SIMULATION OF CONTINUOUS REACTIVE DISTILLATION COLUMN

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Chemical Engineering

by

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Abstract

The present work is concerned with constructing a computer program to simulate the analysis of multi-component, multistage continuous reactive distillation processes.

The rigorous method was used to build computer programs simulation for non ideal mixtures. The MATLAB $_{6.5}$ program as listed in appendix (D-1,2). The computer programs validity and accuracy were checked with Suzuki [5] using the esterification of acetic acid with ethanol to produce ethyl acetate and water.

The influence of various parameters upon the performance of the continuous reactive distillation column was studied. The parameters include feed plate location, reflux ratio, and number of stages. The influence of each parameter upon the distillation accompanied with chemical reaction was studied through vapor and liquid profiles, temperature profile, liquid composition and reaction rate profile.

The result obtained for the one feed reaction distillation column (esterification of acetic acid and ethanol to produce ethyl acetate and water, as an example) show that the purity of ethyl acetate is 48.70 % mole, when the reflux ratio is 10, the number of stages is 13 and the feed stage is 6. For a feed composition (acetic acid 0.4962, ethanol 0.4808, water 0.0229, ethyl acetate 0.0001).

The result obtained for the two feed reaction distillation column (esterification of acetic acid and ethanol to produce ethyl acetate and water, as an example) show that the purity of ethyl acetate increases 52.20 mole % when the reflux ratio is 10, the number of stages is 13 and the feed stage is 6. For a feed composition (acetic acid 1.0, ethanol 0.85, water 0.15).

The best design condition obtained from the present work using one feed gave 44.67 mole % of the ethyl acetate in distillate with reflux ratio of 13. Using a number of stages of 15, the ethyl acetate in distillate was 49.65 mole %. While using a feed location of 9, the ethyl acetate was 49.51 mole %.

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Notations

Symbols	definitions	units
A, B, C and D	constant of ideal gas specific heat, equation (2.39**)**	-
A, B, C and D	Tridiagonal matrix coefficient, equation (3.19)	mole/sec
A	Wilson constant, equation	-
C_p	Specific Heat, Equation	J/mole.K
H	Enthalpy	J/mole
H°_{fi}	Enthalpy of formation	J/ mole
H_L	Enthalpy of liquid phase	J/mole
H_{L_I}	Total enthalpy of liquid phase	J/mole
H_{mix}	Enthalpy of mixing J/mole	
H°_{v}	Ideal gas state enthalpy J/mole	
H_v	Enthalpy of liquid phase J/mole	
K	Equilibrium Constant	-
k	Reaction rate constant	
L	liquid flow rate	mole/sec
P	Pressure	N/m^2
P	Partial pressure	Kpa
R	Universal gas constant =8.314	J/mole.K

r	Reaction rate	mole/sec
T	Temperature	K
U	Liquid side stream	mole/sec
V	Vapor flow rate	mole/sec
VLE	Vapor liquid equilibrium	
W	Vapor side stream	mole/sec
x	Liquid mole fraction	
y	Vapor mole fraction	
z	Feed mole fraction	
p_i^{sat}	Partial pressure	
ai,j	NRTL non-randomness constants interaction	
v_k^i	Number of K groups in molecule i	

Greek letters

Λ	Wilson equation constant, equation (2.17)
γ	Activity coefficient, equation (2.16)
λ	Latent heat of vaporization, equation (3.5)
Δ	Change of difference
ϕ_{vi}^{Λ}	Vapor phase fugacity coefficient form equation (2.3)
ϕ_{li}^{Λ}	Liquid phase fugacity coefficient form equation (2.4)
ρ	Component density

Subscript

i	Component i in the mixture
j	Component j in the mixture
k	Type of function group
n	Number of stages
m	Number of component
f	Feed
V	Vapor phase
L	Liquid phase

Superscript

$\circ$	Pure component
id	ideal solution
mix	mixing
$c_\circ$	Combinational part
R_s	Residual part

Abbreviations

MESHR	Material balance, Equilibrium, mole fraction Summations, Enthalpy Balance, Reaction Rate
NRTL	Non-random, two liquid model.
VLE	Vapor – Liquid Equilibrium
RD	Reactive Distillation

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Chapter one
Introduction

1.1 Introduction

Reactive distillation is old but it is used for some outstanding applications in the recent years and hence the various aspects of it are being investigated worldwide, increasing attention has been directed towards continuous reactive distillation processes as an alternative to conventional processes. This has led to the development of a varity of techniques for simulating reactive multistage continuous columns.

Most of the distillation synthesis studies to data have been concerned with multi- components non ideal mixtures. The main advantages of this process relative to the conventional alternatives are the possibility of carrying equilibrium-limited chemical reactions to completion, and the simultaneous separation of the reaction products in only one unit. This reduces or eliminates reactor and recycle costs.

Reactive distillation processes, gained importance in process design. They are economically favorable in many cases [1], it has important alternative to the usual reaction separation processes.

Reactive distillation exploits chemical reactivity differences between the isomers. Especially for equilibrium limited reaction such as esterfication and ester hydrolysis reaction, conversion can be increased for beyond chemical equilibrium conversion due to the continuous removal of reaction products from the reaction zone. It has proved to be an important process alternative to the conventional reactor-separate configuration [3]. Reactive distillation involves simultaneous chemical reaction and distillation, the chemical reaction usually take place in liquid phase or at the surface of the solid catalyst in constant with the liquid phase [4].

1.2 The benefits of reactive distillation

The benefits of distillation with chemical reaction are:

Reactive distillation process for separation of isomeric mixtures that close boiling point, separation these mixtures very high cost. Reactive distillation exploits chemical reactivity differences between the isomers and separation [8].Second application of reactive distillation involves taking into account undesirable chemical reaction that may occur distillation .for example, separation of cyclopentadiene from c_7 hydrocarbons [19].

Achieve higher conversion rates for an equilibrium-limited reaction because of the continuous remotion of products begin formed and the heat of reaction can reduce the heat load of condensers or reboiler[20].

1.3 Commercial application of reactive distillation

The use of distillation column to carry out estification reaction has been considered since 1921[3].

More recently, reactive distillation has been proposed for the separation of close boiling mixtures, and the production of methyl tert-butyl ether (MTBE), an important anti-knock improver to replace tetra-ethyl lead in gasoline. Reactive distillation can also be found in process such as the production of condensation polymers the commercial applications of reactive distillation chemical companies strive to produce their products at lower costs through more efficient utilization of energy, reactants and industrial hardware (e.g. the conventional reactor separator combination) to intensified process.

Examples of reaction distillation processes [21]:

1- The esterification of acetic acid with ethanol to produce ethyl acetate and water.

2-The reaction of formaldehyde and methanol to produce methyl and water, using a solid acid catalyst

3-Esterification of acetic acid with methanol to produce methyl acetate
and water using sulfuric acid as a catalyst. The conventional process required distillation columns for separation. By using a reactive distillation this can be reduced to a single vessel with nearly 100% conversion.

4-Reaction of isobutene with methanol to produce methyl-tetr-butyl ether (MTBE), this is a complex process for the standard reactor and column setup since the mixture from 3 minimum boiling azeotropes. Using reactive distillation only one column is required .The butanes feed (isobutene and non-reactive n-butene) and methanol feed are both fed to the reactor near the bottom of reactive section .This give nearly 100% conversion and the formation of a product dimethyl ether is suppressed. The azeotropes are reacted away, due to the presence of extra components.

5- Separation of meta-xylene and Para-xylene. This mixture is very close boiling and hard to separate by using reactive distillation one component can be reacted away by using di-tert-butyl benzene as an extractive agent.

1.4 Aim of the Project

The aim of this work is to simulate multi-component multi-stages continuous reactive distillation for acetic acid and ethanol to produce ethyl acetate and water using rigorous method. The results of the developed model programs compared with the results obtained by Suzuki
[5] and AL-Khazraji [30], using different thermodynamic models (Wilson, UNIQUAC) were studied to obtain the best representation of the vapor-liquid equilibrium for the mixture used. Different variables were studied such as reflux ratio, number of stages, and location of the feed plates and number of feed.

Chapter two

Literature Survey

2.1 Introduction:

Distillation is the separation of chemicals by difference in how easily they vaporize, two major types of classical distillation include continuous distillation and batch distillation [1].

Continuous distillation process is one of the most important industrial processes for separating the different components of liquid mixtures [2]. Continuous processing is more cost effective for processing larger quantities, it often leads to a better product as continuous flow of material in and out of the processing equipment eliminates batch to batch variations in the product quality and prevents by product formation.

Reactive Distillation (RD) is a combination of reaction and distillation in a single vessel owing to which it enjoys a number of specific advantages over conventional sequential approach of reaction followed by distillation or other separation techniques. Improved selectivity, increased conversion, better heat control and avoidance of azoetrope[3].

Reaction depends on various factors such as volatilities of reactants and products along with the feasible reaction and distillation temperature. Although invented in 1921, the industrial application of (RD) did not take place before the 1980`s [3].

2.2 Reactive Distillation

Reactive distillation combines both the reactive and separations of mechanic of a distillation into a single unit [4] .Reactants are converted to products with the simultaneous separation of products and recycle of the unused reactants. It has become an important alternative to the usual separation processes considering a reversible reaction

$$A + B \Leftrightarrow C + D$$

Where the boiling point of components follow the sequence (A, C, D, and B), the conventional process consists of reactor followed by sequence of distillation columns. The mixture of A and B fed to the reactor, where the reaction takes place in the presence of a catalyst and reaches equilibrium.

A distillation train is required to produce pure products C and D the unreacted components A and B are recycled back to the reactor, figure (2.1a). The alterative configuration figure (2.1b) is the reactive distillation ,It consists of a reactive section in the middle with non-reactive rectifying and stripping sections at the top and bottom, respectively .The task of the rectifying section to recover reactant B from the product stream C. In the stripping section, the reactant A is stripped from the product stream D. In the reactive section the products are separation in situ, driving the equilibrium to the right and preventing any undesired side reactions between the reactants A (or) B with the product C (or) D. For a properly designed reactive distillation column, virtually 100% conversion can be achieved [30]. Figure (2.2) shows the different between used conventional distillation and reactive distillation.

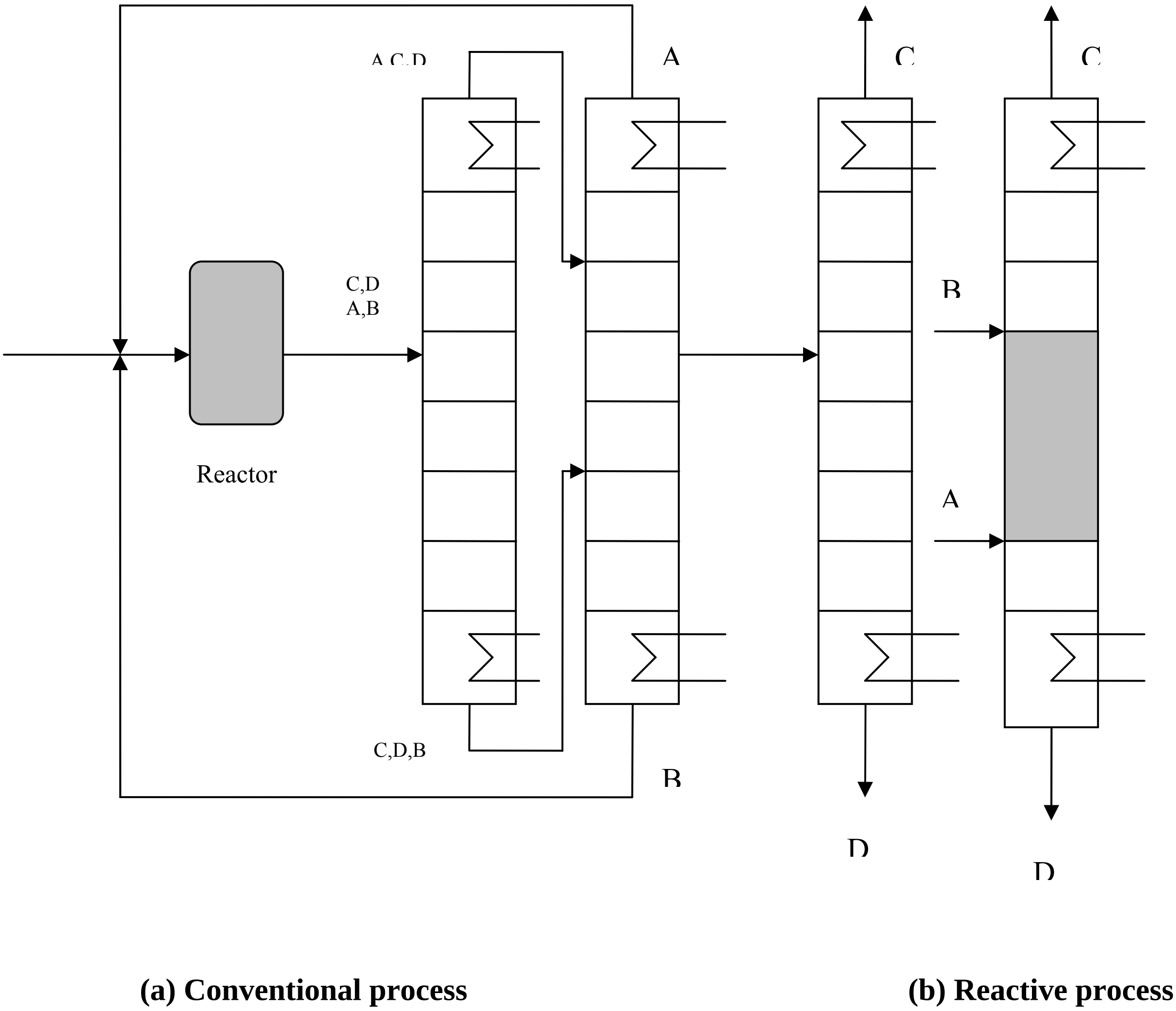
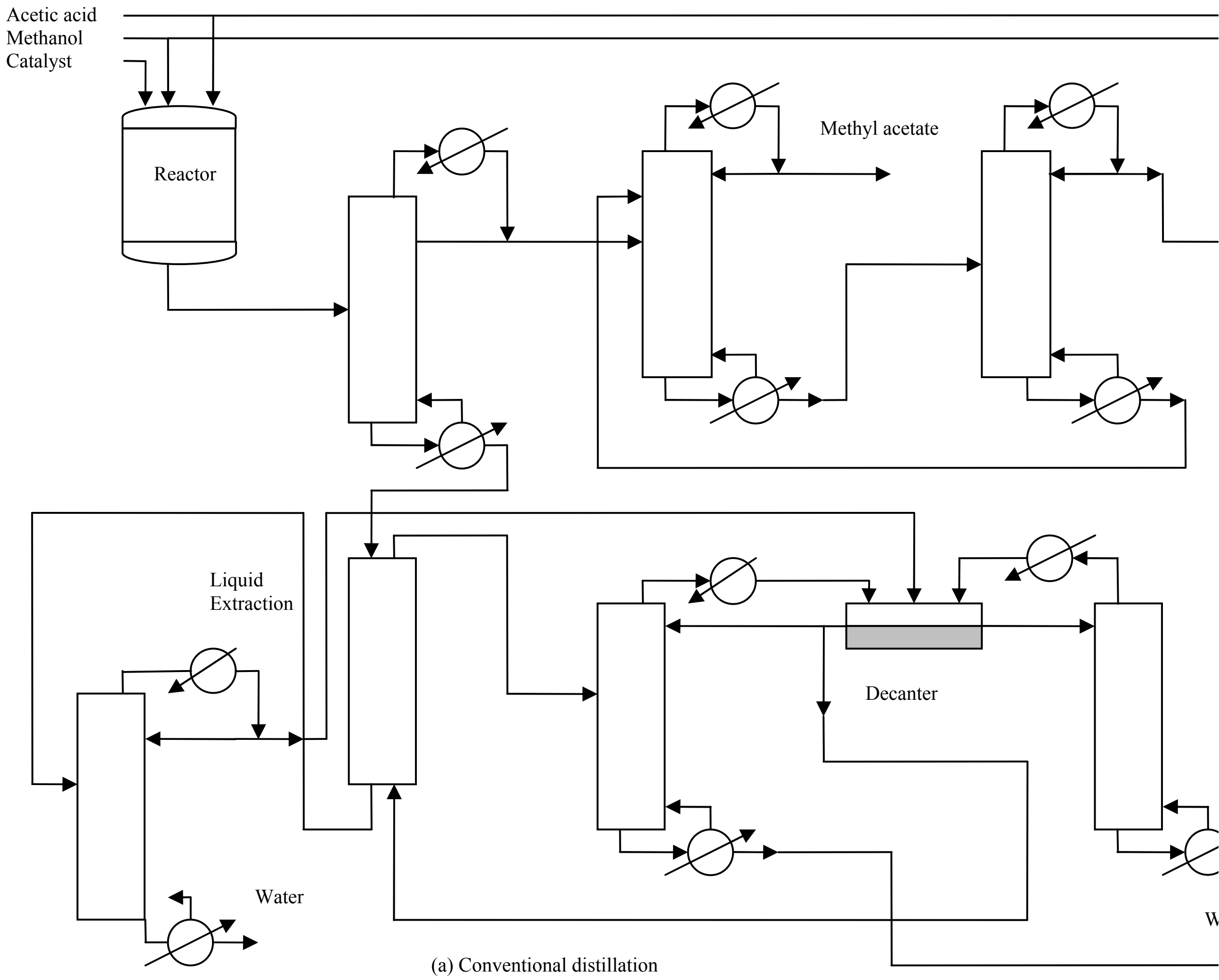


Figure (2.1) processing for a reaction $A + B \Leftrightarrow C + D$ (30)
(a) Conventional process consisting of reactor followed by distillation train.
(b) The reaction distillation configuration.



(a) Conventional distillation

Figure (2.2) processing schemes for the esterification reaction(6) .

Reactive distillation processes, gained an importance in process design. They are economically favorable in many cases and important alternative to the usual reaction separation processes.

Reactive distillation exploits chemical reactivity differences between the isomers, for example separation of meta-and para xylene has not been commercially feasible, very expensive because of the closeness of their boiling points. Meta-and para-xylene are similar in molecular structure[8],Especially for equilibrium limited reaction such as esterfication and ester hydrolysis reaction, conversion can be increased for beyond chemical equilibrium conversion due to the continuous removal of reaction products from the reaction zone. It has proved to be an important process alternative to the conventional reactor-separate configuration.

2.2.1 Reactive Distillation Processes

Some of the proposed systems for reactive distillation processes[7].

$$A+B \leftrightarrow C$$

A	B	C	Reference
Adipic acid	Hexamethyl-enediamine	Salt	Grosser el al. (1986)
Butadiene	Sulfur dioxide	Butadiene sulfone	A.I.Ch.E.(1970)
Ethylene oxide	Water	Ethylene glycol	Corrigan and Miller (1968)
Isobutene	Methanol	Methyl tera-butyl ether	Smith et al. (1984)

Some of the proposed systems for reactive distillation processes.

$A+B \leftrightarrow 2C$

A	B	C	Reference
Benzene	Xylene	Toluene	Bawa et al. (1975)
Acetic anhyride	Water	Acetic acid	Costa and Canepa (1969)

Some of the proposed systems for reactive distillation processes

$A+B \leftrightarrow C+D$

A	B	C	D	Reference
Acetic acid	Ethanol	Ethyl acetate	Water	Komatsu and Holland (1977)
Acetic acid	Methanol	Methyl acetate	Water	Corrigan and Ferris(1969)
Butanol	Ethyl acetate	Ethanol	Water	Davies and jeffreys (1973)
Butanol	Monobutyl phthalate	Dibutyl phthalate	Water	Berman et al.(1948)
Metr- Xylene	Sodium para-xylene	Sodium meta-xylene	para-xylene	Terril et al. (1985)

Some of the proposed systems for reactive distillation processes

$A+2B \leftrightarrow C+2D$

A	B	C	D	Reference
2,3-Butylene glycol	Acetic acid	2,3-Butylene glycol diacetate	Water	Schniepp et al.(1945)
Dimethyl terephthalate	Ethylene glycol	Diglycol terephthalate	Methanol	Baratella et al. (1974)

2.2.2 Continuous Reactive Distillation Operation

The combination of chemical reaction with continuous distillation in only one unit is called continuous reactive distillation.

The two main advantage of this process relative to the conventional alternatives are the possibility of carrying equilibrium limited chemical reactions to completion, and the simultaneous separation of reaction products in only one unit. This reduces or eliminates reactor and recycle costs [2].

Suzuki [5] described experimental results for the continuous

production of ethyl acetate in a distillation column reactor with sieve tray, and successive plate to plate design calculation with graphical techniques and empirical correlation. Also described the iterative method for the determination of stage temperatures, stage reaction rates and inter stage flow rates in the problem of multi component discussed, and the use of amodified Muller`s method for the convergence of the column temperatures profiles is proposed. Derivation of the equation is simplified by using matrix notation, which also has the advantage that any inter stage flow pattern is allowed. For the solution of the linearization material balance equation, the traditional matrix algorithm is employed.

Komatsu [9] performed correction of liquid composition by the relaxation method, this method consists of the normalization between liquid compositions calculated at n- th trial and these resulting from the material balance at hypothetical steady state. It has been confirmed that calculated results by using of this correction method converge to the actual values given by experimental data and that changes of the system from the start-up to the final steady state is simulated.

Barbosa, D. et al. [10] introduced a new set of transformed composition variables to simplify the design equation for double- feed multicompoent reactive distillation column. These new equations are used to develop a general method of calculating minimum reflux ratio for reactive distillation columns for etherification processes discussed.

Agreda et al. [11] used Computer simulations to test a method of minimizing the size of reactors and recycle stream, maximizing yields and conversions, and refining the product in as few steps as possible. This article describes the development of commercial process for the production of high-purity methyl acetate via counter current reactive distillation. The development and scale-up steps described include concept inception, laboratory testing, bench-scale testing, pilot plant development modeling and design, full-scale construction and operation, and final troubleshooting and optimization.

Platt, G. M. [12] developed a steady-state simulator for reactive distillation processes, in the transformed context proposed by UNG and DHERTY. In this transformed context, reactive stage equations and the reactive cascade equation are presented. Using the reactive extension of McCabe- Thiele approximations, an algorithm for solution of the reactive cascade is depicted. Compositional profiles in the column are obtained by the Newton- Raphson method. In this algorithm reactive bubble point calculation are substituted by the direct access to the locus of reactive vapor-liquid equilibrium, improving the simulator performance. Result is obtained for a reactive column for production of Methyl acetate where occurs the well-known etherification reaction, and presented in graphical from. These result shows that a reactive azeotropic is obtained in the top of column and pure water in the bottom

Bruggemann, S., et al. [13] described that shortcut method is a suitable tool for the assessment of feasibility and economic attractiveness of single distillation column. They presented two design algorithms for the synthesis of distillation sequences with minimum operation cost that rely on the analysis of each single split with a suitable shortcut model. The exhaustive enumeration of all sequences, which is widely used for zeotropic mixtures, is compared to an evolutionary optimization strategy. The performance of the evolutionary optimization strategy is assessed by studying one zeotropic and two azeotropic mixtures. The results show that the reliable determination of the best design alternative requires large computational effort.

Zhe Guo, et al. [14] u sing phase and reaction equilibrium information, the feasibility criteria for single-feed and double-feed reactive distillation systems are derived: When the products are a stable node and an unstable node and a part of the reaction equilibrium curve lies in the same distillation region as the products, both reactive rectifying and reactive stripping sections can feasibly produce pure products in a single-feed column. If one of the products is a saddle and no azeotrope exists between the products, a single-feed column is still feasible, but only with large reaction equilibrium constants. If a saddle product forms a minimum-boiling azeotrope with another product, an entrainer is needed to break this azeotrope in a double-feed column. If both reaction products are saddles, the same double-feed column configuration with an entrainer can produce pure products.

AL-Khazraji [30] discussed that continuous reactive distillation for the ideal and non ideal reactive distillation column for esterfication, using fortran program. then study the influence of various parameters , no. of stages, reflux ratio , location feed plate. check the accuracy of program with Isao and Holland.

2.2.3 Batch Reactive Distillation

Reactive distillation has been proved to be an important process alternative to the conventional reactor-separator configuration. Advantage of reactive distillation and flexibility of a batch process can be combined in batch reactive distillation. A simple method to estimate the advantage of using batch reactive distillation over conventional technology, for example in the production of low volume, high value specialty chemical batch distillation is one of the most common operations [2].

Reactive batch distillation columns. given the current applications of batch distillation in small-scale industries producing high-value-added specialty chemicals (pharmaceutical industry, fertilizers).

Mujtaba and Macchietto[15] considered a therotical comparative study with conventional and unconventional column for simultaneous chemical reaction and distillation,with the following reversible reaction scheme:

$$A + B \Leftrightarrow C + D$$

The reaction products are C (main product) and D. D being the most volatile component and C being volatile component in the reaction mixture. They found that the products are removed simultaneously with good conversion and the amount of the distillate product is achieved.

Sabine Giessler, et al. [16] the optimal operation problem of a reactive batch distillation column is solved for various types of models and also for different objective function. As the base case a detailed model, including a dynamic energy balance, is developed for the process producing ethyl acetate. The reflux ratio and the heat duty are selected as the variables to be optimized and are assumed to be piecewise constant. First, the effect of the number of piecewise and are assumed to be piecewise constant time period on the value of objective function investigation. The result indicated that performance is considerable improved with increased the number of time periods. Effect of the reaction on the trays, compared with case where reactions occur in reboiler only.

Kian Huat [17] discussed that batch distillation which is often directly coupled with chemical reactor such that the reactor acts as the reboiler of the column, This combined process increases the conversion of equilibrium reaction, making high conversions easily achievable, by the removal of one of the products through the distillation column.

Maria E. Huerta- Garrido and et al. [18] his work proposes a simplified methodology for the analysis and design of reactive batch distillation columns based on the McCab-Thiele method for reactive continuous columns and on the concept of a reactive difference point for reactive batch distillation columns, expressions for the Mc Cab-Thiele operating Line and for the dynamics of the reboiler in the reactive case have been derived; two cases are considered depending upon the phase in which reactions occur (i.e., liquid or vapor).

Haider, M.H [2] using computer simulation to study batch distillation for with or without reaction for the non ideal using esterification for example and MATLAB programs ,discussed the influence of various parameters ,such as no. of stages, batch time and liquid hold up checked the accuracy of program with Elgue.

2.3 Vapor- liquid equilibrium (VLE):

Modelling and design of distillation column requires tower related liquid and vapor phases compositions. Complexity of this correlation depends on the components number, their nature and the interaction between mixture components .

2.3.1 Ideal solution

Simplest model applies when both liquid and vapor phases are ideal solution call activity coefficients equal and the vapor is an ideal gas.Ideal solution behavior is often approximated by a solution comprised to molecules not too different in size and of the same chemical nature.

General to any solution where all molecules are of the same size and all forces between molecules (like and unlike) are equal. Equitation based on these characteristics provide a model of breviaries known as the ideal solution[22].

For pure ideal gas, fugacity is equal to its partial pressure

$$p_i = y_i p \qquad \dots (2.1)$$

Because of the close relation ship between fugacity and pressure, it is convenient to define their ratio for a pyre substance as

$$\phi_i = \frac{f_i}{p} \qquad \dots (2.2)$$

Which has a value of 1.0 for an ideal gas, for mixture partial fugacity, the coefficients are defined by.

$$\phi_{i_v} = \frac{f_{i_v}^{'}}{y_i p} \qquad \dots (2.3)$$

$$\phi_{i_l} = \frac{f_{i_l}^{'}}{x_i p} \qquad \dots (2.4)$$

As ideal gas behavior is approached $\phi_{i_v} \rightarrow 1.0$ and $\phi_{i_l} \rightarrow \frac{p_i^s}{p}$ where $p^s{}_i$= vapor (saturation) pressure.

$$a_i = \frac{f_i^{'}}{f_i^{\circ}} \qquad \ldots (2.5)$$

For ideal solution $a_{i_v} = y_i$ and $a_{i_l} = x_i p$ .When solutions are non ideal activity, coefficients based on concentrations in mole fraction are defined by

$$\gamma_{i_v} = \frac{a_{i_v}}{y_i} \qquad \ldots (2.6)$$

$$\gamma_{i_l} = \frac{a_{i_l}}{x_i} \qquad \ldots (2.7)$$

For ideal solution $\gamma_{i_v} = 1.0$ and $\gamma_{i_l} = 1.0$

Ideal solution occurs when molecular diameter is equal to the chemical interactions present, inter molecular forces between like and unlike molecules are equal, and in which all the activity coefficients are unity.Vapor phases are ideal solution and the vapor is an ideal gas. Ideal gas mixture is an ideal solution, and any equation applying toideal solution can also be applied to ideal gas mixture.

Converse is not true; there are many ideal solutions that are not ideal gases. The ideal gas mixture is an imaginary gas mixture and every component of the ideal gas obeys the ideal gas law equation.

$$z = \frac{pv}{RT} = 1 \qquad \ldots (2.8)$$

Ideal mixture, whose vapor –liquid equilibrium relationships depend on temperature only, but not on composition.

2.3.2 Non ideal solution

Most of distillation synthesis studies to date have been concerned with multi-component ideal mixture, a technique has been devised for
the synthesis of distillation processes for non-ideal mixtures.
At low pressure, both effects are negligible, at moderate pressure vapor solution may still be ideal even though the gas mixture does not follow
the ideal gas law.
Non idealities in liquid phase are severe even at low pressures.
ϕ_{i_l} Was used to express liquid phase non idealities for non-polar species. Polar species are present, mixture can be modified to include binary interaction parameters, k_{ij} as in (2-9)

$$a = \sum_{i=1}^{c}\left[\sum_{i=1}^{c} y_i y_j \left(a_i a_j\right)^{0.5}\left(1 - k_{ij}\right)\right] \qquad \ldots (2.9)$$

To describe the phase equilibrium of a system on N components at a temperature. Pressure and at equilibrium, fugacity of vapor equal of liquid phase

$$f_{i_v}{}^{\wedge} = f^{\wedge}{}_{i_v} \quad \text{For i= (1, 2, and 3, n)} \qquad \ldots (2.10)$$

To form an equilibrium ratio, these partial fugacity are common
replaced by expression involving mole fraction derived from the
definitions.

$$f_{i_l} = \gamma_{i_l} x_i f_{i_l} \qquad \ldots (2.11)$$

$$f_{i_v} = \phi_{i_l} x_{i_l} p \qquad \ldots (2.12)$$

$$f_{i_v} = \phi_{i_v} y_i p \qquad \ldots (2.13)$$

$$k = \frac{\phi_{i_{l;}}}{\phi_{i_v}} \qquad \ldots (2.14)$$

If we used equation (2.12), (2.13) in equation (2.14) we obtain

$$k_i = \frac{\gamma_{i_l} f_{i_l}^{\circ}}{\phi_{i_v} p} = \frac{\gamma_{i_l} \phi_{i_l}}{\phi_{i_v}} \quad \ldots (2.15)$$

At low pressure $\phi_{i_l} = \frac{p_{i_s}}{p}$ and $\phi_{i_v} = 1.0$ so

$$k_i = \frac{\gamma_{i_l} p_{i_s}}{p} \quad \ldots (2.15.a)$$

There are several models to calculate activity coefficient in multi-component system. The most important models are (Wilson, NRTL, UINIQUA and UNIFAC)

2.3.2.1Wilson model

The models proposed by Wilson in 1964 [26,27] is based on the concept of local composition and leads to an expression for the Gibbs free energy, the distribution of molecules is not purely random and that non- ideal mixing is associated with this fact, is useful for calculation the activity coefficient of any component in quaternary solution using only parameters obtain from binary vapor-liquid equilibrium data. These parameters $(\Lambda_{ij}, \Lambda_{ji})$ are assumed to be independent of temperature although, for the best accuracy they should not be used at temperature too far from that at which they were determined . Wilson equations include the superior representation of activity coefficient for both polar and non-polar mixtures.

Wilson received wide attention because of its ability to fit strongly non ideal mixtures to become highly non ideal, but still miscible, Wilson equation become markedly superior to another models.

Wilson equation has been very often used in calculation of vapor-liquid equilibrium .However, it is not easy to obtain the parameters Λ_{ij} and Λ_{ji} which can be determined from the binary data only.

$$\ln \gamma_i = 1 - \ln \sum_{j=1}^{C} x_j \Lambda_{ij} - \sum_{k=1}^{C} \left[\frac{x_k \Lambda_{ki}}{\sum_{j=1}^{C} x_j \Lambda_{kj}} \right] \qquad \text{... (2.16)}$$

Where

$$\Lambda_{ij} = \frac{V_j^L}{V_i^L} \exp\left(- \frac{\lambda_{ij} - \lambda_{ii}}{RT} \right) = \frac{V_j^L}{V_i^L} \exp\left(- \frac{A_{ij}}{RT} \right) \qquad \text{... (2.17)}$$

where

$\lambda ii=\lambda jj=1$
$Aii=Ajj=0$
$\Lambda ii=\Lambda jj=1$

Characteristics of Wilson model [28, 29]

a. Relatively flexible model.

b. suitable for large variety of non ideal mixtures except systems of limited solubility .

c. Wilson model for a multi-component solution requires only parameters which can be obtained from binary mixtures data.

d. not applicable to partiality miscible system .

2.3.2.2 Non- Random two –liquid (NRTL model)

The NRTL model was developed by Renon and Prausnitz [31,32] describing liquid-liquid equilibrium, NRTL model contains three parameters per binary interaction compared with the two parameters of Wilson models, but based on similar local composition treatment.

Equations of NRTL model

$$G_{ij} = \exp\left(-\alpha_{ij}\tau_{ij}\right) \qquad \ldots (2.18)$$

$$\ln\gamma_i = \frac{\sum_{j=1}^{nc}\tau_{ij}G_{ij}x_i}{\sum_{j=1}^{nc}G_{ij}x_i} + \sum_{j=1}^{nc}\frac{x_j}{\sum_{j=1}^{k}G_{kj}x_k}\left[\tau_{ij} - \frac{\sum_{k=1}^{nc}x_k\tau_{kj}G_{kj}}{\sum_{k=1}^{nc}x_kG_{kj}}\right] \qquad \ldots (2.19)$$

2.3.2.3 UNIQUAC model

The UNIQAC (Universal Quasi-Chemical) equation, were develop by Abrams and Prausniz [33,36], based on a semi-theoretical approach to the mixture problem that includes a local composition model.Non- ideality of liquid mixtures has contributions not only fromspecific interaction but also from the difference in the size and shape of the molecules .The UNIQUAC equation is modified slightly to yield better results for those binary systems where an alcohol is one of the components. UNIQUAC parameters are at least weakly temperature dependent. A particularly useful equation, applicable to a wide variety of liquid mixtures, used only two adjustable parameters per binary in addition to pure-component parameters reflecting the sizes and outer surface areas of the molecules. (short for universal quasi chemical) developed by Abram's and Prausnitz. In this model, the liquid-phase activity coefficients can be individually differentiated in the combinatorial part, which includes the geometric significance for combining molecules of different shapes and sizes, and the residual part, which includes the energy parameters

$$\ln\gamma_i = \ln\gamma_i^{Co} + \ln\gamma_i^{Rs} \qquad \ldots (2.20)$$

Where,

$$\ln\gamma_i^{Co} = \ln\frac{\phi_i}{x_i} + \frac{z}{2}q_i\ln\frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i}\sum_{j=1}^{C}x_jl_j \qquad \ldots (2.21)$$

$$\ln\gamma_i^{Rs} = -q_i\ln\left(\sum_{j=1}^{c}\theta_i\cdot\tau_{ji}\right) + q_i - q_i\sum_{j=1}^{c}\frac{\theta_i\cdot\tau_{ij}}{\sum_{c}^{j=1}\theta_k\tau_{kj}} \qquad \ldots (2.22)$$

Where,

$$\tau_{ij} = \exp\left(-\frac{u_{ij} - u_{jj}}{RT}\right) = \exp\left(-\frac{A_{ij}}{RT}\right) \quad \ldots (2.23)$$

$$\phi_i = \frac{r_i x_i}{\sum_{j=1}^{C} r_j x_j} \quad \ldots (2.24)$$

$$\theta_i = \frac{q_i x_i}{\sum_{j=1}^{C} q_j x_j} \quad \ldots (2.25)$$

$$ri = \sum_k v_k^i R_k \quad \ldots (2.26)$$

$$qi = \sum_k v_k^i Q_k \quad \ldots (2.27)$$

$$l_j = (\frac{z}{2})(r_i - q_j) - (r_j - 1) \quad \ldots (2.28)$$

Models in use today and extensive tabulations of the pure-component and binary parameters are available. Only pure-component and binary parameters are required for application to multi-component systems and the model is useful in both vapor-liquid and liquid-liquid equilibrium.

2.3.2.4 UNIFAC model

The UNIFAC (UNIQUAC) functional Group activity coefficients was developed largely by Fredenslud el .al. [34,35], Application of the model is restricted to the temperature rang 273 to 373 K.

The model is based on the UNIQUAC equations with all pure- substance and binary parameters determined by empirical group-contribution methods.

$$\tau_{ij} = \exp\left(A_{ij}\right) \qquad \text{... (2.29)}$$

$$\phi_i = \frac{r_i x_i}{\sum_{j=1}^{C} r_j x_j} \qquad \text{… (2.30)}$$

$$\theta_i = \frac{q_i x_i}{\sum_{j=1}^{C} q_j x_j} \qquad \text{… (2.31)}$$

$$l_j = (\frac{z}{2})(r_i - q_j) - (r_j - 1) \qquad \text{… (2.32)}$$

$$\ln \gamma_i^{Co} = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_{j=1}^{C} x_j l_j \qquad \text{… (2.33)}$$

$$\ln \gamma_i^{Rs} = -q_i \ln\left(\sum_{j=1}^{c} \theta_i \cdot \tau_{ji} \right) + q_i - q_i \sum_{j=1}^{c} \frac{\theta_i \cdot \tau_{ij}}{\sum_{c}^{j=1} \theta_k \tau_{kj}} \qquad \text{… (2.34)}$$

$$\ln \gamma_i = \ln \gamma_i^{Co} + \ln \gamma_i^{Rs} \qquad \text{… (2.35)}$$

2.4 Enthalpy for Multi-component

The enthalpies of pure species or mixture at temperature and pressure are as follow[19].

$$H_v = \left[\sum_{i=1}^{m} y_i H_{V_I}^{\circ} \right] + \left(H_V - H_V^{\circ} \right) \qquad \text{… (2.36.a)}$$

$$H_l = \left[\sum_{i=1}^{m} x_i H_{v_i}^{\circ} \right] + \left(H_l - H_v^{\circ} \right) \qquad \text{… (2.36.b)}$$

Where H_v° is ideal gas state enthalpy and it is identical to the zero pressure enthalpy of real fluid at the same temperature, i.e,

$H_v^{\circ} = H(T, P = 0)$ [23],

This can also be defined as the integral of specific heat of gases. The specific heat of gases is conventionally given as a polynomial in temperature.

The total enthalpy of liquid phase is given by:

$$H_{l_i} = \sum_{i}^{n} x_{ij} H_l + H_{mix} \qquad \ldots (2.37)$$

Where:

$$H_{mix} = RT \sum_{i=1}^{c} (x \ln \gamma_i) \qquad \ldots (2.38)$$

$$cp_v^\circ = A + BT + CT^2 + DT^3 \qquad \ldots (2.39)$$

Integration of equation (2.39)

$$H_v^\circ = \int_{T^\circ}^{T} cp_V^\circ dt \qquad \ldots (2.40)$$

For ideal gas solution, vapor enthalpy is simply

$$H_v^{id} = \sum_{i=1}^{m} (y_i H_{v_i}^\circ) \qquad \ldots (2.41)$$

$$H_l^{id} = \sum_{i=1}^{m} (x_1 H_{v_i}^\circ - \lambda_i) \qquad \ldots (2.42)$$

For total enthalpy of vapor phase

$$H_v = \sum_{1}^{m} \sum_{i}^{nt} (k_i(j) * x_i(j) * H_v(j)) \qquad \ldots (2.43)$$

2.4.1 Enthalpy of vaporization

The enthalpy of vaporization or the enthalpy of the saturated vapor is that of saturated liquid at the same temperature, because of the forces of attraction between the molecules of the liquid, the molecules escaping are those of higher energy of the remaining molecules in the liquid ,and energy must be supplied to maintain the temperature constant [24].

2.5 Thermodynamic of reaction

The reaction of acetic acid and ethanol has been studied to produce ethyl acetate and water. The over al reaction rates to be calculated by the summation of the reaction rate on each stage [19]:

$$\sum \Delta R_j - \Delta R = 0 \quad \ldots (2.44)$$

The value of the reaction term may be calculated for a given hold up, composition, molar volume and temperature of the liquid. The dependence of rate constant on the temperature and concentration of non-reacting components is needed.

2.6 Heat of reaction

Reactive distillation efficiently uses the heat released by a reaction. In conventional reactors. The heat of reaction is removed by cooling coil or heat exchangers. Since a boiling liquid in the RD process surrounds the catalyst, the heat of reaction improves distillation by increasing the vapor flow. The result energy saving since reboiler duties can be lowered in RD column [30].

Heat of reaction at any temperature can be calculated from heat capacity data if the value for one temperature is known; the tabulation of data can, therefore, be reduced to the compilation of standard heats of formation at a single temperature [19].

The calculation of standard reaction at other temperatures from knowledge of the value at the reference temperature has been given in the following equations [2]:

$$\Delta H^{\circ} = \sum_{i}^{m} v_i H_{f_i}^{\circ} \quad \ldots (2.45)$$

Where the sign convention for v_i is as follow:

Positive (+) for products and negative (-) for reactants

$$\Delta H_T = \Delta H^{\circ} + \int_{T^{\circ}}^{T} \Delta cpdt \quad \ldots (2.46)$$

Where

$T_{\circ}$ = reference temperature

Chapter Three

Theoretical Aspects of Continuous Reactive Distillation

3.1 Introduction

The calculation of reactive distillation has become more and more important in modern process design.

Reactive distillation involves simultaneous chemical reaction and distillation, the chemical reaction takes place in the liquid phase .One general application of reactive distillation is the separation of a close-boiling or azeoropic mixture.

The theoretical models of various process units are derived by using the fundamental principles of conservation of mass, energy and momentum. In its most general form, the conservation principle states that:

Input+ generation=output+ accumulation

For steady state systems, the accumulation terms are always equal to zero and no generation therefore the total input of any conserved quantity to a particular unit must be equal to the total out put.

In this chapter, the mathematical model for simulating a multi-component continuous distillation with chemical reaction is considered to calculate the mole fraction of components by using fundamental principles of mass and energy balances , vapor-liquid equilibrium and reaction rate in a developed program written in (MATLAB); to give composition profile , temperature profile , vapor and liquid flow rate and reaction rate profile .

3.2 Simulation model of multi-component continuous reactive distillation

The Simulation model of multi-component continuous reactive distillation can be divided into:

3.2.1 Method of analysis

The analysis emphasized to simulate a multistage multi- component steady state continuous reactive distillation of N feed components in non-ideal case into relatively pure products.

The widely used system in the study of reactive distillation is the estrification of acetic acid (A) with ethanol (B) to produce ethyl acetate (D)and water (C) was used in the simulation calculation .The reaction is :

$$CH_3COOH + CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + H_2O$$

(Acetic acid) + (Ethanol) → (Ethyl acetate) + (water)

A B C D

The material and energy balances were carried out using rigorous method plate-to- plate calculation to solve MESHR equations of continuous steady state distillation with chemical reaction, to give the composition, internal flow rates of vapor and liquid, reaction rate and temperature profiles for each stages in the column . The feed is assumed liquid at its boiling point.

3.2.1.1 Model assumptions

The simulation model is formulated using the following assumptions:

1- Steady-state continuous operation.

2- Thermal condition of feed (feed at boiling point).

3- The distillation is performed adiabatically.

4- Perfect mixing on all stages.

5- Total condensation.

6- Ideal vapor phase $\phi = 1$ and non-ideal in liquid $\gamma \neq 1$ for all components in mixture.

7- Operating pressure is 1 atm.

Different feed plate location, different number of stage and different reflux ratio were considered.

3.2.2 Specifications of variables

The variables considered for the process system are:

1- Reflux ratio (7, 10, 13).

2- Feed plate location for one feed or two feeds to the tower (3, 6, 9).

3- Number of stage (11, 13,15).

Table (3.1) shows the feed system that has been studied with its composition for single feed. The physical and chemical properties are variable in literature and are given in appendix A table (A-1).

Table (3.1) feed system and its composition (Suzuki, AL-Khazraji)

Components	Composition (mole fraction)
Acetic acid (A)	0.4962
Ethanol (B)	0.4808
Water (C)	0.0229
Ethyl acetate(D)	0.0001

The initial input data to the developed computer program for the simulation model for single feed figure (3.1) are as follows:

1- Number of stages =13.

2- Reflux ratio =10.

3- Temperature of feed, top and bottom are 79, 72, and 92 in C° .

4- Feed flow rate =0.1076 mole/min.

5- Location of the feed plate is (6) from top.

6- Distillat flow rate = 0.0208 mole/min.

7- Bottom flow rate =0.0868 mole/min.

8- hold-up is taken 1.0 *L* at the bottom and 0.3 *L*at each stage.

Table (3.2) shows the feed system that has been studied with its composition for double feed. The physical and chemical properties are variable in literature and are given in appendix A table (A-1).

Table (3.2) feed system and its composition Suzuki

Components	Composition (mole fraction)
Acetic acid (A)	1.0
Ethanol (B)	0.85
Water (C)	0.15
Ethyl acetate(D)	0.0

The initial input data to the developed computer program for the simulation model for double feed figure (3.2) are as follows:

1- Number of stages =13.

2- Reflux ratio =10.

3- Temperature of feed, top and bottom are 72.13, 79, and 92 in C°.

4- Feed flow rate =0.0538 mole/min.

5- Acetic acid, fed to six stage from the top and ethanol fed to the second stage from the bottom.

6- Distillation flow rate = 0.0208 mole/min.

7- Bottom flow rate =0.0868 mole/min.

8- hold-up is taken 1.0 *L* at the bottom and 0.3 *L*at each stage.

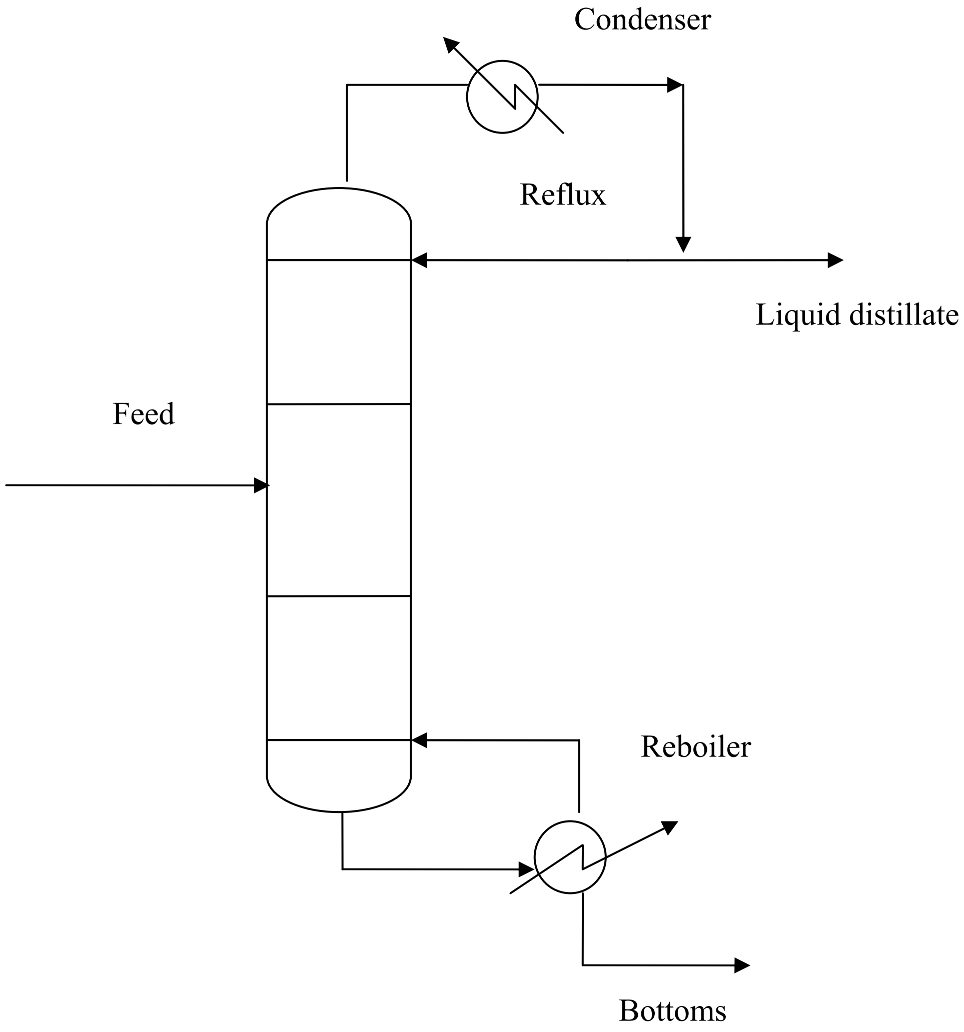


Fig (3.1) Reactive Distillation Column for one feed system.

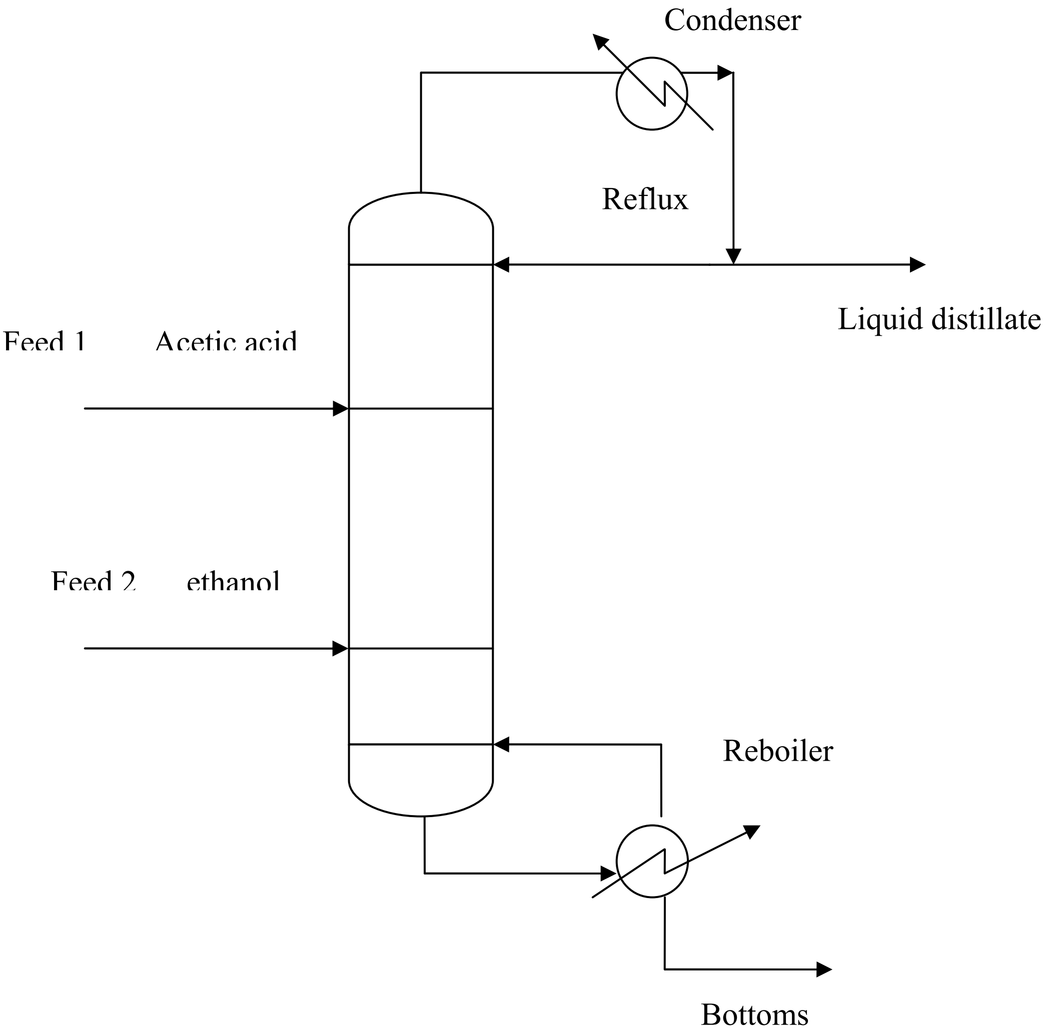


Figure (3.2) Reactive distillation column with two feeds

3.3 Vapor-liquid equilibrium for non ideal system

Vapor –liquid equilibrium is one of the fundamental properties necessary for the calculation of separation process in chemical industry, a simple expression of vapor-liquid equilibrium is Raout's law.

For non-ideal mixture variable (activity coefficient) is appeared in vapor-liquid equilibrium equation to represent the deviation from ideality in liquid phase. In vapor phase ϕ_i (fugacity coefficient) is used to represent the degree of deviation from ideality in vapor phase

The value of $\phi_i \cong 1.0$ for the system used in the present work, and solutions are shown in appendix C(C-1) Therefore,

$$y_i = \frac{\gamma_i p_{sat}}{p} x_i \qquad \dots (3.1)$$

When $\gamma_{\circ} = 1$ the mixture is ideal when the mixture is non-ideal the deviation from ideality is either positive $\gamma_i > 1$ or negative $\gamma_i < 1$.

Several models have been used to calculate the activity coefficient and the most useful models are (Wilson, NRTL , UINQUAC and UNIFAC). In this work Wilson and UNIQUAC have been used and explained in chapter (2).

The value of γ_i is positive deviation from ideality [2].

3.3.1 vapor-liquid equilibrium ratio (K)

Vapor-liquid equilibrium (distribution coefficient) depends on total pressure, temperature and composition; so it is a function of temperature, pressure and the composition of both phases. The distribution coefficient for non-ideal mixture is:

$$K_j = \frac{y_i}{x_i} = \frac{\gamma_i p_i^{sat}}{p} \qquad \dots (3.2)$$

3.3.2 Antoine equation

The vapor pressure at ideal condition is satisfactory for general use; the vapor pressure of each component in this study is calculated by using Antoine equation.

$$Inp_i^{sat} = A_i - \frac{B_i}{C_i + T_{ij}} \qquad \text{… (3.3)}$$

Where the temperature T is in C° and the pressure in atm [25] .Antoine parameters for all components are given in appendix A, Table (A-2).

3.4 Vapor and Liquid Enthalpy

The vapor enthalpy is calculated using the following [30]

$$H_{vi} = a_{1i} + a_{2i}T + a_{3i}T^2 + a_{4i}T^3 \qquad \text{… (3.4)}$$

The parameter a_{1i}, a_{2i}, a_{3i} and a_{4i} for each component are given in appendix A table (A-4).

The enthalpy of liquid is calculated from vapor enthalpy and latent heat.
The latent heat equation used for this system is.

$$\lambda_{i2} = \lambda_{i1}\left(\frac{1 - Tr_2}{1 - Tr_1}\right)^{0.38} \qquad \text{… (3.5)}$$

Where

λ_{i1} = latent heat at normal boiling point.

$$T_r = \frac{T}{T_c}$$

T_r = Reduced temperature

T_c = Critical temperature

T_c Listed in appendix A table (A-1).

3.5 Rate of Reaction

In reaction distillation process, reaction and separation occurs simultaneously. The value of reaction term have been calculated in this work for a given hold-up , composition , molar volume ,and temperature of the liquid if we know the dependence of the rate constant on the temperature and concentration of non-reacting components. The reaction term for the production of ethyl acetate is as follows [5]:

$$\Delta R_j = k_j \phi_j \left(\frac{x_{1j}}{\sum_{i=1}^{m} x_{ij} \rho_{ij}} \right)^2 10^6 \qquad \ldots (3.6)$$

Where k_j reaction rate constant depends on the temperature and concentration of non-reacting components is calculated as follows [5]:

$$\log k = -\frac{2.71 * 10^3}{T} + 3.7 \qquad \ldots. (3.7)$$

The molar volume (ρ_{ij}) is a function of temperature and is calculated as.

$$\rho_{ij} = \frac{A}{B^{\wedge(1+(1-T/C)\wedge D)}} \qquad \ldots (3.8)$$

Where A, B, C and D are constants for each component and are give in appendix A table (A-3).

T is in Kelvin

ϕ_i The liquid hold up is taken 1.0 *L* at the bottom; on each stage and top taken 0.3*L*.

3.6 Heat of Reaction

A process involves chemical reaction; heat will invariably be added or removed.

The moment of heat given out in chemical reaction depends on the conditions under which the reaction is carried out. The standard heat of reaction is the heat released when the reaction is carried out under standard conditions: pure components, pressure 1 atm, temperature usually, but not necessarily, $25\,C^\circ$.

The average heat of reaction over the whole temperature range can be determined by using the following equation [2].

$$\Delta H_T = \Delta H^\circ + \int_{T^\circ}^{T} \Delta cpdt \qquad \ldots (3.9)$$

$$\Delta H^\circ = \sum_i^m v_i H_{f_i}^{\ \circ} \qquad \ldots (3.10)$$

Where $H_{f_i}^{\ \circ}$ is the heat of formation of component and is given in appendix A table (A-1).

and v_i is the stoichiometric number and is positive (+) for products and negative (-) for reactants.

3.8 Bubble Point Calculation

Bubble point (BP) is calculated, because a new set of stage temperature is computed during each iteration from bubble point equations.A new set of temperatures Ti_N is computed stage by stage by computing bubble point temperatures from the normalized $x_{i,N}$ values; the necessary (BP) equation is non-linear in TN and must be solved iteratively. The bubble point temperature has been evaluated by trial and error calculations using Newton's method.

According to this method the correct temperature was calculated. For each assumption, the value of sum is computed from

$$sum=\sum_{i=1}^{C}(K_{i,N}x_{i,N})-1=0 \qquad 1\leq N\geq Nt \qquad \dots (3.11)$$

To normalize $x_{i,N}$ and to decrease the percentage error, *sum* should be between 0.999 and 1.0 [22].

3.9 Design Method

The composition, temperature, flow rate profiles and heat transfer at each stage were determined by using rigorous method [19].

3.9.1 Rigorous Method Algorithm with Chemical Reaction

Theoretical model for an equilibrium stage consider a general, continuous, steady–state reactive distillation column consisting of a number of stages arranged in a counter current cascade Figure (3.3) .A general schematic representation of equilibrium stage j is shown in Figure (3.4), where the stages are numbered down from the top .

Entering stage j can be one phase feed of molar flow-rate F_j, with overall composition in mole fraction z_{ij} of component i, temperature T_{fj}, pressure P_{fj}, and corresponding overall molar enthalpy H_{fj}. Also entering stage j can be inter stage liquid from stage j-1 above , if any of molar flow-rate L_{j-1} with composition in molar fraction x_{ij-1}, enthalpy H_{lJ-1} ,temperature T_{j-1}, pressure P_{j-1} , which is equal to or less than the pressure of static head change across head L, reaction rate ΔR_{j-1} , similarly , from stagej+1 below interstage of molar flow-rate V_{j+1} , with composition y_{ij+1}, enthalpy $H_{v\ j+1}$, temperature T_{j+1} ,pressure P_{j+1} ,and reaction- rate ΔR_{J+1} , can inter stage j; leaving stage j is vapor of intensive properties $y_{ij}, H_{vj}, T_j, P_j,$ and ΔR_J, this stream can be divided into a vapor side stream of molar flow-rate W_j and an inter stage stream of molar flow-rate $V_{j,}$ to be sent to stage j-1 or ,if j=1 to leave the column as product. Also leaving stage j is liquid of intensive properties x_{ij}, H_{ij}, P_j, and ΔR_j when it is in equilibrium with vapor ($V_j + W_j$). This liquid L_j produced from molar flow-rate, is sent to stage j+1, or if j=n to leave the tower as a product. Heat can be transferred at a rate Q_i from (+) or (-) to stage j to simulate stage intercoolers and interheaters.

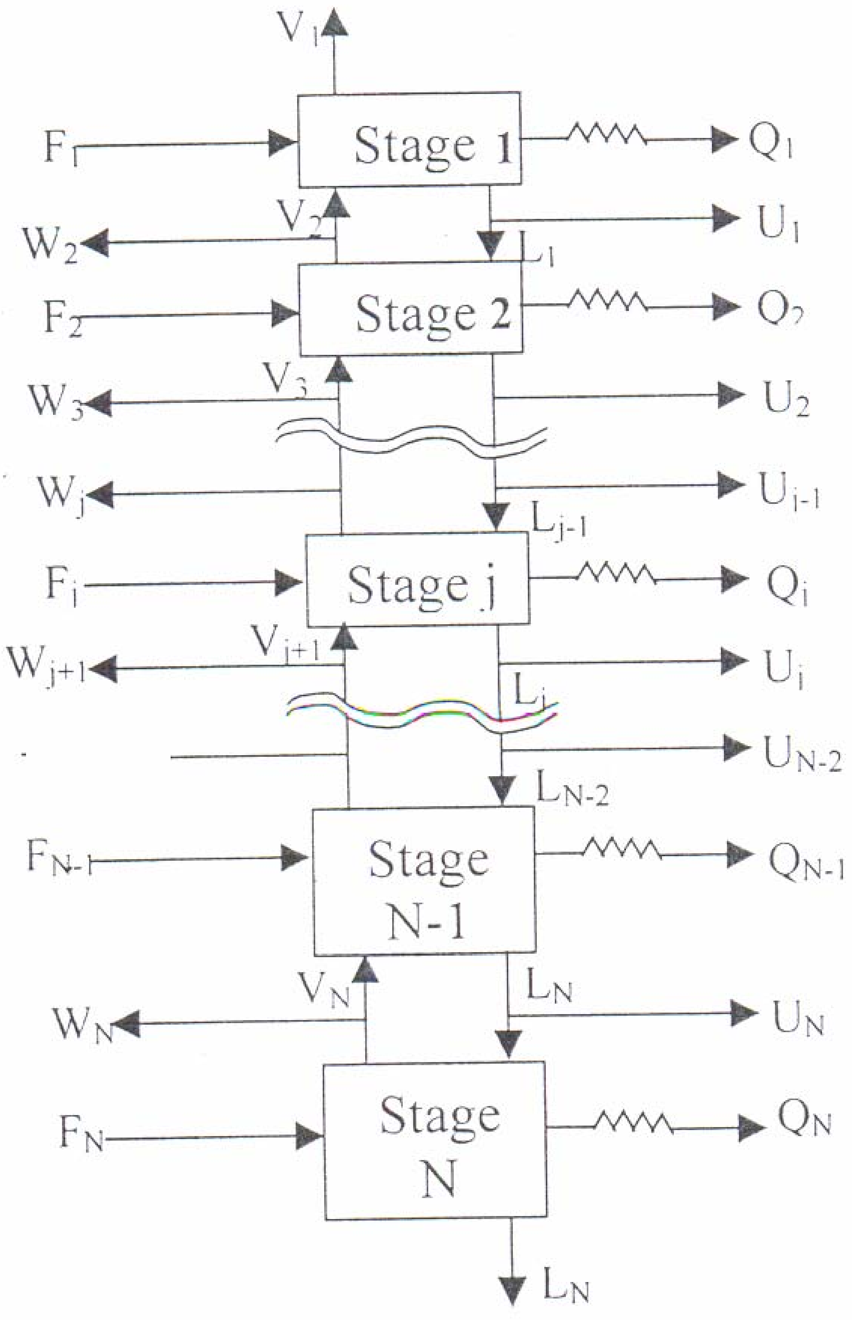


Fig. (3.3) General Reactive Distillation Column [19]

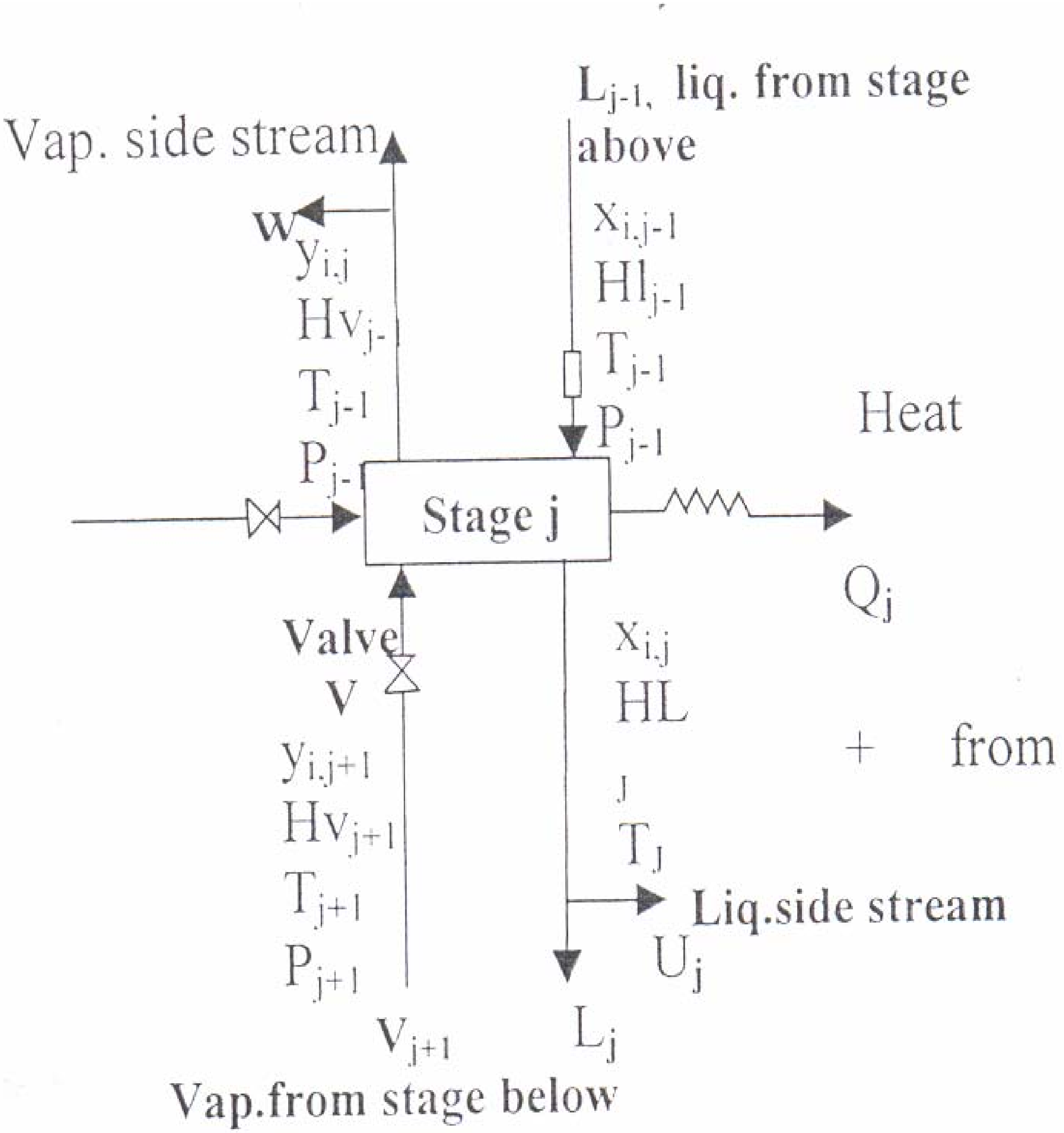


Figure (3.4) General Equilibrium Stage [19].

The model equation may be expressed as follows:

1- The material balance equation (M-equation).

$$\begin{aligned} M_{ij} &= L_{j-1}x_{ij-1} - (V_j + W_j)y_{ij} - (L_J + U_j)x_{ij} + V_{J+1}y_{ij+1} \\ &+ F_j z_{ij} \pm \Delta R_j = 0 \end{aligned} \quad \ldots (3.12)$$

Where the sign of reactants in ΔR_j is negative and positive for only one of the products.

2-Phase equilibrium relation (E-equations).

$$E_{ij} = y_{ij} - K_{ij}x_{ij} \quad \ldots (3.13)$$

3-Mole fraction summations equations (S-equations).

$$(Sy)_i = \sum_{i=1}^{m} y_{ij} - 1 = 0 \quad \ldots (3.14a)$$

$$(Sx)_i = \sum_{i=1}^{m} x_{ij} - 1 = 0 \quad \ldots (3.14b)$$

Where: m is the number of component.

4-Energy balance equations (H-equations).

$$\begin{aligned} H_i &= L_{j-1}H_{LJ-1} - (V_J + W_J)H_{VJ} - (L_J + V_J)H_{LJ} + V_{J+1}H_{VJ+1} \\ &+ F_J H_{Fj} - Q_j + \Delta R_j H_{rj} = 0 \end{aligned} \quad \ldots (3.15)$$

5-Reaction rate equations (R-equations).

$$\sum_{j=1}^{n} \Delta R_j - R = 0 \quad \ldots (3.16)$$

N= number of stages.

The solution of (MESHR) equations for multi-component reactive distillation problems is obtained by finding a set of temperature , phase rate ,reaction rate and compositions which satisfied all the equations of the model described above (i.e. (MESHR)equations) .

Unfortunately, these (MESHR) equations are non-linear algebraic equations that interact strongly. Consequently, solution procedure is relatively difficult and tedious.

3.9.2 Specify Independent Variables

It is important to specify the necessary number of independent variables in advance for reactive distillation must specify the condition, composition and flow rates of feed, the number of stages , column pressure amount and locations of side streams, and inter-cooler and heater loads if a variable .

The object of the design calculation is to find asset of vapor and liquid flow rates , reaction rates , temperature and compositions (these also termed as dependent variable) , which satisfied all equations of (MESHR) equations , or in more general terms it is desired to determine the values of remaining variables when an appropriate number of independent variables are fixed .

3.9.3 Preliminary Assumptions

The Preliminary Assumptions provide initial values for the assumed interaction variables or the dependent variables, which must be assumed to start the trial and error. The computational methods assumed the following variables:

a- Temperature profiles (i.e. temperature on each stage of the column).
b- Vapor and liquid flow rate on each stage of the column).
c- Reaction rate profiles (i.e. reaction rate on each stage).

d- Hold up in vapor phase over a particular stage is negligible as compared to the corresponding hold up in the liquid phase.

e- The column is adiabatic in operation giving constant molar overflow.

f- The liquid hold up is well mixed and same for each stage 0.3 except for reboiler 0.1

The iteration variables may be termed as initial set of tear variables $(T_J, V_J, L_J, \Delta R_J)$ for each stage. For most multi-component continuous physical reactive distillation problems, it is sufficient to assume asset of vapor flow rate (V_J) values, and temperature (T_J) values and reaction rate (ΔR_J) values.

An adequate initial set of vapor flow rate values, and temperature values can be derived from the top-stage and bottom-stage and linear variation with stages in between is assumed.

A strategy for initializing the reaction rate values is to set all of these values corresponding to stages to be zero, and assigning random numbers to the other stages. This is dictated by the nature of feed mixture, since it is a liquid that moves downward.

3.10 Solution of Equation

3.10.1 Solution of Material Balance

The determination of phase composition can be done by the solution of material balance equation .The key to the solution is the tridiagonal matrix that results from modified form of M-equation (3.12),when they are torn from the other equations by selecting $T_j, V_j and \Delta R_j$ as the tear variables, which leaves the modified M-equations linear in the liquid mole fractions.

The modified M- equations are obtained by substituting equation (3.11) into (3.10) and the liquid rate is expressed as function of the vapor rate by an overall material balance. Then the material balance equation is reduced to a tridiagonal matrix form.

$$L_j = V_{J+1} + \sum_{K=2}^{J-1} (F_K - W_K - U_K) - D \qquad \ldots (3.17)$$

$$D = V_1 + U_1 \qquad \ldots (3.18)$$

$$\begin{bmatrix} B_1 & C_1 & & & \\ A_2 & B_2 & C_2 & & \\ & A_j & B_j & C_j & \\ & & A_{n-1} & B_{n-1} & C_{n-1} \\ & & & A_n & B_n \end{bmatrix} \begin{bmatrix} x_{i1} \\ x_{i2} \\ x_{ij} \\ x_{in-1} \\ x_{in} \end{bmatrix} = \begin{bmatrix} D_1 \\ D_2 \\ D_j \\ D_{n-1} \\ D_n \end{bmatrix} \qquad \ldots (3.19)$$

Where

$$A_1 = 0 \qquad \ldots (3.20a)$$

$$B_1 = -V_1 K_{I1} - L_1 - U_1 \qquad \ldots (3.20b)$$

$$C1 = V_2 * K_{I2} \qquad \ldots (3.20c)$$

$$D_1 = \pm \Delta R_1 \qquad \ldots (3.20d)$$

$$A_J = L_{J-1} = V_J + \sum_{K=2}^{J-1} (F_K - W_K - U_K) - D \qquad 2 \le j \le n-1 \qquad \ldots (3.21a)$$

$$B_J = -\left[(V_J + W_J)K_{IJ} + V_{J-1} + \sum_{K=2}^{J}(F_K - W_K - U_K) - D + U_J\right] 2 \qquad \ldots (3.21b)$$

$$C_J = V_{J+1}K_{IJ-1} \qquad 2 \le j \le n-1 \qquad \ldots (3.21c)$$

$$D_J = -F_J Z_{IJ} \pm \Delta R_J \qquad 2 \le j \le n \qquad \ldots (3.21d)$$

$$An = V_n + W_n + G - F_n \qquad \ldots (3.22a)$$

$$B_n = -(V_n + W_n)K_{in} - G \qquad \ldots (3.22b)$$

$$C_n = 0.0 \qquad \ldots (3.22c)$$

$$D_n = -F_n Z_{in} \pm \Delta R_n \qquad \ldots (3.22d)$$

Where G is the bottom product

This set of equations may by formally written as the following matrix equation:

[A] [X] = [D] … (3.23)

With the above manipulation of the material and equilibrium equations, a further manipulation summation of heat balance equation. These is performed equations at constant pressure in a complex column become:

$$\sum_{i=1}^{m} K_{ij}x_{ij} - 1.0 = 0 \qquad 1 \le j \le n \qquad \ldots (3.24)$$

$$\begin{aligned}&(H_{v_{j+1}} - H_{lj})V_{j+1} - (H_{vj} - H_{lj})(V_j + W_j)\\ &- (H_{lj} - H_{l_{j+1}})L_j + F_j(H_{v_{fj}} - H_{lj}) - Q_j + \Delta R_j H_{rj} = 0\end{aligned} \qquad 1 \le j \le n \qquad \ldots (3.25)$$

When the flow rates and composition of feed streams are given, and the amounts of all the product streams are specified $F_J, Z_{ij}, W_j, U_j, D\ andG$ are all constants. If an initial set of $V_j, T_j and\Delta R_j assumed, A_j, B_j, C_j andD_j$ in equation (3.22) are also constant provided that the equilibrium ratios K_{ij} can be expressed as functions of T_J only in the ideal system, while for non ideal mixture the equilibrium ratios is a function of $T_J andX_{IJ}$.

Then the material balance equation (3.22) is a linear system.

The solution of equation (3.25) or X_{ij} can be readily obtained by use of a simple algorithm derived from the Gauss elimination method. Using this algorithm value of X_{ij} is calculated by the first evaluating X_{ij} and receding backward with j decreasing until X_{ij} is reached.

The equations are shown as follows

$$x_{in} = q_n \qquad 1 \le j \le n-1 \qquad \text{… (3.26)}$$

$$x_{ij} = q_j p_j x_{ij+1} \qquad \text{... (3.27)}$$

$$p_1 = \frac{C_1}{B_1} \qquad \text{… (3.28)}$$

$$q_1 = \frac{D_1}{B_1} \qquad \text{… (3.29)}$$

$$p_j = \frac{C_j}{(B_j - A_j P_{j-1})} \qquad 2 \le j \le n-1 \qquad \text{… (3.30)}$$

$$q_j = \frac{(D_j - A_j q_{j-1})}{(B_j - A_j p_{j-1})} \qquad 2 \le j \le n-1 \qquad \text{… (3.31)}$$

When the x_{ij} obtained from the above algorithm is substituted into the reaction rate equation (3.27) and K_{ij} can be expressed as a function of temperature and pressure equation (3.27) becomes a function of T_j only for ideal system, while for non ideal system K_{ij} are expressed as a function of

temperature, pressure and composition , Wilson and UNIQUAQ method is employed for the solution of this equation

$$K_{ij} = \frac{\gamma_{ij}(x_{i\,i}, T_j)P_{ij}}{P} \qquad \text{… (3.32)}$$

$$P_{ij} = EXP(Ai + \frac{Bi}{Ci + T}) \qquad \ldots (3.33)$$

$$S_j(T_j) = \sum_{i=1}^{m} (\frac{\gamma_{ij} P_{ij}}{P}) x_{ij} - 1.0 = 0 \qquad 1 \le j \le n \qquad \ldots (3.34)$$

The values of x_{ij} are corrected to provide better values of the assumed iteration variables for the next trial; therefore for each iteration , the computed set of x_{ij} values for each stage will , in general , not satisfy the summation constraint given by equation (3.17b) . The values of x_{ij} can be normalized by using the relation:

$$(x_{ij})_{normalized} = \frac{x_{ij}}{\sum_{i=1}^{m} x_{ij}} \qquad \ldots (3.35)$$

When a quadratic curve is drawn though three points of temperature and the root of this equation is taken as the approximation, one point is taken such that a value of the project function calculated from one point is contrary in sign to the values from other points. The real root can be always obtained by the above procedure, and then this method can provide the desired solution at the stable state.

When the x_{ij} is obtained from material balance equation , ΔR_j is calculated from the reaction rate equation (3.35) and T_j is obtained from the summation equation (3.17a) ,new values of V_J can be calculated directly from heat balance equation (3.36) if enthalpies of feed streams and heat duties of intercooler or interheater are given.

3.11 Calculation of Vapor Flow Rate from Energy Balance Equations

A new set of V_j tear variable is computed by applying the following modified energy balance , which is obtained by combining equation (3.18) and (3.20) twice to eliminate L_{j-1} and L_J .

After rearrangement,

$$\alpha_j V_j + \beta_j V_{j-1} = \mu_j \qquad \text{… (3.36)}$$

Where

$$\alpha_j = H_{L_{j-1}} - H_{V_j} \qquad \text{… (3.37)}$$

$$\beta_j = H_{V_{j+1}} - H_{L_j} \qquad \text{… (3.38)}$$

$$\begin{aligned}\mu_j = {} & \left[\sum_{m=1}^{j-1}\left(F_m - G_m - U_m\right) - V_1\right]\left(H_{L_i} - H_{F_j}\right) + G_j\left(H_{V_j} - H_{L_j}\right) \\ & + Q_j \pm \Delta R_j H_{rj}\end{aligned} \qquad \text{… (3.39)}$$

And enthalpies are evaluated at the stage temperatures which last computed rather than at those used to initiate the iteration. Written in didiagonal matrix which from equation (3.39) applied over stages 2 to N-1 is:

$$\begin{bmatrix} \beta_2 & 0 & 0 & 0 & & & & 0 \\ \alpha_3 & \beta_3 & 0 & 0 & & & & 0 \\ 0 & \alpha_4 & \beta_4 & 0 & & & & 0 \\ & & & & & & & \\ 0 & & & 0 & \alpha_{N-3} & \beta_{N-3} & 0 & 0 \\ 0 & & & 0 & 0 & \alpha_{N-2} & \beta_{N-2} & 0 \\ 0 & & & 0 & 0 & 0 & \alpha_{N-1} & \beta_{N-1} \end{bmatrix} \begin{bmatrix} V_3 \\ V_4 \\ V_5 \\ \\ V_{N-2} \\ V_{N-1} \\ V_N \end{bmatrix} = \begin{bmatrix} \mu_2 - \alpha_2 V_2 \\ \mu_3 \\ \mu_4 \\ \\ \mu_{N-2} \\ \mu_{N-1} \\ \mu_N \end{bmatrix} \qquad \text{… (3.40)}$$

Matrix equation (3.43) is readily solved one equation at time by starting at the top where V_2 is known and working down recursively .thus is

$$V_2 = \frac{\mu_2 - \alpha_2 V_2}{\beta_2} \qquad \ldots (3.41)$$

$$V_3 = \frac{\mu_3 - \alpha_3 V_3}{\beta_3} \qquad \ldots (3.42)$$

Or, in general

$$V_{j+1} = \frac{\mu_{J+1} - \alpha_{J+1} V_{J+1}}{\beta_{J+1}} \qquad \ldots (3.43)$$

And so on

3.12 Computational Procedure

Assume an initial vapor rate profile by means of constants molar overflow and linear temperature and reaction rate profile.

1- Calculate K_{ij} and then calculate the elements of the matrix A_j, B_j, C_j and D_j.

2- Solve the material balance equation for x_{ij} by using the tridiagonal matrix algorithm.

3- Normalize the compositions of liquid.

4- Substitute the calculated values of x_{ij} and assumed values of T_J into the rate equation, and ΔR_J is calculated for new set.

5- Calculate the enthalpies of the internal vapor and liquid streams.

6- Solve the heat balance equation for a new set of Repeat steps (2) through (7) until the desired accuracy is obtained $\sum y_i = 1$.

Chapter four

Results and Discussion

4.1 Introduction

In the previous chapter, the analysis of the design method for multistage multi component reactive distillation has been considered In this chapter the final results of the vapor and liquid flow rates, temperature, reaction rate and liquid composition profile, using the developed computer program written in MATLAB for continuous reactive distillation with chemical reaction rigorous method) for the esterification of acetic acid with ethanol to produce ethyl acetate and water. The results are compared with previous work of Suzuki [5].

The effects of some process variables such as number of stages, feed location and reflux ratio on the performance of multi component continuous multi stage reactive distillation have been studied. The total vapor and liquid flow rates, temperature, reaction rate and the liquid composition profiles at various processes variables have been presented graphically for comparison purpose.

4.2 The Design Model

Rigorous model has been used to calculate the temperature, liquid and vapor flow rates profiles, reaction rate, and composition profiles. The input parameters needed in the design model were: reflux ratio, number of plates, feed location, temperature of top and bottom, feed flow rate distillate and bottom flow rates and liquid hold up at the top, bottom and for each plate.

Four sets of equations are required (material balance, vapor-liquid relation, rate of reaction and heat balance) in the calculation of rigorous equilibrium stage accompanied by chemical reaction.

The material balance equation is reduced to a tridiagonal matrix form, initial set of V_j, T_j and ΔR_j are assumed, A_j, B_j, C_j, and D in tridiagonal matrix are constant ,provided that the equilibrium ratio K_{ij} can be expressed as a function of T_j. Then the solutions of tridiagonal matrix given in x_{ij} obtained by use of simple algorithm derived from Gauss elimination method then substituted into the reaction rate and K_{ij} can be expressed as function of T_j only. Muller's method is employed for the solution of this equation. When x_{ij} obtained from material balance, ΔR_j calculated from reaction rate and T_j is obtained from the summation equation by Muller's method, new set of V_j can be calculated directly from the heat balance equation if enthalpies of feed streams and heat duties of the intercoolers or interheaters are given.A computer program for the rigorous model has been given in appendix D.

4.3 Selection of Activity Coefficient Model

Wilson and UNIQUAC models have been used to calculate the activity coefficient for system AcOEt and the appropriate model was selected according to the purity of ethyl acetate that is separated as a top product in the distillation. Table (4-1) gives the composition of the AcOEt in the distillate for the different models used.

Table (4-1) composition of AcOEt in distillate

Distillate composition	Wilson	UNIQUAC
AcOEt	0.4870	0.4777

The results show that Wilson model gives the more acceptable results. Therefore, in the present work, Wilson model has been used and because this model is recommended for polar systems.

Figure (4-1) shows the composition of ethyl acetate vs. number of stages for two models.

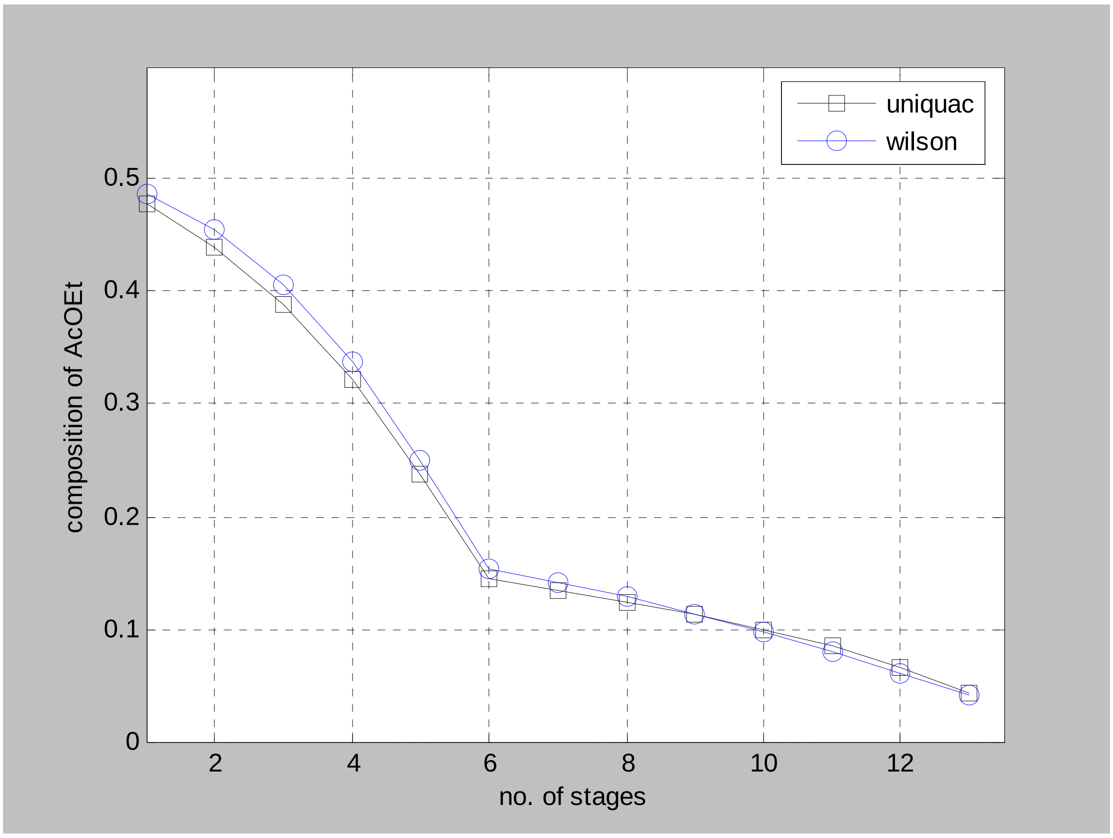


Figure (4-1) mole fraction of ethyl acetate vs. no. of stage

4.4 Model Results

Much more results can be predicted from the simulation model of continuous reactive distillation. This model can be used to predict the composition profile, temperature, liquid and vapor flow rate and reaction rate profiles.

The initial conditions that have been used in this simulation model are the same as those used in the previous work of AL-Khazraji [30] for the production of ethyl acetate-water by reacting acetic acid and ethanol Acetic acid and ethanol enter at same feed location stage (six- stages).

Results of liquid flow rate, vapor flow rate, temperature and reaction rate profiles are depicted in figures (4-2), (4-3), (4-4), (4-5), (4-6) for one feed and figures.

Figure (4-2) shows the changes in liquid composition of each component with stage number. Four components appear in both products, observed that there is increasing in acetic acid composition after the feed stage, because the feed enters at stage six and it contain much quantity of acetic acid ,while liquid composition of ethanol decreases after the feed stage, where reaction and separation is started. The water composition has small change in all stages, while the composition of ethyl acetate in the first six stages increases. The (AcOEt) is 82.30 mole % going to distillate, distillate contain 48.70% mole of (AcOEt) and bottom 16.97% mole of water.

Figure (4-3) shows vapor flow rate versus stage number, it is observed that after the condenser the rate remains almost constant.

The variation of liquid flow rate with stage number is shown in figure (4-4) liquid flow rate decreases slightly in first six stages then there is a sudden increase in the sixth stage where feed enters and it remains constant up to the final where stage there is a sharp decrease because of reboiled stage.

Figure (4-5) shows reaction rate profile results, reaction rate is constant in the first six stages before feed stage. There is slightly increase until the final stage, this means that the reaction is almost finished.

Figure (4-6) shows that the temperature profile increases at the feed stage where the feed enters, reaction and separation start.

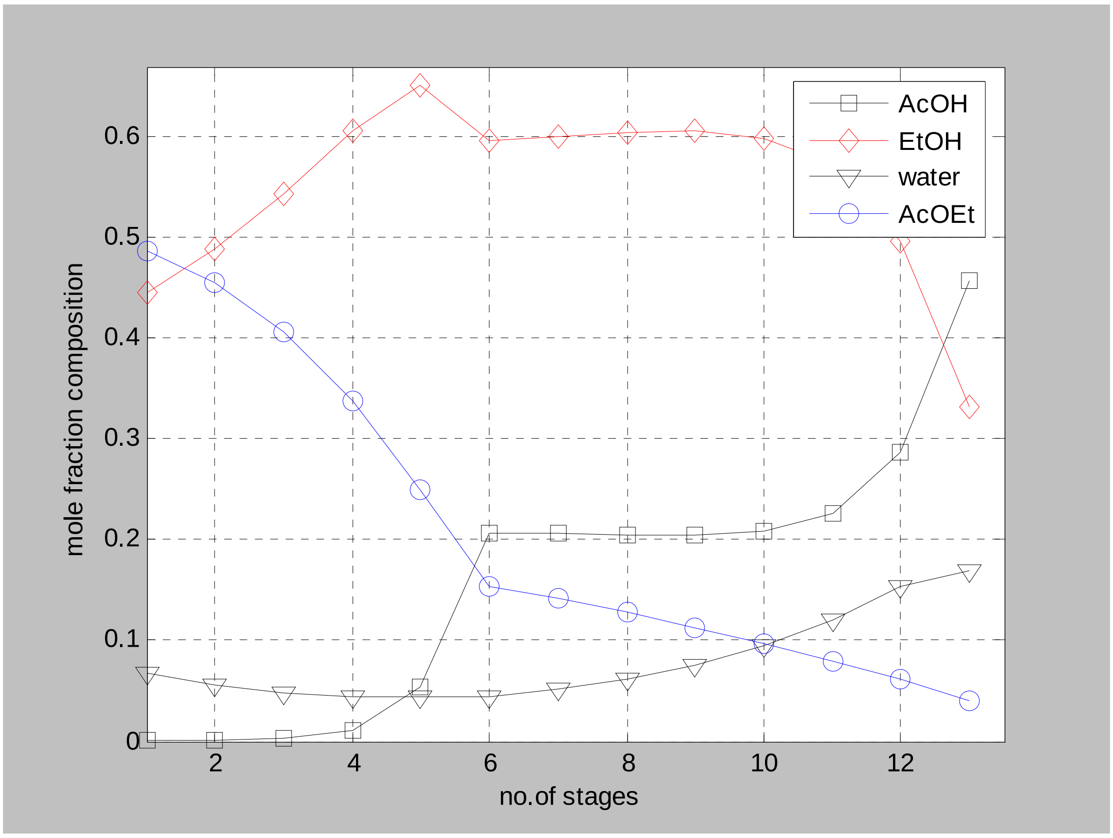


Figure (4-2) liquid composition profile vs. no of stages using one feed

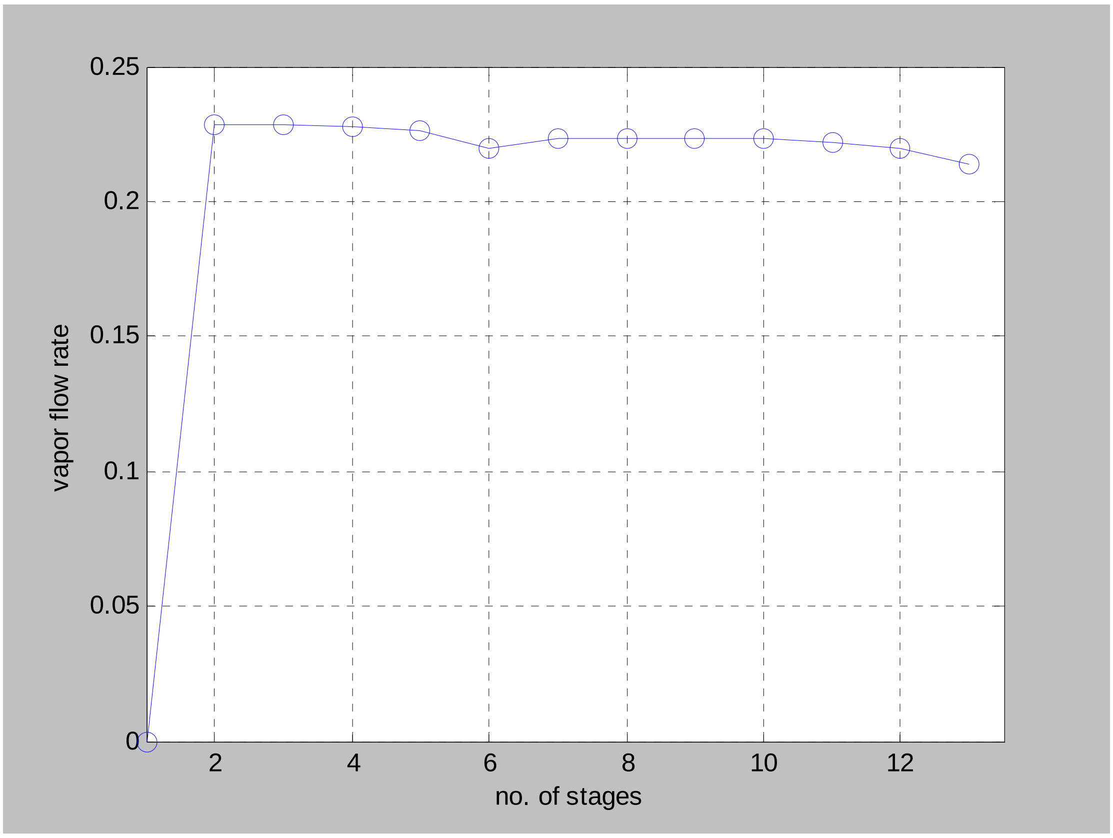


Figure (4-3) vapor flow rate vs. no. of stages using one feed

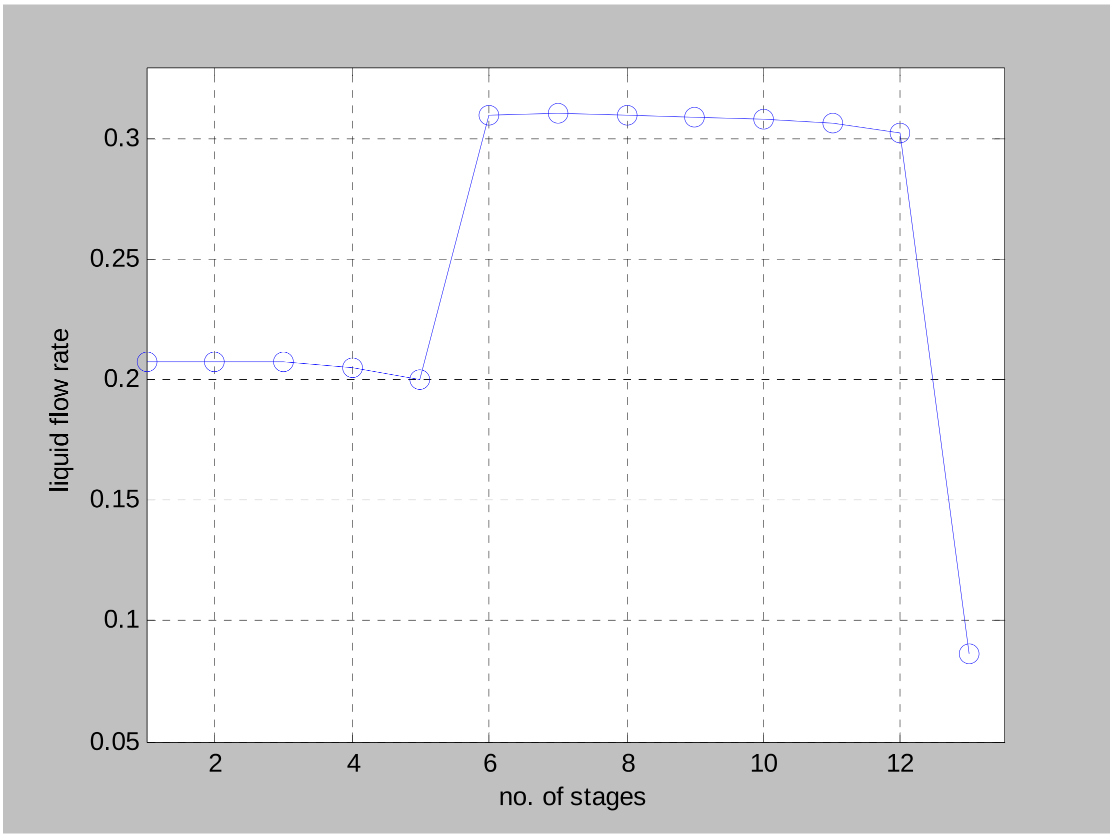


Figure (4-4) liquid flow rate vs. no. of stages using one feed

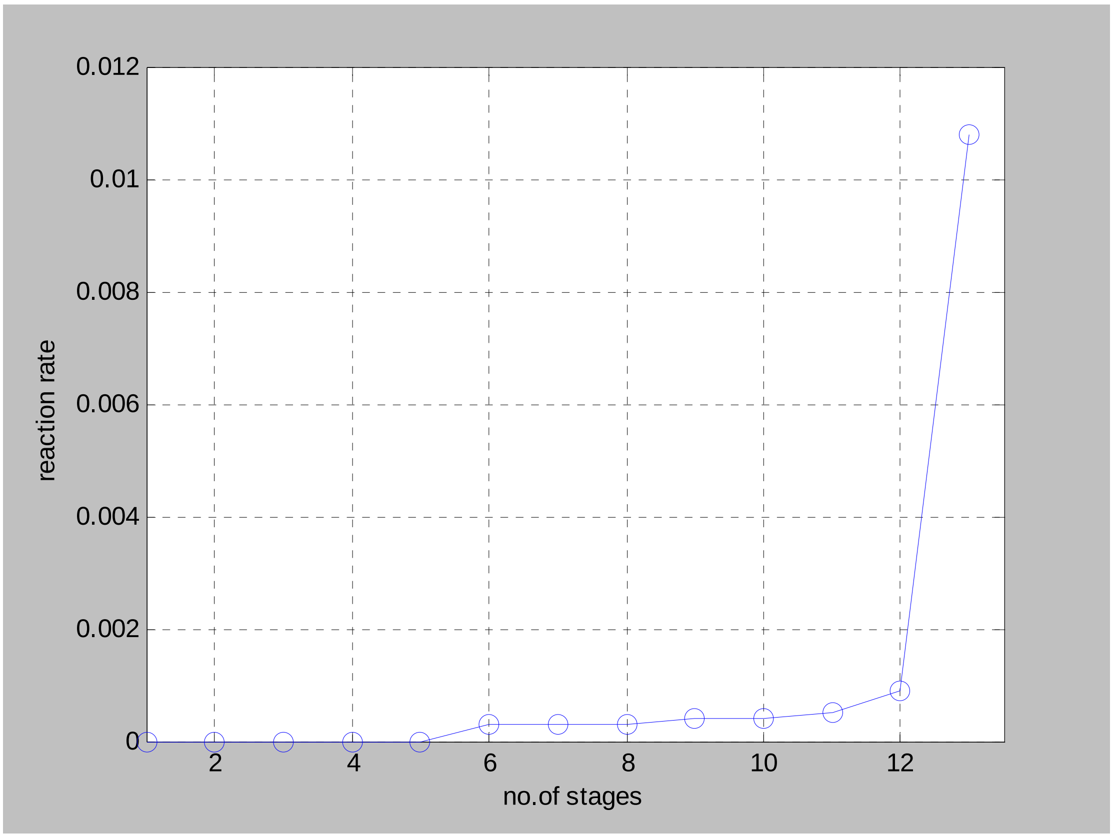


Figure (4-5**)** reaction rate vs. no. of stages using one feed

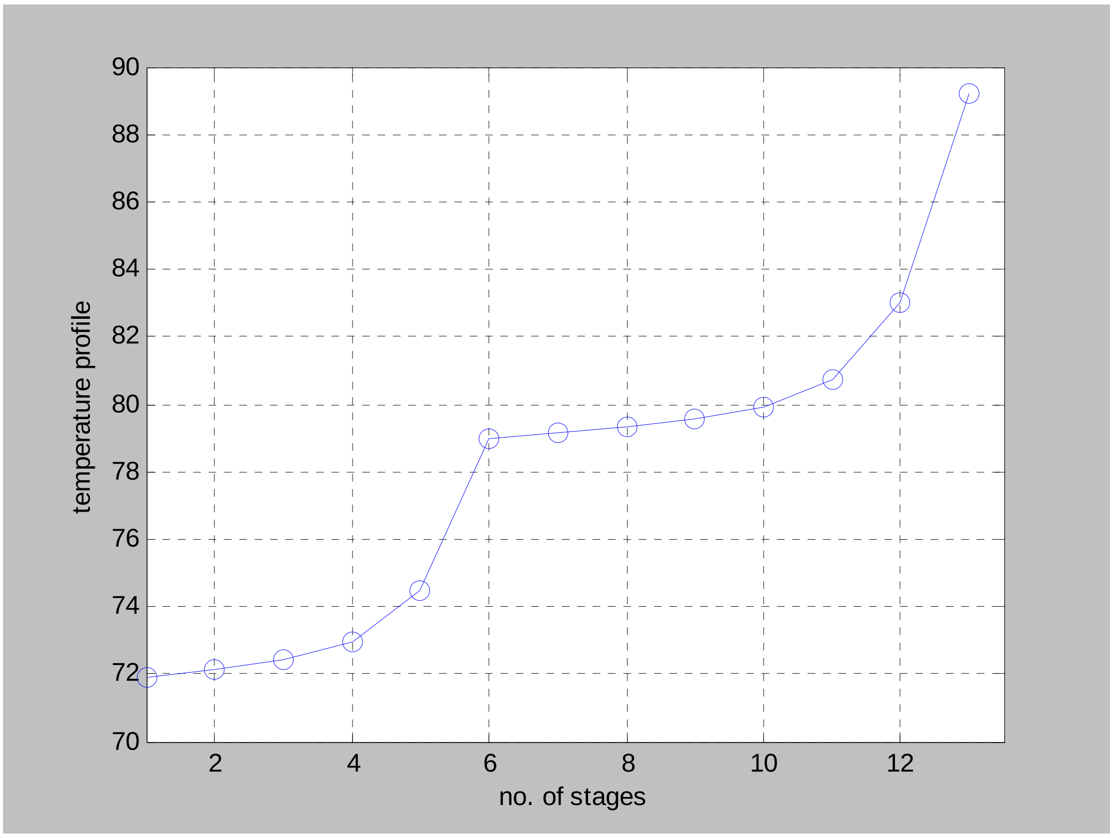


Figure (4-6**)** temperature profile vs. no. of stages using one feed

4.5 Comparison of present model results with previous work Suzuki [5]

Figure (4-7) shows that the liquid composition profile results obtained with Suzuki [5] gives well an agreement.

The presented work shows good agreement with Suzuki [5].

The liquid and vapor profiles Figure (4-8) and (4-9) show a good agreement with Suzuki [5].

Also the temperature and reaction rate profile give a good agreement with the previous work of Suzuki [5]. Figure (4-10) and (4-11).

Ethyl acetate profile figure (4-12) shows a good agreement with Suzuki [5].

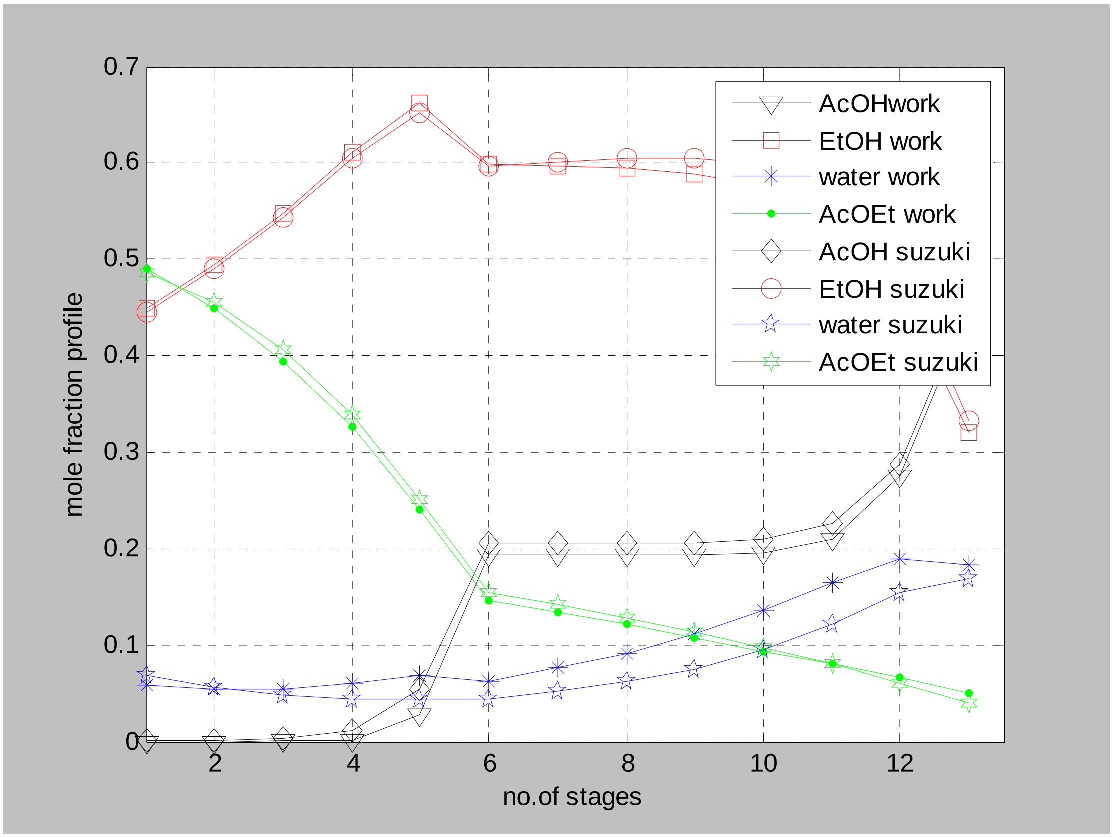


Figure (4-7**)** liquid composition profile comparison using one feed

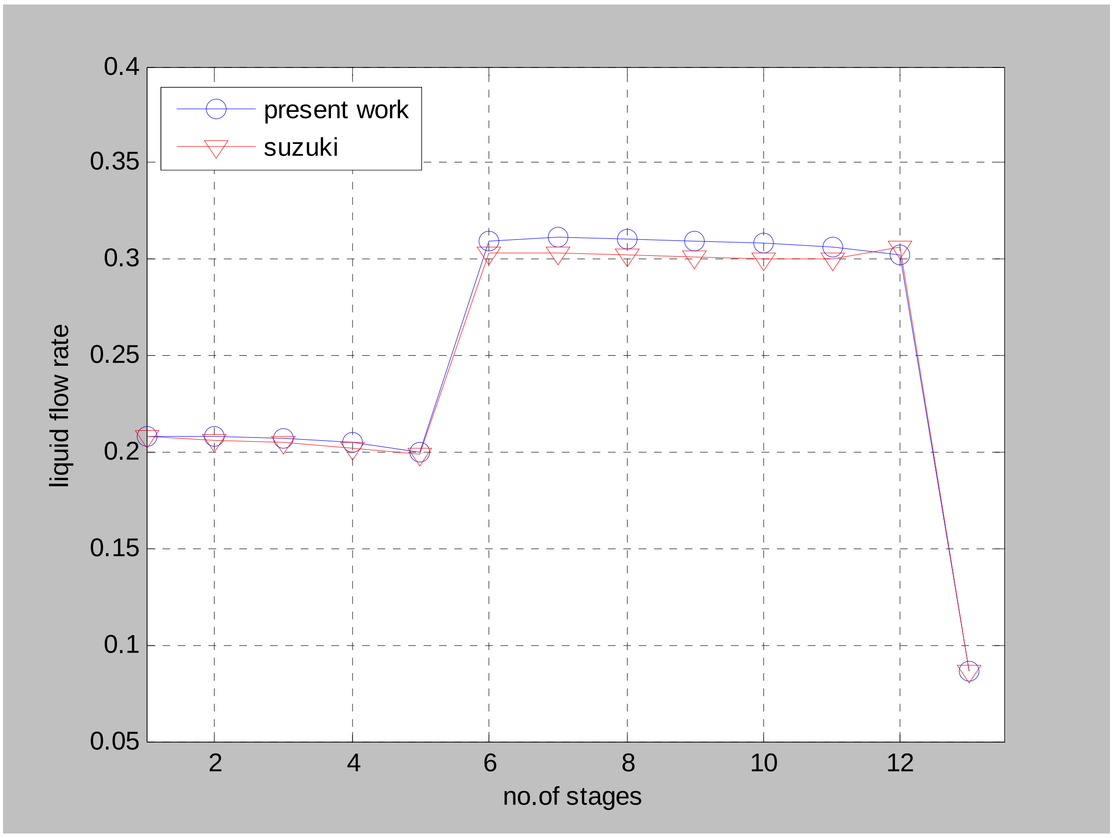


Figure (4-8**)** liquid flow rate profile comparison using one feed

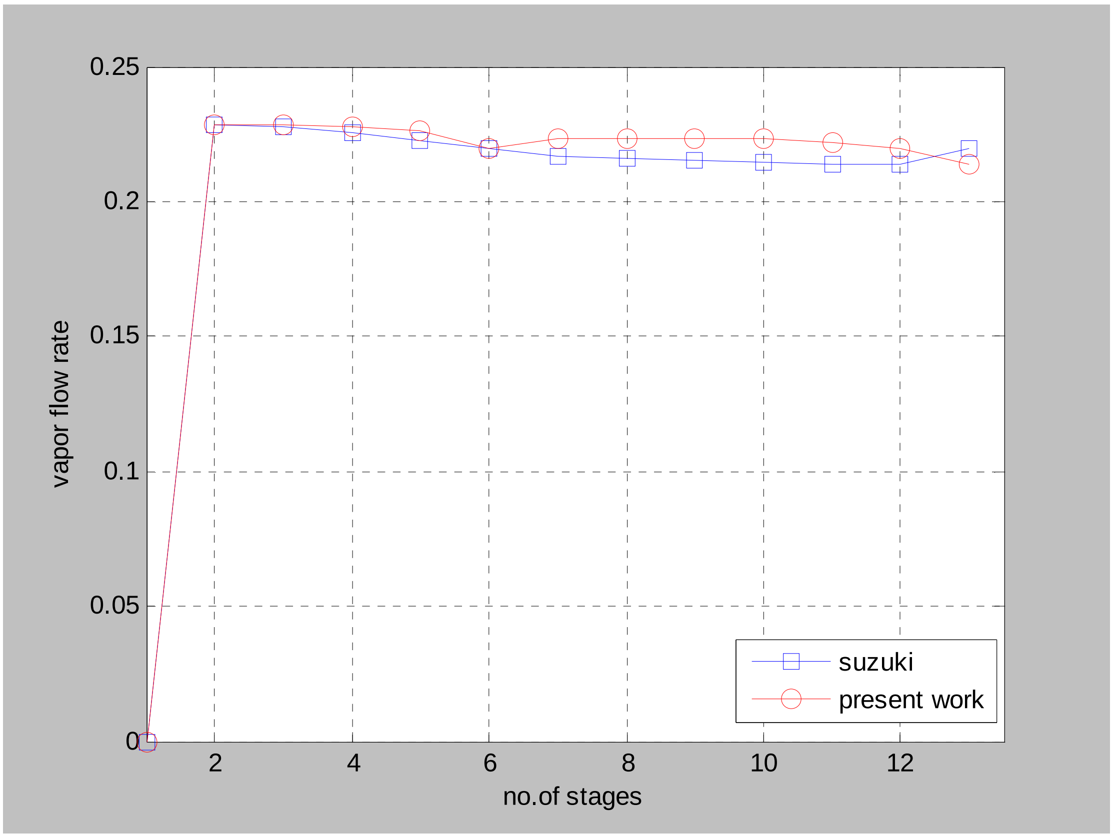


Figure (4-9) vapor flow rate profile comparison using one feed

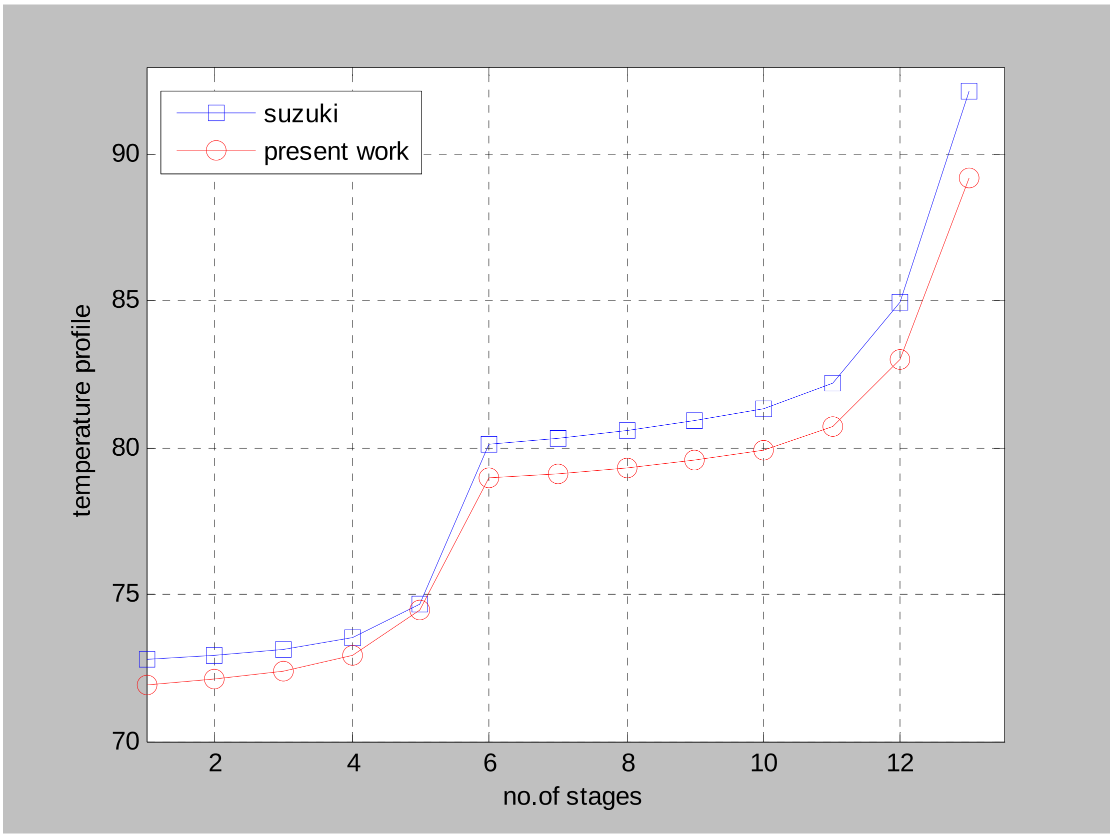


Figure (4-10**)** temperature profile comparison using one feed

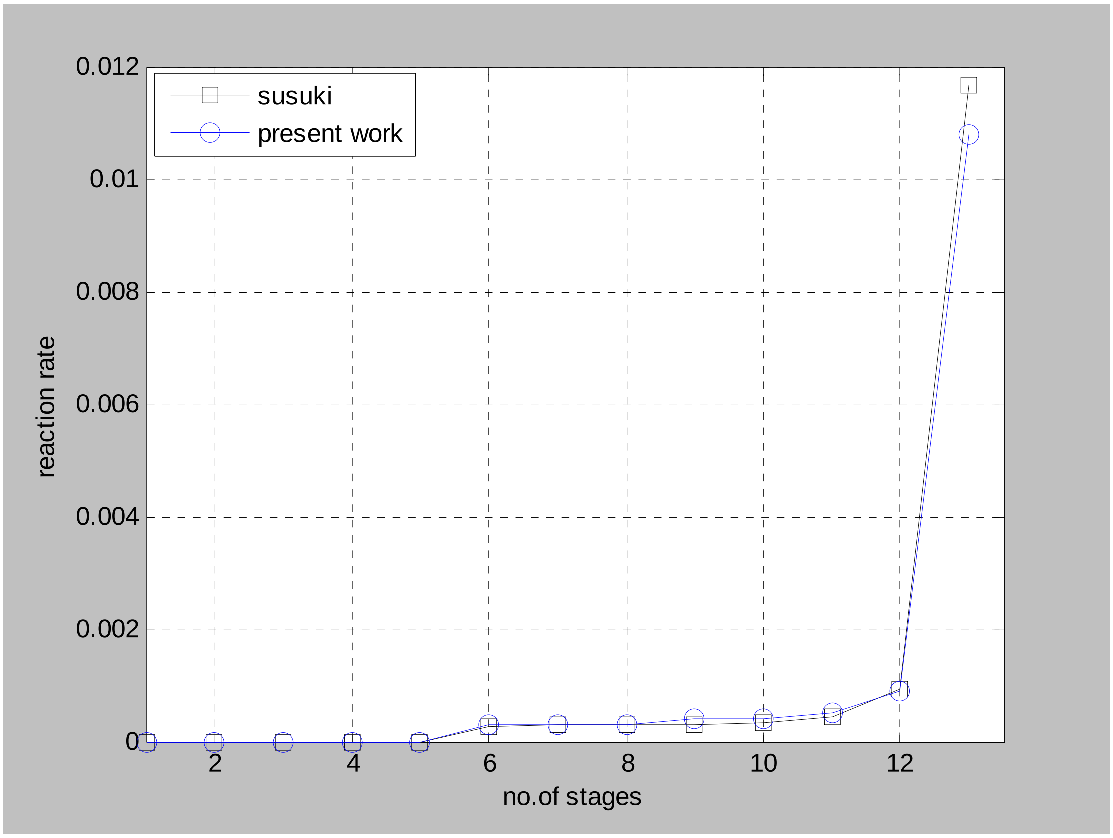


Figure (4-11**)** reaction rate profile comparison using one feed

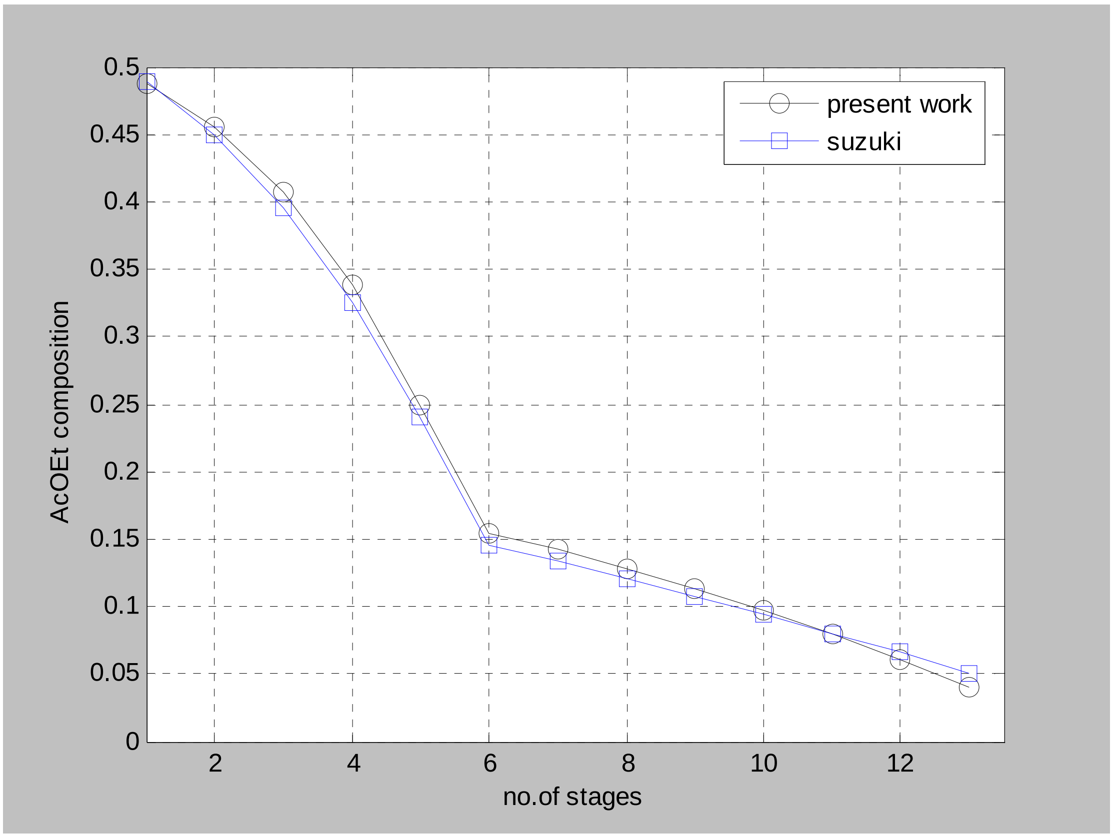


Figure (4-12**)** AcOEt composition profile comparison using one feed

4.6 Effect of Process Variables on the Performance of Multistage Multi-Component Reactive Distillation

Study of the effect of some process variables such as, feed plate location, reflux ratio, number of stages, on the performance of multi-component reactive distillation (i.e., the effects of these variables on the vapor and liquid flow rate profiles, temperature profiles, liquid composition profiles and total reaction rate profiles).

The effect of each process variable is studied under constant of another specified variable, the liquid hold up through the column is constant above the feed and below it, the work done for one feed of ethanol and acetic acid.

4.6.1 Effect of Changing the Reflux Ratio

The effect of changing the reflux ratio on the separation of ethyl acetate from acetic acid and ethanol mixture using continuous reactive distillation process is first considered.

The total liquid and vapor flow rates profiles are decreased with decreasing the reflux ratio, figure (4-13), (4-14).

Figure (4-15) shows that the increase in reflux ratio, causes the stage temperature to decrease, because of the increase of liquid flow rate.

Figure (4-16) shows that the reaction rate is not affected with changing the reflux ratio, this is because the reaction rate is a function of temperature.

Figure (4-17) shows AcOEt composition profile at different reflux ratio 7, 10, and 13.

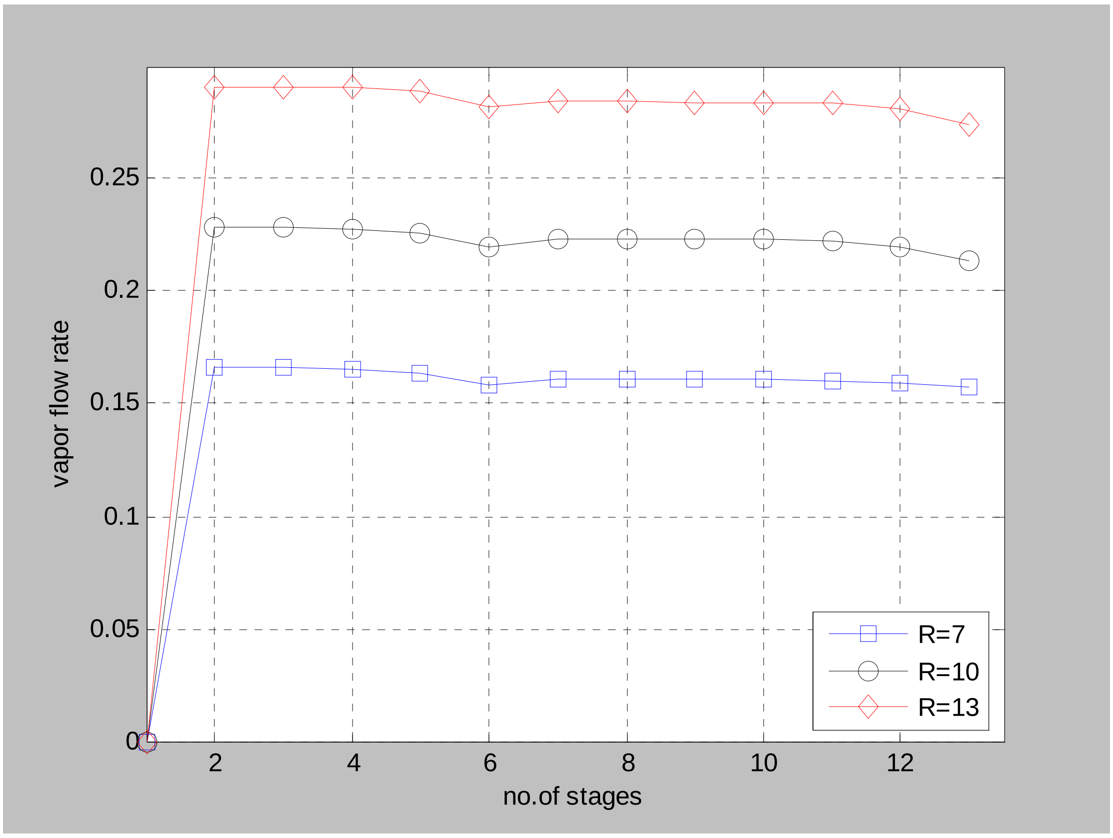


Figure (4-13) vapor flow rate at different reflux ratio 7, 10, 13

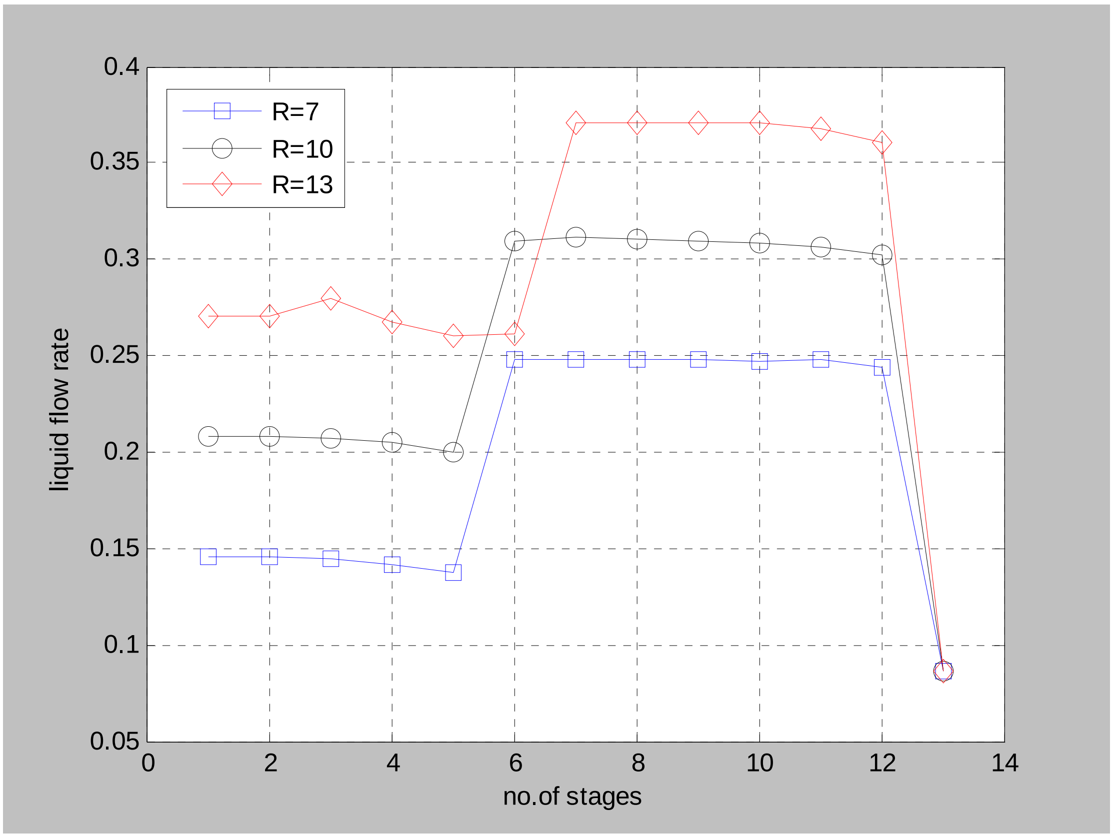


Figure (4-14) liquid flow rate at different reflux ratio 7, 10, 13

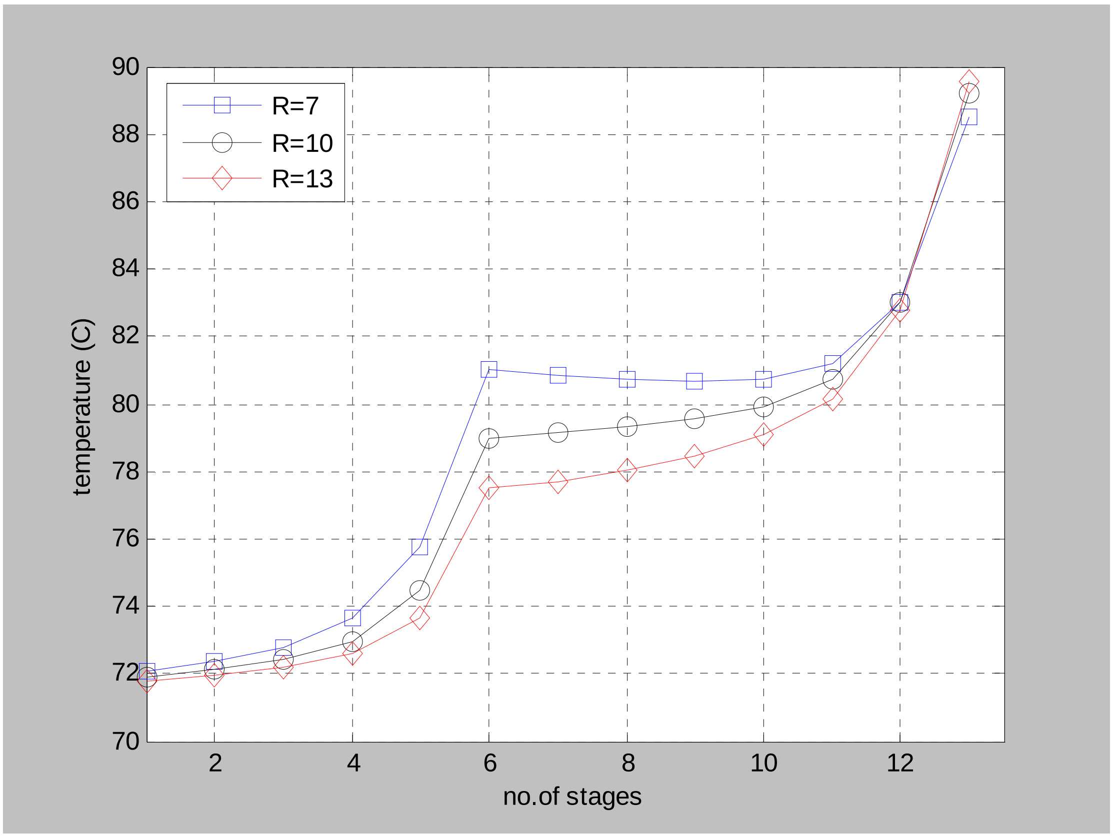


Figure (4-15) temperature (C°) at different reflux ratio 7, 10, 13

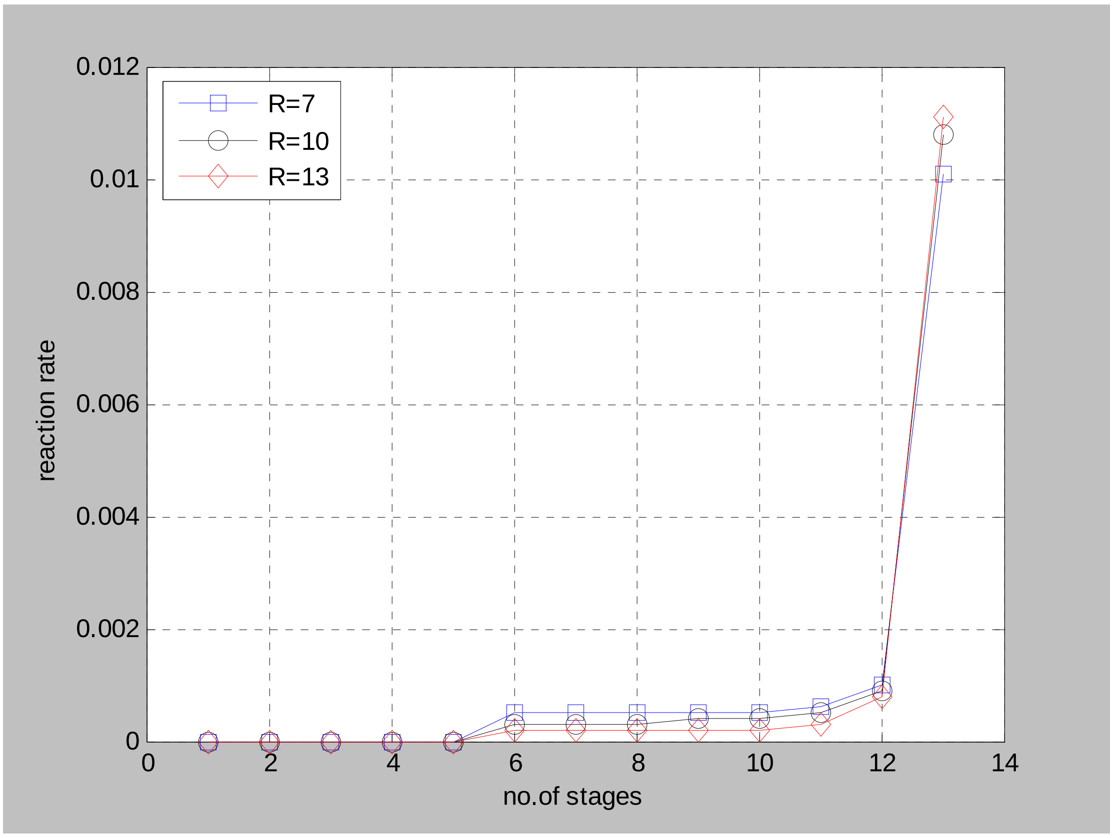


Figure (4-16) reaction rate at different reflux ratio 7, 10, 13

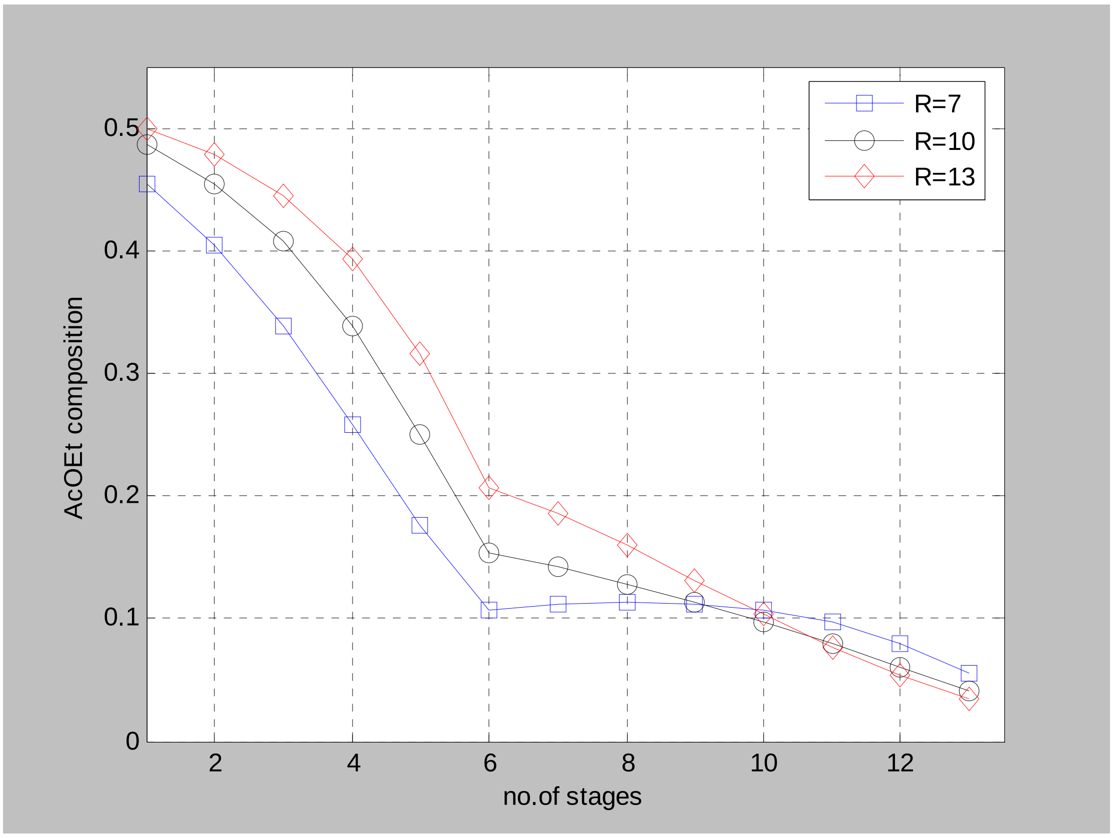


Figure (4-17) AcOEt composition at different reflux ratio 7, 10, 13

4.6.2 Effect of Changing Number of Stages

Figure (4-18) shows AcOEt composition profile at different number of stage 11, 13, and 15. The composition increase with the increase in number of stages because the area of contact between liquid and vapor increases. Figure (4-19) shows the effect of changing the number of stages on temperature profile; when the number of stage the stages increases, the temperature decreases because liquid flow rate increases.

Figure (4-20) shows a small change in reaction rate profile with changing the number of stages.

Figure (4-21) and figure (4-22) show an increase in liquid and vapor flow rate with increasing number of stages, because of the increases of area of contact between vapor and liquid.

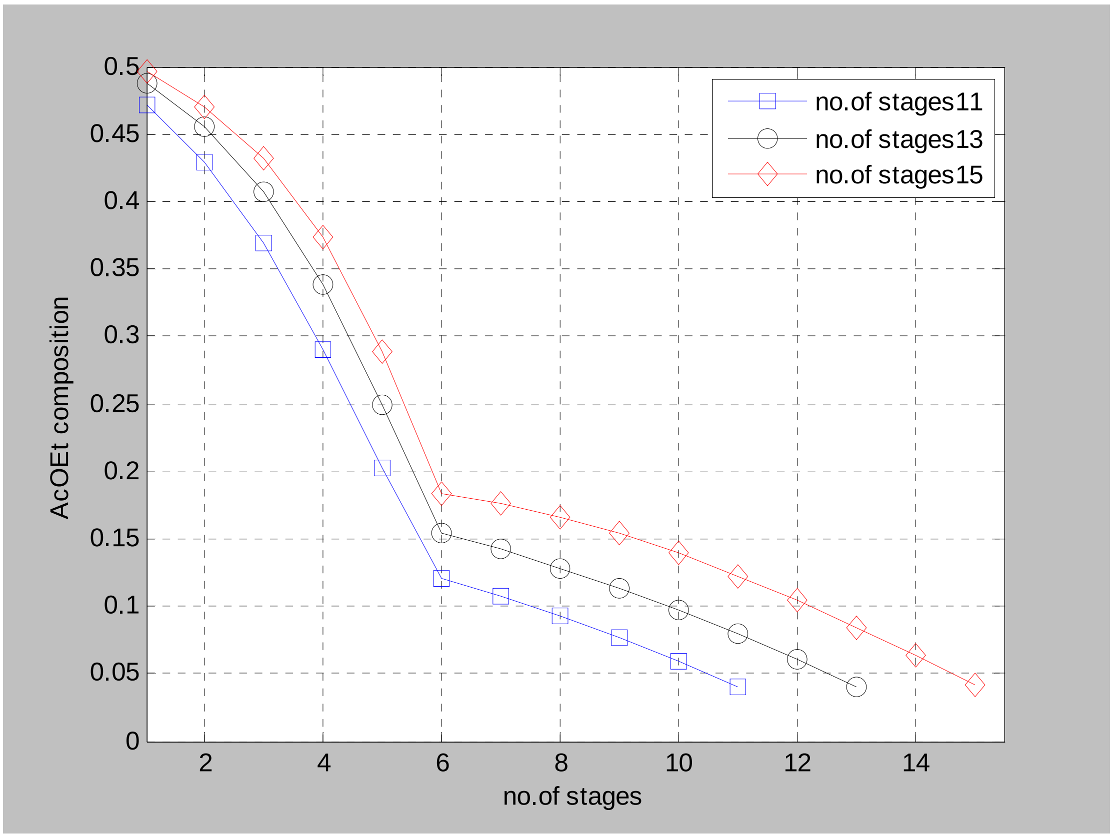


Figure (4-18) AcOEt composition at different number of stages 11, 13, 15

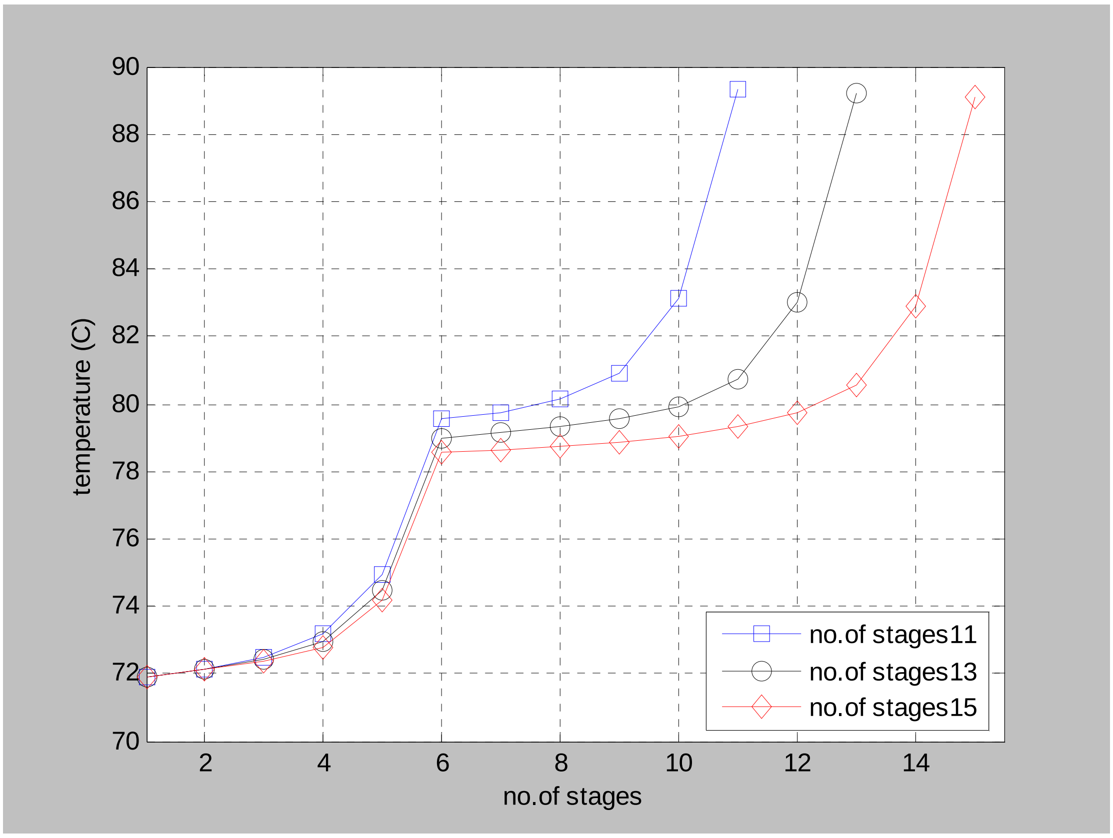


Figure (4-19) temperature (C°) at different number of stages 11, 13, 15

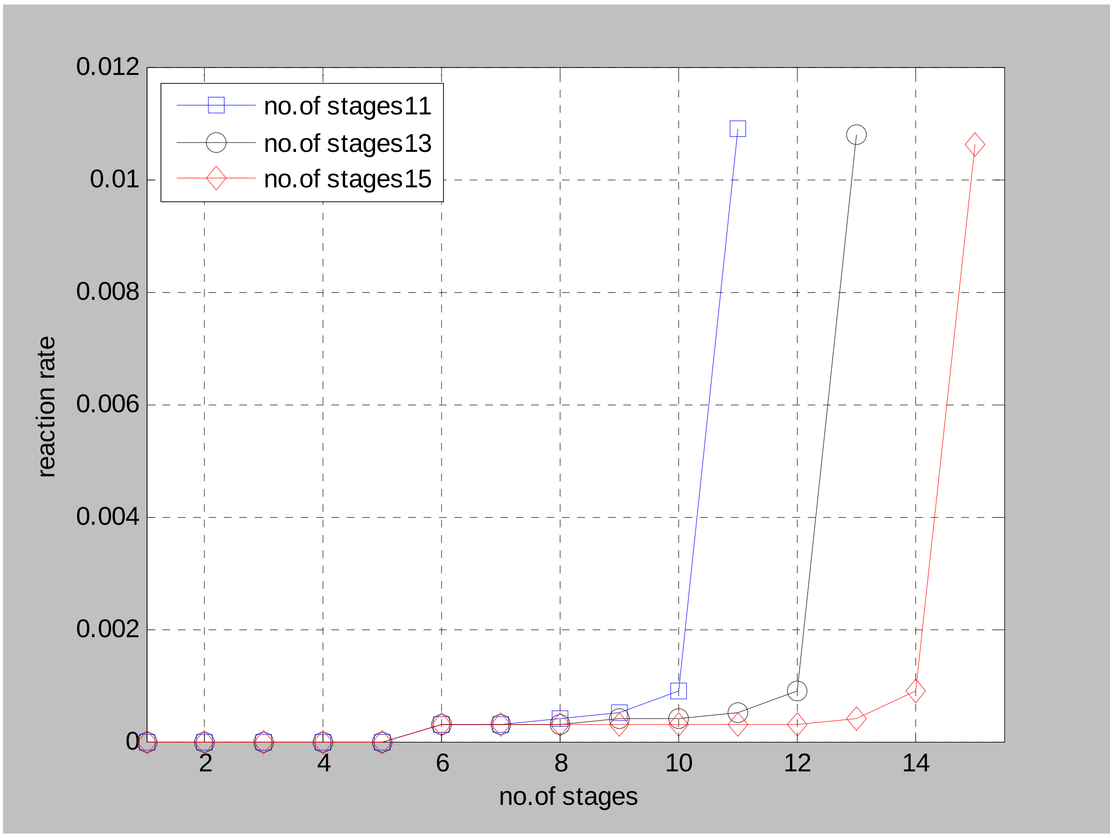


Figure (4-20) reaction rate at different number of stages 11, 13, 15

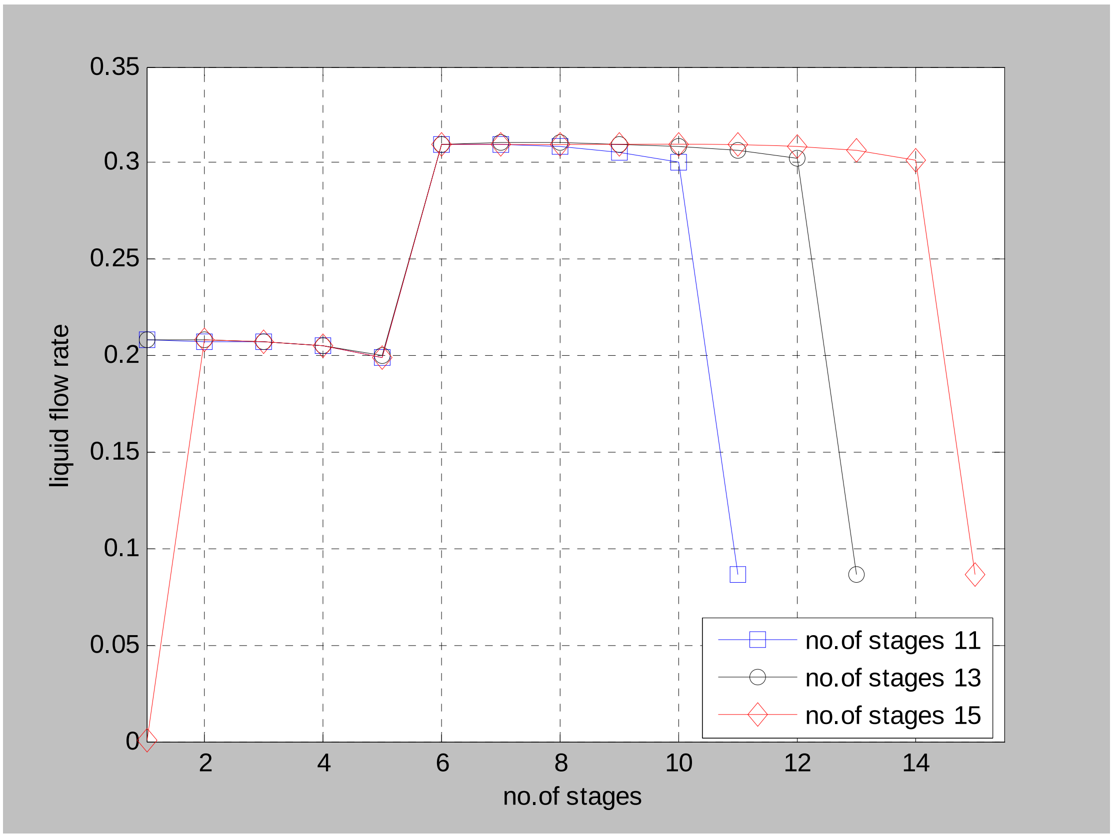


Figure (4-21) liquid flow rate at different number of stages 11, 13, 15

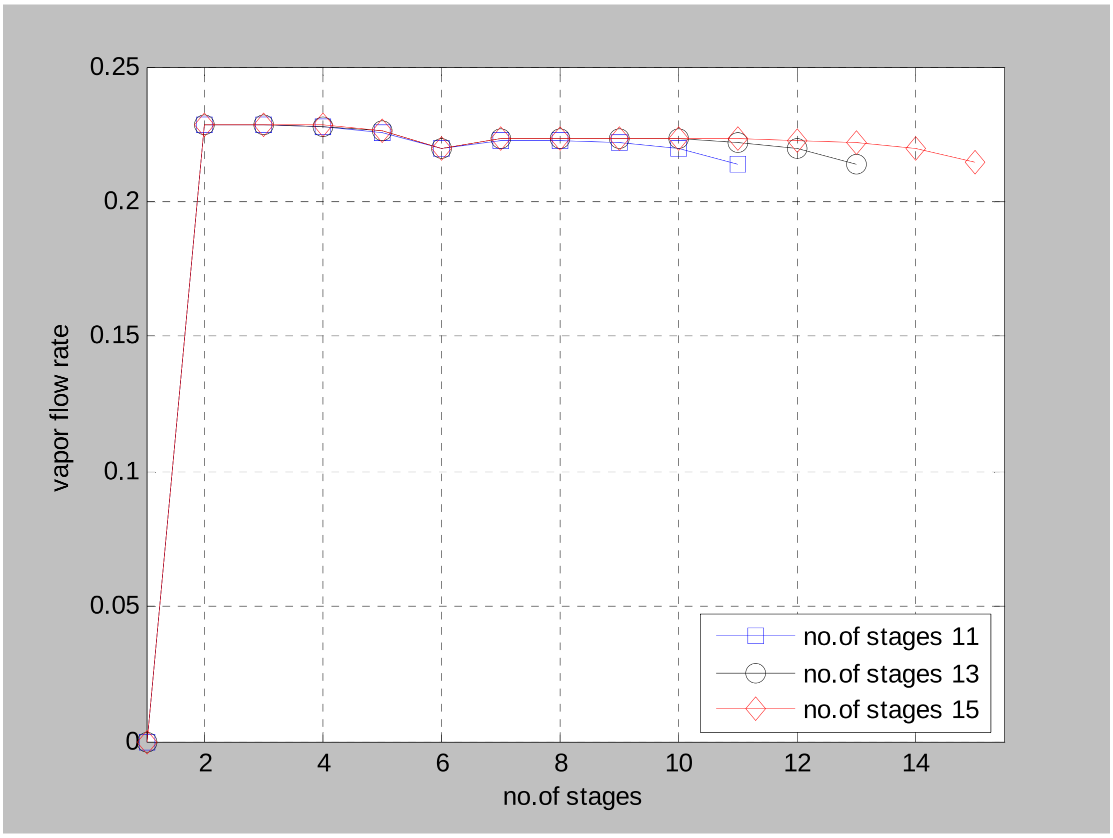


Figure (4-22) vapor flow rate at different number of stages 11, 13, 15

4.6.3 Effect of Changing the Location of Feed plate

Figure (4-23) shows the behavior of liquid flow rate profile. By changing the feed plate stage location,the liquid profile increases when the feed plate location changes to 9, because increasing the area ,allows the separation and reaction to be done.

There is a slight change in vapor flow rate profile with the change the feed plate location. It figure (4-24).

Figure (4-25) shows the stage temperature profile behavior with changing the feed plate location. It decreases when the feed location stages increases to 9 because of increasing liquid flow rate.

The reaction rate profile figure (4-26) shows that it is almost constant with the change of feed plate location.

Figure (4-27) shows the behavior of AcOEt composition profile after changing feed plate location from stage 6 to stage 3 and to stage 9 ,the best composition in feed location is stage 9,because there is enough area for the component reaction and separation.

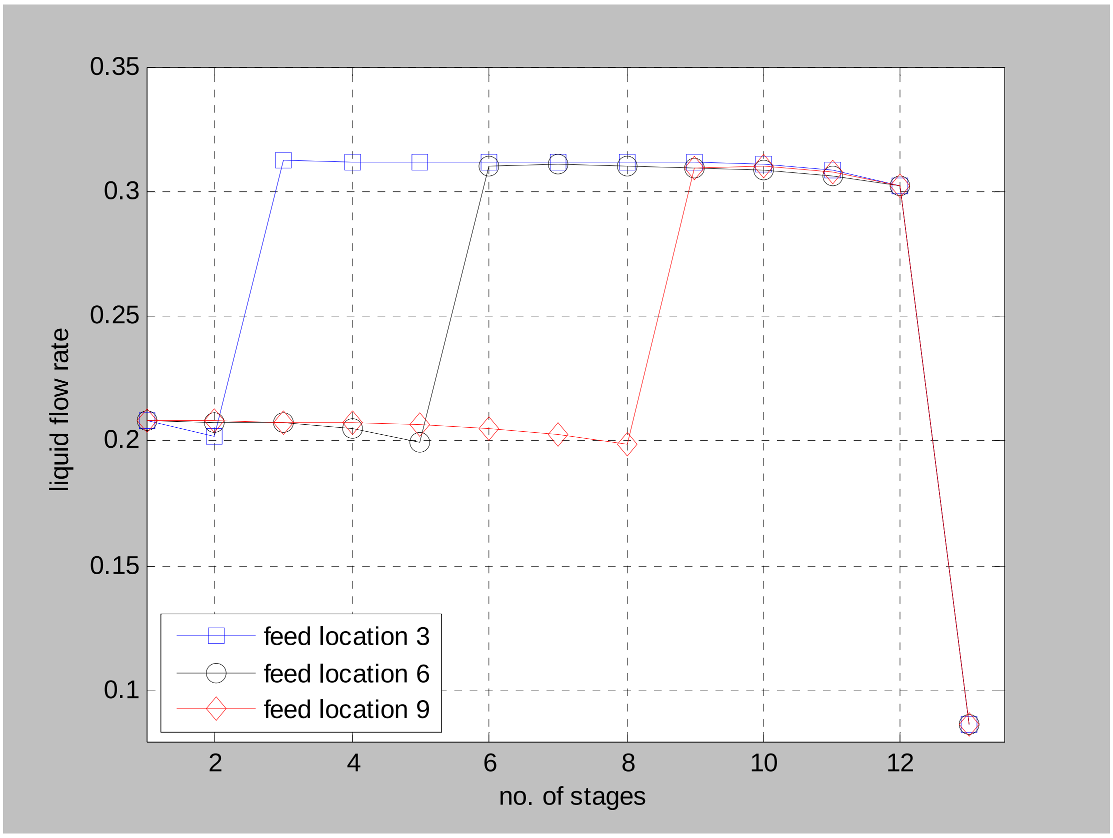


Figure (4-23) liquid flow rate at different feed location 3, 6, 9

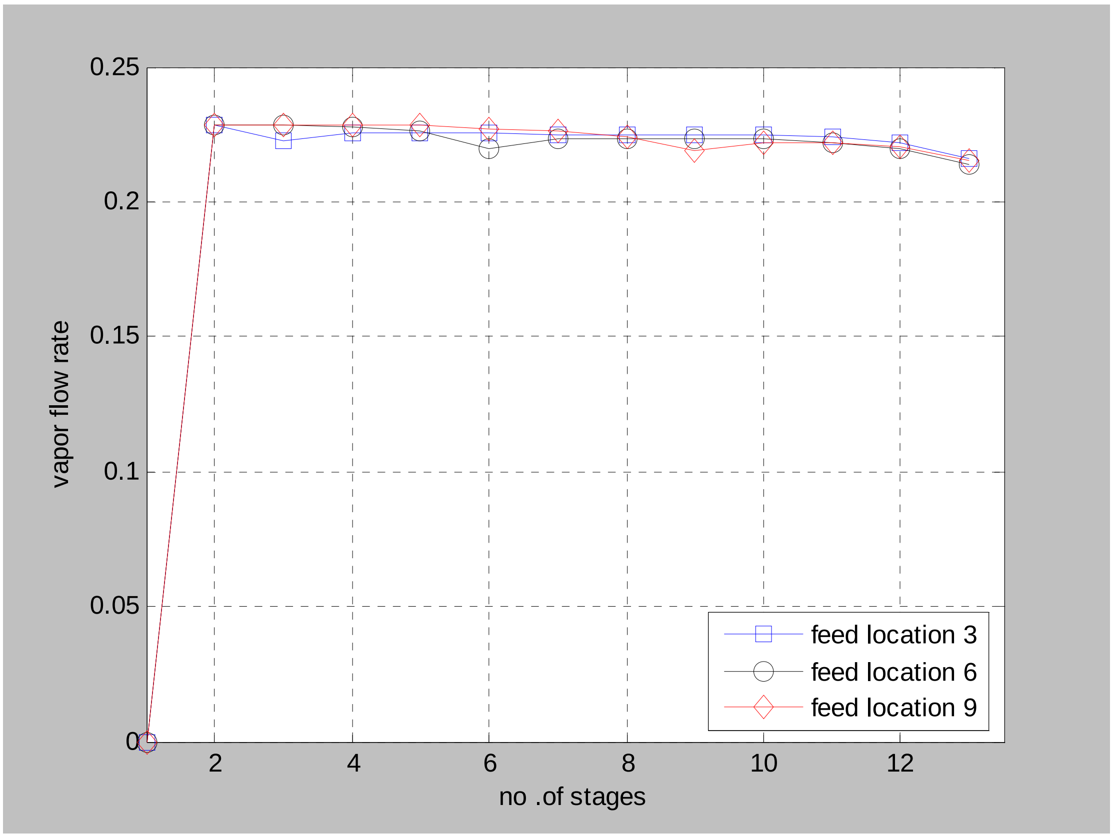


Figure (4-24) vapor flow rate at different feed location 3, 6, 9

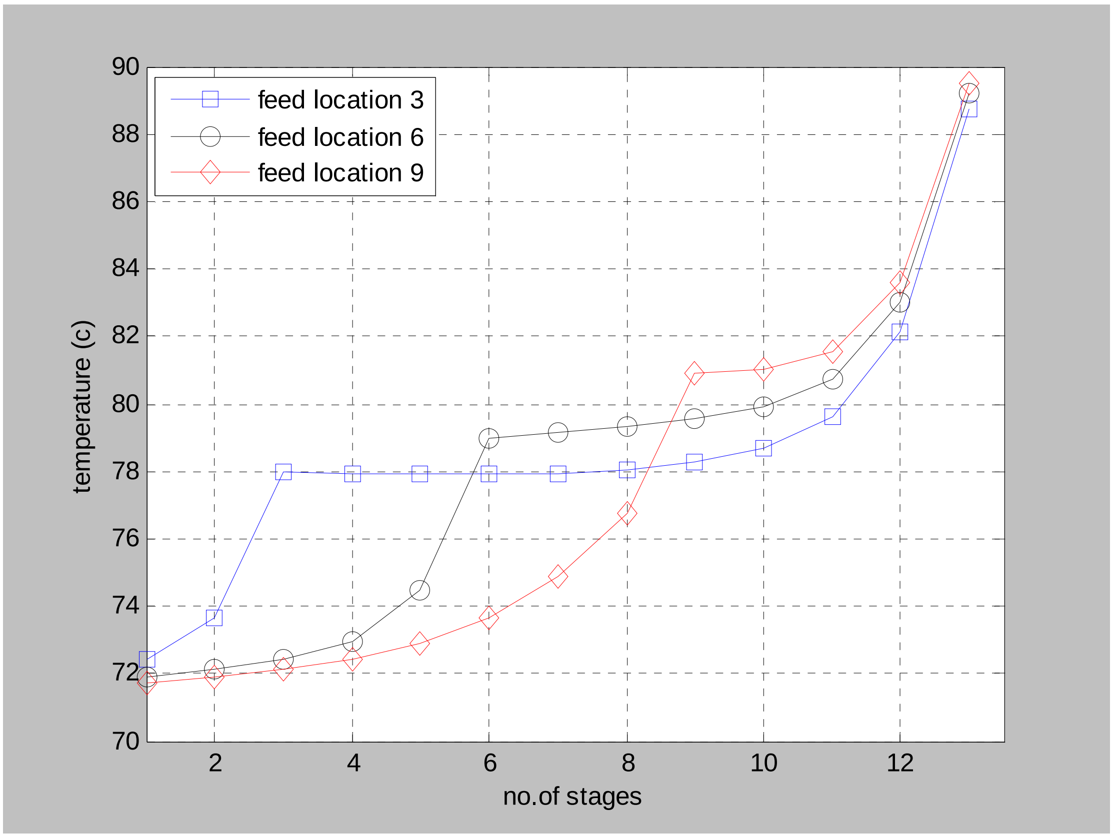


Figure (4-25) temperature (C°) at different feed location 3, 6, 9

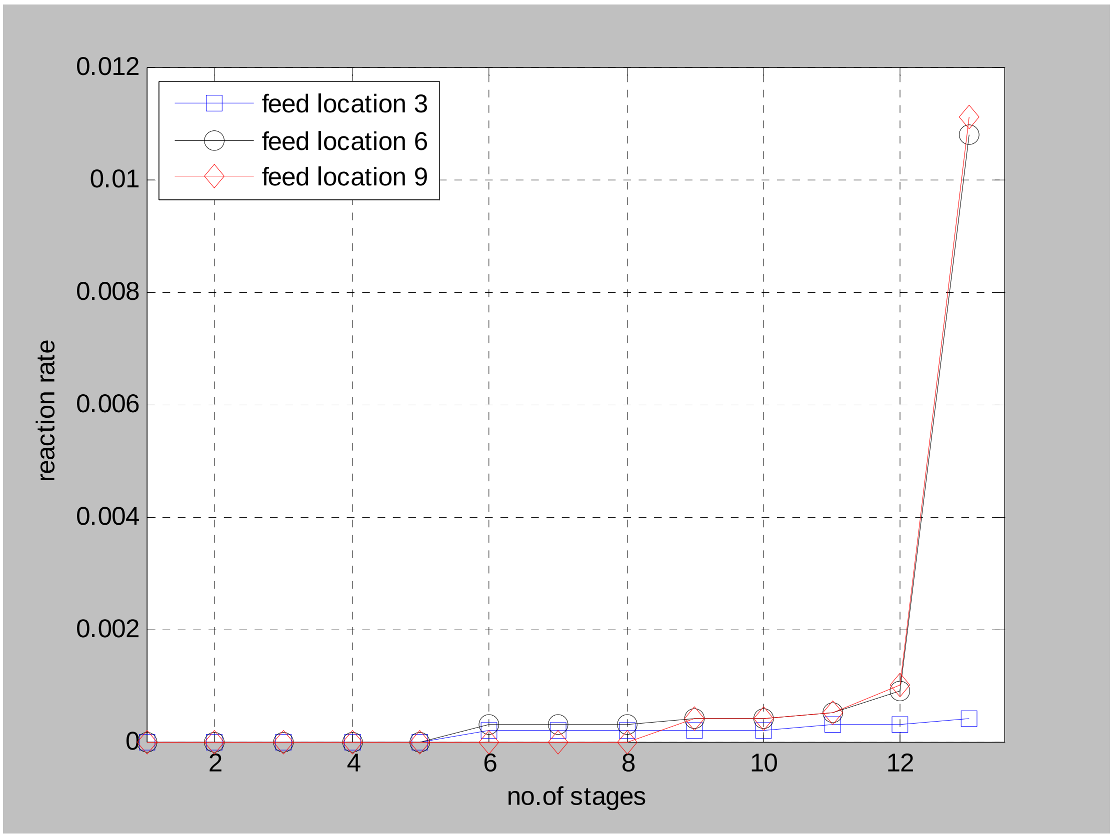


Figure (4-26) reaction rate at different feed location 3, 6, 9

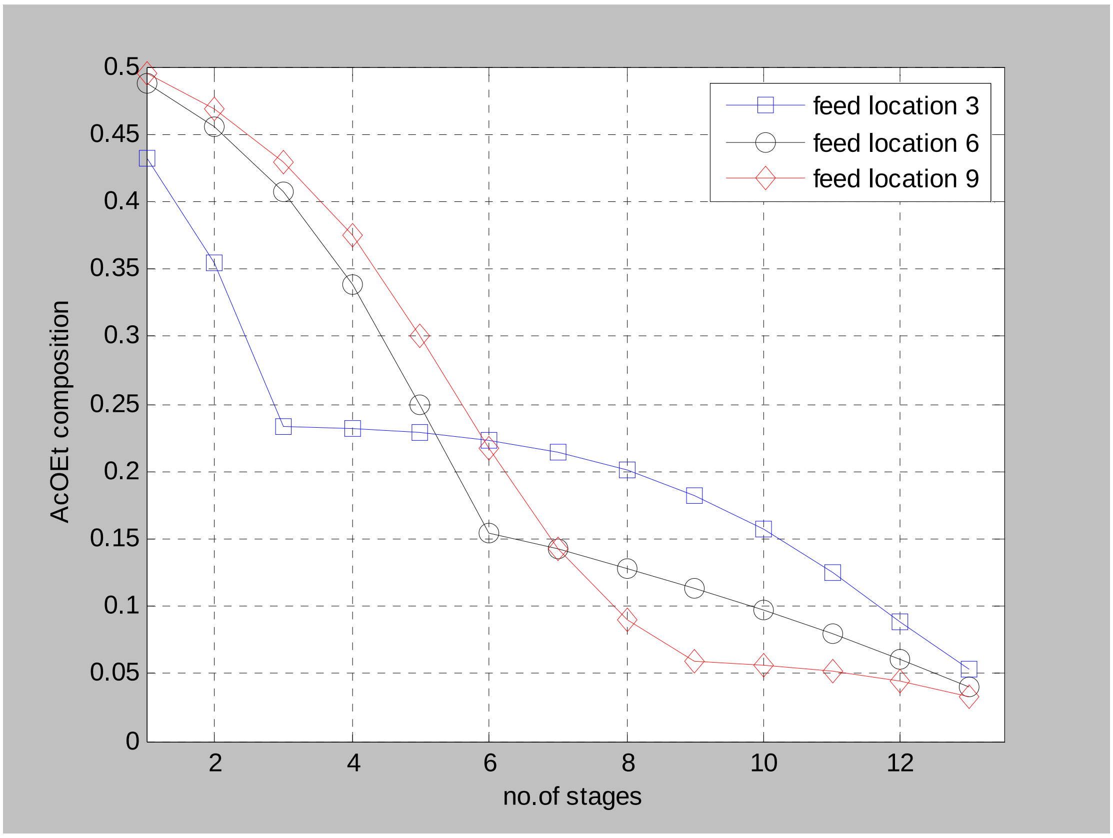


Figure (4-27) AcOEt composition at different feed location 3, 6, 9

4.6.4 Effect of Changing the Number of Feed

Acetic acid enters at the 6th stage from the top and ethanol at the 2nd stage from the bottom. Results of liquid flow rate, vapor flow rate, temperature and reaction rate profiles are depicted in figures (4-28), (4-29), (4-30), (4-31), (4-32).

Figure (4-28) shows the liquid composition profile of each component using two feeds, there is an increase in acetic acid composition after the sixth stage. While liquid composition of ethanol increases in first stage then decreases in the sixth stage AcOEt started to form almost constantly decreased until stage eleven, when ethanol enters and decreased continuously because ethanol is the base of reaction, water composition has small change in all stages and the composition of ethyl acetate in the first stage increases because of that separation process is in the final steps.

The vapor flow rate profile increases after stage one figure (4-29), there is an increase in vapor after the condenser stage.

The liquid flow rate profile is almost constant except in stage 6 and stage 11 figure (4-30), where the two feeds enter the stages, then there is a sharp decrease in final stage.

Figure (4-31) shows the reaction rate profile, where it is observed that the quantity of rate is almost constant in stage 6 before feed one, this is because the reaction is not started, after feed one stage 6, the reaction rate increases until increasing the feed to stage 11 but increases more in the final stage where the reaction operation is finished.

Figure (4-32) shows the temperature profile increases especially when it reaches stage 6 and stage 11 where the two feeds enter.

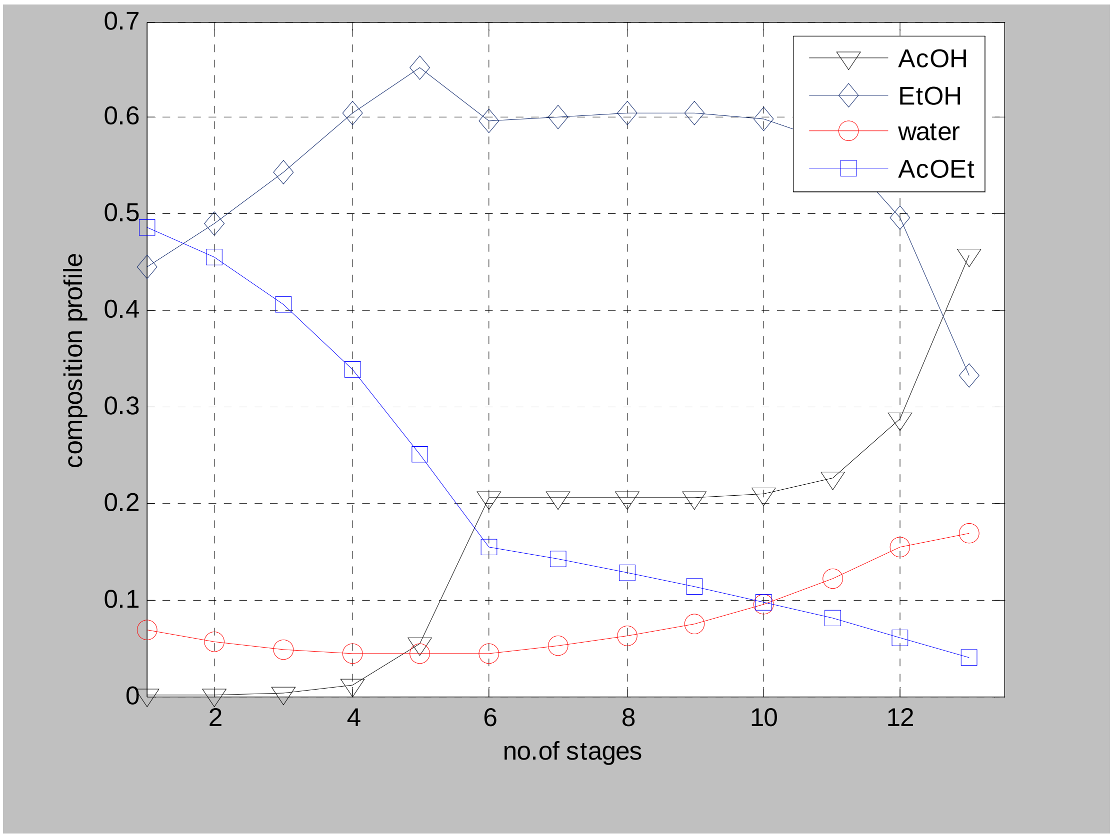


Figure (4-28**)** temperature profile vs. no. of stages using two feed

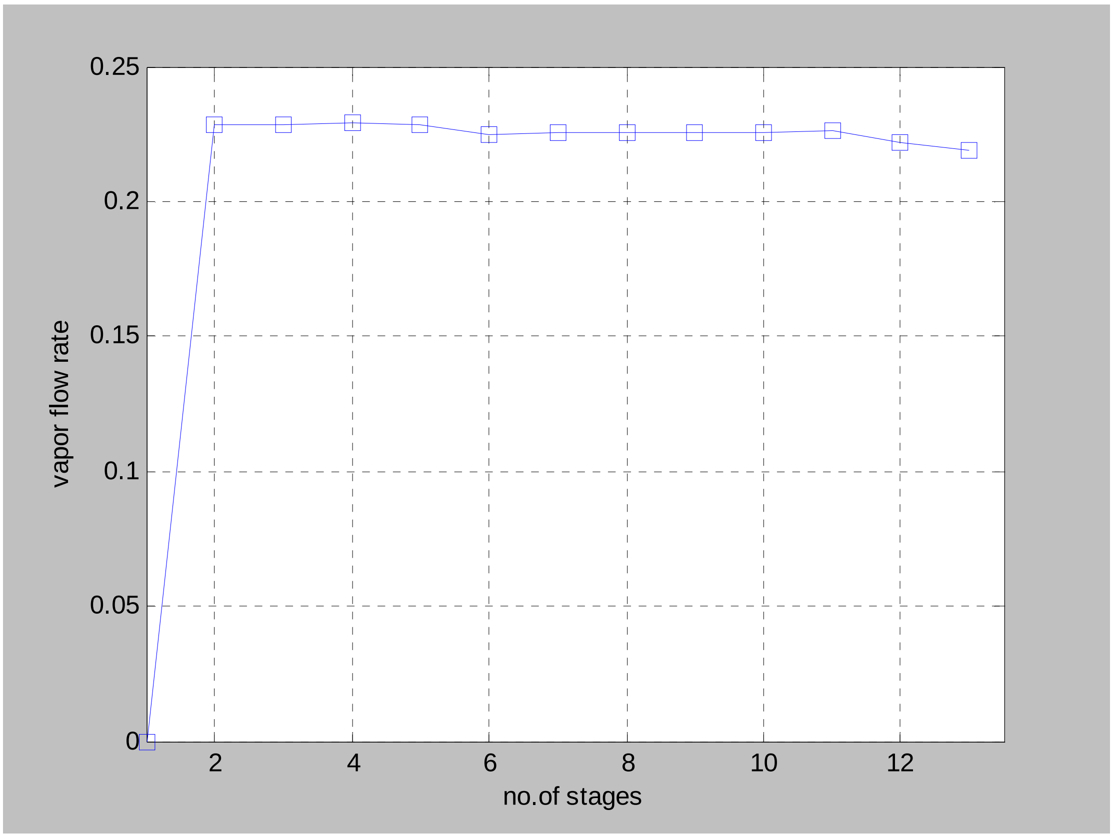


Figure (4-29) vapor flow rate vs. no. of stages using two feed

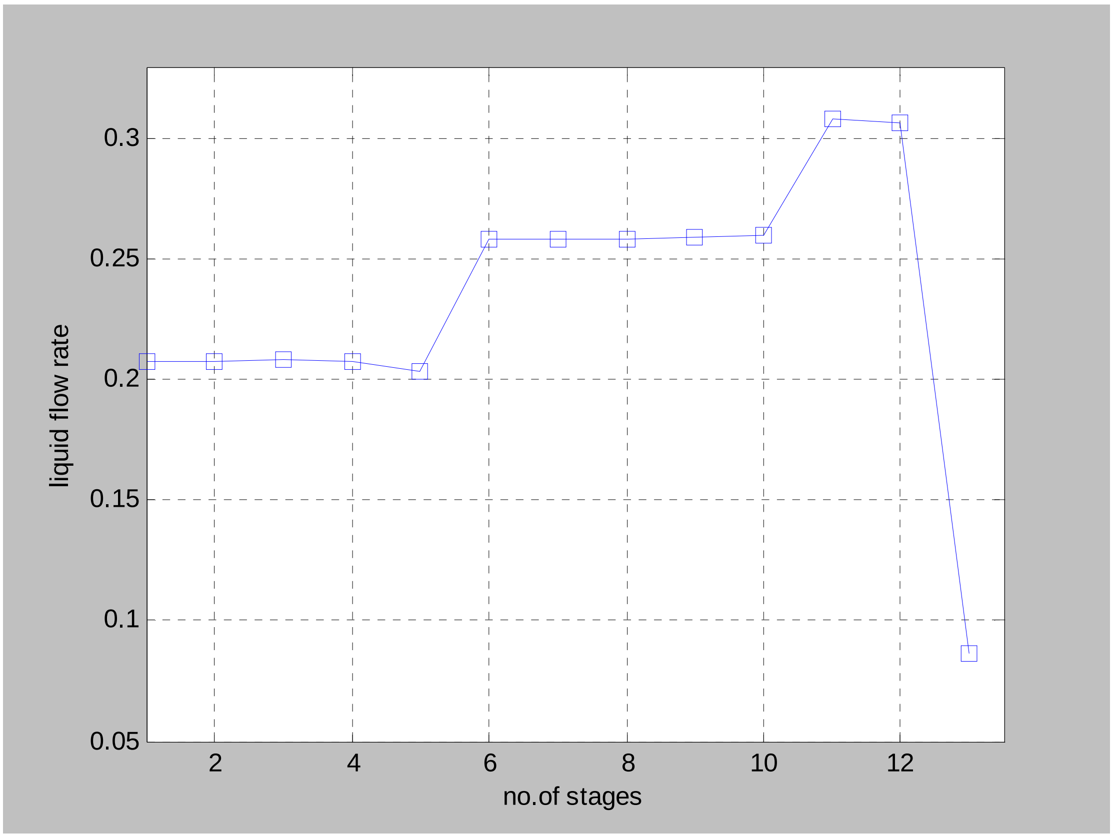


Figure (4-30) liquid flow rate vs. no. of stages using two feed

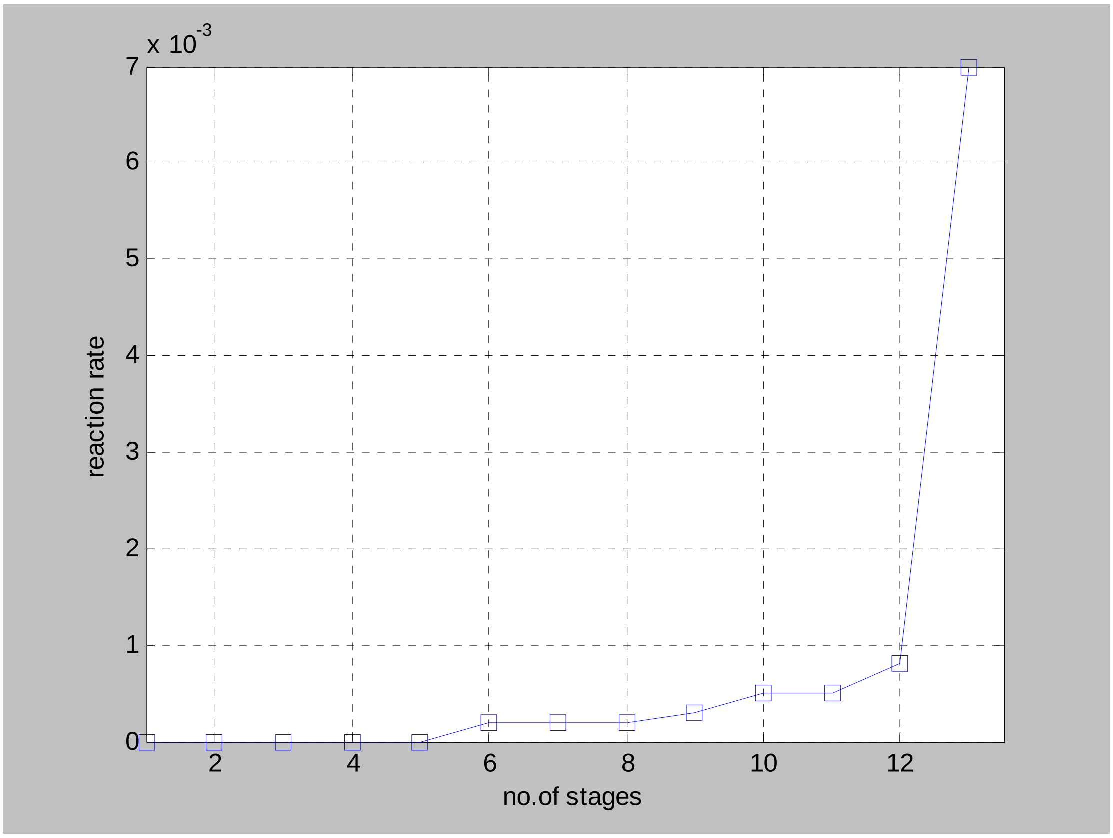


Figure (4-31**)** reaction rate vs. no. of stages using two feed

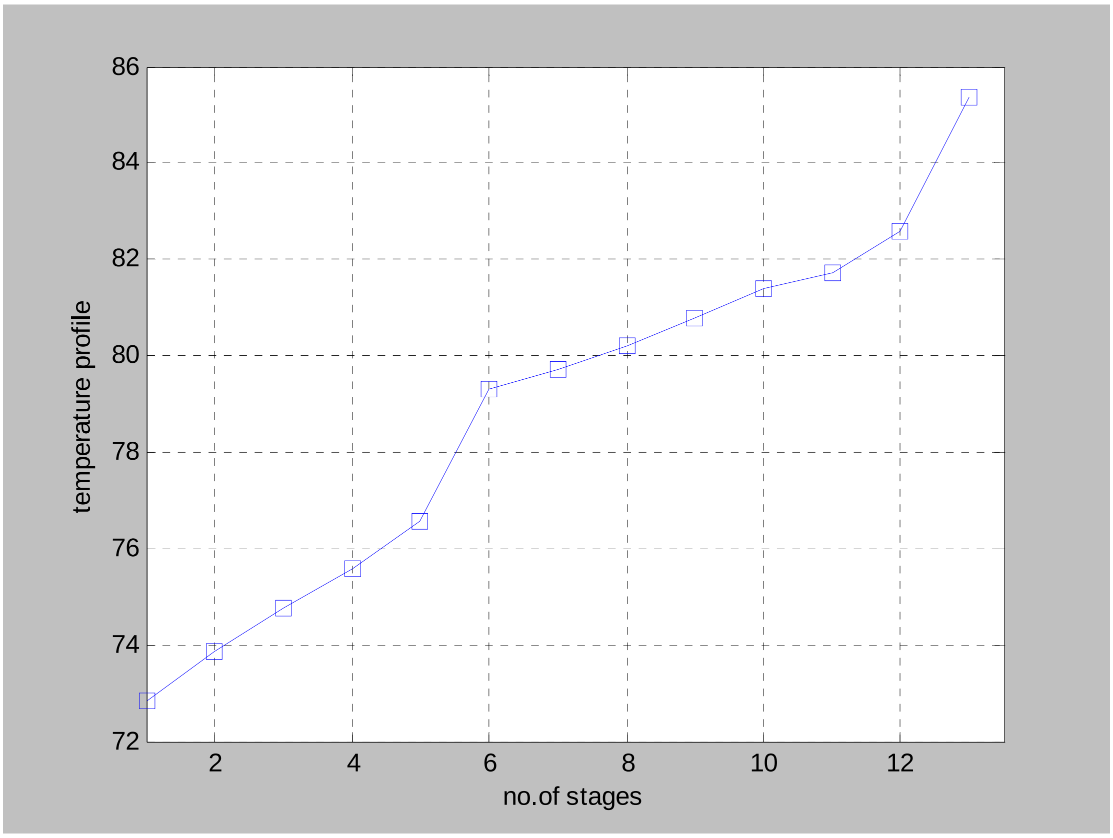


Figure (4-32**)** temperature profile vs. no. of stages using two feed

4.6.4.1 Comparison of present model results with previous work Suzuki [5]

The results obtained by the present work is compared with previous previous work of Suzuki [5]. Results show that vapor, liquid and reaction rate profile give good agreement with the previous work Suzuki [5], figures (4-33), (4-34), (4-35). While there is a small difference in temperature profile due to using another composition, figure (4.36)

The liquid composition profile figure (4-37) shows that there is 33.33 % difference between the present work and Suzuki [5].This is due to using another composition.

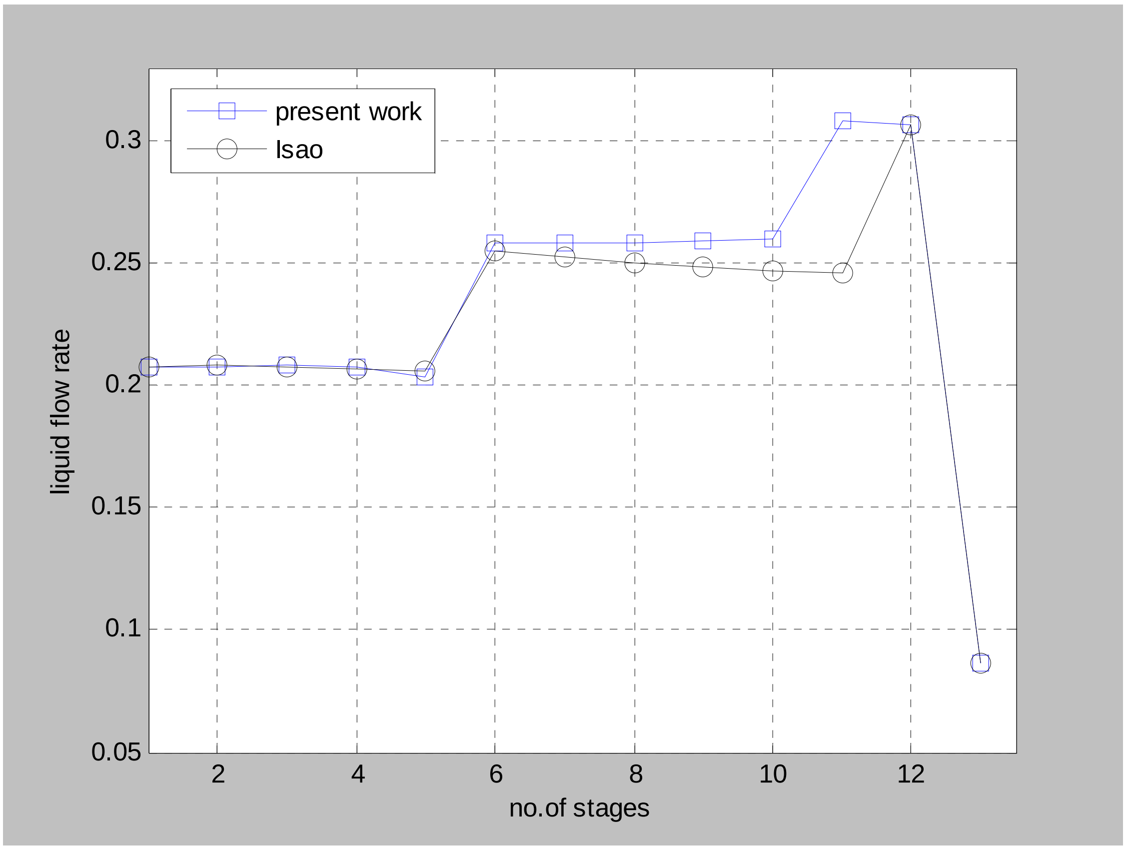


Figure (4- 33**)** liquid flow rate profile comparison using two feed

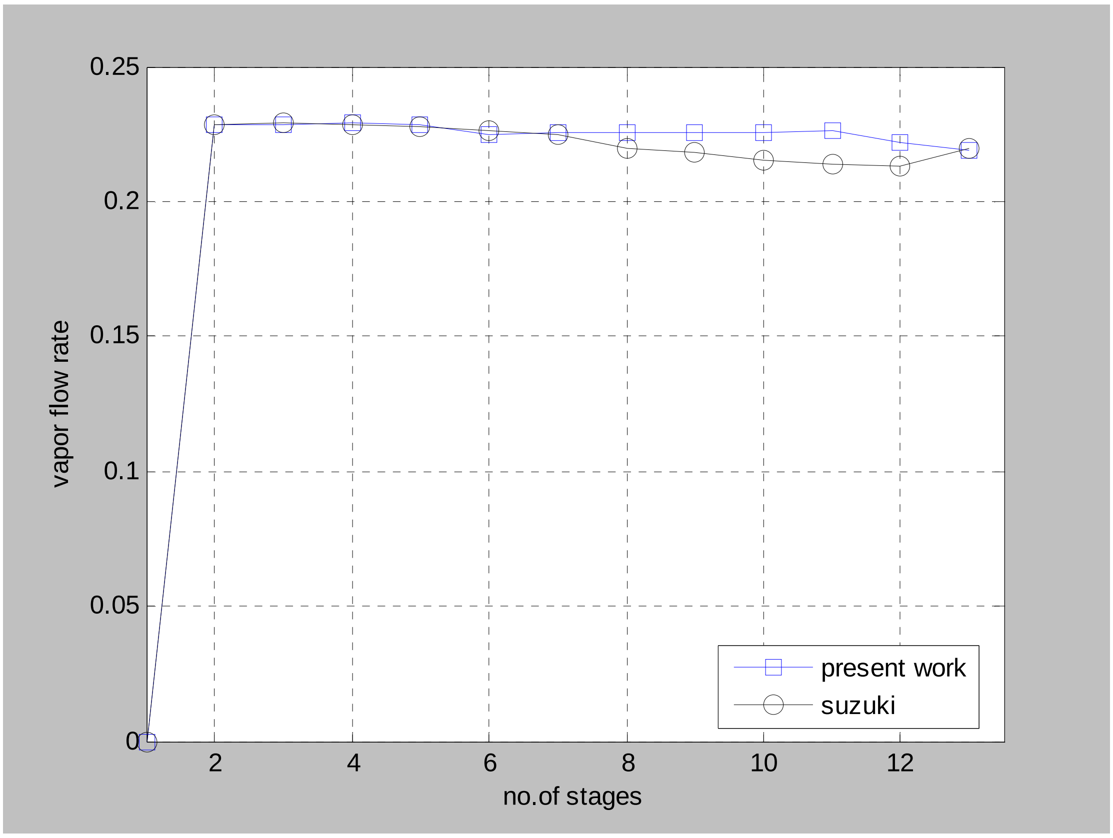


Figure (4-34**)** vapor flow rate profile comparison using two feed

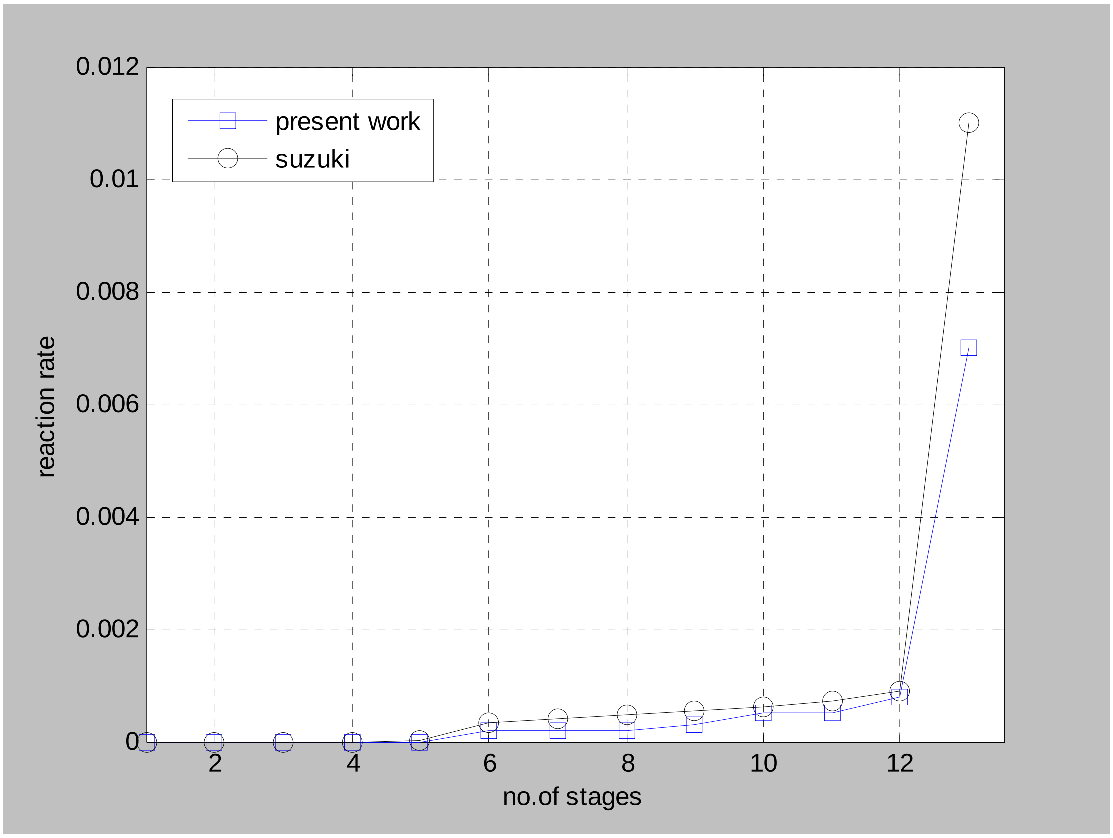


Figure (4-35**)** reaction rate profile comparison using two feed

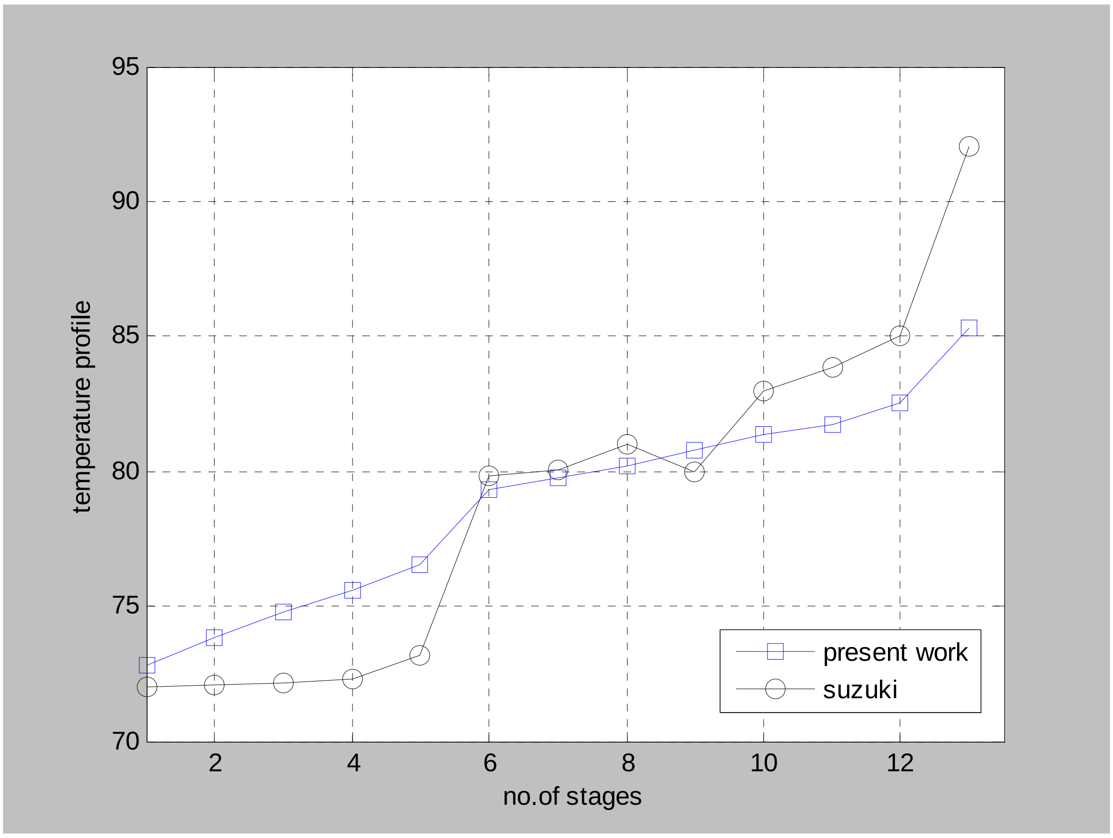


Figure (4-36**)** temperature profile comparison using two feed

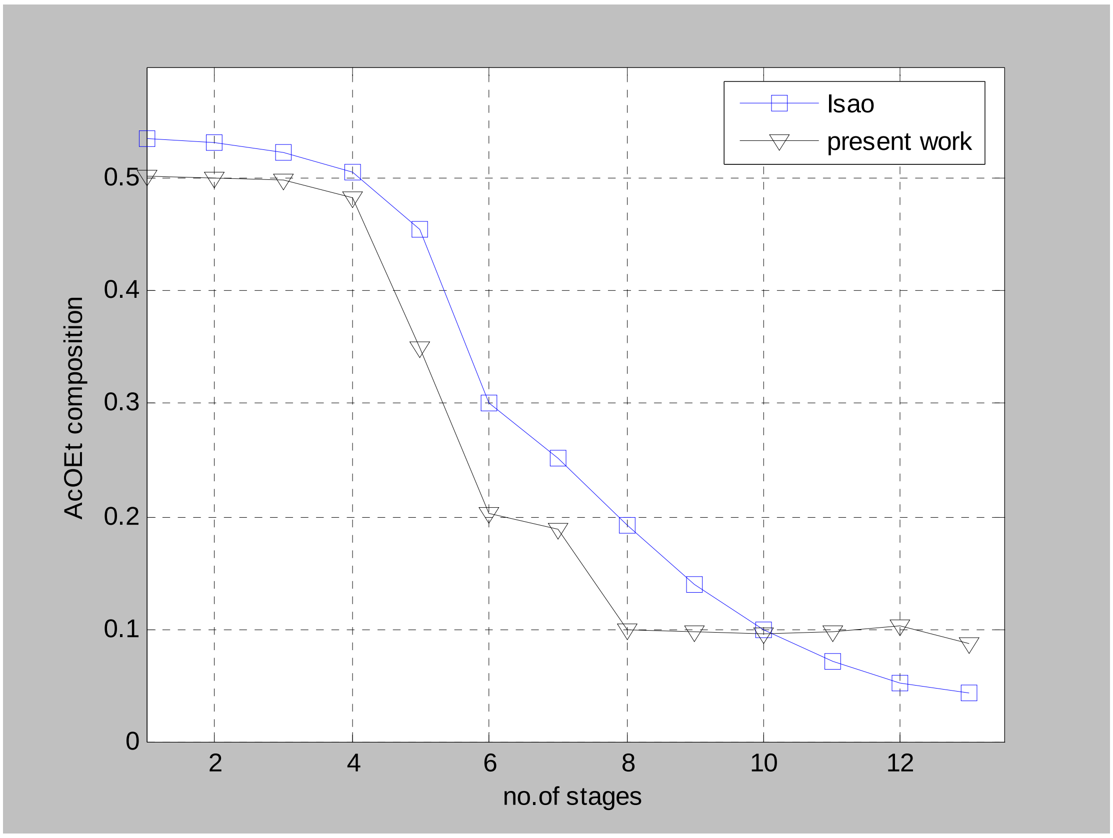


Figure (4-37**)** AcOEt composition profile comparison using two feed

4.6.4.2 Comparison of one feed results with two feed results

The liquid composition profile figure (4-38) shows that there is few difference between the one and two feed].This is due to using another composition.

The results obtained by the one feed is compared with two feed work of present work . Results show that liquid ,vapor and reaction rate profile give good few different between then figures (4-39), (4-40), (4-41). While there is a small difference in temperature profile due to using another composition, figure (4.42)

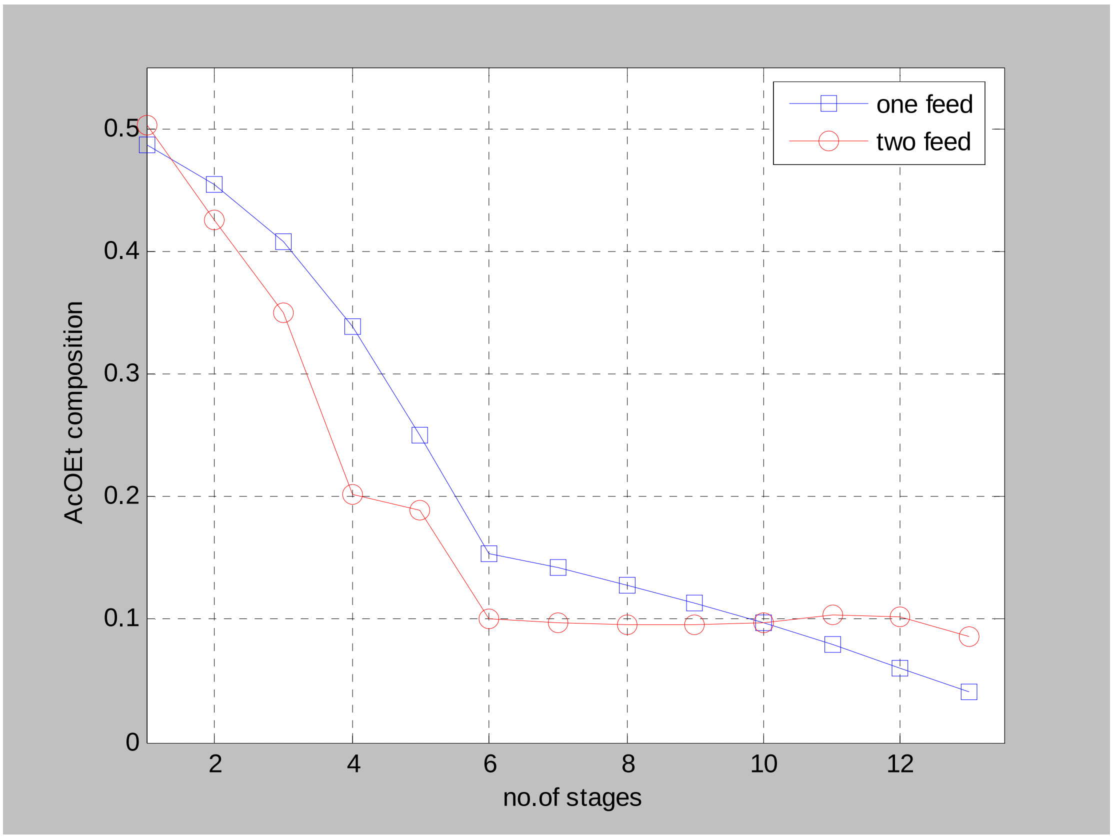


Figure (4-38**)** AcOEt composition profile comparison using two feed one feed

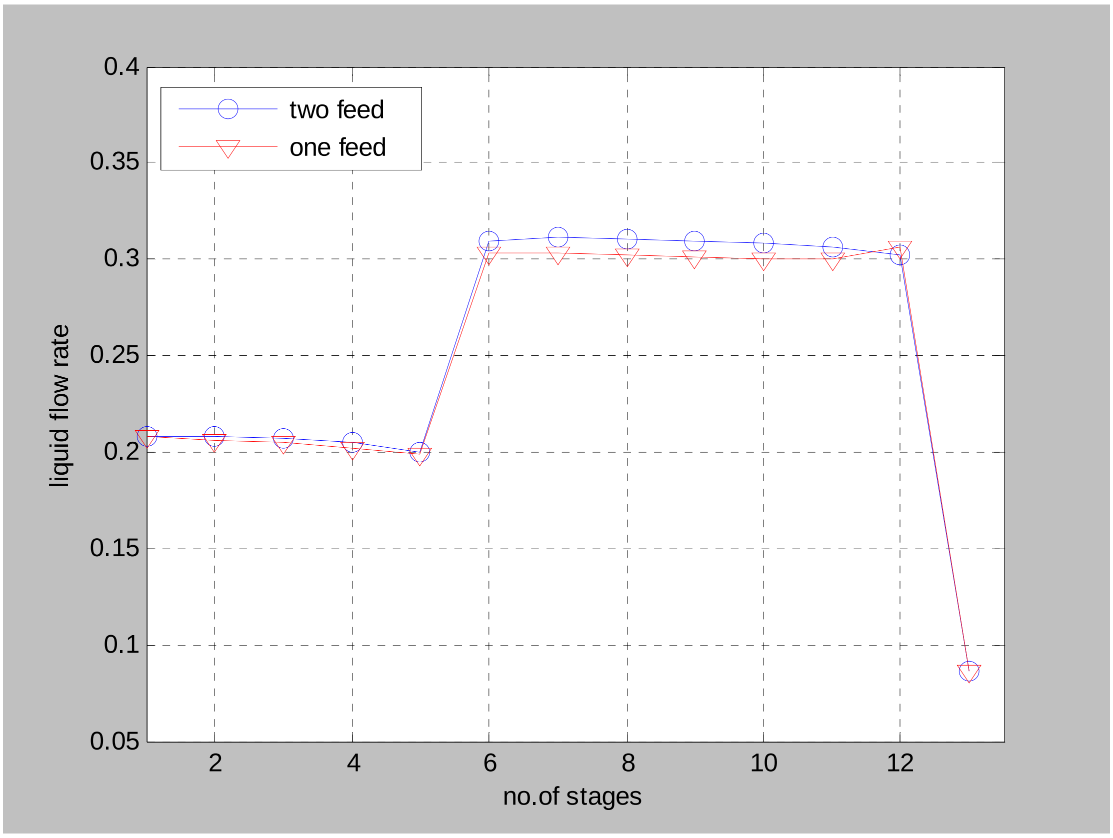


Figure (4- 39**)** liquid flow rate profile comparison using two feed one feed

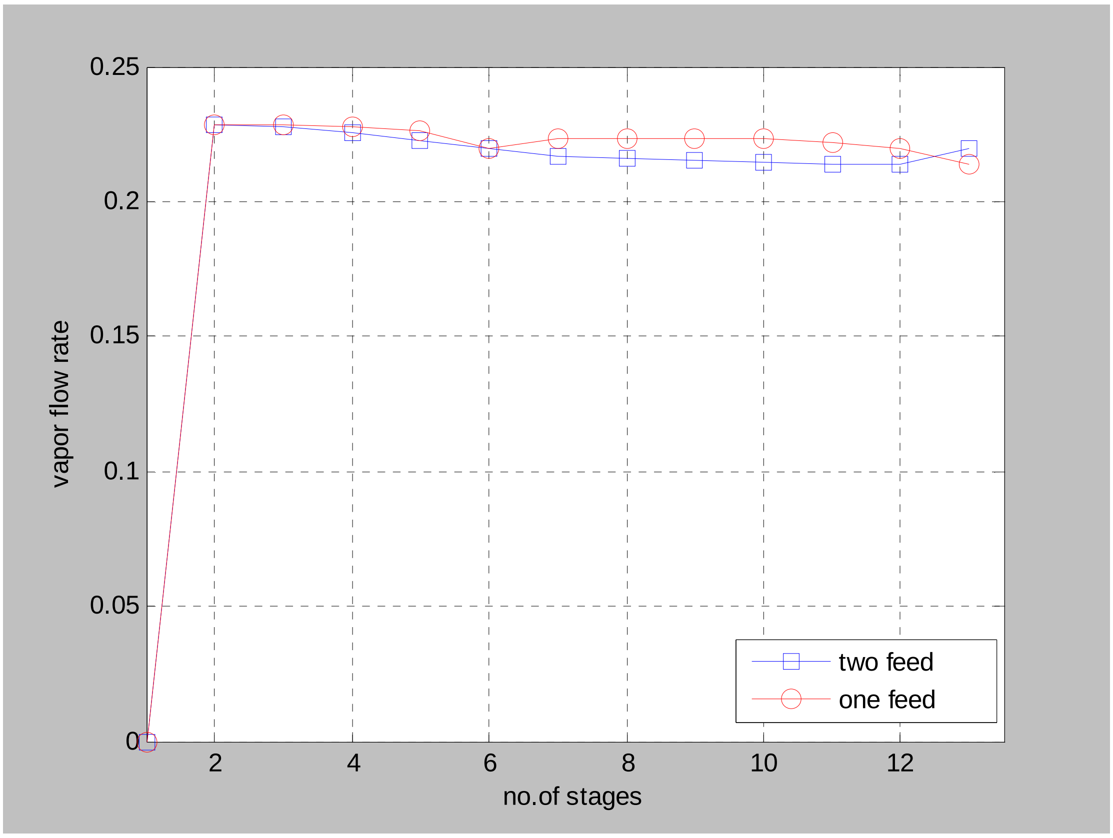


Figure (4- 40**)** vapor flow rate profile comparison using two feed one feed

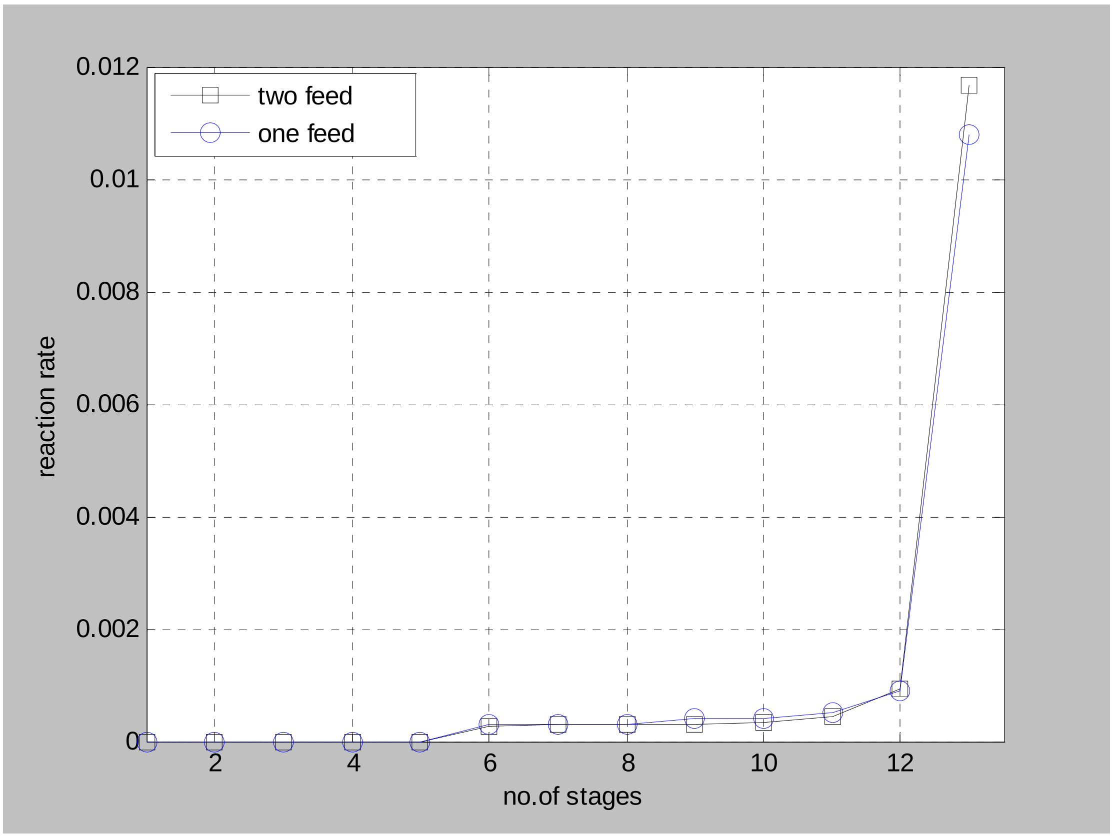


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Figure (4- 41**)** reaction rate profile comparison using two feed one feed

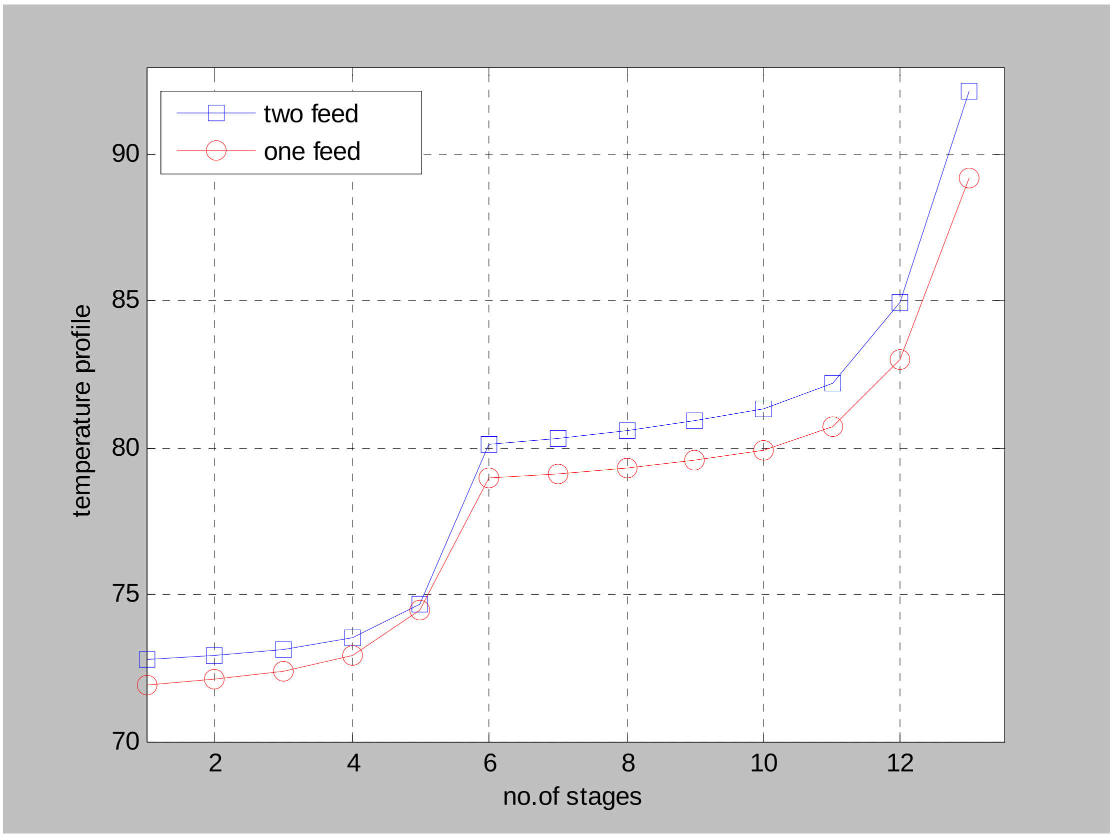

Figure (4- 42**)** temperature profile comparison using two feed one feed

Chapter five

Conclusions and Future Work

5.1 Conclusions

The following conclusions have been drawn from this work

1- The selectivity of liquid phase activity coefficient models, based on the purity of ethyl acetate that is separated, produced an ethyl acetate in the Wilson equation of 48.70 % while in the UNIQUAC is 47.77%.

2- The result obtained from the developed model using rigorous method one feed gave a good agreement with Suzuki [5] and Al- Khazraji [30].

3- The liquid composition of ethyl acetate in distillate in one feed is 48.70 mole % while in double feed is 50.20 mole %.

4- The highest liquid composition (mole fraction) on product distillate obtained is 0.4965 when the reflux ratio was 10 and the number of stages was 15 and feed enters at stage 6.

5-The results of simulate for the present work show that the best condition is, reflux ratio 13, location of feed plate stage 9 and number of stages 15.

6- The results obtained from the model using rigorous method with two feeds give a good agreement with Suzuki [5].

7- The results show that best condition for simulation is by using two feeds where the composition of ethyl acetate increases 52.20 mole% in distillate but when using one feed it is 48.70 mole% .

5.2 Future Work

For the future works, the following recommendations are put forward:

1- Using the equation of state such as NRTL and UNIFAC model to calculate the vapor liquid equilibrium relation in liquid phase and compare the results.

2- Modification of the computer program by studying the effects of other process variables such as changing liquid hold up, the range of temperature.

3- Application of the program on other industrial systems such as methyl acetate and methyl tert-butyl ether (MTBE) productions.

4- Experimental work is required to compare the results with those obtain from the simulation.

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Appendix A

Appendix (A-1) physical properties

Component	Latent heat λ_i (J/mol)	Enthalpy of formation H_f(J/mol)	T_c[K]	T_b[K]	M.W
Acetic acid	5660	-486.2	594.4	391.1	60.052
Ethanol	9260	-277.63	516.2	351.5	46.064
Water	9717	-285.84	647.3	373.2	18.015
Ethyl acetate	7700	-442.92	523.2	350.3	88.107

Appendix (A-2) Coefficient of Antoine equation

Component	A	B	C
Acetic acid	16.808	3405.57	-56.34
Ethanol	18.5242	3578.91	-50.5
Water	18.3036	3816.44	-46.13
Ethyl acetate	16.1516	2790.5	-57.15

Appendix (A-3) Coefficient of the liquid molar density

Component	A	B	C	D
Acetic acid	1.4486	0.25892	591.95	0.2529
Ethanol	1.648	0.27627	513.92	0.2331
Water	5.459	0.30542	647.13	0.081
Ethyl acetate	0.8996	0.2586	523.3	0.278

Appendix (A-4) Vapor enthalpy coefficients

Component	A	B	C	D	E
Acetic acid	-2421.29	2.0142	2.80325e-2	.11363	.002005e-6
Ethanol	-3003.24	4.75	2.503e-2	.8263e-5	1.1975e-3
Water	.4083193	0.0036710	0.0616e-4	3442.355	0
Ethyl acetate	-4981.59	10.31	30.495e-3	5.39e-6	0

Appendix (A-5) UNIQUAC thermodynamic model coefficients

Component	r	q	qpr
Acetic acid	2.2023	2.2072	2.072
Ethanol	2.1054	1.972	0.92
Water	0.95	1.3997	1.0
Ethyl acetate	3.4786	3.1159	3.1159

Appendix B (B-1)

Homogeneous, Heterogeneous catalysis using in reactive distillation [21]

Description	Application	Reference
Liquid-phase mineral-acid catalyst added to column or reboiler	Esterifications Dibutyl phlalate Methyl acetate	Keyes,Ind.Eng.Chem,24,1096(1932)Berman et al.,Ind.Eng.chem.,40,2139(1984)Agreda et al.,U.S.patent 4,435,595(1984)
Homogeneous catalysis		
Catalyst-resin beads placed in cloth bags attached to fiberglass strip.strip wound around helical stainless steel mesh spacer	Etherifications Cumene	Smith et al., U.S. Patent 4,443,559 (1932) Shoemaker and Jones,Hyd. 57(6),(1987)
Ion exchange resin beads used as column packing	Hydrolysis of methyl acetate	Fuchigami, J. Chem. Eng. Jap., 23, 354(1990)
Molecular sieves placed in bags or porous containers Ion exchange resins formed into raschig rings	Alkylation of aromaldehyde MTBE	Crossland, U.S. Patent 5,043,506 (1991) Flato and Hoffman, Chem. Eng., 15,193 (1992)
Granular catalyst resin loaded in corrugated sheet casings Trays modified to hold catalyst bed	Dimethyl acetals of formaldehydehyde MTBE	Zhang et al., Chinese Patent 1,065,412 (1992) Sanfilippo et al., Eur.Pat.Appl. Ep 470,625 (1992)
Distillation trays constructed of porous catalytically active material and reinforcing resins	None specified	Wang et al., Chinese Patent 1,060,228 (1992)

Method described for removing or replacing catalyst on trays as a liquid slurry	None specified	Jones, U.S.Patent, 5,133,942(1992)
Catalyst bed placed in downcomer,designed to prevent vapor flow through bed	Etherifications, Alkylations	Asselineau, Eur. Pat. Appl. EP 547,939(1993)
Slotted plate for catalyst support designed with openings for vapor flow	None specified	Evans and Stark, Eur.Pat. Appl. EP 571,163(1993)
Ion exchanger fibers (reinforced ion exchange polymer)used as solid-acid catalyst	Hydrolysis of methyl acetate	Hirata et al., Jap. Patent 05,212,290 (1993)
High-liquid holdup trays designed with catalyst bed extending below tray level,perforated for vapor-liquid contact	None specified	Yeoman et al., Int. Pat. Appl., WO 9408679(1994)
Catalyst bed placed in Downcomer,in-line Withdrawal/addition system	None specified	Carland, U.S. Patent, 5,308,451 (1994)

Appendix C (C-1)

The fundamental thermodynamic condition for equilibrium between phases is given by the equality of fugacities ,f_i, in all phases for each component. For equilibrium between a vapor and a liquid.

$$f_{i_v} = f_{i_l} \qquad i=1,.....,nc\,, \qquad ...(2.1)$$

The fugacity of a component in a mixture depends on the temperature, pressure, and composition of that mixture. In principle, any measure of composition can be used. For the vapor phase, the composition always expressed by the mole fraction y. To relate f_{iv} to temperature, pressure, and mole fraction, it is useful to introduce the fugacity coefficient Φi

$$\Phi_i = \frac{f_{i_v}}{y_i . p} \qquad ...(2.2)$$

The vapor phase fugacity can be written in terms of the vapor phase fugacity coefficient Φi ,vapor mole fraction yi, and total pressure p as follows

$$f_{i_v} = \Phi_i . y_i . p \qquad ...(2.3)$$

The fugacity of a component in the liquid phase is related to the composition of that phase through the activity coefficient γi

$$\gamma_i = \frac{f_{i_l}}{x_i . f_i} \qquad ...\ (2.4)$$

Also the liquid phase fugacity can be written in terms of the liquid phase activity coefficient γi ,liquid mole fraction xi, and liquid phase properties fi as follows.

$$f_{i_l} = \gamma_i . x_i . f_i \qquad \text{… (2.5)}$$

where

$$f_i(T,p,x)_i = p_{i_{sat}}(T).\Phi_{i_{sat}}(T).\exp \int_{p_{sat}}^{p} \frac{v_{l_i}(T,p)}{RT} dp \qquad \text{...(2.6)}$$

Integrate equation (2.6)

$$f_{i_l} = p_{i_{sat}}.\Phi_{i_{sat}}.\exp\left[\frac{v_{l_i}(p - p_{i_{sat}})}{RT}\right] \qquad \text{...(2.7)}$$

Sub equation (2.7) in equation (2.5)

$$f_{i_l} = \gamma_i . x_i . p_{i_{sat}}.\Phi_{i_{sat}}.\exp\left[\frac{v_{l_i}(p - p_{i_{sat}})}{RT}\right] \qquad \text{...(2.8)}$$

Sub equation (2.8)&(2.3) in (2.1)

$$\Phi_i . y_i . p = \gamma_i . x_i . p_{i_{sat}}.\Phi_{i_{sat}}.\exp\left[\frac{v_{l_i}(p - p_{i_{sat}})}{RT}\right] \qquad \text{...(2.9)}$$

$$y_i = \frac{\gamma_i x_i p_{i_{sat}}}{\Phi_i p} \qquad \text{...(2.10)}$$

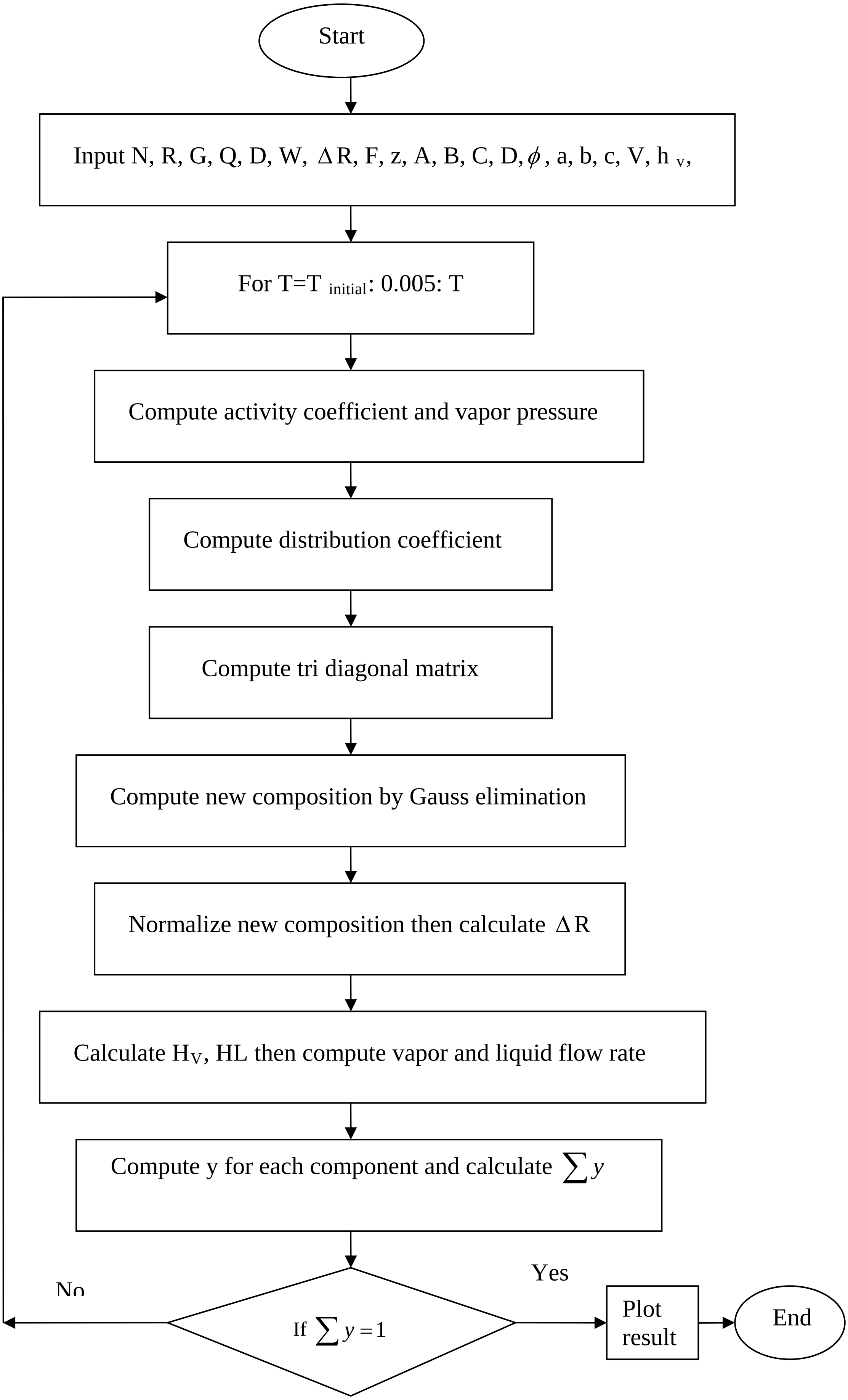
where *Φi* is given by equation ;

$$\Phi_i = \frac{\hat{\Phi}_i}{\Phi_{i_{sat}}}.\exp\left[-\frac{v_{l_i}(p - p_{i_{sat}})}{RT}\right] \qquad \text{…(2.11)}$$

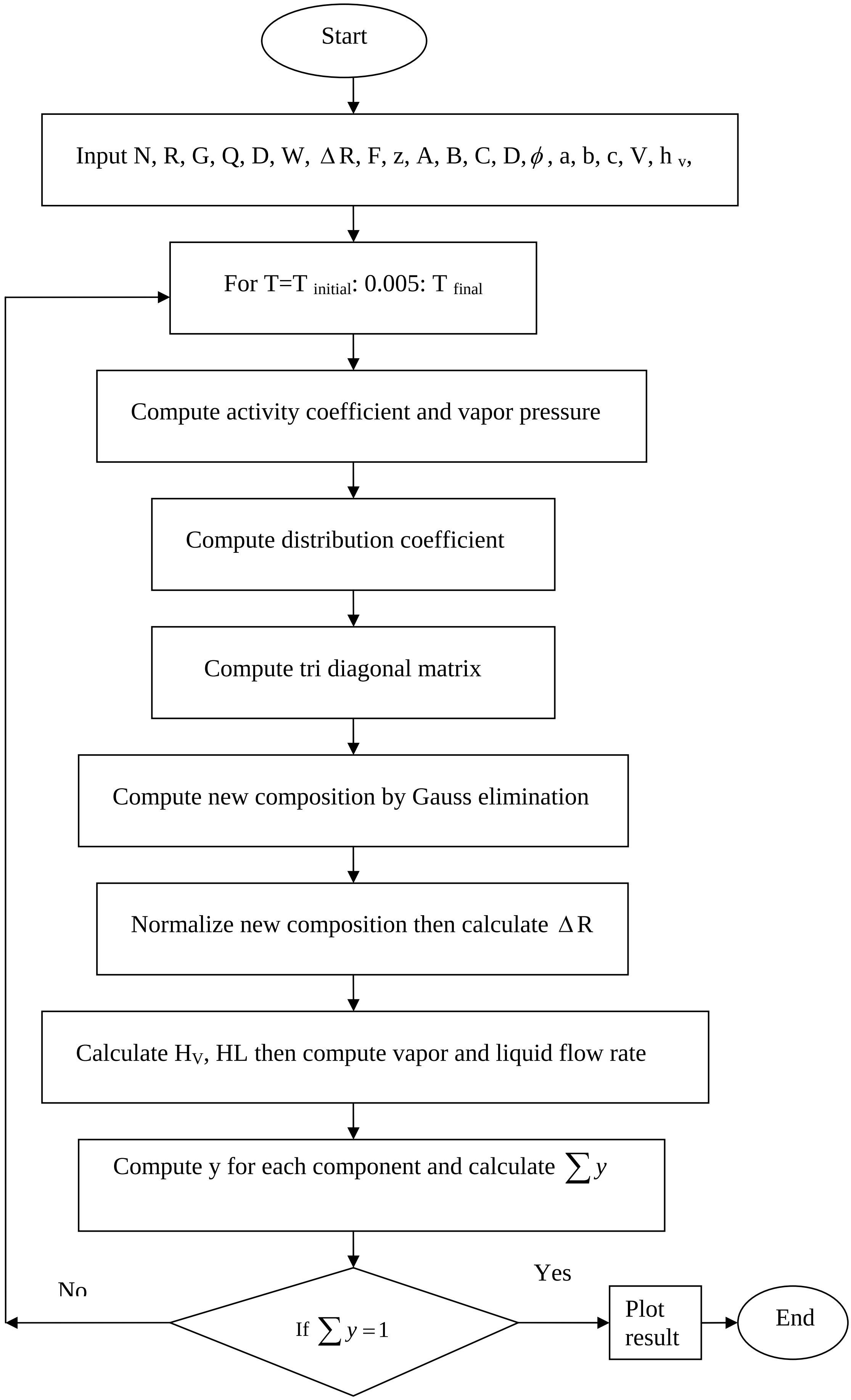
At low pressures(up to at least 1 bar), vapor phases usually approximate ideal gases for which $\Phi\hat{}i = \Phi i_{sat} = 1$ and poynthing factor which represented by the exponential differs from unity by only a few parts per thousand . Therefore equation (2.10) become.

$$y_i = \frac{\gamma_i x_i p_{i_{sat}}}{p} \qquad \text{...(2.12)}$$

Appendix D (D-1)



Appendix D (D-2)



شكر وتقدير

أود أن أعبر عن خالص شكري و تقريري وامتناني العميق للمشرفه الدكتورة ندى بهجت النقاش لما قدمته لي من توجيهات قيمة ونصائح سديدة طوال فترة البحث .

أود أيضا" أن أشكر الدكتورقاسم جبار سيلمان رئيس قسم الهندسة الكيمياوية وجميع أساتذة والموظفي قسم الهندسة الكيمياوية في جامعة النهرين لابدائهم المساعدة اللازمة أثناء هذا العمل. ولا أنسى بالشكر جميع من مد لي يد العون

وأتقدم بالشكر و الامتنان الى من لازمني طوال فترة البحث وخلال أصعب الظروف الى أعز من في الوجود الى أفراد عائلتي فلهم جزيل الشكر والتقدير .

نور قيس رشيد

الخلاصة

يعني هذا العمل بانشاء برامج محاكات حاسوبية لتحليل عمليات التقطير التفاعلي المتصل متعدد المراحل والمركبات.

استخدمت الطريقة المضبوطة لبناء البرامج للخلائط المثالية وغير المثالية .كتبت هذه البرامج بلغة مات لاب وبقصد التوافق مه الحواسيب الشخصية وكما هو مدرج في الملحقين (D -1,2).

دققت صلاحية ودقة هذه البرامج بمقارنة النتائج مع كل من Suzuki [5] باستخدام تفاعل الاسترة لحامض الخليك مع الايثانول لانتاج خلات الاثيل والماء.

درس تأثير العديد من المتغيرات على اداء ابراج التقطير التفاعلي المستمر .تضم هذه المتغيرات موقع صفيحة التغذية ونسبة الانعكاس عدد المراحل.

اجريت هذه الدراسة من خلال فحص مناسيب البخار والسائل ودرجات الحرارة والكسور المولية للسائل ومعدل التفاعل.

وكانت النتائج المستحصلة لابراج التقطير التفاعلي متعدد المراحل في الحالة المغذي الواحد(استره حامض الخليك مع الايثانول لانتاج خلات الاثيل والماء، كمثال)، ان نسبة خلات الاثيل في حاصل التقطير كانت 48.70 مول %عندما كانت نسبة النعكاس 10 وعدد الصفائح 13 وصفيحة التغذية هي السادسة . لكمية التغذية (حامض الخليك 0.4962 ، الايثانول .4808، خلات الاثيل 0.0229 ، الماء 0.0001)

كانت النتائج المستحصلة في الحالة المغذي الثنائي لابراج التقطير التفاعلي متعدد المراحل ، ان نسبة خلات الاثيل في حاصل التقطير كانت 52.20 مول %عندما كانت نسبة النعكاس 10 وعدد الصفائح 13 وصفيحة التغذية هي السادسة . . لكمية التغذية (حامض الخليك 1.0 ، الايثانول 0.85، الماء 0.15).

وان افضل تصميم للعمل هوعندما كانت نسبة النعكاس13 نسبة خلات الاثيل في حاصل التقطير كانت 44.67 مول % 13 وصفيحة التغذية هي االتاسعة نسبة خلات الاثيل في حاصل التقطير كانت 49.65 مول % وعدد المراحل15 نسبة خلات الاثيل في حاصل التقطير كانت 49.51 مول % .

محاكاة عن التقطير المستمر
للتفاعل الكيمياوي

رسالة

مقدمة الى كلية الهندسة في جامعة النهرين وهي جزء من متطلبات نيل درجة ماجستير علوم في الهندسة الكيمياوية

من قبل

نور قيس رشيد

(بكالوريوس علوم في الهندسة الكيمياوية 2004)

رمضان 1429هـ

ايلول 2008م