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**MODELLING AND OPTIMISATION OF BATCH  
DISTILLATION INVOLVING ESTERIFICATION AND  
HYDROLYSIS REACTION SYSTEMS**

Modelling and Optimisation of Conventional and Unconventional Batch  
Distillation Process: Application to Esterification of Methanol and Ethanol  
using Acetic Acid and Hydrolysis of Methyl Lactate System.

**Elmahboub A. EDREDER**

*BSc. and MSc. Chem. Eng.*

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School of Engineering, Design and Technology

University of Bradford

United Kingdom

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## Abstract

**Keyword:** Conventional batch distillation, Inverted batch distillation, Batch reactive distillation, Semi-batch distillation, Fixed product demand, Dynamic modelling and optimisation, Esterification, Hydrolysis, gPROMS

Batch distillation with chemical reaction when takes place in the same unit is referred to as batch reactive distillation process. The combination reduces the capital and operating costs considerably. Among many different types of batch reactive distillation column configurations, (a) conventional (b) inverted (c) semi-batch columns are considered here.

Three reaction schemes such as (a) esterification of methanol (b) esterification of ethanol (c) hydrolysis of methyl lactate are studied here. Four different types of dynamic optimisation problems such as (a) maximum conversion (b) maximum productivity (c) maximum profit and (d) minimum time are formulated in this work. Optimal design and or operation policies are obtained for all the reaction schemes.

A detailed rigorous dynamic model consisting of mass, energy balances, chemical reaction and thermodynamic properties is considered for the process. The model was incorporated within the dynamic optimisation problems. Control Vector Parameterisation (CVP) technique was used to convert the dynamic optimisation problem into a nonlinear programming problem which was solved using efficient SQP (Successive Quadratic Programming) method available within the gPROMS (general PROcess Modelling System) software.

It is observed that multi-reflux ratio or linear reflux operation always led to better performance in terms of conversion, productivity for all reaction schemes compared to that obtained using single reflux operation.

Feed dilution (in the case of ethanol esterification) led to more profit even though productivity was found to be lower. This was due to reduction in feed price because of feed dilution. Semi-batch reactive distillation operation (for ethanol esterification) led to better conversion compared to conventional batch distillation, however, the total amount of acetic acid (reactant) was greater in semi-batch operation. Optimisation of design and operation (for ethanol esterification) clearly showed that a single column will not lead to profitable operation for all possible product demand profile. Also change in feed and /or product price may lead to adjust the production target to maximise the profitability.

In batch distillation, total reflux operation is recommended or observed at the beginning of the operation (as is the case for methanol or ethanol esterification). However, in the case of hydrolysis, total reflux operation was observed at the end of the operation. This was due to lactic acid (being the heaviest) was withdrawn as the final bottom product.

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## Nomenclature and Abbreviation

|                  |   |
|------------------|---|
| ACC              | annualised capital cost (\$/year)                                 |
| AcOH             | acetic acid   |
| $C_i$            | stands for concentration in gmol/litter for the $i$ th component  |
| CBD              | conventional batch distillation                                   |
| CVP              | Control Vector Parameterisation                                   |
| D                | distillate product (kmol)   |
| DAE              | differential algebraic equations                                  |
| EtOH             | ethanol   |
| EtAc             | ethyl acetate   |
| F                | feed of semi-batch (kmol/hr)                                      |
| $F^{\max}$       | the maximum feed as semi-batch in time interval 1 and 2, kmol /hr |
| $H_a, H_c$       | accumulator and condenser holdup respectively (kmol)              |
| $H_j, H_N$       | plate and reboiler holdup respectively (kmol)                     |
| H                | operation time per year (h/year)                                  |
| $h^L, h^V,$      | liquid, vapour enthalpy (kJ/kmol)                                 |
| IPPFO            | Ideal Physical Properties Foreign Objective                       |
| IBD              | inverted batch distillation                                       |
| K                | vapour-liquid equilibrium constant                                |
| $k_f, k_r$       | forward and backward reaction rate constant                       |
| L                | liquid flow rate in the column (kmol/hr)                          |
| $L_D$            | distillate flow rate (kmol/hr)                                    |
| MVC              | middle vessel batch distillation                                  |
| <i>Multi</i> VBD | Multivessel batch distillation column                             |
| MeOH             | methanol  |

|                 |  |
|-----------------|--|
| MA              | methyl acetate                                     |
| N               | number of plates                                   |
| $n_c$           | number of components.                              |
| $N_{CI}$        | number of control intervals                        |
| $N_B$           | number of batches/year                             |
| OP              | optimisation                                       |
| OC              | operating cost/year (\$/yr)                        |
| $P$             | pressure (bar)                                     |
| \$P             | profit (\$/yr)                                     |
| Prod            | productivity (kmol/hr)                             |
| PD              | product demand (kmol/yr)                           |
| $p^{sat}$       | vapour pressure of pure component $i$              |
| $Q_C, Q_R$      | condenser or reboiler duty (kJ/hr)                 |
| $r$             | reaction rate                                      |
| $R, R_{max}$    | reflux ratio                                       |
| $R_1, R_2, R_3$ | reflux ratio in time interval 1, 2 and 3           |
| SQP             | Successive Quadratic Programming algorithm         |
| $T,$            | temperature (K)                                    |
| $t, t_f$        | batch time , final batch time (hr)                 |
| $t_1, t_2, t_3$ | length of interval 1, 2 and 3, hr                  |
| $u(t)$          | control variable                                   |
| $V$             | vapour flow rate in the column (kmol/hr)           |
| VLE             | vapour-liquid equilibrium                          |
| $H_2O$          | water  |
| $x, y$          | liquid or vapour composition (mole fraction)       |
| $x_a$           | accumulated distillate composition (mole fraction) |

$x_D$  instant distillate composition (mole fraction)

$X$  conversion

*Superscripts and subscripts*

$\varepsilon$  small positive number of the order of  $10^{-3}$

$i$  component number

$j$  stage number

$\gamma_i$  activity coefficient of component  $i$

$\lambda_i$  latent heat of vaporisation (kJ/kmol) of component  $i$

$\Delta n$  change in moles due to chemical reaction

# Chapter One

## Introduction

Distillation is the most widely used technique for separating liquid mixtures. Depending on the applications, the distillation process can be divided into two categories: (1) continuous distillation, which is primarily used in the petrochemical and bulk chemical industries and (2) batch distillation, which is mainly used in specialty chemical, biochemical, and pharmaceutical industries. In addition, the distillation process can be carried out in semi-batch (or semi-continuous) mode. All these types of distillation can be carried out with or without chemical reaction.

This chapter sets out the historical background of distillation, brief description of different batch column configurations and their importance and applications. Next the scope, the aim and objectives of this research is summarised. Finally the layout of this thesis is outlined.

### 1.1 Continuous Distillation Columns

Figure 1.1 shows a typical continuous distillation column. In this column, the liquid mixture (feed), which is to be separated into fractions, is introduced at one or more points along the column shell. Because of difference in gravity between vapour and liquid phases, liquid runs down the column while vapour flows up the column, contacting liquid at each tray. Liquid reaching the bottom of the column is partially vaporized in a reboiler to provide boil-up, which is sent back up to the column. The remaining liquids are withdrawn as bottom product. Vapour reaching the top of the column is cooled and condensed to liquid in overhead condenser. Part of this liquid is returned to the column as reflux to provide liquid overflow. The remainder of the liquid is withdrawn as distillate (Perry and Green, 1997) from the top of the column.

Continuous distillation columns operate at constant reflux and reboil ratio during the year. The optimal values of reflux and reboil ratio are determined at the design stage. The overall separation achieved between the distillate and the bottom products depends primarily on relative volatilities of the components, the number of trays, and the ratio of the liquid and vapour flows ratio (i.e. the reflux) (Hines and Maddox,1985). For a given separation task, an optimum combination of reflux and number of stages can be sought by applying optimisation techniques which will, say, maximize profitability.

Continuous distillation is used widely where large quantities of liquids have to be distilled. It finds its widest application in petroleum refineries. In refineries, the crude oil feedstock is separated into their fractions, e.g. light gases, naphtha, diesel, etc. (Gary and Handwerk, 1984) in a multiple product tower (Figure 1.2).

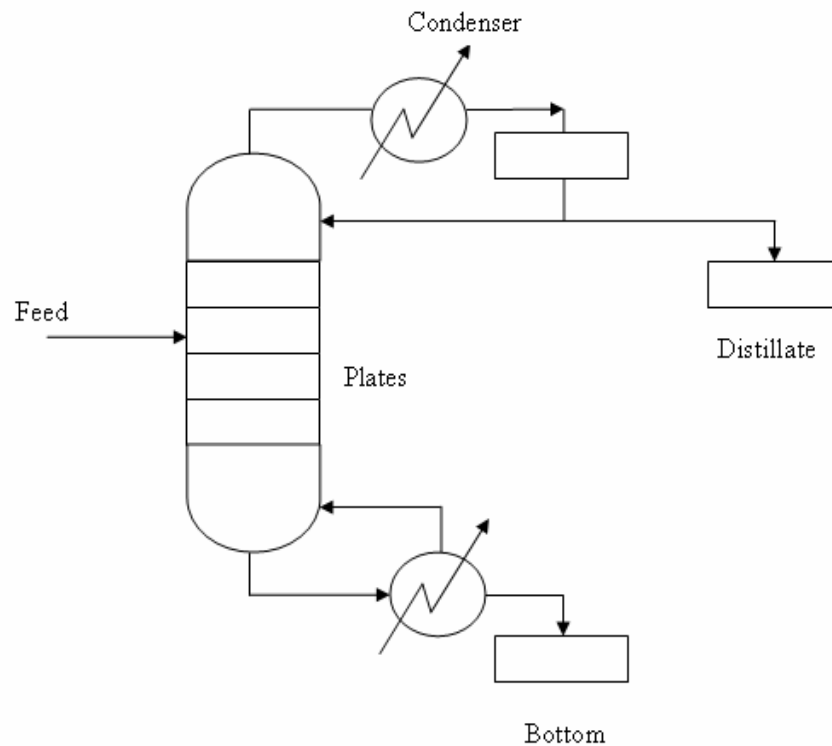


Figure 1.1 Continuous Distillation Column

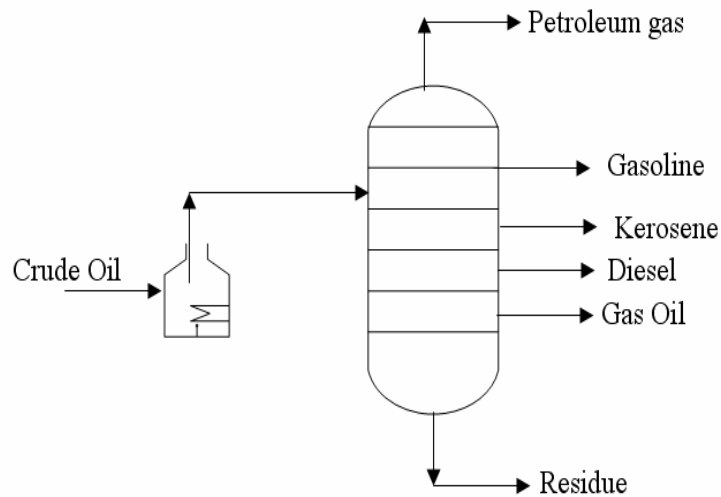


Figure 1.2 Crude Oil Distillation Tower

## 1.2 Batch Distillation

Batch distillation is highly preferable to continuous distillation when high-value-added, low-volume chemicals must be separated (*e.g* making alcohols from artificial wine Osorio *et al.*, 2005; recovery of limonene and myrcene from essential oil of orange , Zamar *et al.*,2005). Furthermore it is widely used in chemical processing industries where small quantities of materials are to be handled in irregularly or seasonally scheduled periods, and it is applied when the feed composition varies widely from period to period or where completely different feed stocks have to be handled (Cuille and Reklaitis, 1986; Wilson, 1987; Logsdon *et al.*, 1990; Albet *et al.*, 1991; Sorensen and Skogestad, 1996; Mujtaba and Macchietto 1992, 1997; Tomazi, 1997; Sharif *et al.*,1998; Mujtaba, 2004).

The most important advantages of batch distillation over a continuous distillation lie in the use of a single column as opposed to multiple columns and its flexible operation. For a multicomponent liquid mixture with  $nc$ , number of components, usually  $(nc-1)$  number of continuous columns will be necessary to separate all the components from the mixture while with the batch distillation, only one column is necessary to separate

all the components in a mixture (Mujtaba, 2004). The other advantages are that it incurs low capital costs and it is able to accept a wide range of feed compositions.

### 1.2.1. Conventional Batch Distillation

Traditionally, the most popular kind of batch column is conventional (regular) batch column (CBD). Figure 1.3 shows a schematic diagram of conventional batch distillation column. It consists of a bottom receiver/reboiler, rectifying column (either a tray or packed column) placed over the reboiler, connected to a total condenser or a partial condenser system and distillate receivers. In this column, the charge is loaded into the reboiler at the beginning of the process and heated to its boiling point. Vapour flows upwards in the column and condenses at the top. After some time, a part of the overhead condensate is withdrawn continuously as distillate, and the other part is returned to the column section as reflux. The liquid in the reboiler is increasingly depleted of the more volatile components. As the amount of liquid in the reboiler decreases, the concentration of high boiling constituents increases.

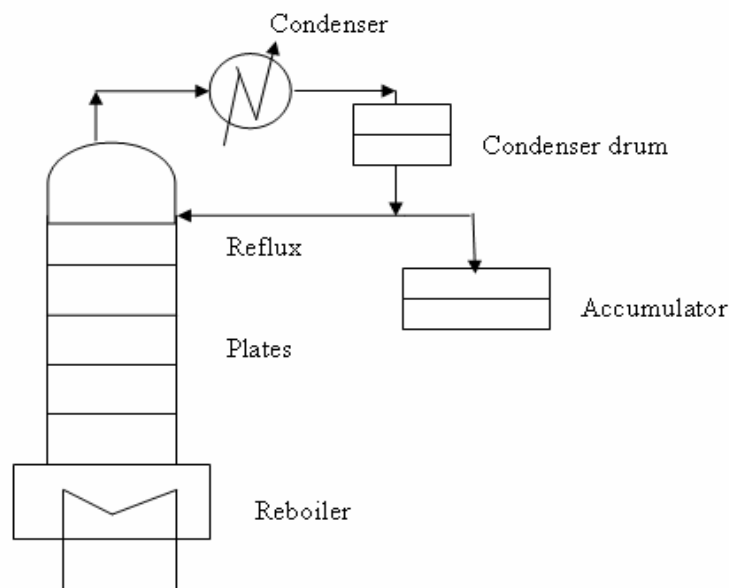


Figure 1.3 Conventional Batch Distillation (CBD)

The column usually operates under three operating modes:

- a) Constant reflux ratio (with variable distillate composition).
- b) Constant distillate composition (with variable reflux ratio).
- c) Total reflux.

Combination of these three basic modes of operation can be used to optimise the operation of a given separation task.

The optimal reflux ratio policy has been confirmed to be significantly advantageous in some cases over other policies such as constant reflux ratio or constant distillate composition in terms of saving batch operating time up to 28 % (Mayur and Jackson, 1971); maximising the quantity of distillate collected by up to 11% (Farhat *et al.*, 1990). Kerkhof and Vissers (1978) showed that for difficult separations an optimal reflux control policy yields up to 5 % more distillate, corresponding to 20-40 % higher profit, compared to that with either constant distillate or constant reflux ratio policies (Mujtaba, 2004).

### **1.2.2 Inverted Batch Distillation**

The use of inverted or stripping batch columns was originally proposed by Robinson and Gilliland (1950). In the inverted column, IBD (Figure 1.4) the feed is charged to the condenser drum. The liquid flowing down the column is vaporized in the reboiler and a fraction is removed as product accumulator. The products are taken out with the heaviest component first, then the second heaviest, etc.

Mujtaba and Macchietto (1994) considered simultaneous reaction and distillation in an inverted column to maximize the conversion of the limiting reactant, obtaining the main product (highest boiling component in the mixture) at specified purity by optimizing reboil ratio. Sorensen and Skogestad (1996) compared the differences between inverted



and conventional columns and investigated the effect on minimum batch time. They found out that when lighter components are present in the feed in small quantity but need to be recovered at high purity, the removal of a large amount of heavy component from the column in inverted columns required less time compared to the batch time that would be required in a conventional column.

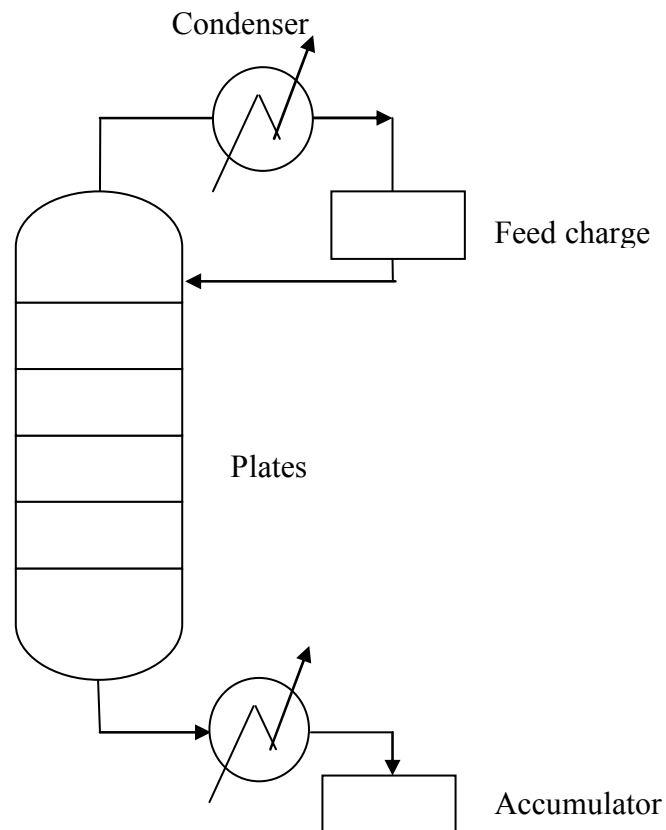


Figure 1.4 Inverted Batch Distillation Column (IBD)

Recently, Masoud and Mujtaba (2005, 2009) addressed the effect of operating decision (e.g. constant reboil ratio or time sequenced reboil ratio) on the design, utility (energy) cost and profitability of inverted batch distillation column.

### 1.2.3 Semi-batch (Semi-continuous) Distillation Column

A typical semi-batch (semi-continuous) distillation column is shown in Figure 1.5. The operation of such columns is very similar to conventional batch distillation except that a part of the feed is introduced to the column in a continuous or semi-continuous mode.

This type of the column is suitable for extractive distillation, reactive distillation, etc. (Lang and co-worker, 1994, 1995; Li *et al.*, 1998; Mujtaba 1999, Fernholz *et al.*, 2000).

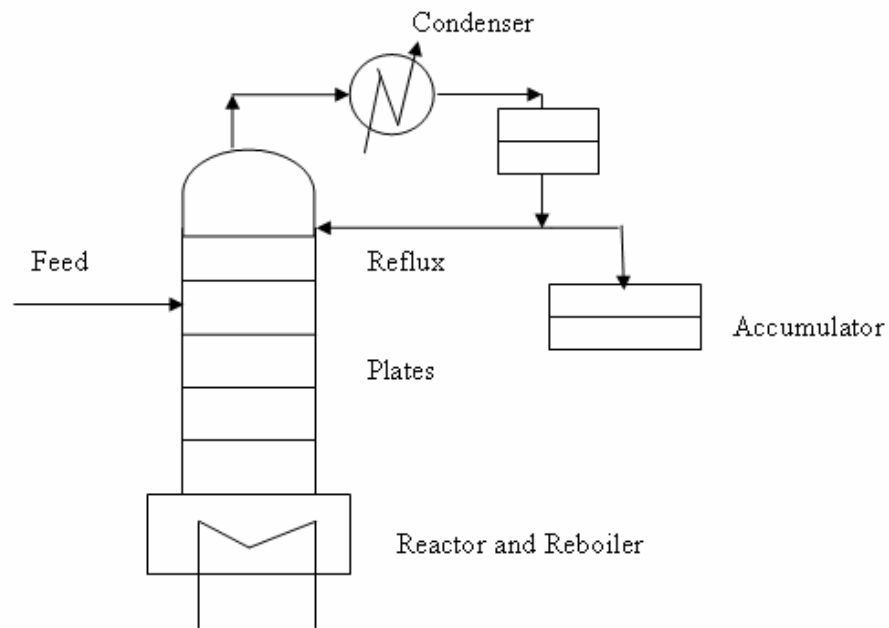


Figure 1.5 Semi-batch Distillation Column

Phimister and Seider (2000) outlined several features of distillation processes to compare semi-continuous with batch and continuous columns. It can be seen in Table 1.1

Table 1.1 Comparisons of Distillation Processes

|                                      | Batch    | Semi-continuous | Continuous |
|--------------------------------------|----------|-----------------|------------|
| Throughput                           | Low      | Intermediate    | High       |
| Flexible                             | Yes      | Yes             | No         |
| Automatic control                    | Uncommon | Possible        | Often      |
| Investment                           | Lowest   | Middle          | Highest    |
| Heat integration                     | No       | No              | Yes        |
| Single column for ternary separation | Yes      | Yes             | No         |

### 1.2.4 Middle Vessel Distillation Column

The middle vessel column (MVC) is a combination of a batch rectifier (conventional column) and a batch stripper (inverted column) (Figure 1.6). Therefore it is possible to obtain a light and a heavy fraction simultaneously from the top and the bottom of the column while an intermediate fraction may also be recovered in the middle vessel. This configuration was first mentioned by Robinson and Gilliland (1950) and was first analysed for binary mixture by Bortolini and Guarise (1971). Hasebe *et al.* (1992); Barolo *et al.* (1996); Mujtaba and Macchietto (1992, 1994); Sorensen and Skogestad (2004); Warter and Stichlmair, 2000; Warter, 2001; Warter *et al.*, 2004 and Rodriguez-Donis *et al.* (2001) reported further use of MVC.

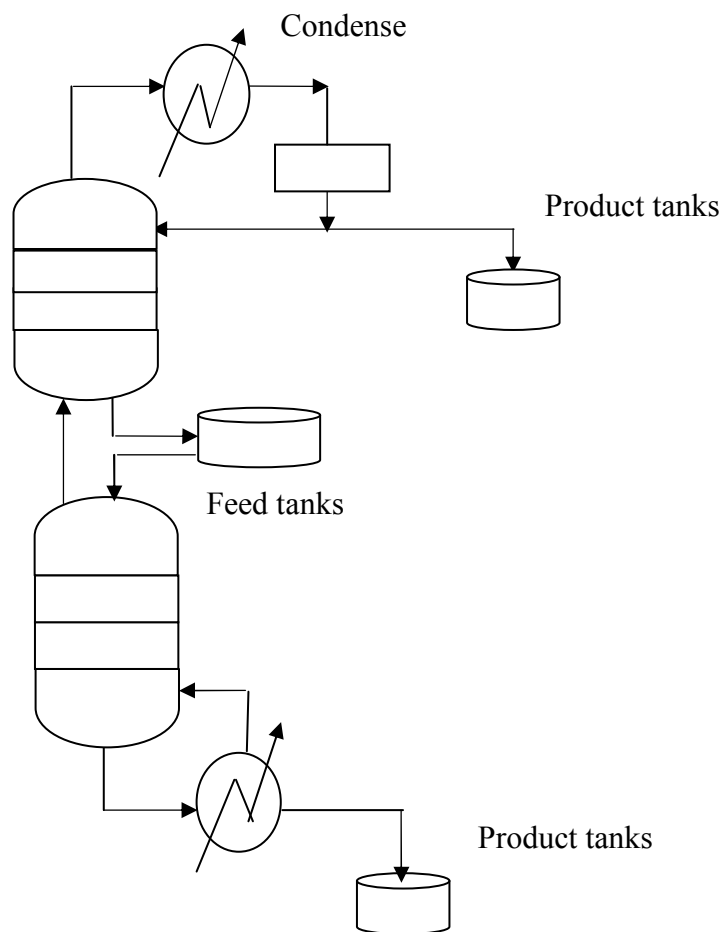


Figure 1.6 Middle Vessel Batch Distillation Column (MVC)

### 1.2.5 Multivessel Batch Distillation Column

The multivessel batch distillation column (*MultiVBD*) (Figure 1.7) consists of a reboiler, several column sections and intermediate vessels and a condenser vessel. Separation of  $n_c$  components would require  $n_c-1$  accumulators. Furlonge *et al.* (1999) minimised the mean rate of energy consumption required for producing products of specified purity while optimising heat input to the reboiler subject to product specifications. Low and Sorenson (2003) maximised profit while optimising the number of stages in different column sections and reflux ratio. More recently, Mahmud *et al.* (2008) considered an optimal design and operation of *MultiVBD* column producing two desired products from a ternary mixture with fixed yearly product demand and strict product specification.

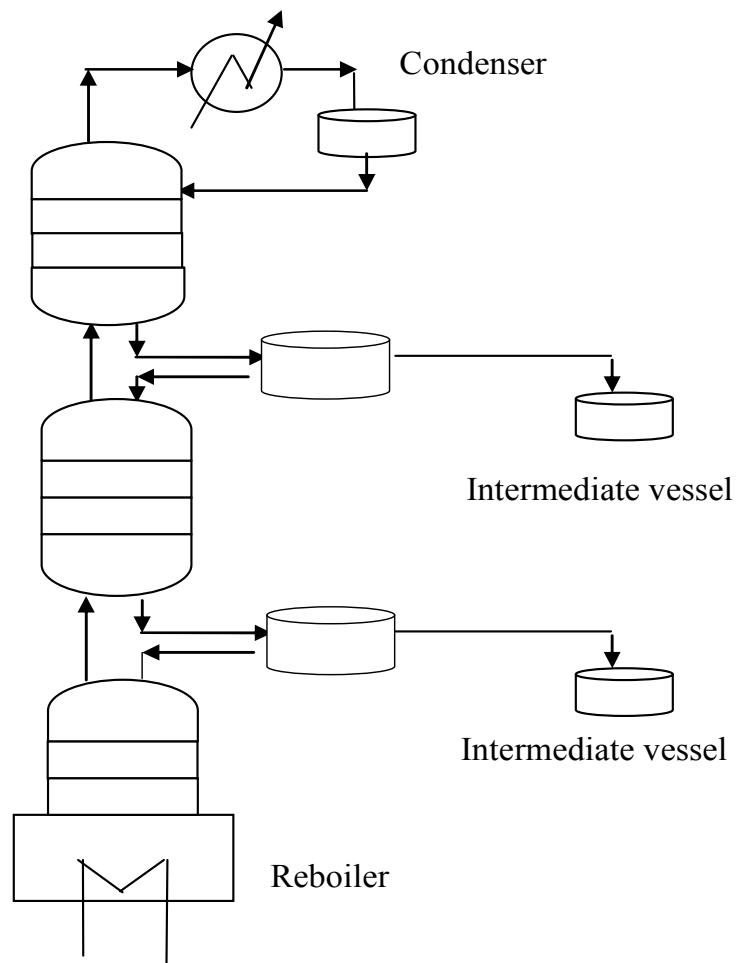


Figure 1.7 Multivessel Batch Distillation Column (*MultiVBD*)

### 1.3 Batch Distillation with Chemical Reaction

It has been a common practice to carry out the reaction and separation in the industrial processes sequentially in separate unit operations. With a reversible reaction system  $A+B \rightleftharpoons C+D$ , the traditional process consists of a reactor followed by a sequence of distillation columns (Figure 1.8). The mixture A and B is fed to the reactor, where the reaction takes place in the presence of a catalyst and reaches equilibrium. A distillation column is then required to separate the products C and D while the unreacted components A and B are recycled back to the reactor. In recent years, the development and application of integrated processes combining the mechanisms of reaction and separation in one single unit has attracted growing interest in the chemical and process industry, although the advantages of continuous reactive distillation has been known in the process industry since 1921 specifically with esterification reactions (Backhaus, 1921).

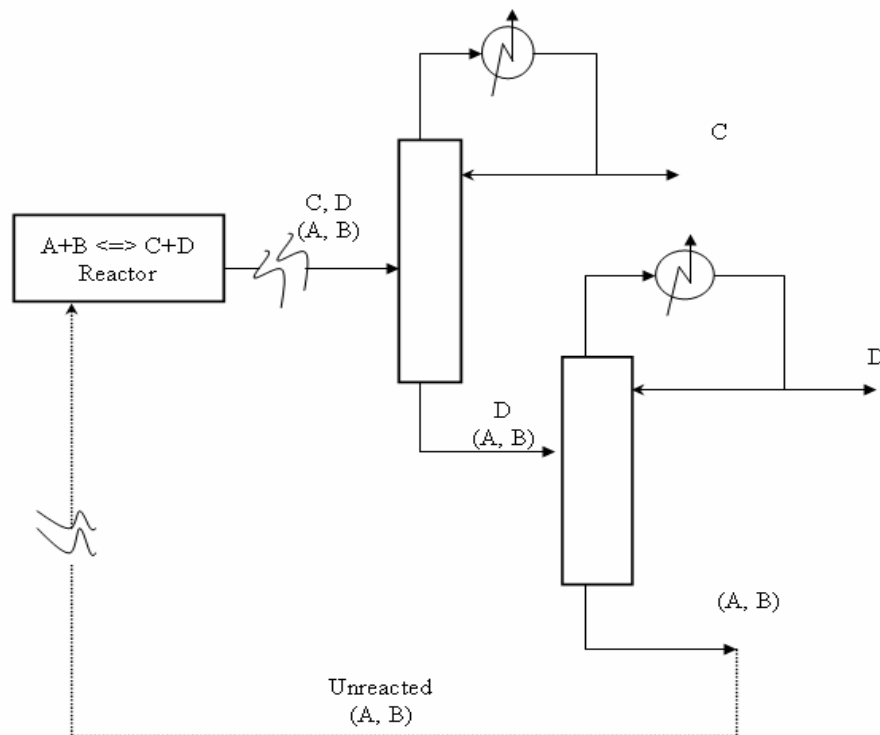


Figure 1.8 Traditional Reaction Distillation Process

The benefits of reactive distillation are clear and can be summarized as follows (Taylor and Krishna, 2000):

- Simplification of the separation system can lead to significant capital savings.
- Improved conversion of reactant, this increase in conversion gives a benefit in reduced recycle costs.
- Improved selectivity, removing one of the products from the reaction mixture or maintaining a low concentration of one of reagents can lead to reduction of the rates of side reactions and hence improved selectivity for the desired products.
- Avoidance of azeotropes.
- Reduced by-product formation.
- Heat integration benefits. If the reaction is exothermic; the heat of reaction can be used to provide the heat of vaporisation and reduce the reboiler duty.

There are so many instances where reactive distillation is of great importance in the chemical industries. One of the frequently treated processes is the esterification of acetic acid with ethanol (Suzuki *et al.*, 1970; Komatsu, 1977; Alejski *et al.*, 1989a; Simandl and Svrcek, 1991; Mujtaba and Macchietto, 1992 and 1997; Greaves, 2003; Greaves *et al.*, 2003).

In batch reactive distillation, a batch reactor can be combined with a distillation column. This combined unit operation is especially useful for those chemical reactions for which chemical equilibrium limits the conversion. By continuous separation of products from reactants while the reaction is in progress, the reaction can proceed to a much higher level of conversion that can be obtained without separation. Reboiler in conventional batch distillation column acts as reactor and reboiler at the same time (Figure 1.9). In this column the feed is charged into a large reboiler or reactor at the bottom of the rectifying column. The reaction temperature can be increased to the boiling point of the

mixture to improve the product yield of equilibrium reactions in the reactor. In fact the higher volatility of one of the reaction products decreases its concentration in the liquid phase, therefore increasing the reaction temperature and rate. The use of conventional batch distillation in which chemical reaction takes place has been noted by many researchers (Egly *et al.*, 1979, Cuille and Raklaties, 1986; Wilson, 1987, Mujtaba and Macchietto 1992, 1997 and Masoud, 2008).

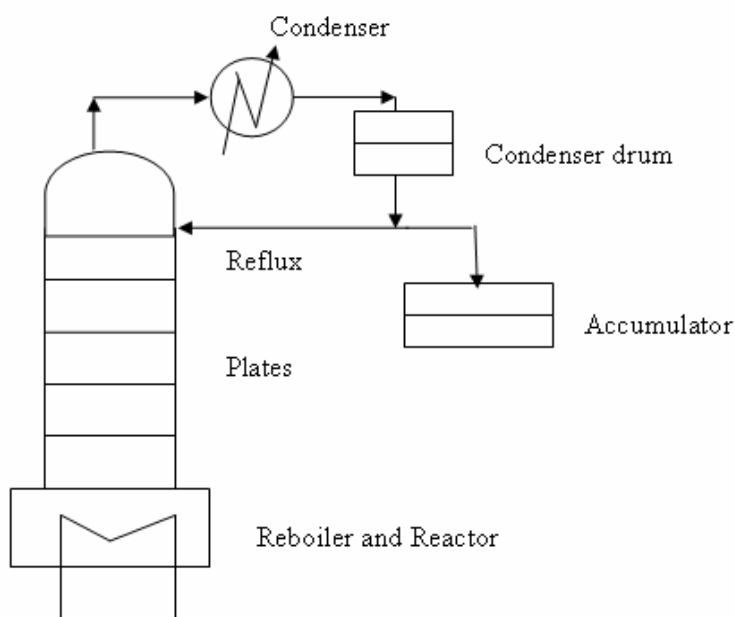


Figure 1.9 Batch Reactive Distillation Column

## 1.4 Scope of the Research

This research is focused on the optimisation of batch distillation for a number of reaction schemes, such as (a) esterification of methanol with acetic acid. (b) esterification of ethanol with acetic acid and (c) hydrolysis of methyl lactate. The main issues in batch reactive distillation are:

- Improving the conversion of limiting reactant.
- Improving the yield in a given batch time or productivity.

- Minimising the batch time.
- Maximising the profitability for a given product demand and product purity in a given column.
- Minimising the utility cost (operating cost).
- Optimising the design and operation of the system for a given product demand.

Several studies developed the optimisation framework for batch reactive distillation systems (both conventional and unconventional) in terms of maximum conversion, maximum profit with unlimited product demand and minimum utility cost in the past.

Kreul *et al.* (1998) studied the esterification reaction between methanol and acetic acid in a semi-continuous (e.g., acetic acid was fed during the operation) catalytic batch distillation to produce methyl acetate and water. Fernholz *et al.* (2000) considered minimum time and maximum productivity optimisation problems in heterogeneous semi-batch reactive distillation process with catalyzed esterification of methanol and acetic acid. Elgue *et al.* (2002) presented the dynamic simulation and optimisation of methyl acetate synthesis in batch reactive distillation. They validated a rigorous dynamic model using experimental data of Bonnaillei *et al.* (2001) who considered esterification of methanol using sulphuric acid as homogenous catalyst. The model was then used in optimisation. They considered two types of optimisation problems: the first one was minimum operating time necessary to obtain the desired reactant conversion while the second one was the combination of operating time and conversion.

For given feed (reactants) composition, Mujtaba and Macchietto (1994) considered a maximum conversion problem in conventional, inverted and middle vessel columns for general reaction scheme of type  $A+B \rightleftharpoons C+D$  with simple column model and kinetic model. Reflux ratio and or reboil ratio and or both were selected as the control parameter to be optimised for fixed batch time.



Mujtaba and Macchietto (1997); Greaves (2003) and Wajge and Reklaitis (1999) considered a maximum conversion problem, subject to a given product purity constraint with rigorous model for catalysed ethanol esterification process (ethanol + acetic acid  $\rightleftharpoons$  ethyl acetate + water). Reflux ratio was selected as the control parameter to be optimised for fixed batch time. However, Wajge and Reklaities (1999) used VLE model different to Mujtaba and Macchietto (1997).

Several researchers in the past have proposed the esterification of lactic acid (impure) with alcohol to obtain lactate ester which is then separated in batch distillation. The distilled lactate ester is then hydrolysed into lactic acid with lower concentration (Choi and Hong, 1999; Kim *et al.*, 2002; Hong *et al.*, 2000; Li *et al.*, 2005; Kumar *et al.*, 2006 a, b).

Most studies in the past were assumed that there is an unlimited market demand for the amount of products being produced (Mujtaba and Macchietto, 1994 and 1996; Greaves *et al.* 2003, Mujtaba and Greaves, 2006). In reality, unplanned and unlimited production of products are not sustainable and may lead to significant losses in the case of large inventory requirements of any excess products produced (Miladi and Mujtaba, 2004; Mahmud *et al.* 2008). Only Masoud (2008) considered the optimal design and operation policy of conventional batch reactive distillation with fixed product demand for a general reversible reaction scheme such as  $A+B \rightleftharpoons C+D$  using simple model equations (see Model Type III, Chapter 4) and reaction rate. In fact, to the author's knowledge, no studies have been reported to date on optimisation of batch reactive process involving ethanol esterification reaction system with strict product specification and fixed product demand using a rigorous process to model (see Model Type V, Chapter 4).

Clearly there is a lot of scope of further research in batch reactive distillation when the existing work (with all the three chemical reaction schemes in different types of batch reactive distillation columns) is compared with the issue highlighted at the beginning of this section.

With this backdrop, this research is focused on the following:

- Maximise the conversion of methyl acetate in conventional batch reactive distillation process involving esterification of methanol with acetic acid. A detailed and rigorous dynamic model incorporating the kinetic model of Popken *et al.* (2001) is developed and used in the optimisation framework.
- Maximise the conversion and productivity of ethyl acetate in conventional batch reactive distillation and conversion in semi-batch reactive distillation. A rigorous dynamic model of Mujtaba and Macchietto (1997) is used for conventional column. A similar model for semi-batch column is developed. Both models are then utilised in the optimisation framework.
- Maximise profitability and optimise design and operation of a batch reactive distillation column for ethanol esterification process with fixed yearly product demand and strict product specifications. The dynamic model of Mujtaba and Macchietto (1997) is used for this purpose.
- Minimise the batch time for the hydrolysis of methyl lactate using both the conventional and inverted batch reactive distillation columns. A rigorous model for conventional and inverted columns are developed and utilised in the optimisation framework.

In all case studies, rigorous dynamic models described by sets of differential and algebraic equations (see Type V, Chapter 4) are considered for simulation as well as optimisation of conventional and unconventional (inverted and semi-batch columns)

batch distillation operations with chemical reaction. The dynamic optimisation problem is converted to nonlinear programming problem by Control Vector Parameterization (CVP) technique and is solved by using efficient SQP method (Mujtaba, 2004) within gPROMS software (general PROcess Modelling System, 2004).

## **1.5 The Aim and the Objectives of This Work**

The aim of this thesis is to study the optimisation of conventional and unconventional batch distillation processes involving esterification of acetic acid with both methanol and ethanol and hydrolysis of methyl lactate. Different optimisation problems are formulated and solved.

The objectives of this research can be highlighted as follows:

- To carry out literature survey on the modelling, simulation and optimisation of batch reactive distillation (conventional and unconventional) column. Reaction kinetics and vapour-liquid equilibrium of esterification and hydrolysis systems.
- To maximise the conversion for methanol esterification process in conventional batch reactive distillation column with varying feed of composition subject to a given product purity of methyl acetate. The optimisation problem is formulated and solved with different batch time. Piecewise constant reflux ratio as a control variable (single time interval) is investigated and optimised.
- To maximise the conversion of ethanol to ethyl acetate in a conventional batch reactive distillation. Different cases with varying amount of reactants (including the cases with the reduced amount of water in the feed and keep the amount of acetic acid and ethanol fixed) are utilised to improve the conversion of ethanol to ethyl acetate. Both piecewise constant and linear reflux ratio profiles (single time interval) are considered as a control variables which are optimised. The

effect of water feed composition on the maximum conversion is also considered in this work.

- To maximise the productivity for ethanol esterification process in a conventional batch reactive distillation for a range of feed compositions. Piecewise constant reflux ratio profile (with single and multiple time intervals) is considered as a control variable.
- To develop the optimisation problem framework for ethanol esterification process in a conventional batch reactive distillation with fixed yearly product demand and strict product specifications. The effect of feed dilution on the system performance in terms of the profitability is investigated also for the representative system. A profit function is maximised while the design parameters (vapour load,  $V$ ) and operation parameters (such as reflux ratio  $R$ ; batch time,  $t_b$ ) are optimised. The control variables are treated as piecewise constant variable.
- To maximise the conversion of ethanol to ethyl acetate in semi-batch reactive distillation column. Piecewise constant reflux ratio (in single and two intervals) together with the rate of acetic acid feed are optimised. As the column is fully charged initially, flooding condition is imposed as a constraint to avoid column flooding due to additional continuous feeding of acetic acid.
- To minimise the batch time of the hydrolysis reaction of methyl lactate in both CBD and IBD. The reflux ratio for the CBD and reboil ratio for IBD are selected as control variables which are optimised (assumed piecewise constant) for a given purity and amount of lactic acid.

## **1.6 Thesis Organisation**

This thesis focuses on the optimisation of conventional and unconventional batch distillation configurations involving an esterification and hydrolysis reactions. The layout is presented below:

### Chapter 1: Introduction

Chapter one presents overview on distillation in general, brief introduction, operation and their applications of conventional and unconventional batch distillation columns. The scope of this research, aim and objectives has been stated.

### Chapter 2: Literature review

Chapter Two takes a look at the past work on continuous reactive distillation and review related to issues the modelling and optimisation of batch reactive distillation column. The knowledge gap in the research is identified which sets the scene for this research.

### Chapter 3: gPROMS Software

Chapter Three introduces overview, application and the advantages of the (gPROMS) software which has been used for modelling and optimisation of the processes in this work. The comparison in terms of the benefit of using the gPROMS rather than other modelling packages is provided at the end of this chapter.

### Chapter 4: Modelling and optimisation

Chapter Four describes the mathematical models and different types of optimisation problems considered in the literature. The Control Vector Parameterisation (CVP) for dynamic optimisation is briefly outlined. Some of the past work on optimisation of batch distillation is presented at the end of the chapter.

## Chapter 5: Optimisation of methanol esterification process

Chapter Five is devoted to study of esterification of methanol and acetic acid to produce methyl acetate using batch reactive distillation column. Different case studies are considered with different feed compositions and with an objective function to maximise the conversion of methanol to methyl acetate.

## Chapter 6: Dynamic optimisation of ethanol esterification process

In Chapter Six, two types of batch reactive distillation configurations (batch and semi-batch) are considered for ethanol esterification reaction. Different optimisation problems are investigated such as maximum conversion problem using both columns. Piecewise reflux ratio strategy with single and multi time intervals was considered. Maximum profit with strict product specifications and fixed product demand are considered using conventional batch reactive distillation column only. The effect of water present in the feed on the maximum productivity is considered also in this work. At the end of this chapter a comparison between batch and semi-batch distillation columns in terms of maximum conversion problem is also presented.

## Chapter 7: Optimisation of methyl lactate hydrolysis process

Chapter Seven addresses the optimal operation of regular and inverted batch distillation columns involving the hydrolysis of methyl lactate to produce lactic acid at high purity. Operating time used as the measure to compare the performances of such columns. A regular and an inverted column will be compared in terms of minimum operating time at the end of this chapter.

## Chapter 8: Conclusions and future work.

Chapter Eight presented the final conclusions reached during the course of this work and suggestions for future work.

## Chapter Two

### Literature Review

#### 2.1 Introduction

This chapter reviews in brief the past work on continuous reactive distillation and conventional, inverted and semi-batch reactive distillation process involving esterification of methanol and ethanol using acetic acid to produce methyl acetate and ethyl acetate and hydrolysis of methyl lactate to produce lactic acid. The aspects of modelling, simulation and optimisation are considered briefly here. Further literature reviews on these are presented in later chapters for convenience.

#### 2.2 Continuous Reactive Distillation

Reactive distillation (RD) has been successfully used and investigated in the past for several reactions such as etherification, esterification, hydrogenation, hydrodesulphurisation and polymerization. The earliest patents of methyl acetate process registered to Backhaus in the 1920s. The reactive distillation process appeared first in 1932 for the production of Ethyl Acetate and became a new focus in 1980's, since Eastman Chemical Company owned a commercial reactive distillation process for the production of methyl acetate.

Various other reviews have been published on reactive distillation (Doherty and Buzad, 1992; Podrebarac *et al.*, 1997; Taylor and Krishna, 2000). Barbosa and Doherty (1988) listed a number of reaction schemes used mainly in continuous reactive distillation. Doherty and Buzad (1992) presented different numerical methods for solving reactive distillation problems (e.g. MTBE process, Methyl Acetate process, Nylon 6,6 process).

Reactive distillation for the synthesis of methyl acetate has been investigated by many researchers in the past (Agreda *et al.*, 1979; Agreda *et al.*, 1990; Rönnback *et al.*, 1997;

Song *et al.*, 1998; Bessling *et al.*, 1998; Krishna, 2002; Popken *et al.*, 2000; Popken *et al.*, 2001; Hoyme and Holcomb 2003; Huss *et al.*, 2003; Sharma and Mahajani, 2003; Ehteshami *et al.*, 2006; Liu *et al.*, 2006 and Lin *et al.*, 2008).

Most of the publications in the literature deal with the modelling and numerical integration of the resulting dynamic equations systems with some presenting experimental results involving esterification of ethanol with acetic acid to produce ethyl acetate (Suzuki *et al.*, 1970; Suzuki *et al.*, 1971; Komatsu, 1977; Izarazz *et al.*, 1980; Holland, 1981; Sawistowski and Pilavakis, 1988; Chang and Seader, 1988; Bogacki *et al.*, 1989; Simandl and Svrcek, 1991; Aljski and Duprat, 1996; Bock *et al.*, 1997; Lee and Dudukovic, 1998; Vora and Daoutidis, 2001; Calvar *et al.*, 2007 and Lai *et al.*, 2008). The optimal design and operation of continuous reactive distillation has been also discussed by some authors (Tang *et al.*, 2003; Chien *et al.*, 2005).

The esterification of lactic acid (impure) with methanol is carried out to obtain lactate ester. The distilled lactate ester is then hydrolyzed into pure lactic acid (with low concentration) using continuous reactive distillation process. This is studied in the past by some researchers (Li *et al.*, 2005; Kumar *et al.*, 2006 b and Rahman *et al.*, 2008).

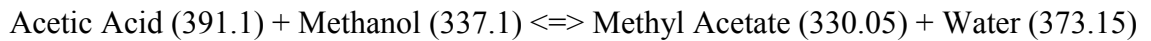
### **2.3 Batch Reactive Distillation in Conventional Column**

The use of conventional batch distillation in which chemical reaction takes place is common practice in the chemical industries (Egly *et al.*, 1979, Cuille and Raklaties, 1986; Wilson, 1987; Logsdon *et al.*, 1990; Albet *et al.*, 1991; Mujtaba and Macchietto, 1992; Mujtaba and Macchietto, 1997 and Mujtaba, 2004).



### 2.3.1 Methanol Esterification Process

The reversible reaction schemes together with the boiling temperatures (K) of the components for esterification of methanol and acetic acid to produce methyl acetate and water are:



The reaction products are methyl acetate and water, with methyl acetate being the main product. Methyl acetate has the lowest boiling temperature in the mixture and therefore has the highest volatility. Controlled removal of methyl acetate by distillation will improve the conversion of the reactants by shifting the chemical equilibrium further to the right. This will also increase the yield proportionately.

#### 2.3.1.1 Modelling

Corrigan and Ferries (1969) studied the methanol esterification with acetic acid in an experimental batch distillation column with emphasis on the design and construction of the equipment.

Wajge and Reklaitis (1999) demonstrated rigorous model within the batch reactive distillation optimisation (RBD OPT) to simulate batch reactive distillation for the production of methyl acetate by esterification of methanol and acetic acid using total and different reflux ratio values. For column operation with 10 stages at 18 hrs the composition of methyl acetate in the accumulated distillate was found 0.75 molefraction.

Elgue *et al.* (2002) developed a rigorous model for methanol esterification process. The experiments performed by Bonnaillet *et al.*, (2001) were used to validate their dynamic model. The model was then used for optimisation of batch reactive distillation column.

### 2.3.1.2 Optimisation

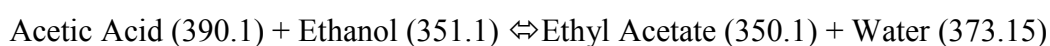
Elgue *et al.* (2002) also presented the dynamic optimisation of methyl acetate synthesis. They considered two types of optimisation problems, the first one is minimising operating time necessary to obtain the desired reactant conversion while the second one is minimising an objective function which is a combination of operating time and conversion. They show that a significant total reflux operation time (more than 15 min) is required for high conversion of reactant in the first type. The second type of the optimisation problem shows that a total reflux time of around 23 min is required if the conversion is privileged and only further operating time would allow reaching higher conversion.

It can be seen that the research work concerning the use of a batch reactive distillation column to produce methyl acetate is very limited compared to that by using continuous reactive distillation. This work will focus into the optimisation of batch reactive distillation process involving methanol esterification process in terms of maximum conversion of limiting reactant to product.

### 2.3.2 Ethanol Esterification Process

Organic esters are important fine chemicals used widely in the manufacturing of flavors, pharmaceuticals, plasticizers, and polymerization monomers. They are also used as emulsifiers in the food and cosmetic industries (Liu *et al.*, 2006). An environmental use of ethyl acetate is in the reduction of pollution associated with wood pulping, whilst improving the economic viability. It is also used as an extraction solvent in the production of pharmaceuticals (Kenig *et al.*, 2001).

Ethyl acetate is produced by the esterification of ethanol with acetic acid. The reaction together with the boiling points (K) of the components is shown below:



Ethyl acetate is the lightest in the mixture, therefore has the highest volatility. Controlled removal of ethyl acetate by distillation will improve the conversion of the reactants by shifting the chemical equilibrium further to the right.

### 2.3.2.1 Modelling

Basualdo and Ruiz (1995) developed the software called READYS (Reactive Distillation Dynamic Simulator) and used it to predict batch operations behaviour of batch reactive distillation. A rigorous model was used for ethanol esterification process. Both start-up and production periods were considered and the simulated results for ethyl acetate synthesis were analyzed.

Mujtaba and Macchietto (1997) developed a rigorous model for ethanol esterification process to use the model for optimisation. Balasubramhanya and Doyle (2000) considered a reduced model for batch reactive distillation column based on the travelling wave phenomena for ethyl acetate process and used this model successfully in a nonlinear MPC scheme.

The esterification reaction between ethanol and acetic acid over an acidic ion exchange resin (Amberlyst 15) was carried out in packed bed reactive distillation in both batch and continuous modes by Kirbaslar *et al.* (2001). Kinetic data and a model covering a wide range of operating conditions were presented with the parameters. They showed that the combination of an esterification reaction with distillation in a reactive distillation column either in batch or continuous mode leads to a large increase in the purity of ethyl acetate in the distillate.

Patel *et al.* (2007) outlines a detailed mathematical modelling and simulation of batch reactive distillation column for ethyl acetate synthesis. They developed a MATLAB program to perform the dynamic simulation which was used to derive the optimum operating profiles. They found for given product purity (50 % of Ethyl Acetate)

optimum operation reflux ratio (internal) was found to be around 0.875 with a batch time of 8.3 hours.

Bahar and Özgen (2008) designed an Artificial Neural Network (ANN) estimator for the esterification reaction of ethanol and acetic acid in a batch reactive distillation. They found that, it is possible to predict the distillate composition values of the column from available four temperature measurements using designed ANN estimator.

Recently, Prakash and Jana (2009) presented a systematic study on both batch and continuous reactive distillation process for the homogeneous catalysed ethanol esterification reaction process to produce ethyl acetate. The equilibrium stage model was incorporated in both columns. The batch column was simulated under total reflux during the start-up period and the open-loop process dynamics was examined during the production period under partial reflux condition.

Also, Jana and Adari (2009) proposed the advanced nonlinear adoptive control law which consists of the generic model controller (GMC) and an adaptive state estimator (ASE) for the ethyl acetate batch reactive column. They showed that, the proposed control structure provides high-quality performance mainly due to the exponential error convergence capability of the ASE estimator.

Literature related VLE and kinetic models for ethanol esterification system are described in Chapter 6.

#### *2.3.2.2 Optimisation*

Mujtaba and Macchietto (1997) presented a computationally efficient framework for dynamic optimisation of batch reactive distillation. They considered a maximum conversion problem, subject to given product purity constraints. Reflux ratio was selected as the control parameters to be optimised for fixed batch time for catalysed

esterification of acetic acid with ethanol, and parametric solutions of the problem were obtained. In their work polynomial curve fitting techniques were proposed and applied to the results of the dynamic optimisation problem (optimal product yield, optimal reflux and optimal heat load profiles). These polynomials were used to formulate a nonlinear algebraic maximum profit problem.

Wajge and Reklaitis (1999) developed an optimisation framework (RBD OPT) allowing campaign optimisation of batch reactive distillation processes with minimal input from the user. The esterification process of acetic acid with ethanol was modelled based on a rigorous model. They solved maximum conversion problem subject to product purity constraint. Reflux level (constant for entire product cut) and its duration were the two control variables in the optimisation problem. They reported lower product purity and conversion compared to those reported by Mujtaba and Macchietto (1997). They explained that the optimal results for this chemical system are relatively insensitive to the operation policy. The small conversion obtained despite the use of a reactive distillation column suggests the necessity of a suitable policy for further reprocessing of the off-cut. However, use of non-catalysed reaction kinetics could be factor of obtaining lower conversion and thus lower purity.

A nonlinear PID –type top product composition controller for batch reactive distillation involving ethanol esterification with acetic acid process was developed by Monroy-Loperena and Alvarez-Ramirez (2000). Reflux ratio was selected as the control variable. They show that their scheme produces the same reflux ratio profile as the optimisation-based approach followed by Mujtaba and Macchietto (1997).

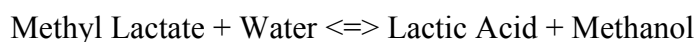
Giessler *et al.* (2001) solved the optimal operation problems of a batch reactive distillation process for different types of models and also for different objective functions. A detailed model, including a dynamic energy balance was developed for the

process producing ethyl acetate. The reflux ratio and heat duty were selected as the control variables which were optimised. They showed clearly that the column stages and initial holdup have a significant effect on the production performance. Their results showed that when a conventional batch reactive distillation column was used, it is impossible to obtain the same results which were reported by Mujtaba and Macchietto (1992, 1997), because it is difficult to cross the distillation boundaries caused by the azeotropes. Note, Mujtaba and Macchietto (1992, 1997) did not account for azeotropes in their study.

Mujtaba *et al.* (2003) and Mujtaba and Greaves (2006) developed a quick and efficient neural network (NN) based Business Decision Making tool. They demonstrated this tool in batch reactive distillation to produce ethyl acetate as an application where product specifications and market demand prices may change. Maximum profit problem was considered based on maximum conversion results achieved using NN based techniques. They showed that the computation time was significantly reduced compared to those obtained by Mujtaba and Macchietto (1997).

### **2.3.3 Hydrolysis of Methyl Lactate**

The hydrolysis of methyl lactate catalyzed by Amberlyst 15 (2.5 %w/w) can be expressed as follows:



The boiling temperatures of methyl lactate, water, lactic acid and methanol are: 417.15, 373.15, 490.47 and 337.15 K, respectively.

Lactic acid is the highest boiling component and methanol is the lightest boiling component in the mixture. Removal of methanol in a conventional column will shift the reaction forward. Finally lactic acid will be collected as bottom product. Removal of lactic acid from the bottom in a inverted column will also shift the reaction forward.

### 2.3.3.1 Modelling

Choi *et al* (1996) considered esterification of lactic acid followed by hydrolysis in batch system. Acidic resins were used as catalyst and the activity of this catalyst was compared with that of sulphuric acid as catalyst. They concluded that the activity of resins was lower than sulphuric acid but it was easily removed and reused.

Choi and Hong (1999) investigated an apparatus (two reactors and two batch distillation columns) to carry out the esterification of impure lactic acid and hydrolysis reactions and achieved pure lactic acid but at low concentration (17 mole %). They showed that these processes were complex for recovery of pure lactic acid and capital cost of equipment was high. To overcome these disadvantages the batch distillation with simultaneous reaction was recommended.

Seo *et al.* (1999) investigated two reactions, esterification followed by hydrolysis for recovery of lactic acid by batch reactive distillation using cation exchange resin as a catalyst. The effects of some operation variables such as catalyst loading, reactant mole ratio, feed concentration, type of alcohols and partial condenser temperature on the yield were studied. The reaction products of the esterification (methyl lactate and water) were distilled and fed to the hydrolysis part to recover pure lactic acid. They showed the yield of lactic acid increased as catalyst loading in the esterification part increased and reactant mole ratio and feed lactic acid concentration decreased. Methanol as a reactant gave higher yield than any other alcohols.

Kim *et al.* (2000) considered a batch reactive distillation with esterification and hydrolysis for the recovery of lactic acid using experiments and simple modelling to obtain optimum design and effective operation.

Kim *et al.* (2002) analyzed the dynamic behaviour of batch reactive distillation of lactic acid in terms of instantaneous rate of esterification reaction. They observed that the rate

increased by controlling of boil up rate and residence time during the operation by changing both the methanol recycle stream and feeding mode. They also compared semi-batch operation with the batch mode. It was found that continuous feeding of methanol enhanced the recovery of lactic acid.

Kumar *et al.* (2006 b) explored and investigated a novel reactive distillation strategy involving experimental esterification and hydrolysis reaction for recovery of pure lactic acid. They studied the effect of operating parameters such as feed concentration, mole ratio; catalyst loaded, and boil up-rate on the recovery of lactic acid. They indicated from their results that lactic acid can be recovered by using batch reactive distillation from its aqueous solution.

#### *2.3.3.2 Optimisation*

As seen most of the work has been focused on the experiments to recover lactic acid. No work has been done in terms of optimisation of the process for production of lactic acid.

#### **2.3.4 Other Reaction Schemes in Conventional Column**

Cuille and Reklaitis (1986) considered the simulation of batch reactive distillation with reaction occurring on the plates, in the condenser and in the reboiler. They presented a numerical solution technique for esterification of 1-propanol with acetic acid as an example. They found it was not suitable for use in batch distillation. Since 1-propanol (one of reactants) was the more volatile component in the system and the removal of species by distillation causes the removal of reactant from the column thus decreases the conversion.

Wilson (1987) discussed the optimal design of batch distillation processes using a simplified column model involving chemical reaction (parallel reaction) and using repetitive simulation. For a commercially used complex parallel reaction scheme and



using a simple economic model, he showed the benefit of integrating reaction and distillation. He generated a number of plots of process efficiency (in terms of product cost contribution per unit product) for a range of alternative process and design variable choices and suggested an optimal design and operation of batch reactive distillation.

Leversund, *et al.* (1994) considered the maximising profit for batch reactive distillation subject to constraints in the reboiler temperature and the accumulator composition. Their study was a condensation polymerisation between a dibasic acid and two glycols. The effect of design variables (for example number of stages) on the profitability was not considered in their paper.

Li *et al.* (1997) used a more detailed dynamic model for batch distillation with reaction in the reboiler. A reversible chemical reaction of the type:  $A + B \rightleftharpoons C + D$  was considered. For the resulting differential algebraic equations they applied the collocation on finite elements and Successive Quadratic Programming (SQP) method to solve the maximum profit problem. They assumed constant molar tray holdup, constant reflux drum capacity, and constant tray efficiencies in their model.

Delgado *et al.* (2007) investigated the kinetics for the esterification of lactic acid with ethanol and the hydrolysis of the corresponding ester, ethyl lactate, catalysed by Amberlyst 15. The influence of different operating parameters such as stirrer speed, catalyst particle size, initial reactant molar ratio, reaction temperature and catalyst loading, has been examined.

Kumar and Mahajani (2007) performed esterification of lactic acid with n-butanol to produce n-butyl lactate in the presence of acid resin as catalyst. They estimated the kinetic parameters using a pseudo-homogeneous model. The results obtained in the experiments through batch and continuous reactive distillation columns were compared with the simulation results. The effect of operating parameters (e.g. feed mole ratio,

catalyst loading, and boilup rate) on the conversion of lactic acid in batch reactive distillation was studied.

Arellano Garcia *et al.* (2008) proposed a new operation mode for batch reactive distillation in middle-vessel column for a generic typical reversible reaction of the form  $B+C \leftrightarrow A+D$  representing A and D the components with the lowest and highest boiling point, respectively. A detailed dynamic model of an industrial process was developed and validated. The optimisation problem in terms of minimisation the total batch time was considered to generate optimal policies for the reflux ratio and the feed flow rate into the reboiler. They showed the benefit of using this configuration rather than a conventional batch distillation process in terms of total batch time and purity restrictions.

Masoud (2008) studied the effect of reaction rate constant, product demand and reflux ratio policy on the design, operating cost and profitability for two different reactive mixtures (in terms of relative volatiles) with reversible reaction scheme. A reversible chemical reaction of the type:  $A + B \rightleftharpoons C + D$  was used in his work with A being the highest boiling and C being the lowest boiling component in the mixture. He showed that the product demand for difficult separation or increased product demand for easy separation can be achieved by enhancing the rate of reaction.

## **2.4 Batch Reactive Distillation in an Inverted Column**

The inverted batch distillation (with chemical reaction) is suitable when the reaction products have higher boiling temperatures (Mujtaba and Macchietto, 1994). While the area of batch reactive distillation by conventional columns has received much attention the research in inverted columns in these aspects is very limited.

## **2.4.1 Other Reaction Schemes in Inverted Batch Distillation**

### *2.4.1.1 Modelling*

Mujtaba and Macchietto (1994) considered the system in which the chemical reaction involves two reactants (A and B) producing two products C (main product) and D. The reversible reaction is modelled by simple model equations for different batch distillation (Conventional, Inverted and Middle Vessel) columns. The reaction is modelled by simple rate equations.

### *2.4.1.2 Optimisation*

Mujtaba and Macchietto (1994) presented a comparative study in terms of maximum conversion to obtain the main product (highest boiling component in the mixture) at specified purity using different batch distillation configurations. Simple models were used for each configuration. Reflux and/or reboil ratio is selected as control variables which were optimised. They found that for reactions involving a product which has the lowest boiling point in the mixture conventional column performed better than an inverted column.

To the best of our knowledge, no work has been carried out concerning modelling and optimisation of esterification of methanol and ethanol with acetic acid or hydrolysis of methyl lactate in the past using batch reactive distillation in an inverted column. Therefore this work will cover the hydrolysis of methyl lactate process as a suitable system for inverted column.

## **2.5 Semi-batch Reactive Distillation**

### **2.5.1 Methanol Esterification Process**

As mentioned in chapter one, the operation of semi-batch columns is very similar to conventional batch distillation except that a part of the feed is introduced to the column in a continuous or semi-continuous mode.

### 2.5.1.1 Modelling

Kreul *et al.* (1998) studied the esterification reaction between methanol and acetic acid in a semi-continuous (e.g, acetic acid was fed during the operation) catalytic batch distillation to produce methyl acetate and water. Dynamic material and energy balances and thermodynamic relationships were used. The mass transfer relationship, column hydraulics and reaction kinetics parameters were experimentally derived. They showed by a combination of detailed modelling and experimental determination of the model parameters that a close matches between simulation and experimental results was possible.

Schneider *et al.* (2001) developed a rigorous dynamic rate-based approach including heat and mass transfer, coupled with chemical reaction for the simulation of the semi-batch packed process for production of methyl acetate and accounted diffusional interactions via the Maxwell-Stefan equations and overall reaction kinetics for determination of total conversion. Several experiments have been carried out in pilot plant column and compared with the simulation results.

### 2.5.1.2 Optimisation

Li *et al.* (1998) optimised an industrial semi-batch distillation process with a chemical reaction (transesterification of two esters and two alcohols) in the reboiler to minimize the batch operation time. The optimal reflux ratio and the feed rate policies of the process were developed with an efficient optimization approach. They showed that up to 30% of the operation time can be saved with the optimal policies developed in comparison to the conventional operation.

Fernholz *et al.* (2000) considered the optimisation of heterogeneous semi-batch reactive distillation process for catalyzed esterification of methanol and acetic acid. Minimum time and maximum productivity problems were set up, including constraints on the

product purity as well as on the conversions of the raw materials and on the manipulated variables. Reflux ratio, heat duty, feed rate, and the initial amount of methanol were optimized. They found that the productivity based optimal problem formulation leads to higher conversion rates for identical batch times. They also concluded from the results that the process is limited by reaction kinetics rather than by the separation.

### **2.5.2. Ethanol Esterification Process**

No work so far has been reported on the use of semi-batch distillation process for ethanol esterification system. In this work, the performance of semi-batch reactive distillation is evaluated in terms of maximum conversion of ethanol to ethyl acetate.

### **2.5.3 Hydrolysis of Methyl Lactate Process**

No work has been carried out using semi-batch reactive distillation column for hydrolysis of methyl lactate to produce lactic acid.

### **2.5.4 Other Reactions Schemes in Semi-batch Reactive Distillation**

Xu and Duduković (1999) developed a rigorous model (considered two phases) for the photo reactive distillation column operated in a semi-batch mode to simulate the chlorination of toluene. Simulation and experimental results were compared and found to be close in the trend.

Adams and Seider (2008) demonstrated the feasibility of using semi-continuous process for the production of ethyl lactate from ethanol and lactic acid. Rigorous simulation and cost estimation was considered and they showed that this technique is more effective compared with batch and continuous processes.

More recently, Suman *et al.* (2009) investigated esterification of ethylene glycol with acetic acid in the presence of Amberlyst 36. They chose 1, 2-dichloro ethane (EDC), as an entrainer. They studied the potential of entrainer in reactive distillation involving

high boiling reactants to decrease the reactive stage temperature and for separation of one of the products to enhance the conversion

## 2.6 Conclusions

This chapter reviews the past work using continuous and batch (conventional, inverted and semi-batch) reactive distillation processes. The conclusions of this chapter can be summarised as follows:

- The research work concerning the use of batch reactive distillation column to produce methyl acetate is very limited compared with that by using continuous reactive distillation. Corrigan and Ferries (1969), Wajge and Reklaitis (1999) and Elgue *et al.* (2002) considered the aspects of modelling and simulation of synthesis of methyl acetate from methanol esterification process. While the optimisation aspect in terms of minimum time was considered by Elgue *et al.* (2002). No work has been considered in terms of maximum conversion for this system.
- The aspects of modelling and simulation of ethanol esterification process in conventional batch reactive distillation process was considered by many researchers (Basualdo and Ruiz, 1995; Balasubramhanya and Doyle, 2000; Kirbaslar *et al.* 2001; Monroy-Loperena and Alvarez-Ramirez, 2000; Patel *et al.* 2007; Bahar and Özgen, 2008; Prakash and Jana, 2009). The optimisation problems were also addressed by many researchers. Maximising conversion was investigated by (Mujtaba and Macchietto, 1997 and Wajge and Reklaitis, 1999). Maximising Profit was considered by Giessler *et al.*, (2001); Mujtaba *et al.*, (2003) and Mujtaba and Greaves, (2006) for this system. On the other hand, maximum productivity, optimisation of semi-batch reactive distillation column and optimal design and operation of a batch reactive distillation column for

ethanol esterification process with fixed yearly product demand and strict product specifications have not yet been explored.

- Most of the work has been focused on experiments with batch reactive processes to recover lactic acid (low concentration) by hydrolysis of methyl lactate (Choi and Hong, 1999; Kim *et al.*, 2000; Kim *et al.*, 2002 and Li *et al.*, 2005; Kumar *et al.*, 2006 Kumar *et al.*, 2006 a, b and Rahman *et al.*, 2008).

While the area of batch distillation, design and operation of conventional column with chemical reaction has received much attention (Mujtaba, 2004), the research in inverted column in these respects is very limited. To date, to the best of our knowledge, no work has reported on the optimal operation of inverted batch distillation except that presented by Mujtaba and Macchietto (1994) for general reaction scheme.

This work will highlight the following contributions (Table 2.1) for optimisation of Methanol, Ethanol Esterification processes and hydrolysis of Methyl Lactate in terms of different optimisation problems.

Table 2.1 Contributions of This Work

| Column       | System         | Modelling           | Optimisation  |
|--------------|----------------|---------------------|---|
| Conventional | Methanol       | Yes ( VLE+ Kinetic) | Max. Conversion   |
|              |                | No                  | Max. Conversion<br>Max. Productivity<br>Max. Profit (Fixed Demand)<br>Sensitivity of Feed Composition |
|              | Ethanol        | Yes (VLE + Kinetic) | Minimum Time  |
|              |                |                     | Methyl Lactate  |
| Inverted     | Methyl Lactate | Yes (VLE + Kinetic) | Minimum Time  |
| Semi-batch   | Ethanol        | No                  | Max. Conversion   |

# Chapter Three

## gPROMS Software

### 3.1 Introductions

This chapter provides an overview of the main features and some applications of gPROMS. The model and dynamic optimisation of batch reactive distillation process for ethanol esterification system (as an example) implemented within gPROMS are shown as a text file. The ideal physical properties foreign object (IPPFO) package which is linked with the gPROMS in the context of thesis is described briefly. Finally the comparison between gPROMS and other software packages is discussed.

### 3.2 The Features of gPROMS

Many different types of software packages are available in the market. Modern tools are numerically powerful, highly interactive and allow sophisticated types of graphical and numerical output. They also allow optimisation and parameter estimation. Here the conventional and unconventional batch distillation configuration processes considered in the course of this thesis are modelled and optimised using the software package “general PROcess Modelling System” (gPROMS) developed by Process Systems Enterprise Ltd., London.

gPROMS (**g**eneral **P**rocess **M**odelling **S**ystem) is a powerful general purpose modelling and optimisation environment, used to enhance the design and operation of continuous and dynamic processes.

The gPROMS has been used for a wide variety of applications in petrochemicals, food, pharmaceuticals, specialty chemicals and automation. Furthermore, it has the potential to be used for any process that can be described by a set of mathematical equations. gPROMS can be used for (PSE, 2004):



- Steady state simulation.
- Dynamic simulation.
- Steady-state optimisation.
- Dynamic optimisation.
- Steady-state parameter estimation.
- Dynamic parameter estimation.

gPROMS has a number of advanced features including the ability to estimate an unlimited number of parameters and to use data from multiple steady-state and dynamic experiments. It also gives the user complete flexibility in that they can specify different variance models for different variables in different experiments. Moreover, it has a built-in interface to MS Excel that allows the user to automatically test the statistical significance of results, generate plots overlaying model data and experimental data, plot confidence ellipsoids.

gPROMS has many advantages that make it an attractive tool for solving dynamic and steady state modelling problems. Some of its numerous advantages include; clear and concise language, unparalleled modelling power and the ability to model process discontinuities and operating conditions among many others (gPROMS Introductory User Guide, 2004).

### **3.3 The Advantages of gPROMS**

The key benefits of using gPROMS are:

- gPROMS is specifically designed for the exacting requirements of the process industries, with a unique and powerful set of modelling and solution facilities.
- gPROMS has powerful custom modelling capabilities. This allows a user to develop a competitive advantage by representing their own processes-rather than using off the shelf block-box models-to a high degree of accuracy.

- gPROMS open model approach enable a user to capture valuable corporate information in usable, maintainable and extendable form.

The key benefits of using gPROMS rather than other modeling systems are (gPROMS guide user, 2004):

- It is specifically designed for the exacting requirements of the process industries, with a unique and powerful set of modeling and solution facilities.
- It can be used specific processes-rather than using black-box models, this is because it has powerful modeling capabilities.
- It adopts open model approach, that means it allows to capture valuable information in usable, maintainable and extendable form

### **3.4 Some Typical Application of gPROMS**

Some typical application areas using gPROMS are those that involve complex physical and chemical phenomena, such as reaction engineering, crystallisation and complex separation processes. It can be summarised as follows (Masoud, 2008):

- Optimisation of reflux policy, reboiler duty and off-cut recycle
- Optimal design and operation of multiphase batch reactors
- Optimal grade-switching policies for continuous polymerisation reactors.
- Optimal design and operation of multiple batch reactor

There are a number of entries corresponding to a group of gPROMS entities, some of these entries are Variable Types, Stream Types, Tasks, Processes, Optimisation, etc. in this work only four of these were used. These are; Variable Types (to specify the types and ranges of the variables used in the model), Models, where the process model (set of differential and algebraic equations) is written in the model file in gPROMS which consists of a minimum of three sections: Parameters, Variables and Equations. Processes (contain specification for simulating the batch column).

Due to the advantages mentioned above, and many others not outlined here for lack of space, gPROMS was chosen as the software of choice for the modelling and dynamic optimisation of the batch distillation configurations which were carried out in the course of this thesis.

### **3.5 gPROMS Entities**

Here, the gPROMS model builder is selected due to:

- Time saving for developing the model because the solution algorithm needs to be specified rather than to be written.
- Different simulation and optimisation activity can be run using the same model.
- gPROMS has an intellectual editors for easy creation and repairs.

#### **3.5.1 Model Entity**

The general information to be specified in any MODEL is described in the following:

- A set of constant parameters that clarify the system. They are declared in the PARAMETER section.
- A set of variables that describe the time-dependent behaviour of the system. They are declared in the VARIABLE section.
- A set of equations involving the stated variables and parameters. They are declared in the EQUATION section.

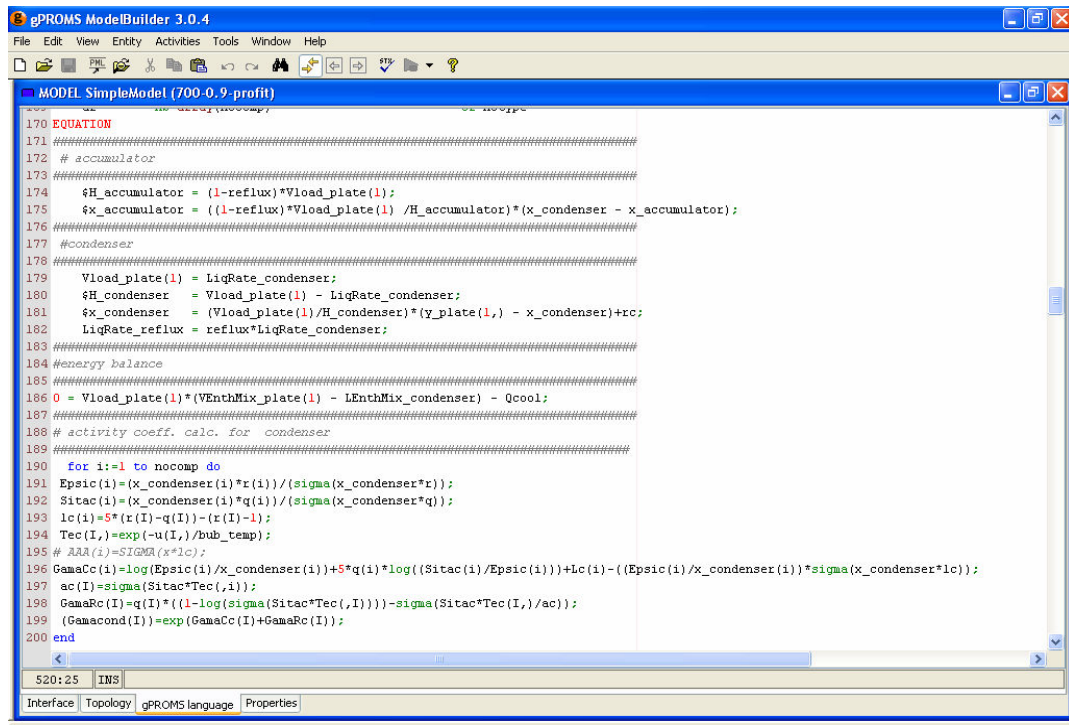
Model equations for batch reactive process which are mentioned in Chapter 4 are modelled within gPROMS model builder and shown in Figure 3.1

#### **3.5.2 Process Entity**

The Processes (contains specification for simulating the batch column). It is separated into sections that contain information necessary to define a dynamic simulation activity.

The main process sections used to carry out simulation studies in this work are UNIT, SET, ASSIGN, INTIAL, SOLUTIONPARAMETERS and SCHEDULE.

The Screenshot of entity PROCESS for dynamic simulation involving the batch reactive process is shown in Figure 3.2



```
170 EQUATION
171 #####
172 # accumulator
173 #####
174 $H_accumulator = (1-reflux)*Vload_plate(1);
175 $x_accumulator = ((1-reflux)*Vload_plate(1) /H_accumulator)*(x_condenser - x_accumulator);
176 #####
177 #condenser
178 #####
179 Vload_plate(1) = LiqRate_condenser;
180 $H_condenser = Vload_plate(1) - LiqRate_condenser;
181 $x_condenser = (Vload_plate(1)/H_condenser)*(y_plate(1,) - x_condenser)+rc;
182 LiqRate_reflux = reflux*LiqRate_condenser;
183 #####
184 #energy balance
185 #####
186 0 = Vload_plate(1)*(VenthMix_plate(1) - LenthMix_condenser) - Qcool;
187 #####
188 # activity coeff. calc. for condenser
189 #####
190 for i:=1 to nocomp do
191 Epsic(i)=(x_condenser(i)*r(i))/(sigma(x_condenser*r));
192 Sitac(i)=(x_condenser(i)*q(i))/(sigma(x_condenser*q));
193 lc(i)=5*(r(I)-q(I))-(r(I)-1);
194 Tec(I)=exp(-u(I)/bub_temp);
195 # AAA(i)=SIGMA(x*lc);
196 GamaCc(i)=log(Epsic(i)/x_condenser(i))+5*q(i)*log((Sitac(i)/Epsic(i))+Lc(i)-((Epsic(i)/x_condenser(i))*sigma(x_condenser*lc)));
197 ac(I)=sigma(Sitac*Tec(I));
198 GamaRc(I)=q(I)*((1-log(sigma(Sitac*Tec(I))))-sigma(Sitac*Tec(I),/ac));
199 (GamaRcond(I))=exp(GamaCc(I)+GamaRc(I));
200 end
```

Figure 3.1 Snapshot of the Model Entity for The Batch Process gPROMS Mode

```

1 UNIT
2   TerBD AS simplemodel
3 SET
4
5   WITHIN TerBD DO
6
7     NoComp      := 4;
8     NoPlate     := 8;
9     R_gas      := 8.314; # J/mol-kelvin
10    Tboiling :=[417.95,373.15,490.15,337.799];#K
11    Tcritical:=[584.0,    647.14,627.0,512.64];#K
12    dHvnormal :=[38177,    40651,54670,    35290    ];#KJ/KMOL
13    kf0:=1.16*10^6;# mol/g.min
14    kb0:=1.65*10^5;
15    Eaf:= 48.52*1000;#J/MOL
16    Ebf:= 50.91*1000;
17    Ptotal      := 1.0;
18    AA:=[0.00000E+00,    -1.03219E+02,0.0, 0.0    ];
19    BB:=[-3.10602E+01,    3.44899E+01,3.40129E+00,    2.11541E+01    ];
20    CC:=[3.56254E-01,    -7.12930E-03,2.17927E-01,    3.54768E-02    ];
21    DD:=[-2.53352E-04,    1.57849E-05,-1.24677E-04,    8.62747E-06    ];
22    EE:=[1.06432E-07,    -8.91847E-09,4.35934E-08,    -7.13272E-09    ];
23    FF:=[-1.84327E-11,    1.87080E-12,-6.92161E-12,    0.00000E+00    ];
24    x:=[0.5,0.498,0.001,0.001];
25    Antoine_A      := [7.24147,7.0436,7.51107,    7.21274    ];
26    Antoine_B      := [2016.46 , 1636.909,1965.7,    1588.63    ];

```

Figure 3.2 Screenshot Showing The gPROMS Process Entity.

The mathematical solvers provided as standard within gPROMS; these fall in several categories (gPROMS Introductory User Guide, 2004):

- Solvers for sets of linear algebraic equations:

There are two standard mathematical solvers for the solution of sets of linear algebraic equations in gPROMS, namely MA28 and MA48.

- Solvers for sets of nonlinear algebraic equations:

There are three standard mathematical solvers for the solution of sets of nonlinear algebraic equations in gPROMS, namely BDNLSOL, NLSOL and SPARSE

- Solvers for mixed sets of nonlinear algebraic and differential equations:

There are two standard mathematical solvers for the solution of mixed sets of differential and algebraic equations in gPROMS, namely DASOLV and SRADAU

- Solvers for optimisation problems.

There are two standard mathematical solvers available in gPROMS for solving dynamic optimization problems. Both are based on a CVP approach which assumes that the time varying control intervals are piecewise constant (or piecewise linear) functions of time over a specified number of control intervals. The first solver implements a single-shooting dynamic optimization algorithm while the second implements the CVP technique via multiple shooting. The first solver is used in this work. These can be specified in the SOLUTIONPARAMETERS section of a PROCESS entity through the syntax:

```
SOLUTIONPARAMETERS
```

```
DOSolver: = "CVP_SS" ;
```

```
SOLUTIONPARAMETERS
```

```
DOSolver: = "CVP_MS" ;
```

### 3.5.3 Optimisation Entity

In the optimisation entity, the parameters for dynamic optimisation problems are specified in many cases, the values are expressed in the form: [guessed value, lower bound, upper bound].

Some of the specifications for the optimisation include (user of Guide gPROMS, 2004):

- The time horizon for the process
- The number of intervals.
- The control values within the intervals
- The end point of constraints.
- The objective function to be minimised or maximised.

The mathematical statement of the dynamic optimization problem can be summarized in Figure 3.3

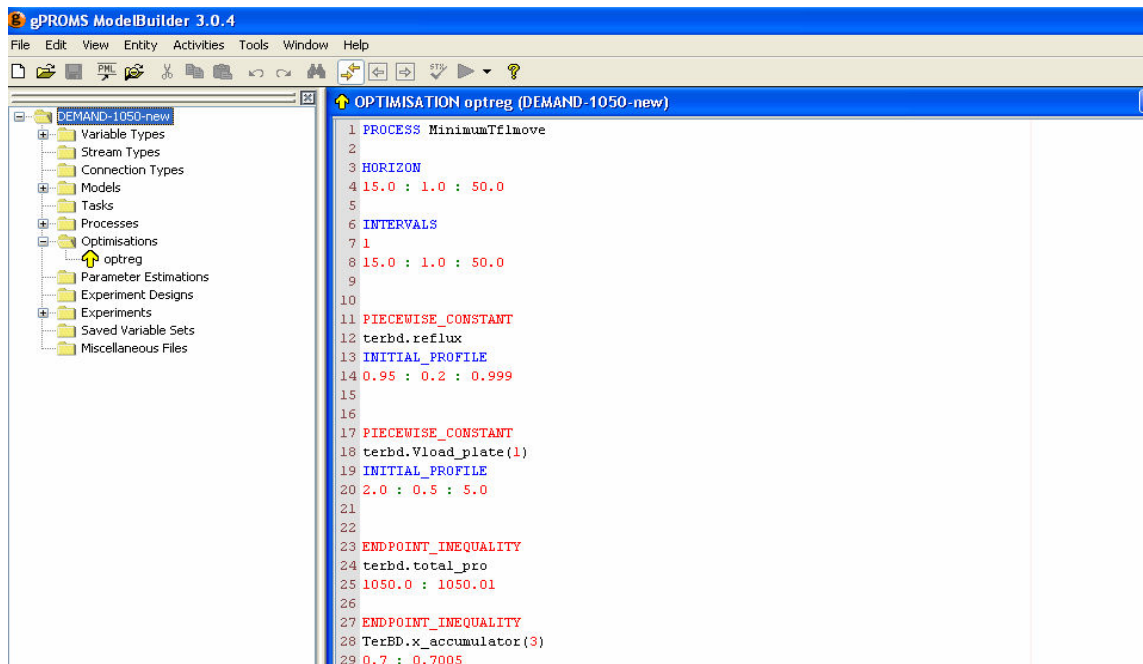


Fig 3.3 Screenshot Showing The gPROMS Optimisation Entity

In gPROMS, the aim of an optimisation framework is to determine the control variables and the time-invariant parameters which minimise or maximise a specified objective function and at the same time satisfying any imposed constraints. There are different types of constraints such as:

- Path constraints.
- Interior constraints.
- End-point constraints.

The solution of this problem comprises three key elements:

- The time horizon ( $t_f$ ) value.
- The time invariant parameters ( $v$ ) values.
- The variation of the control variables  $u(t)$  over the time horizon from  $t = 0$  to

$$t = t_f$$

### 3.6 Control Variable Profiles in gPROMS

Two types of the control variable profiles shown in Figure 3.4 are supported in the dynamic optimisation framework in gPROMS. These are:

- Piecewise-constant controls.
- Piecewise-linear controls.

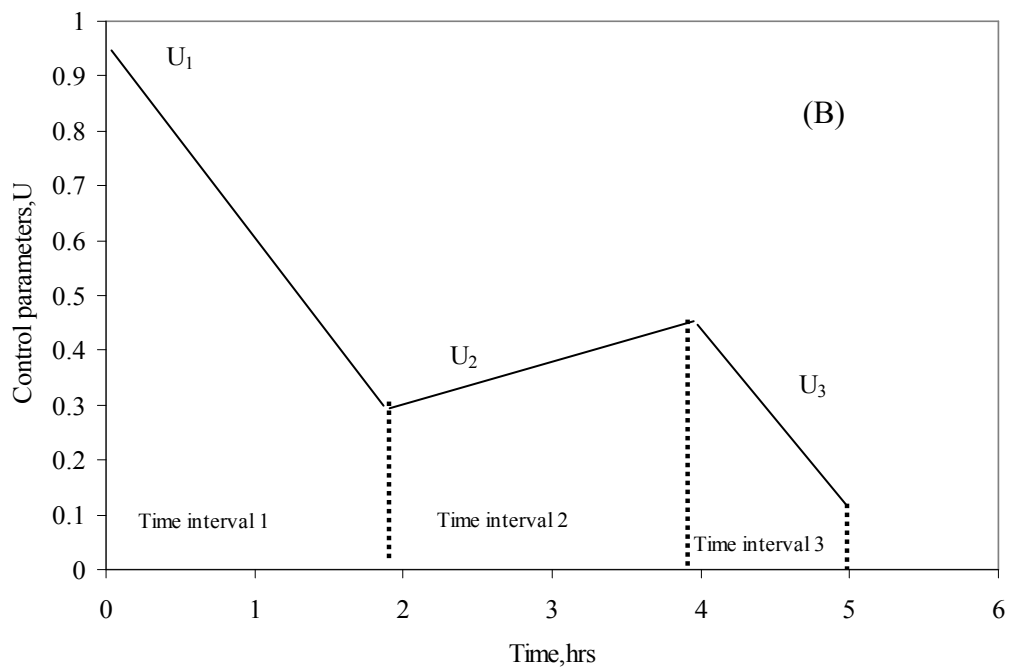
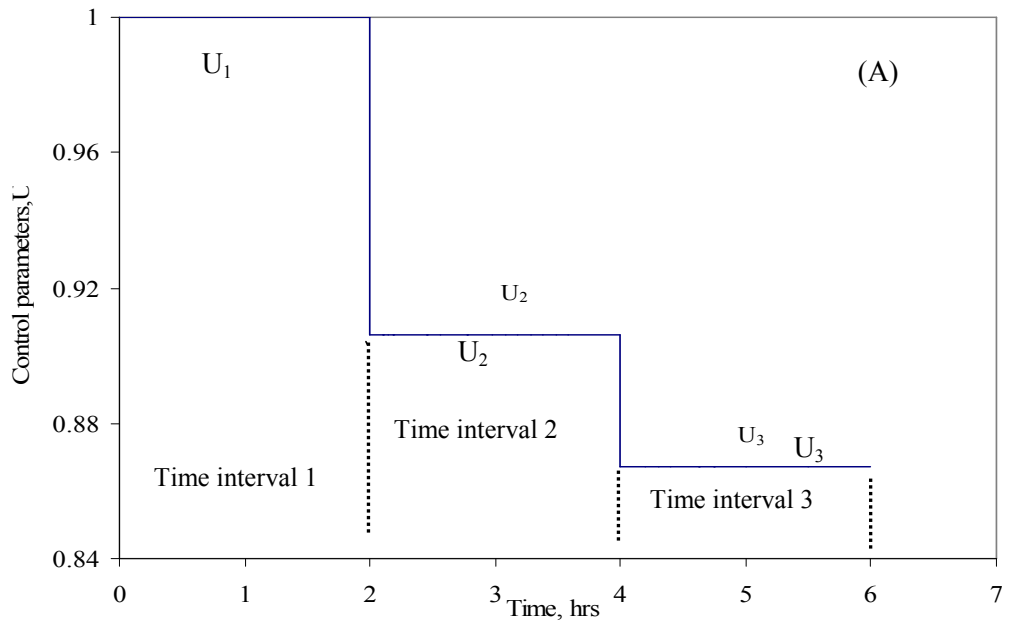


Figure 3.4 Different Types of Reflux Ratio Profiles  
(A) Piecewise Constant Reflux Ratio (B) Piecewise Linear Reflux Ratio



Both types are considered in the optimisation problems for different case studies in this work (see Chapters 5, 6 and 7).

### **3.7 Ideal Physical Properties Foreign Object (IPPFO)**

IPPFO package gives the physical and thermodynamic properties of components. It is linked to the gPROMS software package for the properties calculation such as:

- Constant properties such as molecular weights and standard enthalpies of formation.
- Single-phase properties such as enthalpies, specific heat capacities, densities, viscosities and activity coefficients.
- Two-phase properties such as enthalpies, densities, bubble and dew points.
- Two phase (T, P)-flash calculations.

In this thesis, the liquid and vapour enthalpies which constitute the energy balance equations and other physical properties such as densities were calculated using Ideal Physical Properties Foreign Objective (IPPFO) package interfaced to gPROMS.

### **3.8 Comparison of gPROMS with other Commercial Software**

There are many commercial software packages available for simulations, optimisations, and optimal control of batch distillation. Each of these commercial packages is developed with different characteristics. These include Bdist-SimOPT (Batch Process Technologies), BatchSim (Simulation Sciences), BatchFrac (Aspen Technology, based on Boston et al.), MultiBatchDS (Batch Process Research Company), Hysys, CEMCAD, Matlab, PROII, gPROMS, SpeedUp (Pantelides, 1988a), OMOLA (Andersson, 1990) and ASCEND (Piela *et al.*, 1991) etc...provide modelling languages that allow the transient behaviour of individual unit operations to be described in terms of mixed systems of ordinary differential and algebraic equations (DAEs).

A single software tool may be insufficient for the complex problems. An interface specifically developed for process engineering software, CAPE-OPEN, provides a solution to readily link software packages; for example, a custom unit operation model developed in gPROMS can be inserted into an Aspen Plus flowsheet (Gosling, 2005).

Tjil (2005) compared the performance of Aspen Custom Modeller (ACM) with the performance of gPROMS to optimise the Sec-Butyl Alcohol (SBA) stripper. The SBA model was built in both softwares to perform parameter estimation and assesses their capabilities. CAPE-OPEN was utilised to use the some physical and thermodynamic properties of the components in both softwares (ASC and gPROMS). The model developed in gPROMS consists of vapour-liquid equilibrium which described the distribution of nine components with reactions taking place in the liquid phase. Different aspects of parameter estimation were assessed for both softwares such as: experimental data input, output interpretation, combination of objective functions and optimisation solvers and their ability. Tjil (2005) concluded that the parameter estimation capabilities of gPROMS were better than ACM.

### **3.9 Conclusions**

This chapter includes brief general overview of the gPROMS modelling environment, some benefits and applications in the academic and industrial processes. Types of controls which were found in this package were mentioned and in the next section the general information's about IPPFO property package was presented. Finally the comparison between gPROMS and other software were investigated. Because of the advantages and applications outlined above, and many others not mentioned here for be short of space, gPROMS was chosen as the software for the modelling and dynamic optimisation of an unconventional distillation processes involving esterification and hydrolysis systems carried out in the course of this thesis. Further information can be

found in Oh and Pantelides (1996), Georgiadis *et al.* (2005) and at [www.psenderprise.com](http://www.psenderprise.com).

## **Chapter Four**

### **Process Modelling and Optimisation Problem Formulation**

#### **4.1 Introduction**

Batch processes, as opposed to continuous operation, are characterised by non-steady state behaviour. Their mathematical description is therefore based on time dependent mass and energy balances, resulting in systems of equations which include both differential and algebraic equations.

This chapter provides an overview of the literature concerning modelling, simulation and dynamic optimisation framework in batch distillation process. The numerical techniques for solving the optimization problems are outlined. An overview of some papers considering modelling, simulation and optimisation of batch distillation are presented.

#### **4.2 Modelling of Batch Distillation Process**

Modelling of engineering systems involves the use of mathematical equations to study the dynamics of a real system. It played an important role over the years in achieving better design and in understanding the dynamic behaviour of the systems. There are many attractions for model (based studies of process equations) rather than using the processes itself. Some of these are summarised as follows:

- a) Comprehensive studies (simulation, optimisation, control) using a model are less time consuming compared to that by a real process.
- b) It is cheaper than using real a process.
- c) It is safer, and the outcome is much less fatal if something goes wrong with the study.

Before any optimisation or control can be implemented, the models have to be in place and give a fair representation of the system to be studied. Modelling batch distillation systems were the main interest area of many researchers in the past (Corrigan and Ferris, 1969; Holland and Liapis, 1983; Cuille and Reklaitis, 1986; Diwekar *et al.* 1995; Nad and Spiegel, 1987; Ruiz, 1988; Mujtaba, 1989, 1992, 1997; Diwekar, 1995; Lang *et al.*, 1994).

In general, a batch distillation process model can be categorised as follows:

*Model I:* Rayleigh model.

*Model II:* Shortcut model (based on continuous distillation).

*Model III:* Simple model.

*Model IV:* Rigorous model (constant molar holdup, constant volume holdup).

*Model V:* Rigorous model with chemical reaction (constant molar holdup).

Mujtaba (2004) mentioned that the choice of a model in many cases depends on the numerical techniques available for the solution of the equations. A brief general overview of these models is presented in this thesis. However, this thesis will focus (in detail) on the rigorous model equations with chemical reaction for different batch distillation configurations.

#### **4.2.1 Model I: Rayleigh Model**

The Rayleigh model (Rayleigh, 1902) was developed for a single stage batch distillation where a liquid mixture is charged in a still and a vapour is produced by heating the liquid. At any time, the vapour is removed as soon as it is produced but no part of the vapour is returned as reflux to the still after condensation.

#### **4.2.2 Model II: Short-cut Model**

The short cut model was developed based on the assumption that batch distillation operation can be represented by a series of continuous distillation operation of short

duration and employs modified Fenske-Underwood-Gilliland (FUG) shortcut model of continuous distillation (Diwekar and Madhavan, (1991a,b); Sundaram and Evans, (1993a,b). Seader and Henley (1998) considered the separation of a ternary mixture in batch distillation column using this model. Sundaram and Evans (1993a) simulated the column operation using the short-cut model.

#### **4.2.3 Model III: Simple Model**

The model is developed based on constant relative volatility and equimolar overflow assumptions. The overall common assumptions are:

- Negligible vapour holdup.
- Adiabatic plates.
- Perfect mixing and equilibrium on all trays.
- Constant pressure.
- Total condensation with no sub-cooling.
- Constant tray holdup.
- Feed is saturated liquid.

Robinson (1970); Mayur and Jackson (1971); Luyben (1988); Mujtaba and Macchietto (1992) used this model for simulation and optimisation of conventional batch distillation.

#### **4.2.4 Model IV: Rigorous Model**

The model includes mass and energy balances, column hold up, rigorous phase equilibrium. The dominant assumptions which are mentioned in section 4.2.3 are used in this model. There are two types of rigorous model, first one with constant volume holdup (CVH) and the second one constant molar holdup (CMH) assumptions. Boston *et al.* (1980); Galindez and Fredenslund (1988); Bosley and Edgar (1994); Mori *et al.* (1995); Mujtaba and Macchietto (1998) used rigorous models with constant volume

holdup in their simulation and optimisation studies while, Mujtaba and Macchietto (1992, 1993, 1996, 1998), Greaves (2003), used rigorous models with constant molar holdup in their studies.

The model (models, I,II,III,VI,V) describing a batch distillation column is always dynamic in nature and results in a system of ordinary differential equations (ODEs) or a coupled system of differential and algebraic equations (DAEs) which are derived from the mass and energy balances around each plate of the column, reboiler, condenser and accumulator.

### **4.3 Model V: Rigorous Model with Chemical Reaction**

#### **4.3.1 Conventional Batch Distillation**

The model equations developed by Mujtaba and Macchietto (1997) are presented in the following section, with reference to the column configuration shown in Figure 4.1. The model includes column holdup, rigorous phase equilibria, and chemical reaction on the plates, in the reboiler and in the condenser. The stages are counted from the top to the bottom. In each stage, the vapour stream leaving the stage is in equilibrium with liquid stream leaving the same stage. The main assumptions are listed below:

- 1) Negligible vapour holdup.
- 2) Adiabatic plates.
- 3) Constant molar holdup on plates and in the condenser.
- 4) Perfect mixing on trays.
- 5) Fast energy dynamics.
- 6) Constant operating pressure.
- 7) Total condensation with no sub-cooling.
- 8) No azeotrope formation.
- 9) Feed mixture at its bubble point.

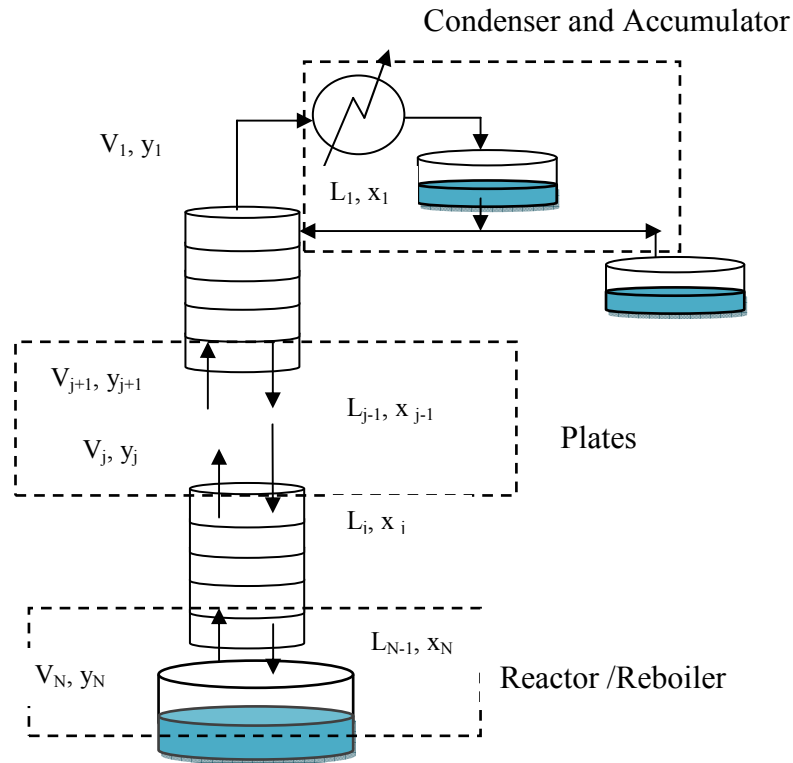


Figure 4.1 Batch Reactive Distillation Column

First the equations for the condenser and accumulator are presented. Then the equations for the plates in the column and the reboiler are presented: The plates are counted from the top to the bottom.  $j$  refers to plates and  $i$  refers to components.

Condenser and Distillate Accumulator:  $j=1$

Accumulator Total Mass Balance

$$\frac{dH_a}{dt} = L_D \quad (4.1)$$

Component Mass Balance:

a) Accumulator

$$H_a \frac{dx_a}{dt} = L_D (x_{D,i} - x_{a,i}) \quad (4.2)$$

b) Condenser Holdup Tank



$$H_c \frac{dx_c}{dt} = V_2 y_{2,i} + r_{1,i} H_c - (V_2 + \Delta n_1 H_c) x_{D,i} \quad (4.3)$$

Energy Balance:

$$0 = V_2 h_2^V - (V_2 + \Delta n_1 H_c) h_1^L - Q_c \quad (4.4)$$

Other Equation

$$L_1 = R(V_2 + \Delta n_1 H_c) \quad (4.5)$$

$$L_D = (V_2 + \Delta n_1 H_c)(1 - R) \quad (4.6)$$

$$T_1 = T_1(x_{D,i}, P) \quad (4.7)$$

$$h_1^L = h_1^L(x_{D,i}, T_1, P) \quad (4.8)$$

Plates,  $j = 2, N-1$

Total Mass Balance:

$$0 = L_{j-1} + V_{j+1} - L_j - V_j + \Delta n_j H_j \quad (4.9)$$

Component Mass Balance:

$$H_j \frac{dx_{j,i}}{dt} = L_{j-1} x_{j-1,i} + V_{j+1} y_{j+1,i} - L_j x_{j,i} - V_j y_{j,i} + r_{j,i} H_j \quad (4.10)$$

Energy Balance:

$$0 = L_{j-1} h_{j-1}^L + V_{j+1} h_{j+1}^V - L_j h_j^L - V_j h_j^V \quad (4.11)$$

Equilibrium:

$$y_{j,i} = K_{j,i} x_{j,i} \quad (4.12)$$

Restrictions:

$$\sum y_{j,i} = 1 \quad (4.13)$$

Relations defining physical properties:

$$K_{j,i} = K_{j,i}(y_{j,i}, x_{j,i}, T_j, P) \quad (4.14)$$

$$h_j^L = h_j^L(x_{j,i}, T_j, P) \quad (4.15)$$

$$h_j^V = h_j^V(y_{j,i}, T_j, P) \quad (4.16)$$

$$r_{j,i} = r_{j,i}(k_{j,i}, x_{j,i}) \quad (4.17)$$

$$\Delta n_j = \sum r_{j,i} \quad (4.18)$$

Reboiler: j = N

Total Mass Balance

$$\frac{dH_N}{dt} = L_{N-1} - V_N + \Delta n_N H_N \quad (4.19)$$

Component Mass Balance:

$$H_N \frac{dx_{N,i}}{dt} = L_{N-1}(x_{N-1,i} - x_{N,i}) - V_N(y_{N,i} - x_{N,i}) + r_N H_N - \Delta n_N H_N x_{N,i} \quad (4.20)$$

Energy Balance:

$$0 = L_{N-1}(h_{N-1}^L - h_N^L) - V_N(h_N^V - h_N^L) + Q_R \quad (4.21)$$

The other equations for the reboiler are the same as Equations (4.14-4.18) where j is replaced by N.

In this work, several case studies using batch reactive distillation column involving methanol, ethanol esterification systems and hydrolysis of methyl lactate and different optimisation problem formulations are considered.

### 4.3.2 Semi-batch Distillation Column

Here, the accumulator, condenser, and reboiler equations in the detailed dynamic model presented in Section 4.3.1 will remain the same. The model equation for the intermediate plates referring to the scheme of a typical plate (Figure 4.2) can be presented as follows:

Internal Plates j= 1 to N (N, Intermediate Plates)

- Total Mass Balance

$$0 = L_{j-1} + V_{j+1} - L_j - V_j + F + \Delta n_j H_j \quad (4.22)$$

- Component Mass Balance

$$H_j \frac{dx_j}{dt} = L_{j-1}x_{j-1,i} + V_{j+1}y_{j+1,i} - L_jx_j - V_jy_j + Fx_{fi} \quad (4.23)$$

- Energy balance

$$0 = L_{j-1}h_{j-1}^L + V_{j+1}h_{j+1}^V - L_jh_j^L - V_jh_j^V + Fh_f \quad (4.24)$$

Relations defining Physical Properties and Chemical Reactions

$$h_f = h_f(x_{f,i}, T_f, P) \quad (4.25)$$

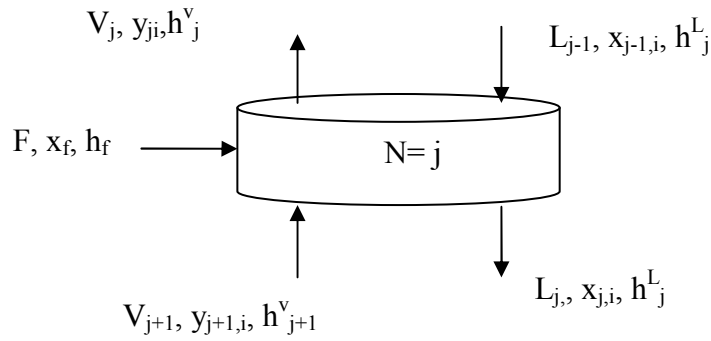


Figure 4.2 Configuration of Typical Plate ( $N = j$ ).

### 4.3.3 Inverted Batch Distillation Column

Referring to Figure 4.3 for an inverted batch distillation column (IBD), the equations for intermediate plates presented in Section 4.3.1 will remain the same. The model equations for the condenser and for the reboiler are presented below.

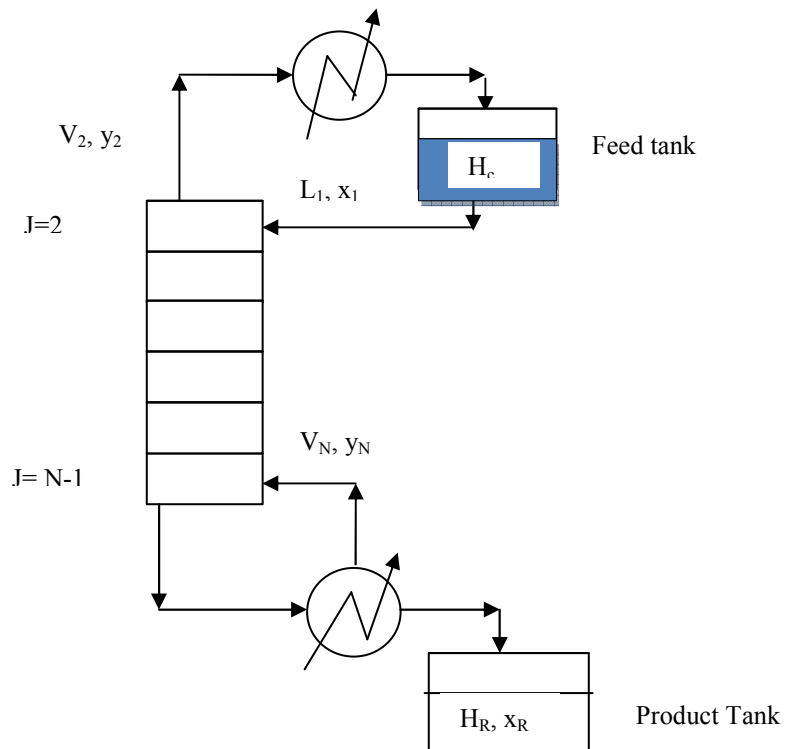


Figure 4.3 Inverted Batch Distillation Column (IBD)

Condenser:  $j = 1; i = 1$  to  $n_c$

Total mass balance:

$$\frac{dH_c}{dt} = V_2 - L_1 + \Delta n_1 H_c \quad (4.26)$$

Component mass balance

$$\frac{dH_c x_{c,i}}{dt} = V_2 y_{2,i} - L_1 x_{1,i} + r_{c,i} H_c \quad (4.27)$$

Energy balance:

$$V_2 h_2^V - L_1 h_1^L - Q_c \quad (4.28)$$

Reboiler Holdup and Product Tanks:  $j=N, i = 1$  to  $n_c$

Total mass balance:

a) Product Tank

$$\frac{dH_B}{dt} = L_B \quad (4.29)$$

b) Reboiler Holdup Tank

$$\frac{dH_N}{dt} = L_{N-1} - L_B - V_N + \Delta n_N H_N \quad (4.30)$$

Component mass balance:

a) Product Tank

$$\frac{d(H_R x_R)}{dt} = L_B (x_{N,i} - x_{R,i}) \quad (4.31)$$

b) Reboiler Holdup Tank

$$\frac{d(H_N x_N)}{dt} = L_{N-1} x_{N-1,i} - L_B x_{N,i} - V_N y_{N,i} + r_{N,i} H_N \quad (4.32)$$

Energy balance:

$$L_{N-1} h_{N-1}^L - L_B h_N^L - V_N h_N^V + Q_R \quad (4.33)$$

Reboil ratio definition:

$$R_B = \frac{V_N}{L_{N-1}} \quad (4.34)$$

Note, thermodynamic, kinetic and other physical properties can be calculated using the appropriate equations defined in Section 4.3.1.

The model equations which are used in this work were tested using the case studies presented in Mujtaba (2004) for conventional and inverted batch reactive distillation to validate the accuracy of the models.

#### **4.4 Optimisation**

Normally, the problems in engineering process design or plant operation have many, and possibly an infinite number of solutions. Optimisation provides a complete range of techniques from the basic multiple run approach of trial and error to highly complex numerical strategies. This assortment stems from the fact that optimisation is not idyllic in the real world but there are a lot of issues that require a practical approach. However, it is the next logical step after developing a process model.

A benefit of optimisation would include: improved product yield, conversion, productivity, profit or operating time. There are many ways optimisation techniques and decisions come into play when applied to the design and operation of chemical processes and plants. Some of them can be stated as follows (Ekpo, 2006):

- Determining the best sites to locate a process.
- Optimal pipeline sizing and layout.
- The entire design of the plant, as well as the “best” location for each piece of equipment.
- Plant operation for maximum productivity and profit.
- Bloated inventories are a major cause of inefficient operations. Optimisation can help in the slashing or minimisation of inventory costs.

The first discussion about seeking the optimal operating strategy of unsteady systems, so-called dynamic optimisation problem (DOP), was conducted by Aris (1960). With the increased importance of an unsteady state operation in chemical industries, many dynamic optimisation strategies have been proposed in the last several decades. The common solution techniques used in the literature to solve the optimal control problem are (Korovessi and Linninger, 2006):

- Pontryagin's maximum principle: it was first proposed by Pontryagin in 1956. In this technique the objective function is formulated as a linear function in terms of the final values of a state vector and a vector of constants.
- Dynamic programming: it is based on the principle of optimality which states that the minimum value of a function is a function of the initial state and the initial time. The application of this technique to a continuously operating systems leads to a set of nonlinear partial differential equations.
- Non Linear Programming optimisation techniques (NLP): they are the numerical tools used by models involving nonlinear algebraic equations. Applying NLP techniques to optimal control problems involved discretisation of control profile by applying orthogonal collocation on finite elements, the control vector parameterisation approach or the polynomial approximation.

Batch distillation is a dynamic process. The determination of optimal control strategy with respect to a maximal gain in the products and minimal production time is one of the main goals in the design and operation of the production processes (Perkins and Walsh, 1996).

The general form of mathematical model can be written as follows:

$$f(x(t_f), \dot{x}(t_f), y(t_f), u(t_f), v, t_f) = 0 \quad \forall t \in [0, t_f] \quad (4.35)$$

Where  $x(t)$  and  $y(t)$  are the differential and algebraic variables respectively both of which are function of time. The control variables  $u(t)$  represent time dependent decision variables while  $v$  is the set of constant parameters and  $t$  is the time.

The initial conditions required for initialisation of the DAE system are of the general form:

$$f(x(0), \dot{x}(0), y(0), u(0), v, t_f) = 0 \quad (4.36)$$

There are usually different types of constraints which hold at all times may generally be represented as

$$h(x(t), \dot{x}(t), y(t), u(t), v, t_f) \leq 0 \quad \forall t \in [0, t_f] \quad (4.37)$$

Constraints which hold at a particular instant in time ( $t_\lambda$ ) are referred to as point constraints and these have the following general form:

$$g(x(t_\lambda), \dot{x}(t_\lambda), y(t_\lambda), u(t_\lambda), v, t_\lambda) \leq 0 \quad (4.38)$$

The control variables and on the time invariant parameters also bounds on which define the optimisation search space:

$$u^{\min} \leq u(t) \leq u^{\max} \quad \forall t \in [0, t_f] \quad (4.39)$$

$$v^{\min} \leq v(t) \leq v^{\max} \quad (4.40)$$

There may also be limitations on the batch processing time:

$$t_f^{\min} \leq t_f \leq t_f^{\max} \quad (4.41)$$

NLP techniques are able to handle larger systems of equations, and hence allow the utilisation of more detailed models. Two general approaches have appeared in the chemical engineering literature in recent years. These are either based on:

- Control Vector Parameterisation, CVP (e.g. Sargent and Sullivan, 1979, Morison, 1984, Farhat *et al.*, 1991; Vassiliadis, 1993).
- Collocation method (e.g. Logsdon and Biegler, 1989).

The CVP method (which is used in this work) is described below.

#### 4.4.1 Control Vector Parameterisation

To pose the optimal control problem as a nonlinear programming (NLP) problem the controls  $u(t)$  are approximated by a finite number of subintervals (NCI), each with a set of basis functions involving a finite number of parameters as follows:

$$u(i) = \phi^j(t, z_j), t \in [(t_{j-1}, t_j), j = 1, 2, 3, \dots, J] \quad (4.42)$$

Where  $t_j = t_f$ . The functions  $\phi^j(t, z_j)$  are assumed to be continuously differentiable with respect to  $t$  and  $z_j$ , and derivatives are uniformly bounded. The control is thus defined by the parameters  $z_j$  and the switching time  $t_j, j = 1, 2, \dots, j$ . The control constraints become:

$$a^u \leq \phi^j(t, z_j) \leq b^u \quad t \in [(t_{j-1}, t_j), j = 1, 2, 3, \dots, J = 2 \times \text{NCI}] \quad (4.43)$$

The set of decision variables for the nonlinear programme can

$$y = \{z_1, z_2, \dots, z_j, t_1, t_2, \dots, t_j\} \quad (4.44)$$

Single and multi time intervals are used for optimisation in this work.  $z_1, z_2, z_3 \dots z_j$  are the optimal reflux ratio values within the time intervals.

An algorithm for the CVP approach is shown schematically in Figure 4.4. It involves the discretisation of the time horizon,  $t_f$ , into NCI control intervals, each of which may be of a different length.



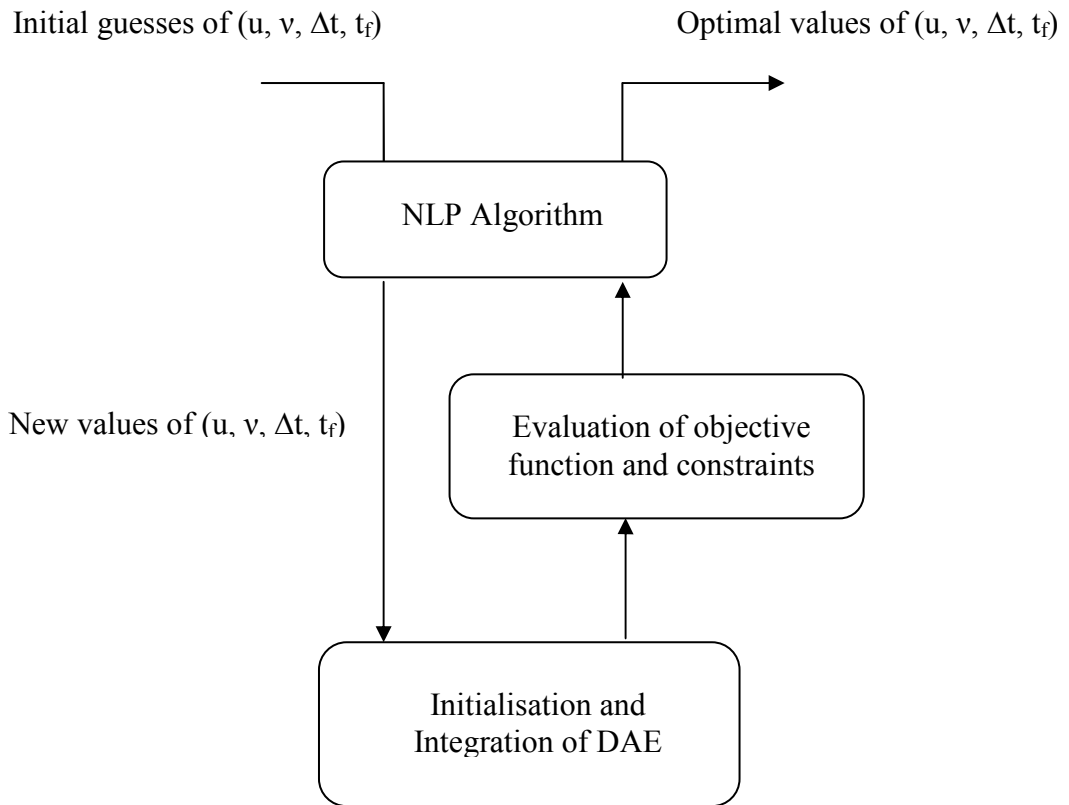


Figure 4.4 Control Vector Parameterisation (Furlonge, 2000)

#### 4.2.2 Dynamic Optimisation Problems Formulation

In general, three areas can be identified in any optimisation problem. These are:

- a) An objective function to be optimised.
- b) Equality constraints, these are the sets of model equations that describe the process to be optimised.
- c) Inequality Constraints (e.g. lower and upper bounds of the operating variables and constraints in the process).

The constraint in conventional batch reactive distillation considered in this work is the purity of the product at the end of the process. The control variables of the process are reflux ratio for conventional column and reboil ratio for an inverted column while in semi-batch reactive distillation is the feed of acetic acid and reflux ratio. The constraint is the purity of the product (Methyl Acetate, Ethyl Acetate, Lactic acid).

The optimisation problem to optimise the operation of a CBD column can be stated as follows (Mujtaba, 2004):

*given:* the column configuration, the feed mixture, vapour boilup rate a separation task in terms of product purity (+ recovery or amount of product or operation time or none)

*determine:* optimal reflux ratio which governs the operation

*so as to:* *minimise* the operation time  
or maximise the conversion  
or *maximise* the amount of product  
or *maximise* the profit  
or maximise the productivity

*subject to:* equality and inequality constraints (e.g. model equations)

Mathematically it can be represented as:

$$\begin{array}{llll}
 \text{OP} & \text{Minimise (or Maximise)} & J \text{ (Objective function)} & (4.45) \\
 & u(t) & & \\
 & \text{subject to :} & \text{Equality Constraints (Model)} & \\
 & & \text{Inequality Constraints} & 
 \end{array}$$

Where  $u(t)$  denotes all the optimisation variables such as reflux ratio and its switching times and or the final time. Inequality constraints refer to simple bounds on  $u(t)$  and final time constraints to the amount and or purity of top or bottom product.

The types of dynamic optimisation problem considered in this work are described below.

#### 4.4.2.1 Maximum Conversion Problem (OPI)

The optimization problem can be stated as:

*Given:* the column configuration, the feed mixture, condenser vapour load, a separation task (i.e. achieve the product with purity specification for a key distillate component) and the batch time ( $t_f^*$ ).

*Determine:* the optimal reflux ratio profile  $R(t)$

*So as to maximise:* an objective function defined for instance the conversion.

*Subject to:* equality and inequality constraints.

Mathematically the optimisation problem *OPI* can be written as:

$$\begin{aligned}
 \text{OPI} \quad & \text{Max } X \\
 & R(t) \\
 \text{subject to :} & \\
 & t = t_f^* \\
 & x_p = x_p^* + \varepsilon \quad \text{(Inequality constraint)} \\
 & \text{and } f(t, x', x, u, v) = 0 \quad \text{(Model Equation, equality constraint)} \\
 & \text{with } f(t_0, x'_0, x_0, u_0, v) = 0 \quad \text{(Initial condition, equality constraint)}
 \end{aligned} \tag{4.46}$$

Where  $X$  is the conversion of limiting reactant to product,  $R(t)$  is the reflux ratio as a function of time ( $t$ ) and  $x_p$  is the composition of product at final time  $t_f$ ,  $x_p^*$  is the desired composition of product and  $\varepsilon$  is a small positive numbering the order of  $10^{-3}$ . Mujtaba and Macchietto (1992, 1997); Mujtaba and Greaves (2006) and Wajge and Reklaitis (1999) considered this type of optimisation problem in their studies.

#### 4.4.2.2 Minimum Time Problem (OP2)

Optimisation problem (OP2) formulated as follows:

$$\begin{aligned}
 OP2 \quad & \min t_f \\
 & R(t) \tag{4.47} \\
 \text{subject to :} \\
 & B = B^* \quad \text{(Inequality constraint)} \\
 & x_p = x_p^* \pm \varepsilon \quad \text{(Inequality constraint)} \\
 & \text{and } f(t, x', x, u, v) = 0 \quad \text{(Model Equation, equality constraint)} \\
 & \text{with } f(t_0, x'_0, x_0, u_0, v) = 0 \quad \text{(Initial condition, equality constraint)} \\
 & \text{Linear bound on } R \quad \text{(Inequality constraint)}
 \end{aligned}$$

Where  $B$ ,  $x_p$  are the amount of bottom product and composition at the final time  $t_f$ .  $B^*$ ,  $x_p^*$  are the specified amount of bottom product and purity.  $R(t)$  is the reflux ratio profile which is optimised and  $\varepsilon$  is small positive numbering the order of  $10^{-3}$ . Mayur and Jackson (1971), Mujtaba (1989) and Mujtaba and Macchietto (1992, 1993, 1996, 1998) considered this type of optimisation.

#### 4.4.2.3 Maximum Profit Problem

Mathematically the optimization problem (OP3) can be represented as:

$$\begin{aligned}
 OP3 \quad & \max \$P \\
 & R(t) \tag{4.48} \\
 \text{subject to :} \\
 & x_p = x_p^* \pm \varepsilon \quad \text{(Inequality constraint)} \\
 & \text{and } f(t, x', x, u, v) = 0 \quad \text{(Model Equation, equality constraint)} \\
 & \text{with } f(t_0, x'_0, x_0, u_0, v) = 0 \quad \text{(Initial condition, equality constraint)} \\
 & \text{Linear bound on } R \quad \text{(Inequality constraint)}
 \end{aligned}$$

Kerkhof and Vissers, 1978; Diwekar *et al.*, 1989, Logsdon *et al.*, 1990; Mujtaba and Macchietto, 1996, 1997; Low and Sorensen, 2004; Mujtaba and Greaves (2006);

Masoud (2008); Mahmud *et al.* (2008) and Mujtaba and Masoud (2009) considered this type of optimisation.

#### 4.4.2.4 Maximum Productivity (OP4)

Mathematically the optimisation problem can be stated as:

$$\begin{aligned}
 \text{OP4} \quad & \max \quad \text{Prod} = \text{amount of distillate} / t_f \\
 & R(t) \tag{4.49} \\
 \text{subject to :} & \\
 & x_p = x_p^* \pm \varepsilon \quad \text{(Inequality constraint)} \\
 & \text{and } f(t, x', x, u, v) = 0 \quad \text{(Model Equation, equality constraint)} \\
 & \text{with } f(t_0, x'_0, x_0, u_0, v) = 0 \quad \text{(Initial condition, equality constraint)} \\
 & \text{Linear bound on } R \quad \text{(Inequality constraint)}
 \end{aligned}$$

Fernholz *et al.* (2000) considered this optimisation problem for semi-batch reactive distillation.

Some of the past work on dynamic optimisation of batch distillation using different types of column configurations are summarised in Table 4.1.

Table 4.1 Some of the Past Work on Optimisation of Batch Reactive Distillation

| Reference                     | Model Type | Column Type                 | Objective function   |
|-------------------------------|------------|-----------------------------|--|
| Egly <i>et al.</i> (1979)     | III        | CBD                         | Min. Time  |
| Wilson (1987)                 | III        | CBD                         | Max. Profit  |
| Mujtaba and Macchietto (1992) | III        | CBD+MVC                     | Max. Conversion  |
| Mujtaba and Macchietto (1994) | III        | IBD                         | Max. Conversion  |
| Mujtaba and Macchietto (1997) | V          | CBD                         | Max. Conversion  |
| Li <i>et al.</i> (1997)       | V          | Semi-batch                  | Max. Profit  |
| Wajge and Reklaitis (1999)    | V          | CBD                         | Max. Conversion  |
| Fernholz <i>et al.</i> (2000) | V          | Semi-batch                  | Min. Time<br>Max. Productivity                                   |
| Giessler <i>et al.</i> (2001) | V          | CBD                         | Max. Profit  |
| Elgue <i>et al.</i> (2002)    | V          | CBD                         | Min. Time  |
| Mujtaba and Greaves (2003)    | V          | CBD                         | Max. Profit  |
| Greaves (2003)                | V          | CBD                         | Max. Profit<br>Max. Conversion                                   |
| This work                     | V          | CBD+<br>Semi-batch<br>+ IBD | Max. Conversion<br>Max. Productivity<br>Max. Profit<br>Min. Time |

## 4.5 Conclusions

This chapter discussed briefly different types of models which have been found in the open literature on batch distillation. Rigorous models with chemical reaction presented in this chapter for batch, semi-batch and inverted distillation columns will be used in Chapters 5, 6 and 7. Different types of optimisation problems which have been found in the literature are described and will be used the course of this work. Also the solution

techniques for dynamic optimisation problems which provide optimal operation policies for a variety of objective functions involving these models are outlined. The dynamic optimization problem is converted to a nonlinear programming problem by Control Vector Parameterization (CVP) technique and is solved using efficient SQP method. Finally at the end of this chapter some of the past work on optimisation of batch distillation has been highlighted.

In this work, gPROMS modelling software is used for the modelling and dynamic optimisation of the batch reactive process. For the solution of set of differential and algebraic variables such as that described early, the DASOLV solver based on a variable time step/backward differentiation formulae (BDF) is used for integrations of the model equations and their sensitivity equations at each iteration of the optimization. There are two standard mathematical solvers available in gPROMS for solving dynamic optimization problems. Both are based on a CVP approach which assumes that the time varying control intervals are piecewise constant (or piecewise linear) functions of time over a specified number of control intervals. The first solver implements a single-shooting dynamic optimization algorithm while the second implements multiple shooting. The first solver is used in this work.

# Chapter Five

## Optimisation of Methanol Esterification Process

### 5.1 Introduction

This chapter deals with optimal operation of a batch reactive distillation process involving esterification of methanol (MeOH) with acetic acid (AA) to produce methyl acetate (MeAc) and water (H<sub>2</sub>O). An objective to maximise the conversion of the limiting reactant (methanol) dynamic optimisation problem (*maximum conversion problem*) is formulated.

A series of optimisation problems for different but fixed batch times  $t_f$  (between 5 and 15 hr) and for given product purity, ( $x^*_{\text{MeAc}} = 0.70$ ) is solved. Note, Greaves (2003) and Mujtaba and Greaves (2006) have considered the optimisation of batch reactive distillation for ethanol esterification process for product purity ranging from 0.6 to 0.85 molefraction and Mujtaba and Macchietto (1997) considered the optimisation problem for the same process for two product purities (0.7 and 0.8). However, in this work, product purity 0.7 is selected in all the optimisation problems. One constant reflux ratio level was optimised over the batch time of operation. Two case studies with varying amount of the reactants are considered and discussed in this purpose.

### 5.2 Methanol Esterification Process

Methyl acetate is used as an intermediate in the manufacture of a variety of polyesters such as photographic film base, cellulose acetate, Tenite cellulosic plastics and Estron acetate. The conventional processes before 1980's used multiple reactors with large excess of one of the reactants to achieve high conversion of the ester (Krishna, 2002).



The methanol esterification process is considered in a conventional batch reactive distillation process described in Chapter 1 (Figure 5.1). The feed charged at the beginning of the batch operation consists of methanol and acetic acid takes place in the reboiler. The reaction products collected in the receiver one are methyl acetate (main product) and methanol (unreacted) and in receiver two are methanol and water. At the end of the batch, a mixture of the unreacted acetic acid and water will be achieved in the reboiler. The reversible reaction schemes together with the boiling temperatures of the components are shown below:



|         |       |        |        |         |
|---------|-------|--------|--------|---------|
| B.P (K) | 391.1 | 337.65 | 330.05 | 373.15K |
|---------|-------|--------|--------|---------|

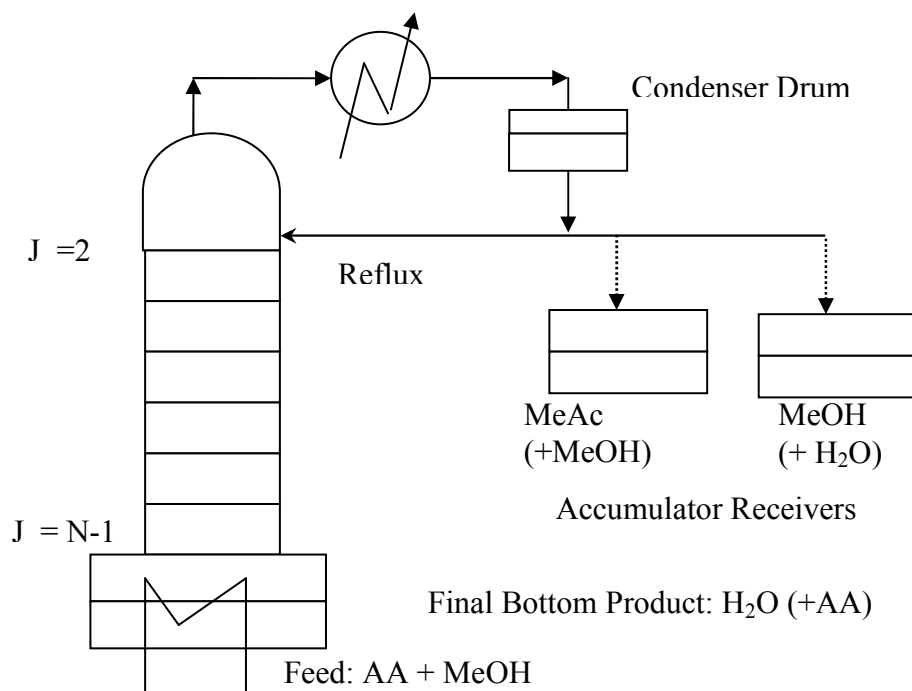


Figure 5.1 Methanol Esterification Process

Note, methanol and methyl acetate are wide boiling compare to ethanol and ethyl acetate (see Chapter 6). Therefore separation of methyl acetate from the reaction mixture will be comparatively easier (without losing much of the methanol (reactant)).

### 5.3 Model Equations

Referring to the column configuration shown in Figure 5.1, the model equations presented in Section 4.3.1 will be used herein. They include mass and energy balances, column holdup, rigorous phase equilibria, chemical reaction on the plates, in the reboiler, and in the condenser. Further information concerning the model equations and assumptions can be seen in Chapter 4.

#### 5.3.1 Reaction Kinetic Model

Wajge and Reklaitis (1999) considered the kinetic model (Equation 5.2) for esterification of methanol with acetic acid.

$$r_{MeOH} = -X_{AA} X_{MeOH} + X_{MeAc} X_{H_2O} \text{ (hr}^{-1}\text{)} \quad (5.2)$$

Where  $X$  is the liquid mole fraction for each component.

Elgue *et al.* (2002) considered a simple kinetic catalysed (sulphuric acid) model (Equation 5.3) which has been used by Bonnaillie *et al.* (2001)

$$r = k_{ester} \exp\left(\frac{-41800}{RT}\right) \left( C_{AA} C_{MeOH} - \frac{C_{H_2O} C_{MeAc}}{K_{eq}} \right) \quad (5.3)$$

With :  $k_{ester} = 3300 \text{ l. mol.}^{-1} \text{ min.}^{-1} \text{ ml.}^{-1} \text{ H}_2\text{SO}_4$  and  $K_{eq} = 5$ .

In this work, pseudo-homogeneous activity based kinetic model (in the presence of solvated protons as a catalyst) was taken from Popken *et al.* (2001) and can be written as:

$$-r = k_1 a_{AA} a_{MeOH} - k_2 a_{MeAc} a_{H_2O} \quad (5.4)$$

With

$$k_1 = 2.961 \times 10^4 \exp\left(\frac{-49190}{RT}\right) \quad (5.5)$$

$$k_2 = 1.348 \times 10^6 \exp\left(\frac{-69230}{RT}\right)$$

Where  $a_i$  is the activity of each component ( $a_i = \gamma_i x_i$ ).  $\gamma_i$  is the activity coefficient of component  $i$  which is calculated using NRTL equation. The NRTL equation and the coefficients are shown in Table 5.1.

Table 5.1 NRTL Model Parameters

| Comp. $i$     | AA       | AA       | AA               | MeOH    | MeOH             | MeAc             |
|---------------|----------|----------|------------------|---------|------------------|------------------|
| Comp. $j$     | MeOH     | MeAc     | H <sub>2</sub> O | MeAc    | H <sub>2</sub> O | H <sub>2</sub> O |
| $b_{ij}$      | 386.136  | 1439.172 | 1145.884         | 504.601 | 740.34           | 1633.968         |
| $b_{ji}$      | -405.711 | -687.401 | -339.409         | 171.727 | -233.016         | 525.774          |
| $\alpha_{ij}$ | 0.3      | 0.3      | 0.3              | 0.3     | 0.3              | 0.3              |

$\alpha_{ij} = 0.0$  and  $b_{ij} = 0.0$  when  $i = j$

### 5.3.2 Vapour-Liquid Equilibrium and Enthalpy Calculations

The vapour-liquid equilibrium relationship is given by:

$$y_i P = P_i^{sat} \gamma_i x_i \quad (5.6)$$

$P$  (bar) is the total pressure,  $x_i$  and  $y_i$  are the composition of the liquid and vapour phases, respectively,  $\gamma_i$  represents the activity coefficient of component  $i$  which was calculated using NRTL equation.

The vapour pressure ( $P^{sat}$ ) of pure components is obtained by using Antoine's equation:

$$\log P^{sat} = A - \frac{B}{T + C - 273.15} \quad (5.7)$$

Where  $A_i$ ,  $B_i$ ,  $C_i$  are the constants for the Antoine equations and  $T$  is the temperature in Kelvin and are shown in Table 5.2.

Table 5.2 Antoine Equation Parameters for Pure Components (Reid *et al.*, 1997)

| Component      | A       | B        | C      |
|----------------|---------|----------|--------|
| Acetic Acid    | 4.54456 | 1555.12  | 224.27 |
| Methanol       | 5.20277 | 1580.08  | 239.50 |
| Methyl Acetate | 4.18621 | 1156.43  | 219.69 |
| Water          | 5.11564 | 1687.537 | 230.17 |

The liquid and vapour enthalpies and other physical properties such as densities were calculated using Ideal Physical Properties Foreign Objective (IPFFO) which is linked with gPROMS modelling software.

## 5.4 Dynamic Optimisation Problem

In this section the optimal operation problem of batch reactive process is presented as a proper dynamic optimisation problem incorporating a detailed dynamic model. Maximum conversion problem (OP1) presented in Section 4.6.2.1 will be used here to find the optimal operation of the system. The reflux ratio is selected as the control variable to be optimised for a fixed batch time so as to maximise the conversion of the limiting reactant (methanol) subject to product (methyl acetate) purity 0.7 molefraction.

Referring to Figure 5.1, the optimisation problem can be stated as:

*Given:* the column configuration, the feed mixture, condenser vapour load, a separation task (i.e. achieve the product with purity specification for a key distillate component) and the batch time ( $t_f^*$ ).

*Determine:* the optimal reflux ratio profile  $R(t)$

*So as to maximise:* the conversion.

*Subject to:* equality and inequality constraints.

Mathematically the optimisation problem (OP1) can be written as:

$$\begin{aligned}
 \text{OP1} \quad & \text{Max} \quad X \\
 & R(t) \qquad \qquad \qquad (5.6) \\
 \text{subject to :} & \\
 & t = t_f^* \\
 & x_{MeAc} = x_{MeAc}^* \pm \varepsilon \qquad \qquad \qquad \text{(Inequality constraint)} \\
 & \text{and } f(t, x', x, u, v) = 0 \qquad \qquad \qquad \text{(Model Equation, equality constraint)} \\
 & \text{with } f(t_0, x'_0, x_0, u_0, v) = 0 \qquad \qquad \text{(Initial condition, equality constraint)}
 \end{aligned}$$

## 5.5 Case Studies

### 5.5.1 Specifications

Optimisation case studies are carried out using the gPROMS model builder. Here, two cases are considered in a 10 stages column (including condenser and reboiler) with vapour load equal 2.5 kmol/hr. The total column holdup is 4 % of the initial feed (50 % is taken as the condenser hold up and the rest is equally divided in the plates) and the reboiler capacity is 5 kmol. The feeds (kmol) <Acetic acid, methanol, methyl acetate, water> for two cases are given in Table 5.3. Case 2 has proportionally more acetic acid than Case 1. Stage compositions, product accumulator compositions, reboiler compositions are initialised to those of the feed compositions.

Table 5.3 Input Data for Two Case Studies

| Component      | Case 1 |              | Case 2 |              |
|----------------|--------|--------------|--------|--------------|
|                | kmol   | molefraction | kmol   | molefraction |
| Acetic Acid    | 2.5    | 0.5          | 3.0    | 0.6          |
| Methanol       | 2.5    | 0.5          | 2.0    | 0.4          |
| Methyl Acetate | 0.0    | 0.0          | 0.0    | 0.0          |
| Water          | 0.0    | 0.0          | 0.0    | 0.0          |

### 5.5.2 Results and Discussions

#### 5.5.2.1 Case 1

The optimisation problem OP1 mentioned in section 5.4 is considered and solved with varying batch time  $t_f$  (between 5 to 15 hrs) and given product (methyl acetate) purity 0.7 molefraction. One piecewise constant reflux ratio level is optimised over the batch time of operation. Table 5.4 shows the maximum conversion (%) of methanol to produce methyl acetate, optimal reflux ratio profile, and the corresponding amount of distillate product (kmol) for different batch times.

Table 5.4 Maximum Conversion, Reflux Ratio Profile and Distillate Product (Case 1)

| $t_f$ , hr | Max. Conversion % | Reflux Ratio | Distillate, kmol          |
|------------|-------------------|--------------|---------------------------|
| 5.0        | 79.5              | 0.765        | 2.94                      |
| 5.0        | <i>77.09</i>      | <i>0.918</i> | <i>1.025 (Simulation)</i> |
| 7.5        | 81.3              | 0.839        | 3.02                      |
| 10.0       | 82.2              | 0.878        | 3.05                      |
| 12.5       | 82.8              | 0.902        | 3.07                      |
| 15.0       | 83.1              | 0.918        | 3.08                      |

It can be seen from Table 5.4 that at  $t_f = 5$  hrs, the column chose to operate at low reflux ratio to remove acetate as quickly as possible to push the conversion as far as possible. However it is done at the expense of losing methanol and low amount of distillate. Higher reflux (ex.  $R = 0.918$  which is optimum reflux ratio at  $t_f = 15$  hrs) operation at low batch time ( $t_f = 5$ ) reduces the conversion and amount of product (shown in italic in Table 5.4). With longer batch time, the column enjoys more freedom to remove acetate by operating at higher reflux while retaining methanol as much as possible for further reaction. This improves not only the conversion but the amount of product as well at a given purity. It was not possible to simulate the column at 15 hrs using low reflux ratio ( $R = 0.765$  which is optimum reflux ratio at  $t_f = 5$  hrs). The maximum allowable operating time is 8.5 hrs (the reboiler gets empty after that time). It was seen that low reflux operation with longer batch time would lower the conversion and would not produce the distillate at the required purity. Typical plots of accumulator and reboiler composition profiles for different batch time are shown in Figures 5.2, 5.3 and 5.4.

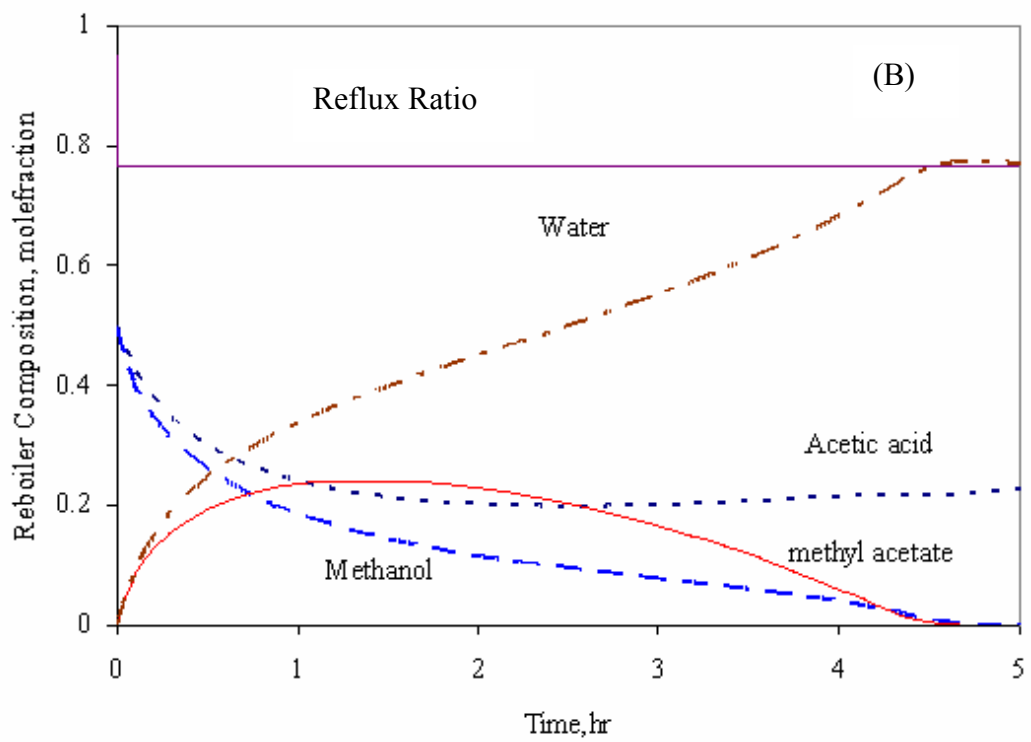
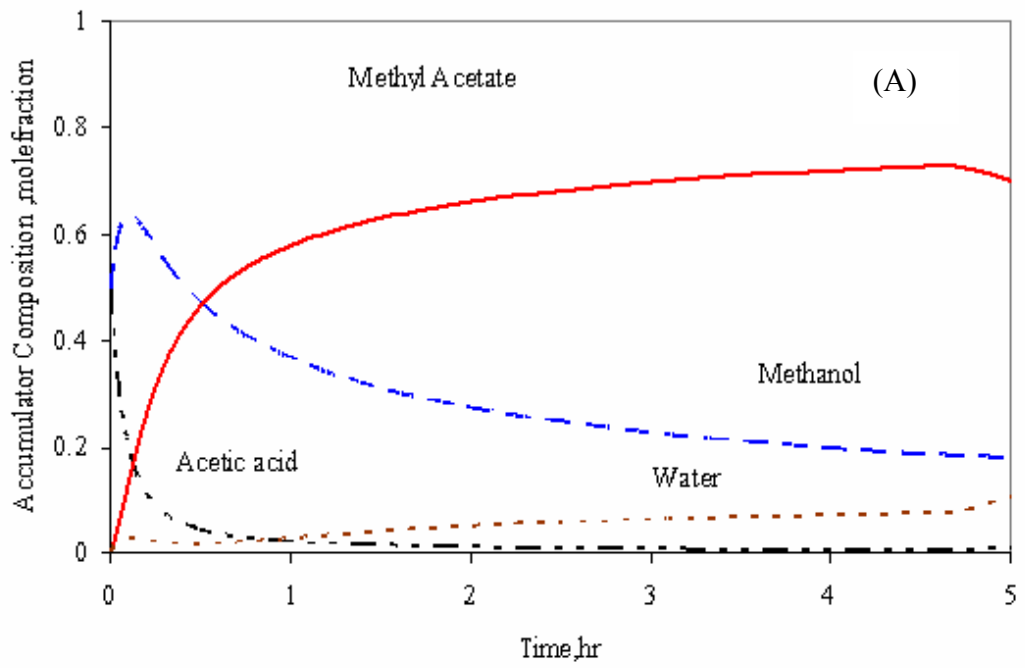


Figure 5.2 Composition and Reflux Ratio Profiles (5 hrs)

(A) Accumulator

(B) Reboiler

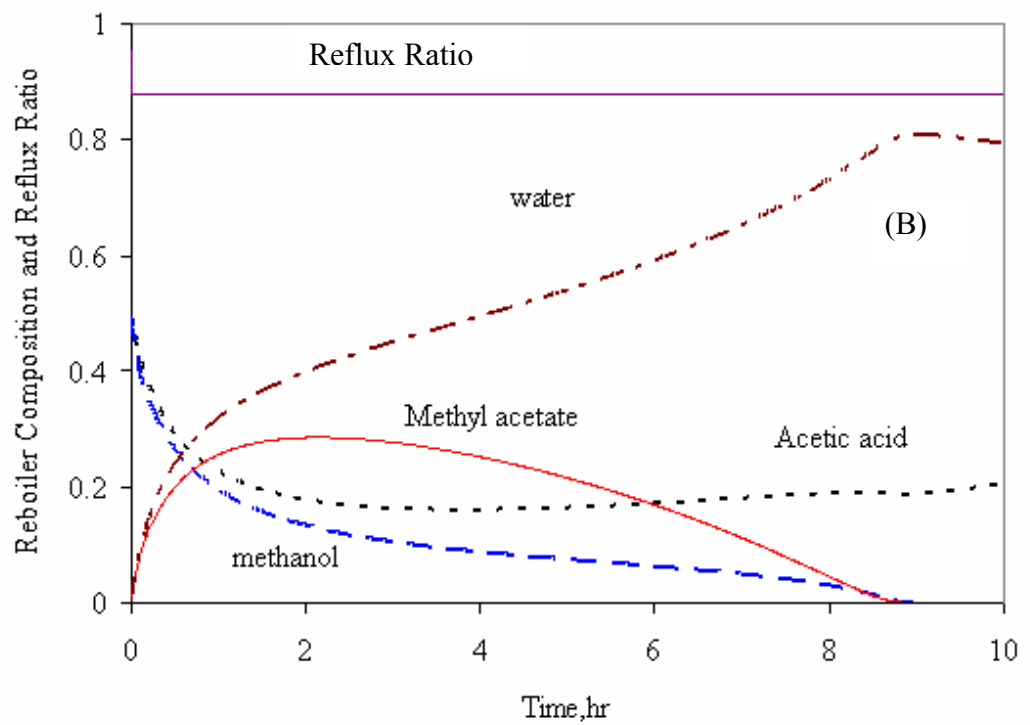
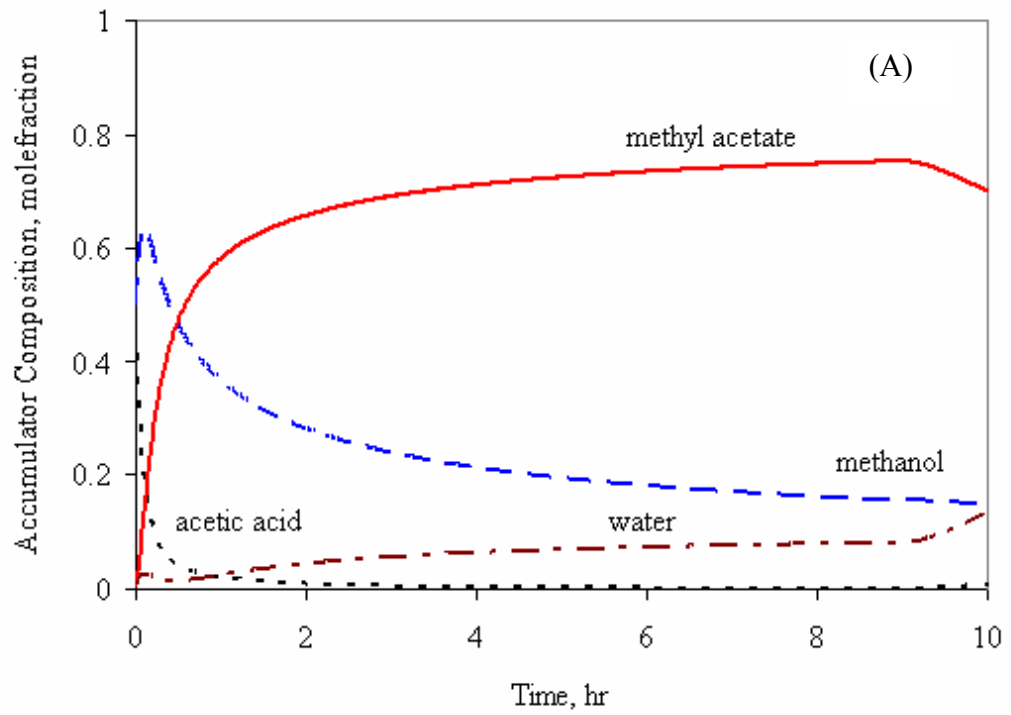


Figure 5.3 Composition and Reflux Ratio Profiles (10 hrs)

(A) Accumulator

(B) Reboiler



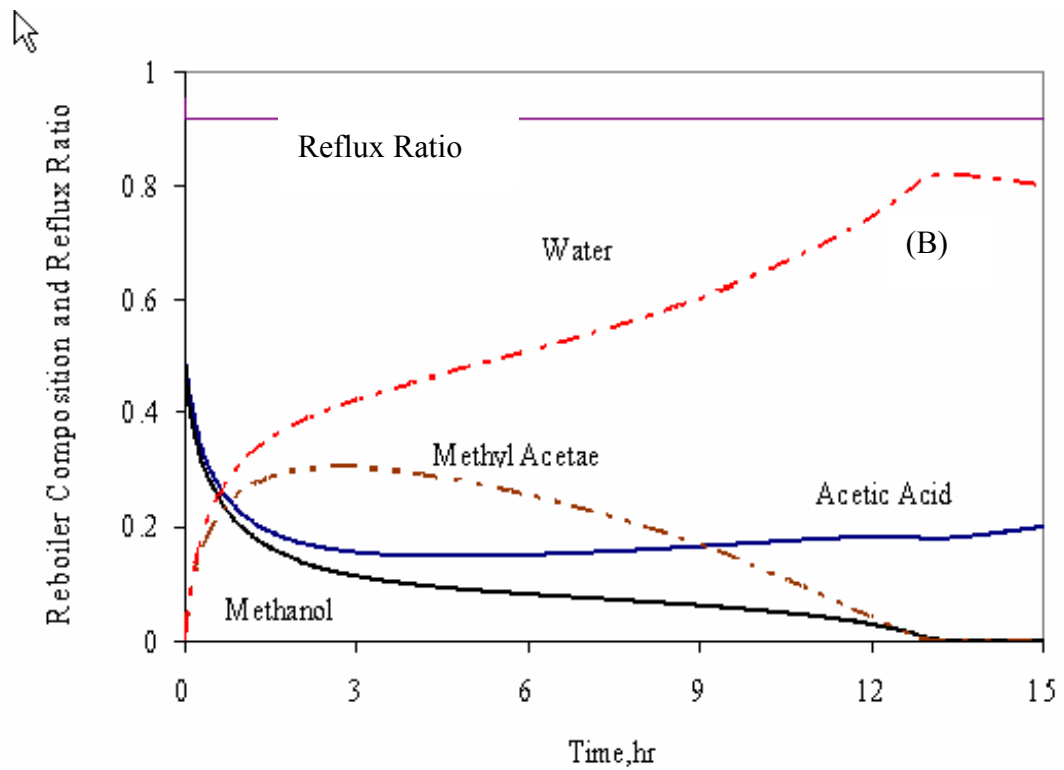
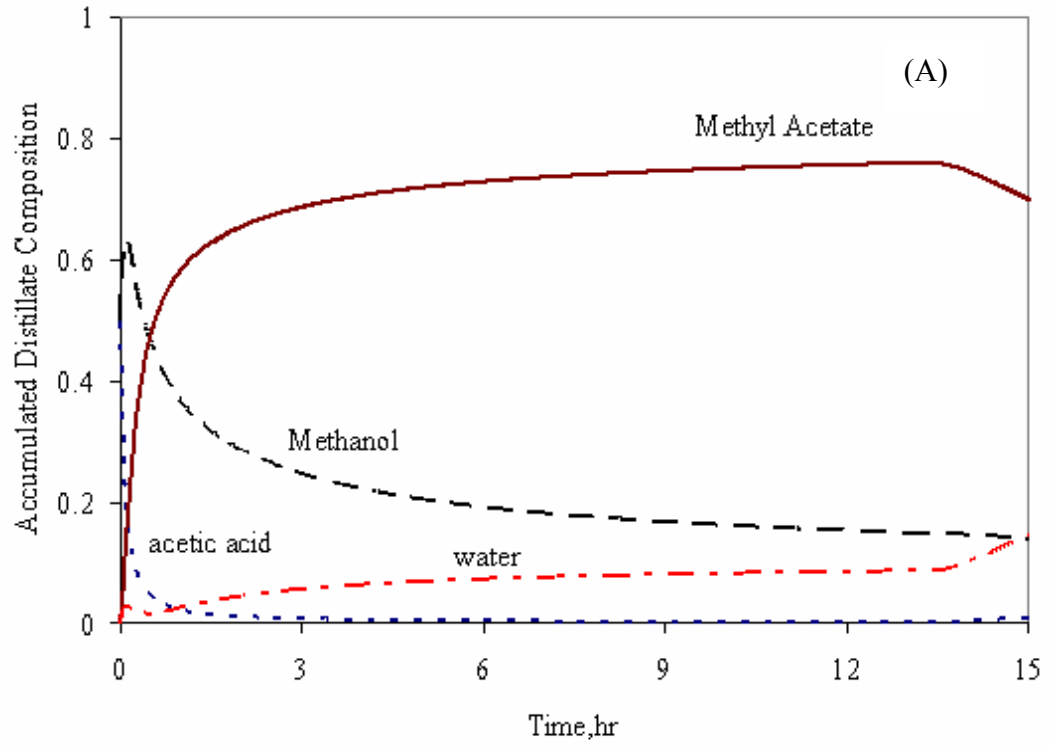


Figure 5.4 Compositions and Reflux Ratio Profiles (15hrs)

(A) Accumulator

(B) Reboiler

### *Analysis of Accumulator Composition Profile*

Observations for operating time of 5, 10 and 15 hrs (Figures 5.2A,5.3A,5.4A) show that initially, the methanol (as reactant) goes up as lower boiling reactant without any reaction and then decreases as it is consumed by reaction. Methyl acetate (as desired product and lower boiling component) steadily increases to the specified composition purity  $x_{MeAc}^* = 0.7$  with time as the reaction goes further to the right. The accumulator composition profiles at the end of operation for a batch time 5, 10 and 15 hrs are shown in Table 5.4. It can be seen from these compositions that more methanol has been reacted to produce more desired product (methyl acetate) therefore the conversion of methanol to product has been increased from 79.5 % for batch time 5 hr to 82.2 % and 83.1 % for batch times 10 and 15 hrs respectively. Higher reflux ratio (for batch time 10 and 15 hrs) would increase the conversion and amount of product compared with 5 hrs. While it leads to more water going up and being trapped in the accumulator.

### *Analysis of the Reboiler Composition Profile*

It can be seen from Figures 5.2B, 5.3B and 5.4B that the mole fraction of methyl acetate in the reboiler rises from zero, reaches a maximum value and then gradually falls to zero. The rise in mole fraction is due to the high rate of reaction initially. Acetic acid composition gradually decreases with time and finally increases at the end of reaction. Methanol mole fraction falls rapidly as it is being consumed by reaction as well as separated by distillation. Methanol is completely consumed in the reboiler at the end of time. At the end of operation, no methanol and methyl acetate were found as they are more volatile and will go up to the accumulator. The column contains more water (at the top and bottom) for operation with more batch time (more evident in Table 5.5).

Table 5.5 Optimisation Results and Composition Profiles Using Three Operation Times.

| $t_f$ , hr | X (%) | R     | D, kmol | X Accumulator    |                 |                 |                  |
|------------|-------|-------|---------|------------------|-----------------|-----------------|------------------|
|            |       |       |         | AA               | MeOH            | MeAc            | H <sub>2</sub> O |
| 5.0        | 79.5  | 0.765 | 2.94    | 0.011<br>(0.229) | 0.180<br>(0.00) | 0.700<br>(0.00) | 0.110<br>(0.771) |
| 10.0       | 82.2  | 0.878 | 3.05    | 0.011<br>(0.210) | 0.150<br>(0.00) | 0.700<br>(0.00) | 0.140<br>(0.790) |
| 15.0       | 83.1  | 0.918 | 3.08    | 0.010<br>(0.20)  | 0.142<br>(0.00) | 0.700<br>(0.00) | 0.148<br>(0.80)  |

Note: the reboiler composition shown in the brackets

### 5.5.2.2 Case 2

In this case the feed mixture contains more acetic acid than methanol (Table 5.3). Maximum conversion problem (*OPI*) is solved for fixed batch time and optimal reflux ratio of operation is determined. The plate compositions, product accumulator compositions and reboiler compositions are initialised at  $t = 0$  to the feed compositions.

The optimisation results in terms of maximum conversion (%) of methanol to methyl acetate, amount of product (methyl acetate) collected for each case and optimal reflux ratios are presented in Table 5.6.

Table 5.6 Maximum Conversion, Reflux Ratio Profile and Distillate Product

| $t_f$ , hr | Max. Conversion % | Reflux Ratio | Distillate, kmol |
|------------|-------------------|--------------|------------------|
| 5.0        | 85.1              | 0.798        | 2.52             |
| 7.5        | 86.6              | 0.863        | 2.57             |
| 10.0       | 87.4              | 0.896        | 2.59             |
| 12.5       | 87.8              | 0.917        | 2.60             |
| 15.0       | 88.0              | 0.930        | 2.61             |

Figure 5.5 (A, B) shows the typical plots of accumulator and reboiler composition profiles for batch time ( $t_f$ ) = 15 hrs. Note in Figure 5.5 the straight line represent the reflux ratio.

The results of Table 5.6 show a trend similar to those observed in Table 5.4. However, as there is less methanol in the feed, there is less amount of distillate.

### *Analysis of Accumulator Composition Profile*

It can be seen from the accumulator profile (Figure 5.5A) that acetic acid directly fall down (as heavier component and a reactant). Methanol decreases as the batch time increases and consumed by the reaction. Methyl acetate composition (main product) achieved from the reaction and rises up slightly until the end decreases to the specified composition. At the end of operation still some methanol and water in the accumulator.

### *Analysis of the Reboiler Composition Profile*

It can be seen that the mole fraction of methyl acetate in reboiler (Figure 5.5 B) rises from zero reaches a maximum value (about 12 hrs) and then gradually falls to zero. The rise in mole fraction is due to the high rate of reaction initially, however after 12 hrs the rate of methyl acetate production by reaction becomes less than the rate of separation by distillation and therefore there is a fall in the mole fraction of methyl acetate. Acetic acid composition gradually decreases with time and finally increases at the end of reaction. This behaviour is due to acetic acid's highest boiling point in the reaction mixture, which retains it in the lower sections of the column to carry out the reaction more efficiently. Methanol mole fraction falls rapidly as it is being consumed by the reaction as well as separated by distillation. Methanol is completely consumed in 12 hrs after which the reaction stops and the column behaves like a non-reactive batch distillation column.

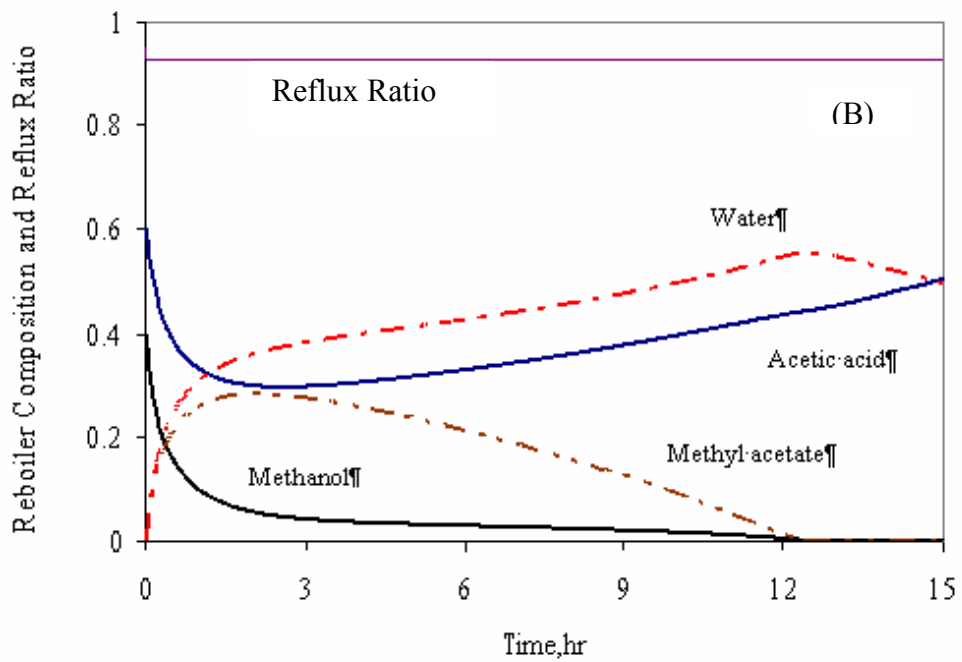
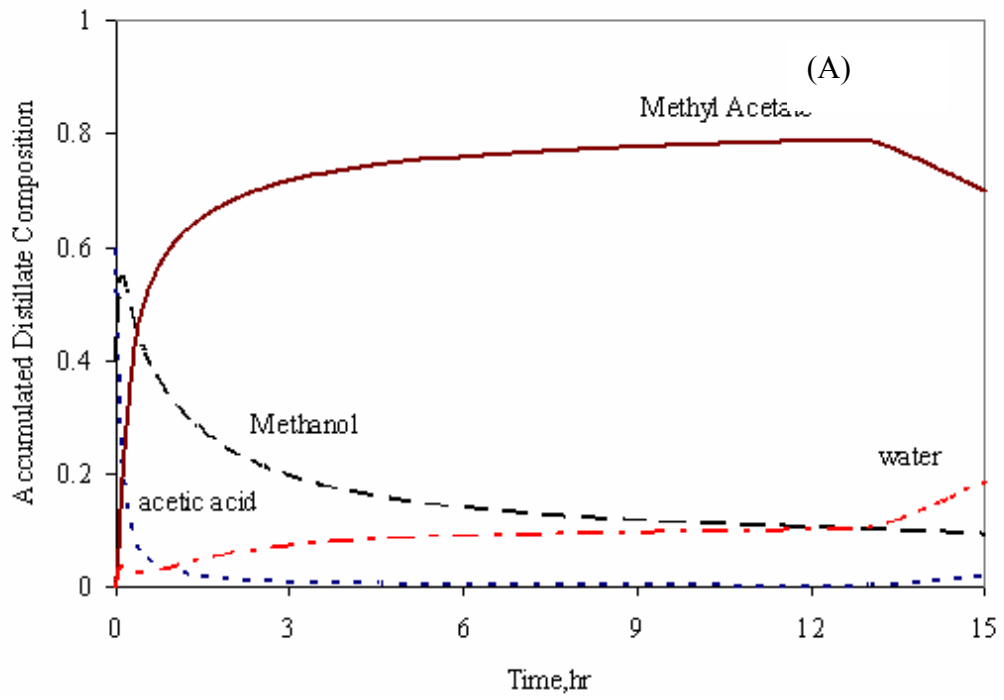


Figure 5.5 Compositions and Reflux Ratio Profiles (15hrs)

(A) Accumulator

(B) Reboiler

### 5.5.3 Comparison Between Two Case Studies

#### 5.5.3.1 With Respect to Conversion

Figure 5.6 shows the maximum conversion achieved for both cases. It can be seen that the conversion has been improved by 6.4 % in the Case 2 (the acetic acid feed increases) because there is sufficient amount of acetic acid reacted with methanol compared with Case 1 (Figure 5.7). Also, at time  $t = 0$  it is assumed that the reboiler content is at its bubble point. With more acetic acid for Case 2, the boiling point for Case 2 at  $t=0$  was higher compared to that in Case 1 (see Figure 5.9) and this enhances the rate of reaction and therefore conversion. Figure 5.6 also shows the maximum conversion profile achieved under total reflux operation (where no product is withdrawn). This scenario is close to the situation when the column operates as the reactor only without distillation. It can be noticed from Figure 5.6 that an improvement in conversion is achieved for the two cases when compared to the conversion achieved under total reflux operation.

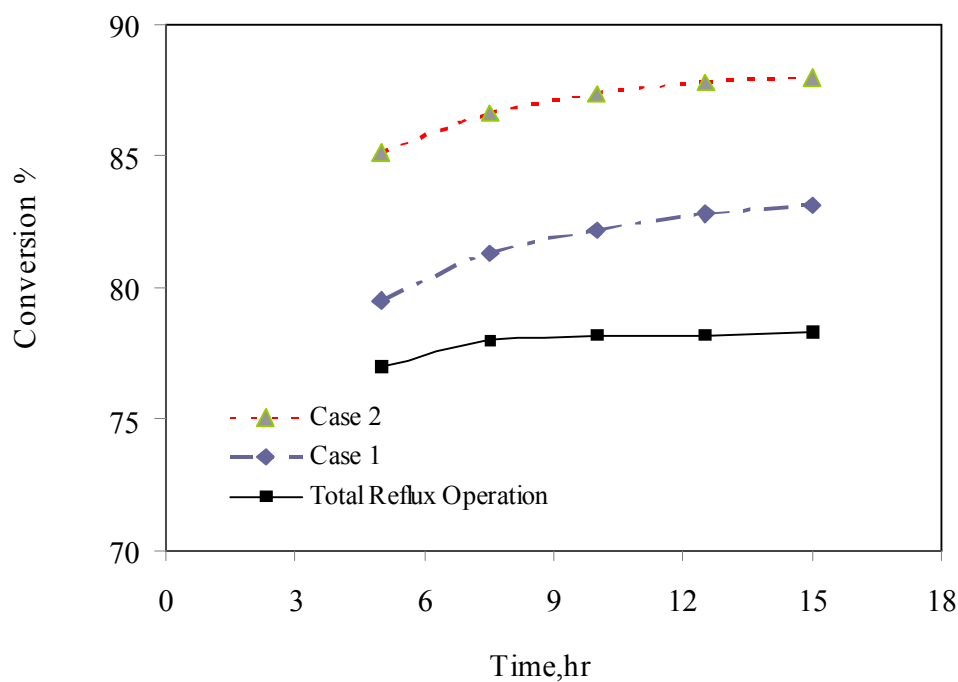


Figure 5.6 Maximum Conversion vs. Batch Time

Figure 5.7 shows the acetic acid composition profile at  $t_f = 15$  hrs for both Case 1 and Case 2. Acetic acid composition gradually decreases until  $t = 3$  hrs and then kept at the same value with increasing the time for Case 1. In Case 2 it gradually increases due to no further reaction (no methanol available).

Figure 5.8 shows the reflux ratio profiles for both cases. As a comparison, at the same operating time, it can be seen that the column operated at lower reflux ratio in Case 1 compared to that in Case 2. This allows more distillate product withdrawn in Case 1 than that achieved in Case 2 (more evident in Table 5.4 and Table 5.6).

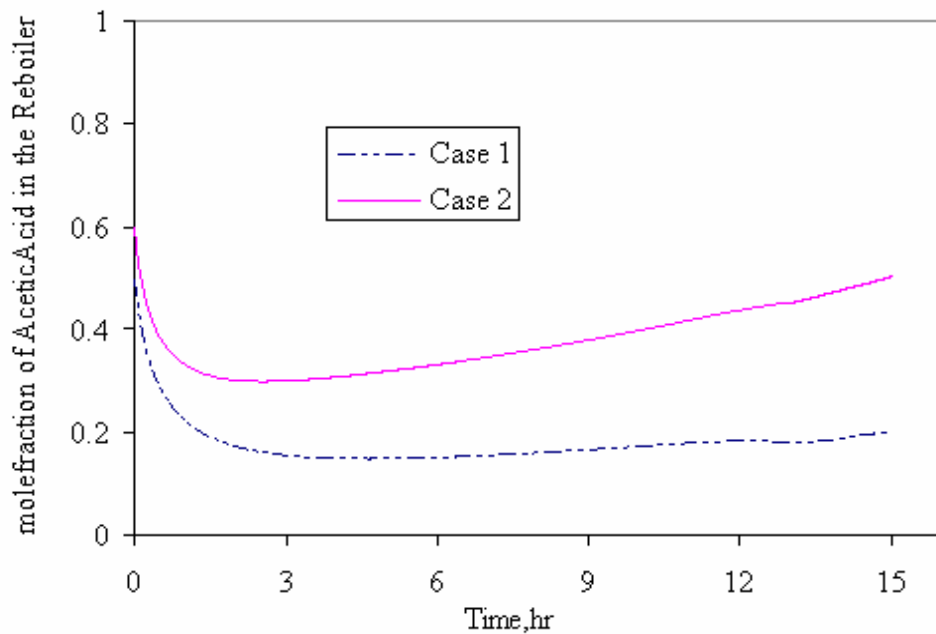


Figure 5.7 Reboiler Composition Profiles for Acetic Acid

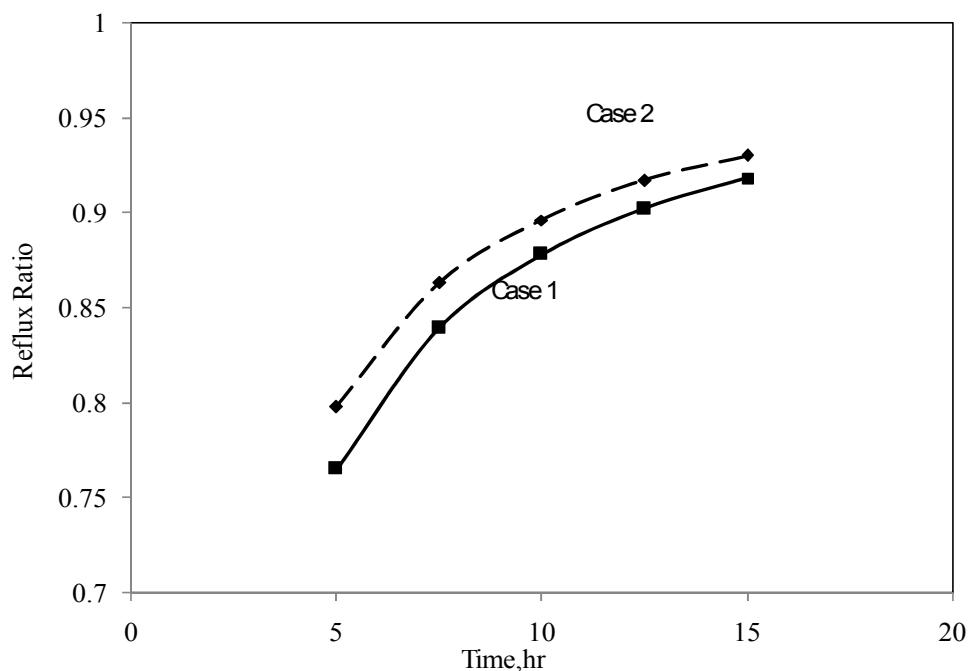


Figure 5.8 Reflux Ratio Profiles vs. Batch Time

#### 5.5.3.2 With Respect to Reboiler Temperature Profiles

The reboiler temperature profile for both cases at operation time 15 hrs and product purity 0.7 (as an example) is shown in Figure 5.9. Similar trend can be observed in both Cases while in Case 2 higher temperature operation is noticed due to more acetic acid in the feed. Higher temperature of the reboiler at initial time is noticed which decreases gradually with time in both cases. The decrease in temperature is due to more volatile components produced by the reaction. After a certain time as the light component is distilled off, the heaviest component is left in the reboiler, therefore the temperature begins to increase.



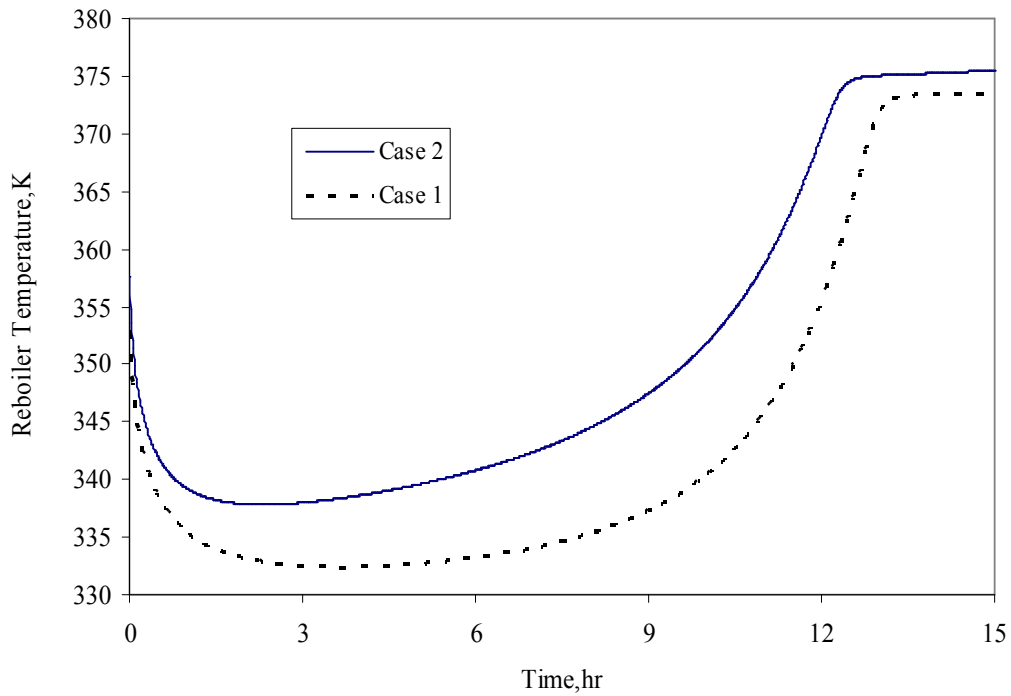


Figure 5.9 Reboiler Temperature Profile for Both Cases ( $t_f = 15$  hr).

## 5.6 Conclusions

In this chapter, optimal operation of batch reactive distillation column involving the esterification process of acetic acid with methanol producing methyl acetate and water was considered. The model equations in terms of mass and energy balances and thermodynamic properties within gPROMS modelling software were used. Two cases are studied. In Case 1 the feed contains 50 % acetic acid and 50 % methanol while in Case 2 the acetic acid feed composition is 60 % and methanol 40 % (by moles). Optimisation problem was formulated to optimise the reflux ratio (assumed piecewise constant) while maximising the conversion of methanol to methyl acetate for different but fixed batch time  $t_f$  (between 5 and 15 hrs) and for given product purity of methyl acetate ( $x_{MeAc} = 0.7$ ). The dynamic optimisation problem is converted to a nonlinear programming problem by Control Vector Parameterization (CVP) technique and is solved by using efficient SQP method. The optimisation results show that as the

methanol and methyl acetate are wide boiling, the separation of methyl acetate is easier without losing much of methanol reactant. Excess acetic acid (Case 2) leads to high temperature operation and therefore high reflux operation (to reduce loss of reactant from the top of the column) to maximise conversion.

## Chapter Six

### Optimisation of Ethanol Esterification Process

#### 6.1 Introduction

In this chapter, optimisation of batch reactive distillation column involving the esterification process of acetic acid with ethanol producing ethyl acetate and water is considered. The following case studies are considered in this chapter:

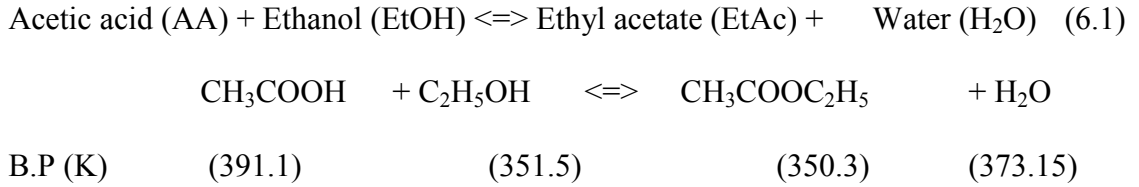
- Case Study 1: Maximising the Conversion of Ethanol to Ethyl Acetate in CBD.
- Case Study 2: Improving the Maximum Conversion of Ethanol Esterification Process in CBD.
- Case Study 3: Maximising the Productivity of Ethyl Acetate in CBD.
- Case Study 4: Maximising the Profitability, while optimising design and operation for fixed product demand.
- Case Study 5: Maximising the Conversion of Ethanol to Ethyl Acetate in Semi-batch Reactive Column.

#### 6.2 Process Description

The main method of the manufacture of ethyl acetate (EtAc) involves the esterification of ethanol (EtOH) and acetic acid (AA) in the presence of catalyst. Ethyl acetate is a colourless liquid with a fruity odour, having a molecular weight of 88.10. It finds use as a solvent in a wide range of applications, across many industries, including:

- Surface coating and thinners.
- Pharmaceuticals.
- Flavours and essences.
- Flexible packaging.

The ethanol esterification process in conventional batch reactive distillation process is shown in Figure 6.1. The esterification of acetic acid with ethanol towards ethyl acetate and water occurs according to the reversible reaction:



The reactants are acetic acid (in some cases diluted) and ethanol, and the products are ethyl acetate (is the main and lightest product) and water. Controlled removal of ethyl acetate by distillation shifts the chemical equilibrium further to right and thus improves conversion of the reactants.

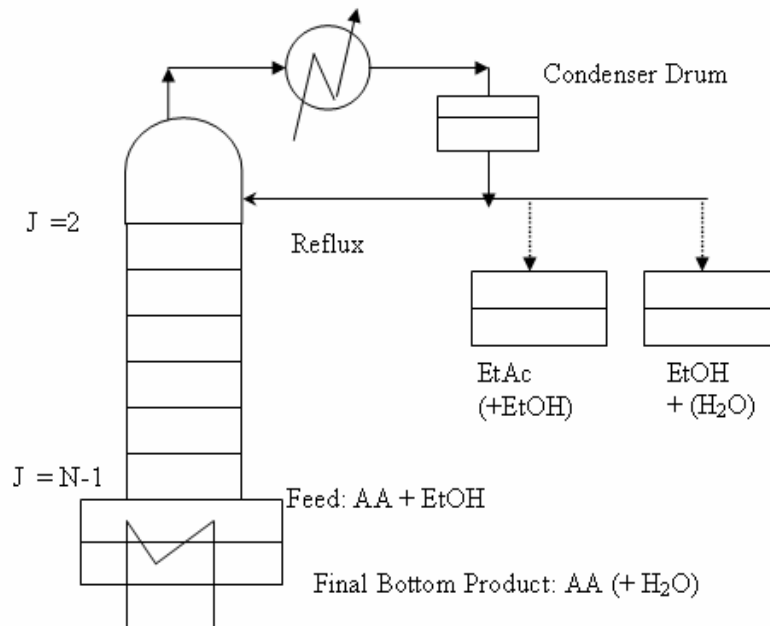


Figure 6.1 Ethanol Esterification Process

Note, while in methanol esterification system, methyl acetate and methanol had wider boiling points compared to ethyl acetate and ethanol in ethanol esterification system. Therefore, separation of ethyl acetate will be comparatively difficult in ethanol

esterification. Ethanol will tend to travel up the column with ethyl acetate and therefore comparatively high reflux operation is anticipated to contain the loss of ethanol (one of the reactants) from the system.

### 6.3 Model Equations

Referring to Figure 6.1 (same as Figure 4.1) the model equations including mass and energy balance equations, column holdup, rigorous phase equilibria, and chemical reaction on the plates, in the reboiler and in the condenser were presented in chapter four (Section 4.3.1).

Several authors have published the modelling of reactive distillation column with different column design, operating conditions and they used different vapour-liquid equilibrium and reaction rate expressions for esterification of acetic acid with ethanol to produce ethyl acetate and water (Suzuki *et al.* 1971; Komatus *et al.* 1977; Izarraraz *et al.* 1980; Chang and Seader, 1988; Alejski *et al.*, 1988, Simandl and Svrcek, 1991; Lee *et al.*, 1998).

#### 6.3.1 Reaction Kinetics

##### 6.3.1.1 Reaction Kinetics (Uncatalysed Type)

In the past, esterification of acetic acid with ethanol was carried out in a liquid phase using uncatalysed and catalyzed reactions. Arnikar *et al.* (1970) were the first to study the kinetics of the uncatalyzed esterification of this system. From the data of a specific rate for esterification reaction, the specific forward reaction rate constant ( $k_1$ ) at various temperatures (333, 338, 343, 353 and 358 K) was found be second order. At equilibrium the kinetics of the reverse reaction ( $k_2$ ) was predicted using the equilibrium constant by  $K = k_1/k_2$  where K was equal to 4.

In Equation 6.1 the esterification system shows the stoichiometric coefficients of all the components in the reaction are equal. The overall reaction rate of this system is

$$r = r_f - r_b = k_1 C_A C_B - k_2 C_C C_D \quad (6.2)$$

Where  $r_f = k_1 C_A C_B$  represents forward reaction rate (esterification) and  $r_b = k_2 C_C C_D$  represents backward reaction rate (hydrolysis).

$$k_1 = 4.85 \times 10^2 \exp\left(\frac{-14300}{RT}\right)$$

$$k_2 = 1.23 \times 10^2 \exp\left(\frac{-14300}{RT}\right) \quad (6.3)$$

Where  $R = 1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$ ,  $T$  is in K and  $C_i$  denotes the molarity of the acetic acid, ethanol ethyl acetate and water component (mol/l) respectively.

The rate constants of the forward and reverse reactions can be written in terms of l/(mol min) as follows:

$$k_1 = 29000 \exp\left(\frac{-7150}{T}\right)$$

$$k_2 = 7380 \exp\left(\frac{-7150}{T}\right) \quad (6.4)$$

### 6.3.1.2 Reaction Kinetics (Catalysed Type)

Smith (1982) presented the catalysed (hydrochloric acid) rate constants at 100 °C in the presence of water. It is written as:

$$k_1 = 4.76 \times 10^{-4} \text{ and } k_2 = 1.63 \times 10^{-4} \text{ (liter/g mol min)} \quad (6.5)$$

Suzuki *et al.* (1971) have considered the esterification of acetic acid with ethanol and used the reaction kinetic equation (an irreversible) forward reaction only. The forward irreversible reaction rate constant was:

$$\log k = \frac{-2.71 \times 10^3}{T} + 3.7 \quad (6.6)$$

### 6.3.2 Vapour-Liquid Equilibrium (VLE)

The vapour-liquid equilibrium coefficients ( $K_i$ ) can be calculated according to the method proposed by Suzuki *et al.* (1970). It can be written as follows:

$$\begin{aligned} K_{AA} &= 2.25 \times 10^{-2} T - 7.812 & T > 347.6 \text{ K} \\ K_{AA} &= 0.001 & T \leq 347.6 \text{ K} \\ \log K_{EtOH} &= \frac{-2.3 \times 10^3}{T} + 6.588 \\ \log K_{EtAc} &= \frac{-2.3 \times 10^3}{T} + 6.742 \\ \log K_{H_2O} &= \frac{-2.3 \times 10^3}{T} + 6.484 \end{aligned} \quad (6.7)$$

The K-values were estimated from the following form (Chang and Seader, 1988):

$$K_i = \frac{\gamma_i P^{sat}}{P} \quad (6.8)$$

Where  $\gamma_i$  is activity coefficient of component  $i$  which can be estimated using different models,  $P^{sat}$  and  $P$  are vapour pressure for pure component and total pressure respectively.

The kinetic rate model given in Eq. (6.2) with the rate constants ( $k_i$ ) in Eq. (6.5) and VLE (Eq. 6.7) are used in all the case studies presented in this chapter.

## 6.4 Case Study 1: Maximising Conversion of Ethanol to Ethyl Acetate

### 6.4.1 Optimisation Problem

The performance of batch (conventional) reactive distillation is defined in terms of maximum conversion of the limiting reactant (ethanol) subject to given product purity of main product (0.7 mole fraction of ethyl acetate).

Referring to Figure 6.1, the optimisation problem can be stated as:

*Given:* the column configuration, the feed mixture, condenser vapour load, a separation task (i.e. achieve the product with purity specification for distillate component) and the batch time ( $t_f^*$ ).

*Determine:* the optimal reflux ratio profile  $R(t)$ .

*So as to maximise:* the conversion.

*Subject to:* equality and inequality constraints.

Mathematically the optimisation problem (*OPI*) can be written as:

$$\begin{aligned}
 \text{OPI} \quad & \text{Max } X \\
 & R(t) \tag{6.9} \\
 \text{subject to :} & \\
 & t = t_f^* \\
 & x_{EtAc} = x_{EtAc}^* \pm \varepsilon \quad \text{(Inequality constraint)} \\
 & \text{and } f(t, x', x, u, v) = 0 \quad \text{(Model Equation, equality constraint)} \\
 & \text{with } f(t_0, x'_0, x_0, u_0, v) = 0 \quad \text{(Initial condition, equality constraint)}
 \end{aligned}$$

Where  $X$  is the conversion of ethanol to ethyl acetate,  $R(t)$  is the reflux ratio as a function of time ( $t$ ),  $x_{EtAc}$  is the composition of ethyl acetate in the product at final time  $t_f$ ,  $x_{EtAc}^*$  is the desired composition of ethyl acetate and  $\varepsilon$  is small positive numbering the order of  $10^{-3}$ .

The maximum conversion problem (*OPI*) solved for different but fixed batch time  $t_f$  (between 5 to 20 hrs). Piecewise constant reflux ratio was optimised (discretised into one and three control intervals). Furthermore, piecewise linear reflux ratio also considered as control variable over the batch time operations.

#### 6.4.2 Problem Specification

The feed to the still consists of a mixture <Acetic Acid, Ethanol, Ethyl Acetate, Water>, with composition (0.45, 0.45, 0.00, 0.10) molefraction and total fresh feed = 5 kmol.

The other input data are presented in Table 6.1.



**Table 6.1 Column Specifications for Ethanol Esterification Process**

|                               |          |                                 |           |
|-------------------------------|----------|---------------------------------|-----------|
| No of ideal stages*           | = 10     | Condenser hold up (kmol)        | = 0.10    |
| Internal plate hold up (kmol) | = 0.0125 | Condenser Vapour load (kmol/hr) | = 2.50    |
| Total fresh feed (kmol)       | = 5      | Column pressure (bar)           | = 1.01325 |

\*including reboiler and condenser

The kinetic model data utilized in this case for the ethanol esterification reaction are mentioned in (Eq. 6.2) with rate constants ( $k_i$ ) taken from (Eq. 6.5) and vapour-liquid equilibrium were given in (Eq. 6.7) respectively. The liquid and vapour enthalpies which constitute the energy balance equations and other physical properties such as densities were calculated using Ideal Physical Properties Foreign Objective (IPFPO) package interfaced to gPROMS. Stage compositions, product accumulator compositions, reboiler compositions are initialized to those of the feed compositions.

### 6.4.3 Results and Discussions

#### 6.4.3.1 Single Reflux Ratio (Piecewise Constant Type)

Table 6.2 shows the optimisation results in terms of the maximum conversion, optimal single reflux ratio, and the corresponding amount of ethyl acetate (kmol) for different batch times (between 5 to 20 hrs). Table 6.2 also shows the maximum conversion (shown in the brackets) achieved under total reflux operation (where no product is withdrawn). It can be seen that no significant increases in terms of conversion when the column operated under total reflux (absence of distillation). The results show that about 10.5 % more conversion is possible when the column is operated optimally compared to total reflux operation.

**Table 6.2 Summary of Maximum Conversion problem (constant Reflux Ratio)**

| $t_f$ , hr | Max. Conversion % | R     | D, kmol |
|------------|-------------------|-------|---------|
| 5          | 50.1 (49.1)       | 0.988 | 0.15    |
| 7.5        | 57.8 (55.9)       | 0.944 | 1.05    |
| 10         | 63.1 (58.5)       | 0.936 | 1.61    |
| 15         | 69.9 (60.0)       | 0.943 | 2.14    |
| 20         | 74.2 (60.5)       | 0.953 | 2.36    |

It can be seen from Table 6.2 that maximum conversion increases with increasing batch time (between 5 to 20 hrs). Higher reflux ratio for batch time 5 hrs is required to produce ethyl acetate product at purity 0.7 mole fraction and then falls as the available batch time increases. With only a short available batch time, only small amount product is produced by reaction and separating it in the distillate requires high reflux ratio. With larger batch times, more products are produced by reaction and separation becomes easier (hence lower reflux ratio). Finally the batch time is increased; high reflux ratio is required again to achieve products at given purity. The product amount achieved increases with increasing batch time. These observations are in line with those of Mujtaba and Macchietto (1997). Also see the methanol esterification case study in chapter five for further qualitative behaviour of the system.

The final amount of distillate and bottom products (kmol) distribution when the optimization problem OP1 was solved using one constant reflux ratio level for different batch operation times are shown in Table 6.3 and Table 6.4 respectively.

It can be seen from Table 6.3 that the amount of ethyl acetate increases with increasing batch time due to removal of it by distillation and as there is more time available the reaction goes further to the right. A Considerable amount of ethanol (reactant) is lost in the accumulator without reaction. Since there is very little acetic acid at the top of the column, no further forward reaction is possible. It can be seen from Table 6.4 that considerable amounts of acetic and ethanol are still available in the reboiler for further reaction (if there was more time available).

Table 6.3 Distillate Product Distribution (kmol) for Different Batch Time

| $t_f$ ,hr | Acetic acid | Ethanol | Ethyl acetate | Water | Total |
|-----------|-------------|---------|---------------|-------|-------|
| 5.0       | 0.00        | 0.041   | 0.105         | 0.004 | 0.15  |
| 7.50      | 0.003       | 0.276   | 0.735         | 0.036 | 1.05  |
| 10.0      | 0.003       | 0.401   | 1.127         | 0.079 | 1.61  |
| 15.0      | 0.004       | 0.462   | 1.498         | 0.176 | 2.14  |
| 20.0      | 0.005       | 0.450   | 1.659         | 0.256 | 2.37  |

Table 6.4 Bottom Product Distribution (kmol) for Different Batch Time

| $t_f$ , hr | Acetic acid | Ethanol | Ethyl acetate | Water | Total |
|------------|-------------|---------|---------------|-------|-------|
| 5.0        | 1.16        | 1.10    | 0.91          | 1.67  | 4.84  |
| 7.50       | 0.984       | 0.675   | 0.482         | 1.805 | 3.95  |
| 10.0       | 0.861       | 0.424   | 0.244         | 1.861 | 3.39  |
| 15.0       | 0.698       | 0.200   | 0.080         | 1.882 | 2.86  |
| 20.0       | 0.600       | 0.118   | 0.037         | 1.875 | 2.63  |

#### 6.4.3.2 Multi-Reflux Ratio (Piecewise Constant Type)

The reflux ratio is discretised into three control intervals for each operation time (from 5 to 20 hrs). Table 6.5 shows the maximum conversion of ethanol to ethyl acetate, optimal reflux ratio ( $R_1$ ,  $R_2$ ,  $R_3$ ), and optimal time intervals ( $t_1$ ,  $t_2$ ,  $t_3$ ), amount of product (kmol) for different batch time from 5 to 20 hrs. Furthermore, reflux ratio profiles for each case are shown in Figure 6.2.

It can be seen from reflux ratio profile (Table 6.5) that, for the first time period an initial total reflux operation was required for all cases before any product was withdrawn from the column. The optimal period time of total reflux operation with batch time 20 hrs was longer compared to that with the other values of batch time. The reflux ratio values in interval 2 and interval 3 increase with increasing the operating times.

In Table 6.5 the results clearly show that the amount of products increases with increasing batch operation time between 5 to 20 hrs.

Table 6.5 Summary of the Maximum Conversion Problem (Multi-Reflux Interval)

| $t_f$ , hr | Max.Conv. % | $t_1, R_1$ | $t_2, R_2$  | $t_3, R_3$  | D, kmol |
|------------|-------------|------------|-------------|-------------|---------|
| 5.0        | 51.3        | 1.80, 1.0  | 1.92, 0.906 | 1.28, 0.867 | 0.88    |
| 7.5        | 59.8        | 1.94, 1.0  | 2.69, 0.908 | 2.87, 0.885 | 1.45    |
| 10.0       | 65.4        | 2.19, 1.0  | 2.56, 0.910 | 5.29, 0.904 | 1.84    |
| 15.0       | 72.4        | 2.46, 1.0  | 7.66, 0.923 | 4.88, 0.935 | 2.27    |
| 20.0       | 76.4        | 2.78, 1.0  | 8.03, 0.934 | 9.19, 0.950 | 2.47    |

The final amounts of distillate and bottom products distribution when time dependent reflux ratio profile is used are shown in Table 6.6 and Table 6.7 respectively.

Comparison between Table 6.3 and Table 6.6 for accumulator product shows that, multi reflux operation allows producing more ethyl acetate (main product) for each operation time.

It can be noticed from Table 6.4 and 6.7 for the reboiler products that less reactants are available in the reboiler with multi-reflux operation.

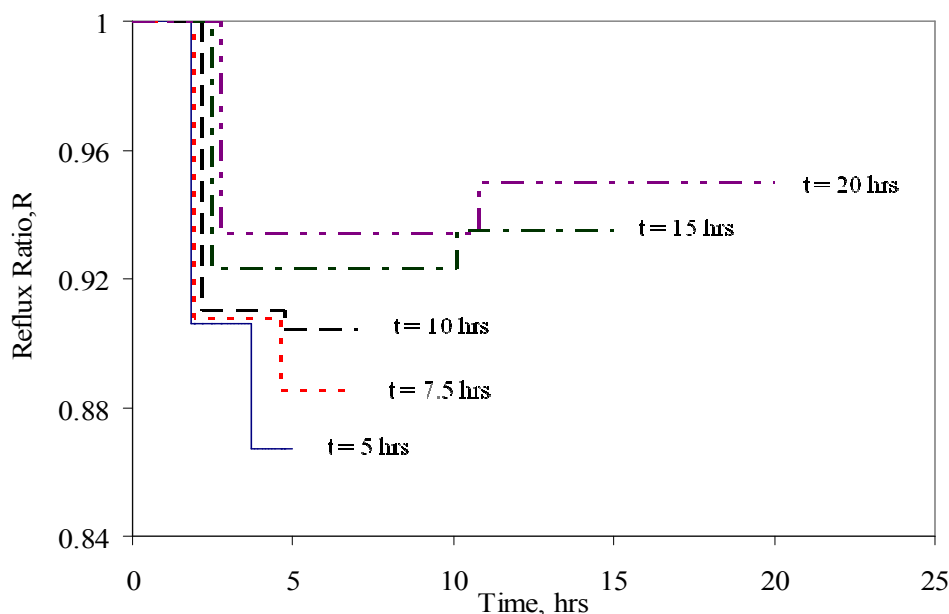


Figure 6.2 Reflux Ratio Profile vs. Batch Time (Multi-Reflux Ratio) NCI = 3

Table 6.6 Distillate Product Distribution (kmol) at Different Batch Time

| $t_f$ ,hr | Acetic acid | Ethanol | Ethyl acetate | Water | Total |
|-----------|-------------|---------|---------------|-------|-------|
| 5.0       | 0.000       | 0.218   | 0.616         | 0.046 | 0.88  |
| 7.50      | 0.000       | 0.335   | 1.015         | 0.100 | 1.45  |
| 10.0      | 0.000       | 0.390   | 1.288         | 0.158 | 1.84  |
| 15.0      | 0.000       | 0.429   | 1.589         | 0.252 | 2.27  |
| 20.0      | 0.000       | 0.415   | 1.729         | 0.326 | 2.47  |

Table 6.7 Bottom Product Distribution (kmol) at Different Batch Time

| $t_f$ ,hr | Acetic acid | Ethanol | Ethyl acetate | Water | Total |
|-----------|-------------|---------|---------------|-------|-------|
| 5.0       | 1.137       | 0.861   | 0.490         | 1.632 | 4.12  |
| 7.50      | 0.937       | 0.550   | 0.302         | 1.757 | 3.55  |
| 10.0      | 0.809       | 0.367   | 0.174         | 1.811 | 3.16  |
| 15.0      | 0.644       | 0.177   | 0.063         | 1.845 | 2.73  |
| 20.0      | 0.549       | 0.104   | 0.030         | 1.847 | 2.53  |

For batch time 20 hrs Reboiler temperature profile, accumulated distillate composition and reboiler composition profiles using one interval reflux ratio and multi reflux ratios are shown in Figures 6.3, 6.4, and 6.5 respectively.

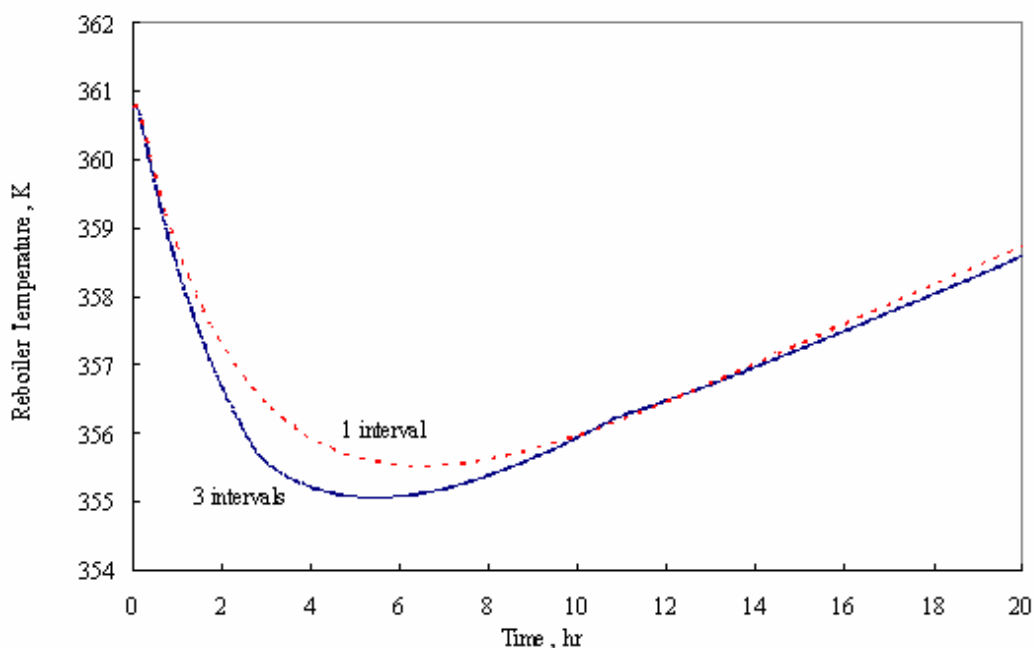


Figure 6.3 Reboiler Temperature Profile ( $NCI = 1$  and  $NCI = 3$ )

For both Cases using single and multi-reflux ratio operation (Figure 6.3) shows that the reboiler starts at a high temperature operation at the beginning (at bubble point temperature of the mixture) and then decreases within about 6 hrs and then increasing gradually. The initial decrease in temperature is due to more volatile component produced (ethyl acetate) by reaction, however, as the separation of these components continues, the reboiler temperature starts increasing. Further decreases in the reboiler temperature are observed (Figure 6.3) when the column is operated using multi-reflux ratio policy than single reflux strategy. This is due to having more ethanol reacting with acetic acid in the reboiler (decreasing ethanol in the accumulator) and producing more (thus lowering the boiling point of the reboiler mixture). Figure 6.4 and 6.5 support this observation.

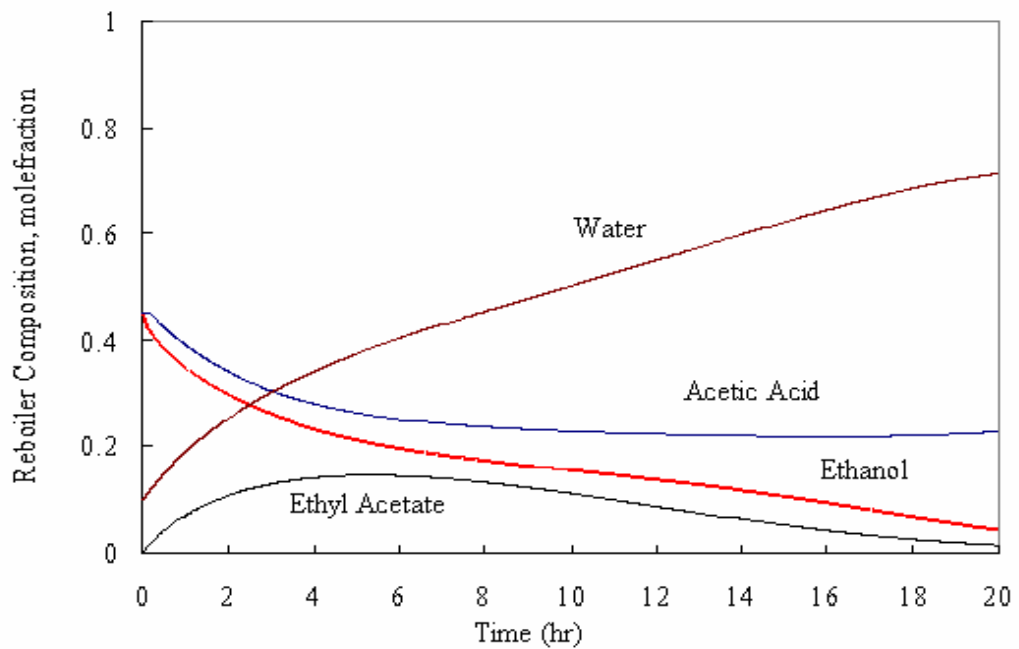
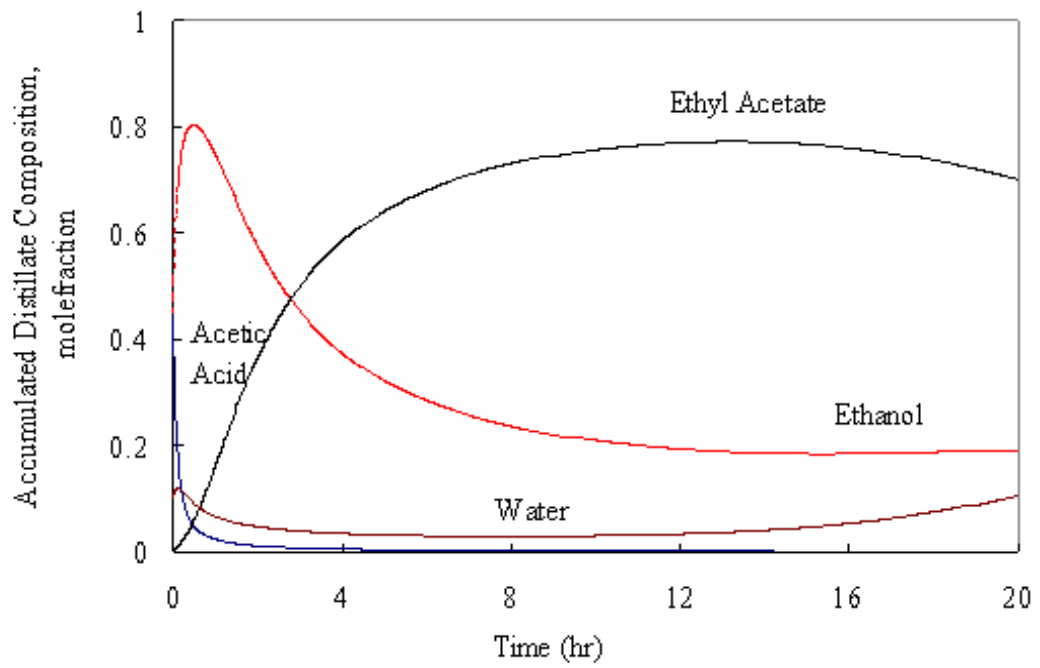


Figure 6.4 Composition Profile using Time Interval (NCI=1)

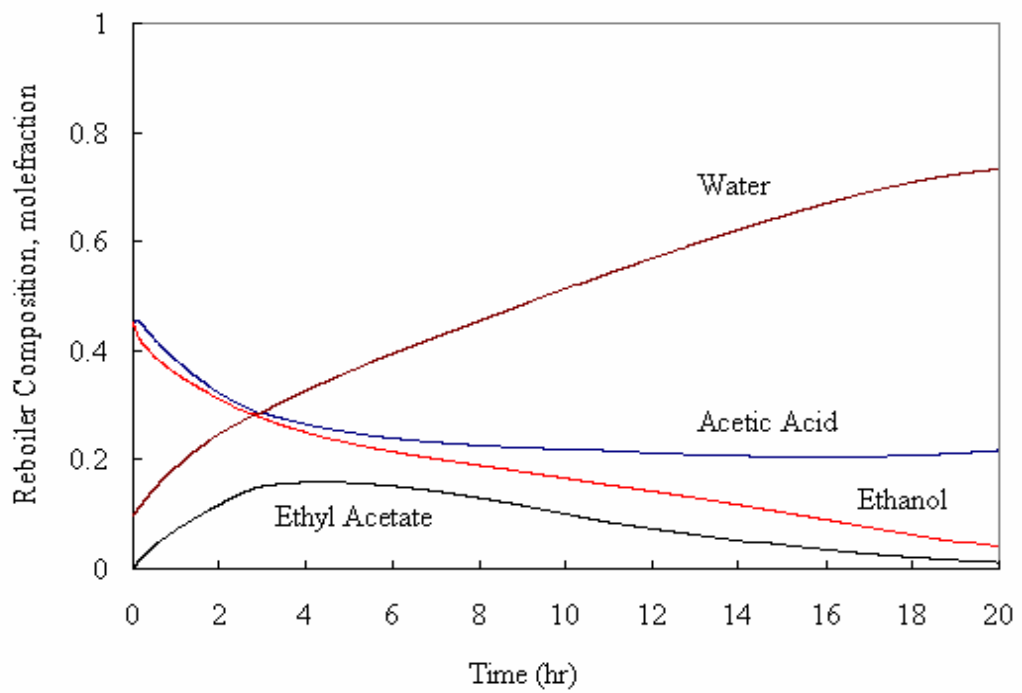
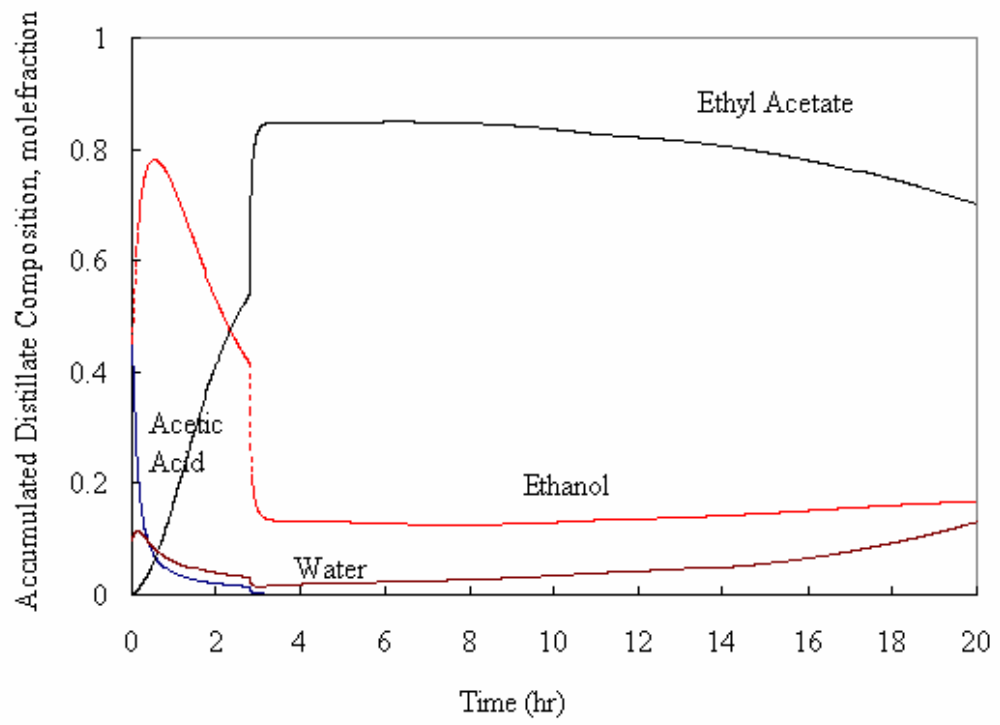


Figure 6.5 Composition Profile for Multi Reflux Ratio ( $NCI = 3$ )

### 6.4.3.3 Single Reflux Ratio (Piecewise Linear Type)

The optimisation results in terms of maximum conversion of ethanol to ethyl acetate, optimal reflux ratio profile and amount of ethyl acetate at different operation batch time using piecewise single linear strategy is shown in Table 6.8.

Table 6.8 Optimisation Results at Different Batch Time (Linear Reflux Ratio)

| $t_f$ , hr | Max. Conversion % | Opt. Reflux Ratio | D, kmol |
|------------|-------------------|-------------------|---------|
| 5          | 51.0              | 1.0- 0.0261t      | 0.83    |
| 7.5        | 59.5              | 1.0-0.0200t       | 1.43    |
| 10         | 65.9              | 1.0-0.0140t       | 1.80    |
| 15         | 71.2              | 1.0-0.0080t       | 2.19    |
| 20         | 74.9              | 0.983-0.003t      | 2.39    |

It can be seen from Table 6.8 that the column operates at total reflux at the initial time and then decreases with increase the operating time for up to batch time 15 hrs. The product amount achieved increases with increasing batch time. Figure 6.6 shows the reflux ratio profiles for each operation time.

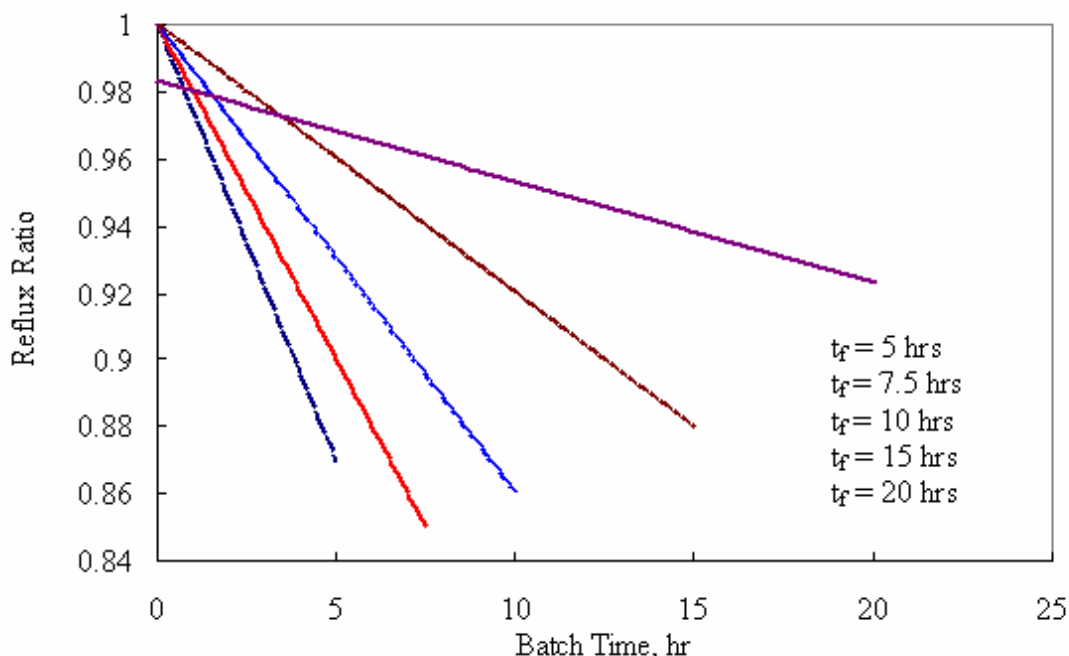


Figure 6.6 Reflux Ratio Profile vs. Batch Time (Linear Reflux Ratio) NCI = 1



#### **6.4.4 Comparison of the Results**

As a comparison, the optimisation results (Table 6.2 and Table 6.5) show that the conversion and the amount of product improve by about 3 % and 14 % respectively for the conventional column when time dependent reflux ratio profile is used. Note, for all cases in Table 6.5 an initial total reflux operation (first interval) was required before any product was withdrawn from the column due to remove all acetic acid from the top.

It can be seen from obtained results (Table 6.2 and Table 6.8) that the conversion slightly improved using single linear reflux strategy as a control variable compared to that using the single constant reflux profile. Moreover, distillate product achieved when the column operated using optimal linear reflux ratio profile is higher than that using constant reflux ratio strategy.

As a comparison the optimisation results between multi-reflux operation (Table 6.5) and that using linear reflux ratio (Table 6.8) shows that up to 10 hrs similar observation in terms of conversion and amount of ethyl acetate have been observed. After that more effective operation was found with multi-reflux than linear reflux strategy (allows more ethanol to react and therefore more acetate is achieved). Both cases required initial total reflux operation in the first interval (multi-reflux case) and in linear reflux case at the initial time. This is required to avoid loss of ethanol as much as possible.

### **6.5 Case Study 2: Improving the Maximum Conversion of Ethanol Esterification Process**

#### **6.5.1 Motivation**

In this Case study, the effect of water in feed on the maximum conversion for ethanol esterification reaction process is considered and the performance of batch reactive distillation is evaluated in terms of maximum conversion of ethanol to ethyl acetate. Again the optimisation problem is solved with varying batch time (between 5 to 25 hrs).

Piecewise constant reflux ratio (single interval) control variable optimised for different case studies.

### 6.5.2 Problem Specifications

For different cases, the amount of feed (kmol): <acetic acid, ethanol, ethyl acetate, water> is presented in Table 6.9. The other input data, such as total fresh feed, number of stages, vapour boil up rate, column holdup etc. are reported in Case Study 1 and were presented in Table 6.1.

Table 6.9 Amount of Feed (kmol) for Different Case Studies

| Component     | Base Case | Case 1 | Case 2 | Case 3 | Case 4 |
|---------------|-----------|--------|--------|--------|--------|
| Acetic Acid   | 2.25      | 2.50   | 2.00   | 2.00   | 2.00   |
| Ethanol       | 2.25      | 2.50   | 2.00   | 2.00   | 2.00   |
| Ethyl Acetate | 0.00      | 0.00   | 0.00   | 0.00   | 0.00   |
| Water         | 0.50      | 0.00   | 0.00   | 0.20   | 0.40   |
| Total         | 5.00      | 5.00   | 4.00   | 4.20   | 4.40   |

### 6.5.3 Results and Discussions

For each case, the optimisation results (maximum conversion and amount of ethyl acetate) are presented in Tables 6.10 and 6.11 respectively. Figure 6.6 shows the reflux ratio profiles for each case with different operation time.

Table 6.10 Maximum Conversion (%) at Different Batch Time

| $t_f$ | Base Case | Case 1 | Case 2 | Case 3 | Case 4 |
|-------|-----------|--------|--------|--------|--------|
| 5     | 50.1      | 52.2   | 52.4   | 51.4   | 50.4   |
| 7.5   | 57.8      | 60.0   | 60.4   | 59.4   | 58.3   |
| 10    | 63.1      | 65.2   | 65.8   | 64.8   | 63.7   |
| 15    | 69.9      | 72.0   | 72.7   | 71.7   | 70.6   |
| 20    | 74.2      | 76.8   | 76.6   | 75.7   | 74.8   |
| 25    | 76.9      | 78.8   | 79.2   | 78.3   | 77.4   |

Table 6.11 Amount of Ethyl Acetate at Different Batch Time

| $t_f$ | Base Case | Case 1 | Case 2 | Case 3 | Case 4 |
|-------|-----------|--------|--------|--------|--------|
| 5     | 0.15      | 0.36   | 0.30   | 0.22   | 0.15   |
| 7.5   | 1.05      | 1.37   | 1.20   | 1.09   | 1.00   |
| 10    | 1.61      | 1.99   | 1.68   | 1.59   | 1.50   |
| 15    | 2.14      | 2.52   | 2.07   | 2.01   | 1.96   |
| 20    | 2.36      | 2.75   | 2.25   | 2.20   | 2.15   |
| 25    | 2.50      | 2.88   | 2.34   | 2.30   | 2.26   |

As a comparison between Case 1 and Base Case (same amount of total feed) that more reactants leading to more reaction and hence increases in conversion and ethyl acetate. While comparison between Case 1 and Case 2 for same amount of the reactant but less amount of total feed in Case 2 show that the conversion is very similar but the amount of product (ethyl acetate) is less due to less availability of reactant.

A comparison between Case 2 and Case 3 (same amount of reactant but small quantity of water in Case 3) might trigger reaction to the left as soon as some acetate produced and hence low conversion and low acetate. Moreover the column operated at lower reflux ratio (Figure 6.7) in Case 2 (no water in the feed) compared to Case 3.

A comparison of the results between (Case 2, 3 and 4) more water in Case 4 (compared to Case 3) shows that further reduces conversion and amount of acetate was observed and the column needed to operate at higher reflux ratio. It can be concluded from the observation results that increasing amount of water in the feed will decrease both the conversion of ethanol to ethyl acetate and the distillate product. Further discussion in terms of productivity will be considered in the next Case study.

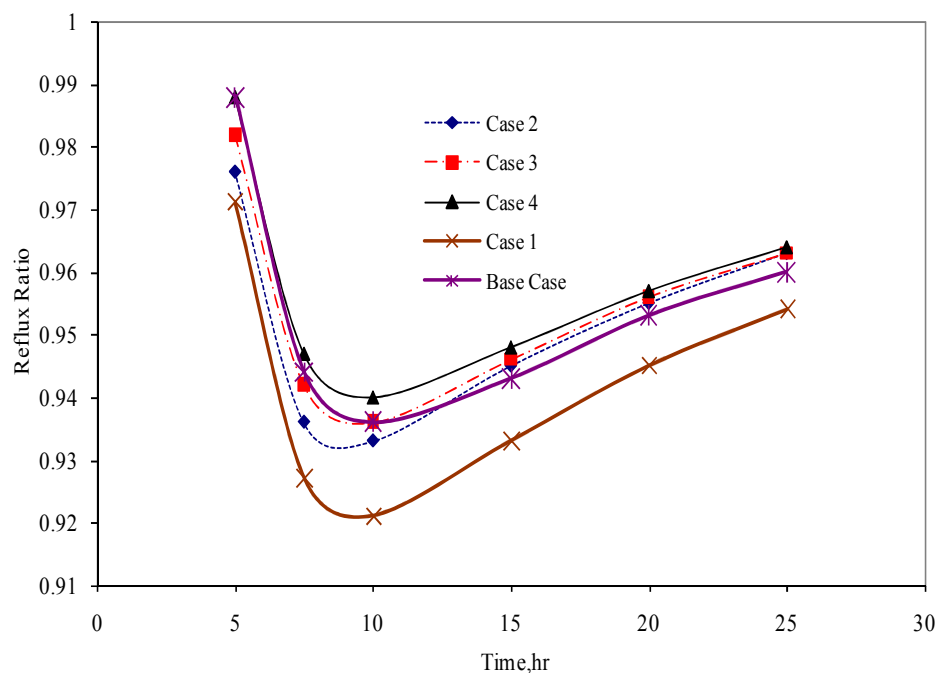


Figure 6.7 Reflux Ratio Profile vs. Batch Time

## 6.6 Case Study 3: Maximising Productivity of Ethyl Acetate

In this study, productivity ( $\text{Prod} = \text{amount of distillate} / \text{batch time}$ ) of ethyl acetate is maximised for different cases with varying amount of reactants in the feed (including the cases with no water in the feed). For this a dynamic optimisation problem is considered piecewise constant reflux ratio profile (with multiple time intervals) and batch times are optimised subject to product purity.

### 6.6.1 Problem Specification

In ethanol esterification, diluted feed is usually considered to reduce the cost of feedstock (Mujtaba and Macchietto, 1997). However, this can affect productivity and or profitability of the operation. In this work, five case studies are investigated with varying amount of water in the feed. Similar to Case studies 1 and 2 the column consists of 10 plates (including condenser and reboiler) and run with condenser vapour load of 2.5 kmol/hr. The total column holdup is 4 % of the initial feed and the maximum

reboiler capacity is 5 kmol. The specification of the feed is the same as that presented in Table 6.9 and is shown again in Table 6.12 for convenience. The given product purity of the main product is 0.7 molefraction of ethyl acetate for different cases (as before).

Table 6.12 Amount of Feed (kmol) for Different Case Studies

| Component     | Base Case | Case 1 | Case 2 | Case 3 | Case 4 |
|---------------|-----------|--------|--------|--------|--------|
| Acetic Acid   | 2.25      | 2.50   | 2.00   | 2.00   | 2.00   |
| Ethanol       | 2.25      | 2.50   | 2.00   | 2.00   | 2.00   |
| Ethyl Acetate | 0.00      | 0.00   | 0.00   | 0.00   | 0.00   |
| Water         | 0.50      | 0.00   | 0.00   | 0.20   | 0.40   |
| Total         | 5.00      | 5.00   | 4.00   | 4.20   | 4.40   |

### 6.6.2 Optimisation Problem

The optimization problem (*OP4*) (discussed in Chapter Four) is again presented below for the reader's convenience:

$$OP4 \quad \max_{R(t)} \quad Prod = \text{amount of distillate} / t_f \quad (6.10)$$

subject to :

$$\begin{aligned}
 x_{EtAc} &= x_{EtAc}^* \pm \varepsilon && \text{(Inequality constraint)} \\
 \text{and } f(t, x', x, u, v) &= 0 && \text{(Model Equation, equality constraint)} \\
 \text{with } f(t_0, x'_0, x_0, u_0, v) &= 0 && \text{(Initial condition, equality constraint)} \\
 \text{Linear bound on } R &&& \text{(Equality constraint)}
 \end{aligned}$$

### 6.6.3 Results and Discussions

Optimisation results in terms of optimal reflux ratio, optimal batch time, amount of product achieved and maximum productivity for each case study using single (scenario 1) and multi time interval (scenario 2) are presented below:

#### 6.6.3.1 Single reflux ratio operation (Scenario 1)

Table 6.13 presents the optimisation results in terms of optimal reflux ratio, optimal batch time, amount of product achieved and maximum productivity for all the case studies using single reflux ratio.

Table 6.13 Summary of the results Scenario 1 ( $NCI = 1$ )

| Case      | $t_f$ , hr | R     | D, kmol | Prod.1 |
|-----------|------------|-------|---------|--------|
| Base Case | 10.21      | 0.935 | 1.63    | 0.16   |
| 1         | 9.60       | 0.920 | 1.92    | 0.20   |
| 2         | 9.12       | 0.932 | 1.55    | 0.17   |
| 3         | 9.51       | 0.936 | 1.52    | 0.16   |
| 4         | 9.90       | 0.940 | 1.49    | 0.15   |

According to the optimal amount of product (ethyl acetate) produced in Case Study 2, the productivity (kmol/hr) has been calculated for each case at different batch time and shown in Table 6.14.

It can be seen from Table 6.14 that maximum productivity have been achieved for batch time 10 hrs for all the cases which are with the line of the optimisation results showed in Table 6.13. Although, the maximum conversion problem (Case 2) shows higher batch time improves conversion and amount of product, but it does not focus on the production rate. The maximum productivity problem straightaway identifies the best productivity straightaway.

Table 6.14 Productivity Results (kmol/hr) at Different Batch Time (Case Study 2)

| $t_f$     | Base Case   | Case 1      | Case 2      | Case 3      | Case 4      |
|-----------|-------------|-------------|-------------|-------------|-------------|
| 5         | 0.03        | 0.07        | 0.06        | 0.04        | 0.03        |
| 7.5       | 0.14        | 0.18        | 0.16        | 0.15        | 0.13        |
| <b>10</b> | <b>0.16</b> | <b>0.20</b> | <b>0.17</b> | <b>0.16</b> | <b>0.15</b> |
| 15        | 0.14        | 0.17        | 0.14        | 0.13        | 0.13        |
| 20        | 0.12        | 0.14        | 0.11        | 0.11        | 0.11        |
| 25        | 0.10        | 0.12        | 0.09        | 0.09        | 0.09        |

### 6.6.3.2 Multi Reflux Ratio Operation (Scenario 2)

The optimisation results for all the case studies using multi reflux ratio are also shown in Table 6.15. It can be seen that in the first time interval, an initial total reflux operation was required for all cases. Increasing amount of water in the feed (Cases 2, 3, 5) leads to higher reflux ratio for the second time interval. Moreover the productivity decreases with increasing amount of water in the feed.

Table 6.15 Summary of the Results Scenario 2 ( $NCI = 2$ )

| Case      | $t_f$ , hr | $t_1, R_1$ | $R_2$ | D, kmol | Prod. 2 |
|-----------|------------|------------|-------|---------|---------|
| Base Case | 7.86       | 2.02,1.0   | 0.896 | 1.47    | 0.19    |
| 1         | 7.35       | 1.92,1.0   | 0.873 | 1.72    | 0.24    |
| 2         | 6.78       | 1.99,1.0   | 0.884 | 1.39    | 0.21    |
| 3         | 7.06       | 1.99,1.0   | 0.895 | 1.36    | 0.19    |
| 4         | 7.28       | 2.06,1.0   | 0.899 | 1.32    | 0.18    |

Table 6.16 gives the percent improvement (IP) in productivity for Scenario 2 compared to Scenario 1. It can be seen that the benefit of using multi reflux policy (scenario 2) is very clear and more effective operation.

Table 6.16 Percent Improvements in the Productivity

| Case | Base Case | 1    | 2    | 3    | 4    |
|------|-----------|------|------|------|------|
| IP % | 18.8      | 20.0 | 23.5 | 18.8 | 20.0 |

Note:  $IP = 100.0 * (Prod\ 2 - Prod\ 1) / Prod\ 1$

The optimisation results show that, increasing the amount of water in the feed leads to a reduction in the productivity of the distillate product. The results also show that the productivity of the desired product improves significantly when the column operates with multi-reflux policy.

## 6.7 Maximum Profitability for Fixed Product Demand

In this work, the optimal of design and operation of a conventional batch reactive distillation column is studied, where the market demand for the product is fixed in terms of total distillate product and its specification. For a given market demand, this work investigates how the design parameters (number of stages  $N$  and vapour load  $V$ ), operation parameters (e.g. reflux ratio  $R$ ; batch time,  $t_b$ ) and schedule in terms of number of batches  $N_B$  are to be adjusted to maximise a profit function. The capability (in terms of  $t_b$ ,  $N_B$ ) of the existing design to meet variable product demands is also investigated. Two cases are considered.

Case 1: To maximise profitability while optimising design and operating parameters.

Case 2: To study sensitivity of feed and product prices on the profitability, design and operation. Change in feed composition reflects the change in feed price.

### 6.7.1 Optimisation Problem

Optimisation Problem (OP3) (described in Chapter Four) is considered and represented here for the reader's convenience:

$$\begin{aligned}
 OP3 \quad & \max \quad \$P \\
 & V, R(t), t_b \hspace{15em} (6.11) \\
 \text{subject to :} & \\
 & x_{EtAc} = x_{EtAc}^* \pm \varepsilon \hspace{10em} (\text{Inequality constraint}) \\
 & PD = D_1(V, R, t_b) \times N_B \hspace{10em} \text{Fixed} \\
 & \text{and } f(t, x', x, u, v) = 0 \hspace{10em} (\text{Model Equation, equality constraint}) \\
 & \text{with } f(t_0, x'_0, x_0, u_0, v) = 0 \hspace{10em} (\text{Initial condition, equality constraint}) \\
 & \text{Linear bound on } R \hspace{10em} (\text{Inequality constraint})
 \end{aligned}$$

### 6.7.2 Case 1

#### 6.7.2.1 Specification

In previous case studies (section 6.4-6.6) the column consists of 10 plates (including reboiler and a total condenser). The amount of feed ( $B_0$ ) is 5 kmol. 4 % of the total feed charge is the total column holdup. 50 % of this holdup is taken as the condenser holdup and the rest is equally divided for the plate holdup. The feed to the still consists of a mixture <acetic acid, ethanol, ethyl acetate, water>, with composition [0.45, 0.45, 0.00, 0.10]. Plates, product accumulator and reboiler compositions are initialized to those of the feed compositions. The given product purity is 0.7 mole fraction of ethyl acetate.

#### 6.7.2.2 Profit Function and Product Demand

Profit function,  $\$P$  (\$/year) for ethanol esterification problem is defined (Mujtaba and Macchietto, 1997) as follows:

$$\$P(\$/yr) = (C_1 D_1 - C_2 B_0 - OC) \times N_B - ACC \hspace{10em} (6.12)$$



$$OC = \left( \frac{K_3 V}{A} \right) \times (t_b + t_s) \quad (6.13)$$

$$ACC = K_1(V)^{0.5}(N)^{0.8} + K_2(V)^{0.65} \quad (6.14)$$

$$N_B = \frac{(H / yr)}{(t_b + t_s)} \quad (6.15)$$

$$PD = D_1(V, R, t_b) \times N_B \quad (6.16)$$

Where,  $OC$  is operating cost (\$/batch),  $ACC$  is Annualised capital cost (\$/year),  $K_1 = 1500$ ;  $K_2 = 9500$ ;  $K_3 = 180$ ;  $A = 8000$ ; Set-up time ( $t_s$ ) = 0.5 hr;  $H = 8000$  hr/yr and  $PD$  is the total yearly product (kmol/yr).  $C_1 = 80$ ,  $C_2 = 22.45$  are the prices (\$/kmol) of the desired product and raw material respectively (taken from Mujtaba and Macchietto, 1997).

### 6.7.2.3 Results and Discussions

For a given column design (i.e. number of stages) the product demand ( $PD$ ) is varied (ranging from 700 to 1200 kmol/yr). For each  $N$ , the summary of the results in terms of optimum batch time (hr), vapour load (kmol/hr), reflux ratio ( $R$ ), number of batches ( $N_B$ ) and distillate product per batch ( $D$ ) are presented.

Table 6.17 presents the optimisation results for  $N = 8$ . It can be seen that, the optimal vapour load and reflux ratio increase while the batch time decreases with increasing product demand. The batch time has to decrease to increase the number of batches ( $N_B$ ) according to Equation (6.15) so that the required amount of product can be produced. Higher  $V$  leads to lower batch time (Miladi and Mujtaba, 2004). Table 6.17 also shows that the operating cost, annual capital cost increase with increasing  $V$ . The results clearly show that a maximum profit of 1414.4 (\$/year) achievable with an optimum  $V$  of 1.87 kmol/hr for product demand 900 kmol (shown in bold), the column with any other  $V$  ( $V > 1.87$ ) will not achieve the maximum profit but will achieve a lower profit

for increasing product demand, because a higher vapour load leads to increased operating and annual capital costs. Moreover the profit sharply decreased after product demand 1000 kmol and negative profit beyond demand of 1100 kmol/yr. OC and ACC increase as product demand and V increase.

Table 6.18 shows the summary of the results for each product demand and  $N = 9$ . The observation is similar to that for  $N = 8$  in terms of vapour load, reflux ratio and batch time. The maximum achievable profit of (2008.4 \$/yr) with an optimum V of 2.06 kmol/hr (Table 6.18) for 1000 kmol fixed demand of the product. The column with any other V ( $V > 2.060$ ) will not achieve the maximum profit but will achieve a lower profit with increased products. Similar trend (as Table 6.17) concerning OC and ACC has been observed.

Table 6.17 Summary of the Results with  $N = 8$

| PD         | $t_f$       | V           | R            | OC           | ACC            | $N_B$        | D           | \$P           |
|------------|-------------|-------------|--------------|--------------|----------------|--------------|-------------|---------------|
| 700        | 25.4        | 1.28        | 0.930        | 230.7        | 20122.4        | 308.8        | 2.27        | 988.4         |
| 800        | 22.1        | 1.56        | 0.934        | 280.6        | 22562.5        | 354.8        | 2.25        | 1332.1        |
| <b>900</b> | <b>19.4</b> | <b>1.87</b> | <b>0.938</b> | <b>337.8</b> | <b>25121.9</b> | <b>402.1</b> | <b>2.24</b> | <b>1414.2</b> |
| 1000       | 17.3        | 2.23        | 0.942        | 401.1        | 27829.3        | 450.7        | 2.22        | 1174.7        |
| 1100       | 15.45       | 2.64        | 0.946        | 475.5        | 30737.9        | 501.1        | 2.20        | 540.1         |
| 1200       | 13.96       | 3.12        | 0.951        | 559.0        | 33896.8        | 553.4        | 2.17        | -574.1        |

Table 6.18 Summary of the Results - ( $N = 9$ )

| PD          | $t_f$        | V           | R            | OC           | ACC            | $N_B$        | D           | \$P           |
|-------------|--------------|-------------|--------------|--------------|----------------|--------------|-------------|---------------|
| 700         | 25.71        | 1.21        | 0.926        | 217.4        | 20301.1        | 305.3        | 2.29        | 1216.2        |
| 800         | 22.30        | 1.46        | 0.930        | 262.9        | 22682.1        | 350.4        | 2.28        | 1717.0        |
| 900         | 19.66        | 1.75        | 0.934        | 314.7        | 25150.9        | 396.8        | 2.27        | 1999.7        |
| <b>1000</b> | <b>17.50</b> | <b>2.06</b> | <b>0.938</b> | <b>372.4</b> | <b>27740.7</b> | <b>444.4</b> | <b>2.25</b> | <b>2008.4</b> |
| 1100        | 15.71        | 2.43        | 0.942        | 437.2        | 30484.5        | 493.5        | 2.23        | 1685.2        |
| 1200        | 14.20        | 2.84        | 0.946        | 511.6        | 33404.6        | 544.3        | 2.20        | 995.2         |

For  $N = 10$ , Table 6.19 shows that the maximum profit (2244.8 \$/year) is achieved at product demand of ethyl acetate 1000 kmol with optimum  $V = 1.95$  kmol/hr and  $R = 0.934$ . The column with any other V ( $V > 1.95$ ) will not achieve the maximum profit but will achieve a lower profit with increased products.

Table 6.19 Summary of the Results - (N = 10)

| PD          | $t_f$        | V           | R            | OC           | ACC            | $N_B$        | D           | \$P           |
|-------------|--------------|-------------|--------------|--------------|----------------|--------------|-------------|---------------|
| 700         | 25.9         | 1.15        | 0.922        | 206.8        | 20557.0        | 303.0        | 2.31        | 1159.1        |
| 800         | 22.47        | 1.39        | 0.926        | 250.1        | 22916.9        | 347.6        | 2.30        | 1733.4        |
| 900         | 19.80        | 1.65        | 0.930        | 297.6        | 25351.5        | 393.3        | 2.29        | 2110.6        |
| <b>1000</b> | <b>17.63</b> | <b>1.95</b> | <b>0.934</b> | <b>351.2</b> | <b>27879.6</b> | <b>440.2</b> | <b>2.27</b> | <b>2244.8</b> |
| 1100        | 15.84        | 2.28        | 0.938        | 410.3        | 30529.0        | 489.6        | 2.25        | 2101.8        |
| 1200        | 14.33        | 2.65        | 0.942        | 478.0        | 33332.2        | 540.0        | 2.22        | 1621.6        |

For N = 11, Table 6.20 shows that the maximum profit (2072.0 \$/year) is achieved at product demand of ethyl acetate 1000 kmol with optimum V = 1.89 kmol/hr and R = 0.932. The column with any other V (V > 1.89) will not achieve the maximum profit but will achieve a lower profit with increased products.

Table 6.20 Summary of the Results - (N = 11)

| PD          | $t_f$        | V           | R            | OC           | ACC            | $N_B$        | D           | \$P           |
|-------------|--------------|-------------|--------------|--------------|----------------|--------------|-------------|---------------|
| 700         | 26.0         | 1.12        | 0.920        | 202.5        | 21465.0        | 302.3        | 2.32        | 855.1         |
| 800         | 22.58        | 1.35        | 0.924        | 242.6        | 23872.3        | 346.6        | 2.31        | 1456.2        |
| 900         | 19.91        | 1.60        | 0.928        | 295.1        | 26338.0        | 392.0        | 2.30        | 1877.7        |
| <b>1000</b> | <b>17.74</b> | <b>1.89</b> | <b>0.932</b> | <b>340.0</b> | <b>28866.3</b> | <b>438.5</b> | <b>2.28</b> | <b>2072.0</b> |
| 1100        | 15.95        | 2.20        | 0.936        | 395.8        | 31513.5        | 486.3        | 2.26        | 2014.6        |
| 1200        | 14.43        | 2.55        | 0.939        | 459.6        | 34286.5        | 535.7        | 2.24        | 1620.5        |

The maximum profit (\$/ year) profile for each of N is shown in Figure 6.8. The results show that higher N allows the column to operate at lower reflux ratio to produce almost constant D (distillate per batch) and on specification. Moreover, at low product demand and higher N more batch time is available. This decreases vapour load (V) and operating cost. Figure 6.8 also clearly shows that for each N, the column can only meet a certain demand to maximise the profit and then the profit will be lower for any other demand. Also one single column is not optimal for the whole range of product demand.

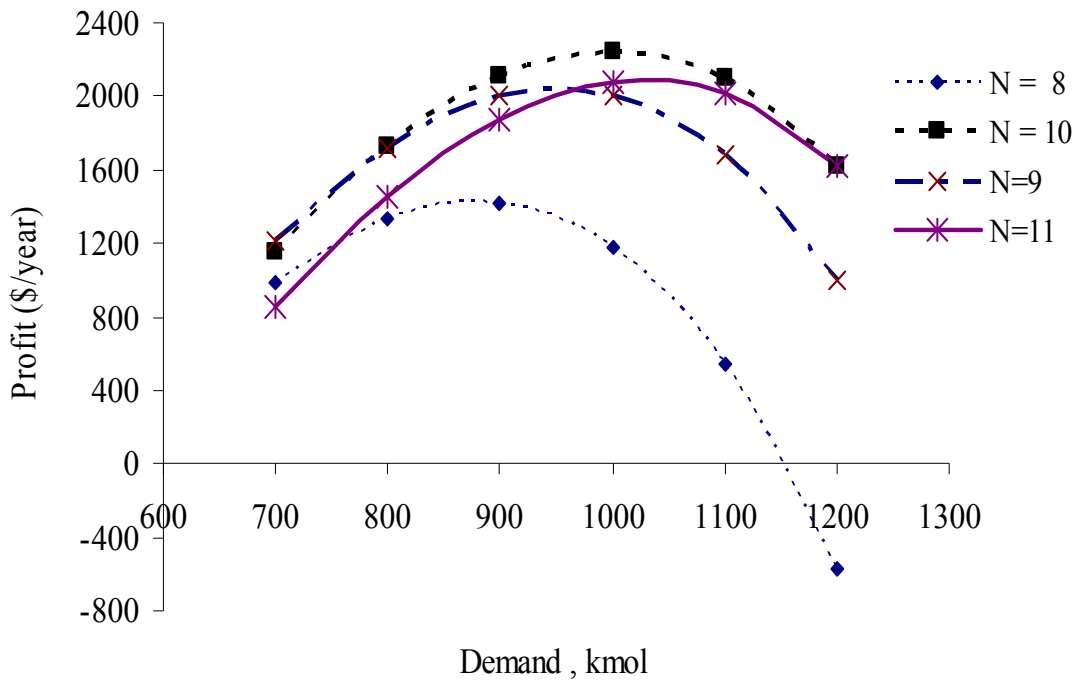


Figure.6.8 Profit vs. Demand

#### 6.7.2.4 Sensitivity Analysis

For product demand of 700 kmol/yr, comparison of the maximum profit using an existing column (e.g.  $N = 8$ ) with the profit which can be obtained using the optimal design ( $N = 9$ ,  $V = 1.21$  kmol/hr), operation ( $R = 0.93$ ,  $t_b = 25.7$  hr) and schedule (number of batches,  $N_B = 306$ ) shows 20 % more profit. And, for the product demand of 1000 kmol/yr, the profit increase is 80 %. This also shows the limit (or capability) of an existing column (i.e. fixed design) delivering products to a changing market demand. For example, it was not possible to make any operational and scheduling plan using the existing column (e.g.  $N = 8$ ) to meet product demand over 1100 kmol/yr profitably (Figure 6.8). The maximum possible profit (2244.8 \$/yr) can be achieved when the product demand is 1000 kmol/yr and a column with  $N = 10$  is operated with  $R = 0.95$  and  $V = 1.95$  kmol/hr.

It is interesting to note that with the given product specification (0.7 mole fraction of ethyl acetate in the distillate) it is less profitable to use the single column to produce products over 1000 kmol/yr. It can be also deduced from optimisation results that an increase in the value of N will lead to decrease in V (measure of external heat).

Figures 6.9, 6.10 and 6.11 show the plot of Annual Capital Cost (ACC), Operating Cost (OC) and yearly vapour load (VT) against the product demand (PD) for each N respectively. Annualised capital cost (ACC) for N = 9 to N = 11 is almost constant, while V (total) decreases significantly with N and so does the operating cost (OC). Energy consumption is thus minimised and the environmental impact is reduced.

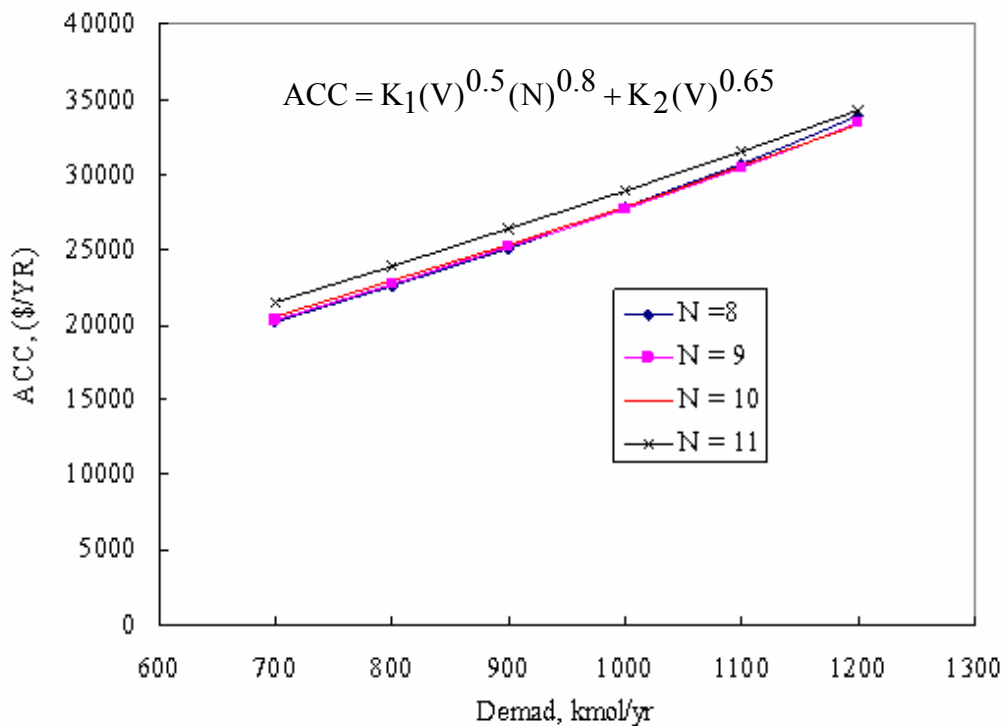


Figure 6.9 Annual Capital Cost vs. Demand

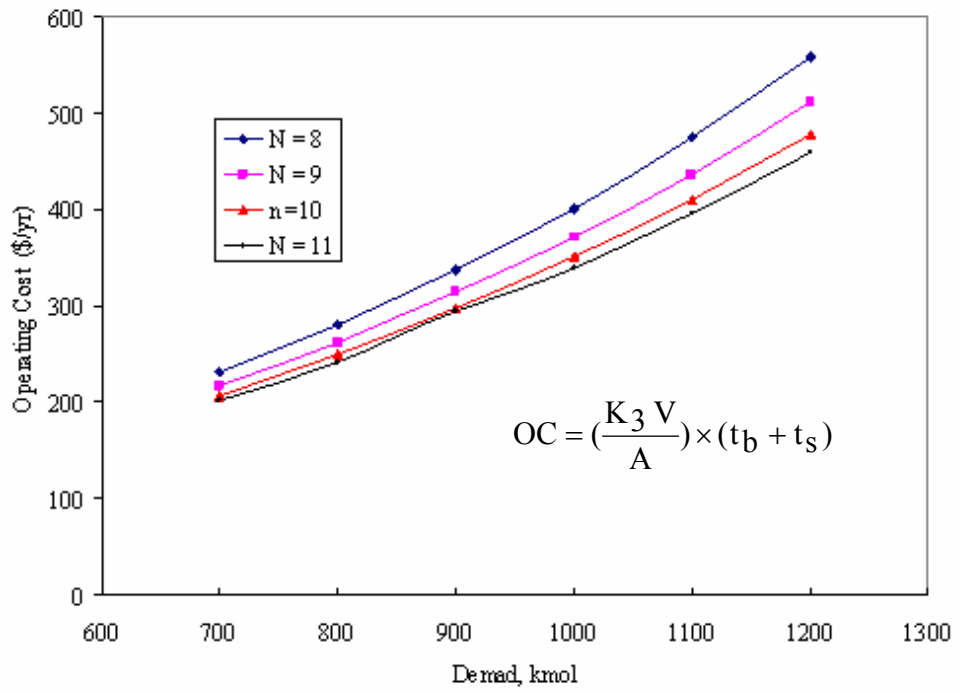


Figure 6.10 Operating Cost vs. Demand

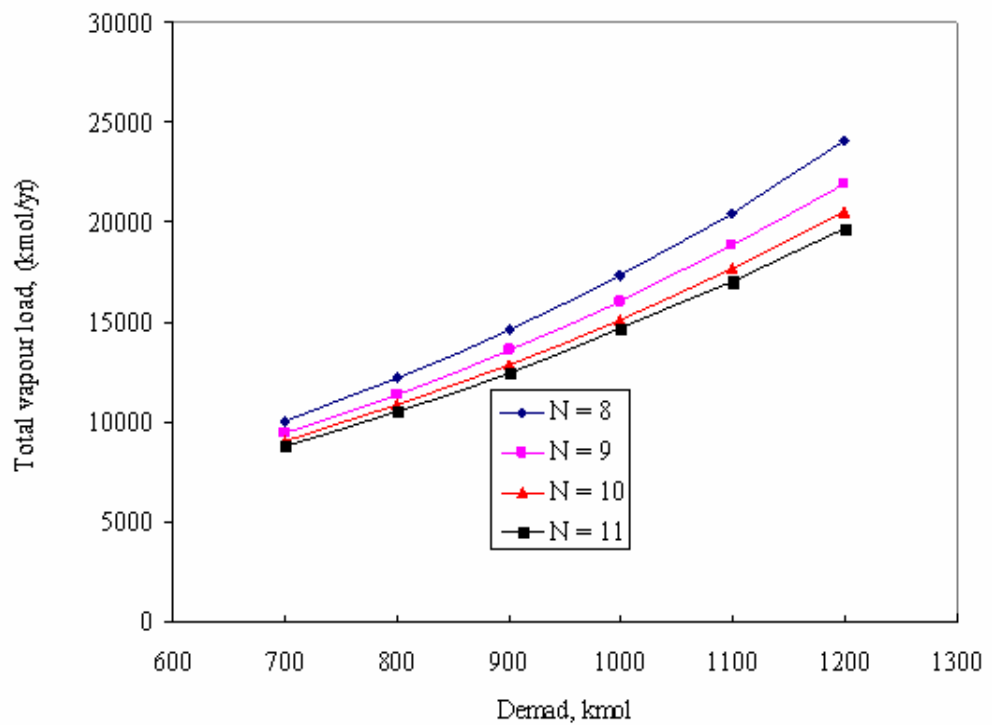


Figure 6.11 Total Vapour Load vs. Demand

Finally note, unlike the previous work (Diwekar and Madhavan, 1989 and Low and Sorensen, 2003 and 2004) the vapour load and the batch time are bounded by the product demand constraints.

### 6.7.3 Case 2: Sensitivity of Feed and Product Prices

Here, two feed conditions are considered: Feed 1 is composed of only the reactants (pure feed) and Feed 2 is composed of reactants as well as a small fraction of one of the reaction products (say water). The Feed 2 composition is same as that used in Case 1. Presence of water dilutes the feed but can cost less. The profit is maximised with fixed product demand ranging from 800 to 1200 kmol/year.

#### 6.7.3.1 Specifications

Again a 10-stage batch distillation column is considered. The total column holdup is 4 % of the initial feed (50 % is taken as the condenser hold up and the rest is equally divided in the plates) and the reboiler capacity is 5 kmol. The feeds (kmol) <Acetic Acid, Ethanol, Ethyl Acetate, Water> are: Feed 1 - <2.5, 2.5, 0.0, 0.0> and Feed 2 - <2.25, 2.25, 0.0, 0.5>.

For Feed 1, the sensitivity of feed and or product prices on the design, operation and profitability is carried out. Two scenarios are considered. In Scenario 1, the price of the feed is increased by 5% while the product price is kept constant. In Scenario 2, both feed and the product prices are increased by 5%.

The optimisation problem (OP3) is same as that used in the previous case. The cost parameters for ethanol esterification reaction are shown in Table 6.21, the feed prices have been assumed (based on inflation on the prices used by Mujtaba and Macchietto, 1997) and the price of the product was taken from Greaves *et al.* (2003).  $C_2$ , the raw material cost is calculated by:

$$C_2 = x_{\text{Acetic Acid}} \times \text{Cost}_{\text{Acetic Acid}} + x_{\text{Ethanol}} \times \text{Cost}_{\text{Ethanol}} \quad (6.17)$$

Table 6.21 Cost Parameters

|   | Feed 1 (pure feed) | Feed 2 (diluted feed) |
|---|--------------------|-----------------------|
| Acetic acid, \$/kmol                        | 50                 | 40                    |
| Ethanol, \$/kmol                            | 20                 | 18                    |
| C <sub>2</sub> = raw material cost, \$/kmol | 35                 | 26.1                  |
| Ethyl acetate at 70 % purity, \$/kmol       | 96                 | 96                    |

Note, the prices for Feed 2 are inflated to those used for Case1 section 6.7.2

### 6.7.3.2 Results and Discussions

Feed 1: The results in terms of optimal design, operation, operating cost, annualised capital cost, amount of distillate and the maximum profit (\$/yr) for each fixed product demand (ranging from 800 to 1200 kmol /yr) are summarized in Table 6.22. As before, the optimal vapour load (V) and reflux ratio (R) increase while the batch time (t<sub>b</sub>) decreases with increasing product demand and consequently leads to increased number of batches (N<sub>B</sub>). The maximum profit (5757.9 \$/yr) has been achieved for product demand of 1100 kmol/yr with optimum (V = 2.11 kmol/hr, R = 0.933, t<sub>b</sub> = 18.8 hr and N<sub>B</sub> = 414.5). Also as before, the operating cost and annual capital cost are directly proportional to increases in vapour load.

Table 6.22 Summary of the Results – Feed 1

| PD          | t <sub>b</sub> (hr) | V           | R            | OC           | ACC            | N <sub>B</sub> | D           | X %         | \$P           |
|-------------|---------------------|-------------|--------------|--------------|----------------|----------------|-------------|-------------|---------------|
| 800         | 26.49               | 1.29        | 0.921        | 231.3        | 20154.0        | 296.5          | 2.70        | 75.6        | 4556.8        |
| 900         | 23.36               | 1.52        | 0.924        | 275.0        | 22236.9        | 335.4          | 2.68        | 75.04       | 5203.1        |
| 1000        | 20.79               | 1.77        | 0.928        | 319.3        | 24312.6        | 375.7          | 2.66        | 74.5        | 5621.6        |
| <b>1100</b> | <b>18.80</b>        | <b>2.11</b> | <b>0.933</b> | <b>381.3</b> | <b>26926.3</b> | <b>414.5</b>   | <b>2.65</b> | <b>74.2</b> | <b>5757.9</b> |
| 1200        | 16.77               | 2.28        | 0.934        | 407.7        | 28167.4        | 463.3          | 2.59        | 72.5        | 5542.3        |

Feed 2: The results are summarised in Table 6.23. For each product demand comparison of the results with those in Table 6.22 clearly shows the effect of feed dilution on the design, operation and profitability. Although the maximum profit is achieved for the product demand of 1100 kmol/yr (same as Feed 1), feed dilution not only reduces the raw material costs but results in much higher profit for each product demand. For example, for product demand 800 kmol/yr, the profitability has improved by almost 70%. Note for Feed 2, the column needs to operate at higher reflux ratio but



with higher  $V$  and thus decreasing the batch time compared to those in Feed 1. This results in producing less amount of distillate (on specification) per batch and more batches in the production campaign.

Table 6.23 Summary of the Results – Feed 2

| PD          | $t_b$ (hr)   | $V$         | R            | OC           | ACC            | $N_B$        | D           | X %         | \$P           |
|-------------|--------------|-------------|--------------|--------------|----------------|--------------|-------------|-------------|---------------|
| 800         | 22.36        | 1.63        | 0.937        | 294.0        | 23135.5        | 350.0        | 2.29        | 71.2        | 7702.6        |
| 900         | 19.66        | 1.95        | 0.941        | 353.2        | 25743.9        | 396.8        | 2.27        | 70.6        | 8527.2        |
| 1000        | 17.48        | 2.32        | 0.945        | 418.3        | 28507.3        | 445.0        | 2.25        | 70.0        | 9002.3        |
| <b>1100</b> | <b>15.66</b> | <b>2.75</b> | <b>0.948</b> | <b>494.9</b> | <b>31468.0</b> | <b>494.9</b> | <b>2.22</b> | <b>69.1</b> | <b>9051.2</b> |
| 1200        | 14.13        | 3.24        | 0.952        | 585.0        | 34676.5        | 546.7        | 2.19        | 68.1        | 8595.4        |

Table 6.22 and 6.23 also show the calculated conversion (X %) for Feed 1 and Feed 2. It is interesting to note that in Case Study 2 (in section 6.5) the presence of water in the feed led to lower conversion (similar observation made in Table 6.23). However, as the dilution of feed with water reduces the price of the reactants it enhances the ultimate profitability of the operation. The results in terms of the conversion values shows that Feed 1 gives a higher conversion than Feed 2 and these observations are in line with the conclusion in the Case Study 2 (Section 6.5) as the presence of water in the feed will reduce the conversion. As both cases (Feed 1 and Feed 2) operated with fixed product demand therefore no comparison can be done with respect the productivity.

### 6.7.3.3 Price Sensitivity

The optimisation results of Scenario 1 (Feed 1: feed price increased by 5 %) are presented in Table 6.24. The optimal design and operation are found to be very close to that of Feed 1. Since feed prices are increased, it directly reduces the maximum profit for each case (almost by 60% compared to Feed 1). From the manufacturer's point view, the production target should be reduced to 1000 kmol/yr to make most money.

Table 6.24 Summary of the Results – Scenario 1 (5% Increase of Feed Price)

| PD          | $t_b$ (hr)   | V           | R            | OC(\$/year)  | ACC(\$/year)   | $N_B$        | D           | \$P(\$/year)  |
|-------------|--------------|-------------|--------------|--------------|----------------|--------------|-------------|---------------|
| 800         | 26.55        | 1.30        | 0.921        | 233.7        | 20256.1        | 295.8        | 2.70        | 1965.7        |
| 900         | 23.41        | 1.54        | 0.925        | 277.7        | 22364.9        | 334.6        | 2.69        | 2270.7        |
| <b>1000</b> | <b>20.87</b> | <b>1.80</b> | <b>0.929</b> | <b>325.7</b> | <b>24544.4</b> | <b>374.4</b> | <b>2.67</b> | <b>2341.6</b> |
| 1100        | 18.77        | 2.09        | 0.933        | 377.7        | 26812.8        | 415.1        | 2.63        | 2133.9        |
| 1200        | 16.95        | 2.39        | 0.935        | 430.9        | 28942.9        | 458.4        | 2.62        | 1591.6        |

The optimisation results of Scenario 2 (Feed 1: feed and product price increased by 5 %) are presented in Table 6.25. It is observed that the profit has been improved by 28 % compared to Feed 1 due to increase in product price and raw material prices. Also it reveals that the production target should remain the same as in Feed 1 (1100 kmol/year). Also similar observations are made in terms of the other optimisation parameters such as (V, R,  $t_b$ ).

Table 6.25 Summary of the Results - Scenario 2 (+5% Both Feed and Product Price)

| PD          | $t_b$ (hr)   | V           | R            | OC(\$/year)  | ACC(\$/year)   | $N_B$        | D           | \$P(\$/year)  |
|-------------|--------------|-------------|--------------|--------------|----------------|--------------|-------------|---------------|
| 800         | 26.55        | 1.30        | 0.921        | 233.6        | 20266.3        | 295.7        | 2.71        | 5804.1        |
| 900         | 23.41        | 1.54        | 0.925        | 277.7        | 22365.1        | 334.6        | 2.69        | 6589.7        |
| 1000        | 20.87        | 1.80        | 0.929        | 325.7        | 24544.3        | 374.4        | 2.67        | 7140.2        |
| <b>1100</b> | <b>18.60</b> | <b>2.01</b> | <b>0.931</b> | <b>372.6</b> | <b>26210.7</b> | <b>418.7</b> | <b>2.63</b> | <b>7370.8</b> |
| 1200        | 16.98        | 2.40        | 0.936        | 430.2        | 29068.6        | 457.7        | 2.62        | 7354.4        |

## 6.8 Dynamic Optimisation of Semi-batch Reactive Distillation Column

In this Case study, optimisation of semi-batch reactive distillation column for ethanol esterification reaction (catalysed) is presented based on a maximum conversion of ethanol to ethyl acetate. Two cases are studied. Case one uses single control interval and Case two uses two control intervals for reflux ratio. In addition to the initial feed of acetic acid and ethanol, acetic acid is fed to the column in a continuous mode. The optimisation problem is solved with varying batch time (between 7.5 to 20 hrs) to maximise the conversion while optimising the reflux ratio and the acetic acid feed rate subject to satisfaction of given ethyl acetate purity specification in the distillate product.

As the column is fully charged initially, flooding condition is imposed as a constraint to avoid column flooding due to additional continuous feeding of acetic acid.

In this case study the column has 10 stages (reboiler, eight plates and condenser). The other specifications are presented in Table 6.1. During the operation, acetic acid is fed in a continuous mode in stage 9 (stages counted from top to bottom).

### 6.8.1 Optimisation Problem

The optimisation problem can be described as:

*Given:* the column configuration, the feed mixture, condenser vapour load, a separation task (i.e. achieve the product with purity specification for a key distillate component) and the batch time.

*Determine:* the optimal reflux ratio profile  $R(t)$ , and acetic acid flow rate,  $F(t)$

*So as to maximize:* the conversion.

*Subject to:* equality and inequality constraints

Mathematically the optimization problem (OP5) can be represented as:

$$OP5 \quad \max_{R(t), F(t)} X \quad (5.18)$$

*subject to :*

$$x_{EtAc} = x_{EtAc}^* \pm \varepsilon \quad (\text{Inequality constraint})$$

$$F^l \leq F \leq F^u \quad (\text{Inequality constraint})$$

$$\text{and } f(t, x', x, u, v) = 0 \quad (\text{Model Equation, equality constraint})$$

$$\text{with } f(t_0, x'_0, x_0, u_0, v) = 0 \quad (\text{Initial condition, equality constraint})$$

#### 6.8.1.1 Operation Constraints

The feed mixture is charged in the reboiler to its maximum capacity at the beginning of the process. For a given condenser vapour load  $V$  if the reflux ratio  $R$  (which governs the distillate rate,  $L_D$ , kmol /hr) and the feed rate  $F$  (kmol/hr) are not carefully controlled, the column will be flooded. The reboiler will overflow and will push the liquid up the column which will disturb the column hydraulics. The following constraint must be satisfied to avoid column flooding (Mujtaba, 1999).

$$L_D \geq F \quad (5.19)$$

Where  $L_D = V(1 - R)$ . This leads to  $R \leq 1 - \left(\frac{F}{V}\right)$  and  $R_{max} = 1 - \left(\frac{F}{V}\right)$

## 6.8.2 Results and Discussions

### 6.8.2.1 Case 1: (NCI = 1)

Table 6.26 presents the optimisation results in terms of optimal reflux ratio and acetic acid feed for Case 1 (NCI = 1). Table 6.26 shows that higher reflux ratio for batch time 7.5 hrs is required to satisfy the product (ethyl acetate) purity specification (0.7 mole fraction) and then falls as the available batch time increases. With larger batch times, more products are produced by reaction and separation becomes easier (hence lower reflux ratio). Finally when the batch time is increased; high reflux ratio is required again to achieve products at given purity.

Table 6.26 Optimal Reflux Ratio and Acetic Acid Feed (NCI = 1)

| $t_f$ , hrs     | 7.5   | 10    | 15    | 20    |
|-----------------|-------|-------|-------|-------|
| R               | 0.935 | 0.926 | 0.935 | 0.947 |
| F, kmol (total) | 1.20  | 1.90  | 2.40  | 2.60  |

Figure 6.12 and Figure 6.13 show the optimisation results in terms of maximum conversion and amount of distillate product (ethyl acetate). It can be noticed from these Figures that both the conversion and amount of ethyl acetate (kmol) increases with increasing batch time.

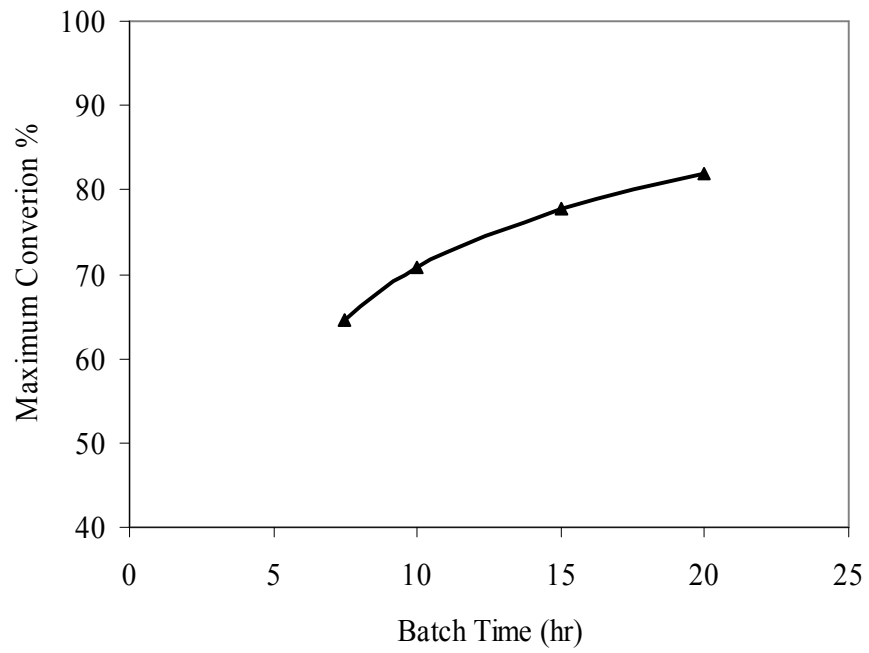


Figure 6.12 Maximum Conversion vs. Batch Time ( $NCI=1$ )

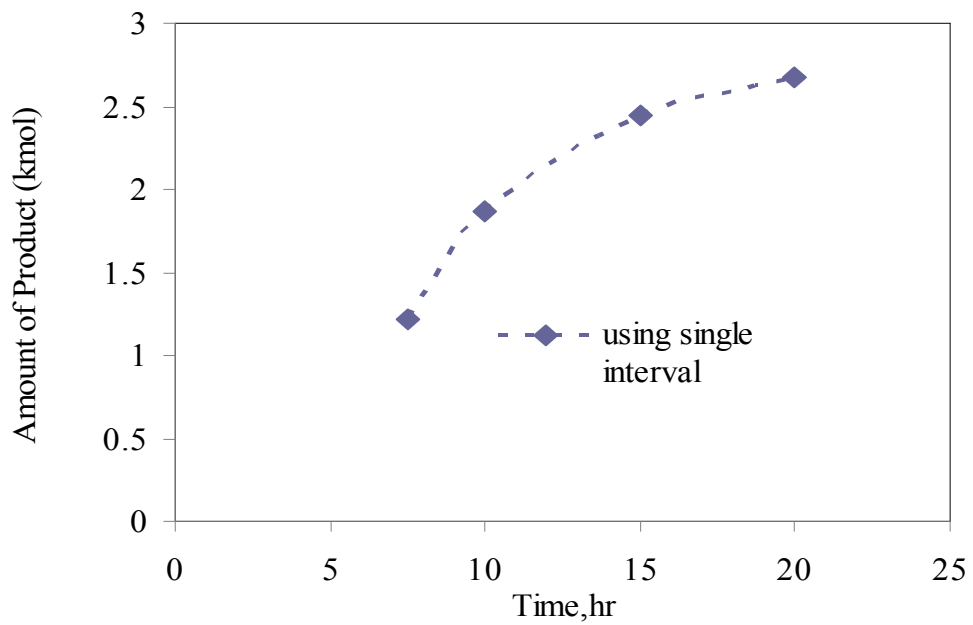


Figure 6.13 Amount of Distillate Product vs. Batch Time ( $NCI=1$ )

### 6.8.2.2 Case 2 ( $NCI = 2$ )

Table 6.27 shows the optimisation results in terms of maximum conversion of ethanol to ethyl acetate, optimal reflux ratio, and optimal length time for each interval, amount of product (kmol) for different batch time when time dependent reflux ratio profile is used ( $NCI = 2$ ).

Multiple reflux operation (Table 6.27) allows initial total reflux operation ( $R_1 = 1$ ) without any acetic acid ( $F_1 = 0.0$ ) feed (thus avoiding column flooding) but operates at comparatively lower reflux ratio with higher acetic acid feed in the second interval (again ensuring no column flooding) to maximise the conversion. It can be noticed from Table 6.27 that the amount of acetic acid added in the second period increases with the operation time of the column. Therefore it needs a longer time to remove all acetic acid from the top and leads to operate at higher reflux ratio as seen in the case when the column operated at 20 hrs.

Table 6.27 Optimal Reflux Ratio and Acetic Acid Feed ( $NCI = 2$ )

| $t_f$ | $t_1$ | $F_2, \text{kmol}$ | $R_1, R_2$ | $D, \text{kmol}$ | Max. Conversion % |
|-------|-------|--------------------|------------|------------------|-------------------|
| 7.5   | 1.44  | 1.95               | 1.0, 0.897 | 1.57             | 66.4              |
| 10    | 1.62  | 2.5                | 1.0, 0.901 | 2.10             | 73.3              |
| 15    | 2.30  | 3.0                | 1.0, 0.920 | 2.57             | 81.1              |
| 20    | 2.62  | 3.2                | 1.0, 0.936 | 2.80             | 85.5              |

Note:  $t_2 = t_f - t_1$ .

### 6.8.2.3 Comparison between Case 1 ( $NCI = 1$ ) and Case 2 ( $NCI = 2$ )

It can be seen from Figures (6.12 and 6.13) and Table 6.27 that the maximum conversion and distillate product (ethyl acetate) are improved by 4 % and 13 % respectively using two reflux ratio intervals compared to those obtained using one interval as a control variable. However, more acetic acid will be added when multi-reflux strategy is used as control variable (increasing by about 14 % compared with the single reflux ratio interval). Figure 6.14 show the amount of acetic acid feed added for both cases.

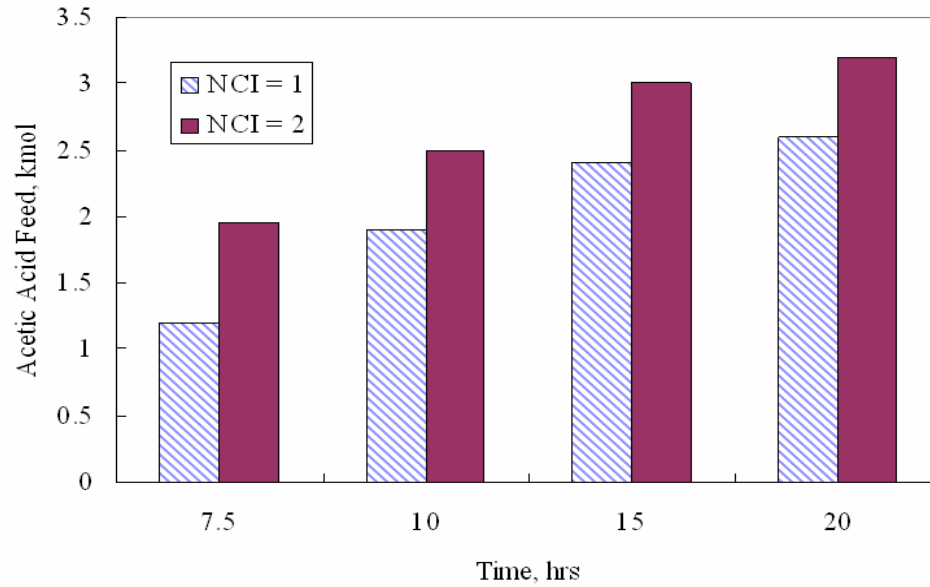


Figure 6.14 Acetic Acid Feed (Semi-continuous) vs. Time ( $NCI=1$  &  $NCI=2$ )

## 6.9 Comparison between Batch and Semi-batch Distillation Columns

### 6.9.1 With Respect to Maximum Conversion

Figure 6.15 shows the conversion vs. batch time for both the conventional and semi-batch distillation processes (using single and multi-reflux strategy). It can be noticed that semi-batch operation (single reflux) and semi-batch operation (multi-reflux) outperforms conventional operation by 11.4 % and 15.8 % respectively.

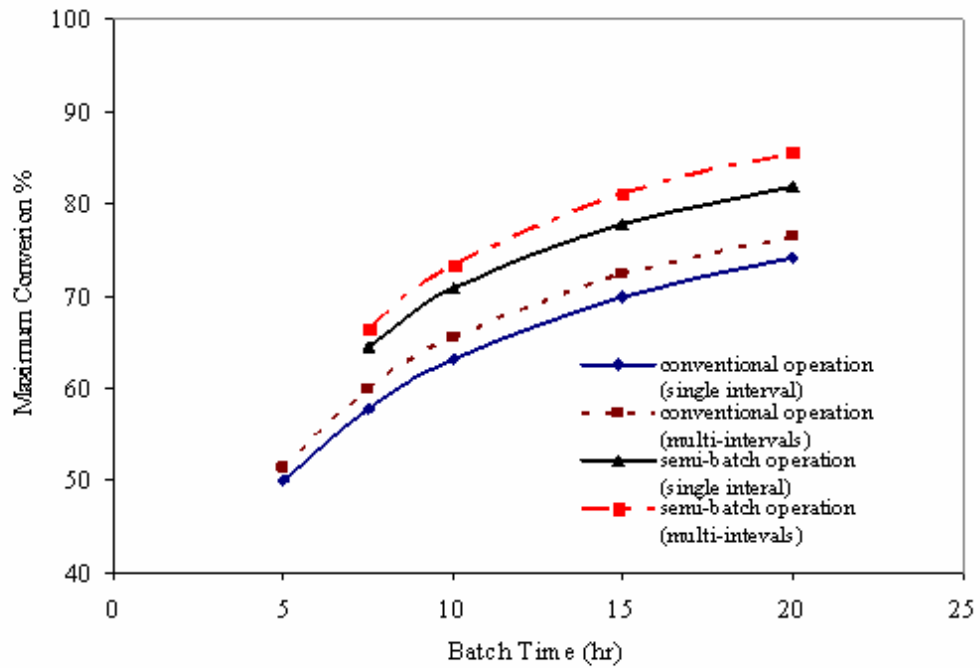


Figure 6.15 Maximum Conversion vs. Batch Time

### 6.9.2 With Respect to Amount of Distillate Product

Figure 6.16 shows the corresponding amount of distillate product (Ethyl acetate) for different batch times using batch and semi-batch operation modes using single and time dependent reflux ratio.

As a comparison, the distillate product (ethyl acetate) is improved by 12 % and 12.4 % using single and multi reflux ratio intervals respectively when the column operated on the semi-batch mode compared to those obtained when the column operated on the batch mode.

Furthermore, comparison of multi-reflux semi-batch operation with conventional single reflux operation (Figure 6.16) shows that semi-batch operation outperforms conventional operation by 29.7 % in terms of distillate product.



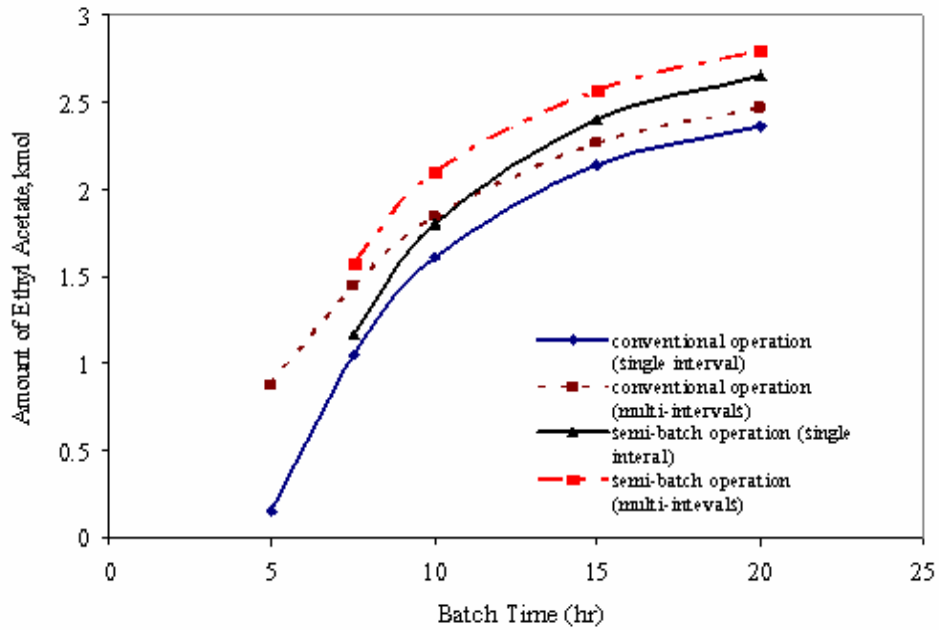


Figure 6.16 Amount of Ethyl Acetate vs. Batch Time

## 6.10 Conclusions

This chapter presented a study on optimal operation of batch reactive distillation operation involving an esterification of ethanol with acetic acid to produce ethyl acetate (main product) and water. A maximum conversion problem is considered in a conventional batch reactive distillation. Both piecewise constant (single and multi intervals) and linear reflux ratio (single time interval) profiles are considered as a control variables which are optimised. The effect of feed dilution on the system performance in terms of conversion has been considered. Maximising the productivity of ethyl acetate is carried out for a range of feed compositions. Piecewise constant reflux ratio profile (with single and multiple time intervals) is considered as a control variable.

This chapter also presented an optimal design and operation of a batch reactive distillation column with fixed yearly product demand (Ethyl Acetate) and strict product specifications. A profit function is maximised while the design parameters, (number of stages  $N$  and vapour load  $V$ ) and operation parameters (such as reflux ratio  $R$ ; batch time,  $t_b$ ) are optimised. Sensitivity of the feed and the product prices on the profitability, design and operation has been studied. The results indicate that the operation with diluted feed is more profitable compared to the case with undiluted feed. Also price increase in feed, although does not affect the design and operation significantly, it can lead to reduced production target to make a profitable operation.

Optimisation of semi-batch reactive distillation column for ethanol esterification system which has not yet been explored in the past is considered in this work and the performance of this process is evaluated in terms of maximum conversion of ethanol to ethyl acetate. A dynamic model for the process is developed which is incorporated into the optimisation framework.

Finally, comparison between batch and semi-batch reactive distillation process to produce ethyl acetate has been considered in terms of maximum conversion. The observation results shows that the significant improvement in the maximum conversion when the column operated in the semi-batch operation mode.

# Chapter Seven

## Optimisation of Methyl Lactate Hydrolysis Process

### 7.1 Introduction

This chapter addresses the performance of conventional and inverted batch reactive distillation columns in terms of minimum operating time for a hydrolysis reaction involving methyl lactate to produce lactic acid and methanol. A rigorous model for the system is developed within gPROMS. Product amount and purity are used as constraints. Reflux ratio for regular column and reboil ratio for inverted column is used as control variable. At the end of this Chapter, a comparison between both columns will be presented.

### 7.2 Lactic Acid Production

The industrial manufacture of lactic acid is carried out by chemical synthesis or by fermentation. It is widely used as a raw material for the production of biodegradable polymers, food, chemical and pharmaceutical industries (Kumar *et al.* (2006). The global market for lactic acid is set to reach 259 thousand metric tons by year 2012. It has received a significant amount of attention as a chemical with many applications and uses. Some the potential applications are illustrated in Table 7.1.

Table 7.1 Some commercial uses and applications of lactic acid and its salt

| Chemical industry   | Chemical feedstock  | Pharmaceutical industry  |
|---|---|--|
| <ul style="list-style-type: none"><li>• Descaling agents</li><li>• Ph regulators</li><li>• Green solvent</li><li>• Cleaning agents</li><li>• Slow acid release agent</li><li>• Metal complexing agent</li></ul> | <ul style="list-style-type: none"><li>• Propylene oxide</li><li>• Acetaldehyde</li><li>• Acrylic acid</li><li>• Propanoic acid</li><li>• Ethyl lactate</li><li>• Poly (lactic acid)</li></ul> | <ul style="list-style-type: none"><li>• Tablettings</li><li>• Mineral preparations</li><li>• Surgical sutures</li><li>• Dialysis solution</li><li>• Prostheses</li></ul> |

Esterification of lactic acid (from impure raw material) with methanol is carried out to obtain lactate ester which is then hydrolysed into lactic acid (Figure 7.1). this scheme has been proposed by several researchers in the past. Both continuous (Li *et al.*, 2005; Kumar *et al.*, 2006 b and Rahman *et al.*, 2008) and batch (Choi and Hong, 1999; Kim *et al.*, 2000; Kim *et al.*, 2002 and Kumar *et al.*, 2006 a) have been employed for the recovery of lactic acid. As seen from the previous researches that most of the work has been focused on experiments to recover lactic acid. Optimisation problem in terms of minimum batch time for hydrolysis of methyl lactate to lactic acid has not been considered in the past. Therefore, in this work, the performance of conventional and an inverted batch reactive distillation process in terms of minimum batch time is considered with the hydrolysis reaction of methyl lactate.

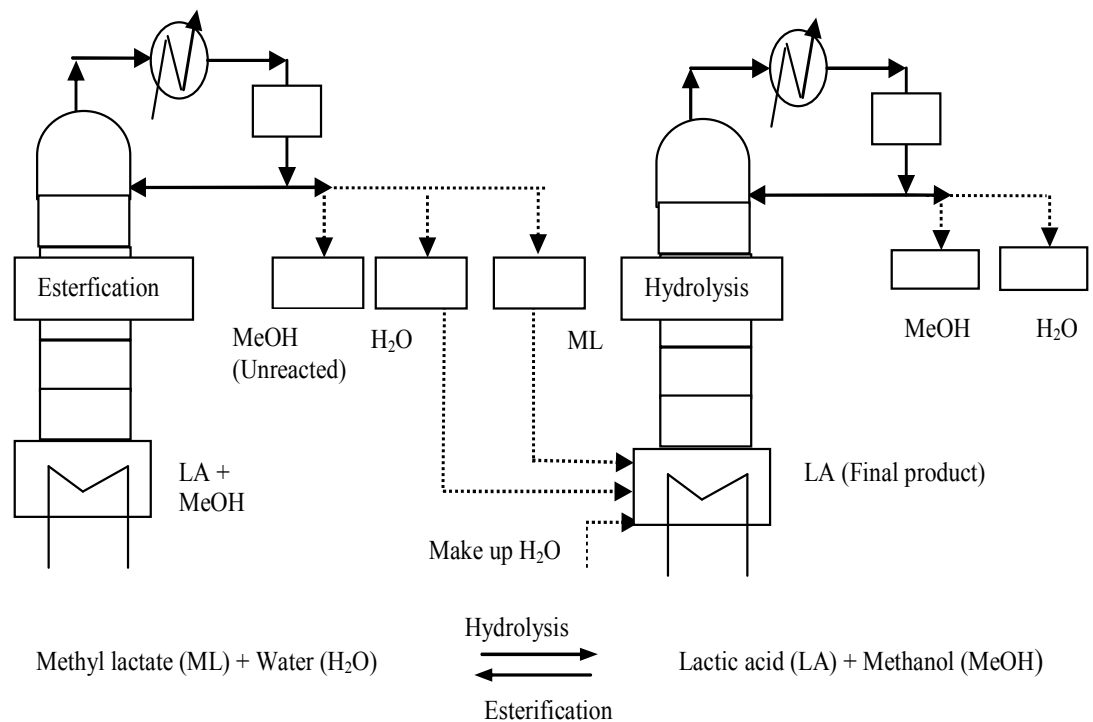


Figure 7.1 Batch Reactive Distillation Process for Lactic Acid Synthesis

## 7.3 Model Equations

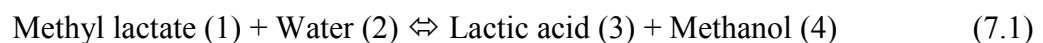
The model equations are presented in chapter four.

### 7.3.1 Reaction Kinetics

Seo and Hong (2000) developed the kinetic equation for esterification of lactic acid with methanol in the presence of an acid catalyst (DOWEX-50W) to use in the design of the reactive distillation process. They studied the effect of reaction temperature (232, 333, 343, 353 K) and catalyst loading on the reaction rate using CSTR under atmospheric pressure.

Hydrolysis of methyl lactate was carried out in a stirred tank batch reactor (CSTR) using Amberlyst 15 as a catalyst (Sanz, 2004). The effects of operating parameters such as temperature, catalyst loading and feed composition were investigated. Three kinetic models (a quasi-homogeneous (QH) model, Langmur-Hinshelwood (L-H) and Eley-Rideal (E-R) model) were tested to correlate the kinetic experimental data of methyl lactate hydrolysis and reverse reaction in order to obtain the general kinetic model.

The hydrolysis of methyl lactate can be expressed as follows:



B.P (K)            (417.15)            (373.15)            (490.47)            (337.15)

A quasi-homogeneous (QH) activity ( $a_i = \gamma_i x_i$ ) based kinetic model was taken from Sanz *et al.* (2004) and can be written as:

$$-r = 1.65 \times 10^5 \exp\left(\frac{-50.91}{RT}\right) a_1 a_2 - 1.16 \times 10^6 \exp\left(\frac{-48.52}{RT}\right) a_3 a_4 \quad (7.2)$$

### 7.3.2 Vapour-Liquid Equilibrium (VLE)

The vapour-liquid equilibrium relationship is given by:

$$y_i P = P_i^{sat} \gamma_i x_i \quad (7.3)$$

$P$  (kPa) is the total pressure,  $x_i$  and  $y_i$  are the composition of the liquid and vapour phases respectively,  $\gamma_i$  is the activity coefficient of component  $i$  which is calculated using UNIQUAC equation, The vapour pressure ( $P^{sat}$ ) of pure components has been obtained by using Antoine's equation. The UNIQUAC binary interaction parameters and Antoine parameters (Table 7.2) were taken from Sanz *et al.* (2003). Volume and area parameters were taken from the data bank of HYSYS and given Tables 7.2 and The UNIQUAC binary interaction parameters are given in Table 7.3.

Table 7.2 The Antoine equation parameters and the area and volume parameters for the UNIQUAC equation

| Component          | A       | B        | C        | r       | q       |
|--------------------|---------|----------|----------|---------|---------|
| Methyl Lactate (1) | 7.24147 | 2016.46  | -32.104  | 5.95005 | 5.01723 |
| Water (2)          | 7.0436  | 1636.909 | -48.230  | 0.92000 | 1.39970 |
| Lactic Acid(3)     | 7.51107 | 1965.7   | -91.021  | 5.27432 | 4.47617 |
| Methanol (4)       | 7.21274 | 1588.63  | -32.5988 | 1.4311  | 1.4320  |

Table 7.3 Binary interaction parameters for UNIQUAC Equation

|                             | $A_{ij}/K$ | $A_{ji}/K$ |
|-----------------------------|------------|------------|
| methanol ,water             | -192.6     | 325.0      |
| Methanol-methyl lactate     | 866.6      | -164.4     |
| Methanol - Lactic acid      | 322.59     | 17.14      |
| Water – methyl lactate      | -20.05     | 325.31     |
| Water- lactic acid          | -84.80     | -26.1      |
| methyl lactate- lactic acid | 367.14     | -302.09    |

The liquid and vapour enthalpies ( $h^L, h^V$ ) which constitute the energy balance equations are usually expressed as a function of liquid/vapour mole fractions, temperature and pressure. The physical and thermodynamic properties data and enthalpy equations for all pure components are given in Table 7.4 and Table 7.5.

Table 7.4 Physical and Thermodynamic Properties for Pure Components

|                       | Methyl Lactate (1) | Water (2) | Lactic acid (3) | Methanol (4) |
|-----------------------|--------------------|-----------|-----------------|--------------|
| $T_c$ (K)             | 584.0              | 647.3     | 627.0           | 512.6        |
| M.wt                  | 104.11             | 18.02     | 90.08           | 32.04        |
| $\lambda_1$ (KJ/kmol) | 38177              | 40651     | 54670           | 35290        |
| $T_b$ (K)             | 417.95             | 373.15    | 490.0           | 337.8        |

Table 7.5 Vapour Enthalpy Equations for All Pure Components

$$\begin{aligned}
 h_1^V &= 104.11 \times (0.0 - 2.9834 \times 10^{-1} T + 3.4219 \times 10^{-3} T^2 - 2.43350 \times 10^{-6} T^3 \\
 &\quad + 1.0223 \times 10^{-9} T^4 - 1.7705 \times 10^{-13} T^5) \\
 h_2^V &= 2.32 \times (0.1545871 \times 10^5 + 0.8022526 \times 10(T \times 1.8) - 0.4745722 \times 10^{-3}(T \times 1.8)^2 \\
 &\quad - 0.6878047 \times 10^{-6}(T \times 1.8)^3 - 0.1439752 \times 10^{-9}(T \times 1.8)^4) \\
 h_3^V &= 90.0784 \times (0.0 - 3.77592 \times 10^{-2} T + 2.41939 \times 10^{-3} T^2 - 1.38409 \times 10^{-6} T^3 \\
 &\quad + 4.8395 \times 10^{-10} T^4 - 7.68398 \times 10^{-14} T^5) \\
 h_4^V &= 2.32 \times (0.1174119 \times 10^5 + 0.7121495 \times 10(T \times 1.8) + 0.5579442 \times 10^{-2}(T \times 1.8)^2 \\
 &\quad - 0.4506170 \times 10^{-6}(T \times 1.8)^3 - 0.2091904 \times 10^{-10}(T \times 1.8)^4)
 \end{aligned}$$

Where:  $H^V$  in kJ/kmol and T is in °K.

The liquid phase enthalpies were calculated by subtracting the heat of vaporisation from the vapour enthalpies.

$$h_j^V = \sum y_i h_i^V$$

$$h_j^L = \sum x_i (h_i^V - \lambda_i)$$

$$\lambda_2 = \lambda_1 \left( \frac{[1 - Tr_2]}{[1 - Tr_1]} \right)^{0.38}, \quad Tr = \frac{T}{T_c} \quad (7.4)$$

Where  $\lambda_i$  is the latent heat of vaporisation (kJ/kmol) of component

## 7.4 Optimisation Problem

The performance of conventional batch reactive distillation column is evaluated in terms of minimising the operating time. Single and multiple reflux ratio strategies are used, yielding an optimal reflux ratio policy. For multiple reflux ratio policy, within each interval the reflux ratio (assumed piecewise) together with the switching time from one to other interval is optimized. Values of profile over time intervals concerned are assumed.

given: the column configuration, the feed mixture, vapour boilup rate, product purity, amount of bottom product.

determine: optimal reflux ratio which governs the operation

so as to minimise: the operation time.

subject to: equality and inequality constraints (e.g. model equations).

Mathematically, the Optimisation Problem (OP) can be represented as:

$$\begin{aligned}
 OP2 \quad & \min \quad t_f \\
 & R(t) \tag{7.5} \\
 \text{subject to :} \\
 & B = B^* \quad \text{(Inequality constraint)} \\
 & x_3 = x_3^* \pm \varepsilon \quad \text{(Inequality constraint)} \\
 & \text{and } f(t, x', x, u, v) = 0 \quad \text{(Model Equation, equality constraint)} \\
 & \text{with } f(t_0, x'_0, x_0, u_0, v) = 0 \quad \text{(Initial condition, equality constraint)} \\
 & \text{Linear bound on } R \quad \text{(Equality constraint)}
 \end{aligned}$$

Where  $B$ ,  $x_3$  are the amount of bottom product and composition of lactic acid at the final time  $t_f$ , (denotes that the  $B$  and  $x_3^*$  are specified).  $R(t)$  is the reflux ratio profile which is optimized and  $\varepsilon$  is small positive numbering the order of  $10^{-3}$ .

The amount of bottom product (lactic acid) and product purity are specified as constraints bounds in the optimization problem. In addition to the constraints mentioned the differential algebraic equations (DAE) process model act as equality constraints to the optimisation problem.

## 7.5 Case Study

### 7.5.1 Specification

The case study is carried out in a 10 stages column (including condenser and reboiler) with condenser vapour load of 2.5 (kmol/hr). The total column holdup is 4 % of the initial feed (50 % is taken as the condenser hold up and the rest is equally divided in the plates) and the reboiler capacity is 5 kmol. The feed composition <Methyl Lactate (1), Water (2), Lactic acid (3), Methanol (4)> is : <0.5, 0.5, 0.0, 0.0>.



## 7.5.2 Results and Discussions

A series of minimum time problems were solved at different values of product purity between 0.8 and 0.99 molefraction and the impact of time dependant reflux ratio policy on product quality and batch time are analysed.

### 7.5.2.1 Case 1: Optimisation Results using Single Time Interval ( $NCI = 1$ )

Table 7.6 summarises the optimum results (optimal reflux ratios, conversion of methyl lactate to lactic acid and minimum operating time) for each of product purity  $NCI = 1$ .

It can be seen from Table 7.6 that, the operating time increases gradually with increasing product purity until 0.9 molefraction. There is a sharp increase in batch time beyond purity of 0.9 molefraction. Beyond 0.9 there are still small amount of reactants (mainly in the reboiler) and a higher reflux ratio with longer operation time can achieve the product specification. As expected conversion (Table 7.6) increases with purity as higher reflux operation ensures retention of reactants (especially water as it is 2<sup>nd</sup> boiling component in the mixture) in the column longer leading to further reaction. It was not possible to achieve lactic acid at purity  $> 0.95$  using single reflux policy.

Table 7.6 Summary of Optimisation Results using  $NCI = 1$

| Purity of Lactic acid, $x_3^*$<br>(molefraction) | Minimum Batch Time,<br>$t_f$ (hr) | Reflux<br>Ratio | Conversion<br>% |
|--|-----------------------------------|-----------------|-----------------|
| 0.80   | 14.88                             | 0.933           | 77.69           |
| 0.85   | 23.28                             | 0.957           | 82.46           |
| 0.90   | 46.04                             | 0.973           | 86.92           |
| 0.925  | 135.4                             | 0.993           | 89.19           |
| 0.950*   | *                                 | *               | *               |

\*no results obtained

Figure 7.2 shows the accumulated distillate, condenser and reboiler profiles for product purity ( $x_{B^*} = 0.8$ ). It can be seen from Figure 7.2 that the composition of methanol rises

from zero reaches the maximum value (in both reboiler and accumulator) and then gradually falls to zero in the reboiler. The rise in mole fraction is due to high rate of reaction initially in the reboiler. Little water goes to the accumulator without any reaction when the column operated with lower reflux ratio. As batch time increases more lactic acid is produced in the reboiler and methanol is removed more quickly in the top. At the end of the reaction, unreacted water and methyl lactate can be separated (if needed) in an inverted distillation column (removing lactic acid first), as water the lightest component it follows upward in to the top of the column while methyl lactate (heavy component) may remain in the reboiler.

Figure 7.3 presents the accumulator, condenser and reboiler composition profiles for product purity 0.9. Initially the composition of water (2<sup>nd</sup> boiling component and a reactant) increases in accumulator (Figure 7.3A, same observation in Figure 7.2A) and then decreases. Methanol rises to the maximum values (in accumulator and reboiler) and then decreases in the reboiler as the operating time increases (due to the lower boiling component and product). Methyl lactate decreases with increasing time (due to consumption by reaction with water). At the end of operation no methanol was found in the reboiler and no lactic acid (heavier product) in the accumulator while some traces of unreacted feed (water and methyl lactate) were trapped in accumulator and in the reboiler (Figure 7.3C). In Figure 7.3B the methanol composition has the maximum values and all the water dropped in the reboiler while some methyl lactate remains in the condenser until about 35 hrs the water increases and therefore the methanol decreases and the remaining methyl lactate will fall down in the reboiler as unreacted feed.

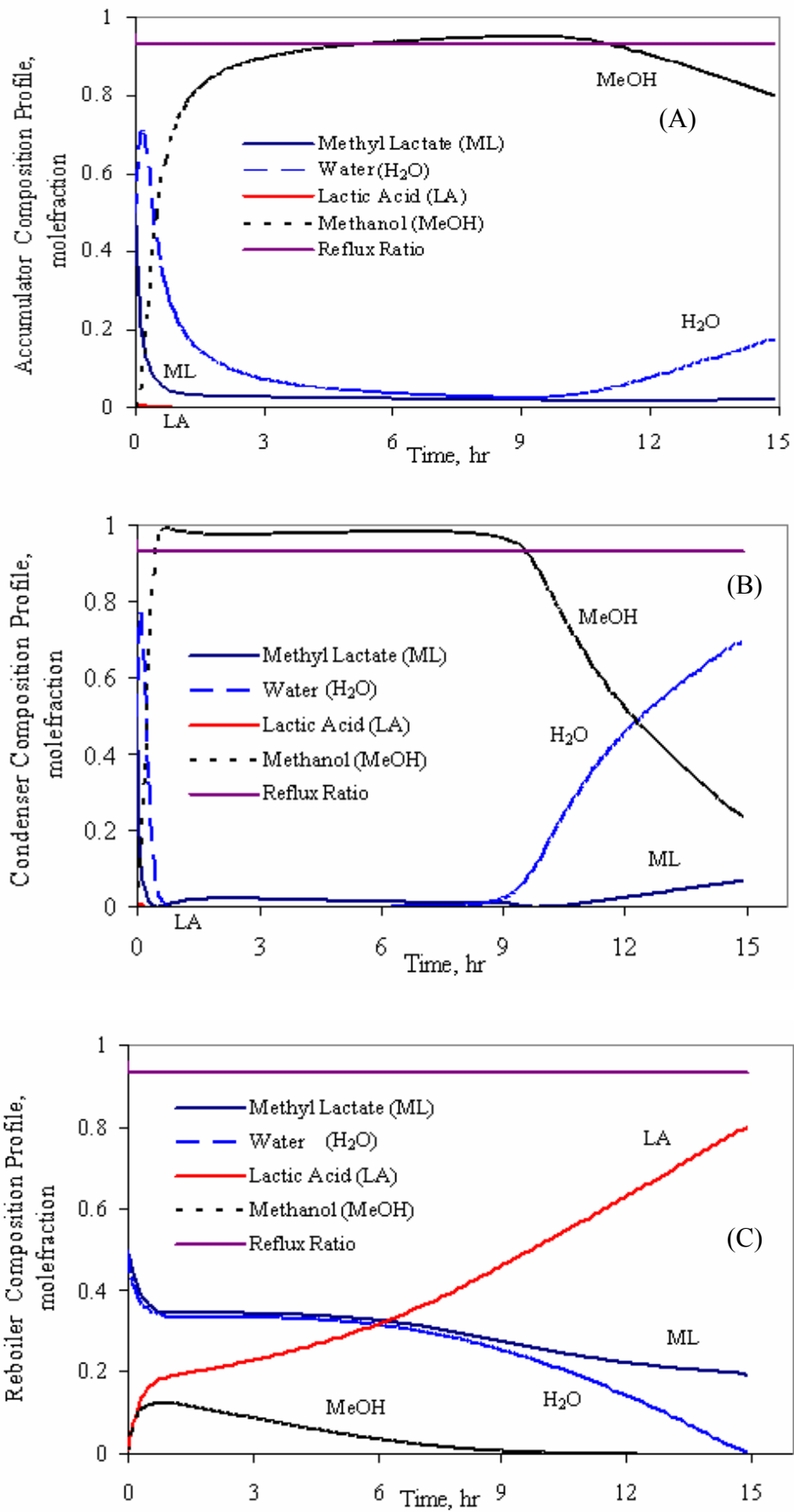


Figure 7.2 Composition and Reflux Ratio Profiles,  $NCI = 1$  ( $x_3^* = 0.8$ )  
 (A) Accumulator (B) Condenser (C) Reboiler

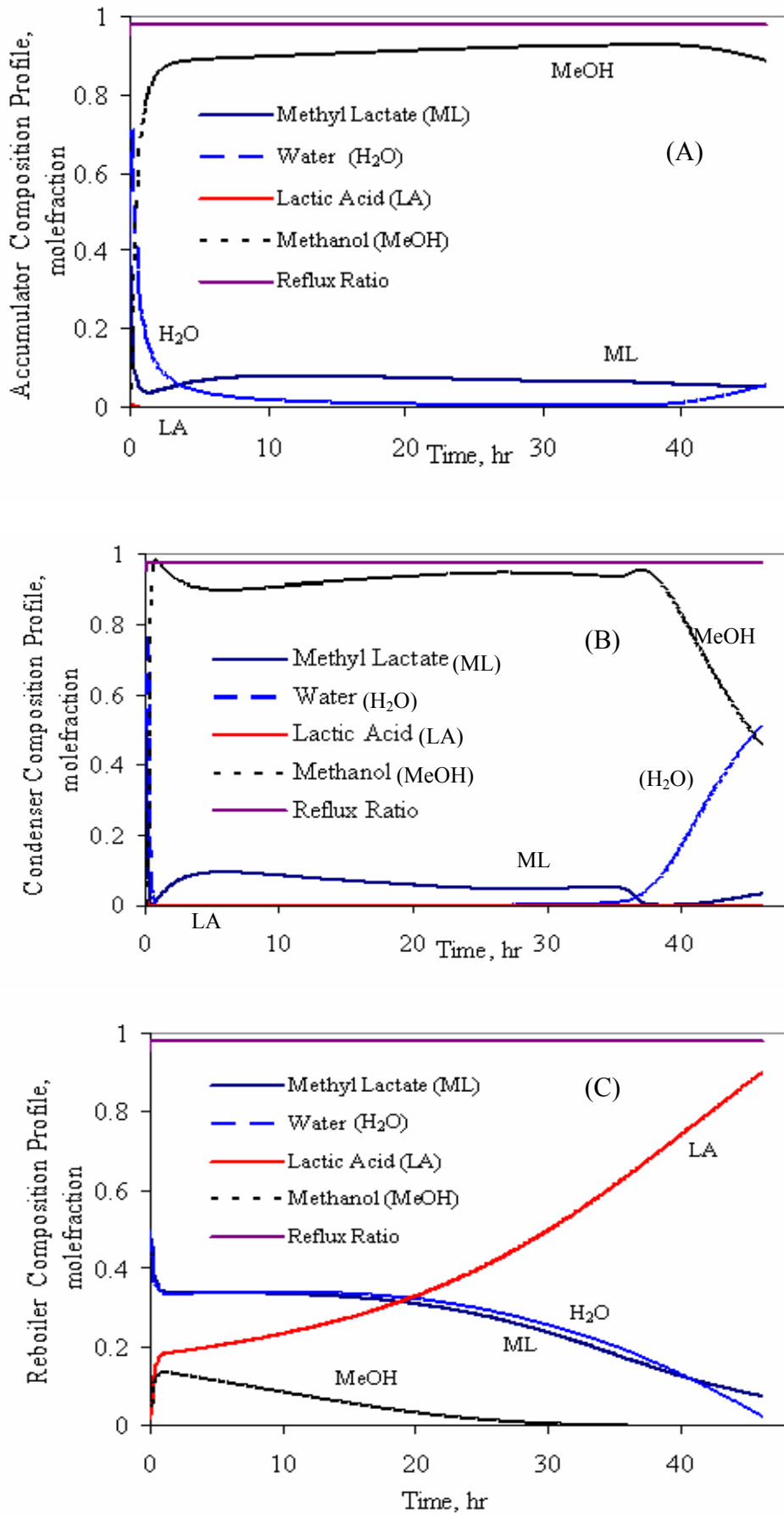


Figure 7.3 Composition and Reflux Ratio Profiles,  $NCI = 1$  ( $x_3^* = 0.9$ )  
 (A) Accumulator (B) Condenser (C) Reboiler

### 7.5.2.2 Case 2: Two time Intervals ( $NCI=2$ )

Two reflux ratio intervals strategy of operation is considered in this work. For each purity specification, Table 7.7 gives the optimisation results in terms of optimal reflux ratio, optimal operating time in each interval and total minimum operating time to achieve the product within the specifications. Table 7.7 also presents the conversion of methyl lactate to lactic acid. Figure 7.4 shows the accumulated distillate, condenser and reboiler composition profiles and optimal reflux ratio profile for product purity 0.8 molefraction, Figure 7.5 shows for product purity 0.90 and Figure 7.6 for product purity 0.95.

Table 7.7 Summary of the optimization results using 2 time intervals ( $NCI=2$ )

| $x_3^*$ | $t_1, R_1$   | $t_f, R_2$   | Conversion % |
|---------|--------------|--------------|--------------|
| 0.80    | 9.54, 0.914  | 13.72, 0.957 | 77.7         |
| 0.85    | 9.43, 0.937  | 19.04, 0.957 | 82.7         |
| 0.90    | 8.66, 0.922  | 23.95, 0.979 | 87.9         |
| 0.925   | 12.50, 0.950 | 31.41, 0.983 | 90.1         |
| 0.950   | 10.55, 0.935 | 44.73, 0.990 | 92.5         |
| 0.975   | *            | *            | *            |

\* No results obtained

For each purity specification, it can be seen from Table 7.7 that, the column operates at lower reflux ratio for the first interval to remove methanol as quickly as it is produced as a distillate product. In the second interval, higher reflux and higher batch time allows retention of methyl lactate and water in the reaction zone to have further reaction improving the conversion (see Figure 7.4 - 7.6, the reduction of water in the accumulator and retention of water in the reboiler are visible). Since there is no methanol in the reboiler and no lactic acid in the accumulator the reversible reaction (esterification) does not take place. Note, with 2 time intervals lactic acid with purity more than 0.95 molefraction was not possible.

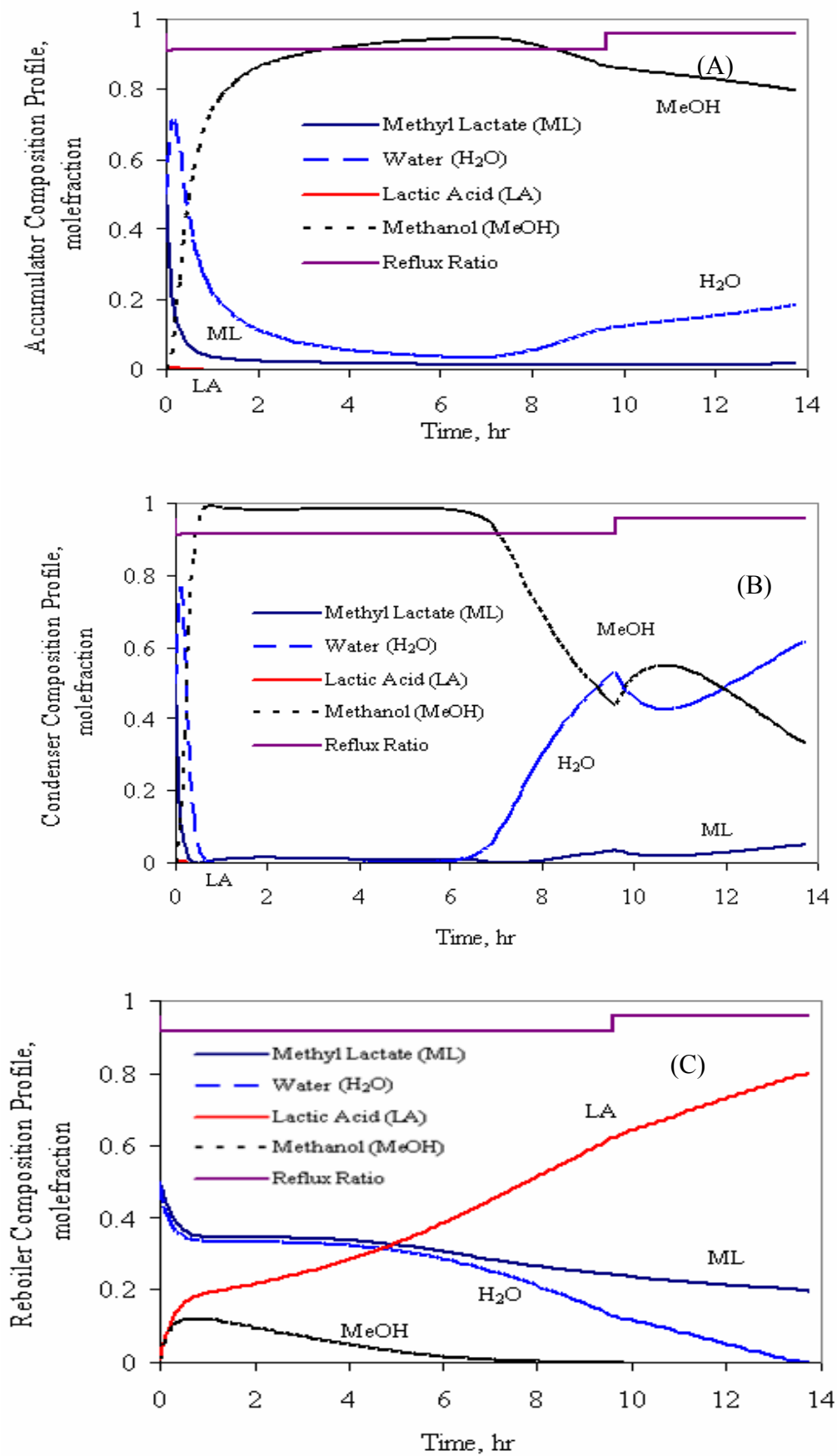


Figure 7.4 Composition and Reflux Ratio Profiles,  $NCI = 2$  ( $x_3^* = 0.8$ )

(A) Accumulator      (B) Condenser      (C) Reboiler

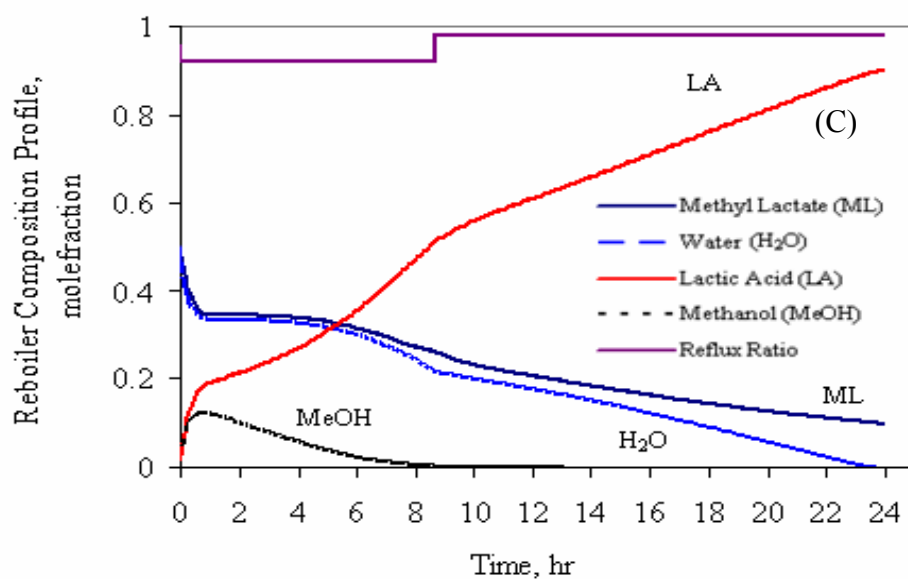
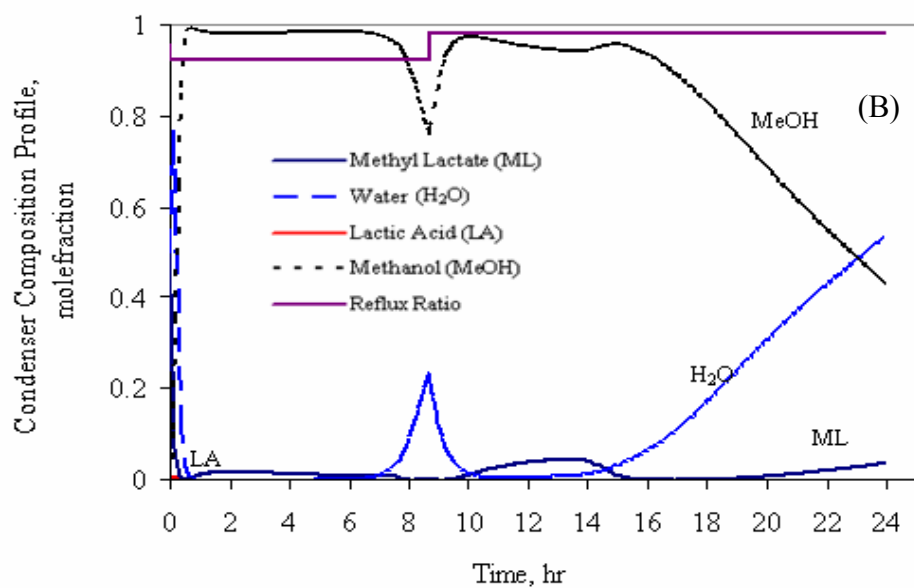
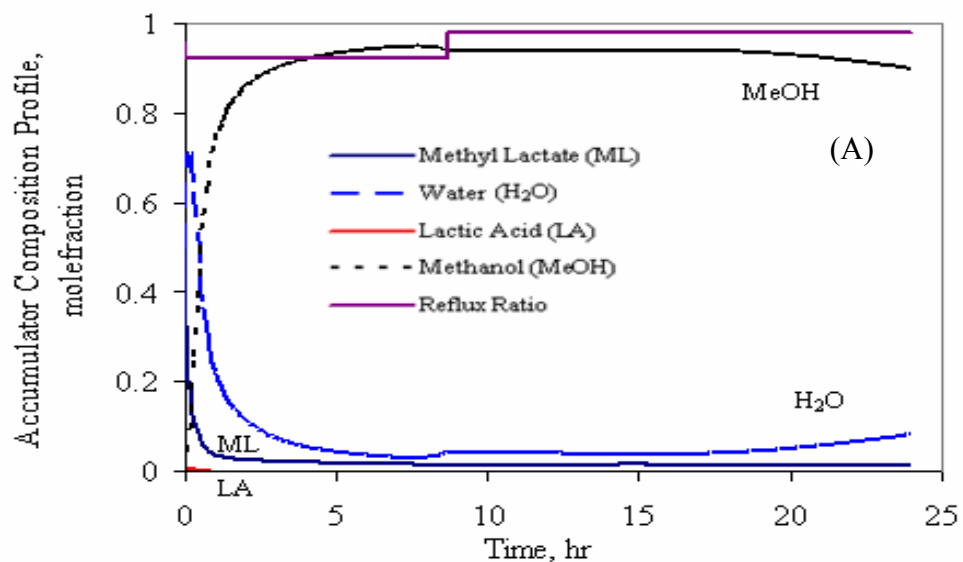


Figure 7.5 Composition and Reflux Ratio Profiles,  $NCI = 2$  ( $x_3^* = 0.90$ )  
 (A) Accumulator (B) Condenser (C) Reboiler

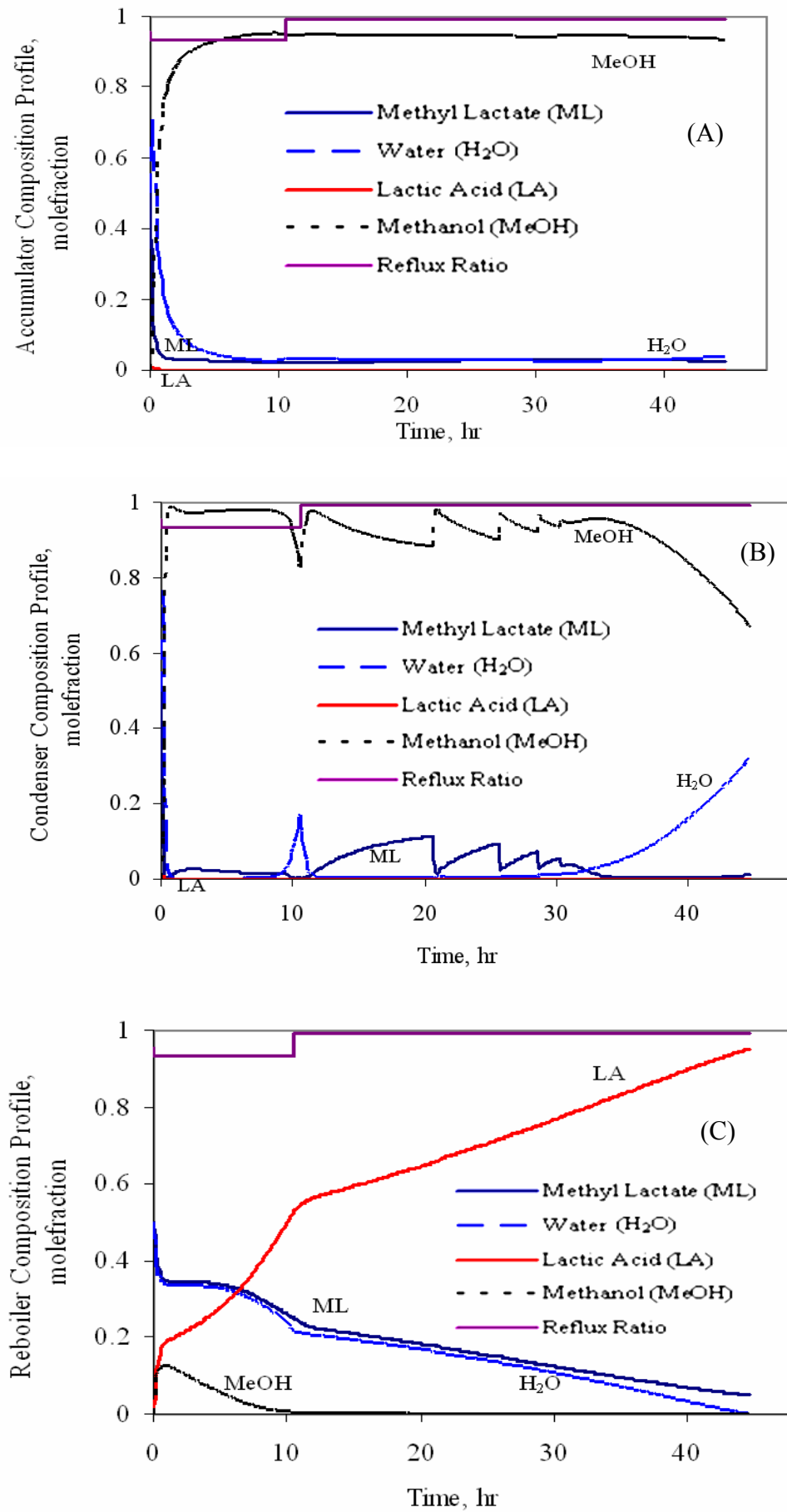


Figure 7.6 Composition and Reflux Ratio Profiles,  $NCI = 2$  ( $x_3^* = 0.95$ )  
 (A) Accumulator (B) Condenser (C) Reboiler



### 7.5.2.3 Case 3 (Three Time Intervals) $NCI = 3$ :

Three time intervals for the reflux ratio profile is considered here. For each case of product purity, the optimisation results for each interval in terms of optimal reflux ratio, optimal time interval and total minimum operating time are shown in Table 7.8. The conversion of methyl lactate into lactic acid is also shown in Table 7.8.

It is clearly seen from the results that, the column operated with lower reflux ratio for the first two intervals, to remove methanol. In the third interval higher reflux ratio is required to retain the reactants (especially water) in the reaction zone and to have further reaction and to meet the product specifications. The operating time gradually increases with increasing product purity of the product which is obvious.

Table 7.8 Summary of the optimization results ( $NCI= 3$ )

| $x_3^*$ | $t_1, R_1$   | $t_2, R_2$   | $t_f, R_3$   | Conversion. % |
|---------|--------------|--------------|--------------|---------------|
| 0.800   | 2.33, 0.813  | 2.00, 0.907  | 11.27, 0.945 | 77.8          |
| 0.850   | 7.49, 0.907  | 3.99, 0.971  | 16.72, 0.964 | 82.9          |
| 0.900   | 4.86, 0.886  | 3.74, 0.950  | 21.90, 0.980 | 88.1          |
| 0.925   | 5.75, 0.899  | 12.08, 0.975 | 28.88, 0.989 | 90.5          |
| 0.950   | 6.24, 0.909  | 11.09, 0.975 | 37.82, 0.992 | 92.9          |
| 0.975   | 16.31, 0.956 | 17.70, 0.988 | 55.07, 0.996 | 94.8          |
| 0.990   | *            | *            | *            | *             |

\* No results obtained

Note, with 3 reflux interval lactic acid with 0.99 could not be produced. Typical plots of accumulated distillate, condenser and reboiler composition profiles for product purities 0.8 and 0.975 are shown in Figures 7.7 and 7.8 respectively. Following points are noted from these plots:

### *Analysis of Accumulator Composition Profile*

Figure 7.7A and Figure 7.7B present the accumulated distillate composition profiles for product purities 0.8 and 0.975 molefraction respectively. Initially, the composition of water (2<sup>nd</sup> boiling component and reactant) increases in the accumulator (more evident in Figure 7.7A) and then decreases. Due to high reflux operation for purity 0.975 there is only a small trace of water in the accumulator (Figure 7.7B). Methyl lactate composition (being heavier and reactant) decreases with increasing batch time. Lactic acid being the heaviest component will be trapped in the bottom and therefore there is no lactic acid found in the distillate products.

It can be seen from Figure 7.7B that, increasing product purity ( $x_3^* = 0.975$ ) leads to less loss of reactants in the distillate. Mainly methanol is removed from the top of the column compared to the case with low product purity (0.8).

### *Analysis of Condenser Composition Profile*

Figure 7.8A and Figure 7.8B present the condenser composition profiles for product purities 0.8 and 0.975 molefraction respectively. From  $t = 0$  all methyl lactate returns to the reboiler therefore no amount was found in the condenser (Figure 7.8A) compared with that in the case of product purity 0.975 (Figure 7.8B). As batch time increases, the reflux ratio in the second and third intervals increases and more water goes up to the condenser.

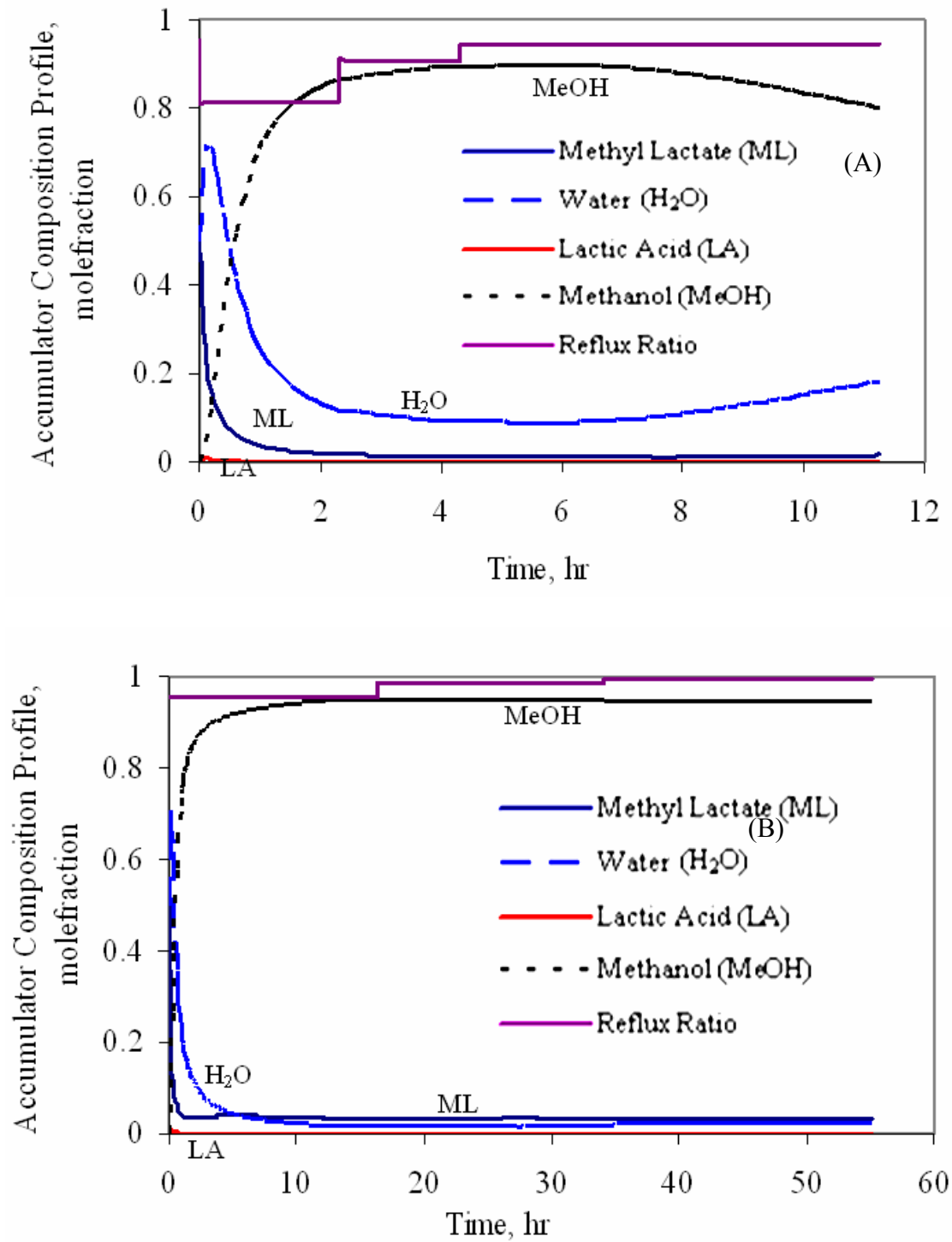


Figure 7.7 Accumulator Composition and Reflux Ratio Profiles,  $NCI = 3$

(A)  $x_3^* = 0.8$

(B)  $x_3^* = 0.975$

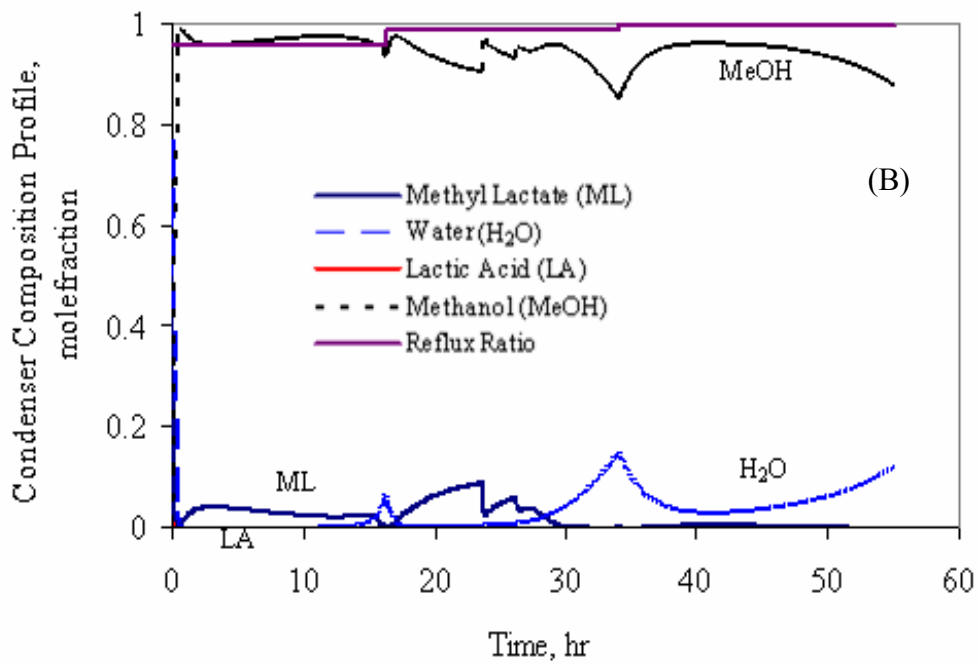
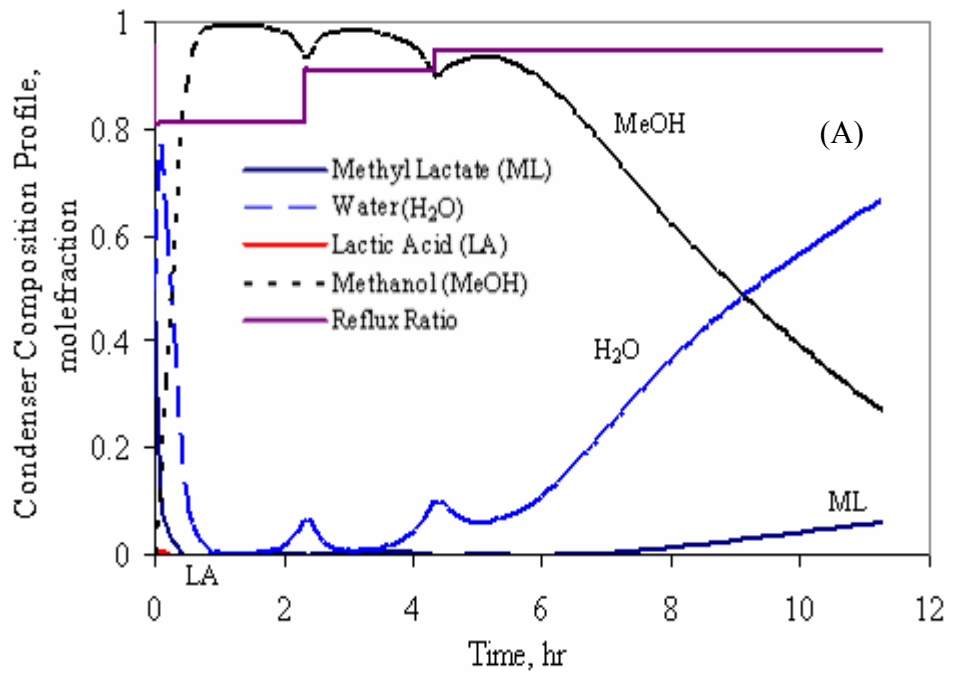


Figure 7.8 Condenser Composition and Reflux Ratio Profiles,  $NCI = 3$   
 (A)  $x_3^* = 0.8$  (B)  $x_3^* = 0.975$

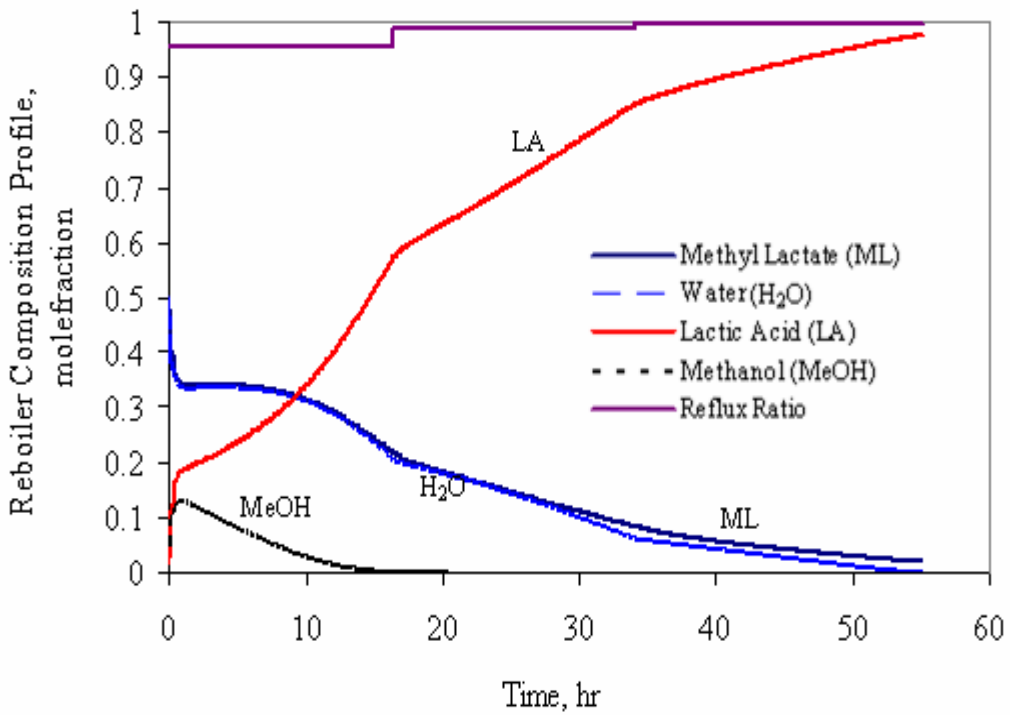
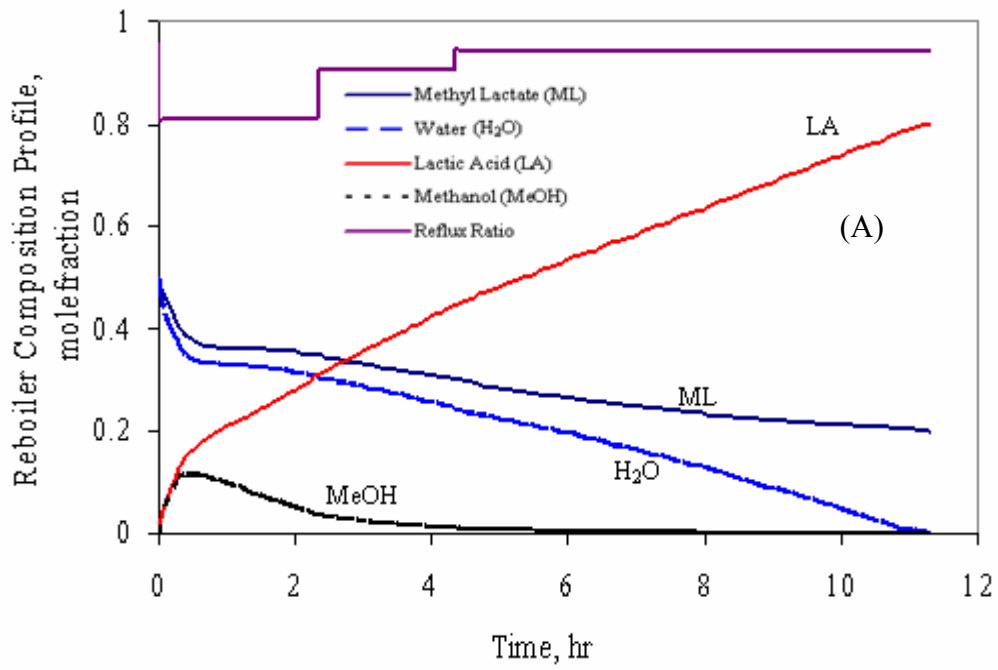
### *Analysis of Reboiler Composition Profile*

Figure 7.9 presents the reboiler composition profiles for product purity of 0.8 and 0.975 respectively. For purity 0.8, the column operates at lower reflux ratio (Figure 7.9A) and there is a substantial amount of reactants (more lactate than water) still available in the reboiler. Clearly at this purity more lactic acid product could have been produced (note in this example the product amount is constrained to 2.5 kmol). Note, for high purity operation (Figure 7.9B), both the reactants are retained in the reboiler (similar composition almost all the way) but at a lower value near the end of the operation. Therefore, further gain (at this product purity) in the amount of lactic acid product would be limited.

The mole fraction of lightest component (methanol) rises from zero, reaches the maximum value and then gradually falls to zero. The rise in mole fraction is due to high rate of reaction initially. Lactic acid composition gradually increases while the reactants are consumed and their compositions gradually decrease as batch time increases.

As seen from Figure 7.9B that, it can not be possible to achieve higher purity more than 97.5 % mole for bottom product using three time intervals. Some water is trapped in the column. Also since there is no substantial amount of methanol in the reboiler or in the column the esterification reaction (reversible) does not take place. Also for all the cases, since there is no lactic acid in the column or in the condenser, the reversible esterification reaction does not take place.

As observed from the profiles at product purity 0.95 molefraction using two time intervals (Figure 7.6) and product purity 0.975 molefraction using three time intervals that, the similar trend are shown for both accumulator and reboiler composition profiles.



(B)

Figure 7.9 Reboiler Composition and Reflux Ratio Profiles,  $NCI = 3$   
 (A)  $x_3^* = 0.8$  (B)  $x_3^* = 0.975$  molefraction

#### 7.5.2.4 Case 4 (Four Time Intervals) $NCI = 4$

Four time intervals are considered in this case. For each product purity, the optimisation results for each interval in terms of optimal reflux ratio, optimal time interval and total minimum operating time are shown in Table 7.9. The conversion of methyl lactate into lactic acid is also shown in Table 7.9.

It can be observed from the results that up to product purity 0.975 molefraction no significant improvement in terms of operating time is achieved when results are compared with those obtained using 3 reflux ratio intervals. In some cases, an initial total reflux with limited time for the first interval was found to be necessary. The reflux ratio goes down in the second interval and up again at the end to satisfy the product specifications. However, 99 % purity of lactic acid can be achieved using 4 reflux ratio intervals and 96 % of methyl lactate has been converted to lactic acid.

Table 7.9 Summary of the optimisation results using 4 time intervals ( $NCI = 4$ )

| $x_3^*$ | $t_1, R_1$   | $t_2, R_2$   | $t_3, R_3$   | $t_4, R_4$   | Conversion. % |
|---------|--------------|--------------|--------------|--------------|---------------|
| 0.800   | 0.500, 1.00  | 2.11, 0.800  | 2.63, 0.918  | 10.80, 0.935 | 77.9          |
| 0.850   | 1.280, 0.921 | 5.49, 0.908  | 5.10, 0.962  | 16.55, 0.957 | 82.9          |
| 0.900   | 0.420, 1.00  | 2.70, 0.835  | 3.88, 0.937  | 20.09, 0.976 | 88.3          |
| 0.925   | 0.500, 1.00  | 1.26, 0.779  | 4.61, 0.924  | 27.26, 0.982 | 90.7          |
| 0.950   | 0.540, 1.00  | 2.93, 0.848  | 8.79, 0.964  | 34.17, 0.989 | 93.3          |
| 0.975   | 6.03, 0.962  | 10.95, 0.955 | 17.43, 0.988 | 54.88, 0.996 | 94.7          |
| 0.990   | 15.34, 0.954 | 20.72, 0.994 | 51.10, 0.996 | 142.08, 1.00 | 96.0          |

Typical plots of accumulator, condenser and reboiler composition profiles for product purity 0.99 are shown in Figure 7.10. It can be seen from Figure 7.10A and 7.10B that the molefraction of methanol (as lower boiling product) rises from zero reaches the maximum values (in both reboiler and accumulator) and then gradually falls to zero (in the reboiler). Little water goes to the accumulator without any reaction when the column operates with the lower reflux ratio. Methyl lactate falls rapidly from the accumulator (as the heavier reactant components). As batch time increases more water and methyl lactate reacted and consumed. Note, in the last time interval ( $R_4$ ) the column operates at total reflux for a long period ( $\sim 91$  hrs). Although there was no distillate withdrawn during that period, changes in composition profiles in the condenser holdup tank, internal stages and in the reboiler took place to purify the bottom product to the desired purity. Finally, note for each product purity, the amount of bottom product could be further improved by multi-reflux policy.



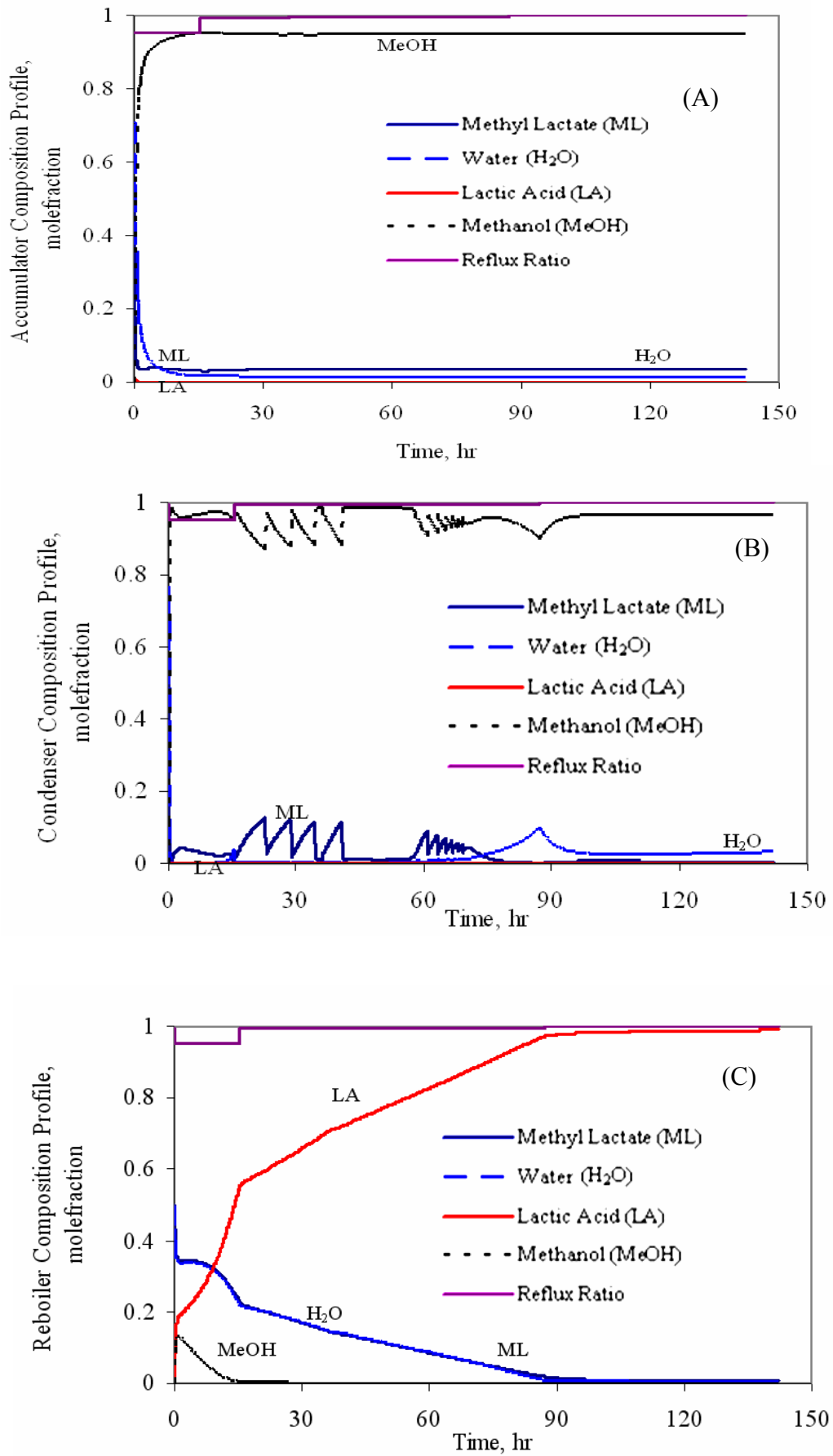


Figure 7.10 Composition and Reflux Ratio Profiles,  $NCI = 4$  ( $x_3^* = 0.99$ )  
 (A) Accumulator (B) Condenser (C) Reboiler

### 7.5.3 Comparison Between Single and Multi Reflux Ratio Strategy

It is noticed from the optimisation results that, the column operated with single time interval for reflux ratio was not sufficient to produce the main product at high purity specifications ( $> 0.925$  mole fraction a lactic and in the bottom product). The multi-reflux interval strategies (Case 2-4) were found to be better to produce products with higher purity specifications with shorter batch time. Figure 7.11 proves this fact in terms of minimum operating time as a function of bottom product purity specifications and reflux ratio policy. For example the operation time using two time intervals (in case of product purity 0.925) is reduced by 76.8 % compared to that obtained by using single interval. This is due to the fact that the column initially operated at lower reflux ratio ( $R_1$ ) to remove the light component (methanol) and then at higher reflux ( $R_2$ ) to meet the product specification in a shorter time.

Observation also shows that the operating time for some cases can be saved by 79 % when the column operated using 3 reflux ratio intervals compared to the operation times obtained using single interval. Moreover the operating time has been saved by an average of 37 %, 46 % and 48 % using 2, 3 and 4 time intervals respectively for the purity range from 0.8 to 0.925. This clearly shows the benefit of using multi reflux intervals. It can be observed also that at product purity 0.975 no significant improvement is noticed in terms of operating time when the column operates with 3 or 4 reflux ratio level intervals.

Unlike esterification reaction in conventional batch reactive distillation where the reaction product (ester) is the lightest (see Chapters 5 and 6), the hydrolysis reaction considered here produces the product (lactic acid) which is the heaviest in the mixture. The column has to always operate at high reflux ratio so that both the reactants are available in the reaction zone (reboiler and stages). Low reflux ratio operation will

separate the reactants from the system and will thus lower the conversion (as can be seen in Case 1). It can be seen from the composition profiles (Figure 7.2 – 7.10) that the multi-reflux strategy allows more reactant to be consumed with shorter period of time and therefore will increase the production of desired product. Multi-reflux operation enjoys more freedom to balance between the conversion and product purity (as can be seen in Cases 2-4) Unlike esterification reactions (Chapters 5 and 6) where the desired product is in the distillate, the desired product in the case of hydrolysis reaction (as in this case) is in the reboiler, purification of such product required total reflux operation at the end of the process rather than at the beginning of the processes (refer to the results of the other chapters). Table 7.10 shows the composition of each component at the end of the operation for each case (Case 1-4). Figure 7.11 shows the condenser composition of each component at the end of the operation for each case (Case 1- 4)

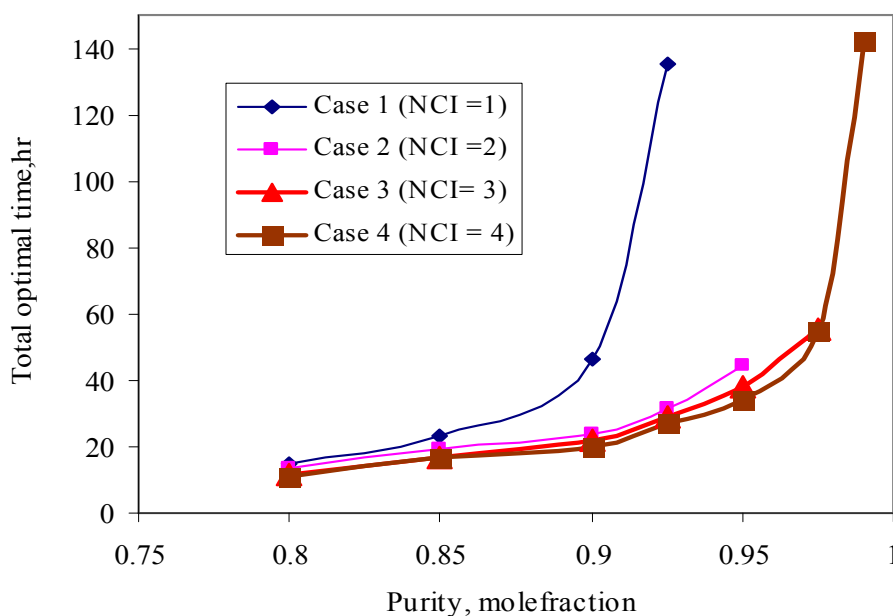


Figure 7.11 Total Minimum Operating Time vs. Purity Specification

Table 7.10 Distillate and Reboiler Composition at Different Purities at the End of Operating Time

Case 1: Single time intervals

| Purity | X Accumulator |                  |       |       | X Reboiler |                  |              |       |
|--------|---------------|------------------|-------|-------|------------|------------------|--------------|-------|
|        | ML            | H <sub>2</sub> O | LA    | MeOH  | ML         | H <sub>2</sub> O | LA           | MeOH  |
| 0.800  | 0.024         | 0.176            | 0.000 | 0.800 | 0.195      | 0.005            | <b>0.800</b> | 0.000 |
| 0.850  | 0.029         | 0.124            | 0.000 | 0.847 | 0.144      | 0.006            | <b>0.850</b> | 0.000 |
| 0.900  | 0.055         | 0.058            | 0.000 | 0.887 | 0.076      | 0.024            | <b>0.900</b> | 0.000 |
| 0.925  | 0.093         | 0.011            | 0.000 | 0.896 | 0.018      | 0.057            | <b>0.925</b> | 0.000 |
| 0.950  | *             | *                | *     | *     | *          | *                | *            | *     |

Case 2: Two time intervals

| Purity | X Accumulator |                  |       |       | X Reboiler |                  |              |       |
|--------|---------------|------------------|-------|-------|------------|------------------|--------------|-------|
|        | ML            | H <sub>2</sub> O | LA    | MeOH  | ML         | H <sub>2</sub> O | LA           | MeOH  |
| 0.800  | 0.019         | 0.185            | 0.000 | 0.796 | 0.198      | 0.002            | <b>0.800</b> | 0.000 |
| 0.850  | 0.023         | 0.128            | 0.000 | 0.849 | 0.147      | 0.003            | <b>0.850</b> | 0.000 |
| 0.900  | 0.017         | 0.085            | 0.000 | 0.898 | 0.100      | 0.000            | <b>0.900</b> | 0.000 |
| 0.925  | 0.024         | 0.058            | 0.000 | 0.918 | 0.073      | 0.002            | <b>0.925</b> | 0.000 |
| 0.950  | 0.024         | 0.040            | 0.000 | 0.936 | 0.048      | 0.002            | <b>0.950</b> | 0.000 |
| 0.975  | *             | *                | *     | *     | *          | *                | *            | *     |

Case 3: Three time intervals

| Purity | X Accumulator |                  |       |       | X Reboiler |                  |              |       |
|--------|---------------|------------------|-------|-------|------------|------------------|--------------|-------|
|        | ML            | H <sub>2</sub> O | LA    | MeOH  | ML         | H <sub>2</sub> O | LA           | MeOH  |
| 0.800  | 0.016         | 0.184            | 0.000 | 0.800 | 0.198      | 0.002            | <b>0.800</b> | 0.000 |
| 0.850  | 0.015         | 0.135            | 0.000 | 0.850 | 0.149      | 0.001            | <b>0.850</b> | 0.000 |
| 0.900  | 0.013         | 0.088            | 0.000 | 0.899 | 0.100      | 0.000            | <b>0.900</b> | 0.000 |
| 0.925  | 0.016         | 0.067            | 0.000 | 0.917 | 0.075      | 0.000            | <b>0.925</b> | 0.000 |
| 0.950  | 0.020         | 0.040            | 0.000 | 0.940 | 0.050      | 0.000            | <b>0.950</b> | 0.000 |
| 0.975  | 0.030         | 0.023            | 0.000 | 0.947 | 0.025      | 0.000            | <b>0.975</b> | 0.000 |
| 0.990  | *             | *                | *     | *     | *          | *                | *            | *     |

Case 4: Four time intervals

| Purity | X Accumulator |                  |       |       | X Reboiler |                  |              |       |
|--------|---------------|------------------|-------|-------|------------|------------------|--------------|-------|
|        | ML            | H <sub>2</sub> O | LA    | MeOH  | ML         | H <sub>2</sub> O | LA           | MeOH  |
| 0.800  | 0.013         | 0.185            | 0.000 | 0.802 | 0.198      | 0.002            | <b>0.800</b> | 0.000 |
| 0.850  | 0.017         | 0.132            | 0.000 | 0.851 | 0.148      | 0.002            | <b>0.850</b> | 0.000 |
| 0.900  | 0.008         | 0.088            | 0.000 | 0.904 | 0.100      | 0.000            | <b>0.900</b> | 0.000 |
| 0.925  | 0.014         | 0.060            | 0.000 | 0.926 | 0.075      | 0.000            | <b>0.925</b> | 0.000 |
| 0.950  | 0.014         | 0.037            | 0.000 | 0.949 | 0.050      | 0.000            | <b>0.950</b> | 0.000 |
| 0.975  | 0.032         | 0.022            | 0.000 | 0.946 | 0.023      | 0.002            | <b>0.975</b> | 0.000 |
| 0.990  | 0.034         | 0.016            | 0.000 | 0.950 | 0.006      | 0.004            | <b>0.990</b> | 0.000 |

\* Not achieved

Table 7.11 Condenser Composition Profile at the End of Operation Time for Each Case and Purity

| Case 1: Single time interval |       |                  |       |       |
|------------------------------|-------|------------------|-------|-------|
| Purity                       | ML    | H <sub>2</sub> O | LA    | MeOH  |
| 0.800                        | 0.069 | 0.694            | 0.002 | 0.235 |
| 0.850                        | 0.059 | 0.645            | 0.001 | 0.295 |
| 0.900                        | 0.035 | 0.512            | 0.000 | 0.453 |
| 0.925                        | 0.005 | 0.228            | 0.000 | 0.767 |
| 0.950                        | *     | *                | *     | *     |

| Case 2: Two time intervals |       |                  |       |       |
|----------------------------|-------|------------------|-------|-------|
| Purity                     | ML    | H <sub>2</sub> O | LA    | MeOH  |
| 0.800                      | 0.053 | 0.616            | 0.000 | 0.331 |
| 0.850                      | 0.059 | 0.648            | 0.001 | 0.292 |
| 0.900                      | 0.038 | 0.535            | 0.000 | 0.427 |
| 0.925                      | 0.031 | 0.486            | 0.000 | 0.483 |
| 0.950                      | 0.011 | 0.322            | 0.000 | 0.667 |
| 0.975                      | *     | *                | *     | *     |

| Case 3: Three time intervals |       |                  |       |       |
|------------------------------|-------|------------------|-------|-------|
| Purity                       | ML    | H <sub>2</sub> O | LA    | MeOH  |
| 0.800                        | 0.063 | 0.664            | 0.000 | 0.273 |
| 0.850                        | 0.053 | 0.616            | 0.001 | 0.330 |
| 0.900                        | 0.036 | 0.519            | 0.000 | 0.445 |
| 0.925                        | 0.015 | 0.362            | 0.000 | 0.623 |
| 0.950                        | 0.009 | 0.299            | 0.000 | 0.692 |
| 0.975                        | 0.002 | 0.124            | 0.000 | 0.874 |
| 0.990                        | *     | *                | *     | *     |

| Case 4: Four time intervals |       |                  |       |       |
|-----------------------------|-------|------------------|-------|-------|
| Purity                      | ML    | H <sub>2</sub> O | LA    | MeOH  |
| 0.800                       | 0.069 | 0.696            | 0.001 | 0.234 |
| 0.850                       | 0.060 | 0.651            | 0.001 | 0.288 |
| 0.900                       | 0.050 | 0.577            | 0.000 | 0.373 |
| 0.925                       | 0.038 | 0.531            | 0.000 | 0.431 |
| 0.950                       | 0.023 | 0.434            | 0.000 | 0.543 |
| 0.975                       | 0.003 | 0.122            | 0.000 | 0.875 |
| 0.990                       | 0.003 | 0.033            | 0.000 | 0.964 |

\* Not achieved

## 7.6 Production of Lactic Acid in Inverted Batch Distillation Column

### 7.6.1 Introduction

This work will investigate the production of lactic acid by hydrolysis of methyl lactate (Figure 7.12). The feed (ML+H<sub>2</sub>O) is charged to the condenser drum and the products are taken out with the heaviest (LA). Unreacted methyl lactate as the second heavier (reactant) will also fall down in the bottom drum.

Theoretically, from  $t = 0$ , most of the reaction will start at the condenser feed tank. As methanol and lactic acid is produced, methanol will remain in the condenser tank, lactic acid and then methyl lactate will travel down the column. Water will be trapped at the top and intermediate stages with methanol. After certain time reaction zone will shift from condenser to probably in middle to lower stages. Since the holdup in stages is small, the rate of reaction will be slow and conversion will be limited.

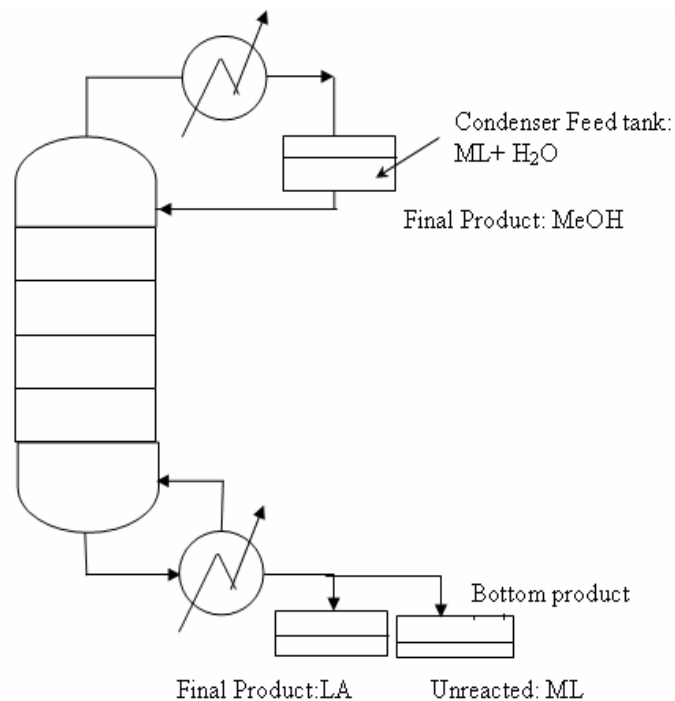


Figure 7.12 Inverted Batch Distillation Process for Lactic Acid Synthesis

### 7.6.2 Model Equations

Hydrolysis of methyl lactate to produce lactic acid and methanol is modelled using a rigorous mathematical model in an inverted distillation process (Figure 7.12) and incorporated into the minimum time optimisation problem which was numerically solved within gPROMS modelling software. The model equations were presented in chapter four. The kinetic reaction and VLE models are given in (Eq. 7.2) and (Eq. 7.3) respectively. The enthalpies of the vapour and liquid are calculated using Eq. 7.4.

### 7.6.3 Optimisation Problem Formulation

The performance of inverted column is evaluated in terms of minimum batch time subject to constraints on the bottom product ( $B^* = 2.5$  kmol) and different purities of main product (Lactic acid) between (0.8 and 0.99). Reboil ratio (single time interval,  $NCI = 1$ ) is selected as control variable which is optimised.

Mathematically, the Optimisation Problem (OP) can be represented as:

$$\begin{aligned}
 OP2 \quad & \min t_f \\
 & R_B(t) \\
 \text{subject to :} & \\
 & B = B^* \quad (\text{Inequality constraint}) \\
 & x_3 = x_3^* \pm \varepsilon \quad (\text{Inequality constraint}) \\
 & \text{and } f(t, x', x, u, v) = 0 \quad (\text{Model Equation, equality constraint}) \\
 & \text{with } f(t_0, x'_0, x_0, u_0, v) = 0 \quad (\text{Initial condition, equality constraint}) \\
 & \text{Linear bound on } R \quad (\text{Inequality constraint})
 \end{aligned} \tag{7.16}$$

Where  $B$ ,  $x_3$  are the amount of bottom product and composition of lactic acid at the final time  $t_f$ ,  $B^*$ ,  $x_3^*$  are the specified amount of bottom product (2.5 kmol) and purity of Lactic acid.  $R_B(t)$  is the reboil ratio profile which is optimised and  $\varepsilon$  is small positive numbering the order of  $10^{-3}$

## 7.6.4 Case Study

### 7.6.4.1 Problem specification

Hydrolysis of methyl lactate to produce lactic acid is carried out in 10 stages of an inverted batch column. The total column holdup is 4 % of the initial feed (50 % is taken as the reboiler hold up and the rest is equally divided in the plates) and the condenser capacity is 5 kmol. The feed composition of <Methyl Lactate, Water, Lactic acid, Methanol> is: <0.5, 0.5, 0.0, 0.0>.

### 7.6.4.2 Results and Discussions

Results in terms of optimal reboil ratio ( $R_B$ ) which minimises the operating time  $t_f$  subject to constraints on the amount and purity of main product at the final time are shown in Table 7.12. The reboil ratio ( $R_B$ ) is defined over single control interval ( $NCI = 1$ ) and is assumed piecewise constant control type.

The minimum operating time (hrs) needed to produce the required amount of product and purity and optimal reboil ratio for each purity are presented in Table 7.12 and shown graphically in Figure 7.13 for minimum operating time and Figure 7.14 for optimal reboil ratio. For each purity specification Table 7.12 also gives the conversion of methyl lactate to lactic acid.

Table 7.12 Summary of optimisation results ( $NCI=1$ )

| $x_3^*$ | Minimum Batch Time, ( $t_f$ ) | Reboil Ratio ( $R_B$ ) | Conversion % |
|---------|-------------------------------|------------------------|--------------|
| 0.80    | 29.81                         | 0.967                  | 79.14        |
| 0.85    | 47.63                         | 0.979                  | 83.75        |
| 0.90    | 92.14                         | 0.989                  | 89.82        |
| 0.925   | 121.58                        | 0.991                  | 92.12        |
| 0.950   | 193.17                        | 0.994                  | 94.78        |
| 0.975*  | *                             | *                      | *            |

\* No results obtained



It can be seen from the results that the trend in terms of operating time and optimal reboil ratio against the product purity is the same as that observed for conventional column with  $NCI = 1$ , although the actual numbers vary quite interestingly (further explanations are provided in section 7.7)

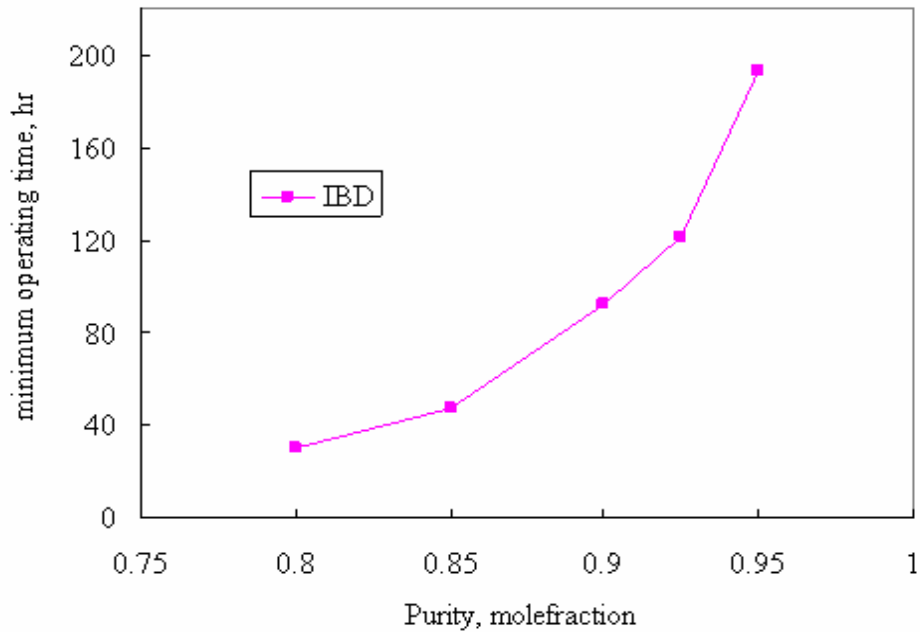


Figure 7.13: Minimum Operating Time vs. Product Purity Specification

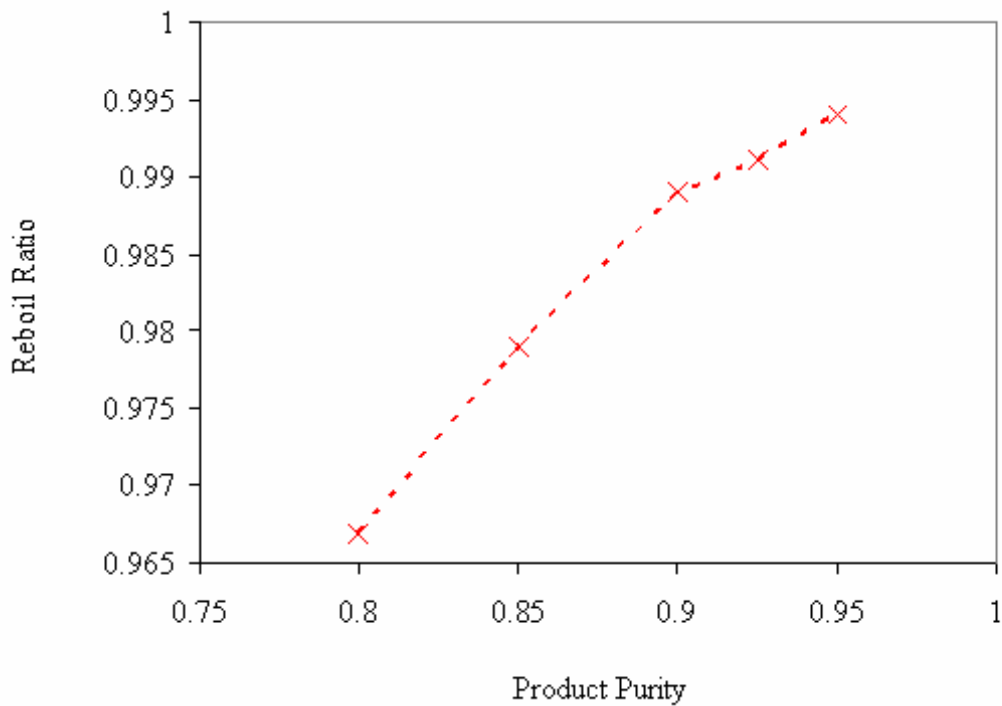


Figure 7.14: Reboil ratio as a Function of Product Purity Specification

For product purities ( $x_3^* = 0.8$  and  $0.95$  molefraction), the composition of the products in the condenser and in the bottom tank and reboil ratio profiles are given in Figures 7.15 and 7.16 respectively.

In Figure 7.15A it can be seen from condenser composition profile that unreacted reactants will remain in the condenser depending on the volatility. While the water remains in the condenser, methyl lactate (heavier than water) component is transported downwards from the condenser to the bottom which reduces conversion. Furthermore the composition of methanol (as light product) gradually increases and trapped in the condenser and not any amount in the reboiler while the lactic acid in the condenser raises from zero reaches the maximum value and then gradually falls to zero. The rise in mole fraction is due to high rate of reaction initially in the condenser.

It can be seen from bottom composition profile (Figure 7.15B) that, initially some methyl lactate goes down in the reboiler without any reaction and no water available in the reboiler. The composition of the main product (Lactic acid) is higher than the specification during most of the run as the rate of reaction initially increased and then decreasing at the end of 5 hrs to reaches the specified value. As batch time increases the reactants are gradually consumed to produce more valuable product. After 20 hrs of operation, it is noticed that there is no substantial amount of lactate in the condenser (Figure 7.15A) and no water in the reboiler (Figure 7.15B) to have further reaction. Beyond this operation time, the reboiler composition profiles are adjusted to match the product specifications.

The condenser composition profile in Figure 7.16A shows trend similar to that in Figure 7.15A but with more decreasing in the reactants to achieve more lactic acid with the specification. As no substantial amount of lactic acid in the condenser therefore the esterification reaction does not take place.

It can be seen from the bottom composition profile (Figure 7.16B) that all the lactic acid will be downward directly as bottom product. As batch time increases the composition of the product slightly higher than the specification and reached the specified value at the end of batch time. Higher reboil ratio leads to no water and methanol in the bottom as they are the lightest components. Compared to the case presented in Figure 7.15, in this case high reboil ratio ensures lactate in the condenser (as perhaps in the plates). As no substantial amount of methanol is found in the bottom tank the esterification reaction does not take place.

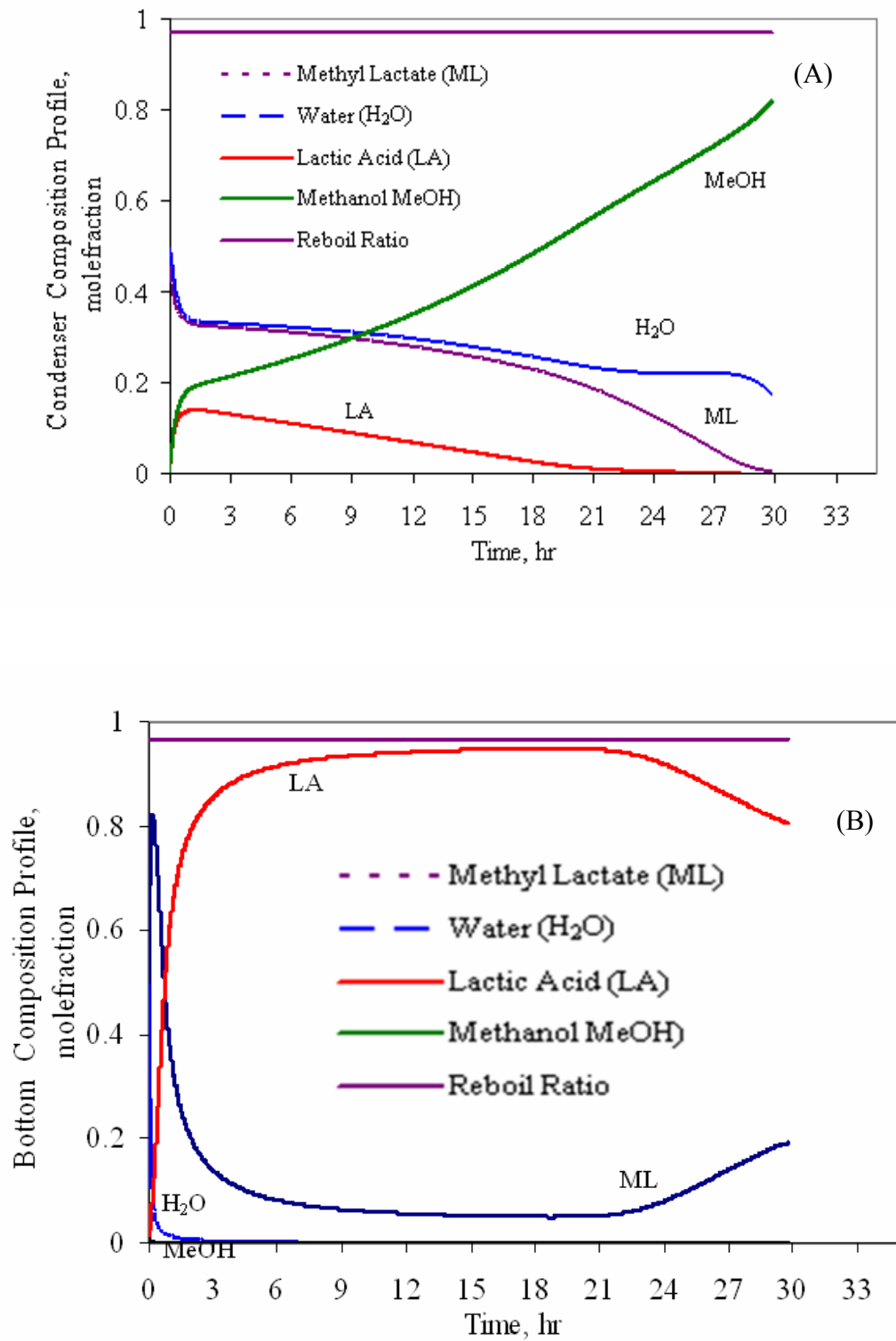


Figure 7.15 Composition and Reboil Ratio Profiles –NCI = 1 ( $x_3^* = 0.8$ )

(A) Condenser

(B) Bottom Product

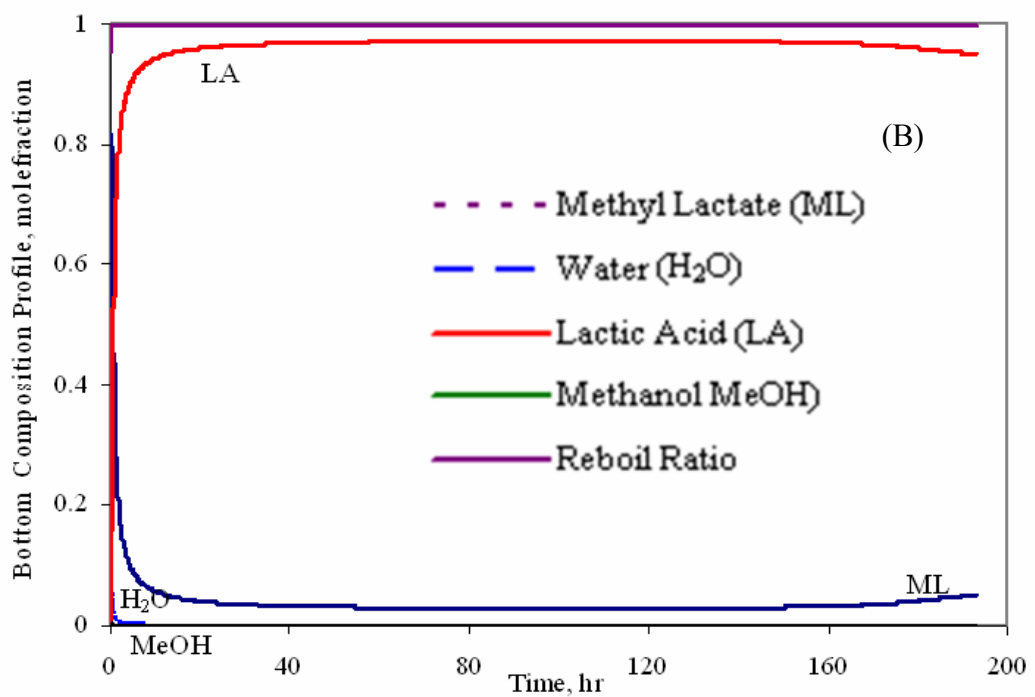
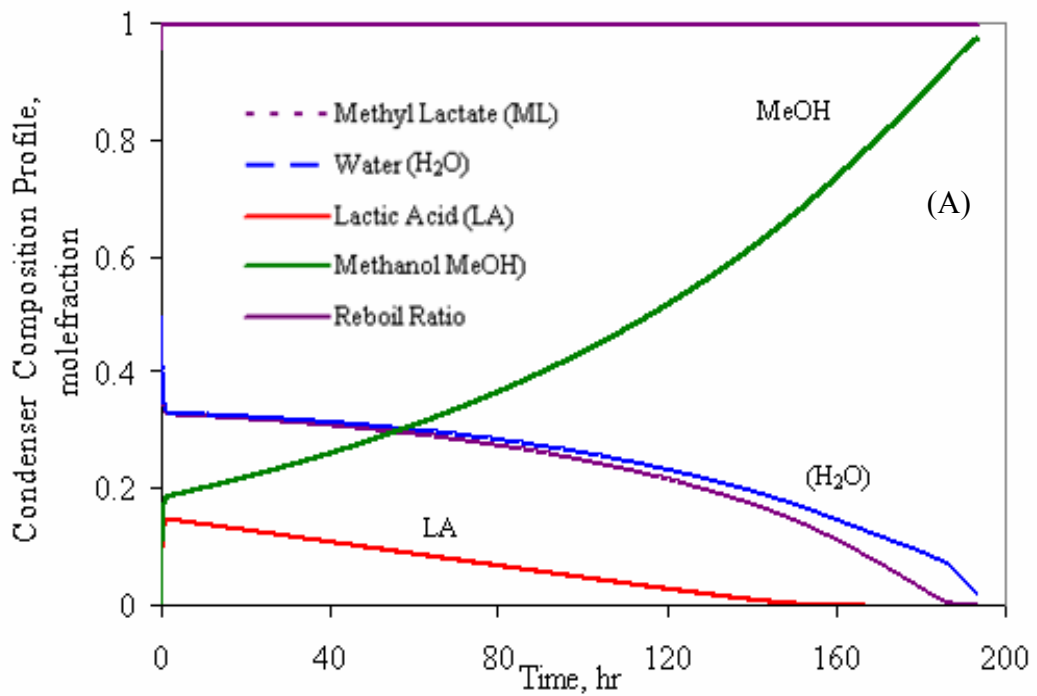


Figure 7.16: Composition and Reboil ratio Profiles- NCI = 1 ( $x_3^* = 0.95$ )  
 (A) Condenser (B) Bottom Product

Interesting observation shows that the time has been increased by about 570 % at the purity of product 0.95 compared with that for product purity 0.8 molefraction to meet the constraint specifications which will affect the operating cost of the process. In such circumstances single reboil inverted batch distillation will not be suitable and multi-reboil of short duration operation might have to be sought to satisfy high product purity (more than 0.95 mole fraction of lactic acid).

## **7.7 Comparison of Inverted and Conventional Batch Distillation**

### **Columns**

To the best of author's knowledge, no work has been reported with the comparison between inverted and conventional batch distillation columns with chemical reaction in terms of optimal operating time for hydrolysis reactions. The performance of conventional and the inverted batch distillation column are compared in this section based on the optimisation results presented in section 7.5.2.1 (Case1) and section 7.6.4. In the conventional case, the feed takes place in the reboiler and the products as it is the heaviest component (Lactic Acid) will be remaining in the bottom product with the purity specifications. Unreacted methyl acetate (as the heaviest reactant) will also be kept in the reboiler. While the methanol (second product and lower boiling) will go up and taken out in the accumulator. In the inverted case, the feed is charged into the condenser and the products are taken out with the heaviest first.

Table 7.13 summaries the results (for inverted and conventional columns) in terms of optimal reflux, optimum operating time and maximum conversion for each product purity using single constant reflux ratio (conventional column) and reboil ratio (inverted column),  $NCI = 1$ . Figure 7.17 shows the minimum operating time for different product purity using CBD and IBD columns. From Table 7.13 and Figure 7.17 it can be seen that at low product purity required CBD column is more effective operation than an

IBD column while at high product purity an IBD column superior to a CBD column in terms of operating time.

The composition profiles using product purity 0.925 molefraction for the Case when the IBD is the best are shown in Figure 7.18 and Figure 7.19 respectively. For the inverted column (Figure 7.18), the composition of lactic acid is slightly higher than the specification during most of the run and reaches the specified values at the final time. The bottom product contains only lactic acid and unreacted methyl lactate. No water was found. In the conventional column, lactic acid has been increased with more reaction of reactants. There is substantial amount of reactant (more water than lactate) still available in the reboiler. As the column operated at higher reflux ratio there is some amount available in the accumulator (Figure 7.19).

As explained in section 7.6.1, IBD suffers from split of reactants as soon as the process starts (unlike CBD). A higher reboil ratio ensures pushing of methyl lactate up the column to react further with water trapped in the middle of the column and therefore takes longer batch time compared to CBD for up to product purity 0.9. Beyond 0.9 product purity IBD seems to perform better in terms of batch time compared to CBD. This is due to further push of methyl lactate up the column for IBD. But for CBD, at high purity (say 0.925), a very high reflux ratio is required to push the water down the column and to have further reaction. With high reflux, however methyl lactate does not travel up the column too far and therefore does not allow further purification of lactic acid (beyond 0.925) in the reboiler. However, with IBD very high reboil ratio pushes both methyl lactate and water up the column to have further reaction and to purify bottom product to 0.95.

Table 7.13 Summary of the results (CBD and IBD columns)

| $x_3^*$ | CBD Column |                   |                 | IBD Column |                       |                 |
|---------|------------|-------------------|-----------------|------------|-----------------------|-----------------|
|         | $t_f$ (hr) | Reflux Ratio<br>R | Conversion<br>% | $t_f$ (hr) | Reboil Ratio<br>$R_B$ | Conversion<br>% |
| 0.80    | 14.88      | 0.933             | 77.69           | 29.81      | 0.967                 | 79.14           |
| 0.85    | 23.28      | 0.957             | 82.46           | 47.63      | 0.979                 | 83.75           |
| 0.90    | 46.04      | 0.973             | 86.92           | 92.14      | 0.989                 | 89.82           |
| 0.925   | 135.4      | 0.993             | 89.19           | 121.58     | 0.991                 | 92.12           |
| 0.950   | *          | *                 | *               | 193.17     | 0.994                 | 94.78           |

\*No results obtained

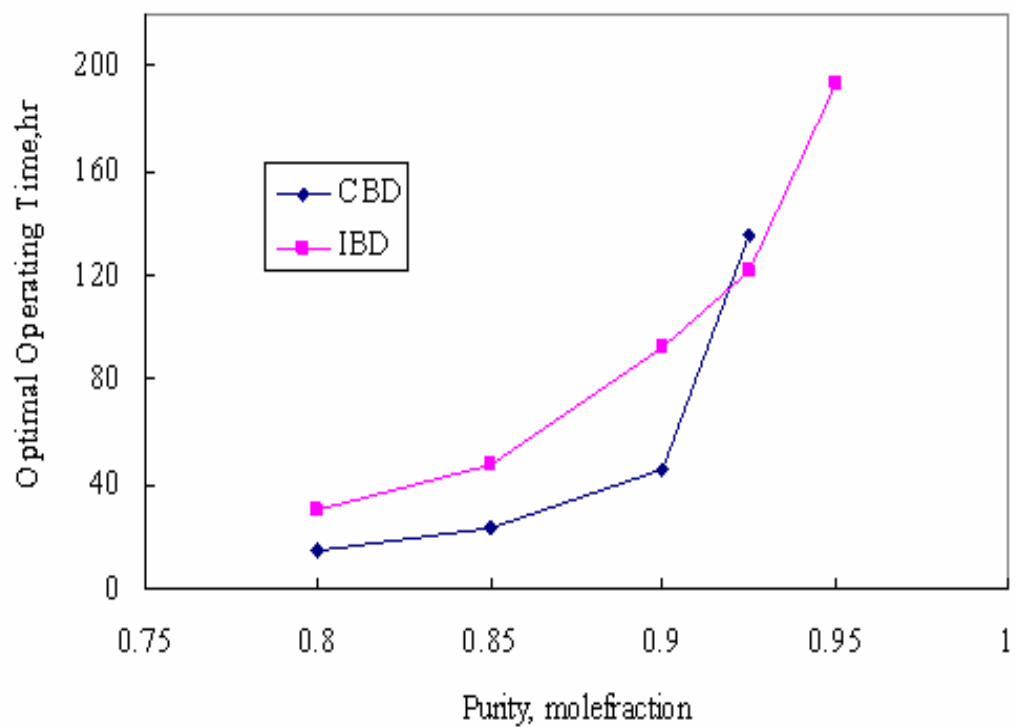


Figure 7.17 Operating Time vs. Purity (using CBD and IBD)



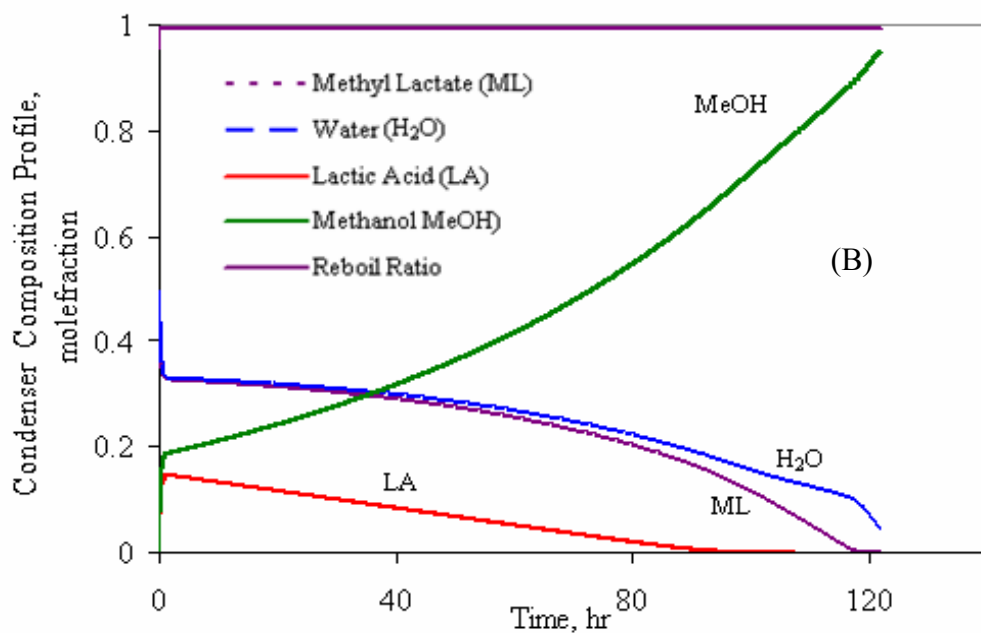
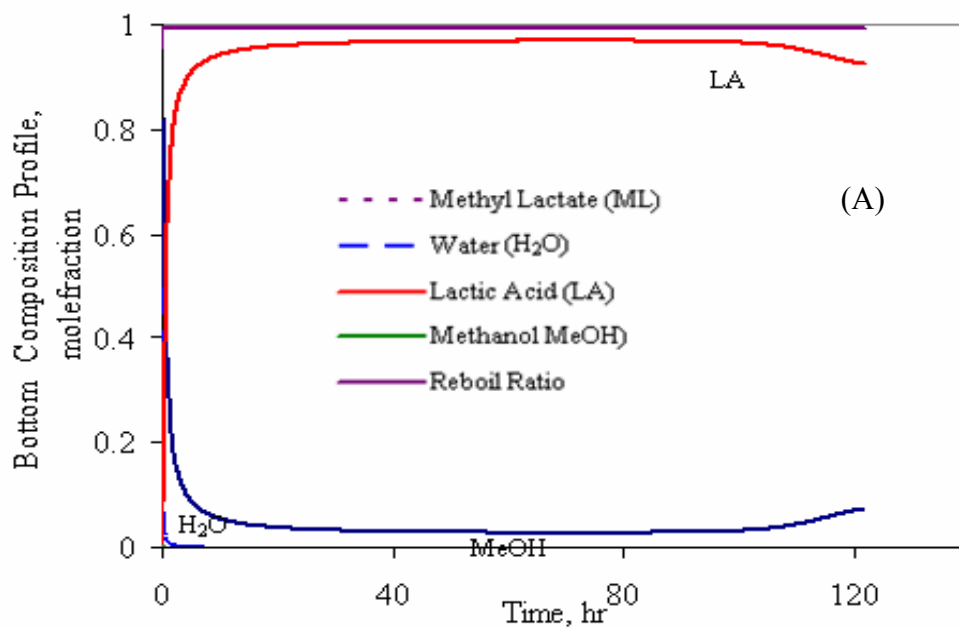


Figure 7.18: Composition and Reboil ratio Profiles- NCI = 1 ( $x_3^* = 0.925$ )  
 (A) Condenser (B) Bottom Product (Inverted)

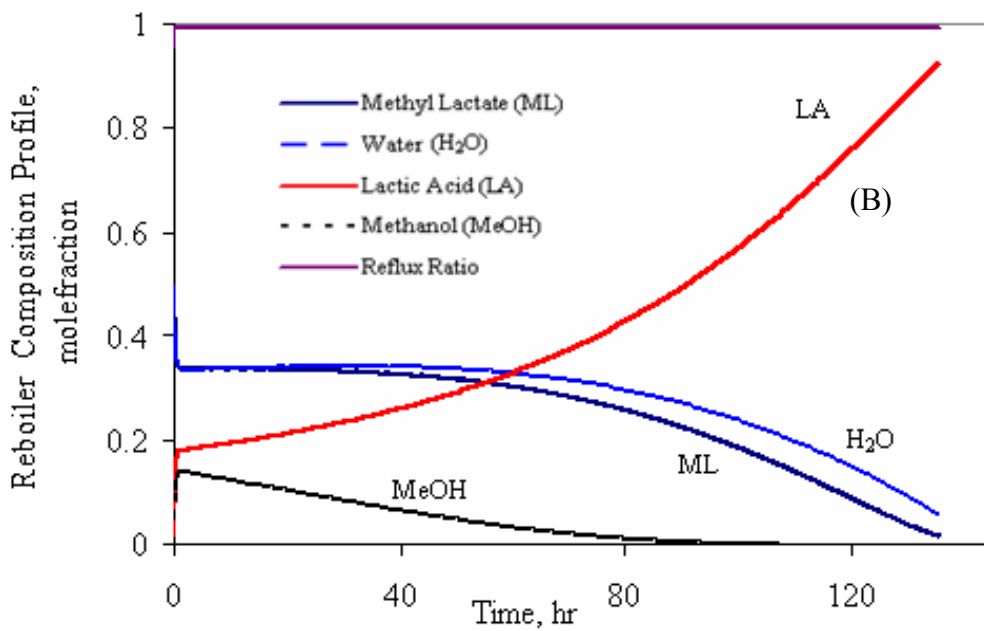
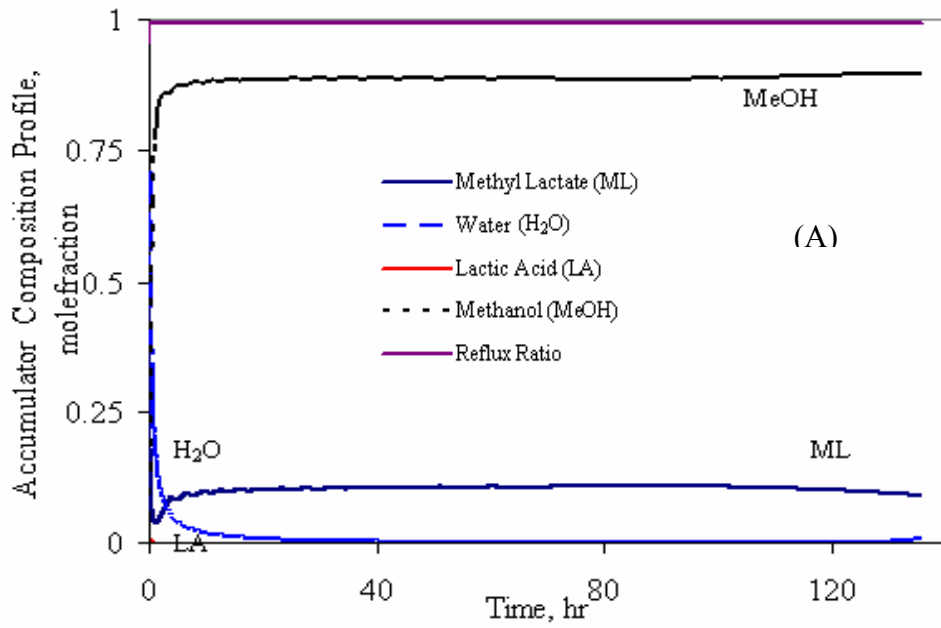


Figure 7.19: Composition and Reflux Ratio Profiles- NCI = 1 ( $x_3^* = 0.925$ )  
 (A) Accumulator (B) Reboiler (Conventional)

## 7.8 Conclusions

This chapter provides the optimisation of methyl lactate hydrolysis process. Unlike the previous studies, in this work hydrolysis reaction of methyl lactate in the presence of Amberlyst 15 (2.5 % w/w) toward pure lactic acid and methanol is carried out using both conventional and inverted reactive distillation columns. A minimum time optimisation problem is developed incorporating the process model within gPROMS. Product amount and purity are used as constraints. Reflux ratio is used as control variable which is discretised using Control Vector Parameterisation technique.

The optimisation results indicate that, highly purified lactic acid can be achieved directly from hydrolysis of methyl lactate in the presence of catalyst using a batch reactive distillation process. For a given column configuration, it is noticed that, the column operated with single time interval for reflux ratio was not sufficient to produce main product at high purity specifications ( $> 0.925$  mole fraction). However, more than 99 % purity of lactic acid can be achieved using multi reflux intervals operation. Observation results using single reflux ratio (CBD) and reboil ratio (IBD) show that CBD more suitable at lower product purity while at higher purity required an IBD is more effective operation in terms of optimum operating time.

## Chapter Eight

### Conclusions and Future Work

#### 8.1 Conclusions

This research was focused on the optimisation of batch distillation (conventional, inverted semi-batch) for esterification of methanol and ethanol and hydrolysis of methyl lactate. The main issues considered in this work were:

- Maximising the conversion of the limiting reactant.
- Maximising the productivity.
- Maximising the profitability.
- Minimising the batch time.

Three reaction schemes were considered:

- Methanol + Acetic Acid  $\rightleftharpoons$  Methyl Acetate + Water (Esterification)
- Ethanol + Acetic Acid  $\rightleftharpoons$  Ethyl Acetate + Water (Esterification)
- Methyl Lactate + Water  $\rightleftharpoons$  Lactic acid + Methanol. (Hydrolysis)

Methanol esterification was carried out using conventional batch distillation. Ethanol esterification was carried out using conventional and semi-batch distillation columns. Methyl Lactate hydrolysis was carried out using conventional and inverted batch distillation columns.

Different types of dynamic optimisation problems were formulated which included a detailed process model and was converted to nonlinear programming problem by Control Vector Parameterisation (CVP) technique and was solved by using efficient SQP method within gPROMS.

The following conclusions are drawn from this work.

#### *Chapter Five*

Optimisation of batch reactive distillation column involving the esterification of methanol with acetic acid producing methyl acetate and water was considered. Two cases were studied with different feed composition. An optimisation problem was formulated to optimise the reflux ratio (assumed piecewise constant) while maximising an objective function (conversion of methanol to methyl acetate) for different but fixed batch time  $t_f$  (between 5 and 15 hrs) and for given product purity of methyl acetate ( $x_{MeAc} = 0.7$ ). The optimisation results showed that as the methanol and methyl acetate were wide boiling the separation of methyl acetate was easier without losing much of methanol reactant. Use of excess acetic acid (Case 2) led to further reaction with methanol and required the column to operate at higher reflux ratio compared to Case 1.

#### *Chapter Six*

Different optimisation problems formulations (e.g. productivity and profit) for ethanol esterification process using conventional batch distillation were considered and discussed. While maximising the conversion of ethanol to ethyl acetate was considered using both conventional and semi-batch distillation columns.

Results in terms of maximum conversion indicated that the multi-reflux ratio intervals and linear reflux ratio operation helped retaining reactants in the column leading to further conversion and production of ethyl acetate compared to the cases with constant reflux ratio profile.

The optimisation results in terms of productivity showed that, increasing the amount of water in the feed led to a reduction in the productivity of the distillate product (Ethyl acetate). This was probably due to some backward reaction taking place (note, the forward reaction rate for esterification reaction is given by  $r_f = k_1 C_A C_B$  and

hydrolysis reaction is given by  $r_b = k_2 C_A C_B$ , see Eq. 6.2) or due to slow forward reaction (because of the presence of water). The results also showed that the productivity of the desired product improves significantly when the column operates with multi-reflux policy.

An optimal design and operation of a batch reactive distillation column with fixed yearly product demand (ranging from 700 to 1200 kmol) and strict product specification was then considered with the objective of maximising profit. Unlike previous works, vapour load and batch time were bounded by the product demand constraints. The design, operation and schedule were found to be different for all cases. The column with  $N=10$  indicated the best profitability profile for all product demand scenarios although product demand of 1000 kmol/yr was the best. Vapour load decreased significantly with  $N$  and so did the utility cost (OC) minimising energy consumption and the environmental impact.

For the maximum profit problem, sensitivity of the feed and product prices on the design and operation were also studied. For a given product demand, the optimisation results showed that, operating with diluted feed was always more profitable compared to the case with undiluted feed (as the raw material cost of diluted feed is usually low). However, significant change in design and operation was noticed in diluted feed compared to non-diluted feed. Also, changes in feed/product prices led to different design and operation as well as production target.

Semi-batch reactive distillation operation was considered to maximise the conversion of ethanol to ethyl acetate. Piecewise constant reflux ratio (in single and two intervals) together with the rate of acetic acid feed are optimised. The multi reflux operation was found to be more effective than single reflux ratio operation. Furthermore it led to better conversion compared to conventional batch distillation.

## *Chapter Seven*

The hydrolysis reaction of methyl lactate in the presence of Amberlyst 15 (2.5 % w/w) to produce lactic acid and methanol is carried out using both conventional and inverted batch distillation columns. A series of minimum time problems were solved at different values of product purity ranging from 0.8 to 0.99 and with fixed bottom product amount of 2.5 kmol. In conventional mode, the results showed that, 99 % purity of lactic acid was achieved using multi reflux intervals operation. As the lactic acid was the bottom product, total reflux operation at the end of operation was noticed as opposed to that observed for esterification reactions. The dynamic optimisation of an inverted batch distillation column with chemical reaction received very limited case studies. Therefore this work also considered the minimum time optimisation problem of hydrolysis of methyl lactate using inverted column. While low reflux operation for conventional column was good enough to keep the reactants in the reaction zone, high reboil ratio was required for the inverted column for the same purpose. For certain product purity, thus inverted column needed more batch time.

## **8.2 Future Work**

Some suggestions for future are outlined below.

- The accuracy of the results presented in this thesis is dependent on the models used which may not be completely in agreement with the real plant. Therefore, the results achieved in this thesis should be validated experimentally in the future work.
- The effect of kinetic and VLE models available in the literature for selected esterification systems using rigorous and simple models should be studied further.
- In this work only reversible reaction scheme is considered, other types of reactions should be studied in future.

- Optimisation of design ( $V$ ), operation ( $R$  and  $t_f$ ) of batch reactive distillation process with strict product specification and fixed product demand was considered using single reflux ratio strategy. In optimal design (both  $N$  and  $V$ ) and operation problem should be studied using MINLP or Genetic Algorithm and with time dependent reflux ratio profile. Sharif *et al.* (1998) and Low and Sorensen (2005) utilized such methods for non-reactive batch distillations which can be used for batch reactive distillation.
- The optimal design and operation policies in batch distillation with strict product specification and fixed product demand can be studied for other reaction schemes.
- Optimisation of semi-batch distillation in terms of maximum conversion for ethanol esterification process has been discussed. Maximum profit problems for such system can also be considered in future.
- Network of methyl lactate hydrolysis process using different batch distillation configurations as shown in Figure 8.1 can be considered in future for improved separation of the desired product. Note, study with middle vessel column would be interesting as both methyl lactate and water are mid-boiling components in the mixture. The reaction products methanol (lightest) and lactic acid (heaviest) can be withdrawn simultaneously from the top and bottom of the column in such case.



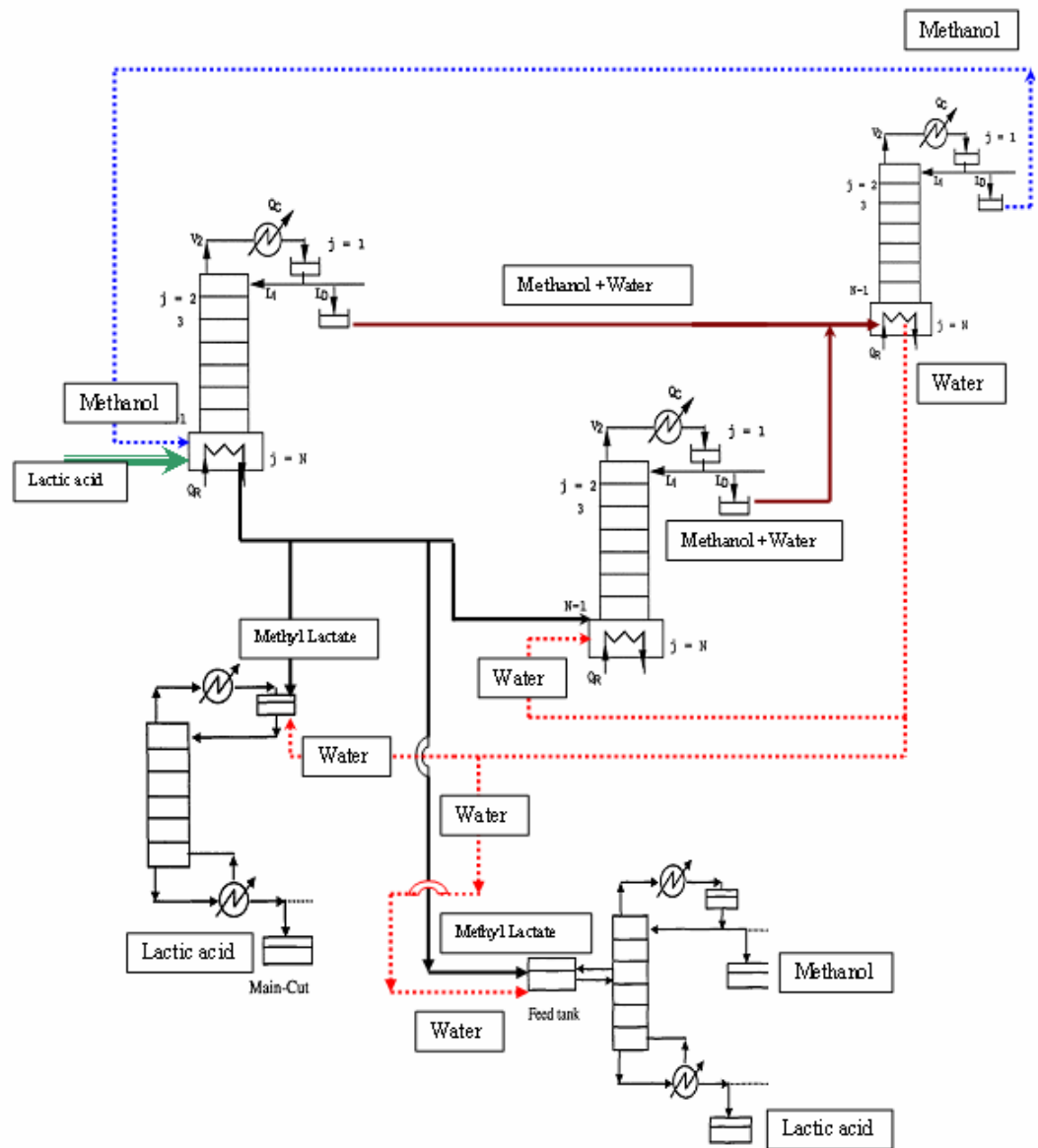


Figure 8.1 Improvement of Separation of Desired Product using Different Batch Distillation Configuration

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## Appendix

### Publications Made from This Work

1. E.A. Edreder, I.M. Mujtaba, M.M. Emtir. Performance of esterification system in reaction-distillation column *Proceeding of European Congress of Chemical Engineering*, 16-20 September 2007, Copenhagen-Denmark, ISBN-978-87-91435-57-9.
2. E.A. Edreder, M.M Emtir, I.M. Mujtaba. Improving the maximum conversion of ethanol esterification, *Chemical Product and Process Modeling*, The Berkeley Electronic Press, vol. 3, Issue 1, Art. 36,2008  
<http://www.bepress.com/cppm/vol3/iss1/36>
3. M. Emtir, I. M. Mujtaba, and E. A. Edreder. Improving the maximum conversion of ethanol esterification, *CAPE Forum-2008*, Thessaloniki-Greece, 7-8 February 2008.
4. E.A. Edreder, I.M. Mujtaba, M.M Emtir An Optimal Operation of Batch and Semi-Batch Reactive Distillation for Production of Ethyl Acetate , 11th Conference on Process Integration, Modelling and Optimisation for Energy Saving and Pollution Reduction, 2008.
5. E.A. Edreder, I.M. Mujtaba, M. Emtir .Dynamic Optimization of Semi-batch Reactive Distillation Column, *Proceedings of the International Conference on Chemical Engineering (ICChE2008)*, 29-30 December 2008, Dhaka, Bangladesh
6. Edreder, E.A., Mujtaba, I.M., Emtir, M.M. Optimisation of Design, Operation and Scheduling of Batch Reactive Distillation Process with Strict Product Specification and Fixed Product Demand using gPROMS, In *Computer Aided Chemical Engineering*, vol. 26, 411-415, Elsevier B.V., 2009.
7. E.A. Edreder, I.M. Mujtaba, M. Emtir. Profitability Analysis for Batch Reactive Distillation Process Based on Fixed Product Demand, *Chemical Engineering Transactions*, Volume 18, pp 701-706, 2009.