SIMULATION OF BATCH DISTILLATION

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in
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by

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Certification

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Abstract

The importance of batch distillation process in chemical, petroleum and pharmaceutical industries to separating the liquid mixture into their constituent components. The present work is concerned with developing a computer program using short-cut model and a simulation computer program using rigorous model to analyze multi-components non ideal mixture, multistage batch distillation column using MATLAB.

The short-cut model has been used to calculate minimum number of stage using Fenske equation and minimum reflux ratio using Underwood equation. The Theoretical number of stages required to distillate the mixture of Benzene-Toluene-Ethylebenzene is calculated by Gilliland correlation that related minimum number of stage with the actual number , and that have been used in rigorous method to calculate the concentration profile, temperature profile, vapor and liquid flow rate on each stage. Rigorous model composed of the MESH (Material balance, Equilibrium , Sum of mole fractions ,Heat balance) equations.

The results obtained from short-cut model gave good agreement with previous work [seader] and a rigorous model gave good agreement with experimental work [Salah] for the system Benzene-Toluene-Ethylebenzene .

Rigorous model for the ideal system Hexane-Heptane-Octane gave a good agreement with the previous work [Bernot].

Different liquid phase activity coefficient models have been studied such as (Wilson, NRTL, UNIQUAC, UNIFAC) for Benzene-Toluene-Ethylebenzene system and the appropriate model was selected according to the purity of the benzene that is separated as a top product.

The results showed that UNIFAC and NRTL models give more acceptable results. In the present work the UNIFAC model has been used because it is modern and the parameters used in this model are easy to obtain.

The distillation column was operated under constant operating pressure of 1 atm, 8 number of theoretical stages and initial feed temperature at 298.15 K.

The influence of various parameters such as reflux ratio (1 , 2 , 4), batch time (0.5 - 2 hr), liquid hold up in condenser and on each tray ((1.25 , 0.5) , (5 , 1) , (20 , 5) mole), respectively and initial feed composition of benzene in the still (0.2 , 0.3 , 0.5 mole) upon the performance of the batch non-ideal distillation have been studied through vapor and liquid flow rate profiles, temperature profile, liquid mole fraction profile ,heat input to the still and heat out put from the condenser.

Increasing the reflux ratio the composition of the desired component (Benzene) decreases in the distillate comparison with the composition of benzene in the distillate when decreasing the reflux ratio.

Increasing the batch time the distillate composition of benzene decreased .Changing the liquid hold up in plates and in condenser give different results, increasing the liquid hold up in plates and condenser cause decreasing in distillate composition.

Increasing the initial feed composition of light component in the still give high quantity in distillate.

The best design condition for operating batch distillation to obtain purity of the desired product was reflux ratio equal to 1 , batch time less than 1 hr, liquid hold up in condenser and in each tray is 1.25 and 0.25 mole, respectively and the initial feed composition of benzene is 0.5 mole in the still.

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Notations

Symbols		Notations	Units
A,B,C	=	Antoine's coefficient	-
A_l,B_l,C_l	=	Constant of specific heat of liquid	-
A_v,B_v,C_v,D_v	=	Constant of specific of vapor	-
Btime	=	Batch time	hr
C_0	=	Combinational part	-
Cp	=	Specific heat of component	j/mol.k
D	=	Distillate flow rate	mol/hr
f	=	Fugacity	atm
Gc	=	Constant volume holdup in the condenser	m^3
G_N	=	Constant volume holdup in the plate	m^3
h_i	=	Enthalpy of a liquid phase	j/mol
h°	=	Enthalpy of formation	j/mol
H_{Li}	=	Total Enthalpy of a liquid phase	j/mol
H_{mix}	=	Enthalpy of mixing	j/mol
H_i	=	Enthalpy of a vapor phase	j/mol
K	=	Distribution coefficient	-
L	=	Liquid flow rate	mol/hr
M_N	=	Molar holdup on N tray	mol
Mc	=	Molar holdup on condenser	mol
Mr	=	Molar holdup on still	mol
M_0	=	Initial charge to the still	mol
M_{wi}	=	Molecular weight of component i	kg/mol
N_t	=	Total number of stage	-
P	=	Pressure	atm
P^{sat}	=	Saturated pressure of pure component	atm

Q_r = Still heat duty w

Q_c = Condenser heat w

q_i = Van Der Waals area parameter -

R_r = Reflux ratio -

R = Constant of ideal gas j/mol.k

R_s = Residual part -

r_i = Van Der Waals volume parameter -

Stime = Step time hr

T = Temperature k

t = Time -

v = Molar volume of i component m^3/mol

V = Vapor flow rate mol/hr

x = Liquid mole fraction mol/mol

z = Co-ordination number -

Greek Symblos

α = Relative volatility -

$a_{i,j}$ = NRTL non-randomness constants interaction -

γ_i = Activity of a component I in a mixture -

v_k^i = Number of K groups in molecule i -

Γ_k = Residual activity coefficient of group K -

λ = Latent heat of vaporization j/mol

ρ = Component density kg/m^3

Φ = Fugacity coefficient -

Δ = Difference -

Abbreviations

BTEb = Benzene, toluene and Ethylebenzene.

MESH = (Material balance, Equilibrium, Summation of mole, Heat balance).

NRTL = Non-random, two liquid model.

ODE'S = Ordinary Differential Equations.

VLE = Vapor – Liquid Equilibrium

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Chapter One
Introduction

1.1 Introduction

One of the major operation in the chemical and pharmaceutical industries is the separation of liquids mixtures into their components by distillation.

Distillation is a process in which a liquid or vapor mixture of two or more substances is separated into its component fractions of desired purity, by the application and removal of heat.

Distillation is based on the fact that the vapor of a boiling mixture will be richer in the components that have lower boiling points, when this vapor is cooled and condensed, the condensate will contain more of the high volatile material.

Although the meaning of "Distillation" is fairly understood the important aspects that seem to be missed from the manufacturing point of view are that:

1. Distillation is the most common separation technique.
2. It consumes enormous amounts of energy, both in terms of cooling and heating requirements.
3. It can contribute to more than 50% of plant operating costs.

The best way to reduce operating costs of existing units, is to improve their efficiency and operation via process optimization and control. To achieve this improvement, a thorough understanding of distillation principles and how distillation systems are designed is essential.

One way of classifying distillation column type is to look at how they are operated. Thus distillation is operated as:-

1. Batch Distillation or.
2. Continuous Distillation.

In batch operation, the feed to the column is introduced batch-wise. That is, the column is charged with a 'batch' and then the distillation process is carried out. When the desired task is achieved, a next batch of feed is introduced.

In contrast, continuous columns process a continuous feed stream. No interruptions occur unless there is a problem with the column or surrounding process units, they are capable of handling high throughputs.

Batch distillation has the advantage of being much more flexible than continuous distillation. This flexibility makes batch distillation suitable to separate high purity products using the same column. Further more batch distillation often means simpler operation and lower capital cost than continuous distillation[4].

The increasing production of high value added, low -volume specialty chemicals , biochemical and pharmaceutical, in recent years, have generated a renewed interest in batch processing technology [5].However , most of the research in batch processing focused on developing methodologies for synthesizing and sizing equipment network ,where performance characteristics of the process units are assumed to be given. This is because time -dependent nature of batch processes and units make the models to be complex. Another major issue in batch process design or synthesis is operational flexibility, which gives rise to a large number of alternative evaluations [6].

1.2 The Benefits of Batch Distillation

Batch processing is becoming increasingly important in many chemical companies as the trend to specialty, small-volume and high-value chemicals continues. Batch distillation columns are frequently an important part of these processes. Batch distillation has the advantage of being able to produce a number of products from a single column. Even though batch distillation typically consumes more energy than continuous distillation. It provides more flexibility and involves less capital investment. A single column can be also handle a wide range of feed compositions, number of components, and degrees of difficulty of separation. Since energy costs are not too significant in small-volume, high value products, batch distillation is often attractive for this class of products [6].

In batch distillation little change is required when switching from one mixture to another. Reflux ratio and throughput can be varied easily. No balance of feed and drawoff need be maintained. In situations where the composition of the feed may change frequently or where different mixtures must be handled. The versatility of the batch distillation unit is excellent [7].

1.3 The Project Aims

1- Simulate multi-component batch distillation using two methods of calculations short-cut method under unsteady state condition to calculate the number of stages roughly and rigorous method to give the exact results.

2- The results obtained by short-cut method was compared with the result obtained by [Seader] , and the result of the rigorous method was compared with the experimental data taken from previous work [Salah] for benezene, toluene and ethylebenzene.

3- The results of the simulation model for the system hexane, heptane and octane was compared with the results obtained by [Doherty].

4- Different thermodynamic models (Wilson, NRTL, UNIQUAC and UNIFAC) were considered in the theoretical work to obtain the best representation of the vapor-liquid equilibrium for the mixture used.

5- Different variables were studied such as batch time, reflux ratio, composition of the component and liquid holdup.

Chapter Two
Literature survey

2.1 Introduction

Distillation is one of the most important separation processes used by the chemical industry. It is used for separating mixtures into two or more fractions of different composition .Inherent in the process, is the countercurrent contacting of liquid and vapor phases moving relative to one another in a tower or column as a result of differences in density [8].

There are two main types of distillation; batch and continuous. The process of continuous or steady state distillation ,as distinguished from transient or unsteady -state ,denotes that flow rate, composition temperature, and pressure tend to be independent of time at every position in the operation. Batch distillation , a special case of transient behavior , signifies starting with a single charge and continuously with drawing an overhead product [4].

Batch distillation is a very simple and efficient unit operation for the separation of multi component mixtures into pure components due to the low investment cost and the high purity of products [9].

2. 2 Distillation Processes Techniques

Two or more components differ in boiling point by less than approximately 50˚C and form a non-ideal liquid solution. The relative volatility may be below 1.10 . Then ordinary distillation may be uneconomic, and if an azeotrope forms even impossible. There are several techniques referred to as enhanced distillation to separate of azeotropic mixture, but all of these techniques depend on the idea of improving the vapor-liquid equilibrium of the mixture to be separated. This can be done either by changing column pressure or by adding other components to the mixture called an extraneous liquid, when present in the column ,changes the relative volatilities of the original components and thus facilities the separation .

2.2.1 Extractive Distillation

In extractive distillation a miscible, high boiling relatively non-volatile component is used as a solvent. The solvent is fed at the upper part of distillation column and interacts differently with the components of the original mixture (increases the volatility difference between the components to be separated and pulls some of the components down the column). Extractive distillation is commonly used to separate azeotropic mixtures that display minimum azeotropes.

The selection of an appropriate solvent is one of the most important steps in designing of extractive distillation [10]. The best solvent must obey the following conditions:-

1. It should enhance the volatility of the key component.
2. It should remain soluble in the feed components and should not lead to the formation of two phases.
3. It should be easily separated from the bottom product.
4. It should be inexpensive and readily available.
5. It should be stable at the temperature of the distillation and solvent separation.
6. It should be non-reactive with the components in the feed mixture.
7. It should have low latent heat.
8. It should be non-corrosive and nontoxic.

However satisfying all these conditions is very difficult if not impossible, therefore, the selected solvent must obey as many as possible of theses conditions.

2.2.2 Salt Distillation

Salt distillation adds a salt to the system to modify the thermodynamic behavior of the system. The salt is normally added to the mixture to separate in distillation column[11,12].The salt dissociates in the feed mixture and reduces the vapor pressure of the more soluble component and then the separation by distillation is possible.

2.2.3 Pressure-Swing Distillation

To make a required separation by using pressure swing distillation, it is possible to change the vapor-liquid equilibrium at azeotropic point by changing the column pressure (either increasing or decreasing), and then a good separation could be attained by simple distillation. This method is used to separate methyl ethyl-ketone (MEK)/water system [12]. For some mixtures, a significant change in the azeotropic point could result by simple change in operating pressure. Before selecting this method to separate any azeotropic mixture, it is very important to examine the equilibrium data at various pressures and temperature to obtain the best condition to operate pressure swing distillation. According to a specific pressure and temperature one could choose optimum thermodynamic model, which can accurately predict the behavior of azeotrope.

2.2.4 Azeotropic Distillation

The driving force for any distillation process is the difference between the liquid and vapor composition in the mixture. When the liquid and the vapor have the same composition at a certain point, this mixture is called azeotropic mixture and this point is called azeotropic point. Therefore there is no driving force for separation at this point, and the azeotropic mixtures cannot be separated by conventional distillation technique.

Azeotropic Distillation is an important separation technique to separate azeotropic mixtures. In azeotropic distillation of binary mixture, a third component (entrainer) is added to the mixture. This entrainer either breaks the azeotrope or forms another azeotrope with one of the components in the initial mixture. Then it is easy to separate the ternary mixture by conventional distillation [13].Azeotropes are formed due to differences in intermolecular forces of attraction among the mixture component (hydrogen bounding and others). A mixture consists of close boiling point components which may form an azeotrope when only a small deviation from ideal liquid solution occurs.

There are two main types of azeotropic mixtures. An azeotrope that contains one liquid phase in contact with the vapor phase is called homogeneous azeotrpe, while when azeotropic mixture contains two liquid phases in equilibrium with vapor phase. This mixture is called heterogeneous azeotropic.

2.2.4a Homogeneous Azeotropic Distillation

Homogeneous Azeotropic Distillation is a method of separating a mixture by adding an entertainer that forms a homogeneous minimum-or maximum-boiling azeotrope with one or more feed components. The entertainer is added near the top of the column, to the feed, or near the bottom of the column, depending upon whether the azeotrope is removed from the top or bottom [1].

2.2.4b Heterogeneous Azeotropic Distillation

Heterogeneous Azeotropic Distillation is a more useful azeotropic distillation in which a minimum-boiling heterogeneous azeotrope is formed by the entertainer. The azeotrope splits into two liquid phases in the overhead condensing system. One liquid phase is sent back to the column as reflux, while the other liquid phase is sent to another separation step or is a product [1].

An alternative technique that dose find wide industrial application is heterogeneous azeotropic distillation, which is used to separate close-boiling binary mixtures and minimum-boiling binary azeotropes by employing an entertainer that forms a binary and/or ternary heterogeneous azeotrope [1].

2.2.5 Reactive Distillation

Reactive distillation is a method that uses a reaction in the distillation equipment to help the separation by add a separating agent to react selectively and reversibly with one or more of the constituents of the feed. Reactive distillation involves simultaneous chemical reaction and distillation. The chemical reaction usually takes place in the liquid phase or at the surface of a solid catalyst in contact with the liquid phase. One generally application of reactive distillation, described by [14] , is the separation of a close-boiling or azeotropic mixture of components A and B, where a reactive entrainer E is introduced into the distillation column. If A is the lower-boiling component, it is preferable that E be higher boiling than B and that it react selectively and reversibly with B to produce reaction product C, which also has a higher boiling point than component A and does not form an azeotrope with A,B, or E. Component A is removed from the distillation column as distillate, and component B and C, together with an excess E, are removed as bottoms. Components B and E are recovered from C in a separate distillation step, where the reaction is reversed to completely react C back to B and E; B is taken off as distillate, and E is taken off as bottoms and recycled to the first column .In recent years there has been an increasing interest in reactive distillation to purify the close boiling compounds [15]. Also reactive distillation can purify the compounds that are very expensive to separate by using conventional techniques cheaply, cleanly and efficiently. Reactive distillation is used in production of methyl tert-butyl ether (MTBE) which is used as an octane enhancer.

2.3 Distillation Process

The general objective of distillation is the separation of compounds that have different vapor pressures at any given temperature . The word distillation as used refers to the physical separation of mixture in to two or more fractions that have different boiling points. If a liquid mixture of two volatile materials is heated , the vapor that comes off will have a higher concentration of the lower boiling material than the liquid from which it was evolved . Conversely , if a warm vapor is cooled , the higher boiling material has a tendency to condense in a greater proportion than the lower boiling material . Although distillation was known and practiced in antiquity and commercial still had been developed by **Coffey**, the theory of distillation was not studied until the work of **Sorel** cited in [16].Other early workers were **Lord Rayleigh and lewis (1902) [16]**.

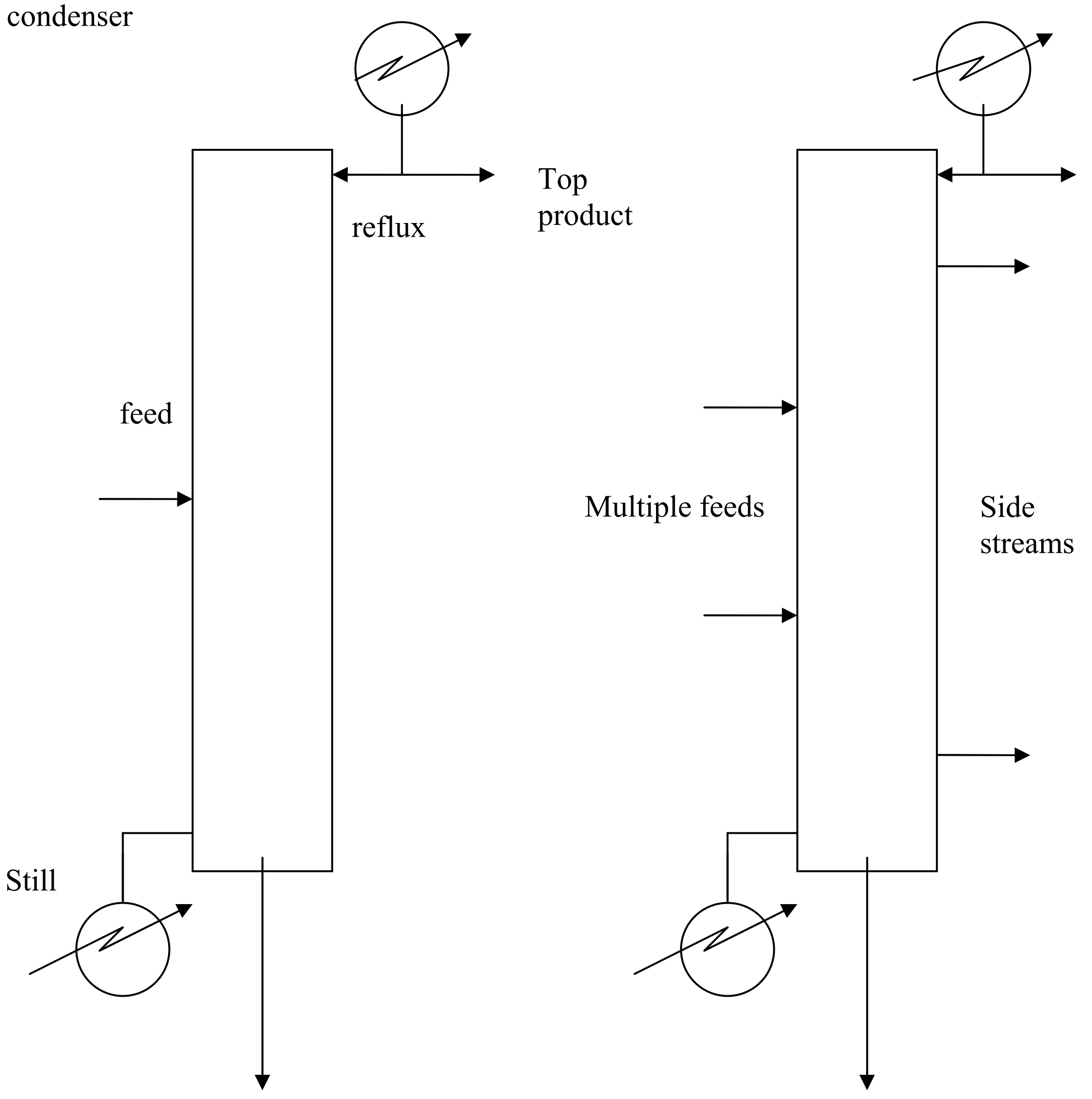
Continuous Distillation Process

The separation of liquid mixtures by distillation depends on differences in volatility between the components . The greater the relative volatilities, the easier the separation [17].From industrial perspective , the choice of distillation process depends primarily on the amount of feed to be processed , other aspects include the complexity of the mixture of if a flexible multi purpose facility is required . In general , continuous distillation column will be chosen for separating large feed flow rate [13].

Continuous distillation process is one of the most important industrial processes for separating the different components of liquid mixtures . One of the most well - known applications of distillation is the separation of crude oil in to several light and heavy fractions , depending on their varying boiling point [18].

Figure 2.1 shows the basic equipment required for continuous distillation .Vapor flows up the column and liquid counter-currently down the column . The vapor and liquid are brought into contact on plates , or packing . Part of the condensate from the condenser is returned to the top of the column to provide liquid flow above the feed point(reflux), and part of the liquid from the base of the column is vaporized in the still and returned to provide the vapor flow .In the section below the feed , the more volatile components are stripped from the liquid and this is known as the *stripping section* . Above the feed , the concentration of the more volatile components is increased and this is called the enrichment , or more commonly, the *rectifying section* .Figure 2.1a shows the column producing two product streams, referred to as tops and bottoms, from a single feed .

Columns are occasionally used with more than one feed , and with side streams withdrawn at points up the column , Fig 2.1b this complicates the analysis of the process [17].



(a) Basic column (b) Multiple feeds and side streams

Fig 2-1 Continuous Distillation

2.3.2 Batch Distillation Process

Batch distillation , which is the predecessor of continuous distillation , has tended to be supplanted by the letter process with it's higher throughputs. However, in recent years, the increasing consideration being given to fine chemistry and the need to improve the recovery of useful resources from waste products has forced a reappraisal of batch distillation.

Batch distillation can be represented by differential equations, and recent research on this aspect has been in one of two directions : either as a problem of optimum operation or as an exercise in simulation [19].

In batch separation operations , a feed mixture is charged to the equipment and one or more products are withdrawn , where a liquid mixture is charged to still pot and heated to boiling .The vapor formed and condensed to produce a distillate. The composition of both the initial charge and distillate change with time ; there is no steady state . The still temperature increasing and relative amount of lower boiling components in the charge decrease as distillation proceeds [1].

Differential Distillation

Literature on batch distillation goes back to (1902), when Lord Rayleigh produced the first mathematical treatment of batch distillation [6]. Figure 2.2 shows the simplest case of batch distillation (Differential distillation) which was considered by Rayleigh .There is no reflux ratio ; at any instant , vapor leaving the still pot with composition y_d is assumed to be in equilibrium with perfectly mixed liquid in the still. For total condensation, $y_d= x_d$. Thus , there is only a single equilibrium stage , the still pot . This apparatus is useful for separation wide-boiling mixtures.

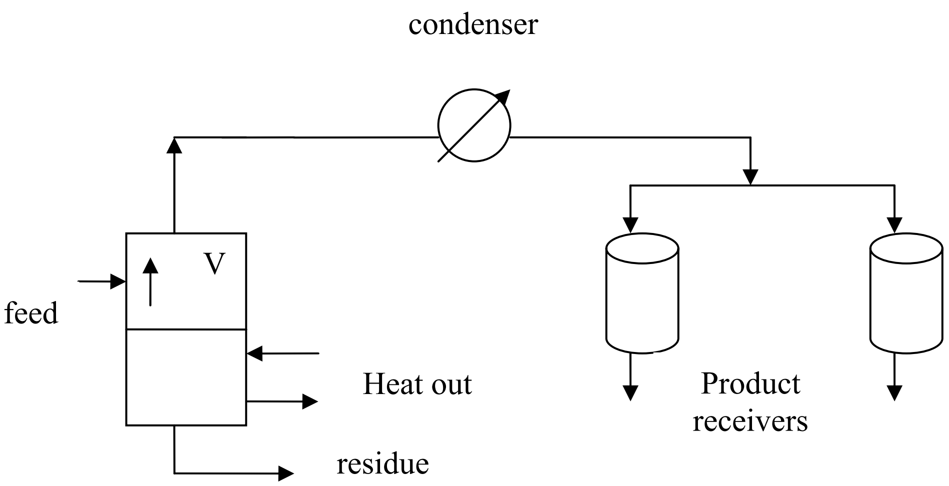


Fig 2-2 Differential Distillation

Batch Rectification

To achieve a sharp separation and/or reduce the intermediate cut fraction **Smoker and Rose (1940)** presented an analysis of the constant reflux case. They suggested a trayed or packed column , located above the still , and a means of sending reflux to the column .

Fig 2.3 shows batch rectifier for a column of a given diameter , the molar vapor boilup rate is usually fixed at a value safely below the column flooding point . If the reflux ratio R is fixed , distillate and still bottoms compositions vary with time . for a total condenser , negligible holdup of vapor and liquid in the column , phase equilibrium at each stage and constant molar over flow , still apply with yd=xd. The constant reflux policy is simple and easy to implement for small batch rectification system.

Bogart (1937) analyzed the case of constant overhead composition . This requires a more complex control system , including a composition monitor (or suitable substitute) on the distillation , which may be justified only for large batch rectification system , negligible liquid holdup and constant molar over flow was assumed. These models were developed based on McCabe-Thiele's graphical method for continuous distillation and were applicable to binary system.

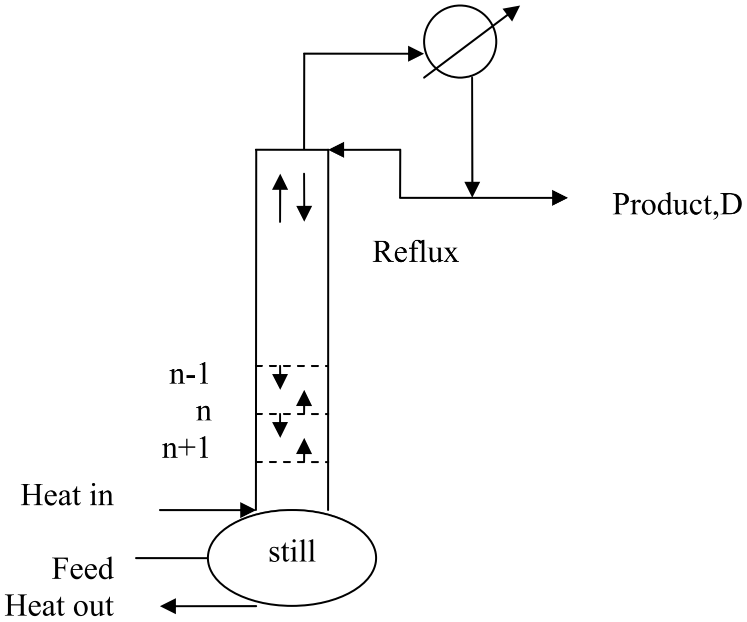


Fig 2-3 Batch rectification

Ellerebe 1973 [20] described the methods of operation batch columns . Batch rectification problems generally fall into two groups-constant and variable reflux .

a- constant-reflux batch rectification

In this mode of operation , the column has a fixed number of theoretical stages and variable overhead composition . Column holdup is assumed to be negligible.

b- variable-reflux batch rectification

Operation of batch column under variable reflux requires the continuous adjustment to maintain a distillate-purity specification.

Initial still liquid is rich in the more volatile component a low reflux-ratio will produce the desired distillate-purity . As the distillation proceeds , the reflux rate be continuously increased until a practical material reached .

Batch Stripping

For batch stripper Fig 2.4 consisting of a large accumulator , a trayed or packed stripping column and a still . The mixture in the accumulator is fed to the top of the column and the bottoms cut is removed from the still. A batch stripping is useful for removing small quantities of volatile impurities.

For binary mixtures , McCabe-Thiele construction is applied and the graphical method can be modified to follow with time . The change in composition in the accumulator and the corresponding instantaneous and average composition of the bottom cut [5].

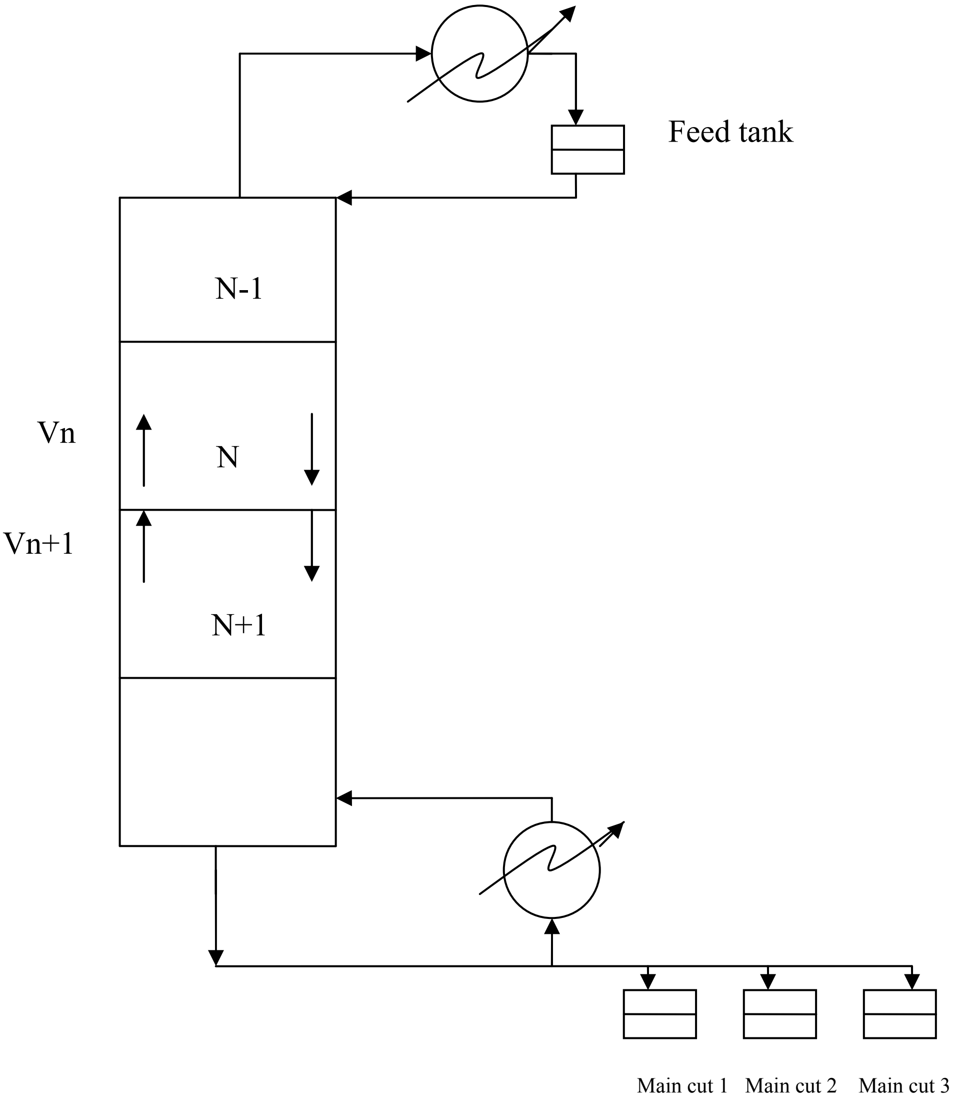


Fig 2-4 Batch Stripping

Complex Batch Distillation

A complex batch distillation unit , of the type described by **Hasebe et al (1992) [21]** , the permit considerable operating flexibility is shown in figure 2.5. The charge in the feed tank fed to the suitable column location . Holdup in the still and condenser are kept minimum . Products or intermediate cuts are withdrawn from the condenser , the still or both . In addition , the liquid in the column at the feed location can be recycled to feed tank if it is desirable to make the composition in the feed tank close to the composition of the liquid at the feed location.

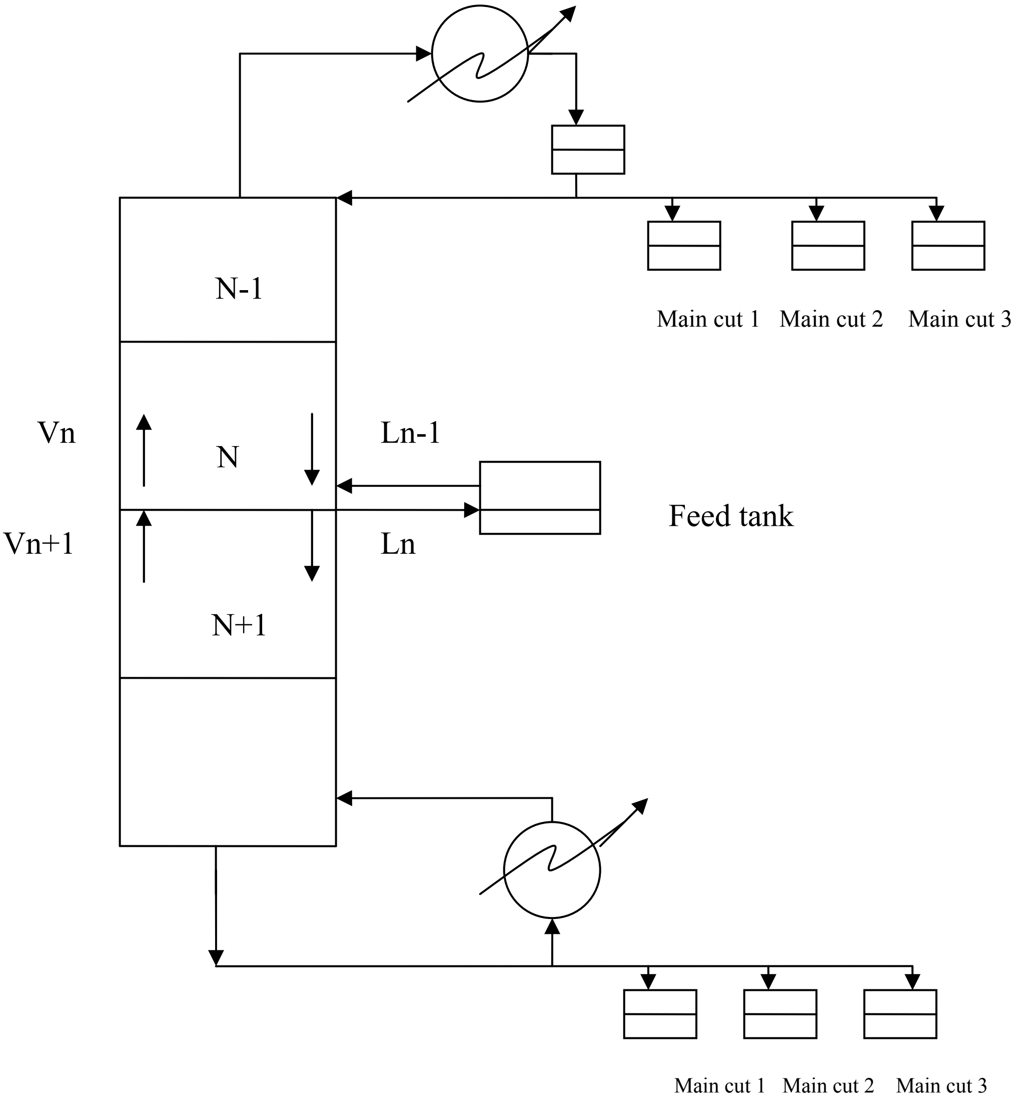


Fig 2-5 Complex batch distillation

The capacity factor methodology developed by **Luyben 1988 [22]** for binary batch distillation is extended to the separation of ternary mixtures . The processing strategy of recycling the two slope cuts back into the next batch is used . The effects of both design and operating parameters are explored by using digital simulation : number of trays , reflux ratio (both fixed and variable) , initial still charge , relative volatility , and product purity . The capacity factor can be used to determine the optimum number of stages and the optimum reflux ratio . Results show little difference in capacity increases with increasing number of trays and increasing relative volatility .

Luyben 1992 [23] developed the first work regarding inferential control strategy with batch distillation.

The work by **Henson and seborg 1997 [24]** lists a number of simulation and experimental cases in which feedback controllers were used . In this work , a nonlinear model-based strategy was developed with commercial software specifically suitable for modeling batch distillation operation. Batch distillation is a very simple and efficient unit operation for the separation of multi-component zeotropic mixtures into pure components due to the low investment cost and the high purity of products . Generally , a regular batch column Fig2.6a is used for batch distillation . In this type of column the feed vessel is located at the bottom of the rectifying column . If a regular batch column used to separate a ternary zeotropic mixture , the first phase of the process pure low boiler is the top product and , therefore , the still depletes in low boiler . In the second phase the intermediate boiler is the top product and , therefore , the concentration of the liquid in the still moves further on to the high boiler , which remains at the end of the process in the still. It is also possible to locate the feed vessel at the top of a stripping column and to operate the column as an inverted batch column Fig2.6b . If an inverted batch column used to separate a ternary azeotropic mixture , the first product is the high boiler and , because of this the feed vessel depletes in high boiler .At the end of the process remains the low boiler in the feed vessel of the inverted batch column .The middle vessel column Fig2.6c is a combination of a regular and an inverted batch distillation column . It was originally proposed by Robinson and [25] . The separation section of the column is divided into a rectifying and a stripping section with the feed vessel in between . Therefore , it is possible to obtain the light and heavy fractions *D* and *B* simultaneously from the top and bottom of the column , while an intermediate boiling fraction *M* may recovered at the end of a process from the middle vessel . Columns with more than two column sections and feed vessel are called multi-vessel-column [9] .

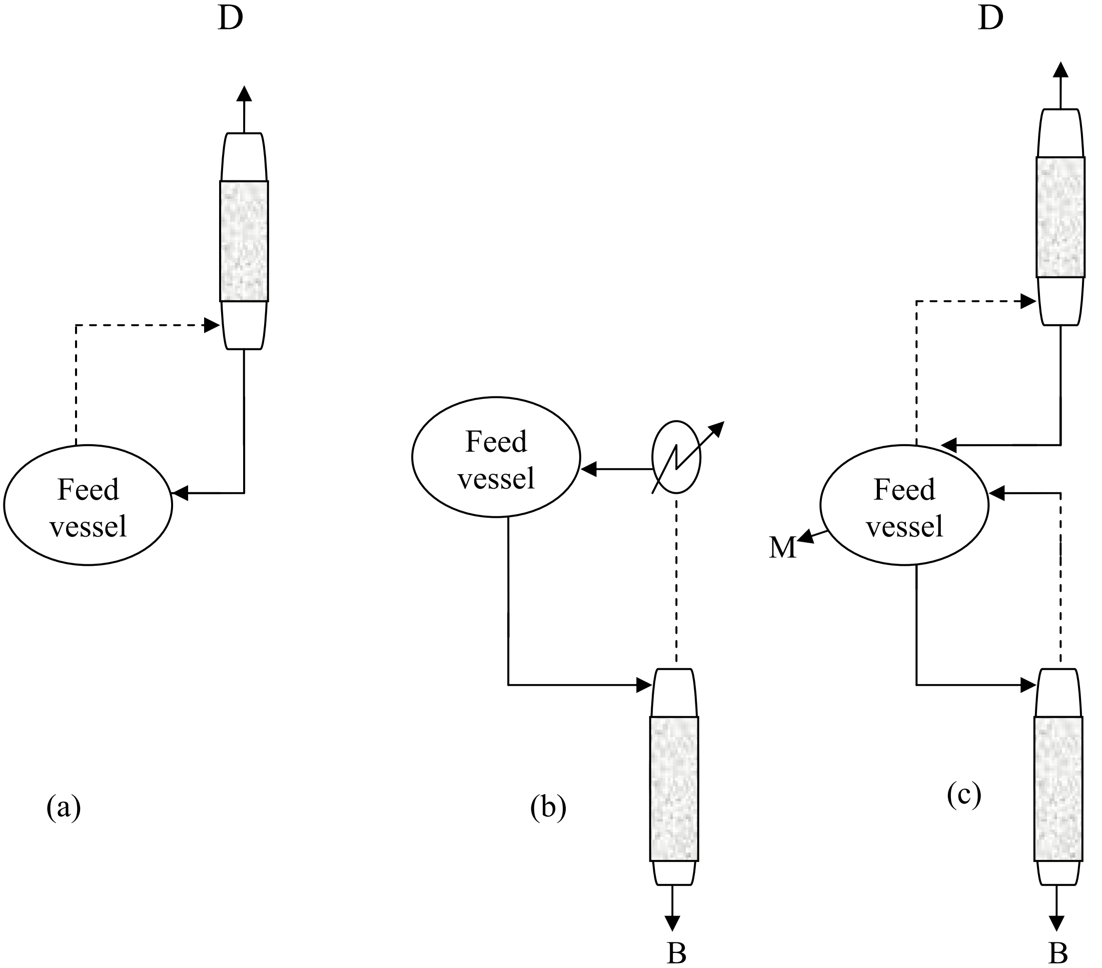


Fig 2-6 Types of batch columns(a)regular batch column , (b) inverted batch column , (c) middle vessel column.

An operation with a middle vessel column may have several advantages over an operation with a regular column like a lower temperature in the feed vessel during the process (this can be important for substances which tend to decomposite at high temperatures) , lower energy-and time demand for the process , a shorter duration of the start-up phase of process , a lower entrainer demand for the batchwise extractive distillation of azeotropic mixtures.

2.4 Batch Vs Continuous Distillation

Although batch distillation is generally less energy efficient than continuous distillation, it has received increased attention during the last few years along with the expansion in the pharmaceutical and fine and specialty chemical industries [12] This attention is due to the following reasons [26] :-

1. Batch distillation offers the possibility of separating multi-component mixtures into high purity products using a single column.
2. Batch distillation columns are flexible and robust to variation in feed composition and specification.
3. Batch distillation can be used for liquids with contaminants (such as solids and tars or resins).
4. Batch equipment can be cleaned or sterilized between the batch operation. .

The choice between continuous and batch distillation operations usually depends on the amount of feed to be processed, but sometimes other aspects are consider such as the complexity of the mixture (multi-component, low relative volatility or non-deal, feed composition). Usually, continuous distillation is chosen for large throughputs (above 5000 tons per year) and batch distillation is chosen for low throughputs (less than 5000 ton per year), batch production and multi-purpose plant [27]

Batch distillation is generally less expensive than continuous distillation in terms of costs per unit of product [26]. However, for multi-component mixtures with a large number of components it may be less expensive to use batch distillation since only one batch column is required to separate a number of products. Because the distillate composition varies in the case of batch distillation, while it remains constant in the case of continuous distillation. Therefore a single batch column can be used to separate a Nc component mixture whereas (Nc-1) continuous distillation columns would be required to separate Nc components mixture.

Batch distillation also preferred when there are special operational condition that make continuous operation difficult, for example, processes that require very long residence times, material that are difficult to pump and processes where the equipment needs frequent cleaning.

2.5 Thermodynamics of Vapor – Liquid Equilibria

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

$$\hat{f}_{iv} = \hat{f}_{il} \qquad i=1,.....,nc\,, \qquad ...(2.1)$$

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 Φ_i

$$\hat{\Phi}_i = \frac{\hat{f}_{i_v}}{y_i.p} \qquad ...(2.2)$$

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

$$\hat{f}_{i_v} = \hat{\Phi}_i.y_i.p \qquad ...(2.3)$$

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

$$\gamma_i = \frac{\hat{f}_{i_l}}{x_i.f_i} \qquad ...(2.4)$$

Also the liquid phase fugacity can be written in terms of the liquid phase activity coefficient γ_i ,liquid mole fraction x_i, and liquid phase properties f_i as follows[28].

$$\hat{f}_{i_l} = \gamma_i.x_i.f_i \qquad ...(2.5)$$

where

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

Integrate equation (2.6)

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

Substituting equation (2.7) in equation (2.5)

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

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

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

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

where Φ_i is given by equation ;

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

At low pressures(up to at least 1 bar), vapor phases usually approximate ideal gases for which $\Phi\hat{}_i = \Phi_{isat}$=1 and poynting factor [28] which represented by the exponential differs from unity by only a few parts per thousand . Therefore equation (2.10) become.

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

2.5.1 Ideal Vapor – Liquid Equilbrium

Vapor liquid equilibrium is one of the most important fundamental properties in simulation, optimization and design of any distillation process.

The mixture is called ideal if both liquid and vapor are ideal mixtures of ideal components, thus in the vapor phase the partial pressure of component P_{isat} is proportional to its mole fraction in the vapor phase according to Daltons law.

$$p_{i_{sat}} = y_i p \qquad ...(2.13)$$

The equilibrium relationship for any component is defined as.

$$k_i = \frac{y_i}{x_i} \qquad \text{... (2.14)}$$

For ideal mixtures the relationship between the liquid and vapor compositions is given by Raoult's law,where

$$y_i = \frac{p_i^0 x_i}{p} \qquad \text{... (2.15)}$$

For ideal mixture the *k* value can be predicted from Raoult's law, where

$$k_i = \frac{y_i}{x_i} = \frac{p_{i_{sat}}}{p} \qquad \text{... (2.16)}$$

Ideal solutions occur when molecular diameter is equal, no chemical interactions are present, intermolecular forces between like and unlike molecules are equal, and in which all the activity coefficients are unity (i.e. $\gamma_i=1$ for all *i)*[29]. The simplest model applies when both liquid and vapor phases are ideal solution and the vapor is an ideal gas. Ideal gas mixture is an ideal solution, and any equation applying to ideal solution can also be applied to ideal gas mixture. The 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 (2.17) in pure state as well as in mixture environment. However, the real gases do not obey the ideal gas law expect at very low pressures.

$$z = \frac{pv}{RT} = 1 \qquad \text{...(2.17)}$$

2.5.2 Fugacity Coefficient Models and Their Parameters

Deviations from the ideal gas law can be accounted for by the use of fugicity coefficients Φ_i

There are several methods could be used in order to determine the vapor fugacity coefficient in pure and vapor mixture. In this study two models will be given for evaluating the component fugacity coefficient in vapor phase.

2.5.2.1 Virial Equation

The general equation of fugacity coefficient of component in multicomponent vapor mixtures is

$$\ln \hat{\phi}_k^V = \frac{P}{RT}\left[B_{kk} + \frac{1}{2}\sum_i \sum_l y_i y_l (2\delta_{ik} - \delta_{il})\right] \quad \text{... (2.18)}$$

where the dummy indices i and l run over all species, and

$\delta_{ik} \equiv 2B_{ik} - B_{ii} - B_{kk}$, and $\delta_{il} \equiv 2B_{il} - B_{ii} - B_{ll}$

with $\delta_{ii} = 0$, $\delta_{kk} = 0$, and $\delta_{ik} = \delta_{ki}$, etc.

The cross-coefficients, B_{ik}, where determined using the mixing rule recommended by **Prausnitz 1980 [36]**.

$$B_{ij} = \frac{RT_{cij}}{P_{cij}}(B^0 + \omega B^1) \quad \text{... (2.19)}$$

$$B^0 = 0.083 - \frac{0.422}{T_{rij}^{1.6}} \quad \text{... (2.20)}$$

$$B^1 = 0.139 - \frac{0.172}{T_{rij}^{4.2}} \quad \text{... (2.21)}$$

where,

$$\omega_{ij} = \frac{\omega_i + \omega_j}{2} \quad \text{... (2.22)}$$

$$T_{cij} = \left(T_{ci} T_{cj}\right)^{1/2} \quad \text{... (2.23)}$$

$$P_{cij} = \frac{Z_{cij} R T_{cij}}{V_{cij}} \quad \text{... (2.24)}$$

$$T_{rij} = \frac{T}{T_{cij}} \quad \text{... (2.25)}$$

$$Z_{cij} = \frac{Z_{ci} + Z_{cj}}{2} \quad \text{...(2.26)}$$

and

$$V_{cij} = \left(\frac{V_{ci}^{1/3} + V_{cj}^{1/3}}{2}\right)^3 \quad \text{...(2.27)}$$

2.5.2.2 Redlich/Kwng Equation

$$\ln \hat{\phi}_i^V = \frac{b_i}{b}(Z-1) - \ln Z(1-h) + \frac{a}{bRT^{1.5}}\left(\frac{b_i}{b} - \frac{2\sum_k y_k a_{ki}}{a}\right)\ln(1+h) \quad \text{... (2.28)}$$

The mixing rules that have found greatest favor are:

$$a = \sum_i \sum_j y_i y_j a_{ij} \quad \text{... (2.29)}$$

with $a_{ij} = a_{ji}$,

$$b = \sum_i y_i b_i \quad \text{... (2.30)}$$

$$a_{ij} = \frac{0.42748 R^2 T_{cij}^{2.5}}{P_{cij}} \quad \text{... (2.31)}$$

and

$$b = \frac{0.08664 R T_{ci}}{P_{ci}} \quad \text{... (2.32)}$$

$$Z = \frac{1}{1-h} - \frac{a}{bRT^{1.5}}\left(\frac{h}{1+h}\right) \quad \text{... (2.33)}$$

$$Z-1=\frac{h}{1-h}-\frac{a}{bRT^{1.5}}\left(\frac{h}{1+h}\right) \qquad \text{... (2.34)}$$

$$h=\frac{bP}{ZRT} \qquad \text{... (2.35)}$$

The procedure requires initial solution of equations (2.34) and (2.35), usually by an iterative scheme.

2.5.3 Non Ideal Vapor – Liquid Equilbrium

The departures from Raoult's law with real mixtures are due to deviations in the liquid phase from the ideal mixture law; and deviations in the gas phase from the ideal mixture laws and from the ideal gas law .Deviations from the ideal mixture law can be accounted for by the use of activity coefficients γ_i

$$y_i=\frac{\gamma_i x_i p_{i_{sat}}}{p} \qquad \text{... (2.36)}$$

represented the deviation from the reality when $\gamma_i=1$, the mixture is said to be ideal which simplifies the equation to Raoult's law. For non-ideal mixture $\gamma_i \neq 1$, exhibits either positive deviation from Raoult's law ($\gamma_i > 1$), or negative deviation from Raoult's law ($\gamma_i < 1$). And deviations from the gas laws in the vapor phase by the fugacity coefficient Φ_i.

$$y_i=\frac{\gamma_i x_i p_{i_{sat}}}{\Phi_i \cdot p} \qquad \text{... (2.37)}$$

2.5.4 Calculation of activity coefficient.

The prediction of liquid phase activity coefficient is most important for design calculation of non-ideal distillation. Before calculating vapor-liquid equilibrium of non-ideal mixture, the activity coefficient of each component must be calculated.

Simple models for the liquid-phase activity coefficient base only on properties of pure species are not generally accurate . However, for hydrocarbon mixtures, regular solution theory is convenient and widely applied. The theory is based on the premise that non-ideality is due to differences in van der waals forces of attraction among the different molecule present

Two major methods frequently employed to calculate the activity coefficient of component *i* in a multi-component mixture.

These methods can be divided into those which required binary pair interactions, and those which split the component molecules into fundamental groups.

The most common of the binary interaction methods are Wilson ,NRTL and UNIQUAC and the most common of the major group contribution method is UNIFAC and ASOG [30].

The disadvantage of the binary interaction methods the that binary pair interactions are required, making the parameters for a mixture of more than three or four components difficult to obtain. This problem is removed by the group contribution approach because the molecules are broken into groups, and these groups are assigned the interaction parameters, the advantage is that a large number of components can be represented by relatively few groups.

All these models, the model parameters are determined by fitting the experimental data of binary mixtures.

The selection of appropriate model for a given mixture based on three characteristics, which are temperature, pressure and composition. If inappropriate model is selected, the design and simulation of the process will not work well.

The separation of multi-component mixtures by distillation can be difficult when the system VLE is non-ideal and azeotropes are present. Then there are severe problems in even estimating the products that can be obtained from a distillation column. It is found that the simulated separation at total reflux is dependent on the predictive thermodynamic package . Extensive results using Wilson, NRTL, UNIQUC and UNIFAC show the wide range of separations that can be obtained. These differences become more severe when the liquid- phase behaviour highly non-idealty .

2.5.4.1Wilson Model

Wilson (1964) [1] predicted the following equation to calculate the liquid phase activity coefficient .

$$\ln \gamma_i = 1 - \ln \sum_{j=1}^{C} x_j \Lambda_{ij} - \sum_{k=1}^{C} \left[\frac{x_k \Lambda_{ki}}{\sum_{j=1}^{C} x_j \Lambda_{kj}} \right] \qquad \text{... (2.38)}$$

where,

$$\Lambda_{ij} = \frac{v_j^L}{v_i^L} \exp\left(- \frac{\lambda_{ij} - \lambda_{ii}}{RT} \right) = \frac{v_j^L}{v_i^L} \exp\left(- \frac{A_{ij}}{RT} \right) \qquad \text{... (2.39)}$$

where

$\lambda_{ii}=\lambda_{jj}=1$

$A_{ii}=A_{jj}=0$

$\Lambda_{ii}=\Lambda_{jj}=1$

The molar volume v calculation is based on the component molecular weight and the liquid density at 25°C (no temperature dependence is assumed).

The Wilson model has advantage it is new flexible model, suitable for a large variety of non-ideal mixtures and completely miscible solutions and that can be extended to multi-component systems without involving any additional parameters except systems of limited solubility. However, Wilson's equation is not applicable to partially miscible system. To remove this serious disadvantage, a third binary constant has been introduced, which permits the Wilson equation to correlate partially miscible system. Unless the third binary constants are the same for all the constituent binary pairs, however, the three-parameter Wilson equation cannot be generalized for multi-component systems. In addition, the derivation of both the Wilson and the three-parameter Wilson equations has remained obscure and Wilson model has the disadvantage that cannot be described liquid-liquid equilibrium restricts its use [31].

2.5.4.2 NRTL Model

The nonrandom, two-liquid (NRTL) equation developed by Renon and **Prausnitz (1968 and 1969)[32,33]** represented an accepted extension of Wilson's concept. The NRTL equation is applicable to multi-component vapor-liquid, liquid-liquid, and vapor-liquid-liquid systems. The NRTL contains three parameters per binary interaction, compared with the two parameter of the Wilson model but is based on a similar local composition treatment. The NRTL expression for the activity coefficient is

$$\ln\gamma_i = \frac{\sum_{j=1}^{C}\tau_{ji}x_jG_{ji}}{\sum_{k=1}^{C}x_kG_{ki}} + \sum_{j=1}^{C}\frac{x_jG_{ij}}{\sum_{k=1}^{C}x_kG_{kj}}\left(\tau_{ij} - \frac{\sum_{m=1}^{C}\tau_{mj}x_mG_{mj}}{\sum_{k=1}^{C}x_kG_{ki}}\right) \qquad \text{... (2.40)}$$

where $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$ ... *(2.41)*

$$\tau_{ji} = \frac{g_{ji} - gii}{RT} = \frac{A_{ji}}{RT} \qquad \text{... (2.43)}$$

where

$G_{ji} \neq G_{ij}$

$\tau_{ij} \neq \tau_{ji}$

$G_{ii} = G_{jj} = 1$

$\tau_{jj} = \tau_{ii} = 0$

2.5.4.3UNIQUAC Model

The UNIQUAC [34,35,36] (short for universal quasi chemical) Were developed by **Abrams and Prausnitz (1974 and 1975)**. 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

$$\ln\gamma_i = \ln\gamma_i^{Co} + \ln\gamma_i^{Rs} \qquad \text{... (2.44)}$$

where,

$$\ln\gamma_i^{Co} = \ln\frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln\frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i}\sum_{j=1}^{C} x_j l_j \qquad \text{... (2.45)}$$

$$\ln\gamma_i^{Rs} = -q_i \ln\left(\sum_{j=1}^{C}\theta_i\tau_{ji}\right) + q_i - q_i\sum_{j=1}^{C}\frac{\theta_j\tau_{ij}}{\sum_{k=1}^{C}\theta_k\tau_{kj}} \qquad \text{... (2.46)}$$

where,

$$\tau_{ij} = \exp\left(-\frac{u_{ij}-u_{jj}}{RT}\right) = \exp\left(-\frac{A_{ij}}{RT}\right) \qquad \text{... (2.47)}$$

$$\phi_i = \frac{r_i x_i}{\sum_{j=1}^{C} r_j x_j} \qquad \text{... (2.48)}$$

$$\theta_i = \frac{q_i x_i}{\sum_{j=1}^{C} q_j x_j} \qquad \text{... (2.49)}$$

$$ri = \sum_k v_k^i R_k \qquad \text{... (2.50)}$$

$$qi = \sum_k v_k^i Q_k \qquad \text{... (2.51)}$$

$$l_j = \left(\frac{z}{2}\right)(r_i - q_j) - (r_j - 1) \qquad \text{... (2.52)}$$

The UNIQUAC model is one of he most successful two parameter 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 .

2.5.4.4 UNIFAC Model

Fredensland et al (1976) [37] described UNIFAC (UNIQUAC functional group model). In UNIFAC model each molecule is taken as a composite of subgroups; for example t-butanol is composed of 3 "CH3" groups, 1 "C" group and 1 "OH" group and Ethan, which contain 2 "CH3" groups. The interaction parameters between different molecules are defined in literature.This model, also called group contribution method, is based theoretically on UNIQUAC equation (2.26). The activity coefficient consists of two parts, combinational and residual contribution.

$$\ln \gamma_i = \ln \gamma_i^{Co} + \ln \gamma_i^{Rs} \qquad \text{... (2.53)}$$

Combinational contribution γ_i^{Co} taking into account effects arising from difference in molecular size and shape while residual contribution γ_i^{Rs} taking into account energetic interactions between the functional group in the mixture, the combinational parts is given in equation .

$$\ln \gamma_i^{Rs} = \sum_k v_k^i (\ln \Gamma_k - \ln \Gamma_k^i) \qquad \text{... (2.54)}$$

UNIFAC activity coefficient model has several advantages over the other models because :

1. It has an explicit temperature dependence.
2. It has a large library of functional groups from which thousand of chemicals can be built.
3. It can be update and expanded, as more experimental data become available .

Therefore UNIFAC model can be used when the binary interaction parameters are not available for Wilson, NRTL or UNIQUAC models.

2.6 Enthalpy for Multi-component

The enthalpy of the component in liquid-phase was estimated through basing on the heat of formation at reference temperature and adding the sensible heat to a desired temperature as the following:

$$h_L = \Delta H_{f(L)}^{298.15} + \int_{298.15}^{T} Cp_L dt \qquad \text{... (2.55)}$$

The values of the heat of formation can be found in appendix A table A.1

In order to evaluate the liquid phase heat capacity we used this equation [13]:

$$Cp_i^L = A_{i,Cp} + B_{i,Cp}T + C_{i,Cp}T^2 \qquad \text{... (2.56)}$$

Where the constants a $A_{i,cp}$, $B_{i,cp}$ and $C_{i,cp}$ can be found in appendix A table A.2

And for mixture, heat capacity evaluated as [17]

$$Cp_{mix} = \sum_{i=1}^{C} x_i Cp_i \qquad \text{... (2.57)}$$

The total enthalpy of liquid phase is given by :

$$h_{L_{i,j}} = \sum_{i=1}^{C} x_{i,j} h_L + H_{mix} \qquad \text{... (2.58)}$$

Each model have different heat of mixing or excess energy

For wilson model heat of mixing is:

$$H_{mix} = H^{E} = \sum_{i=1}^{C}[x_i[\frac{\sum_{i,j\neq 1}^{C} x_j(\frac{\partial \Lambda_{ij}}{\partial T})RT^2}{x_i + \sum_{i,j\neq 1}^{C} x_i\Lambda_{ij}}]]$$

... *(2.59a)*

$$(\frac{\partial \Lambda_{ij}}{\partial T})RT^2 = (\lambda_{ij} - \lambda_{ii})\Lambda_{ij}$$

For NRTL model heat of mixing is:

$$H_{mix} = H^{E} = x_1x_2R[\frac{x_1\tau_{21}G_{21}^{'}}{(x_1 + x_2G_{21})^2} + \frac{x_2\tau_{12}G_{12}^{'}}{(x_2 + x_1G_{12})^2}$$

... *(2.59b)*

$$G_{ij}^{'} = \frac{\partial G_{ij}}{\partial(1/T)}$$

And for UNIQUAC and UNIFAC model heat of mixing is:

$$H_{mix} = H^{E} = RT\sum_{i=1}^{C}(x_i \ln \gamma_i) \qquad \text{... (2.59c)}$$

where H_{mix} is the heat of mixing when 1 mol of solution is formed, at temperature t.

Heat of mixing and heat of solution are determined experimentally and are available in the handbooks for the more commonly used solution . For organic solutions the heat of mixing is usually small compared with the other heat quantities, and can usually be neglected when carrying out a heat balance to determine the process heating or cooling requirments, and for the gases , the heats of mixing are usually negligible . [17].

The enthalpy of the component in vapor-phase was estimated through basing on the enthalpy in liquid-phase at its bubble point and the heat of vaporization at bubble point and the sensible heat from bubble point of the mixture in vapor-phase to a desired temperature as the following:

$$h_v = \int_0^{Tb} Cp_L dt + \lambda_i + \int_{Tb}^{T} Cp_v dt \qquad \text{... (2.60)}$$

In order to evaluate the vapor phase heat capacity we used this equation

$$Cp_i^V = A_{i,Cp} + B_{i,Cp}T + C_{i,Cp}T^2 + D_{i,Cp}T^3 \qquad \text{...(2.61)}$$

where the constants $A_{i,cp}$, $B_{i,cp}$,$C_{i,cp}$ and $D_{i,cp}$ can be found in appendix A table A.3

For gases, the heats of mixing are usually negligible and the heat capacities and enthalpy can be taken without introducing any significant error into design calculation [17]: .

2.6.1 Heat of Vaporization (Latent Heat)

If a phase transition take place between the specified and dutm temperatures, the latent heat of the phase transition is added to the sensible-heat . **Haggenmacher (1946)** equation was used to estimate the latent heat, which was derived from the Antoine vapor pressure equation:

$$\lambda_i = \frac{8.32 B_{i,VP} T^2 \Delta z}{(T + C_{i,VP})} \qquad \text{... (2.62)}$$

$$\Delta z = \left[1 - \frac{P_{ri}}{T_{ri}^3}\right]^{1/2} \qquad \text{... (2.63)}$$

where $B_{i,vp}$ and $C_{i,vp}$ is the coefficient in the Antoine equation , and P_{ri} is the reduced pressure and T_{ri} is the reduced temperature.

At bubble point can be obtained latent heat from Trouton's rule, one of the oldest prediction method.

$$\frac{\lambda_i}{Tb} = \text{constant} \qquad ...(2.64)$$

For organic liquid the constant can be taken as 100.

2.7 Mathematical Model of Multi-Component Batch Distillation

Since batch distillation is an important unit operation in the batch processing industry and is most widely used , a fast and accurate model for this unit operation would be very useful**.**

Many methods for multi-component distillation calculation have been published to date. These methods can be broadly classified as short-cut and tray-by-tray methods . Both methods possess merites and demerits regarding simplicity, accuracy, possibility or otherwise of design calculations, required computer capacity and running time .

2.7.1 Short-Cut Model

The short-cut model for batch distillation is based on the assumption that the batch distillation column can be considered as a continuous distillation column with changing feed at any time instant .In other words , the bottom product of one time step forms the feed for the next time step . This is equivalent to having bottom plate as the feed plate and the feed at its boiling point .

The short-cut method was shown in figure 2.7. Since continuous distillation theory is well-developed and tested , the short-cut method [Fenske-Underwood-Gillilande (FUG) method] for continuous distillation can be modified for batch distillation. The batch time is implicit and can be calculated if the vaporization rate V of the still is known . Because of the algebraic-equation-oriented short-cut method , it is possible to adapt the model for optimal control calculations very easily .

At each time instant, there is a change in the still composition of the key component, resulting in changes in the still composition of all other components calculated by the differential material balance equations (DMB). Hengestebeck-Geddes'equation relates the distillate composition to the new still composition in terms of the constant $C1$. The constant $C1$ in Hengestebeck-Geddes'equation is equivalent to the minimum number of plates, Nmin in Fenske's equation.

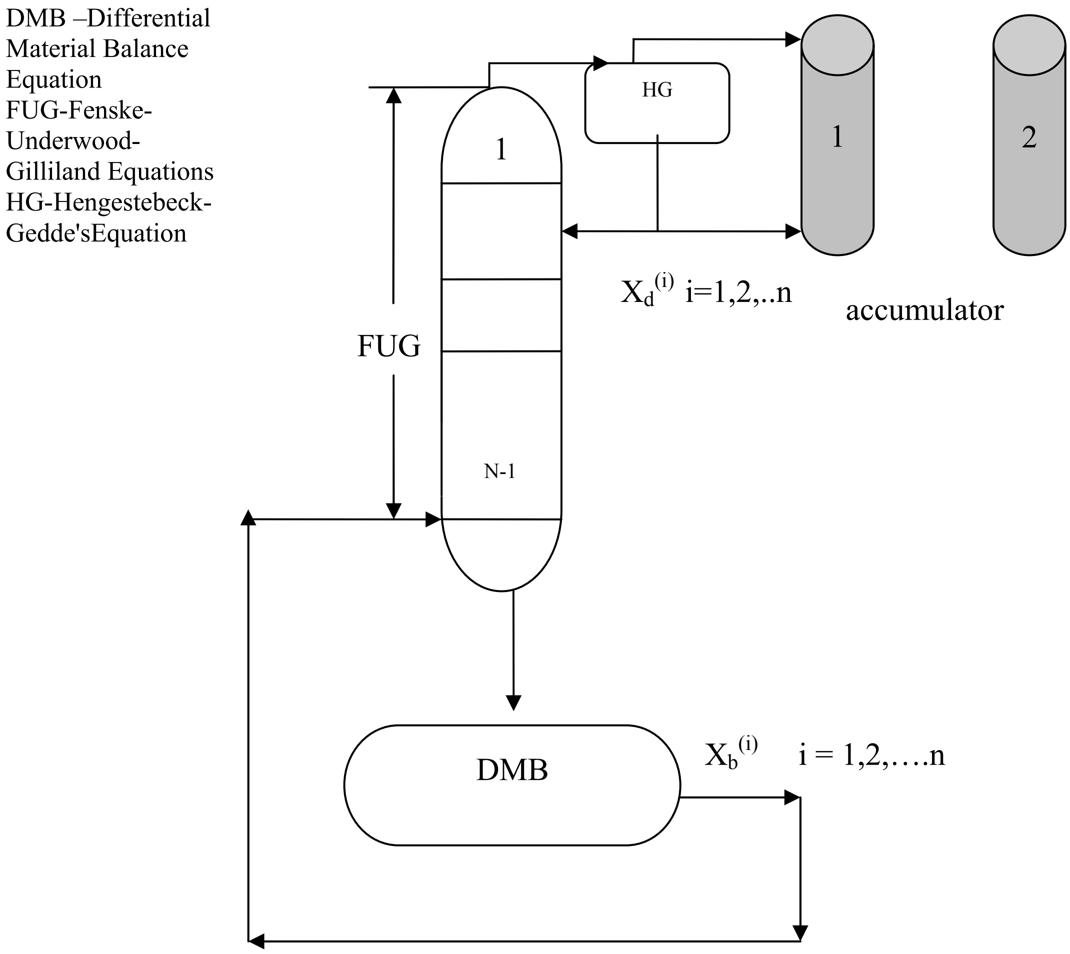


Fig 2.7 Short-cut method

The empirical short-cut models for binary systems preceded the graphical models. The short –cut models for batch distillation have been very widely used in the literature .Short-cut techniques develop a direct relationship between the composition in the still drum and the distillate , thus avoiding the modeling of individual trays . This leads to a significant reduction in model size This further means that the computational effort is reduced , which was of crucial importance before today's powerful computer hardware became available .

Diwekar and and Madhaven (1991) [38] developed short-cut method for handling multi-component mixtures under the assumption of constant
molar over flow , and negligible vapor and liquid holdup for the two cases of constant distillate composition and constant reflux, and by Sundaram and **Evans (1993) [39]** for constant reflux .

Both methods avoid tedious stage-by-stage calculation of vapor and liquid composition employing the Fenske-Underwood-Gilliland short cut procedure for continuous distillation .

They treat batch rectification as a sequence of continuous ,steady-state rectification .As in the FUG method ,no estimations of composition or temperatures are made for intermediate stages.

2.7.2 Rigorous Model

The rigorous modeling of batch distillation operation involves solutions for a large number of stiff differential equation . The computational intensity and memory requirement of the problem increase with an increase in the number of the plates and components . For an *n*-component system and a column with *N* number of plates , the simulation of constant reflux or variable reflux operation requires simultaneous solution of *n* x *N* material balance differential equations, *N* energy balance differential or difference equations and the vapor - liquid equilibrium calculation associated with each differential material balance equation . The vapor - liquid equilibrium calculations are iterative in nature and become more complicated for azeotropic systems [38].

A rigorous approach to batch distillation involves the solution of the material balance equations in the differential form **Huckaba and Danly (1960) [40]** proposed the for binary system.

The schematic of the process of abstraction for the batch distillation column model was shown in figure 2.8

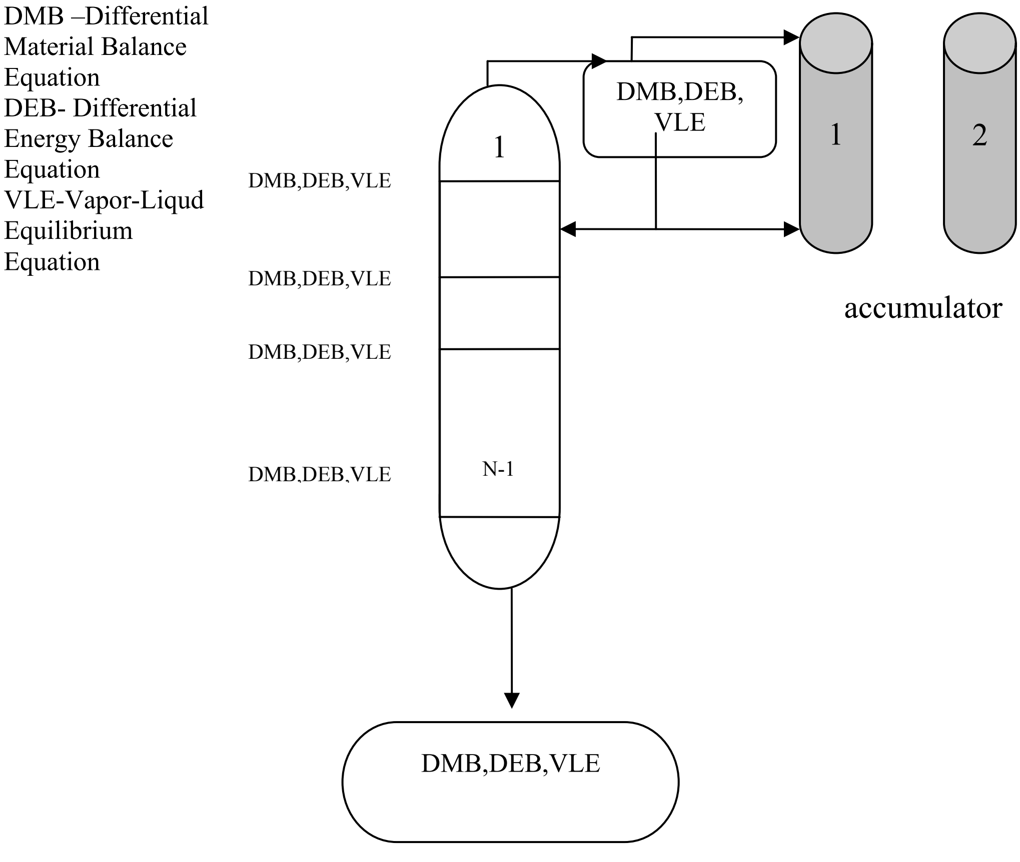


Fig 2.8 Rigorous method

Meadows (1963) [41] developed the first rigorous multi-component batch distillation model , based on the assumption of equilibrium stages , perfect mixing of liquid and vapor phase at each stage , negligible vapor holdup , constant molar liquid holdup on a stage and n the condenser system , and adiabatic stages in the column.

Distefano (1968) [42] analyzed the applicability of different numerical integration techniques for solving the rigorous dynamic model for multi-component batch distillation in detail and reported the cause of numerical instabilities . Distefano model is the most cited Rigorous model for batch rectification operation was shown in figure 2.9.

The equipment consist of a partial still , a column with N equilibrium stages or equivalent in packing , and a total condenser with a reflux drum .

To initial operation , the feed is charged to the still , to which heat is supplied . Vapor leaving stage 1 at the top of the column is totally condensed and passed to the reflux drum . At first ,at total reflux condition is established for a steady – state fixed overhead vapor flow rate .

Depending upon the amount of liquid holdup in the column and in the condenser system , the amount and composition of the liquid in the still at total reflux differs to some extent from the original feed [42].

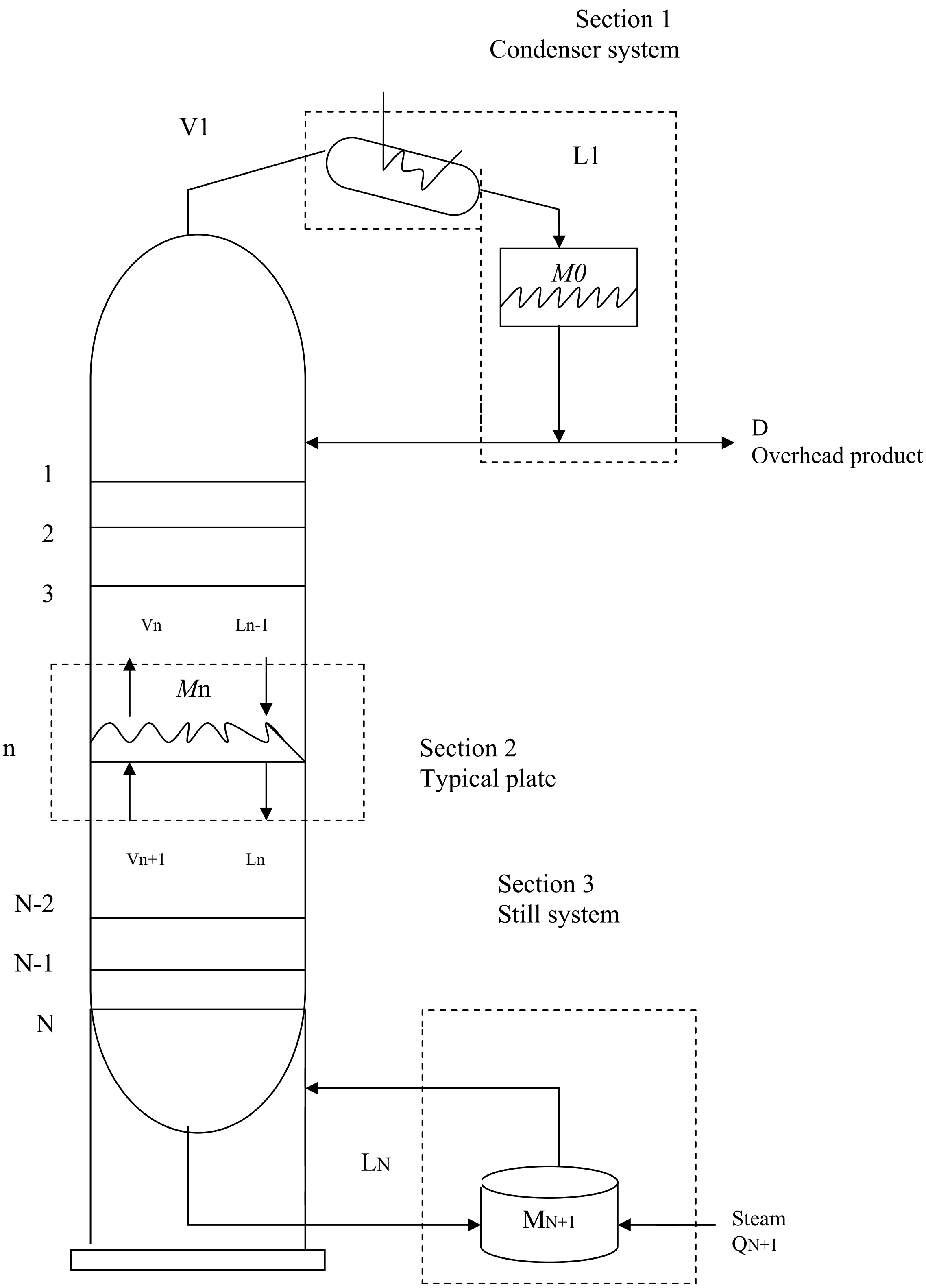


Fig 2.9 Rigorous model for batch rectification operation

The most of the studies and simulation models, which have appeared since 1968 are based on this model[38].

Boston et al. (1981) [43] described a traditional programs for computer simulation of batch distillation processes use rigorous calculation algorithm for the time integration of the differential equation, used Runge-Kutta method and based on the Distefano's model.

Domenech and Enjalbert (1981) [44] use the classical method of rigorous calculation and the traditional 4th-order Runge-Kutta-Merson method , with variable step size for the time integration . Ideal solution is assumed. **Galindez and Fredenslund (1988) [45]** developed a quasi steady-state solution procedure for more rapid calculation.

The mathematical model is based on UNIDIST, a computer program for simulation of continuous distillation column developed by **Christiansen et al (1979) [46]** . The thermodynamic models used are UNIFAC,UNIQUAC, the soave-Redlich-Kwong equation of state and ideal solution .

A detailed account of the program is given by **Fredenslund et al in (1977) [47]** .

The UNIDIST model assumption are :

- Constant total molar flowrates in each section.
- Enthalpy balance are neglected.
- Hydrodunamic effects of vapor and liquid flows are neglected.

Thus the dynamics of the initial startup of the column cannot be simulated.

Marta and Juan Carlos (2000) [48] described a case study to fit a rigorous model using the commercial package HYSYS, for multi-component batch distillation processes.

Ping Zhang (2002) [49] formulated a rigorous model for the dynamic simulation of a multiphase batch distillation in the software gPROMS.

Jimenez, L. et. Al (2002) [50] used rigorous models as an alternative to predict the concentration profile and to specify the optimal switching time from products to stop cuts for nonlinear dynamic modeling of multi-component batch distillation . **Nad and Spiegel (1987) [51]** described a nonlinear model for the system [n-heptane+cyclohexane+toluene] and developed it with commercial software specifically suitable for modeling batch distillation operation. BATCHFRAC (Aspen Technology Inc, Cambridge, MA, USA) and HYSYS.Plant (AEA Technology, Calgary, Canada) , use rigorous calculations, with several methods available to integrate the differential equations while CHEMCAD BATCH (Chemstation Inc., Houston, TX, USA) uses a pseudostationary model performances were tested to evaluate whether their potentialities in other applications such as inferential control structure and/or soft sensor could be attractive.

Chapter Three
Theoretical Aspects of Batch Distillation

3.1 Introduction

The mathematical model of any process is a system of equations whose solution gives a specified data representative of the response of the process to a corresponding set of inputs [52].

Computer simulation is used extensively to analyze the dynamics of chemical processes or design controllers and study their effectiveness in controlling the process. The simulation operations make it possible to evaluate the influence of the variables on any process theoretically. The simulation is also used to fix the experimental conditions needed for design, optimization and control.

In this chapter a dynamic model has been studied the behavior of multi-component batch distillation columns. The set of nonlinear ordinary differential equations governing the unsteady state composition profile in the model were integrated by using eigenvalue method .The powerful MATLAB program was used to give the composition profile, temperature profile, vapor and liquid flow rate profiles .

3.2 Simulation Model of Multi-Component Batch Distillation

3.2.1 Method of Analysis

The analysis emphasized to develop computer programs to simulate multistage multi-component unsteady state batch multi-component distillation of N feed components in the non-ideal cases into a relatively pure products .

The simulations presented in this section, the initial compositions along the column and in the still are equal to that of the original feed mixture.The (benzene,toluene and ethylebenzene) and (hexane,heptane and octane) systems were used in simulation of batch distillation . The model gave a system of ordinary differential equations (ODE'S) and algebraic equations, the algebraic equation includes physical properties and vapor liquid equilibrium equations, where the differential equations include total material, heat and component balance equations.

The design model based on the multi-component batch rectification operation figure 3.1. It consists of a still and a fractionating column on top. The vapors coming from the topmost plate of the column are condensed in the total condenser, and the distillate is collected in the receiver.

3.2.1.1 Model Assumptions

Consider the batch distillation column shown in figure 3.1. The mathematical model is formulated using the following assumptions:

1. The liquid on a plate has a constant molar holdup (constant volume holdup and molar density).
2. The vapor hold up is negligible(smaller molar density of the vapor phase).
3. The distillation is performed adiabatically.
4. Perfect mixing on all trays and in all vessels (condenser and still).
5. Total condensation.
6. Ideal vapor phase(Φ_i=1) and non-ideal liquid phase ($\gamma_i \neq 1$) for all components in mixture.
7. There is non azeotropes in the system.
8. The separation system has sufficient stages and reflux to achieve the desired distillate composition.

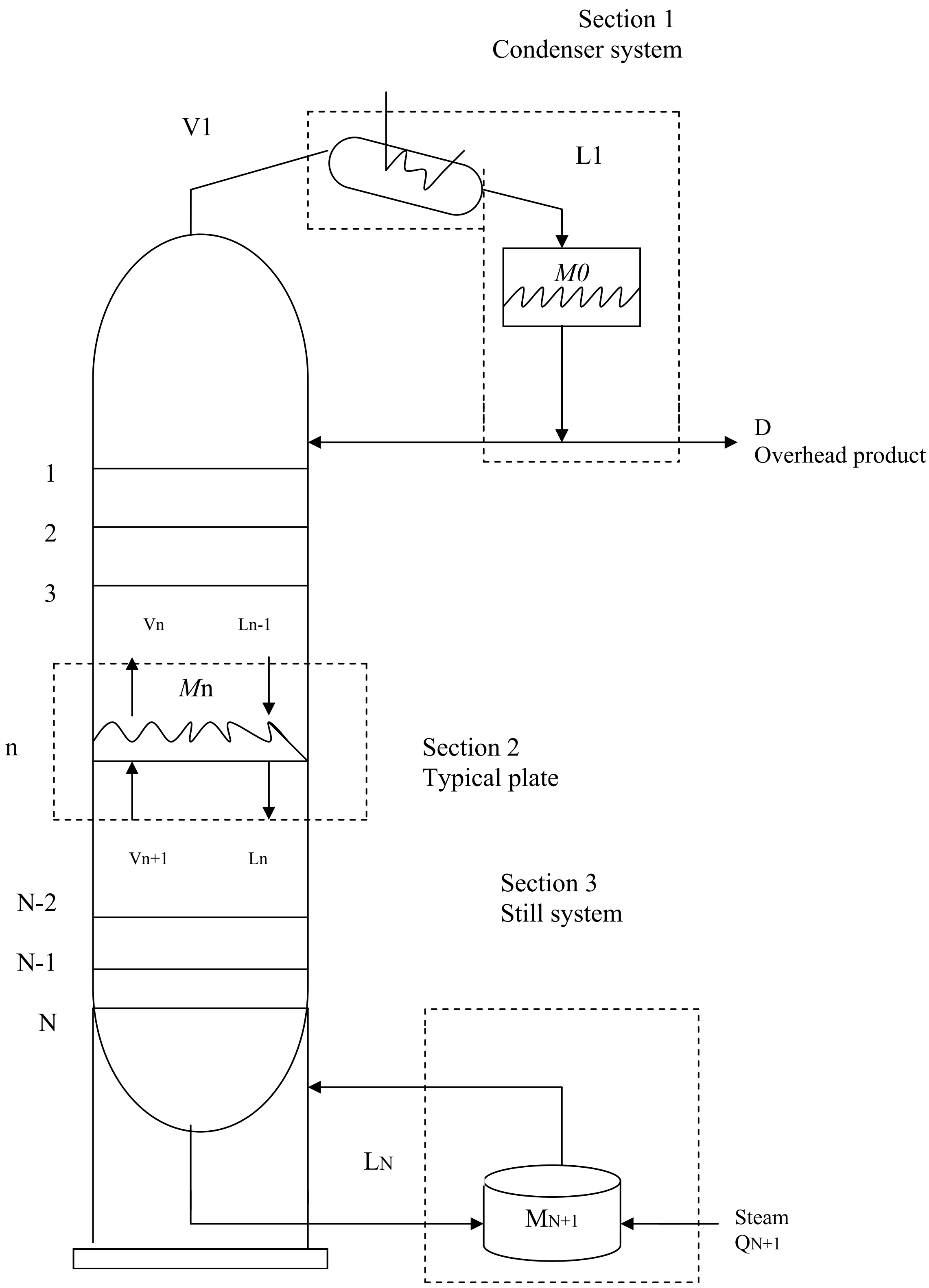


Fig 3.1 General Batch distillation column

The design calculations were considered for varying initial composition for constant reflux ratio, and varying reflux ratio for constant initial composition

The material and energy balances were carried out for each case using rigorous method plate to plate calculation at unsteady state condition .

3.2.2 Specification of Variables

The variables considered for the process system are:

1. Reflux ratio.
2. Batch time.
3. Liquid holdup.
4. Initial composition.

A Ternary feed system has been chosen, and the initial feed composition is given in table 3.1 and 3.2 . The physical and chemical properties are available in the literature and are given in appendix A table A-1.

Table 3.1: Initial feed composition for system benzene-toluene-ethylebenzene

Component	Composition
Benzene	0.3
Toluene	0.4
Ethylebenzene	0.3

Table 3.2: Initial feed composition for system hexane-heptane-Octane

Component	Composition
Hexane	0.3
Heptane	0.3
Octane	0.4

Two simulation computer programs were developed using two different methods of design calculations. Short-cut method distillation and rigorous method to give the exact solution. The validity of these two simulation programs were cheeked with the previous design model [1,2] and with the experimental work [3].

3.2.3 Vapor-Liquid Equilibria

Vapor-Liquid Equilibrium distribution ratios (i.e. equilibrium constants) are used to predict the composition and coexisting phases of systems. For non-ideal mixture additional variable γ_i (activity coefficient) appears to represent the degree of deviation from ideality in liquid phase and Φ_i (fugacity coefficient) to represent the degree of deviation in vapor phase. Where Virial equation has been used to estimate the value of the fugacity coefficient for the system (Benzene-Toluene-ethylebenzene) respectively. The vapor phase is nearly ideal $\Phi_i \approx 1$ therefore .

$$y_i = k_i x_i = \frac{\gamma_i p_{isat}}{p} x_i \qquad \text{... (3.1)}$$

When $\gamma_i=1$, the mixture is said to be ideal which simplifies the equation to Raoult's law. For non-ideal mixture $\gamma_i \neq 1$, exhibits either positive deviation from Raoult's law ($\gamma_i > 1$), or negative deviation from Raoult's law ($\gamma_i < 1$) . Where the UNIFAC equation has been used to calculate the activity coefficient for the system (Benzene-Toluene-ethylebenzene) respectively. $\gamma_i > 1$, positive deviation for the system studied in this work. The prediction of liquid phase activity coefficient is most important for design calculation of non-ideal distillation.

In this work Wilson ,NRTL and UNIQUAC and UNIFAC equations have been used. The parameters of these models are given in appendix A, table A.4,A.5,A.6 and A.7 .

3.2.4 Antoine Model

The vapor pressure of each component in this study was calculated by using Antoine equation .

$$\ln P_{i_{sat}} = A_{i,vp} - \frac{B_{i,vp}}{T + C_{i,vp}} \qquad \ldots (3.2)$$

Where the temperature T is in Kelvin and the pressure in mm Hg. The parameters in Antoine equation for all components are given in appendix A, table A.8

3.2.5 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 T_{i_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 T_N and must be solved iteratively. The bubble point temperature has been evaluated by trial and error calculation. According to this method correct temperature was calculated. For each assumption, the value of sum is computed from

$$sum = \sum_{i=1}^{C} (K_{i,N} x_{i,N}) - 1 = 0 \qquad 1 \le N \ge Nt \qquad \ldots (3.3)$$

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

3.2.6 Effect of Liquid Holdup

A batch rectifier is usually operated under total reflux conditions for an initial period of time prior to the withdrawal of distillate product. During this initial time period, liquid holdup in the column increases and approaches a value that is reasonably constant for the remainder of the distillation cycle. Because of the total-reflux concentration profile, the initial concentration of light components in the remaining charge to the still is less than in the original charge. At high liquid holdups, this causes the initial purity and degree of difficulty of separation to be reduced from estimates based on methods that ignore liquid holdup. Liquid holdup can reduce the size of product cuts, increase the size of intermediate fractions that are recycled, increase the amount of residue, increase the batch cycle time, and increase the total energy input. Although approximate methods for predicting the effect of liquid holdup were developed, the complexity of the holdup effect is such that it is now considered best to use the rigorous computer-base batch-distillation algorithms described later to study the effect on a case-by-case basis . In general, the effect of holdup in a trayed column is greater than in a packed column because of the lower amount of holdup in the latter.

The model based on constant volume holdup on trays and condenser , thereforethe molar holdup on all trays and in the still was calculated in the present work by using the equations [1].

$$M_{condenser} = \frac{Gc}{\sum_{i=1}^{C} \frac{x_i . Mw_i}{\rho_i}} \qquad \text{... (3.4)}$$

$$M_{plate} = \frac{G_N}{\sum_{i=1}^{C} \frac{x_i . Mw_i}{\rho_i}} \qquad \textit{from } N = 1\text{- } Nt \qquad \text{...(3.5)}$$

$$M_{reboiler} = Mr^{0} - \sum_{j=0}^{Nt} Mj - \int_{0}^{t} Ddt \qquad \text{... (3.6)}$$

Effect of Time

One of the most important variables that have the major effect in batch distillation column is the time .

In batch distillation process there is usually no feed flow rate, but there is a liquid charge in the still pot (still) which will change its amount and composition with time.

In batch distillation process, the composition, the temperature profiles, vapor and liquid flowrate along the column and the heat input to the still and heat output from the condenser change with time. During each step of batch distillation process, the concentration of the liquid on each stage is change from $x_i(t_0)$ to $x_i(t_1)$; and the temperature of each component is changed from $T_{i,N}(t_0)$ to $T_{i,N}(t_1)$.

3.3 Design Methods for Batch Distillation

Minimum number of stage, minimum reflux ratio, actual reflux ratio and theoretical number of stages have been estimated using short-cut method which gives the initial values that can be used in rigorous method. The composition, temperature, flow of liquid and vapor profiles rates , liquid holdup and enthalpy of vapor and liquid have been estimated using rigorous method stage by stage calculation.

3.3.1 Short-cut Method for Batch Distillation

One of the major purpose of this work is to calculate the number of stages required to distill a mixture contains a certain number of the components by using short-cut method.

Equation (3.7) is used to calculate minimum number of stage required.

$$N_{\min} = \frac{\log\left[\left(\frac{Xd_{LK}}{Xw_{LK}}\right)\left(\frac{Xw_{HK}}{xd_{HK}}\right)\right]}{\log \alpha_{i,r_{LK}}} \qquad \text{... (3.7)}$$

$$Xdi = Xwi \,.\left(\frac{Xd_{HK}}{Xw_{HK}}\right).\alpha_{i,r}^{N_{\min}} \qquad \text{... (3.8)}$$

$$Xd_{HK} = \frac{Xw_{HK}}{\sum_{i=1}^{C} Xwi \,.\alpha_{i,r}^{N_{\min}}} \qquad \text{... (3.9)}$$

Substitute equations (3.9)and (3.8) into (3.7)

$$N_{\min} = \frac{\log\left\lfloor .\alpha_{i,r}^{N_{\min}}{}_{LK}\right\rfloor}{\log \alpha_{i,r_{LK}}} \qquad \text{... (3.10)}$$

By using Newton's Raphson method equation (3.10) has been solved. Equations (3.11)and (3.12) have been used to calculate the minimum reflux ratio and the actual reflux ratio, and equations (3.10), (3.11) and (3.12) are used in equation (3.13) for calculating the theoretical l number of stages.

$$R_{\min} = \frac{\left(\frac{Xd_{LK}}{Xw_{LK}}\right) - \alpha_{LK,HK}\left(\frac{Xd_{Hk}}{Xw_{Hk}}\right)}{\alpha_{LK,HK} - 1} \quad \text{... (3.11)}$$

$$R_{act} = R_{\min} * 1.25 \quad \text{... (3.12)}$$

$$\frac{N_{act} - N_{\min}}{N_{act} + 1} = 0.75\left[1 - \left(\frac{R_{act} - R_{\min}}{R_{act} + 1}\right)^{0.5668}\right] \quad \text{... (3.13)}$$

Trial and error calculations have been used to solve equation (3.13) by suggesting N_{act} in each time and where the equation (3.13) equal to zero then we have the theoretical number of stage.

A computer program return in MATLAB were developed and the result were compared with the result of previous model [1].

3.3.2 Rigorous Method for Batch Distillation

Theoretical model for an equilibrium stage consider a general, batch unsteady-state distillation column consisting of a number of stages arranged in a counter current cascade figure 3.1.

A general schematic representation of equilibrium stage j is shown in figure 3.2, where the stage is numbered from top to bottom. Entering stage j as shown in figure 3.2, with overall composition in mole fractions x_{in} of component i ,temperature T_{iN}, liquid holdup Mn_{in}, and pressure P_{in}. During each step of batch process, the conversion of the liquid on each stage effected by time interval Δt so that change from $X_i(t_0)$ to $X_i(t_1)$; also the effect of time interval on the temperature $T_{i,N}(t_0)$ to $T_{i,N}(t_1)$, and the effect of time interval on liquid holdup $Mn_{iN}(t_0)$ to $Mn_{iN}(t_1)$. At stage j where the liquid flow rate $L_{i,N-1}$ entering stage N from stage N-1 above, with composition in all mole fractions $X_{i,N-1}$, temperature $T_{i,N-1}$, and pressure $P_{i,N-1}$, similarly from stage N+1 below, so the vapor flow rate $V_{i,N+1}$ entering stage N, with composition $y_{i,N+1}$,temperature $T_{i,N+1}$, and pressure $p_{i,N+1}$.

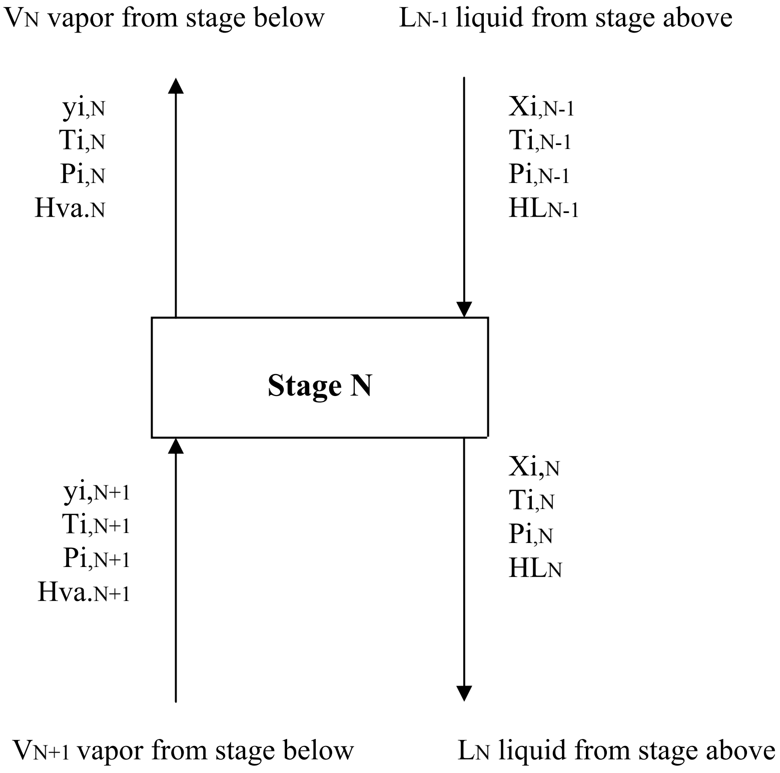


Fig 3.2 General Equilibrium Stage

3.4 Simulation of Batch Distillation Column Using MESH Equations

To simulate and model a multi-component batch distillation, the complete stage temperature, internal flow and composition with time are required, and could be calculated by solving MESH (a material balance, equilibrium, summation of mole, heat balance) equations for all trays simultaneously.

The simulation rigorous model of batch distillation involves solving a large number of stiff ordinary equations. For the system of C component distilled in a batch column with Nt number of trays, simulation by using MESH model involves solution:

- C × (Nt+1) differential equations for material balance.
- C × (Nt+1) vapor liquid equilibrium calculation associated with each material balance equation,
- Nt+1 summation equations.
- Nt+1 differential or difference equations for heat balance.

The calculations of the total number of variables, total number of equations and degree of freedom for multi-component batch distillation column as shown in figure 3-1 have been given in appendix B (B.1) . The total number of variables are (2NC+6N+10C+34) and the number of equations are (2NC+5N+5C+16) therefore the degree of freedom in batch distillation column in figure 3.1 is (N+5C+18).

Knowing that this large number of equations must be solved for each time step (few seconds), one could imagine the problem size for simulation of this type of system if the total time is a few hours .

The earliest studies on simulation of multi-component distillation columns are limited by using fixed step time in integration of MESH ordinary differential equations(ODE'S).In this algorithm to produce a stable system, small step time is necessary.

The model equations are derived for the overhead condensing system, the column stages, and the still, so these are:

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

$$V_1 y_{i,1} - L_0 x_{i,0} - D x_{i,D} = \frac{d\left(M_0 x_{i,0}\right)}{dt} \qquad \text{... (3.14)}$$

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

$$(Sx)_i = \sum_{i=1}^{C} \frac{y_{i,N}}{K_{i,N}} - 1 \qquad \text{... (3.15)}$$

$$(Sy)_i = \sum_{i=1}^{C} x_{i,N} * K_{i,N} - 1 \qquad \text{... (3.16)}$$

3- Phase equilibrium relations (E-equations).

$$E_{i,N} = y_{i,N} - K_{i,N} X_{i,N} \qquad \text{... (3.17)}$$

4- The overall energy balance equations(H-equations).

$$V_1 h_{v1} - (L_0 + D) h_{Li0} = Q_{Nt+1} + \frac{d(Mo.h_{Li0})}{dt} \qquad \text{... (3.18)}$$

The solution of (MESH) equations for multi-component batch distillation is obtained by finding a set of temperature, phase rate, batch time and compositions which satisfies all the equations of the model that described above (MESH equations).

3.4.1 Model Equations

Figure (3.3) represents the conventional batch distillation column. In this column, there is vapor liquid equilibrium in the still, therefore the still can be assumed as a theoretical stage. Making the total material ,component and energy balances on the various sections of the batch distillation column, and by further simplifications of the differential equations lead to the model.

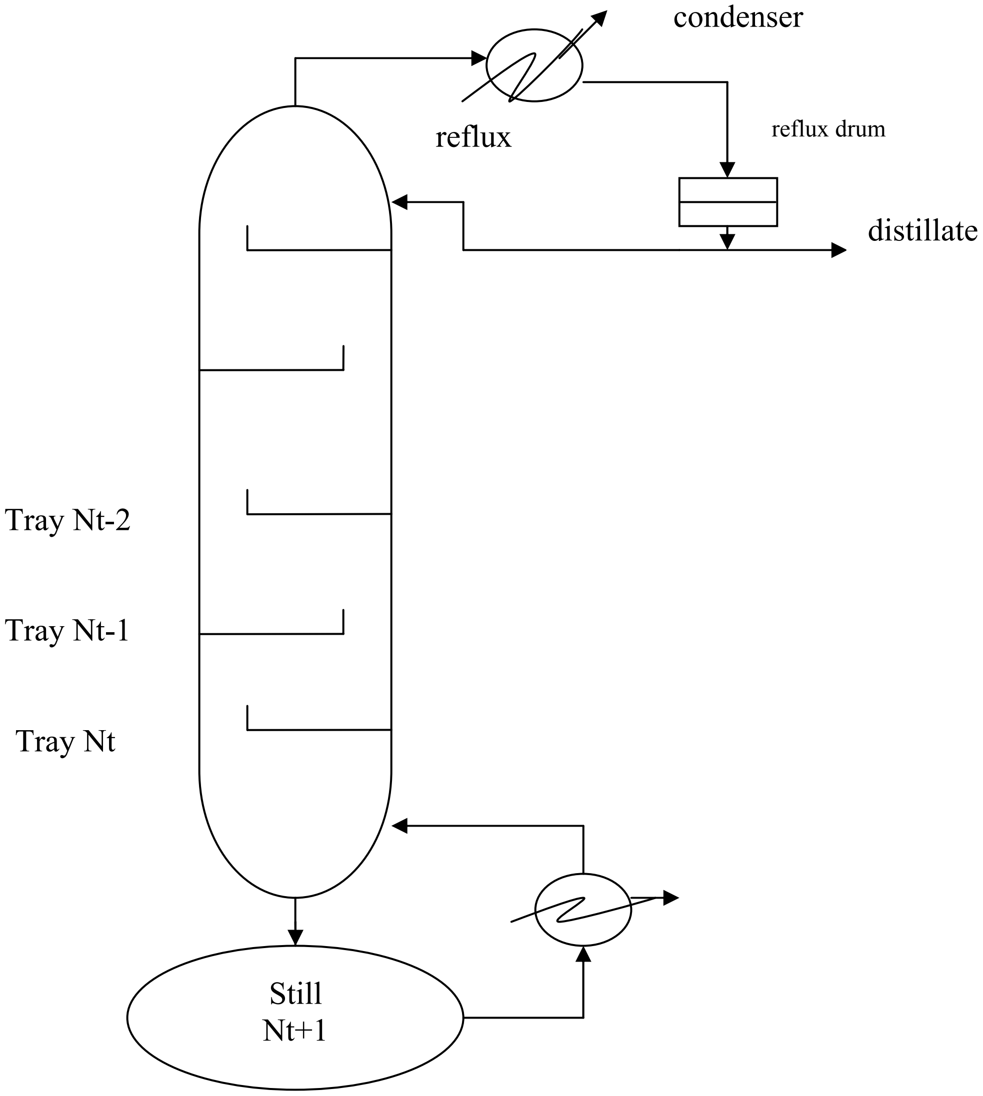
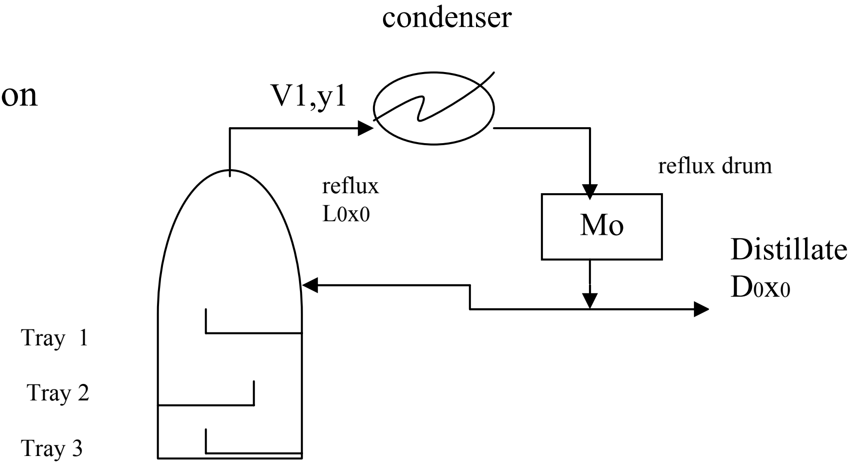


Fig 3.3 Conventional Batch Distillation Column

3.4.1.1 Material Balance
3.4.1.1a Material Balance on Condenser



In-Out=Generation +Accumulation
No reaction
Generation=0
In-Out= Accumulation

a. Total Material Balance

$$\frac{dMo}{dt} = V_1 - L_0 - D_0 \quad \text{... (3.19)}$$

b. Component Material Balance

$$\frac{dM_0 x_0}{dt} = V_1 y_1 - L_0 x_0 - D_0 x_0 \quad \text{... (3.20)}$$

By expanding the first term of equation (3.20).

$$M_0 . \frac{dx_0}{dt} + x_0 . \frac{dM_0}{dt} = V_1 y_1 - L_0 x_0 - D_0 x_0 \quad \text{... (3.21)}$$

$$y_1 = k_1 . x_1 \quad \text{... (3.22)}$$

Substitution of equation (3.22) in equation (3.21) the following equation will produce.

$$M_0 . \frac{dx_0}{dt} = V_1 k_1 x_1 - L_0 x_0 - D_0 x_0 - x_0 . \frac{dM_0}{dt} \quad \text{... (3.23)}$$

$$\frac{dx_0}{dt} = \left(\frac{V_1 k_1}{M_0} \right) x_1 - \left(\frac{L_0 + D_0 + \frac{dM_0}{dt}}{M_0} \right) x_0 \quad \text{... (3.24)}$$

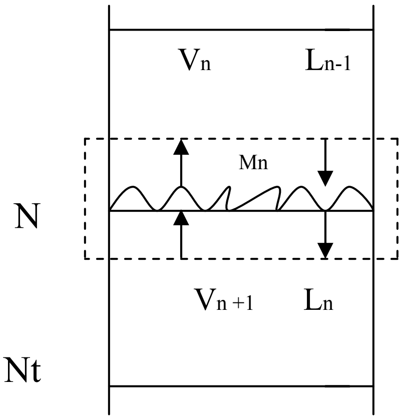
where

$$Mo = \frac{Gc}{\sum_{i=1}^{C} \frac{Xi.Mwi}{\rho i}} \quad \textit{... (3.25)}$$

$$V_1 = D(R+1) + \frac{dM_0}{dt} \quad \textit{... (3.26)}$$

$$L_0 = R * D \quad \textit{... (3.27)}$$

3.4.1.1b Material Balance on General Tray



a. Total Material Balance

$$\frac{dM_n}{dt} = V_{n+1} + L_{n-1} - V_n - L_n \quad \textit{... (3.28)}$$

b. Component Material Balance

$$\frac{d(M_n x_n)}{dt} = V_{n+1} y_{n+1} + L_{n-1} x_{n-1} - V_n y_n - L_n x_n \quad \textit{...(3.29)}$$

By expanding the first term of equation (3.29).

$$M_n . \frac{dx_n}{dt} + x_n . \frac{dM_n}{dt} = V_{n+1} y_{n+1} + L_{n-1} x_{n-1} - V_n y_n - L_n x_n \quad \textit{... (3.30)}$$

$$y_n = k_n . x_n \quad \textit{... (3.31)}$$

By substitution (3.31) in equ. (3.30) the following equation will produce.

$$\frac{dx_n}{dt} = \left(\frac{L_{n-1}}{M_n}\right)x_{n-1} + \left(\frac{V_{n+1}.k_{n+1}}{M_n}\right)x_{n+1} - \left(\frac{V_n k_n + L_n + \frac{dM_n}{dt}}{M_n}\right)x_n \qquad \text{... (3.32)}$$

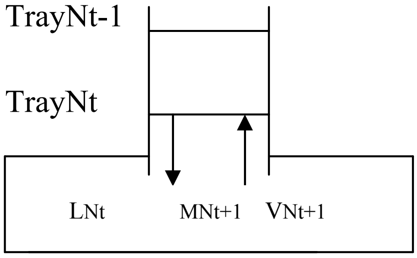
Where

$$M_N = \frac{G_N}{\sum_{i=1}^{C} \frac{Xi.Mwi}{\rho i}} \qquad N=1 \text{ to } Nt \qquad \text{...(3.33)}$$

$$L_N = V_{N+1} + L_{N-1} - V_N - \frac{dM_N}{dt} \qquad \text{... (3.34)}$$

$$V_{N+1} = \frac{1}{\left(h_{v_{N+1}} - h_{L_N}\right)}\left[V_N\left(h_{VN} - h_{LN}\right) - L_{N-1}\left(h_{L_{N-1}} - h_{LN}\right) + M_N\frac{dh_{LN}}{dt}\right] \qquad \text{... (3.35)}$$

3.4.1.1c Material Balance on Still



a.Total Mterial Balance.

$$\frac{dM_{Nt+1}}{dt} = L_{Nt} - V_{Nt+1} \qquad \text{... (3.36)}$$

b. Component Material Balance

$$\frac{dM_{Nt+1}x_{Nt+1}}{dt} = L_{Nt}x_{Nt} - V_{Nt+1}y_{Nt+1} \qquad \text{... (3.37)}$$

By expanding the first term of equation (3.37).

$$M_{Nt+1}.\frac{dx_{Nt+1}}{dt} + x_{Nt+1}.\frac{dM_{Nt+1}}{dt} = L_{Nt}x_{Nt} - V_{Nt+1}y_{Nt+1} \qquad \text{... (3.38)}$$

$$y_{Nt+1} = k_{Nt+1}.x_{Nt+1} \qquad \text{... (3.39)}$$

By substitution (3.39) in equ. (3.38) the following equation will produce.

$$\frac{dx_{Nt+1}}{dt} = -\left(\frac{V_{Nt+1}k_{Nt+1} + \frac{dM_{Nt+1}}{dt}}{M_{Nt+1}}\right)x_{Nt+1} + \left(\frac{L_{Nt}}{M_{Nt+1}}\right)x_{Nt} \qquad \text{...(3.40)}$$

Where

$$M_{Nt+1} = Mr = Mr^0 - \sum_{j=0}^{C} Mj - \int_0^t Ddt \qquad \text{... (3.41)}$$

Then the material balance equations are reduced to a tri-diagonal matrix form[53] .

$$\begin{bmatrix} B_0 & C_0 & 0 & 0 & 0 \\ A_1 & B_1 & C_1 & 0 & 0 \\ 0 & A_N & B_N & C_N & 0 \\ 0 & 0 & A_{Nt-1} & B_{Nt-1} & C_{Nt-1} \\ 0 & 0 & 0 & A_{Nt} & B_{Nt} \end{bmatrix} \cdot \begin{bmatrix} x_0 \\ x_1 \\ x_N \\ x_{Nt-1} \\ x_{Nt} \end{bmatrix} = \begin{bmatrix} dx_0/dt \\ dx_1/dt \\ dx_N/dt \\ dx_{Nt-1}/dt \\ dx_N/dt \end{bmatrix} \qquad \text{... (3.42)}$$

Where

$$A_0 = 0 \qquad \text{...(3.43a)}$$

$$B_0 = -\left(\frac{L_0 + D_0 + \frac{dM_0}{dt}}{M_0}\right) \qquad Nt=0 \qquad \text{...(3.43b)}$$

$$C_0 = \left(\frac{V_1k_1}{M_0}\right) \qquad Nt=0 \qquad \text{...(3.43c)}$$

$$B_N = -\left(\frac{V_n k_n + L_n + \frac{dM_n}{dt}}{M_n} \right) \quad \text{for } N = 1\ 10\ Nt \qquad \text{... (3.44b)}$$

$$C_N = \left(\frac{V_{n+1} . k_{n+1}}{M_n} \right) \quad \text{for } N = 1\ 10\ Nt \qquad \text{...(3.44c)}$$

$$A_{Nt} = \left(\frac{L_{Nt}}{M_{Nt+1}} \right) \qquad \text{...(3.45a)}$$

$$B_{Nt} = -\left(\frac{V_{Nt+1} k_{Nt+1} + \frac{dM_{Nt+1}}{dt}}{M_{Nt+1}} \right) \qquad \text{...(3.45b)}$$

$$C_{Nt} = 0 \qquad \text{...(3.45c)}$$

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

$$A.X = d\, x_N/dt \qquad \text{...(3.46)}$$

After calculating dx_N/dt from the algorithm Matrix we can calculate the mole fraction x_N from eigen-value.

The values of mole fraction x_N are corrected to provide better values of the assumed iteration variables for the next trial; therefore, for each iteration, the computed set of x_N values for each stage will in general, not satisfy the summation constraint given by equation (3.47). the values of x_N can be normalized using the following relation:

$$(x_{i,N})normalized = \frac{x_{iN}}{\sum_{i=1}^{C} x_{iN}} \qquad \text{... (3.47)}$$

After normalization of x_N we can calculate the correct temperature $T_{i,N}$ for each component I by the same loop for vapor-liquid equilibrium for calculation of partial pressure from Antoine equation $p_{i,N}$, distribution constant $K_{i,N}$, and the bubble point calculation for $x_{i,N}$ after normalizing in equation below:

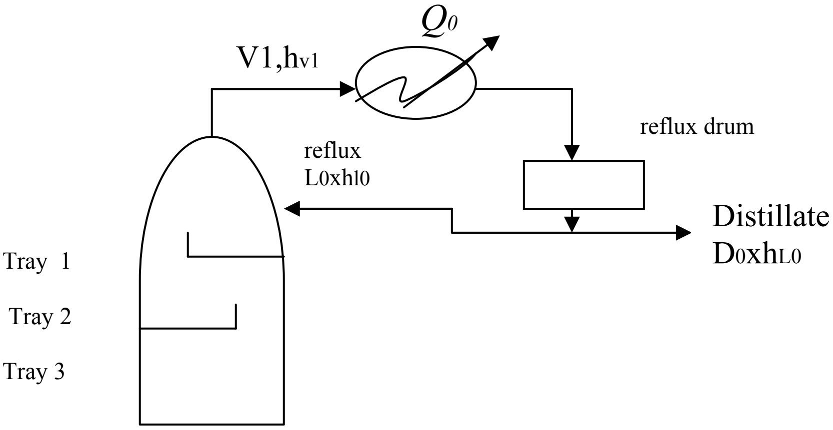
$$k_{i,N} = \frac{y_{i,N}}{x_{i,N}} \qquad ...(3.48)$$

$$\ln\ Pisat = A_{i,vp} - \frac{B_{i,vp}}{T + C_{i,vp}} \qquad ...(3.49)$$

$$Sum(N) = \sum_{i=1}^{C} (x_{i,N} * K_{i,N}) - 1 = 0 \qquad ...\ (3.50)$$

3.4.1.2 Energy Balance

3.4.1.2a Energy Balance on Condenser



$$\frac{dM_0 h_{L0}}{dt} = V_1 h_{v1} - L_0 h_{l0} - D_0 h_{l0} - Q_0 \qquad ...(3.51)$$

By expanding the first term of equation (3.25).

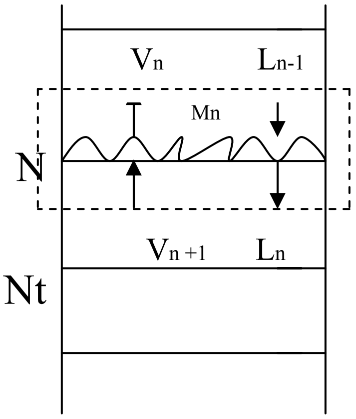
$$h_{L0}.\frac{dM_0}{dt} + M_0.\frac{dh_{l0}}{dt} = V_1 h_{v1} - L_0 h_{l0} - D_0 h_{l0} - Q_0 \qquad ...\ (3.52)$$

$$V_1 = L_0 + D_0 \qquad ...\ (3.53)$$

By substitution (3.53) in equ. (3.52) the following equation will produce.

$$Q_0 = M_0.\frac{dh_{l0}}{dt} + V_1\left(h_{L0} - h_{V1}\right) \qquad ...\ (3.54)$$

3.4.1.2b Energy Balance on General Tray



$$\frac{d(M_n h_{Ln})}{dt} = V_{n+1} h_{vn+1} + L_{n-1} h_{Ln-1} - V_n h_{vn} - L_n h_{Ln} \quad \text{... (3.55)}$$

By expanding the first term of equation (3.55).

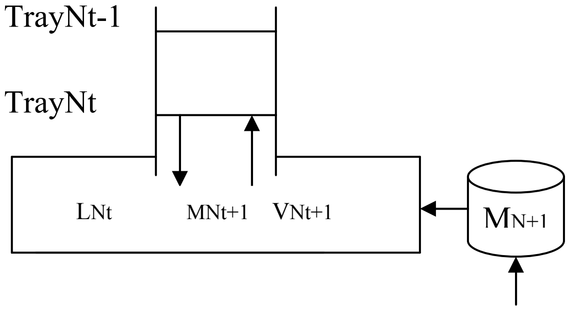
$$M_n . \frac{dh_{Ln}}{dt} + h_{Ln} . \frac{dM_n}{dt} = V_{n+1} h_{vn+1} + L_{n-1} h_{Ln-1} - V_n h_{vn} - L_n h_{Ln} \quad \text{... (3.56)}$$

By substitution (3.28) in equ. (3.56) the following equation will produce.

$$M_n \frac{dh_{Ln}}{dt} = V_{n+1} h_{vn+1} + L_{n-1} h_{Ln-1} - V_n h_{vn} - L_n h_{Ln} - h_{Ln}(V_{n+1} + L_{n-1} - V_n - L_{n)} \quad \text{... (3.57)}$$

$$V_{n+1} = \frac{1}{(h_{vn+1} - h_{Ln})} \left[V_n (h_{vn} - h_{Ln}) - L_{n-1}(h_{Ln-1} - h_{Ln}) + M_n \frac{dh_{Ln}}{dt} \right] \quad \text{... (3.58)}$$

3.4.1.2c Energy Balance on Still



$$\frac{d(M_{Nt+1}.h_{LNt+1})}{dt} = L_{Nt}h_{LNt} - V_{Nt+1}h_{vNt+1} + Q \qquad \text{... (3.59)}$$

By expanding the first term of equation (3.59)

$$M_{Nt+1}\frac{d(h_{LNt+1})}{dt} + h_{LNt+1}\frac{d(M_{Nt+1})}{dt} = L_{Nt}h_{LNt} - V_{Nt+1}h_{vNt+1} + Q \qquad \text{... (3.60)}$$

by substitution equ.(3.36) in equ.(3.60)

$$Q = M_{Nt+1}\frac{d(h_{LNt+1})}{dt} + h_{LNt+1}(L_{Nt} - V_{Nt+1}) - L_{Nt}h_{LNt} + V_{Nt+1}h_{vNt+1} \qquad \text{... (3.61)}$$

$$Q = V_{Nt+1}(h_{vNt+1} - h_{LNt+1}) - L_{Nt}(h_{LNt} - h_{LNt+1}) + M_{Nt+1}\frac{d(h_{LNt+1})}{dt} \qquad \text{... (3.62)}$$

Where

$$h_L = \Delta H_{f(L)}^{298.15} + \int_{298.15}^{T} Cp_L dt \qquad \text{... (3.63)}$$

$$h_v = \int_{0}^{Tb} Cp_L dt + \lambda_i + \int_{Tb}^{T} Cp_v dt \qquad \text{... (3.64)}$$

$$Cp_i^L = A_{i,Cp} + B_{i,Cp}T + C_{i,Cp}T^2 \qquad \text{... (3.65)}$$

$$H_{L_{i,j}} = \sum_{i=1}^{C} x_{i,j} h_j + H_{mix} \qquad \text{... (3.66)}$$

$$Cp_i^V = A_{i,Cp} + B_{i,Cp}T + C_{i,Cp}T^2 + D_{i,Cp}T^3 \qquad \text{...(3.67)}$$

With the aid of the finite-difference representation, it is useful to evaluate the values of liquid and vapor enthalpy derivatives dh_L/dt and dh_v/dt depending on the values of h_L and h_v at previous time steps, by using the following equations.

$$\frac{dh_L}{dt} \approx \frac{h_L(t) - h_L(t+\Delta t)}{\Delta t} \qquad \text{... (3.68)}$$

$$\frac{dh_v}{dt} \approx \frac{h_v(t) - h_v(t+\Delta t)}{\Delta t} \qquad \text{... (3.69)}$$

These two equations give very good results because the contribution to the energy balance from the change in enthalpy with time is very small.

Chapter Four
Experimental Work

4.1 Introduction

This chapter explains in detail the apparatus and the main instruments that have been used in the present work. The experimental work of batch distillation is discussed separately and performed by measuring the following operating variables:

1- Temperature in the still, condenser and trays.
2- Composition in the still and in the condenser.
3- The column pressure drop.

4.2 Column Description

The experiments were carried out using laboratory scale batch distillation column as shown in figures (4.1 and 4.2) . Figure 4.1 represents the diagram of the experimental column. The general view of the main experimental is shown in figure 4.2.

The distillation column manufactured of heat resistance glass consist of a still pot, which is heated using heat mantle. The column is located above the still pot and consist of eight bubble-cup tray, each equipped with sampling valve and thermocouple sensor. At the top of the column bulb-condenser is connected which is used to condense the vapor leaving the top of the column. Another condenser consist of double pipe is located prior to the distillate collection pot is used to ensure that there is no vapor exit as product and cool the distillate. A magnetic reflux unit (Solenoid valve) situated near the top of the column controls the rate of condensate being set to distillate collection pot.

To reduce the heat losses to minimum value, the still wall and the vessel were insulated with a mineral wool; also the column wall was insulated with a thin layer of mineral wool. Each two parts of this plant were connected using a flange with Teflon gasket.

There was also a computer system with a temperature interface unit, which can be used efficiently to translate and record the temperature signal along the column.

4.2.1 The Still

The column is connected at lower part to 2 liter capacity spherical heat resistant glass vessel (A) with four necks for installing instruments, as well as sampling valve. The still pot (B) is equipped with 500 watt electrical heating mantle. The electrical heater power is regulated by an interface unit connected to a personal computer.

The actual reading of the heater power (actual heating rate) is calibrated by using ethylbenzene (136.1 C^o boiling point).

4.2.2 Main Column

The main column(C) is manufactured from a heat resistance glass and fitted with a glass jacket plated with double vision fringe in order to reduce heat losses as far as possible. The main column of 1m height and 8.1 cm inner diameter consist of eight bubble-cup tray of 30 cm^3 liquid holdup for each tray.

The vapor rises from the lower tray and enters the upper tray then passes through the cap and out through the slots to give a stream of bubbles that passes through the upper liquid.

4.2.3 The Condenser

The upper part of the main column contains bulb condenser (E) . The cooling water enters the condenser at room temperature, and flows through the two pipe condenser(F) . The length of the bulb condenser is 18 cm.

Total vapor raising from the upper tray is condensed in the condenser. The condensate is collected in a glass walled distillate receiver and passes directly through reflux ratio control valve (G, electromagnetic valve). The valve configuration is either totally open or totally closed. However, the reflux ratio is controlled by selecting the time constants for open and for close, also duration time that the valve is open or close.

Depending on reflux ratio a part of the condensed mixture returns to the top of the column as reflux and the other part is withdrawn and collected in a 2 litter distillation collecting tank (H) as top product.

4.2.4 The Temperature Interface Unit

There are several assignments of the temperature interface unit (I) with personal computer (J). They are the temperature data reading and acquisition, regulating heater power supply and also selecting of the reflux ratio.

The interface consist of an interface box and interface card. The box contains electrical and electronic parts that offer the connections of the wires of each thermocouple, heater and the solenoid valve.

These devices are connected are connected to a personal computer unit through an interface card fixed inside the Pc case. The Pc used is Pentium III operated with windows millennium as an operating system. The visual interface program written in visual basic language was designed for selecting the process parameters reading and saving the experimental data.

4.3 Studied System

Why choose the Benzene-Toluene-Ethylebenzene system ?

1- The availability of experimental vapor-liquid equilibrium data for this ternary system and their parameters of liquid phase activity coefficient model.

2- The component of this system are commonly used in academic studies and researches, so that physical properties of these component are available in literatures.

3- The availability of these components in the land market.

4.4 Experimental Procedure

At the start of the process the amount of the components have been putted in the vessel shown in table 4.1

Table 4.1 Amount and initial composition of the components

Component	Amount(Litter)	Initial composition
Benzene	0.503	0.3
Toluene	0.807	0.4
Ethylebenzene	0.690	0.3

In batch distillation, there are three essential modes of operation, which are:

1- Start-up and production period. During the start-up period, the column was operated at total reflux. Because there was no product withdrawn at this period, the column achieved a steady state, the start-up period begins at the point at which the liquid on trays starts to boil.

2- Production period the distillate was withdrawn, and unsteady state operation of the column was inherent because the composition of the liquid in the still was changing continuously.

3- Shut-down period.

4.5 Measurements

In this section the measurement of temperature, pressure and concentration are described.

4.5.1 Temperature Measurement

The temperature of the column was read continuously by using fourteen J-type sensors placed in various section of the plant. These sensors (T_1, T_2, T_3, T_4, T_5, T_6, T_7, T_8, T_9, T_{10}, T_{11}, T_{12}, T_{13} and T_{14}) were placed in the still , eight points along the column, the bulb condenser contain two sensor, two pipe condenser contain two sensor, plain column contain sensor. Each one of these sensor measures the liquid temperature and sends the data to a computer by using a temperature interface; these data were recorded with time in the computer as notepad file.

4.5.2 Pressure Measurement

The total pressure drop in the column was read by using a U tube-mercury manometer (K) as shown in figure 4.1. The manometer is connected to bottom vessel from one side and to the upper part of the column from other side. From experimental work the column was operates at atmospheric pressure.

4.5.3 Composition Measurement

The measuring of the composition of any mixture is a complicated process. The selection of a device to measure the composition is very importance . The most accurate on-line instrument in industry is the gas chromatograph. Numerous operational difficulties characterize these instruments such as sampling and sample time, calibration and sensitivity of the sensor to impurities. Sampling time of a gas chromatograph can be in the range of 10 - 30 minutes and gives rise to severe control limitations. The long sampling time is caused by time consuming analysis and transport delay from the process to the analyzer.

During the experiment run, liquid samples were taken from the bottom vessel and the distillate every (20 minute). The samples are withdrawn in test tubes. It is important to take such a small amount of sample to avoid the significant change of the bottom vessel composition.

Note: It was difficult to get a suitable GC to analyze any samples then done the experimental work and the analysis of this sample was taken from the experimental data (Salah)

Table 4.2 and 4.3 shows the results of the composition in the still and in the condenser that have been taken from experimental work from Salah [3]

Table 4.2 Composition of the component in the still

Time(min)	**Benzene**	**Toluene**	**Ethylebenzene**
0	0.3	0.4	0.3
20	0.009	0.59	0.45
40	0.005	0.57	0.48
60	0.001	0.55	0.5

Table 4.3 Composition of the component in the condenser

Time(min)	Benzene	Toluene	Ethylebenzene
0	0.3	0.4	0.3
20	0.69	0.29	0.009
40	0.44	0.57	0.001
60	0.21	0.78	0.001

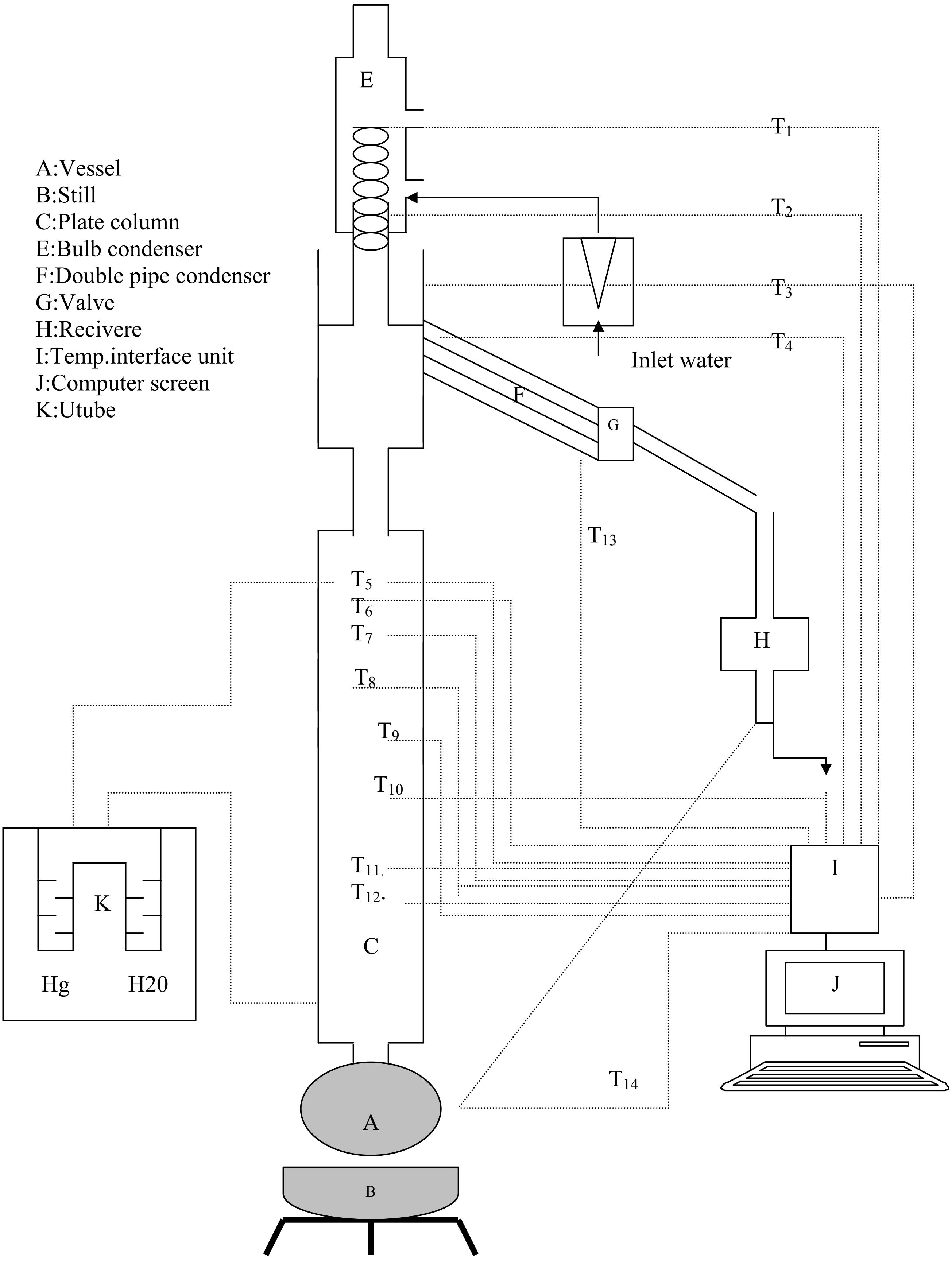


Fig 4.1 Flow Diagram of Experimental Plant

Fig 4.2 General View of Experimental Plant

Chapter Five
Results and Discussion

5.1 Introduction

In the previous chapter, the analysis of the design method for the multi-component batch distillation for multistage column has been considered.

This chapter includes the results of the models developed for batch non-ideal multi-component distillation, which consists of liquid composition profile, vapor and liquid flow rates profiles, temperature profile for different time interval and total heat input to the still and heat output from the condenser at the end of batch time.

The effects of some process variables on the performance of multi-component batch distillation process have been studied. All the results have been taken from the developed computer programs using MATLAB. The total vapor and liquid flow rates, Temperature and the liquid composition profiles at various process, variables have been presented graphically for comparison purposes.

5.2 Computational Procedure
5.2a The Short-Cut Model

In the present work, a developed computer program using MATLAB$_{6.5}$ has been constructed for solving short-cut models that performs calculation of minimum number of stages N_{min} using Fenske equation and the minimum reflux ratio R_{min}, using the Underwood equation. The theoretical number of stage N required to distillate the mixture is calculated by Gilliland correlation that relate N_{min} with N_{act} . The results obtained have been compared with the previous work [1].

The developed computer program to calculate activity and fugacity coefficient by using different models have been shown in appendix C Wilson, NRTL, UNIQUAC and UNIFAC models have been used to calculate the activity coefficient as shown in appendices (C.1),(C.2),(C.3),(C.4) respectively and Virial equation is used to estimate the fugacity coefficient as shown in appendix (C.5) for the system BTEb. The values of the activity coefficient and fugacity coefficient from the above models for the system BTEb have been given in table 5.1 .

Table 5.1 Results of activity and fugacity coefficient for the initial mixture

component	**Activity: Wilson**	**Activity: UNIFAC**	**Activity: UNIQUAC**	**Activity: NRTL**	**Fugacity: Virial**
Benzene	0.0505	2.6774	0.4018	1.2463	0.9637
Toluene	0.0963	2.7118	0.3729	0.9183	0.9454
Ethylebenzene	0.004	2.7143	0.6854	0.7807	0.925

A block diagram for the short-cut model has been shown in appendix D(D.1).

5.2b The Rigorous Model

This model is used to calculate the temperature, liquid and vapor flow rates profiles, still hold-up, composition profile, heat input in the still and removed from the condenser.

The input parameters needed in simulation program were: reflux ratio, number of plates, initial charge to the still, holdup on plates, holdup in condenser, and the initial concentration on each plates and in the still.

By using trial and error method with the aid of the summation equations, the equilibrium equation are solved to predict the distribution coefficient $K_{i,j}$, and the temperature T_j in the condenser, plates and still. Finally the program is checked when the boiling point temperature of each component i on each stage is between 0.999 and 1.0.

The values of the distribution coefficient $K_{i,j}$ was necessary in integration of the component material balance equations, since $K_{i,j}$ is a function of local composition and temperature.

The component material balance equations have been arranged as differential matrix and solved to calculate the new composition $x_{i+1,j}$ by tri-diagonal matrix using eigenvalues. Then the mole fraction of each component i at each time step is normalized to force them to sum to 1. After normalization the mole fraction of each component i is used as input to another batch time loop.

This new temperature and compositions have been used to compute liquid and vapor specific enthalpies.

The differential matrix contains terms of internal vapor and liquid flow rates, which must be update during the simulation for each time period .

Calculations are continued for a period of time with total reflux until the temperature equal to the same value in each tray .Then the new period is initially by making a step change from total reflux to any value of reflux ratio , this period may be continued for any specified period of time or until the desired still pot liquid composition has been achieved.

The step time Δt has been taken as a variable value and 0.5 min has been chosen because it give an accurate prediction in the results when have been compared with the experimental work. On the other hand, if the step time decreases the calculation should take much more time and the accuracy would not improve very much. Every time interval Δt the change in composition and temperature on each tray cause a change in liquid phase activity coefficient and hence a change in distribution coefficient K_{ij} value. A block diagram for the rigorous model has been shown in appendix D(D.2) .

5.3 Selection of Activity Coefficient Model

Different liquid phase activity coefficient models have been studied for Benzene-Toluene-Ethylebenzene system and the appropriate model was selected according to the purity of the benzene that is separated as a top product. Table 5.2 gives the composition of the Benzene in the condenser for the different models used.

Table 5.2 Composition of Benzene in the distillate

	Wilson	**UNIFAC**	**UNIQUAC**	**NRTL**
Benzene	0.355	0.9804	0.9733	0.9919

The results shows that UNIFAC and NRTL models give the more acceptable results. In the present work the UNIFAC model has been used because is modern and a parameters were used in this model is easy to get.

5.4 Model Results

Much more results can be predicted from the simulation model of batch distillation. This model can be used to predict the composition, temperature, liquid and vapor flow rates .

The initial conditions that have been used in this simulation are same as that used in the experimental work [3] for the system Benzene-Toluene and Ethylebenzene. Where the mole fraction in the still is 0.3,0.4 and 0.3 ,eight theoretical stags ,reflux ratio equal 1, simulation batch time is 1 hr and step time equal 0.5 min .Figures 5.1 shows the change of still liquid composition profile for each feed components with batch time. This is expected and it is a positive sign regarding the program validity.

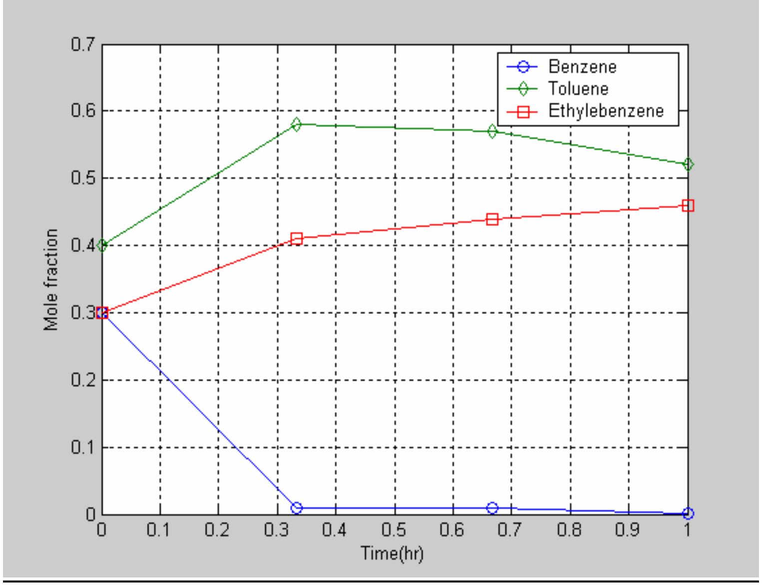


Figure 5-1 Mole fraction of each component vs. batch time at still

Figure 5.2 shows the results obtained from the simulation model at the still for the composition profile and have been compared with the experimental data [3] by taking the initial mole fraction in the still 0.3, 0.4 and 0.3, reflux ratio of 1.0, ten theoretical stages and with step time equal 20 min. Also, the present model results was compared with the previous model [1] results as shown in figure 5.3 for Hexane-Heptane and Octane ideal system 0.3, 0.3 and 0.4 initial composition, reflux ratio of 5, seven theoretical stages, batch time of 1.6 hr and step time change of 4 min.

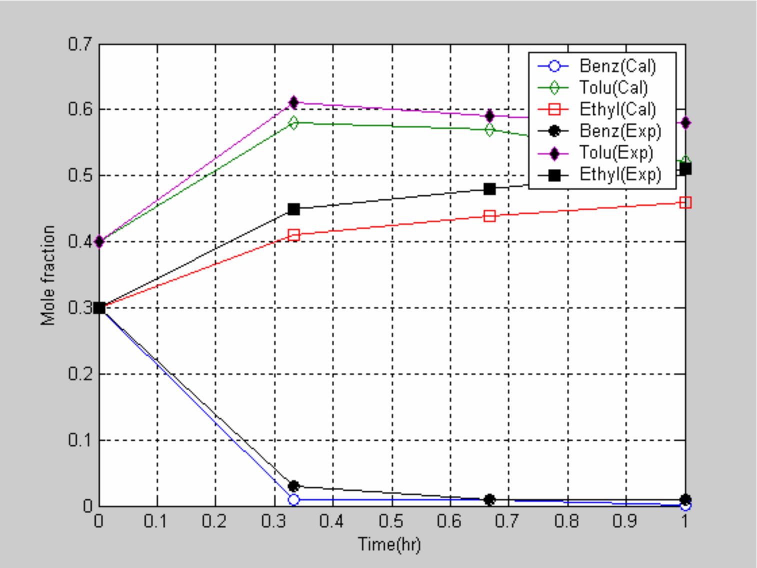


Figure 5-2 Comparison between the present model results for the mole fraction in the still with the experimental data [3] for Benzene-Toulene-Ethylebenzene system.

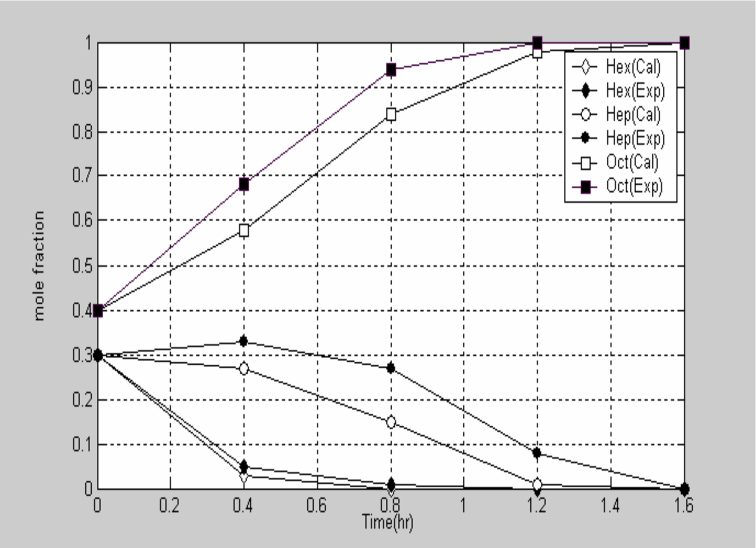


Figure 5-3 Comparison between the present model results for the mole fraction in the still with the experimental data for ideal system Hexane-Heptane-Octane[2].

The results give a good agreement for liquid composition at the still. The difference is due to the thermodynamic non-ideal models used, the kinetic model simplicity, conditions of experimental work, and the initial experimental variables that inputs to the simulation model. In fact complex models taking into account the non-ideality of the mixture and so integrating thermodynamic models would provide more accuracy. Nevertheless, the good agreement between experiments and their mathematical representation allows validating the simulation environment.Figure 5.4 shows the change in mole fraction profile of the benzene that gradually increases with batch time range from 0 – 0.05 hr for the still (stage 8) to distillate (stage 1). The maximum purity for the benzene is in the distillate is equal to 0.9832.

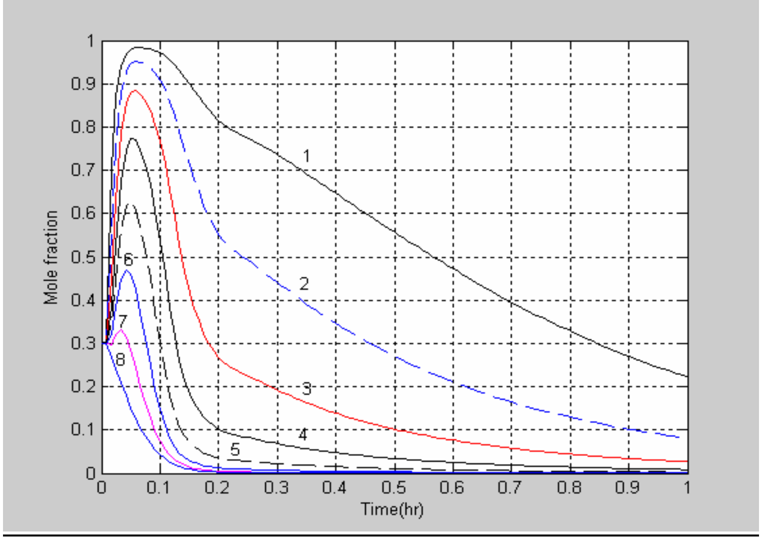


Figure 5-4 Mole fraction of the benzene vs. batch time in each stage (R=1)

While the mole fraction of ethylebenzene decreases from the still to distillate because it is the heaviest , the mole fraction in still is 0.46 and in the distillate is .0001 as shown in figure 5.5.

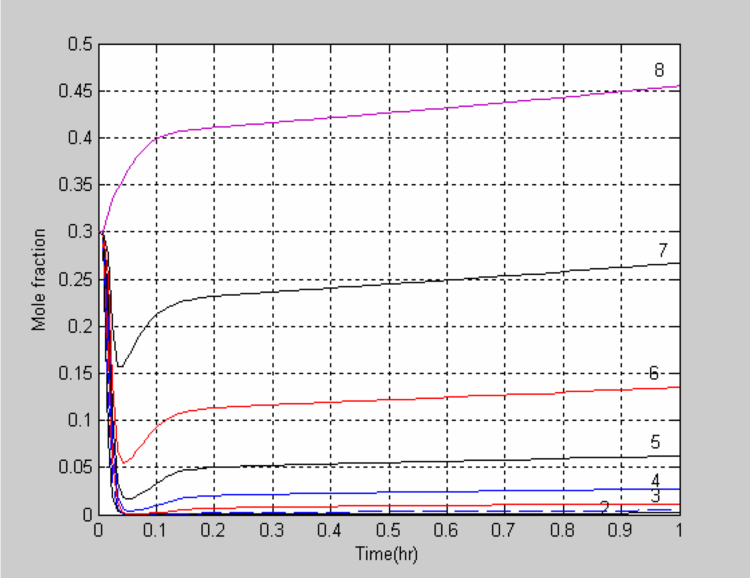


Figure 5-5 Mole fraction of the ethylebenzene vs. batch time in each stage (R=1)

Figure 5.6 shows a gradually decreasing in mole fraction of toluene from the still to the distillate for the same batch time . The maximum purity of toluene is 0.98 in fourth stage.

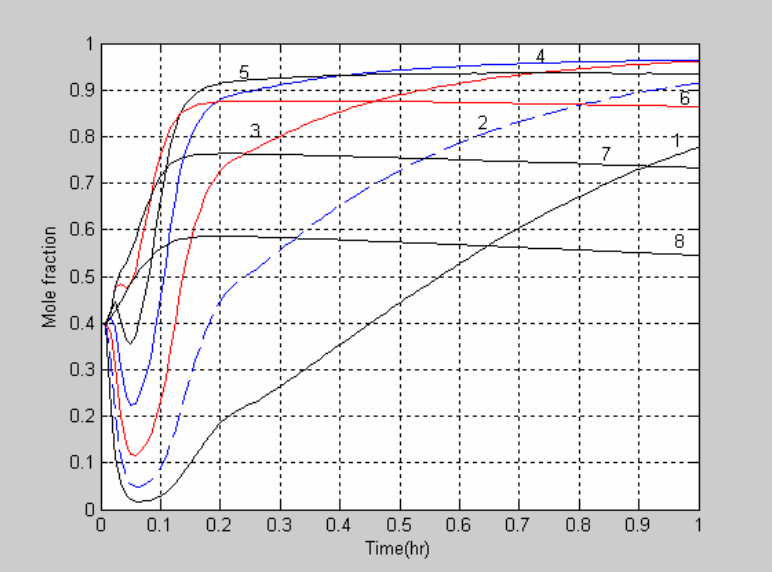


Figure 5-6 Mole fraction of the toluene vs. batch time in each stage (R=1)

5.5 Effect of Process Variables on The Performance of Multistage Multi-Component Batch Distillation

Study of the effect of some process variables such as, reflux ratio, batch time, different composition and variable holdup in the condenser and plates, on the performance of multi-component batch distillation (i.e, the effects of these variables on the temperature profiles ,liquid composition profiles and liquid and vapor flow rate, heat input to the still and output from the condenser) .

The effect of each process variable is studied under constant of another specified variable, for example when changing the feed composition , the batch time, reflux ratio and effect hold up remain constant.

5.5.1 Effect of Reflux Ratio

The effect of changing the reflux ratio on the separation of benzene from BTEb mixture using batch distillation process is first considered. Figures 5.4,5.7 and 5.8 shows the composition profile of benzene on each tray. When the reflux is 1 and batch time 1 hr the mole fraction of benzene is 0.21, figure 5.4. When the reflux ratio increased to 2 and to 4 the purity of benzene increase to 0.33 and 0.41 respectively figures 5.7 and 5.8. In the same figures when the batch time is 0.07 hr the mole fraction of benzene increase with decreasing reflux ratio. That mean we can get more quantity of benzene in less batch time when decreasing reflux ratio.

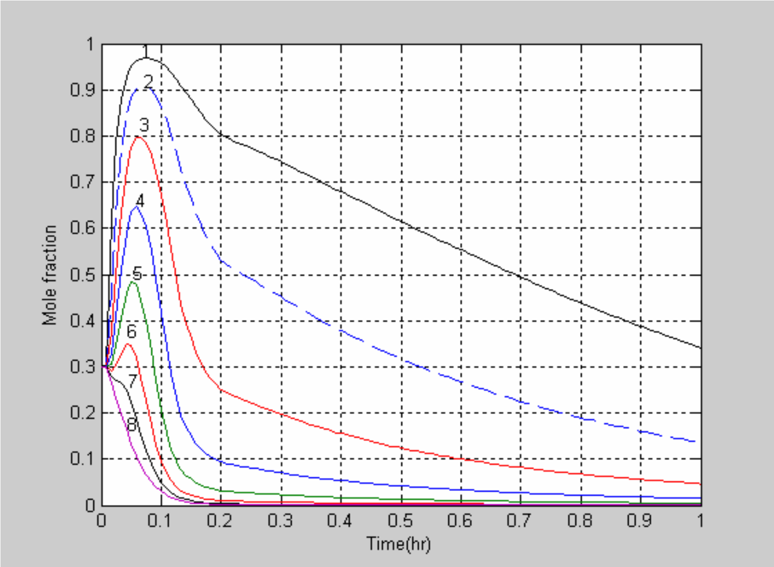


Figure 5-7 Mole fraction of the benzene vs. batch time in each stage (R=2)

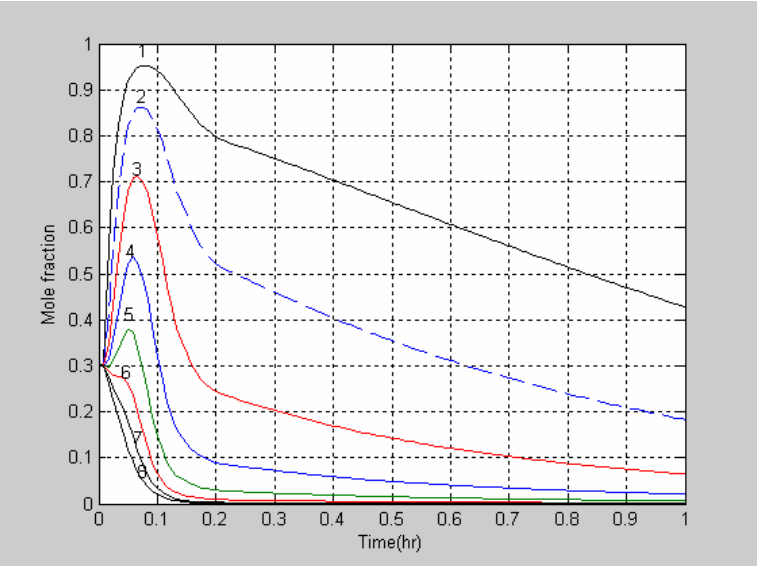


Figure 5-8 Mole fraction of the benzene vs. batch time in each stage (R=4)

In figure 5.5, 5.9 and 5.10 show that when the reflux ratio is 1 the composition of ethylebenzene in the still is 0.455 at the end of the batch time as the reflux increase s to 2 the composition becomes 0.41 and for reflux ratio of 4 the composition of ethylebenzene is 0.39.

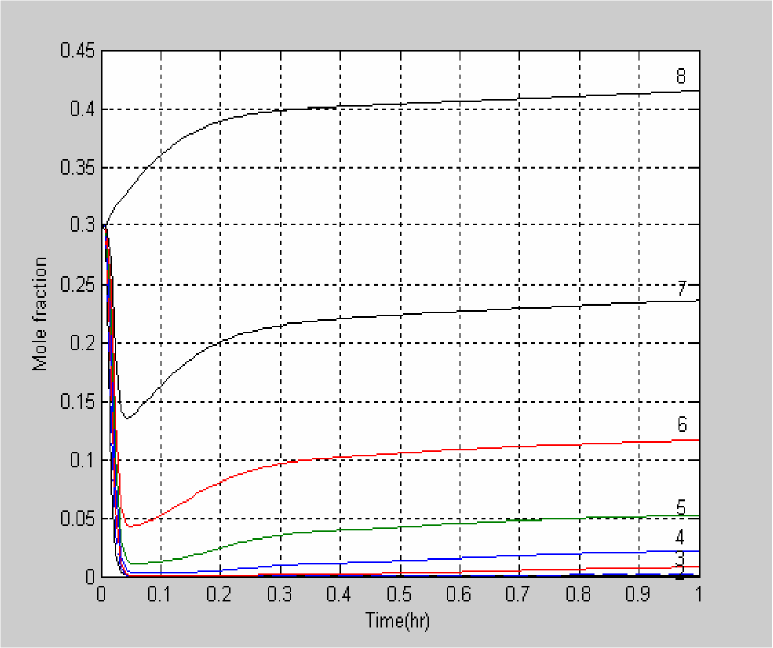


Figure 5-9 Mole fraction of the ethylebenzene vs. batch time in each stage (R=2)

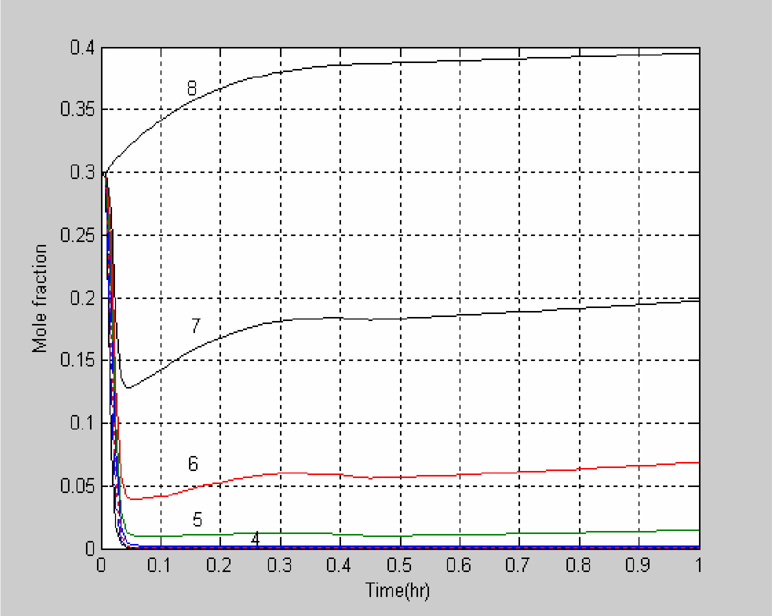


Figure 5-10 Mole fraction of the ethylebenzene vs. batch time in each stage (R=4)

For toluene when increasing the reflux ratio from 1 to 2 and to 4 the mole fraction of toluene stay constant at 0.55 as shown in figure 5.6

This mean that when the reflux ratio is low the composition of the light component is small and the composition of the heavy component is large in the still for the same batch time. This because when the reflux is small the more quantity of light component is drawn from the distillate. Therefore the best reflux ratio is less 4

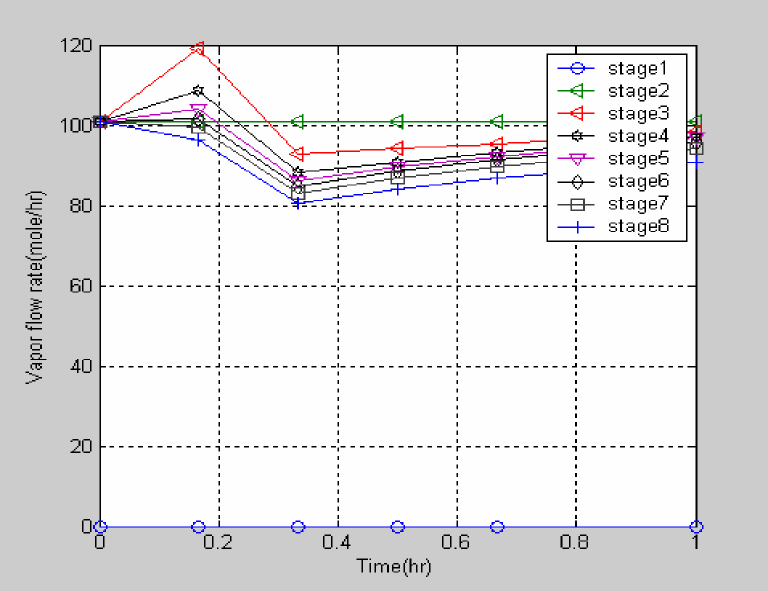


Figure 5-11 Vapor flow rate vs. batch time at each stage

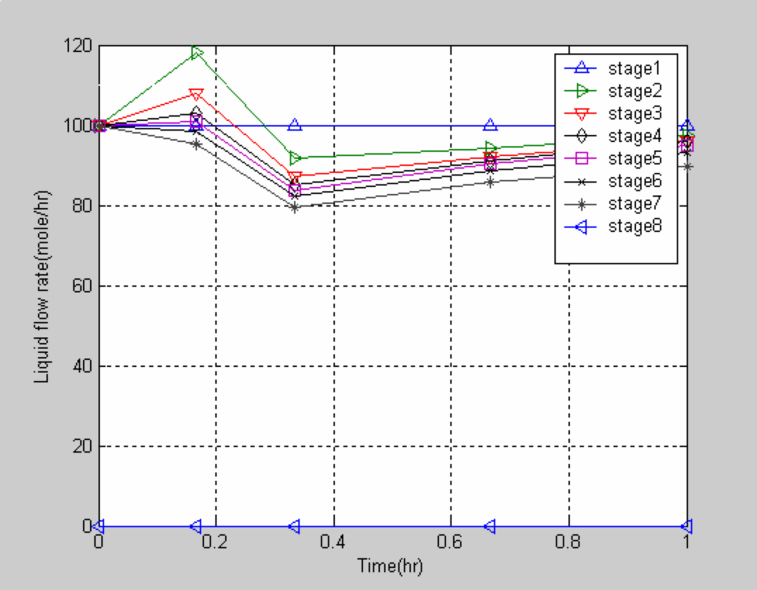


Figure 5-12 Liquid flow rate vs. batch time at each stage

Temperature profile in variable reflux ratio has been shown in figure 5.13, 5.14 and 5.15 , this figures shows that the temperature profile is decrease in the still and the stages above the still when the value of the reflux ratio increasing because when the value of reflux is high the quantity of the lightest component in the reflux if is very high and that cause decrease in the temperature of the mixture that return from the distillate to the still.

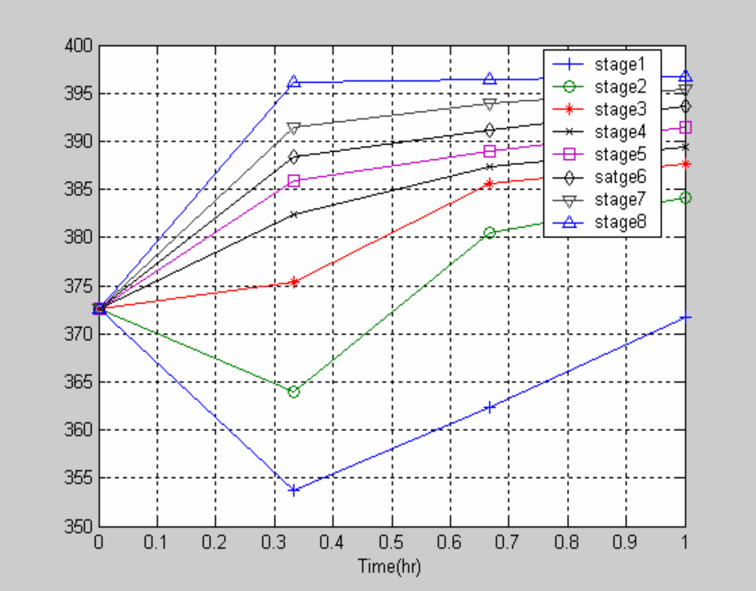


Figure 5-13 Temperature profile vs. batch time at each stage (R=1)

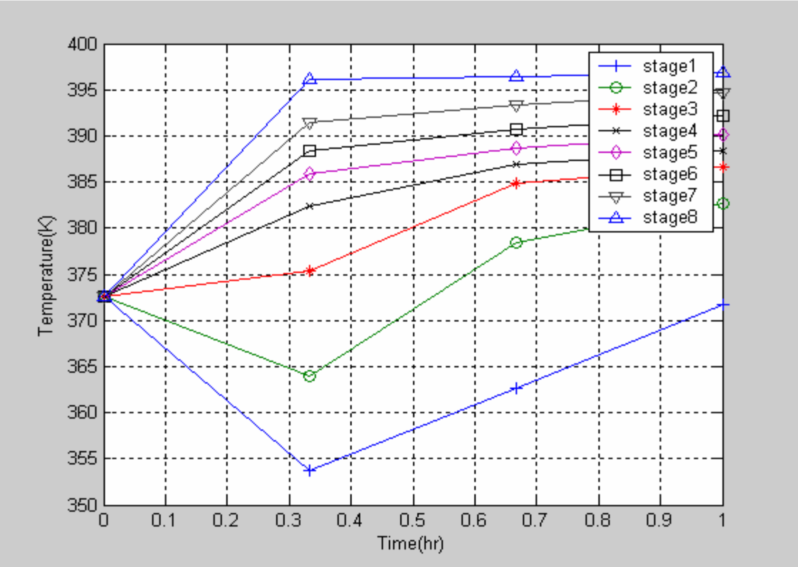


Figure 5-14 Temperature profile vs. batch time at each stage (R=2)

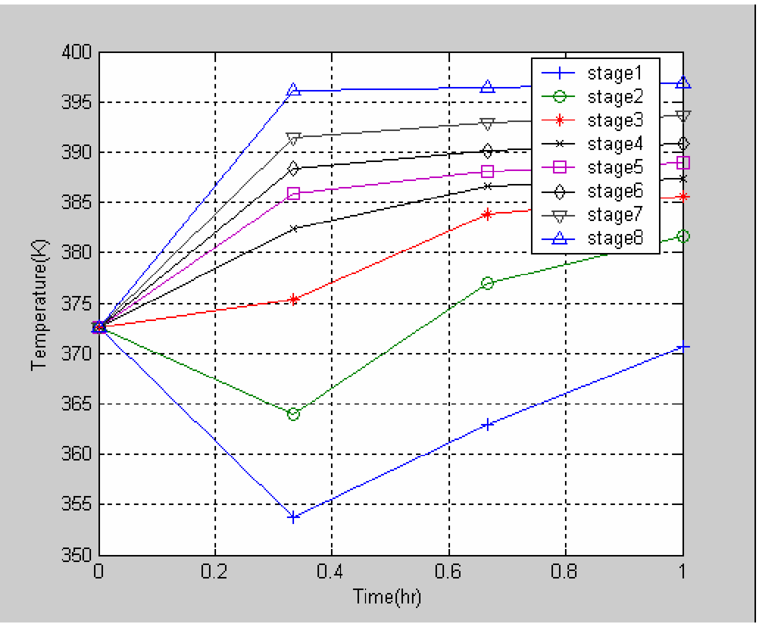


Figure 5-15 Temperature profile vs. batch time at each stage (R=4)

The quantity of heat input to the still and removed from the condenser at different reflux ratio is given in table 5.3. This results show that when the reflux increases the quantity of heat input to the still is increasing this due to increasing the amount of mixture that retain to the still, (more reflux mean high still duty).

Table 5.3 Heat input to the still and output from the condenser in different reflux ratio

Reflux	Qstill (w)	Qcondenser(w)
1	201.83	194.74
2	501.13	496.67
4	843.09	827.77

5.5.2 Effect of Changing The Batch Time

The effect of changing batch time on the separation of benzene from the BTEb mixture is most important. Figure 5.4 shows the liquid composition of benzene at each stage vs. batch time. When batch time is 1 hr the mole fraction of benzene is 0.22 in distillate.

When the batch time decreased to 0.5 hr the mole fraction of the benzene in the distillate increases to 0.56 and for 1.5 hr the mole fraction is 0.09 and for 2 hr batch time the mole fraction of the benzene is 0.02 as shown in figures 5.16. Therefore changing the mole fraction of benzene depends on the simulation curve of the lightest component vs. batch time. This curve increase in the time less 0.5 hr , and begin to decrease this due to the effect of temperature of the mixture When the batch time is less than 0.5 temperature is very far from the boiling point of toluene and ethylebenzene and near to the boiling point of benzene thus benzene boiled before toluene and ethylebenzene .When the temperature increases ,it reached the boiling point of toluene, it begins to boil . Therefore, the best batch time is less 1 hr.

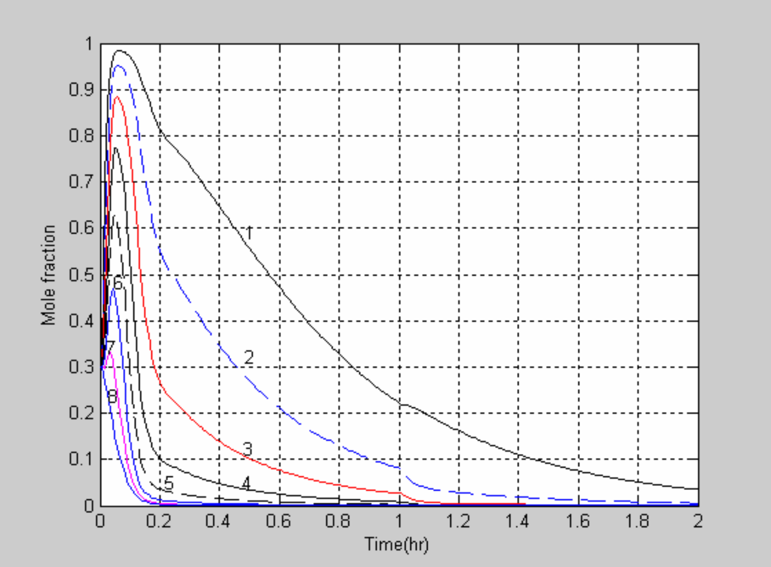


Figure 5-16 Mole fraction of the benzene vs. batch time at each stage (2) hr.

The mole fraction of the toluene is increasing from 0.44 to 0.92 with increasing the batch time from 0.5hr to 2hr as shown in figures 5.6 and 5.17.

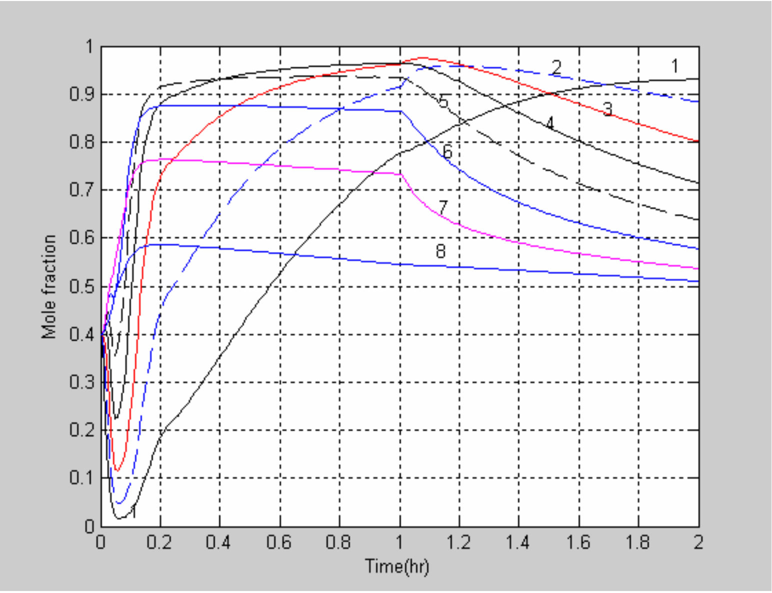


Figure 5-17 Mole fraction of the toluene vs. batch time at each stage (2) hr

Figure 5.18 shows that there is a drop of mole fraction of ethylebenzene initially and after that the mole fraction start to increase slightly until batch time 1 hr after that there is a large increase in the mole fraction of ethylebenzene with batch time at all the stages. This due to when increasing the batch time the quantity of the light component in the tower is finished and the quantity of the heavy component is began boil and reached to the distillate.

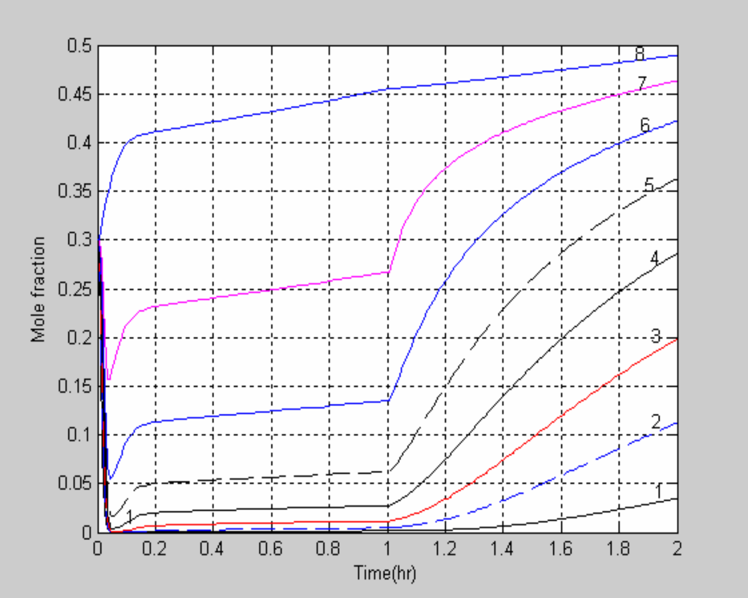


Figure 5-18 Mole fraction of the ethylebenzene vs. batch time at each stage (2) hr.

The temperature of the distillate is 358 K when the batch time is 0.5 hr. When increase the batch time to 1 hr the temperature of the distillate increase to 371.2 K and becomes 380.4 k at 1.5 hr and 384.7 k at 2 hr batch time as shown in figures 5.19 . This depends on the concentration of the lightest component.

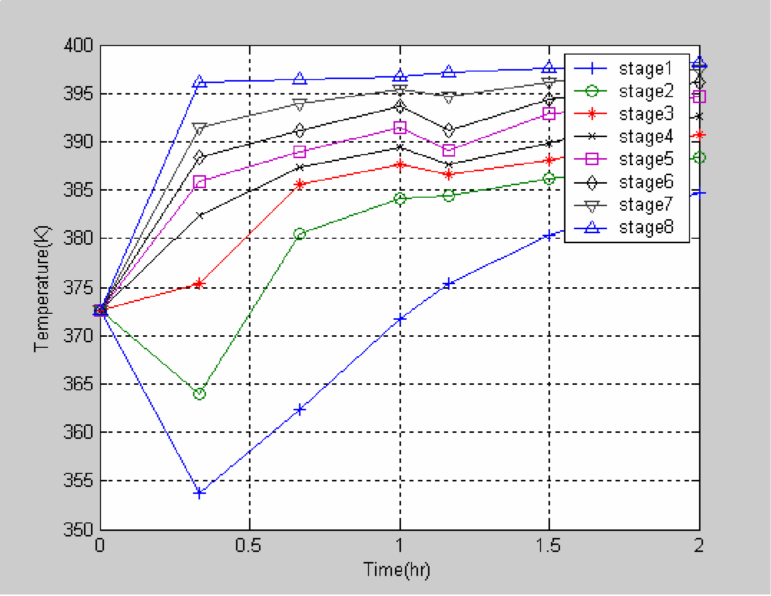


Figure 5-19 Temperature profile vs. batch time at each stage (2) hr

The vapor flow rate profile figure 5.20 decreases with increasing the batch time on each tray and approaches zero at 1.5 hr batch time this is because the quantity of the light components is consumed . Increasing the batch time to 2 hr the vapor flow rate start to increase and stay constant for all stages due to increasing the temperature of mixture and approaches to the boiling temperature of the heavy component.

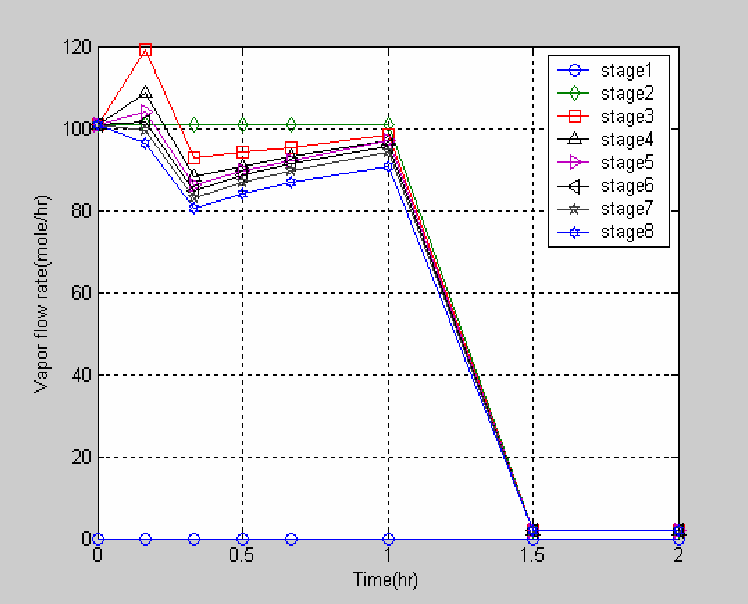


Figure 5-20 Vapor flow rate vs. batch time at each stage (2) hr.

The liquid profile on each stages figure 5.21 show that increasing until reached to 1 hr and after that began decreasing with increasing the batch time because with increasing the batch time the heavy component began boil and the quantity of the liquid decrease.

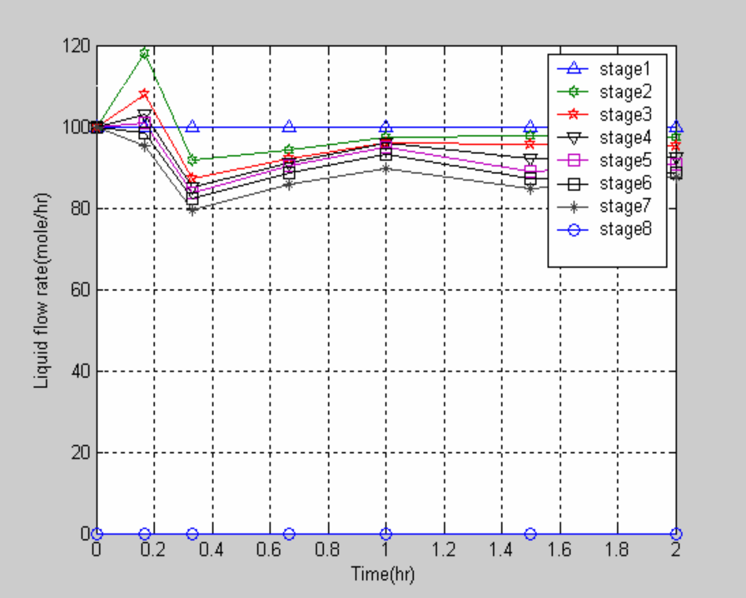


Figure 5-21 Liquid flow rate vs. batch time at each stage (2) hr.

The heat input to the still and the heat output from the condenser decreased with increasing the batch time. Table 5.4 , this due to in start of distillation process the mixture heating from initial temperature to the boiling temperature of the light component and this has high difference in the temperature and after that the mixing heating to the boiling temperature of the second component and that has low difference in the temperature, therefore it is needed low energy.

Table 5.4 Heat input to the still and output from the condenser in different batch time

Batch time(hr)	**Qstill(w)**	**Qcondenser(w)**
0.5	850.4	791.6
1	201.83	194.74
1.5	400.16	401.38
2	403.6	407.12

5.5.3 Effect of Liquid Hold up

In present work the volume hold up assumed constant and the liquid molar density is changed or volume holdup is changed and liquid molar density is constant that mean a change in liquid hold up in condenser, plates and still .The effect of changing the liquid hold up on mole fraction profile, temperature, vapor and liquid flow rates profile and heat duty is considered.

The best hold up that gives the higher purity of the desired component is chosen. In figure 5.22 when the plates and condenser hold up is 0.25 and 1.25 mole respectively and initial charge is 100 mole the mole fraction of benzene at the end 1 hr is 0.02 , while when hold up in plates and condenser change to 1 and 5 mole the purity of benzene is 0.23 as shown in figure 5.4. When increasing the plates and condenser hold up to 5 and 20 mole the purity of benzene is 0.57 at the end of batch time as shown in figure 5.23 . But when decreasing hold up in condenser and plate we can get more quantity of benzene in less batch time as shown in figure 5.4, 5.22 and 5.23.

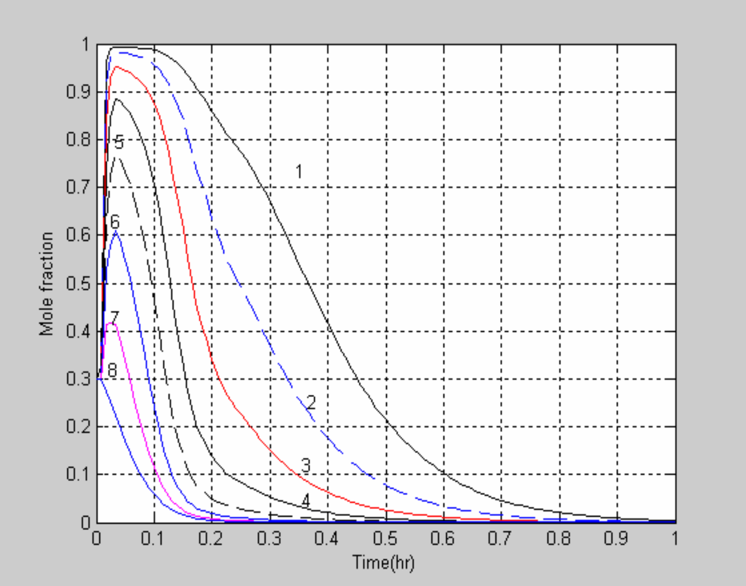


Figure 5-22 Mole fraction of the benzene vs. batch time (Mc=1.25, Mp=0.25 mole)

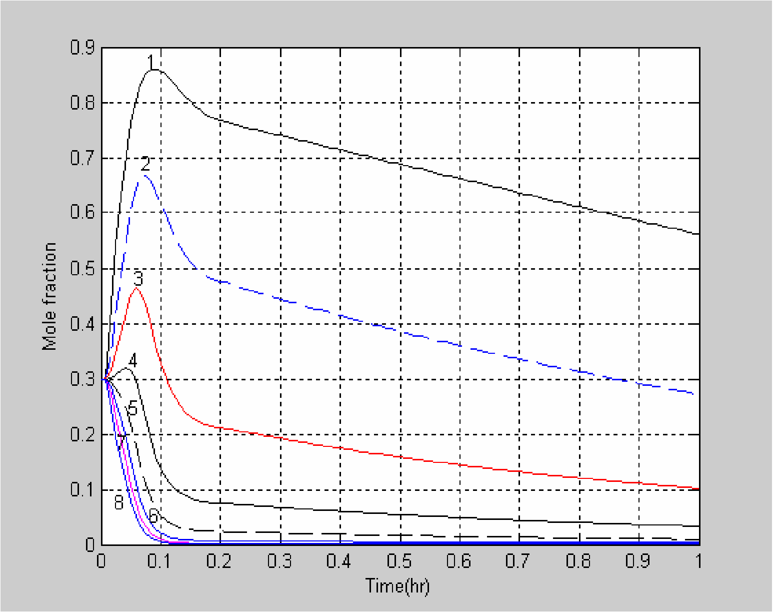


Figure 5-23 Mole fraction of the benzene vs. batch time (Mc=20, Mp=5 mole)

The mole fraction of toluene in distillate has been shown in figure 5.24 is 0.99 when the plates and condenser hold up is 0.25 and 1.25 mole respectively , while in figure 4.6 the mole fraction is 0.78 when the plates and condenser hold up is 1 and 5 mole respectively, and decrease the mole fraction of toluene to 0.43 when the initial charge is 100 mole, plates and condenser hold up is 5 and 20 mole respectively as shown in figure 5.25 .

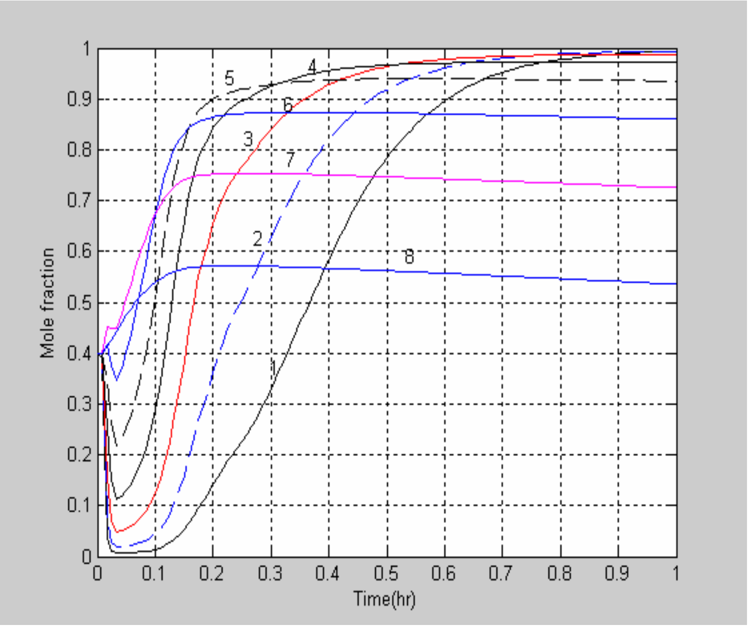


Figure 5-24 mole fraction of the toluene vs. batch time (Mc=1.25, Mp=0.25 mole)

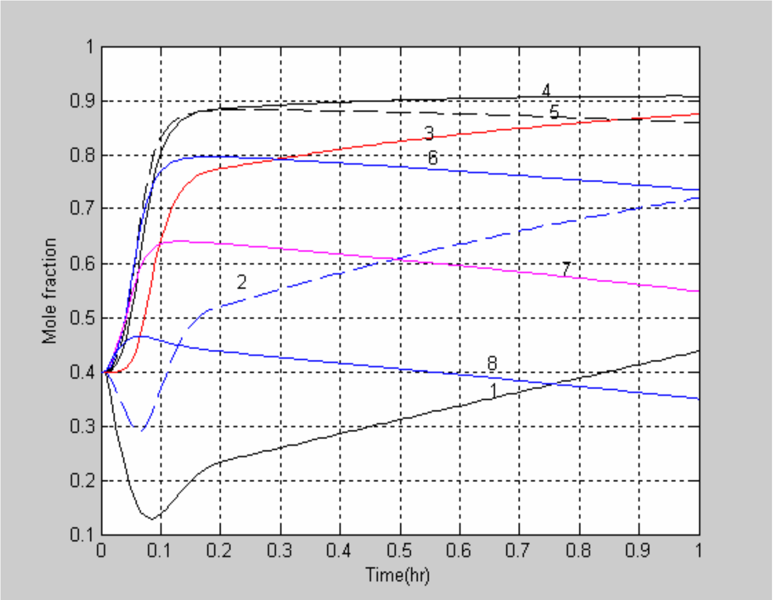


Figure 5-25 Mole fraction of the toluene vs. batch time (Mc=20, Mp=5 mole)

Finally the mole fraction of ethylebenzene in figure 5.5 ,5.26 and 5.27 , when increasing the liquid hold up in plates and condenser increasing the mole fraction of ethylebenzene in distillate

Therefore from the above the best concentration of the desired component in less time has been when the small hold up in plates and condenser.

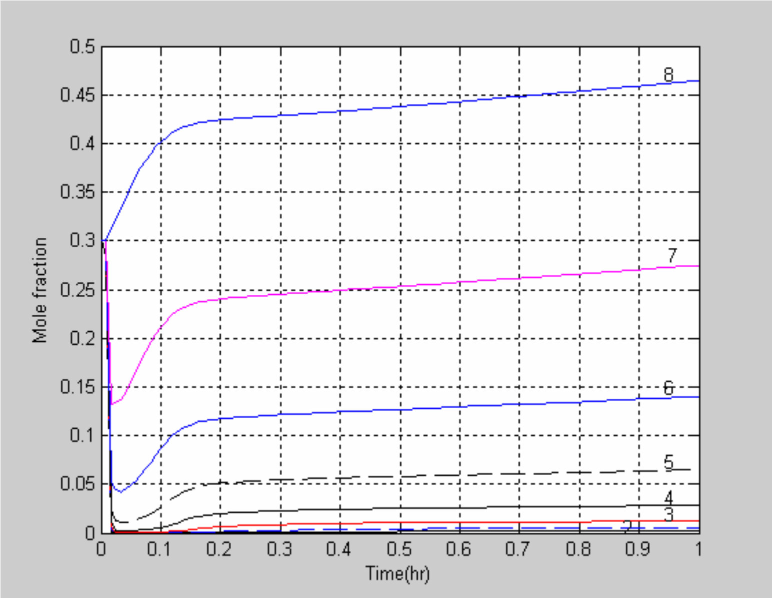


Figure 5-26 Mole fraction of the ethylebenzene vs. batch time (Mc=1.25, Mp=0.25 mole)

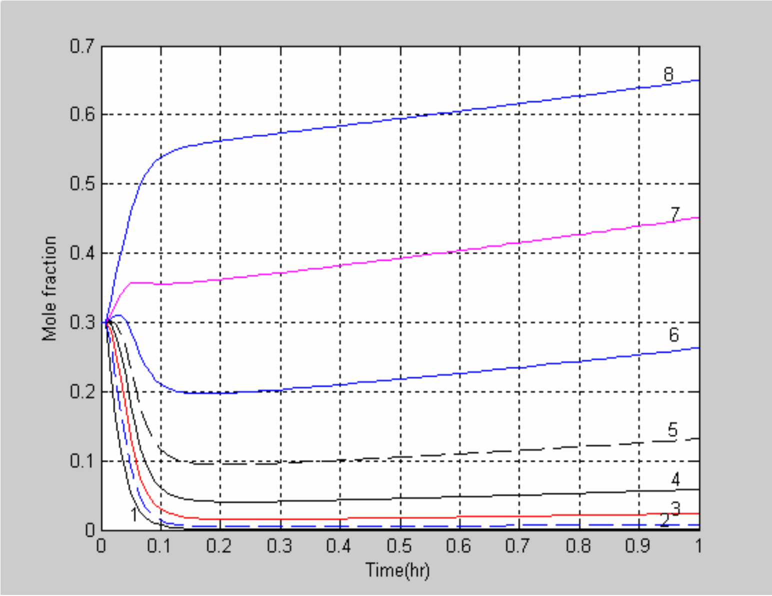


Figure 5-27 Mole fraction of the ethylebenzene vs. batch time (Mc=20, Mp=5 mole)

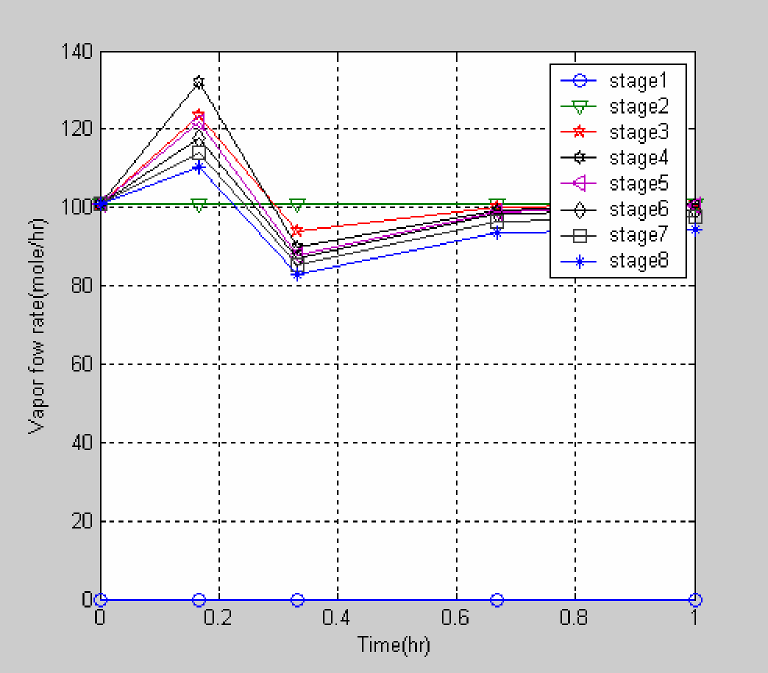


Figure 5-28 Vapor flow rate vs. batch time (Mc=1.25, Mp=0.25 mole)

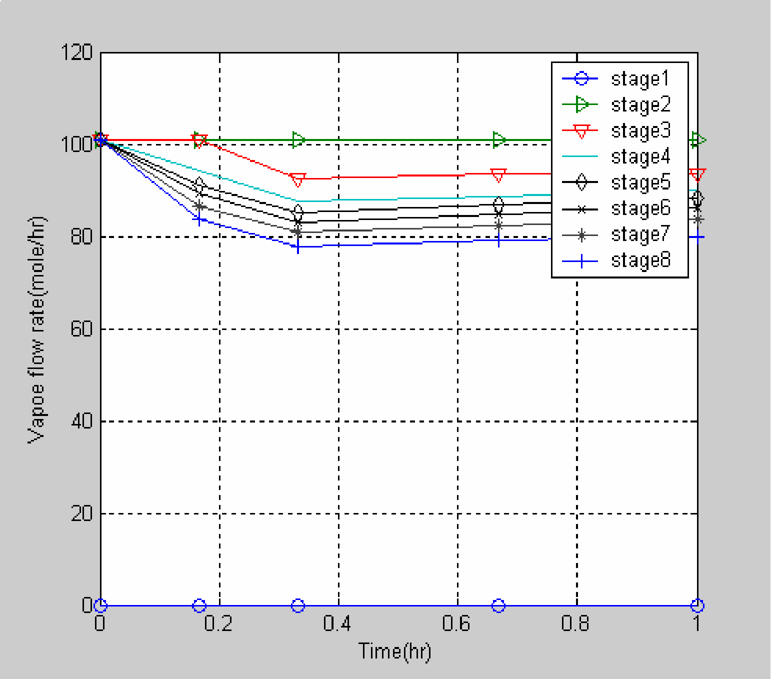


Figure 5-29 Vapor flow rate vs. batch time (Mc=20, Mp=5 mole)

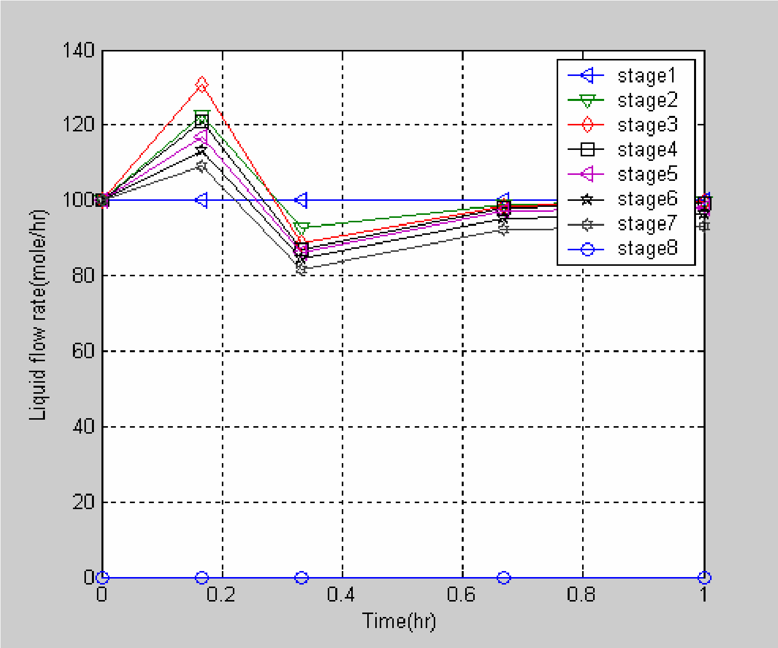


Figure 5-30 Liquid flow rate vs. batch time (Mc=1.25, Mp=0.25 mole)

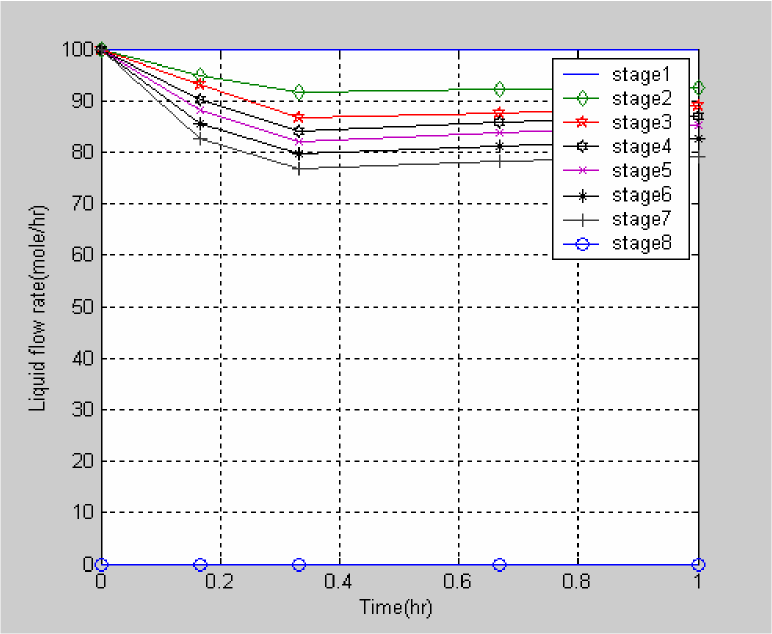


Figure 5-31 Liquid flow rate vs. batch time (Mc=20, Mp=5 mole)

Figures 5.32, 5.13 and 5.33 show the temperature profile with batch time on each stage at different hold up. The temperature profile decreases with increasing the hold up due to increasing the quantity of the low boiling point in the distillate section.

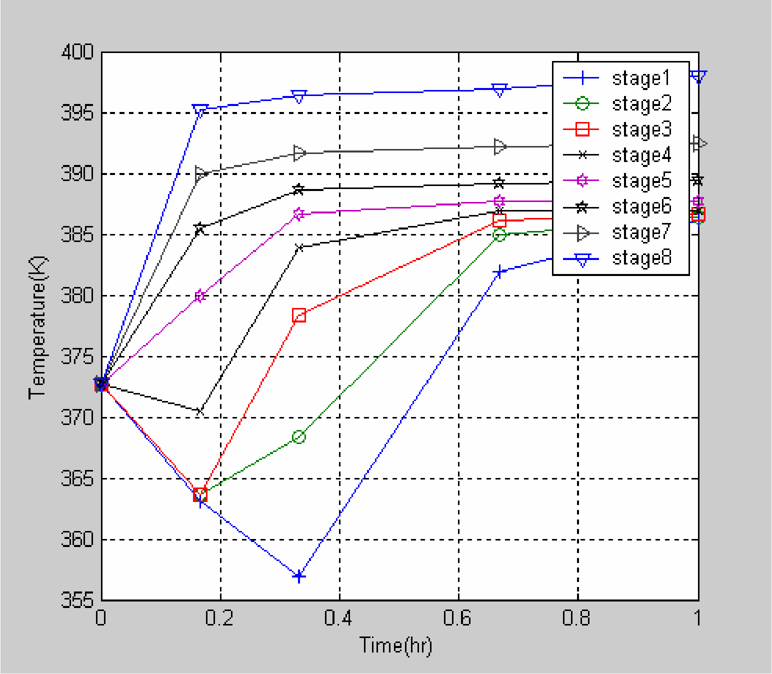


Figure 5-32 Temperature profile vs. batch time (Mc=1.25, Mp=0.25 mole)

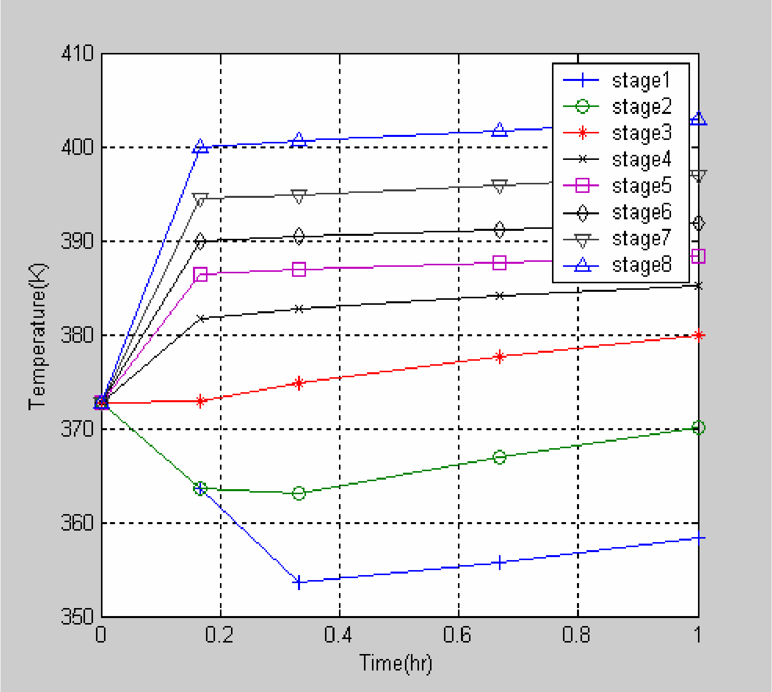


Figure 5-33 Temperature profile vs. batch time (Mc=20, Mp=5 mole)

The still hold up is changed when changing the condenser and plates hold up, as shown in figures 5.34 , 5.35 and 5.36 .Increasing the liquid hold up in the plates and in the condenser the still hold up decreases.

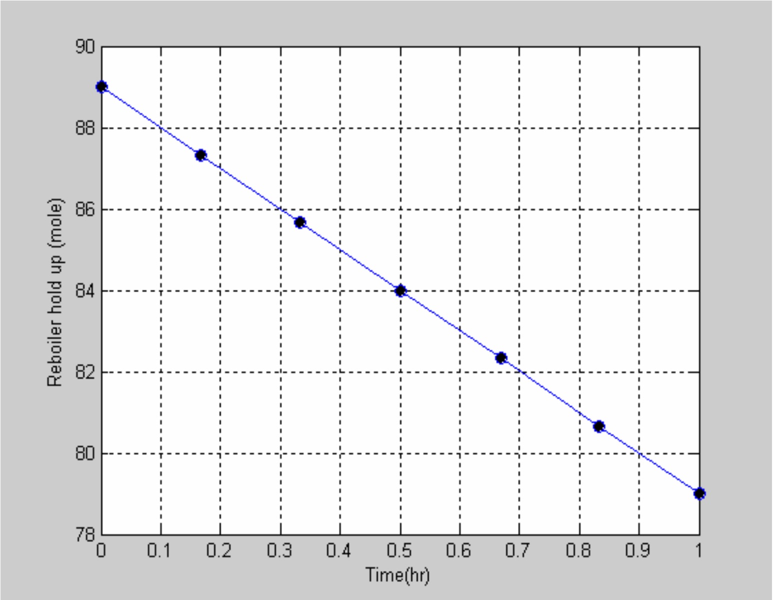


Figure 5-34 Still hold up vs. batch time (Mc=5, Mp=1 mole)

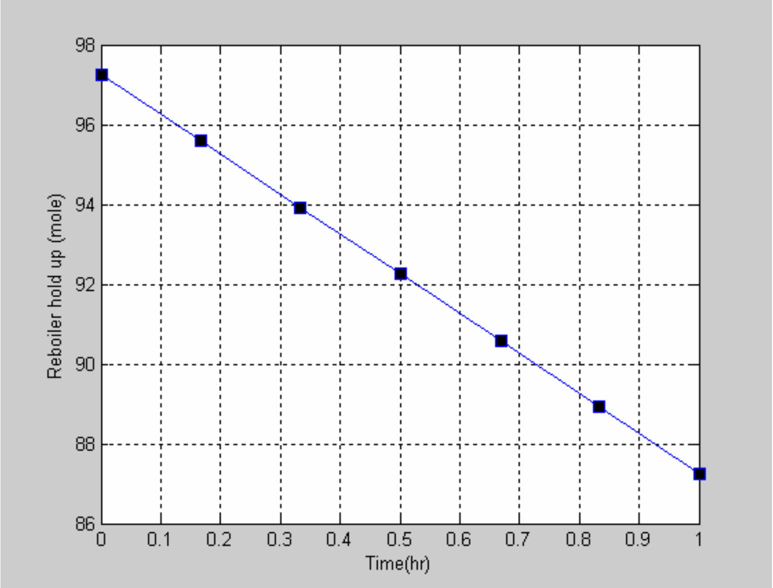


Figure 5-35 Still hold up vs. batch time (Mc=1.25, Mp=0.25 mole)

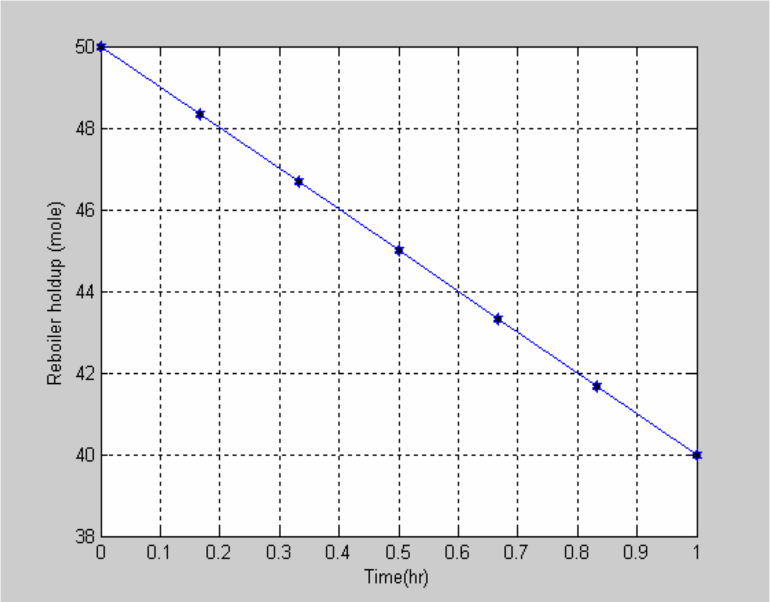


Figure 5-36 Still hold up vs. batch time (Mc=20, Mp=5mole)

The heat input to the still and heat out put from the condenser decreases with increasing the hold up. Table 5.5 this is due to decrease the hold up in the still and that mean less energy to less quantity.

Table 5.5 Heat input to the still and output from the condenser with different condenser and plates hold up

Hold up(mole)	Qstill (w)	Qcondenser(w)
1.25 , 0.25	209.3	202.2
5 , 1	201.83	194.74
20 , 5	186.17	178.55

5.5.4 Effect of Changing The Initial Composition

The effect of change the initial composition of the light component on the mole fraction, temperature profile and on the liquid and vapor profile and on heat duty has been studied in this section .

When the composition of the benzene is 0.2 in the still and 1 reflux ratio and 1 hr the composition of benzene is 0.11 in the distillate as shown in figure 5.37. In figure 5.4 when increasing the initial mole fraction of benzene to 0.3 the composition of it is 0.22 in the distillate at the end of batch time and when increasing the initial composition to 0.5 the composition of benzene is 0.38 in the distillate as shown in figure 5.38.

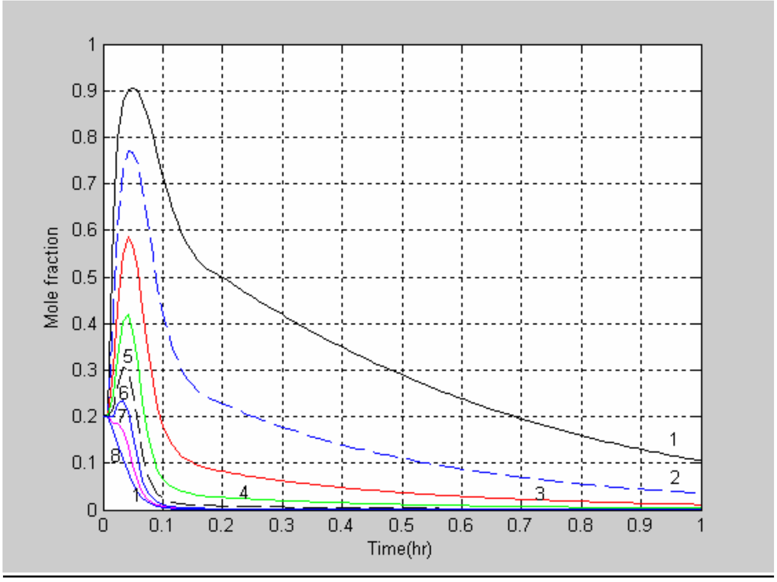


Figure 5-37 Mole fraction of the benzene vs. batch time at each stage, initial composition (Xb0=0.2 , Xt0=0.3 , Xeb0=0.5)

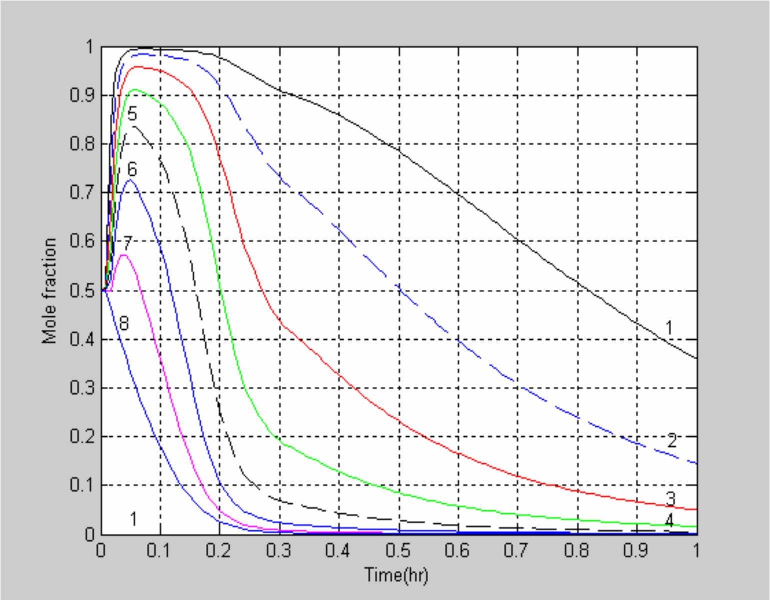


Figure 5-38 Mole fraction of the benzene vs. batch time at each stage, initial composition (Xb0=0.5 , Xt0=0.3 , Xeb0=0.2)

Figures 5.39 , 5.6 and 5.40 shows the composition of the toluene with different initial composition. When increasing the initial composition of the light component the composition of toluene is decreases

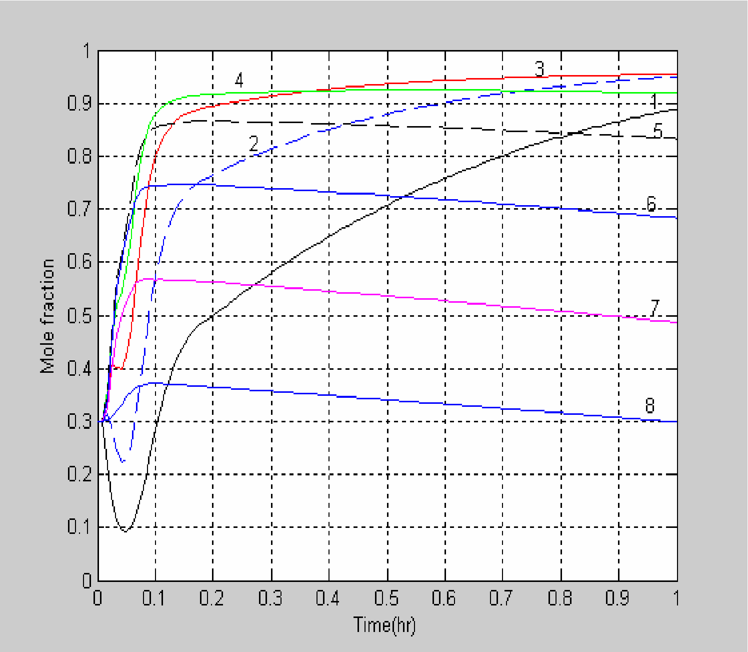


Figure 5-39 Mole fraction of the toluene vs. batch time at each stage, initial composition (Xb0=0.2 , Xt0=0.3 , Xeb0=0.5)

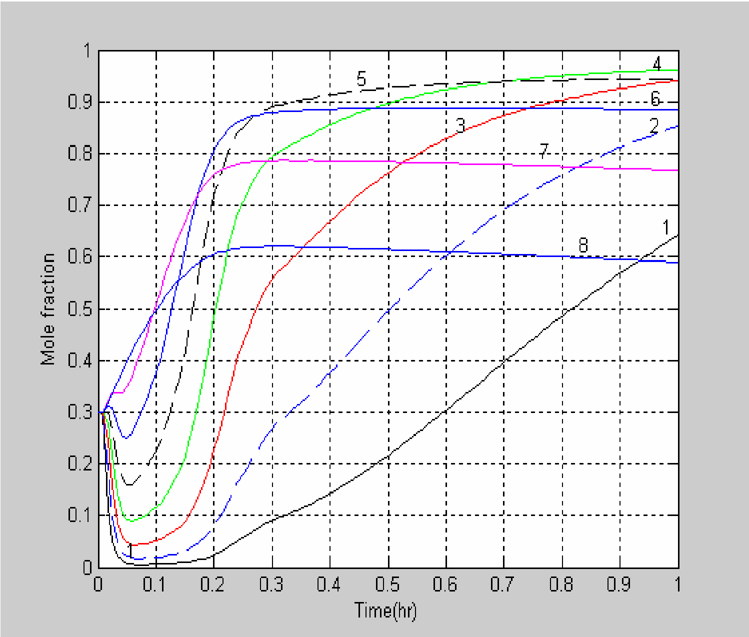


Figure 5-40 Mole fraction of the toluene vs. batch time at each stage, initial composition (Xb0=0.5 , Xt0=0.3 , Xeb0=0.2)

When increasing the initial composition of ethylebenzene from 0.2,0.3 to 0.5 as shown in figures 5.41 , 5.5 and 5.42 the composition of ethylebenzene increasing the mole fraction of ethylebenzene in distillate because the light component has the small initial composition and it is consumed from the tower so the heavy component began boil and approach from the distillate section.

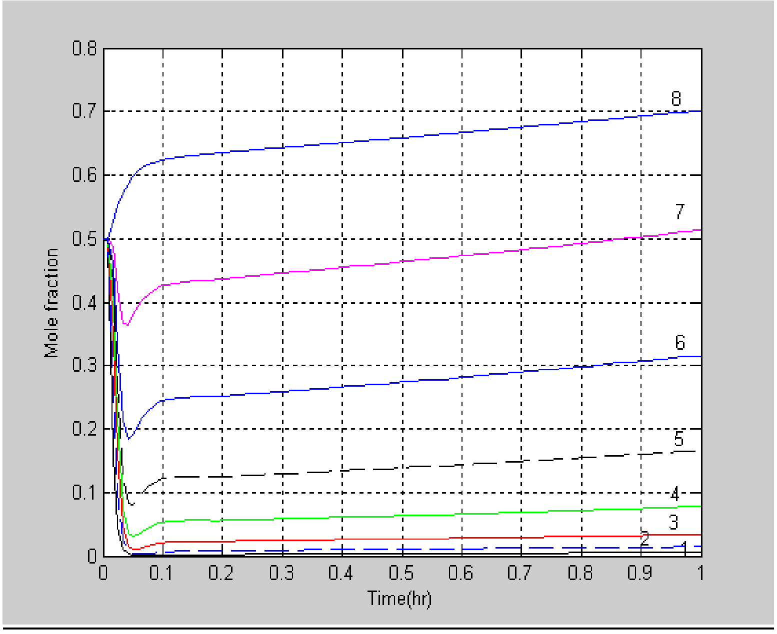


Figure 5-41 Mole fraction of the ethylebenzene vs. batch time at each stage, initial composition (Xb0=0.2 , Xt0=0.3 , Xeb0=0.5)

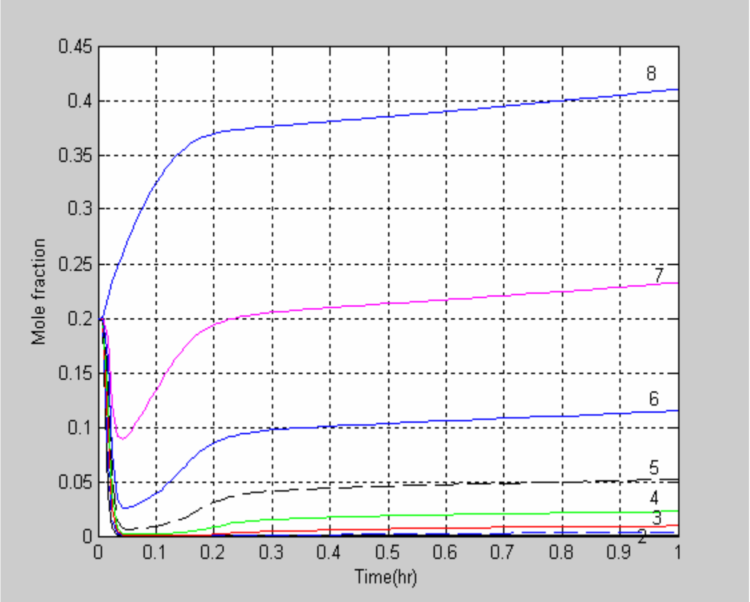


Figure 5-42 Mole fraction of the ethylebenzene vs. batch time at each stage , initial composition (Xb0=0.5 , Xt0=0.3 , Xeb0=0.2)

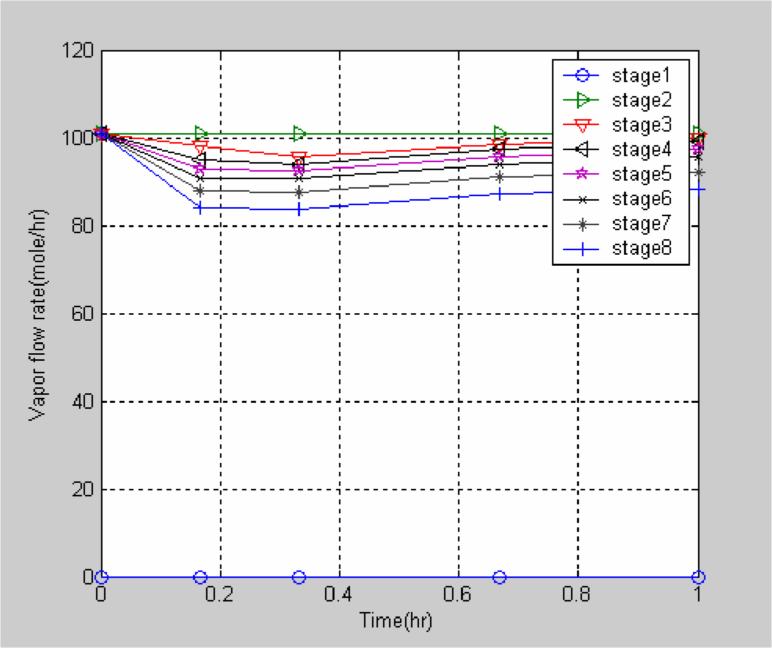


Figure 5-43 Vapor flow rate vs. batch time at each stage , initial composition (Xb0=0.2 , Xt0=0.3 , Xeb0=0.5)

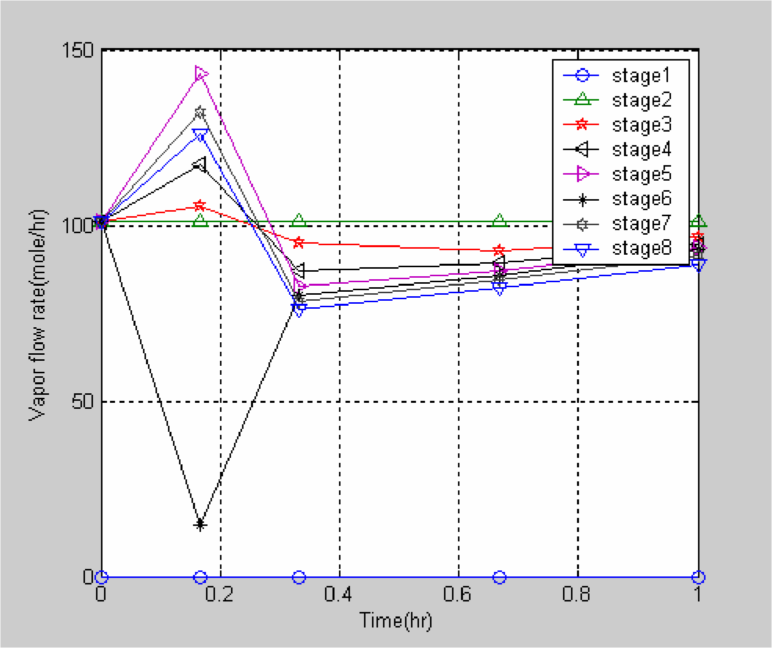


Figure 5-44 Vapor flow rate vs. batch time at each stage, initial composition (Xb0=0.5 , Xt0=0.3 , Xeb0=0.2)

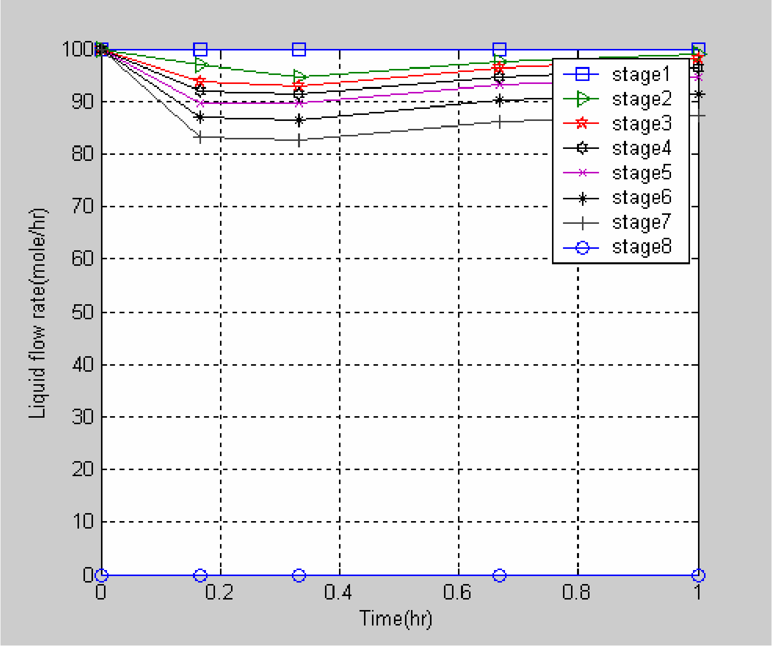


Figure 5-45 Liquid flow rate vs. batch time at each stage, initial composition (Xb0=0.2 , Xt0=0.3 , Xeb0=0.5)

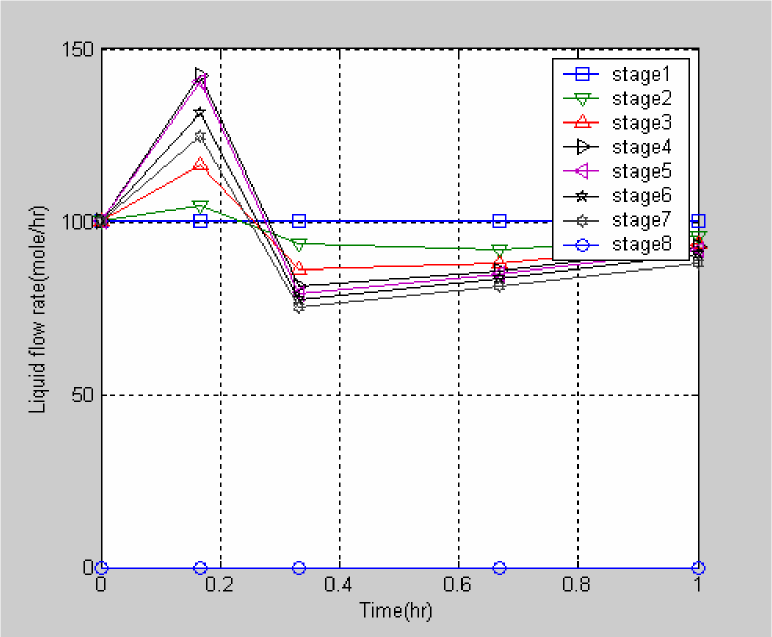


Figure 5-46 Liquid flow rate vs. batch time at each stage, initial composition (Xb0=0.5 , Xt0=0.3 , Xeb0=0.2)

The temperature in the distillate is changed when the initial composition of the lightest component is changed . Figures 5.47 , 5.13 and 5.48 show the temperature profile with batch time in each stage ,in this figure we can conclude the temperature of the trays is decrease with increasing the initial composition of the light component because it is has the low boiling point.

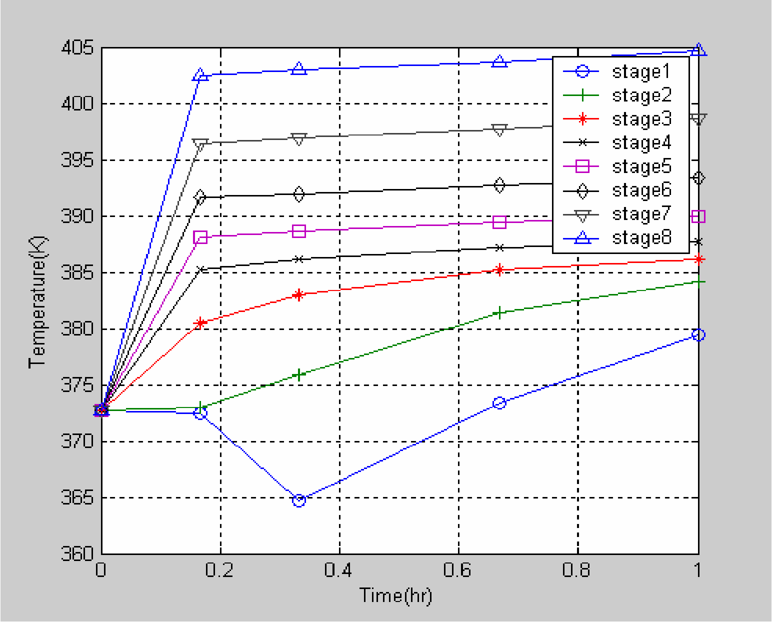


Figure 5-47 Temperature profile vs. batch time at each stage, initial composition (Xb0=0.2 , Xt0=0.3 , Xeb0=0.5)

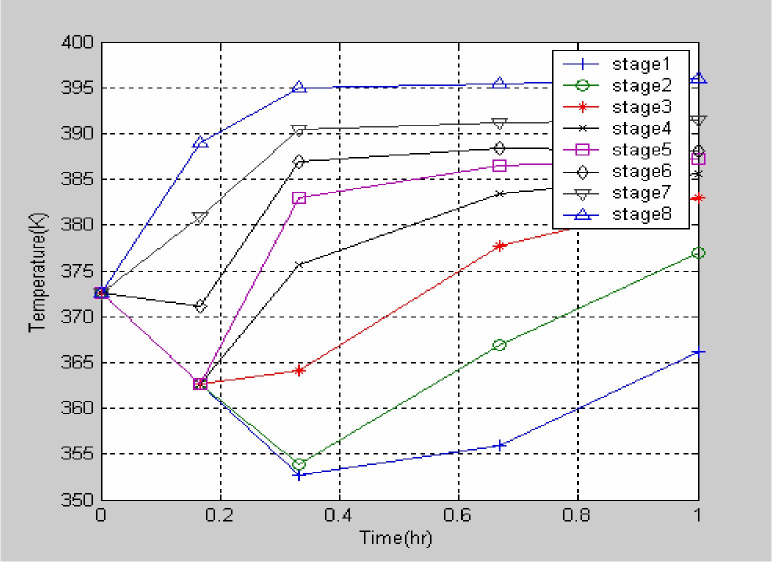


Figure 5-48 Temperature profile vs. batch time at each stage , initial composition (Xb0=0.5 , Xt0=0.3 , Xeb0=0.2)

The heat input to the still and output from the condenser at the end of the batch time is dencrease with increasing the initial composition of the light component as shown in table 5.6. This due to the light component has less boiling point.

Table 5.6 Heat input to the still and output from the condenser with different composition

initial composition	**Qstill (w)**	**Qcondenser(w)**
0.2,0.3,0.5	208.43	199.33
0.3,0.4,0.3	201.83	194.74
0.5,0.3,0.2	194.29	188.75

Chapter Six
Conclusions and Suggestions for Future Work

6.1 Conclusions

The following conclusions have been drawn from this work regarding the conventional batch distillation column:

1- The results obtained from the developed model using short-cut method gives a good agreement with those in reference [1].

2- The results of the simulation model developed using rigorous method give good agreements with the experimental data [3] and with the model developed by [2].

3- The NRTL and UNIFAC liquid phase activity coefficient models are the most appropriate model to describe the non-ideality of Benzene – Toluene – Ethylebenzene ternary mixture.

4- The reflux ratio has the major effect on the separation of BTEb mixture. Therefore any reflux ratio less 4 can gives better results.

5- The selection batch time for the separation of BTEb system is important, so any batch time less 1 hr give good result.

6- To obtain a good result for the mixture the lower value for the hold up in condenser (1.25 mole) and plates (0.25mole) give high purity of benzene with less time.

7- Selection of the initial composition in the still is very important in designing the non ideal batch distillation column. The purity of top and bottom products depends on the initial feed composition for the light and heavy components. So when the light component has higher initial composition in the still give a high purity of the light component in distillate in less batch time.

6.2 Suggestions for Future Work

For the future work, the following suggestions are put forward :

1- Modification the computer program by taking the non ideality of vapor phase into account.

2- Using the ASOG model in prediction the vapor-liquid equilibria and compared the result with UNIFAC model.

3- Predict the parameters have been used in liquid phase activity coefficient from infinite – dilution activity coefficients that predicted by the method of Pierotti et al.

4- Extending this model to study the dynamics and optimization non ideal distillation columns, such as pressure swing distillation, salt distillation azeotropic and extractive distillation.

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Appendix A

Table A.1 Properties of the component

Component	Heat of formation (J/mole)	Boiling point (K)	Molecular weight	Density (Kg/m³)	Heat of vaporization (J/mol)
Benzene	49080	353.25	78.114	885	30781
Toluene	12180	383.75	92.141	867	33201
Ethylebenzene	-12668	409.75	106.168	867	35588
Hexane	-166920	341.85	86.178	659	28872
Heptane	-187780	371.55	100.25	684	31719
Octane	-208750	398.75	114.232	703	34436

Table A.2 Specific heat capacity of liquid.

Component	$A_{i,Cp}$	$10^3\,B_{i,Cp}$	$10^6\,C_{i,Cp}$
Benzene	129.44	-169.5	647.81
Toluene	140.41	-152.3	695
Ethylebenzene	133.16	44.507	396.45
Hexane	41.653	-210.32	427.20
Heptane	22.626	-100.75	192.71
Octane	33.866	-172.60	349.17

Table A.3 Specific heat capacity of vapor.

Component	$A_{i,Cp}$	$10\,B_{i,Cp}$	$10^4\,C_{i,Cp}$	$10^8\,D_{i,Cp}$
Benzene	-33.917	4.743	-3.017	7.13
Toluene	-24.355	5.124	-2.765	4.911
Ethylebenzene	-43.099	7.071	-4.81	13
Hexane	-4.413	5.819	-3.118	8.084
Heptane	-5.146	6.761	-3.650	7.657
Octane	-6.096	7.712	-4.195	8.855

Table A.4 Parameters of Wilson equation

Benzene (1)	Toluene (2)	Ethylbenzene (3)
V_1=89.41 cm^3/mol	V_2=106.85 cm^3/mol	V_3=123.07 cm^3/mol
$A_{11}=\lambda_{11}-\lambda_{11}=0$	$A_{12}=\lambda_{12}-\lambda_{11}=-423.437$	$A_{13}=\lambda_{13}-\lambda_{11}=789.146$
$A_{21}=\lambda_{21}-\lambda_{22}=1646.709$	$A_{22}=\lambda_{22}-\lambda_{22}=0$	$A_{23}=\lambda_{23}-\lambda_{22}=1384.090$
$A_{31}=\lambda_{31}-\lambda_{33}=-733.790$	$A_{32}=\lambda_{32}-\lambda_{33}=-1131.223$	$A_{33}=\lambda_{33}-\lambda_{33}=0$

Table A.5 Parameters of NRTL equation

Benzene (1)	Toluene (2)	Ethylbenzene (3)
$A_{11}=g_{11}-g_{11}=0$	$A_{12}=g_{12}-g_{22}=1910.423$	$A_{13}=g_{13}-g_{33}=-423.966$
$A_{21}=g_{21}-g_{11}=-811.861$	$A_{22}=g_{22}-g_{22}=0$	$A_{23}=g_{23}-g_{33}=-1208.87$
$A_{31}=g_{31}-g_{11}=389.236$	$A_{32}=g_{32}-g_{22}=1333.039$	$A_{33}=g_{33}-g_{33}=0$
$\alpha_{11}=0$	$\alpha_{21}=0.304$	$\alpha_{11}=0$
$\alpha_{12}=0.304$	$\alpha_{22}=0$	$\alpha_{11}=0$
$\alpha_{13}=0.283$	$\alpha_{11}=0$	$\alpha_{33}=0$

Table A.6 Parameters of UNIQUAC equation

Benzene (1)	Toluene (2)	Ethylbenzene (3)
$A_{11}=u_{11}-u_{11}=0$	$A_{12}=u_{12}-u_{22}=-771.757$	$A_{13}=u_{13}-u_{33}=-513.547$
$A_{21}=u_{21}-u_{11}=4723.19$	$A_{22}=u_{22}-u_{22}=0$	$A_{23}=u_{23}-u_{33}=144.557$
$A_{31}=u_{31}-u_{11}=770.656$	$A_{32}=u_{32}-u_{22}=-323.13$	$A_{33}=u_{33}-u_{33}=0$
$r = 3.1878$	$r = 3.9228$	$r = 4.5972$
$q = 2.4$	$q = 2.968$	$q = 3.509$

Table A.7 Parameters of UNIFAC equation

Benzene(1)		Toluene(2)		Ethylebenzene(3)		
Group	K	R_k	Q_k	V_{k1}	V_{k2}	V_{k3}
ACH	10	0.5313	0.4	6	5	5
ACCH3	12	1.2663	0.968	0	1	0
ACCH2	13	1.0396	0.66	0	0	1
CH3	1	0.9011	0.848	0	0	1
$a_{10,10}=a_{12,12}=a_{13,13}=0$	$a_{10,12}=167$	$a_{10,13}=167$	$a_{10,1}=-11.12$	$a_{12,10}=-146$	$a_{12,13}=0$	$a_{12,1}=-69.7$
$a_{13,10}=-146$	$a_{13,12}=0$	$a_{13,1}=-69.7$	$a_{1,10}=61.130$	$a_{1,12}=76$	$a_{1,13}=76.5$	$a_{1,1}=0$

Table A.8 Parameters of Antoine equation

Component	$A_{i,VP}$	$B_{i,VP}$	$C_{i,VP}$
Benzene	15.9008	2788.51	-52.36
Toluene	16.0137	3096.52	-53.67
Ethylbenzene	16.0195	3272.47	-59.95

Table A.9 Critical properties

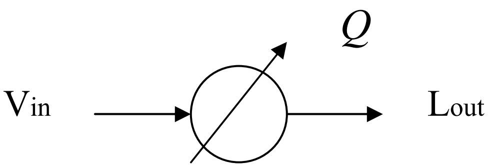
Component	T_c (K)	P_c (bar)	V_c (m^3/kmol)	Z_c	ω
Benzene	562.1	48.9	0.259	0.271	0.212
Toluene	591.7	41.1	0.316	0.264	0.262
Ethylbenzene	617.1	36.1	0.374	0.2632	0.302

Appendix B (B.1)

Single stream contain C component

Equation	Number of equation
Composition	C-1
Temperature	1
Pressure	1
total flow rate	1
Mole fraction constraints	1
	C+3

Total condenser



Degree of freedom = number of variables – number of equations

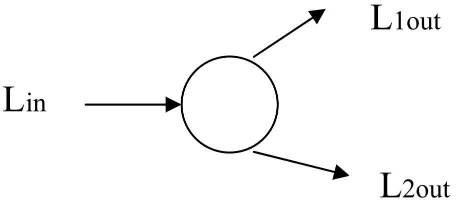
$N_D=N_V-N_E$

$N_V=2*(C+3)+1=2C+7$

Equation	Number of equation
Component material balances	C-1
Total material balances	1
Enthalpy balances	1
Mole fraction constraint	2
	NE=C+3

$N_D= 2c+7 – (C+3) =C+4$

Divider

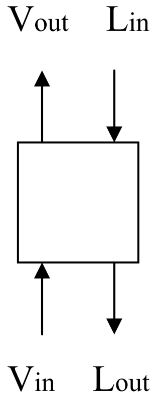


$N_V=3*(C+3)+1=3C+10$

Equation	Number of equation
Component material balances	2*(C-1)
Total material balances	1
Enthalpy balances	1
Mole fraction constraint	3
Pressure equality	1
Temperature equality	1
	NE=2C+5

$N_D= 3C+10 – (2C+5) =C+5$

Adiabatic equilibrium stage

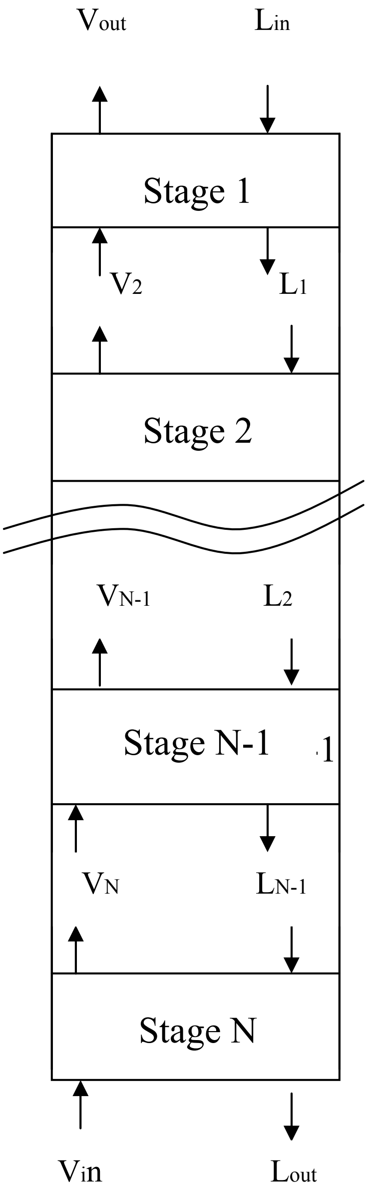


$N_V=4*(C+3=4C+12$

Equation	Number of equation
Component material balances	C-1
$L_{in}(x_i)_{L_{in}}+V_{in}(y_i)_{V_{in}}=L_{out}(x_i)_{L_{out}}+V_{out}(y_i)_{V_{out}}$	
Total material balances, $L_{in}+V_{in} =L_{out} +V_{out}$	1
Adiabatic enthalpy balances,	1
$H_{L_{in}}L_{in}+H_{V_{in}}V_{in} =H_{L_{out}}L_{out} +H_{V_{out}}V_{out}$	
Mole fraction constraint	4

Pressure equality, $P_{Vout}=P_{Lout}$	1
Temperature equality, $T_{Vout}=T_{Lout}$	1
Phase equilibrium relationships, $(y_i)_{Vout}=k_i(x_i)_{Lout}$	C
	$N_E=2C+6$

$N_D=4C+12-(2C+7)=2C+5$



$(N_V)_{unit}=\Sigma(N_V)_e-N_R*(C-3)+N_A$

$(N_V)_{unit}=N(4C+12)-[2(N-1)(C+3)]+1$

$(N_V)_{unit}=2NC+6N+2C+7$

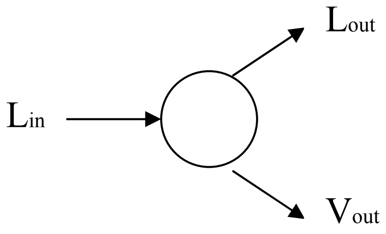
$(N_E)_{unit}=\Sigma(N_E)_e-N_R$

$(N_E)_{unit}=N(2C+7)-2(N-1)$

$(N_E)_{unit}=2NC+5N+2$

$(N_D)_{unit}= (N_V)_{unit}- (N_E)_{unit}=N+2C+5$

Partial reboiler



$N_V=3*(C+3)+1=3C+10$

Equation	Number of equation
Component material balances $L_{in}(x_i)_{Lin} = L_{out}(x_i)_{Lout}+V_{out}(y_i)_{Vout}$	C-1
Total material balances, $L_{in} = L_{out} + V_{out}$	1
Adiabatic enthalpy balances, $H_{Lin}L_{in} = H_{Lout}L_{out} + H_{Vout}V_{out}$	1
Mole fraction constraint	4
Pressure equality,$P_{Vout}=P_{Lout}$	1
Temperature equality,$T_{Vout}=T_{Lout}$	1
Phase equilibrium relationships,$(y_i)_{Vout}=K_i(x_i)_{Lout}$	C
	NE=2C+6

$N_D=3C+12-(2C+6)=C+4$

Total degree of freedom in batch distillation unit

$(N_D)_{total}=(N_D)_{Total\ condenser} + (N_D)_{Divider} + (N_D)_{Adiabatic\ stage} + (N_D)_{partial\ reboiler}$

$(N_D)_{total}= 5C+N+18$

Appendix C

Appendix (C.1): Wilson Model

```
%=================================================================
% input temperature in kelvin
T=input('Temperature(K):')
% Loop to input liquid mole fraction for Benzene(1)-Toluene(2)-ethylbenzene(3)
for i=1:3
m=input('Liquid mole fraction:')
x(i)=m
end
R=1.98721;
% Binary interaction force
a=[0,-423.437,789.146;1646.709,0,1384.09;-733.79,1131.223,0];
% Molar volume (cm3/mol)
V=[89.41,106.85,123.07];
for i=1:3
L1=0;
for j=1:3
A(i,j)=V(j)/V(i)*exp(-a(i,j)/(R*T));
L1=L1+x(j)*A(i,j);
end
N1(i)=L1;
end
for i=1:3
L2=0;
for j=1:3
L2=L2+x(j)*A (j,i)/N1(j);
end
N2(i)=L2;
gama(i)=exp(1-log(N1(i))-N2(i));
end
```

Appendix (C.2): NRTL Model

```
%==========================================================
% input temperature in kelvin
T=input('Temperature(K):')
% Loop to input liquid mole fraction for Benzene(1)-Toluene(2)-ethylbenzene(3)
for i=1:3
m=input('Liquid mole fraction:')
x(i)=m
end
% Binary interaction force
a=[0,1910.423,-423.966;-811.861,0,-1208.87;389.236,1333.038,0];
% purly emperical parameter for the system Benzene(1)-Toluene(2)-ethylbenzene(3)
F=[1,.304,.283;.304,1,.306;.283,.306,1];    R=1.98721;
 t=a./(R*T);
 g=exp(-t.*F);
for i=1:3
L1=0;   L2=0;
for j=1:3
L1=L1+(t (j,i)*x(j)*g(j,i));
L2=L2+(x(j)*g(j,i));
end
N1(i)=L1;     N2(i)=L2;
end
for i=1:3
L3=0;
for j=1:3
L3=L3+x(j)*g(i,j)/N2(j)*(t(i,j)-N1(j)/N2(j));
end
N3(i)=L3;
gama(i)=exp(N1(i)/N2(i)+N3(i));
end
```

Appendix (C.3): UNIQUAC Model

```
%==========================================================
% input temperature in kelvin
T=input('Temperature(K):')
% Loop to input liquid mole fraction for Benzene(1)-Toluene(2)-ethylbenzene(3)
for i=1:3
m=input('Liquid mole fraction:')
x(i)=m
end
R=8.314;
% Binary interaction force
u=[0,-771.757,-513.547;4723.19,0,144.557;770.656,-323.13,0];
r=[3.1878 3.9228 4.5972]';
q=[2.4 2.968 3.508]';
z=10;
qs=0;   rs=0;
for i=1:3
qs=qs+x(i)*q(i);
rs=rs+x(i)*r(i);
for j=1:3
t(i,j)=exp(-u(i,j)/(R*T));
end
L(i)=z/2*(r(i)-q(i))-(r(i)-1);
end
NL3=0;
for i=1:3
V(i)=q(i)*x(i)/qs;
B(i)=r(i)*x(i)/rs;
end
for i=1:3
NL1=0;
for j=1:3
```

```
NL1=NL1+(V(j)*t(j,i));
NL2(i,j)=V(j)*t(i,j);
end
N1(i)=NL1;
NL3=NL3+x(i)*L(i);
end
for i=1:3
NL4=0;
gama_C(i)=log(B(i)/x(i))+z/2*q(i)*log(V(i)/B(i))+L(i)-B(i)/x(i)*NL3;
for j=1:3
NL4=NL4+NL2(i,j)/N1(j);
end
N4(i)=NL4;
gama_R(i)=q(i)*(1-log(N1(i))-N4(i));
gama(i)=exp(gama_C(i)+gama_R(i));
 end
```

Appendix (C.4): UNIFAC Model

```
%=========================================================

% input temperature in kelvin
T=input('Temperature(K):')
% Loop to input liquid mole fraction for Benzene(1)-Toluene(2)-ethylbenzene(3)
for i=1:3
m=input('Liquid mole fraction:')
x(i)=m
end
R=8.314;
%UNIFAC constants for(ACH,ACCH3,ACCH2,CH3)
k=[10 12 13 1];
Rk=[.5313 1.2663 1.0396 .9011];
Qk=[.4 .968 .66 .848];
Vk=[6 5 5;0 1 0;0 0 1;0 0 1];
qs=0;   rs=0;
for i=1:3
for j=1:4
qs=qs+ Vk (j,i)* Rk (j);
rs=rs+ Vk (j,i)* Qk (j);
end
q(i)=qs;
r(i)=rs;
end
rx=0; qx=0;
for i=1:3
rx=rx+r(i)*x(i);
qx=qx+q(i)*x(i);
end
for i=1:3
j(i)=r(i)./rx;
```

```
l(i)=q(i)./qx;
end
for i=1:4
for m=1:3
Gk(i,m)= Vk(i,m)*Qk(i);
end
end
ok=0
for i=1:4
for m=1:3
ok= ok+ Gk(i,m)*x(m);
end
Ok(i)=ok;
end
A=[0 167 167 -11.120;-146.8 0 0 -69.7;-146 0 0 -69.7;61.13 76.5 76.5 0];
H=exp(-A./(R*T));
s11=H(1,1)*Gk(1,1)+H(1,2)*Gk(2,1)+H(1,3)*Gk(3,1)+H(1,4)*Gk(4,1);
s12=H(2,1)*Gk(1,1)+H(2,2)*Gk(2,1)+H(2,3)*Gk(3,1)+H(2,4)*Gk(4,1);
s13=H(3,1)*Gk(1,1)+H(3,2)*Gk(2,1)+H(3,3)*Gk(3,1)+H(3,4)*Gk(4,1);
s14=H(4,1)*Gk(1,1)+H(4,2)*Gk(2,1)+H(4,3)*Gk(3,1)+H(4,4)*Gk(4,1);

s21=H(1,1)*Gk(1,2)+H(1,2)*Gk(2,2)+H(1,3)*Gk(3,2)+H(1,4)*Gk(4,2);
s22=H(2,1)*Gk(1,2)+H(2,2)*Gk(2,2)+H(2,3)*Gk(3,2)+H(2,4)*Gk(4,2);
s23=H(3,1)*Gk(1,2)+H(3,2)*Gk(2,2)+H(3,3)*Gk(3,2)+H(3,4)*Gk(4,2);
s24=H(4,1)*Gk(1,2)+H(4,2)*Gk(2,2)+H(4,3)*Gk(3,2)+H(4,4)*Gk(4,2);

s31=H(1,1)*Gk(1,3)+H(1,2)*Gk(2,3)+H(1,3)*Gk(3,3)+H(1,4)*Gk(4,3);
s32=H(2,1)*Gk(1,3)+H(2,2)*Gk(2,3)+H(2,3)*Gk(3,3)+H(2,4)*Gk(4,3);
s33=H(3,1)*Gk(1,3)+H(3,2)*Gk(2,3)+H(3,3)*Gk(3,3)+H(3,4)*Gk(4,3);
s34=H(4,1)*Gk(1,3)+H(4,2)*Gk(2,3)+H(4,3)*Gk(3,3)+H(4,4)*Gk(4,3);

N10=s11*x(1)+s21*x(2)+s31*x(3);
```

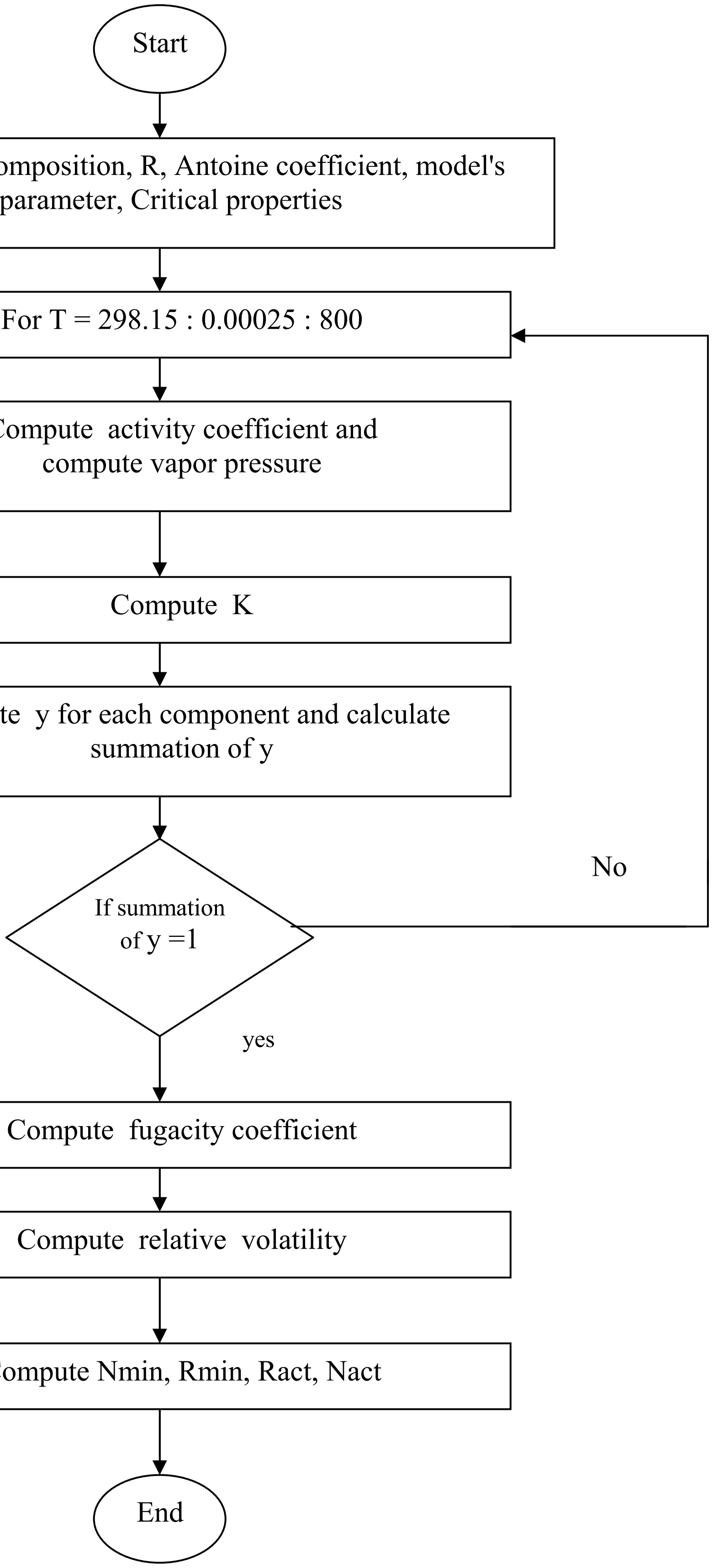
```
N12=s12*x(1)+s22*x(2)+s32*x(3);
N13=s13*x(1)+s23*x(2)+s33*x(3);
N1=s14*x(1)+s24*x(2)+s34*x(3);

u1=(1-j(1)+log(j(1))-5*q(1)*(1-(j(1)./l(1))+log(j(1)./l(1))));
u2=(1-j(2)+log(j(2))-5*q(2)*(1-(j(2)./l(2))+log(j(2)./l(2))));
u3=(1-j(3)+log(j(3))-5*q(3)*(1-(j(3)./l(3))+log(j(3)./l(3))));

O1=exp(q(1)*(1-log(l(1)))-((Ok(1)*(s11/N10)-Gk(1,1)*log(s11/N10))+(Ok(2)*(s12/N12)-Gk(2,1)*log(s12/N12))+(Ok(3)*(s13/N13)-Gk(3,1)*log(s13/N13))+(Ok(4)*(s14/N1)-Gk(4,1)*log(s14/N1))));

O2=exp(q(2)*(1-log(l(2)))-((Ok(1)*(s21/N10)-Gk(1,2)*log(s21/N10))+(Ok(2)*(s22/N12)-Gk(2,2)*log(s22/N12))+(Ok(3)*(s23/N13)-Gk(3,2)*log(s23/N13))+(Ok(4)*(s24/N1)-Gk(4,2)*log(s24/N1))));

O3=exp(q(3)*(1-log(l(3)))-((Ok(1)*(s31/N10)-Gk(1,3)*log(s31/N10))+(Ok(2)*(s32/N12)-Gk(2,3)*log(s32/N12))+(Ok(3)*(s33/N13)-Gk(3,3)*log(s33/N13))+(Ok(4)*(s34/N1)-Gk(4,3)*log(s34/N1))));

gama_1=exp(u1+O1);
gama_2=exp(u2+O2);
gama_3=exp(u3+O3);
```

Appendix (C.5): Virial Model

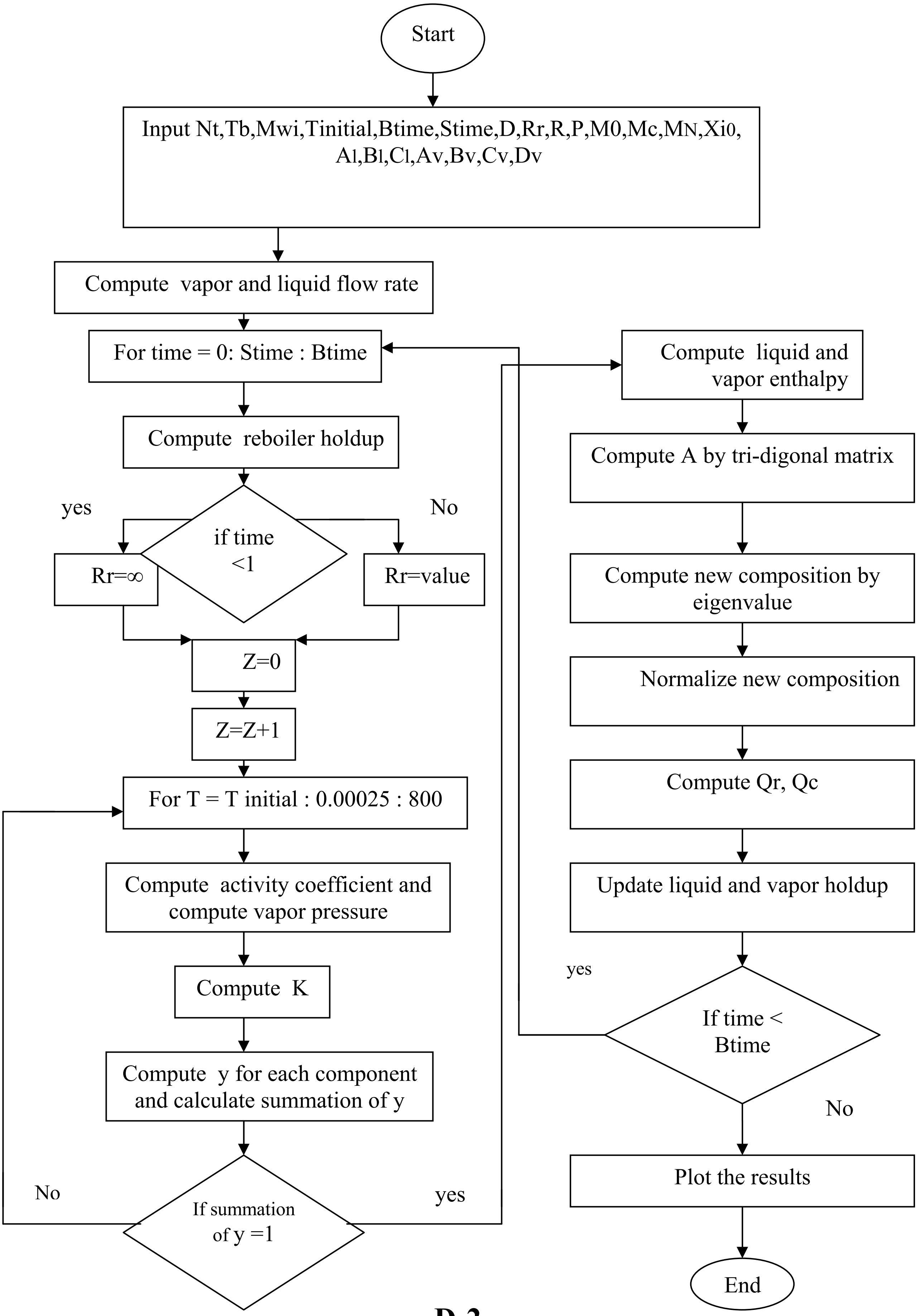
```
%=========================================================
% input temperature in kelvin
T=input('Temperature(K):')
% Loop to input vapor mole fraction for Benzene(1)-Toluene(2)-ethylbenzene(3)
for i=1:3
m=input('Vapor mole fraction:')
y(i)=m
end
R=0.08314;
P=1.01;
%critical properties
Tc=[562.1 591.7 617.1];
Pc=[48.9 41.1 36.1];
Vc=[0.259 0.316 0.374];
Zc=[0.271 0.264 0.2632];
w=[0.212 0.2621 0.3026];
Tr=T./Tc;
Bo=0.083-0.422./Tr.^1.6;
B1=0.139-0.172./Tr.^4.2;
for i=1:3
for j=1:3
Tcij(i,j)=(Tc(i)*Tc(j))^.5;
Zcij(i,j)=(Zc(i)+Zc(j))/2;
Vcij(i,j)=((Vc(i)^(1/3)+Vc(j)^(1/3))/2)^3;
Pcij(i,j)=Tcij(i,j)*R*Zcij(i,j)/Vcij(i,j);
wij(i,j)=(w(i)+w(j))/2;
Trij(i,j)=T /Tcij(i,j);
Boij(i,j)=0.083-0.422/Trij(i,j)^1.6;
B1ij(i,j)=0.139-0.172/Trij(i,j)^4.2;
Bij(i,j)=R*Tcij(i,j)/Pcij(i,j)*(Boij(i,j)+wij(i,j)*B1ij(i,j));
end
```

```
end
for k=1:3
for i=1:3
delta_ik(i,k)=2*Bij(i,k)-Bij(i,i)-Bij(k,k);
for l=1:3
delta_il(i,l)=2*Bij(i,l)-Bij(i,i)-Bij(l,l);
sum_delta(l)=y (i)*y (l)*(2*delta_ik(i,k)-delta_il(i,l));
end
sum_delta(i)=sum(sum_delta(l));
end
sum_delta(k)=sum(sum_delta(i));
fi(k)=exp(P/(R*T)*(Bij(k,k)+1/2*sum_delta(k)));
end
```

Appendix D (D.1)



Appendix D (D.2)



الخلاصة

لأهمية ابراج تقطير ذو الدفعات في المواد الكيمياوية والصناعات النفطية والدوائية لفصل الخليط السائل الى مكوناته النقية . تم التركيز في هذا البحث بتطوير نموذج طريقة استعمال برنامج حاسوب باستعمال طريقة (short-cut) وبرنامج حاسوب محاكاة باستعمال طريقة (rigorous) لتحليل خليط غير مثالي, متعدد المكونات باستعمال البرنامج الرياضي MATLAB6.5.

طريقة (short-cut) تستعمل لحساب الحد الادنى من المراحل باستعمال معادلة (Fenske) وحساب الحد الادنى من الراجع الجزئى باستعمال معادلة (Underwood) . العدد النظرى للمراحل المحتاجة لتقطير خليط من البنزين-التلوين-اثيل البنزين بحسب علاقة (Gillilland) التي تربط الحد الادنى من المراحل مع العدد النظري والذي استعمل في نموذج (rigorous) لحساب التركيز, درجة الحرارة و نسبة البخار والسائل المتدفق مع الزمن في كل صينية وكمية الطاقة المجهزة للبرج و وكمية الطاقة المنبعثة من المكثف.

النتائج المحصلة من كلا النموذجين أعطت تطابق جيد مع النتائج النظرية للموديل الرياضي والنتائج العملية.

عدة نماذج لمعامل الطور نشاط السائل مثل (Wilson, NRTL, UNIQUAC, UNIFAC) درست لخليط من البنزين-تلوين-أثيل البنزين والنموذج الملائم أختير طبقا" لنقاوة البنزين المنفصل في اعلى برج التقطير, النتائج المحصلة من UNIFAC , NRTL كانت أكثر قبولا في العمل الحالي. نموذج UNIFAC استعمل لانه الأحدث والثوابت المستعملة في هذا النموذج يمكن الحصول عليها بسهولة.

برج التقطير شغل تحت ضغط تشغيل ثابت وهو 1 ضغط جوي, وعدد المراحل النظرية هي 8 ودرجة الحرارة المحيط 298.15 K

تأثير العوامل المختلفة مثل نسبة الراجع الجزئي, وقت الدفعة, كمية العالق من السائل في كل صينية و في المكثف, الكمية الابتدائية للمادة المطلوبة في بداية العملية على اداء برج التقطير الغير مثالى درست لحساب التركيز, درجة الحرارة و نسبة البخار والسائل المتدفق مع الزمن في كل صينية وكمية الطاقة المجهزة للبرج و وكمية الطاقة المنبعثة من المكثف.

ان زيادة نسبة الراجع تسبب نقصان تركيز البنزين في اعلى البرج عند 0.5 hr مقارنة مع تركيز البنزين في اعلى البرج عند نقصان نسبة الراجع.

زيادة مدة التشغيل تسبب نقصان تركيز البنزين في اعلى البرج. تغير نسبة العالق من السائل في كل صينية وفي المكثف تسبب نقصان تركيز البنزين في اعلى البرج. ان زيادة النسبة الابتدائية للبنزين تؤدي الى زيادة تركيزه في اعلى البرج.

أحسن الظروف الملائمة لتشغيل برج تقطير الدفعة للحصول على نقاوة المنتج المطلوب كان نسبة الراجع الجزئي 1, وقت تشغيل دفعة اقل من 1 hr, كمية السائل العالق في المكثف وفي كل صينية هو 0.25 , 1.25 مول , على التوالي ونسبة التركيز الابتدائي للبنزين هو 0.5

شكر وتقدير

اولا وقبل كل شئ الحمد والشكر لله على تمام الصحة وقوة الايمان التي ساعدتني على تخطي جميع الصعاب التي واجهتها طيلة فترة البحث.

اود ان اعبر عن خالص شكري وتقديري وعرفاني بالجميل للمشرفة **ا.د. ندى بهجت النقاش** لما قدمته لي من اهتمام كبيروجهد بالغ ولما ابدته من توجيهات قيمة ساعدت على انجاز هذا العمل.

اود ان اشكر جميع منتسبي قسم الهندسة الكيمياوية واخص بالذكر **ا.د قاسم جبار سليمان** لابدائه المساعدة اللازمة اثناء هذا العمل.

ولا انسى ان اتقدم بجزيل الشكر والتقدير الى من ساندني وساعدني على تخطي الصعوبات خلال فترة البحث الى الذين لا مثيل لهم في الدنيا الى أبي وأمي الأعزاء، أخوتي وأخواتي.

م. اسراء سعد نوشي

محاكاة جهاز التقطير
ذو الدفعات

رسالة

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

من قبل

أسراء سعد نوشي

(بكالوريوس علوم في الهندسة الكيمياوية 2004)

رمضان 1428 هـ

أيلول 2007 م