SIMULATION OF BATCH REACTIVE DISTILLATION FOR PRODUCING OF METHYL ACETATE

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Requirements for the Degree of Master of
Science in Chemical Engineering

by

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CERTIFICATION

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Abstract

Batch distillation process is one of the major operations in the chemical, petroleum and pharmaceutical industries for the separation of liquid mixtures into their pure components

The present work is concerned with constructing a simulation computer programs to analyze multi-components, multistage batch distillation without and with chemical reaction.

The rigorous method was used to build the simulation computer programs for non ideal mixtures, by using $MATLAB_{6.1}$ package to solve MESH and MESHR equations. The validity and accuracy of the results obtained from the developed computer programs for both without and with chemical reaction were checked with Elgue [55] using the esterfication of acetic acid with methanol methyl acetate and water. The results obtained gave good agreement with accuracy 4.7% for maximum producing of methyl acetate at batch time 0.4hr, which are shown the programs in appendix B (B-1, B-2, and B-3).

The influence of various parameters, such as number of stages, batch time, and liquid holdup upon the performance of the batch distillation column operating with chemical reaction were studied. Through vapor and liquid profiles, temperature profile, reaction rate profile, and liquid composition profiles.

The results obtained for the non ideal reactive multistage batch distillation column show that the overall conversion to methyl- acetate is 49.41%, and the distillate composition is 24.7% for methyl acetate, with

90.7% recovery, when reflux ratio is 2.5, the number of stages is 6 theoretical stages with constant liquid holdup and batch time are 1.7hr. When decreasing the number of theoretical stages to 4 the mole fraction of methyl- acetate in the distillate decreased to 5% and the overall conversion becomes 10%. Increasing the number of theoretical stages to 8 the overall conversion to methyl- acetate is 5.1% with 10.2% conversion at batch time of 1.7hr. Decreasing the batch time to 1hr the distillation composition decreased to 22.5% with overall conversion of methyl- acetate of 45%, for 6 theoretical stages and 2.5 reflux ratio and constant holdup. Increasing the batch time to 3hrs the overall conversion becomes 43.4% and the mole fraction of methyl acetate decreased to 21.7%.

The best design condition obtained from the present work was 1.7hr batch time, 6 theoretical of stages, 2.5 reflux ratio to give 90.7% recovery of methyl acetate and 49.41% overall conversion with constant liquid holdup through out the tower.

Changing the liquid holdup throughout the tower will affect the performance of tower and increases the overall conversion to methyl acetate to 50.4% and the distillate composition to 25.2%.

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Nomenclature

Symbols	***Definitions***	***Units***
A, B, C, and D	Constant of ideal gas specific heat, from equation (2.41)	—
$Btime$	Batch time	hr
Cc_i	Concentration of each component i at any time from equation (3.19)	—
Cm_o	Initial concentration for chemical reaction from equation (3.19.1)	—
Cp	Specific heat from equation (3.20)	cal/mol.K
$C1_i, C2_i,$ $C3_i, C4_i$	Constant molar density	—
D	Distillate flow rate from equation (3.22)	Mole/hr
$Dens$	Density from equation (3.15)	kg/m^3
E	Activation energy from equation (3.19)	kJ/kmol
Gc	Constant volume holdup in the condenser from equation (3.16)	m^3
Gp	Constant volume holdup in the plates from equation (3.15)	m^3
H	Enthalpy	J/mol
H^o_{fi}	Enthalpy of formation from equation (3.21)	J/mol
H_L	Enthalpy of liquid phase from equation (2.37)	J/mol
HLi	Total enthalpy of liquid phase from equation (2.38)	J/mol
H_{mix}	Enthalpy of mixing from equation (2.39)	J/mol
H^o_v	Ideal gas state enthalpy from equation (2.36)	J/mol

H_V	Enthalpy of vapor phase from equation (2.36)	J/mol
HV_a	Total enthalpy of vapor phase from equation (2.43)	J/mol
L	Liquid flow rate	mole/hr
L_D	Liquid molar density	—
L_V	Latent heat of vaporization	kJ/kgmol
K	Distribution coefficient from equation 3.13	—
K_{eq}	Equilibrium constant for chemical reaction from equation (3.19)	—
K_{ester}	Pre-exponential factor from equation (3.19)	1/kgmol.min H_2S0_4.l
Mc	Liquid holdup in the condenser section from equation (3.16)	mole
Mn	Liquid holdup on each tray from equation (3.15)	mole
Mt	Liquid holdup in the reboiler section from equation (3.17)	mole
N	Number of feed component.	—
Nt	Total number of stages	—
P	Pressure	mmHg
Q_r	Inter-heater at the reboiler section	kJ/min
Rate	Rate of reaction from equation (3.19)	mole/hr
r_i	Molecular Vander walls volume from equation (2.28)	—
Rr	Reflux ratio	—
$Stime$	Step time	sec

T	Temperature	K
V	Vapor flow rate	mole/hr
v	Molecular Volume from equation (2.13)	—
vol	Volume of one tray	m^3
$V_{reboiler}$	Volume of liquid in the reboiler section from equation (3.18)	cm^3
Wm	Molecular Weight from equation (3.15)	kg/kgmole
x_i	Liquid mole fraction from equation (2.2)	—
X	The experimental conversion (from reference [55])	—
y_i	Vapor mole fraction from equation (2.2)	—

Greek Letter

$\hat{\Phi}_{Vi}$	Vapor phase fugacity coefficient from equation (2.2)
$\hat{\Phi}_{Li}$	Liquid phase fugacity coefficient from equation (2.2)
P_i^o	Partial pressure from equation (2.14)
γ	Liquid phase activity coefficient from equation (2.8)
Δ	Change of Differences

Subscript

i	Component i in the mixture
j	Component i in the mixture at stage j
k	Type of functional group
m	Number of stages
V	Vapor phase
L	Liquid phase
f	Feed

Superscript

^{o}	Pure component

id	Ideal solution
eq	equilibrium
mix	Mixing

Abbreviation

MESH	Material balance, Equilibrium, mole fraction Summations, enthalpy balance
MESHR	Material balance, Equilibrium, mole fraction Summations, enthalpy balance, Reaction rate
NRTL	Non-random, two liquid model
BRD	Batch reactive distillation
VLE	Vapor-Liquid Equilibrium

Chapter one
Introduction

1.1 Introduction

In recent years, increasing attention has been directed towards batch reactive distillation processes as alternative to conventional processes. This has led to the development of a variety of techniques for simulating reactive multistage batch columns; however the problem of design and synthesis of batch reactive distillation processes have not yet been addressed.

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

Reactive distillation has proved to be an important process alternative to the conventional reactor-separator configuration. Advantages of reactive distillation and flexibility of a batch process can be combined in batch reactive distillation. The yield and selectivity target is determined for batch reactive distillation device, and the effect of operating parameters on yield and selectivity is studied. The advantage of using batch reactive distillation equipment is more significant for systems with fast side reactions. Comparison of these estimates with those for conventional reactors is useful for quick screening of process alternatives during process synthesis [1].

The aim of this work is to develop a simple model to quantify the performance of a batch reactive distillation device. The model considers stage-by-stage calculations for the rectification column. The model assumes that the specified distillate composition is always achievable for the given column configuration; e.g. for simple mixtures without azeotropes, the lightest boiling component can be removed as distillate. However, in mixtures with azeotropes, it is not always possible to meet the specified distillate composition; for these mixtures a vapor-liquid equilibrium model is necessary to assess the feasibility of separation and also to determine the boiling point of the reaction mixture. Also this work presents a method for the rigorous solution of problems in multi-component multistage batch with and without reactive distillation. In batch reactive distillation where the reaction occurs on each stage in a column, the material balance for each component and the heat balance on each stage will give a set of algebraic equations which may be expressed in a matrix if the effect of chemical reaction in the basic relation is included. For agreement between the assumed and the calculated conversion of reaction, no method has more stable and rapid convergence than does the iterative method.

Chapter two
Literature Survey

2.1 Introduction

Distillation process is one of the major operations in the chemical, petroleum and pharmaceutical industries in the separation of liquid mixtures into their pure components. Distillation process is either batch or continuous.

Batch distillation is one of the oldest separation processes. It is used in the chemical industries and has several advantages. It is often used in industries where high purity products are required than continuous distillation [2].

The combination of chemical reaction with distillation in only one unit is called reactive distillation. The performance of reaction with separation in one piece of equipment offers distinct advantages over the conventional, sequential approach. Especially for equilibrium limited reactions such as esterification and ester hydrolysis reactions, conversion can be increased far beyond chemical equilibrium conversion due to the continuous removal of reaction products from the reactive zone [3].

Reactive distillation has proved to be an important process alternative to the conventional reactor-separator configuration. Advantages of reactive distillation and flexibility of a batch process can be combined in batch reactive distillation [1].

2.2 Distillation Process

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 [4].

Distillation is based on the fact that the vapor of a boiling mixture will be richer in the components that have lower boiling points. Therefore, when this vapor is cooled and condensed, the condensate will contain more volatile components. At the same time, the original mixture will contain more of the less volatile material. Distillation columns are designed to achieve this separation efficiently [4].

Distillation is the most common separation technique. It consumes enormous amounts of energy, both in terms of cooling and heating requirements and it can contribute to more than 50% of plant operating costs [5].

2.2.1 Continuous Distillation Operation

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 or if a flexible multi-purpose facility is required. In general, continuous distillation column will be chosen for separating large feed flow rates [5].

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 into several light and heavy fractions, depending on their varying boiling points [6].

Continuous distillation process is used for the separation of bulk chemicals where high throughput and few feed or product changes are expected [7].

Continuous distillation achieves objective by the creation of two or more coexisting zones which differ in temperature, pressure, component composition position, and/or phase state. Each molecular species in the mixture to be separated reacts in a unique way to differing environments offered by these zones as shown in Figure 2.1 [5].

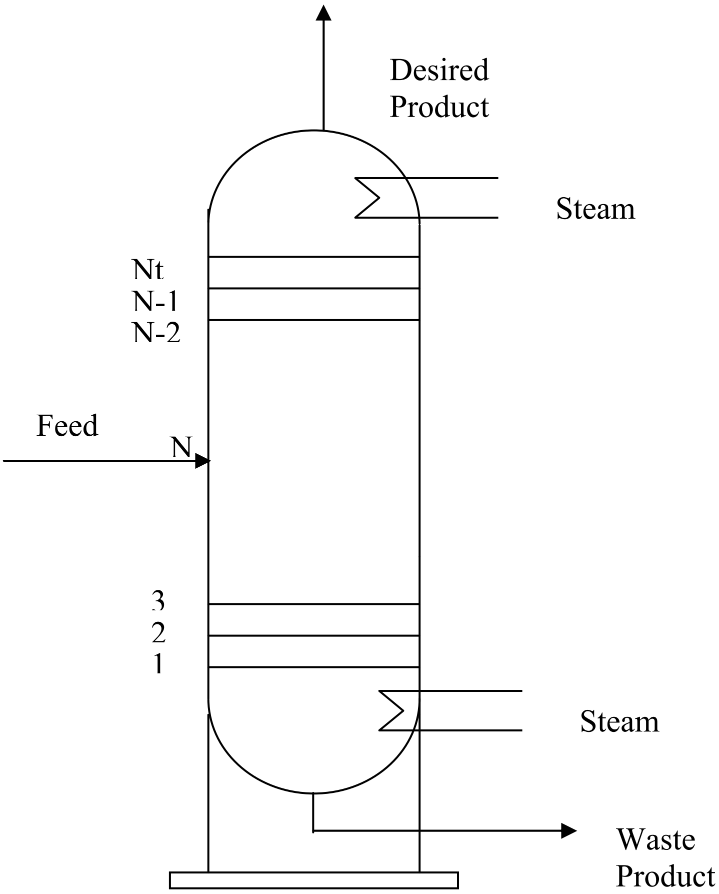


Figure 2.1: Continuous Distillation Operation (5)

2.2.2 Batch Distillation Operation

Batch distillation is an old unit operation in the chemical industry. There has been an increased interest in batch distillation processes because of its applicability to small-scale production of specialty chemicals [8].

Batch distillation is becoming increasingly important as high-value small-volume specialty chemical, biochemical, pharmaceutical and food manufacturing industries continue to gain momentum. Batch distillation continues to be the preferred unit operation because of its flexibility [9].

Rayleigh [10] discussed the simplest case of batch distillation which is the differential distillation, figure 2.2. There is no reflux 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 $y_D = x_D$. Therefore, there is only a single equilibrium stage, the still pot. This is useful for separating wide boiling mixture.

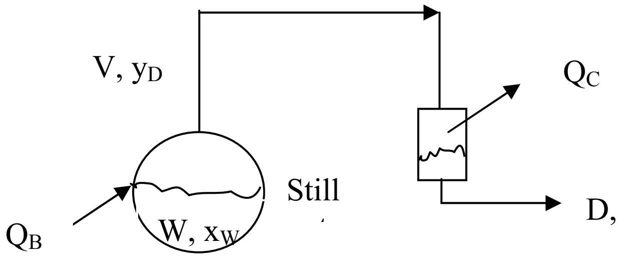


Figure 2.2: Differential batch distillation

To achieve a sharp separation and/or reduce the intermediate-cut fraction, a trayed or packed column, located above the still, and a means of sending reflux to the column is provided, figure 2.3. For a column of a given diameter, the molar vapor boilup rate is usually fixed at a value below the column flooding point. If the reflux ratio 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 overflow is achieved [10]. Smoker and Rose [11] gave a method to analysis such a binary batch rectification with constant reflux and variable distillate composition with McCabe-Thiele diagram.

The more optimal operating policy for batch rectification is to maintain a constant molar vapor rate, but continuously vary the reflux ratio to achieve a constant distillate composition that meets the specified purity. The calculation for this policy was made with McCabe-Thiele diagram by Bogart [12] and Ellerbe [13].

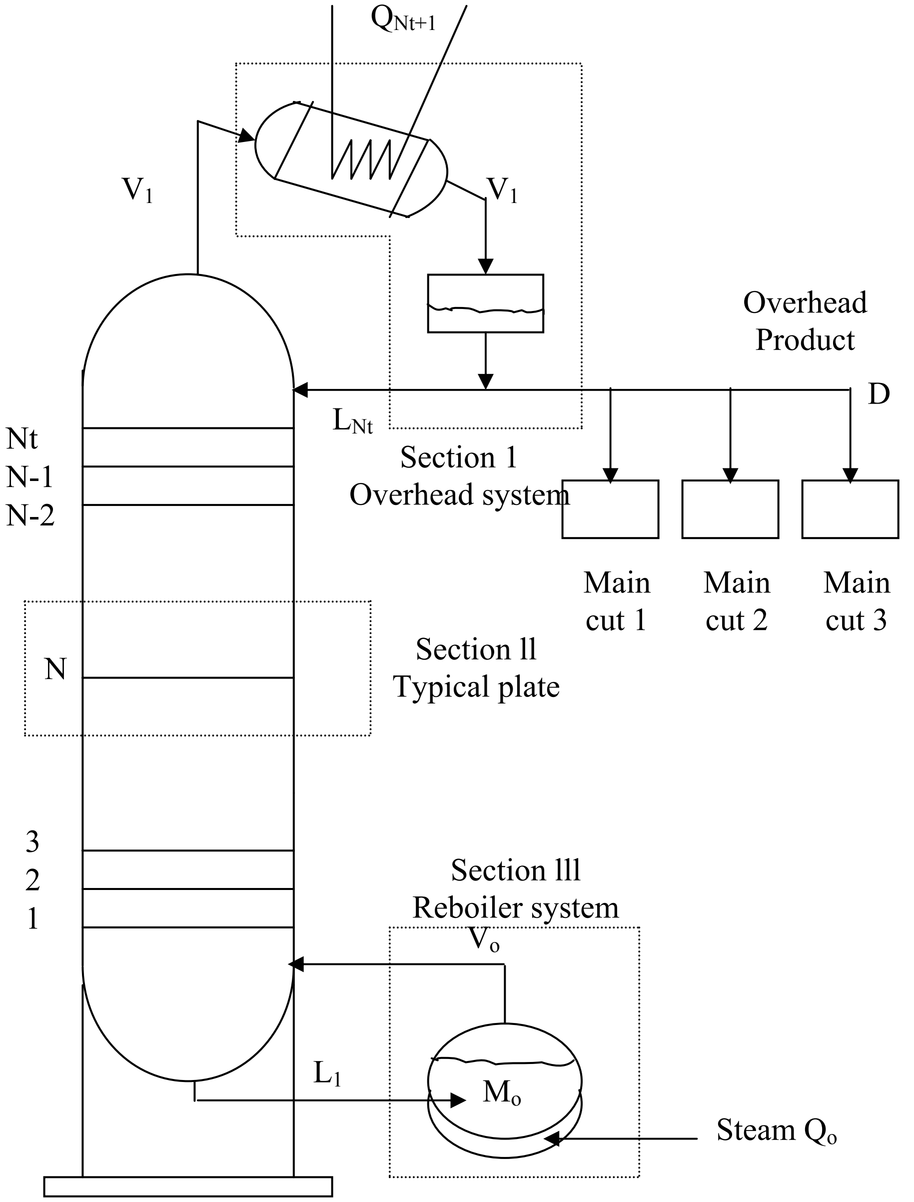


Figure 2.3: Batch Rectification Operation

For batch stripper figure 2.4 consisting of a large accumulator, a trayed or packed stripping column and a reboiler. The initial charge is placed in the accumulator rather than the reboiler. The mixture in the accumulator is fed to the top of the column and the bottoms cut is removed from the reboiler. A batch stripping is useful for removing small quantities of volatile impurities. For binary mixtures, McCabe-Thiele construction is applied and the graphical methods 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 [10].

Hasebe et al. [14] described a more complex batch distillation unit figure 2.5. The charge in the feed tank is fed to a suitable column location. Holdups in the reboiler and condenser are kept to a minimum. Products or intermediate cuts are withdrawn from the condenser, the reboiler or both. In addition, the liquid in the column at the feed location can be recycled to the 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.

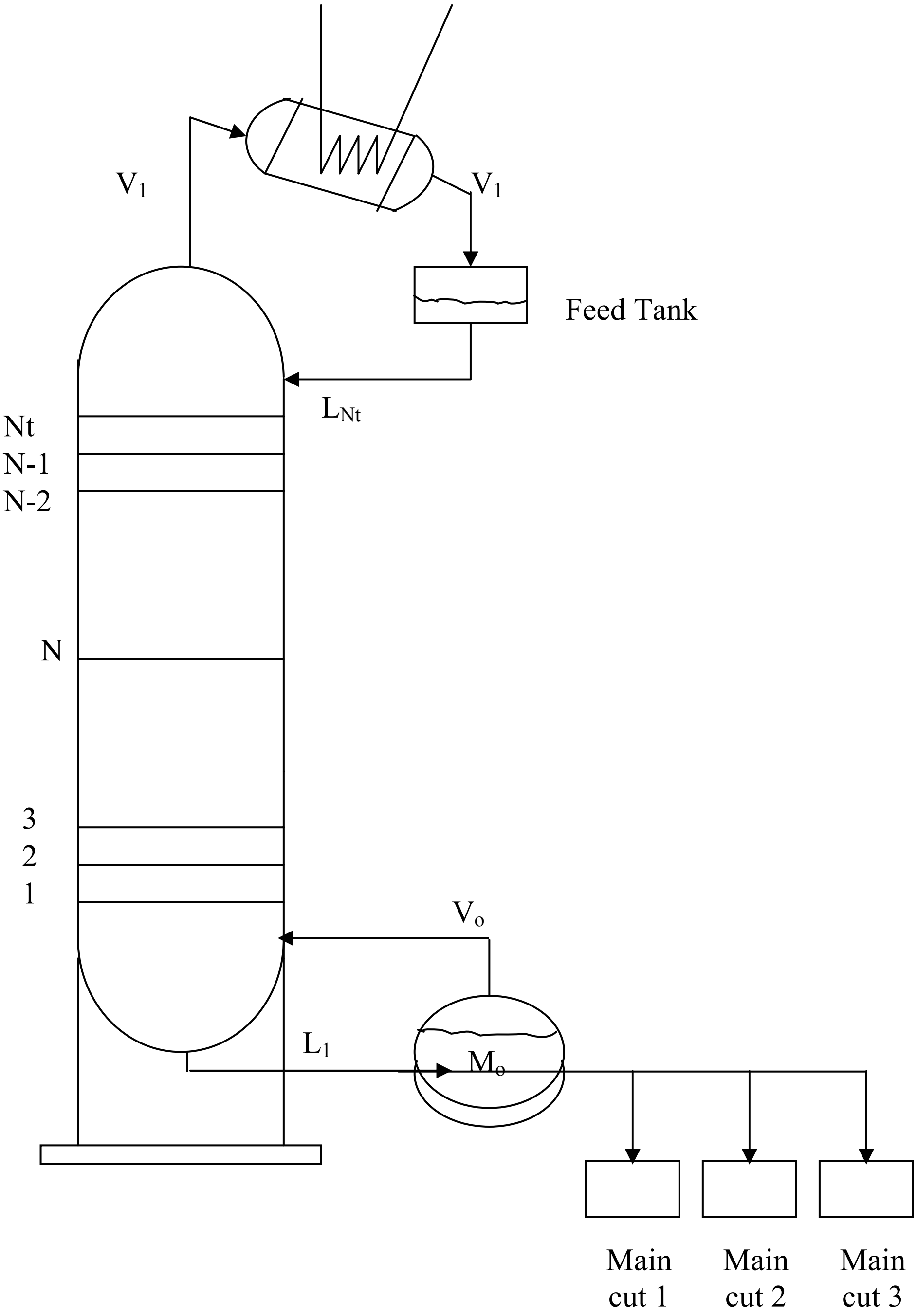


Figure 2.4: Batch Stripping Operation

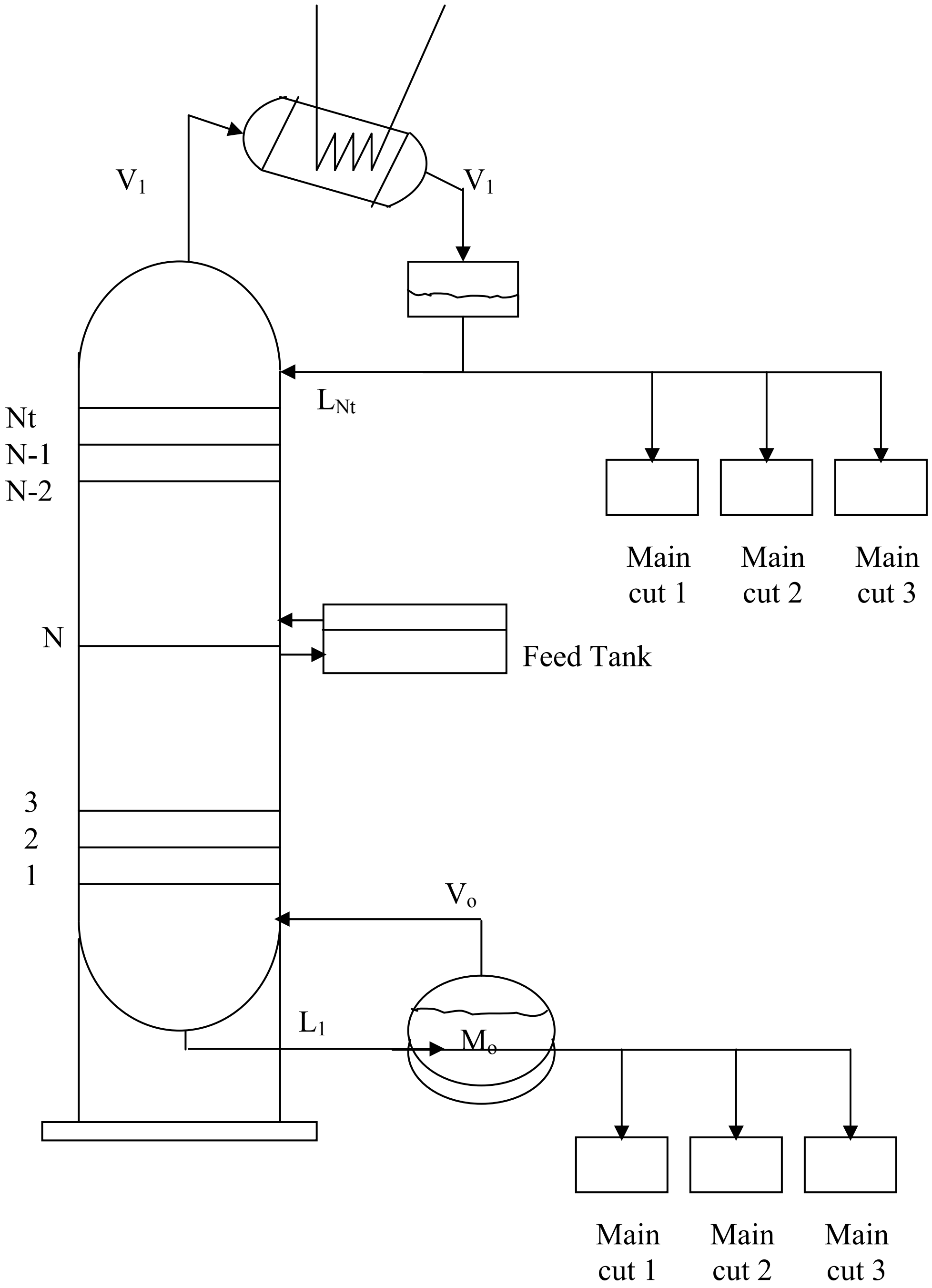


Figure 2.5: Complex Batch Distillation Operation

In batch separation operations, a feed mixture is charged to the equipment and one or more products are withdrawn. In Figure 2.2, where a liquid mixture is charged to a still pot, retort, or flask and heated to boiling. The vapor formed is continuously removed and condensed to produce a distillate. The composition of both the initial charge and distillate change with time. The still temperature increases and the relative amount of lower-boiling components in the charge decreases as distillation proceeds. Batch operations can be used for several advantages under the following circumstances [10]:

1- The capacity of a facility is too small to permit continuous operation at a practical rate.
2- It is necessary, because of seasonal demands, to distill with one unit, different feedstocks to produce different products.
3- It is desired to produce several new products with one distillation unit for evaluation by potential buyers.
4- Upstream process operations are batchwise and the composition of feedstocks for distillation vary with time or from batch to batch.

The feed contains solids or materials that form solids, tars, or resin that plug or foul a continuous distillation column.

Batch distillation is a very simple and efficient unit operation for the separation of multi-component azeotropic mixtures into pure components due to the low investment cost and the high purity of products. Generally, a regular batch column Figure 2.6a is used for batch distillation. In this type of column the feed vessel is located at the bottom of a rectifying column. 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 Figure 2.6b. The combination of the regular and inverted batch column can be divided into two types. First is called middle vessel column Figure 2.6c and consists of a rectifying and a stripping section. The second is called cyclic column Figure 2.6d. Columns with more than two column sections and feed vessels are called multi-vessel-columns [15].

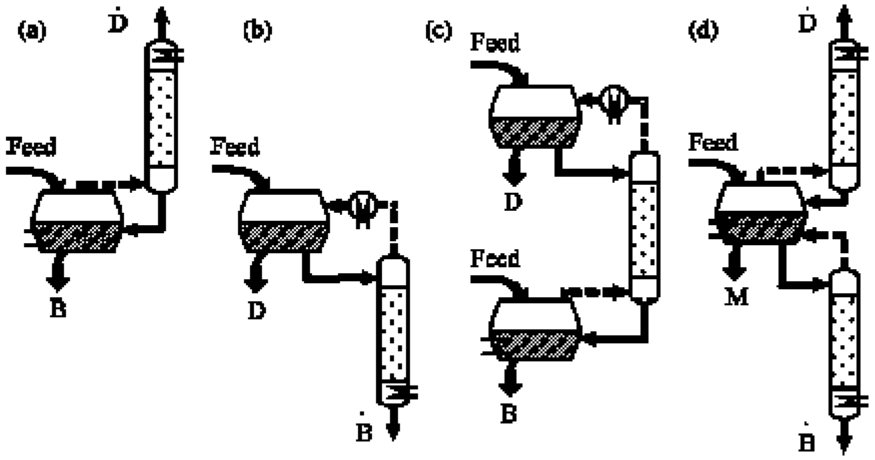


Figure: 2.6 Different Batch column types – (a) regular (b) inverted
(a) cyclic and (d) middle vessel

This system can be described as a “batch reactor-rectifier”, because the products are obtained in the distillate. It consists of a reboiler 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 and the following assumptions were made [15]:

a- The separation system has sufficient stages and reflux to achieve the desired distillate composition.
b- There are no reactive or non-reactive azeotropes in the system.
c- A total condenser produces a saturated liquid product.
d- Constant plate efficiency.
e- Neglect the vapor holdup.
f- Perfect mixing in all trays.
g- Constant pressure drop.
h- Variable liquid holdup.
i- Ideal vapor phase and non-ideal liquid phase.

Multi-effect batch distillation system (MEBAD), which separates multiple components simultaneously, has higher efficiency compared with an ordinary batch distillation column. In order to make the characteristics of the (MEBAD) clearer, the energy consumption of the (MEBAD) is compared with that of a conventional continuous distillation system for various feed conditions. Results of the exhaustive simulations show that the (MEBAD) has the potential for having higher energy efficiency than a continuous system when the number of components is increased or relative volatilities among the components are decreased. Furthermore, it is shown that there is little relationship between the number of column stages and the energy consumption at the reboiler of the (MEBAD) while the number of stages strongly affects the energy consumption of the continuous system[16].

2.2.2.1 The Benefits of Batch Distillation

Batch distillation is an important unit operation in the batch processing industry and is widely used for the production of high value-added, low-volume chemicals. This has generated a renewed interest in batch processing technologies [10].

The batch distillation operation requires a much simpler apparatus, but is complicated because the process is a function of time so that batch distillation operates at un-steady states, and that only one pure product is removed [17].

2.2.3 Comparison between Batch and Continuous Distillation

Batch distillation is a very efficient and advantageous unit operation for the separation of multi-component mixtures into pure components. Due to its flexibility and low capital costs, batch distillation is becoming increasingly important in the fine chemicals and pharmaceutical industries [15].

Batch distillation may be preferable to continuous distillation where relatively small quantities of material are to be separated at irregularly scheduled periods. In many cases, the composition of the initial feed may vary from period to period. Furthermore, a general-purpose batch still is often desired to be used in handling a number of different products [17].

The most outstanding attribute of batch distillation is its flexibility. Little change is required when switching from one mixture to another. Reflux ratio and throughput can be varied easily. No balance of feed and draw off 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 [17].

2.3 Distillation Processes Techniques

Where 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 1.1. Then ordinary distillation may be uneconomic, and if an azeotrope forms even impossible. A number of separation techniques, referred to as enhanced distillation have been considered by Fair and Bravo [10]:-

2.3.1 Extractive Distillation

A method that uses a large amount of relatively high-boiling solvent to alter the liquid phase activity coefficients of the mixture, so that the relative volatility of the key components becomes more favorable. The solvent enters the column above the feed entry and a few trays below the top, and exits from the bottom of the column without causing an azeotrope to be formed. If the feed to the column is an azeotrope, the solvent breaks it. Also, the solvent may reverse volatilities [10].

Extractive distillation is a common process for the separation of homogeneous azeotropic mixtures and other mixtures that have key components with relative volatility below 1.1 over an appreciable range of concentration. If the feed is a minimum boiling azeotrope, a solvent with a lower volatility than the key components of the feed mixture, is added to a tray above the feed stage and a few trays below the top of the column so that [10]:

1- The solvent is present in the down flowing liquid phase to the bottom of the column.

2- Little solvent is stripped and last to the overhead vapor.

If the feed is a maximum-boiling azeotrope, the solvent enters the column with the feed. The components in the feed must have different affinities for the solvent so that the solvent cause an increase in the relative volatility.

2.3.2 Salt Distillation

A variation of extractive distillation in which the relative volatility of the key components is altered by dissolving a soluble, ionic salt in the top reflux. Because the salt is nonvolatile, it stays in the liquid phase as it passes down the column [10].

Rather that using a solvent that contains a dissolved salt, the salt can be added as a solid or melt directly into the column by dissolving it in the liquid reflux before it enters the column. This technique was demonstrated experimentally by Cook and Furter [18].

2.3.3 Pressure-Swing Distillation

Pressure-Swing Distillation is a method for separating a pressure-sensitive azeotrope that utilizes two columns operated in sequence at two different pressures [10].

When a binary azeotrope disappears at some pressure or changes composition by 5mol% or more over a moderate range of pressure, consideration should be given to using, without a solvent, two distillation columns operating in series at different pressures. This process is referred to as pressure-swing distillation or two-column distillation [10]. Knapp and Doherty [19] list 36 pressure-sensitive binary azeotropes, taken mainly from the compilation of Horsley [20].

2.3.4 Homogeneous Azeotropic Distillation

Homogeneous Azeotropic Distillation is a method of separating a mixture by adding an entrainer that forms a homogeneous minimum-or maximum-boiling azeotrope with one or more feed components. The entrainer 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 [10].

2.3.5 Heterogeneous Azeotropic Distillation

Heterogeneous Azeotropic Distillation is a more useful azeotropic distillation in which a minimum-boiling heterogeneous azeotrope is formed by the entrainer. The azeotrope splits into two liquid phases in the overhead condensing system. One liquid phase is sent back to the column as reflux, while the other liquid phase is sent to another separation step or is a product [10].

An alternative technique that does 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 entrainer that forms a binary and/or ternary heterogeneous azeotrope [10].

2.3.6 Reactive Distillation

Reactive distillation (RD) combines chemical reaction and distillation into a single process unit.

The combination of chemical reaction and distillation product separation offered several advantages in composition with conventional process, in which the reaction and product separation take place in series. Since the products are separated simultaneously from the reaction mixture, no chemical equilibrium can be established, and therefore the reaction velocity is maintained at a high rate consequently. This also applies to processes for the production and hydrolysis of acetates. Reactive distillation may facilitate the suppression of side reactions. In addition, the heat of reaction can be utilized for the mass transfer operation in a reactive distillation column [3].

In some application particularly in cases when thermodynamic reaction equilibrium prevents high conversions, the coupling of distillation to remove the reaction products from the reaction zone can improve the overall conversion and selectivity significantly. In other applications reactions are utilized to overcome the separation problems caused by azeotropes. This combination of reaction and distillation often results into simpler processes, with less recycle streams and reduced need for waste handling resulting into lower investment and operating costs [21].

The reaction product is subsequently distilled from the non-reacting components. The reaction is then reversed to recover the separating agent and the other reacting components. Reactive distillation also refers to the case where a chemical reaction and multistage distillation are conducted simultaneously in the same apparatus to produce other chemicals. This combined operation, sometimes referred to as catalytic distillation if a catalyst is used, is especially suited to chemical reactions limited by equilibrium constraints, since one or more of the products of the reaction are continuously separated from the reactants [10].

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 general application of reactive distillation, described by Terrill et. al., Sylvestre, and Doherty [22], 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 reacts 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 components B and C, together with any 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. Terrill et. al. Sylvestre, and Doherty [22] discussed the application of reactive entrainers to the separation of mixtures of *p-xylene* and *m-xylene*, whose normal boiling points differ by only 0.8°C, resulting in a relative volatility of only 1.029. Separation by ordinary distillation is impractical because, for example, to produce 99 mol% pure products from an equi-molar feed, more than 500 theoretical stages are required. By reacting the *m-xylene* with a reactive entrained such as *tert*-butylbenzene accompanied a solid aluminum chloride catalyst, or cheated *m-xylene* dissolved in cumene, the stage requirements are drastically reduced.

Closely related to the use of reactive entrainers in distillation is the use of reactive absorbents in absorption, which finds wide application in industry. For example, sour natural gas is sweetened by the removal of hydrogen sulfide and carbon dioxide acid gases by absorption into aqueous alkaline solutions of mono-and diethanolamines. Fast and reversible reactions occur to form soluble salt complexes such as carbonates, bicarbonates sulfides, and mercaptans. The rich solution leaving the absorber is sent to a reboiler stripper where the reactions are reversed at higher temperatures to regenerate the amine solution as the bottoms and deliver the acid gases as overhead vapor.

Reactive distillation involves taking into account undesirable chemical reactions that may occur during distillation. Robinson and Gilliland [23] present an example involving the separation of cyclopentadiene from C_7 hydrocarbons. During distillation, cyclopentadiene dimerizes. The more volatile cyclopentadiene is taken overhead as distillate, but a small amount dimerizes in the lower section of the column and leaves in the bottoms with the C_7s. Alternatively, the cyclopentadiene can be dimerized to facilitate its separation by distillation from other constituents of a mixture. Then the dicyclopentadience is removed as bottoms from the distillation column. However during distillation, it is also necessary to account for possible depolymerization to produce cyclopentadiene, which would migrate to the distillate.

Reactive distillation involves combining chemical reaction (s) and separation by distillation in a single distillation apparatus. This concept appeared first by Backhaus, 1921 [24], who obtained a series of patents for esterification reactions in a distillation column. This-concept of continuous and simultaneous chemical reaction and distillation in a single vessel was verified experimentally by Leyes and Othmer [25] for the esterification of acetic acid with an excess of *n*-butanol in the presence of sulfuric acid catalyst to produce butyl acetate and water. This type of reactive distillation should be considered as an alternative to the use of separate reactor and distillation vessel whenever the following hold:

1-The chemical reaction occurs in the liquid phase, in the presence or absence of a homogeneous catalyst, or at the interface of a liquid and a solid catalyst.

2-Feasible temperature and pressure for the reaction and distillation are the same. That reaction rates and distillation rates are of the same order of magnitude.

3-The reaction is equilibrium-limited such that if one or more of the products formed can be removed, the reaction can be driven to completion; thus, a large excess of a reactant is not necessary to achieve a high conversion. This is particularly advantageous when recovery of the excess reagent is difficult because of azeotrope formation. For reactions that are irreversible, it is more economical to take the reactions to completion in a reactor and then separate the products in a separate distillation column. In general, reactive distillation is not attractive for supercritical conditions, for gas-phase reactions, and for reactions that must take place at high temperatures and pressure, and/or that involve solid reactants or products.

Careful consideration must be given to the configuration of the distillation column when employing reactive distillation. Important factors are feed entry and product removal stages, the possible need for intercoolers and interheaters when the heat of reaction is appreciable and the method for obtaining required residence time for the liquid phase. In the following ideal cases, it is possible, as shown by Belck [26] and others for several two-, three-, and four-component systems, to obtain the desired products without the need for additional distillation.

Case 1: The reactions A ↔ R or A↔2R, where R has a higher volatility than A. In this case, only a reboiled rectification section is needed. Pure A is sent to the column reboiler where all or most of the reaction takes place. As R is produced, it is vaporized, passing to the rectification column where it is purified. Overhead vapor from the column is condensed, with part of the condensate returned to the column as reflux. Chemical reaction may also take place in the column. If A and R form a maximum-boiling azeotrope, this configuration is still applicable under steady-state conditions, the mole fraction of R in the reboiler is greater than the azeotropic composition.

Case 2: The reactions A ↔ R or 2A↔2R, where A has the lower boiling point or higher volatility. In this case, only a stripping section is needed. The feed of pure liquid A is sent to the top of the column, from which it flows down the column, reacting to produce R. The column is provided with a total condenser and a partial reboiler. No product is withdrawn from the top of the column. Product R is withdrawn from the reboiler. This configuration requires close examination because at a certain location in the column, chemical equilibrium may be achieved, and if the reaction is allowed to proceed below that point, the reverse reaction can occur.

Case 3: The reactions 2A ↔ R + S or A + B ↔R + S, where A and B are intermediate in volatility to R and S, and R has the highest volatility. In this case, the feed enters an ordinary distillation column somewhere near the middle; with R withdraw as distillate and S withdraw as bottoms. If B is less volatile than A, then B may enter the column separately and at a higher level than A.

Commercial applications of reactive distillation include the following:

1- The esterification of acetic acid with ethanol to produce ethyl acetate and water.
2- The reaction of formaldehyde and methanol to produce methylal and water, using a solid acid catalyst, as described by Masamoto and Matsuzaki [27].
3- The esterification of acetic acid with methanol to produce methyl acetate and water, using sulfuric acid catalyst, as patented by Agreda and Partin [28], and described by Agreda, Partin, and Heise [29].
4-The reaction of isobutene with methanol to produce methyl-*tert*-butyl ether (MTBE), using a solid, and strong-acid ion-exchange resin catalyst, as patented by Smith [30, 31, and 32] and further developed by DeGarmo. Parulekar, and Pinjala [33].

The production of ester like methyl-acetate, ethyl-acetate, and butyl-acetate has been for years an interesting (RD) application. Very important application of (RD) is the production of methyl tertiary butyl ether (MTBE) that is used for gasoline component. Other potential applications include ethyl tertiary butyl ether (ETBE), tertiary amyl methyl ether (TAME) and tertiary amyl ethyl ether which are also widely used in modern gasoline [21].

Güttinger and Morari (1998) [34] developed graphical methods for the prediction of output multiplicities caused by the reactive vapor-liquid equilibrium in reactive distillation. These methods rest upon the limiting case of reactive columns of infinite length operated at infinite internal flows (infinity/infinity analysis), and are directly applicable to systems where the reactions take place in the entire column ("non-hybrid" columns).

2.3.6.1 Continuous Reactive Distillation Operation

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

The two main advantages of this process relative to the conventional alternatives are the possibility of carrying equilibrium limited chemical reactions to completion, and the simultaneous separation of the reaction products in only one unit. This reduces or eliminates reactor and recycle costs [35].

Suzuki [36] described experimental results for the continuous production of ethyl acetate in a distillation column reactor with sieve tray, and successive plate to plate design calculation with graphical techniques and empirical correlation. Also described the Iterative method for the determination of stage temperatures, stage reaction rates and inter stage flow rates. In the problem of multi component distillation acompanied by simultaneous chemical reaction is discussed, and the use of a modified Muller's method for the convergence of the column temperature profile is proposed. Derivation of the equation is simplified by-using matrix notation, which also has the advantage that any inter stage flow pattern is allowed. For the solution of the linearized material balance equation, the tridiagonal matrix algorithm is employed.

Komatsn and Holland [37] three methods are presented for solving problems of this type. The first method θ method of convergence is applied to conventional and complex distillation columns. The second is 2n Newton-Rhaphson method is applied to absorbers and distillation columns in which one or more chemical reactions occur per stage. The first two methods are recommended for mixtures which form highly non-ideal solutions and one or more chemical reactions occur per stage.

In this work of Barbosa, D. and Doherty, M. F. [38] a new set of transformed composition variables is introduced to simplify the design equations for double-feed multicomponent reactive distillation columns. These new equations are used to develop a general method of calculating minimum reflux ratios for reactive distillation columns. The application of these equations to the reactive distillation columns for etherification processes is discussed.

Agreda et. al. [29] used Computer simulations to test methods of minimizing the size of reactors and recycle streams, maximizing yields and conversions, and refining the product in as few steps as possible. This article describes the development of commercial process for the production of high-purity methyl acetate via counter current reactive distillation. The development and scale -up steps described include concept inception, laboratory testing, bench- scale testing, pilot plant development modeling and design, full-scale construction and operation, and final troubleshooting and optimization.

Platt, G. M. [40] developed; a steady-state simulator for reactive distillation processes, in the transformed context proposed by UNG and DOHERTY. In this transformed context, reactive stage equations and the reactive cascade equations are presented. Using the reactive extension of McCabe - Thiele approximations, an algorithm for solution of the reactive cascade is depicted. Compositional profiles in the column are obtained by the Newton- Raphson method. In this algorithm reactive bubble point calculations are substituted by the direct access to the locus of reactive vapor – liquid equilibrium, improving the simulator performance. Results are obtained for a reactive column for production of Methylactate [where occurs the well - known esterification reaction

[Acetic acid + methanol<=> Methyl acetate + water]

, and presented in graphical form. These results show that a reactive azoetrope is obtained in the top of the column and pure water in the bottom.

Bruggemann, S., and Marquardt, W.[41] described that shortcut methods are suitable tool for the assessment of feasibility and economic attractiveness of single distillation columns. In this work they presented two design algorithms for the synthesis of distillation sequences with minimum operation cost that rely on the analysis of each single split with a suitable shortcut model. The exhaustive enumeration of all sequences, which is widely used for zeotropic mixtures, is compared to an evolutionary optimization strategy. The performance of the evolutionary optimization strategy is assessed by studying one zeotropic and two azeotropic mixtures. The results show that the reliable determination of the best design alternative requires large computational effort.

Aittamaa, J. [42] states that reactive Distillation (RD) is a new unit operation of Chemical Engineering. It combines chemical reaction and distillation into a single process unit. The combination (reaction and distillation) is particularly advantageous when the rate of chemical reaction is decreased by the reaction equilibrium resulting into poor yield, selectivity and conversion. By combining the separation process within the reactor, the reaction products can be removed from the reaction zone significantly improving the overall yield, selectivity and conversion compared to a conventional process. In reactive distillation process the number of process equipment and the energy needs are often much lower than in a conventional process. The design of a reactive distillation process is much more demanding than the design of a conventional process that consists of separate reactors and separation equipment. This is because there reaction and the distillation take place in a single unit.

2.3.6.2 Batch Reactive Distillation Operation

Reactive distillation has proved to be an important process alternative to the conventional reactor-separator configuration. Advantages of reactive distillation and flexibility of a batch process can be combined in batch reactive distillation. A simple method to estimate the advantage of using batch reactive distillation over conventional technology. For example in the production of low volume, high value specialty chemicals batch distillation is one of the most common operations [1].

Sagar et. al. [1] viewed batch reactive distillation (BRD) as an important process alternative to conventional batch processing. Distillation with chemical reaction also offers advantages in overcoming the equilibrium limitation for reversible reactions and separations of undesired byproducts. In a typical BRD process, reaction and separation occur simultaneously. The removal of one or more products from the reaction mixture not only increase the conversion of equilibrium limited reactions but also increases or decreases the reaction vessel temperature if the product removed is lower or higher boiling, respectively.

Kian Huat [9] discussed that batch distillation which is often directly coupled with chemical reactors such that the reactor acts as the reboiler of the column. This combined process increases the conversion of equilibrium reaction, making high conversions easily achievable, by the removal of one of the products through the distillation column.

Sundmacher, and Steyer [43] stated that the crude lactic mixture can be reacted with alcohols like methanol etc. in a batch reactive distillation apparatus with simultaneous distillation of the voltaic methyl lactate as a distillate. Then this methyl lactate is fed to another batch reactive distillation apparatus where hydrolysis of the methyl lactate to form lactic acid and methanol is performed.

Batch distillation is often directly coupled with chemical reactors such that the reactor acts as the reboiler of the column. This combined process increases the conversion of equilibrium reaction, making high conversions easily achievable, by the removal of one of the products through the distillation column [5].

Mujtaba and Macchietto (1994) [44] considered a theoretical comparative study with conventional and unconventional columns for simultaneous chemical reaction and distillation, with the following reversible reaction scheme:

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

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

2.4 Vapor-liquid Equilibrium for Multi-component Distillation

Vapor-liquid equilibrium calculations are usually carried out for separation processes, with several versions of the EOS. The prediction of mixture vapor-liquid equilibrium is more complicated than the prediction of pure component.

Phase equilibrium relation is one of the fundamental properties which are necessary for the calculation of separation processes, and useful equations have been proposed for expressing these relations.

The local-composition models have limited flexibility in the fitting of data, but they are adequate for most engineering purpose. Moreover, they are implicitly generalized to multi-component systems without the introduction of any parameters beyond those required to describe the constituent binary systems.

Efficient design of distillation equipment requires quantitative understanding of vapor-liquid equilibria in multi-component mixtures as expressed through vapor-phase fugacity coefficients and liquid-phase activity coefficients [45].

2.4.1 Fundamental Equations for the VLE Relation

To describe the phase equilibrium of a system of N components at a temperature T, pressure P and at equilibrium, the vapor phase fugacity is equal to the liquid phase fugacity for every component [10].

$$f_{iV}^{\wedge} = f_{iL}^{\wedge} \quad \text{For } i = 1,2,3,.........N \qquad (2.1)$$

Equation of states in both phases

$$\hat{\phi}_{iL} = \frac{\hat{f}_{iL}}{x_i P}, \quad \hat{\phi}_{iV} = \frac{\hat{f}_{iV}}{y_i P} \tag{2.2}$$

$$\hat{\phi}_{iL} x_i = \hat{\phi}_{iV} y_i \tag{2.3}$$

$$K = \frac{\hat{\phi}_{iL}}{\hat{\phi}_{iV}} \tag{2.4}$$

Equation of states in vapor phase and activity coefficient in liquid phase

$$\hat{f}_{iV} = \hat{f}_{iL} \tag{2.5}$$

The vapor phase fugacity can be written in terms of the vapor phase fugacity coefficient Φ_i^V vapor mole fraction y_i and total pressure P as following.

$$\hat{f}_{iV} = \hat{\Phi}_{iV} y_i P \tag{2.6}$$

$$\hat{a}_{iL} = \frac{\hat{f}_{iL}}{f_{iV}^o} \tag{2.7}$$

Also the liquid phase fugacity can be written in terms of liquid phase activity coefficient γ_i, and liquid mole fraction x_i as following:

$$\hat{f}_{iL} = \gamma_i x_i f_{iL}^o \tag{2.8}$$

$$\ln \frac{f_{iL}^o}{f_{isat}^o} = \frac{V}{RT}\left(P - P_i^{sat}\right) \tag{2.9}$$

$$\hat{f}_{iL} = f_{isat}^o \exp^{\frac{V}{RT}\left(P - P_i^{sast}\right)} \tag{2.10}$$

$$\phi_i^{osat} = \frac{f_i^{osat}}{P_i^{sat}} \tag{2.11}$$

$$\hat{f}_{iL} = \phi_i^{osat} P_i^{sat} \exp^{\frac{V}{RT}\left(P - P_i^{sat}\right)} \tag{2.12}$$

$$\hat{\phi}_{iV} y_i P = \gamma_i x_i \phi_i^{osat} P_i^{sat} \exp^{\frac{V}{RT}\left(P - P_i^{sat}\right)} \tag{2.13}$$

2.4.2 Ideal Vapor Liquid Equilibrium

A mixture is called ideal if both liquid and vapor are ideal mixtures of ideal components, thus the partial pressure of component i, P_i in the vapor phase is proportional to its mole fraction in the vapor phase according to Dalton's law:

$$P_i^o = y_i P \tag{2.14}$$

For an ideal mixture, the equilibrium relationship for any component is defined as:

$$K_j = \frac{y_i}{x_i} \tag{2.15}$$

The K_j value can be predicted from Raoult's law, where:

$$K_j = \frac{P_i^o}{P} \tag{2.16}$$

Ideal solutions occur when molecular diameter is equal, chemical interactions are present, intermolecular forces between like and unlike molecules are equal, and in which all the activity coefficients are unity (i.e. $y_i = 1$ for all i) [45]. 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 mixture 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.

$$Z = \frac{PV}{RT} = 1 \tag{2.17}$$

2.4.3 Non Ideal Vapor liquid Equilibrium

For non-ideal mixture or azeotropic mixture additional variable γ_i (activity coefficient) appears in vapor-liquid equilibrium equation.

$$y_i = \frac{\gamma_i P_i^o}{P_t} \cdot x_i \tag{2.18}$$

Where γ_i represent degree of deviation from reality. When $\gamma_i = 1$, the mixture is said to be ideal simplifies the equation to Raoult's law. For non-ideal mixture $\gamma_i \neq 1$, exhibit either positive deviation from Raoult's law $(\gamma_i > 1)$, or negative deviation from Raoult's law $(\gamma_i < 1)$.

The prediction of liquid phase activity coefficient is most important for non-ideal distillation design calculation.

There are several excess energy g^E models to calculate activity coefficient in multi-component systems. The most important models are (Wilson, NRTL, UNIQUAC, and UNIFAC) [46]. In all these models, the model parameters are determined by fitting the experimental data of binary mixtures. Using binary interaction data only can make the prediction of vapor-liquid equilibrium of multi-component mixture possible.

Each one of these models has advantages and disadvantages. The selection of appropriate model for a given mixture is based on the three characteristics, which are temperature, pressure, and composition.

2.4.3a Wilson model:

Wilson [10] predicted his equation to calculate the liquid phase activity coefficient.

$$\gamma_K = \ln\left[\sum_{j=1}^{n} x_j \Lambda_{ij}\right] + \sum_{K=1}^{n}\left[\frac{x_K \Lambda_{Ki}}{\sum_{K=1}^{n} \Lambda_{Kj}}\right] \qquad (2.19)$$

Where

$$\Lambda_{ij} = \frac{v_j^L}{v_i^L} \cdot \exp\left[-\left(\lambda_{ij} - \lambda_{ii}\right)/RT\right] \qquad (2.20)$$

$$\Lambda_{ij} = \lambda_{ji} \qquad (2.21)$$

$$\lambda_{ij} = \lambda_{ji} \qquad (2.22)$$

$$\Lambda_{ii} = \Lambda_{jj} = 1 \qquad (2.23)$$

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

The Wilson model has the disadvantage that cannot predict vapor-liquid equilibrium when two liquids exist in the liquid phase.

2.4.3b NRTL model:

The NRTL [10] (non-random, two liquid model) developed by Renon and Prausnitz [47, 48]. This model uses three binary interaction parameters for each binary pair in multi-component mixture-pairs. For N-components system, it's required $\frac{N(N-1)}{2}$ molecular binary pair. This equation is applicable to multi-component vapor-liquid, liquid-liquid, and vapor-liquid-liquid systems.

The following equations represent NRTL model:

$$G_{ij} = \exp\left(-\alpha_{ij}\tau_{ij}\right) \tag{2.24}$$

$$\ln\gamma_i = \frac{\sum_{j=1}^{n_C}\tau_{ji}G_{ji}x_j}{\sum_{j=1}^{n_C}G_{ji}x_j} + \sum_{j=1}^{n_C}\frac{x_j}{\sum G_{Kj}x_K}\cdot\left(\tau_{ij} - \frac{\sum_{K=1}^{n_C}x_K\tau_{Kj}G_{Kj}}{\sum_{K=1}^{n_C}x_K G_{Kj}}\right) \tag{2.25}$$

The NRTL group interaction parameters are $\tau_{12} = {}^{b_{12}}\!/_{RT}$, α, b_{12}, and b_{21} are NRTL constant.

2.4.3c UNICQUIC model:

Abrams and Prausnitz [49, 50, and 51] developed the UNIQUIC (universal quasi Chemical) activity coefficient model. This model distinguishes two contributions termed configurationally (C) and (R).

$$\ln\gamma_i = \ln\gamma_i^C(combinational) + \ln\gamma_i^R(residual) \tag{2.26}$$

The combinational part basically accounts for non-ideality of a mixture arising from differences in size and shape of constituent molecular species; whereas the residual part considers the difference between inter-molecular and interaction energies.

The two-parameter in UNIQUIC equation gives a good representation of the vapor-liquid equilibria for binary and multi-component mixture.

$$\tau_{ij} = \exp\left(A_{ij}\right) \tag{2.27}$$

$$\phi = \frac{r_i x_i}{\sum_{j=1}^{n_C} r_i x_i} \tag{2.28}$$

$$\theta = \frac{q_i x_i}{\sum_{j=1}^{n_C} q_i x_i} \tag{2.29}$$

$$L_j = Z(r_i - q) - (r - 1) \quad \text{Where Z=10} \tag{2.30}$$

$$\ln \gamma_i^c = \ln \frac{\phi_i}{x_i} + \frac{Z}{2} q_i \ln \frac{\theta_i}{\phi_i} + L_i - \frac{\phi_i}{x_i} \sum_{j=1}^{n_C} x_i L_j \tag{2.31}$$

$$\ln \gamma_i^r = -q_i \ln\left(\sum_{j=1}^{n_C} \theta_i \tau_{ij} \right) + q_i - q_i \sum_{j=1}^{n_C} \frac{\theta_j \tau_{ij}}{\sum_{K=1}^{n_C} \theta_K \tau_{Kj}} \tag{2.32}$$

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^r \tag{2.33}$$

The molecular Vander walls volume r_i and the molecular surface q_i are usually calculated as the sum of the group volume and area parameters.

2.4.3d UNIFAC model

Fredensland et al [46] 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 “CH_3” groups, 1 “C” group and 1 “OH” group and Ethane, which contain two “CH_3” groups. The interaction parameters between different molecules are defined in literature.

This model, also called group contribution method, is based theoretically on UNIQUAC equation (2.33). The activity coefficient consists of two parts, combinational and residual contribution.

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^r \tag{2.34}$$

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

$$\ln \gamma_i^c = \ln \frac{\phi_i}{x_i} + 5q_i \ln \frac{{}_i i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j \tag{2.35}$$

The residual contribution is given by:

$$\ln \gamma_i^r = \sum_K v_K^i \left(\ln \Gamma_K - \ln \Gamma_K^i \right) \tag{2.36}$$

Hansen et al. [10] provides a computer aided system for UNIFAC parameters calculation.

UNIFAC model is extensively used to describe thermodynamics in chemical engineering literature (Skjold-Jorgensen et al.; Kikic ; Gmehling et al. ; Macedo et al. ; Tiegs and Gmehling ; Hansen et al. [10]) and is widely used in process simulation.

2.5 Enthalpy for Multi-component

The enthalpies of pure species or mixture at temperature T and pressure P are as follows [10]:

$$H_v = \left[\sum_{i=1}^{m} y_i H_{vi}^o \right] + (H_v - H_v^o) \tag{2.37}$$

$$H_L = \left[\sum_{i=1}^{m} x_i H_{vi}^o \right] + (H_L - H_v^o) \tag{2.38}$$

Where H_V^o is the ideal gas state enthalpy it is identical to the zero pressure enthalpy of real fluid at the same temperature, i.e.,$H_V^o = H(T, P = 0)$ [52], which also can be defined as the integral of the specific heat of gases. The specific heat of gases is conventionally given as polynomial in temperature.

The total enthalpy of liquid phase is given by:

$$HLi_j = \sum_i^N X_{i,j} H_L + H_{mix} \tag{2.39}$$

Where:

$$H_{mix} = RT \sum_{i=1}^{C} (x \ln \gamma_i) \tag{2.40}$$

$$Cp_v^o = A + BT + CT^2 + DT^3 \tag{2.41}$$

The integration of equation (2.35) provides an equation for ideal gas state enthalpy at any temperature T referred to a datum temperature T_o.

$$H_v^o = \int_{T_o}^{T} Cp_v^o \, dT \tag{2.42}$$

Where the constant A, B, C, and D can be found in appendix A table A-2 from equation(2.41)with assumption of ideal gas law and an ideal gas solution, vapor enthalpy is simply

$$H_v^{id} = \sum_{i=1}^{m} (y_i H_{vi}^o) \tag{2.43}$$

, and the liquid enthalpy for ideal solutions is obtained from equation(2.43), which is simplified to:

$$H_L^{id} = \sum_{i=1}^{m} (x_i H_{vi}^{o} - \lambda_i) \qquad (2.44)$$

For total enthalpy of vapor phase:

$$HV_a(j) = \sum_{1}^{m} \sum_{i}^{Nt} (K_i(j) * x_i(j) * H_V(j)) \qquad (2.45)$$

2.5.1 Enthalpy of vaporization

The enthalpy of vaporization or the latent heat of vaporization is the difference between the enthalpy of the saturated vapor and that of saturated liquid at the same temperature.

Because of the forces of attraction between the molecules of the liquid, the molecules escaping are those of higher energy of the remaining molecules in the liquid, and energy must be supplied to maintain the temperature constant [53].

2.6 Thermodynamics of the reaction

The reaction of acetic acid and methanol has been studied to produce methyl-acetate and water. The over all reaction rates to be calculated by the summation of the reaction rate on each stage [10]:

$$\sum \Delta R_j - \Delta R = 0 \qquad (2.46)$$

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

2.6.1 Heat of reaction

Chemical reactions also are accompanied either by the transfer of heat or by temperature changes during the course of reaction, in some cases by both. These effects are manifestations of the differences in molecular structure; therefore, in energy of the products and reactants. For example, the reactants in the combustion reaction possess greater energy on account of their structure than do the products, and this energy must either be transferred to the surroundings as heat or produce products at elevated temperature [10].

The amount of heat required for specific chemical reaction depends on the temperatures of both the reactant and products. A consistent basis for treatment of reaction heat effects results when the products of reaction and the reactants are all at the same temperature.

Heats of reaction at any temperature can be calculated from heat capacity data if the value for one temperature is known; the tabulation of data can, therefore, be reduced to the compilation of standard heats of formation at a single temperature [10].

The calculation of standard heats of reaction at other temperatures from knowledge of the value at the reference temperature has been given in the following equations [54]:

$$h_{oi} = \sum_{i}^{m} \upsilon_i \Delta H_{fi}^{o} \tag{2.47}$$

Where the sign convention for υ_i is as follow:

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

$$HVai = h_{oi} + \int_{T_o}^{T} \Delta Cp_v^o \, dT \qquad (2.48)$$

2.7 Mathematical Models and Design of Multi-component Batch Distillation without and with Chemical Reaction

The basic equations for the batch distillation calculations are the same as those for continuous distillation processes. Material balance, phase equilibrium correlations and energy balances are formulated for simulation purposes. The balance equations are applied on each tray [55].

Although there is an extensive literature on batch distillation, relatively little has been published on batch distillation with reaction. No systematic design methods are available for batch reactive distillation devices because most of the earlier work focused on detailed models for simulation and process optimization.

Rigorous calculation of multi-component distillation are so tedious that chemical engineers have long been looking for a simple shortcut methods that would be capable of accurately and rapidly calculating multi-component distillation with several efforts. However shortcut methods cannot be used in the design of non-ideal systems because they are based on the assumptions involving ideality and constant relative volatility. So plate to plate calculation are more accurate and convenient to give the temperature, composition, steam flow rates and load reaction at each stage.

2.7.1 Shortcut Model

For preliminary studies of batch rectification of multi-component mixtures, shortcut methods that assume constant molal overflow and negligible vapor and liquid holdup are useful.

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 reboiler 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 Madhaven [56] developed the shortcut methods for handling multi-component mixtures under assumption of constant molar overflow, and negligible vapor and liquid holdup.

Sundaram and Evans [57] applied their shortcut method to batch rectification only to the case of constant reflux.

Jae W. Lee [58] developed a shortcut procedure to approximate the operating policies (dynamic behavior) of batch reactive separation systems.

2.7.2 Rigorous Model

The early 1960s, when large digital computers became available, interest has been generated in developing rigorous calculation procedures for binary and multi-component batch distillation [5].

BatchFrac is a batch distillation model that solves unsteady-state heat and material balance equations by rigorous equations. These equations describe the behavior of a multistage batch distillation column. BatchFrac applies rigorous heat balances, material balances, and equilibrium relationships at each stage. BatchFrac calculates the profiles of column composition, temperature, pressure, and vapor and liquid flows as a function of time [59].

Huckaba and Danly [60] developed a computer program that assumed constant mass tray holdups, adiabatic tray operation, and linear enthalpy relationships included energy balances around each tray efficiencies.

Destefano [61] extended the model and developed a computer-based-solution procedure that was used to simulate successfully several commercial batch distillation columns.

Boston [62] extended the model, provided a variety of practical sets of specifications, and utilized modern numerical procedures and equation formulations to handle efficiently the nonlinear and often stiff nature of multi-component batch distillation problem.

Marta and Juan Carlos [63] described a case study to fit a rigorous model using the commercial package HYSYS, for multi-component batch distillation processes.

Galindez H. and Fredenslund [16] developed to simulate the operation of multistage, multi-component batch distillation operations using rigorous algorithms for the integration of the differential equations.

Ping Zhang [64] formulated a rigorous model for the dynamic simulation of a multiphase batch distillation in the software gPROMS.

Meadows [65] developed the first rigorous multi-component batch distillation model, based on assumptions of equilibrium stages, perfect mixing of liquid and vapor phases at each stage, negligible vapor holdup and constant molar holdup.

Jimenez, L. et. Al. [66] used rigorous models as an alternative to predict the concentration profile and to specify the optimal switching time from products to slop cuts for nonlinear dynamic modeling of multi-component batch distillation.

Different methods of solution have been presented by Distefano, Boston and Britt developed the program (BATCHFRAC) as a general simulation package for batch distillation. Holland and Liapis proposed a combination of the two-point implicit method and the theta method for the start-up period and the actual, time dependent, reaction period. Gallun and Holland proposed improvements of the Gear method for the numerical solution of the coupled algebraic and differential equations. Sadotomo and Miyahara used an eigenvalue procedure for solving the balance equations. This method is supposed to be 20 times faster than the Runge-Kutta-Gill method. Guille Reklaitis proposed a method for modeling multi-component distillation with overlaid chemical reaction [3].

Mujtaba and Macchietto [1] described the dynamic optimization of batch reactive distillation with an objective, so they used a detailed model including mass and energy balances.

Elgue [55] developed the rigorous model to solve the differential equations that consist of total and component material balances, total energy balance, negligible vapor holdup, and constant liquid holdup for batch reactive distillation.

Chapter Three

Theoretical Aspects of Batch Reactive Distillation

3.1 Introduction

One of the major operations in the chemical and pharmaceutical industries is the separation of liquid mixtures into their components using distillation. The distillation can be preformed as either a continuous or a batch process.

In this chapter, the mathematical model for simulating a multi-component batch distillation with and without chemical reaction is considered to calculate the mole fraction of the components by using the fundamental principle of mass and energy balance, vapor-liquid equilibrium and reaction rate in a developed program ($\text{MATLAB}_{6.1}$); to give the composition profile, temperature profile, vapor and liquid flow rate profiles and reaction profile.

3.2 Simulation model of multi-component batch distillation with and without chemical reaction

The simulation model of multi-component batch distillation without and with chemical reaction is divided into:

3.2.1 Method of analysis:

The analysis emphasized to develop computer programs to simulate multistage multi-component unsteady state batch distillation with and without chemical reaction of N feed components in the non-ideal cases into a relatively pure products.

The complete stage temperature, internal flow rate (vapor-liquid flow rate), liquid holdup, reaction rate, and composition for all components with time are required and can be calculated by solving (MESH) equations for batch distillation without chemical reaction and (MESHR) for batch with chemical reaction for all trays.

The design model based on the multi-component batch rectification operation Figure 3.1, similarly to a conventional batch distillation column except that for the reaction occurring in the reboiler. This system can be described as a “batch reactor-rectifier” Figure 3.2. It consists of a reaction vessel (reboiler) 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. Where methanol reacted with acetic acid with sulfuric acid as homogenous catalyst in reaction vessel (reboiler) after reaction, water and methyl-acetate are produced, all components are vaporized, so that the reaction takes place in all trays, the desired product input to the condenser section, and collected in the receiver and produced as top product. The rate of reaction is a function of temperature, catalyst concentration of the products and reactants. The following assumptions are made for the developed model:

a- The liquid-phase reaction takes place in all stages.
b- The separation system has sufficient stages and reflux to achieve the desired distillate composition.
c- There are no reactive or non-reactive azeotropes in the system.
d- A total condenser produces a saturated liquid product.

e- Constant plate efficiency.

f- Neglect the vapor holdup.

g- Perfect mixing in all trays.

h- Constant pressure drop.

i- Variable liquid holdup.

j- Ideal vapor phase and non-ideal liquid phase.

k- Homogeneous catalyst (sulfuric acid).

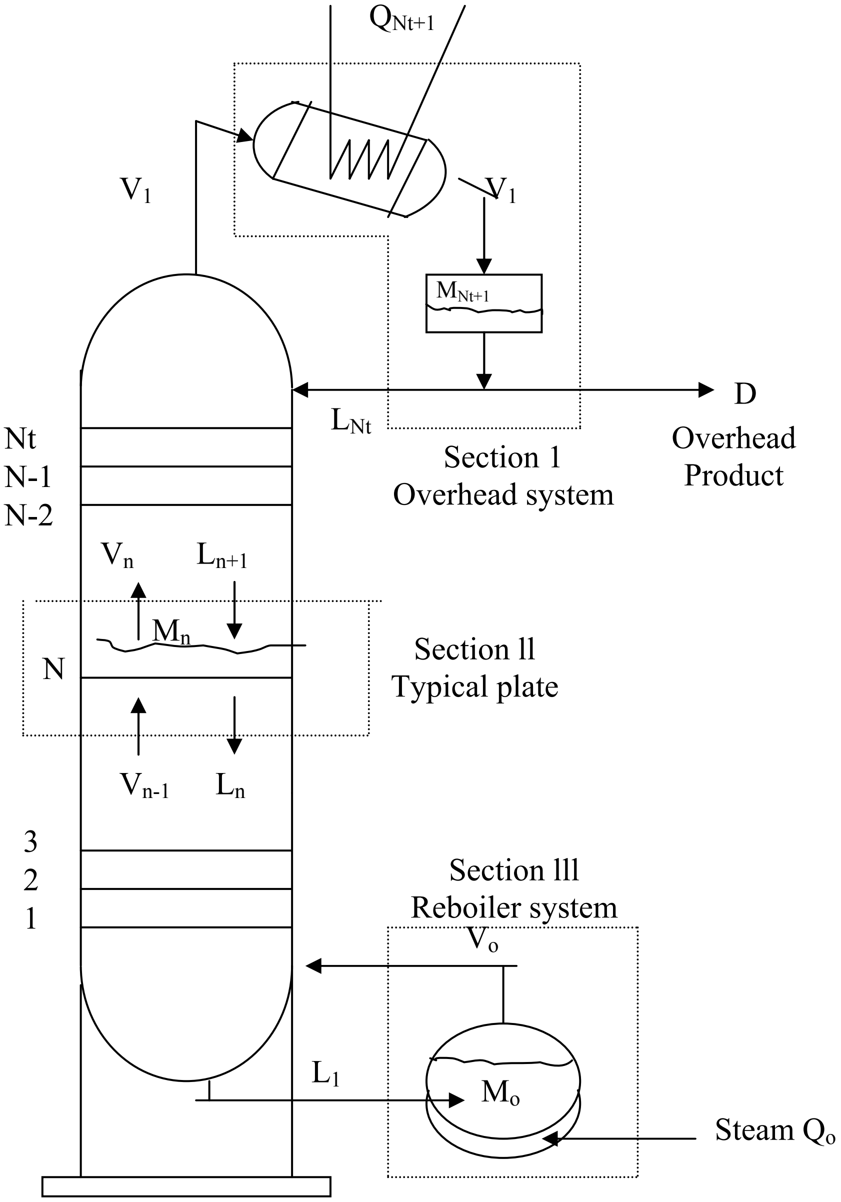


Figure 3.1: General Batch distillation column

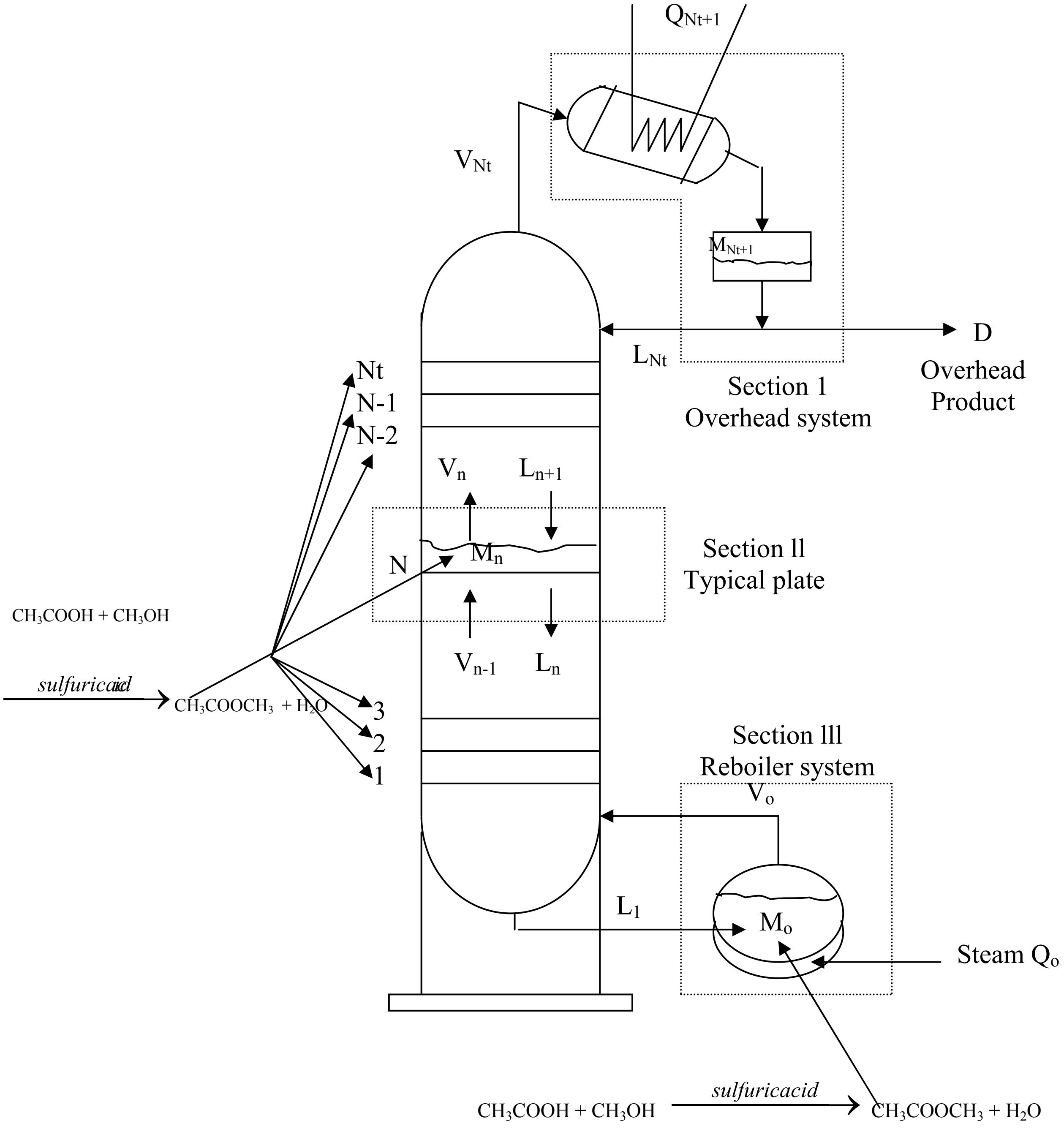


Figure 3.2: Batch Reactive Distillation

The reaction is:

$$CH_3COOH + CH_3OH \xrightarrow{sulfuricacid} CH_3COOCH_3 + H_2O$$

$$\text{(Acetic acid)+ (methanol)} \xrightarrow{sulfuricacid} \text{(methyl-acetate) + (water)}$$

The design calculations are considered for varying batch times, number of stages, and liquid holdup for constant reflux ratio.

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

In all cases the feed is assumed as liquid at its boiling point.

The composition, flow rates of vapor and liquid, reaction rate, temperature profile and liquid holdup for each stage were obtained using developed programs.

3.2.2 Specification of variables

The variables considered for the process system are:

1- Batch time.
2- Number of stages.
3- Liquid holdup.

These variables are studied and the results are compared with previous work(55).

Ternary feed system table 3.1 has been chosen depending on previous work(55), where the feed composition is shown in appendix A table A.9 and table A.10 for batch distillation without and with chemical reaction, and the physical and chemical properties are available in the literature and are given in appendix A table A.3.

Table 3.1: Feed system component

Component	Ternary feed
A	Methanol
B	Acetic acid
C	Water

This system is studied with different number of theoretical stages 4, 6, and 8, different batch time 1, 1.7 and 3 hr. The effect of liquid holdup on the performance of reactive distillation column for the production of methyl acetate, water from methanol and acetic acid.

The initial input data to the developed computer programs for the design method to check its validity are as follows [55]:

1- Number of stages = 6.
2- Reflux Ratio = 2.5.
3- Liquid holdup (reboiler, plates, and condenser) respectively = 85, 0.5, and 14.5 mole.
4- Feed input = 100 mole.
5- Feed composition input for batch distillation without and with chemical reaction respectively:
A- Methanol = 0.25, and 0.5.
B- Acetic Acid =0.07, and 0.46.
C- Water = 0.3, and 0.03.
D- Methyl Acetate = 0.38, and 0.01.
6- Batch Time = 1.7hr.
7- Operating pressure = 1 atm.
8- Initial temperature = 310.15 K.

9- Distillate flow rate = 10 mole/hr.

3.2.3 Vapor-liquid equilibrium relation for non ideal system

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

For non-ideal mixture additional variable γ_i(activity coefficient) is appeared in vapor-liquid equilibrium equation, where the non ideality is in the liquid phase.

$$y_i = \frac{\gamma_i p_i^o}{p} \cdot x_i \tag{3.1}$$

Where γ_i represent degree of deviation from ideality. When $\gamma_i = 1$, the mixture is said to be ideal simplifies the equation to Raoult's law. For non-ideal mixture $\gamma_i \neq 1$, exhibit positive deviation from Raoult's law $(\gamma_i > 1)$, or negative deviation from Raoult's law $(\gamma_i < 1)$, where in this system $\gamma_i > \mathbf{1}$, because there is positive deviation.

The prediction of liquid phase activity coefficient is most important for non-ideal distillation design calculation.

There are several excess energy g^E models to calculate the activity coefficient in multi-component systems, the most important models are (Wilson (10), NRTL (10), UNIQUAC (10), and UNIFAC (10)) [10]. In all these models, the model parameters are determined by fitting the experimental data of binary mixtures. Using binary interaction data only can make the prediction of vapor-liquid equilibrium of multi-component mixture possible.

3.2.3a UNIFAC model

Fredensland et al [46] described UNIFAC (UNIQUAC functional group model). In UNIFAC model each molecule is taken as a composite of subgroups; for example methanol is composed of 1 “CH_3” group, and 1 “OH” group and acetic acid, which contains 1 “CH_3” group and 1 “COOH” group. The interaction parameters between different molecules are defined in literature.

This model also called group contribution method is based theoretically on UNIQUAC equation. The activity coefficient consists of two parts, combinational and residual contribution that is shown in equation 3.2:

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^r \tag{3.2}$$

Combinational contribution γ_i^c takes into account effects arising from difference in molecular size and shape while residual contribution γ_i^r taking into account energetic interactions between the functional group in the mixture, the combinational parts are given as:

$$\ln \gamma_i^c = \ln \frac{\phi_i}{x_i} + 5q_i \ln \frac{{}_i i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j \tag{3.3}$$

Where:

$$\phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \text{ (Volume fraction)} \tag{3.4}$$

$$\vartheta_i = \frac{q_i x_i}{\sum_j q_j x_j} \text{(Area fraction)} \tag{3.5}$$

$$l_i = 5(r_i - q_i) - (r_i - 1) \tag{3.6}$$

The residual contribution is given by:

$$\ln \gamma_i^r = \sum_K v_K^i \left(\ln \Gamma_K - \ln \Gamma_K^i \right) \tag{3.7}$$

In which

$$\ln \Gamma_K = \theta_K \left[1 - \ln \left(\sum_m \theta_m \psi_{mK} \right) - \sum_m \left(\theta_m \psi_{Km} \Big/ \sum_n \theta_n \psi_{nm} \right) \right] \tag{3.8}$$

$$\psi_{nm} = \exp(-a_{nm} / T) \tag{3.9}$$

$$\theta_m = \vartheta_m x_m / \sum_n \vartheta_n x_n \tag{3.10}$$

$$x_m = \frac{\sum_j v_{mj} x_j}{\sum_j \sum_n v_{nj} x_j} \tag{3.11}$$

The efficiency of this method depends on the volume parameters (R_K), group surface area (Q_K) and the group interaction parameters (a_{nm} and a_{mn}) all of these parameters are shown in appendix A table A.5.

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

1- Flexibility, because UNIFAC has a well founded basis for establishing group sizes and shapes.
2- Simplicity, because UNIFAC parameters are nearly independent of temperature for the temperature range considered in this study.
3- Large range of applicability, because UNIFAC parameters are available for a considerable number of different functional groups.

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

In this work the UNIFAC equation was chosen because of its simplicity coupled with it's accuracy compared to that obtained by the other more complex equations, also that it is more correct than other methods.

3.2.3b Antoine Equation:

Antoine equation is mainly used in the calculation of distribution coefficient (K) for ideal system [46]:

$$\ln p_i^o = A_i - B_i /(C_i + T_{ij}) \tag{3.12}$$

This is dimensional equation with p_i^o in mmHg, T_{ij} in C^o. The parameters A_i, B_i, and C_i for each component of the chosen system are given in appendix (table A.1).

3.2.3c Distribution coefficient (K):

Equilibrium VL-distribution ratios (i.e. equilibrium constants) are used to predict the composition and coexisting phases of systems occurring in many problems of industrial interest.

Therefore the equilibrium constant (K) for non-ideal mixture is:

$$K_i = \frac{y_i}{x_i} = \gamma_i \frac{p_i^o}{p} \tag{3.13}$$

3.2.3d Bubble Point Calculation:

Bubble point (BP) is calculated, because a new set of stage temperature is computed during each iteration from bubble point equations.

A new set of temperatures Ti_j is computed stage by stage by computing bubble point temperatures from the normalized $X_{i,j}$ values. The necessary (BP) equation is non- linear in T_j and must be solved iteratively. It is prefered to use UNIFAC iterative method because it is reliable and does not require the calculation of derivatives. UNIFAC method requires the initial assumptions of $X_{i,j}$. For each assumption, the value of $Sum(j)$ is computed from equation 3.14:

$$Sum(j) = \sum_{i=1}^{m} \left(K_{i,j} X_{i,j}\right) - 1 = 0 \qquad 1 \le j \le Nt \qquad (3.14)$$

To normalize $X_{i,j}$ to more corrected value and to decrease the percentage error, the quantity of $Sum(j)$ should be between 0.999 and 1.0

3.2.4 Effect of liquid holdup

At high pressure, vapor holdup in a rectifying column is negligible in batch distillation because of the small molar density of the vapor phase. However, the effect of liquid holdup on the trays and in the condensing and reflux system can be significant when the molar ratio of holdup to original charge is more than a few percent. This is especially true when a charge contains low concentrations of one or more of the components to be separated. 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.

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-based batch-distillation algorithms described later to study the effect on a case-by-case basis [10].

The liquid holdup in the batch distillation system is:

$$Mn_j = {}^{1000*Gp}\Big/ \sum_{i=1}^{N} x_{i,j} * {}^{Wm_i}\!/_{Dens_i} \qquad 2 \le j \le Nt-1 \qquad (3.15)$$

$$Mc_j = {}^{1000*Gc}\Big/ \sum_{i=1}^{N} x_{i,j} * {}^{Wm_i}\!/_{Dens_i} \qquad j = 1 \qquad (3.16)$$

$$Mt_j = Mr_j - (V_{j+1} - V_j) * Stime \qquad j = Nt \qquad (3.17)$$

Where:

$$Mr_j = \frac{1000 * V_{reboiler}}{\sum_{i=1}^{N} x_{i,j} * Wm_i / Dens_i} \qquad j = Nt \qquad (3.18)$$

3.2.5 Batch distillation with chemical reaction

In a typical BRD process, reaction and separation occur simultaneously. The removal of one or more products from the reaction mixture not only increase the conversion of equilibrium limited reactions but also increases or decreases the reaction vessel temperature if the product removed is lower or higher boiling, respectively.

In the system studied, liquid methanol is reacted with liquid acetic acid in the presence of sulfuric acid as homogeneous catalyst to form methyl-acetate and water. The rate of reaction is a function of the temperature, and composition [55].

$$\begin{aligned} Rate\ (j) &= \Delta R_j = Kester * \exp(-E / R * Ti(j)))) \\ &* (Cc_m(j) * Cc_a(j) - (Cc_w(j) * Cc_{ma}(j)) / Keq) \end{aligned} \qquad (3.19)$$

Where:

$$\begin{aligned} Ccm(j) &= Cmo(j) * (1 - Xm(j)) * (Ti(j) / To) * (P / Pm) \\ Ccw(j) &= Cmo(j) * (Zw + Xm(j)) * (Ti(j) / To) * (P / Pw) \\ Cca(j) &= Cmo(j) * (Za - Xm(j)) * (Ti(j) / To) * (P / Pa) \\ Ccma(j) &= Cmo(j) * (Zma + Xm(j)) * (Ti(j) / To) * (P / Pma) \end{aligned} \qquad (3.19.1)$$

Where: $(Kester, E)$ are data in appendix (table A.7).

3.2.6 Heat of Reaction

Batch distillation with chemical reaction efficiently uses the heat released by a reaction. In conventional reactors, the heat of reaction is removed by cooling coil or heat exchangers. Since a boiling liquid in the BRD process surrounds the catalyst, the heat of reaction improves distillation by increasing the vapor flow. This result in energy saving since reboiler duties can be lowered in BRD column [46].

The average heat of reaction over the whole temperature range can be determined by using the following equation 3.20:

$$\Delta H_T = \Delta H^o + \int_{To}^{T} \Delta Cpdt \qquad (3.20)$$

$$\Delta H^\circ = \sum_{i}^{m} \upsilon_i H_{fi}^\circ \qquad (3.21)$$

Where:

H_{fi}° are the heats of formation of component i and υ_i are the stoichiometric numbers positive (+) for products and negative (-) for reactant , Appendix (table A.3).

3.2.7 Effect of time

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

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

In batch distillation process, the composition and temperature profiles along the column change with time. During each step of batch distillation process, the concentration of the liquid on each stage is changed from $x_i(t_o)$ to $x_i(t_1)$; and the temperature of each component is changed from $T_{ij}(t_o)$ to $T_{ij}(t_1)$.

3.3 Design Method for Batch Distillation

The composition, temperature, flow rate, liquid molar density and heat transfer at each stage were determined by using rigorous method stage by stage calculation.

3.3.1 Rigorous Method Algorithm for Batch distillation without chemical reaction

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 and Figure 3.2, a general schematic representation of equilibrium stage j is shown in Figure 3.3, where the stage is numbered top from the bottom.

Entering stage j as shown in Figure 3.3, with overall composition in mole fractions Z_{ij} of component i, temperature T_{ij}, liquid holdup Mn_{ij}, and pressure P_{ij}. During each step of batch process, the conversion of the liquid on each stage effected by time interval Δt so that changed from $x(t_o)$ to $x(t_1)$, also the effect of time interval on the temperature $T_{ij}(t_0)$ to $T_{ij}(t_1)$, and the effect of time interval on liquid holdup $Mn_{ij}(t_o)$ to $Mn_{ij}(t_1)$. At stage j where the liquid flow rate $L_{i,j-1}$ entering stage j from stage $j-1$ above, with compositions in mole fractions $x_{i,j-1}$, temperature $T_{i,j-1}$, and pressure $P_{i,j-1}$, similarly from stage $j+1$ below, so the vapor flow rate $V_{i,j+1}$ enterring stage j, with composition $y_{i,j+1}$, temperature $T_{i,j+1}$, and pressure $P_{i,j+1}$.

3.3.2 Rigorous Method Algorithm for Batch distillation with chemical reaction

A similar mathematical model is considered for batch distillation with chemical reaction, except that the rate of reaction must be introduced in the calculation, where the rate of reaction $\Delta R_{i,j}$ in stage j is changed with time interval Δt from $\Delta R_{i,j}(t_o)$ to $\Delta R_{i,j}(t_1)$.

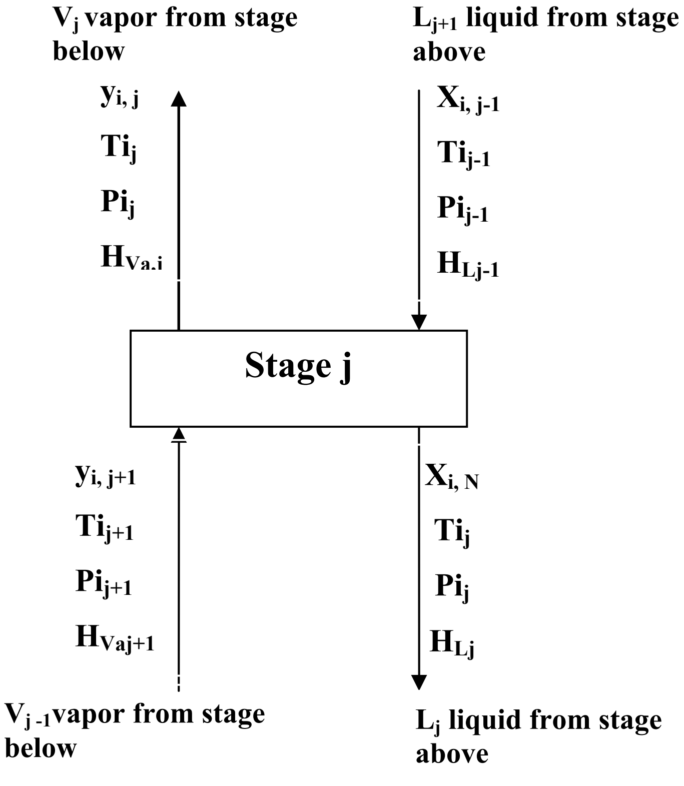


Figure 3.3: General Equilibrium Stage

3.4 Simulation of Batch distillation column without and with reaction

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

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

$$V_1 \mathrm{y}_{\mathrm{i},1} - \mathrm{L}_\mathrm{o}\mathrm{x}_{\mathrm{i,o}} - \mathrm{Dx}_{\mathrm{i,D}} = \mathrm{d}(\mathrm{M}_\mathrm{o} x_{i,o}) \big/ dt \tag{3.22}$$

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

$$(Sx)_i = \sum_{i=1}^{m} y_{ij} / K_{i,j} - 1 = 0 \tag{3.23}$$

$$(Sy)_i = \sum_{i=1}^{m} x_{ij} * K_{i,j} - 1 = 0 \tag{3.24}$$

Where: $m =$ is the number of component.

3- Phase equilibrium relations (E-equations).

$$E_{i,j} = y_{i,j} - K_{i,j} x_{i,j} \tag{3.25}$$

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

$$V_1 h_{V1} - (L_o + D) h_{Li_o} = Q_{Nt+1} + \frac{d(Mc \cdot h_{Li_o})}{dt} \tag{3.26}$$

Where:

Nt = number of stages.

5- Reaction rate equations (R-equation)

$$\sum_{j=1}^{m} \Delta R_j - \Delta R = 0 \tag{3.27}$$

The solution of (MESH) equations for multi-component batch distillation without chemical reaction and (MESHR) equations for multi-component batch distillation with chemical reaction problems is obtained by finding a set of temperature, phase rate, batch time, rate of reaction and compositions which satisfies all the equations of the model that described above (i.e. (MESH and MESHR) equations).

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

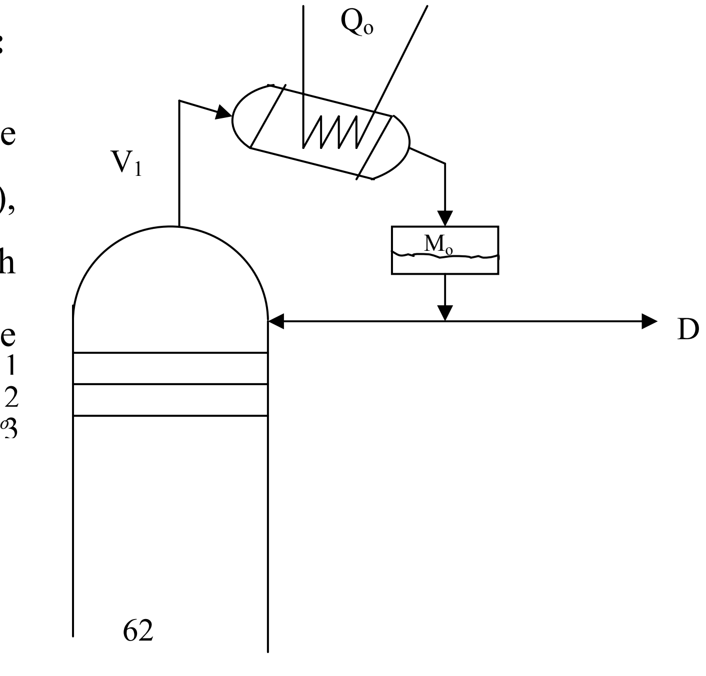
To solve the equations below the initial value problem for the system of ordinary differential and algebraic equations (DAES). The total number of equations for batch distillation model is (2CN+3C+4N+7). If variables N_t, D, Rr, M^o_{Nt-1} and all G_j are specified and the correlations for computing liquid densities, vapor and liquid enthalpies and K-values are available. The number of unknown variables, distributed is equal to number of equations (2CN+3C+4N+7).

3.4.1 Solution of Material Balance

The determination of phase composition and its temperature can be done by solution of material balance equations.

3.4.1a The overhead section:

At the top part of the column (condenser section), the composition of each component $x_{i,o}$, temperature $T_{i,o}$, and liquid holdup $Mc_{i,o}$



is calculated using the following equations:

$$dxi,o\big/dt = -\left(\left(L_o + D + dMc_o / dt\big/Mc_{i,o}\right)\right) * X_{i,o} \; + \left(\left(\left(V_1 * K_{i,1}\right)\big/Mc_{i,o}\right)\right)\cdot X_{i,1}$$

(component material balance) (3.28)

Where

$$Mc_{i,o} = Gc * L_{D_{i,j}} \qquad (3.29)$$

$$dMc_o / dt = V_1 - L_O - D \qquad (3.30)$$

$$L_O = R * D \qquad (3.31)$$

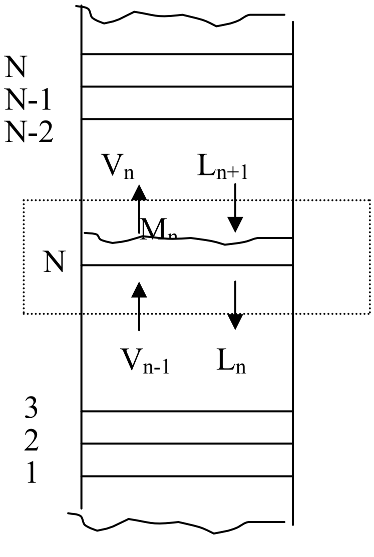
For batch reactive distillation the chemical reaction term is added to the equation (3.32):

$$dxi,o\big/dt = -\left(\left(L_o + D + Mc_o\big/Mc_{i,o}\right)\right) * X_{i,o}$$

$$+\left(\left(\left(V_1 * K_{i,1}\right)\big/Mc_{i,o}\right)\right)\cdot X_{i,1} + \Delta R_i + vol \qquad (3.32)$$

3.4.1b The typical stage section:

At the main part of the column (typical stage section), the conversion of each component x_{ij}, temperature $T_{i,j}$, and liquid holdup $Mn_{i,j}$ are calculated as:



$$\frac{dxi,j}{dt} = \left(\frac{L_{j-1}}{Mpi_j}\right) * X_{i,j-1} - \left(\left(L_j + \left(K_{i,j} * V_j\right) + \frac{dM_j / dt}{Mp_{i,j}}\right)\right) * X_{i,j} + \left(\frac{K_{i,j+1} * V_{j+1}}{Mp_{i,j}}\right) * X_{i,j+1} \quad \text{(component material balance)} \qquad (3.33)$$

Where:

$$Mp_{i,j} = Gp * L_{D_{i,j}} \qquad (3.34)$$

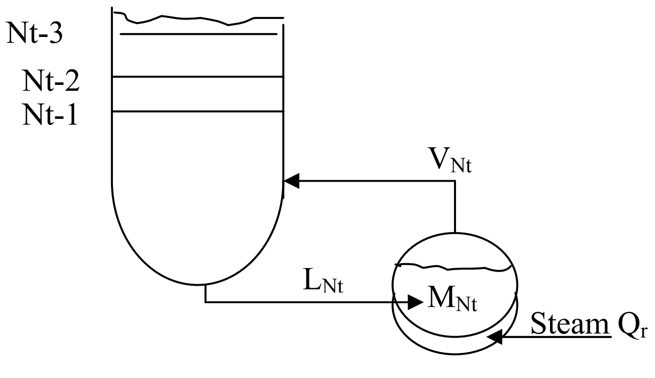
$$L_j = V_{j+1} + L_{j-1} - V_j - dM_j / dt \qquad (3.35)$$

For batch reactive distillation the chemical reaction term must be added to equation 3.36; therefore:

$$\frac{dxi,j}{dt} = \left(\frac{L_{j-1}}{Mpi_j}\right) * X_{i,j-1} - \left(\left(L_j + \left(K_{i,j} * V_j\right) + \frac{dM_j / dt}{Mp_{i,j}}\right)\right) * X_{i,j} + \left(\frac{K_{i,j+1} * V_{j+1}}{Mp_{i,j}}\right) * X_{i,j+1} + (\Delta R_i + vol) \qquad (3.36)$$

3.4.1c The reboiler section:

At the lower part of the column (reboiler section), the mole fraction of each feed component $x_{i,Nt}$,temperature $T_{i,Nt}$, and liquid holdup $Mt_{i,Nt}$ are calculated as:



$$\frac{dxi_{,Nt}}{dt} = \left(\frac{L(Nt-1)}{Mr}\right) * X_i(Nt-1) - \left(\left(\left(\left(V(Nt) * K_i(Nt)\right) + Mt\right) / Mr\right) * X_i(Nt)\right)$$

(component material balance) (3.37)

$$Mr_j = M^o_{Nt+1} - \sum_{j=0}^{Nt} M_j - \int_0^t D dt \qquad (3.38)$$

When batch reactive distillation is considered the term of chemical reaction is added to equation (3.39):

$$dxi,o \big/ dt = \left(L(1) \big/ Mr \right) * X_i(1) - ((((V(1) * K_i(1)) + Mt) / Mr) * X_i(1)) + \Delta R_i + \text{vol} \qquad (3.39)$$

Then the material balance equations are reduced to a tri-diagonal matrix form for batch reactive distillation:

$$\begin{pmatrix} B_1 & C_1 & 0 & 0 & 0 \\ A_2 & B_2 & C_2 & 0 & 0 \\ 0 & A_j & B_j & C_j & 0 \\ 0 & 0 & A_{j-1} & B_{j-1} & C_{j-1} \\ 0 & 0 & 0 & A_{Nt} & B_{Nt} \end{pmatrix} \begin{pmatrix} X_{i1} \\ X_{i2} \\ X_{i,j} \\ X_{ij-1} \\ X_{iNt} \end{pmatrix} = \begin{pmatrix} dxi,1 \big/ dt \\ dxi,2 \big/ dt \\ dxi,j \big/ dt \\ dxi,j-1 \big/ dt \\ dxi,Nt \big/ dt \end{pmatrix} \qquad (3.40)$$

Where

$$A_1 = 0 \qquad (3.41a)$$

$$B_1 = -\left(\left(L_o + D + dMc_o / dt \Big/ Mc_{i,o} \right) \right) \qquad j = 0 \qquad (3.41b)$$

$$C_1 = \left(\left(\left(V_1 * K_{i,1} \right) \Big/ Mc_{i,o} \right) \right) + rate(o) * Vol \qquad j = 0 \qquad (3.41c)$$

$$A_j = \left(L_{j-1} \Big/ Mpi_j \right) \qquad 2 \le j \le Nt - 1 \qquad (3.42a)$$

$$\mathrm{B_j} = -\left(\left(L_j + \left(K_{i,j} * V_j\right) + {}^{Mn_j}\!\big/_{Mp_{i,j}}\right)\right) \qquad 2 \le j \le Nt-1 \qquad (3.42b)$$

$$\mathrm{C_j} = \left({}^{K_{i,j+1} * V_{j+1}}\!\big/_{Mp_{i,j}}\right) + rate(j) * Vol \qquad 2 \le j \le Nt-1 \qquad (3.42c)$$

$$\mathrm{A_n} = \left({}^{L(Nt-1)}\!\big/_{Mr}\right) \qquad j = Nt \qquad (3.43a)$$

$$\mathrm{B_n} = -\left(\left(\left(\left(V(Nt) * K_i(Nt)\right) + Mt\right)/Mr\right)\right) + rate(1) * Vol \qquad j = Nt \qquad (3.43b)$$

$$\mathrm{C_n} = 0 \qquad (3.43c)$$

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

$$A.X = {}^{dx_{i,j}}\!\big/_{dt} \qquad (3.44)$$

When the initial composition of the feed streams and stage composition are given [55], and the amounts of Q_r, R_r, Vol, $Dens$, Wm, Gc, Gp, L_V, T_B, and D are all constants specified in appendix A table A.3, table A.4, and table A.8, so that we can calculate the variables $V_j, L_j, K_j, T_{i,j}, L_{D_{i,j}}, P_i, Cc_{i,j}, Mp_{i,j}, Mc_{i,j}, Mn_j, Mc_j, Mt$ by:

$$V_j = {}^{3600 * Qr}\!\Big/_{\sum_{i=1}^{N} x_{i,j} L_{V_i}} \qquad \text{(at initial mole fraction)} \qquad (3.45)$$

$$V_{j+1} = \left[\left(\frac{1}{\left(HVa_{j+1} - H_{Lij}\right)}\right) \bullet \begin{pmatrix} V_j \cdot \left(HVa_j - H_{Lij}\right) - \\ L_{j-1} \cdot \left(H_{Lij-1} - H_{Lij}\right) + Mn_j \cdot \dfrac{dH_{Lij}}{dt} \end{pmatrix}\right] \qquad (3.46)$$

$$L_j = V_{j+1} + L_{j-1} - V_j - dM_j / dt \qquad (3.47)$$

$$K_{i,j} = {y_{i,j}}/{x_{i,j}} \qquad (3.48)$$

$T_{i,j} =$ (is calculated from UNIFAC method)

$$P_{i,j} = \exp\left(A_i + {B_i}/{C_i + T_i} \right) \qquad (3.49)$$

$$Cc_{i,j} = C_{i,o}(j) * (1 - x_{i,j}) * \left({Ti_j}/{To} \right) * \left({P}/{P_i} \right) \qquad (3.50)$$

$$L_{D_{i,j}} = {C1_i}/{C2_i \wedge \left[1 + \left(1 - \left({Ti_j}/{C3_i} \right) \right) \wedge C4_i \right]} \qquad (3.51)$$

$$Mp_{i,j} = Gp * L_{D_{i,j}} \qquad (3.52)$$

$$Mc_{i,j} = Gc * L_{D_{i,j}} \qquad (3.54)$$

$$dM_j / dt = V_{j+1} + L_{j-1} - V_j - L_j \qquad 2 \le j \le Nt - 1 \qquad (3.55)$$

$$dMc_o / dt = V_1 - L_O - D \qquad j = 0 \qquad (3.56)$$

$$Mr_j = M^o_{Nt+1} - \sum_{j=0}^{Nt} M_j - \int_0^t D dt \qquad j = 0 \qquad (3.57)$$

After calculating ${dxi,j}/{dt}$ from the algorithm Matrix we can calculate the mole fraction $X_{i,j}$ from eigen-value.

The values of mole fraction $X_{i,j}$ are corrected to provide better values of the assumed iteration variables for the next trial; therefore, for each iteration, the computed set of $X_{i,j}$ values for each stage will in general, not satisfy the summation constraint given by equation 3.58. The values of $X_{i,j}$ can be normalized using the following relation:

$$(x_{i,j})_{normalized} = \frac{x_{ij}}{\sum_{i=1}^{m} x_{ij}} \qquad (3.58)$$

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

$$K_{i,j} = {}^{y_{i,j}}\!\big/_{x_{i,j}} \qquad (3.59)$$

$$P_{i,j} = \exp\left(A_i + {}^{B_i}\!\big/_{C_i + T_i} \right) \qquad (3.60)$$

$$Sum(j) = \sum_{i=1}^{m} \left(K_{i,j} X_{i,j} \right) - 1 = 0 \qquad 1 \le j \le Nt \qquad (3.61)$$

3.4.2 Solution of Energy Balance

The determination of energy balance can be done by the solution of energy balance equations for batch distillation column without and with chemical reaction. The key to the solution is the results from modified form H-equations 3.26.

The modified H-equations are obtained first by calculating the liquid phase enthalpy (H_{Li}), and then we calculate the enthalpy of vapor phase (Hva). Second calculating the vapor flow rates (V_{j+1}), then the heat supplied to the condenser (Qc) is calculated.

3.4.2a For Ideal system:

The liquid phase (H_{Li}), and the vapor phase (Hva), are calculated by the equations:

$$H_{Li} = Cpm_i * (Ti_j - T_o) \quad \text{(Enthalpy of liquid phase)} \tag{3.62}$$

Where: the mean heat capacity Cpm_i is give in appendix A table A.6

$$\begin{aligned} HV_{ai}(j) &= h_{oi} + C1iV * (Ti(j) - To) \\ &+ C2iV * ((Ti(j)^\wedge 2 - To^\wedge 2)/2) + C3iV * \\ &((Ti(j)^\wedge 3 - To^\wedge 3)/3) + \\ &C4iV * ((Ti(j)^\wedge 4 - To^\wedge 4)/4) \end{aligned} \tag{3.63}$$

(Enthalpy of vapor phase)

Where:

[C1iV, C2iV, C3iV, C4iV] are the constant enthalpy coefficients and are available in Appendix A table A.2.

$$\begin{aligned} h_{oi} &= C1iV * (To) + C2iV * (To^\wedge 2/2) + \\ &C3iV * (To^\wedge 3/3) + C4iV * (To^\wedge 4/4) \end{aligned} \tag{3.64}$$

$$HLi_j = \sum_i^{Nt} X_{i,j} H_{Li} \quad \text{(Total enthalpy of liquid phase)} \tag{3.65}$$

A new set of V_{j+1} tear variables is computed by applying the following modified energy balance, which is obtained by the calculation of liquid and vapor enthalpies:

$$V_{j+1} = \left[\left(\frac{1}{\left(HVa_{j+1} - H_{Lij} \right)} \right) \bullet \left(\begin{array}{l} V_j \cdot \left(HVa_j - H_{Lij} \right) - \\ L_{j-1} \cdot \left(H_{Lij-1} - H_{Lij} \right) + Mn_j \cdot \dfrac{dH_{Lij}}{dt} \end{array} \right) \right] \qquad (3.66)$$

Where:

$$\frac{dH_{Lij}}{dt} = H_{Li(i,j)} - H_{L(i,j-1)} \qquad (3.67)$$

Then the heat supplied to the condenser (Qc), is calculated by equation below:

$$Qc = V_j * \left(\sum_{i}^{N} X_{i,j} \left(Hva_{i,j} - H_{Li,j} \right) \right) - Mr * HLi_j \qquad (3.68)$$

3.4.2b For Non-Ideal system:

For non-ideal system heat of mixing was added to the total enthalpy liquid phase:

$$H_{mix} = RT \sum_{i=1}^{C} \left(x \ln \gamma_i \right) \qquad (3.69)$$

$$HLi_j = \sum_{i}^{N} X_{i,j} H_{Li} + H_{mix} \qquad (3.70)$$

In batch reactive distillation the term of chemical reaction is added to the enthalpy in Liquid phase:

$$H_{Li} = Cpm_i * \left(Ti_j - T_o \right) * rate(j) * Vol \qquad (3.71)$$

3.5 Computational Procedure

3.5.1 Batch distillation process:

A computer program is developed using $\text{Matlab}_{6.1}$ version as shown in appendix B (B-1) to determine the phase composition and its temperature in a batch distillation process. This program is operated by:

1- Time loop that begins at $t = 0$, time interval $\Delta t = 0.0017 \sec$, and batch time $Btime = 1.7hr$ (according to reference [55] for checking the model).

2- Stage loop that begins at $m = 1$, to $m = Nt$ (where $Nt =$ the total number of stages).So that this program was operated for any number of stages.

3- Temperature loop to calculate the boiling point or tray temperature that begins at $T_{initial} = 298^0 K$ reference temperature which depends on the boiling point of the feed components input. This loop calculates the partial pressure of each component i using Antoine equation, the activity coefficient γ_i using UNIFAC equations, then the equilibrium constant $K_{i,j}$. 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 calculation of vapor and liquid flow rates are calculated after the temperature on each stage is corrected. The concentration of each component i is calculated by tri-diagonal matrix, and solved using Igion value. Then we normalized the mole fraction of each component i. After normalization the mole fraction of each component i is calculated as input to another batch time loop.

From energy balance the total liquid enthalpy and vapor enthalpy are calculated by tray loop, and then the inter-cooler load Qc_{Nt+1} is obtained.

3.5.2 Batch reactive distillation process:

The developed model for computer program for batch distillation is modified by adding the reaction rate term to the material balance to obtain the mole fraction of each component as shown in appendix B (B-2), and (B-3).

The energy balance is modified by adding the reaction effect to the liquid enthalpy term.

Chapter Four
Results and Discussions

4.1 Introduction

In the previous chapter, the analysis of the design method for the multi-component batch distillation with and without chemical reaction for multistage column was considered.

In this chapter the final results of the vapor and liquid flow rates, temperature, liquid holdup in (reboiler, plates, and condenser), and liquid composition profile, using the developed computer programs MATLAB$_{6.1}$ for batch distillation without and with chemical reaction to produce water and methyl-acetate are presented and compared with the results obtained by Elgue, and Lann [55].

The effects of some process variables on the performance of multi-component batch reactive distillation process were studied. All the results are taken from the developed computer programs using MATLB$_{6.1}$. The total vapor and liquid flow rates, temperature, reaction rate, and the liquid composition profile at various process, variables are presented graphically for comparison purposes.

In batch reactive distillation the reaction takes place along the distillation column:

$$CH_3COOH + CH_3OH \xrightarrow{H_2SO_4 \text{ as a Catalyst}} CH_3COOCH_3 + H_2O$$

$$\text{(Acetic acid)} + \text{(methanol)} \longrightarrow \text{(methyl-acetate)} + \text{(water)}$$

In this chapter the effect of number of stages, effect of liquid holdup and batch time on the estrification of methanol with acetic acid to produce methyl-acetate and water using batch reactive distillation are considered.

4.2 Batch distillation without chemical reaction

In the present work, and as a preliminary step, a developed computer program using MATLAB$_{6.1}$ was constructed that performs calculations of temperature profile, liquid mole fraction, heat supply to the reboiler (Q_r), with constant reflux ratio, liquid ,and vapor flow rate profiles and liquid holdup, in batch distillation column. Figure 4.1 shows the change of reboiler liquid composition profile of each feed components with batch time. This is expected and it is a positive sign regarding the program validity, since up to the test under hand, no reaction terms were added to the mathematical model. In order to correct one has to add the reaction term to the material and energy balance under batch reactive distillation (i.e. computing distillation conditions). So the results for reboiler composition Figure 4.1 were compared with experimental reference data [55], this is shown in Figure 4.2, the results give a good agreement for liquid composition in the reboiler. 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 in the simulation procedure. In fact complex models and 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 representations allows validating the simulation environment. Figure 4.3, shows the change in composition profile of the methyl acetate product that gradually decreased with batch time range 0-1.7hr from the reboiler (stage 1) to distillate (stage 6).

The mole fraction of methyl acetate in the reboiler and distillate reached 0.75 and 0.197 respectively, while for water figure 4.5 shows a gradual increase in composition profile from the reboiler to distillate for the same batch time range. Figures 4.4 and 4.6 show the change in composition profile for both methanol and acetic acid with batch time. As the batch time is increased the composition profile of methanol and acetic acid increased from the reboiler to the distillate, the maximum purity for methanol 0.315 and for acetic acid 0.098 at distillate section. No reaction takes place but a conventional batch distillation process. These figures show the selectivity of methyl acetate is 0.197 and for water 0.4 and the recovery fraction of both methyl acetate and water is 19.03% and 49.56% respectively, when batch distillation without chemical reaction is considered as a conventional system.

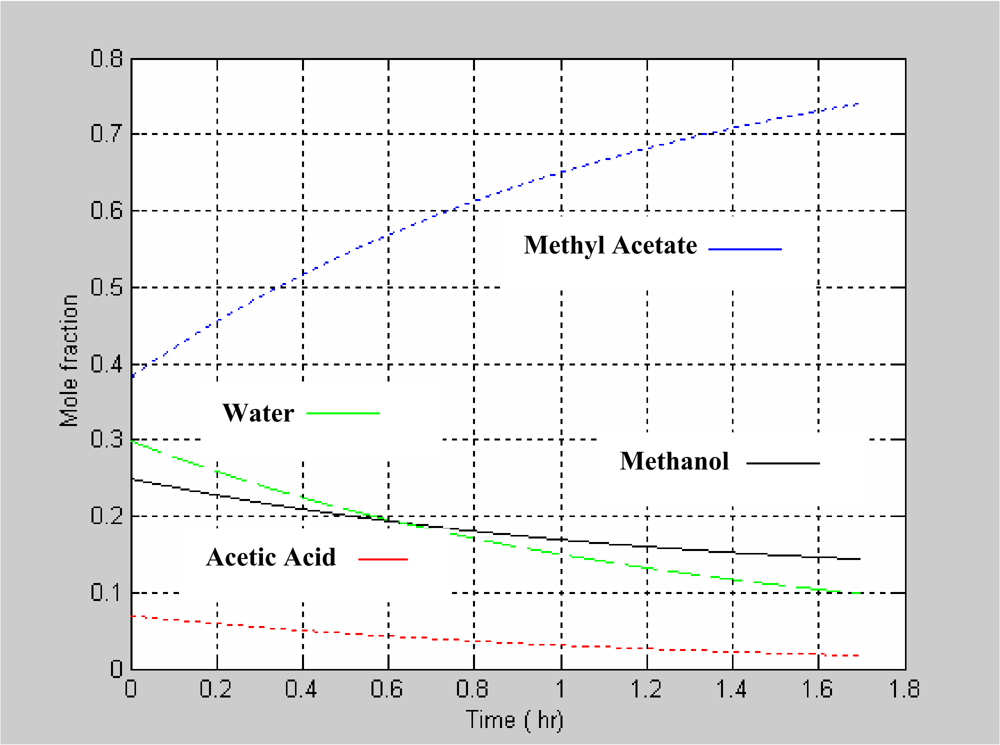


Figure 4.1: mole fraction of each component vs. batch time at reboiler without chemical reaction

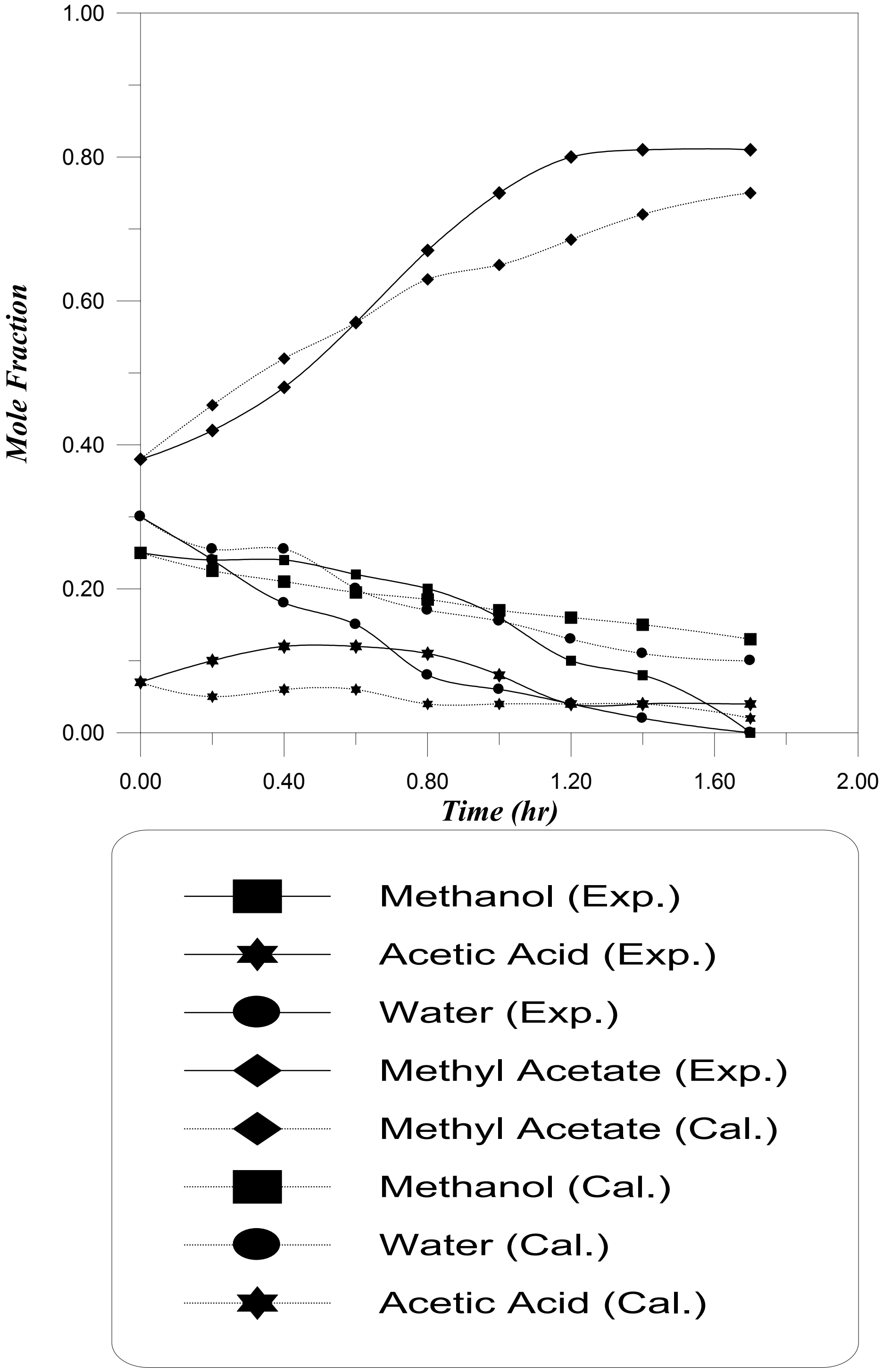


Figure 4.2: Comparison between the mole fractions of the experimental and calculated works at reboiler(without chemical reaction)

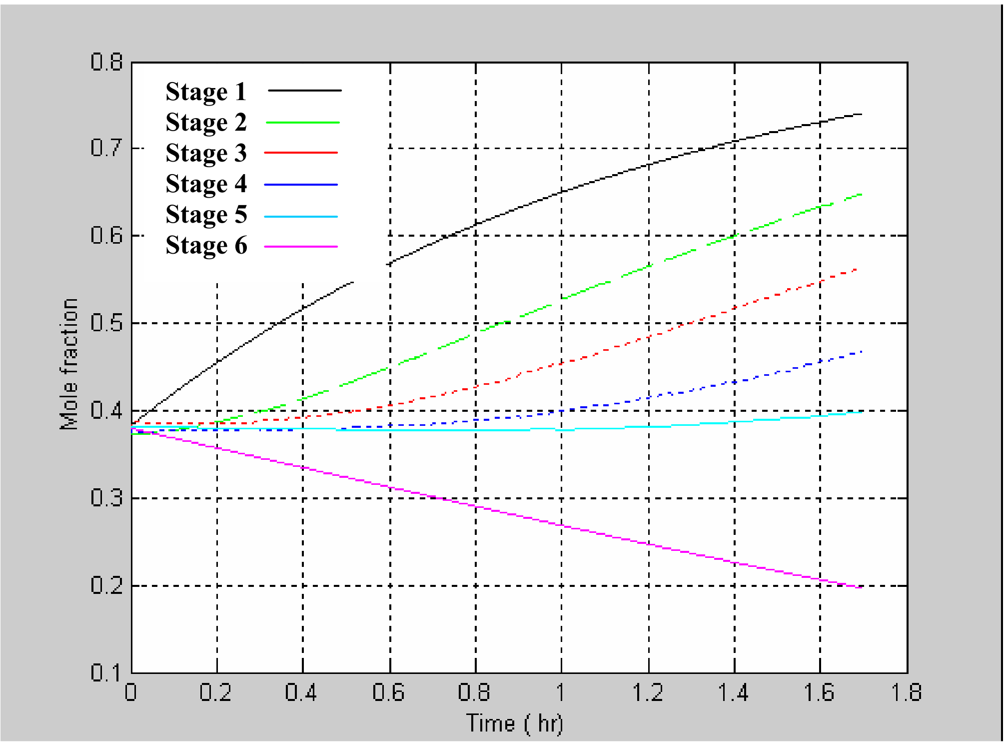


Figure 4.3: mole fraction of the product water vs. batch time at each stage (without chemical reaction)

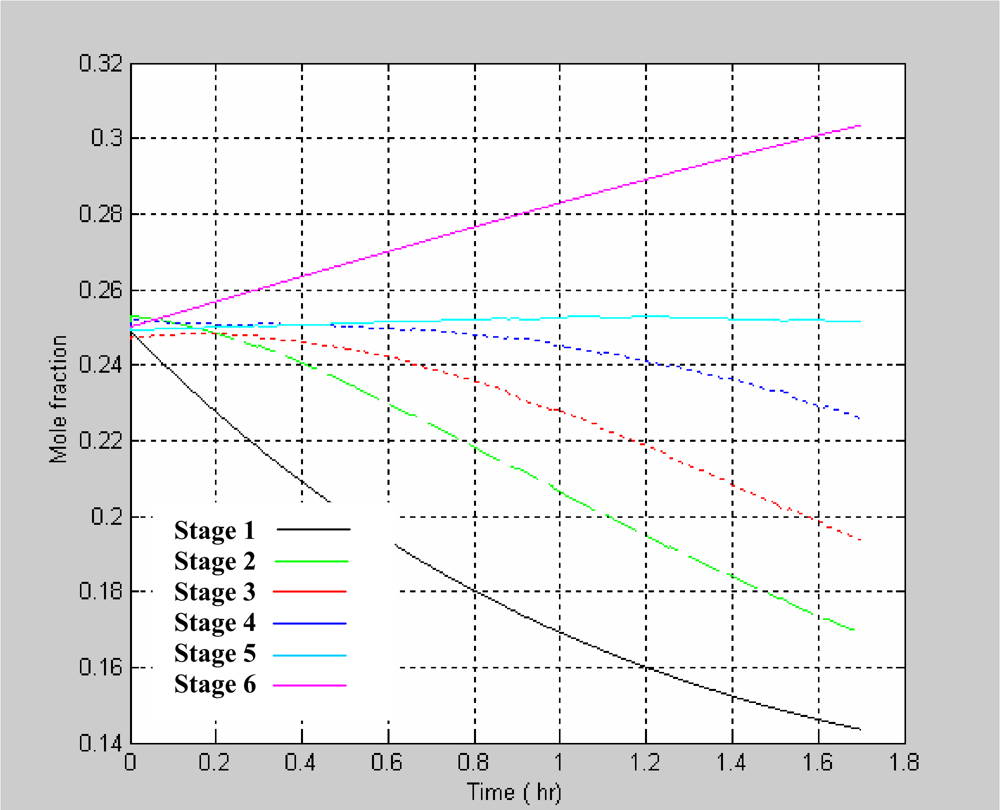


Figure 4.4: mole fraction of the methanol vs. batch time at each stage without chemical reaction

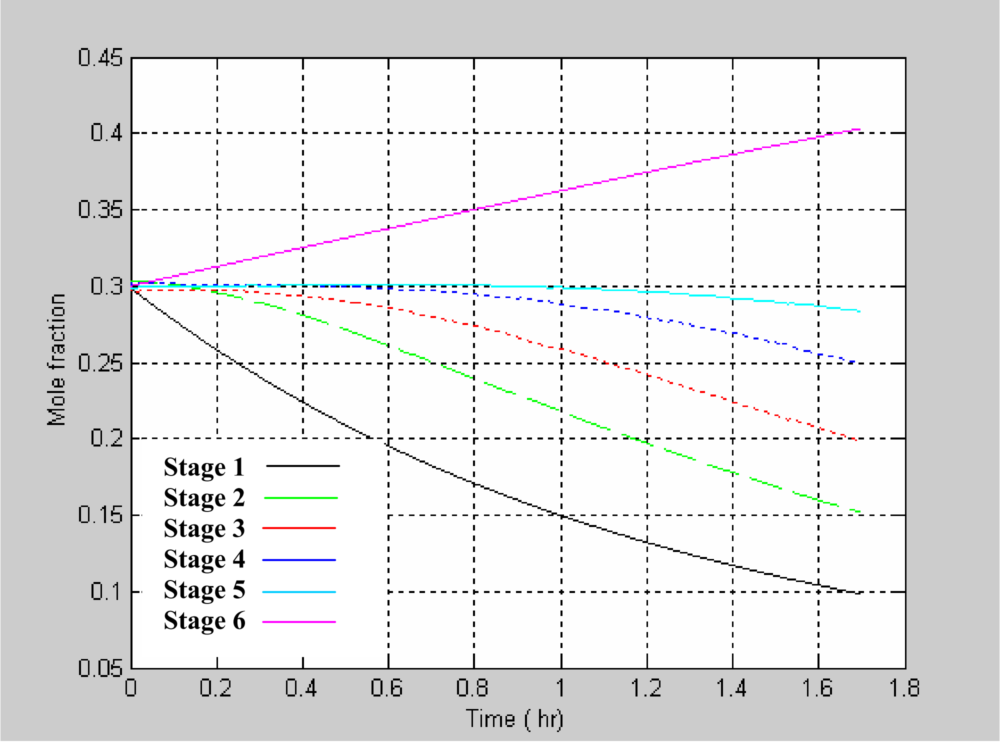


Figure 4.5: mole fraction of the methylacetate vs. batch time at each stage without chemical reaction

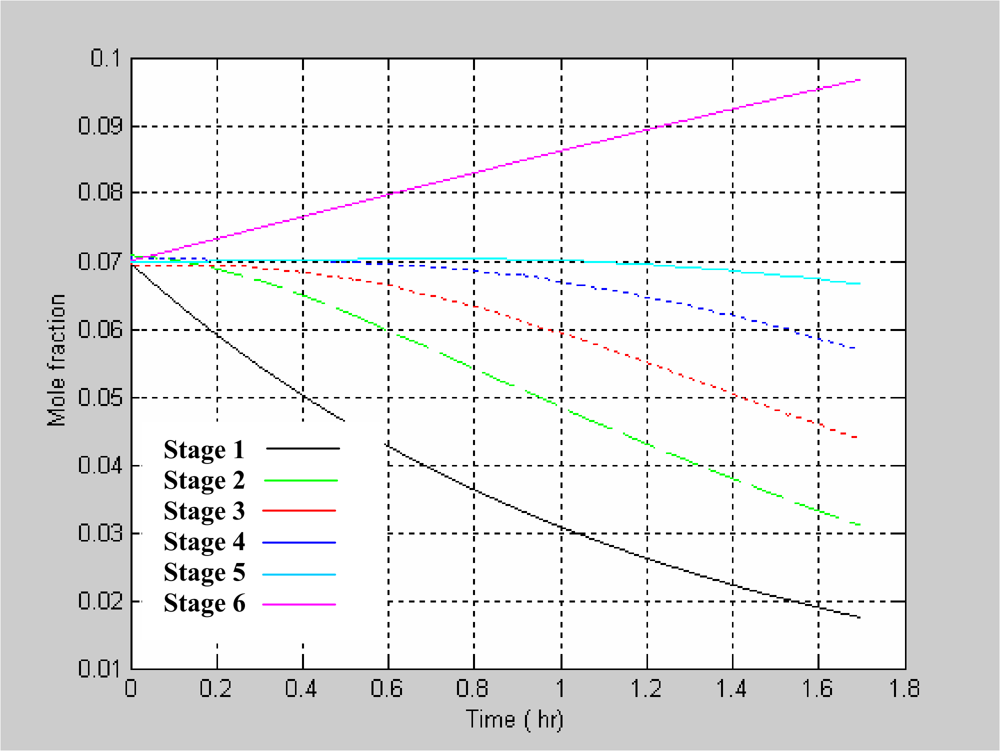


Figure 4.6: mole fraction of the Acetic acid vs. batch time at each stage without chemical reaction

4.3 Batch distillation Column with Chemical Reaction

When the reaction term was added to the model calculation, together, with the necessary modifications. The modified program was run to solve the reaction of acetic acid and methanol with sulfuric acid as homogeneous catalyst to produce water and methyl-acetate with reaction corrections. The developed model calculation was checked with the conditions taken from reference [55]:

Take a single un-reversible chemical reaction at each stage. This modification was affected by incorporating temperature profile, liquid mole fraction, heat supply to the reboiler (Q_r), reaction rate profiles and constant vapor and liquid flow rates in batch reactive distillation column.

Figure 4.7 shows the changes in still liquid composition of each feed component with batch time. As batch time is increased, the concentrations of methyl acetate, methanol and acetic acid decreased while for water increased at the reboiler section. Figure 4.8 shows the comparison of still liquid composition profile of each component versus batch time for present work with the operating reference data [55], so it gives a good agreement, with deviation due to thermodynamic models used, the non-ideal model and the kinetic model simplicity.

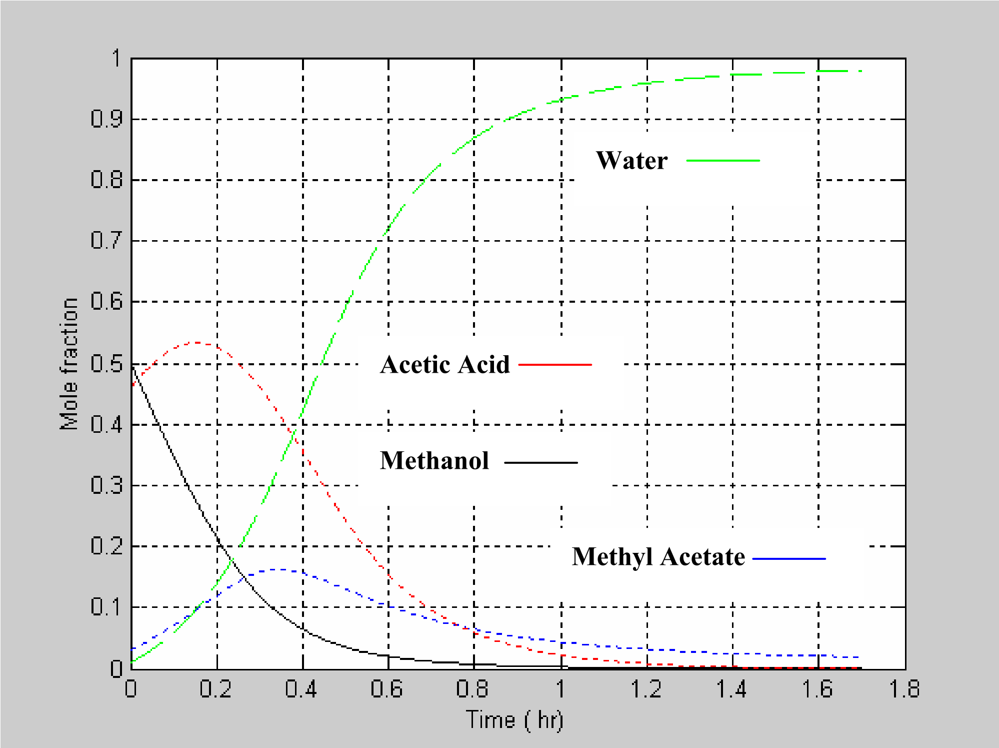


Figure 4.7: mole fraction of each component vs. batch time at reboiler section with chemical reaction

Figure 4.9, shows the composition profile of methyl acetate that increased form the reboiler to distillate section, the mole fraction of methyl acetate in the distillate section 0.247, % conversion is 49.41%, and recovery fraction is 0.907kmol/hr while for water the composition profile decreased from the reboiler to the distillate section as shown in Figure 4.11. Figure 4.10 and 4.12 show a decrease in composition of the reactants methanol and acetic acid with batch time from the distillate to reboiler section, which approached zero at time above 1.2hr for acetic acid and 0.8hr for methanol at reboiler section. This is due to the fact that methanol and acetic acid react with the presence sulfuric acid as a catalyst to produce methyl acetate and water; the maximum purity for methanol is 0.01 and for acetic acid is 0.04. This reaction takes place in the reboiler and in each tray through out the tower. Figure 4.13 shows that the change of reaction rate profile with batch time on each tray and in reboiler section. In this Figure the reaction profile was decreasing from the reboiler to distillate section with batch time range 0-1.2hr, which approaches 0.118. Above 1.2hr the reaction rate profile at distillate section was increased to 0.14, where the reaction profile for plates and reboiler section stayed constant at 0.12. Due to reaction there is a change in temperature profile with batch time as shown in Figure 4.14, from this Figure the temperature profile was increased from the reboiler to distillate section with batch time range 0-1hr, which approach 326.5 K, above 1hr the temperature profile at distillate section decreased to 324 K, where the temperature for plates and reboiler section stayed constant at 326 K, all with constant reflux ratio of 2.5 and constant liquid holdup reboiler, plate, and condenser being 85, 0.5, and 14.5 respectively. These Figures show the selectivity of methyl acetate being 0.247 and for water 0.7 at distillate section. The recovery fraction of both methyl acetate and water are 0.907 and 0.858 respectively.

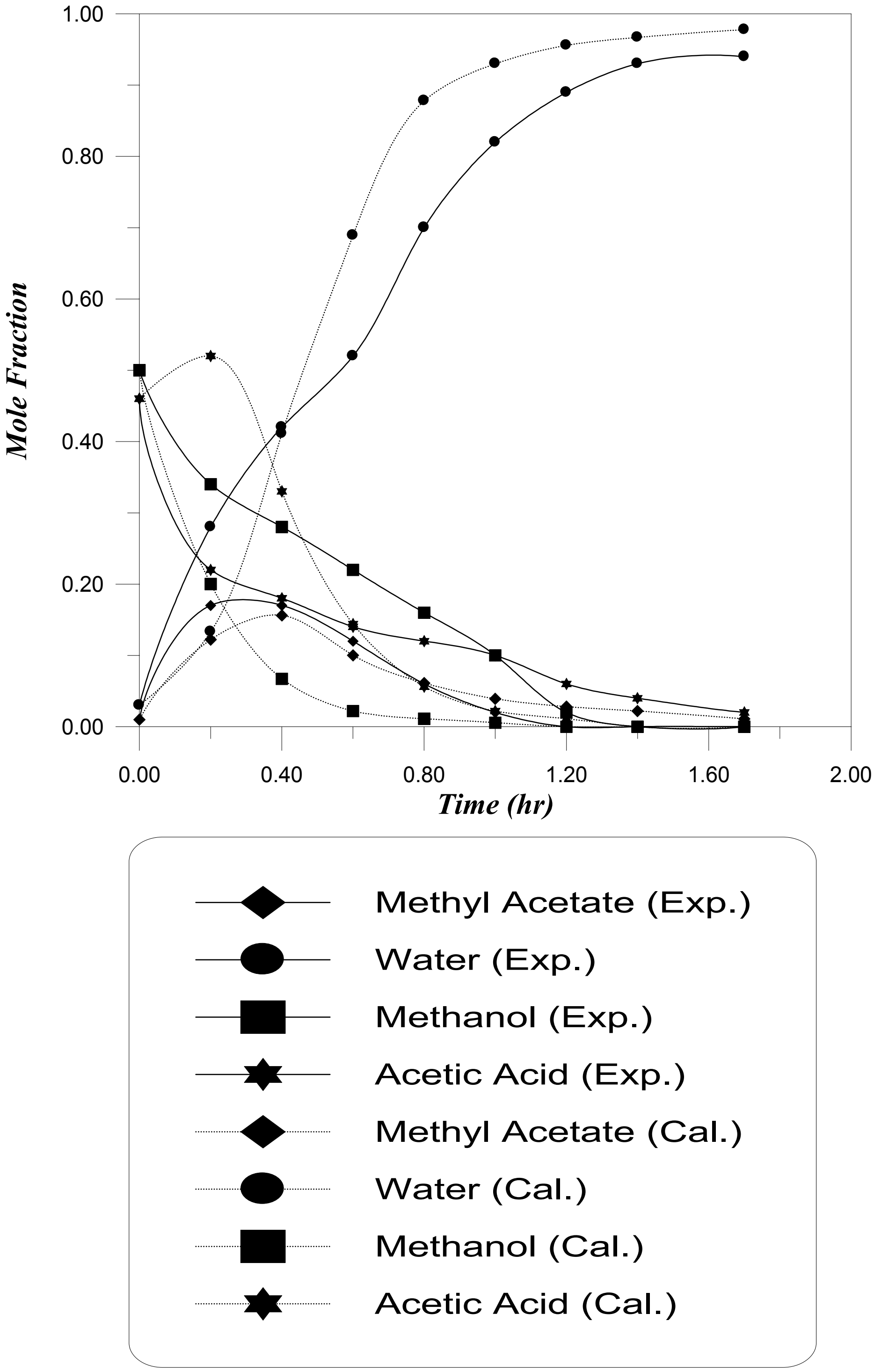


Figure 4.8: Comparison between the mole fractions of the experimental and calculated works at reboiler(with chemical reaction)

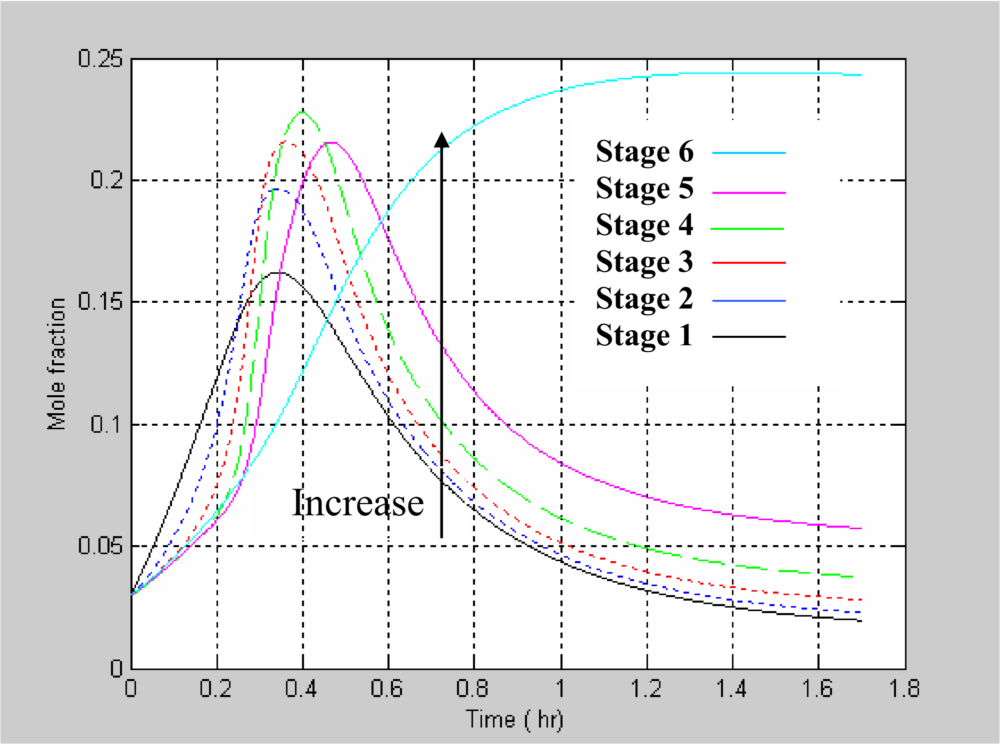


Figure 4.9: mole fraction of the desired product methyl acetate vs. batch time at each stage with chemical reaction

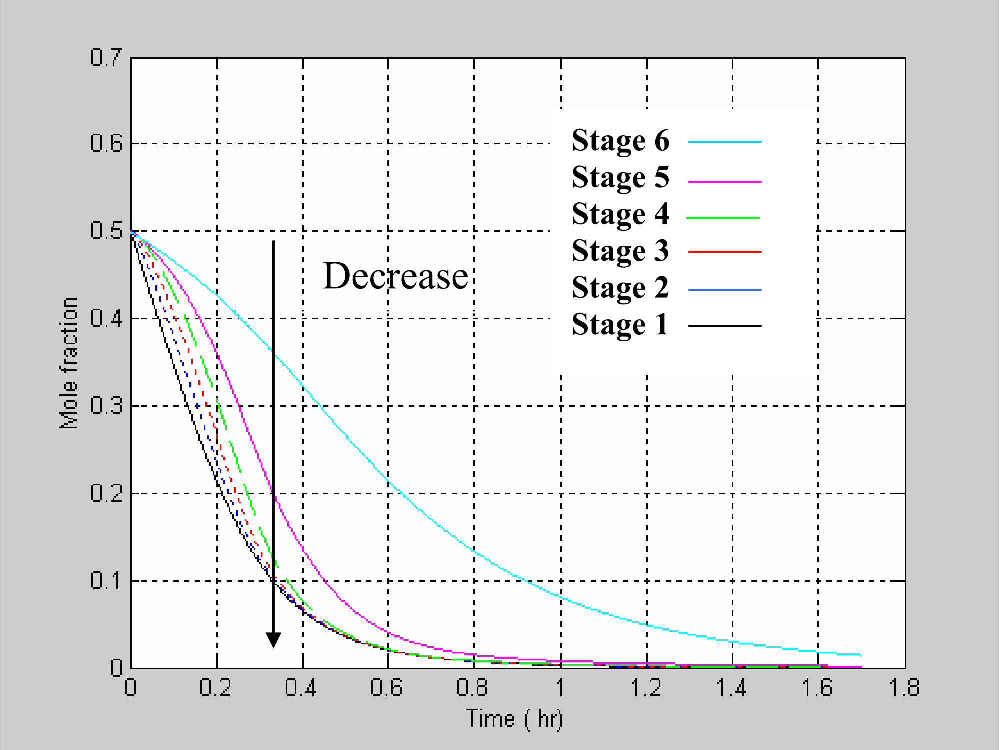


Figure 4.10: mole fraction of the methanol vs. batch time at each stage with chemical reaction

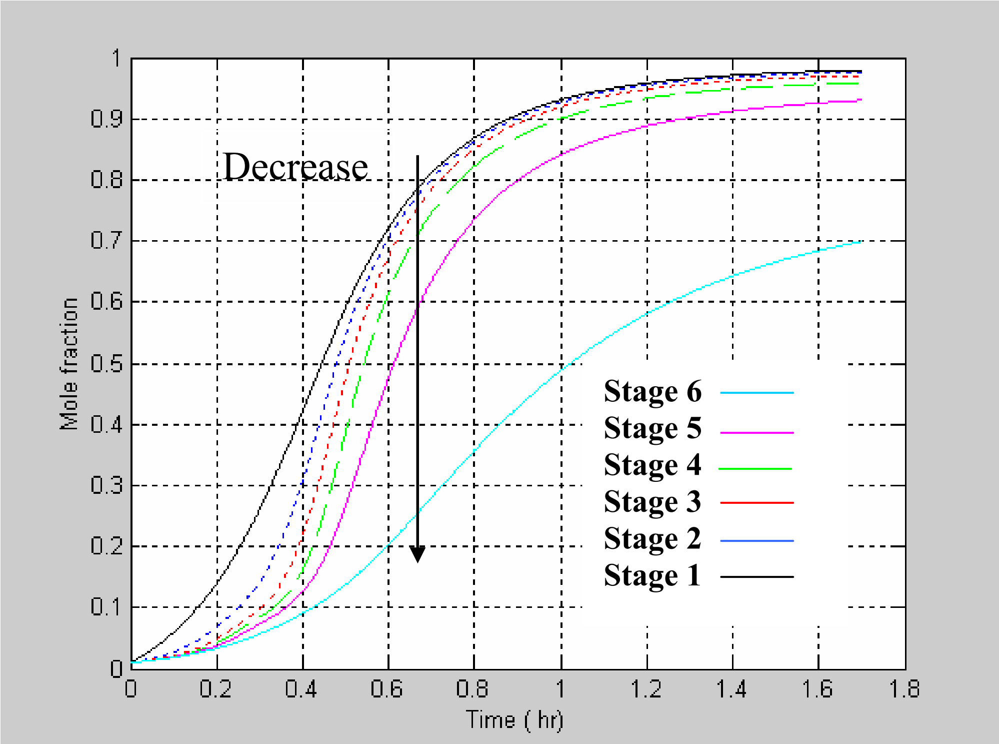


Figure 4.11: mole fraction of the water vs. batch time at each stage with chemical reaction

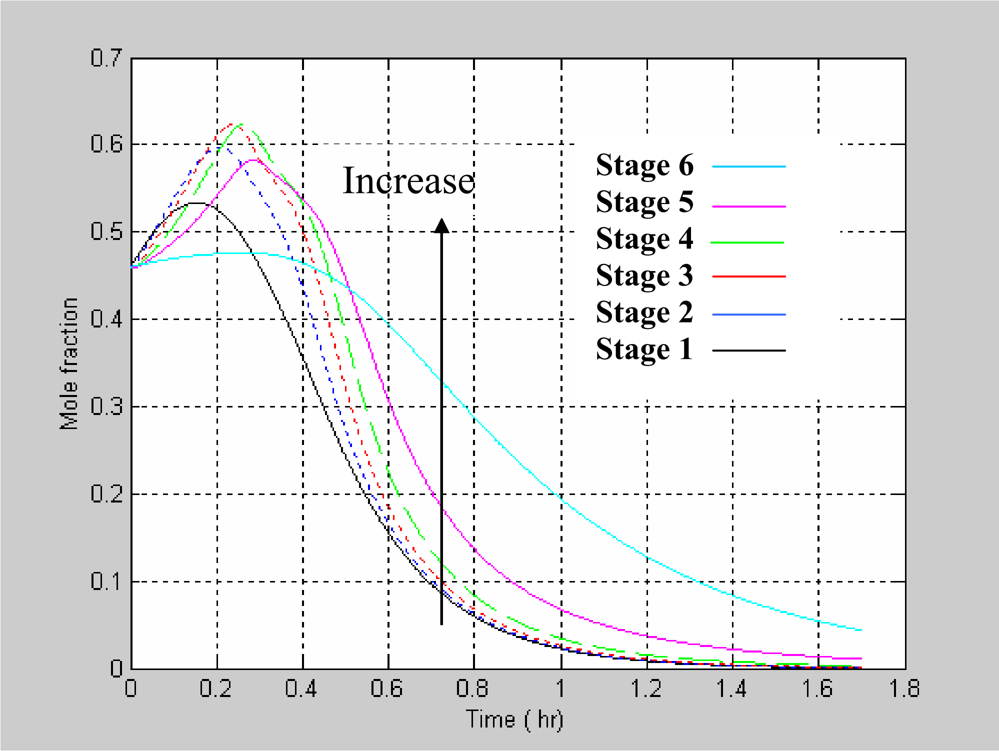


Figure 4.12: mole fraction of the Acetic acid vs. batch time at each stage with chemical reaction

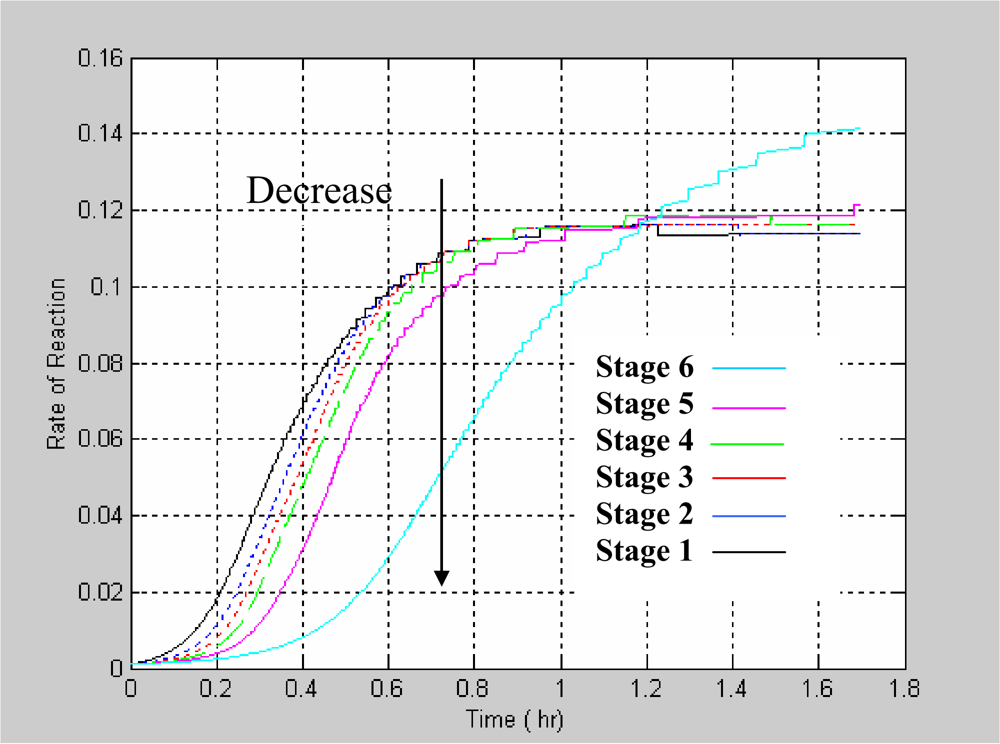


Figure 4.13: rate of reaction vs. batch time at each stage

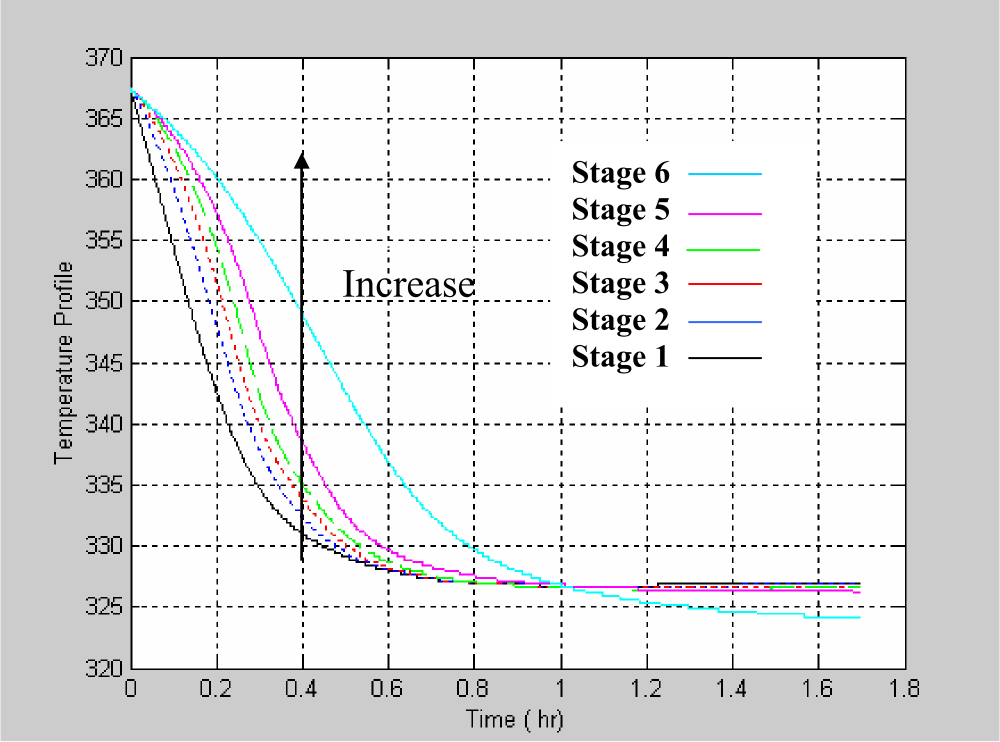


Figure 4.14: temperature profile vs. batch time at each stage with chemical reaction

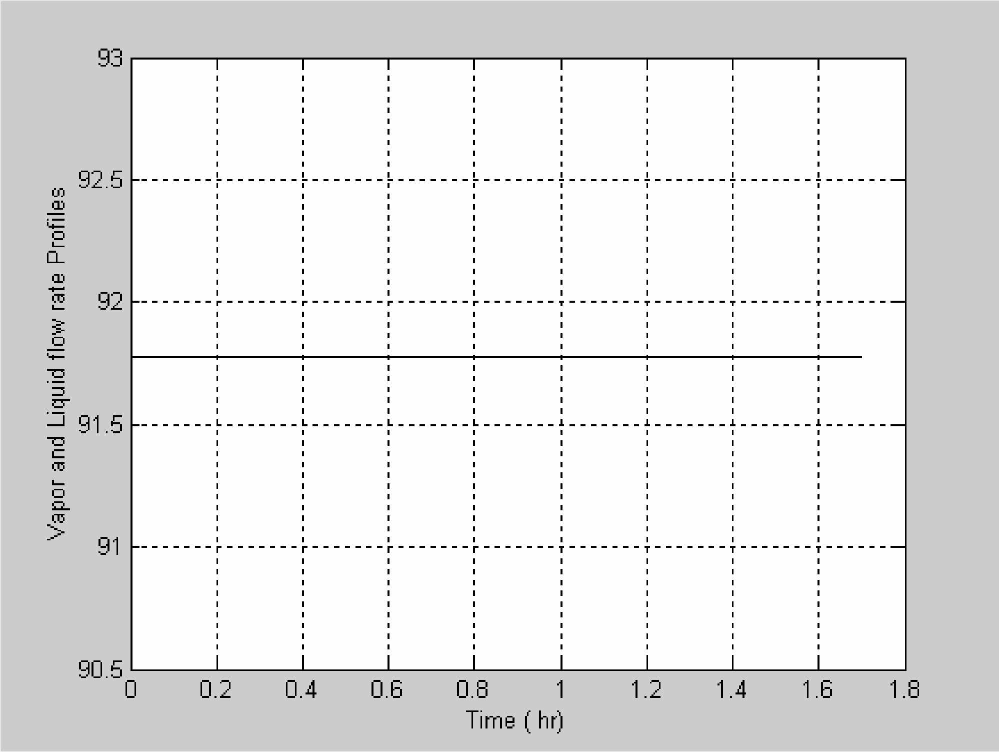


Figure 4.15: vapor and liquid flow rate profiles vs. batch time at each stage with chemical reaction

4.4 Comparison between Batch Distillation with and without Chemical Reaction for the Desired Product Methyl Acetate

Reactive distillation has proved to be an important process alternative to the conventional reactor-separator configuration. Advantages of reactive distillation and flexibility of a batch process can be combined in batch reactive distillation, a simple method to estimate the advantage of using batch reactive distillation over conventional technology is found in the production of low volume, high value specialty chemicals where batch distillation is one of the most common operations [1].

Figures 4.3 and 4.9 shows the change of mole fraction of the product methyl acetate in each stage vs. batch time in batch distillation without and with chemical reaction. Where the mole fraction of methyl acetate in the distillate in batch distillation without chemical reaction equals to 0.197, while in batch distillation with chemical reaction equals to 0.247 and %conversion is 49.64%. This change in mole fraction is due to the effect of chemical reaction that occurs in reboiler and at all stages along the distillation column.

4.5 Effect of process Variables on the Performance of Multistage Multi-component Batch Reactive Distillation

The reaction of acetic acid with methanol to produce the desired product methyl acetate and water is used to study the effect of some process variables such as batch time, number of stages, and effect of liquid holdup, on the performance of multi-component batch reactive distillation (i.e., the effects of these variables on the temperature profiles, liquid composition profiles, and the reaction rate profiles.

Before dealing with the analysis of the process variables effects, the following point must be considered:

- The effect of each process variable is studied under constant of another specified variable, for example when changing the feed batch time, the number of stages, and effect of the liquid hold up remain constant.

4.5.1 Effect of changing the Batch Time

The effect of changing batch time on the reaction of acetic acid and methanol to produce methyl-acetate and water is first considered. Figure 4.9 shows the liquid composition of methyl-acetate at each stage vs. batch time when this equals to 1.7hr from this figure the mole fraction of methyl acetate is 0.247 at distillate.

When the batch time changed to 1hr the mole fraction of the methyl-acetate at top decreased to 0.225 with 45%conversion and for 3hrs batch time the mole fraction of the methyl-acetate decreased to 0.217 with 43.4%conversion, as shown in Figures 4.16 and 4.17. From these one can conclude that changing the mole fraction of methyl acetate depends on the simulation curve of the desired product vs. batch time this curve increased until it reached to 1.7hr, this curve begin to decrease until it becomes constant at 5hrs batch time shown in Figure 4.18. Therefore, the best batch time is 1.7hr.

Figures 4.20 and 4.23 show that the concentration of water in the reboiler is 0.98 at batch time 1.7hr, when decreasing the batch time to 1hr the concentration decreased to 93% and at higher batch time above 1.7hr the mole fraction stayed constant at 98%.

The mole fraction of the reactants methanol and acetic acid decreased and approached zero in the reboiler at batch time 1.7hr, this means that the methanol and acetic acid are converted to the products water and methyl acetate at this time. When decreasing the batch time to 1hr the concentration of the reactant increased in the reboiler and at 3hrs and above, the concentration stayed constant approximately zero as shown in Figures 4.19, 4.22, 4.21, and 4.24, respectively. Therefore, from the above the best batch time for this operating condition is 1.7hr.

Figures 4.25 and 4.26 show that the reaction rate profiles at each stage vs. batch time, where in the distillate section is 0.14 at batch time 1.7, when decreasing the batch time to 1hr the reaction rate profile decreased to 0.096 and at higher batch time above 1.7hr the reaction rate profile increased and stayed constant at 0.157 at the distillate.

Figures 4.27 and 4.28 show that the temperature profiles at each stage vs. batch time. At the distillate section, the temperature is 324 K at batch time 1.7, when decreasing the batch time to 1hr the temperature increased to 326.7 K and at higher batch time above 1.7hr the temperature decreased and stayed constant at 322.8 K. This depends on the concentration of products and reactants at the top section.

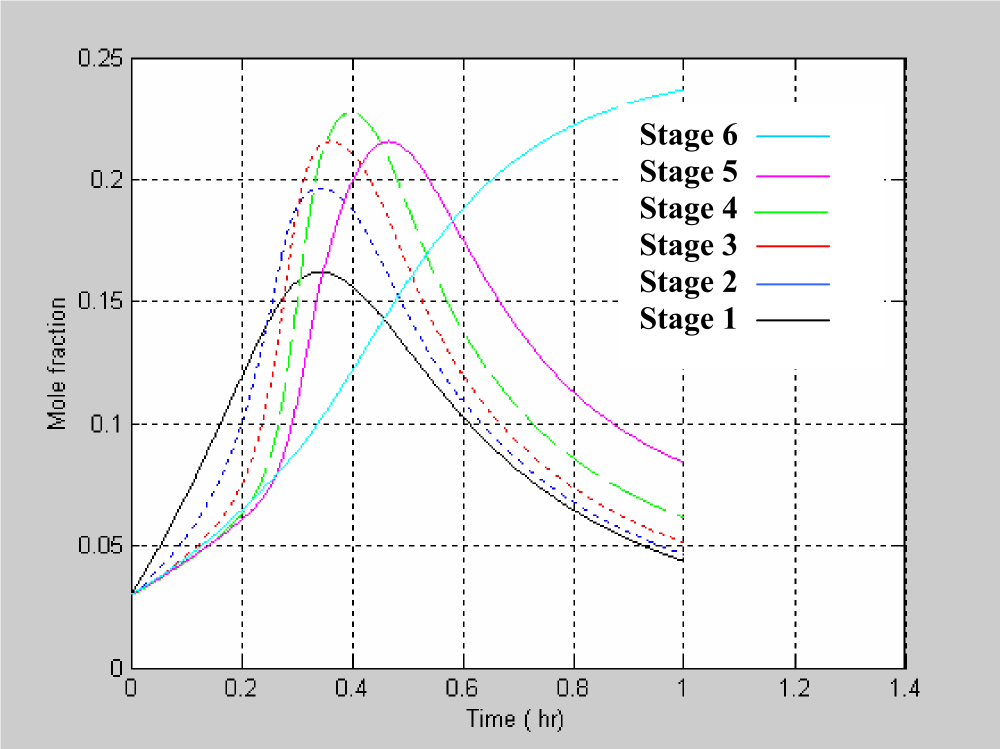


Figure 4.16: mole fraction of the desired product methyl acetate vs. batch time at each stage (1hr), where the distillate (stage 6) and the reboiler (stage 1)

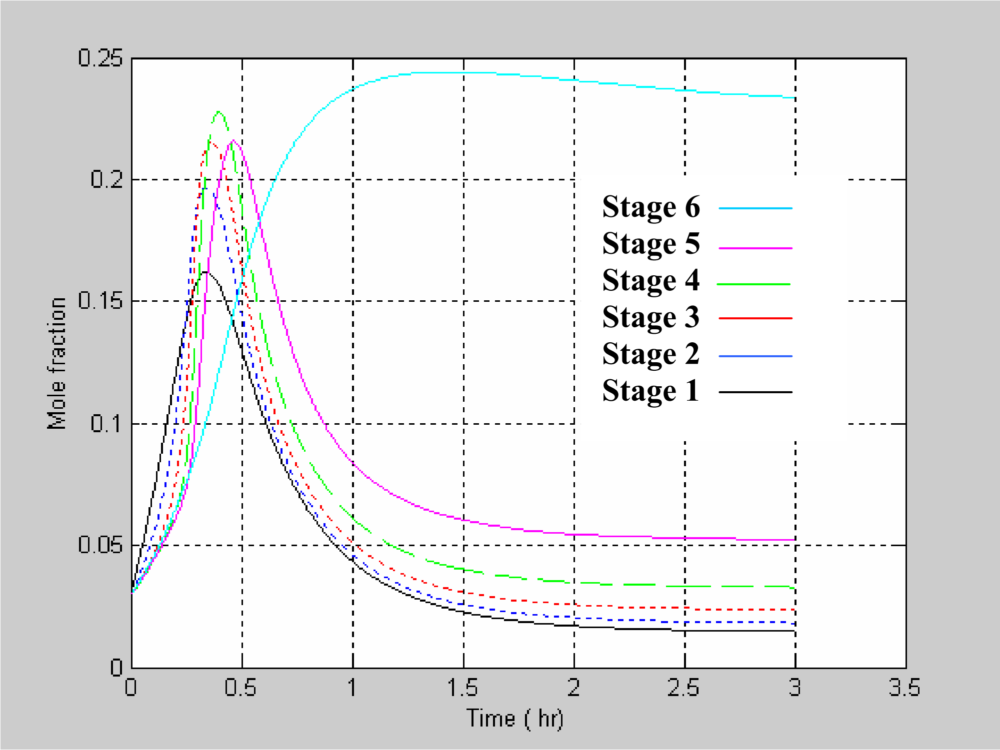


Figure 4.17: mole fraction of the desired product methyl acetate vs. batch time at each stage (3hr)

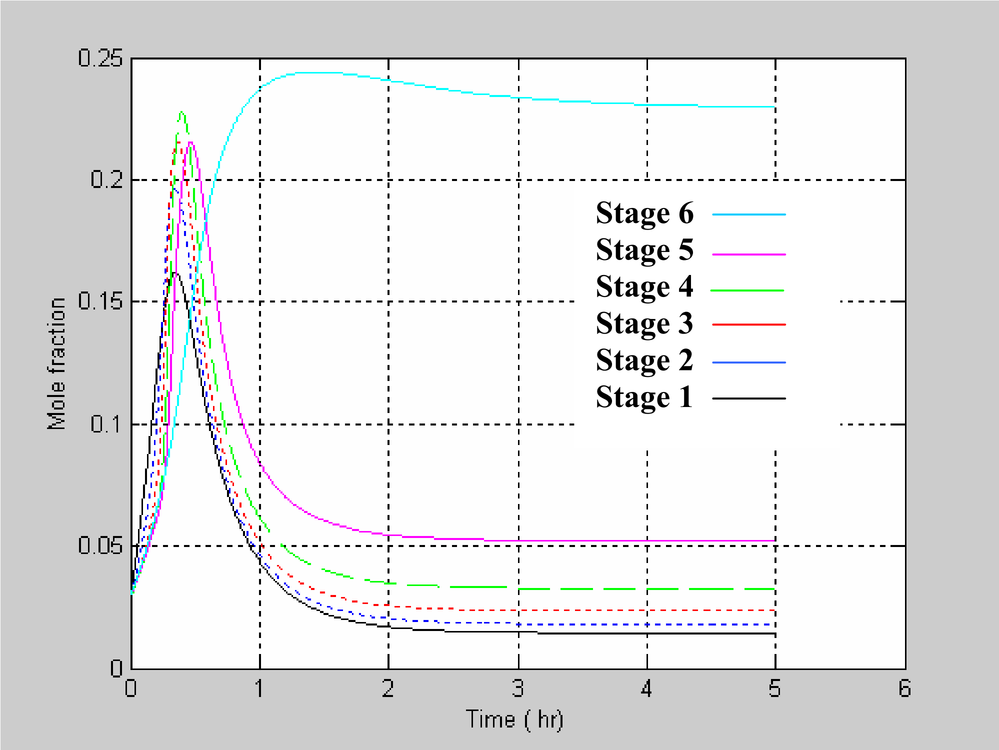


Figure 4.18: mole fraction of the methyl acetate vs. batch time at each stage (5hr)

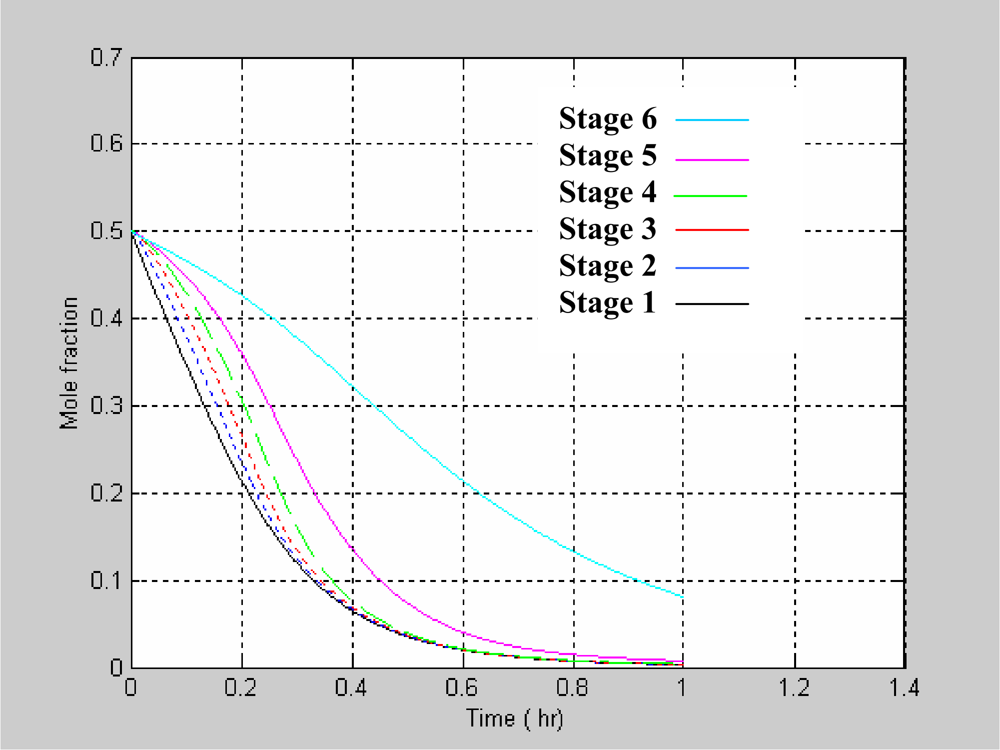


Figure 4.19: mole fraction of the methanol vs. batch time at each stage (1hr)

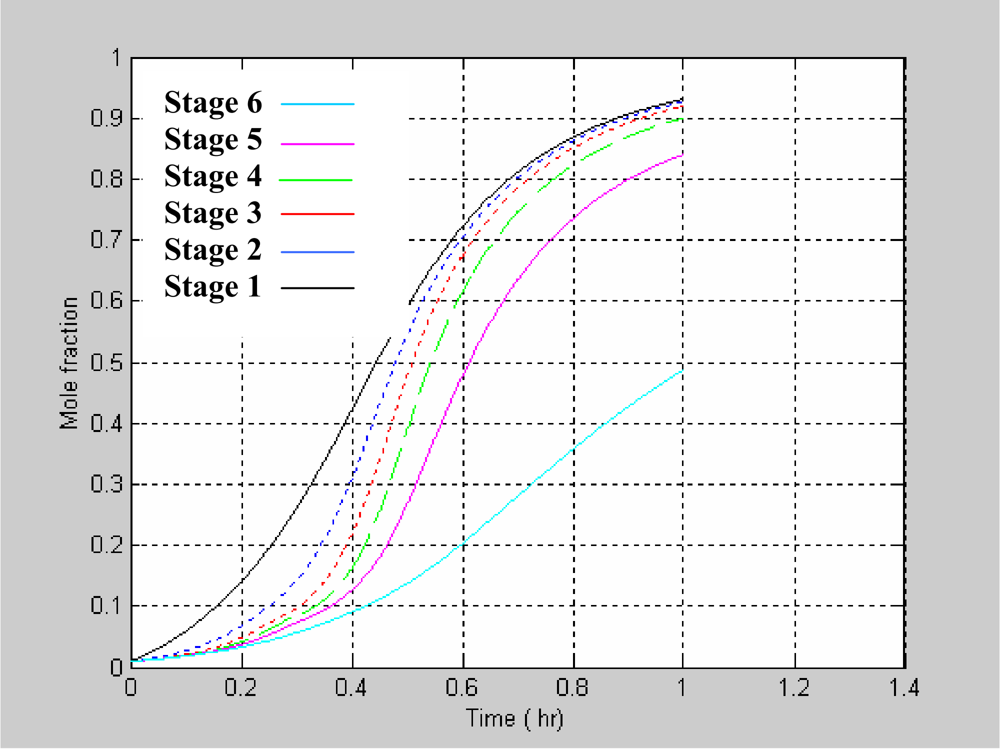


Figure 4.20: mole fraction of the water vs. batch time at each stage (1hr)

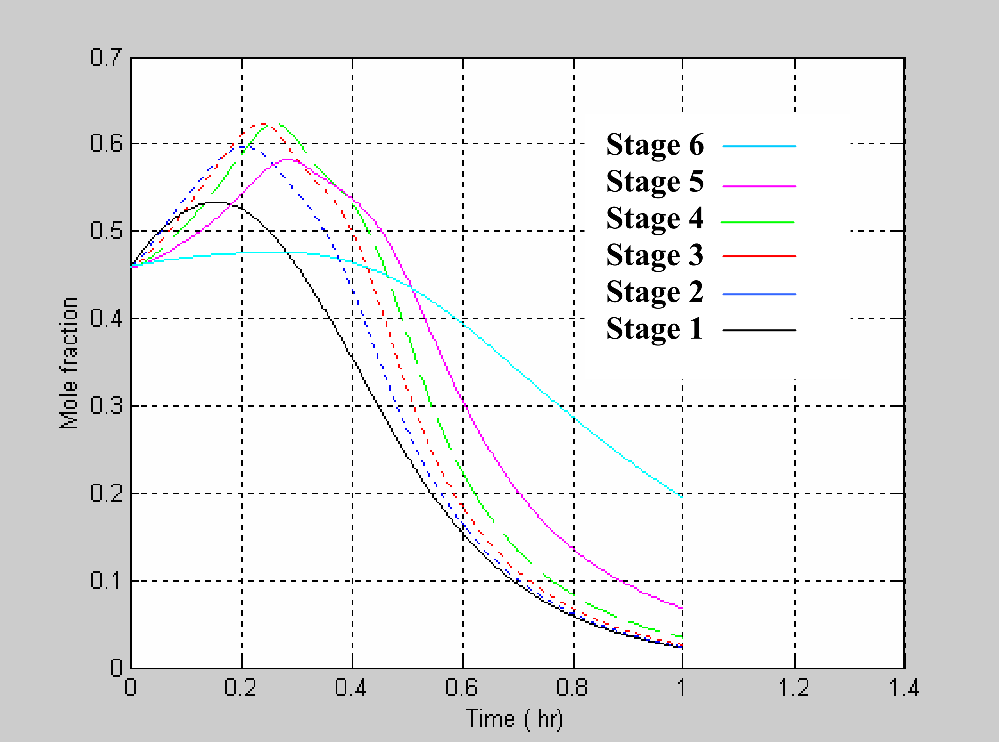


Figure 4.21: mole fraction of the Acetic acid vs. batch time at each stage (1hr)

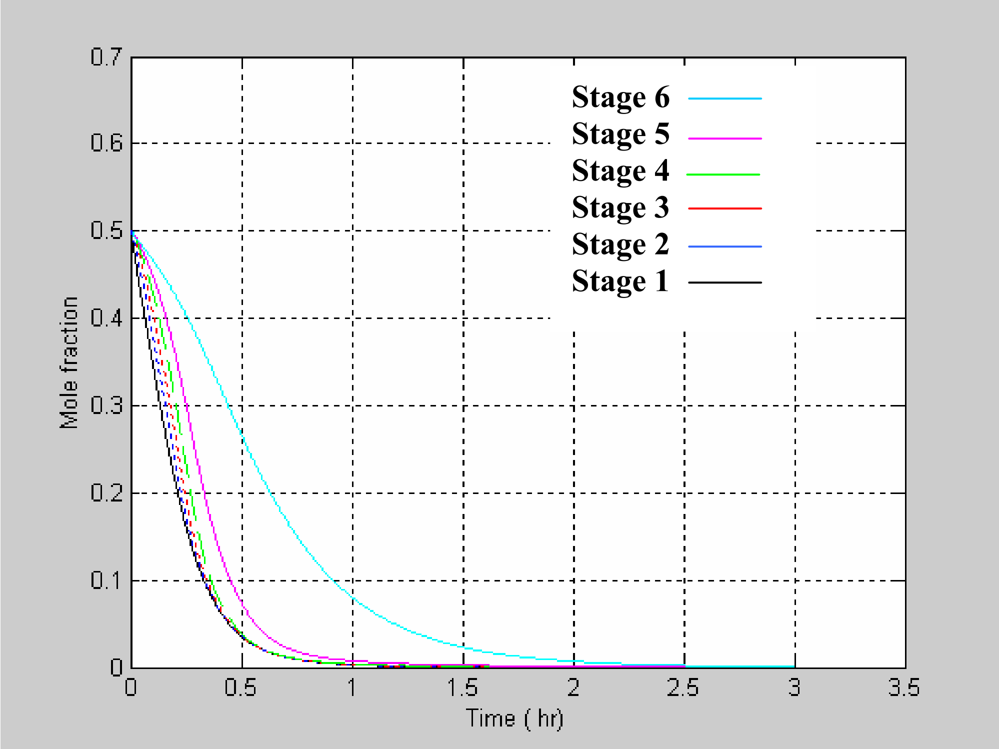


Figure 4.22: mole fraction of the methanol vs. batch time at each stage (3hr)

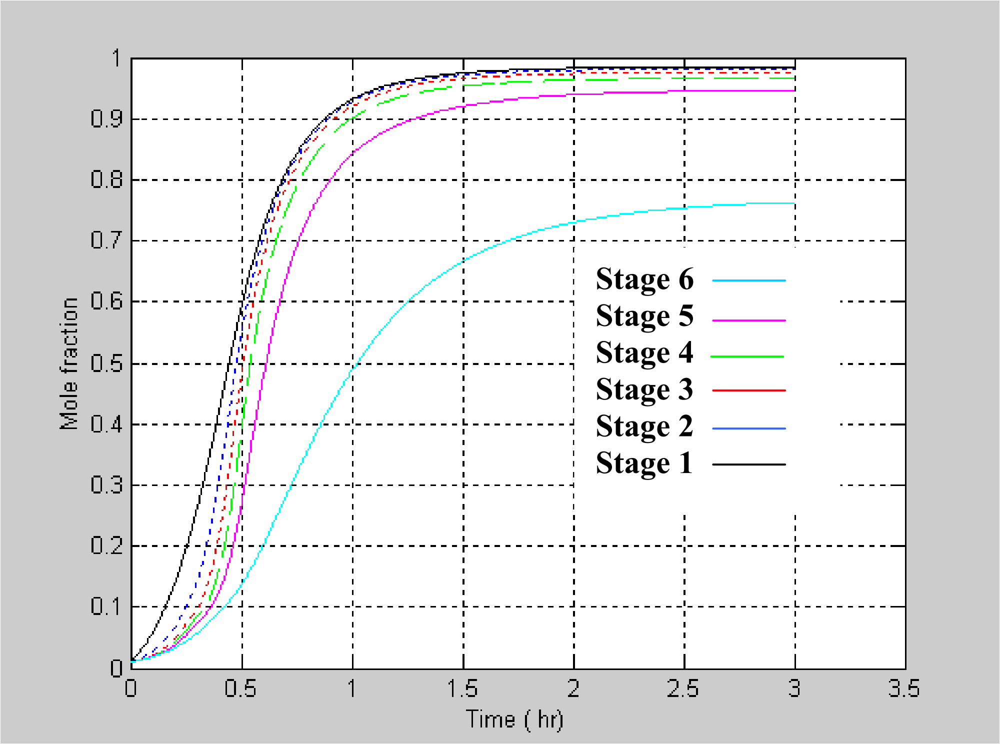


Figure 4.23: mole fraction of the water vs. batch time at each stage (3hr)

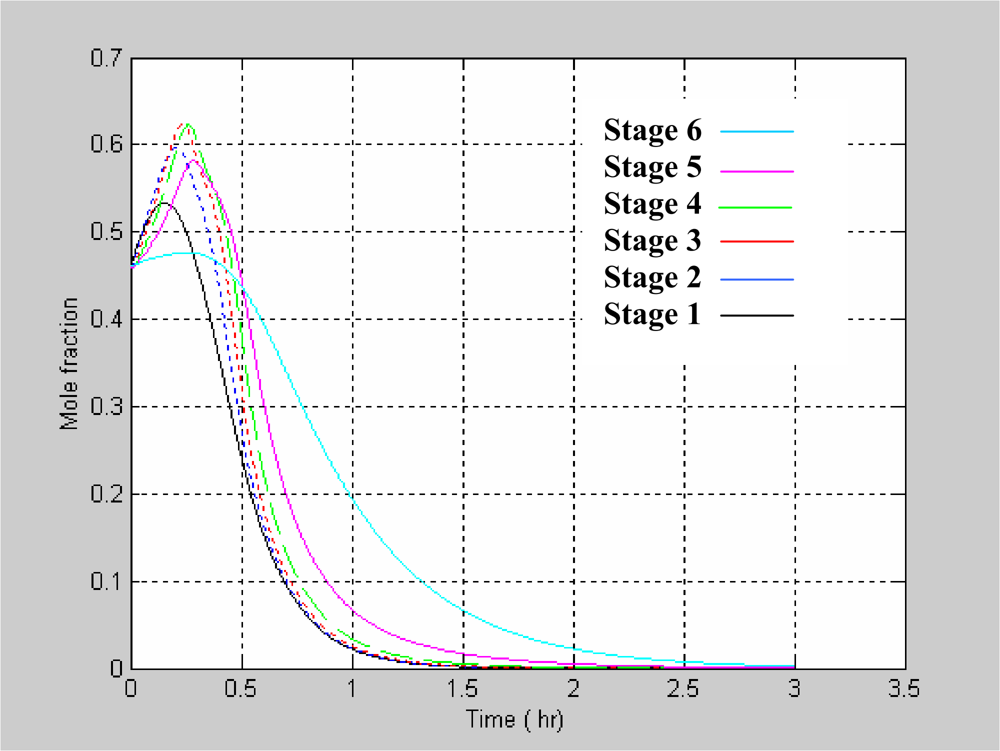


Figure 4.24: mole fraction of the Acetic acid vs. batch time at each stage (3hr)

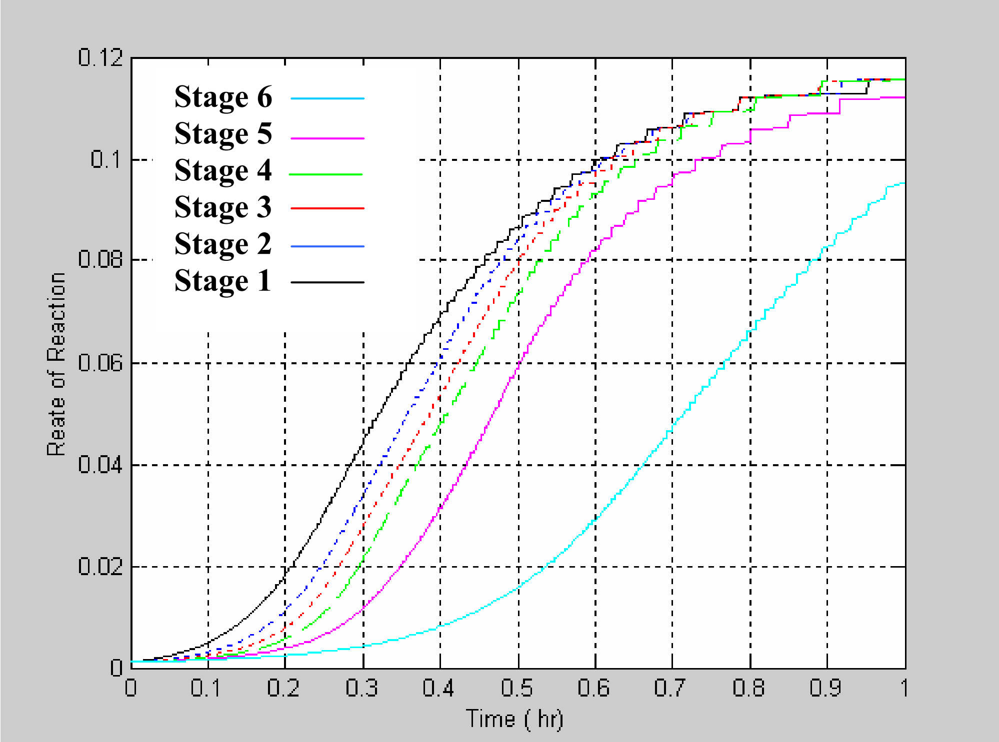


Figure 4.25: reaction rate profile vs. batch time at each stage (1hr)

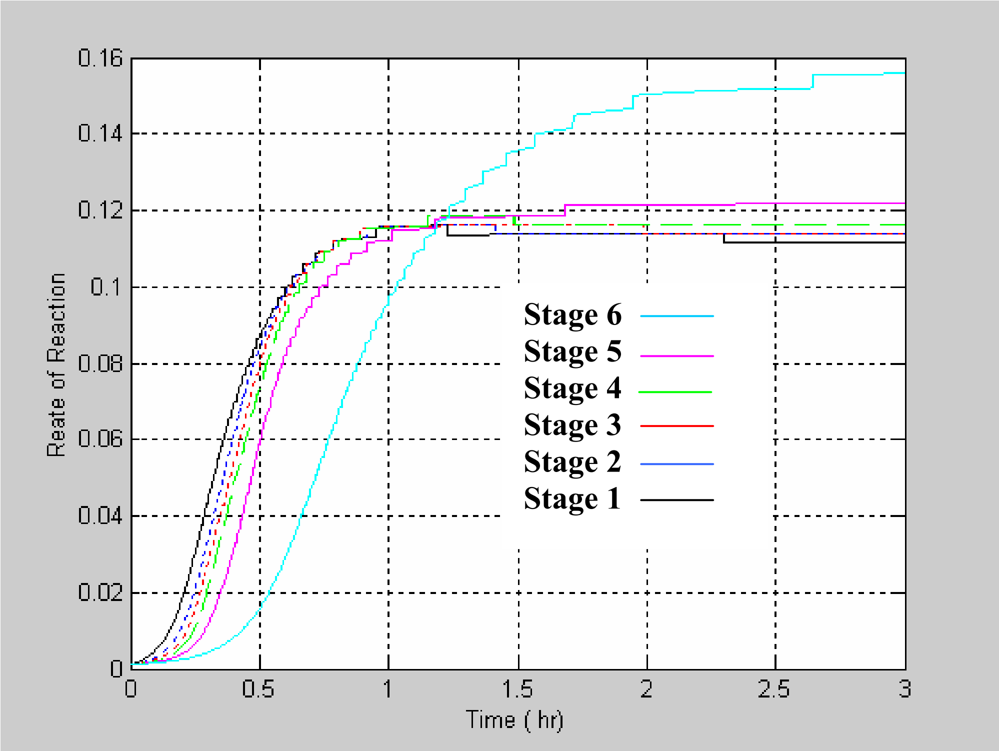


Figure 4.26: reaction rate profile vs. batch time at each stage (3hr)

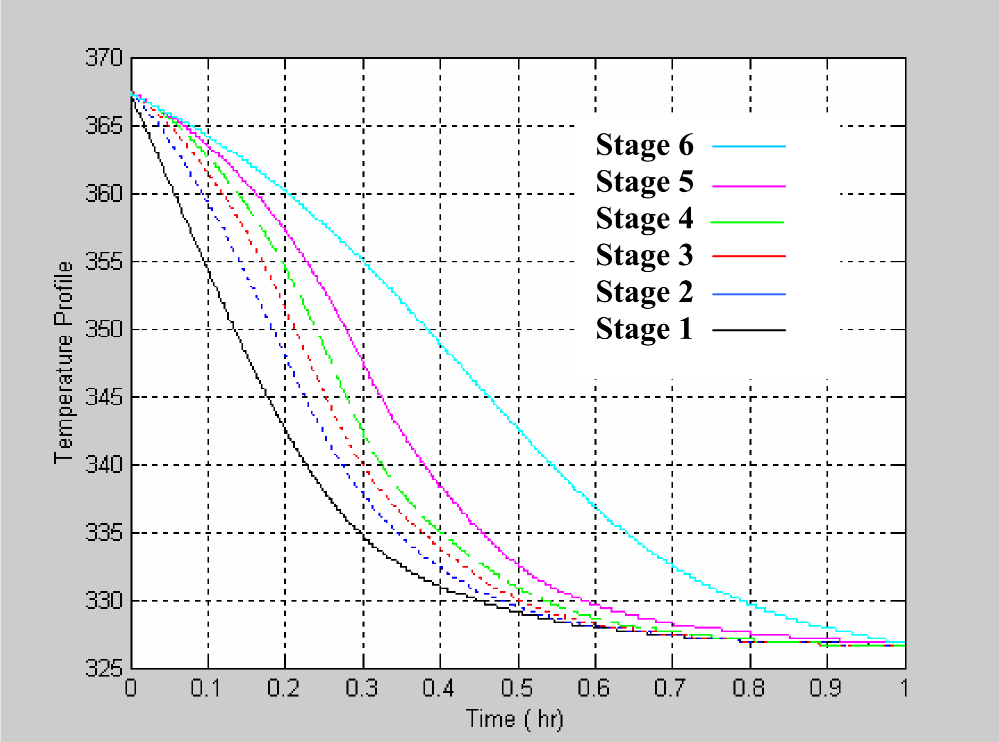


Figure 4.27: temperature profile vs. batch time at each stage (1hr)

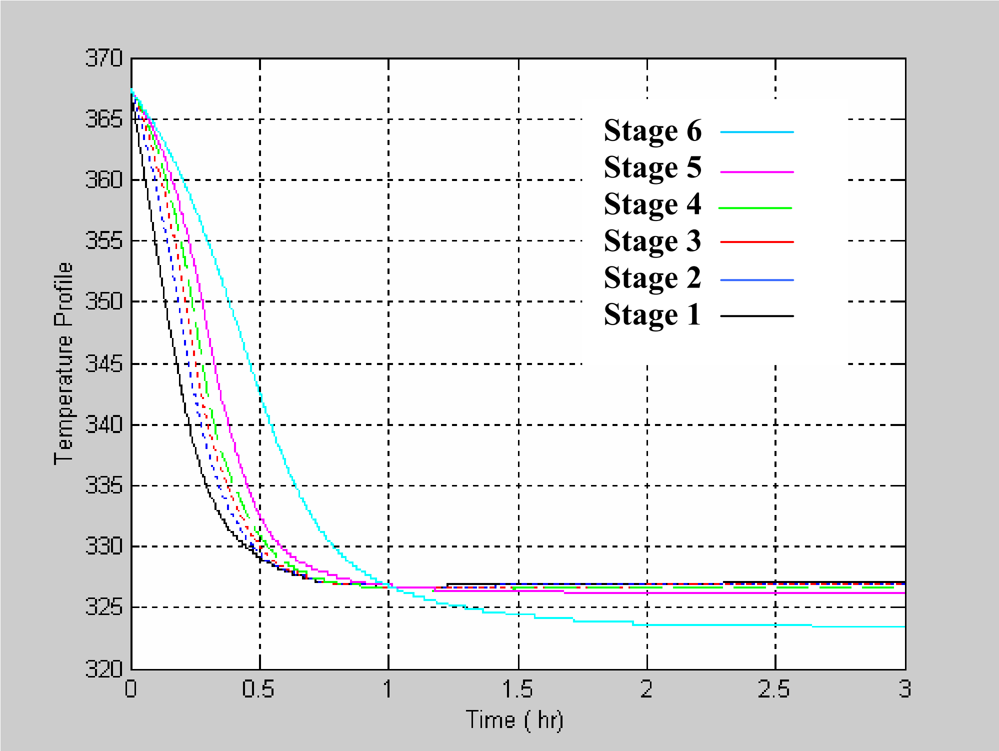


Figure 4.28: temperature profile vs. batch time at each stage (3hr)

4.5.2 Effect of Changing Number of Stages

The effect of changing number of stages on the reaction of acetic acid and methanol to produce methyl-acetate and water is now considered. Figure 4.9 shows that the liquid composition of methyl-acetate at the top section using 6 theoretical stages is 0.247, with 49.4%conversion. When the number of stages changed to 4 theoretical stages the mole fraction of the methyl-acetate decreased to 0.05 at the top as shown in Figure 4.29 with 10% conversion. Increasing the number of theoretical stages to 8 the mole fraction of the methyl-acetate decreased to 0.051 with 10.2% conversion, as shown in Figure 4.30. So when decreasing the number of stages to 4 stages the mole fraction decreased, also when increasing the number of stages to 8 stages the mole fraction decreased. Therefore, the best condition to produce methyl acetate and water for the given feed analysis is 6 theoretical stages.

Figures 4.32 and 4.35 show that the concentration of water in the reboiler is 0.98 for 6 theoretical stages, when decreasing to 4 theoretical stages the concentration decreased to 0.84 and at higher theoretical stages the mole fraction also decreased to 0.82.

The mole fraction of the reactants methanol and acetic acid decreased and approached to zero in the reboiler at 6 theoretical stages, this means that methanol and acetic acid are converted to water and methyl acetate at this number of stages. When decreasing the theoretical stages to 4 and increasing to 8, the concentration of the reactant decreased. In the reboiler the concentration becomes constant at approximately zero, Figures 4.31, 4.33, 4.34, and 4.36, respectively. Therefore, from above, the best number of theoretical stages for the operating conditions in the analysis is 6 theoretical stages.

Figures 4.37 and 4.38 show the reaction rate profiles at each stage vs. batch time, where in the distillate section is 0.14 at 6 theoretical stages, when decreasing the theoretical stages to 4 stages the reaction rate profile decreased to 0.098 and at higher theoretical stages the mole fraction also decreased to 0.1.

Figures 4.38 and 4.40 show the temperature profiles at each stage vs. batch time, when decreasing and increasing the theoretical stages to 4 and 8, respectively the temperature profile increased to 327 K.

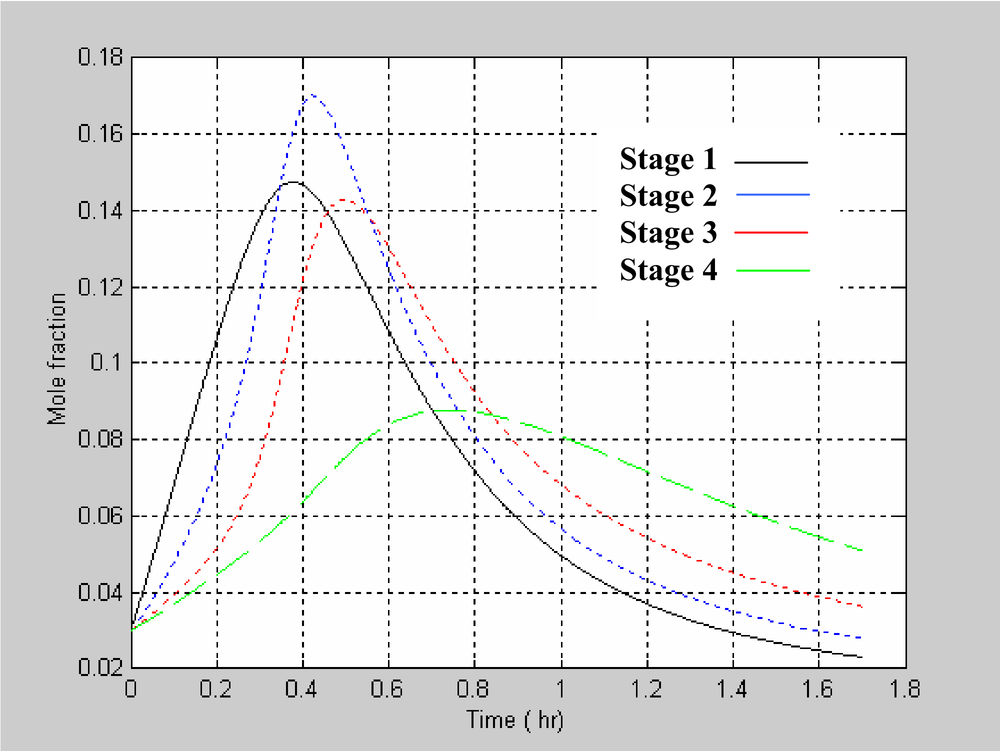


Figure 4.29: mole fraction of the product methyl acetate vs. batch time at each stage (4 stages)

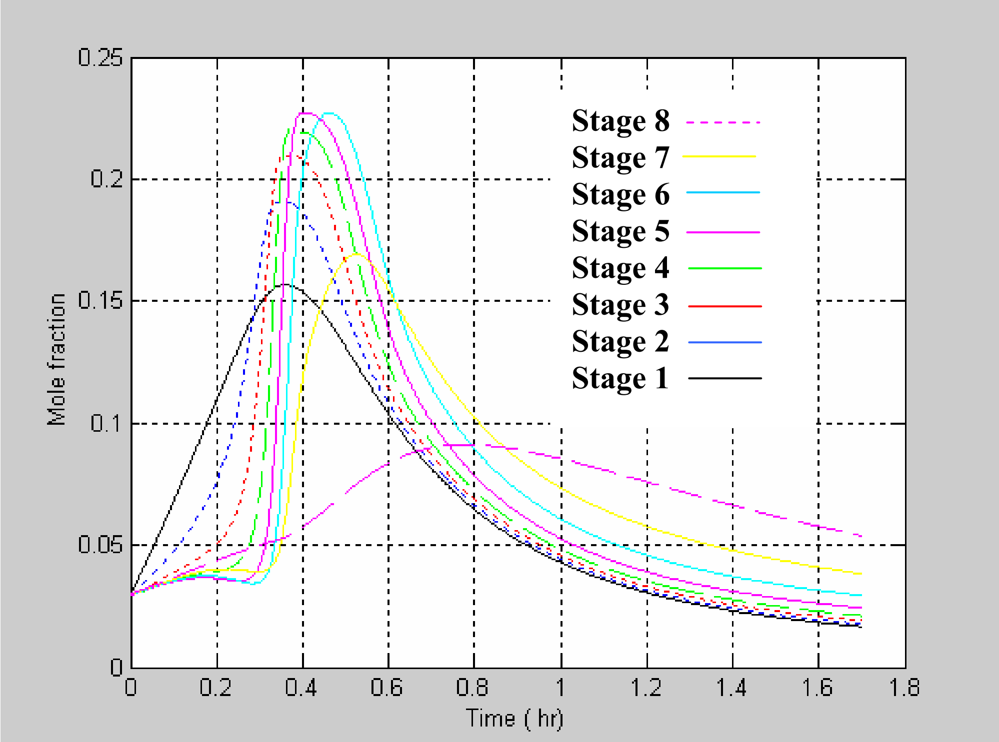


Figure 4.30: mole fraction of the product methyl acetate vs. batch time at each stage (8 stages)

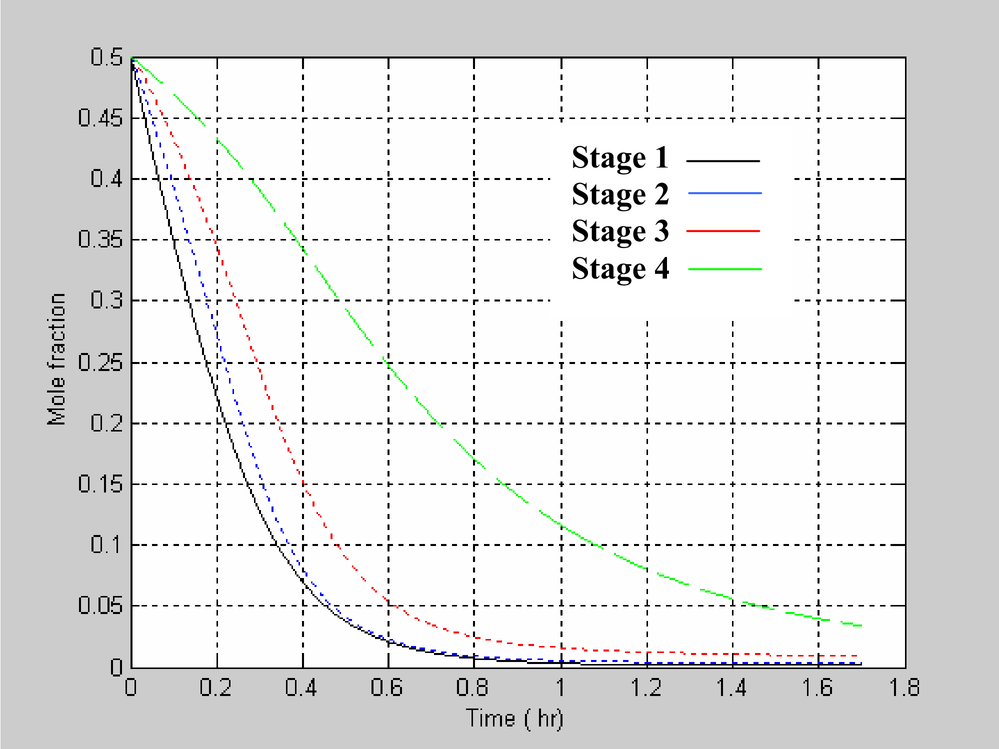


Figure 4.31: mole fraction of the methanol vs. batch time at each stage (4 stages)

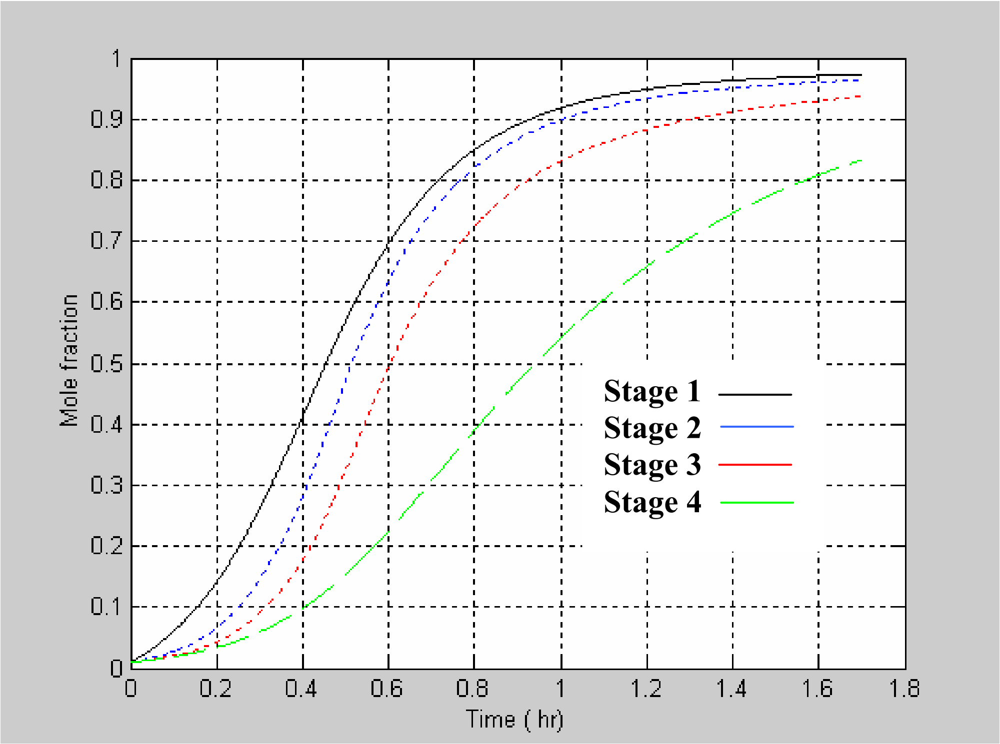


Figure 4.32: mole fraction of the water vs. batch time at each stage (4 stages)

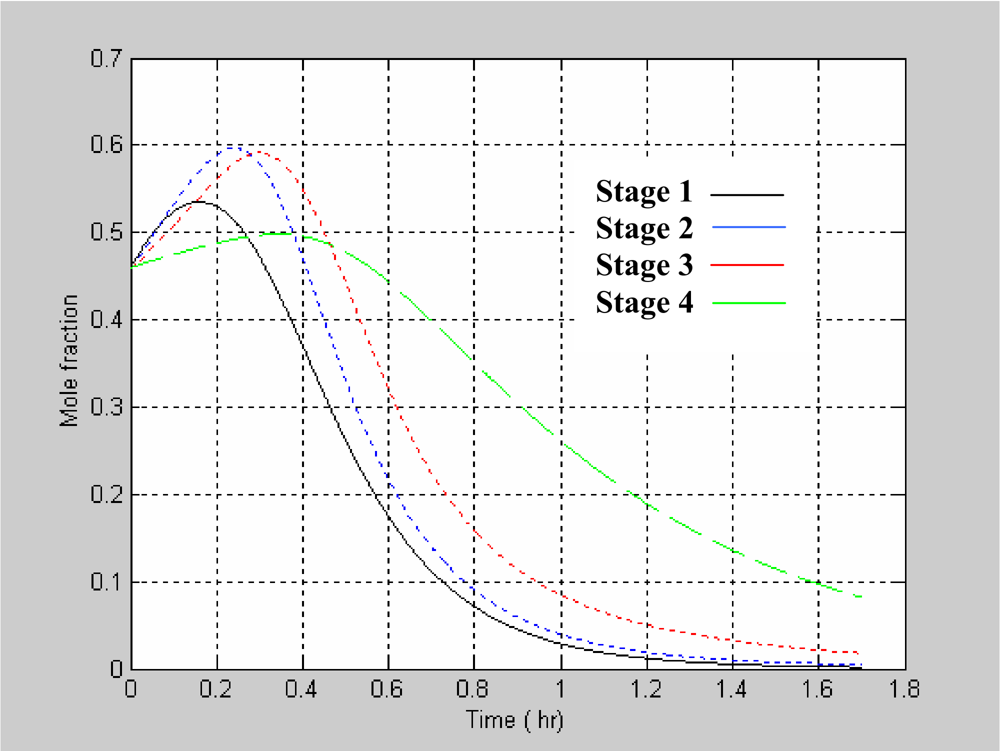


Figure 4.33: mole fraction of the Acetic acid vs. batch time at each stage (4 stages)

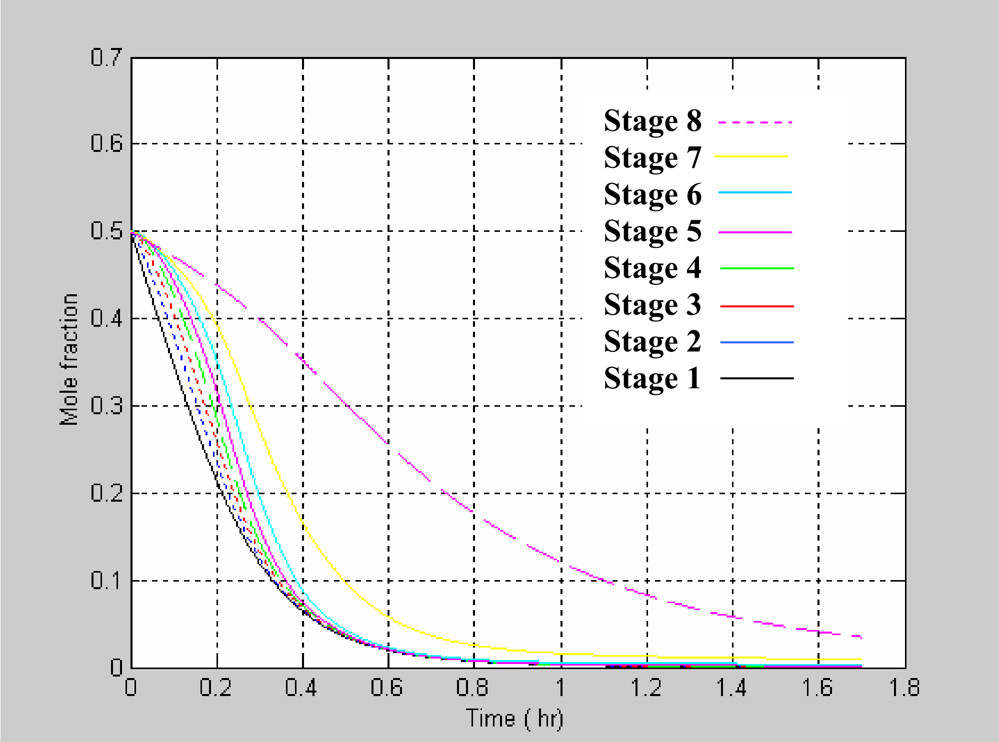


Figure 4.34: mole fraction of the methanol vs. batch time at each stage (8 stages)

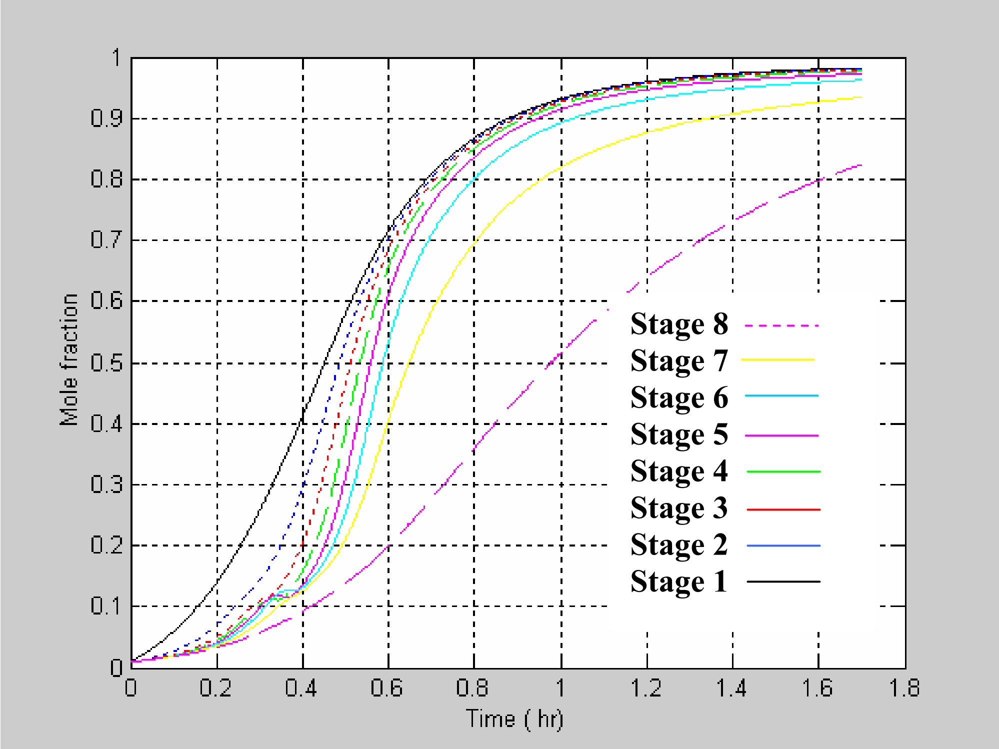


Figure 4.35: mole fraction of the water vs. batch time at each stage (8 stages)

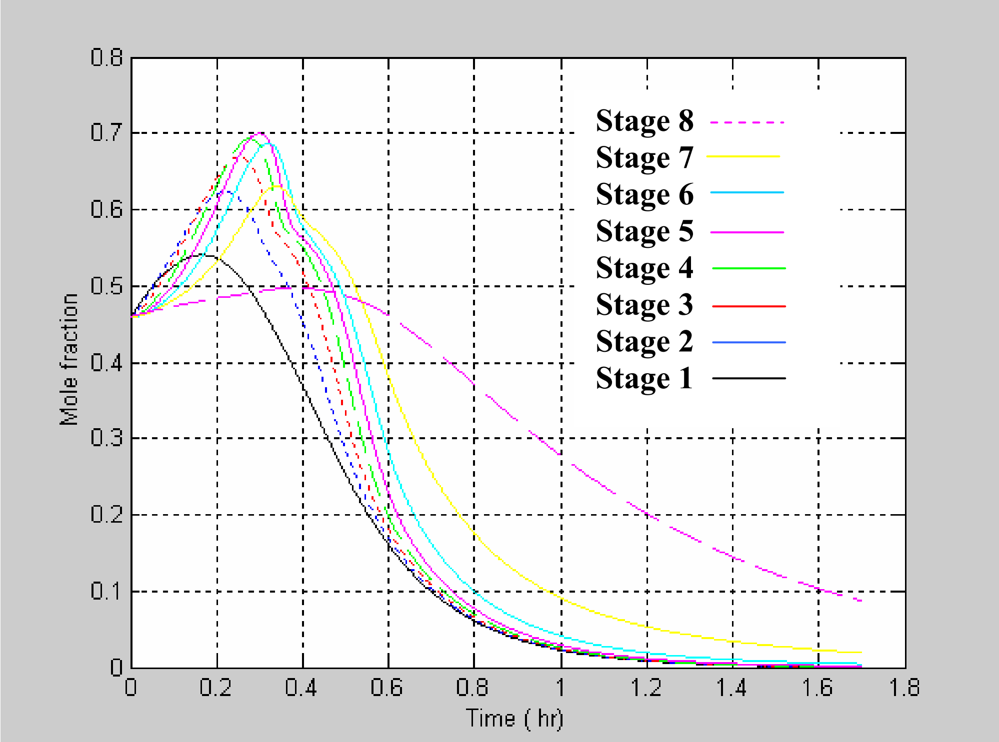


Figure 4.36: mole fraction of the Acetic acid vs. batch time at each stage (8 stages)

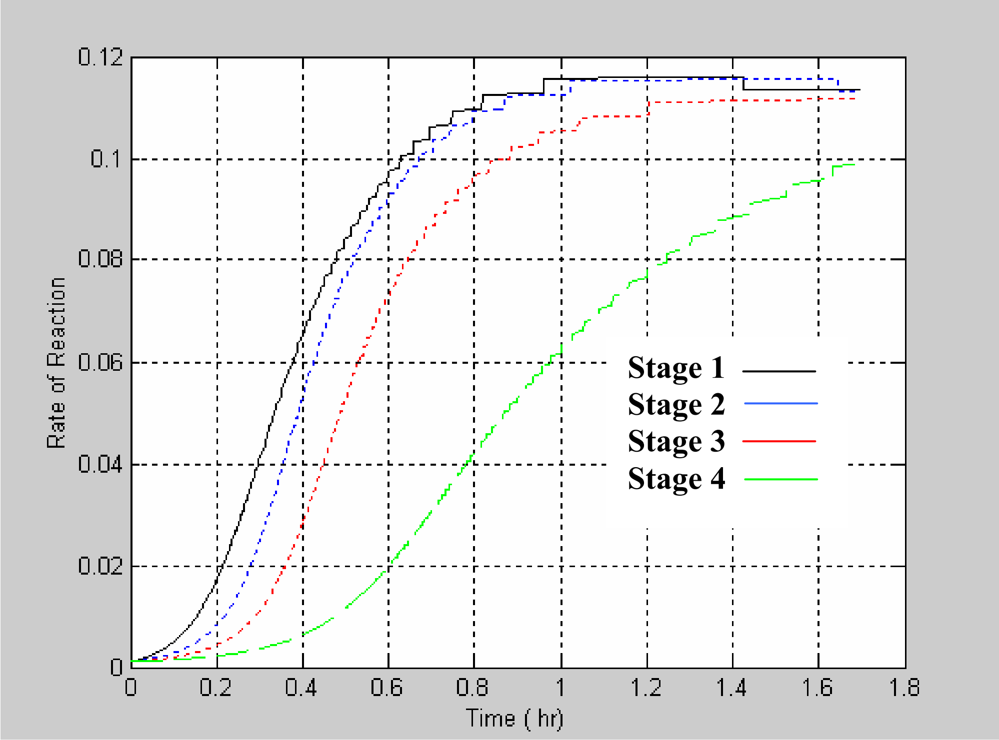


Figure 4.37: rate of reaction profile vs. batch time at each stage (4 stages)

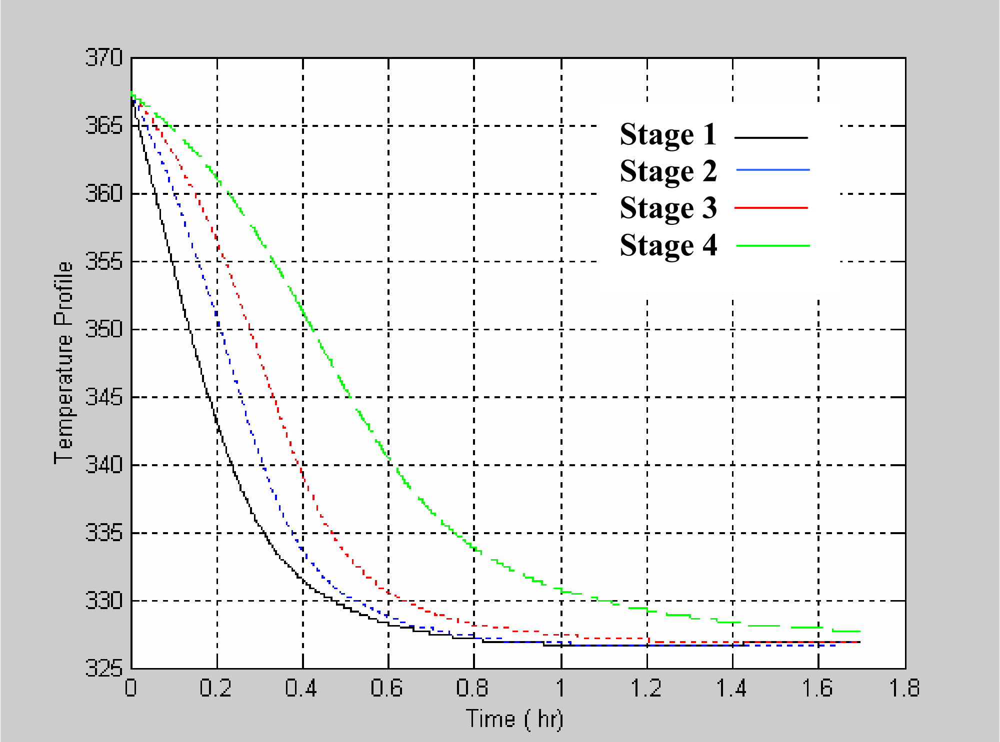


Figure 4.38: rate of temperature profile vs. batch time at each stage (4 stages)

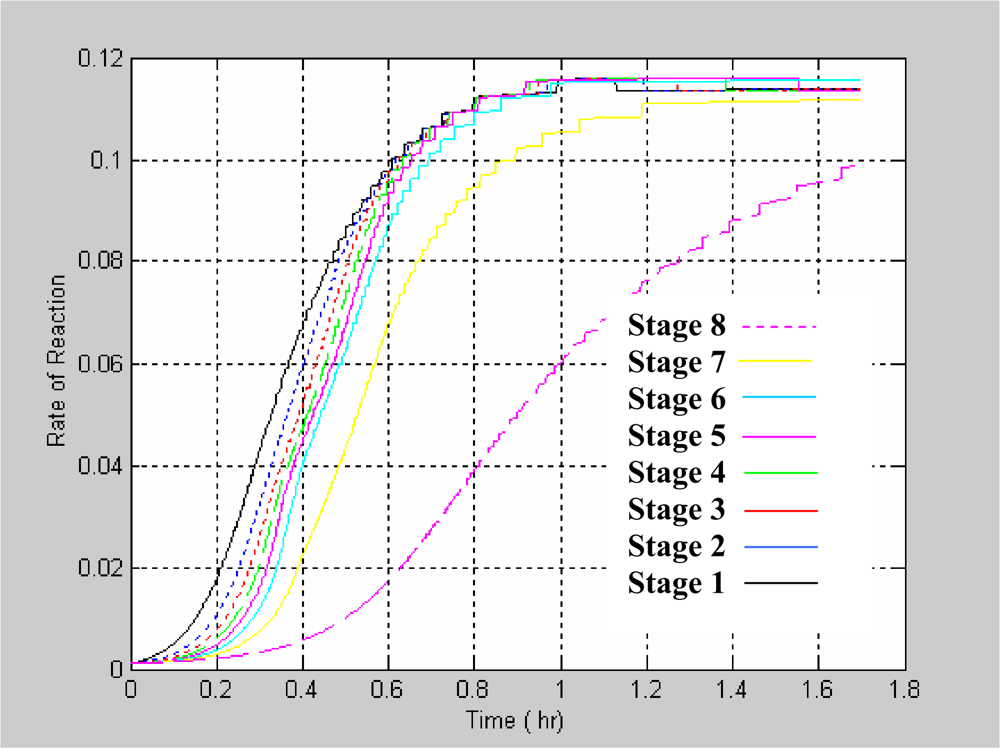


Figure 4.39: rate of reaction profile vs. batch time at each stage (8 stages)

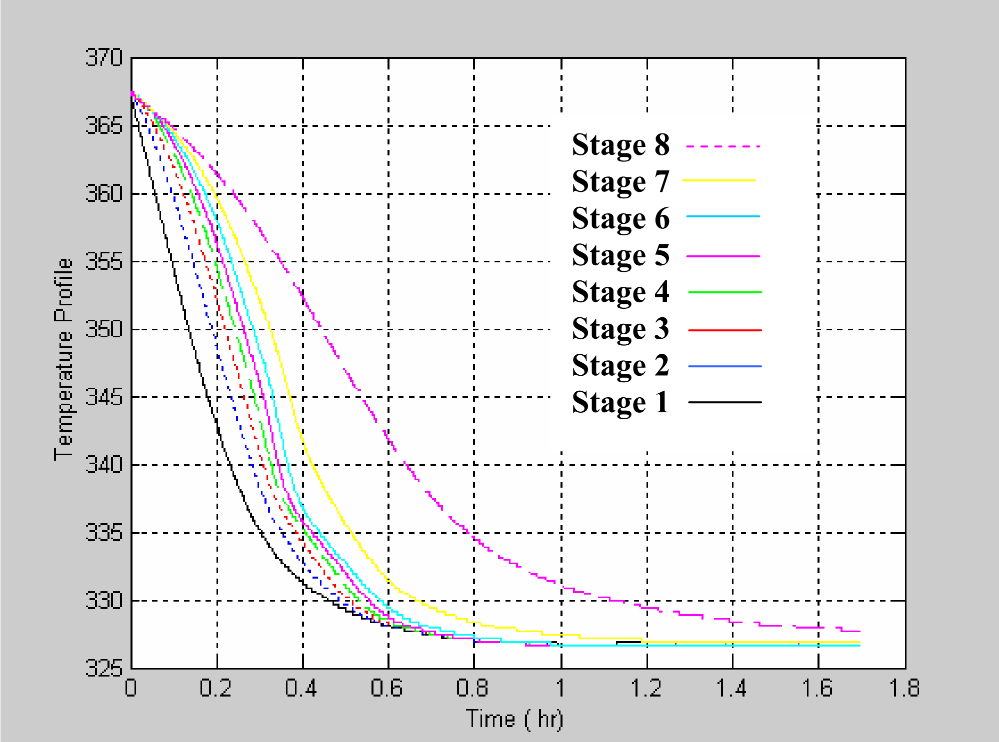


Figure 4.40: rate of temperature profile vs. batch time at each stage (8 stages)

4.6 Effect of Liquid Holdup

In the previous sections the liquid holdup was assumed to be constant throughout the column, when the effect of liquid holdup on the reaction of acetic acid and methanol to produce methyl-acetate and water is studied, the results show that the effect of liquid holdup on the simulation curve of methyl acetate in the distillate section, reach to maximum at 0.252 at batch time range 0.4-0.8hr with 50.4% conversion Figure 4.41, while, for constant holdup the simulation curve reach to a maximum of 0.247 at batch time range 1.2-1.4hr. Therefore the effect of liquid holdup on the concentration of methyl acetate required less batch time than for constant liquid holdup.

Figure 4.43 shows that the concentration of water in the distillate is increased to 0.78 with liquid holdup, while with constant liquid holdup it was 0.7.

The mole fraction of methanol and acetic acid decreased and approached zero in the reboiler at constant liquid holdup. This means that the methanol and acetic acid are converted to water and methyl acetate. When the effect of liquid holdup is considered the concentration of the reactant decreased in the reboiler and the concentration stayed constant approximately equals to zero, Figures 4.42 and 4.44 respectively.

Figure 4.45 shows that the reaction rate profile at each stage vs. batch time, in the distillate section is 0.14 at constant liquid holdup, while with liquid holdup the reaction rate profile increased to 0.159.

Figure 4.46 shows that the temperature profiles decreased with batch time at each stage. It reduced to 324 K in the distillate section and kept constant for batch time range 0.8-1.7hr. While for constant liquid holdup the profile decreased and reached to 325 K and kept constant for batch time range 1.2-1.7hr.

Figures 4.47 and 4.48 show that the vapor and liquid flow rate profiles at each stage vs. batch time, in the distillate section is 91.77 kg/hr at constant liquid holdup, while with liquid holdup effect the vapor and liquid flow rate profiles was changing until the batch time is 1.5hr, where above 1.5hr the vapor and liquid flow rates stayed constant at 104.6 mole/hr and 103.7 mole/hr respectively.

Figures 4.49, 4.50, and 4.51 show that the liquid holdup in reboiler, plates, and distillate is 13, 2.5, and 12.8 respectively for batch time of 1.7hr.

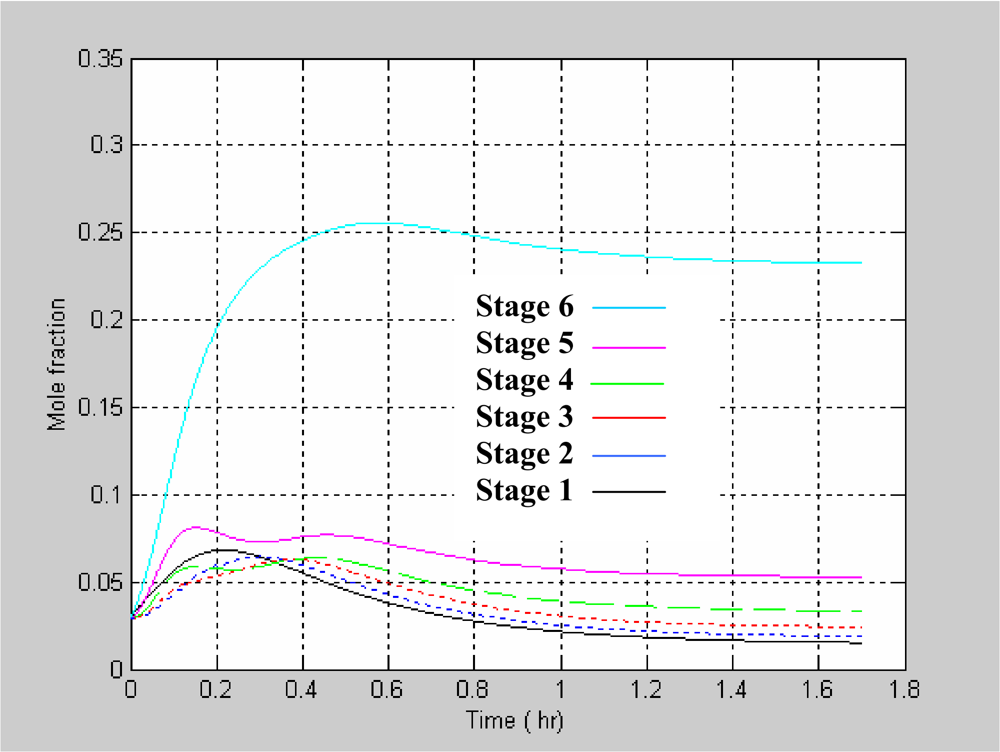


Figure 4.41: mole fraction of the product methyl acetate vs. batch time at each stage

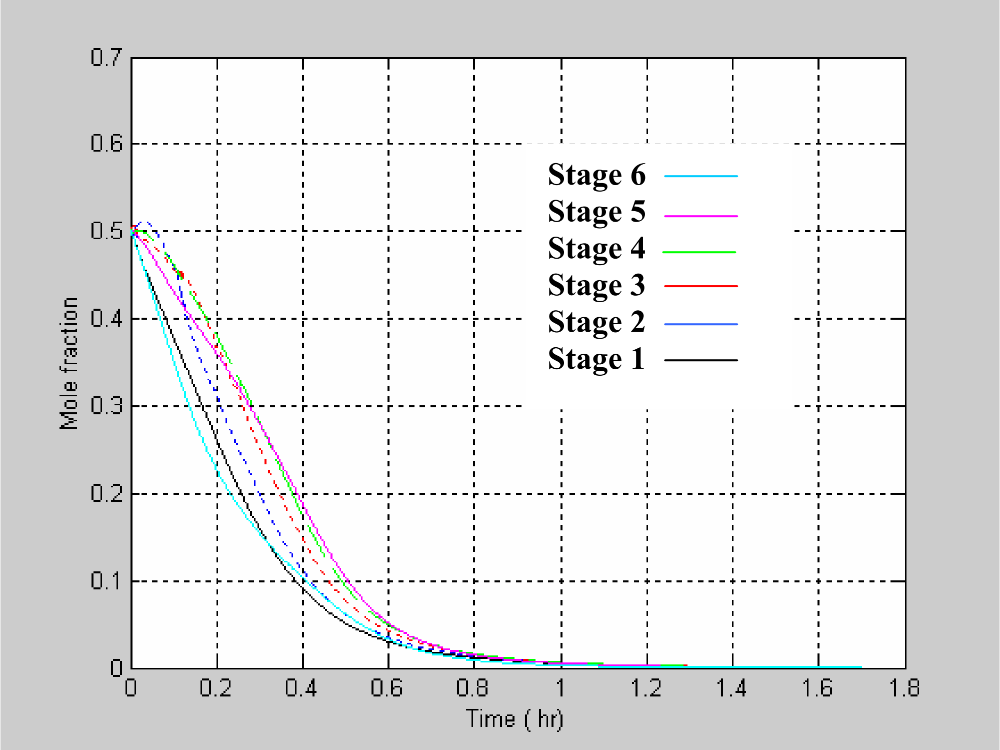


Figure 4.42: mole fraction of the methanol vs. batch time at each stage

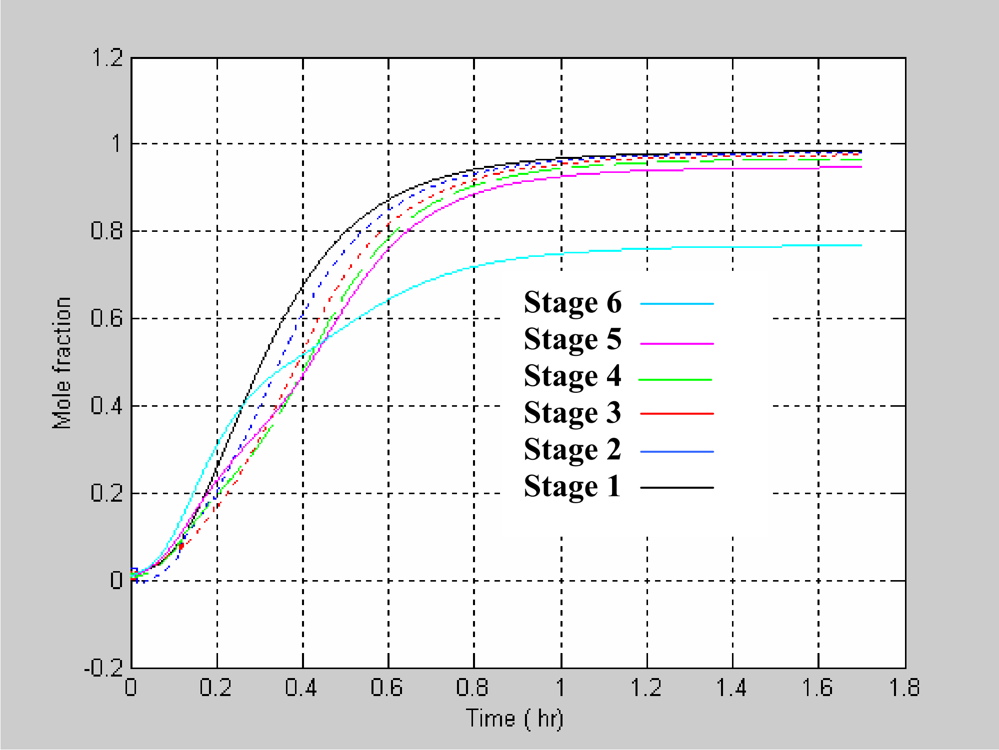


Figure 4.43: mole fraction of the water vs. batch time at each stage

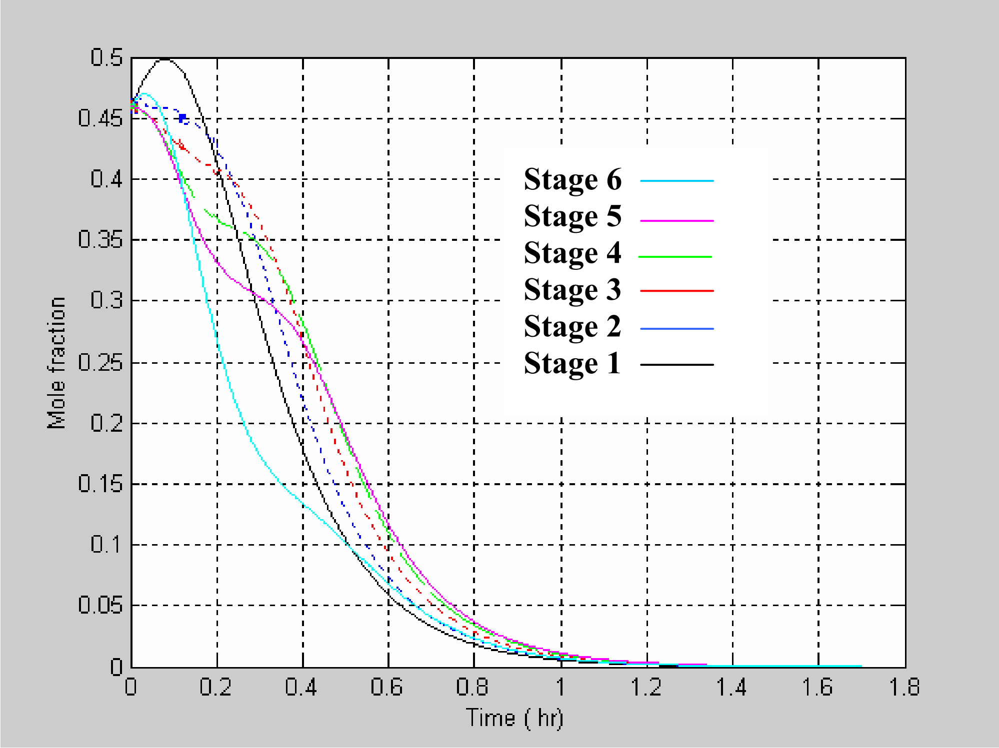


Figure 4.44: mole fraction of the acetic acid vs. batch time at each stage

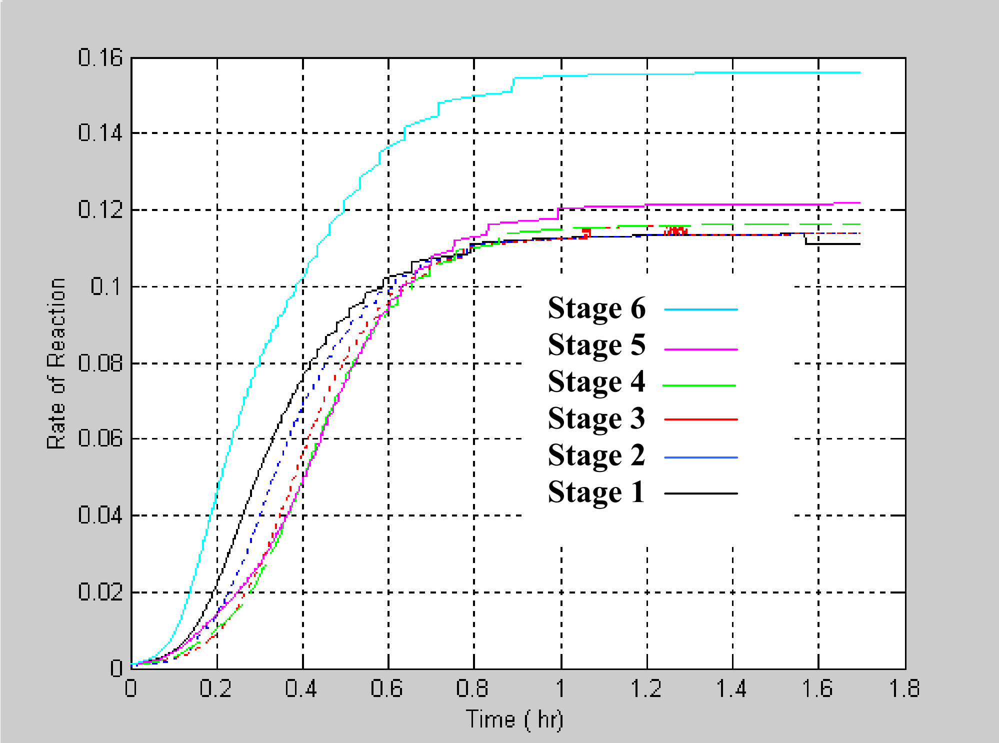


Figure 4.45: reaction rate profile vs. batch time at each stage

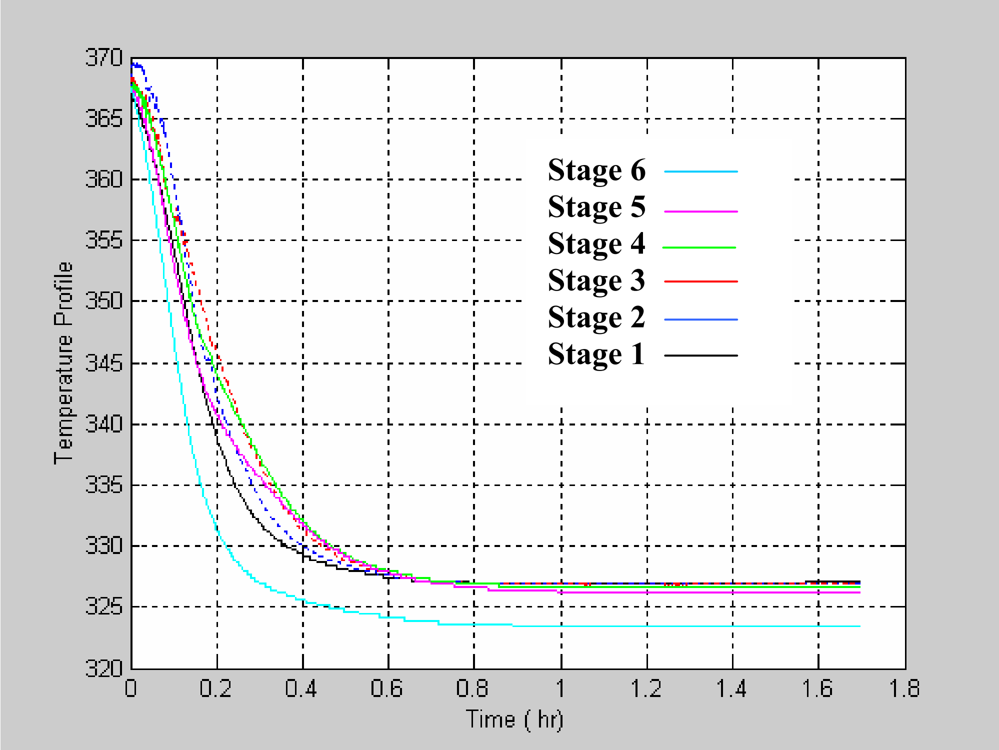


Figure 4.46: temperature profile vs. batch time at each stage

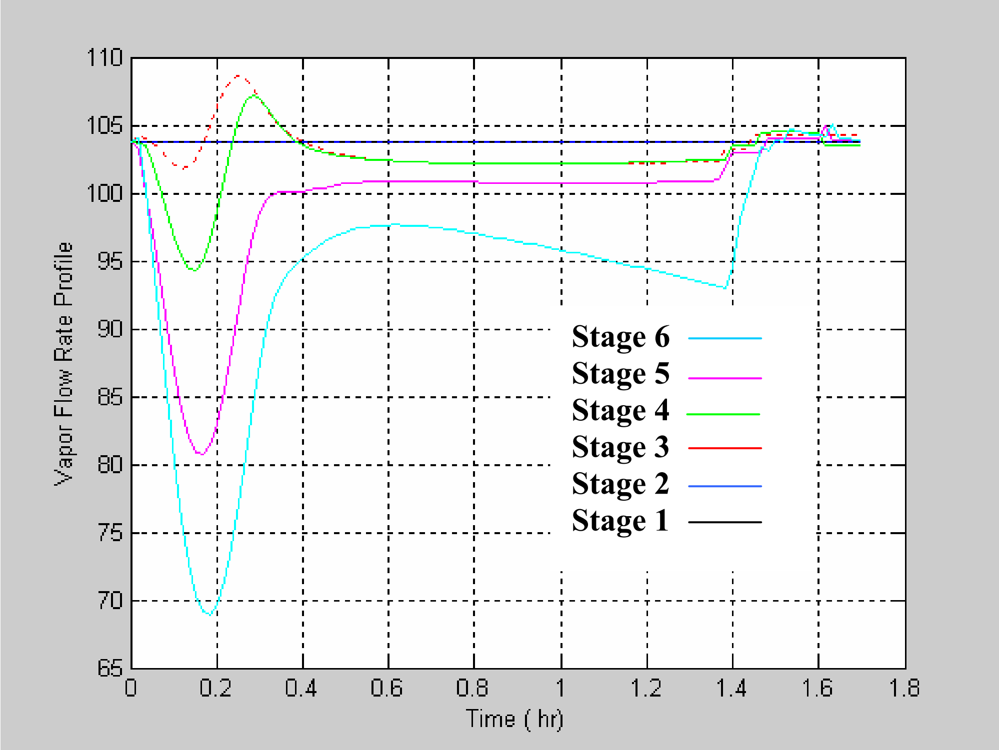


Figure 4.47: vapor flow rate profile vs. batch time at each stage

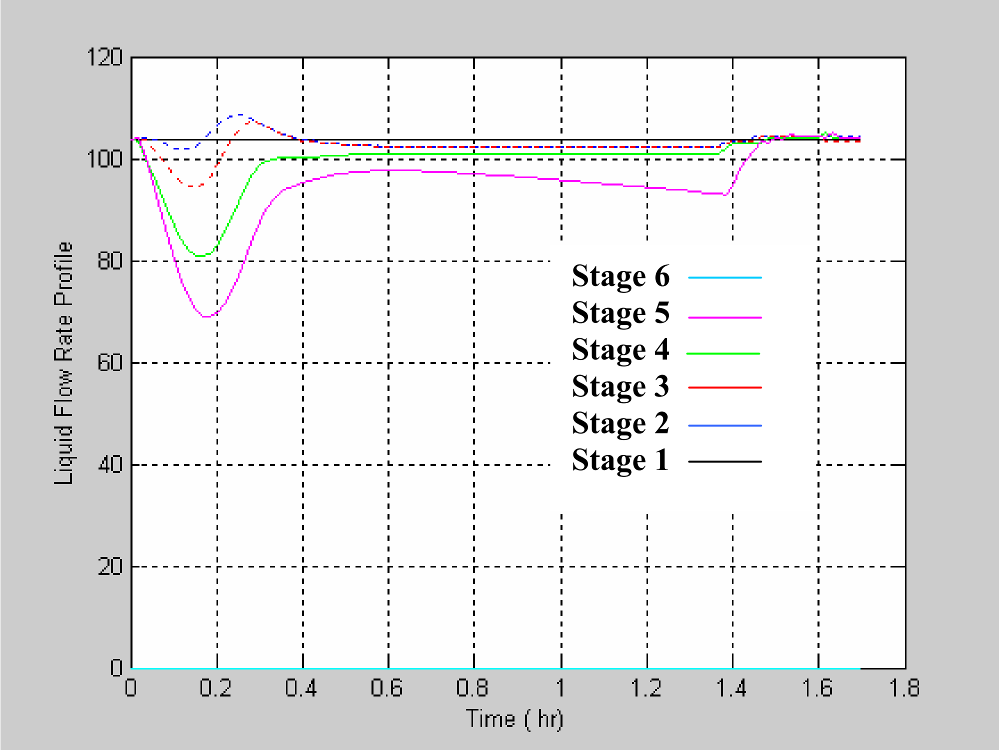


Figure 4.48: liquid flow rate profile vs. batch time at each stage

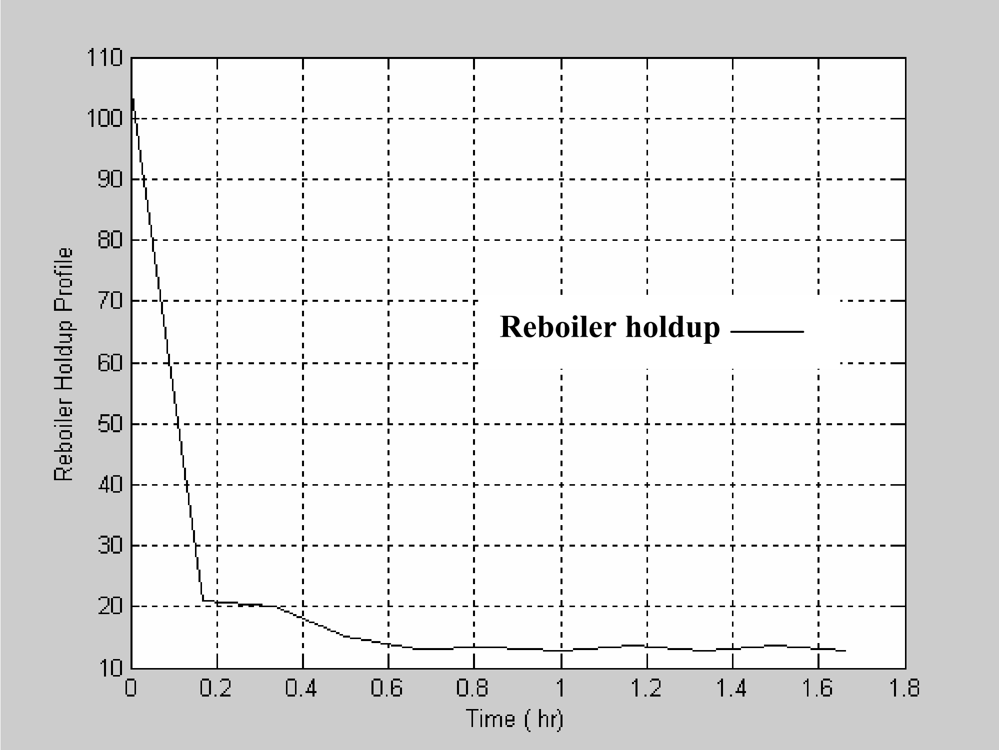


Figure 4.49: reboiler holdup profile vs. batch time at each stage

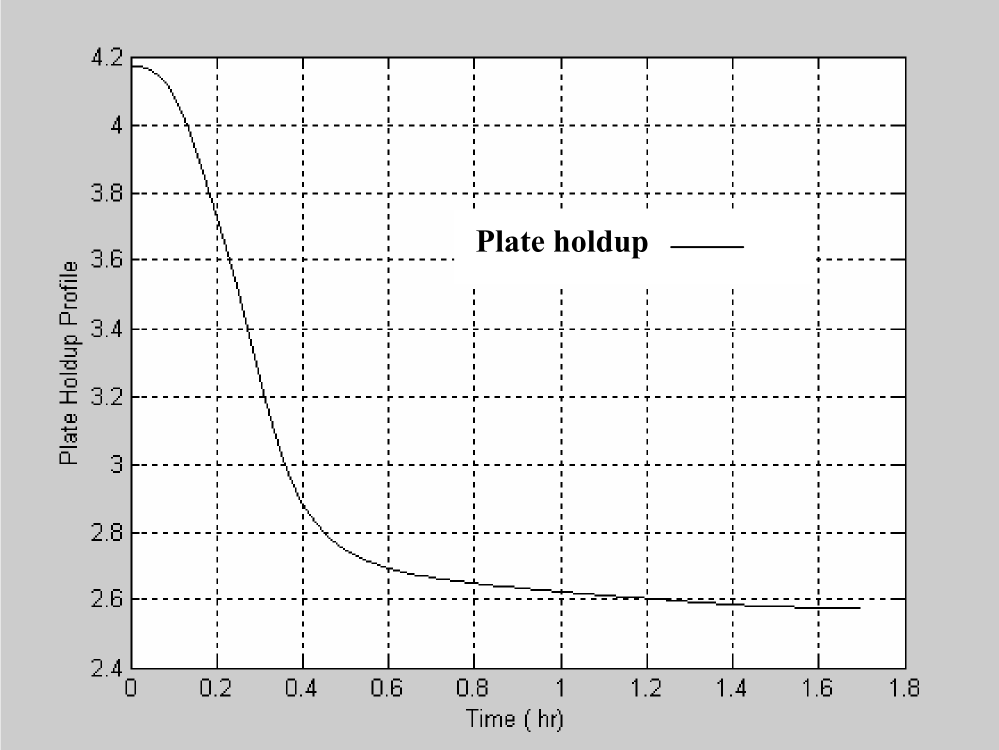


Figure 4.50: plate holdup profile vs. batch time at each stage

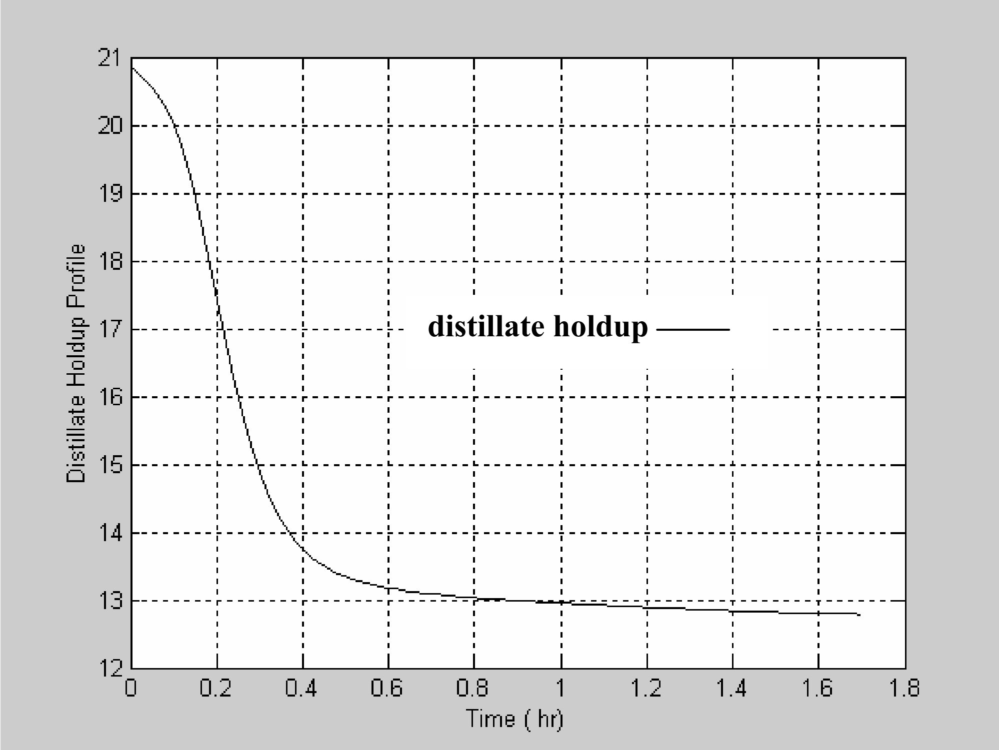


Figure 4.51: distillate holdup profile vs. batch time at each stage

The results show the best conditions to simulate the system studied is:

1- Number of stages = 6.

2- Reflux Ratio = 2.5.

3- Liquid holdup (reboiler, plates, and condenser) respectively = 85, 0.5, and 14.5 mole.

4- Batch Time = 1.7hr.

5- Operating pressure = 1 atm.

6- Feed temperature = 310.15 K.

Chapter Five

Conclusions and Future Work

5.1 Conclusions

In recent years there was an increasing tendency in publication for using batch distillation especially with chemical reaction. The present research is concerned with modeling and simulation.

Our goal in this work was the separation of multi-component mixture into its pure components by using batch distillation process. In this study, two main processes were used to separate this multi-component mixture were discussed to obtain a good condition for optimum separation, so that the aim of this work was to build a computer program to design a multi-component batch distillation process without and with chemical reaction using a rigorous method and applying a program for the production of methyl acetate as the desired product and water by the reaction of methanol and acetic acid and sulfuric acid as homogeneous catalyst in order to compute temperature, reaction rate and liquid composition profiles, and to study the effect of liquid holdup, change in batch time, and change in number of stages, which were discussed in the previous chapter for batch distillation with chemical reaction.

For the present system the following points can be concluded for the production of the desired product that is methyl acetate:

5.1.1 Batch distillation without chemical reaction

1- The results obtained from the developed computer program for conventional separation give a good agreement with Eluge [55].

2- The liquid composition of methyl acetate at distillate section is 19.7%, with recovery fraction of 19.03%, while for water the mole fraction is 40%, with recovery fraction of 48.945%, which agreed with the results obtained by [55] for constant vapor and liquid flow rates, constant reflux ratio, without chemical reaction, and constant liquid holdup.

5.1.2 Batch distillation with chemical reaction

1- The results obtained from the developed computer program conventional separation give a good agreement with Eluge [55].

2- The liquid composition of the desired product methyl acetate at distillate section is 24.7%; with 49.4% conversion, while for water the mole fraction is 40%.

3- The effect of changing batch time on the product of methyl acetate is studied, while decreasing the batch time than 1.7hr, the liquid mole fraction of methyl acetate decreased to 22.5%, with 45% conversion. When increasing the batch time the liquid mole fraction of methyl acetate decreased to21.7, with 43.4% conversion. The best condition for the design analysis of produced methyl acetate was when batch time equals to 1.7hr.

4- The effect of changing number of stages product methyl acetate is studied, while decreasing the number of stages to 4 stages the liquid mole fraction of methyl acetate decreased to 5%, with 10% conversion, when increasing to 8 stages the liquid mole fraction of methyl acetate also decreased to 5.15%, with

10.2% conversion. The best condition for the design analysis of produced methyl acetate was when number of stages equals to 6 theoretical stages.

5- The effect of liquid holdup through the column on the production of methyl acetate, where the mole fraction is 23%, with 46% conversion.

5.2 Future Work

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

1. Using another equation of state such as Wilson, NRTL, and UNIQUIC models to calculate the vapor-liquid equilibrium relations in liquid phase and compare the results.
2. Modification the computer program by taking the non ideality of vapor phase into account.
3. Application of the program on the other industrial systems such as ethyl acetate and methyl tert-butyl ether (MTBE) productions.
4. Experimental work is required to compare the results with the simulation findings.

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Appendices

Appendix A

Component	Antoine coefficient		
	A	B	C
Methanol	18.5875	3626.55	34.29
Acetic Acid	16.8080	3405.57	56.34
Water	18.3036	3816.44	46.13
Methyl acetate	16.1295	2601.92	56.15

Table (A-1) Coefficients of Antoine equation [5]

Component	Constant of gas heat capacity			
	C_1	C_2	C_3	C_4
Methanol	19.238	0.0521	1.197 E-5	-1.131 E-8
Acetic Acid	4.837	0.2547	-1.7519 E-4	4.9456 E-8
Water	32.2218	0.001923	1.0502 E-5	-3.5941 E-8
Methyl acetate	16.5397	0.22439	-4.3389 E-5	2.91255 E-8

Table (A-2) Constant of gas heat capacity [67]

Component	Latent Heat λi (kj/kmol)	Enthalpy of Formation H_f (Kj/kmol)	Boiling Point Temperature T_B (k)	Molecular Weight (M.W.)
Methanol	35255.227	-238.655	337.8	32.042
Acetic Acid	23682.006	-674.461	391.1	60.052
Water	40656.9	-285.840	373.2	18.015
Methyl acetate	30125.52	-509.193	330.1	74.080

Table (A-3) Physical Properties [5]

Component	Liquid Molar Density Constants			
	C_1	C_2	C_3	C_4
Methanol	**2.288**	**0.2685**	**512.64**	**0.2453**
Acetic Acid	**1.4486**	**0.25892**	**591.95**	**0.2529**
Water	**5.459**	**0.30542**	**647.13**	**0.081**
Methyl acetate	**1.13**	**0.2593**	**506.55**	**0.2764**

Table (A-4) Liquid Molar Density Constants [5]

Component	UNIFAC Constants		
	R_K	Q_K	No
Methanol	**1.4311**	**1.432**	**19**
Acetic Acid	**1.3013**	**1.224**	**40**
Water	**0.92**	**1.40**	**20**
Methyl acetate	**2.85**	**2.5**	**50**

Table (A-5) Constants of UNIFAC equation [69]

Component	Constants liquid mean heat capacity
Methanol	**81.6**
Acetic Acid	**124.3**
Water	**75.291**
Methyl acetate	**120.2**

Table (A-6) Constants liquid mean heat capacity [68]

Rate of reaction		
Pre-exponential factor (K_{ester}) (1/Kmol.mn.ml H_2SO_4)	Activation energy E (kj/kmol)	Equilibrium constant of chemical reaction (k_{eq})
3300	41800	5

Table (A-7) Constant rate of reaction [55]

Component	Density (kg/m^3)
Methanol	791
Acetic Acid	1049
Water	1000
Methyl acetate	934

Table (A-8) Density of components at reference temperature [5]

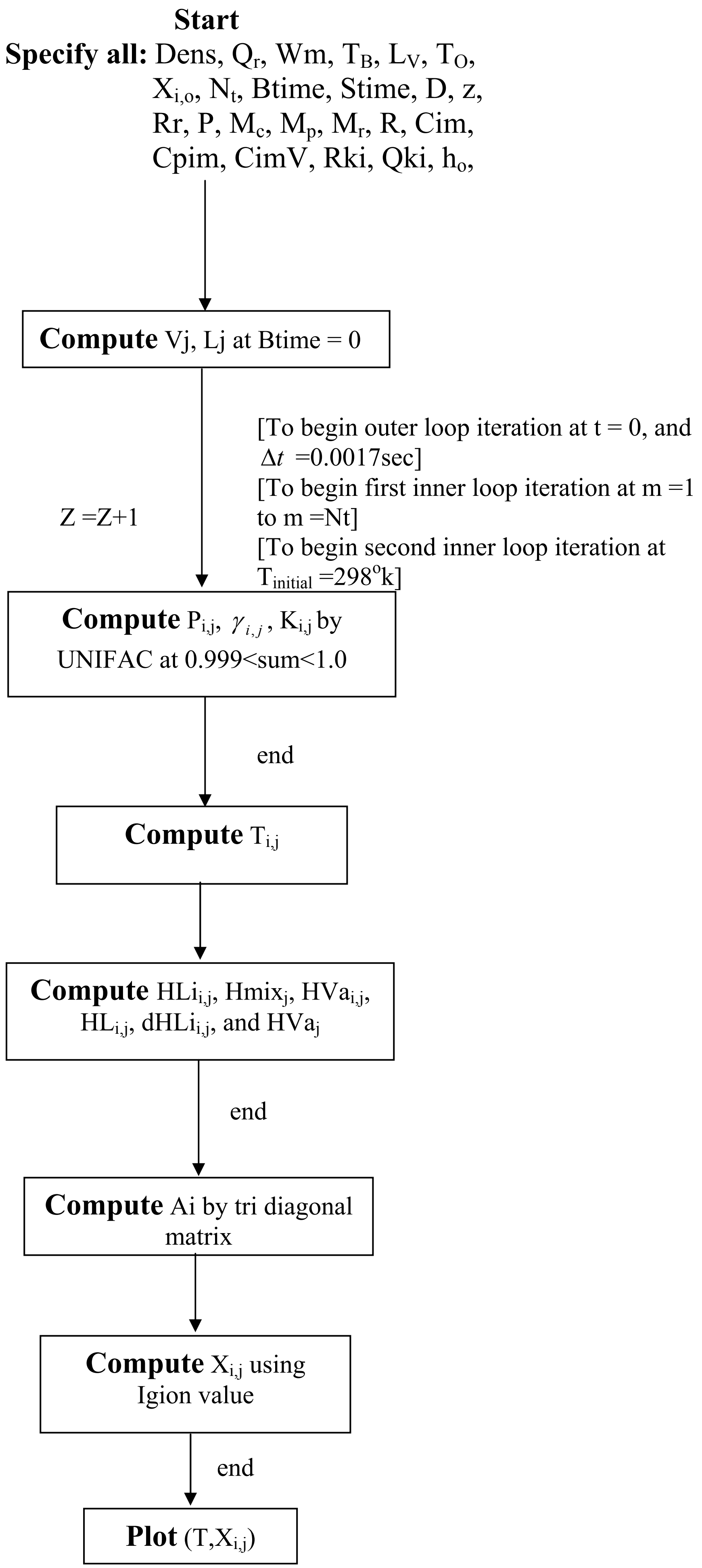
Initial Feed composition for Batch Distillation without Chemical Reaction	
Component	Mole Fraction
Methanol	0.25
Acetic Acid	0.07
Water	0.30
Methyl acetate	0.38

Table (A-9) Initial feed composition for conventional batch distillation [55]

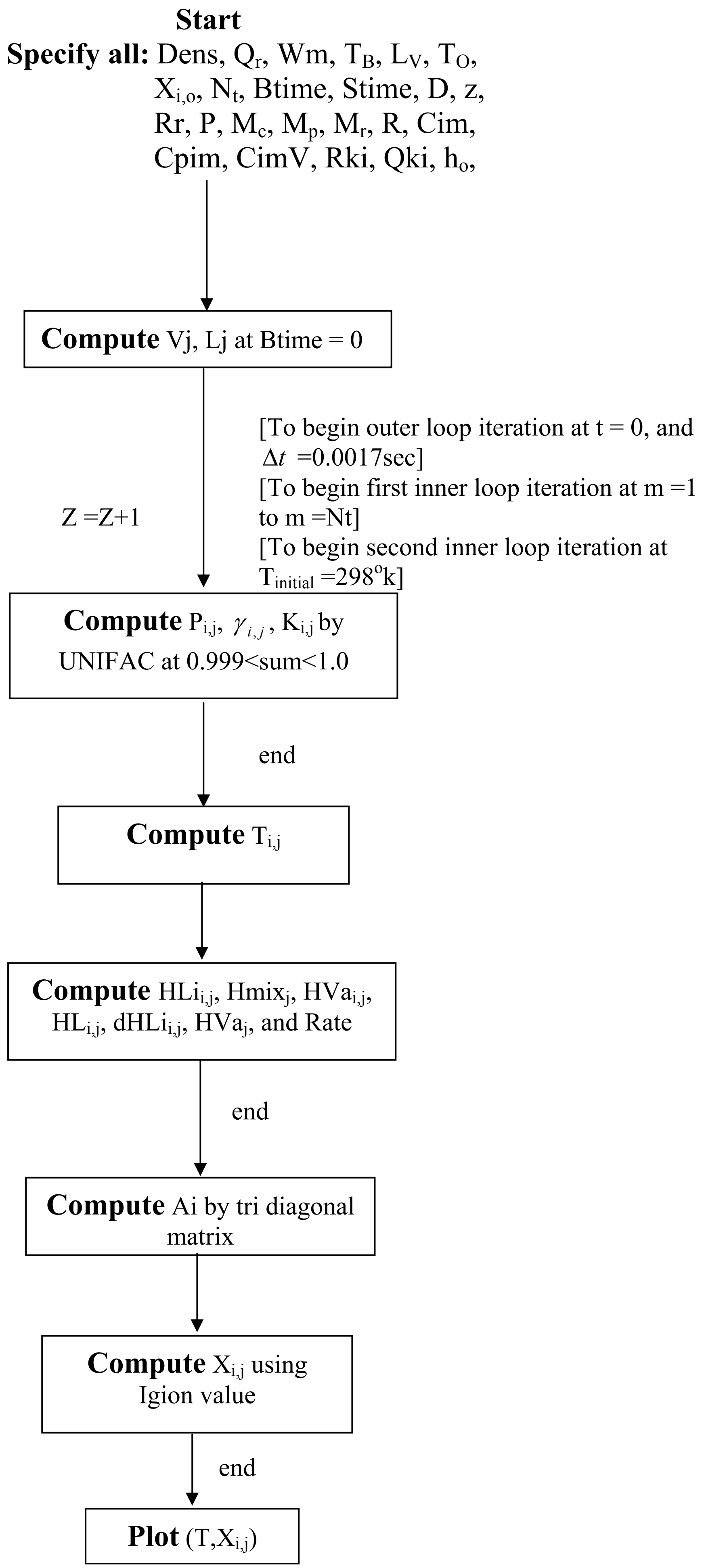
Initial Feed composition for Batch Distillation with Chemical Reaction	
Component	Mole Fraction
Methanol	0.5
Acetic Acid	0.46
Water	0.03
Methyl acetate	0.01

Table (A-10) Initial feed composition for rectifier batch distillation [55]

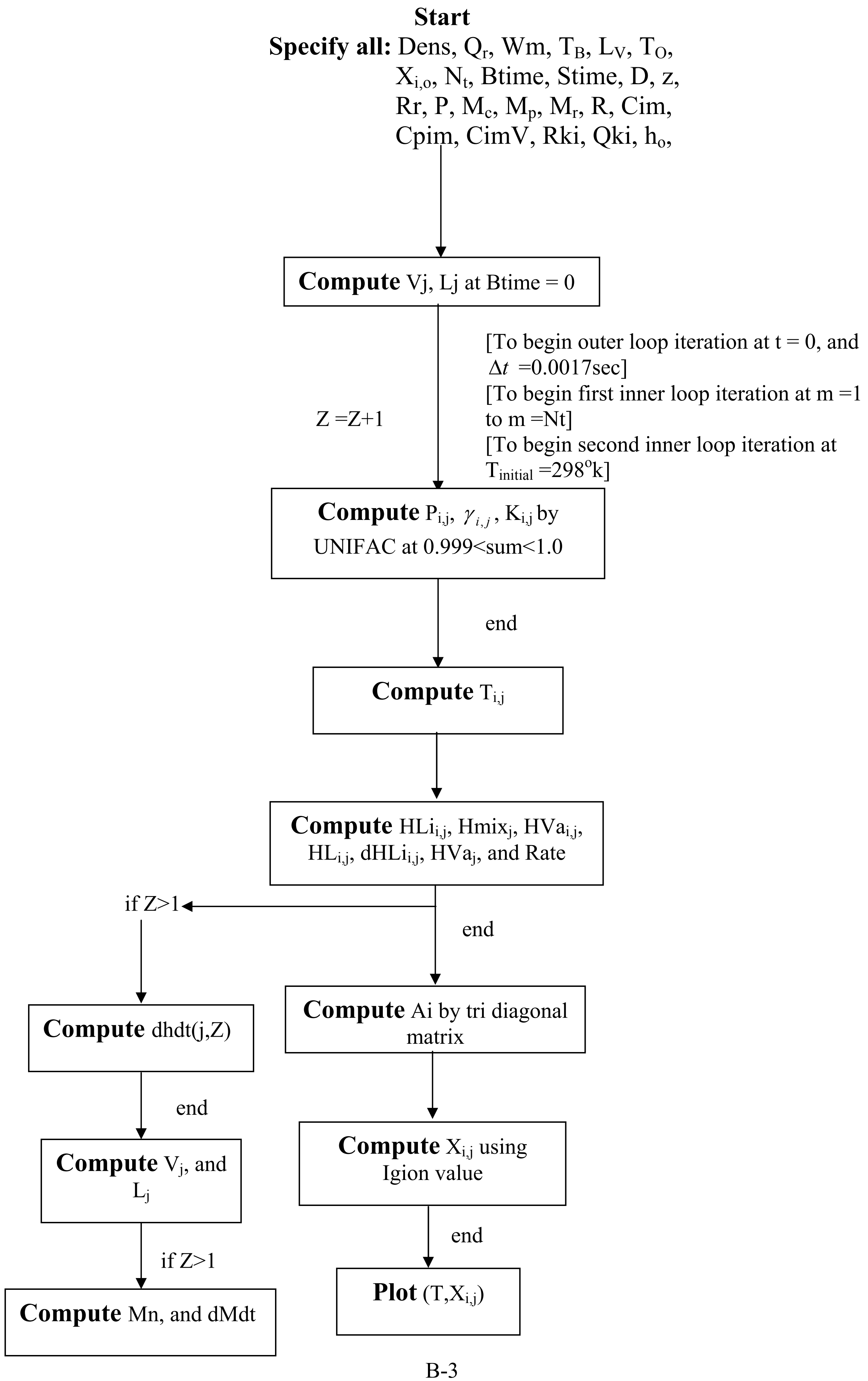
Appendix B (B-1)



Appendix B (B-2)



Appendix B (B-3)



شكر وتقدير

أود أن اعبر عن خالص شكري وتقديري وامتناني العميق للمشرفين الدكتورة ندى بهجت نقاش والدكتور نصير الحبوبي لما قدماه لي من توجيهات قيمة ونصائح سديدة طوال فترة إنجاز البحث.

أود أيضاً أن اشكر المشرف الدكتور قاسم جابر سلمان وجميع أساتذة وموظفي قسم الهندسة الكيمياوية في جامعة النهرين لإبدائهم المساعدة اللازمة أثناء هذا العمل.

ولا أنسى أن أتقدم بالشكر والامتنان إلى من لازمني طوال فترة البحث وخلال اصعب الظروف إلى أعز من في الوجود إلى أبى وأمي وجميع أفراد عائلتي فلهم جزيل الشكر والتقدير.

حيدر محمد حمودي الزبيدي

الخلاصة

نظام جهاز التقطير ذو الدفعات يعتبر واحد من اهم الجهزة التي تستخدم في المصانع الكيمياوية و النفطية و الدوية لفصل خلائط السوائل الى مركباتها النقية.

استخدمة هذا العمل لأنشاء برامج محاكات حاسوبية لتحليل عمليات جهاز التقطير ذو الدفعات الغير مصاحب و المصاحب بتفاعل كيمياوي متعدد المراحل و المركبات.

استخدمة الطريقة المضبوطة (Rigorous Method) لبناء البرنامج للخلط الغير مثالية، كتبت هذه البرامج بلغة $MATLAB_{6.1}$ و بقصد التوافق مع الحواسيب الشخصية و كما هو مدرج في الملاحق (B-1, B-2, and B-3).

دققت صلاحية ودقة هذه البرامج بمقارنة النتائج مع Eluge [55] بإستخدام تفاعل الأسترة لحامض الخليك مع الميثانول لإنتاج خلات المثيل والماء .

درس تأثير العديد من المتغيرات منها تأثير عدد الصواني ، تأثير الوقت ، وتأثير حساب الماء المتبقي في الصينية على أداء برج التقطير ذو الدفعات المصاحب للتفاعل الكيمياوي خلال جريان السائل والبخار داخل البرج وتأثيرها على درجات الحرارة وسرعة التفاعل وكميات السوائل الناتجة .

النتائج حصلنا عليها للخلائط الغير مثالية لجهاز التقطير ذو الدفعات حيث رأينا نسبة التحول لخلات المثيل الكلية تساوي 49.41 مول % ونسبة خلات المثيل في المقطر 24.7 مول % ونسبة المستلم لهذه المادة 90.7% عندما تكون نسبة الراجع 2.5 وعدد المراحل 6 عند ثبوت الماء التبقي في الصينية الواحدة ووقت التقطير يساوي 1.7 ساعة . عندما نقلل عدد المراحل إلى 4 حيث كمية خلات المثيل في المقطر تقل إلى 5 مول % ونسبة التحول الكلية تصبح 10 مول % . عند زيادة عدد المراحل إلى 8 تقل أيضاً كمية خلات المثيل في المقطر إلى 5.1 مول % ونسبة التحول الكلية تصبح 10.2 مول % عندما يكون وقت التقطير يساوي 1.7 ساعة . عند تقليل وقت التقطير إلى 1 ساعة تقل

كمية خلات المثيل في المقطر إلى 22.5 مول % وكمية التحول الكلية إلى 45 مول % بينما عند زيادة وقت التقطير إلى 3 ساعة نلاحظ أيضاً نقصان في كمية خلات المثيل في المقطر إلى 21.7 مول % ونسبة التحول الكلية تساوي 43.4 مول % عندما تكون عدد المراحل تساوي 6 .

إختيار ظروف التصميم الأفضل للحصول على هذه النتائج عندما يكون وقت التقطير يساوي 1.7 ساعة وعدد المراحل تساوي 6 ونسبة الراجع تساوي 2.5 وذلك للحصول على 90.7 % من خلات المثيل ونسبة التحول الكلية 49.41 مول % عندما تكون نسبة الماء التبقي في الصينية الواحدة ثابته لكل جهاز تقطير ذو الدفعات .

درس تأثير الماء التبقي في الصينية الواحدة لكل جهاز تقطير ذو الدفعات حيث تؤثر على عمل جهاز التقطير وتزيد من نسبة التحول الكلية لخلات المثيل حيث تساوي 50.4 مول % وكمية خلات المثيل في المقطر تساوي 25.2 مول % .

التمثيل بجهاز التقطير ذو الدفعات المصاحب بتفاعل كيمياوي لأنتاج المثيل أسيتيت

رسالة
مقدمة الى كلية الهندسة في جامعة النهرين و هي جزء من متطلبات
نيل درجة ماجستير علوم في الهندسة الكيمياوية

من قبل
حيدر محمد حمودي الزبيدي
(بكالوريوس في الهندسة الكيمياوية ٢٠٠١)

شعبان ١٤٢٥ هـ
تشرين الاول ٢٠٠٤م