed. An equation tearing method is purposed for solving non-linear equations describing the distillation column.

CHAPTER 3

MODEL DEVELOPMENT

This Chapter discusses an investigation for the development of a mathematical model to describe underlying phenomena occurring in a multicomponent reactive distillation column. The model has been build by the basic equations of individual component and overall material balance, enthalpy balance, phase equilibria and reaction rate equation. It also considers the nonideal behavior for the system. Finally, it describes a method for the evaluation of minimum value of reflux ratio for a multicomponent reactive distillation column.

3.1 GENERAL

Fig. 3.1 depicts the distillation column having N equilibrium stages including a condenser and a reboiler. The stages are numbered from top to bottom with the condenser as the first stage and the reboiler as the N-th stage. It is assumed that one feed stream, one vapor side stream, one liquid side stream and one intercooler or interheater exist at each stage except for the condenser and reboiler.

Fig. 3.2 depicts an equilibrium stage where the vapor stream leaving the stage is in equilibrium with the liquid stream leaving the same stage.

3.2 MODEL BUILDING

Following assumptions are made to simplify the model:

1. The heat losses from the column walls are negligible.
2. The heat of mixing in both the vapor and liquid is negligible.
3. The increase in sensible heat of the components with increase in temperature through the column is negligible.
4. The heat of reaction is negligible compared to the enthalpy of the vapor phase.
5. The feed is a saturated liquid.
6. Vapor -liquid equilibrium is achieved on each plate.

7. The irreversible chemical reaction proceeds in the liquid phase only and is described by appropriate kinetic equation.
8. The molar vapor hold up is negligible compared to the molar liquid hold up.

There are generally four sets of equations, which must be satisfied in a calculation for the equilibrium stage accompanied by a chemical reaction. They are the material balance equations, the vapor-liquid equilibrium relationships, mole fraction summation equations, and the enthalpy balance equations. In case of a multicomponent reactive distillation column, the material and enthalpy balances should also include the terms expressing the influence of the reaction on the moles of various components. These are given below:

- Material balance for component i at stage j is:

$$L_{j-1}x_{i,j-1} - (V_j + G_j)\, y_{i,j} - (L_j+U_j)x_{i,j} + V_{j+1}y_{i,j+1} + F_j z_{i,j} \pm \Delta R_{i,j} = 0 \qquad (3.1)$$

The value of $\Delta R_{i,j}$ is positive when the i-th component is produced by the reaction and negative when it disappears.

- Phase equilibrium relation for component i at stage j is:

$$y_{i,j} - K_{i,j}\, x_{i,j} = 0 \qquad (3.2)$$

where $K_{i,j} = \gamma_{i,j}\, P_{i,j}^{*} / Z_{i,j}\, P$

- Summations of mole fraction of components yields the following expressions:

For vapor phase

$$\sum_{i=1}^{C} y_{i,j} - 1.0 = 0 \qquad (3.3)$$

For liquid phase

$$\sum_{i=1}^{C} x_{i,j} - 1.0 = 0 \qquad (3.4)$$

- Enthalpy balance at stage j is as follows:

$$L_{j-1}h_{j-1} - (V_j+G_j)H_j - (L_j+U_j)h_j + V_{j+1}\, H_{j+1} + F_j H_{f,j} - Q_j + \Delta R_{1,j} H_{r,j} = 0 \qquad (3.5)$$

where kinetic and potential energy changes are ignored.

The variables $K_{i,j}$, H_j, and h_j and ΔR_j are functions of temperature, pressure and compositions. If these relations are not included in equations and the four properties are not counted as variables, each equilibrium stage is defined only by the 2C+3 equations. A countercurrent cascade of N such stages, as shown in Figure 3.1, is represented by N(2C+3) such equations.

A conventional distillation column usually has one feed and two product streams. The following specifications are required for a column at steady state operation.

1. Number of stages in the column.
2. Quantity, composition, and thermal condition of the feed.
3. Type of condenser.
4. Column pressure.
5. Reflux ratio.
6. Temperature of the distillate or the total distillate rate.

For a column;number of stages, feed plate location, condenser type and condition of feed have been specified, the remaining variables to be obtained are as follows:

Vapor and liquid mole fractions (2CN), molar flow rates (2N), temperature at each stage (N), reboiler and condenser duties (2), and column pressure (1). Hence the number of variables in a column of N atages are [N(2C+3)+3] and the number of independent equations relating them are N(2C+3). Based upon this, the degree of freedom for this system becomes [(N(2C+3)+3) - N(2C+3)] i.e. equal to 3.

In other words, three variables can be taken as the design variables. In the present investigation on multicomponent reactive distillation, distillate flow rate, reflux ratio and column pressure have been considered as the specified variable and thus the above systems becomes fully defined one.

Equation (3.1-3.5) represents the model of the multicomponent reactive distillation systems. These equations are highly nonlinear in nature. So they invariably need the use of iterative method for their solution.

3.3 NONIDEAL BEHAVIOUR OF THE SYSTEM

Before attempting the solution of the model for the set of equations (3.1-3.5), it is necessary to discuss salient features of the systems.

Usually in case of multicomponent reactive distillation, association of one component occurs in vapor phase. This can be taken into account by introducing a correction factor (Z_i) into modified Raoults law which relates the mole fraction of a component in vapor phase with that in the liquid phase given by

$$y_i Z_i P = x_i \gamma_i P_i^* \qquad i = 1,\ldots\ldots,C \qquad (3.6)$$

Where

$$Z_A = \frac{1+(1+4k_A P_A^*)^{0.5}}{1+[1+4k\ P y_A(2-y_A)]^{0.5}} \qquad (3.7)$$

if A is the associating component(acetic acid), and

$$Z_i = \frac{2\{1-y_A+[1+4k\ P y_A(2-y_A)]^{0.5}\}}{(2-y_A)\{1+[1+4k\ P y_A(2+y_A)]^{0.5}\}} \qquad (3.8)$$

if i is non associating component. In this expression k_A is the dimerization equilibrium constant for pure component A, and k is the dimerization equilibrium constant of A in the mixture. It is usually a good assumption to consider $k = k_A$. Value of this can be calculated as

$\log k_A = C_1 + C_2/T$,where C_1 and C_2 are constants given in Table C-8 of Appendix C.

Here Z_i is the correction factor that allows us to convert a chemical equilibrium problem into a pseudo phase-equilibrium problem.

Activity model

Activity coefficient is another parameter of vital importance in multicomponent reactive distillation systems. There are various equations, which can be used for its determination such as NRTL, UNIQUAC, Wilson, Margules equations etc. In this investigation UNIQUAC equation has been employed as recommended by Kang et. al., 1992 to determine the value of activity coefficients.

UNIQUAC Equation

An equation for the liquid-phase activity coefficient for a component in a multicomponent mixture is:

$$\text{In}\,\gamma_i = \text{In}\,\gamma_i^C + \text{In}\,\gamma_i^R = \underbrace{\text{In}\,(\psi_i / x_i) + (\bar{Z}/2\, q_i\ \text{In}\,(\theta_i / \psi_i) + l_i - (\psi_i / x_i) \sum_{j=1}^{C} x_j l_j}_{\text{C.combinational}}$$

$$\underbrace{+\, q_i \left[1 - \text{In}\left(\sum_{j=1}^{C} \theta_j T_{ji} \right) - \sum_{j=1}^{C} \left(\frac{\theta_j T_{ij}}{\sum_{k=1}^{C} \theta_k T_{kj}} \right) \right]}_{R,residual} \qquad (3.10)$$

Where

$$l_j = \left(\frac{\bar{Z}}{2} \right) (r_j - q_j) - (r_j - 1)$$

The first term on the right-hand side account for *combinatorial* effects due to differences in molecule size and shape; the second term provides a residual contribution due to differences in intermolecular forces, where

$$\psi_i = \frac{x_i r_i}{\sum_{i=1}^{C} x_i r_i} = \text{Segment fraction}$$

$$\theta = \frac{x_i q_i}{\sum_{i=1}^{C} x_i q_i} = \text{area fraction}$$

Here, two structural parameters r (volume parameter) and q (surface parameter) are the relative number of segments per molecule, and the relative surface area of the molecule respectively, Z is defined as lattice coordination number set equal to 10, and

$$T_{ij} = \exp\left(\frac{u_{ji} - u_{ii}}{RT}\right)$$

Where $u_{i,j}$ and $u_{j,i}$ are binary interaction parameters.

3.4 DETERMINATION OF MINIMUM REFLUX RATIO

Reflux ratio plays an important role to affect the product quality and its economics. It is directly responsible to the requirement of utilities in a distillation column. Generally, the columns are operated at low values of reflux ratio to reduce the consumption of energy. Therefore, the determination of minimum value of reflux ratio is of paramount importance. It is quite often calculated by the equation recommended by Under-wood for ideal systems having constant relative volatility. It can not be applied to systems, which show non-ideal behavior and significant variation in the value of relative volatility. This section pertains to a method, which can be employed directly for the determination of minimum value of reflux ratio for nonideal systems.

Reflux ratio affects the vapor and liquid flow rates and thereby the material balance profiles. As the value of reflux ratio is decreased, the profiles move towards the equilibrium. At minimum value, one of the profiles ends as it reaches the other profile. In this situation infinite number of stages are required to achieve the desired separation. The value of reflux ratio corresponding to it is termed as minimum reflux ratio. The geometrical condition for it is that the tangent to saddle pinch profile at the point where the feed pinch profile just ends is a straight line through the feed composition.

Feed pinch and saddle pinch points are located by solving the following two equations:

$$s^* Y_i^S - (s^* + 1) X_i^S + X_{i,B} = 0 \qquad i = 1,2 \qquad (3.11)$$

$$r^* X_i^r - (r^* + 1) Y_i^r + X_{i,D} = 0 \qquad i = 1,2 \qquad (3.12)$$

In this the value of reflux ratio for which feed pinch, saddle pinch point and the feed composition are collinear is determined by solving the set of algebraic equations.

The details of this method are given in Appendix B.

Eqs (3.1-3.5) describe a model for multicomponent reactive distillation. The nonideal behavior for the system has been considered by the inclusion of activity coefficient and correction factor for association in vapor phase in the model. A method has also been described to calculate the value of minimum reflux ratio for multicomponent reactive distillation column. To solve the model a method has been described in the following chapter.

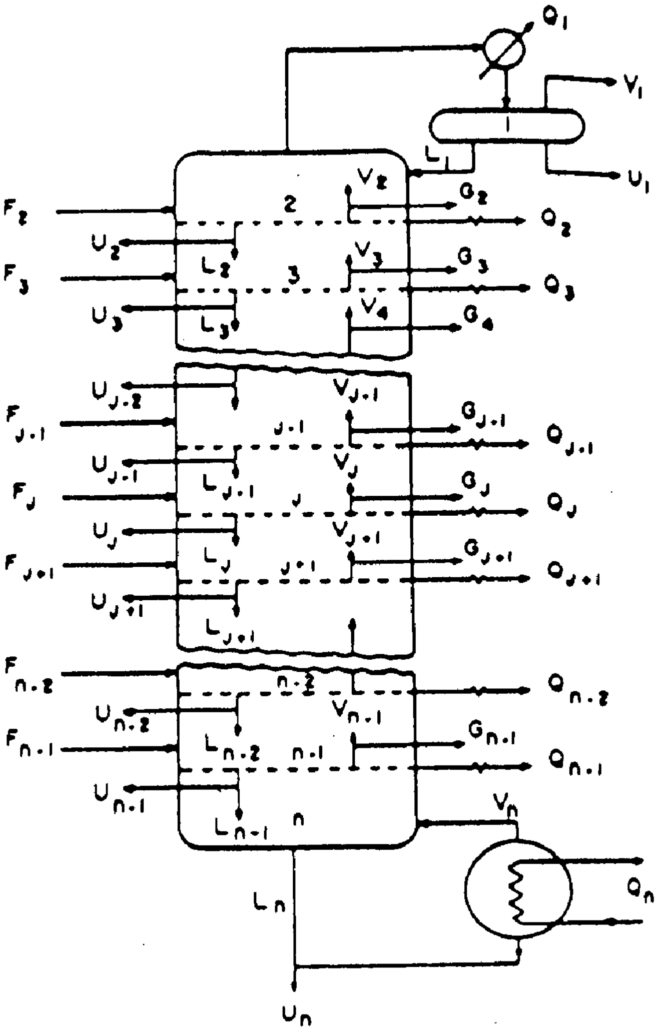

Fig. 3.1 Schematic diagram of distillation column

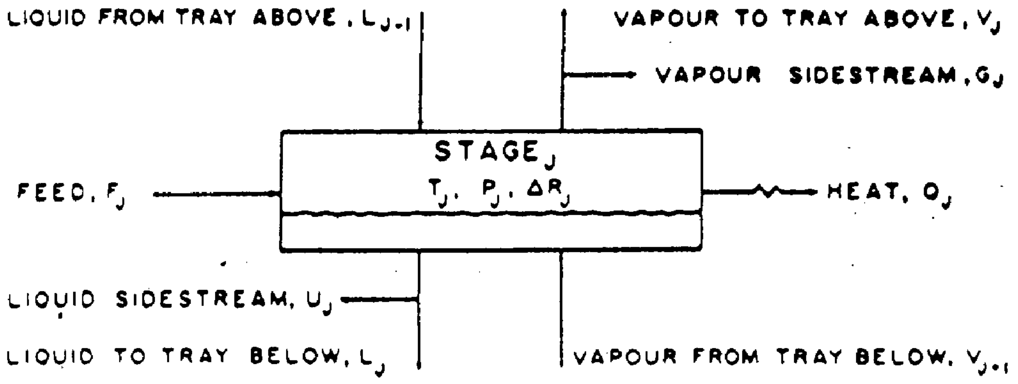

Fig. 3.2 Schematic diagram of equilibrium stage

CHAPTER 4

COMPUTATIONAL TECHNIQUES AND COMPUTER PROGRAM

This Chapter presents a method for solution of a model, which has already been discussed and developed in preceeding chapter, for multicomponent reactive distillation column. Material balance equations and phase equilibrium relationships provide a set of equations. This set of equations are expressed in the form a tridiagonal matrix, which has been solved by the use of a Gauss elimination algorithm. The solution of the model leads to the determination of vapor and liquid compositions profiles, molar flow rates, temperature profile, extent of reaction at stage j, overall conversion and the amount of heat duties for a reboiler and a condenser.

4.1 TRIDIAGONAL MATRIX ALGORITHM

A tridiagonal matrix is formed from a modified form of the material balance equations. Here, temperature T_j; vapor flow rate, V_j; and rate of reaction, ΔR_j at a stage j are considered as tear variables. The unknown liquid mole fractions, $x_{i,j}$ are calculated by employing Gauss elimination algorithm.

A total material balance equation can be used in place of Eqs. (3.3) and (3.4). It is obtained by combining these two equations and following the condition that summation of feed mole fractions is equal to one. The material balance equation, Eq. (3.1) is summed over all the components at each stage and then over stages 1 to j to give the following equation:

$$L_j = V_{j+1} + \sum_{k=2}^{j}(F_k - B_k - U_k) - D \qquad (4.1)$$

Where,

$D = V_1 + U_1$

Following modified material balance equations are obtained by eliminating L by the use of Eq. (4.1) and substituting the value of y from Eq.(3.2).

The result for each component and each stage is as follows, where the i subscripts have been deleted from the A, B, C and D terms:

$$A_j x_{i,j-1} + B_j x_{i,j} + C_j x_{i,j+1} = D_j \qquad (4.2)$$

It can also be written in following matrix form:

$$\left|\begin{array}{cccccccc} B_1 & C_1 & 0 & \cdot & \cdot & \cdot & \cdot & 0 \\ A_2 & B_2 & C_2 & \cdot & \cdot & \cdot & \cdot & 0 \\ & \cdot & \cdot & \cdot & \cdot & & \cdot & \cdot \\ & \cdot & \cdot & \cdot & \cdot & & \cdot & \cdot \\ & \cdot & \cdot & \cdot & \cdot & & \cdot & \cdot \\ & \cdot & \cdot & \cdot & \cdot & & \cdot & \cdot \\ & \cdot & \cdot & \cdot & \cdot & & \cdot & \cdot \\ 0 & \cdot & \cdot & \cdot & \cdot & A_{N-1} & B_{N-1} & C_{N-1} \\ 0 & \cdot & \cdot & \cdot & \cdot & 0 & A_N & B_N \end{array}\right| \left|\begin{array}{c} x_{i1} \\ x_{i2} \\ \cdot \\ \cdot \\ x_{ij} \\ \cdot \\ \cdot \\ x_{iN-1} \\ x_{iN} \end{array}\right| = \left|\begin{array}{c} D_1 \\ D_2 \\ \cdot \\ \cdot \\ D_j \\ \cdot \\ \cdot \\ D_{N-1} \\ D_N \end{array}\right|$$

Where

$$A_j = L_{j-1} = V_j + \sum_{k=2}^{j-1}(F_k - G_k - U_k) - D \qquad 2 \le j \le N \qquad (4.3)$$

$$B_j = -[(V_j + G_j)K_{ij} + V_{j+1} + \sum_{k=2}^{j}(F_k - G_k - U_k) - D + U_j] \qquad 1 \le j \le N \qquad (4.4)$$

$$C_j = V_{j+1} K_{ij+1} \qquad 1 \le j \le N-1 \qquad (4.5)$$

$$D_j = -F_j z_{ij} \pm \Delta R_j \qquad 1 \le j \le N \qquad (4.6)$$

4.2 SOLUTION PROCEDURE

To solve the above equations, values of $K_{i,j}$, T_j, V_j, and ΔR_j are required. For this an initial set of V_j values is taken based on the assumption of constant molal flow rates.

A initial set of T_j values is also computed by computing a temperature at a condenser and a reboiler. The approximate of condenser and reboiler temperature are obtained by making an estimate of top and bottom compositions. A linear temperature profile is assumed between the condenser and reboiler.

The value of equilibrium constant, $K_{i,j}$ is obtained by the following relationship

$$K_{i,j} = P_{i,j}^*/P \tag{4.7}$$

Where vapor pressure, P^* is expressed as a function of temperature, T by the following equation:

$$\ln(P_{i,j}^*) = A + B/(T_j+C) + D\ln(T_j) + ET_j^F \tag{4.8}$$

where value of constants are given in Table C-4 of Appendix C.

From the above liquid mole fraction, $x_{i,j}$; is calculated which in turn leads to the determination of $y_{i,j}$ by the use of Eq. (3.2).

Using these values of $x_{i,j}$ and $y_{i,j}$, the values of equilibrium constant. $K_{i,j}$ are again calculated by

$$K_{i,j} = \gamma_{i,j} P_{i,j}^*/Z_{i,j} P \tag{4.9}$$

Here, activity coefficient (γ) of ith component at jth stage are dependent on liquid mole fraction and the correction factor (Z) of ith component at jth stage are dependent on vapor mole fraction.

Values of activity coefficients ($\gamma_{i,j}$) and correction factor ($Z_{i,j}$) are calculated by Eqs. (3.10) and (3.7 & 3.8).

The solution of equation (4.2) for x_{ij} has been obtained by use the Gauss elimination method. Using this algorithm, values of x_{ij} are calculated by first evaluating x_{iN} and receding backward with j decreasing until x_{ij} is reached. These equations are shown as follows:

$$\begin{aligned}
&x_{iN} = q_N \\
&x_{ij} = q_j - p_j x_{ij+1} && 1 \le j \le N-1 && (4.10) \\
&p_1 = C_1/B_1 \\
&q_1 = D_1/B_1 \\
&p_j = C_j/(B_j - A_j p_{j-1}) && 2 \le j \le N-1 \\
&q_j = (D_j - A_j q_{j-1})/(B_j - A_j p_{j-1}) && 2 \le j \le N-1
\end{aligned}$$

When applied in this fashion, it generally avoids build-up of computer truncation errors because usually none of the steps involves subtraction of nearly equal quantities. Furthermore, computed values of $x_{i,j}$ are almost always positive.

For each iteration, the computed set of $x_{i,j}$ values for each stage will, in general, not satisfy the summation constraint given by (3.4), we will normalise the set of computed $x_{i,j}$ values by the relation.

$$(x_{i,j})_{normalised} = \frac{x_{i,j}}{\sum_{i=1}^{C} x_{i,j}} \tag{4.11}$$

These normalized values are used for all subsequent calculations involving $x_{i,j}$ during the iteration.

Calculation of reaction rate at each stage is expressed in terms of a tray hold up, liquid compositons, molar volume and temperature.

For the production of ethyl acetate from ethanol-actic acid, reaction rate term ΔR_j (Suzuki et. al., 1971) is as follows:

$$\Delta R_j = K_{Rj}\, \phi_j \left(\frac{x_{1j}}{\sum_{i=1}^{C} \rho_{ij} x_{ij}} \right)^2 10^6 \tag{4.12}$$

Where,K_R is expressed as a function of temperature, T which is as follows:

$$\log K_{Rj} = \frac{-2.71 \text{ x } 10^3}{T_j} + 3.70$$

Similarly, for the production of methyl acetate, the reaction rate term ΔR_j (Hinshelwood, C.N. taken from Bamford, C.H., 1972) is as follows:

$$\Delta R_j = K_{Rj}\phi_j \left(\frac{1}{\sum_{i=1}^{C} \rho_{ij} x_{ij}} \right)^2 \frac{x_{1j}\, x_{2j}\, x_c}{x_{2j} + K_1\, x_{3j}} \tag{4.13}$$

Where 1, 2, 3 and c represents acetic acid, methanol, water and catalyst (sulphuric acid) respectively. In this equation K_R and K_1 are related to temperature by the following relationships:

$K_1 = 1000\ ((0.11 + 0.0007043t^{1.556})\ \rho_{2j})^{-1}$
Where t is in °C.

and $K_R = 1.2 \times 10^6 \exp(-10{,}200/RT)$

Muller's method is employed for the solution of mole fraction summation equations to obtain temperature profile in the column. Muller's iterative method has been employed because it is reliable and does not require the calculation of derivatives. It requires three initial assumptions of T_j. For each assumption, the value of S_j is computed from the following relationship:

$$S_j = \sum_{i=1}^{C} K_{i,j} x_{i,j} - 1.0 \tag{4.14}$$

The three sets of (T_j, S_j) are fitted into a quadratic equation for S_j in terms of T_j. The resulting quadratic equation is then solved to determine the value of T_j for S_j=0. The validity of this value of T_j is examined by using it to compute S_j in (4.11). Above step involving the formation of quadratic equation and its checking is repeated with the three best sets of (T_j, S_j) until desired convergence tolerance is achieved.

Liquid and vapor enthalpies are calculated, which are utilised to calculate condenser and reboiler duty.

Heat duty of the condenser is derived from the enthalpy balance about the condenser, which is as follows:

$$Q_c = -V_1H_1+V_2H_2+(L_1+U_1)\, h_1 \tag{4.15}$$

And reboiler duty (Q_R) is determined by taking heat balance around the entire column. It is as follows:

$$Q_R = V_1H_1 + U_1h_1 + Bh_N + Q_C + \sum_{j=2}^{N-1}(G_jH_j + U_jh_j - F_jH_{F_j}) \tag{4.16}$$

Substitution of total material balance equation into enthalpy equations gives a vapor profile, which is as follows:

$$V_{j+1} = \frac{(V_j + G_j)(H_j - h_j) + L_{j-1}(h_j - h_{j-1}) - F_j(H_{Fj} - h_j)}{H_{j+1} - h_j} \tag{4.17}$$

Convergence Criteria

The solution procedure is considered to be converged when sets of $T_j^{(k)}$ and $\Delta R_j^{(k)}$ values are within a prescribed tolerance for corresponding sets of $T_j^{(k-1)}$ and $\Delta R_j^{(k-1)}$ values, where k is the iteration index. Convergence criterions are as follows:

1. $$\sum_{j=1}^{N}\Delta T_j^2 = \sum_{j=1}^{N}((T_j)_k - (T_j)_{k-1})^2 \le 0.01N \tag{4.18}$$

and

2. $$|TR_k - TR_{k-1}| \le \varepsilon \tag{4.19}$$

where, TR is total mole of reaction in a column.

In this investigation, ε has been taken equal to 10^{-5}.

4.3 PHYSICAL AND THERMODYNAMIC DATA

Enthalpies: Enthalpies of all the components have been calculated with respect to the enthalpies of components in liquid state, at a reference temperature of 298 K. At this reference temperature, the enthalpies of the components in the liquid state are assumed to be equal to zero.

Enthalpy correlation and related data has been given in Table C-6 and C-7 of Appendix C.

Activity Coefficients: Value of activity coefficients are calculated by UNIQUAC method. Binary interaction parameters and structural parameters are given in Table C-1 and C-2 of Appendix C.

Vapor Pressure: The values of constants for calculating vapor pressure are listed in Table C-4 of Appendix C.

Molar Volume: The correlation and related data for calculating molar volume has been listed in Table C-5 of Appendix C.

4.4 ALGORITHM FOR MULTICOMPONENT REACTIVE DISTILLATION COLUMN

1. Assume an initial vapor rate profile by means of constant molal overflow, linear temperature profile and approximate reaction rate profile
2. Total condenser is considered and is assumed to be first stage in the column.
3. The liquid interstage flow rates L_j are calculated
4. Rate constant (K_{ij}) is calculated depending whether it is composition dependent or independent.
5. Tridiagonal matrix with elements A_j, B_j, C_j and D_j is formed.
6. Matrix is solved for liquid compositions (x_{ij}) by using Gauss elimination method.
7. The compositions of liquid phase are normalised.
8. Compositions in vapor phase are calculated.
9. Calculated values of liquid compositions and temperatures are substituted into the reaction rate term, and ΔR_j is calculated.
10. Muller's method is employed on summation equations for the convergence of temperature.

11. Liquid and vapour enthalpies are calculated.
12. Heat duties for a condenser and a reboiler are calculated.
13. Enthalpy balance equation is solved for calculating vapor profile.
14. Steps (3) to (13) are repeated until the reaction term converges.
15. Value of activity coefficients is calculated by UNIQUAC equation dependent on liquid compositions.
16. Value of association factors in vapor phase is determined by Marek's equation dependent on vapor compositions.
17. Steps (3) through (14) are repeated until the desired convergence is achieved.

4.5 COMPUTATION OF MINIMUM REFLUX RATIO

With a new set of transformed composition variables it is possible to reduce the conservation equations that describe the simple distillation of reactive mixtures to a form, which is identical to that for non-reactive mixtures. One can use this set of transformed composition variables to derive the design equations for reactive distillation columns. These new equations are identical, in form to the corresponding equation for conventional distillation. This leads to the development of a general method for calculating minimum reflux ratios in reactive distillation columns.

The geometrical condition for minimum reflux is that the tangent to the saddle pinch profile at the point where the feed pinch profile just ends (at its feed pinch) is a straight line through the feed composition. This procedure finds the value of r, which makes the feed pinch point, the saddle pinch point and the feed composition collinear.

The feed pinch and saddle pinch points can be located by

$$s^* Y_i^s - (s^* + 1) Y_i^s + X_{i,B} = 0 \qquad i=1,2 \tag{4.20}$$

$$r^* Y_i^r - (r^* + 1) Y_i^r + Y_{i,D} = 0 \qquad i=1,2 \tag{4.21}$$

The value of r_{min} can be calculated by using the following algorithm to solve these equations.

4.6 ALGORITHM FOR MINIMUM REFLUX RATIO

1. Values of x_F, x_D and x_B are specified. These are converted into transformed composition variables.
2. A value for r_{ext} is assumed.
3. Calculate s_{ext} using Eq. (B.18) of Appendix B.
4. If Eqs. (4.20) and (4.21) are solved for the pinch components(i.e. X_r and X_s)
5. Check whether X_r, X_s and X_F are collinear i.e. check whether

   $(X^S_2 - X_{2,F}) (X^r_1 - X_{1,F}) - (X^r_2 - X_{2,F}) (X^S_1 - X_{1,F}) = 0$

$$\frac{(X_{D,2} - X_{F,2})((R+1)K_{D,2} + R)}{(X_{D,1} - X_{F,1})((R+1)K_{D,1} + R)} - \frac{(X_{B,2} - X_{F,2})((S+1-S \times K_{W,2})}{(X_{B,1} - X_{F,1})((S+1-S \times K_{W,1})} = 0 \tag{4.22}$$

6. Eq. (4.22) is found to be satisfied, the chosen value of r_{ext} is equal to r_{min}. Otherwise, go to step (2) and repeat this procedure.

4.7 COMPUTER PROGRAM

Computer programs are developed in FORTRAN VISUAL WORKBENCH to perform the computational and simulation work in this thesis. The details of the program, associated files are described below:

Main Program

The major parts of computations are done in main program. We have developed a efficient program which calculates temperature profile, liquid and vapor compositions at each stage, molar flow rate profiles along the multicomponent reactive distillation column. Extent of reaction at each stage, overall reaction and conversion are also calculated with the help of suitable reaction rate equations available in literature. Reboiler and condenser duties are also among the outputs of program. It takes few iterations to converge to solution. Following are the subroutines utilised in the main program

ACTIVE: It uses the UNIQUAC method to calculate the liquid phase activity coefficients.

ZCOR: It is used for calculating association factors (Z_{ij}) for components in vapour phase.

PS: It uses the Antoine's equation to calculate the vapour pressure.

CTEMP: It returns the value of summation equation whenever called.

MULL: It returns the value of converged temperature at a stage.

Minimum Reflux ratio

This program calculates the minimum reflux ratio for multicomponent reactive distillation column. It is employed for calculation of minimum reflux ratio for Methanol-Acetic acid system. For computing, distillate and feed compositions along with molar flow rates are provided as inputs and program gives the value of minimum reflux ratio.

CHAPTER 5

RESULTS AND DISCUSSION

This Chapter discusses the results obtained from a simulation model for a multicomponent reactive distillation column. Basically, it includes the validation of present model and methodology to solve it by comparing the results so obtained with those available in literature and extending the model for simulation studies of another system. It has also been used to obtain the parametric effect of operating variables namely stage hold up, feed molar flow rate, number of stages, reflux ratio, feed composition and column pressure on top ester mole fraction and percent conversion of acetic acid into ester for methanol-acetic acid system. It also discusses the results of a distillation column with two feeds, in which acetic acid feed entered separately at a higher feed position. Minimum reflux ratio has also been computed by using the method described earlier. Finally, multicomponent reactive distillation column has been solved using HYSYS package.

In this investigation, ethanol-acetic acid system has been considered for the testing model because data for this system are available in literature. These data pertains to Suzuki et. al.,1971. Further the model, after examining its validity over ethanol-acetic acid system has been extended to methanol-acetic acid system, which is quite similar in nature to previous one. Here, it may be mentioned that data are not available for methanol-acetic acid system. Hence, the results obtained on this system could not be checked.

5.1 MODEL VALIDATION AND COMPARISON

The model developed for multicomponent reactive distillation has been validated by employing it on ethanol-acetic acid system for which the simulated results due to Suzuki et. al., 1971 are available.

System Description: A conventional multicomponent reactive distillation column for ethanol-acetic acid system has been considered. The column is operated at atmospheric pressure. It has 13 number of trays including a reboiler and a total condenser. A feed of 0.1076 moles per minute is fed to the column. The distillate flow rate is 0.0208 mol/min.

The feed is a saturated liquid. The reflux ratio is taken to be as 10. The feed stage location is sixth from the top and has the following molar composition:

Acetic acid = 0.4963
Ethanol = 0.4808
Water = 0.0229
Ethyl acetate = 0.0000

Considering that the value of vapor-liquid equilibrium constant depends on temperature as given in Table C.9 of Appendix. A linear temperature profile, a vapor flow rate profile corresponding to a constant molal flow rate and a value of conversion of reaction at each stage are assumed by approximate calculation for initialisation.

The hold up at each stage has been taken as 300 ml except for a reboiler where its value has been taken to be 1000 ml.

For the validation of the model, the reaction between acetic acid and ethanol has been considered to be irreversible so that the results obtained from the model simulation may be directly compared with the values available in literature due to Suzuki et. al., 1971. The simulated values as well as those available in literature are given in Tables A.2 and A.1 of Appendix A. There comparisons have been shown in Figures 5.1 to 5.5 for better interpretation.

Figure 5.1 shows a comparison of temperature profiles obtained by simulation with that due to Suzuki et. al., 1971 for ethanol-acetic acid system. This figure indicates an excellent matching between the two.

Figures 5.2 and 5.3 shows a comparison of stage-wise liquid phase and vapour phase compositions of the components obtained in this study respectively. These plots also contain data for above cases due to Suzuki et. al., 1971. As can be seen again an excellent agreement between the two is observed for all the components from top to bottom of the column.

Figure 5.4 shows a comparison of molar flow rates obtained by simulation with that due to Suzuki et. al., 1971. This figure also indicates an excellent matching between the two.

Comparison of stage-wise rate of production of ethyl acetate is shown in Fig. 5.6. From this plot it is seen that no production of ethyl acetate occurs up to the fifth stage. Its production starts from fifth stage onwards and a steep increase in production rate is observed at 13th stage. Further, in this case also an excellent agreement exists between the two.

In the present case condenser and reboiler duties calculated are 2309 cal/min and -2296 cal/min, respectively. The change in number of moles for all the components is 0.0127 and the conversion is 24.51% with respect to ethanol. These values compare very close to the values reported by Suzuki et. al., 1971. The reported values are 0.01261 and 24.37 % for change in number of moles for all the components and the percent conversion with respect to ethanol respectively.

From the above, it can be concluded that the present model and the methodology of its solution has succeeded in computing liquid and vapour molar flow rate profiles, temperature profiles, composition profiles and rate of production of product (ethyl acetate), which are in excellent agreement with the values available in literature.

On the basis of above, it can be said that ethanol-acetic acid simulation results clearly demonstrates the adequacy of the modeling process and validates its extension to methanol-acetic acid multicomponent reactive distillation column.

5.2 MODEL APPLICATION TO METHANOL-ACETIC ACID SYSTEM

The manufacture of high-purity methyl acetate via the reaction of methanol and acetic acid is difficult because of reaction equilibrium limitations and the formation of methyl acetate-methanol and methyl acetate-water minimum-boiling azeotropes. Conventional processes use schemes with multiple reactors in which a large amount of excess of one of the reactants is used to achieve the high conversion of the reactant. In some cases a series of vacuum and atmospheric distillation columns are used to change the composition of the methyl acetate-water azeotrope. The refined methyl acetate is separated from the unconverted reactants, and the methyl acetate-methanol azeotrope is then recycled to the reactors. Other schemes include the use of several atmospheric distillation columns and a column with an extractive agent, such as ethylene glycol monomethyl ether, to act as an entrainer to separate the methyl acetate from methanol.

In multicomponent reactive distillation column, enrichment beyond the methyl acetate-methanol azeotrope can occur. Chemical reaction in this system is as follows:

$$CH_3OH + CH_3COOH \rightarrow CH_3COOCH_3 + H_2O$$

Methanol Acetic acid Methyl acetate water

System Description: Operating conditions and specifications for this system is same as for ethanol-acetic acid. These have been described in Section 5.1. The molar composition of the feed is as follows:

Acetic Acid = 0.6290
Methanol = 0.3316
Water = 0.0266
Methyl acetate = 0.0128

As can be seen from the above molar composition of the feed, it usually contains small amount of methyl acetate and water. These components are formed in the feed tank by above chemical reaction. An important point worth mentioning is that the above chemical reaction occurs in presence of a small quantity (0.8% of reflux rate) of sulphuric acid as the catalyst. It is fed into the column through the reflux at the top.

The vapour-liquid equilibrium behaviour of the quaternary system methyl acetate-methanol-water-acetic acid was modelled by using the UNIQUAC equation in combination with Marek's method for the association of acetic acid.

Table A.3 of Appendix A provides the results of simulation of methanol-acetic acid multicomponent reactive distillation column. These have been clearly shown in Figures 5.6 to 5.10.

Figure 5.6 shows a temperature profile for the above system. The profile is found to be smooth except for a discontinuity at the feed point.

Figures 5.7 and 5.8 shows liquid and vapor phase composition profiles. For above systems respectively. It is also seen that both the plots have almost the same nature of curves. From these plots it can be inferred that mole fraction of methyl acetate (the most volatile component) increases up the column, methanol (the second most volatile component) in general decreases down the column, water and acetic acid (these being the two less volatile components) increases down the column. At the top of the column the vapor and liquid phases consisted mainly of methyl acetate and methanol although some traces of acetic acid and water were also present.

Fig. 5.9 shows inter stage liquid and vapor molar flow rates for methanol-acetic acid multicomponent reactive distillation column. As can be seen, there is a sudden increase in the liquid molar flow from stage 5 to stage 6. This might be due to the introduction of saturated liquid feed at stage 6. However, vapor molar flow rate remains nearly constant throughout the column.

Fig. 5.10 shows rate of production of methyl acetate across the column. As liquid hold up in the column is small, most of reaction occurs in the reboiler.

The change in number of moles for all the components is 0.0168 and the conversion is 24.867 % with respect to acetic acid and 47.157 % with respect to methanol. In the present case condenser and reboiler duties calculated are 1293 cal/min and –1030 cal/min, respectively.

5.3 PARAMETRIC STUDIES FOR METHANOL-ACETIC ACID SYSTEM

This Section discusses the effect of operating parameters namely stage hold up, feed molar flow rate, number of stages, reflux ratio, feed composition and column pressure on top ester mole fraction and percent conversion of acetic acid into ester for methanol-acetic acid systems. The chemical reaction is as follows:

$$\underset{\text{Methanol}}{CH_3OH} + \underset{\text{Acetic acid}}{CH_3COOH} \rightarrow \underset{\text{Methyl acetate}}{CH_3COOCH_3} + \underset{\text{water}}{H_2O}$$

Operating conditions and other specifications are the same as mentioned in case of methanol-acetic acid system in Section 5.2.

5.3.1 EFFECT OF STAGE HOLD-UP ON TOP ESTER MOLE FRACTION AND PERCENT CONVERSION

Figure 5.11 shows a plot between top ester mole fraction and stage hold up for the methanol-acetic acid system. From this figure it can be seen that an increase in the stage hold up causes an increase in mole fraction of methyl acetate (top ester). The chemical reaction occurs in liquid phase, which leads to increase the degree of completion of reaction due to increased residence time with increase in stage hold up.

Figure 5.12 shows a plot between percent conversion and stage hold up. It shows that with increase in stage hold up, percent conversion with respect to acetic acid increases.

5.3.2 EFFECT OF FEED FLOW RATE ON TOP ESTER MOLE FRACTION AND PERCENT CONVERSION

Fig. 5.13 shows a plot between top ester mole fraction and feed flow rate for the methanol-acetic acid system. From this plot, it is seen as feed flow rate is increased, top ester mole fraction continuously decreases however the rate of decrease becomes a small when feed flow rate change from 0.11 mol/min to 0.12 mol/min. This behaviour can be explained by the fact that an increase in feed flow rate causes the catalyst concentration in liquid phase to decrease. It may be mentioned here sulphuric acid acts as a catalyst and it is fed from top of the column. This decrease in the concentration of catalyst is responsible for decrease in the production of methyl acetate.

Fig. 5.14 shows a plot between percent conversion and feed flow rate. The above reason can be given for a decrease in the percent conversion with increase in feed flow rate.

5.3.3 EFFECT OF NUMBER OF STAGES ON TOP ESTER MOLE FRACTION AND PERCENT CONVERSION

Fig. 5.15 shows a plot between top ester mole fraction and number of stages. The feed location remains fixed at the centre of distillation column. This plot clearly indicates that an increase in number of stages also increases top ester mole fraction. An increase in number of stages means liquid and vapor will interact for more number of times resulting in enrichment of vapor with more volatile component. This increases top ester mole fraction.

Fig. 5.16 shows a plot between overall conversion and number of stages. This plot show that with increase in number of stages, the percent conversion will increase.

5.3.4 EFFECT OF REFLUX RATIO ON TOP ESTER MOLE FRACTION AND PERCENT CONVERSION

Fig. 5.17 shows that the top ester mole fraction increases with increase in reflux ratio. Even though the increase in the reflux ratio suppresses the reaction rate in the column, it can enhance the purity of the more volatile component in the distillate i.e. methyl acetate.

Fig. 5.18 shows that overall conversion decreased with increase of the reflux ratio, since the reactants are diluted with ester. This excess of ester causes lowering of boiling points and hence production rate goes down.

5.3.5 EFFECT OF FEED COMPOSITION ON TOP ESTER MOLE FRACTION AND PERCENT CONVERSION

Fig. 5.19 shows a plot between top ester mole fraction and feed composition. These plot shows that with increase in acetic acid mole fraction in feed, top ester mole fraction increases.

Fig. 5.20 shows a plot between percent conversion and feed composition. This shows that as the feed composition is varied, it is found that there is a minimum conversion at the acetic acid mole fraction in feed of 0.5. This is explained since the two definitions of conversion (5.1) and (5.2) are symmetrical and the reboiler concentrations of acetic acid and methanol are proportional to the respective feed concentrations.

The overall conversion can be expressed in one of the following forms:

$$\text{Conversion} = \frac{\mathrm{Fx}_{\mathrm{FA}} - (Dx_{DA} + Bx_{BA})}{\mathrm{Fx}_{\mathrm{FA}}} = \frac{\mathrm{Dx}_{\mathrm{DE}} + Bx_{BE}}{\mathrm{Fx}_{\mathrm{FA}}}, \quad \text{for } x_{\mathrm{FA}} \le 0.5 \qquad (5.1)$$

$$\text{Conversion} = \frac{\mathrm{Fx}_{\mathrm{FA}} - (Dx_{DA} + Bx_{BA})}{\mathrm{Fx}_{\mathrm{FM}}} = \frac{\mathrm{Dx}_{\mathrm{DE}} + Bx_{BE}}{\mathrm{Fx}_{\mathrm{FM}}}, \quad \text{for } x_{\mathrm{FA}} \ge 0.5 \qquad (5.2)$$

where F, D and B are the feed, top and bottom molar flow rates respectively, x_{FA} and x_{FM} are the acetic acid and methanol feed mole fractions, x_{DA} and x_{DE} are the acetic acid and ester top mole fractions, x_{BA} and x_{BE} are the acetic acid and ester bottom mole fractions.

5.3.6 EFFECT OF COLUMN PRESSURE ON TOP ESTER MOLE FRACTION AND PERCENT CONVERSION

Fig. 21 shows a plot between top ester mole fraction and column pressure.

Fig. 22 shows a plot between top ester mole fraction and percent conversion. Both the plots clearly indicate that with increasing column pressure, the top ester mole fraction and percent conversion will increase. This is due to higher operating pressure resulted in higher boiling points and thus increased the liquid and vapour temperatures in the column as well as the reaction rate constant. This resulted in a higher conversion.

On the basis of above studies, it can be said that increase in stage hold up, number of stages, reflux ratio, acetic acid feed composition and column pressure favours higher product yield i.e. top ester mole fraction but increase in feed flow rate shows reverse trend. It should be taken into account that no consideration is being given to the design aspect. The independent changes in parameters are considered.

5.4 MULTIPLE FEED COLUMN

A distillation column with two feeds, in which acetic acid feed entered separately at a higher feed position and methanol to the eleventh tray from the top, is considered. The feed flow rate of acetic acid and methanol is 0.0538 mole per minute each. Counter current flow of acetic acid and methanol occurs in a multicomponent reactive distillation column. Consequently, acetic acid acts as an extractive agent and distillation took place, sometimes resulting in top ester mole fraction higher than the azeotropic value (at 0.677 mole fraction of methyl acetate).

Fig. 5.23 displays the variation of acetic acid feed stage location. As the acetic acid feed position changed to approach the top, the top ester mole fraction increases.

The main advantage of this is that we can combine the reactive and extractive distillation in only one column, by a convenient choice for the introduction of acetic acid feed stage location.

5.5 SIMULATION OF ETHANOL-ACETIC ACID SYSTEM USING HYSYS

A conventional multicomponent reactive distillation column for ethanol-acetic acid system has been considered. The column is operated at atmospheric pressure. It has 13 number of trays including a reboiler and a total condenser. A feed of 0.1076 moles per minute is fed to the column. The distillate flow rate is 0.0208 mol/min. The feed is a saturated liquid. The reflux ratio is taken to be as 10. The feed stage location is sixth from the top and has the following molar composition:

Acetic acid = 0.4963
Ethanol = 0.4808
Water = 0.0229
Ethyl acetate = 0.0000

A reversible rate equation is taken as

$$r = K_1 c_A c_B - K_2 c_C c_D$$

where, $K_1 = 485\exp(-14300/RT)$

$K_2 = 123\exp(-14300/RT)$, T is in K.

Simultaneous correction method is employed for solution of multicomponent reactive distillation column. Heat of reaction is taken into considered. UNIFAC method is employed for calculation of activity coefficients, enthalpy calculations are done with the help of Soave-Redlich-Kwong equation.

Fig. 5.24 displays the temperature profile for column. It is found to be smooth except for a discontinuity at the feed point.

Fig. 5.25 and 5.26 displays the liquid and vapor composition profiles respectively.

Fig. 5.27 displays the interstage molar liquid and vapor rates profile.

Fig. 5.28 displays the relative volatility of all the components with respect to water.

Two important factors in the failure to achieve a high conversion and nearly pure products are (1) the highly nonideal nature of the quaternary mixture, accompanied by the large number of azeotropes, and (2) the tendency of the reverse reaction to occur. The change in number of moles for all the components is 0.0222 and the conversion is 63.26 % with respect to ethanol.

5.6 MINIMUM REFLUX CALCULATION

The minimum reflux is calculated for methyl acetate system. This method predicts a minimum reflux of 0.76, which is in good agreement with reported value of 0.78 [Barbosa and Doherty, 1988].

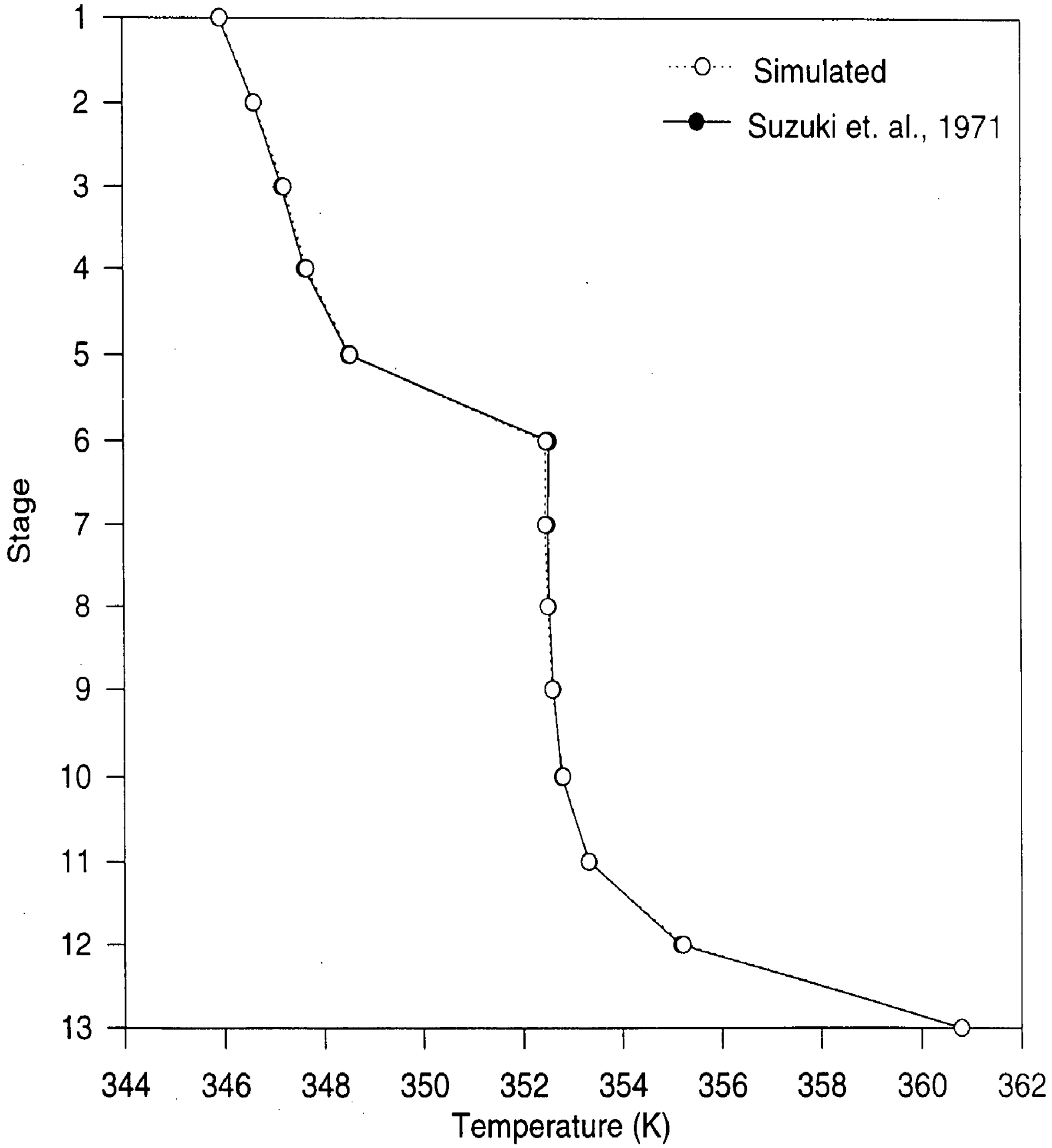

Fig. 5.1 Comparison of temperature profiles for Ethanol-Acetic acid

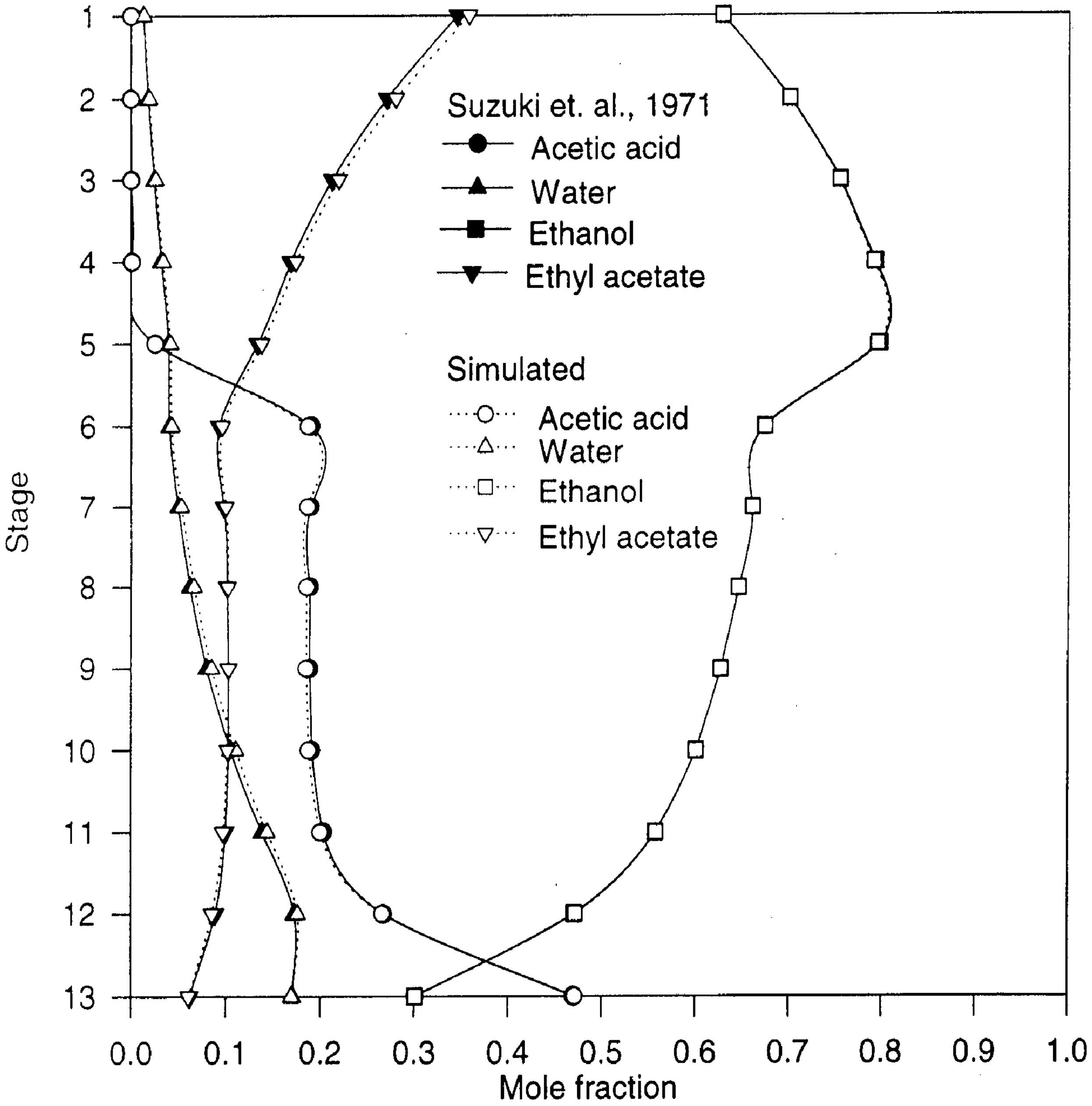

Fig. 5.2 Comparison of composition profiles in liquid phase for Ethanol-Acetic acid

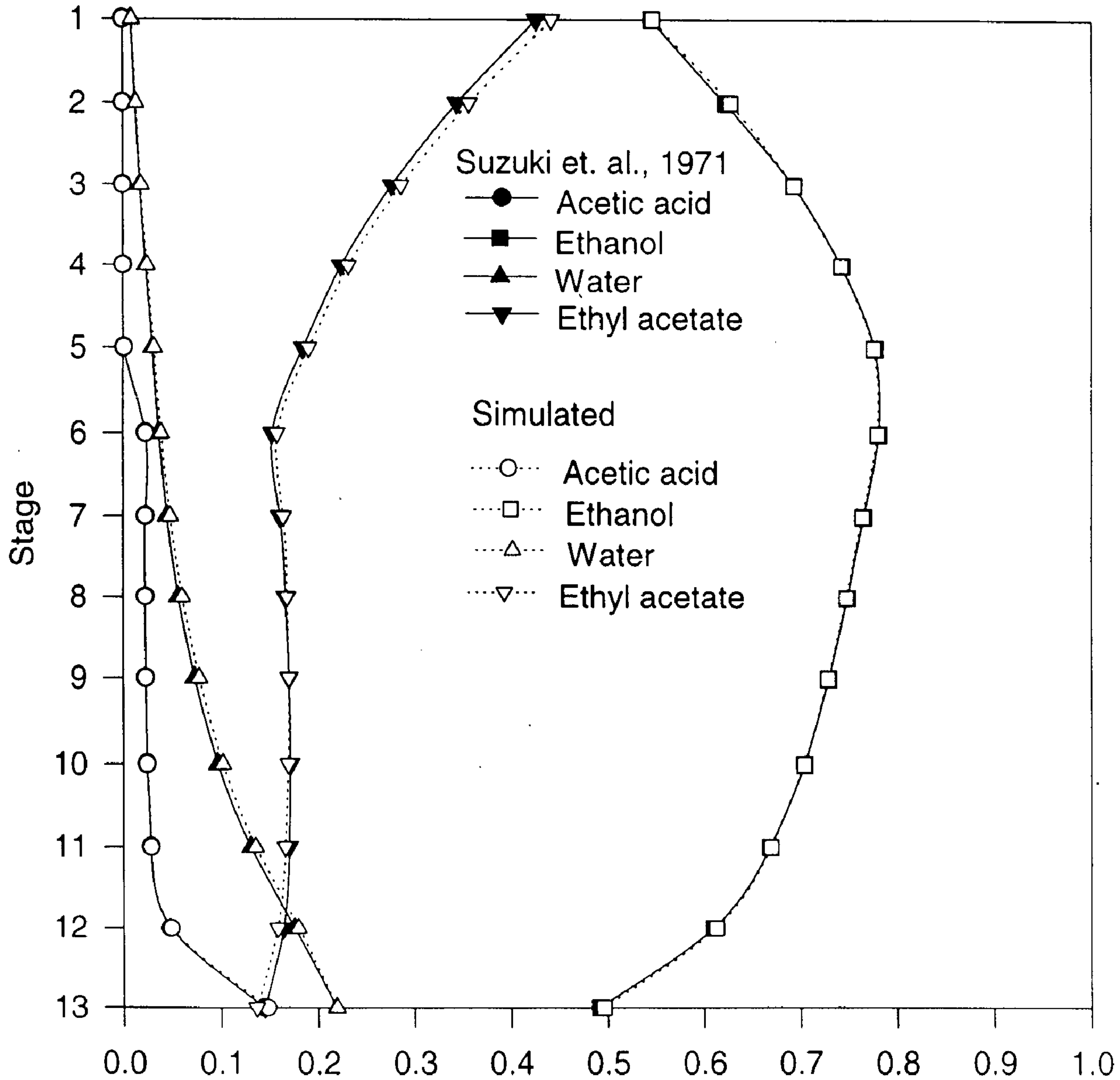

Fig. 5.3 Comparison of composition profiles in vapor phase for Ethanol-Acetic acid

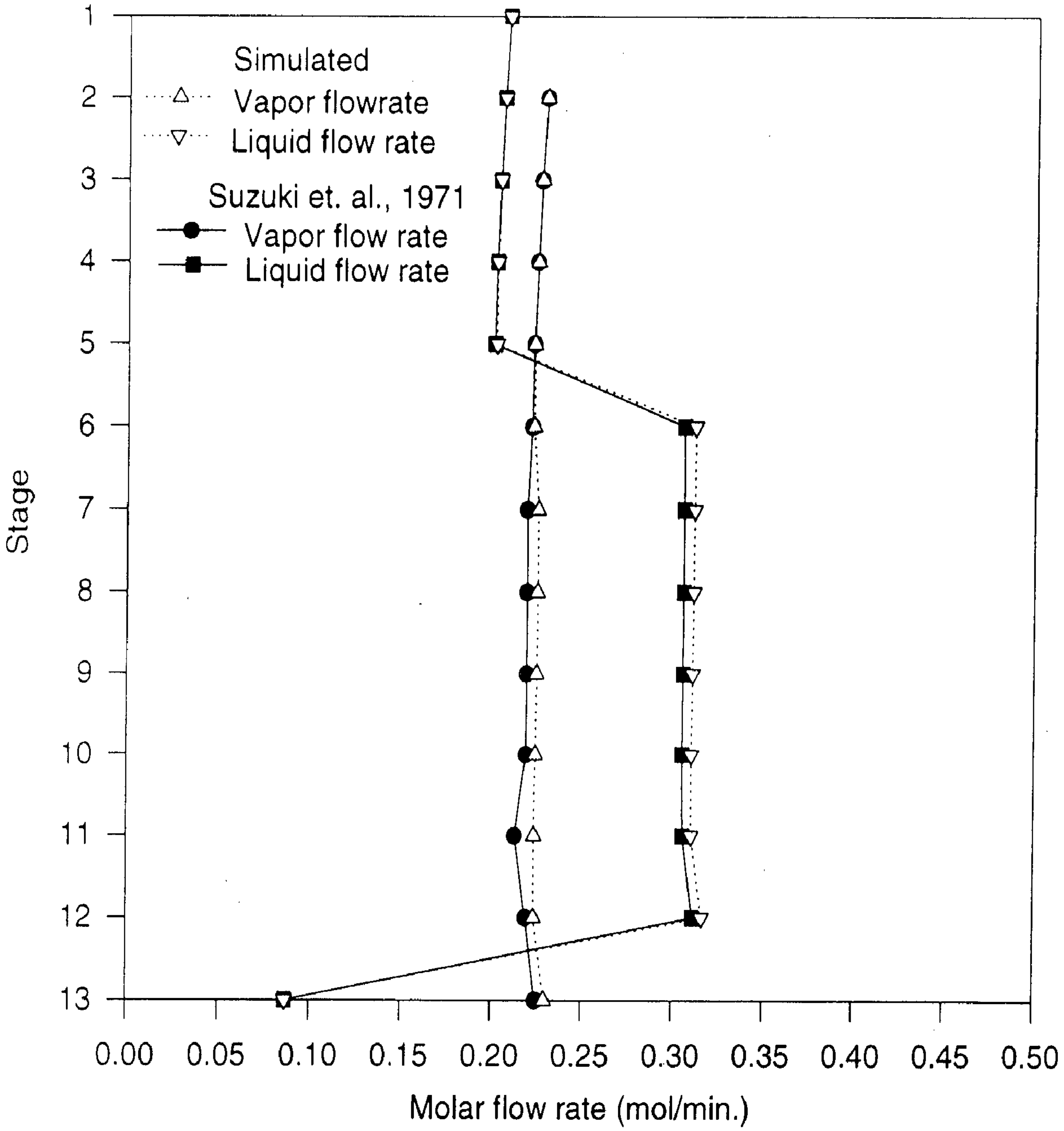

Fig. 5.4 Comparison of molar flow rate profiles for Ethanol-Acetic acid

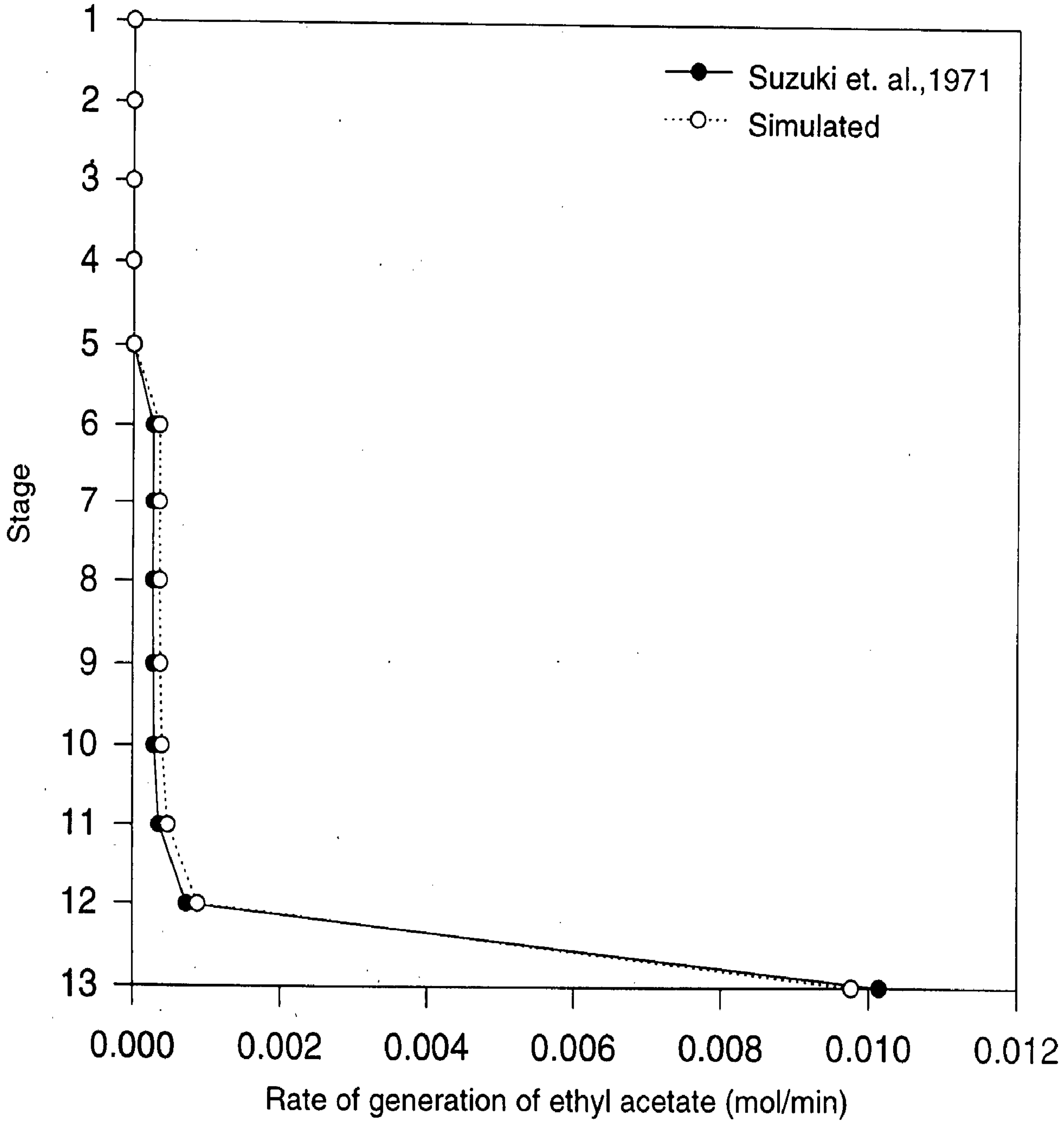

Fig. 5.5 Comparison of rate of generation of Ethyl acetate

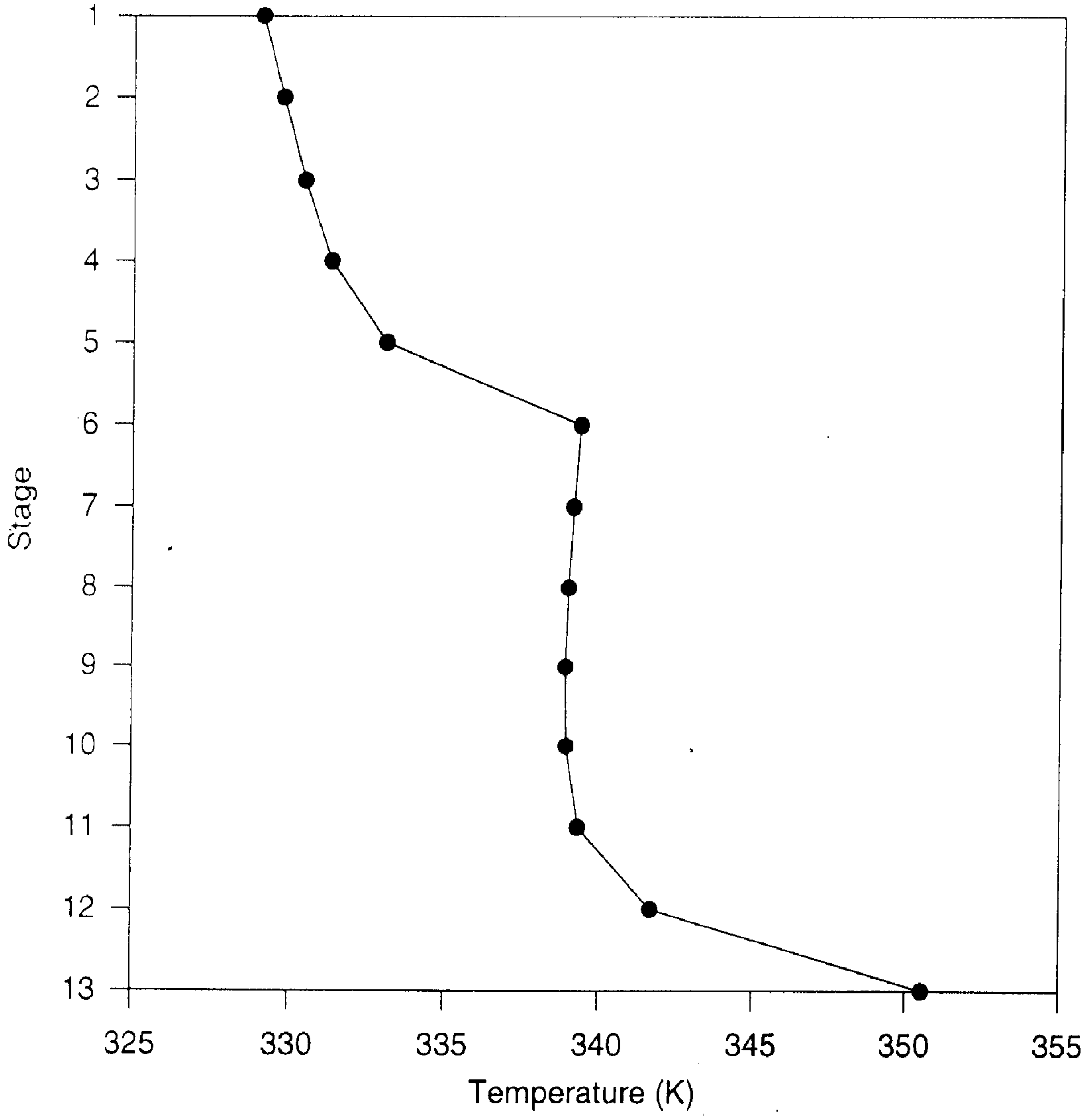

Fig. 5.6 Temperature profile for Methanol-Acetic acid

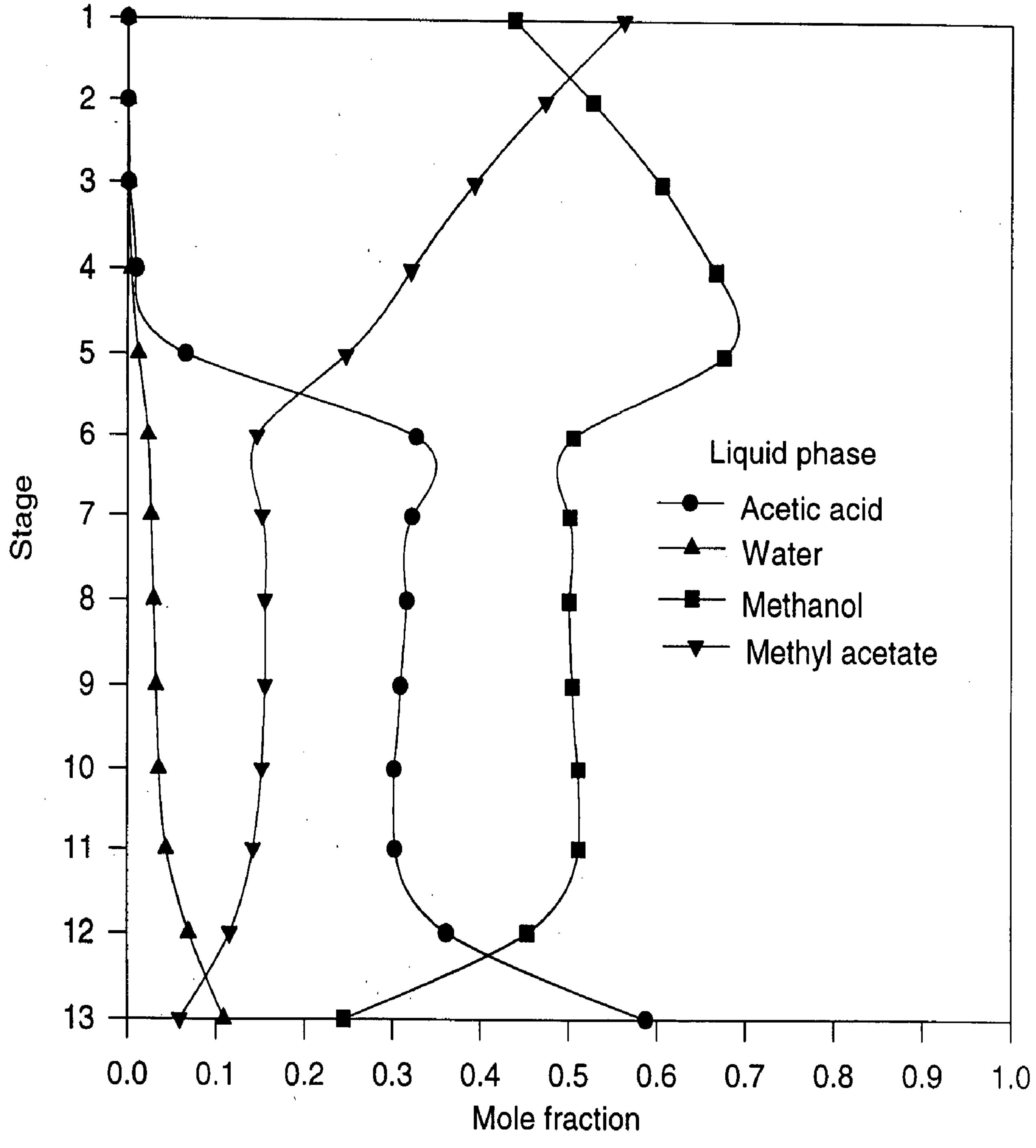

Fig. 5.7 Composition profiles in liquid phase for Methanol-Acetic acid

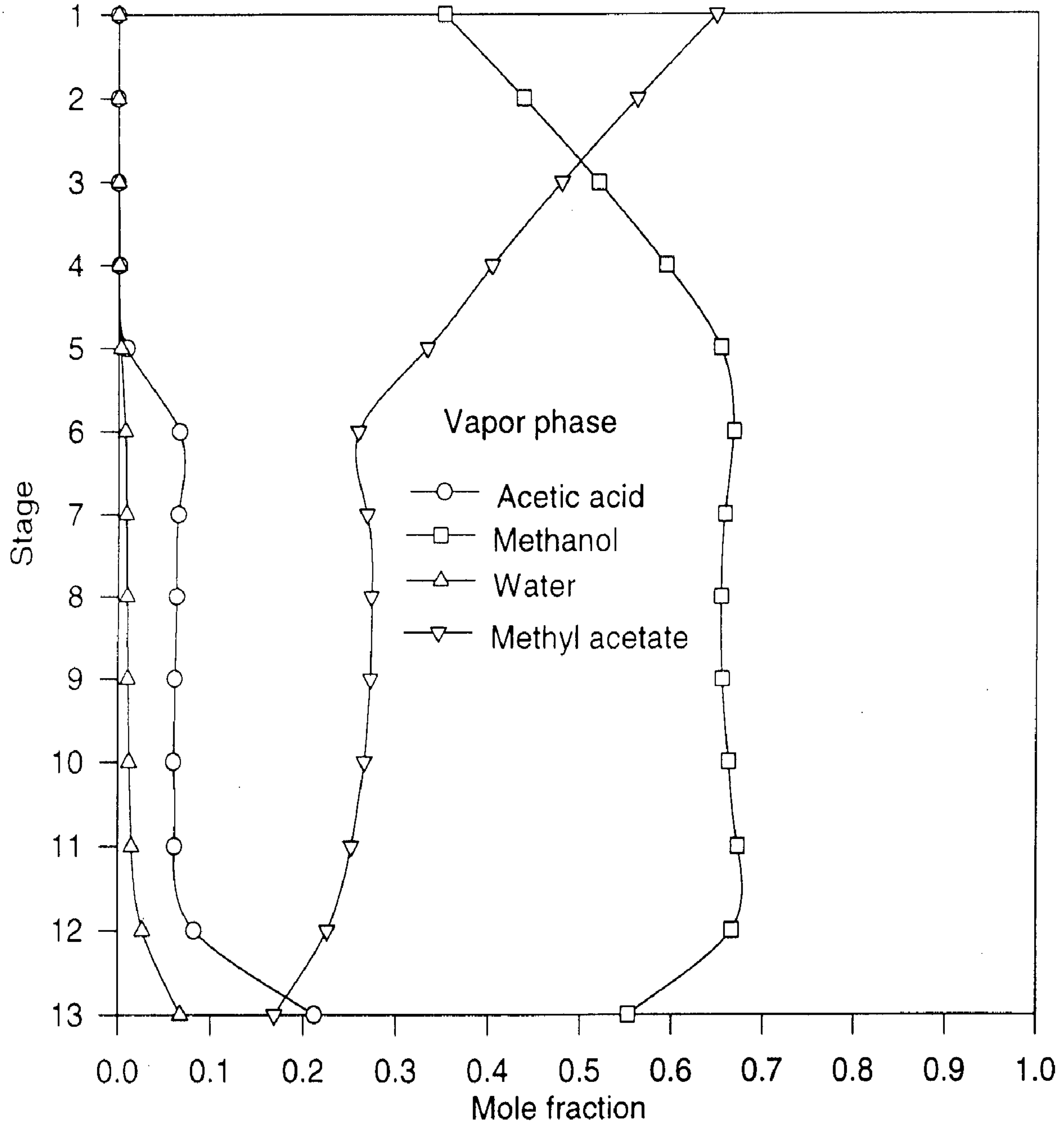

Fig. 5.8 Composition profiles in vapor phase for Methanol-Acetic acid

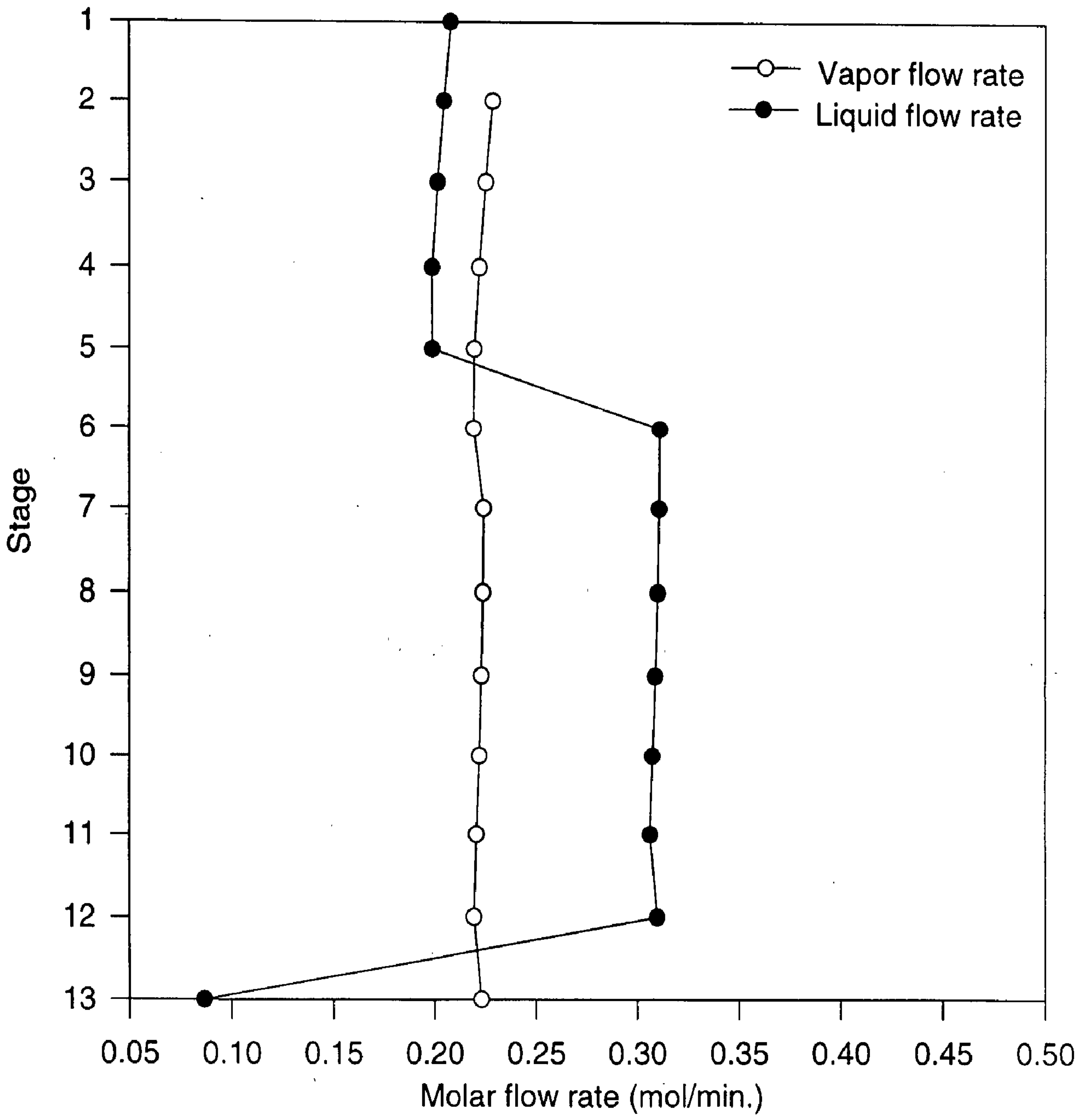

Fig. 5.9 Molar flow rate profiles for Methanol-Acetic acid

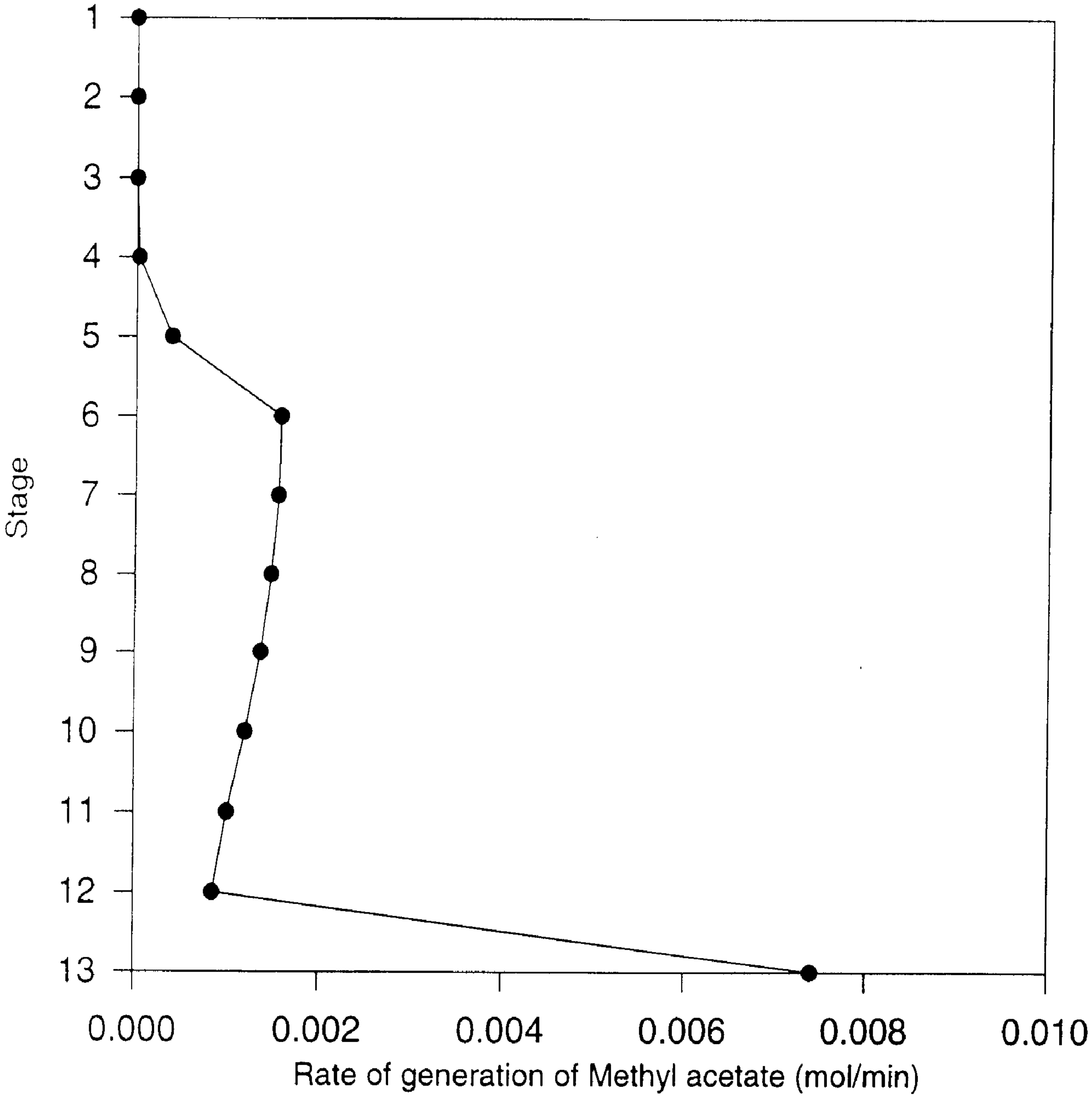

Fig. 5.10 Rate of generation of Methyl acetate

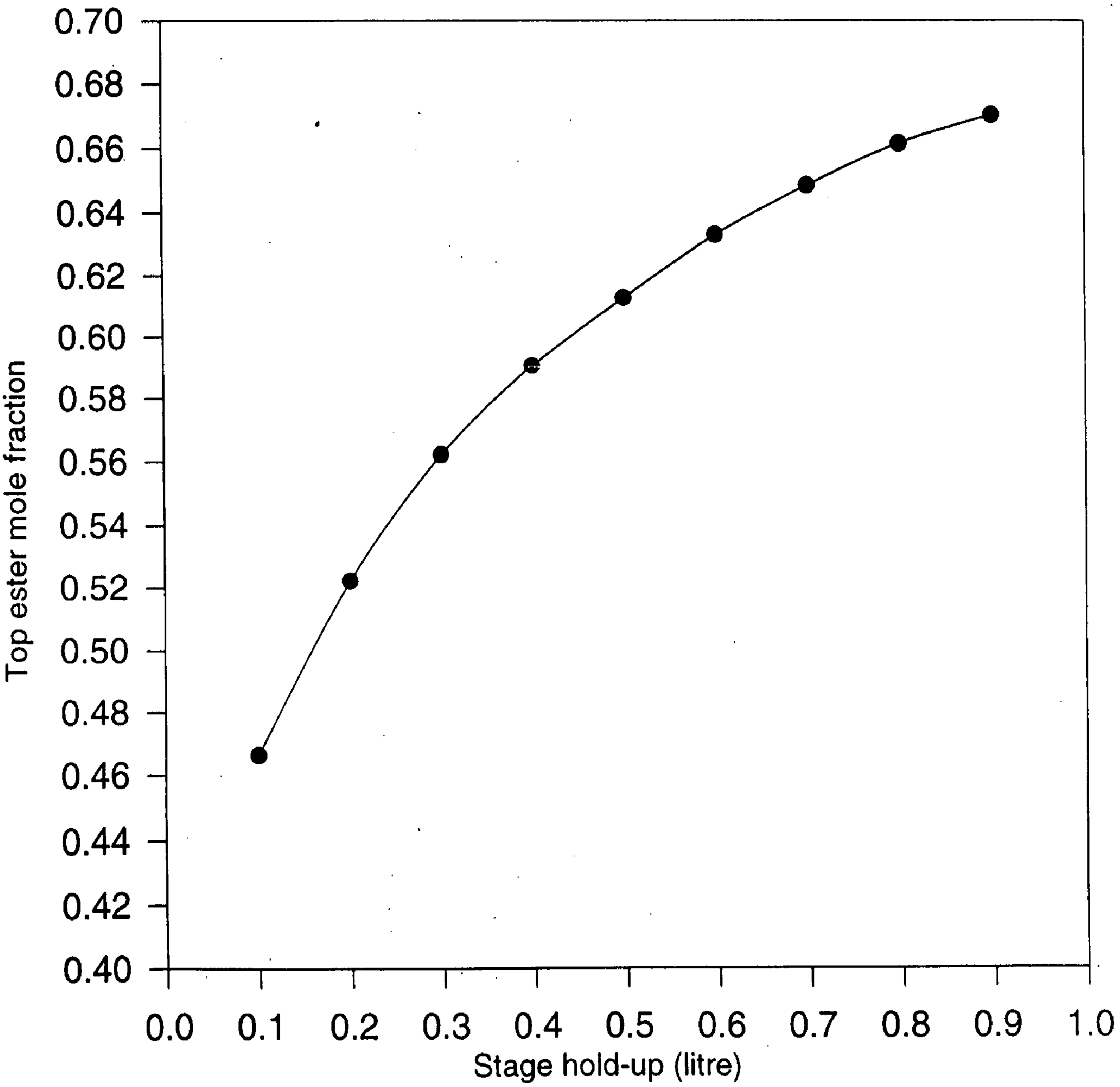

Fig. 5.11 Effect of stage hold-up on top ester mole fraction for Methanol-Acetic acid

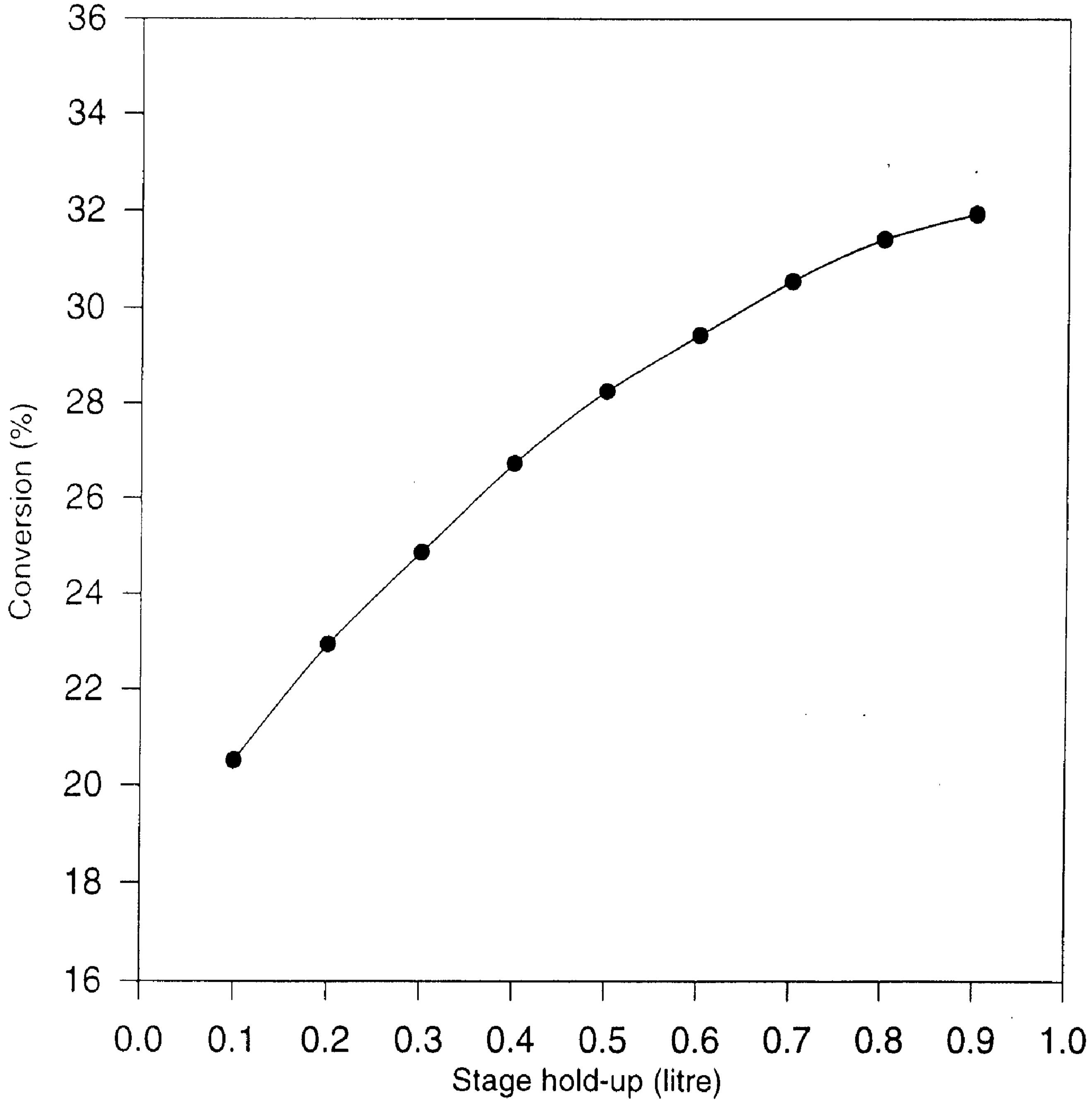

Fig. 5.12 Effect of stage hold-up on percent conversion for Methanol-Acetic acid

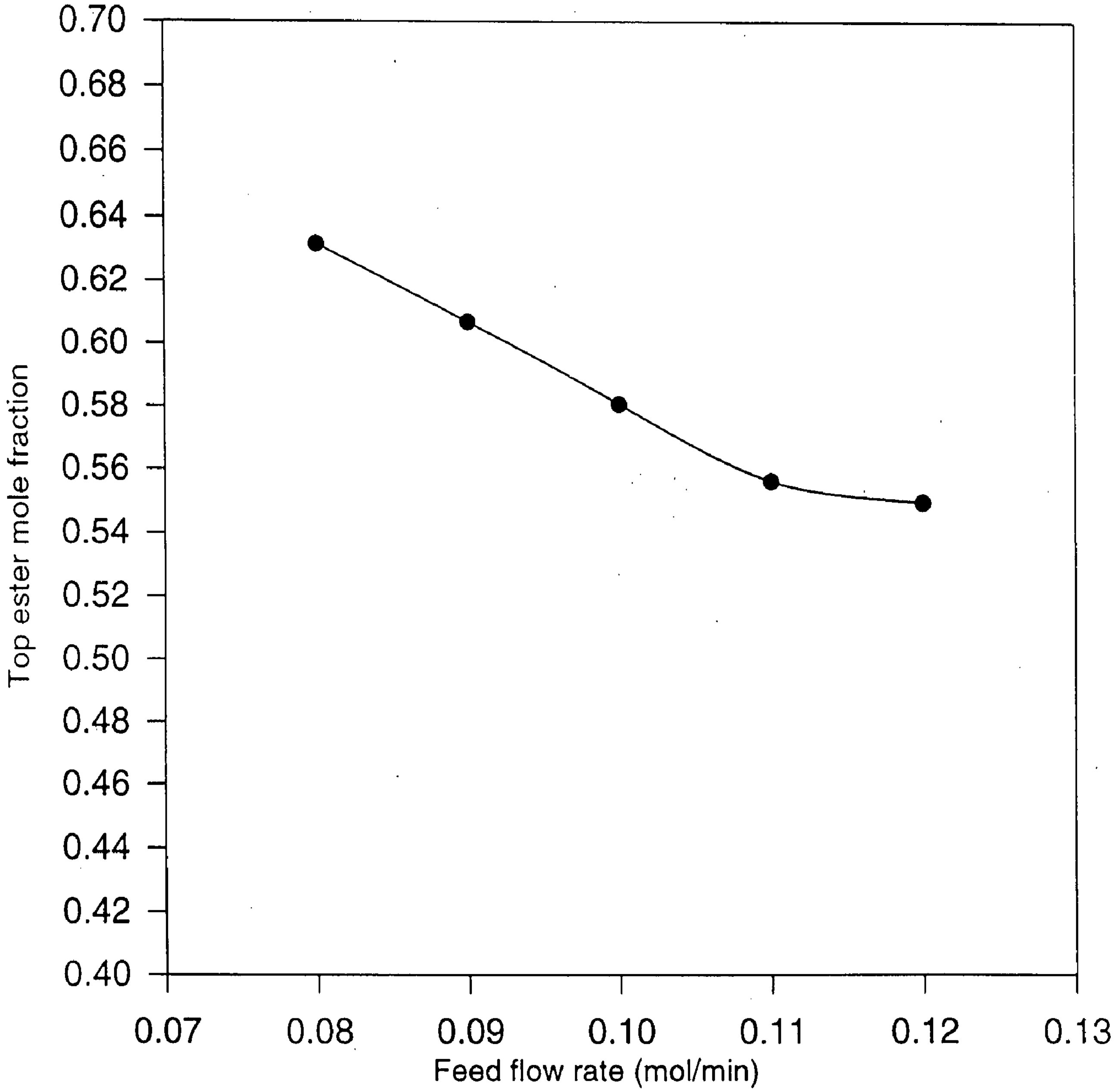

Fig. 5.13 Effect of feed flow rate on top ester mole fraction for Methanol-Acetic acid

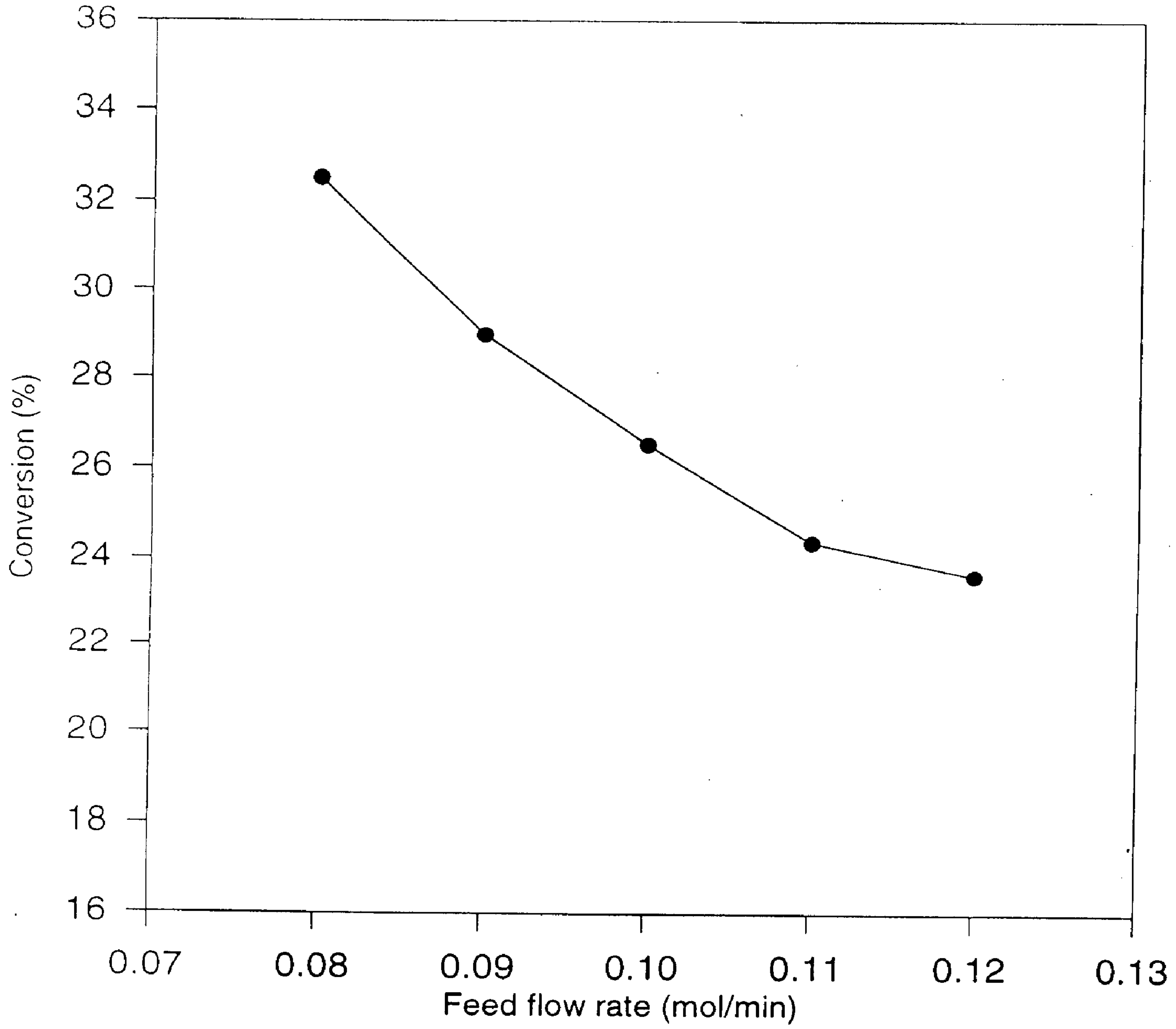

Fig. 5.14 Effect of feed flow rate on percent conversion for Methanol-Acetic acid

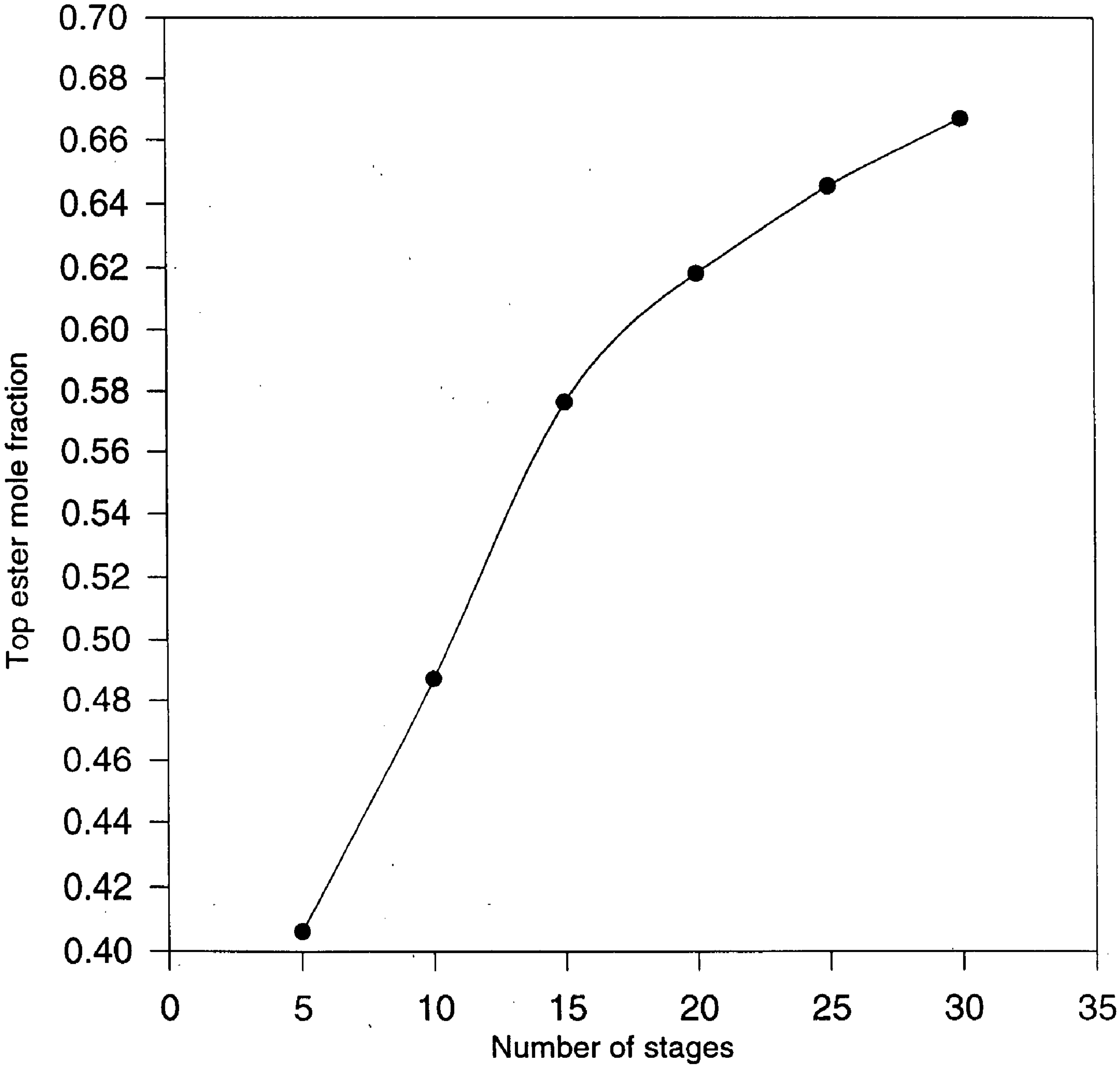

Fig. 5.15 Effect of number of stages on top ester mole fraction for Methanol-Acetic acid

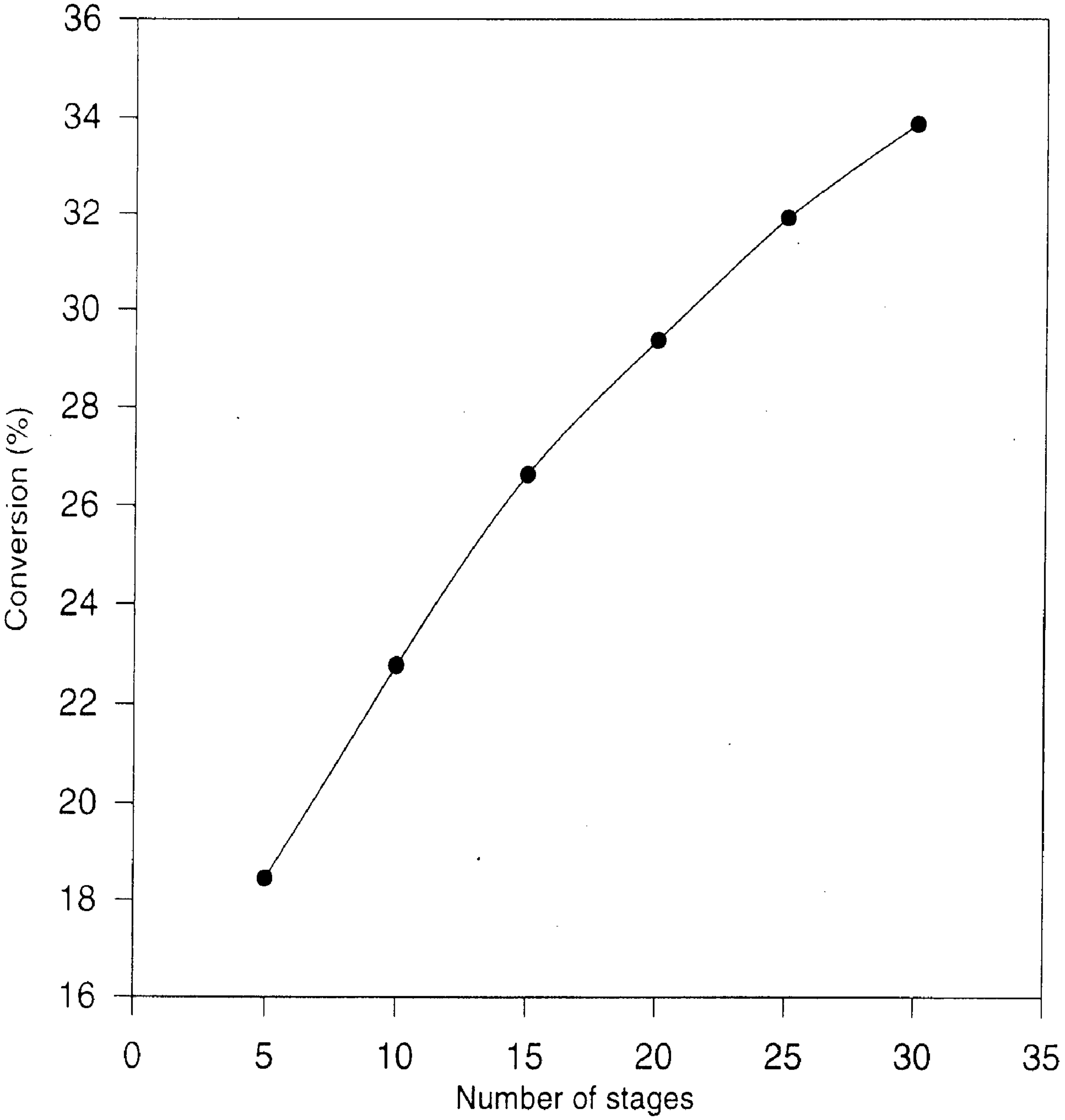

Fig. 5.16 Effect of number of stages on percent conversion for Methanol-Acetic acid

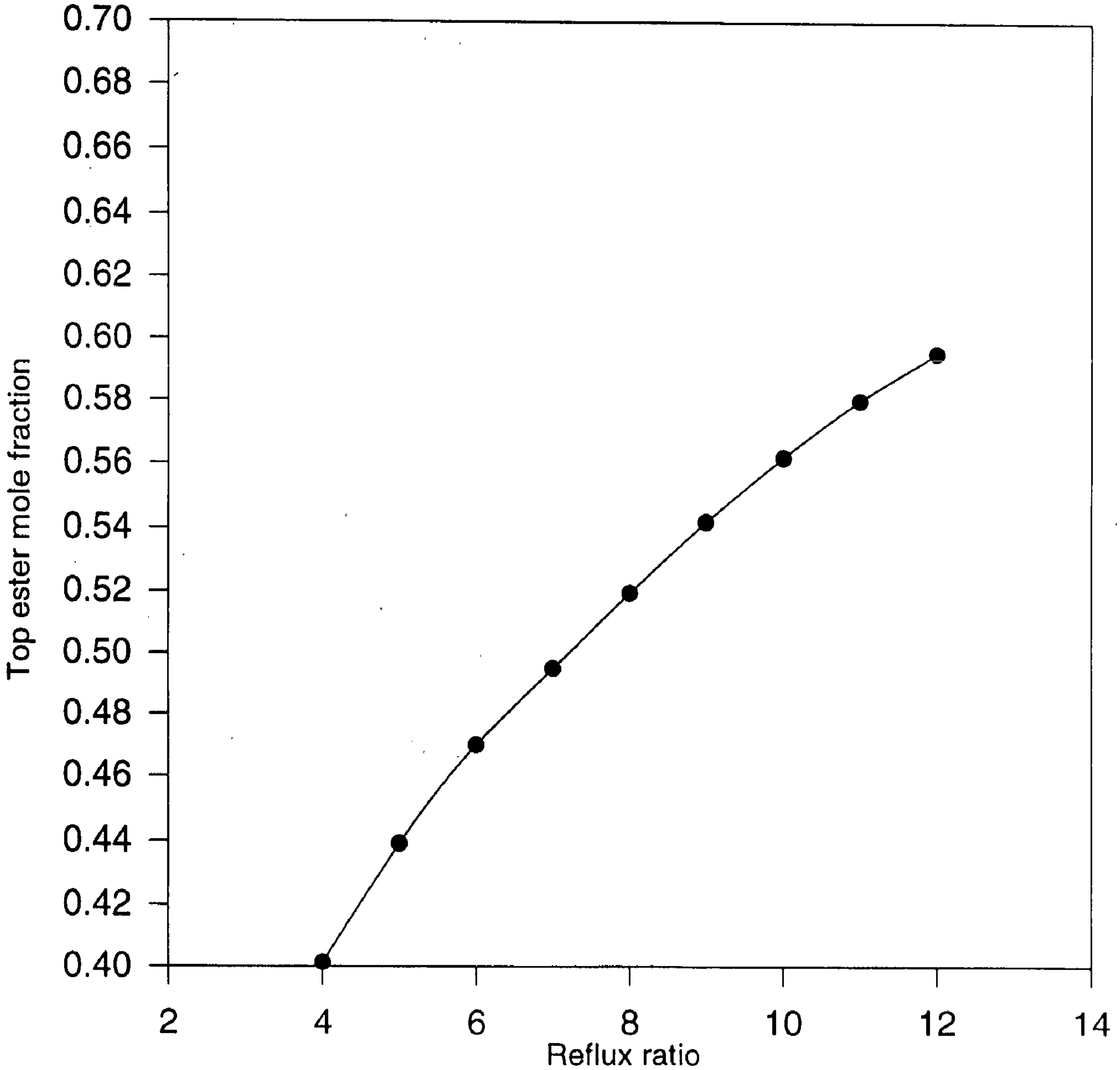

Fig. 5.17 Effect of reflux ratio on top ester mole fraction for Methanol-Acetic acid

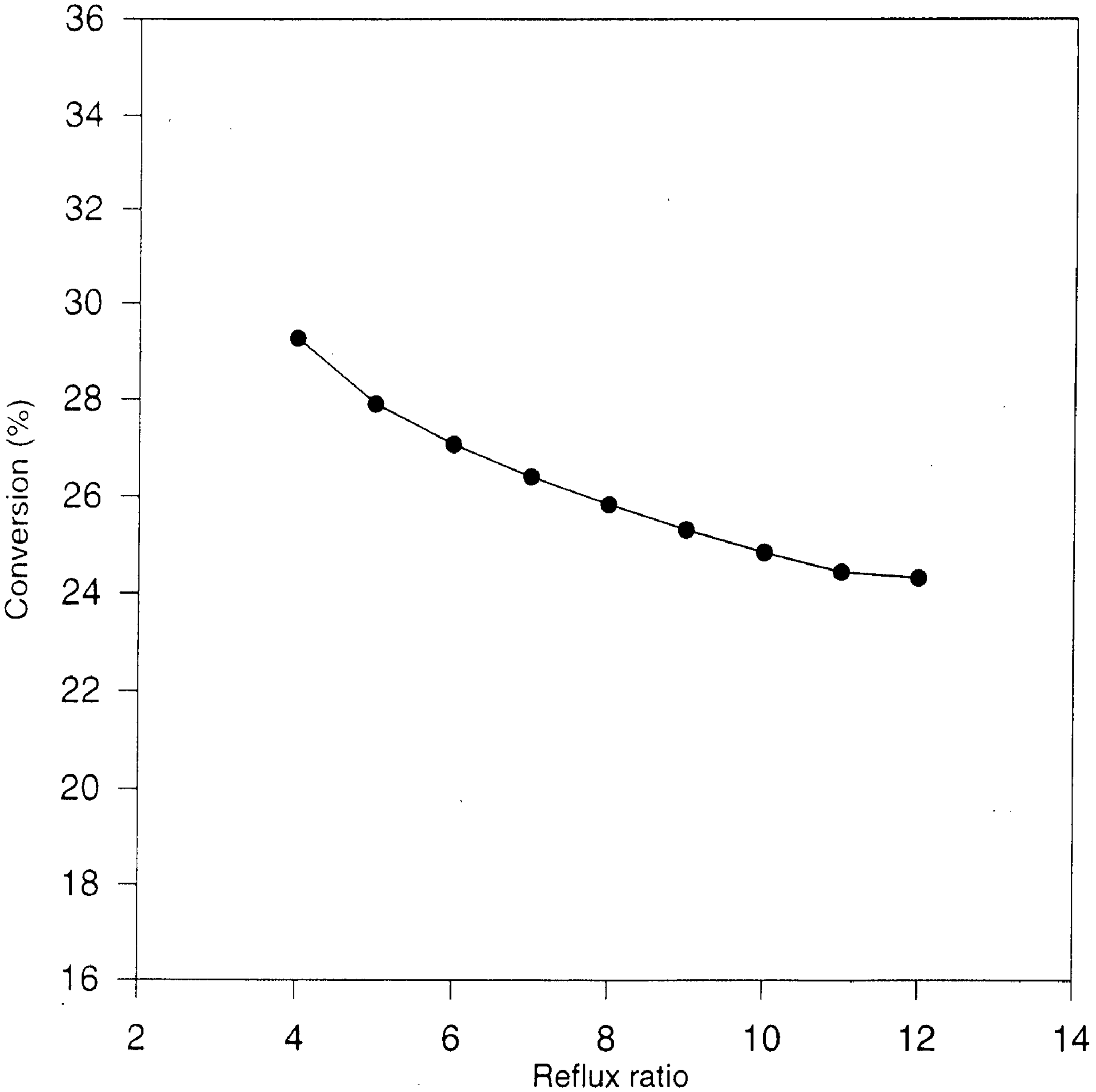

Fig. 5.18 Effect of reflux ratio on percent conversion
for Methanol-Acetic acid

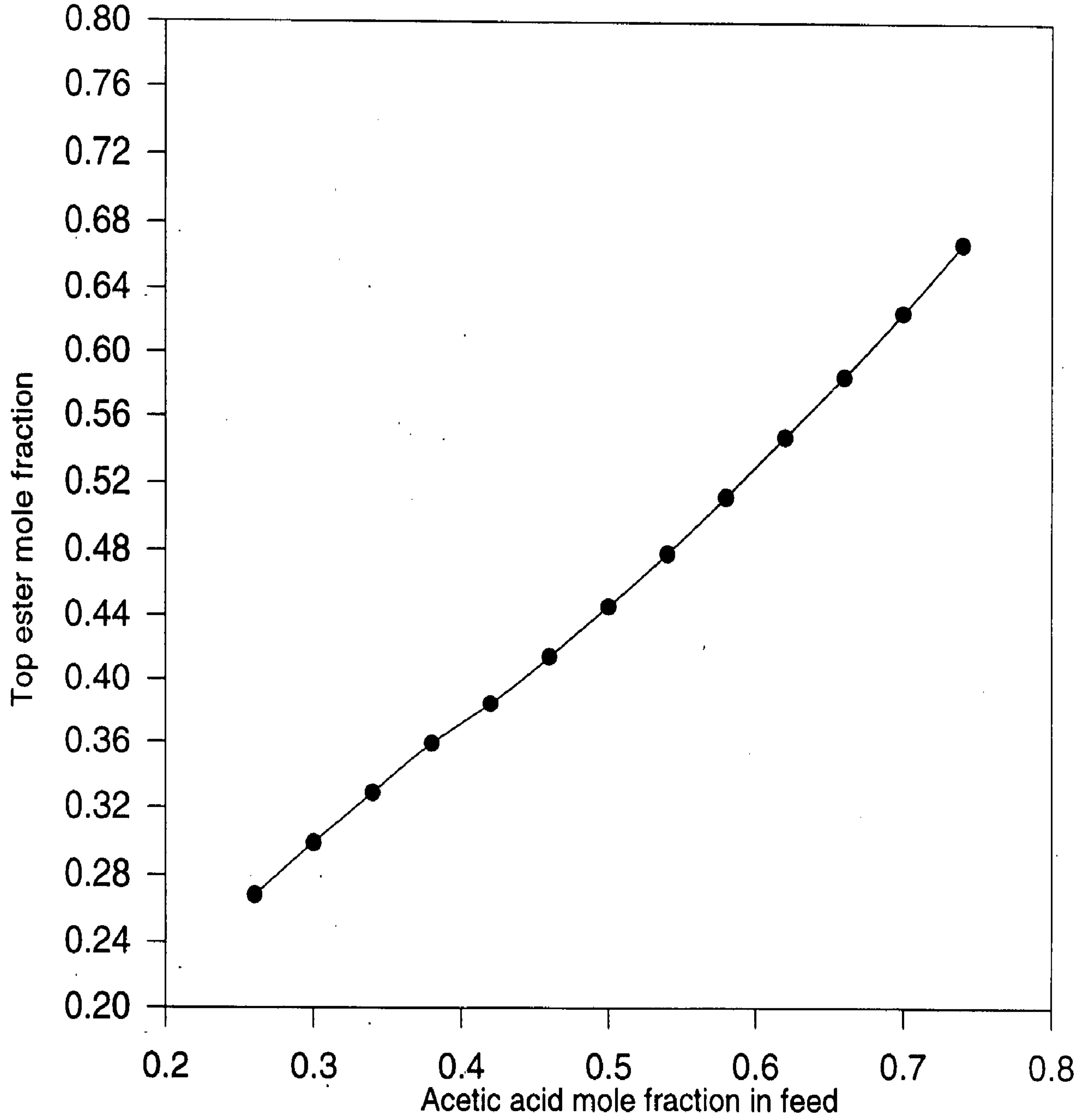

Fig. 5.19 Effect of feed composition on top ester mole fraction for Methanol-Acetic acid

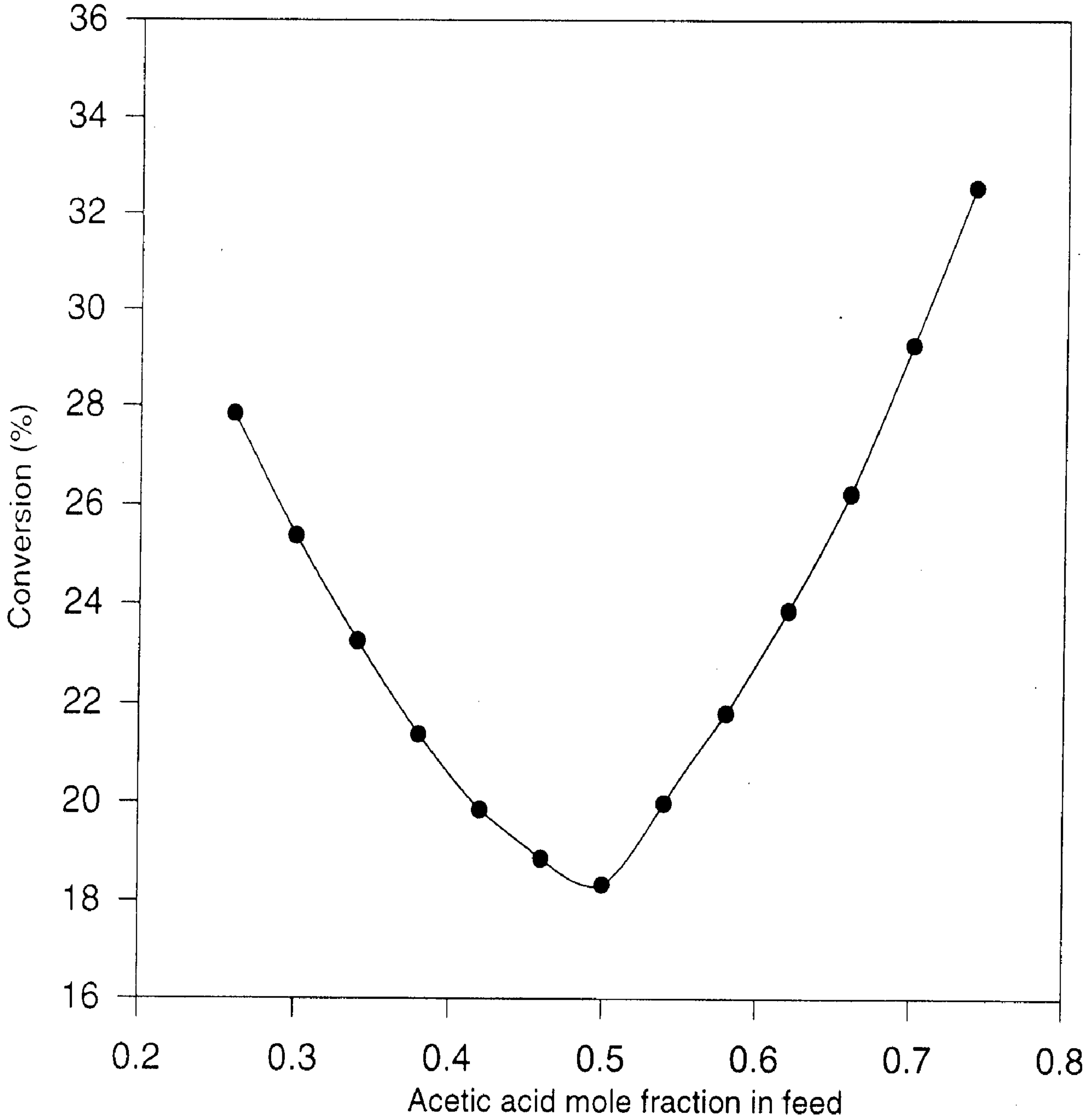

Fig. 5.20 Effect of feed composition on percent conversion for Methanol-Acetic acid

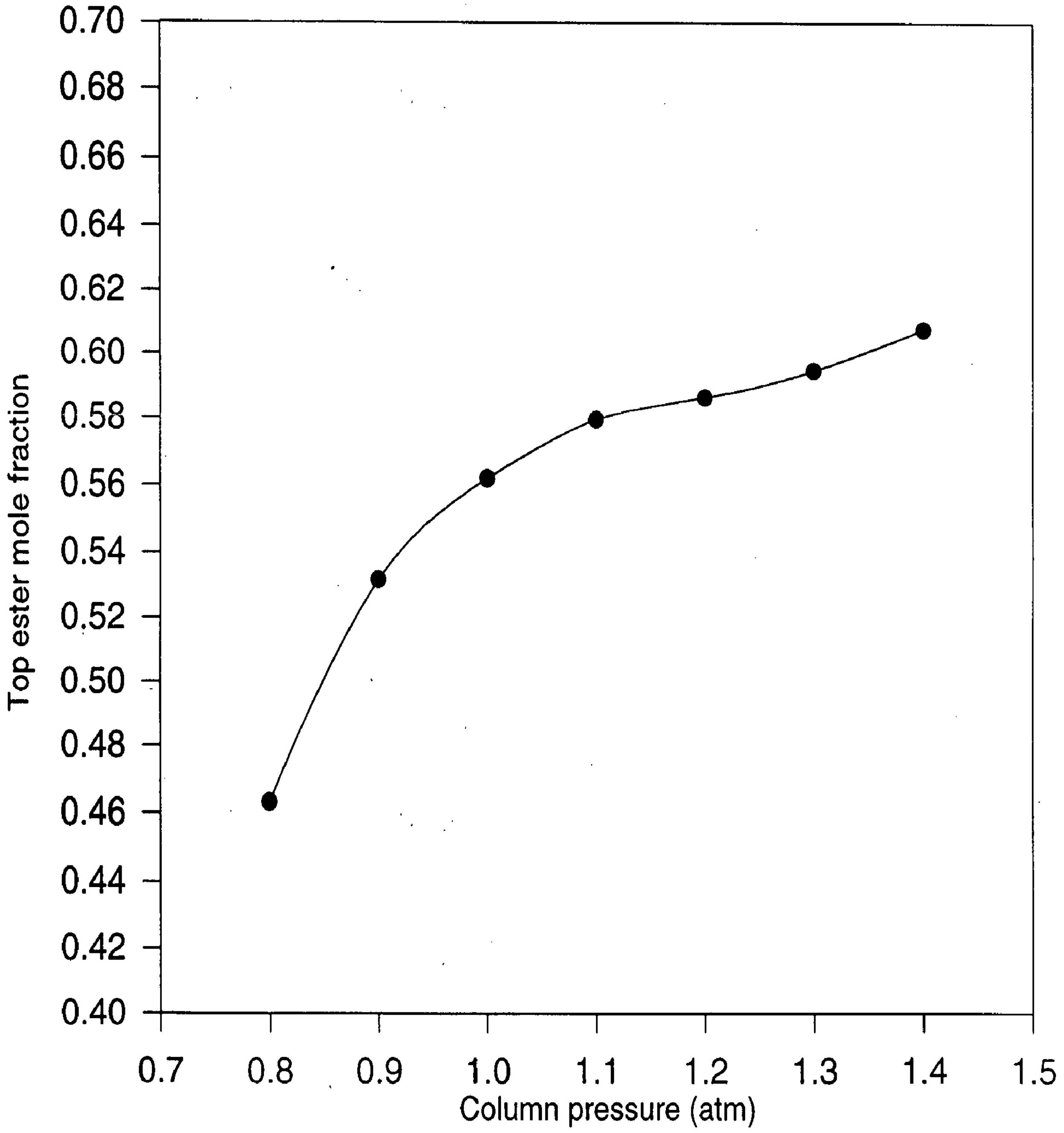

Fig. 5.21 Effect of column pressure on top ester mole fraction
for Methanol-Acetic acid

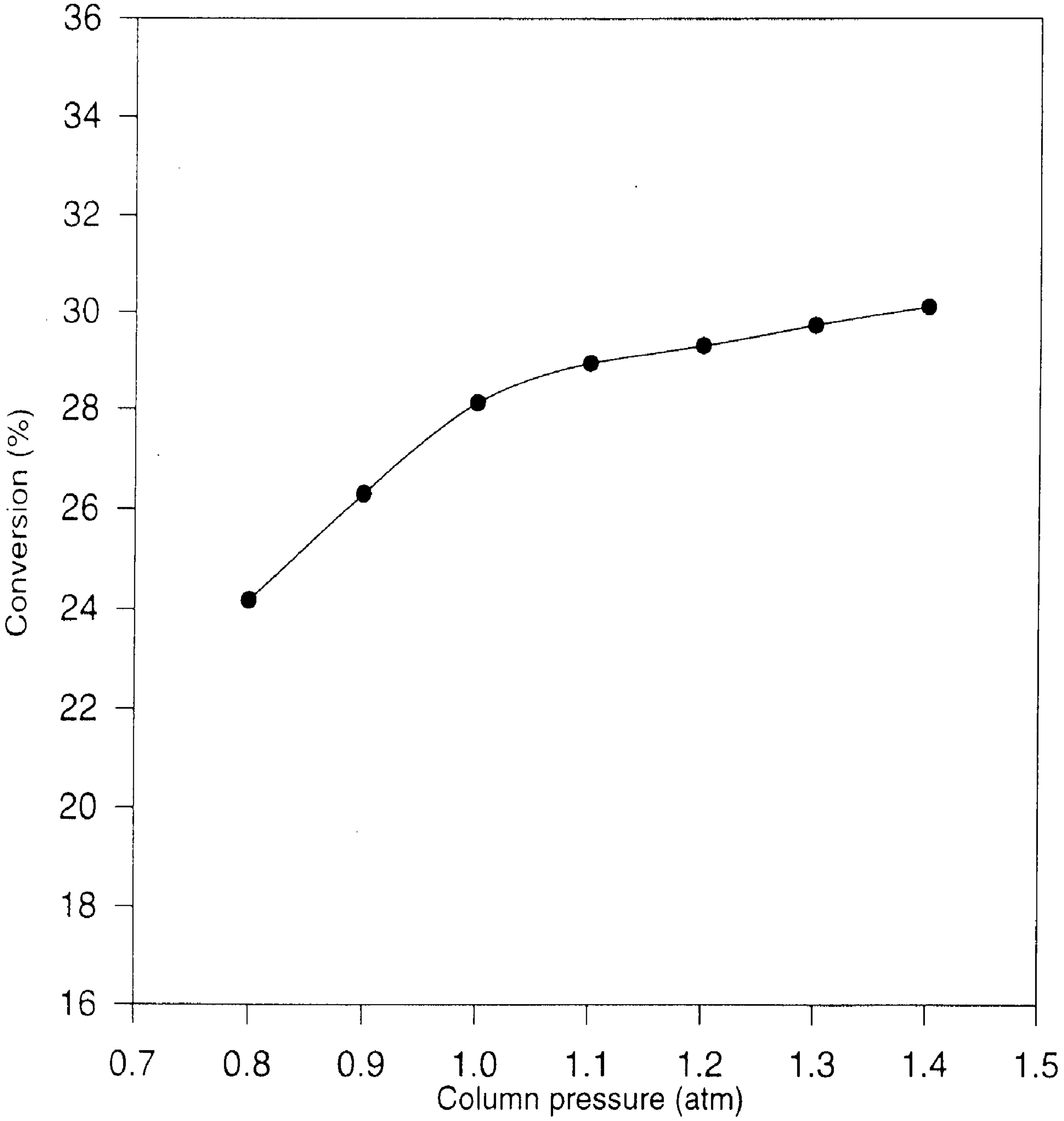

Fig. 5.22 Effect of column pressure on percent conversion for Methanol-Acetic acid

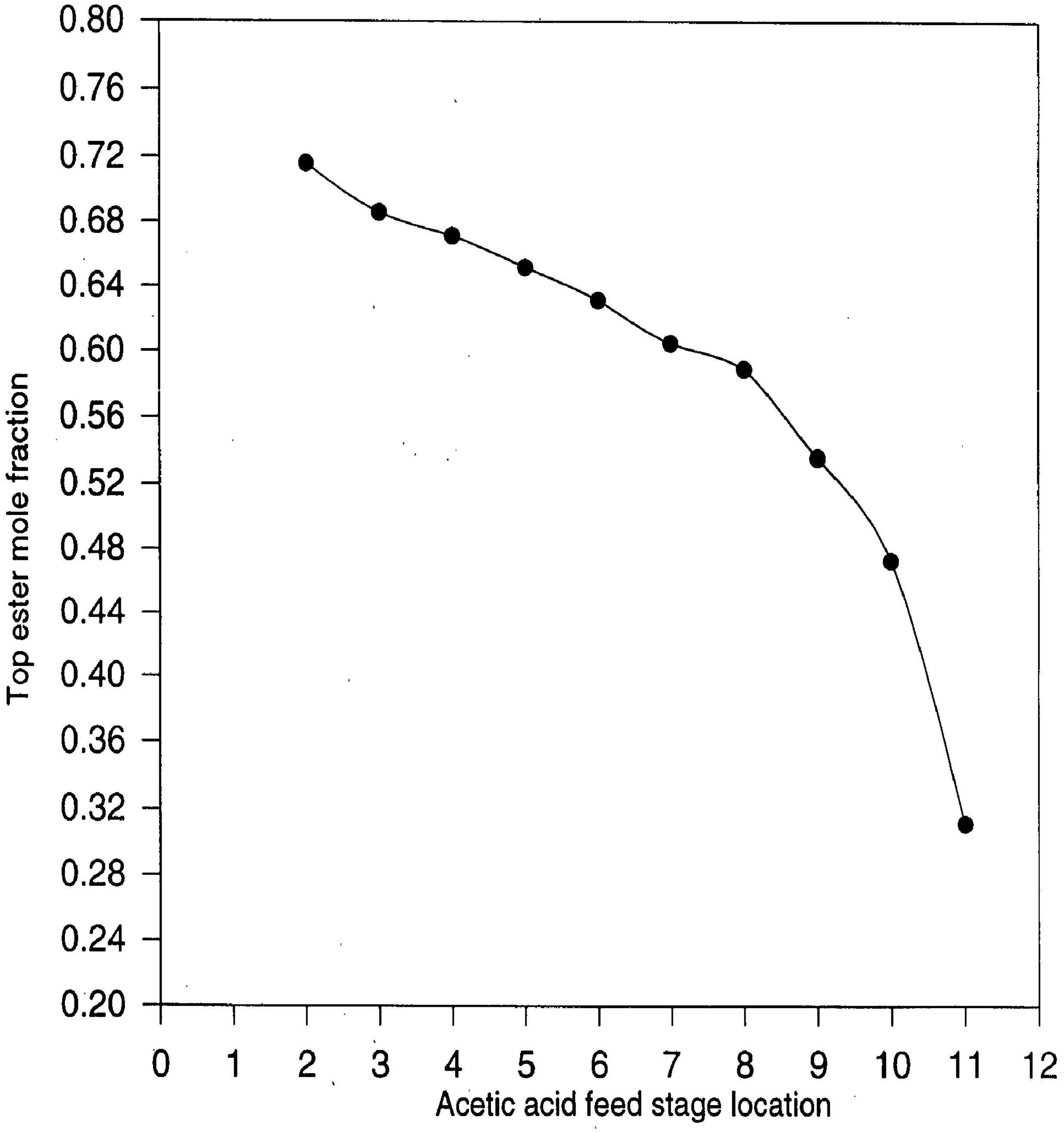

Fig. 5.23 Effect of acetic acid feed stage location on top ester mole fraction for Methanol-Acetic acid (Multiple feed)

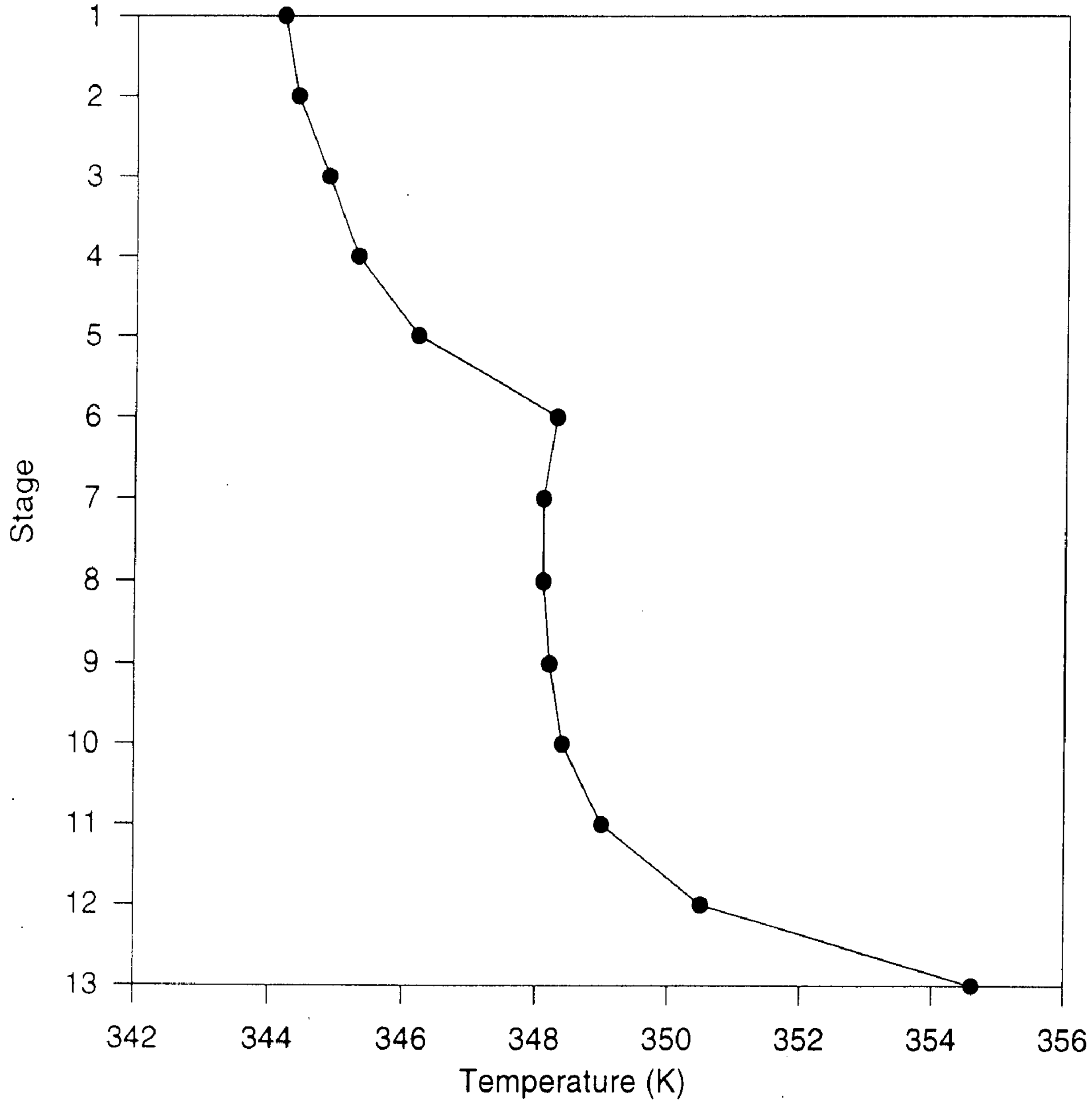

Fig. 5. 24 Temperature profile for Ethanol-Acetic acid using HYSYS

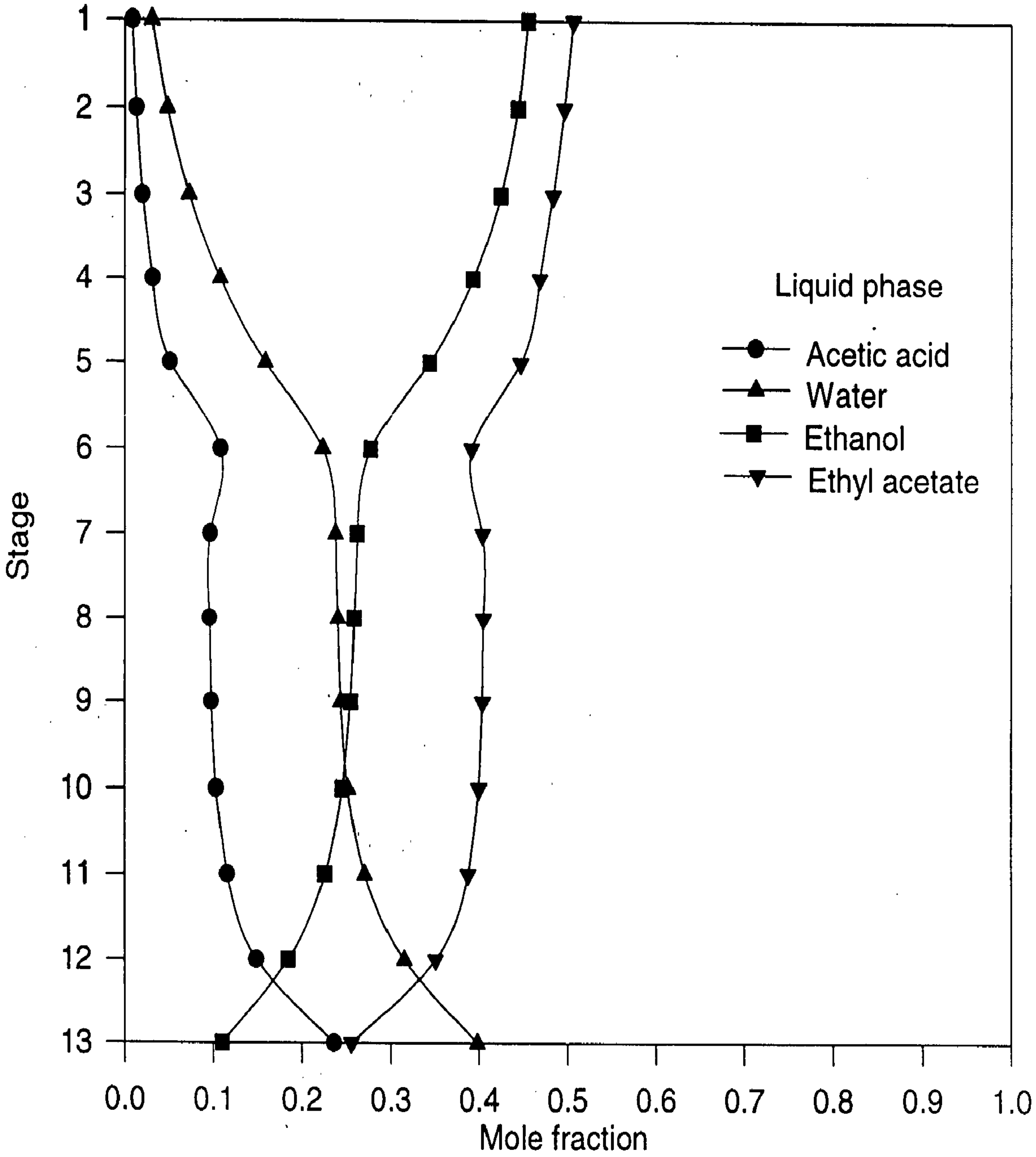

Fig 5.25 Composition profiles in liquid phase for Ethanol-Acetic acid using HYSYS

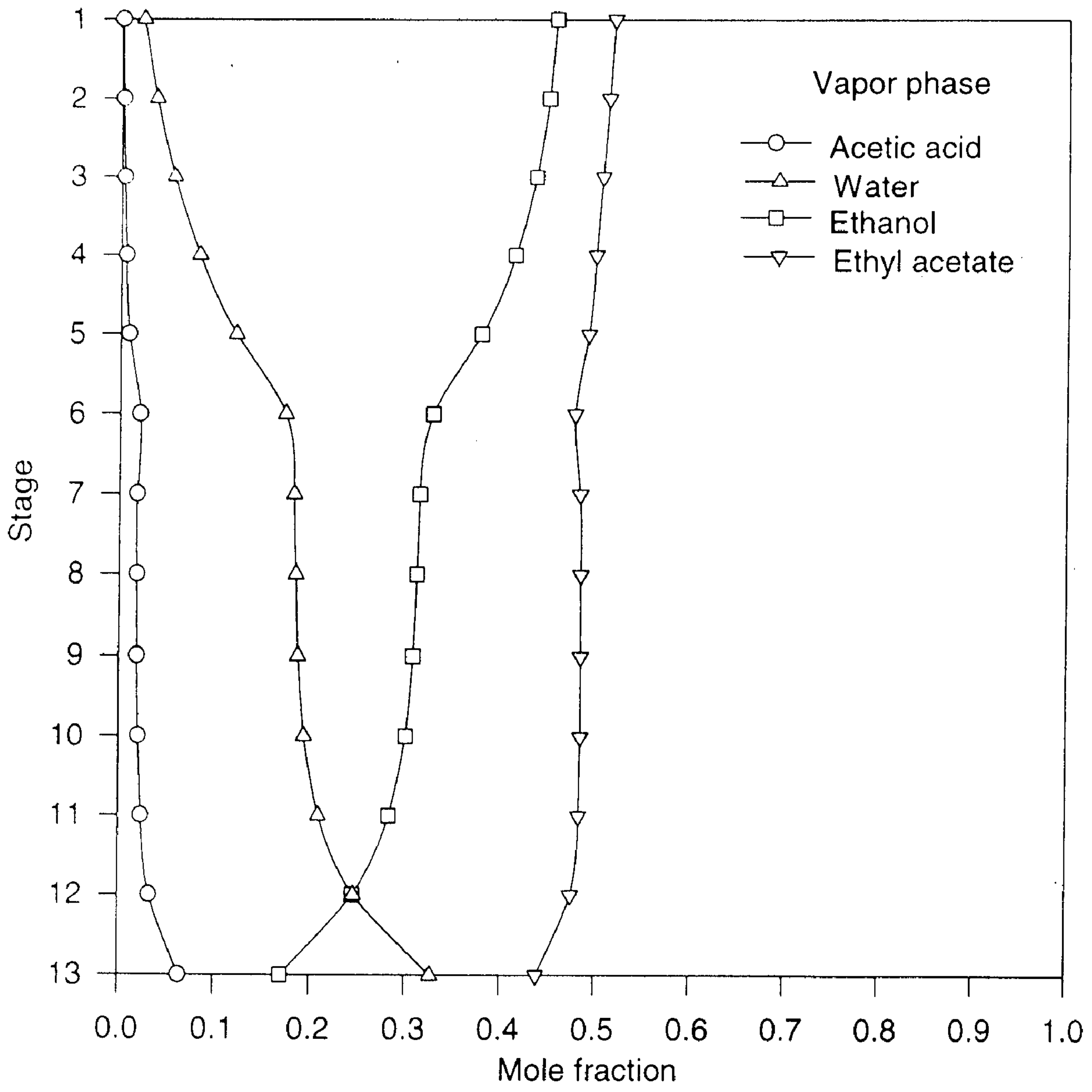

Fig 5.26 Composition profiles in vapor phase for Ethanol-Acetic acid using HYSYS

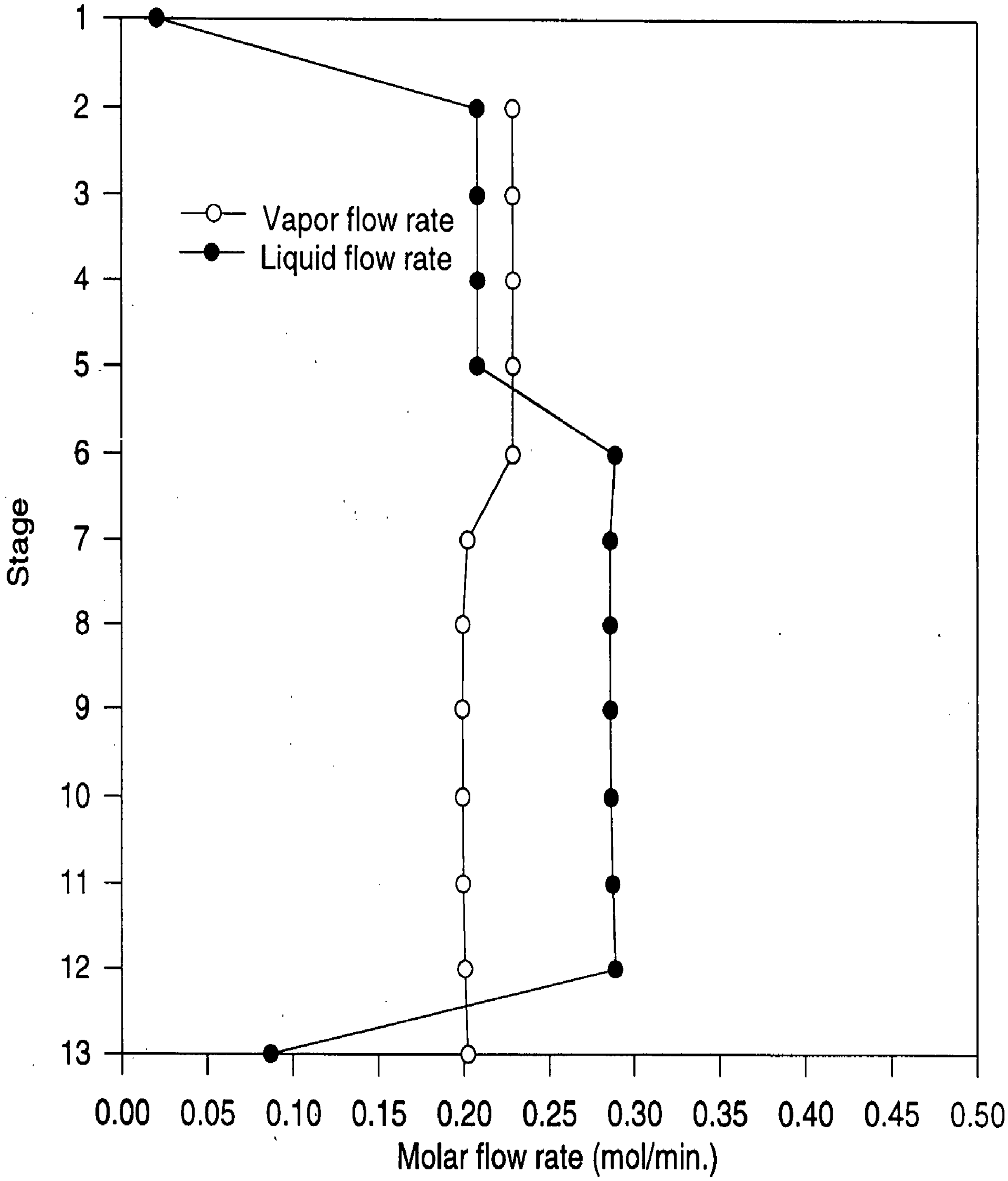

Fig 5.27 Molar flow rate profiles for Ethanol-Acetic acid using HYSYS

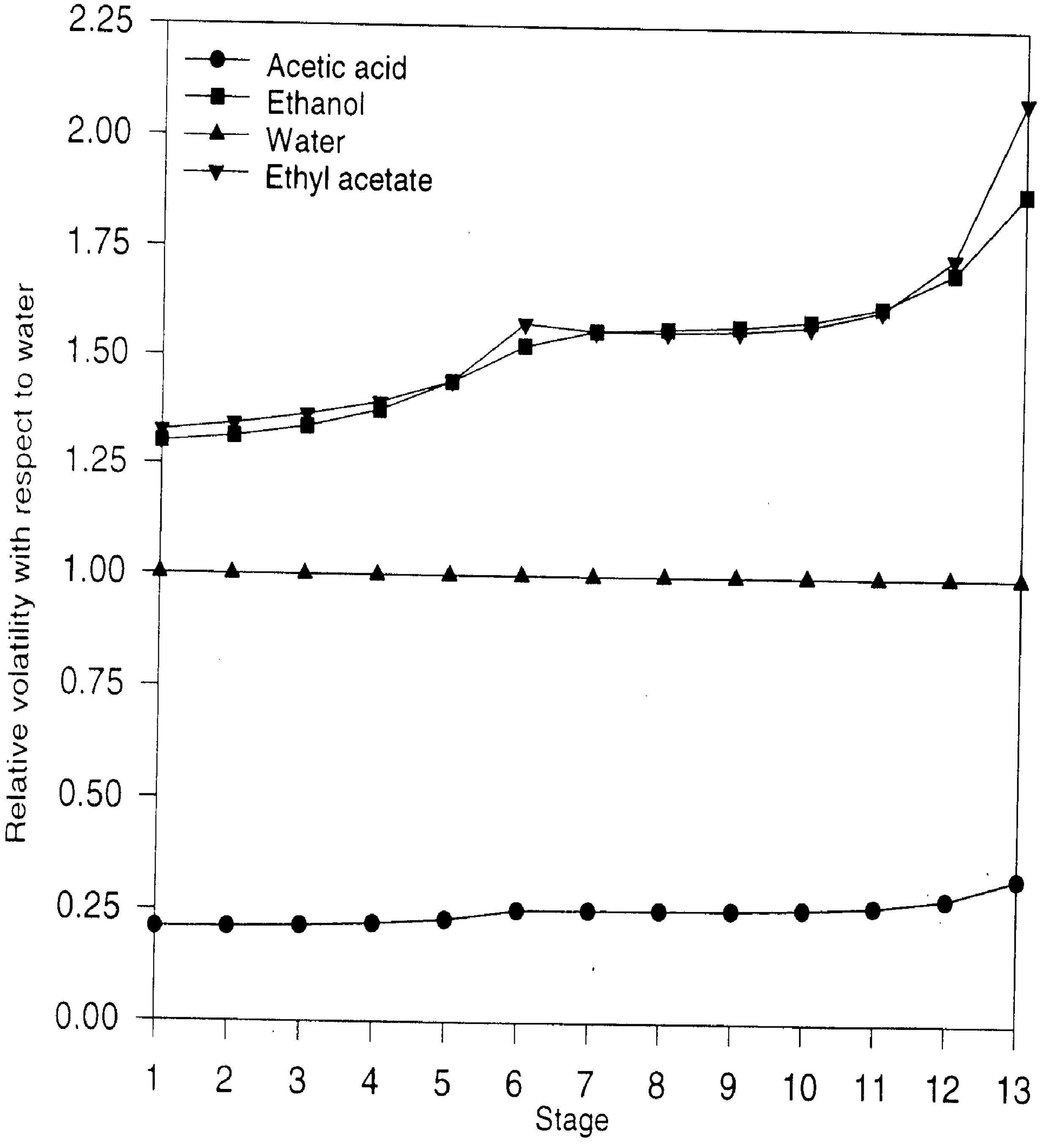

Fig 5.28 Relative volatility profiles for Ethanol-Acetic acid using HYSYS

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

As a result of this investigations following conclusions have emerged out:

1. A model has been developed and validated for ethanol-acetic acid system against the data reported by Suzuki et al., 1971. Excellent agreements in respect of temperature profile, liquid and vapor molar flow rates, liquid and vapor compositions and extent of reaction at each stage have been obtained.
2. A model has been further developed with inclusion of UNIQUAC equation in combination with Marek's method for the association in vapor phase. Using the above model methanol-acetic acid system has been simulated. Profiles for temperature, molar flow rate, liquid and vapor compositions and extent of reaction at each stage have been determined. Further effect of stage hold up, feed molar flow rate, number of stages, reflux ratio, feed composition and column pressure on top ester mole fraction and percent conversion of acetic acid have been studied.
3. The system has also been investigated when two feeds have been introduced at two different stages of the column. As a result, it has been found that it improves the product yield.

   In fact, when methanol was introduced at eleventh stage and acetic acid on second stage in a column of 13 equilibrium stages including a reboiler and a condenser, a maximum yield of methyl acetate was obtained. Lowering the introduction stage of acetic acid while keeping methanol on eleventh stage resulted in lowering of methyl acetate yield in the process.
4. The differential equations for rectification and stripping section have been simultaneously solved along with appropriate condition for minimum reflux ratio and the value of the minimum reflux ratio has been computed. This has been found to be

   eement with the value reported by Doherty and Barbosa, 1988.

5. HYSYS software package has been used successfully for the simulation of ethanol - acetic acid reactive system and the profiles for temperature, liquid and vapor composition, molar flow rates have been obtained.

Following recommendations are made for future work:

1. In the present model developed in this investigation, the chemical reaction has been considered to be irreversible due to insufficient data available in literature. It will be better if the values of rate constants are experimentally determined and reaction is considered to be reversible. This is likely to improve the feasibility of system.
2. The present simulation study has been confined to steady state operation only. It is worthwhile to mention that a dynamic simulation of multicomponent reactive distillation column will give more insight about the system.
3. In this investigation, stages of the distillation column have been considered to be at equilibrium condition. This is far from reality. Therefore, it will be worthwhile to develop a non-equilibrium model by including tray hydraulics, heat and mass transfer coefficients and other pertinent phenomena-taking place.

APPENDIX A
Tables

TABLE A-1: RESULTS OF ETHANOL-ACETIC ACID (SUZUKI ET. AL. (1971))

STAGE	T K	V mol/min	L mol/min	X(AcOH)	X(EtOH)	X(H_2O)	X(EtOAc)
1	345.93	0.0000	0.2080	0.0000	0.6288	0.0128	0.3450
2	346.61	0.2288	0.2053	0.0000	0.7007	0.0182	0.2704
3	347.17	0.2261	0.2033	1.0000e-5	0.7552	0.0245	0.2120
4	347.63	0.2241	0.2015	8.3000e-4	0.7928	0.0318	0.1681
5	348.52	0.2223	0.2005	0.0252	0.7975	0.0392	0.1331
6	352.54	0.2213	0.3058	0.1900	0.6740	0.0403	0.0927
7	352.52	0.2190	0.3058	0.1891	0.6612	0.0494	0.0977
8	352.53	0.2190	0.3057	0.1885	0.6463	0.0621	0.1011
9	352.61	0.2189	0.3055	0.1885	0.6274	0.0800	0.1029
10	352.78	0.2187	0.3053	0.1906	0.6008	0.1051	0.1029
11	353.33	0.2128	0.3057	0.2034	0.5578	0.1386	0.0998
12	355.17	0.2189	0.3115	0.2674	0.4708	0.1725	0.0891
13	360.79	0.2247	0.0868	0.4703	0.3006	0.1701	0.0622

STAGE	Y(AcOH)	Y(EtOH)	Y(H_2O)	Y(EtOAc)	DELR mol/min
1	0.0000	0.5466	8.7600e-3	0.4272	0.0000
2	0.0000	0.6232	0.0128	0.3450	0.0000
3	0.0000	0.6940	0.0177	0.2772	0.0000
4	1.0000e-5	0.7434	0.0234	0.2243	0.0000
5	7.5000e-4	0.7774	0.0300	0.1846	0.0000
6	0.0229	0.7816	0.0367	0.1530	2.7000e-4
7	0.0227	0.7658	0.0450	0.1610	2.7000e-4
8	0.0227	0.7491	0.0566	0.1667	2.7000e-4
9	0.0230	0.7296	0.0731	0.1703	2.8000e-4
10	0.0241	0.7044	0.0968	0.1716	2.9000e-4
11	0.0281	0.6688	0.1306	0.1704	3.6000e-4
12	0.0480	0.6101	0.1757	0.1644	7.3000e-4
13	0.1439	0.4915	0.2185	0.1446	0.0101

Total mole of reaction = 0.01261

Conversion = 24.371 % with respect to ethanol

Note: T, V, L, X , Y and DELR denotes temperature, vapor flow rate, liquid flow rate, liquid phase mole fraction, vapor phase mole fraction and extent of reaction at each stage respectively.

TABLE A-2: RESULTS OF ETHANOL-ACETIC ACID (SIMULATED)

STAGE	T K	V mol/min	L mol/min	X(AcOH)	X(EtOH)	X(H_2O)	X(EtOAc)
1	345.95	0.0000	0.2080	0.0000	0.6289	0.0137	0.3574
2	346.63	0.2288	0.2055	0.0000	0.7007	0.0194	0.2798
3	347.22	0.2263	0.2035	1.4000e-5	0.7546	0.0261	0.2192
4	347.67	0.2243	0.2019	9.4100e-4	0.7915	0.0339	0.1737
5	348.55	0.2227	0.2016	0.0252	0.7956	0.0417	0.1375
6	352.48	0.2225	0.3119	0.1864	0.6746	0.0430	0.0960
7	352.47	0.2251	0.3117	0.1855	0.6614	0.0531	0.1000
8	352.51	0.2249	0.3114	0.1848	0.6462	0.0667	0.1022
9	352.60	0.2246	0.3109	0.1848	0.6271	0.0853	0.1029
10	352.81	0.2241	0.3103	0.1868	0.6008	0.1108	0.1016
11	353.32	0.2235	0.3105	0.2000	0.5585	0.1441	0.0974
12	355.23	0.2236	0.3165	0.2662	0.4721	0.1762	0.0856
13	360.80	0.2297	0.0868	0.4716	0.3010	0.1692	0.0608

STAGE	Y(AcOH)	Y(EtOH)	Y(H_2O)	Y(EtOAc)	DELR mol/min
1	0.0000	0.5477	9.366e-3	0.4430	0.0000
2	0.0000	0.6289	0.0137	0.3574	0.0000
3	0.0000	0.6941	0.0189	0.2870	0.0000
4	1.3000e-5	0.7430	0.0250	0.2321	0.0000
5	8.5300e-4	0.7763	0.0320	0.1909	7.0000e-6
6	0.0229	0.7800	0.0391	0.1580	3.6100e-4
7	0.0227	0.7646	0.0482	0.1645	3.6200e-4
8	0.0228	0.7481	0.0607	0.1684	3.6700e-4
9	0.0231	0.7288	0.0779	0.1701	3.7600e-4
10	0.0242	0.7042	0.1020	0.1695	3.9900e-4
11	0.0283	0.6697	0.1357	0.1662	4.8000e-4
12	0.0489	0.6131	0.1798	0.1582	8.8100e-4
13	0.1480	0.4964	0.2192	0.1364	9.7670e-3

Total mole of reaction = 0.0127

Conversion = 24.519 % with respect to ethanol

Q_1 = 2309 cal/min

Q_N = -2296 cal/min

TABLE A-3: RESULTS OF METHANOL-ACETIC ACID (SIMULATED)

STAGE	T K	V mol/min	L mol/min	X(AcOH)	X(MeOH)	X(H_2O)	X(MeOAc)
1	329.10		0.2080	1.6000e-5	0.4378	5.2000e-5	0.5621
2	329.76	0.2288	0.2046	1.4500e-4	0.5267	2.5100e-4	0.4729
3	330.45	0.2254	0.2014	1.1790e-3	0.6052	1.0530e-3	0.3926
4	331.31	0.2222	0.1988	9.2050e-3	0.6665	3.9770e-3	0.3203
5	333.09	0.2196	0.1987	0.0654	0.6758	0.0123	0.2465
6	339.40	0.2195	0.3112	0.3264	0.5053	0.0229	0.1455
7	339.17	0.2243	0.3108	0.3215	0.5007	0.0263	0.1515
8	339.01	0.2239	0.3101	0.3157	0.5003	0.0293	0.1548
9	338.92	0.2232	0.3089	0.3087	0.5041	0.0321	0.1551
10	338.95	0.2221	0.3075	0.3016	0.5112	0.0356	0.1517
11	339.35	0.2208	0.3064	0.3026	0.5116	0.0437	0.1421
12	341.70	0.2196	0.3099	0.3614	0.4536	0.0694	0.1156
13	350.54	0.2232	0.0868	0.5876	0.2443	0.1089	0.0592

STAGE	Y(AcOH)	Y(MeOH)	Y(H_2O)	Y(MeOAc)	DELR mol/min
1	2.0000e-6	0.3517	1.0000e-5	0.6483	0.0000
2	1.8000e-5	0.4378	5.1000e-5	0.5621	0.0000
3	1.5000e-4	0.5197	2.2000e-4	0.4799	1.6154e-6
4	1.2180e-3	0.5940	8.6800e-4	0.4040	2.7462e-5
5	9.4640e-3	0.6539	2.9470e-3	0.3337	3.8931e-4
6	0.0660	0.6676	7.7710e-3	0.2586	1.5734e-3
7	0.0646	0.6582	8.8640e-3	0.2683	1.5508e-3
8	0.0631	0.6541	9.8130e-3	0.2730	1.4765e-3
9	0.0613	0.6557	0.0107	0.2722	1.3666e-3
10	0.0597	0.6629	0.0118	0.2655	1.2035e-3
11	0.0609	0.6728	0.0148	0.2515	1.0096e-3
12	0.0819	0.6661	0.0265	0.2255	8.5615e-4
13	0.2116	0.5526	0.0673	0.1685	7.3920e-3

Total mole of reaction = 0.0168

Conversion = 24.867 % with respect to acetic acid.

Conversion = 47.157 % with respect to methanol

Q_1 = 1293 cal/min

Q_N = -1030 cal/min

TABLE A-4: Effect of stage hold-up for methanol-acetic acid

Stage hold-up (litre)	Top ester mole fraction	Conversion %
0.1	0.4664	20.505
0.2	0.5222	22.929
0.3	0.5621	24.867
0.4	0.5906	26.731
0.5	0.6129	28.259
0.6	0.6330	29.436
0.7	0.6484	30.557
0.8	0.6614	31.655
0.9	0.6700	31.934

TABLE A-5: Effect of feed flow rate for methanol-acetic acid

Feed flow rate (mol/min)	Top ester mole fraction	Conversion %
0.08	0.6316	32.497
0.09	0.6069	28.977
0.10	0.5807	26.523
0.11	0.5563	24.380
0.12	0.5497	23.630

TABLE A-6: Effect of number of stages for methanol-acetic acid

Number of stages	Top ester mole fraction	Conversion %
5	0.4064	18.444
10	0.4871	22.764
15	0.5763	26.646
20	0.6184	29.389
25	0.6457	31.923
30	0.6670	33.863

TABLE A-7: Effect of reflux ratio for methanol-acetic acid

Reflux ratio	Top ester mole fraction	Conversion %
4	0.4013	29.266
5	0.4392	27.905
6	0.4700	27.078
7	0.4953	26.414
8	0.5198	25.842
9	0.5421	25.327
10	0.5621	24.867
11	0.5801	24.456
12	0.5956	24.341

TABLE A-8: Effect of feed composition for methanol-acetic acid

Acetic acid mole fraction in feed	Top ester mole fraction	Conversion %
0.26	0.2685	27.842
0.30	0.2991	25.381
0.34	0.3290	23.260
0.38	0.3593	21.381
0.42	0.3845	19.848
0.46	0.4148	18.869
0.50	0.4462	18.345
0.54	0.4786	19.995
0.58	0.5126	21.820
0.62	0.5481	23.876
0.66	0.5855	26.247
0.70	0.6258	29.280
0.74	0.6681	32.547

TABLE A-9: Effect of column pressure for methanol-acetic acid

Pressure (atm)	Top ester mole fraction	Conversion %
0.8	0.4632	24.181
0.9	0.5318	26.306
1.0	0.5621	28.123
1.1	0.5795	28.942
1.2	0.5863	29.313
1.3	0.5946	29.743
1.4	0.6079	30.121

TABLE A-10: Effect of Acetic acid feed stage location (Multiple feed)

Acetic acid feed location	Top ester mole fraction
2	0.7159
3	0.6859
4	0.6714
5	0.6520
6	0.6314
7	0.6049
8	0.5891
9	0.5365
10	0.4733
11	0.3113

TABLE A-11: RESULTS OF ETHANOL-ACETIC ACID USING HYSYS

STAGE	T K	V mol/min	L mol/min	X(AcOH)	X(EtOH)	X(H2O)	X(EtOAc)
1	344.20		0.0208	8.5120e-3	0.4548	0.0305	0.5061
2	344.40	0.2288	0.2079	0.0131	0.4434	0.0479	0.4957
3	344.86	0.2287	0.2079	0.0201	0.4242	0.0725	0.4832
4	345.30	0.2289	0.2081	0.0314	0.3927	0.1078	0.4682
5	346.20	0.2289	0.2080	0.0511	0.3436	0.1586	0.4466
6	348.30	0.2288	0.2890	0.1082	0.2772	0.2233	0.3913
7	348.10	0.2022	0.2863	0.0963	0.2621	0.2378	0.4038
8	348.10	0.1995	0.2860	0.0958	0.2587	0.2406	0.4049
9	348.20	0.1992	0.2862	0.0977	0.2546	0.2438	0.4039
10	348.40	0.1994	0.2867	0.1029	0.2458	0.2515	0.3999
11	349.00	0.1999	0.2876	0.1157	0.2261	0.2706	0.3876
12	350.50	0.2008	0.2891	0.1485	0.1848	0.3155	0.3512
13	354.60	0.2023	0.0868	0.2361	0.1099	0.3982	0.2558

STAGE	Y(AcOH)	Y(EtOH)	Y(H2O)	Y(EtOAc)
1	1.3870e-3	0.4567	0.0235	0.5184
2	2.1380e-3	0.4484	0.0369	0.5125
3	3.3300e-3	0.4351	0.0556	0.5059
4	5.3100e-3	0.4132	0.0824	0.4990
5	9.0200e-3	0.3780	0.1211	0.4919
6	0.0212	0.3276	0.1731	0.4781
7	0.0188	0.3144	0.1828	0.4841
8	0.0187	0.3115	0.1848	0.4850
9	0.0192	0.3081	0.1874	0.4853
10	0.0204	0.3005	0.1937	0.4854
11	0.0236	0.2833	0.2092	0.4839
12	0.0326	0.2454	0.2464	0.4756
13	0.0637	0.1699	0.3271	0.4392

Total mole of reaction = 0.0222

Conversion = 63.266 % with respect to ethanol

TABLE A-12: **Relative volatility with respect to water for Ethanol-Acetic acid using HYSYS**

STAGE	α(AcOH)	α(EtOH)	α(H2O)	α(EtOAc)
1	0.2111	1.3005	1.0000	1.3264
2	0.2128	1.3132	1.0000	1.3430
3	0.2158	1.3368	1.0000	1.3642
4	0.2214	1.3755	1.0000	1.3938
5	0.2313	1.4415	1.0000	1.4428
6	0.2525	1.5250	1.0000	1.5766
7	0.2533	1.5613	1.0000	1.5600
8	0.2539	1.5671	1.0000	1.5593
9	0.2551	1.5739	1.0000	1.5635
10	0.2577	1.5879	1.0000	1.5762
11	0.2644	1.6210	1.0000	1.6145
12	0.2815	1.7006	1.0000	1.7339
13	0.3289	1.8805	1.0000	2.0898

APPENDIX B

Derivation of differential equations from transformed composition variables

With a set of transformed composition variables it is possible to reduce the conservation equations that describe the simple distillation of reactive mixtures to a form, which is identical to that for non-reactive mixtures. One can use this set of transformed composition variables to derive the design equations for reactive distillation columns. These new equations are identical, in form to the corresponding equation for conventional distillation. This leads to the development of a general method for calculating minimum reflux ratios in reactive distillation columns.

Stripping section: The composition material balance for components i and k are:

$$L_{n+1}x_{i,n+1} = Vy_{i,n} + Bx_{i,n} - v_1\sum_{i=1}^{n}\frac{d\varepsilon_i}{dt} \tag{B.1}$$

$$L_{n+1}x_{kn+1} = Vy_{k,n} + Bx_{k,n} - v_1\sum_{i=1}^{n}\frac{d\varepsilon_i}{dt} \tag{B.2}$$

Where $v_i\sum_{i=1}^{n}\frac{d\in_i}{dt}$ is the number of moles of component i generated by reaction over the entire section of column.

Eliminating the term $\Sigma\ d\in_i/dt$ from equations (B.1) and (B.2), we get

$$L_{n+1}\left(\frac{x_{i,n+1}}{v_i}-\frac{x_{k,n+1}}{v_k}\right) = V\left(\frac{y_{i,n}}{v_i}-\frac{y_{k,n}}{v_k}\right) + B\left(\frac{x_{i,B}}{v_i}-\frac{x_{k,B}}{v_k}\right) \tag{B.3}$$

We define the transformed composition variables as

$$X_i = \left(\frac{x_i}{v_i}-\frac{x_k}{v_k}\right)/(v_k - v_T x_k) \qquad i=1,\dots,C-1\ ;i \neq k \tag{B.4}$$

$$Y_i = \left(\frac{y_i}{v_i}-\frac{y_k}{v_k}\right)/(v_k - v_T y_k) \qquad i=1,\dots,C-1;i \neq k \tag{B.5}$$

Rewriting equation. (B.3) as

$$L_{n+1}(v_k - v_T x_{k,n+1})X_{i,n+1} = V(v_k - v_T y_{k,n})Y_{i,n} + B(v_k - v_T x_{k,B})X_{i,B} \tag{B.6}$$

Overall balance

$$L_{n+1} = V + B - \nu_T \sum_{i=1}^{n} \frac{d\varepsilon_i}{dt} \qquad \text{(B.7)}$$

Where $\nu_T = \sum_{i=1}^{c} \nu_i$

Substituting for reaction term by using equation. (B.2)

$$L_{n+1}(\nu_k - \nu_T x_{k,n+1}) = V(\nu_k - \nu_T y_{k,n}) + B(\nu_k - \nu_T x_{k,B}) \qquad \text{(B.8)}$$

A modified reboil ratio for each plate is defined as

$$S_n^{\cdot} = \frac{V(\nu_k - \nu_T y_{k,n})}{B(\nu_k - \nu_T x_{k,B})} = S_{ext} \frac{(\nu_k - \nu_T y_{k,n})}{(\nu_k - \nu_T X_{k,B})} \qquad \text{(B.9)}$$

Arranging equation. (B.6) by using equation. (B.8) and equation. (B.9).

$$X_{i,n+1} = \frac{S_n^{\cdot}}{S_n^{\cdot} + 1} Y_{i,n} + \frac{1}{S_n^{\cdot} + 1} X_{i,B} \qquad i = 1,\ldots,C\text{-}1; i \neq k \qquad \text{(B.10)}$$

This is the equation of the operating line for the stripping section of a reactive distillation column written in terms of the transformed composition variables.

Rectifying section: The component and overall material balance

$$V(\nu_K - \nu_T y_{k,m-1})Y_{i,m-1} = L_m(\nu_k - \nu_T x_{k,m})X_{i,m} + D(\nu_k - \nu_T x_{k,D})X_{i,D} \qquad \text{(B.11)}$$

$$V(\nu_k - \nu_T y_{k,m-1}) = L_m(\nu_k - \nu_T x_{k,m}) + D(\nu_k - \nu_T x_{k,D}) \qquad i = 1,\ldots,C\text{-}1; i \neq k \quad \text{(B.12)}$$

A modified reflux ratio is defined as:

$$r_m^{\cdot} = \frac{L_m(\nu_k - \nu_T x_{k,m})}{D(\nu_k - \nu_T x_{k,D})} = r_{ext} \frac{(\nu_k - \nu_T x_{k,m})}{(\nu_k - \nu_T x_{k,D})} \qquad \text{(B.13)}$$

Operating line for the rectifying section is written as:

$$X_{i,m} = \frac{r_m^{\cdot} + 1}{r_m^{\cdot}} Y_{i,m-1} - \frac{1}{r_m^{\cdot}} X_{i,D} \qquad i = 1,\ldots,C\text{-}1; i \neq k \qquad \text{(B.14)}$$

In the special case of $\nu_T = 0$, r_m^* is a constant equal to the external reflux ratio.

Overall balances

The composition of the feed and the composition of the two product streams of a distillation column are not independent of each other as they are related by overall material balances around the entire column. Also, the relationship exists between the external reflux ratio and the external reboil ratio, which can be derived as follows:

The component and overall material balances for the entire column

$$F(v_k - v_T x_{k,F})X_{i,F} = D(v_k - v_T x_{k,D})X_{i,D} + B(v_k - v_T x_{k,B})X_{i,B}$$

$$i = 1,\ldots,C\text{-}1 \;\; ; \;\; i \neq k \qquad \text{(B.15)}$$

$$F(v_k - v_T x_{k,F}) = D(v_k - v_T x_{k,D}) + B(v_k - v_T x_{k,B})$$

$$i = 1,\ldots,C\text{-}1 \;\; ; \;\; i \neq k \qquad \text{(B.16)}$$

From equation. (B.15) and (B.16), we get

$$\frac{D(v_k - v_T x_{k,D})}{B(v_k - v_T x_{k,B})} = \frac{X_{i,B} - X_{i,F}}{X_{i,F} - X_{i,D}} \qquad i \text{ -}1,\ldots,C\text{-}1 \;\; ; \;\; i \neq k \qquad \text{(B.17)}$$

which can be rearranged to

$$\frac{S_{ext}(v_k - v_T x_{k,N-1})}{(1 + r_{ext})(v_k - v_T x_{k,B})} = \frac{X_{i,B} - X_{i,F}}{X_{i,F} - X_{i,D}} \qquad i \text{ -}1,\ldots,C\text{-}1 \;\; ; \;\; i \neq k \qquad \text{(B.18)}$$

Equations (B.17) and (B.18) can be used to obtain a relationship between the feed, distillate and bottoms composition i.e.

$$\frac{X_{1,B} - X_{1,F}}{X_{1,F} - X_{1,D}} = \frac{X_{i,B} - X_{i,F}}{X_{i,F} - X_{i,D}} \qquad i = 2,\ldots,C\text{-}1 \;\; ; \;\; i \neq k \qquad \text{(B.19)}$$

The above equation shows that not all the composition variables for the feed, distillate and bottom product are independent design variables. For example, for a four component mixture eq. (B.19) states that the composition of the feed, bottoms and distillate must lie on a straight line in the composition space defined by the transformed composition variables.

In order to study the geometry of distillation processes, it is convenient to approximate the set of discrete points generated by design equation. (B.10) and (B.14) by continuous profiles. This can be done by approximating the finite difference equations by a set of first-order ordinary differential equations. This differential model has the advantage of allowing us to use the extensive literature on ordinary differential equations to interpret the results. Also, it can be used to devise techniques for the calculation of minimum reflux ratios for distillation columns.

If we subtract $X_{i,n}$ from each side of equation. (B.10), we get

$$X_{i,n+1} - X_{i,n} = \frac{S_n^*}{S_n^* + 1} Y_{i,n} - X_{i,n} + \frac{1}{S_n^* + 1} X_{i,B} \qquad \text{(B.20)}$$

The quantity $X_{i,n+1}$ - $X_{i,n}$ is simply the increment in the liquid phase composition between nth and (n+1)th plates and is equal to $\Delta X_i/\Delta h$. In this case $\Delta h=1$. When ΔX_i is small or n is large, we can approximate the first differences $\Delta X_i/ \Delta h_i$ by dX_i/dh_i. equation. (B.20) can be written as

$$\frac{dX_i^s}{dh^s} = \frac{S^*}{S^* + 1} Y_i^* - X_i^S + \frac{1}{s^* + 1} X_{i,B} \qquad \text{(B.21)}$$

with initial condition

$X^S(h^S = 1) = X_B$

Similarly for rectifying section, we can write

$$\frac{dX_i^r}{dh^r} = \frac{r^* + 1}{r^*} Y_i^r - X_i^r + \frac{1}{r^*} X_{i,D} \qquad \text{(B.22)}$$

APPENDIX C

Physical and Thermodynamic Data

TABLE C-1: UNIQUAC Binary Interaction Parameters [HYSYS]

Components in Binary Pair, i – j	**Binary parameters**	
	$u_{i,j}$/R, K	$u_{j,i}$/R, K
Acetic acid-methanol	155.852	-151.546
Acetic acid-water	354.79	-204.473
Acetic acid – methyl acetate	907.555	-458.200
Methanol-water	576.506	-360.106
Methanol-methyl acetate	679.605	-130.742
Water-methyl acetate	617.904	-178.59

TABLE C-2: Structural Parameters [Van Ness and Smith]

Component	**R**	**Q**
Acetic acid	2.20230	2.07200
Methanol	1.4311	1.432
Water	0.92	1.3997
Methyl acetate	2.8041	2.5759

TABLE C-3: Boiling point at 1 atm [HYSYS]

Component	**Boiling point (K)**
Acetic acid	391.10
Methanol	337.80
Ethanol	351.40
Water	373.15
Methyl acetate	330.40
Ethyl acetate	350.30

TABLE C-4: Vapour Pressure [HYSYS]

$\ln P^* = A + B/(T+C) + D \ln(T) + ET^F$, P_{sat} in KPa

	Acetic acid	Methanol	Water	Ethanol	Methyl acetate	Ethyl acetate
A	6.13409E1	5.98373E1	6.59278E1	8.6486E1	9.65245E1	8.8376E1
B	-6.76888E3	-6.28289E3	-7.22753E3	-7.9311E3	-7.05036E3	-7.14786E3
C	0	0	0	0	0	0
D	-6.72663E0	-6.37873E0	07.17695E0	-1.02498E1	-1.23781E1	-1.09917E1
E	4.84265E-6	4.61746E-6	4.0313E-6	6.38949E-6	1.13721E-5	8.54613E-6
F	2	2	2	2	2	2

TABLE C-5: Molar Volume [HYSYS]

Molar volume = A + BT + CT^2 cc/gm mole, T in ^{0}K

Component	A	B	C
Acetic acid	121.7	-0.21808	4.8233E-04
Ethanol	53.7	-3.11071E-02	1.599E-04
Methanol	44.77	-7.17E-02	1.942E-04
Water	22.887	-3.64161E-02	6.855E-05
Ethyl-Acetate	30.61	-5.2404E-02	5.6E-05
Methyl-Acetate	150.998	-.5092	9.308E-04

TABLE C-6: Latent Heat of Vaporisation (λ) [HYSYS]

λ = A + BT + CT^2 cal/gm mole, T in ^{0}K

Component	A	B	C
Acetic acid	8349.9	-5.2695	-0.00298
Ethanol	10287	13.5120	-0.04788
Methanol	8757.278	14.8297	-0.04670
Water	12170.0	-1.7784	-0.01294
Ethyl-Acetate	10993.0	-3.3898	-0.01743
Methyl –Acetate	9038.864	-3.2339	-0.02716

TABLE C-7: Liquid Enthalpy (h) [HYSYS]

h =A + BT + CT^2 + DT^3 cal/gm mole, T in ^{0}K

Component	A	B	C	D
Acetic acid	-4.7224E03	14.0936	0.02584	-6.6967E-05
Ethanol	-3.7412E03	3.3019	0.01346	5.901E-05
Methanol	-2.844E03	3.6156	7.07E-03	4.2927E-05
Water	-5.954E03	23.5459	-0.01735	1.807E-05
Methyl acetate	-11.8102E03	44.8494	-0.03899	0.7207E-05
Ethyl acetate	-11.8187E03	46.089	-0.05635	9.250E-05

TABLE C-8: Dissociation constant of Acetic acid [Barbosa and Doherty, 1988]

log $k_A = C_1 + C_2/T$, T in ^{0}K

Component	C_1	C_2
Acetic acid	-10.4205	3166.00

TABLE C-9: V. L .E. data for Ethyl acetate system [Suzuki et. al., 1971]

Component	Vapour-Liquid Equilibrium
Acetic acid	Log K1 =-2.25E-02 x T-1.666
Ethanol	Log K2 = -2.3E-03 / T + 6.58825
Water	Log K3 = -2.3E-03 / T + 6.48351
Ethyl acetate	Log K4 = -2.3E-03 / T + 6.74151

APPENDIX D

HYSYS is The Integrated Engineering Environment - The Future of Process Modeling. In an Integrated Engineering Environment, all of the necessary applications work inside a common operating environment. There are the four critical advantages to this approach:

- Information is shared, rather than transferred, between applications.
- All applications use common thermodynamic models.
- One can only have to learn one interface.
- One can switch between modeling applications at any time, gaining the most complete understanding of the process.

HYSYS is a high degree of flexibility in how one can perform any task, combined with a consistent and logical approach to how these capabilities are delivered. There are four key aspects of HYSYS that are responsible for how you will use it:

First there is the Event Driven operation of HYSYS, which combines the power of interactive simulation with instantaneous access to information. Interactive simulation means that information is processed as you supply it, with calculations performed automatically. At the same time, you are not tied to the specific location of the program where you are supplying the information. You can access whatever information you need.

Second is the Modular Operation combined with the Non -Sequential solution algorithm. Not only is information processed as you supply it, but the results of any calculation are automatically propagated throughout the flowsheet, both forwards and backwards. The modular structure of the operations means that they can calculate in either direction, using information in an outlet stream to calculate inlet conditions. One can gain process understanding at every step, since the operations calculate the results immediately understanding each piece of the simulation in the greatest possible detail.

Third is the Multi-Flowsheet Architecture which allows you to create any number of flowsheets within a simulation. In addition to satisfying the technical requirement of using multiple property packages within a simulation, this architecture compliments the approach to modeling of interactive simulation.

And what brings all of these together is the Object Oriented Design of HYSYS. The separation of interface elements from the underlying engineering code means that the same information can be displayed simultaneously in a variety of locations. Each display is tied to the same process variable, so that if the information changes it is automatically updated in every location.

Primary Interface Elements

There are four primary interface elements for interacting with HYSYS.

- The PFD is a graphical environment for building your flowsheet and examining process connectivity. Process information can be displayed for each individual stream or operation as needed.
- The Workbook is a collection of Worksheets, displaying information in a tabular format. Each Workbook displays information about a specific object type i.e. all streams, pipes, controllers etc., on a single page. Multiple pages for a given object type can be installed, displaying information in varying levels of details.
- The Property View is a single view with multiple pages, accessed via page tabs. It is used extensively within HYSYS to contain all information about a specific object - an individual stream or operation - within a single view.
- The Summary View displays the currently installed streams and operations.

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