OPTIMAL CONFIGURATION, DESIGN AND OPERATION OF BATCH DISTILLATION PROCESSES

Kian Huat Low

A thesis submitted for the degree of

Doctor of Philosophy

University of London

September 2003

Department of Chemical Engineering

University College London

Abstract

The overall objective of this thesis is to study the optimal configuration, design and operating policy of batch distillation processes in different separation scenarios. In so doing, this work also aims to provide conceptual insights and compare the performance of the traditional regular column against unconventional columns.

In the first part of the thesis, the optimal operation of extractive batch distillation is investigated. A rigorous dynamic optimisation approach based on a detailed model is employed. In addition to the regular column, the optimal operation of the process in the unconventional middle vessel column is examined. The liquid and vapour stream configurations at the middle section of the column is explored for the first time, resulting in improved process performance. The performance of both columns are compared and the results show how their relative performances are affected by different feed compositions.

The second part of the thesis is concerned with the simultaneous design and operation of batch distillation processes. The thesis proposes a stochastic optimisation methodology based on genetic algorithm and penalty function. Using the proposed methodology, the simultaneous optimal designs and operations of the regular column for different design scenarios are investigated using rigorous models. Furthermore, the optimal design of the unconventional multivessel column for multicomponent separation is studied for the first time. The effect of different factors such as objective function, feed composition, relative volatility, product specification and number of components on the optimal design of the multivessel system is investigated. A comparison of the performance of the multivessel system with the regular column is also presented.

In the final part of the thesis, the feasibility of the genetic algorithm-penalty function approach in tackling simultaneous configuration selection, column sizing and operation is explored. In the case of binary mixture separation, the regular column was found to be more profitable for feeds with a high fraction of the light component whilst the inverted column is optimal for heavier feeds. There exists a flip point, the location of which is case study specific. For the multicomponent separation case study, the multivessel system is found to be superior to both the regular and inverted configurations.

Preface

This thesis is submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy of the University of London. The work has been carried out during the period of October 1999 to May 2003 at the Department of Chemical Engineering, University College London, with Dr Eva Sørensen as my main adviser. The work is a project under the broad area of Product and Process Design, conducted in the Computer-Aided Process Engineering (CAPE) research group, which is part of the Centre for Process Systems Engineering, located at Imperial College London and University College London.

I would like to express my greatest thanks to my supervisor, Dr. Eva Sørensen for her invaluable guidance, constructive discussion and encouragement with regards to the research project. Also thanks to Dr. Eric Fraga for his insightful comments and suggestions with regards to my MPhil transfer report, hence influencing the final outcome of this dissertation. To all my colleagues at the Department of Chemical Enginering, UCL, especially those present in the CAPE research group between 1998 and 2003, for their helpful hints and input into this project. Special thanks to Dr. Haydn Furlonge for sharing useful discussions and expert advice in the area of batch distillation. Last, but not least, my appreciation to Sharon Chan for proofreading this thesis.

During the majority of the research period, I acted in the additional capacity of part-time software manager in the department (October 1999 to October 2002), as a means for personal financial support. Conference funding from UCL Graduate School and IChemE Fluid Separation Processes Group is gratefully acknowledged.

Finally, I would like to dedicate this thesis to my parents, Katherine Chan and Robert Low, and to Chris Low and David McLaren, as a token of my gratitude for their support and constant encouragement.

The oral examination for this thesis was held on 12th September 2003 by Professor Costas Pantelides and Dr. Iqbal Mujtaba.

Contents

List of Figures

List of Tables

Chapter 1

Introduction

This thesis is concerned with the conceptual study of the configuration, design and operation of batch distillation processes using computer-aided optimisation techniques. In this chapter, a general background and some definitions of batch distillation processes are presented, followed by the motivation and objectives of this work. Finally, the structure of the thesis is outlined.

1.1 Background

Batch processing has received renewed attention over the past few decades due to the proliferation of low-volume and high-value-added chemical and biochemical industries. The on-going trend towards custom-made rather than commodity chemicals and the increasing cost pressures due to an over-capacity problem with high volume continuous plants, is likely to increase further the importance of batch processing in the future (Sharif, 1999).

The separation principle of batch distillation is based on differences in relative volatilities between the components of a mixture. According to Fair (1988), "if the mixture is amenable to separation by distillation, then that is the method most likely to be economically attractive". Although this suggestion might be debatable, batch distillation remains irrefutably the most widely used separation unit operation in the batch chemical processing industry (Kim and Diwekar, 2001). It finds widespread applications in the

production of fine and specialty chemicals, pharmaceuticals, polymers and biochemical products, either for purification purpose or for recovery of valuable solvents. In these industries, batch distillation is more suitable than its continuous counterpart due to several factors:

- Batch distillation is a single unit solution in multipurpose production plants. Unlike continuous distillation which requires at least *n-1* columns to separate a feed of *n* components, a properly designed batch distillation column can separate mixtures with any number of components into its pure components.

- Arguably the greatest advantage of batch distillation is its ability to cope better with different separation duties, *i.e.* varying feed mixture, composition and product specification, by simply changing the operating conditions and operating policy of the column.

- Batch distillation may be more suitable in terms of economics and operability for small-scale production. For small volume production, the capital cost associated with the equipment size of the column, batch or continuous, is low compared to other costs such as controls, storage and buildings. Hence, the choice of batch or continuous distillation can be made simply on feed pattern, economics and operability grounds on a case-by-case basis (Rose, 1985).

- Batchwise operation provides batch identity, *i.e.* product tracking and traceability, which is imperative in the production of drugs and foodstuffs which has strict quality control requirement.

1.2 Definitions

In the following sections, different column configurations for the batch distillation process and its basic operation are defined. Various ways of distilling non-ideal mixtures are also briefly defined.

1.2.1 Column Configurations

The configuration of a column can be classified primarily by the position of the feed charge, number of column sections and the points from which products are withdrawn. In most industrial cases, the batch distillation column is traditionally utilised in a rectifying mode in what is often termed as the *conventional* regular column or batch rectifier. *Unconventional* columns were first proposed by Robinson and Gilliland (1950). However, these novel unconventional columns are still in theoretical research and pilot plant development stages and have yet to be implemented for industrial usage. The different column configurations considered in this research are defined below (see Figure 1.1):

Regular Column

This traditional configuration consist of a bottom reboiler where the feed is charged, a rectifying column section (trays or packed) and a top total (usually sub-cooled) condenser system. The products are withdrawn from the reflux drum from the top into a series of product accumulator tanks. The overhead composition varies during the operation (most volatile first) and a number of cuts is usually made which are either desired product cuts or intermediate fractions, or offcuts, that may be recycled to subsequent batches. The least volatile component may be recovered as a product in the reboiler at the final stage of the operation. This configuration is also referred to as a batch rectifier or batch rectifying column.

Inverted Column

The inverted configuration was first proposed by Robinson and Gilliland (1950). In this stripping mode column, liquid feed is charged to the top reflux drum while the products and offcuts are withdrawn from the bottom reboiler. High boiling components are withdrawn first, followed by more volatile components. This configuration is also referred to as a batch stripper or batch stripping column.

Middle Vessel Column

This configuration was originally proposed by Robinson and Gilliland (1950) and the interest in it was rekindled when it was re-introduced by Hasebe *et al.* (1992). The feed is mostly charged into a vessel located between two column sections, *i.e.* splitting the column into rectifying and stripping sections. Products and offcuts can be withdrawn simultaneously from both the reflux drum at the top (most volatile first) and from the reboiler at the bottom (least volatile first). There can be great variety within this configuration, as pointed out by Warter and Stichlmair (1999), defined by the way the liquid and vapour streams are arranged between the middle vessel and the rectifying and stripping sections. This configuration is also sometimes referred to as a *complex* column.

Multivessel Column

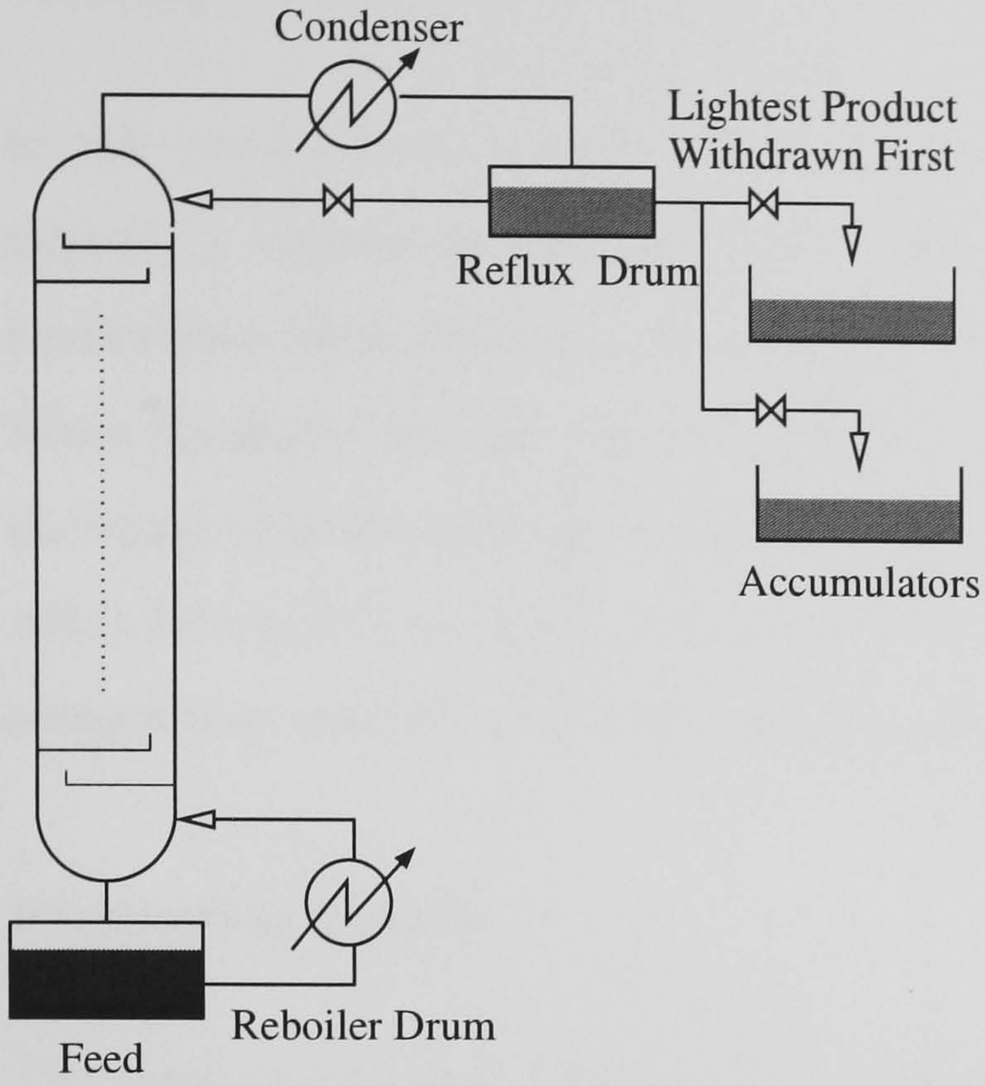
This configuration was proposed by Hasebe *et al.* (1995) and is an extension of the middle vessel column concept. This configuration comprises of three or more column sections with side vessels located between the columns. The feed and products can be charged to, and withdrawn from, these side vessels, respectively, as well as from the reflux drum and reboiler. This type of column gives the greatest flexibility and number of degrees of freedom. It can be converted to the regular, inverted or middle vessel column by fixing some of the parameters. This configuration is also referred to as a *multi-effect* column.

1.2.2 Basic Modes of Operation

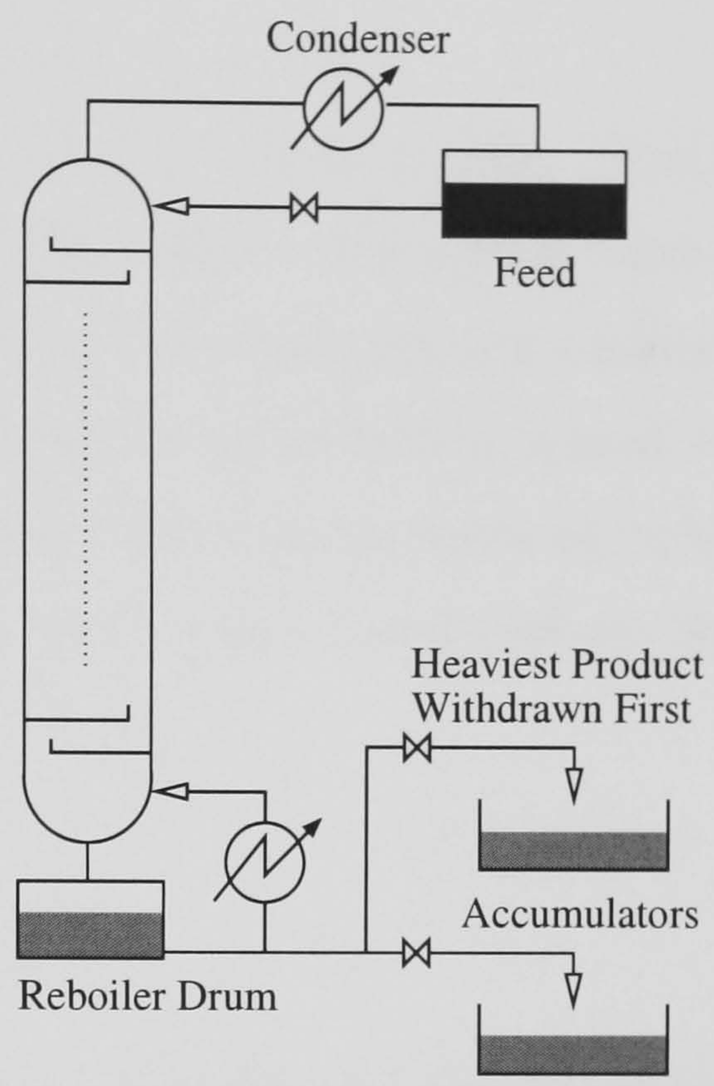
In practice, the operation of a typical batch distillation column can be classified into four periods, *i.e.* set-up, start-up period, production and shutdown periods. These periods are described below:

Set-up Period

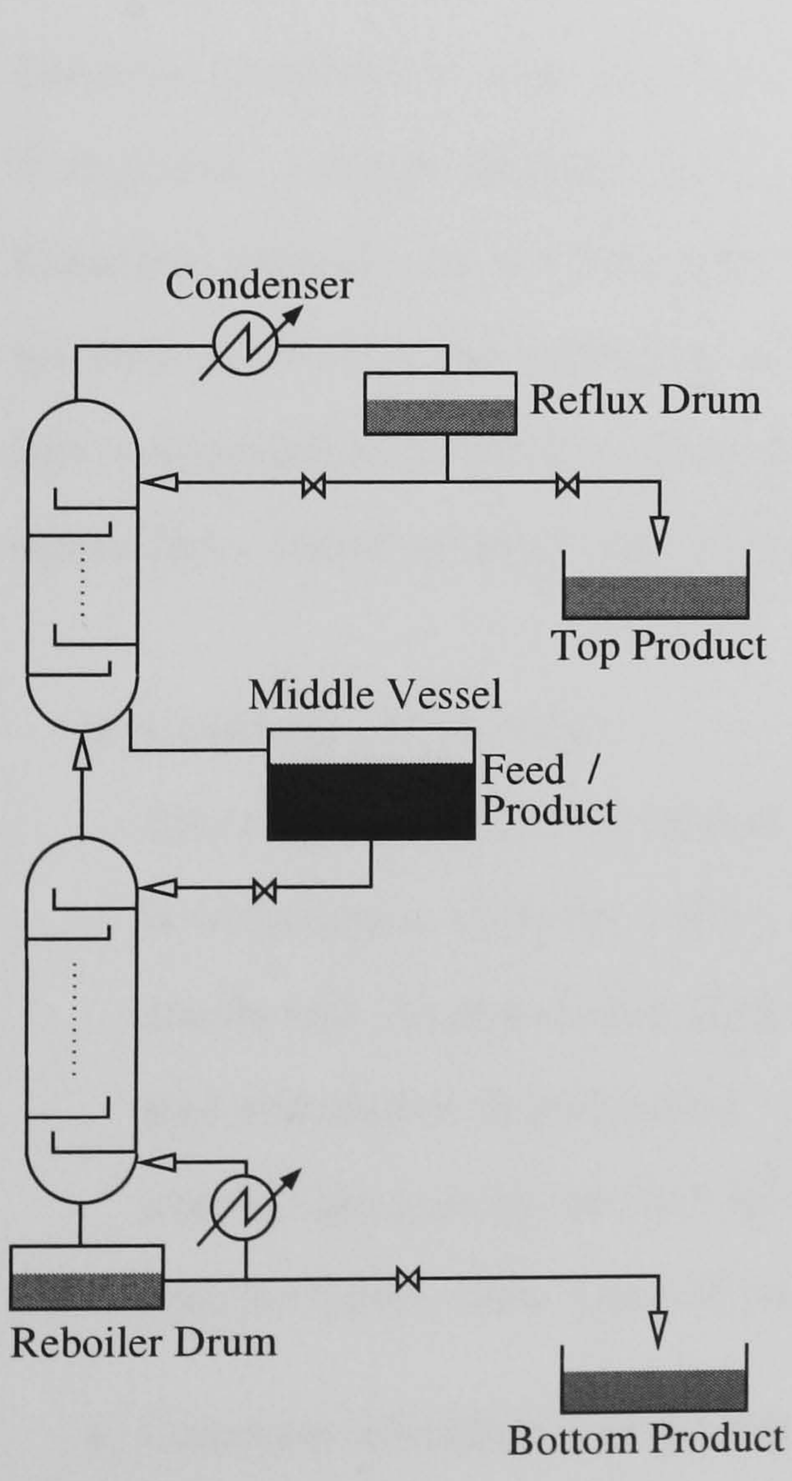
The column and the ancillary equipments are cleaned and prepared. The mixture to be separated is charged into the feed drum.



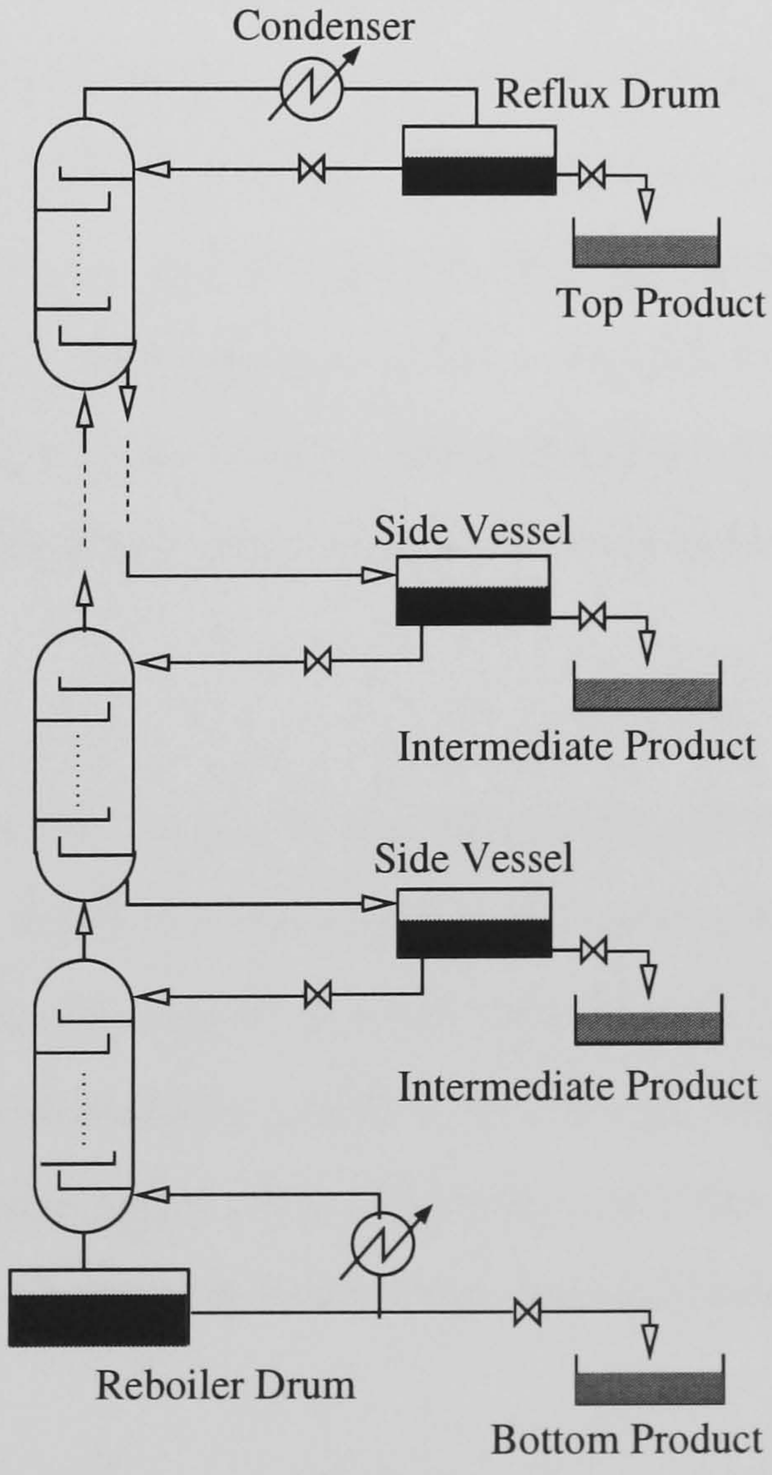
(a) Regular Column



(b) Inverted Column



(c) Middle Vessel Column



(d) Multivessel Column

Figure 1.1: Different batch distillation column configurations

Start-up Period

In this period, heat is applied to bring the mixture to its boiling point. Part of the mixture is vapourised and rises upward through the column. The coolant valve to the condenser is opened causing the vapour to be condensed and collected into a reflux drum. When the liquid fills the reflux drum to a certain level, the reflux valve is opened, causing the liquid to be redirected into the column. Normally, the column is operated under total reflux for a period of time, usually until a steady state is approached or until the distillate composition reaches a desired product purity.

Production Period

The production period starts when the reflux ratio is decreased and part of the distillate is withdrawn into an accumulator. The *operating policy* in this period is the manner in which the column is operated, *i.e.* the choice of values or profiles for the operating decision parameters such as the withdrawal policy, column vapour loading policy and, if required, solvent addition policy and offcut recycling. The operating policy and its duration depends on the requirements of the separation duty and the economics of the process. Conventional operating policies include constant reflux ratio and constant distillate composition whilst less conventional policies include optimal reflux ratio and cyclic operation. These product and offcut withdrawal policies are described below:

- Constant reflux ratio

  The constant reflux operation is the most common practice in the industry. Product is withdrawn with the reflux ratio fixed at a pre-defined constant value during the whole cut. Composition higher than the specification is produced at the beginning and thereafter deteriorates. The accumulated product at the end should be at, or above, the desired purity. In the subsequent cuts, different (constant) reflux ratios may be used. This type of policy is termed as *piecewise constant* policy.

- Constant distillate composition

  The distillate composition is held constant during the operation by varying the reflux ratio, normally using a controller. In this mode of operation, the reflux ratio

is varied continuously to produce on-specification product until a time when the reflux ratio has increased to some value considered to be uneconomical.

- Optimal reflux ratio

  The reflux ratio profile used is optimal with respect to a particular objective function (*e.g.* maximum profit, maximum productivity, minimum time, minimum energy consumption rate *etc.*) and subject to a set of constraints (*e.g.* product amount and purity).

- Cyclic operation

  This mode is characterised by a repetition of three steps which make up one cycle, *i.e.* filling-up, transient total reflux and dumping. In the first step, little or low reflux back to the column and no distillate withdrawal causes the holdup in the reflux drum to increase to a pre-defined level. In the total reflux step, the reflux flowrate is set equal to the vapour flowrate into the reflux drum, so that the reflux drum holdup remains constant. After a sufficient duration (*i.e.* until steady state or a certain product purity is achieved), the distillate is withdrawn with either no reflux or low reflux to the column. The cycle is then repeated until all the desired products are separated. The cyclic operation for batch distillation columns has mainly been mentioned in the context of research and pilot plant testing (*e.g.* Sørensen, 1999 and Noda *et al.*, 1999). The industrial implementation of this policy has so far not been attempted.

In terms of the column vapour loading policy, the choices include:

- Constant reboiler duty

  In this policy, the reboiler heat input is typically set at or near its highest capacity without flooding the column and held constant throughout the batch processing time. Due to the transient state of the composition and holdup in the reboiler. and the rate of vapourisation of the components, the vapour rate out of the reboiler varies continuously.

- Constant boilup rate

  This policy requires the vapour rate out of the reboiler to be kept at a particular level throughout by varying the reboiler duty accordingly.

- Constant condenser vapour load

  Vapour rate into the condenser is held at a constant value throughout the operation by varying the reboiler duty accordingly.

- Constant distillate or bottom rate

  This requires constant rate of distillate (regular column) or bottom (inverted column) throughout by varying the reboiler duty accordingly.

The latter three policies are more commonly used for theoretical or simulation studies rather than in practice due to the greater difficulty involved in their implementation.

Shutdown Period

The heat, and subsequently the coolant supplies, are turned off. The holdup in the column is collapsed and left to drain into the reboiler drum. The liquid collected is either a main product cut or a residual offcut that may be recycled to the next batch. The condenser holdup may be mixed with the final top cut or with the reboiler material.

Further Remarks

The above operating modes apply primarily to a regular column. For other configurations, the operation modes will be a variation of the sequences mentioned above. It is also possible to combine the various operating policies for a given separation. Apart from the withdrawal and column vapour loading policies, there are other operating decision variables, especially for more flexible configurations like the unconventional multivessel column (see section 1.3), the choice of which depends on the properties of the mixture being separated as well as on economics consideration.

1.2.3 Distillation of Complex Systems

Close-boiling and low relative volatility mixtures are difficult and often uneconomical to distill, and azeotropic mixtures are impossible to separate into pure components by

ordinary distillation. Yet such mixtures are quite common and many industrial processes depend on efficient methods for their separation.

An azeotropic mixture is a non-ideal mixture with a deviation so large that the pressure-composition and temperature-composition phase diagrams exhibit a minimum or maximum point. At these minima and maxima, the liquid phase and its equilibrium vapour phase have the same composition and the dew-point and bubble-point curves are tangent with zero slope. These are the defining conditions for a *homogeneous* azeotrope where a single liquid phase is in equilibrium with a vapour phase. Mixtures that form two liquid phases are capable of forming *heterogeneous* azeotropes where the overall liquid composition is identical to the vapour composition, but the vapour and liquid surfaces are not tangent with zero slopes (Fair, 1997).

Azeotropes and low relative volatility mixtures can be separated in a distillation column by altering the relative volatilities, or in the case of azeotropes, shifting the azeotropic point to a more favourable position. This can be done by using appropriate operating pressure or by the addition of specially chosen chemicals to facilitate the separation. The methods of azeotropic separations can be classified as follow:

- Extractive distillation

  Extractive distillation is defined as distillation in the presence of a miscible, high-boiling, relatively non-volatile component (known variously as solvent, entrainer, extractive agent or extractant) that does not form any azeotropes with other components in the mixture. The solvent breaks the azeotrope by altering the relative volatilities of the various components, which then permit the sequential withdrawal of different cuts, each one rich in one of the components of the feed, from the reflux drum at the top. The solvent is retrieved in the bottom stream and may be re-used.

- Homogeneous azeotropic distillation

  Similar to extractive distillation, a miscible liquid separating agent is added to break the azeotrope mixture. However, a light solvent is used and recovered in the distillate.

- Heterogeneous azeotropic distillation

  In this method, commonly referred to simply as *azeotropic distillation*, the liquid separating agent forms one or more azeotropes with the components in the mixture and causes two liquid phases to exist over a broad range of compositions. The immiscible liquid-liquid phases are then separated according to a distillation sequence.

- Distillation in the presence of ionic salts

  The salt dissociates preferentially in the liquid mixture and alters the relative volatilities sufficiently so that the separation becomes possible (*e.g.* Llano-Restrepo and Aguilar-Arias, 2003).

- Reactive distillation

  The separating agent reacts preferentially and reversibly with one or more of the azeotropic components. The reaction product is then distilled from the non-reacting components and the reaction is reversed to recover the initial component.

- Pressure-swing distillation

  A series of columns operating at different pressures are used. A separating agent which forms a pressure-sensitive azeotrope can also be added to ease separation.

1.3 The Batch Distillation Optimal Configuration, Design and Operation Problem

Unlike continuous distillation which is typically studied at steady state for most design, operation and control purposes, batch distillation is inherently a dynamic system due to temporal variations in composition and holdup, *i.e.* the amount and composition of material remaining in the column change over time as the products are withdrawn in the order of their volatilities. As a result, for a tray column, the dynamic mathematical model which describe its operation typically comprises of ordinary differential equations for material and energy balances, and algebraic equations for the equilibrium relationships, hydrodynamics and physical properties.

Typically, the general problem statement for batch distillation design is the specification of the most cost effective batch distillation system for the separation of a mixture (or several mixtures) into its components to a specified or minimum degree of purity. The system to be specified involves the following decision variables categorised as follows (summarised in Table 1.1):

- Configurational Variables
  - number of column sections
  - initial feed charge distribution
  - product, offcut and solvent withdrawal locations
  - feed, offcuts and solvents input locations (semi-batch)
- Design Variables
  - batch size
  - transfer unit capacity (number of plates or height of packing)
  - column holdup
  - column diameter
  - detailed column dimensions
- Operation Variables
  - column pressure
  - task intervals duration (thus, total batch time)
  - column vapour loading
  - reflux or(and) reboil ratios
  - solvent addition rate
  - additional variables

Degrees of Freedom	This Study	Summary Remarks	Chapter†
Configurational Variables			
Number of column sections	S, $\surd$	Different column configurations selection.	6
Initial feed distribution	S, $\surd$	Different column configurations selection.	5, 6
Withdrawal location	S, $\surd$	Different column configurations selection.	6
Input location	S, $\times$	Solvent addition location specified in chapter 4. Semi-batch and off-cut recycling not considered.	(4)
Design Variables			
Batch Size	S	Typically based on an *a priori* specific plant capacity requirement.	-
Transfer unit capacity	S, $\surd$	Only tray column sections are considered.	5, 6
Column holdup	S		-
Column diameter	$\times$	Typically based on detailed calculation after preliminary design.	-
Detailed dimensions	$\times$	Typically based on detailed calculation after preliminary design.	-
Operation Variables			
Column pressure	S	Typically based on thermophysical/chemical properties, safety factor and general economic heuristic.	-
Task intervals	$\surd$		4, 5, 6
Column vapour loading	$\surd$	Constant reboiler duty, constant boilup rate and constant condenser vapour load considered.	4, 5, 6
Reflux and/or reboil ratios	$\surd$	Constant piecewise policy considered.	4, 5, 6
Solvent addition rate	$\surd$	Constant rate considered.	4, 5, 6
Additional variables	S, $\surd$	Extra variables afforded by unconventional columns, *i.e.* inter-column stream configuration and side heat input	4

S specified; $\surd$ optimised; $\times$ not considered
† chapter(s) in which the variable is optimised

Table 1.1: Summary of degrees of freedom in batch distillation design

Configurational Variables

Traditionally, these configurational variables are seldom considered in industrial batch distillation design where the design engineer invariably starts off the design process with a batch rectifier structure in mind. If these fundamental configurational degrees of freedom are explored, novel unconventional columns emerge (as defined in section 1.2.1) that might provide performance advantages over the traditional batch rectifier. These configurational variables are inherent in the highest hierarchy of decision-making, namely - where should the feed be placed, where should the products be collected and should more than one column section be used? The consideration of these configurational decision variables may provide greater gain in the process economics and performance than the optimisation of the design and/or operation variables (described below) as in common design practices. Furthermore, these novel column configurations can themselves evolve additional operation degrees of freedom compared to the traditional batch rectification configuration.

Other configurational decisions look at whether, and where, to introduce the feed intermitently during the process, either in a semi-batch mode where only part of the feed is fed during the process or, to the extreme case of *sequential steady state batch distillation* (Abram *et al.*, 1987 and Mujtaba, 1997) where the whole feed is charged continuously to a suitable location in the middle of the column from a feed tank. The input location of offcuts from the previous batch and solvent (if needed) can also be considered and may be determined optimally.

Design Variables

Theoretically, a batch distillation system capable of handling large batch sizes is more cost effective due to economy of scale and reduction in total set-up time over a production period. However, the nominal batch size is normally dependent on the short or medium term inventory requirement of a particular plant. The batch size can be determined *a priori* via optimal capacity and product portfolio planning, or even as a result of a wider supply chain optimisation study.

The main design variable to be decided upon is the transfer unit capacity, *i.e.* the number of stages or amount of packing. Column liquid holdup also affects the performance (*e.g.* batch processing time) of batch distillation depending on the separation task (*e.g.* *degree of difficulty of separation* as defined and proven by Mujtaba and Macchietto, 1998).

It should also be noted that the column diameter and detailed sizing of the trays' internal dimensions, condenser, reboiler, reflux drum and accumulator units are normally performed during the detailed engineering stage which is *after* the main decision variables (configurational, design and operation variables) have been obtained. For example, when the column holdup and column vapour loading have been set, the column diameter and tray internal dimensions are then designed to adjust the vapour flow conditions so as to take into account foaming, flooding, weeping and entrainment effects. Therefore, the inclusion of these parameters in the optimisation framework, although theoretically possible, is not typically performed because it serves only to increase the complexity and size of the optimisation problem, to a point of very high, and possibly unjustifiable, computational cost and to very little benefit.

Operation Variables

Operation variables are typically concerned with how a *fixed* batch distillation column is to be operated in order to fulfil the separation task cost effectively. Thus, for an *existing* column configuration and design, the operation variables such as operating pressure, tasks intervals, column vapour loading, reflux ratio, reboil ratio and solvent addition rate can be optimised.

The setting of the column operating pressure in practice depends, as a first priority, on the thermal sensitivity of the separation mixture. In the case of thermo-sensitive mixtures like high molecular weight material, vacuum operation might be used in order to reduce the boiling temperature of the material to below a value at which product decomposition occurs. For other mixtures, an optimal pressure can be decided based on economic trade-off, *e.g.* when pressure is raised, the relative volatility decreases resulting in the need for more contact stages and higher reflux. Pressurised and vacuum operation

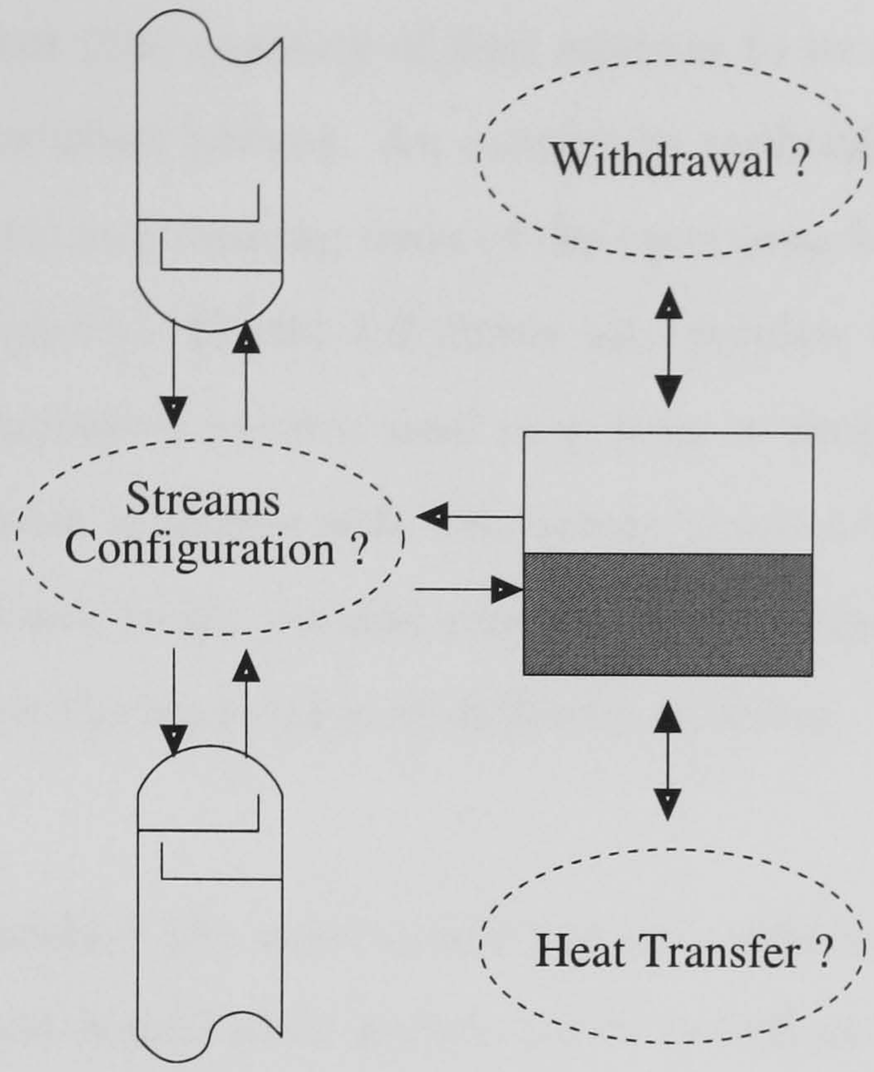


Figure 1.2: Additional operational degrees of freedom in complex columns

are often purposely avoided due to their complexity, their risk factor as well as capital and operating penalties incurred by additional auxiliary equipments for pressurisation and refrigeration. In practice, the determination of pressure via a rigorous economic optimisation framework is seldom deemed necessary considering the computational effort involved and whenever possible, the column is typically operated at atmospheric pressure or slightly above it (Smith, 1995).

As mentioned above, some unconventional column configurations can derive additional variables that can also be taken into consideration and used to improve the performance of the batch distillation process. For example, complex configurations like multivessel and middle vessel columns supply further decisions on how the vapour and liquid streams between their side vessels and column sections ought to be connected, as well as whether the opportunity for additional heat input and material withdrawal from the side vessels should be taken up (Figure 1.2).

Computer-aided Optimal Configuration, Design and Operation

This thesis is concerned with the determination of the optimal, *i.e.* the most economical configurational, design and operation variables for a given separation duty, *i.e.* minimum

product purity requirement (the quantity of feed mixture to be separated and operating pressure are given, as discussed above). An economics optimality criterion is based on production revenue, capital and running costs of the open-loop batch distillation systems operating at nominal capacity. Figure 1.3 shows an overview of the batch distillation design problem. The separation system may vary from a simple ideal binary mixture to complex multicomponent mixtures with azeotropic characteristic. The process constraints may be as varied as a single purified product to a multipurpose scenario whereby a single unit is utilised for the separation of different mixtures.

Note that this study considers the most important and time-consuming period of production (production period described in section 1.2.2) as well as the total reflux duration of the start-up period. The simulation of the start-up period where an empty column is filled progressively requires either a detailed modelling of the plate hydraulics, or the process can be simplified by assuming a certain holdup state during initialisation, *e.g.* at feed composition and the boiling point temperature. The set-up and shutdown periods are normally represented by an estimated fixed time duration (typically based on previous experience of similar batch sizes).

Also note that this study does not consider partially fed batch distillation (*e.g.* semi-batch or sequential steady state) nor the *steady state* design which considers the added dimension of inter-batch offcuts recycling.

A Note on Uncertainty

Like most unit operations, batch distillation is susceptible to internal uncertainty like process disturbances and external uncertainty such as changing feed and product demand. Thus, controllability and flexibility issues may be defined and considered concurrently during the optimal design stage. Other *operability* issues like column availability, safety, environment impact, start-up, shutdown and maintainability may also be quantified in some way and integrated within the process design optimisation problem. The full integration of these process operability issues within the process design stage is beyond the scope of this project where the emphasis is more on economic design and operation

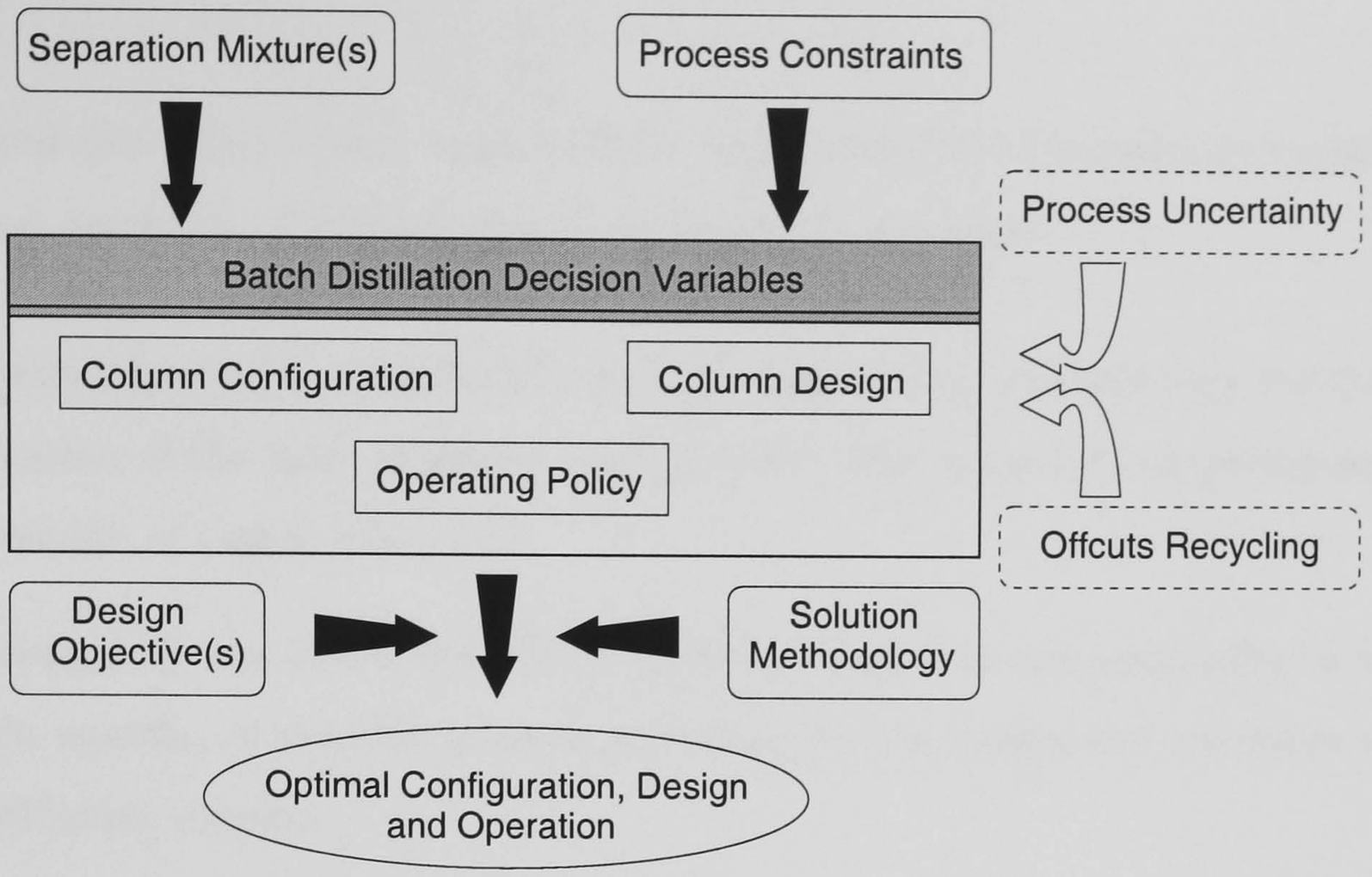


Figure 1.3: Overview of the batch distillation design problem

in a nominal process, as mentioned above. However, closed-loop design based on dual objectives of economics and operability is highlighted as an important direction of future research (chapter 7) following the work in this thesis.

1.4 Motivation and Objectives of This Thesis

Batch distillation is becoming more important in parallel with the recent increase in the industrial production of high value-added and low-volume fine and specialty chemicals, pharmaceuticals, polymers and bioproducts. With high demand growth rates, increased competitiveness and tightened environmental regulations faced by these industries, there is a continuous impetus towards increasing the cost-effectiveness, productivity and efficiency of the production process (Furlonge, 2000).

In recent years, one of the most significant efforts in providing cost effective solutions involves seeking improvement at the fundamental batch distillation configuration itself, resulting in the emergence in academic studies of various novel unconventional columns and their alternative operating policies. Another trend that can be seen in both academic research and industrial practice is the increasing application of computer-aided tools for process engineering studies.

The general aim of this work is to gain further understanding of the optimal configuration. design and operation of different batch distillation systems by:

- developing suitable models and applying optimisation methodology for the determination of the most profitable configuration, design and(or) operating policy for a number of case studies, and
- investigating the effect of different design scenarios on the optimality in order to elicit specific, or possibly general, guidelines for the design and operation of batch distillation columns.

A state-of-the-art literature review in this thesis (see chapter 2) as well as a similar review conducted by Kim and Diwekar (2001) have identified some main motivational areas of research in batch distillation which directs the work conducted in this research:

- operation of complex batch distillation processes
- batch distillation design
- unconventional batch distillation processes

1.4.1 Operation of Complex Batch Distillation Processes

Many separations performed in industry involve low relative volatility and non-ideal mixtures like azeotropic systems. Distillation methods for their separation, as defined in section 1.2.3, are commonly applied in a continuous multi-column mode in industry. However, practical application of complex distillation in the batch mode is still limited. For example, the concept of extractive batch distillation has only been explored recently in the open literature. Although it is believed that the extractive batch distillation process has been attempted in the industrial setting, no reports on this can be found in the open literature.

The majority of the studies available on extractive batch distillation were concerned with background feasibility work, for example, theoretical graphical analysis, as well as

a number of works which attempted simulation studies. The inherent dynamic nature of the batch distillation process coupled with the added complexity of thermodynamic behaviour of azeotropic mixtures and the extra degrees of freedom like solvent addition, make for a challenging problem. As a result, simplified models have been used in order to reduce the computational effort required for the challenging task of dynamic simulation and optimisation. However, the assumptions employed can reduce the accuracy, and thus, the applicability of the solutions obtained (Furlonge, 2000). The optimal operating policy was mostly explored via simulation studies, a method that does not give the whole picture of the process when the degrees of freedom interact with each other. The research to date, coupled with industrial expectation, point to a need for a more rigorous optimisation study of these complex batch distillation systems.

In this work, a comprehensive optimisation of the operation of an extractive batch distillation system is studied based on the feed, products, solvent and operating costs. The study takes into account the utilisation of a detailed model and the exploration of a wider range of degrees of freedom in order to achieve a more realistic and rigorous study of the process (chapter 4).

1.4.2 Design of Zeotropic Batch Distillation Processes

The optimal operation of batch distillation for zeotropic mixture separation has been the subject of extensive research over the years; as such, they are fairly well-understood and well-established. On the other hand, there have been relatively few studies on optimal design of batch distillation. This might be due to optimisation difficulties associated with the inherent transient property of the batch process and the problem of handling discrete design variables, such as the integer number of stages in the column and(or) the disjunction encountered in column configuration selection, in addition to the continuous operation variables. The complexity of the optimisation problem can increase for unconventional columns, for example, in the case of multivessel columns where the lengths of column sections relative to each other are to be determined. The challenge also appears in tackling the nonconvexity of the optimisation solution space especially when the objective function is a nonlinear economics model which encompasses both design and operational economics simultaneously.

In industrial practice, the design of batch distillation columns is still commonly carried out using an heuristic approach that relies on engineering knowledge and experience which starts off with an order of magnitude calculation followed by judgement based on iterative calculations and sensitivity analysis aided by repeated computer simulation runs.

This work aims to present the optimal design of batch distillation processes (chapter 5) using a stochastic optimisation methodology (chapter 3). The optimisation is also expanded to tackle simultaneous optimal column configuration selection, design and operation (chapter 6).

1.4.3 Comparison of Unconventional Batch Distillation Processes

In industry, the batch distillation process is typically operated in the traditional rectification mode which consists of a single column section with the feed charged to the reboiler. In response to industrial impetus for more efficient separation processes, academic research on unconventional column configurations and operating policies has regained considerable activity over the past decade although the introduction of these novel processes were first made by Robinson and Gilliland (1950). Nonetheless, the implementation of these unconventional columns are seldom seen in industrial practice. This may be attributed to the fact that the body of research in this area is still confined to the development stages like feasibility analysis, simulation-based sensitivity studies and optimal control studies. Recently, a few experimental works have begun in the laboratory and pilot-plant scale (Barolo *et al.*, 1996; Wittgens and Skogestad, 2000; Noda *et al.*, 2001 and Warter *et al.*, 2002).

Insofar as works on comparative studies between regular and unconventional columns based on optimisation is concerned, the reported work in this area is rather limited. Thus, there is a need to initiate more rigorous comparative optimisation studies based on the use of a more conclusive economics performance index (instead of the frequently used minimum process time, minimum energy consumption or maximum production rate indices). There is also scope for better exploitation of the additional degrees of

freedom afforded by the unconventional columns and consideration of the influence of a wider range of design scenarios (chapters 4 and 5). This study also aims to expand on the previous optimal operation works to include the consideration of design variables in order to compare optimally-designed unconventional and regular columns for the first time based on the economics objective function (chapter 5).

1.4.4 Summary of Thesis Objectives

The specific objectives of this thesis are as follow:

- To conduct a more rigorous optimisation study on the complex extractive batch distillation operation.
- To investigate the optimal operation of the extractive distillation process in alternative configuration such as the middle vessel column.
- To compare the optimal operation performances of the different column configurations.
- To develop a methodology for optimal design of batch distillation processes.
- To apply the above methodology to the design of both regular and unconventional columns and to conduct a more comprehensive study on the effect of different design scenarios on the optimal results.
- To compare the optimally-designed regular and unconventional columns.
- To develop a methodology for automated determination of optimal batch distillation configuration design.
- To apply the methodology to both binary and multicomponent case studies and to gain insight on the configuration selection under different separation scenarios.

1.5 Outline of The Thesis

Chapter 2 presents a critical survey of selected literature on the modelling of batch distillation followed by a state-of-the-art review on extractive batch distillation, the design

of batch distillation columns and finally, works on unconventional batch distillation processes.

Chapter 3 outlines the dynamic models used in this work. The dynamic simulation technique as well as the deterministic and stochastic approaches used to solve the dynamic optimisation, are presented.

In chapter 4, a comprehensive optimal operation study on the separation of a binary azeotropic mixture using extractive batch distillation is presented. A detailed tray model was used and the operating policies of both regular and middle vessel columns were investigated for different scenarios and compared.

In chapter 5, work on simultaneous design and operation of batch distillation is presented. The effect of different design scenarios for both regular and multivessel columns are studied, followed by a comparison between the two configurations. The optimisation in this chapter is tackled using the stochastic approach.

Chapter 6 attempts the batch distillation configuration design problem by embedding the decision on column configuration selection within the stochastic optimisation approach used in the previous chapter. Case studies for both binary and multicomponent zeotropic mixtures separation are presented.

Finally, in chapter 7, the overall conclusions and main contributions of this project are listed. This thesis concludes with a brief outline of possible future research.

Chapter 2

Literature Review

This chapter presents a detailed literature review on particular areas of past research that motivate the objectives of this work, as outlined in chapter 1. The chapter starts with a classification of batch distillation models followed by a critical chronological review on the research areas of extractive batch distillation, batch distillation design methodology and unconventional columns.

2.1 Review of Batch Distillation Modelling

The theoretical analysis of the elementary *simple distillation* presented by Rayleigh (1902) marks the first theoretical work on batch distillation. The concept of reflux and the use of plates and packing materials to increase the mass transfer converts this simple still into a distillation column. McCabe and Thiele (1925) presented a graphical analysis of the staged distillation column with reflux and thus provided the analytical basis for batch distillation operating modes. Smoker and Rose (1940) presented the first analysis of the constant reflux operation of batch distillation using the Rayleigh equation in conjuction with the McCabe-Thiele graphical method. Bogart (1937) presented the first analysis of the variable reflux policy using a similar method as that of Smoker and Rose (1940). These early models of the regular column, which relied on analytical and graphical analysis, were all limited to ideal binary systems.

Modelling Assumptions	Simplified Models	Rigorous Models	Detailed Models	Rate-based Models
Negligible liquid holdup on the trays	√			
Constant molal overflow	√	√†		
Negligible vapour holdup	√	√		
Phase equilibrium	√	√	√	
Perfect mixing	√	√	√	√
Adiabatic operation	√	√	√	√

† semi-rigorous model

Table 2.1: Classification of batch distillation models

Later, the introduction of digital computers to solve models numerically played an important role in the gradual relaxation of modelling assumptions and in the handling of more complex models (*e.g.* more components and number of trays). However, the stiffness of the set of the DAE system describing the batch distillation model [1] coupled by its complexity [2], used to render digital simulation of the process a non-trivial task, due to the instability of the numerical integration methods used (*i.e.* explicit integration techniques as opposed to implicit) and the initial lack of computational capability (*i.e.* speed and memory), respectively. This led to the development of alternative simplified models that attempt to reduce the computational time in a trade-off with the accuracy of the model prediction. The range of model abstraction studied in the past literature can be broadly classified as follow, according to the assumptions employed (Table 2.1):

- Simplified models
- Rigorous models
- Detailed models
- Rate-based and higher hierarchy models

[1] attributed to the large differences in component volatilities or(and) the much greater ratio of reboiler to tray holdup, compared to continuous distillation. Thus, the tray dynamics are significantly faster than the reboiler dynamics. In addition, batch distillation display severe transients compared to continuous distillation where the variations are relatively smaller.

[2] that grows with the number of stages and components.

Simplified Models

The simplification of the models in this category mainly involves tackling the stiffness during numerical integration caused by the large time constant difference between the reboiler and the trays. The modelling solution (as opposed to integration solution) to this problem is based on splitting the system into two levels - the reboiler, where the dynamics are slower, is represented by differential equations; whilst the rest of the column tray cascade is simplified in some way. For example, the column tray cascade can be assumed to be in a quasi steady state where the composition and enthalpy changes in the condenser and trays were assumed to be zero (*e.g.* Domenech and Enjalbert, 1981 and Bernot *et al.*, 1991). The *pseudo stationary cascade* model presented by Ruiz Ahón and de Medeiros (2001) is another similar variant where the dynamic response delay of the column tray cascade is neglected, thus the cascade model operates in a pseudo stationary state where the internal and output variables change simultaneously with an input change. Also, in this model, the mass balance and equilibrium set of equations are de-coupled from the energy balance equations by relaxing the latter group of equations via a McCabe-Thiele approximation.

In another example, in the *short-cut* model as proposed by Diwekar and Madhavan (1991), the column tray cascade was simplified by developing a more direct relationship between the distillate and bottom reboiler compositions based on the Hengestebeck-Geddes' equilibrium relationship, Fenske and Underwood equations and Gilliland correlation (FUG). It assumes negligible tray liquid holdup and constant molal overflow (*i.e.* negligible sensible heats effect and similar latent heats of the mixture components). The short-cut models have also been modified to incorporate holdup issues (Diwekar, 1994). Other works on short-cut models include Galindez and Fredenslund (1988), Logsdon *et al.* (1990), Chiotti and Iribarren (1991), Al-Tuwain and Luyben (1991), Sundaram and Evans (1993), Zamar *et al.* (1998) *etc.*

Rigorous Models

Unlike the simplified models where the holdup in the column section is neglected, the category of rigorous models considers the stage-by-stage column dynamics, in addition

to the dynamics of the major holdups in the reboiler and condenser. The negligible tray liquid holdup assumption is relaxed, and holdup on each stage is responsible for the dynamics of each stage with differential mass and energy balances being the governing equations. The differential energy balance is sometimes simplified to an algebraic equation by assuming fast energy dynamics or, in the case of *semi-rigorous* models, the assumption of constant molal overflow is retained. The assumptions retained in this type of model include negligible vapour holdup, constant liquid holdup in the trays, phase equilibrium and adiabatic operation. Works with this model include Huckaba and Danly (1960), Meadows (1963), Distefano (1968), Boston *et al.* (1980), Mujtaba and Macchietto (1996) and Sharif *et al.* (1998).

Detailed Models

Works by Bosley and Edgar (1994), Tomazi (1997) and Furlonge *et al.* (1999) have included greater details in batch distillation modelling which relaxes the assumptions of negligible vapour holdup and constant liquid holdup in the trays. Their models took into account variable liquid and vapour holdups by the inclusion of equations describing tray hydraulics like liquid weir overflow, downcomer dynamics and pressure drop-vapour flowrate relationships. For studies involving optimal control, they found that common modelling assumptions such as constant molal overflow and, indeed, constant liquid tray holdup, had significant impact on their results. For example, it was found that the optimal values of decision variables are significantly affected by the degree of detail in modelling, and moreover, the optimal solutions obtained with simpler models were found to violate important constraints when they were implemented in detailed model simulations (Furlonge, 2000).

Rate-based and Higher Hierarchy Models

So far, the categories of models described above assume theoretical stages where the vapour and liquid streams leaving a stage are in equilibrium with each other. The common method of representing non-equilibrium or real trays is to use an efficiency factor of some kind, most likely to be either an overall efficiency or the Murphree efficiency which can be easily incorporated into the equilibrium set of equations. There have been works

that included mass and energy transfer dynamics which are known as non-equilibrium or rate-based models (Mehlhorn *et al.*, 1998 and Kruel *et al.*, 1999). In these models, the balance equations are written for both liquid and vapour phases within the stage and then linked by transport equations around the interface (*e.g.* Maxwell-Stefan diffusion equations for mass transfer). The models mentioned so far assume perfect mixing of the fluid in the stages. To relax this assumption, higher hierarchy models consider partial mixing (non-uniform composition in a stage). This adds greater complexity to the model as the dimension of concentration change increase from one to three taking into account the flow pattern in the stage.

Further Notes

The basic common assumptions among all the models described above are that the phases are prefectly mixed and that the column is operated adiabatically. To the best of our knowledge, there has been no report on study effort involving the modelling aspect of mixing phenomena and heat loss to the column environment.

In terms of the thermodynamics models used, many studies have utilised the ideal behaviour or constant relative volatility assumptions. Using rigorous thermodynamics models, which take into account both liquid and vapour fugacities as a function of temperature, pressure and composition, adds to the complexity of the batch distillation system. Nonetheless, these rigorous thermodynamics models are essential for dealing with the separation of non-ideal and azeotropic systems.

2.1.1 Summary

Over the past four decades, many studies have been conducted on the modelling and simulation of the conventional batch distillation column. Hence the dynamic behaviour for the regular column is a fairly well understood area. Over the course of computational and algorithmic advancement, a wide hierarchy of models have been employed. These models have generally been simplified to aid the numerical solution, namely to tackle the stiffness of the system of describing equations and(or) to reduce the computational times. However, with the advent of more robust solution techniques, the use of simplified

modelling techniques, as opposed to using a more robust solution algorithm such as implicit integrators, to circumvent the numerical solution problem, is no longer warranted in most circumstances.

As a result, the selection of batch distillation models nowadays should be based on the purpose of its usage and thus considering the aspects of computational costs [3], accuracy of model prediction and data availability. For example, in feasibility and quick sensitivity studies, the usefulness of abstracted models depends on the computational ease with which they can be analysed for global behaviours without compromising accuracy.

In the case of simulation and optimal control studies whereby the tray geometry is available, it has been shown that using detailed or rate-based models can achieved better prediction of experimental results with reasonable computational effort, thus the trade-off between computational cost and accuracy becoming less of an issue (Kreul *et al.*, 1999 and Furlonge, 2000). However, for problem such as configuration and design optimisation studies, the complexity of the model to be utilised is limited by the non-availability of preliminary data such as the detailed column internal dimensions (as described in Section 1.3) and to some extent, computational cost.

2.2 Review of The Extractive Batch Distillation Process

Extractive distillation is an important process in the chemical industries for the separation of azeotropes and components with close boiling points. Continuous extractive distillation is a well-known and widespread technology in the chemical industries. In contrast, extractive batch distillation is a relatively new process with limited instances of industrial implementation. This process offers the advantages of both batch and extractive distillations, hence it has been actively studied in recent years. In this section, a chronological review of works conducted on extractive batch distillation is presented, starting with the work by Bernot *et al.* (1990) to the latest work by Warter *et al.* (2002).

[3] Note that some simplified models can be computationally more expensive than the rigorous model, for example in the case of quasi steady state model where an iterative solution of nonlinear tray-to-tray algebraic equations is needed.

Bernot *et al.* (1990) introduced a graphical technique that can be used to determine the sequence of distillate fractions from an initial feed composition of an azeotropic mixture. The method involved defining the different batch distillation regions on the state composition map in the limiting case of infinite number of stages and reflux or reboil ratios. The method is rapid and easy as the residue curve maps required only minimal computational effort to generate and minimum knowledge of the boiling points of the pure components and azeotropes. Once the batch distillation regions have been defined, the sequence of product fractions can be predicted for any initial feed composition depending on which distillation regions the composition lies on. A ternary mixture was presented as an example in their study. Bernot *et al.* (1991) extended their method of sequence and feasibility prediction to inverted columns and quaternary mixtures. They also showed how the analysis of batch distillation regions can help in solvent selection and that the separation sequence can be modified by using appropriate solvents. A similar technique was also used by Düssel and Stichlmair (1995) and Salomone and Espinosa (1999). The possible drawback of this method, which can be useful for preliminary design, is that residue curve maps for mixtures having more than four components cannot be visualised and are difficult to represent.

Although extractive distillation is widely used in industry as a multi-column continuous system, Yatim *et al.* (1993) were the first to consider the application of extractive batch distillation via a pilot plant column and a computer model for comparison. They proposed and simulated a four steps operating policy for extractive batch distillation of binary minimum azeotrope mixtures (with semi-continuous solvent feeding near the top of the column):

Step 1 Total reflux operation without solvent feeding. This establishes the azeotropic composition at the top.

Step 2 Total reflux operation with solvent feeding. This breaks the azeotrope and achieves a high purity of the light component at the top.

Step 3 Finite reflux ratio operation to withdraw the light component.

Step 4 Finite reflux operation without solvent feeding. The heavy component is withdrawn and high purity solvent is left in the reboiler.

The model used by the authors included dynamic mass and energy balances, but constant liquid holdup and negligible vapour holdup in the trays were assumed. Simulation results for an acetone-methanol separation mixture using water as solvent were found to be in close agreement with experimental data. They achieved a recovery of 82% for acetone with 96 *mol*% purity. It was shown that the termination time of the production of the more volatile component due to the deterioration of the distillate quality, can be indicated by the steep rises of temperatures on the trays below the solvent feed tray. The group added some parametric simulation studies in a later paper (Lang *et al.*, 1994). Using a similar model, the effects of various parameters like reflux ratio, solvent feedrate, solvent feed tray, reboiler heat duty, batch size and feed composition were investigated by varying one parameter individually whilst keeping the others constant. Although an optimal operation cannot be determined from these results as the parameters are interdependent, nonetheless, the parametric analysis demonstrated the significant effects of the operation parameters on the separation performance of the extractive batch distillation. Lang *et al.* (2000) investigated the performance of extractive batch distillation for the separation of maximum azeotropes. Again, the effects of various parameters were studied via simulation whilst the optimum values of the parameters were determined through sensitivity analysis.

Watson *et al.* (1995) did work similar to Bernot *et al.* (1991), *i.e.* development of an operating policy for separating a highly non-ideal quarternary mixture which involved firstly the prediction of product sequence using the graphical method of Bernot *et al.* (1991) and then modifying the sequence via solvent addition (near the top of the column) to favour the entrainment of selected components. The thermodynamic analysis of the methanol, cyclohexane, ethanol and water mixture using the NRTL physical property model showed a complex system of four binary azeotropes and a ternary azeotrope, some of which are heterogeneous. They also presented the industrial cyclic operating policy. For this particular industrial separation objective, simulations with a rigorous model showed that cyclic operation offers simpler implementation and more advantages over extractive distillation operation. However, this was a special case where the quantity of some of the components in the initial feed mixture was very small and comparable to the tray and condenser holdups. Therefore, besides the distillation region, the column holdup has a

great influence on product withdrawal and ultimately on the choice of operating strategy.

Safrit *et al.* (1995) was the first published work analysing the potential of the middle vessel column for extractive batch distillation. In their paper, the graphical analysis for continuous extractive columns by Wahnschafft and Westerberg (1993) was applied to batch distillation. Using the insight of a pinch point curve technique, they were able to explain graphically that the limited recovery of the distillate product (82%) seen in the work of Yatim *et al.* (1993), was due to the column's extractive section becoming infeasible during the column operation. They also conclude that it is theoretically possible to recover all the distillate product by avoiding the intersection of the still path and pinch point curve. They argued that increasing the solvent flowrate (near the top of the column) would delay this intersection but this would also require a huge still pot, *i.e.* a total distillate recovery would require an infinite size still pot; however, this problem can be overcome by using the middle vessel column. With more degrees of freedom to influence the still path, *i.e.* top and bottom withdrawals and solvent rates, the middle still pot can be *steered* towards the intermediate component to achieve high recovery in the distillate. The steering was accomplished by adding an equality constraint into their model. The problem of still pot size is also overcome because in this configuration, solvents are continuously withdrawn from the bottom. A simulation was conducted for both the batch regular and middle vessel columns. The operation for the middle vessel was performed in the following steps:

Step 1 Solvent addition with distillate removal but with no bottom removal.

Step 2 Solvent addition with bottom and distillate removal. The bottom is recycled back to the top part of the column as solvent.

For the same distillate purity as seen in Yatim *et al.* (1993), the recovery was increased to 99.5%. Safrit *et al.* (1995) also noted that while the steering of the still path in the middle vessel does determine the 'optimal' solvent withdrawal to addition ratio, the flexibility of the middle vessel column allows for many other column parameters to be optimised. For example, the results of their simulation show that, although the recovery has been improved, large reflux and reboil ratios were needed, which resulted in a long processing time. This trade-off suggest a need for a thorough optimisation in order to

find the most economical performance.

Safrit and Westerberg (1997) conducted simulation studies to find the sensitivity of the column parameters to a profit function, in particular, solvent flowrate and switching times between operation steps. They stated that, although the still path steering operation policy towards the intermediate component may have been an optimal or near optimal way of maximising the product revenue, a more realistic objective function and operation policy should include overall costs, *e.g.* utility consumption, waste costs, inventory and capital investment. The operation steps are similar to Safrit *et al.* (1995) but unlike their operation, not all of the acetone was recovered. Hence, a third step is added to achieved the desired purity of the intermediate component (methanol) in the still:

Step 1 Solvent addition with distillate removal but with no bottom removal.

Step 2 Solvent addition with bottom and distillate removal. The bottom is recycled back to the column as solvent.

Step 3 No solvent addition. Distillate cut is azeotropic mixture. This step purifies methanol in the still.

In this case study, the azeotropic mixture from the third step can be used in the next batch, hence this study neglected waste costs, inventory and capital investment in their objective function. This work again highlighted the need for a thorough optimal operation study involving a wide range of degree of freedoms to find the best economic performance.

Lang *et al.* (1995) and Lelkes *et al.* (1998a) extended the work of Lang *et al.* (1994) by considering other operating policies for the regular column. Instead of constant reflux ratio during the last two steps of the operating policy described by Yatim *et al.* (1993), a constant distillate composition policy and a mixed policy of constant reflux ratio and constant distillate composition were considered and simulation results were compared to experimental results. Improvements in production rate, batch processing time, energy and solvent consumption were obtained in some cases. This again highlights the need for rigorous optimisation to explore the full potential of extractive batch distillation.

Lelkes *et al.* (1998b) presented a method to assess the feasibility of extractive batch distillation for a ternary mixture using a graphical technique. The feasibility, product sequence and limiting values of operation parameters were determined by calculating feasible profiles of the column sections on the triangular composition diagram. They concluded that feasibility and sequence of component withdrawal depend on the location of the extractive column section stable node. They found that for a required distillate purity, there was a minimum solvent flowrate, minimum number of trays for the extractive column section as well as a minimum and a maximum number of trays in the rectifying column section. For sufficiently high solvent flowrates there was no maximum reflux ratio. They performed a pilot plant experiment which agreed with their proposed feasibility method. For the same experiment, the feasibility method by Safrit *et al.* (1995) did not yield proper results. When they compared operation of the regular column to the middle vessel column, they found that, contrary to the results by Safrit *et al.* (1995), the middle vessel column achieved less recovery under the same conditions. Lelkes *et al.* (1998b) supported their analysis with experimental results while Safrit *et al.* (1995) conducted only a simulation study using a short-cut model to back their theoretical analysis.

Warter and Stichlmair (1999) also compared the middle vessel column with the regular column for extractive batch distillation. For the middle vessel column, novel modifications of the stream configuration between the column sections was proposed including feeding the liquid stream from the upper column section directly into the lower column section. Separation of an ethanol-water mixture using ethylene glycol as solvent (fed semi-continuously near the top of the column) in both middle vessel and regular columns, having the same number of trays, were simulated. The operating policy was similar to Safrit *et al.* (1995) with constant solvent rate, fitted for every process, and constant product composition withdrawal. The results showed that the temperature in the feed vessel, the solvent demand and the energy demand for the middle vessel processes were significantly lower than those of the regular batch column. The comparisons were made via simulation without considering the full range of degrees of freedom available to each column configuration. Since the reboiler power used for the simulation is the same for the regular and middle vessel columns, the energy demand difference reported were a result of heat integration.

Cheong and Barton (1999a,b,c) analysed the feasibility and operating policy of extractive batch distillation in the middle vessel column using the graphical technique, *i.e.* locating feasible distillation regions and plotting column composition profiles. Similarly to the previous graphical studies described above, the assumptions underlying their analysis were an infinite number of stages and reflux ratio based on a simplified model of negligible column tray holdup and constant molal overflow. Also similarly to earlier studies, they investigated the concept of steering the middle vessel composition by manipulating the operation parameters to overcome distillation barriers. An operating policy based on a ternary diagram analysis was proposed.

Milani (1999) conducted an experimental study on extractive batch distillation of acetone-methanol in a batch mode of solvent feeding whereby the solvent, *i.e.* water, was charged together with the feed mixture into the reboiler at the beginning of the operation. The purity and recovery of the acetone product were measured for various solvent to feed ratios. However, the operation of the column was not described, thus the significance of the results is unclear. The results showed no distinct trend between the solvent to feed ratios and acetone purity, recovery and productivity and no explanation was given.

Mujtaba (1999) conducted the first dynamic optimisation of extractive batch distillation for a regular column. He considered batch mode and semi-continuous mode of solvent feeding as well as full and partial feed charge operations. With product specifications fixed by customer demand, the operation can be optimised using the maximum profit objective function with switching times, reflux ratio, solvent feed rate and recovery as the optimisation decision variables. The overall optimisation problem was decomposed to separate independent single period dynamic optimisation (SDO) problems. The decomposed SDO are either maximum productivity problems or minimum time problems and are applied to each single task period according to the separation problem. In one of the examples given, he considered semi-continuous solvent feeding mode with partial feed charge for the separation of the acetone-methanol mixture with water as solvent. Reflux ratio and solvent feed rate were the resulting optimisation decision variables after the decomposition. With this decomposition method, certain maximum time constraints

were also needed to avoid exceeding the capacity of the reboiler. The model assumed constant molal liquid holdup and negligible vapour holdup in the column trays.

Phimister and Seider (2000) proposed a new operating policy for the middle vessel column called semi-continuous operation where the process cycles through several campaigns of re-feeding the intermediate withdrawals. In the case of extractive distillation, the semi-continuous policy appears to be more complicated than the other policies studied so far. However, there is potential for reducing the overall processing time for a large number of batches by eliminating start-up and shutdown periods of operation. Nonetheless, no optimisation or comparative study was conducted to investigate this potential as yet.

Ruiz Ahón and de Medeiros (2001) presented another optimisation study on the extractive batch distillation in a middle vessel column based on a profit objective function. The separation is to recover ethanol from its nearly azeotropic hydrated form with ethylene glycol as solvent fed into the middle vessel together with the feed at the beginning. The solvent is recovered at the bottom and recycled to the top of the rectifying column section during the operation. A simplified pseudo stationary cascade model was used which assumed zero column holdup, instantaneous dynamic response in the column and a simple McCabe-Thiele approximation to de-couple the MESH equations. Instead of separating the mixture into required purities, this fundamental product constraint was neglected and replaced by a price function, which meant that all product purities were acceptable and have values corresponding to the price function. The unconstrained optimisation (due to the elimination of the purity constraints) was solved using a Simplex method. Other decision variables like solvent recycle rate and internal vapour flowrate, were specified as constant and not taken into consideration as degrees of freedom.

Furlonge (2000) also attempted an optimisation study on extractive batch distillation in both regular and middle vessel columns based on a profit objective function. The separation of ethanol and water using ethylene glycol as the solvent (added near the top of the column) was considered. A rigorous packed column model assuming fast energy dynamics, constant vapour and liquid holdup in the column and constant pressure was considered. The solution is then checked via simulation using a more detailed model

(where the assumptions mentioned are relaxed). If it was found to be feasible with respect to all the constraints, the solution is accepted as the final solution; otherwise, the solution is modified in an *ad hoc* manner in order to restore feasibility.

Cui *et al.* (2002) performed an experimental study of the extractive batch distillation of a binary azeotropic mixture similar to that considered by Milani (1999) in the middle vessel column and matched the experimental data with simulation results of a rigorous model. Their experimental and simulation results showed that both the solvent at the bottom and the product at the top of the column can be withdrawn simultaneously for a long period of time. However, more time was needed for the solvent to reach the required purity than the time needed for the more volatile component to reach its desired purity, so that the time to withdraw solvent from the bottom is delayed. The operating policy was as follows:

Step 1 Total reflux operation without solvent feeding.

Step 2 Total reflux operation with solvent feeding.

Step 3 Solvent addition with distillate removal but with no bottom removal.

Step 4 Solvent addition with bottom and distillate removal.

Step 5 Top and bottom offcuts without solvent addition.

Warter *et al.* (2002) also performed a pilot plant scale experimental investigation of extractive batch distillation operation in both regular and middle vessel columns. The separation of an equimolal ethanol-water mixture with ethylene glycol as the solvent (added near the top of the column) was considered. The operating policy performed on the regular column was similar to the steps of Yatim *et al.* (1993) but additional offcut periods were required after steps 3 and 4. For the middle vessel column, the operating policy was as follow:

Step 1 Total reflux operation without solvent feeding until azeotrope concentration is reached in the upper column section.

Step 2 Solvent addition with distillate removal.

Step 3 Purification of product in the middle vessel. This step consisted of a period of total reflux with no solvent addition, followed by a period of distillate offcut.

2.2.1 Summary and Research Statement

Extractive distillation in the batch mode to separate azeotropic mixtures has been the subject of active research over the past decade or so (Table 2.2). Many of the works spanning the past decade have been concentrated on the preliminary feasibility issue, or determining whether a specified separation is attainable for a given feed mixture composition and design and operation parameters. The general characteristic of the feasibility studies includes graphical-based techniques which looked at the still location in the ternary or quarternary composition diagrams in distillation regions demarcated by still path and column composition profiles. These studies are also based on simplified models and assumptions of infinite number of stages and reflux or reboil ratios.

Many simulation, and recently, experimental studies (Milani, 1999; Cui *et al.*, 2002 and Warter *et al.*, 2002), have also been reported with some work trying to investigate the effect of various operation variables on the performance of the process via sensitivity analysis. However, this method of analysis does not give the whole picture of the economics of the process since the degrees of freedom interact with each other. In an effort to understand the optimal operation of the process, a few optimisation studies have begun to emerge in recent years using simplified (Ruiz Ahón and de Medeiros, 2001) and rigorous models (Mujtaba, 1999 and Furlonge, 2000).

In line with the progression of work in this area, the work in this thesis aims to present a more comprehensive optimisation study of the extractive batch distillation process. The rigorous study here is based on a detailed model and on the exploration of a wider degrees of freedom than previously considered. The effect of different feed compositions on the optimal operating policy is also investigated. The optimal operating policy for extractive batch distillation in both regular and middle vessel columns are compared (chapter 4).

References	Column	Approach to Feasibility and Operating Policy Study	Model
Bernot *et al.* (1990)	Regular, Inverted	Graphical	Simplified
Yatim *et al.* (1993)	Regular	Simulation, Experiment	Rigorous
Lang *et al.* (1994)	Regular	Graphical	Rigorous
Lang *et al.* (1995)	Regular	Graphical	Rigorous
Watson *et al.* (1995)	Regular	Graphical, Simulation	Simplified, Rigorous
Safrit *et al.* (1995)	Middle vessel	Graphical, Simulation	Simplified
Düssel and Stichlmair (1995)	Regular, Inverted	Graphical	Simplified
Safrit and Westerberg (1997)	Middle vessel	Simulation	Simplified
Lelkes *et al.* (1998a)	Regular	Simulation	Rigorous
Lelkes *et al.* (1998b)	Regular, Middle vessel	Graphical, Simulation, Experiment	Simplified, Rigorous
Warter and Stichlmair (1999)	Regular, Middle vessel	Simulation	Rigorous
Salomone and Espinosa (1999)	Regular	Graphical	Simplified
Cheong and Barton (1999a,b,c)	Middle vessel	Graphical, Simulation	Simplified, Rigorous
Milani (1999)	Regular	Experiment	-
Mujtaba (1999)	Regular	Optimisation	Rigorous
Phimister and Seider (2000)	Middle vessel	Simulation	Rigorous
Ruiz Ahón and de Medeiros (2001)	Regular, Middle vessel	Optimisation	Simplified
Furlonge (2001)	Regular, Middle vessel	Optimisation	Rigorous
Cui *et al.* (2002)	Middle vessel	Experiment, Simulation	Rigorous
Warter *et al.* (2002)	Regular, Middle vessel	Experiment, Simulation	Rigorous
This work (2003)	Regular, Middle vessel	Optimisation	Detailed

Table 2.2: Chronological summary of extractive batch distillation literature

2.3 Review of Batch Distillation Design

Although a great number of works have been devoted to studying the operation and optimal control of zeotropic batch distillation (reviewed by Furlonge, 2000), far fewer studies have been conducted on the design aspect. Here, a chronological review of literature related to batch distillation design is outlined.

Diwekar *et al.* (1989) were among the first to consider the optimal design and operation of batch distillation simultaneously via a computer-aided mathematical programming technique. A simplified model with the assumptions of constant molal overflow, zero column holdup and constant relative volatility, as well as the short-cut approach using the Fenske and Underwood equations and Gilliland correlation (FUG), were used. They formulated the problem as a constrained nonlinear programming problem (NLP) with the number of trays treated as a continuous variable and an economics objective function that included product revenue, capital cost and utility cost. Sequential quadratic programming (SQP) and Pontryagin's maximum principles were used for the optimisation.

Similarly, Logsdon *et al.* (1990) explored the problem of simultaneous optimal design and operation of the regular column. The problem was formulated as a NLP by treating the number of trays as a continuous variable. The FUG short-cut model was used which assumed constant molal overflow, no tray liquid holdup and constant relative volatility. The objective function included product revenue as well as capital and utility costs correlations described in Douglas (1988). The control profiles (*i.e.* differential equations) were discretised using orthogonal collocation on finite elements to obtain a set of algebraic equations which was then placed as constraints within the NLP problem. The NLP utilised a reduced SQP as the optimisation algorithm. Several design scenarios were presented. One case study involved optimising the number of trays and reflux ratio profile given an initial feed composition, feed charge, boilup rate, set-up time and purity constraints. Another case study involved the optimal flexible design and operation of a multipurpose column involving two binary mixtures. In this particular case, the objective function involved maximising the sum of the individual profits but ignoring the downtime for the switching of the feeds.

Al-Tuwaim and Luyben (1991) conducted a comprehensive economic analysis for the design of a regular batch distillation column using a semi-rigorous model assuming constant molal overflow and constant relative volatility. From their multiple simulation results, a set of short-cut design and cost correlations were produced. Hence, for given relative volatilities, product purities, energy cost, payback period and material of construction, the optimum number of trays and reflux ratio can be obtained using the design correlations. However, the repetitive simulation process of obtaining the design correlations data is tedious and computationally expensive and the resulting correlations has very limited coverage, *i.e.* in this case, the correlations are valid only for binary and ternary systems, constant reflux ratio policy, equal fractions feed composition, specific economic data, *etc.*

Diwekar (1992) expanded the work of Diwekar *et al.* (1989) and presented a new approach for the solution of the optimal design and operation problem. A new solution algorithm for optimal control was proposed which combines the feature of both Pontryagin's maximum principle and the NLP technique. The short-cut FUG model approach was then unified with the combined techniques to solve the optimal design and control problem simultaneously. This approach was claimed to be computationally several times faster than that of Logsdon *et al.* (1990) who used the short-cut FUG model approach and the NLP technique.

Bernot *et al.* (1993) proposed a step-by-step design procedure to estimate both design and operation variables without solving the batch distillation optimisation problem. Based on a simplified model with quasi steady state column and constant molal overflow assumptions, the concept of dimensionless *warped* time was used in the model for the purpose of decoupling the variation of flows in the model so that the decoupled model is only described in terms of variation of compositions. The decoupled model is then used to calculate the duration of each cut and number of stage through a complicated calculation algorithm which requires pre-specification of the recoveries in each cut as well as heuristically chosen reflux ratios (*e.g.* $R = 1.5R_{min}$). Finally, the vapour flow rate in the column is calculated from the dimensionless warped time model with an arbritrarily

specified batch operating time. Thus, the design obtained from their proposed step-by-step procedure is not optimal.

Mujtaba and Macchietto (1996) reported another method for simultaneous optimisation of design and operation of a multicomponent batch distillation column using a rigorous model. The problem was solved by a two-level NLP optimisation algorithm. The algorithm consisted of an outer loop where the design variable, *i.e.* number of trays, and other operating decision variables, *i.e.* recoveries in each cut, are optimised based on the overall profit objective function, and a number of inner loop subproblems (according to the number of separation tasks represented by a state-task-network (STN)) where operating control variables, *i.e.* reflux ratios, are optimised based on a decomposed minimum time objective function. In the outer loop problem, the profit objective function evaluation is performed which requires a complete solution of the sequence of the inner loop minimum time subproblems. The number of trays was relaxed to be a continuous variable whilst in the inner loop subproblem, its value would be rounded off to the nearest integer. The gradients with respect to that variable, required by the outer loop, were evaluated by finite differences using the function and constraint values at the rounded off values and its next higher integer value. Control vector parameterisation (CVP) was used for the discretisation of the control profiles and SQP for the optimisation algorithm. The case study presented includes the single separation duty design scenario and design for a multipurpose column. The profit objective function included net product revenue and the same form of operating and capital costs correlation used by Logsdon *et al.* (1990). However, unlike Logsdon *et al.* (1990), the formulation reflects the different *importance* of each duty, which is more realistic when the column is to be designed to handle multiple separation duties. For the design of the multipurpose column, the designer specified the total available annual processing time and how it is to be allocated among the different feed mixtures.

Salomone *et al.* (1997) presented a short-cut design procedure by adapting the FUG approach frequently used in continuous distillation. For a given separation duty, the minimum number of trays and minimum reflux ratio are calculated using the modified Fenske and Underwood methods, respectively. Then, extensive simulations were con-

ducted to construct a correlation in Gilliland coordinates based on these minima trays and reflux values. The resulting correlation between number of trays and reflux ratio can then be used to select the optimal design pair using economic data. However, their work did not proceed to tackle the optimisation.

Sharif *et al.* (1998) presented another mathematical programming approach to tackle the optimal design taking into account column design and operation parameters using a rigorous model. The mathematical formulation led to a mixed integer nonlinear programming problem (MINLP) which was solved via decomposition using an outer approximation and augmented penalty (OA/AP) solution algorithm. Treating the number of trays as a discrete variable required the introduction of a superstructure in the modelling that encompasses all possible numbers of trays between a lower and an upper bound. The OA/AP algorithm comprised of a continuous primal subproblem involving the optimisation of a column with fixed number of trays and a master subproblem involving the solution of a mixed integer linear programming (MILP) problem that determines the number of trays to be considered at the next iteration in the algorithm. The primal subproblem was solved as a standard NLP, *i.e.* CVP discretisation and SQP optimiser algorithm, whilst the master MILP was solved using a branch and bound algorithm. The proposed methodology was demonstrated with a case study involving a sequence of two regular columns.

Instead of considering both design and operation variables simultaneously in a single optimisation framework, Kim (1999) started by obtaining the optimal operations, *i.e.* reflux ratio profiles, for a series of columns with fixed number of trays using a NLP technique (CVP discretisation and SQP optimiser). Then, capital investment cost, *i.e.* heat exchanger, tray and column costs, is deducted from the optimal operating profits. The column having the largest net overall profit is then taken as the optimum design. The study used a semi-rigorous model that assumed constant relative volatility and linear variation for the vapour flowrate in the column.

Oldenburg *et al.* (2002) presented a mixed logic dynamic optimisation (MLDO) approach for the optimal configuration and sequencing of two batch distillation units in series. *i.e.*

to determine whether the columns were to be operated regularly or inversely and which component was to be removed in the first column and which to be fed to the second column. The problem was formulated using disjunctive programming whereby the decisions were represented by boolean variables (true or false) resulting in a MLDO problem. The solution approach has similarity with the typical decomposition approach used to solve MIDO - a primal dynamic optimisation subproblem with fixed boolean variables and a master MILP subproblem which was obtained by transforming the linearised disjunctive program using Big-M constraints (Yeomans and Grossmann, 2000). Although the configurational and operation aspects were optimised, it is important to note that the number of trays was actually specified. It is unsure whether the proposed MLDO approach could be expanded to tackle the number of trays without reverting back to some form of MINLP.

2.3.1 Summary and Research Statement

Over the past decade or so, although considerable progress has been made in the optimal operation of zeotropic batch distillation in the traditional regular column (a comprehensive review in this area has been presented by Furlonge, 2000), far fewer studies have dealt with the computer-aided optimal design issue of batch distillation (Table 2.3). The optimal design aspect of batch distillation is a more challenging problem as it involves simultaneous determination of the discrete design variables (*i.e.* number of stages) combined with the continuous optimal control for an inherently dynamic and nonlinear process.

The previous works in this area include step-by-step calculation algorithms which may result in non-optimal designs (Bernot *et al.*, 1993 and Salomone *et al.*, 1997) to correlations drawn from a series of multiple simulations that can only be applied to a narrow range of design scenarios (Al-Tuwaim and Luyben, 1991). Other works attempted to solve the design optimisation by decomposing the mixed integer dynamic optimisation problem (MIDO) to NLP approaches (Diwekar *et al.*, 1989; Logsdon *et al.*, 1990; Diwekar, 1992; Mujtaba and Macchietto, 1996 and Kim, 1999). The majority of the works also utilised simplified models with short-cut FUG equations or semi-rigorous models with constant molal overflow assumption. Sharif *et al.* (1998) managed for the very first time to tackle

References	Optimal Design	Approach	Model
Diwekar *et al.* (1989)	√	NLP†	Simplified§
Logsdon *et al.* (1990)	√	NLP†	Simplified§
Al-Tuwaim and Luyben (1991)	√	Parametric simulations	Semi-rigorous
Diwekar (1992)	√	Combined NLP/Pontryagin's maximum principle†	Simplified§
Bernot *et al.* (1993)	×	Step-by-step procedure	Simplified¶
Mujtaba and Macchietto (1996)	√	Decomposed NLP†	Rigorous
Salomone *et al.* (1997)	×	Step-by-step procedure	Simplified§
Sharif *et al.* (1998)	√	MINLP	Rigorous
Kim (1999)	√	NLP	Semi-rigorous
Oldenburg *et al.* (2002)	‡	MLDO	Unspecified
This work (2003)	√	Stochastic	Rigorous

† number of trays treated as continuous; ‡ optimal configuration (number of trays fixed)
§ short-cut FUG equations; ¶ dimensionless model

Table 2.3: Chronological summary of computer-aided batch distillation design literature

the problem using a rigorous model and by treating the number of stages directly as an integer variable in a MINLP formulation. In order to do so, mathematical modification had to be introduced to the standard batch distilation model itself in order to convert it into a superstructure.

So far, work on simultaneous optimal configuration and design has not been reported. For example - although Sharif *et al.* (1998) managed to determine the optimal number of trays, the configuration of the two sequential columns, *i.e.* regular mode, considered in the case study, had been pre-assumed. For a similar case of two column series, Oldenburg *et al.* (2002) optimised the configuration and sequencing of the columns, *i.e.* regular versus inverted mode, however, the number of trays in the columns were pre-specified.

In short, there is an impetus for more studies on optimal design, and indeed, simultaneous optimal configuration, design and operation of batch distillation, which has yet to be solved. Therefore, this work aims to propose a stochastic optimisation methodology

for batch distillation design (chapter 3) capable of handling a wider range of degrees of freedom than previously considered in the literature including column configuration selection (chapters 5 and 6).

2.4 Review of Unconventional Batch Distillation Processes

The traditional batch rectifier is a widely used unit operation in the chemical industries. Nevertheless, due to ever pressing need to increase process efficiency and reduce cost, a proliferation of studies concerned with investigating alternative batch distillation processes were seen over the past decade. A chronology of works on unconventional batch distillation processes is reviewed in this section.

Chiotti and Iribarren (1991) considered the optimal operation of the inverted column for the separation of a binary mixture and compared it with the traditional regular column. A simplified model was used with the assumption of pseudo steady state in the column section, constant molal overflow, constant relative volatility and negligible vapour holdup. For a high purity specification on the heavy product, the inverted column was found to be better than the regular column based on a total annual cost objective function. On the other hand, the regular column was better when the purity specification on the light product was high.

Mujtaba and Macchietto (1994) presented a comparative optimal operation study between the middle vessel column and the regular column for the separation of a ternary mixture. They considered minimum batch processing time as the objective function and a semi-rigorous model with the assumptions of constant molal overflow, constant relative volatility, negligible vapour holdup and constant liquid holdup, was used. For a number of different scenarios considered, *i.e.* combinations of various feed compositions, relative volatilities and product specifications, it was found that the middle vessel column gave better results than the regular column in some of the cases. There appeared to be no straightforward guideline to establish the best configuration for a given separation duty.

Davidyan *et al.* (1994) presented a theoretical analysis of the dynamic behaviour of the middle vessel column using a simplified model with the assumption of negligible liquid holdup in the column section, constant molal overflow, constant relative volatility and negligible vapour holdup. The theoretical analysis, based on infinite number of stages, highlighted qualitatively the potential advantage of the middle vessel column over the regular column in terms of the existence of additional steady states and degrees of freedom in the middle vessel column. A simple comparison of the batch processing time between the two columns for a separation of a binary mixture was also conducted using the simplified model. The middle vessel column was operated under constant distillate and bottom flowrates whilst the regular column was operated under a constant distillate composition policy, *i.e.* decreasing distillate flowrates. For the equimolar binary feed, the middle vessel was found to be approximately twice as fast as the regular column.

Meski and Morari (1995) presented comparison similar to that of Davidyan *et al.* (1994), *i.e.* the middle vessel, inverted and regular columns were compared in terms of batch processing time for a separation of a binary mixture via simulation on a simplified model. Again, the middle vessel column was operated under constant distillate and bottom flowrates whilst the regular and inverted columns were operated under the constant distillate composition policy. The middle vessel column was again shown to give the best performance. They also concluded that the inverted column required longer batch time than the regular column due to the non-symmetry of the vapour-liquid equilibria of the binary mixture.

Hasebe *et al.* (1996) simulated the operation of the middle vessel and regular columns using a semi-rigorous model of constant molal overflow, constant relative volatility, negligible vapour holdup and constant tray liquid holdup. The maximum quantity of product collected per unit time, *i.e.* production rate, was used as the performance index. For the separation of a ternary mixture, the middle vessel column was found to be more effective than the regular column for cases in which the separation of the heavy component was easier, *e.g.* higher product purity specification for the top product. The reason postulated was that the stripping column section, which is similar to an inverted column, had a lower separation efficiency; consequently, separations in which removal of the heavy

product was easier than removal of the light product would yield a better performance.

Sørensen and Skogestad (1996) compared the optimal operation of the inverted and regular columns in term of minimum batch processing time for a given product specification. The semi-rigorous model was used with constant molal overflow, negligible vapour holdup, constant tray liquid holdup and constant relative volatility. The inverted column was found to be superior for cases where the products were to be recovered at high purity from a feed low in light component. Below this high purity product specification, the regular column performed better. The regular column was found to be better for cases where the products were to be recovered at high purity from a feed rich in light component; below this high purity product specification, the inverted column performed better. The explanation given was that, for the regular column, it would have been more difficult to transfer a small quantity of light component from the bottom of the column to the top. However, there exists a product purity below which the regular column is better.

Noda *et al.* (1999) and Noda *et al.* (2001) compared the performance of the inverted and regular columns in term of production rate, *i.e.* quantity of product collected per unit time, by optimising the operation in the cases of total reflux, constant reflux and variable reflux policies. They used a semi-rigorous model with constant molal overflow, negligible vapour holdup, constant liquid holdup on the trays and constant relative volatility. For a ternary mixture case study with different feed compositions and product specifications, they found the performance of the inverted column inferior to that of the regular column. For both inverted and regular columns, the total reflux policy was found to give the best performance, followed by the variable reflux policy and constant reflux policy, respectively.

Furlonge *et al.* (1999) presented the optimal operation of the multivessel column for the separation of an equimolar quaternary mixture and compared its performance to that of the regular column. The study was based on a detailed model which considered tray hydraulics and variable liquid and vapour holdup in the column. A wide range of operation variables were explored and the comparison was performed on the basis of the mean energy consumption rate. They found that the mean energy consumption rate of the

multivessel column was about half that of the regular column having the same number of trays.

Kim and Diwekar (2000) compared the performance of the inverted, middle vessel and regular columns based on three performance indices - product purity and yield, column flexibility and thermodynamic efficiency, as defined in their paper. The comparison was conducted for a binary mixture separation and for a range of design and operation variables using parametric simulation based on a statistical sampling technique. Due to the high number of simulations required by this approach, a simplified model was used which assumes zero holdup in the column section, constant molal overflow and constant relative volatility. A number of observations were drawn from the results but ultimately they surmised that the trade-offs between the performances indices should be investigated in a multi-objective optimisation framework.

Ruiz Ahón and de Medeiros (2001) presented an optimal operation study on the inverted, middle vessel and regular columns using a profit objective function that included product revenue and utility cost. However, instead of distilling the feed mixture into specified purities, this fundamental product requirement was neglected and replaced by a price function, which meant that all cuts were acceptable and have values corresponding to the price function, *i.e.* an unconstrained optimisation problem. A simplified pseudo stationary cascade model was used which assumed zero column holdup, instantaneous dynamic response and a simple McCabe-Thiele approximation to decouple the MESH equations. The comparative study considered the separation of a quaternary mixture with different feed compositions. The middle vessel column was found to give the best performance in most cases whilst the inverted column was better in the case of heavy feeds compared to the regular column, and vice versa.

Warter *et al.* (2002) compared the operation of the middle vessel column and the regular column for the separation of a ternary mixture in a pilot plant scale experimental study. The middle vessel and regular columns were operated in the total reflux and constant reflux policies, respectively. The comparison was made on the practical aspects of the operation whereby they claimed that the advantages of the middle vessel column could be

References	Column	Approach to Comparative Study	Performance Index	Model
Chiotti and Iribarren (1991)	Inverted, Regular	Optimal control	Total annual cost	Simplified
Mujtaba and Macchietto (1994)	Middle Vessel, Regular	Optimal control	Batch time	Semi-rigorous
Davidyan *et al.* (1994)	Middle Vessel, Regular	Theoretical analysis and simulation	Batch time	Simplified
Meski and Morari (1995)	Inverted, Middle Vessel, Regular	Theoretical analysis and simulation	Batch time	Simplified
Hasebe *et al.* (1996)	Middle Vessel, Regular	Simulation	Production rate	Semi-rigorous
Sørensen and Skogestad (1996)	Inverted, Regular	Optimal control	Batch time	Semi-rigorous
Noda *et al.* (1999, 2001)	Inverted, Regular	Optimal control	Production rate	Semi-rigorous
Furlonge *et al.* (1999)	Multivessel, Regular	Optimal control	Energy consumption rate	Detailed
Kim and Diwekar (2000)	Inverted, Middle Vessel, Regular	Simulation	Product purity and yield, design feasibility and flexibility, thermodynamic efficiency	Simplified
Ruiz Ahón and de Medeiros (2001)	Inverted, Middle Vessel, Regular	Optimal control	Profit	Simplified
Warter *et al.* (2002)	Middle Vessel, Regular	Experiment	Temperature, batch time	-
This work (2003)	Inverted, Multivessel, Regular	Optimal design and control	Profit	Rigorous

Table 2.4: Chronological summary of comparative unconventional batch distillation processes literature

seen in the lower temperature profile in the feed vessel as well as in the shorter start-up duration in the middle vessel column.

2.4.1 Summary and Research Statement

Numerous comparative studies between the traditional regular column and unconventional columns have been presented in the literature over the past decade or so (Table 2.4). These comparative studies play an important role in pushing these novel unconventional columns to be accepted and adapted as an industrial technology which is a viable and cost effective mean to increase batch distillation performance.

In some works (Davidyan *et al.*, 1994 and Meski and Morari, 1995), the theoretical and simulation analysis on the unconventional columns serve well to highlight the fundamental understanding of the theoretical flexibility, as well as limitation, of these columns compared to the regular column. More practical comparative investigations were also conducted by various researchers who compared the optimised operation of the columns (Chiotti and Iribarren, 1991; Mujtaba and Macchietto, 1994; Sørensen and Skogestad, 1996; Noda *et al.*, 1999, 2001; Furlonge *et al.*, 1999 and Ruiz Ahón and de Medeiros, 2001). However, the performance indices compared are often based on a specific aspect of the operation, *i.e.* batch processing time, production rate and energy consumption. In addition, the comparative studies were usually performed using simplified and semi-rigorous models and for the separation of binary or ternary mixtures.

One of the aims of this project is to conduct a more comprehensive comparative study based on optimisation which considers an economics performance index and the influence of different design scenarios. A comparison between the multivessel column and the regular column based on optimal design for the separation of various multicomponent mixtures, is investigated for the first time (chapter 5).

2.5 Concluding Remarks

Over the past four decades, a great number of studies have been performed on batch distillation (over 150 papers according to Furlonge, 2000). The review conducted in this chapter reveals that over the past decade, these studies have begun to concentrate on more complex areas of batch distillation, namely, the tackling of azeotropic mixtures, optimal design and the potential of alternative configurations which form the motivational basis of this research.

From the literature survey, it is clear that in the area of extractive batch distillation, a rigorous and comprehensive optimisation study is needed in order to gain further understanding on the optimal operation of this complex batch process. The potential of using unconventional columns should be explored by considering all the additional degrees of freedom afforded by these configurations and a thorough comparison with the regular column should be made on the basis of optimal operations obtained through detailed models.

In the batch distillation design aspect, there is scope for the use of optimisation methodology for simultaneous configuration selection, design and operation of the batch distillation process. The application of such a simultaneous optimisation methodology for the comparison of the various column configurations under different design scenarios is lacking in the works reviewed.

These unaddressed issues drawn from the literature review provide the motivation for the main objectives of this research, as outlined in section 1.4.4.

Chapter 3

Modelling and Numerical Solution Techniques

In this chapter, the models of the batch distillation process, as used in this study, are described, followed by the numerical integration technique used for the dynamic simulation. The optimisation solution approaches are then presented, i.e. a deterministic nonlinear programming approach used for the optimal operation case study in chapter 4 and a stochastic genetic algorithm approach used for the optimal design and configuration studies in chapters 5 and 6, respectively.

3.1 Batch Distillation Models

It is evident from the literature survey in the previous chapter that many of the previous studies involving batch distillation based their work on models that simplify the dynamics of the column section cascade. However, the assumptions employed generally reduce the accuracy, and hence, the applicability of the results obtained. With the advances in computational power and solution algorithms, the use of simplified models in the areas of optimal design and optimal operation is no longer justified. As a result, the optimisation work in this research is conducted based on detailed and rigorous models, the exact

Model Characteristics	Rigorous Model	Detailed Model
Mass balance	Dynamic	Dynamic
Energy balance	Fast	Dynamic
Tray liquid holdup	Constant	Variable
Tray vapour holdup	Negligible	Variable
Inter-tray flow	MESH balance	Tray hydraulics and pressure-flow relationship
Total condenser	√	√
Phase equilibrium	√	√
Perfect mixing	√	√
Adiabatic operation	√	√
Thermodynamics model	SRK Equation of State	SRK Equation of State and Wilson model†
Model usage	Suitable for column design and quick feasibility or sensivity studies	Advanced design stage and optimal operation or retrofit of existing column

† in chapter 4 for the liquid phase

Table 3.1: Summary of models used in case studies

complexity of which is dependent on the purpose of the case studies presented in this thesis, as summarised in Table 3.1.

The rigorous model disposes of the common modelling assumptions such as negligible tray holdup, constant molal overflow and constant relative volatility and is characterised by the consideration of the stage-by-stage column dynamics which is described by the set of MESH (material balance, equilibrium, summation of fractions and heat balance) equations. The rigorous model is used for the design optimisation studies presented in chapters 5 and 6, and includes the following features:

- Fast energy dynamics instead of a dynamic energy balance. The need for an initial condition for the temperature is eliminated hence making the model easier to initialise,
- Constant liquid holdup on trays and in reflux drum, hence not requiring details associated with tray hydraulics which are not generally available nor required during

the preliminary design stage,

- Negligible vapour holdup hence eliminating the need to specify detailed flow characteristics during the preliminary design stage,

- Rigorous thermodynamic models which replace the quite common constant relative volatility assumption through the use of liquid and vapour fugacities as functions of temperature, pressure and composition, and

- Total condenser, phase equilibrium, perfect mixing and adiabatic trays.

On the other hand, for the optimal operation study in chapter 4, where the dimensions and dynamic behaviour of an existing column are specified *a priori*, a more detailed model is utilised. The use of a detailed model instead of a rigorous, or more abstracted, model can have a significant impact on the accuracy of the optimal solutions obtained as demonstrated by Tomazi (1997) and Furlonge *et al.* (1999). The detailed model used includes the following main features:

- Dynamic energy balance instead of relying on the usual assumption of constant molal overflow,

- Both liquid and vapour tray holdups, their combined value being a function of the prevailing pressure and the inter-tray spacing,

- Tray hydraulics, the liquid flowrate from the tray being determined by the Francis weir formula,

- Pressure drop-vapour flowrate relationship that takes into account both dry and wet head losses on each tray, and

- Rigorous thermodynamic models which replace the usual constant relative volatility assumption through the use of liquid and vapour fugacities which are functions of temperature, pressure and composition.

Dynamic material and energy balances are also used to model the product accumulators, reflux drum, side vessels and reboiler. In each of these, both liquid and vapor holdups

are taken into account. The condenser model assumes total condensation with no sub-cooling. The assumptions retained for both the rigorous and the detailed models include no entrainment effects, no downcomer dynamics, adiabatic operation with regards to the column's environment, phase equilibrium and perfect mixing. Details of the detailed and rigorous model equations are given in Appendix A.

3.2 Dynamic Simulation Technique

The mathematical model describing the dynamic behaviour of a batch distillation column, consists of a set of differential and algebraic equations (DAE). Implicit numerical integration techniques were found to be better suited than explicit techniques as they overcome the stiffness problem often exhibited during the numerical integration of the batch distillation model (Boston *et al.*, 1980). The backward differentiation formulae (BDF) approach (Gear, 1971), which is a class of implicit methods with varying time step and order of integration, was employed in this study using the *gPROMS* software (Process Systems Enterprise Ltd., 2000). The time step and order of integration were varied automatically during the integration to ensure that the longest possible time steps are taken while satisfying the error tolerences imposed by the user.

3.3 Dynamic Optimisation Techniques

The general form of the dynamic optimisation problem for batch distillation is outlined in Appendix B. In this work, the dynamic optimisation (DO) problem (chapter 4) is solved using a deterministic nonlinear programming (NLP) approach whilst the mixed integer dynamic optimisation problem (MIDO) (chapters 5 and 6) is solved using a stochastic genetic algorithm (GA) approach. The details of both approaches are discussed in the following sections 3.4 and 3.6, respectively.

3.4 Nonlinear Programming Approach

This approach involves transforming the dynamic optimisation (DO) problem, which is of infinite dimension, into a finite dimensional nonlinear programming (NLP) problem

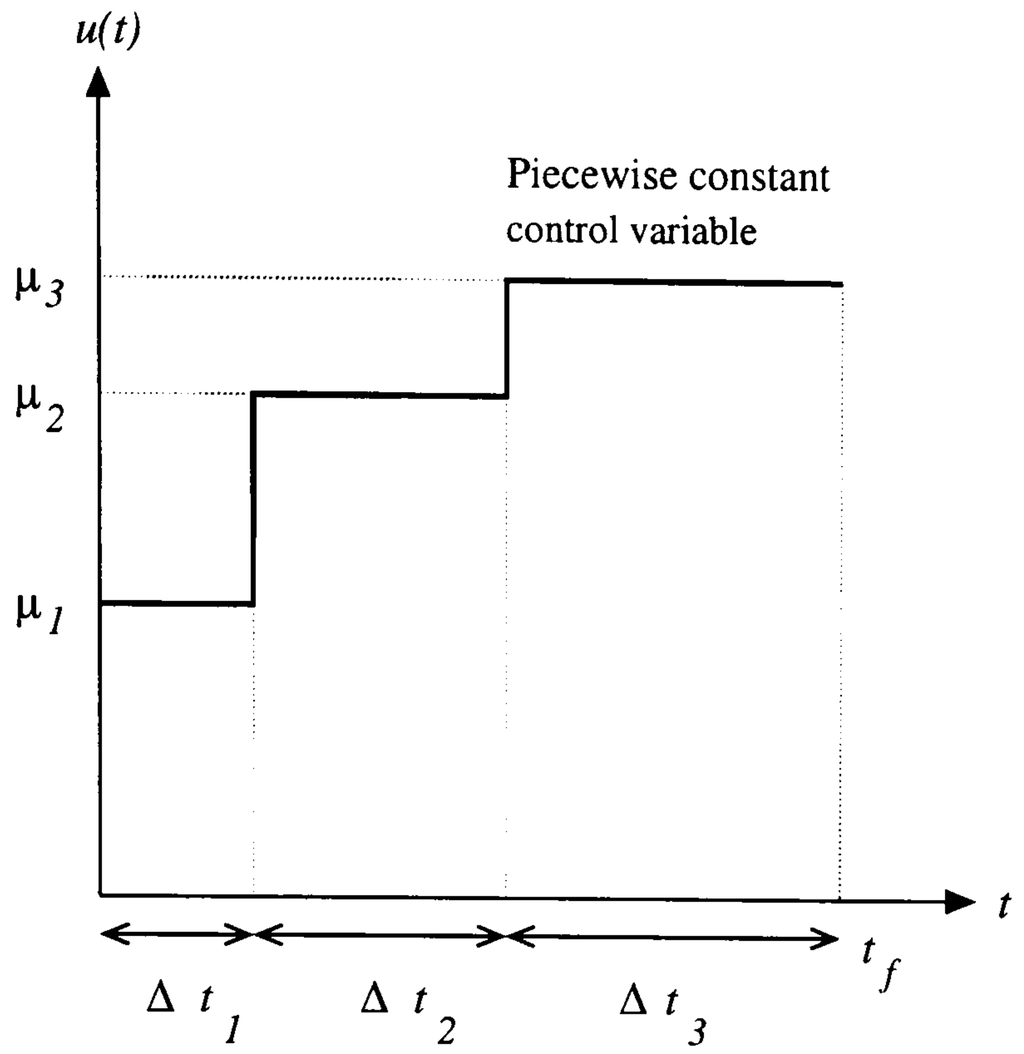


Figure 3.1: Piecewise constant control variable profile

via temporal discretisation. It involves the discretisation of the time horizon, t_f, into a number of N_I control intervals, each of which may be of a different length, Δt_i:

$$t_f = \sum_{i=1}^{N_I} \Delta t_i \tag{3.1}$$

Δt_i are allowed to vary in the optimisation, within a range of specified maximum and minimum lengths:

$$\Delta t_i^{\min} \leq \Delta t_i \leq \Delta t_i^{\max}, \qquad i = 1, .., N_I \tag{3.2}$$

The control variable, $u(t)$, is then restricted to a predefined form of temporal variation (also referred to as a *basis function*), for instance a simple piecewise-constant form[1], over each discretised time interval. The parameters of the basis function, as shown in Figure 3.1, *e.g.* μ_1, μ_2 and μ_3 for each corresponding control interval, Δt_1, Δt_2 and Δt_3, respectively, then become the optimisation decision variables represented by:

$$u(t) = f(\mu, \Delta t, t), \qquad \forall t \in [0, t_f] \tag{3.3}$$

[1]Other forms of temporal variation include for instance piecewise-linear and polynomial.

with the simple lower and upper bounds for μ_i:

$$u_i^{\min} \leq \mu_i \leq u_i^{\max}, \qquad i = 1, .., N_I \tag{3.4}$$

Using the parameters of the control variable (μ_i) and the discrete control intervals (Δt_i), the infinite dimensional dynamic optimisation problem is converted into a finite dimensional nonlinear programming (NLP) problem which is then solved using a sequential quadratic programming (SQP) optimiser. This algorithm, termed the control vector parameterisation[2](CVP) approach (Vassiliadis *et al.*, 1994a,b), is shown schematically in Figure 3.2. Initial guesses of the parameters of control variables (μ), time invariant parameters (ν), control interval durations (Δt) and time horizon (t_f) are provided in the first instance to the algorithm and subsequently the initialisation and integration of the model equations is performed (section 3.2) to evaluate the objective function and constraints using the choice for the decision variables values as determined by the NLP optimiser. This is an iterative procedure which is repeated until an optimal solution has been found.

This control vector parameterisation (CVP) NLP approach is implemented with the *gPROMS* process modelling and optimisation tool (Process System Enterprise Ltd., 2000).

3.5 Mixed Integer Dynamic Optimisation Solution Alternatives

In mathematical terms, the need to consider design and operation simultaneously translates into both discrete (*e.g.* the number of trays) and continuous variables (*e.g.* reflux ratio profile). When configuration decisions are included in the optimisation, additional discrete variables are introduced into the problem (*e.g.* boolean variables, see chapter 6).

[2]In contrast to this approach, another NLP technique termed *complete discretisation* (Logsdon and Biegler, 1989) discretises the set of DAEs, objective function and constraints over the whole time domain, resulting in a set of nonlinear equations. Although integration of the DAE is not required, the size of the fully discretised NLP problem is significantly larger than that of the CVP approach and may result in a NLP problem which is difficult to solve.

Figure 3.2: Algorithm for the control vector parameterisation approach (Vassiliadis *et al.*, 1994a,b)

The optimisation objective function (chapter 5) is nonlinear with a potential nonconvex search space. Coupled with a nonlinear dynamic model of the batch distillation column, this translates into a complex mixed integer dynamic optimisation (MIDO) problem. This type of problem is difficult to solve and there is much ongoing research on developing practical solution algorithms. Different solution techniques have been presented for various chemical engineering problems where the formulation led to an MIDO optimisation problem. For example, Quesada and Grossmann (1992) proposed a branch-and-bound (BB) algorithm that requires the solution of the dynamic optimisation problem with relaxed discrete variables. The other MIDO solution approaches that have appeared in the literature are all based on decomposition principles. One approach is to completely discretise the system into a finite-dimensional mixed integer nonlinear program (MINLP) using a technique such as orthogonal collocation on finite elements (Avraam *et al.*, 1999; Viswanathan and Grossmann, 1990 and Mohideen *et al.*, 1996). The other approach is to decompose the problem into a series of primal problems (typically a dynamic optimisation problem that is solved using a control vector parameterisation approach) where the discrete variables are fixed, and a master MILP. Different variations of this method include outer- approximation (OA) (Duran and Grossmann, 1986), OA/augmented-penalty (OA/AP) (Sharif *et al.*, 1998, who applied it to batch distillation design) and generalised Benders decomposition (GBD) (Geoffrion, 1972).

Conventional deterministic mathematical programming approaches such as OA and GBD, require gradient information for the NLP solver, and therefore, are not robust when solving problems with highly nonlinear functions, stiff models and complex search spaces like that exhibited by the batch distillation column design. The batch distillation design problem is highly nonconvex, thus convexity conditions required by many of these gradient-based approaches to locate the global optimum are not satisfied. Allgor and Barton (1999) proposed an approach where the master MILP is solved on a so-called screening model in an attempt to mitigate the effects of nonconvexity. However, the approach is case-study specific and requires domain specific knowledge gathered from physical laws and engineering insight. Recently, Bansal *et al.* (2003) proposed a new algorithm based on GBD with improved features like dispensing of the need to solve intermediate adjoint problems in order to construct the master problems and independence of the type of method used to solve the dynamic optimisation primal problem. The development of global optimisation algorithms for solving MIDO is a formidable task and still in its infancy (see chapter 7.2.1).

In this thesis, the use of a stochastic algorithmic method to solve the batch distillation design MIDO problem, is proposed. The application of genetic algorithm to the design of chemical engineering systems has been explored only in a limited number of cases and has not previously been considered for the design of batch distillation columns. Genetic algorithm is generally slower than gradient-based solution techniques when used for solving simple optimisation problems. However, the probabilistic nature of the algorithm has the potential to be a more attractive solution technique. There are several potential advantages to the use of genetic algorithm.

3.5.1 Advantages and Drawbacks of The Genetic Algorithm Approach

In this thesis, a non-deterministic algorithm, *i.e.* genetic algorithm, is used to arrive at the optimal batch distillation configuration and design results. In terms of these optimisation problems, where discrete variables are introduced in addition to the continuous variables, only a handful of deterministic works has been reported in the literature - they ranged from various NLP methods where the discrete variable is treated as continuous, to MINLP method that requires superstructure modelling (described in section 2.3).

Compared to these approaches, the genetic algorithm approach provides some inherent advantages as follows:

(1) It offers greater robustness as it can handle nonlinear objective functions with complex search space topography in a single continuous optimisation run without the algorithm terminating due to instability. This is because genetic algorithm is a black box or gradient-free search algorithm which means it only requires scalar values of the objective function, *i.e.* it does not require derivative information or a smooth, continuous and differentiable search space. In addition, the solutions are manipulated in parallel rather than by the sequential adjustment of a single solution performed by more traditional methods. This reduces the dependence on search path history, *e.g.* derivative information, and thus the likelihood of the algorithm failing due to a previous infeasible solution. This is important for the batch distillation model which often experiences initialisation or integration difficulties due to either highly nonlinear functions, stiff models, sharp operational switches, or more likely, infeasible solutions.

(2) It has global optimisation capability and eliminates the difficult task of guessing the initial starting point. The solution obtained by many deterministic methods such as direct search and gradient-based search, depends on manual setting of the initial starting point or the quality of the initial guess, *i.e.* the location of the starting point in the search space. Rather than starting from a single point within the search space, the genetic algorithm is initialised with a population of points which is spread throughout the search space. Furthermore, the mutation operator subsequently ensures the diversity of the population by allowing the algorithm to jump to a new solution and sample the entire search space.

(3) The fitness of the solution set improves over each generation. Since the algorithm operates on a population of solutions and the average population fitness of each generation improves in line with the best genome fitness, the final population may supply some viable alternative designs and operations which are near the optimum solution. This is not generally available from deterministic mathematical programming approaches.

(4) Genetic algorithm offers the opportunity for parallel processing to reduce computational time.

(5) The approach is practical, flexible and easily implemented. Since only the optimised variables and value of the objective function are passed between the algorithm and the model, the approach can be applied to different types and complexities of models with minimal implementation effort, and different modelling packages can be connected to the algorithm. The nature of the approach also means that it can treat continuous variables as well as discrete variables like integer and logical variables easily within its genome set (details in the following sections), and thus, specially tailored procedures to tackle the different types of variables, like that which distinguishes NLP and MINLP techniques, is not required.

The main drawbacks of the genetic algorithm approach are:

(1) Unlike methods which direct the optimisation search based on the sensitivity of an individual solution, the inherent need for a population of solutions in the genetic algorithm approach may translate to a relatively higher computational cost. Note that a possible alternative is to have a population size of one. Since there is only one individual or solution, there would be no crossover, but only mutation. This stochastic method is recognisable as *simulated annealing* where the so-called *mutation* is conventionally called *random move* and the solution typically moves to the next one with a probability function. Hanke and Li (2000) reported the use of simulated annealing approach to solve the optimal operation problem of batch distillation.

(2) The *optimality* (or *accuracy*) of the final solution is actually, since genetic algorithm is stochastic in nature, dependent on the convergence setting. This is one drawback of genetic algorithm - the trade-off between the accuracy and computational time, especially at the latter part of the optimisation where the growth in fitness is slower than in the initial stages (Appendix D). Furthermore, the algorithm itself requires careful tuning of a number of parameters (see section 3.7.9 and Appendix C) in order to obtain an acceptable performance in terms of its effectiveness and computational efficiency.

3.6 Genetic Algorithm Approach

In chemical engineering, genetic algorithms have typically been applied to the design of process plants, albeit only in a limited number of cases (such as Fraga and Senos Matias, 1996; Garrard and Fraga, 1998 and Marriott *et al.*, 2000). As in the case of this research, the application of genetic algorithms to optimise batch processes has only just emerged, for example, Zhang *et al.* (2003), Sarkar and Modak (2003) and Silva and Biscaia (2003) who considered simulated moving bed chromatography, fed-batch reaction and batch polymerization systems, respectively. It also emerged recently that Mukherjee *et al.* (2001), parallel to this research, have also attempted to use genetic algorithm to optimise the batch distillation process. However, theirs was a *unconstrained* optimisation based on the FUG model with fixed purity values. The amount of distillate in each cut is the only variable optimised. In contrast, the application of genetic algorithm for the design of batch distillation is presented in this work. The genetic algorithm-penalty function methodology proposed here is discussed in relation to the batch distillation problem in the following sections.

3.7 Background

Genetic algorithm is an optimisation technique inspired by the theory of biological evolution which attempts to imitate the process of natural selection. In the natural selection process, individuals of high fitness as characterised by their genomes are favoured over weaker individuals and are therefore more likely to survive longer, participate in mating and produce stronger offspring for the next generation. The fitness of the whole population generally increases from generation to generation.

In order to translate this strategy into a search technique for the batch distillation optimisation problem - firstly, the design and operation decision variables of the problem have to be represented as genes in the genome. Then, a measurement of fitness has to be assigned to every genome depending on the quality of its genes. The fitness measurement corresponds to the optimisation objective function and the aim is to maximise (or minimise) its value over time. The genetic algorithm starts by an automatic random

initialisation of a population of genomes. It then employs three operators, *i.e.* selection, crossover and mutation, to evolve the initial population and drive it towards convergence at the global optimum.

3.7.1 Genetic Algorithm Framework

The optimisation framework proceeds according to the following algorithm:

(1) Initialisation - An initial population is created consisting of random points in the search space.

(2) Fitness function evaluation - The fitness of each genome in the population is evaluated through the objective function and penalty function.

(3) Reproduction genetic operators - The search is performed by creating a new population generation from the previous one through the application of genetic operators.

(4) Convergence criteria - Steps 2 and 3 are repeated until the population converges according to a pre-specified optimality criterion.

The detailed genetic algorithm strategy proposed in the work is described in the following sections.

3.7.2 Genome Coding

The batch distillation design problem consists of both design and operation decision variables which are grouped together to represent a solution genome. Similar to the NLP approach described in section 3.4, the control variable, $u(t)$, must be parameterised (here, piecewise-constant) and the time horizon, t_f, discretised into a number of N_I control intervals Δt_i in order to be represented as separate genes in the genome (Figure 3.3):

$$\{\nu_1, \ldots, \nu_j, \overbrace{\underbrace{\mu_1, \ldots, \mu_i}_{u(t)}, \underbrace{\Delta t_1, \ldots, \Delta t_i}_{t_i}}^{\text{parameterised}}\} \tag{3.5}$$

where ν represents the time invariant parameters. Each parameter, or *gene*, in the genome including the control intervals, can have different sets of bounding values, *i.e.* higher and

lower bounds of the decision variables, depending on the design problem. The genome can accommodate logical, discrete and continuous decision variables simultaneously, which is convenient for the batch distillation optimisation problem that needs to tackle column selection, design and operation simultaneously. All the decision variables are represented in the genome as direct real values instead of converted binary bits and mapping which has been found to be less efficient (Coley, 1999).

Figure 3.3: Genome coding

3.7.3 Steady State Genetic Algorithm

Similar to the CVP NLP approach mentioned in section 3.4, initialisation and integration of the model equations using the choice of the decisions variables represented by each genome is required to evaluate the objective function and constraints. However, the optimiser in the genetic algorithm is based on a black box (non gradient-based) adaptive search technique operating on a population of solution genomes (instead of one solution at a time as in the CVP NLP approach).

A steady state genetic algorithm that uses overlapping populations is used in this study, the basic structure of which is shown in Figure 3.4. Firstly, an initial population of a specified size, N_{pop} number of genomes, is generated randomly. This is N_{pop} different combinations of column design and operation variables. Then, in each generation, the fitness of each genome is evaluated (refer to section 3.7.4 below). Based on the fitness function of each genome, the algorithm creates a new set of temporary genomes via the three operators, *i.e.* selection, crossover and mutation, and adds these to the previous population, and at the same time removes the weaker genomes in order to return the population to its original size. The amount of new genomes created in each generation depends on the percentage of population overlap, P_{ss}, specified. In this algorithm, the new genomes may or may not make it into the next population, depending on whether they are better or weaker than the rest in the temporary population. This allows the retention of fitter genomes for use in the next generation as well as provides the opportu-

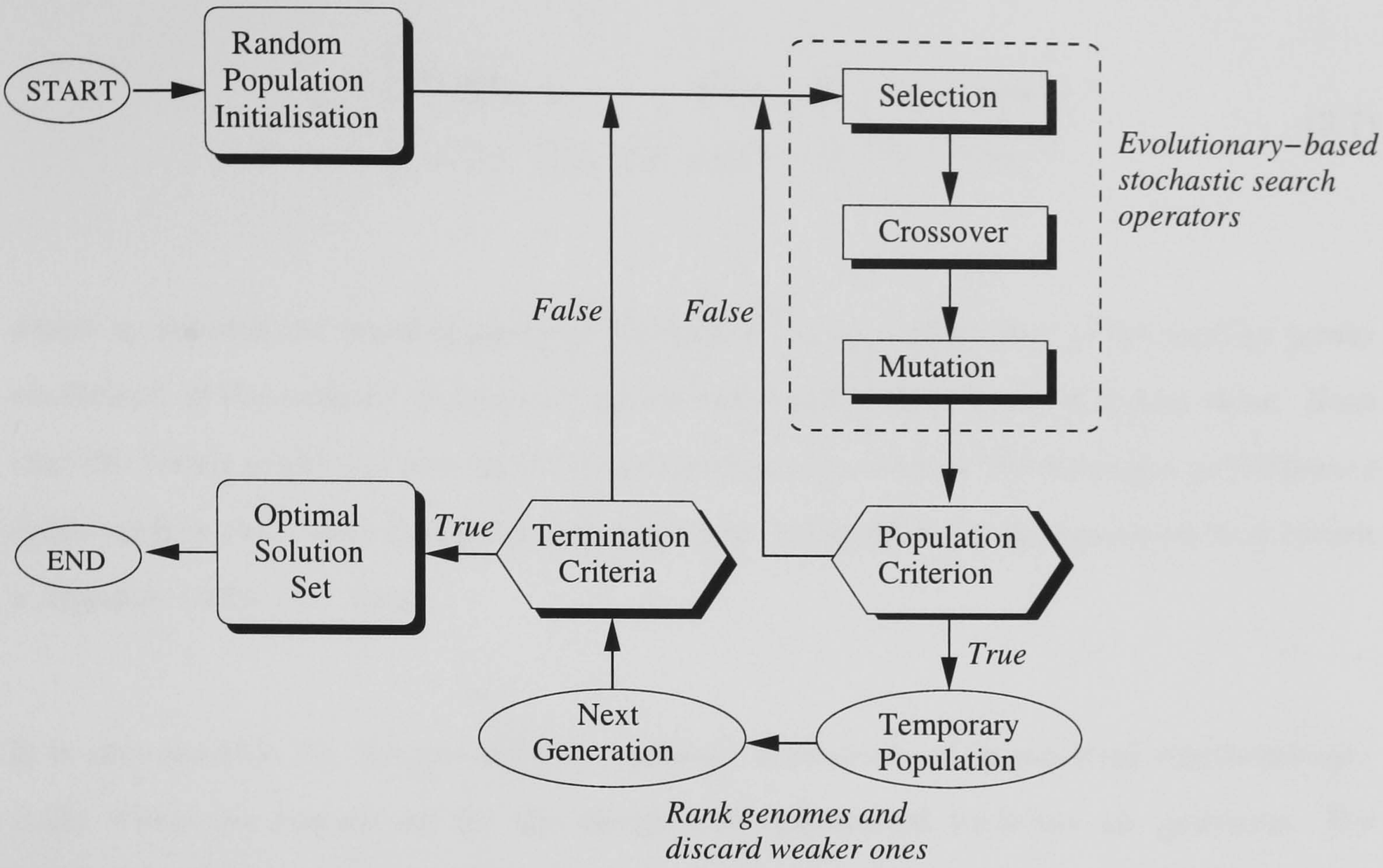


Figure 3.4: General structure of the genetic algorithm

nity to discard new genomes that are weaker than those of the parent's generation. This is done by simply ranking the genomes according to their objective function values.

3.7.4 Fitness Function: Constraints Checking and Solution Infeasibility

In many constrained optimisation problems such as the batch distillation optimal design, the majority of possible solutions represented by the genomes will prove to fall short of the requirement of the constraints. A mechanism is needed to check the constraints of the returned simulation results represented by the genome and to map the evaluated objective function to an appropriate fitness function in accordance with the magnitude of constraint violation, if necessary. In the batch distillation optimal design problem, the purity of the products, $x_i(t_f)$, are checked against the constraints, $x_i^{\min}$, for each returned result and the objective function value is then manipulated using a *penalty function* to obtain a *corrected* fitness value for each genome:

$$\kappa_i = \begin{cases} \left[1 - \frac{x_i^{\min} - x_i(t_f)}{x_i^{\min}}\right]^{p_i} & \text{if} \quad x_i(t_f) < x_i^{\min} \qquad \forall\, i = 1, .., n_c \\ 1 & \text{otherwise} \end{cases} \tag{3.6}$$

$$f = \begin{cases} \Omega \prod_{i=1}^{n_c} \kappa_i & \text{when} \quad \Omega \geq 0 \quad \text{(profit)} \\ \Omega \left(2 - \prod_{i=1}^{n_c} \kappa_i\right) & \text{when} \quad \Omega < 0 \quad \text{(loss)} \end{cases} \tag{3.7}$$

where κ_i denotes the penalty function for each of the n_c constraints, p_i the penalty power coefficient, Ω the original objective function value and f the corrected fitness value. Note that the terms *profit* and *loss* for the objective function refer to the economic performance index used in this study (chapters 5 and 6) where a feasible solution (genome) may return a negative value (*i.e.* loss).

It is also possible for the genomes to represent unrealistic or impractical solutions especially when the bounds set for the design and operational variables are generous. For example, when the maximum bounds or high values are chosen for the boilup rate, product withdrawal rate and control interval, the reboiler pot may run dry during the task causing the simulation to crash due to infeasibility. In this case, a low fitness value is automatically assigned to the genome so that the probability of it being promoted to the next generation is less than those with feasible solutions. Therefore, the fitness value for infeasible solutions should be set well below the fitness of all feasible solutions. This can be easily determined by calculating the objective function for the worst case scenario using the decision variables bounds.

3.7.5 Fitness Scaling

If during an early generation, one particularly fit genome is created, the fitness-proportional selection algorithm can allow a large number of its copies to rapidly dominate the subsequent generations and cause rapid and erroneous convergence towards a local optimum. Once the population has converged, crossover of almost identical genomes produces little that is new and thus the ability of the genetic algorithm to search for better solutions is effectively eliminated. Only mutation remains to explore entirely new space and this only performs a slow and random search.

During later stages of the optimisation, after many generations, the population would

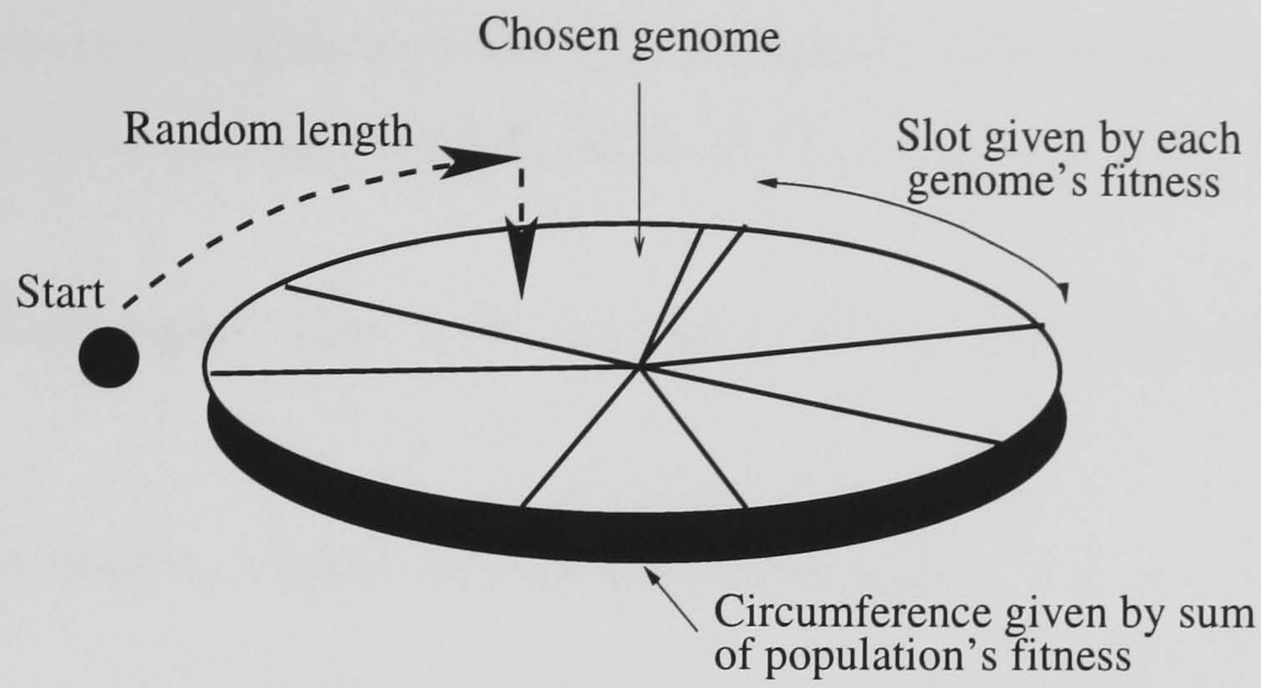


Figure 3.5: Fitness proportional selection

have largely converged but again, there may be little difference between the best and the average genomes. Thus there may be insufficient selection pressure to distinguish between the high fitness genomes and this will push the population quickly towards the global optimum.

In this work, a *sigma scaling* technique (Coley, 1999) is used to overcome both premature convergence and slow finishing difficulties as described above. Fitness scaling works by pivoting the fitness of the population members about the average population fitness value using the population standard deviation. The scaling of the fitness score for each individual is given by:

$$f^{\mathrm{S}} = f - (f_{ave} - cf^{\sigma}) \tag{3.8}$$

where f^{S} the scaled fitness value, f is the corrected fitness of a genome, f_{ave} the average fitness value of the population, c is a reasonable sigma multiplier (typically $1 \leq c \leq 3$; default $= 2$) and f^{σ} the population standard deviation. It is this scaled fitness value, f^{S}, that is utilised by the genetic algorithm selection operator described below.

3.7.6 Selection Operator

In order to obtain good offspring, genomes with higher fitness values should have a greater probability of being selected to undergo reproduction, *i.e.* crossover and mutation. A stochastic sampling method called *fitness proportional* or *roulette wheel* is used here as

the selection operator. In this approach, the probability of selection is proportional to the fitness value of the genome. The algorithm is summarised as follow (Figure 3.5):

- Sum the fitness value (after fitness scaling) of all the population genome members, f_{sum}.
- Generate a random number R_s where $R_s \in [0, f_{sum}]$.
- Add, one at a time, the fitness value of the population members stopping immediately when $f_{sum} \geq R_s$. The last member added is the selected genome.

The selection operation is applied twice in order to select a pair of genomes to undergo crossover. Selection is continued until enough offspring genomes have been created according to the percentage of population overlap specified, P_{ss}.

3.7.7 Crossover and Mutation Operators

After the selection operator, the crossover operator in the genetic algorithm is then employed to mate the genomes to form new offspring. Due to the fact that the genomes hold a mix of discrete and continuous variables and that each gene represents a distinct configuration, design or operation variable, the crossover method have to respect the structure of the genome, *i.e.* crossover is only allowed between genes at the same position of the parent genomes and the resulting length of the offspring genomes must not be altered. This is done via a *uniform crossover* technique as shown in Figure 3.6. The genes in each genome are only allowed to swap with the gene at the same allele location in the other genome with a probability, P_c. A random number, $R_c \in [0,1]$, is generated for each pair of genes along the genome and the genes undergo crossover only if $R_c \leq P_c$, otherwise the pair proceed without crossover.

After passing through the crossover operator, the offspring genomes undergo *Gaussian type mutation* with a probability of P_m. Again a random number, $R_m \in [0,1]$, is generated, and if $R_m \leq P_m$, the gene is mutated using a Gaussian function around the current value. If the mutated value goes out of the gene's bounding range, *i.e.* higher and lower bounds of the decision variables, it is reset to the violated boundary.

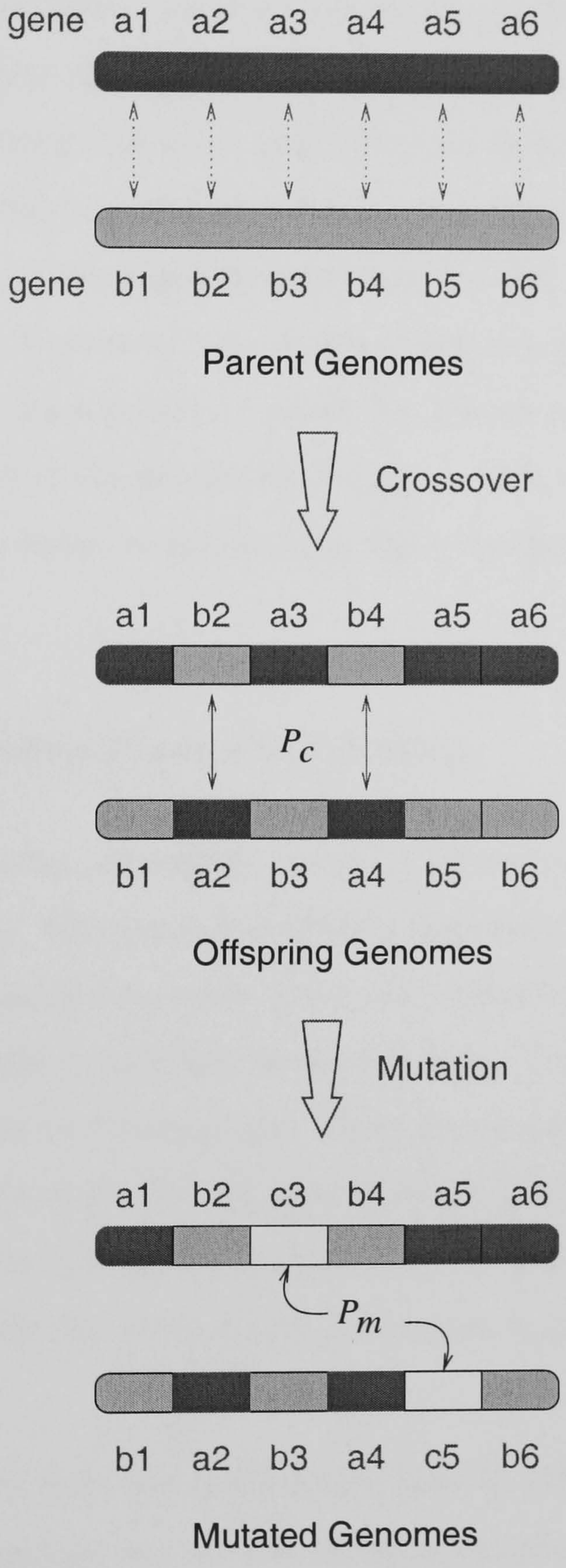


Figure 3.6: Uniform crossover operator and mutation operation

3.7.8 Termination Criteria

If the genetic algorithm is implemented correctly, the population will evolve over sequential generations so that both the fitness of the best genome and the average fitness of the population in each generation increase towards the global optimum. There are a number of ways to terminate the algorithm. One of the criteria is termination when a specified number of generations has been generated and tested. However, the required number of generations to obtain a solution is difficult to estimate for a new problem. The termination can be based on convergence percentage, *i.e.* the current best of generation is compared to either the N previous best of generation or current generation average. Here, termination criteria are combined, namely the algorithm stops when the ratio of the current population best to the population average, *and* to the population best of the previous 30 generations, is equal or greater than the convergence percentage, $P_{converge}$, specified.

3.7.9 Genetic Algorithm Parameters Tuning

The choice of genetic algorithm parameters can play a crucial role in the effectiveness and efficiency of the algorithm. The parameters govern the extent of *exploration* to investigate new and unknown areas in the search space, and *exploitation* of knowledge found at solutions previously obtained to help find better solutions. Therefore, they influence the solution quality and the speed of convergence. There are six parameters (presented in the sections above): the population size in each generation, N_{pop}, the steady state population overlap, P_{ss}, the penalty function power coefficient, p_i, the mutation probability, P_m, the crossover probability, P_c and the convergence percentage, $P_{converge}$.

There are general heuristics and rules of thumb (Goldberg, 1989) that can provide good initial guesses for these parameters. In this study, a sensitivity analysis is performed to study the effect of these parameters on the performance of the algorithm used in the batch distillation optimal design problem (Appendix C). Parameter optimisation, which, however, is often highly computationally intensive, can be performed to obtain the optimal values of the genetic algorithm parameters. The inherent trade-off lies between the additional computational time devoted to parameter optimisation and tuning, versus

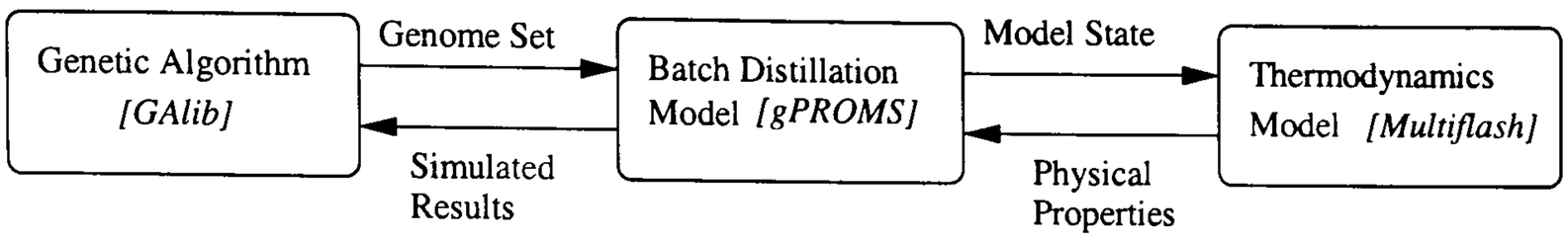


Figure 3.7: Schematic diagram of the genetic algorithm implementation

the additional savings achieved in the objective function value or computational time of the algorithm when it is actually applied to the batch distillation optimisation.

3.7.10 Implementation

The genetic algorithm is implemented with the library *GAlib* (Wall, 1999) (Figure 3.7). The genetic algorithm program operates on the genome populations. During the genome evaluation step, the program performs a foreign process call to the *gPROMS* batch distillation model as well as passes the genome over. In the batch distillation model, the column configuration, design and operating policy represented by the genome is dynamically simulated using an implicit backward differentiation formulae (BDF) method. The objective function, together with the values of the constrained parameters are then passed back to the genetic algorithm program where a fitness value is obtained based on the penalty function.

3.8 Concluding Remarks

In this chapter, the dynamic modelling of batch distillation and the approaches used for dynamic simulation and optimisation in this thesis have been presented.

The stochastic genetic algorithm framework applied in batch distillation design optimisation for the first time in this thesis, was found to be a robust and viable way of solving the optimal batch distillation design problem and can be used with a range of models with different complexities. The proposed algorithm is found to be robust compared to other deterministic approaches (used for optimal batch distillation operation) as it does not rely heavily on information from previous iterations for the search direction or on the topography of the search space. The genetic algorithm is also more robust in absorbing infeasible solutions. However, the genetic algorithm parameters have to be selected

appropriately in order to fulfil the problem constraints as well as to avoid premature convergence. It is hoped that through this work, application of a stochastic method can be seen as a feasible solution choice, in addition to, but not superseding, the extensive deterministic algorithms already used traditionally to solve batch distillation problems. Applying it for the first time in batch distillation optimisation would allay at least some of the initial skepticism of trying out the approach. Note that it is also possible to use alternative, or even more tailored, algorithms to describe the evolution, selection, mutation, crossover, scaling, termination *etc.* (some of these variations is discussed in Coley, 1999). The aim here is to investigate the feasibility of using simple genetic algorithms which are suited to the batch distillation problem and that are more readily available in library codes.

Some computational consideration for the optimisation approaches are presented in Appendix D.

Chapter 4

Optimal Operation of Extractive Batch Distillation

In this chapter, optimal operations of extractive batch distillation for both regular and middle vessel columns are derived based on a profit objective function. Detailed models are used for the rigorous dynamic optimisation which takes into account a wide range of operation decision variables including reflux ratio, solvent feed rate, input heat duties and the possibility of product withdrawals during the process. Optimal feed distribution and liquid and vapour stream configurations at the middle section of the middle vessel column are also investigated. Separation of a minimum boiling azeotropic acetone-methanol mixture using water as solvent and involving different separation duties and feed compositions, is presented as a case study. The performance of the middle vessel column is found to be significantly influenced by the middle section stream configurations, with the highest profit value achieved when the stream configurations are allowed to vary optimally during the operation. The optimal operating policy for the middle vessel column involved the feed being charged predominantly to the reboiler still with low holdup in the middle vessel during the operation.

4.1 Introduction and Aims of This Work

Azeotropic and low relative volatility mixtures are commonly encountered in the fine and specialty industries, and many chemical processes depend on efficient and economical means for their separation. Extractive distillation is widely used in the chemical industry and is commonly applied in a continuous multi-column mode. However, due to the proliferation of low-volume value-added fine chemical and biopharmaceutical industries, and in the current highly competitive climate of changing duty and product demand, extractive distillation in batchwise mode provides an economically attractive and flexible single column process alternative.

Graphical and simulation studies so far have demonstrated that the choice of various operation parameters has a significant effect on the performance of the process, *i.e.* Yatim *et al.* (1993), Safrit *et al.* (1995), Safrit and Westerberg (1997) and Warter and Stichlmair (1999) (details in chapter 2.2). The use of unconventional columns for extractive batch distillation has also been proposed for a few years now, *i.e.* the middle vessel column by Safrit *et al.* (1995). The advantages of this complex column over the regular column, for example with respect to product recovery, were claimed in the literature by Safrit *et al.* (1995) and Warter and Stichlmair (1999) but were contradicted by Lelkes *et al.* (1998b). There are more decision variables available to this configuration than to a regular configuration, which increases the flexibility as well as the complexity of the column. Studies so far have mainly involved feasibility and column sequencing, as well as comparative studies via simulation. Recently, experimental investigation on a laboratory and pilot plant scale has been started by Milani (1999), Cui *et al.* (2002) and Warter *et al.* (2002).

Only a few optimisation studies have been found in the literature survey (chapter 2.2). These studies have only been tackled in recent years, namely Mujtaba (1999), Ruiz Ahón and de Medeiros (2001) and Furlonge (2001). Mujtaba (1999) studied the optimal operation of extractive batch distillation in the regular column with the optimisation problem decomposed into separate independent single-period dynamic optimisation problems. The optimisation study by Ruiz Ahón and de Medeiros (2001) included both regular and

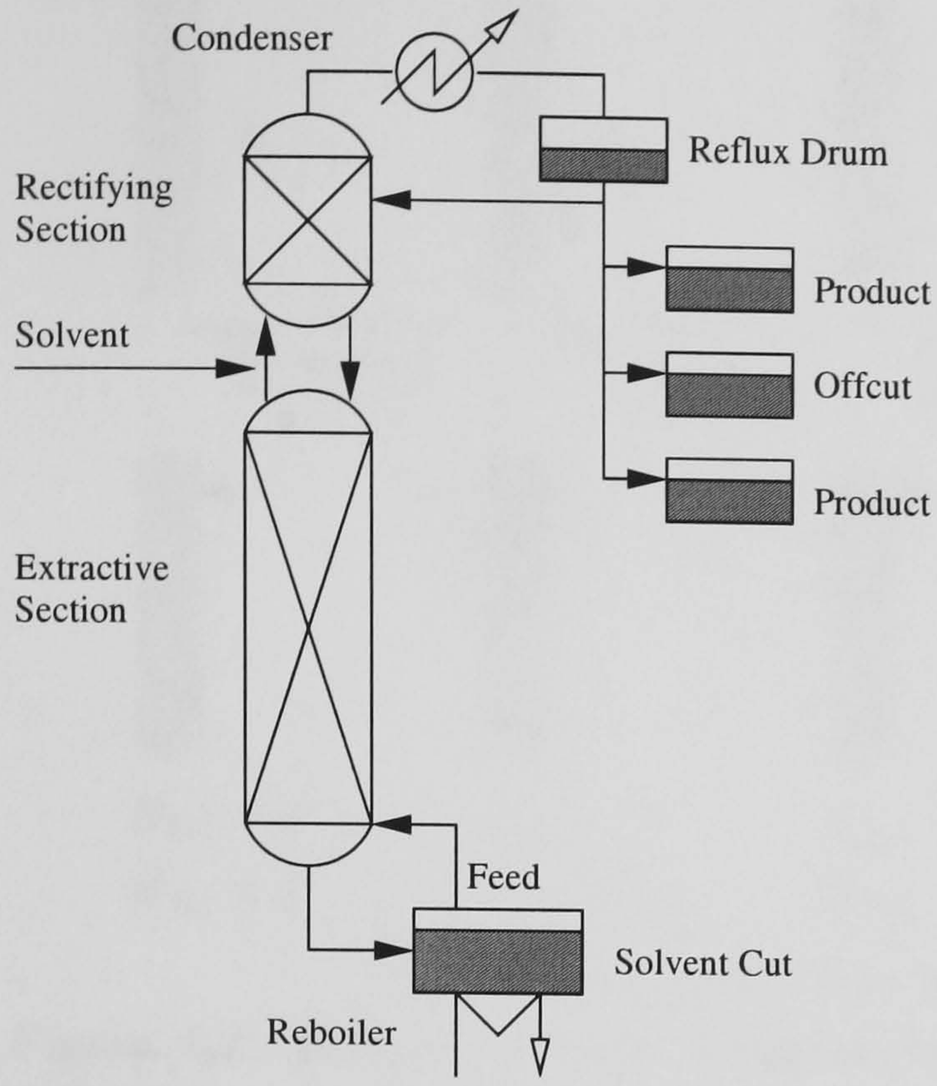
middle vessel columns but the work was based on a simplified pseudo stationary cascade model, a simplified operating procedure, the consideration of only one decision variable, namely the product fraction profile, and unconstrained optimisation whereby every cut has a value corresponding to its purity. Recently, Furlonge (2000) reported in his thesis an optimisation study on the extractive batch distillation on a packed column using a rigorous model. To the best of our knowledge, no industrial attempt has been reported so far in the open literature to realise extractive distillation in a batch system although it is expected that this form of operation does take place.

In this work, the optimal operation of extractive batch distillation in both regular and middle vessel column configurations is presented. The work in this chapter expands on previous works by presenting a more rigorous and comprehensive optimisation case study of extractive batch distillation, based on the exploration of a wider range of degrees of freedom available, including optimal feed placement and optimal stream configuration in the middle vessel column. A detailed tray model is used for the first time taking into account tray hydraulics and variable holdup that closer reflect the operation practicalities. The optimal operations are obtained via a dynamic optimisation technique using a profitability objective function.

In the next section, the different column configurations for extractive batch distillation and their degrees of freedom are outlined, followed by the introduction of the optimisation formulation and the key features of the model used. Next, the solution methodologies for the dynamic simulation and the optimisation problem are presented. This is followed by the description of a case study involving the extractive separation of a binary minimum boiling mixture using both regular and middle vessel columns. Finally, the optimal operations of both columns for different scenarios are compared.

4.2 Column Configurations and Degrees of Freedom

The regular and middle vessel column configurations for extractive batch distillation are shown in Figure 4.1. In the regular column, feed is charged into the reboiler initially.



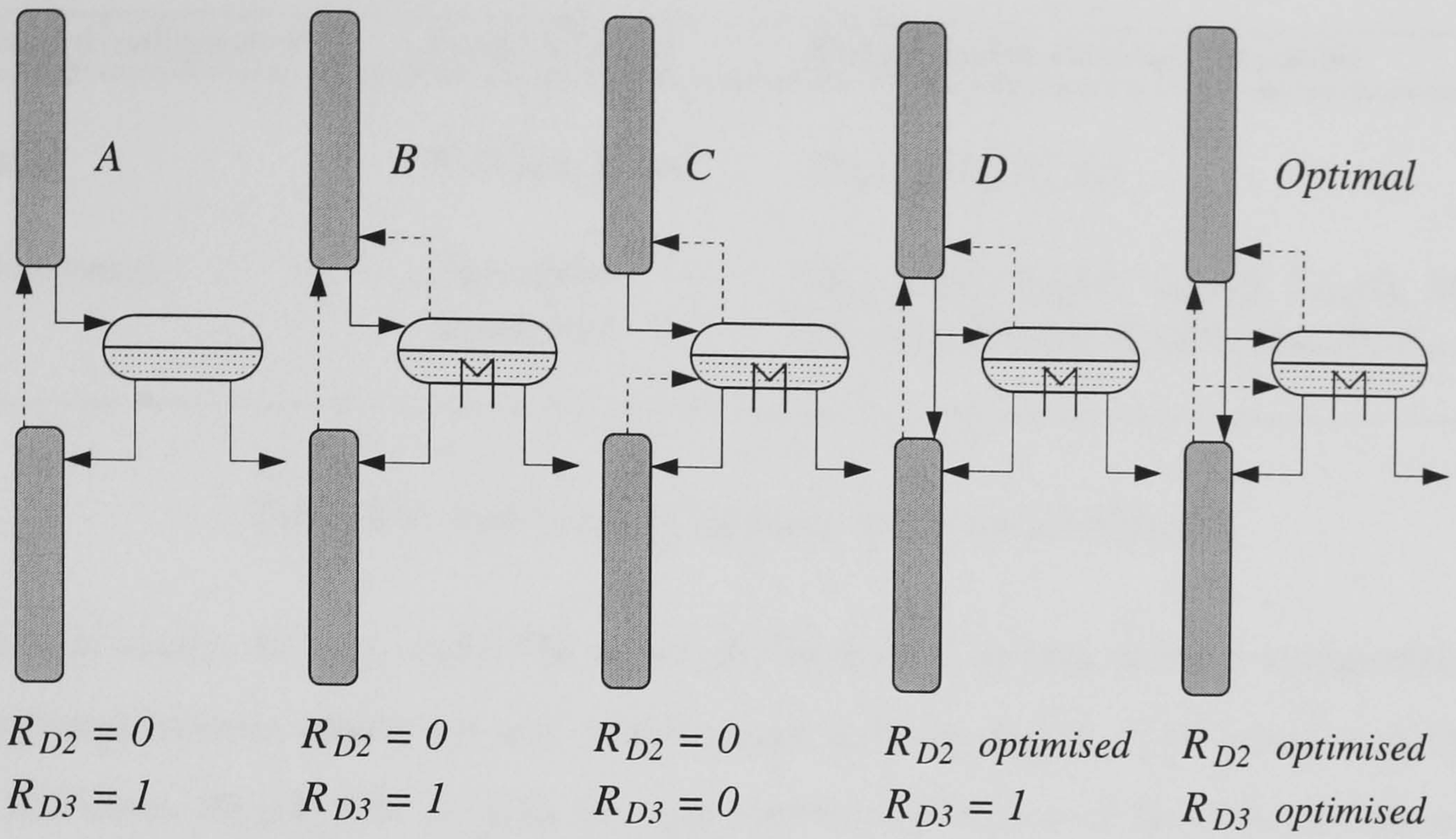
(a) regular column (b) middle vessel column

Figure 4.1: Batch column configurations for extractive distillation

During operation, solvent may be added between the rectifying and extractive sections[1] whilst product and offcuts are withdrawn from the top. The solvent is recovered in the reboiler at the end of the operation. The operating policy can be sufficiently described by the parameters reboiler heat duty, Q_{reb}, reflux ratio, $R(t)$ and solvent feedrate $F_{sol}(t)$.

The middle vessel column is split into three sections. Similar to the regular column, the rectifying section is above the point of solvent addition. Below the solvent feed point, the middle vessel is placed between the extractive and stripping sections. Due to the flexibility of this column, the feed can be charged either to the middle vessel or to the reboiler, hence three different alternatives can be considered, namely feed placed mainly in the middle vessel, feed placed mainly in the reboiler drum and feed optimally distributed between these two. Previous studies on this column were always conducted with feed placed in the middle vessel. In this study, this assumption is relaxed and feed placement is considered as a degree of freedom. Also for the first time, material withdrawal is al-

[1]It is also possible to add the solvent further down the column, or even in the reboiler. However, this is not considered in the case study presented here.



R_{D2} and R_{D3} split fractions (see Appendix A)

Figure 4.2: Different stream configurations at the middle section of the middle vessel column

lowed into accumulators during the operation from both the reboiler (flowrate $F_{reb}(t)$) and the middle vessel (flowrate $F_{mv}(t)$).

Most studies so far on middle vessel column involved only a fixed middle section stream configuration. However, there are several combinations of vapour and liquid streams connection possible between the column and middle vessel as shown in Figure 4.2. Studies on middle vessel columns concentrated mostly on configuration A. The reason for this may be due to the practicality of this configuration where the whole liquid stream, as a result of weir overflow of the bottom extractive tray, is diverted into a middle vessel. The liquid stream from the middle vessel is fed back into the column at the top stripping tray, the rate of which, $L_{mv}(t)$, can be optimised. This configuration can operate without heat addition in the middle vessel and can be easily constructed by modifying an existing regular column. However, there is also an opportunity to introduce heating at the middle vessel, and an additional vapour stream originating from the vessel is possible. Furthermore, the liquid stream leaving the bottom extractive tray and the vapour streams leaving the top stripping tray can be directed in different ways (at least one stream must be fed to the middle vessel). These degrees of freedom lead to the different middle vessel configurations shown in Figure 4.2. Warter and Stichlmair (1999) compared the extractive batch distillation operations in configurations A and C via a

Column Configuration	Feed Location	Optimisation Decision Variables
Regular	Reboiler drum	Q_{reb}, $R(t)$, $F_{sol}(t)$
Middle vessel	Optimally distributed	Q_{reb}, $R(t)$, $F_{sol}(t)$, $L_{mv}(t)$, $F_{reb}(t)$, $M_{reb}(0)$, $M_{mv}(0)$, $R_{D2}(t)$, $R_{D3}(t)$, $Q_{mv}(t)$, $F_{mv}(t)$

Table 4.1: Summary of decision variables considered

simulation study. In this study, the effect of the middle section stream configuration on the optimal column operation and performance is investigated. The liquid and vapour split fractions, $R_{D2}(t)$ and $R_{D3}(t)$, are also treated as degrees of freedom in this study.

Together with the initial feed distribution in the reboiler and middle vessel, $M_{reb}(0)$ and $M_{mv}(0)$, reboiler and middle vessel heat duties, Q_{reb} and $Q_{mv}(t)$, reflux ratio, $R(t)$, solvent feedrate, $F_{sol}(t)$, and both middle and bottom withdrawals, $F_{mv}(t)$ and $F_{reb}(t)$, the optimisation determines all degrees of freedom available and hence the best operating policy for the given feed composition and product requirement without any prior specification on feed placement or middle section stream configuration. The degrees of freedom for both columns are summarised in Table 4.1.

4.3 The Extractive Batch Distillation Operation Problem: Optimisation Formulation

The purities of the main products are normally driven by customer demand and distillation is undertaken to achieve these specifications. The optimal operation of batch distillation is dictated by the economics of the process, *i.e.* to achieve the greatest profit at the shortest possible duration. The optimisation problem considered here aims therefore to find the operating variables (see Table 4.1) which maximise the operating profit per unit time. The profit can be calculated by taking into account sales revenue, inventory cost, utility cost, waste cost and capital investment interest. If the *operation* of a column is to be considered, the capital investment costs associated with any existing column are fixed *a priori* and thus would not be involved in any operating trade-off (unlike

optimal design studies where this parameter must be included to account for the interaction between column sizing and the operation performance afforded by a particular column size). Here, the cost of waste is neglected in the objective function, *i.e.* assuming any waste cuts being relatively valueless compared to the value of the desired products. Since a significant fraction of the solvent used may be recovered at the end of the batch at a purity equal to, or higher than that of the fresh solvent, only the make-up solvent is included in the objective function:

$$Profit = \frac{Sales\,revenue - Feed\,cost - Solvent\,cost - Reboiler\,duty}{Batch\,processing\,time} \tag{4.1}$$

Mathematically, the optimisation problem can be written as:

$$\max \frac{\sum_{i=1}^{N_C} C_i H_{A,i}(t_f) - C_{feed} H_{feed} - C_{sol} H_{sol}^{make-up} - C_Q \int_0^{t_f} Q_T(t) dt}{t_f} \tag{4.2}$$

subject to

Model equations (equality constraints),

$$f(\dot{x}, x, t, u) = 0 \tag{4.3}$$

Control variables bounds,

$$u_o^{\min} \leq u_o \leq u_o^{\max} \tag{4.4}$$

Products purities (inequality constraints),

$$x_{A,i}(t_f) \geq x_{A,i}^{\min} \qquad \forall\, i = 1, .., N_C \tag{4.5}$$

Recovered solvent purity (inequality constraint),

$$x_{A,sol}(t_f) \geq x_{feed,sol} \tag{4.6}$$

Product and solvent recovery (inequality constraints),

$$\frac{H_{A,i}(t_f)}{H_{feed,i}} \geq \Pi_i^{\min} \qquad \forall\, i = 1,..,N_C \tag{4.7}$$

$$\frac{H_{A,sol}(t_f)}{\int_0^{t_f} F_{sol}(t)dt} \geq \Pi_{sol}^{\min} \tag{4.8}$$

If solvent feedrate is much higher than the distillate flowrate and withdrawals, the possibility exists that the reboiler drum may overflow, leading to operational problems. To prevent this situation from arising, a constraint is placed on the liquid level (l_{reb}) in the reboiler drum during the optimisation,

$$l_{reb}(t) < \frac{\nu_{reb}}{A_{reb}} \quad \forall\, t \ \in [0, t_f] \tag{4.9}$$

where C_i, C_{feed}, C_{sol} and C_Q represent the unit costs of product i, feed, solvent and heating, respectively, $H_{A,i}, H_{feed}$ and $H_{sol}^{make-up}$ the amounts of product i, feed and make-up solvent, respectively, $Q_T(t)$ the total reboiler and middle vessel heat duty, t_f the total batch processing time, $x_{A,i}$ and $x_{A,sol}$ the recovered product and solvent purity, respectively, $x_{feed,sol}$ the purity of the solvent feed, ν_{reb} and A_{reb} the reboiler volume and cross-sectional area, respectively, and $\Pi_i^{\min}$ and $\Pi_{sol}^{\min}$ the minimum product and solvent recovery, respectively. $H_{sol}^{make-up}$ is defined as:

$$H_{sol}^{make-up} = \int_0^{t_f} F_{sol}(t)dt \; - \; H_{A,sol}(t_f) \tag{4.10}$$

where $F_{sol}(t)$ is the solvent feedrate, and $H_{A,sol}(t_f)$ is the amount of solvent recovered at the end of the batch.

4.4 Solution Methodology

The control vector parameterisation (CVP) NLP as described in chapter 3 is used here. In order to use the CVP technique, a feasible solution of the model equations must exist for every possible value which the optimisation decision variables may take. This is not a trivial requirement. In the middle vessel column for instance, the reflux flowrate

(L_{mv}) from the middle vessel is allowed to vary within certain bounds in the optimisation. Since the reflux flowrate may exceed the inlet flowrate (L_{mv}^{in}) to the middle vessel (which depends on the column equations), the liquid holdup (M_{mv}) in the middle vessel. determined by the equation:

$$\frac{dM_{mv}}{dt} = L_{mv}^{\text{in}} - L_{mv} \tag{4.11}$$

may fall below zero. This situation is physically unrealistic and must be avoided. A technique (Furlonge *et al.*, 1999) is employed whereby the above mass balance is modified to:

$$\frac{dM_{mv}}{dt} = L_{mv}^{\text{in}} - L'_{mv} \tag{4.12}$$

where L'_{mv} is the *effective* reflux flowrate related to the control variable L_{mv} via:

$$L'_{mv} = L_{mv}\left(1 - e^{-\frac{M_{mv} - M^{\text{min}}}{M^*}}\right) \tag{4.13}$$

where M^* and M^{min} are constant holdup values. These are chosen such that, for $(M_{mv}(t) - M^{\text{min}}) \gg M^*$, the above equation reduces to $L'_{mv} \approx L_{mv}$. On the other hand, as $M_{mv}(t) \rightarrow M^{\text{min}}$, L_{mv} tends to zero. Hence, assuming that the initial holdup value $M_{mv}(0) > M^{\text{min}}$, $M_{mv}(t)$ can never become negative for any control profile of $L_{mv}(t)$.

Similarly, effective liquid withdrawal rate, $F_{mv}(t)$, and effective middle vessel heat duty, $Q_{mv}(t)$, are also used. The same technique is also employed to prevent the reboiler drum from going dry using an effective liquid flowrate leaving the reboiler drum, $F_{reb}(t)$, and an effective reboiler heat duty, Q_{reb}.

4.5 Mathematical Model

In this study, a detailed model is used. The level of abstraction used disposes of the common modelling assumptions such as negligible tray holdup and constant molal overflow

which may have a significant impact on the optimal solutions obtained as demonstrated by Tomazi (1997) and Furlonge *et al.* (1999). The main features of the detailed model are presented in chapter 3.1.

Dynamic material and energy balances are also used to model the accumulator, reflux drum, vessels and reboiler. In each of these, both liquid and vapor holdups are taken into account. The condenser model assumes total condensation with no subcooling. The model assumptions retained include no entrainment effects, no downcomer dynamics, adiabatic operation with regards to the column's outer environment, phase equilibrium and perfect mixing. The implementation and simulation of the model are presented in Appendices A and E, respectively.

4.6 Optimal Operation of Regular and Middle Vessel Columns

Separation of an acetone-methanol mixture using water as solvent, a well known industrial application, is considered. Many studies, from Yatim *et al.* (1993) to Milani (1999), have presented this mixture and solvent as their case study, therefore the same is used here for easy comparison. The mixture forms a minimum boiling azeotrope at $55^{o}C$ with about 0.8 mole fraction of acetone (Gmehling and Onken, 1977). The feed composition is 50 *mol*% each and the batch size is taken to be 100 *mol* plus 5.7 *mol* initial total holdup on the trays and the reflux drum.

The product specification for the acetone cut is 93 *mol*% whilst the specification for water is 99 *mol*%, matching the initial purity of the solvent so that the recovered cut can be re-used in successive batches. For the methanol-rich cut, it is either treated as an offcut or as a product with a specification of 93 *mol*% imposed on it. If it is treated as an offcut, it has negligible sale value. The cost parameters needed in the objective function are given in Table 4.2.

Cost Parameters	
Sale price of acetone, C_1 $(\$/mol)^1$	1.358
Sale price of methanol, C_2 $(\$/mol)^1$	0.606*
Cost price of feed, C_{feed} $(\$/mol)^1$	0.298
Cost price of water, C_{sol} $(\$/mol)^1$	0.0038
Heating cost, C_Q $(\$/MJ)^2$	0.019

1: taken from Mujtaba (1999); 2: taken from Sinnott (1993)
* 0.001 when treated as offcut

Table 4.2: Cost parameters for case study

Accumulator	Volume, v	0.0151 m^3
Reflux drum	Volume, v	0.000079 m^3
Reboiler drum	Cross-sectional area, A_{reb}	0.03 m^2
	Volume, v_{reb}	0.012 m^3
Middle vessel	Volume, v	0.012 m^3
Trays	Number of trays, N	30
	Volume, v_k	0.00012 m^3
	Weir height, h_{weir}	0.006 m
	Weir length, l_{weir}	0.018 m
	Plate area, A_k	0.00196 m^2
	Total hole area, A_{holes}	0.0002244 m^2
	Wall correction factor, F_w	0.98
	Aeration coefficient, β	0.6
	Tray vapour flow coefficient, α	0.003
	Scale parameter, φ	1.0
Condenser	Vapour flow coefficient, γ	0.04

Table 4.3: Column dimensions and other characteristics

4.6.1 Column Specifications

The regular and middle vessel tray column configurations were shown in Figure 4.1. Both columns have the same number of trays. The condenser pressure in both cases is atmospheric. Table 4.3 shows the column dimensions and other characteristics. The typical values of coefficients such as wall correction factor, aeration coefficient, tray and condenser vapour flow coefficients were obtained from Perry and Green (1984).

The rectifying section of the regular column consists of 6 trays. Below the point of solvent addition, the extractive section consists of 24 trays. Depending on the specifications, two or three overhead accumulators are used to collect the acetone product, methanol prod-

	$\lambda_{1,2} - \lambda_{1,1}$ (J/mol)	$\lambda_{2,1} - \lambda_{2,2}$ (J/mol)
acetone(1) methanol(2)	-478.6693	2281.5109
acetone(1) water(2)	1440.6960	6201.5804
methanol(1) water(2)	347.2201	2178.3820

Source: Gmehling and Onken (1977)

Table 4.4: Wilson binary interaction parameters

uct and offcut. The recovered solvent is taken to be the final content of the reboiler drum.

Similarly, the rectifying section of the middle vessel column consists of 6 trays. Both the extractive and stripping sections consist of 12 trays each, making the total number of trays equivalent to that of the regular column. An overhead accumulator is used for collecting the acetone product and another accumulator is made available for a possible offcut. The methanol-rich cut is produced in the middle vessel rather than being withdrawn overhead. The recovered solvent is taken to be the final content of the reboiler drum together with the liquid withdrawn to the bottom accumulator.

4.6.2 Thermophysical Model

Thermophysical properties including density, enthalpy and fugacity are calculated using the *Multiflash* (Infochem Computer Services Ltd., 2000) physical properties package interfaced to *gPROMS*. The pressure range of the system is 1 bar with no liquid-liquid heterogeneity, hence the Wilson model is chosen for the polar liquid phase while the Soave-Redlich-Kwong Equation of State is used for the vapour phase.

The Wilson binary interaction parameters were obtained from Gmehling and Onken (1977), as shown in Table 4.4. The consistency of the parameters were checked by performing simple boiling point flash calculations at atmospheric pressure and the results obtained matched closely the values given by Safrit *et al.* (1995).

Decision Variables	Bounds
Q_{reb} (kW)	[0.5 , 20]
$Q_{mv}(t)$ (kW)	[0.5 , 20]
$R(t)$	[0.5 , 1]
$R_{D2}(t)$	[0 , 1]
$R_{D3}(t)$	[0 , 1]
$F_{sol}(t)$ (mol/s)	[0 , 0.1]
$L_{mv}(t)$ (mol/s)	[0.1 , 1]
$F_{mv}(t)$ (mol/s)	[0 , 0.5]
$F_{reb}(t)$ (mol/s)	[0 , 0.5]
$M_{mv}(0)$ (mol)	[10 , 90]
$M_{reb}(0)$ (mol)	[10 , 90]
Δt (s)	[10 , 2000]

Table 4.5: Decision variable bounds

4.6.3 Initial Conditions

The start-up period of operation, *i.e.* starting from when the column is initially dry and cold feed is placed in the reboiler drum, is not simulated. Rather, it is assumed that the initial liquid composition throughout the column is that of the feed (50 $mol\%$), and the liquid is at its boiling point (*i.e.* 330 K). This was shown by Sadotomo and Miyahara (1983) to be a reasonably accurate approximation for tray columns. The initial liquid holdup on the trays is 0.19 mol to allow liquid flow over the weir from the very beginning of the operation. The reflux drum and all accumulators are assumed to be empty at the start.

4.6.4 Bounds on Decision Variables

For a fixed column design, the operation is likely to be most profitable when operated at maximum available reboiler heat duty to provide maximal column vapour loading (without flooding) and shorter process time. Thus, the optimal *time-invariant* reboiler heat duty is determined. All other control variables are allowed to vary in a *piecewise-constant* manner. The bounds placed on the optimisation decision variables are shown in Table 4.5.

Case Study	Separation Duty (purity)	Middle Stream Configuration (Figure 4.2)	Recovery Constraint
I	Acetone (93 *mol*%) Solvent (99 *mol*%)	A	≥20 %
II	Acetone (93 *mol*%) Methanol (93 *mol*%) Solvent (99 *mol*%)	A, B, C, D and Optimal	≥20 %

Table 4.6: Summary of optimisation cases considered

4.6.5 Case I: Single Product

The separation duty involving only one main product (acetone) and solvent recovery is considered first (Table 4.6). The operating duration is divided into four time intervals for both regular and middle vessel columns, the durations of which are allowed to vary in the optimisation. In the case of the regular column, all of the feed is initially charged to the reboiler drum. The reflux ratio, $R(t)$, the reboiler heat duty, Q_{reb}, and the solvent feedrate $F_{sol}(t)$ are optimised. The column is operated under total reflux (*i.e.* $R(t) = 1$) in the first interval. All other decision variables in this interval, and all decision variables for the subsequent intervals, are free to be determined by the optimisation. The acetone product cut is collected in the first overhead accumulator during the first three intervals. In the last interval, a methanol-rich offcut is withdrawn into the second accumulator whilst the solvent concentrates in the reboiler.

The simplest and most practical middle vessel column configuration (configuration A, Figure 4.2) is considered with three different feed locations, namely feed placed mainly in the middle vessel (90%), feed placed mainly in the reboiler drum (90%) and feed optimally distributed between these two. The reflux ratio, $R(t)$, the reboiler heat duty, Q_{reb}, the solvent feedrate, $F_{sol}(t)$, the reflux flowrate from the middle vessel, $L_{mv}(t)$, and the bottom product withdrawal flowrate, $F_{reb}(t)$, are optimised in all three situations. Similar to the regular column, only the reflux ratio in the first interval is set to total reflux, the rest of the decision variables are optimised throughout the duration of the

Column	Regular	Middle Vessel		
Feed Location	*a*	*a*	*b*	*c*
Reboiler/Middle vessel (*mol*)	100/-	90/10	10/90	90/10
Operating profit ($/*hr*)	149.8	122.5	111.8	122.5
Batch processing time (*min*)	16.6	18.9	21.5	19.0
Heat consumption (*MJ*)	19.9	20.2	22.4	20.3
Acetone recovery (%)	93.0	89.3	91.3	89.7
Methanol recovery (%)	-	-	-	-
Solvent recovery (%)	69.9	52.0	52.7	52.2
Solvent used (*mol*)	78.2	94.8	96.4	95.4

Feed location *a*: reboiler drum; *b*: middle vessel; *c*: optimised
See Appendix F for product purities

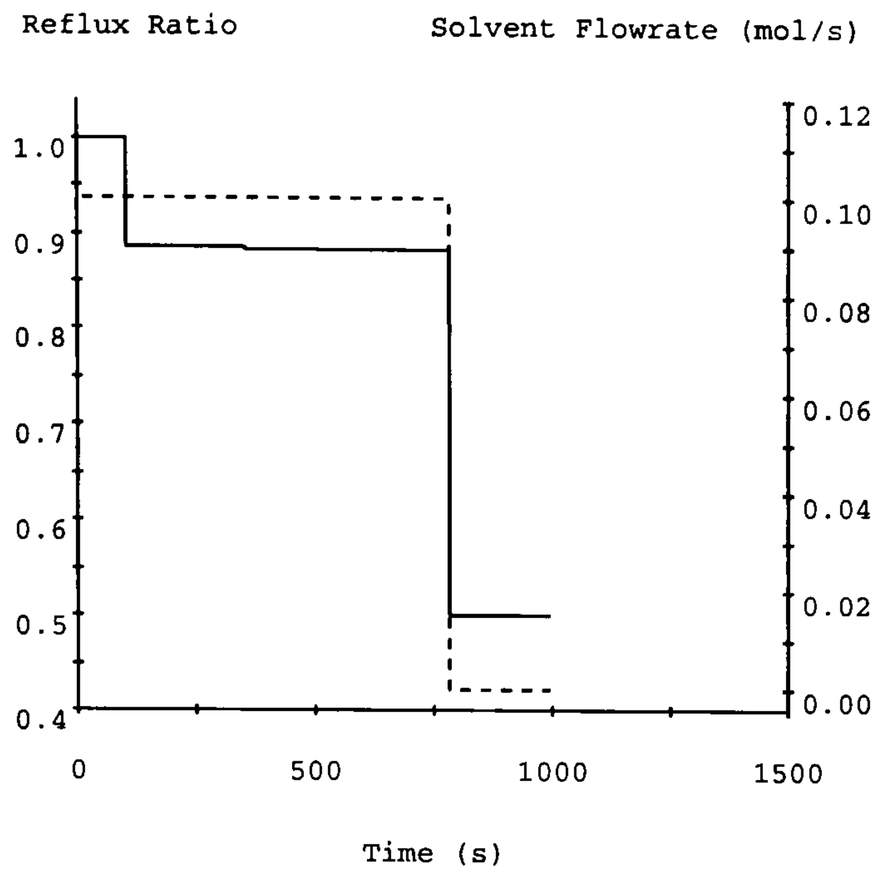
Table 4.7: Summary of optimal results for case study I

operation. The acetone product is collected in the first top accumulator while high purity solvent recovery is collected in the reboiler and bottom accumulator. A summary of the optimisation results for case study I is given in Table 4.7 (see Appendix F for product purities).

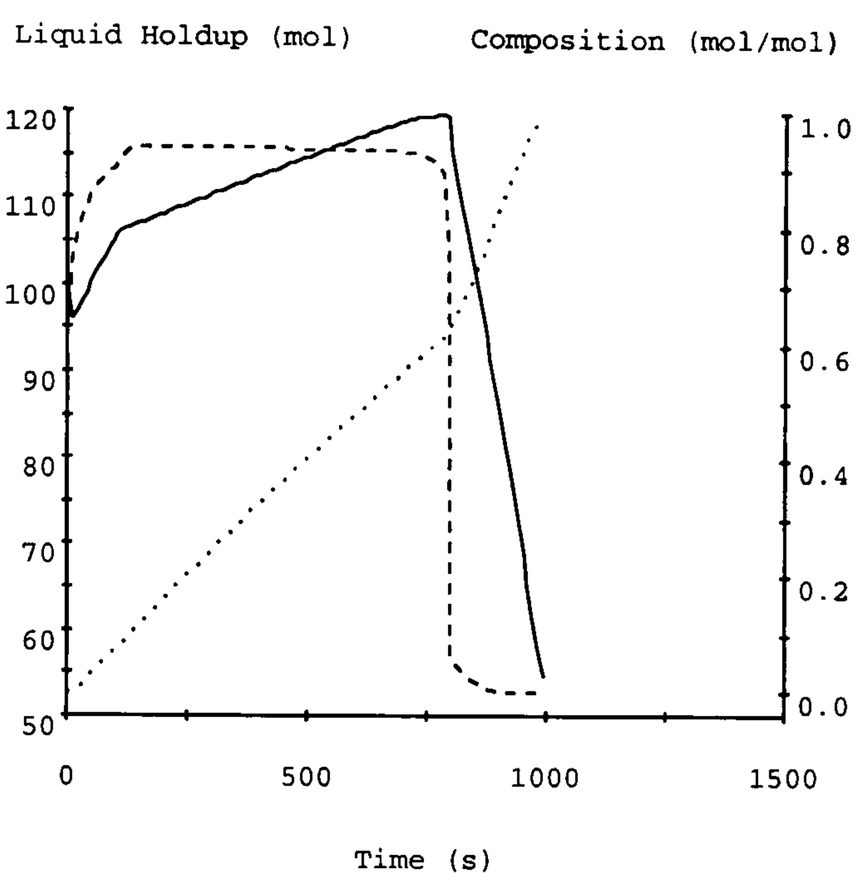
Optimal Operating Policy for Regular Column

Although four control time intervals were allowed in the optimisation, the optimal operating policy suggests that only three steps are required to fulfil the separation duty. As can be seen from the reflux ratio profile in Figure 4.3a, the first step is a short period of total reflux operation (102 *s* duration) with solvent introduced right from the very beginning of the process. Thus, the first period of total reflux without solvent addition, as proposed by Yatim *et al.* (1993), is found here to be redundant for this case, reducing the minimum number of operation steps required to three. The acetone composition in the distillate rises steeply and above the azeotropic composition (80 *mol*%) during this period (Figure 4.3b). The reboiler holdup dips slightly before rising due to the introduction of the solvent.

In the second period of operation, withdrawal of the acetone product cut occurs. The



(a)



(b)

(a) —— reflux ratio; - - - Fsol (b) —— reboiler holdup; - - - composition of acetone in distillate; . . . composition of solvent in reboiler

Figure 4.3: Case I optimal results for regular column

withdrawal period is relatively lengthy compared to the first period due to the high reflux ratio required to maintain a high distillate composition. This reflux ratio is maintained at the same value (0.884 and 0.883) in the two intervals (of 251 s and 428 s). Solvent feedrate (0.1 mol/s) and reboiler duty (20 kW) at the maximum bounds are chosen. The reboiler liquid holdup increases gradually as solvent addition exceeds the product removal rate.

In the final period of operation (212 s duration), solvent feeding terminates and solvent purification takes place. This involves the withdrawal of a methanol-rich cut overhead. Intuitively, a low reflux ratio is used in order to reduce the length of time taken, particularly since no specification is placed on the purity of the methanol-rich cut as it is treated as a waste cut. The reboiler liquid holdup drops sharply as an offcut is withdrawn into the second accumulator at the top, until the purity specification on the solvent in the reboiler (99 $mol\%$) is reached. The total batch processing time is 993 s.

Optimal Operating Policy for Middle Vessel Column

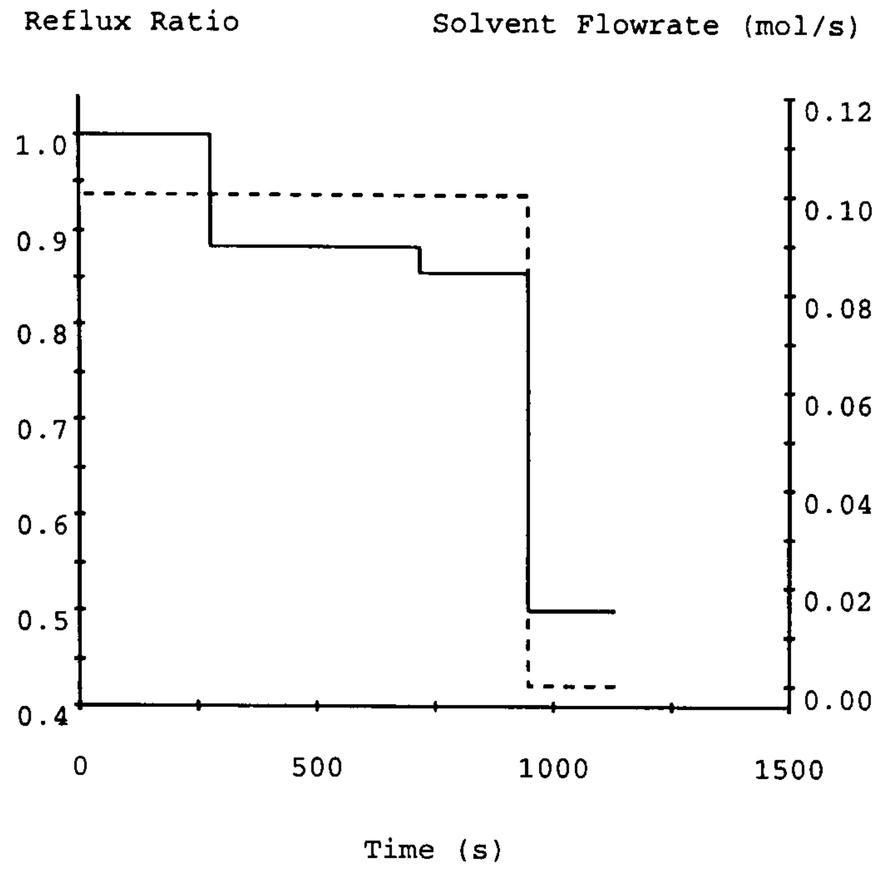
The optimal operation of the middle vessel column with feed mostly charged to the reboiler drum (Table 4.7, case *a*) is found to be quite similar to the optimal operation of the conventional regular column. Again, only three operation steps are required (Figure 4.4).

The first total reflux period (277 *s*) is much longer than that of the regular column. Again, the maximum allowable solvent feed rate is introduced to the column from the very beginning. A high reflux flowrate from the middle vessel is selected which maintains a low liquid holdup in the middle vessel (Figure 4.4c). Note that the effective reflux flowrate, L'_{mv}, is lower than its control value, L_{mv}, due to the low middle vessel holdup (refer to Equation 4.13). This is a result of the mathematical technique used to prevent the vessel from going dry (as described in section 4.4).

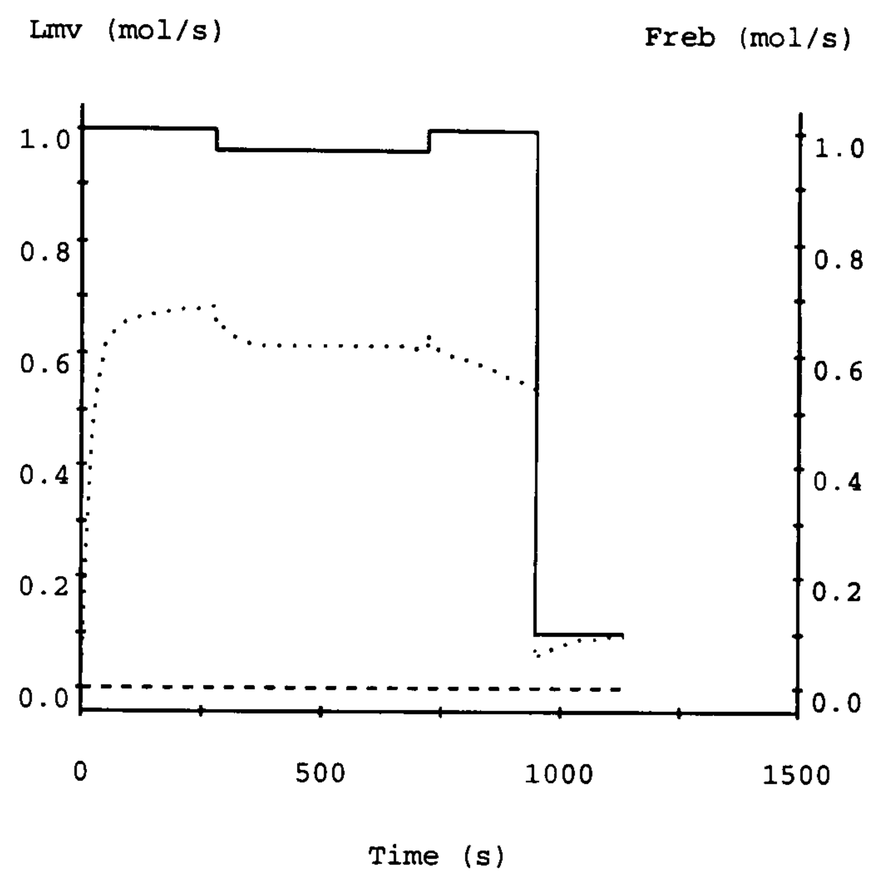
In the second period of operation, the acetone cut is withdrawn at a reflux ratio of 0.881 followed by 0.855 (two intervals of 439 *s* and 232 *s*, respectively). The solvent feedrate is kept at the maximum allowable value during this period. The middle vessel liquid holdup is kept fairly constant and at a low value. As shown in Figure 4.4d, the methanol composition profile in the middle vessel profile rises steeply towards the end of this period.

In the final period (183 *s* duration), purification of the solvent in the reboiler drum occurs. Again, the reflux ratio is lowered to accelerate the removal of the offcut. The reflux flowrate from the middle vessel, L_{mv}, is decreased substantially, causing the liquid holdup in the middle vessel to rise and the methanol purity in the vessel to deteriorate. This is because no specification is imposed on this cut, hence all the decision variables are selected to speed up the concentration of the solvent in the reboiler. Note that, although bottom product withdrawal is allowed throughout the duration of the process, no bottom cut was withdrawn and the solvent concentration in the reboiler only reaches its specification at the end of the process.

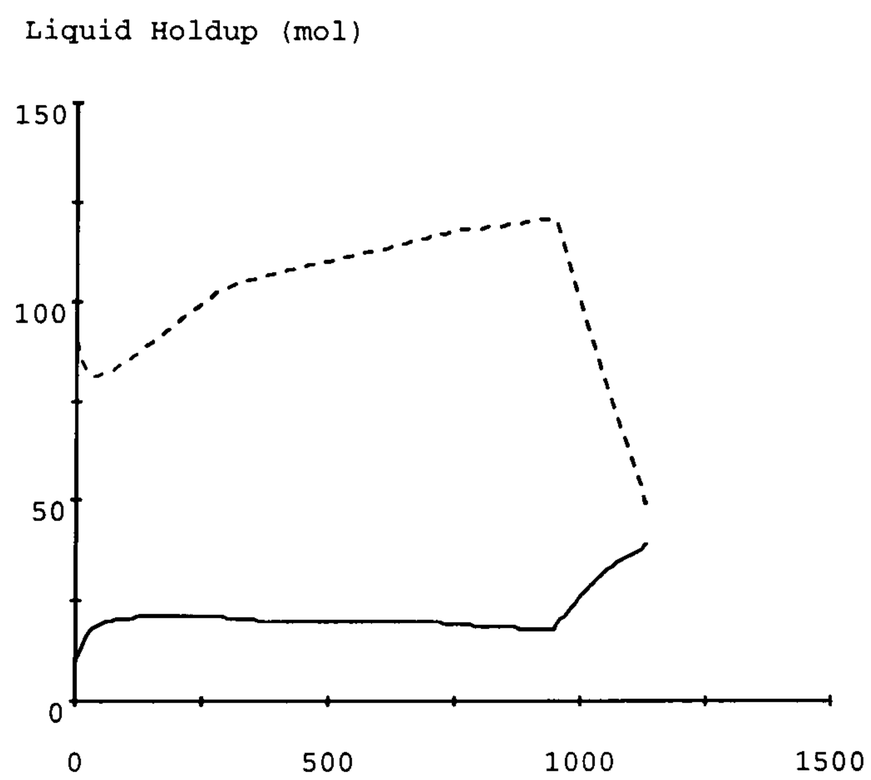
Next, consider the case where the feed is charged to the middle vessel (case *b*). The optimal operation policy involves an initial total reflux period without solvent feeding



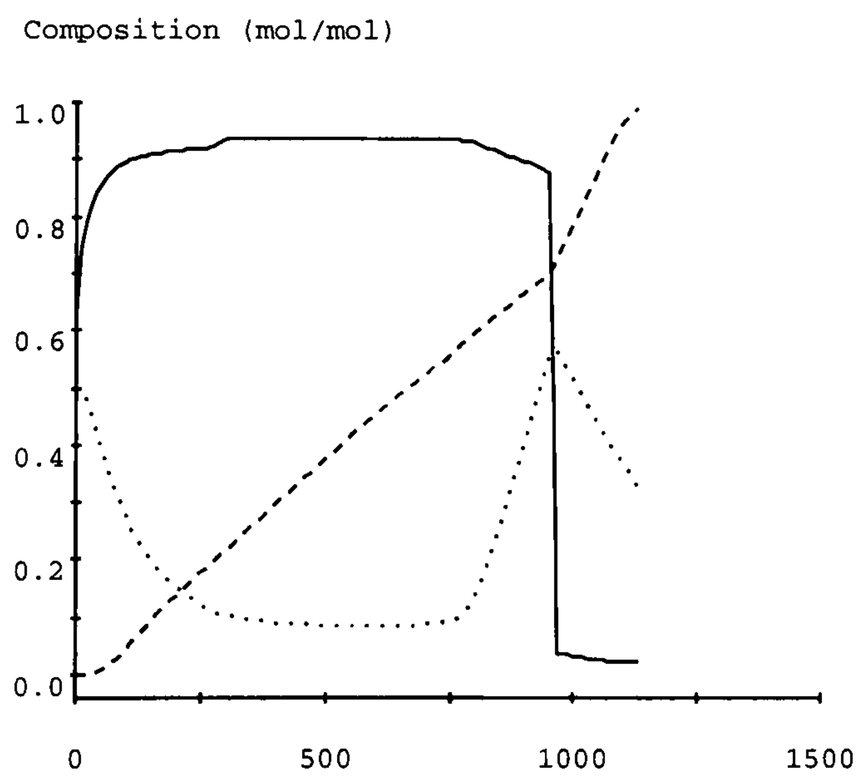
(a)



(b)



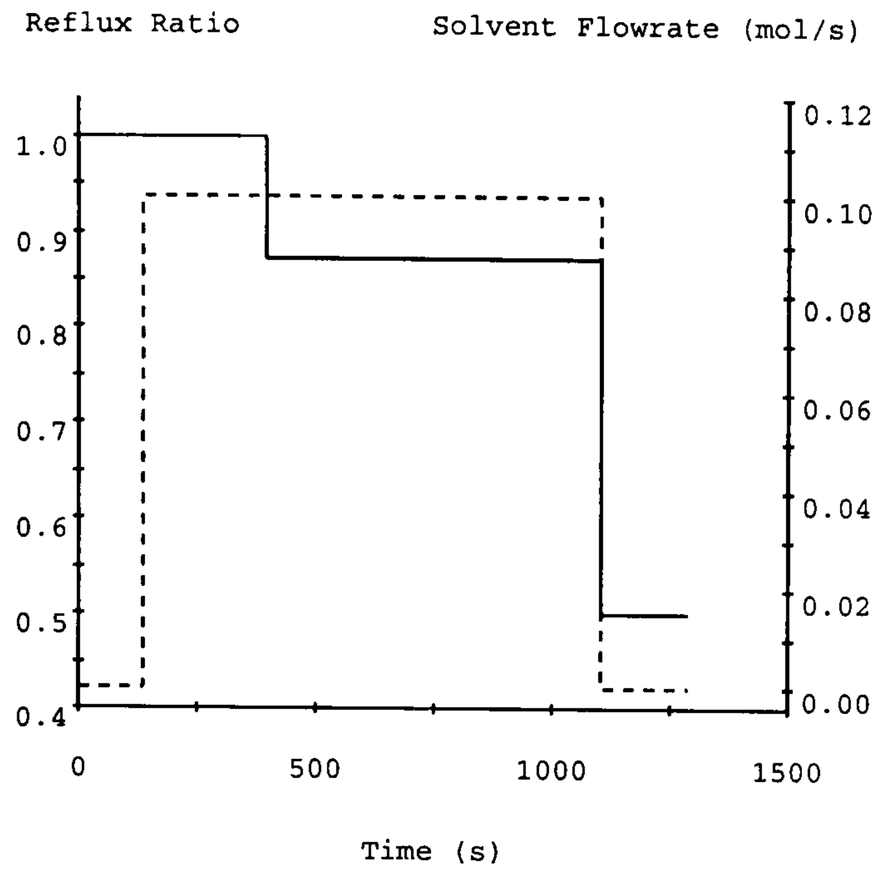
(c)



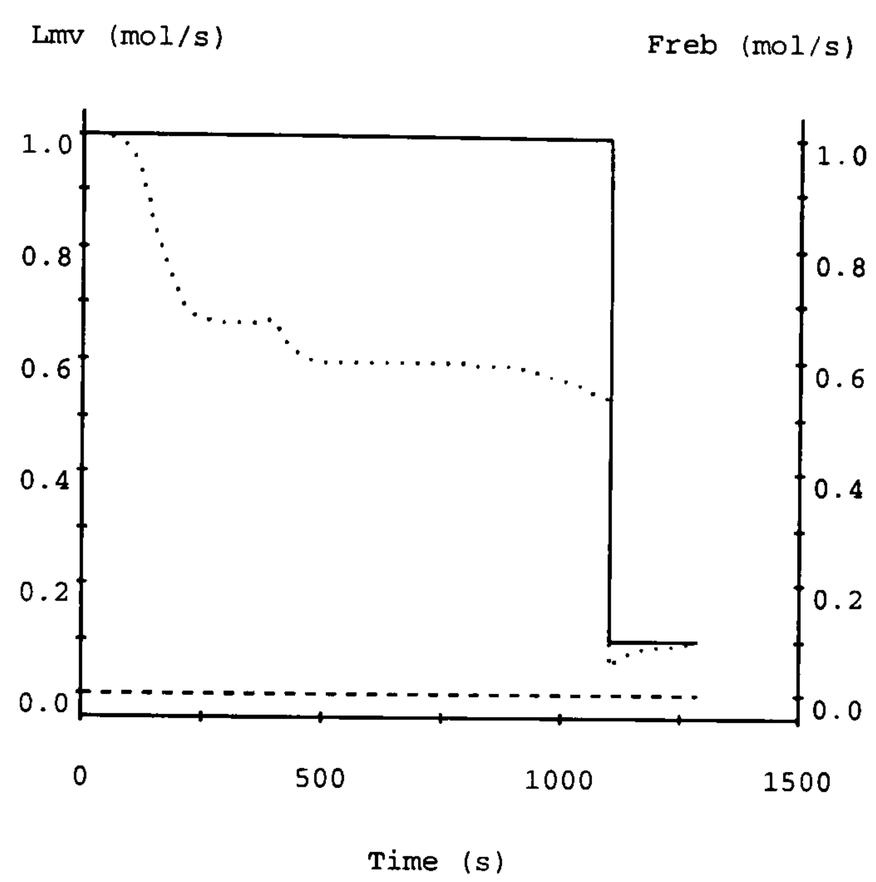
(d)

(a) —— reflux ratio; - - - F_{sol}
(b) —— L_{mv}; . . . effective L_{mv}; - - - F_{reb}
(c) Liquid holdup: —— middle vessel; - - - reboiler
(d) Composition: —— acetone in distillate; - - - solvent in reboiler; . . . methanol in middle vessel

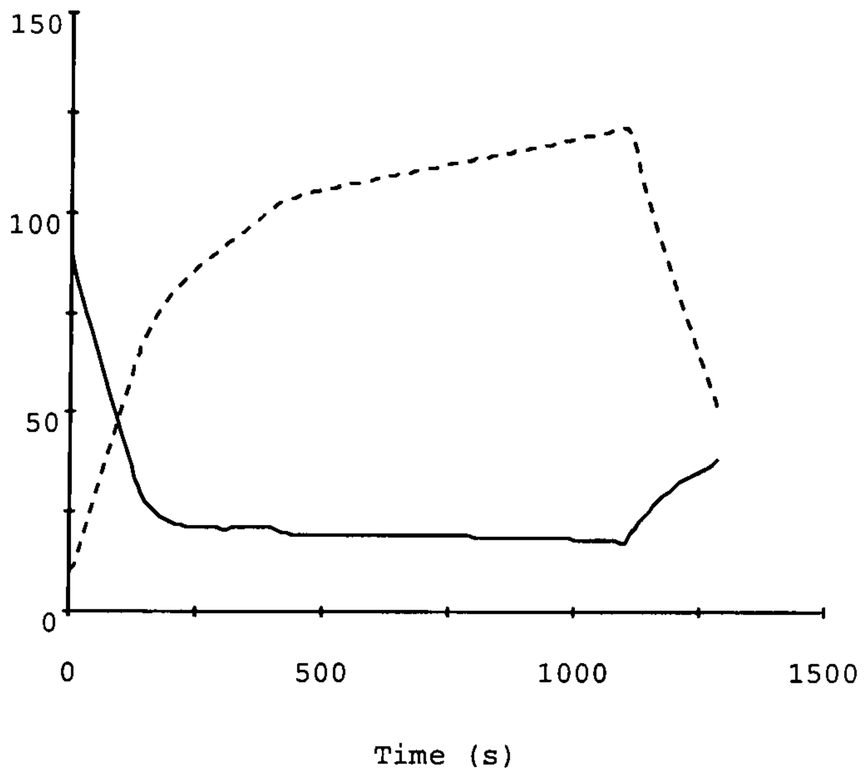
Figure 4.4: Case I optimal control variables, holdup and composition profiles for middle vessel column with reboiler charge (case *a*)



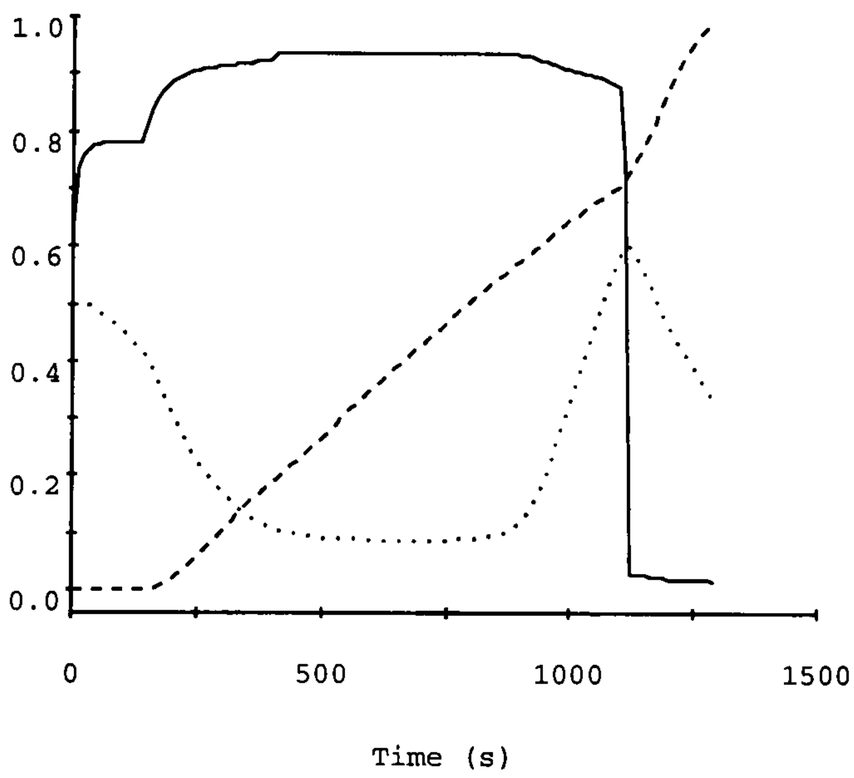
(a)



(b)



(c)



(d)

(a) —— reflux ratio; - - - F_{sol}
(b) —— L_{mv}; . . . effective L_{mv}; - - - F_{reb}
(c) Liquid holdup: —— middle vessel; - - - reboiler
(d) Composition: —— acetone in distillate; - - - solvent in reboiler; . . . methanol in middle vessel

Figure 4.5: Case I optimal control variables, holdup and composition profiles for middle vessel column with middle charge (case *b*)

(Figure 4.5). During this period, a high reflux flowrate from the middle vessel is selected which causes most of the liquid holdup in the middle vessel to be transfered to the reboiler (Figure 4.5c). By the end of the first period, the distillate composition reaches the azeotropic point. Then, maximum solvent feedrate is introduced into the column until the distillate composition approaches the purity specification. Hence, the combined total reflux period is longer (396 s) compared to the previous case (277 s) but the extra time is spent transfering material from the middle vessel to the reboiler.

Finally, the initial feed distribution was determined (case c). As expected, the optimal feed placement is in the reboiler, *i.e.* 90 mol, and the control variables profiles are practically identical (within the optimisation accuracy) to those of case a (Table 4.7).

Comparison of Regular and Middle Vessel Column

For the middle vessel column, the optimal operation for feed charged to the reboiler drum (case a) performed better than for feed charged to the middle vessel (case b). This was confirmed by the optimal feed location results (case c). The operating profit for case b was about 9% lower than that of cases a and c due to the additional interval required at the beginning of the operation to transfer the holdup from the middle vessel to the reboiler.

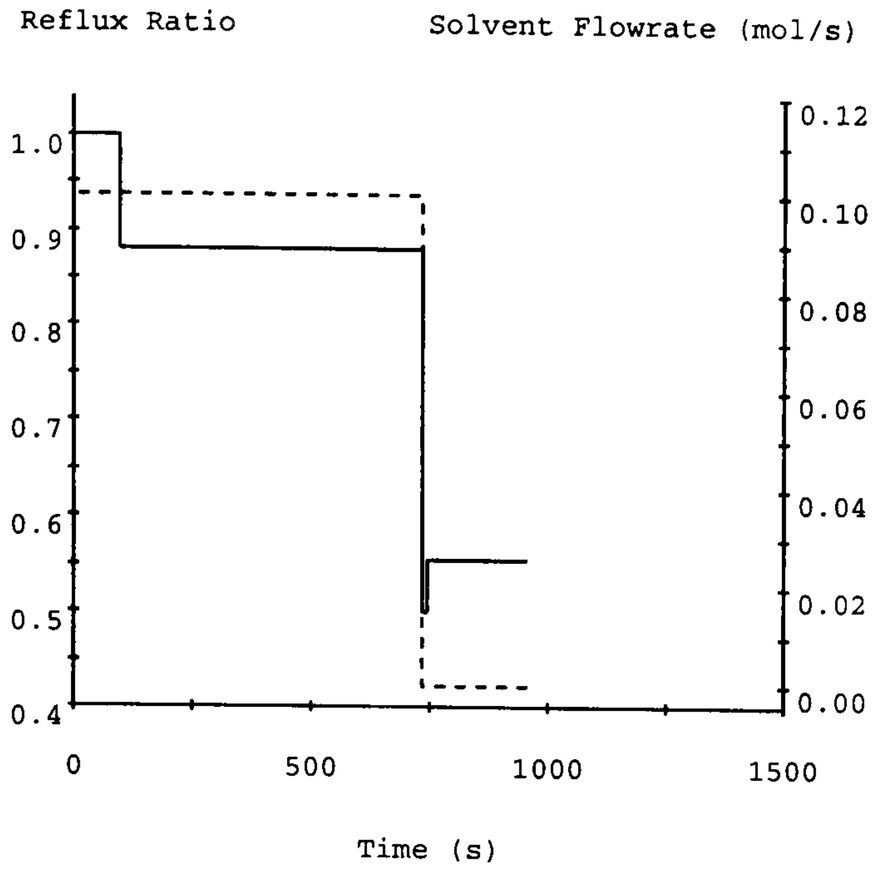
The optimal acetone and solvent recovery of the regular column were found to be higher than that of the middle vessel column. Also, the operating profit of the regular column was 18% higher than that of the simple middle vessel column configuration (case a). This was in part due to the longer total reflux period in the middle vessel column. In this specific case study, where recovery of the intermediate component (methanol) was not considered, the middle vessel did not offer any functional advantage compared to the regular column other than acting as a low level holdup throughout most of the operation duration.

4.6.6 Case II: Multiple Products

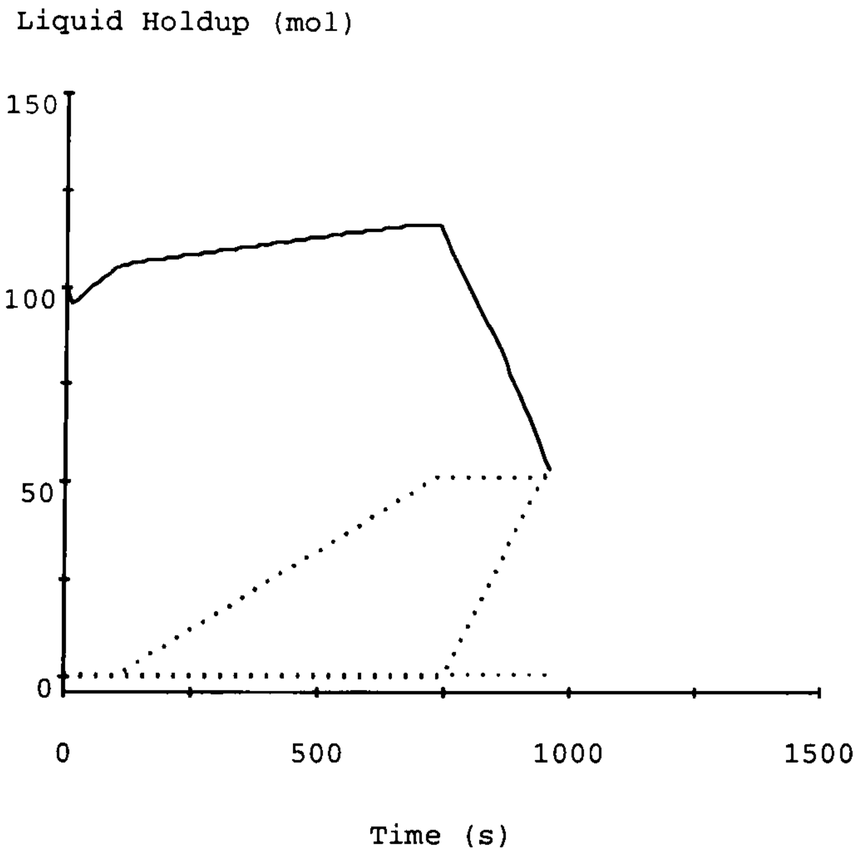
In this example, the less volatile component methanol is also recovered, at a purity specification of 93 *mol*%, in addition to the specifications of acetone and solvent (Table 4.6). For the regular column, results from the first case study suggest that four control intervals are sufficient to fulfil the extra methanol specification. The methanol rich cut is collected in the final accumulator with an additional accumulator made available after the first acetone accumulator to collect a possible offcut. For the middle vessel column, all the different stream configurations are now considered (Figure 4.2). The methanol rich cut is purified in the middle vessel and an additional accumulator is also made available for a possible offcut from the top. Therefore, the number of time intervals is increased to five for all the middle vessel configurations. The optimisation results are discussed below (summarised in Table 4.8).

Optimal Operating Policy for Regular Column

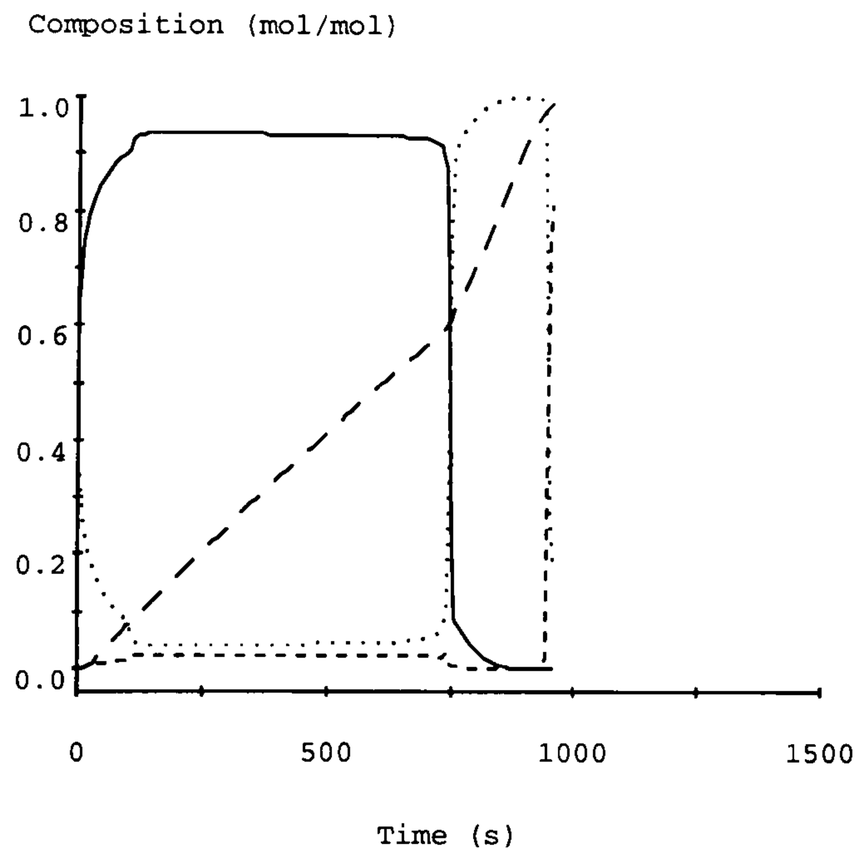
The first period for the regular column is a short total reflux operation (99 s) with solvent feeding at the maximum rate (Figure 4.6). The acetone composition at the top rises steeply from that of the feed to well above the azeotropic point (Figure 4.6c). In the second period of operation (648 s), withdrawal of the first product cut of acetone occurs. This is done rather slowly with a high reflux ratio to maintain the distillate at a fairly constant level of just above the required 93 *mol*%. As shown in Figure 4.6b, the liquid holdup of the first accumulator increases at a constant rate with a final acetone recovery of 90.4% with 93.0 *mol*% purity. At the end of the second period, the composition change in the distillate is very sharp with the methanol profile shooting upwards almost instantaneously to well above the purity specification of 93 *mol*%. Hence, an offcut is not required in the optimal policy as shown in Figure 4.6a where the offcut interval touches the minimum bound of 10 s. In the third period (211 s), solvent addition ceases and a lower reflux ratio is chosen to speed up the relatively easy separation of the remaining methanol from the solvent in the reboiler. As shown in Figure 4.6b, the second accumulator fills up much faster than the first accumulator.



(a)



(b)



(c)

(a) —— reflux ratio; - - - F_{sol}
(b) Liquid holdup: —— reboiler; . . . accumulators
(c) Composition: —— acetone; . . . methanol; - - - solvent in distillate; – – solvent in reboiler

Figure 4.6: Case II optimal control variables, holdup and composition profiles for regular column

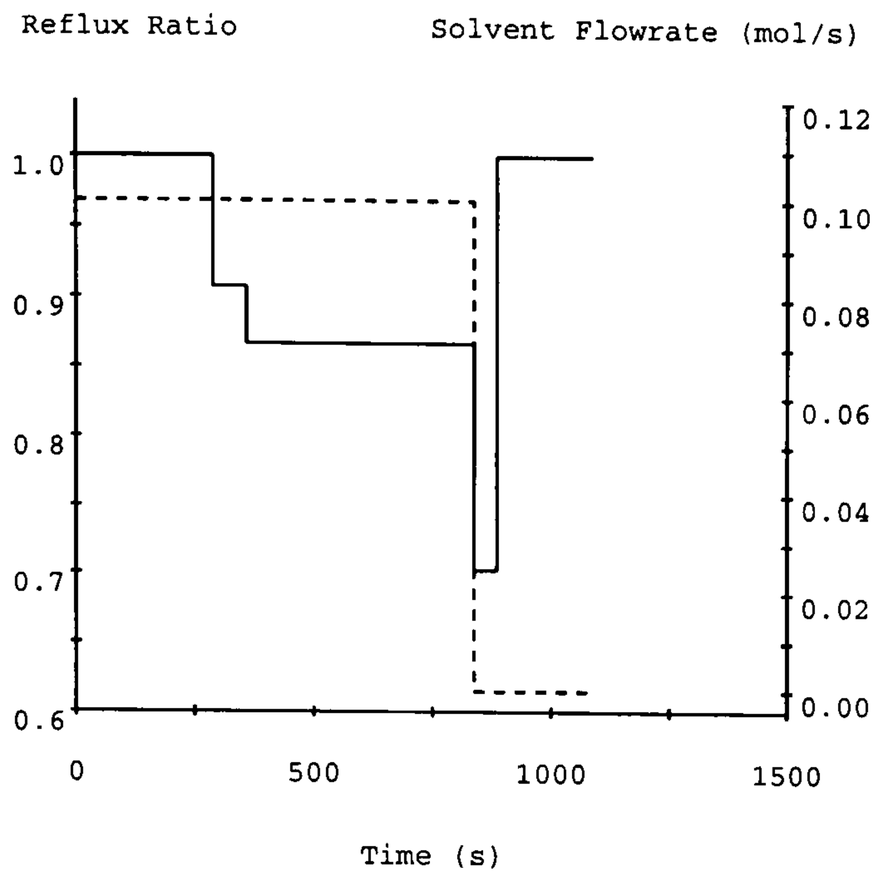
Optimal Operating Policy for Middle Vessel Columns

Five different configurations of the middle vessel column were investigated in this case study (Figure 4.2). For each configuration, the variables which were determined by the optimisation include the reflux ratio, $R(t)$, solvent flowrate, $F_{sol}(t)$, reflux from the middle vessel, $L_{mv}(t)$, reboiler and middle vessel heat duties, Q_{reb} and $Q_{mv}(t)$, withdrawals from the reboiler and middle vessel, $F_{reb}(t)$ and $F_{mv}(t)$, the initial feed placement, $M_{mv}(0)$ and $M_{reb}(0)$, and duration of the process intervals, Δt. In addition, the split ratios of the liquid and vapour streams at the middle vessel section, $R_{D2}(t)$ and $R_{D3}(t)$, were allowed to vary in the optimal case (refer to Table 4.1).

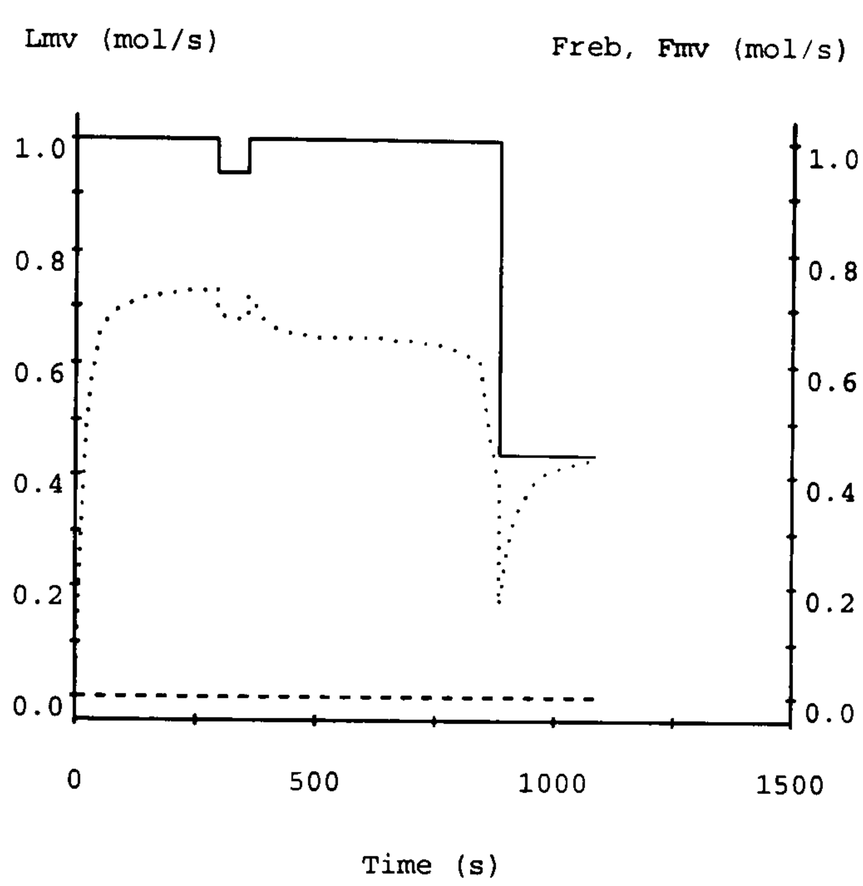
For the most practical configuration A (Figure 4.7), the optimal feed location is the reboiler drum. The total reflux period with solvent addition is followed by the acetone removal period at reflux ratios of 0.907 and 0.867. After a brief period of offcut, the solvent feed is stopped and another total reflux period resumes. Reflux flowrate from the middle vessel is reduced, allowing the methanol cut to accumulate and purify in the middle vessel. At the same time, the solvent is being purified in the reboiler drum. There was no withdrawal from the reboiler nor from the middle vessel.

In configuration B, a heat input is introduced at the middle vessel and vapour is allowed to flow between the middle vessel and the bottom extractive tray. The optimal operating policy is similar to that of configuration A. The introduction of heating at the middle vessel, albeit at only 4.5% (0.9 MJ) of the total heat consumption, improves the performance of the separation in terms of lower processing time and overall heat duty as well as improvement in product recoveries. The objective function increased by 18% from 201.4 $\$/hr$ to 238.0 $\$/hr$ compared to configuration A (Table 4.8).

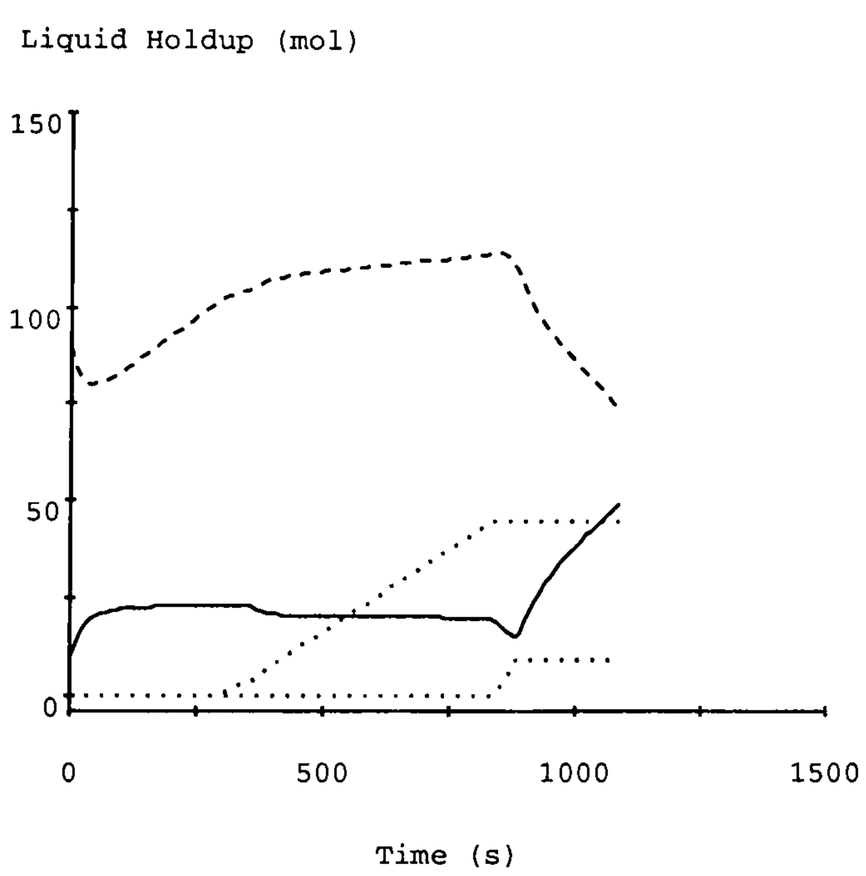
In configuration C, the vapour stream from the stripping section is fed to the middle vessel instead of to the extractive section. Of course, from a practical point of view, diversion of vapour between the trays into a heated middle vessel is difficult, unlike the liquid stream which may be easier to split via the downcomer. Nonetheless, in order to pursue a purely theoretical scenario, the model assumes the vapour stream as being



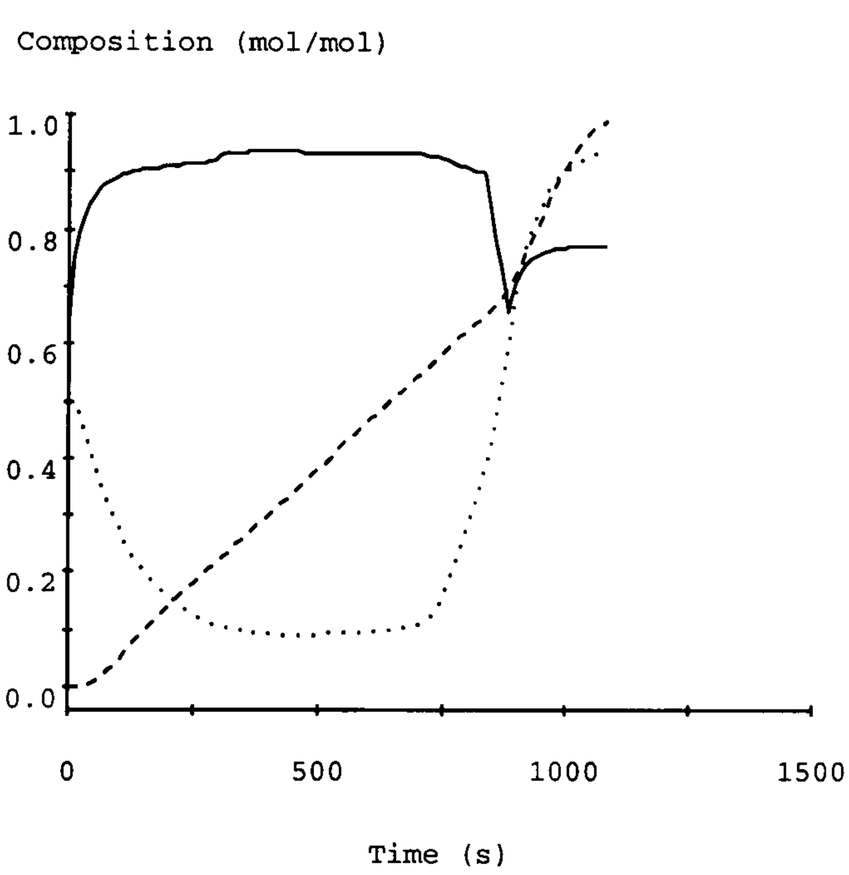
(a)



(b)



(c)



(d)

(a) —— reflux ratio; - - - F_{sol}
(b) —— L_{mv}; . . . effective L_{mv}; - - - F_{reb}, F_{mv}
(c) Liquid holdup: —— middle vessel; - - - reboiler; . . . accumulators
(d) Composition: —— acetone in distillate; - - - solvent in reboiler; . . . methanol in middle vessel

Figure 4.7: Case II optimal control variables, holdup and composition profiles for middle vessel column with configuration A

Column Configuration	Regular	Middle Vessel				
		A	B	C	D	Optimal
Operating profit ($/hr)	270.8	201.4	238.0	257.9	278.7	291.1
Batch processing time (min)	16.0	18.1	16.3	16.0	15.1	14.7
Total heat consumption (MJ)	19.1	21.0	20.0	19.6	18.5	18.0
Total heat consumption to middle vessel (MJ)	-	-	0.9	0.5	2.9	2.1
Acetone recovery (%)	90.4	79.3	83.7	87.9	90.0	91.5
Methanol recovery (%)	94.6	86.7	88.4	90.0	89.9	90.4
Solvent recovery (%)	73.4	88.1	85.3	84.6	83.4	82.8
Amount solvent used (mol)	73.4	83.6	74.6	73.2	67.8	66.0
Optimal feed location (mol) (reboiler/middle vessel)	-	90/10	90/10	90/10	90/10	89/11

See Appendix F for product purities

Table 4.8: Summary of optimal results for case study II

driven by the usual inter-tray pressure difference. With this configuration, the column performance improved further with better processing time, overall heat duty and product recoveries. The profit is 28% higher than that of configuration A.

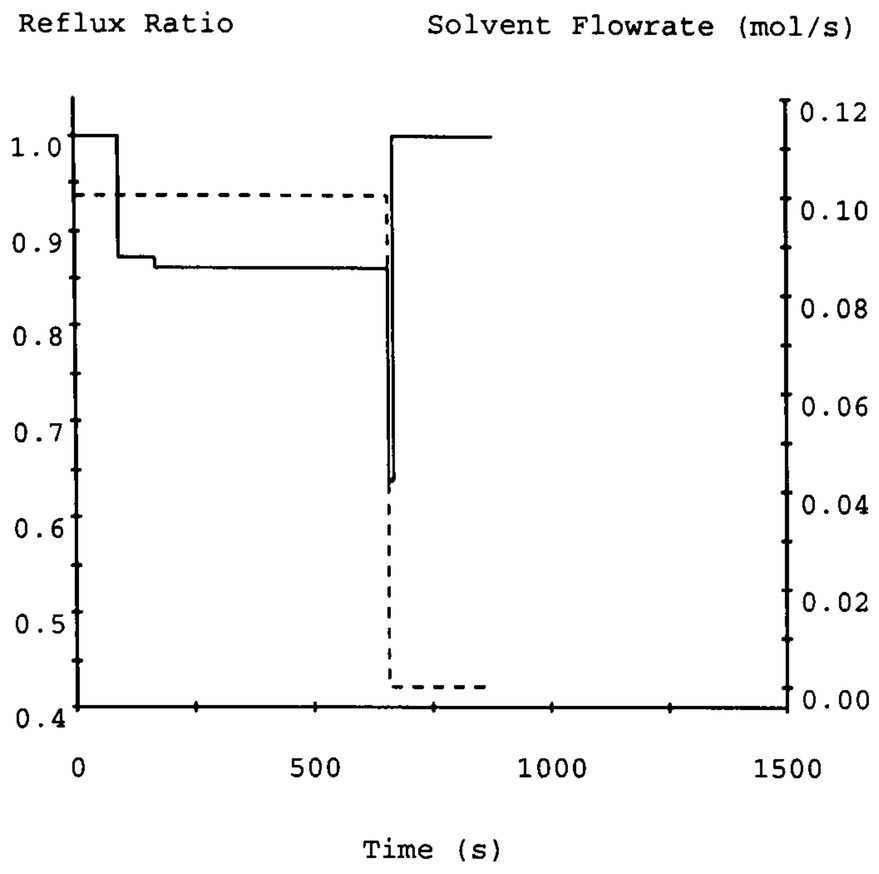
A more practical approach to investigate a possible improvement to configuration B, is to allow the direction of the liquid stream from the extractive section to be determined by the optimisation, *i.e.* configuration D. The downcomer flow could be split using a simple valve connection with the ratio being the decision variable, R_{D2}. The optimal split ratio is at a high value (0.8) during the initial total reflux and acetone withdrawal periods. In other words, the liquid stream is diverted to the stripping section bypassing the middle vessel during the solvent addition periods. This behaviour may be explained by the fact that the solvent-rich stream would be directed towards the reboiler where eventually it would be purified, instead of being forced through the middle vessel where it may contaminate its content. During the final step, where methanol is purified in the middle vessel, the liquid stream switches its direction completely into the middle vessel. Configuration D has an operating profit 17% higher than that of configuration B and

38% higher than configuration A.

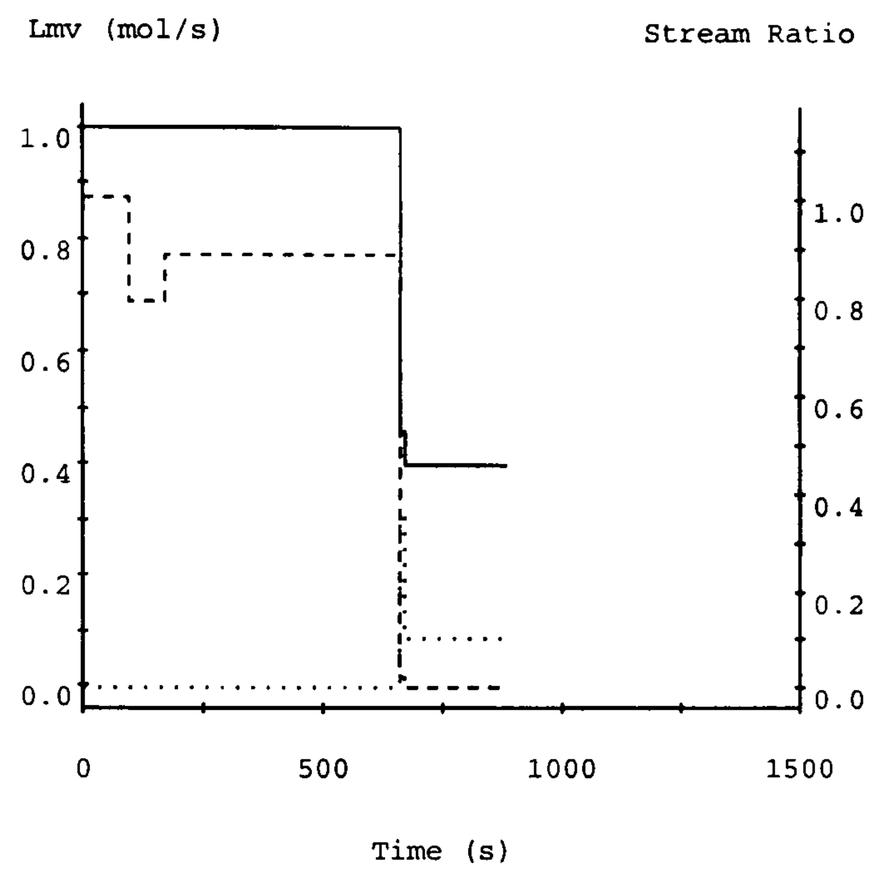
Lastly, for the optimal configuration case (Figure 4.8), all operational degrees of freedom available to this column were examined including the optimal stream configurations between the middle vessel and the column *i.e.* both the vapour and liquid streams split ratios. The optimal feed placement is in the reboiler drum as shown in Figure 4.8c. The control variables profiles show that only three operating steps are required, *i.e.* a short period of total reflux with solvent feeding, a top withdrawal period with solvent feeding and finally another total reflux period without solvent feeding. There is a very short offcut period (10 s, lower bound) before the final total reflux step.

Figure 4.8a,b illustrates the optimal operating steps of the middle vessel column. In the first total reflux period (93 s), solvent is introduced at the maximum allowable flowrate. The heat duty in the middle vessel and reflux flowrate from the middle vessel are at their maximum bounds of 20 kW and 1.0 mol/s, respectively. This keeps the liquid holdup in the vessel low (Figure 4.8c). The entire vapour stream from the stripping section is directed to the middle vessel instead of to the extractive section. Similar to previous observations, the liquid stream, which is rich in the added water solvent and adsorbed methanol, is directed straight down to the stripping section, by-passing the middle vessel. As shown in Figure 4.8d, the acetone composition in the middle vessel improved and contamination by the solvent is kept low.

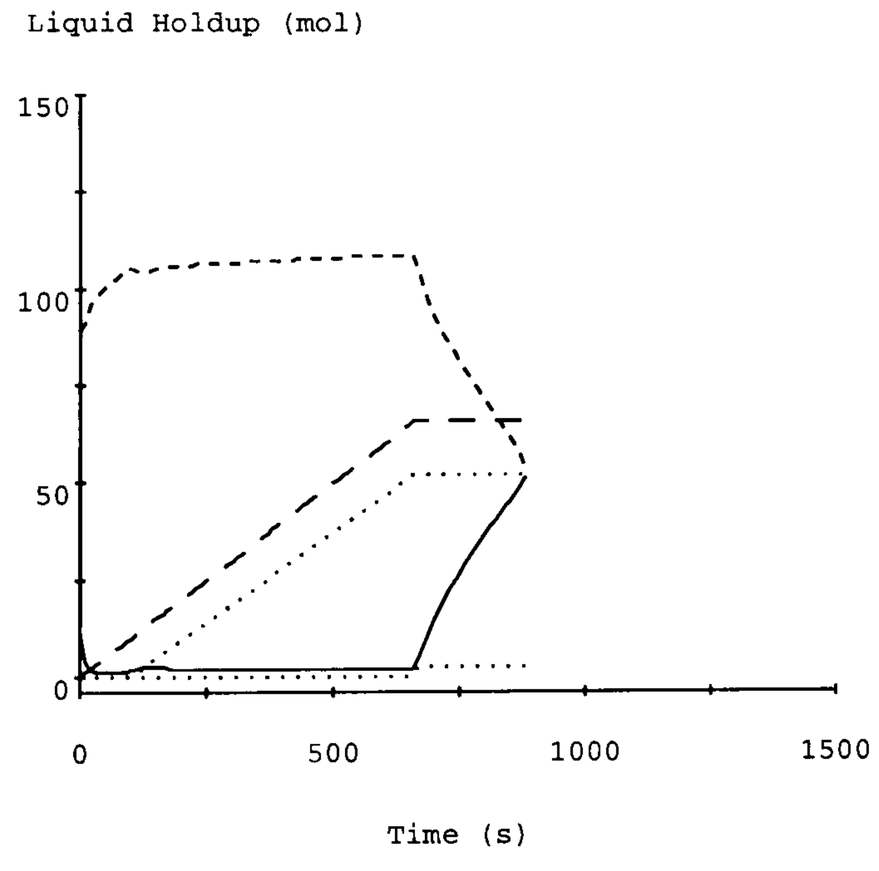
In the second period (75 s and 492 s, durations), solvent feeding is continued at a high flowrate while the acetone product is being withdrawn at a fairly high reflux ratio. Only a minimal amount of heat duty is needed in the middle vessel (1.1 kW, then 0.5 kW, lower bound). During this period, the composition of the middle vessel is kept fairly constant and so are the liquid holdups of the reboiler drum and middle vessel. This is because the rates of solvent addition and product removal are similar. Following a negligible offcut period (10 s, lower bound), the final period (213 s) involves simultaneous purification of the methanol product and the solvent. Solvent feeding is terminated. No top offcut withdrawal is necessary as the column is switched back to total reflux mode. Purification is done by the middle section stream configuration. All the liquid from the



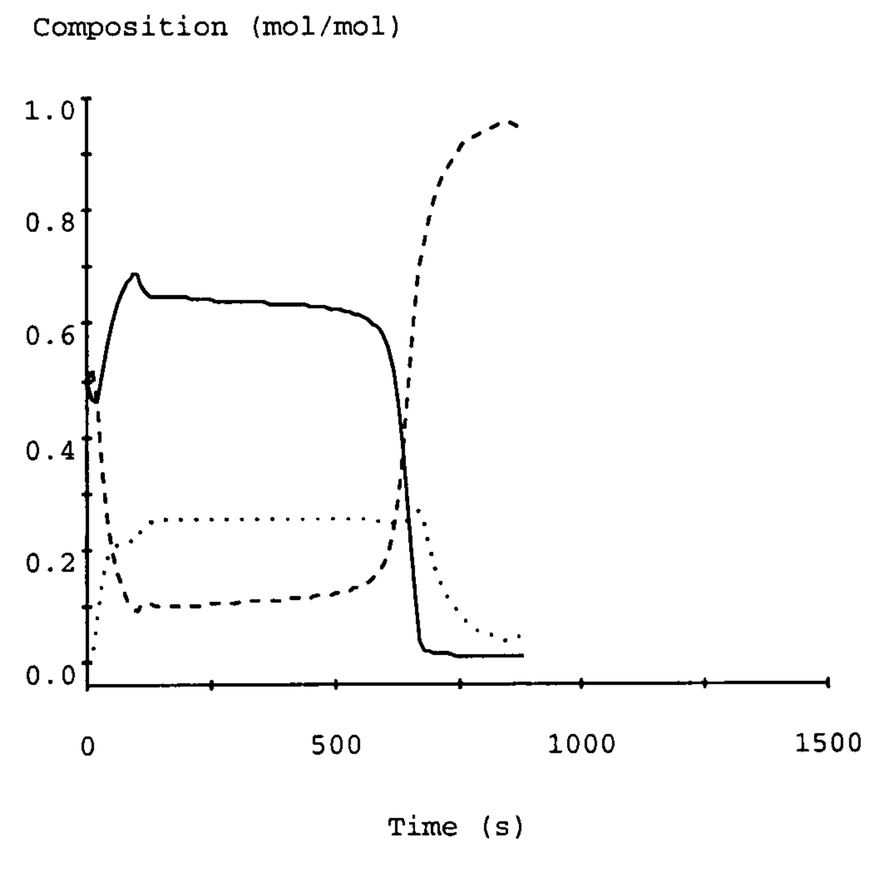
(a)



(b)



(c)



(d)

(a) —— reflux ratio; - - - F_{sol}
(b) —— L_{mv}; - - - liquid stream split ratio; . . . vapour stream split ratio
(c) Liquid holdup: —— middle vessel; - - - reboiler; . . . accumulators; – – amount of solvent fed
(d) Composition: —— acetone; - - - methanol; . . . solvent in middle vessel

Figure 4.8: Case II optimal control variables, holdup and composition profiles for middle vessel column with optimal configuration

column, and most of the vapour stream, is diverted to the middle vessel where methanol is being accumulated. At the same time, the water solvent is being recovered in the reboiler drum at its original purity. No withdrawals were taken from either the middle vessel or the reboiler throughout the process operation.

By allowing both streams to vary in an optimal way, the operating profit increased by 45% from that of the simple configuration A in our case study. The batch processing time and energy consumption decreased by 19% and 14%, respectively.

Comparison of Regular and Middle Vessel Columns

For the middle vessel column, Safrit *et al.* (1995) have proposed a middle vessel steering operating policy which involved a period of solvent addition with no bottom removal but with distillate removal (acetone), followed by a period of normal distillate and bottom (water) removal. During the latter period, the reflux and reboil ratios were calculated in order to maintain the distillate and bottom purities while the middle vessel is being steered towards the required methanol composition. They claimed that the advantage is high distillate recovery of up to 100% by overcoming the need for infinite reboiler size in the regular column. However, they observed high reflux ratio and reboil ratios towards the end of the operation. Thus, the proposed policy may not be attractive from an economic point of view due to requirements such as high number of trays, high utility costs and long processing times. They used a simple model assuming pseudo steady state on the trays and ignoring holdup effects hence the operational feasibility is doubtful. Another study proposed by Lelkes *et al.* (1998b) has since refuted the study by Safrit *et al.* (1995) and even obtained the opposite result where the maximum recovery obtained using the batch rectifier was higher than that obtained with the middle vessel column.

From an industrial point of view, a comparison of operating procedures is best made via a detailed optimal control problem based on the economics of the process which takes into account all revenues and related costs. The optimal economic operation is seldom the maximum production operation, maximum revenue operation nor minimum processing time operation alone. The results of our study suggest that the middle vessel did not

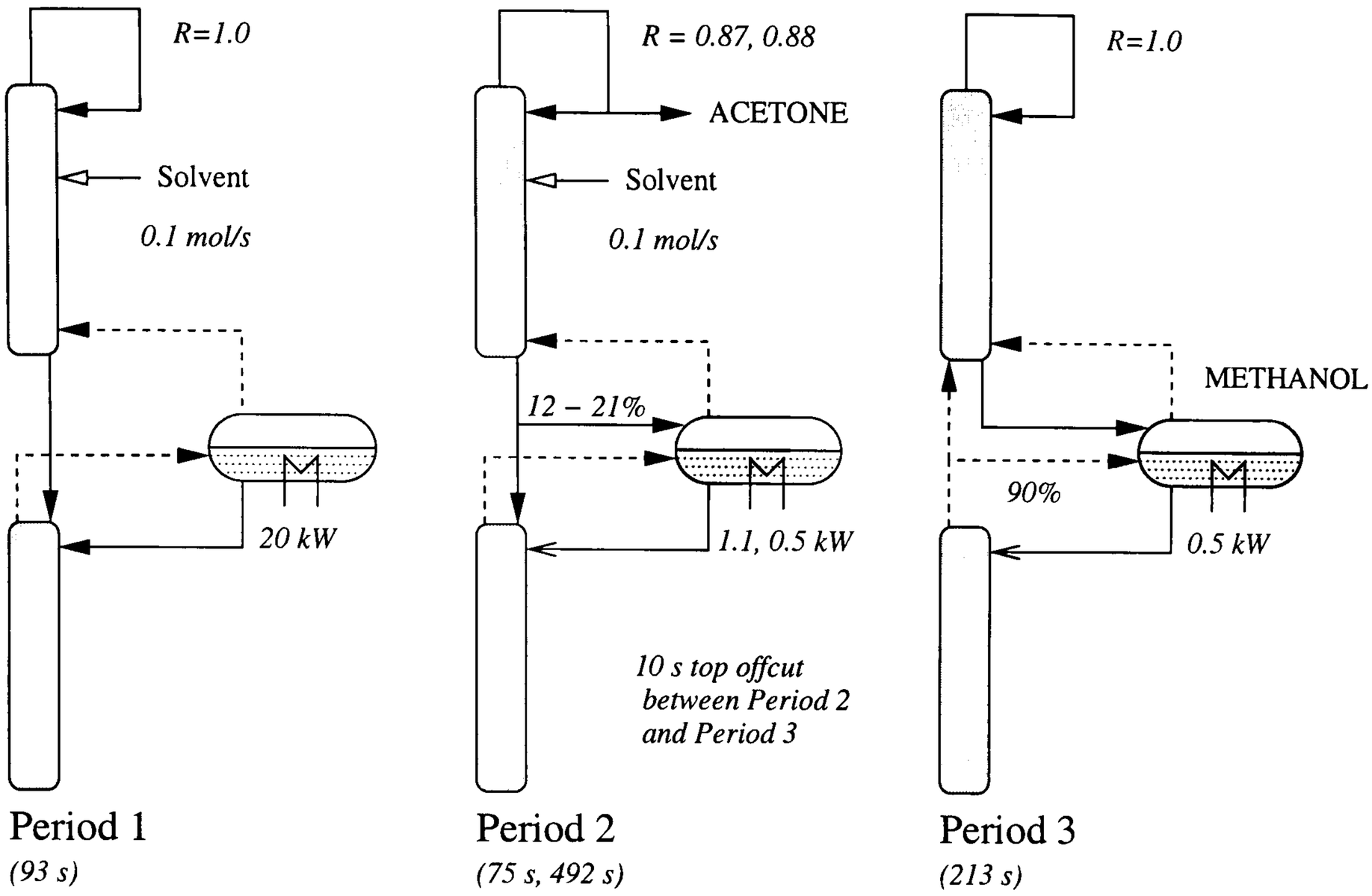
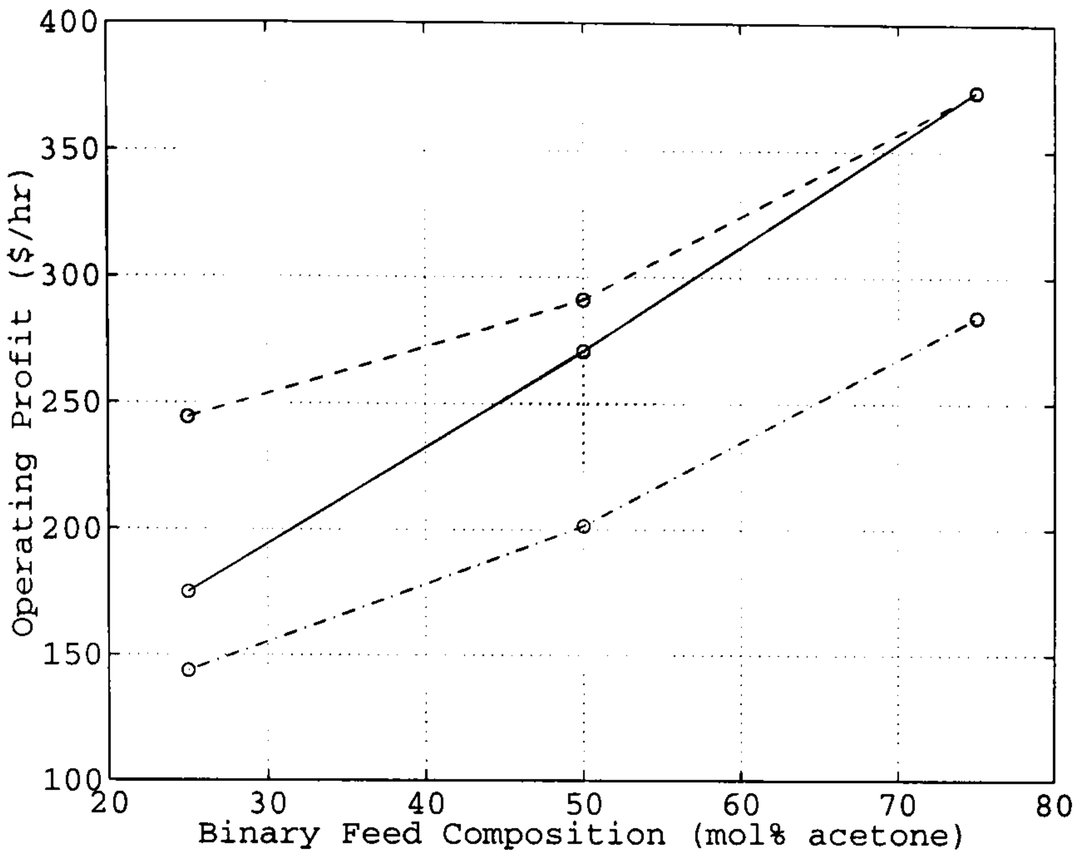


Figure 4.9: Optimal operating policy of middle vessel column

take up the functionality of being steered proposed by Safrit *et al.* (1995). In fact, the optimal feed location in this case study is the reboiler rather than the middle vessel. The optimal middle section stream configuration in the first two steps (Figure 4.9) resulted in the holdup of the middle vessel remaining low thus did not exhibit any advantageous functionality over the regular column. Only in the final step did the middle vessel use this option to accumulate the methanol cut and this is due to the product location being pre-specified.

In this specific case study, it was found that the operating profit of the middle vessel column can be improved by 45% from that of the simple configuration A by allowing both liquid and vapour streams configuration to vary during the operation. The middle vessel column with a flexible middle section stream configuration also performed 7.5% better than the conventional regular column in terms of operating profit. The middle vessel has a slightly shorter batch processing time, heat duty and acetone recovery while the regular column achieved better methanol recovery. It should, however, be noted that the profitability depends on the selling price of the products and other costs.



-.-.- simple configuration middle vessel column; —— regular column; - - - optimal configuration middle vessel column

Figure 4.10: Operating profits for different feed compositions

4.6.7 Case III: Effect of Different Feed Compositions

In the previous case studies, an equimolar mixture of the binary azeotropic feed was used. To the best of our knowledge, all studies of extractive batch distillation so far, including feasibility methods, simulation experiments and optimisation as reported in the literature review (section 2.2), involved only equimolar mixtures and hence their conclusions are valid only for these mixtures. Here, the optimal operating profits and operations for both regular and middle vessel columns using different feed compositions, are presented. Both the simple configuration (configuration A) and optimal stream configuration of the middle vessel are used in our investigation. The production of both feed components and solvent recovery were taken into account as in case study II. The results are displayed in Table 4.9 and the operating profits are as shown in Figure 4.10.

As can be seen from the results (Table 4.9), when the molar ratio of a particular component is large in the feed mixture, the recovery of that component improves for both columns. The change in the amount of solvent used is small (18 - 47%) as compared to the change is feed composition (200%). In the case of the regular column, which has a fixed solvent feedrate capacity, this is because the extension of the total period of solvent feeding (total reflux and acetone withdrawal periods) was not significant as a result of lower reflux ratios used for feed with more acetone.

Column	Regular			Middle Vessel Simple Configuration			Middle Vessel Optimal Configuration		
Feed composition † (*molfraction*)	0.25, 0.75	0.50, 0.50	0.75, 0.25	0.25, 0.75	0.50, 0.50	0.75, 0.25	0.25, 0.75	0.50, 0.50	0.75, 0.25
Operating profit ($/hr)	175.0	270.8	373.7	143.7	201.4	284.4	244.2	291.1	373.3
Batch processing time (*min*)	17.3	16.0	15.5	16.9	18.1	17.5	11.4	14.7	15.3
Heat duty (*MJ*)	18.3	19.1	18.6	17.2	21.0	21.1	13.0	18.0	18.8
Acetone recovery (%)	77.0	90.4	97.1	58.0	79.3	88.5	71.0	91.5	97.5
Methanol recovery (%)	98.7	94.6	83.8	93.3	86.7	64.2	94.8	90.4	74.4
Solvent recovery (%)	69.9	73.4	76.7	82.7	88.1	90.5	69.1	82.8	88.1
Amount solvent used (*mol*)	68.3	73.4	80.9	61.2	83.6	90.0	39.8	66.0	83.1
Optimal feed location (*mol*) (reboiler/middle vessel)	-	-	-	84/16	90/10	90/10	72/25	89/11	86/14
Amount withdrawn from reboiler (*mol*)	-	-	-	0.0	0.0	0.0	0.0	0.0	5.0
Amount withdrawn from middle vessel (*mol*)	-	-	-	0.0	0.0	0.0	0.1	0.1	0.2

† acetone-methanol mixture
See Appendix F for product purities

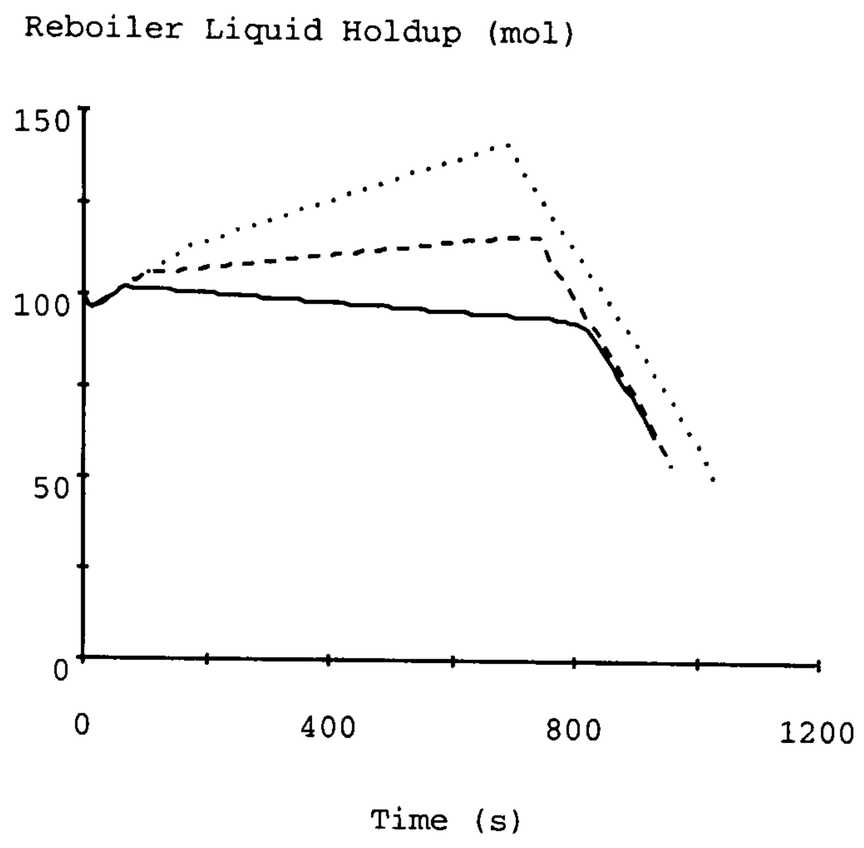
Table 4.9: Summary of optimal results for regular and middle vessel columns using different feed compositions

Using the regular column to separate the various feed compositions, the optimal operating profiles are similar, each with negligible offcuts. The main difference is the duration of the total reflux period. More time is needed to reach the purity specification for feed mixture with lower concentration of acetone (172, 99 and 61s for the feed compositions 25, 50 and 75 $mol\%$ acetone, respectively). However, the total durations of the withdrawal steps of the operation are quite similar (865, 859 and 867s, respectively) as the durations of the acetone withdrawal periods and the methanol withdrawal periods counterbalances each other for the various feed compositions. Thus, the optimal processing time of separating different feed compositions varies only insofar as the total reflux period at the beginning for a column with a maximum feedrate capacity.

For feed composition with a higher acetone fraction (0.75, 0.25), the longer period of solvent addition results in a greater amount of solvent added, and it would be intuitively assumed that the maximum reboiler still holdup would be greater. Contrary to that prediction, the maximum still holdup actually decreases as shown in Figure 4.11. This is because as the acetone composition in the feed increases, the rate of acetone withdrawal is faster due to lower reflux ratio. For the case of feed composition 75 $mol\%$ acetone, the withdrawal rate is actually greater than the rate of solvent addition. This causes the reboiler holdup to decrease rather than increase. Hence, for some separation duties, the capacity of the reboiler is not an operation limitation to batch extractive distillation and in such cases, greater quantities of feed may be processed.

For the middle vessel column, the optimal feed placement is in the reboiler for all feed compositions for this case study. The operating procedures are similar – beginning with a period of total reflux with solvent feeding followed by an acetone withdrawal period, offcut with solvent feeding stopped and finally, a period of methanol concentration in the middle vessel. For feed mixtures richer in acetone, the initial total reflux period and the methanol concentration period gets shorter while the acetone withdrawal periods becomes longer.

Similar to the observation in the regular column, although more solvent is used for sep-



Feed mol fraction: . . . 0.25, 0.75; - - - 0.50, 0.50; —— 0.75, 0.25

Figure 4.11: Case III reboiler liquid holdup profiles in the regular column for different feed compositions

arating a feed mixture rich in acetone, the maximum holdup in the reboiler is the lowest for the feed with 75 *mol*% acetone. In fact, similar to the regular column, the holdup was below the initial charge throughout the operation. Unlike the previous two cases, accumulation of volume is not required in the middle vessel during the methanol concentration period with the middle vessel reflux valve fully open (L_{mv} maximum).

In comparison, the regular column performed better than the simple middle vessel column for all three feed compositions investigated. Interestingly, a linear function can be seen as shown in Figure 4.10, especially for the regular column. However, for feed with a low fraction of methanol, the advantage of the middle vessel column with optimal stream configuration over the regular column is reduced, up to a point whereby the operating profit of the regular column began to overtake that of the middle vessel column. This trend is in accordance with intuition as when the feed to be processed approaches pure acetone, the functionality of the middle vessel, *i.e.* to collect methanol, would diminish and thus it would not be expected to perform better than an straightforward batch rectifier. Hence, it can be assumed that the performance of a column configuration over another is dependent on the composition of the feed mixture and that in certain cases, an

advantage in performance may sometimes be reversed at some different feed composition, as found in our example. The same observation was also found by Sørensen and Skogestad (1996) when they compared the operation of the regular and inverted columns.

4.7 Conclusions

In this chapter, a study on optimal operation of extractive batch distillation operation involving a binary acetone-methanol azeotropic mixture with water as solvent was presented. Both conventional and complex columns with flexible stream configurations were considered and several comparative case studies presented. The dynamic model took into account variable liquid and vapour holdups, tray hydraulics and rigorous mass and energy balances. A rigorous nonlinear programming technique was used for optimisation and all the operational control variables available to both columns were taken into account including reflux ratio, solvent feedrate, heating duties, stream ratios and withdrawals. The effects of feed distribution and stream configuration were also investigated.

For the middle vessel column, the results of this study indicate that the operation is most economical when the feed is placed at the reboiler. The holdup of the middle vessel was kept at a low level throughout the first two steps thus did not exhibit any functional advantages over the conventional regular column in the specific case studies. The batch rectifier performed better than the simple configuration middle vessel column in terms of operating profit for various feed compositions. However, the performance of the middle vessel column can be improved by optimising the liquid and vapour stream configuration at the middle section. Nonetheless, in practice, the switching of the streams during the process is more difficult to implement compared to the more practical simple configuration.

The example highlighted the need for thorough consideration when comparing the economical advantages of different column configurations and before making general conclusion as the performance of a column may be influenced by various factors such as feed composition.

The results obtained are specific to this case study in terms of mixture type, composition, feed amount, operation objective, pricing, column design as well as parameters specification, bounds and constraints. Thus the guidelines drawn from this study are based on these conditions. However, this work shows that rigorous comparative optimisation case studies are now possible with current numerical and computer technology and can be beneficial if applied during column and operational design for batch extractive distillation.

Chapter 5

Optimal Design and Operation of Batch Distillation

In this chapter, the simultaneous optimal design and operation of both regular and multivessel columns based on an economics performance index are investigated. Rigorous models are used for the mixed integer dynamic optimisation which is solved by adopting a stochastic search technique based on a genetic algorithm and penalty function strategy (chapter 3). Given a set of design specifications and separation requirements, the optimal number of stages, column vapour loading, reflux profiles, product recoveries, time interval of each distillation task, process allocation and number of batches are obtained for the regular column. Several design case studies are presented and a comparison of optimal designs for various design scenarios such as different production time, capital costs, process allocation and mixture characteristics, are investigated. Further case studies are also presented to highlight the effect of objective function, feed composition, relative volatility and product specification on the optimal column section configuration and feed distribution of the multivessel system. Finally, a comparison of the optimum performance of the multivessel system and the conventional regular column is presented. The combined energy efficiency and production rate of the multivessel system is found to be greater than that of the regular column and the benefit is more prominent when separating mixtures with more components.

5.1 Introduction and Aims of This Work

Although batch distillation is widely used in high-value and low to medium scale production, such as those found in the fine and speciality chemical and pharmaceutical industries, the development of design methods for batch distillation remains a challenging task. There is a lack of studies on optimal design, which might be due to optimisation difficulties associated with the inherent transient property of the batch process, the greater complexity supplied by the complex configurations, such as the multivessel column, as well as the problem of handling discrete design variables, such as number of stages, in addition to the continuous operation variables. Furthermore, the batch distillation optimisation problem normally entails the solution of model and objective function with nonlinearities as well as a nonconvex solution space. The task is also further complicated when the batch column flexibility as a multipurpose separations unit has to be taken into consideration at the design stage.

Design of batch distillation columns is still being carried out using heuristic approaches which rely on intuition, engineering knowledge and experience, starting with an order of magnitude calculation followed by repeated calculations either by hand or aided by a computer. With the emergence of greater computational power and better solution algorithms, computer-aided optimisation approaches using mathematical programming techniques is beginning to be used to tackle the simultaneous design and operation of batch distillation columns. However, to the best of our knowledge, only works by Diwekar *et al.* (1989), Logsdon *et al.* (1990), Diwekar (1992), Mujtaba and Macchietto (1996), Sharif *et al.* (1998) and Kim (1999) are available in the open literature (details in chapter 2.3). In summary, most of these works involved the use of short-cut methods and decomposition of the mixed integer dynamic optimisation (MIDO) problem into various NLP and MINLP techniques. The nonconvexity of the search space can cause these gradient-based sequential search methods to converge into arbitrary local optimal designs, and this has been the case for many optimal control studies using standard NLP techniques.

The batch distillation design studies so far have concentrated on the conventional regu-

lar column and the problem has mostly been tackled using simplified and semi-rigorous models (except the works by Mujtaba and Macchietto, 1996 and Sharif *et al.*, 1998) and subsets of the available degrees of freedom. The design of columns with complex configuration, such as the multivessel system, has not been attempted. So far, the analysis of the multivessel system had tended to focus exclusively on the operation of the system, *i.e.* the different operating policies and their on-line control schemes implementation. Despite the fact that the column section length and configuration of the multivessel system itself has a major impact on the separation performance, no design study has been reported in the open literature, neither in terms of the effect on the separation process nor in terms of optimisation that takes into account this key design decision variable. The optimal design of the multivessel system should be considered since the main drawback of the multivessel system is the high capital cost associated with the greater number of column sections needed in the system. The total combined column section lengths can be several times that of a regular column. Thus, it is important to take into account the trade-off in capital cost so that the comparison between the regular and multivessel columns can be more conclusive.

The objective of this work is to study the simultaneous optimal design and operation of both the regular and multivessel batch distillation columns in different scenarios by applying the stochastic genetic algorithm and penalty function optimisation solution approach proposed in chapter 3. The work also aims to highlight the effects of different design scenarios, *i.e.* production time, capital costs, process allocation, objective function, feed composition, relative volatility, product specification and number of components, on the optimal design and operation of batch distillation. An economics comparison between optimally designed regular and multivessel columns is also presented for the first time.

In the next section, the batch distillation design problem is presented which include the definition of the optimisation problem and the formulation of the objective function. Next, the mathematical modelling of batch distillation and the optimisation solution technique are introduced. This is followed by case studies demonstrating how the approach can be used to obtain the optimal designs of regular and multivessel columns, respectively, for different design scenarios. Finally, the performance of the regular and multivessel columns are compared.

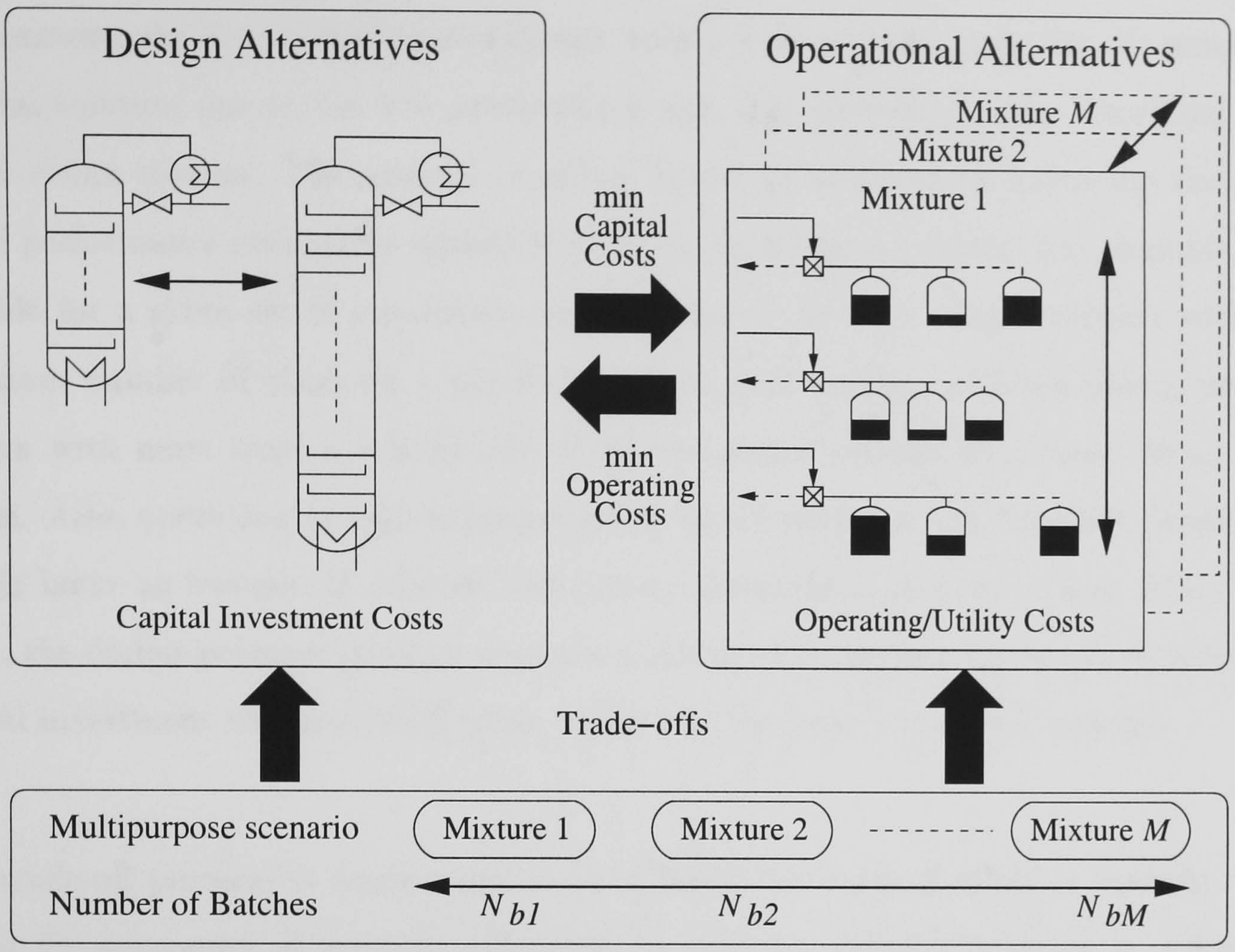


Figure 5.1: Batch distillation design problem

5.2 The Batch Distillation Design Problem

5.2.1 Problem Definition

The objective in batch distillation design is to determine the most economical column specification capable of fulfilling all separation requirements intended for the unit. The design and operation issues are inherently interdependent, and thus they need to be considered simultaneously (Figure 5.1). This interdependency is fundamental as the operation of batch distillation is linked to the reflux ratio profile and column vapour loading, operation parameters which need to be set as a basis for a particular design. For continuous distillation, the design limits are based on these parameters being fixed at the minimum and infinite values, resulting in the highest and lowest investment costs, respectively. However, in the batch mode, even with constant operation parameters, the system is dynamic, hence, a straightforward analytical calculation of the column design is not possible (unlike for continuous distillation where the design can be calculated based on its steady state condition).

Furthermore, the lowest capital cost design does not necessarily make for the most economical solution due to the low performance and high operating costs associated with a high reflux column. The optimal condition might be achieved by balancing the additional performance obtainable against investment in a bigger column. For example, it is possible for a given set of separation requirements to be met using a column with the minimum number of trays for a particular reflux ratio profile, or alternatively, using a column with more trays operated over a shorter period of time at a lower reflux ratio profile. Also, operating at high vapour loading would reduce batch time but would conversely incur an increase in reboiler and column investment costs as well as utility cost. Thus, the design problem involves several complicated economics trade-offs between the capital investment and operating costs, subject to the separation requirements.

The trade-off problem is further complicated when the batch distillation column is designed for separation of multiple mixtures. In industry, batch distillation is commonly used as a flexible multipurpose unit and there may be a need for the same column to be used for a wide range of feed mixtures or at different stages in a single production process. In this multipurpose scenario, the optimal number of stages and optimal control of each of the duty are different and therefore a third dimension is added whereby the design has to take into account the trade-offs among the various duties. Production time allocation, *i.e.* the relative importance of a particular mixture with regard to the others, would also influence the final optimal design solution. For example, if a particular separation is performed much more frequently than others, the ultimate design tends to be biased toward this weighting. The design also depends on the characteristics of the mixtures, such as the difficulty of separation, and the price structure of the separated products. In this work, the process time allocation of different mixtures may be given or can be treated as an extra degree of freedom and incorporated into the optimal design problem. Thus, the optimal design variables, the different optimal operating policies of each mixture, as well as the optimal allocation of process time among the mixtures, will be solved simultaneously.

5.2.2 Objective Function

The general design objective of a batch distillation system is to obtain the most economical column design and operating policy that will satisfy all specified separation requirements. A performance index has to be defined in order to obtain the overall optimality of the design, which can then be used to compare column configurations. Furlonge *et al.* (1999) utilised the mean rate of energy consumption as the performance index for their optimal operation study, defined as:

$$Mean\,energy\,consumption,\; E = \frac{Total\,energy\,consumption\,per\,batch}{Total\,batch\,time} = \frac{\int_0^{t_f} Q(t)dt}{t_f + t_s} \tag{5.1}$$

where $Q(t)$ is the instantaneous rate of energy consumption in the reboiler and t_f and t_s are the batch processing and set-up times, respectively. By restricting the performance measurement to a single quantifiable aspect of the operation, in this case the energy consumption rate, the full optimal potential of the system could not be explored. This might not be the ideal performance measurement in most real industrial scenarios whereby, in addition to minimising the energy consumption, there is a perpetual incentive to increase production yield and to minimise batch time, *i.e.* to increase the number of batches. Thus, a more comprehensive performance index should take all three factors into account:

$$Index = f\,(Product\,yield,\, Batch\,time,\, Energy\,Consumption) \tag{5.2}$$

The performance index above can be translated into an economics model of sales revenue and operating cost using monetary units based on a production time scale, *e.g.* hourly or annually. For an optimal design study, whereby the optimum number of stages, N, is to be included, an additional capital cost term has to be included to account for the trade-off described in the previous section (section 5.2.1). The economical design will be a trade-off between lower capital and operating costs against higher production revenue, thus the objective function must be formulated to encapsulate all of these costs. The performance index for the design of a batch distillation column as used in this study is an overall profitability function given by:

$$Profit,\ P = \frac{Sales\ revenue - Feed\ cost - Operating\ cost - Capital\ cost}{Total\ batch\ time} \tag{5.3}$$

In this work, the economics models for the operating cost and capital cost are based on Guthrie's correlation (Douglas, 1988). The main operating cost in batch distillation is utilities cost, C_{uty}, whilst the main capital cost, C_{cap}, includes the installed column shell, C_{sh}, and the installed heat exchangers costs, C_{ex}. In this type of economics model, the costs are correlated from values in a base case (BC) distillation column, for example from the pre-determined costs associated with installing a carbon steel column of a certain size with hydrocarbon feedstock. Introducing correlation coefficients K_1, K_2 and K_3 for the shell, heat exchangers and utilities costs, respectively, the values of which can be calculated according to the base case distillation column system, the profit function of Equation 5.3 is given by:

$$P = \frac{\sum_{i=1}^{N_C} C_i H_{A,i}(t_f) - C_{feed} H_{feed}}{t_f + t_s} - \left(K_1 N^{0.802} V^{0.533} + K_2 V^{0.65}\right) - K_3 V \tag{5.4}$$

where C_i and C_{feed} represent the unit costs of product i and feed, respectively, H_i and H_{feed} the quantity of on-specification product i collected and feed, respectively, V the column vapour loading, and the economics correlation coefficients, K_1, K_2 and K_3, given by:

$$K_1 = \frac{C_{sh,BC}}{N_{BC}^{0.802} V_{BC}^{0.533}} \tag{5.5}$$

$$K_2 = \frac{C_{ex,BC}}{V_{BC}^{0.65}} \tag{5.6}$$

$$K_3 = \frac{C_{uty,BC}}{V_{BC}} \tag{5.7}$$

The detailed derivation of the objective function is given in Appendix G. In this work, the same economics correlation function is used for both the regular and multivessel columns, although it can be also expected that the capital cost of a multivessel system

might perhaps be marginally higher due to additional construction or pipework associated with more column sections. In the multivessel system, the variable N is the total number of stages of all column sections, $N = \sum_{i=1}^{N_S} N_i$.

The objective function can be expressed as an annualised profitability, based on the total time available for processing per year, T_A:

$$P_A = \left(\frac{\sum_{i=1}^{N_C} C_i H_i(t_f) - C_{feed} H_{feed}}{t_f + t_s} \right) T_A - \left(K_1 N^{0.802} V^{0.533} + K_2 V^{0.65} \right) - K_3 V \quad (5.8)$$

or

$$P_A = \left(\sum_{i=1}^{N_C} C_i H_i(t_f) - C_{feed} H_{feed} \right) B - \left(K_1 N^{0.802} V^{0.533} + K_2 V^{0.65} \right) - K_3 V \quad (5.9)$$

where B is the total number of batches processed per year, calculated as:

$$B = \frac{T_A}{t_f + t_s} \quad (5.10)$$

In a flexible processing scenario, a multipurpose batch column unit is used to separate a number of mixtures. In this study, the objective function for the design of a multipurpose column is given by:

$$P_A = \left(\sum_{m=1}^{N_m} \left(\frac{\sum_{i=1}^{N_C} C_{i,m} H_{i,m}(t_{f,m}) - C_{feed,m} H_{feed,m}}{t_{f,m} + t_{s,m}} \right) \phi_m \right) T_A$$
$$- K_1 N^{0.802} V^{0.533} - K_2 V^{0.65} - K_3 V \quad (5.11)$$

where ϕ_m is a parameter proposed by Mujtaba and Macchietto (1996) as a simple mechanism to describe the degree of influence, or importance, a particular mixture has on the optimal design of a multipurpose unit. It is defined as the fraction of total production time, T_m, allocated to each particular mixture, m:

$$\phi_m = \frac{T_m}{T_A} \tag{5.12}$$

As a result,

$$B_m = \frac{\phi_m T_A}{t_{f,m} + t_{s,m}} \tag{5.13}$$

where B_m is the number of batches processed per year for each mixture, m.

5.2.3 Optimisation Formulation

The aim of the batch distillation design problem is to maximise the objective function, *i.e.* the profitability performance index, P, defined above, subject to the column model equations and all the separation constraints. In this work, it is assumed that the purities of the main products are driven by customer demand and distillation is undertaken to achieve these minimum specifications. The optimisation problem is then:

Given N_m mixtures to be separated, each with $N_{C,m}$ components, minimum products purity specification $x_{i,m}^{\min}$ (where $x_{i,m}$ refer to the recovered product i of mixture m), the price structure of the feed and products, $C_{feed,m}$ and $C_{i,m}$, as well as the total production time available per year, T_A, *determine* the optimum set of design variables, u_d, optimum operating control variables, $u_{o,m}$, and production schedule among the mixtures, $\phi_m \in [0,1]$, so as to maximise the objective function P (Equations 5.4, 5.8, 5.9 or 5.11).

In mathematical terms, the optimisation problem is posed as follow:

$$max_{u_d, u_{o,m}, \phi_m} \; P \tag{5.14}$$

subject to

$$f(\dot{x}_m, x_m, t, u) = 0 \qquad \forall\, m = 1, .., N_m \tag{5.15}$$

$$x_{i,m}(t_f) \geq x_{i,m}^{\min} \qquad \forall\, i = 1,..,N_C;\ m = 1,..,N_m \tag{5.16}$$

$$u_d^{\min} \leq u_d \leq u_d^{\max} \tag{5.17}$$

$$u_{o,m}^{\min} \leq u_{o,m} \leq u_{o,m}^{\max} \tag{5.18}$$

where Equation 5.15 represents the basic mathematical model for the description of a batch distillation process, x is the vector of state variables (*i.e.* holdups, concentrations, temperatures and pressures), u denotes the vector of decision variables (design and control variables, u_d and $u_{o,m}$, respectively) and t is the process time. Equation 5.16 represents the product purity constraints on all main cuts which must be satisfied for all the mixtures. Equations 5.17 and 5.18 represents the physical and optimisation bounds of the design and operating control variables, respectively.

The set of design variables includes the optimal number of trays and the batch size, *i.e.* $u_d = \{N, H_{feed}\}$. The operating control variables includes the column vapour loading and the interval durations of each main and offcut periods for each mixture, $t_{i,m}$, and the corresponding reflux ratio profiles, *i.e.* $u_{o,m} = \{V, R(t_{i,m})\}$. Thus, indirectly, the total batch time for each mixture, $t_{f,m}$, the recovery of each product and offcut and the withdrawal rate profiles, can be obtained in an optimal manner. The optimal column vapour loading, V, can subsequently be used to determine the diameter of the column (*e.g.* using Guthrie's correlation $D \propto \sqrt{V}$) as well as the heat exchanger loading.

Due to the set-up time between batches, t_s, larger batch sizes, H_{feed}, will inevitably be favoured since a greater quantity per batch can be processed for a given production time, resulting in fewer number of batches and greater reduction in set-up time. The longer the set-up time, the stronger is the tendency towards larger batch sizes. Furthermore, at high production rates, the trade-off caused by higher capital costs becomes insignificant compared with the revenue component, as the capital cost typically increases with

capacity by an exponent of less than 1 due to economy of scale (as in the case of the design objective function defined in Equation 5.4). Hence, the design scenario whereby the batch size is specified *a priori* is considered in this study. From a practical point of view, this is an acceptable design scenario as the design engineer would typically have a desired batch capacity suited to a particular plant inventory and short or(and) long term scheduling. Therefore, the optimal batch size could be determined separately via optimal capacity and product portfolio planning, or based on a supply chain optimisation study, perhaps prior to the individual unit design.

In a multiple separation duties scenario, when the optimal process allocation, ϕ_m, is treated as a degree of freedom, the optimisation would supply decision support on the ranking of the duties for maximum profitability, *i.e.* the duration of time allocated to each particular duty, in addition to the optimum column size and all the operating policies.

5.3 Solution Methodology

In mathematical terms, the consideration of design and operation simultaneously translates into both discrete (*e.g.* the number of stages) and continuous variables (*e.g.* reflux ratio profile). The optimisation profit performance index (section 5.2.2) is nonlinear with a potential nonconvex search space. Coupled with a dynamic and nonlinear DAE model of the batch distillation column, this leads to a complicated mixed integer dynamic optimisation (MIDO) problem. This type of problem is difficult to solve and there is much ongoing research on developing practical solution algorithms (chapter 3.5). In this work, a stochastic algorithmic method based on genetic algorithm is used to solve the optimal design MIDO problem (chapter 3.6). Here, the use of a framework consisting of a steady state genetic algorithm and a weighted penalty function to handle the problem constraints (product purities), is used.

5.4 Mathematical Models

The mathematical model of the dynamic batch distillation system is a set of differential-algebraic equations (DAE). The optimisation framework proposed in this study can be

utilised in conjunction with any level of model abstraction and the choice of model is dependent on the level of detail or accuracy required at a particular design stage as well as the computational cost available. In the optimal design case studies presented in this chapter, rigorous models built on first principles are used (details of the model are presented in chapter 3.1). Note that the semi-rigorous model and detailed model are also used in design scenario III (section 5.6.3) and design scenario I (section 5.7.4), respectively.

The models are constructed using the *gPROMS* modelling tool (Process Systems Enterprise Ltd., 2000). The model equations are presented in Appendix A. Thermophysical properties including density, enthalpy and fugacity required in the rigorous model are calculated using the *Multiflash* (Infochem Computer Services Ltd., 2000) physical properties package interfaced to *gPROMS*. The Soave-Redlich-Kwong (SRK) Equation of State is used for both the vapour and liquid phases.

5.5 Case Studies

Optimal design cases studies for the regular and multivessel batch distillation systems are discussed in the following sections 5.6 and 5.7, respectively. The configurations are compared in section 5.8.

5.6 Optimal Design of Regular Columns

In this section, several optimal design case studies for the regular column are presented. Optimal design of a regular column with single separation duty involving multicomponent mixtures is considered in sections 5.6.1 and 5.6.2 and optimal design for a flexible regular column with two separation duties in section 5.6.3.

5.6.1 Design Scenario I: Multicomponent Mixture Separation

The objective in this case study is to find the optimal design and operating policy for a regular batch distillation column with a single separation duty of a multicomponent

Available annual production time, T_A $(h/year)$	8760
Batch set-up time, t_s (s)	1800
Operating pressure, P (Pa)	101 325
Batch size, H_{feed} (mol)	2930
Reflux drum holdup, H_{rd} (mol)	43.95 (1.5% H_{feed})
Tray holdup, H_{tray} (mol)	7.325
Feed composition, $x_{i,feed}$ $(molfraction)$†	
Cyclohexane, $x_{1,feed}$	0.407
n-Heptane, $x_{2,feed}$	0.394
Toluene, $x_{3,feed}$	0.199
Product purity specifications, $(molfraction)$†	
First product, $x_1(t_f)$	0.895 of cyclohexane
Second product, $x_2(t_f)$	0.863 of n-heptane
Final product, $x_3(t_f)$	0.990 of toluene
Cost, C_i $(\$/mol)$†	
Cyclohexane, C_1	0.034
n-Heptane, C_2	0.026
Toluene, C_3	0.024
Feed, C_{feed}	0.002
Waste	negligible

† set to values given by Mujtaba and Macchietto (1996)

Table 5.1: Column specifications and operating conditions for case study I

mixture. A rigorous model is utilised with the thermodynamical properties described by the SRK Equation of State. Table 5.1 gives a summary of the column specifications and operating conditions.

Figure 5.2 shows the schematic of the batch distillation process. The batch distillation operation is separated into five control intervals, starting with a total reflux period followed by a cyclohexane product withdrawal period, an offcut period, a n-heptane product withdrawal period and finally another offcut period to purify the toluene product in the reboiler. The minimum product purity specifications are 89.5, 86.3 and 99.0 $mol\%$ of cyclohexane, n-heptane and toluene, respectively. Given these specifications, the aim is to find the design and operating policy for the separation duty that would give a max-

Decision Variables	Bounds
N	[4 , 30]
V $(kmol/hr)$	[0.6 , 6.0]
$R(t_i)$	[0.4 , 1.0]
$\Delta t_{1,2,4}$ (s)	[1000, 15000]
$\Delta t_{3,5}$ (s)	[0 , 15000]

Table 5.2: Decision variables bounds for the case study I

Optimum Profit $(\$/yr)$	Optimal Genome N, V, $R(t_1)$†, $R(t_2)$, $R(t_3)$, $R(t_4)$, $R(t_5)$, Δt_1 , Δt_2, Δt_3, Δt_4, Δt_5
97942.9	29, 6.00*, 1, 0.86, 0.84, 0.84, 0.99, 1100, 5700, 100, 4400, 500

† set as total reflux; * on bound

Table 5.3: Optimisation solution vector for design scenario I

imum annualised profit. The cost coefficients for the total annual cost were based on a carbon steel column and hydrocarbon feedstock using cost data as shown in Logsdon *et al.* (1990) resulting in the coefficients K_1, K_2 and K_3 (Equation 5.4) having the values of 1500, 9500 and 180, respectively.

The design and control variables considered are the optimum number of trays, N, the optimum constant condenser vapour load, V and optimal reflux ratio profile, *i.e.* the values of the normalised reflux ratios, $R(t_i)$ (except for $R(t_1)$ which is set at 1 for total reflux), and the durations, Δt_i, of each of the five ($i = 5$) task intervals. The bounds for each variable are given is Table 5.2.

Optimal Solution

The optimum solution genome is shown in Table 5.3. The optimal design variables, number of trays and condenser vapour load, are found to be 29 and 6.0 $kmol/hr$, respectively, whilst the optimal operating policy is shown as the distillate composition profiles in Figure 5.3. Assuming non-stop year round production ($T_A = 8760\ hr/yr$), a profit of 97 942 $\$/yr$ is achieved.

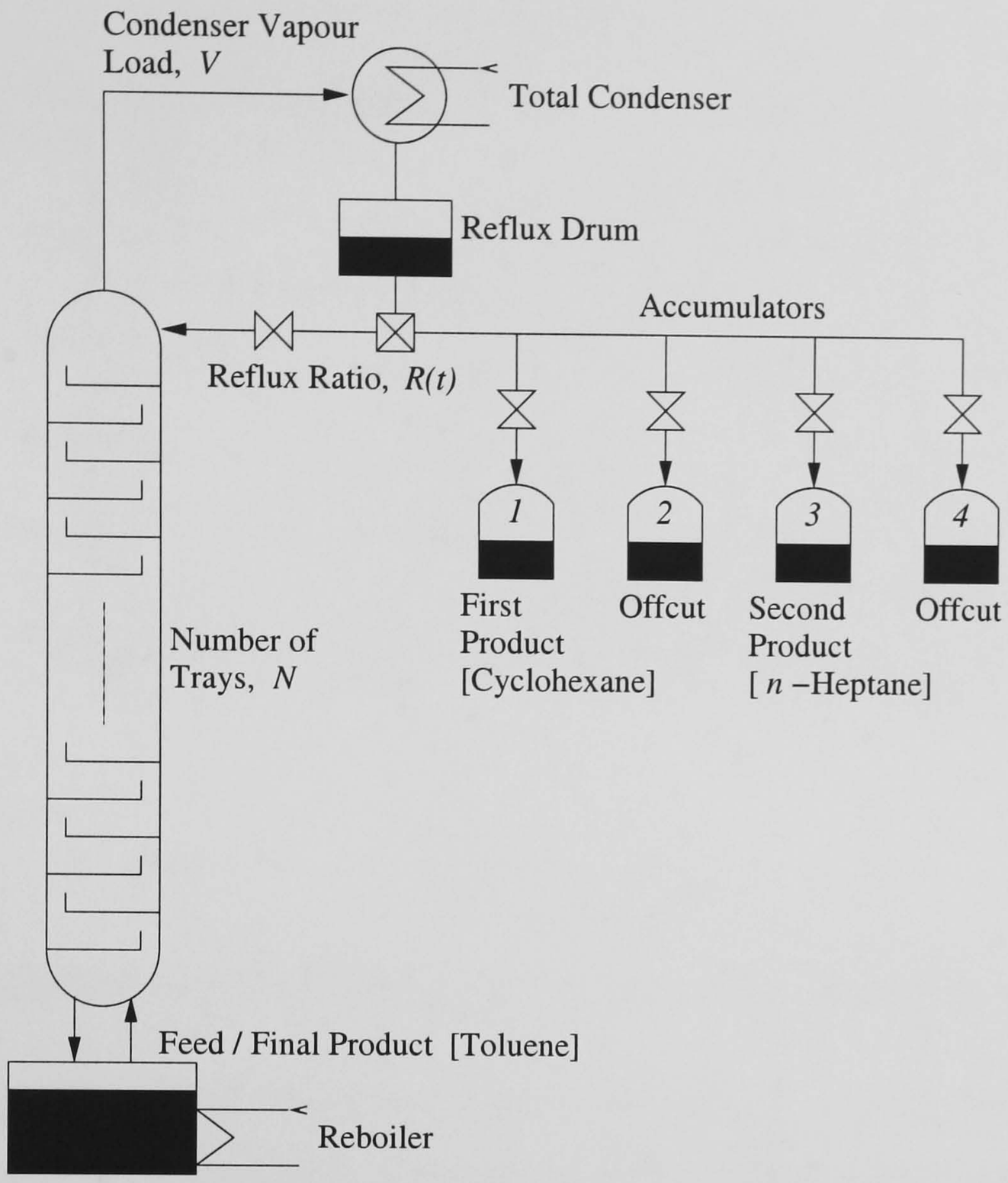
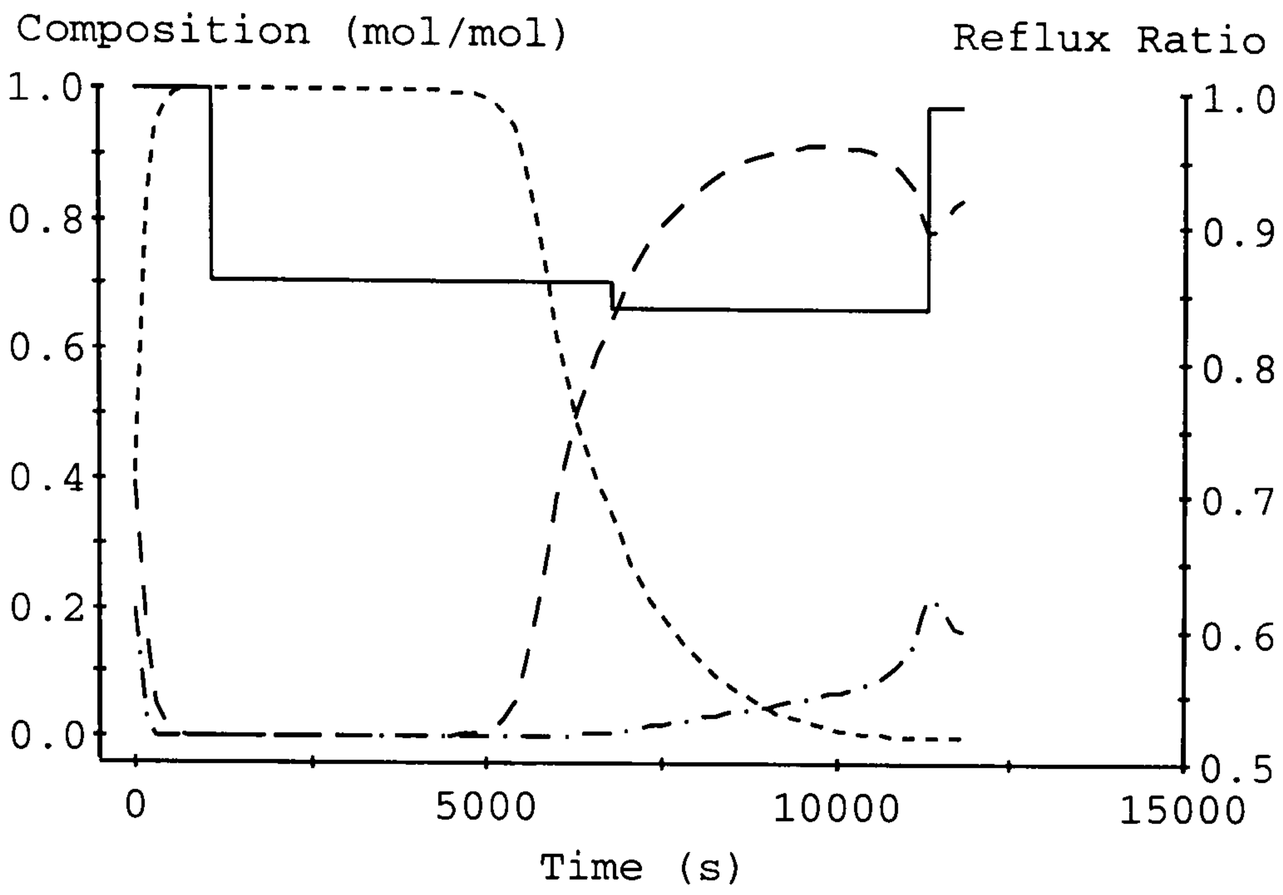


Figure 5.2: Schematic of batch distillation for the case study I

A column size of 29 trays, close to the maximum bound, is found to be optimal in this particular case study. The greater performance obtained from a bigger column achieved a revenue of 187 502 $\$/yr$ which is enough to offset the annual capital investment cost of 88 480 $\$/yr$ for a 29-tray column. This situation is obvious for a production plant where the products are of high relative value. If the design is based on a longer return outlook, *e.g.* biennial or longer, the possibility of a bigger column being more profitable in the long run increases. Similar explanation holds for the condenser vapour load, V. For a specified amount of distillate, the batch time is inversely proportional to V. Alternatively, for a given batch time, the amount of product is directly proportional to V. Since the utility and capital costs grow with V by an economic factor less than 1, a column with large V will be favourable.

The optimal operation consists of a short total reflux period (1100 s) during which the composition of the distillate rises steeply to well above the required purity of 89.5 $mol\%$



—— reflux ratio, - - - cyclohexane , – – *n*-heptane, -.-.- toluene

Figure 5.3: Optimal reflux ratio and distillate composition profiles for case study I

of cyclohexane (Figure 5.3). Then the cyclohexane product is withdrawn for a period (5700 s) with a reflux ratio of 0.86 until the purity in the first accumulator falls below specification. Despite the non-sharp product changeover, the offcut period is very brief (100 s). This is followed by the *n*-heptane withdrawal period (4400 s). Finally, there is a short period of slight offcut or close to total reflux ($R(t_5)$= 0.99) to obtain the final toluene product remaining in the reboiler. The purities obtained are 90.1, 86.5 and 99.0 *mol%* of cyclohexane, *n*-heptane and toluene respectively, which satisfy the separation specifications.

The computational statistics of the stochastic optimisation and the evolution profile of the solution is presented in Appendix D.

5.6.2 Design Scenario II: Effect of Design Parameters

At this point, it would be interesting to see the effect of another design scenario on the optimal design and operating policy. In the previous scenario, the production was run continually all year round without any stoppages. Here, a more realistic annual production time, T_A, with a 20% downtime (0.8 x 8760 = 7008 hr operating time) is

Design Scenario	I	II
Production time per annum, T_A (hr)	8760	7008
Capital costs coefficients, K_1, K_2	1500, 9500	2250, 14250
Utility cost coefficient, K_3	180	270

Table 5.4: Alternative design scenarios

assumed, taking into account labour and maintenance work. Also, a 50% inflation of the capital and utility costs is assumed in order to study the effect of higher costs on column sizing. The new design scenario II is shown in Table 5.4.

Optimal Solution

A feasible solution would be to use the same column and operating policy optimised for the previous scenario I. The separation duty purity constraints would be satisfied as previously and the profit can be calculated (Table 5.5). Due to production downtime, the number of batches processed per year would be reduced from 2318 to 1855, giving a revenue of 150 002 $\$/yr$. The higher capital cost and utility cost are 132 720 $\$/yr$ and 1620 $\$/yr$, respectively (from Equation G.13 plus G.14 and Equation G.15 in Appendix G). This gives an annualised profit of 15 662 $\$/yr$ which is the maximum value achievable for a column with 29 trays, and serve as a base case for scenario II because any better alternative design and operating policy must be able to provide at least this amount of annualised profit.

The genetic algorithm is used to search for possible better solutions for design scenario II. As shown in Table 5.5, the new column design consists of 17 trays and vapour flowrate of 6.0 $kmol/hr$ whilst the new operating policy is shown in Figure 5.4. The smaller column has lower efficiency than the base case column, *i.e.* higher reflux ratios across all the task intervals and longer offcut periods to satisfy the purities requirement, causing an overall longer process time (Figure 5.4) and thus a decrease in number of batches per year (N_b = 1627) compared to the base case. However, the smaller column also reduces the capital investment cost and the overall offset has resulted in a higher profitability than the base case. In other words, the 17% loss in production revenue (from 150002 to 124 524 $\$/yr$)

Design Scenario	I	II	
	Optimised Design	Base Case Design	Revamped Design
Number of trays, N	29	*29*	17
Condenser vapour load, V $(kmol/hr)$	*6.0*	6.0	6.0
Batch processing time, t_f (hrs)	*3.28*	3.28	3.81
Number of batches, N_b (including t_s)	2318	*1855*	1627
Purity constraints, x_i $(mol\%)$	[90.1,86.5,98.9]	*[90.1,86.5,98.9]*	[89.6,86.4,99.0]
Production revenue $(\$/yr)$	187 502	*150 002*	124 524
Capital Costs $(\$/yr)$	88 480	*132 720*	102 390
Utility Costs $(\$/yr)$	1080	*1620*	1620
Profit $(\$/yr)$	**97 942**	*15 662*	**20 514**

Table 5.5: Optimal designs of regular column for different scenarios

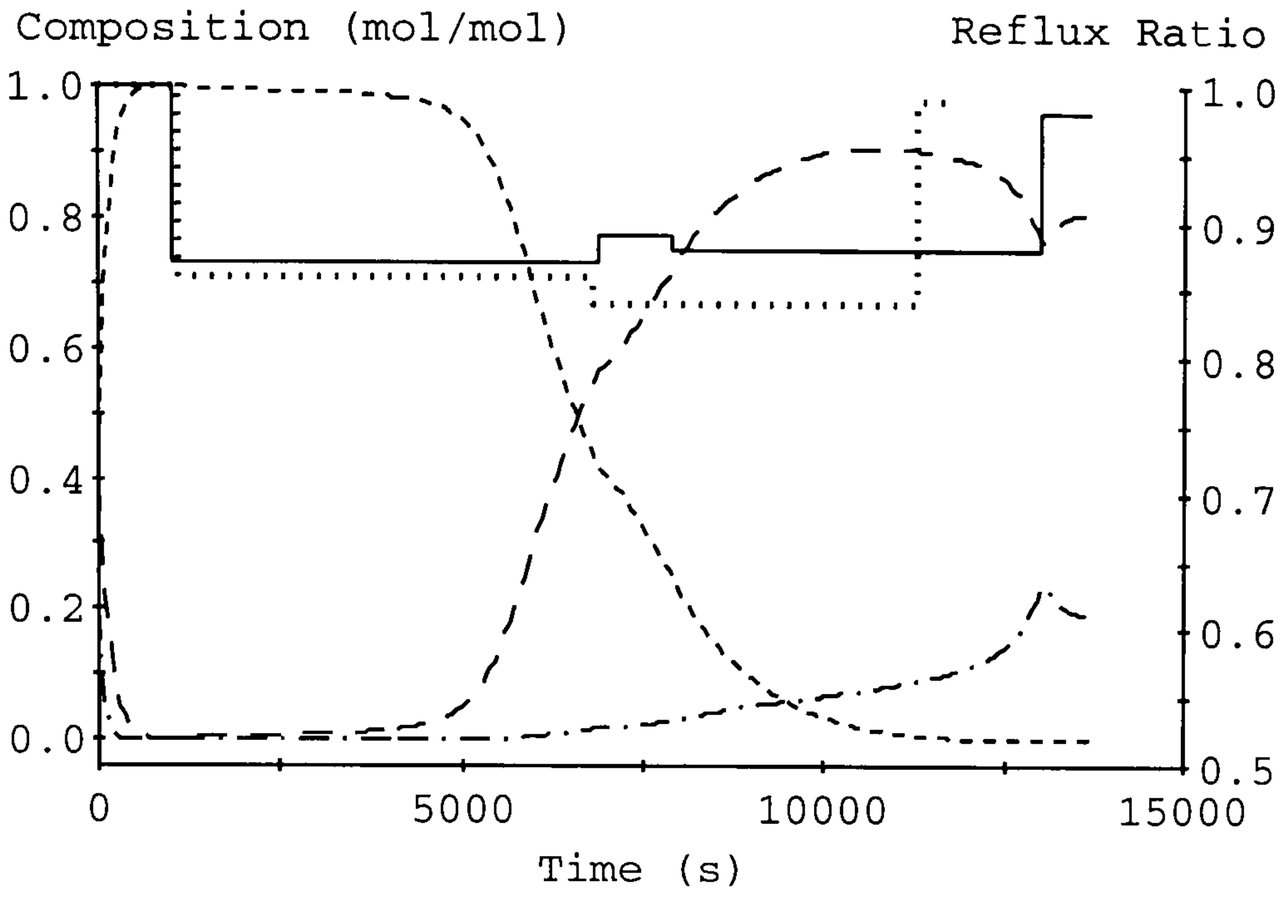
is positively offset by a greater reduction (23%) in the cost of installing a smaller and less efficient column. The net profit for the revamped design and its corresponding operating policy is 20 514 $\$/yr$, a 30% increase from using the base case column with 29 trays.

5.6.3 Design Scenario III: Multiple Separation Duties

In this case study, the design of a column with multiple separation duties (two binary mixtures) is considered. The aim is to obtain the optimal column design, *i.e.* number of trays and condenser vapour load, as well as optimal operating policies for each of the separation duty, in a scenario whereby the column is used to separate mixtures with different thermodynamic characteristics. Here, the ease of separation of one mixture is greater than the other as given by the specification of relative volatilities [1].

Table 5.6 gives the summary of the column specifications and operating conditions. A similar design scenario as that described in Mujtaba and Macchietto (1996) is consid-

[1]The semi-rigorous model with constant molal overflow and constant relative volatility is used here so that the different characteristics of the mixtures can be easily set using the relative volatility parameter and the resulting solution trend obtained.



—— reflux ratio of scenario II; ..... reflux ratio of scenario I;
- - - cyclohexane; – – *n*-heptane; -.-.- toluene

Figure 5.4: Optimal reflux ratio and distillate composition profiles for different scenarios

ered. The two binary feeds are of equimolar composition. The separation requirements is to obtain 95 $mol\%$ of the lighter components for each mixture, both having the same selling price of 20 $\$/kmol$, thus the only difference between the mixtures is the ease of separation. A total production time of 8000 hr (9% downtime) is allocated per year to be distributed between the two separation duties (ϕ_m). The column set-up time for each batch is 1440 s. Figure 5.5 shows the schematic of the batch distillation process whereby each operating policy consists of two time intervals. The same values as in the previous case studies are used for the coefficients K_1, K_2 and K_3 as well as the genetic algorithm parameters. The bounds for each variable are given in Table 5.7.

Optimal Solution

Table 5.8 and Table 5.9 show the optimal column design and optimal operating policies for different cases of process allocation scenario. Cases A and B represent the optimal designs when the column is used exclusively to separate a particular mixture. The optimal number of trays for separating the mixture with a relative volatility of 1.5 is 21 (case A), close to the maximum bound, whilst a column with 12 trays, the minimum

Total Available annual production time, T_A (hr/yr)	8000
Batch set-up time, t_s (s)	1440
Operating pressure, P (Pa)	101 325
Batch size, H_{feed} (mol)	10000
Reflux drum holdup, H_{rd} (mol)	100 (1.0% H_{feed})
Tray holdup, H_{tray} (mol)	3.0% H_{feed}
Number of mixtures, N_m	2 binaries
Relative volatilities, α_{ij}	
Mixture 1	1.5, 1.0
Mixture 2	2.5, 1.0
Feed composition, $x_{i,feed}$ $(molfraction)$	
$x_{1,feed}$, $x_{2,feed}$ of mixture 1	0.5, 0.5
$x_{1,feed}$, $x_{2,feed}$ of mixture 2	0.5, 0.5
Product purity specifications, $(molfraction)$	
First product of mixture 1	0.950
First product of mixture 2	0.950
Cost, C_i $(\$/mol)$	
C_1, C_2 of mixture 1	0.020, 0
C_1, C_2 of mixture 2	0.020, 0
C_{feed} of both mixtures	0.002, 0

Similar to values given by Mujtaba and Macchietto (1996)

Table 5.6: Column specifications and operating conditions for case study III

Decision Variables	Bounds
$N\dagger$	[12 , 22]
V $(kmol/hr)$	[5 , 15]
ϕ_m	[0 , 1]
$R(t_{i,m})$	[0.4 , 1.0]
$\Delta t_{i,m}$ (s)	[100 , 18000]

Bounds similar to that given by Mujtaba and Macchietto (1996)

Table 5.7: Decision variables bounds for the case study III

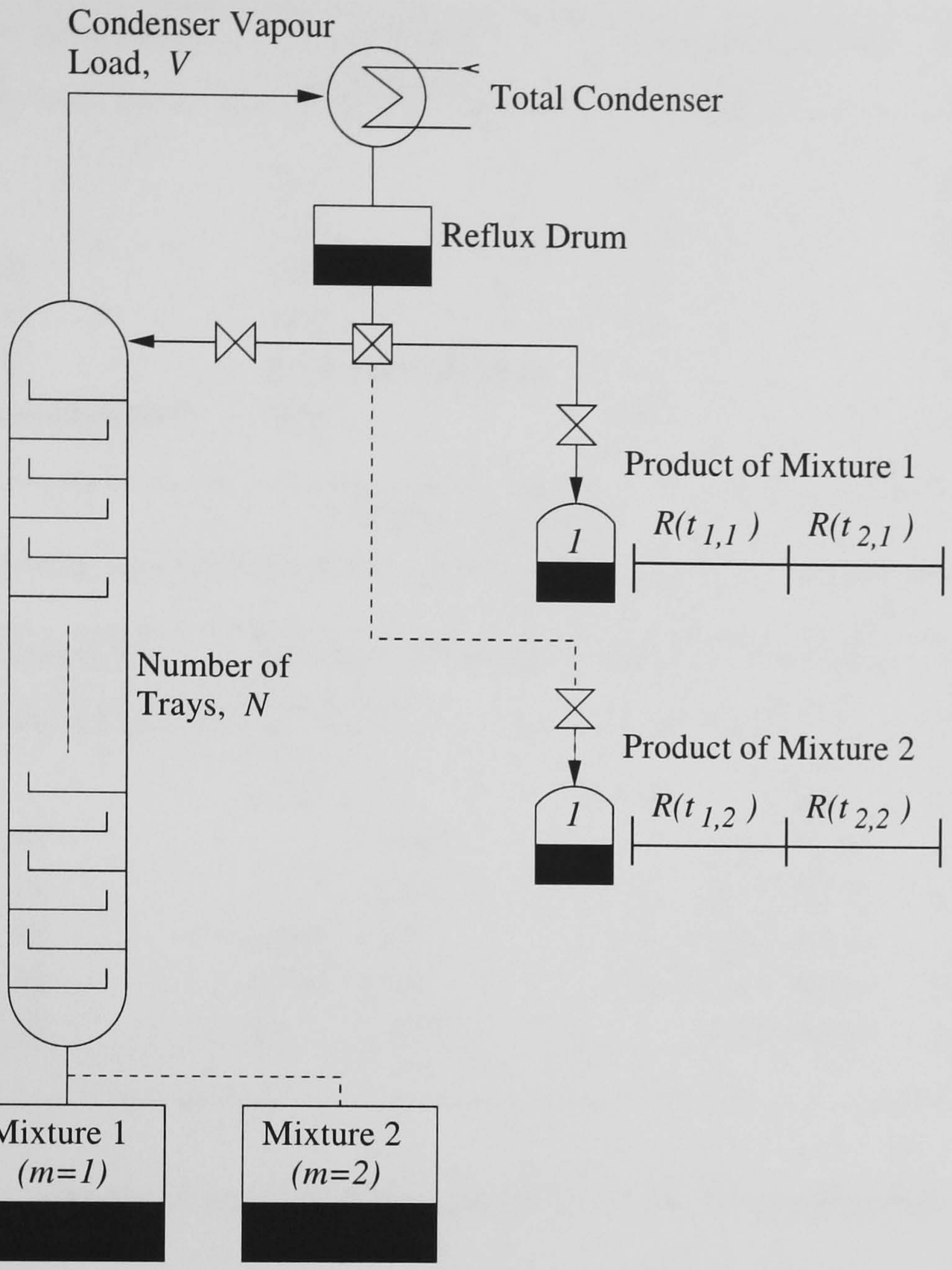


Figure 5.5: Schematic of batch distillation with multiple separation duties for the case study III

bound, is found to be optimal for the separation involving the mixture with a relative volatility of 2.5 (case B). The solution is in accord with engineering intuition, *i.e.* a smaller column can be used to satisfy purity specification for a mixture with greater ease of separation. The results also show that it is more profitable to allocate production time to an easy-to-separate mixture (247 333 $\$/yr$) rather than to the more difficult separation (55 702 $\$/yr$). This is because, in addition to lower capital cost for a smaller column, the operating policy is also economically more advantageous in case B, *i.e.* greater ease of separation allowing for lower reflux ratios and thus lower batch times (1.25 hr compared to 2.47 hr) and greater number of batches processed per year (4848 compared to 2785). In addition to more batches, a greater amount of product is collected per batch in case B (4.364 $kmol$) than in case A (3.767 $kmol$), as well as in total (10 491 $kmol$ and 21 156 $kmol$ per annum for case B and case A, respectively).

Case	Process Allocation $[\phi_1,\phi_2]$	Vapour Load V $(kmol/hr)$	Optimal Number of Trays, N	Profit P_A $(\$/yr)$
A	[1,0]	10.0	**21**	**55 702**
B	[0,1]	10.0	**12†**	**247 333**
C_1	[0.5,0.5]	10.0	**18**	**146 001**
C_2	[0.5,0.5]	10.0	**16**	**144 529**
C_3	[0.5,0.5]	**14.9 (optimised)**	**16**	**204 498**
D	**[0,1] (optimised)**	10.0	**12†**	**245 361**

† minimum bound

Table 5.8: Optimal process allocation and column design for two separation duties

Case	Batch Times (hr) $[t_{1,1}+t_{2,1}],[t_{1,2}+t_{2,2}]$	Amounts of Product $(kmol/batch)$	Number of Batches $N_{b,1},N_{b,2}$ (Total)	Total Production $(kmol/year)$
A	2.47 , —	3.767 , —	2785 , — (2785)	10 491
B	— , 1.25	— , 4.364	— , 4848 (4848)	21 156
C_1	3.00 , 1.19	3.931 , 4.258	1176 , 2509 (3685)	15 306
C_2	2.78 , 1.03	3.986 , 3.908	1259 , 2802 (4061)	15 969
C_3	2.22 , 0.92	4.090 , 4.641	1525 , 3038 (4563)	20 337
D	— , 1.39	0 , 4.625	0 , 4472 (4472)	20 683

Table 5.9: Details of optimal operating policies for two separation duties

Cases $C_{1,2,3}$ represent the design scenario whereby a single column is used for different separation duties. When the production time is distributed equally between the two mixtures ($\phi_1 = \phi_2 = 0.5$), a column with 18 trays is found to be optimum with a profit of 146 001 $\$/yr$. The batch processing time for the easy separation is 1.03 hr compared to 2.78 hr for the more difficult separation. An interesting observation can be seen when case C_1 is contrasted to case A and B whereby a column of 18 trays seems to be a compromise between the optimum 21 trays in case A and the optimum 12 trays in case B. This is reflected in the operation where, as a result of using a smaller column (18 instead of 21 trays), the batch time has decreased for the more difficult duty (2.78 hr compared to 2.47 hr) whereas on the other hand, the batch time has increased slightly (1.03 hr compared to 1.25 hr) for the easier duty when a larger than necessary column is used (18 instead of 12).

Case C_2 highlights the possibility of alternative solutions for a particular design scenario.

The profit objective function is very close to case C_1 (difference of 1.0%). Therefore, there is an option of choosing either a column with 18 trays (case C_1) that processes 4601 batches per year, or a smaller column size of 16 trays (case C_2) which offsets the 9% decrease in the total number of batches processed (4601 to 3685) with a 9% saving in the capital cost (51 978 to 47 293 $\$/yr$). The results highlight the complexity of the batch distillation optimisation problem, *i.e.* the existence of different optimal design and operation solutions with very close objective function values (tolerance of 1%). Due to the closeness of the objective function values, it is plausible for the genetic algorithm to return either solutions. It is demonstrated here that, although the genetic algorithm approach has the potential for global optimisation, in practice, a global optimum can only be guaranteed when a very large population and a very tight convergence criterion is used.

In case C_3, the condenser vapour load, V, is optimised along with the other variables. Similar to the observation in case study I, a high condenser vapour load (14.9 $kmol/hr$, close to the maximum bound) maximises the objective function. The capital and utility costs associated with high condenser vapour load is insignificant relative to the greater performance and production gained from the faster separation and higher number of batches.

Finally, in case D, the process allocation parameter, ϕ_m, is relaxed as a degree of freedom. In other words, the algorithm is free to make the decision on how much importance should be placed on each mixture so as to maximise profit, in addition to determining the column design and its associated operating policies. It can be expected from the previous cases that the highest profit can be obtained when all the available production time is allocated solely on the easier separation (case B), which is duly confirmed in case D. The optimal number of trays, 12, and objective function is the same as case B (-0.8%). However, interestingly, there are alternatives within the operating policy, *i.e.* 4848 batches per year collecting 4.364 $kmol$ per batch (case B, with single batch processing time of 1.25 hr) compared to 4472 batches (376 less) but collecting slightly higher 4.625 $kmol$ per batch (case D, with single batch processing time of 1.39 hr). The total production for case B is 21157 $kmol/yr$ whilst for case D it is 20683 $kmol/yr$ (2.2% less), which account for the slightly lower profit.

5.7 Optimal Design of Multivessel Columns

In this section, the optimal design of unconventional multivessel batch distillation systems is presented. In the following section (section 5.7.1), the body of work found in the literature with regards to this novel configuration is briefly discussed. This is followed by a degrees of freedom analysis and a simulation sensitivity study in sections 5.7.2 and 5.7.3, respectively. Optimal design case studies are then investigated in sections 5.7.4, 5.7.5 and 5.7.6 where the effect of different factors such as the performance index, product purity requirement and feed composition on the optimal design is explored.

5.7.1 Background

In industry, the batch distillation process is generally operated in the conventional rectification mode which consists of a single column with the feed charged to the reboiler. Novel modification of the batch distillation configuration, such as the multivessel system, can offer a significant increase in the flexibility and efficiency of the process, and thus, there has been increased industrial interest in the further study of the potential of this system.

The multivessel system was first proposed by Hasebe *et al.* (1995) whereby the concepts of inverted column and middle vessel column (Robinson and Gilliland, 1950) were extended to what they termed as the *multi-effect*, or multivessel, distillation system. Since then, the multivessel system has been shown, via both simulation and experimental studies, to offer better performance than the conventional regular column system with the same number of stages (*e.g.* Hasebe *et al.*, 1995; Hasebe *et al.*, 1997 and Furlonge *et al.*, 1999). The performance indices used for the comparison included maximum production rate and minimum mean energy consumption.

Hasebe *et al.* (1999) attempted to compare the operation of the multivessel system with the continuous distillation system. They used different performance indices for the mul-

tivessel system (production rate divided by vapour flowrate) and the continuous system (sum of product flowrates divided by the sum of vapour flowrates) and found that the separation performance of the batch multivessel system is comparable to the continuous process from the viewpoint of energy consumption.

Recently, several control strategies for the multivessel system have also been proposed. Simple level controllers can be used to maintain constant vessel holdup (Hasebe *et al.*, 1995). Wittgens *et al.* (1996), Skogestad *et al.* (1997) and Wittgens and Skogestad (2000) proposed and demonstrated via a pilot-plant, an on-line feedback control strategy capable of compensating for feed composition variation. The strategy involves maintaining the temperature at some location in the multivessel column section by manipulating the reflux flowrate out of the corresponding vessel above, thereby adjusting its level to the correct value. Their simulation results indicate that the temperature controller achieved the same steady state product compositions in the vessels independent of the initial feed composition, the system was thus able to tackle feed composition disturbances. Noda *et al.* (2000) later presented a more complex on-line feedback control strategy to optimally operate the multivessel system. The on-line system consists of four subsystems, namely a composition measuring subsystem using a near-infrared analyzer, a composition estimation and model update subsystem, an optimisation subsystem, and finally, a control subsystem.

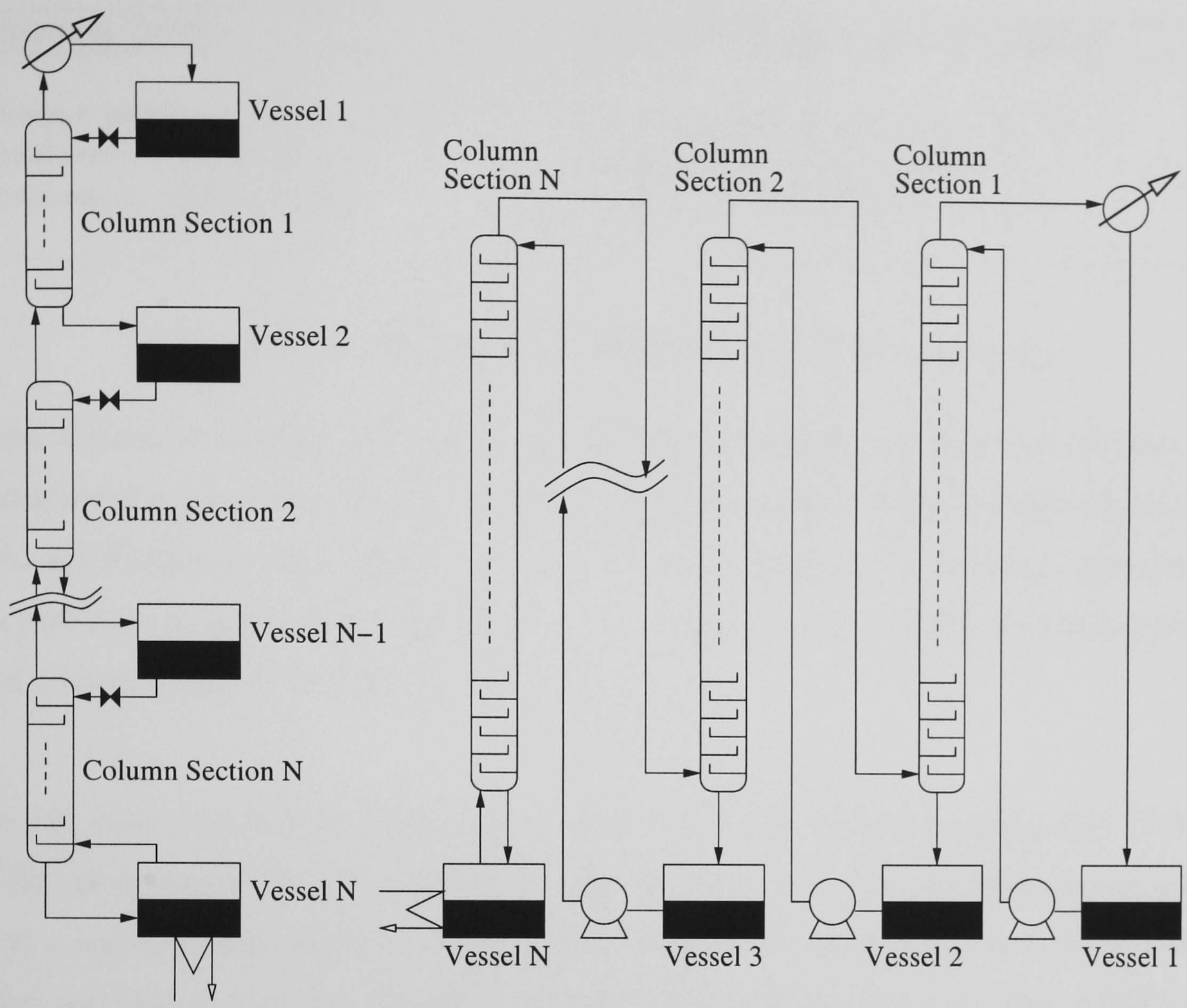
In this study, an optimal design study of the multivessel system is presented. The overall purpose of this investigation is to provide a better understanding of the optimal design of the multivessel system, and more specifically, (i) to show how optimal design and the use of a more general economics performance index, affects the overall optimal performance of the system and (ii) to highlight the effects of factors such as feed composition, relative volatility and product purity specification on the optimal design and operation of the system.

5.7.2 Degrees of Freedom

The multivessel system configuration comprises a set of sequentially connected column sections and holdup vessels (total reflux configurations shown in Figure 5.6). In the basic set-up, only the vessels at both ends are served by utilities for reboiling and condensing purposes. Conceptually, this novel system can be viewed as either a partitioning of a batch rectifier into separate column sections, or alternatively, it can be viewed as an array of multiple batch rectifiers joined together in series. Likewise, the layout of this novel batch distillation system can be implemented practically in either a horizontal or vertical manner (Figure 5.6). In the horizontal format, the column sections are in series with the vessels at ground level. Reflux pumps are then needed to bring the liquid from the vessels to the top of the column sections. In this case, one can easily put several column sections in series to meet the separation requirements for a given mixture. Alternatively, the column sections can be stacked on top of each other, where the liquid then flows by gravity and there is no need for pumps. With the existence of additional holdup vessels in the multivessel system, there is also the freedom to introduce heating on each vessel.

The main feature of the multivessel system is that it allows for the separation of all the components simultaneously (N_C components needing $N_C - 1$ column sections). For the separation of a binary feed mixture ($N_C = 2$), only a single column is needed ($N_C - 1 = 1$) and thus, the multivessel system reverts to the regular column. Therefore, the usage and analysis of the multivessel system is conducted in the context of multicomponent separations. Potentially, the benefit of the multivessel system could be even more prominent if used for separating mixtures with a higher number of components as will be demonstrated in this work.

The multivessel system offers a greater number of degrees of freedom than a conventional regular column system, in terms of both design variables and operation variables. For a regular column, the designer has to decide only on the length, or number of stages, for a single column section, N, whilst for the multivessel system, the length of each column section, N_i, and the initial feed distribution among the vessels, $M_i(0)$, have to be decided upon. The column section configuration, N_i, and the initial feed distribution, $M_i(0)$,



Left: vertical stack format Right: horizontal ground level format

Figure 5.6: Two schematic layouts of total reflux multivessel batch distillation systems

depend on the separation duty such as feed composition, relative volatilities and product specifications.

In terms of the operation decision variables, the multivessel system also offers more degrees of freedom than a regular column; however, it can either be more difficult or easier to operate depending on the actual number of operation decision variables utilised. In this work, the optimisation is focused on the *total reflux constant holdup* policy. It is the simplest operating policy in terms of theoretical analysis as well as practical implementation. The *total reflux holdup* policy is also desirable for its high product yield due to no offcut. From a design study point of view, the focus on the simplest operating policy allows for the benefit of the system design to be highlighted more clearly. In other words, the benefit of the multivessel system can be distinctly studied from the aspect of optimal alteration of the system configuration itself rather than due to the extra operation de-

Operating Policies	Design and Operation Decision Variables
Product withdrawal variable holdup	N_i, $M_i(0)$, $Q(t)$ or $V(t)$, $M_i(t)$, $F_i^W(t)$, t_f
Total reflux variable holdup	N_i, $M_i(0)$, $Q(t)$ or $V(t)$, $M_i(t)$, t_f
Total reflux constant holdup	N_i, $M_i(0) = M_i(t_f)$, $Q(t)$ or $V(t)$, t_f

Table 5.10: Classification of multivessel system operating policies

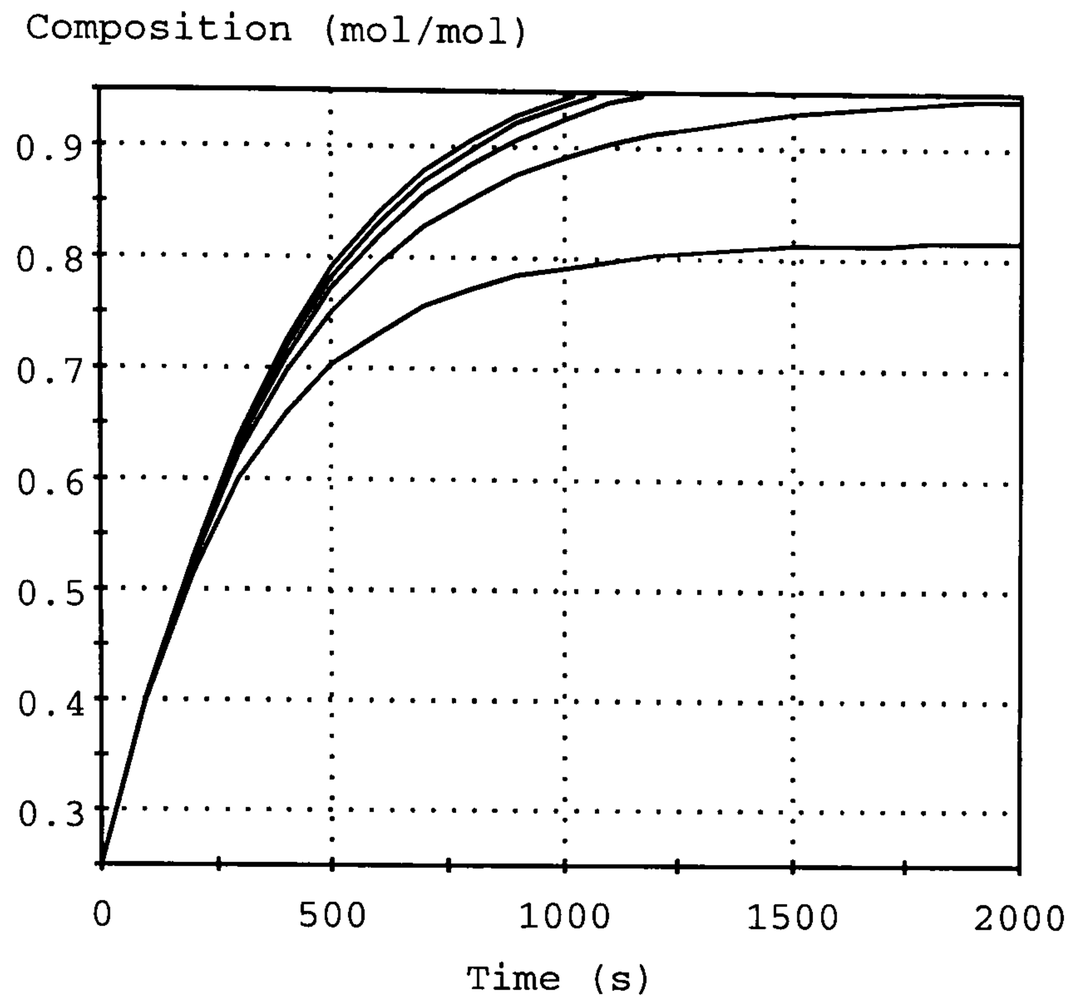
grees of freedom available. Of course, vessel holdup and product withdrawal can also be optimised if needed later on and the various operating policies compared (Hasebe *et al.*, 1997 and Furlonge *et al.*, 1999), *i.e.* especially when the degree of performance increment they afford is needed to decide whether a correspondingly more complex operating policy and control system is justifiable.

For the most complicated policy, *i.e.* *product withdrawal variable holdup* policy (Table 5.10), the operation decision variables are the heat duty, $Q(t)$, (or condenser vapour load, $V(t)$), vessels holdup profiles, $M_i(t)$, product withdrawal flowrate profiles, $F_i^W(t)$, and batch processing time, t_f. In the *total reflux* policy, the products are not withdrawn during the process, *i.e.* $F_i^W(t)$ are set to zero. Within the *total reflux* policy, the vessel holdups, $M_i(t)$, can either be constant or allowed to vary. In this study, the most practical operating policy of having the vessel holdups constant throughout the duration of the process is considered ($M_i(t) = M_i(0), \forall t \in [0, t_f]$).

5.7.3 Simulation Experiment: Effect of Column Section Length and Configuration on Separation Performance

The length of the multivessel column sections is an important design decision variable, the effect of which has, so far, not yet been investigated and included in any optimisation studies in the open literature. As the column section lengths are a trade-off between economics and operation performance, optimum values exist.

Figure 5.7 illustrates what the trade-off may look like. A multivessel system consisting of four vessels and three column sections used to separate a quaternary and equimolar



Left to right: 90, 60, 45, 30, 15 stages

Figure 5.7: Composition of the main lightest distillate for different total column length

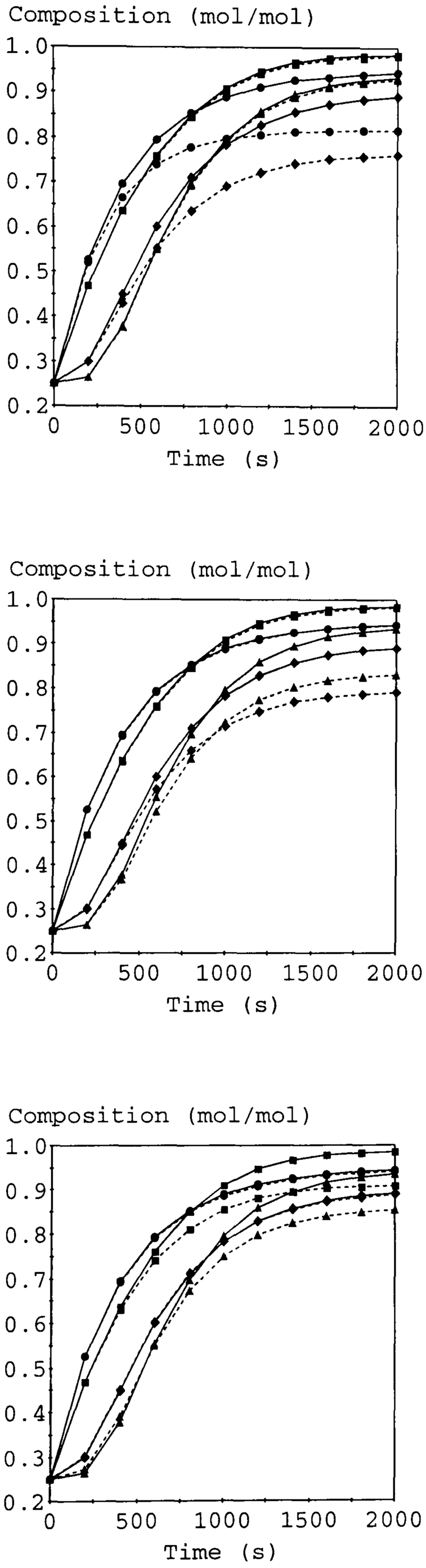
mixture (methanol, ethanol, *n*-propanol and *n*-butanol) is considered. Figure 5.7 shows the total reflux purity profiles of the lightest product (methanol) in the top vessel (reflux drum) for different column section lengths, *i.e.* 15, 30, 45, 60 and 90 stages in total (using an equilibrium model with 1000 *mol* feedstock, 2.5 *mol* constant tray liquid holdup and 1.6 *mol/s* condenser vapour load). If the desired purity of the product is specified as 95 *mol%*, it can be seen from Figure 5.7 that the system with 15 stages does not achieve the specification. The system with 30 stages achieves the specification at its steady state, which makes it the cheapest feasible system design in terms of capital cost. However, longer column sections, for example, the one with a total of 45 stages, can reduce the batch processing time considerably, as shown in Figure 5.7 where it can be seen that the composition profile reaches the 95 *mol%* specification much sooner. As the total column section length increases further, the magnitude of the batch time saving reduces. At the end of the scale, a further increase in total column sections length barely affords any batch time saving at all (see systems with 60 and 90 stages).

The example shown in Figure 5.7 demonstrates that the optimal column sections length is a function of the separation duty (*i.e.* product specification), and that their values

have an impact on capital cost and operating costs (*i.e.* batch time and energy consumption). At one limit, systems with short column sections (*e.g.* $\leq$ 30 stages) were not able to satisfy the products specification whilst, at the other limit, systems with very long column sections (*e.g.* $\geq$ 60 stages) were redundant in terms of unnecessary capital cost spending. In between (*e.g.* 30-60 stages), the optimal column sizing is a trade-off between capital cost and operating cost; thus, this is where the optimum design lies.

In addition to the total column sections length, the configuration (*i.e* the individual column sections length in relation to each other) of the multivessel system also influences the separation performance. To illustrate this, the separation of a quaternary multivessel system with different column section configurations (5:10:10, 10:5:10, 10:10:5 for top:middle:bottom column sections, respectively) but equal total number of stages, was simulated and the results are shown in Figure 5.8. In each sub-figure, the product purity profiles in each of the four vessels are shown (dashed line) and contrasted against the configuration with equal column section length of 10 each (solid lines). The graphs indicate that the separation performance, or specifically, the product composition profiles are significantly affected by the system configuration. It can also be surmised that the final product purities achieved in a particular vessel are most significantly influenced by the column sections directly connected to it, for example, in the quaternary mixture separation example considered here, it is found that the lightest product purity is most directly affected by the top column section length, the second lightest product purity is most directly affected by the top and middle column sections length and so on.

Figures 5.7 and 5.8 highlight that both the total length of the column sections as well as their configuration in relation to each other, can significantly influence the separation performance of the multivessel distillation system, and thus, there is a need to include the section lengths in an optimisation study for a better understanding of the interaction between the system design and operation.



Top: - - - 5:10:10 configuration; Middle: - - - 10:5:10 configuration;
Bottom: - - - 10:10:5 configuration; All: —— 10:10:10 configuration;
◯ reflux drum; ◇ vessel 1; △ vessel 2; □ reboiler

Figure 5.8: Product composition in each vessel for different column sections configurations

5.7.4 Design Scenario I: Effect of Performance Index

The multivessel system separation scenario with three column sections as presented by Furlonge *et al.* (1999) for the separation of a quaternary mixture is considered here. They considered a laboratory size distillation column with given column diameter and internal tray dimensions. The model used to describe the system was the detailed type and takes into account variable liquid and vapour holdups that are determined by tray hydraulics and detailed pressure drop equations (see chapter 3.1).

For fixed column section diameters, the capital cost of the column shell is directly proportional to the number of stages ($C_{sh} \propto N$). Since one of the aims here is to compare the results of Furlonge *et al.* (1999), hence, utilising the same reboiler and condenser units, the heat exchangers installed costs, C_{ex}, can be neglected. Assuming the same Guthrie's correlation coefficients as Equation 5.4, the economics performance index for the detailed model of an existing column can be expressed from Equation 5.3 as[2]:

$$P = \frac{\sum_{i=1}^{N_C} C_i H_{A,i}(t_f) \; - \; C_{feed} H_{feed}}{t_f + t_s} - K_1 \left(\sum_{i=1}^{N_S} N_i \right)^{0.802} - K_3 V_{ave} \qquad (5.19)$$

where N_S is the number of column sections in the multivessel system and V_{ave} the average condenser vapour load over the processing time, given by:

$$V_{ave} = \int_0^{t_f} V(t) dt \; / \; t_f \qquad (5.20)$$

Optimal Operation

The optimal operation of the multivessel system based on the economics performance index (Equation 5.19) is determined and compared to the optimal operating policy based on minimum mean rate of energy consumption as described by Furlonge *et al.* (1999). The multivessel system consists of 10 trays in each of the three column sections (10:10:10). Table 5.11 gives the column specifications and operating conditions. The total batch feed

[2] An alternative for the capital cost correlation function is $K_1 \left(\sum_{i=1}^{N_S} N^{0.802} \right)$. This assumes the construction of a multivessel system as being similar to building N_S separate regular columns; *i.e.* resulting in much greater capital cost.

Batch set-up time, t_s (s)	1800
Operating pressure, P (Pa)	101 325
Batch size, H_{feed} (mol)	100
Reboiler, side vessels and reflux drum holdups (mol)	25 each
Tray holdup, H_{tray} (mol)	0.12
Column dimensions and flow coefficients	as in Furlonge *et al.* (1999)
Feed composition, $x_{i,feed}$ $(molfraction)$	
Methanol, ethanol, *n*-propanol, *n*-butanol	0.25, 0.25, 0.25, 0.25
Product purity specifications, $(molfraction)$	
Reflux drum, $x_1(t_f)$	0.928 of methanol
Vessel 1, $x_2(t_f)$	0.854 of ethanol
Vessel 2, $x_3(t_f)$	0.914 of *n*-propanol
Reboiler, $x_4(t_f)$	0.970 of *n*-butanol
Product price, C_i $(\$/mol)$	0.035 for all
Feed cost, C_{feed} $(\$/mol)$	0.001

Table 5.11: Column specifications and operating conditions for case study I

is 100 *mol* of methanol, ethanol, *n*-propanol and *n*-butanol with the desired minimum purities of 92.8, 85.4, 91.4 and 97.0 *mol*%, respectively.

The feed is distributed equally among the reboiler, two side vessels and reflux drum. All the holdups are kept constant throughout the operation which takes place under total reflux (*total reflux constant holdup* policy, Table 5.10). The operating policy is divided into six control intervals of variable duration bounded between 12 and 5000 s (Table 5.12). In addition, the reboiler capacity, $Q(t_i)$, is in the range between 0.75 and 5.5 kW. K_1 and K_3 are assumed to be 0.0663 and 1.5 based on hourly profit, respectively (Sharif *et al.*, 1998).

The optimal results are shown in Table 5.13. The optimal operation by Furlonge *et al.* (1999) gives a minimum mean energy consumption rate of 1478 W. Also, the optimal production rates were at the lower bounds of 0.209, 0.225, 0.221 and 0.213 mol/min,

Decision Variables	Bounds
N_1, N_2, N_3	[2 , 20]
$Q(t_i)$	[0.75 , 5.50]
t_i	[12 , 5000]

Table 5.12: Decision variables bounds for the case study I

respectively. By considering the performance index given in Equation 5.19, it is found that a better alternative to operating a column with the lowest energy consumption rate (1478 W) is to operate at maximum profit, *i.e.* to operate the column with a 40% increase in energy consumption rate (2065 W) with a reduction in operating time by 46% (5115 to 2774 s). For a production plant with unlimited demand, this would result in a greater number of batches and more than 2.5 fold increase in profitability (0.40 to 1.07 $\$/hr$). From the viewpoint of costs, the significant rise in revenue (1.69 to 2.56 $\$/h$) can more than compensate for the rise in operating costs (0.28 to 0.47 $\$/h$). The optimal production rates are also higher at 0.316, 0.340, 0.335 and 0.321 mol/min, respectively.

As a further note, in the case where a plant is required to produce only a specified amount of product to fulfil a fixed demand, the operating policy of the senario based on optimal profitability remains the preferred choice due to the lower total energy required to separate the same batch size ($2065\ W \times 2274\ s = 5.7\ MJ$ compared to $1478\ W \times 5115\ s = 7.5\ MJ$). Unlike the unlimited demand scenario whereby the economic benefit seems to be garnered from higher *productivity*, the real benefit in this limited demand scenario lies in the *efficiency* of the operation.

The comparison highlights the disadvantage of using an objective function that focuses on a particular aspect of the batch distillation process, such as energy consumption, instead of an overall economics evaluation like profitability which accounts for optimal trade-off in production yield, batch time and energy consumption. The policy obtained in this study appears to be the *"true"* economics optimum and seems to be true for both unlimited and existing demand plant production scenarios.

Performance Index	Mean Energy Consumption, E†	Profit, P	Profit, P
Column section configuration (top:middle:bottom sections)	10:10:10 (fixed)	10:10:10 (fixed)	11:11:9 (optimal)
Total number of stages	30	30	31
Mean energy consumption, E (W)	**1478**	2065	2148
Profit, P $(\$/h)$	0.40	**1.07**	**1.31**
Batch time, t_f (s)	5115	2774	2255
Revenue $(\$/h)$	1.69	2.56	2.89
Operating cost $(\$/h)$	0.28	0.47	0.54
Capital cost $(\$/h)$	1.01	1.01	1.04
Constraints			
Purity 1 $(molfraction)$	0.928*	0.928*	0.928*
Purity 2 $(molfraction)$	0.854*	0.870	0.876
Purity 3 $(molfraction)$	0.914*	0.925	0.914*
Purity 4 $(molfraction)$	0.970*	0.986	0.973
Production rate 1 (mol/min)	0.209*	0.316	0.357
Production rate 2 (mol/min)	0.255*	0.340	0.385
Production rate 3 (mol/min)	0.221*	0.335	0.379
Production rate 4 (mol/min)	0.213*	0.321	0.362

† Furlonge *et al.* (1999); * on the lower bounds

Table 5.13: Summary of optimal results for the case study I

Simultaneous Optimal Design and Operation

Next, the optimal number of trays for each column section, N_i= 1, 2 and 3, were optimised in order to investigate how an optimal design would affect the overall performance of the system. The number of trays are allowed to vary discretely between 2 and 20 for each column section and hence, taking into consideration the capital investment cost trade-off.

The results to the right in Table 5.13 show that, by investing in just one more tray (31 instead of 30), *i.e.* a small increase in capital outlay, and by optimally distributing the trays in the column (11:11:9 configuration instead of 10:10:10 configuration), the profitability can be increased a further 22% from 1.07 to 1.31 $\$/hr$. The optimal multivessel system design increases the revenue of the process (2.56 to 2.89 $\$/hr$) by reducing the

batch time further (2774 to 2255 s).

This comparison shows how economical insight can be gained by considering both design and operating parameters concurrently during the design stage and the benefits of doing so. In this case study, it is found that the performance of the multivessel system and its overall profitability can be significantly improved by optimising the system configuration design.

5.7.5 Design Scenario II: Effect of Product Purity Specification

Here, the effect of product purity specifications on the optimal design of the multivessel system is presented. Although product purity specifications are expected to have a significant influence on the optimal multivessel system design, an investigation of such nature has yet to be performed prior to the study here. Table 5.15 lists the different purity constraint scenarios (cases A to F) for the separation of a 1000 mol quaternary and equimolar mixture of methanol, ethanol, n-propanol and n-butanol. The rigorous model (Table 3.1) utilised here to describe the column assumed negligible vapour holdup and constant tray liquid holdup (2.5 mol per tray), *i.e.* without pre-specified column tray dimensions for tray hydraulics, thus suitable for design study purposes. The multivessel system consists of three column sections as well as the reboiler, two side vessels and a reflux drum where the four products are collected, respectively. To simplify the comparison, all products are assumed to be of equal value for all purity specifications (*i.e.* 35 $\$/kmol$). The comparison is based on atmospheric operation. The cost of the feed is set at 1 $\$/kmol$, the set-up time is 1800 s and the cost correlation coefficients in Equation 5.4 are assumed to be 1500, 9500 and 180 for K_1, K_2 and K_3, respectively (Logsdon *et al.*, 1990). The decision variable bounds are given in Table 5.14.

The optimal multivessel system design results for cases A to F are presented in Table 5.15 and Figure 5.9. The figure clearly illustrates that the optimal multivessel configuration is highly influenced by different separation duties. The general trend confirms the intuition that, the higher the purity specification, the lower the profitability achieved (Table 5.15). This is due mainly to the longer batch processing time needed to achieve

Decision Variables	Bounds
N_1, N_2, N_3	[2 , 20]
V	[0.16 , 1.6]
t_f	[100 , 3000]

Table 5.14: Decision variables bounds for the case study II

the higher specifications. For example, the profit obtained for case A with low product purities is 321 542 $\$/yr$, whilst the profit for case D with higher purity requirements is considerably lower at 187 806 $\$/yr$. The optimal total number of trays varies from 19 trays for case A to 44 trays for case D for the range of combination of purity specifications investigated (between 70 to 95 $mol\%$).

The optimal multivessel configuration for case A (0.70, 0.70, 0.70, 0.70) is 6:9:4 trays for the top, middle and bottom column sections, respectively. The intermediate components of ethanol and n-propanol are at their minimum specifications of 70 $mol\%$ which suggest that they are the limiting components in this particular case study example. This is also shown in case B (0.90, 0.90, 0.90, 0.90) whereby the products collected in the intermediate side vessels achieved only the minimum specifications of 90 $mol\%$.

When the minimum desired purities are increased from 70 $mol\%$ (case A) to 90 $mol\%$ (case B) for all four products, the optimal total number of trays needed increased by 16 trays from 19 to 35 trays. In terms of the individual column sections, all of them increased in length from a 6:9:4 configuration to a 14:12:9 configuration, which indicates that the degree of increase (8, 3 and 5 trays, respectively) are different despite the fact that the purity constraints were raised equally for all four products. The longest column section in case B is the top one compared to the middle one in case A. This shows that the optimal column sections length in relation to each other can change according to the purity specification (even though all four purity constraints were increased by the same magnitude). Nonetheless, both configurations displayed the same characteristic of satisfying the lower bounds of the product purities in the intermediate vessels. In the example, the overall profit of the process with higher purity requirement in case B is

Case	*A*	*B*	*C*	*D*	*E*	*F*
Purity specification for each product (*molfraction*)	0.70, 0.70, 0.70, 0.70	0.90, 0.90, 0.90, 0.90	0.90, 0.70, 0.70, 0.90	0.90, 0.95, 0.95, 0.90	0.70, 0.70, 0.95, 0.95	0.95, 0.95, 0.70, 0.70
Column configuration						
Stages in Section 1	6	14	10	18	4	17
Stages in Section 2	9	12	4	14	17	20‡
Stages in Section 3	4	9	7	12	12	4
Total number of stages	19	35	21	44	33	41
Constraints						
Purity 1 (*molfraction*)	0.81	0.95	0.90*	0.98	0.78	0.98
Purity 2 (*molfraction*)	0.70*	0.90*	0.70*	0.95*	0.71†	0.95*
Purity 3 (*molfraction*)	0.70*	0.90*	0.71†	0.95*	0.95*	0.80
Purity 4 (*molfraction*)	0.82	0.97	0.91†	0.99	0.99	0.88
Profit, P ($/yr$)	321 542	242 721	279 645	187 806	209 609	201 305

Mixture of methanol, ethanol, *n*-propanol and *n*-butanol
* on or † near the lower bounds; ‡ on the upper bound

Table 5.15: Summary of optimal results for case study II

25% lower than the profit achieved for the less demanding separation in case A.

In case C, the purity specifications are 90, 70, 70 and 90 $mol\%$ for methanol, ethanol, n-propanol and n-butanol, respectively. Since the limiting components are the intermediates ethanol and n-propanol, the middle column section, which most directly affects these products, was found to become shorter by two-thirds from 12 trays in case B to only 4 trays. As a result, again only the minimum product purities are achieved in the intermediate vessels. The number of trays in the top and bottom column sections also pivoted accordingly to obtain the minimum purities at the reflux drum and reboiler, respectively.

From another viewpoint, the optimal configuration in case C can also be contrasted against that of case A. When higher product purities are required in the reflux drum and reboiler (90 $mol\%$) with the specifications for the intermediate vessels the same as in case A (70 $mol\%$), the optimal configuration displays an intuitive change (6:9:4 to 10:4:7) where the trays in the middle column section are shifted to the top and bottom column sections to tackle the higher purity requirement in the reflux drum and reboiler. In total, only two extra trays are needed. Note that the purities of product 1 (81 $mol\%$) and product 4 (82 $mol\%$) (see Table 5.15), which were otherwise over-purified in case A, are now brought up to the required minimum specifications of 90 $mol\%$ (but no higher). Thus, all the products are separated to just their minimum purities because there is no economical gain in wasting valuable batch processing time to achieve higher purities than required.

In case D, the purity specifications are 90, 95, 95 and 90 $mol\%$ for methanol, ethanol, n-propanol and n-butanol, respectively. With higher product purities now required in the intermediate vessels, the middle column section length increased more than three fold from 4 trays in case C to 14 trays. Although both the top and bottom column sections also increased in length, their increment is to support the purities of ethanol and n-propanol which again reached the lower limit of 95 $mol\%$ in the intermediate vessels. Since the top and bottom column sections also directly affect methanol and n-butanol, respectively, as a result, their purities went way above the specifications (98 and 99 $mol\%$).

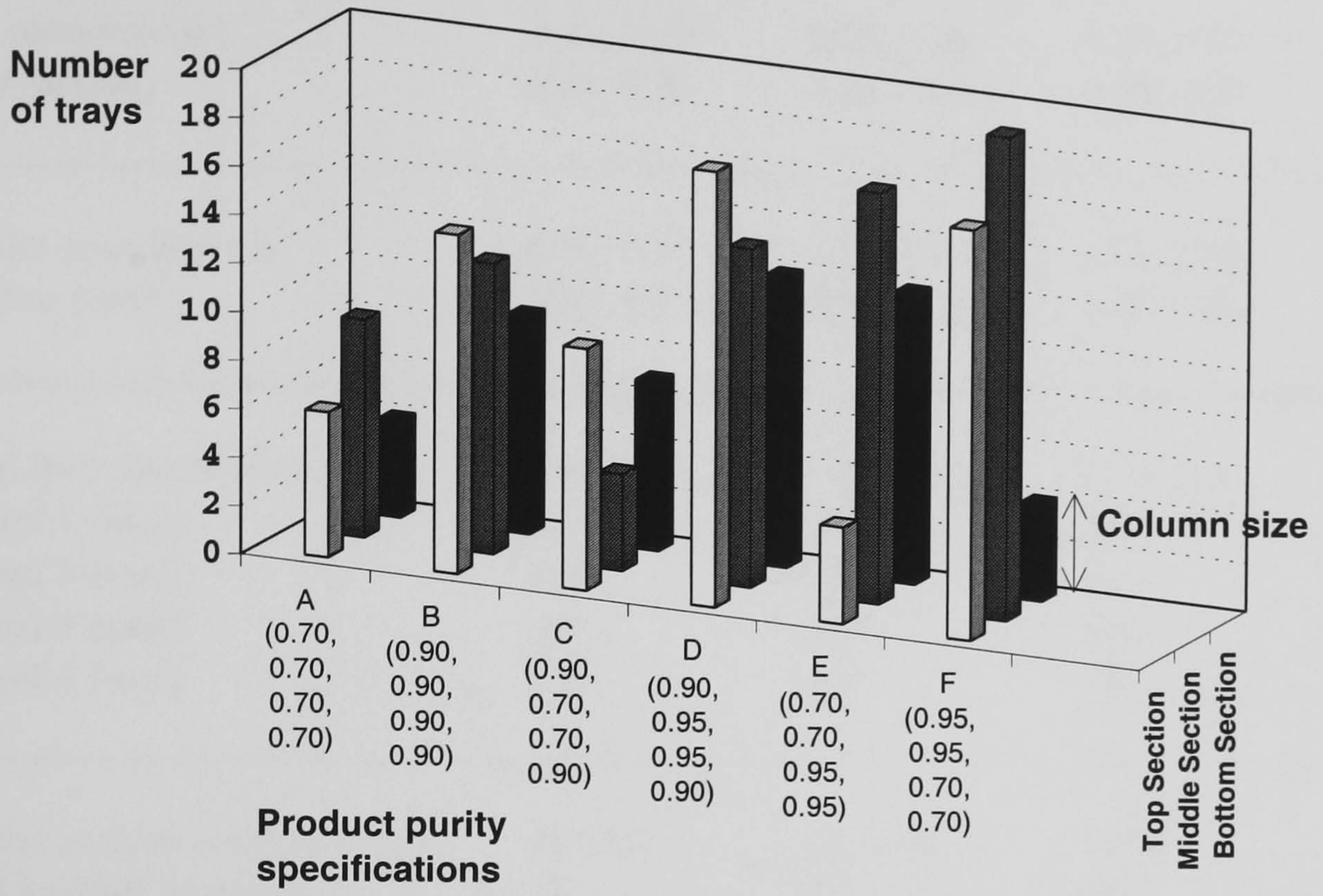


Figure 5.9: Optimal column section configurations of the multivessel system for different product purity specifications

The purity constraints in cases E and F are specified in such a way as to demonstrate how optimal design of the multivessel system configuration is strongly influenced by the separation duty (4:17:12 configuration for purity specifications of 70, 70, 95 and 95 $mol\%$ and 17:20:4 for 95, 95, 70 and 70 $mol\%$). In case E, the top column section is the shortest whilst in case F, the bottom column section is the shortest. This highlights how each column section is affected by the products collected in vessels directly connected to it, thereby confirming the simulation results presented earlier.

5.7.6 Design Scenario III: Optimal Initial Feed Distribution

Unlike the regular column where the feed is charged wholly into the reboiler, the novel configuration of the multivessel system allows the feed to be distributed among the reboiler, reflux drum and the vessels that are attached to each column section. In the previous cases where equimolar mixtures were considered, the feed was equally distributed

Case	Base	*A*	*B*	*C*
Feed composition‡ (*molfraction*)	0.25, 0.25, 0.25, 0.25	0.25, 0.25, 0.25, 0.25	0.25, 0.25, 0.25, 0.25	0.30, 0.10, 0.40, 0.20
Product specification (*molfraction*)	0.90, 0.90, 0.90, 0.90	0.90, 0.90, 0.90, 0.90	0.95, 0.60, 0.60, 0.95	0.90, 0.90, 0.90, 0.90
Initial feed distribution	(specified)	(optimal)	(optimal)	(optimal)
Vessel 1 (*mol*)	250	269	182	324
Vessel 2 (*mol*)	250	227	318	45
Vessel 3 (*mol*)	250	247	318	423
Vessel 4 (*mol*)	250	257	182	208
Column section configuration	14:12:9	11:13:10	13:5:6	11:10:9
Total number of stages	35	34	24	30
Profit, P ($/yr$)	242 721	249 464	310 647	230 816
Batch time, t_f (s)	1400	1350	1000	1600
Constraints				
Purity 1 (*molfraction*)	0.96	0.91†	0.96	0.93
Purity 2 (*molfraction*)	0.90*	0.91†	0.62	0.92
Purity 3 (*molfraction*)	0.90*	0.90*	0.60*	0.91†
Purity 4 (*molfraction*)	0.97	0.95	0.96	0.91†

‡ mixture of methanol, ethanol, *n*-propanol and *n*-butanol
* on or † near the lower bounds

Table 5.16: Summary of optimal results for case study III

among the vessels. Here, the optimal initial holdups of the vessels, $M_i(0)$, are treated as additional decision variables to be optimised (*total reflux variable holdup* policy in Table 5.10). The same quaternary mixture of methanol, ethanol, *n*-propanol and *n*-butanol is used here as an example with the bounds for the vessel holdups $M_i(0)$ set at [50, 500 *mol*] and governed by the constraint $\sum_{i=1}^{N_C} M_i(0) = 1000\ mol$. Again, it is assumed that the final holdups collected in all the vessels are desired products with equal selling price for all purities specified.

The base case in Table 5.16 considers an equimolar feed with the same purity specifi-

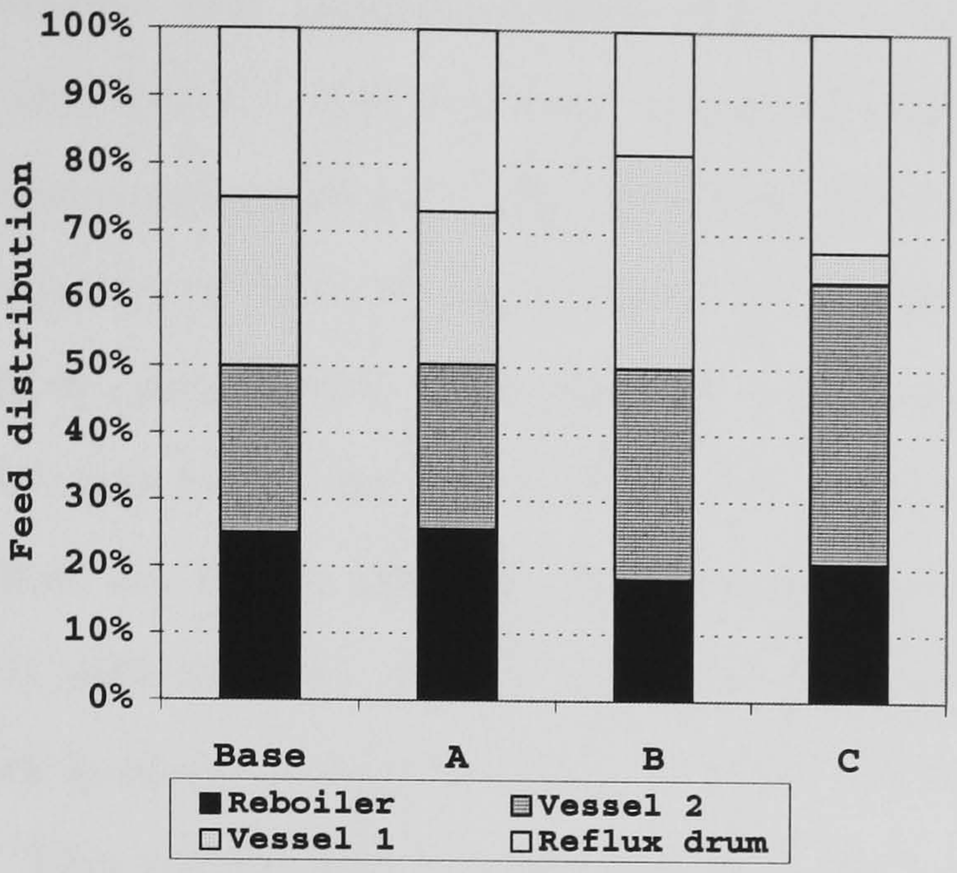


Figure 5.10: Optimal feed distribution for different separation scenarios

cation of 90 *mol*% for each product. The feed is split into four equal portions of 250 *mol*, each charged into the reflux drum, intermediate vessels (vessels 1 and 2) and reboiler, respectively. The optimised profit obtained is 242 721 $\$/yr$. When the vessel holdups are optimised in addition to the other decision variables (case A), the optimal performance index of the multivessel system is increased by 3% to 249 464 $\$/yr$. This is due to a slight redistribution of the holdups and a minor re-adjustment of the system configuration. Figure 5.10 illustrates how the holdups of vessel 1 and vessel 2, where the limiting intermediate components of ethanol and *n*-propanol are purified, have been reduced from 250 *mol* to 227 and 247 *mol*, respectively. Also, the total number of trays has been reduced by one from 35 to 34, and two trays in the top column section have been redistributed to the other two column sections. The combined effect causes the strain of separating the limiting intermediate components in the middle of the system to be reduced, and thus the reduction in both batch processing time and capital cost resulted in the slightly higher annual profit.

The results obtained in cases B and C highlight the fact that the distribution of the feed or product holdups must be optimally determined for different separation scenarios in order to achieve the highest economical efficiency. In case B, it can be seen that the

amount of product for a particular component is directly related to its specification, *i.e.* 318 *mol* for ethanol and *n*-propanol with their lower purity specifications of 60 *mol*% compared to 182 *mol* for methanol and *n*-butanol which has a tougher requirement of 95 *mol*%. When a non-equimolar mixture (0.30, 0.10, 0.40, 0.20 *molfraction*) is to be separated to a purity of 90 *mol*% each (case *C*), the optimal feed or product distribution also changes from the base case. Although this is fundamentally governed by the material balance which exists for a total reflux operation such as the one considered, the optimal distribution does not reflect the feed composition precisely, *i.e.* only 45 *mol* of ethanol-rich product is collected compared to its initial 100 *mol* in the feed whilst sightly more *n*-propanol-rich product is collected (423 *mol*) for the richest feed component (400 *mol* in the feed). This observation is consistent with the result in case *A* which is slightly different from the base case due to the characteristic (*i.e.* the limiting conditions caused by, for example, the relative difference in relative volatilities) of each component. In this case (case *C*), ethanol is both limiting and exists in low purity in the feed, hence a lower recovery. For *n*-propanol, even though it is also a limiting component, the higher recovery is due to the fact that it exists in the largest quantity in the feed.

5.8 Comparison of Regular and Multivessel Columns

There are several works available which compare the optimal *operation* of the novel multivessel system to that of the traditional regular column system (*e.g.* Hasebe *et al.*,1995; Hasebe *et al.*, 1997 and Furlonge *et al.*, 1999). Here, the optimal *design* of the two systems is compared concurrently with the optimal operation for the first time. The column section lengths and configuration, as well as the operation decision variables, are taken into account simultaneously to provide a more comprehensive and objective comparison.

The comparison in this work is based on the separation of 1000 *mol* equimolar feed of hydrocarbon mixtures as detailed in Table 5.17. In the regular column, the feed is charged wholly into the reboiler whilst in the multivessel system, the feed is equally distributed among the reboiler, two side vessels and reflux drum. To simplify the comparison, all feed mixtures are assumed to be of equal cost regardless of the type or number of components (1 $/kmol$). The purity constraints are set at 90 *mol*% for all products which also have

Case	Hydrocarbon Feed Mixture	Feed Composition
A	pentane, hexane, heptane	0.33, 0.33, 0.33
B	pentane, heptane, nonane	0.33, 0.33, 0.33
C	pentane, hexane, heptane, octane	0.25, 0.25, 0.25, 0.25
D	pentane, hexane, heptane, octane, nonane	0.20, 0.20, 0.20, 0.20, 0.20

Table 5.17: Summary of optimisation cases considered for regular and multivessel columns comparison

the same selling price of 35 $\$/kmol$. Both the regular column and the multivessel system are assumed to have the same set-up time of 1800 s and cost correlation coefficients in Equation 5.4 of 1500, 9500 and 180 for K_1, K_2 and K_3, respectively (Logsdon *et al.*, 1990).

For the multivessel system, the decision variables and bounds are the number of trays in each column section, N_i [2, 20], the condenser vapour load, V [0.16, 1.6 mol/s], and the total reflux time, t_f [100, 3000 s]. In the regular column, the first period of operation consists of total reflux until the purity of the most volatile component reaches the specification of 90 $mol\%$. The decision variables optimised include the total number of trays, N [2, 60], the piecewise-constant internal reflux ratio profile, $R(t_i)$ [0.5, 1.0], and the duration of each time interval after the total reflux period, t_i [100, 2000 s], whereby each of the two main product cuts is separated by a possible offcut period, t_c [0, 1000 s] (*i.e.* for a separation involving a mixture with N_C components, there are $N_C - 1$ product withdrawal periods plus $N_C - 1$ offcut periods).

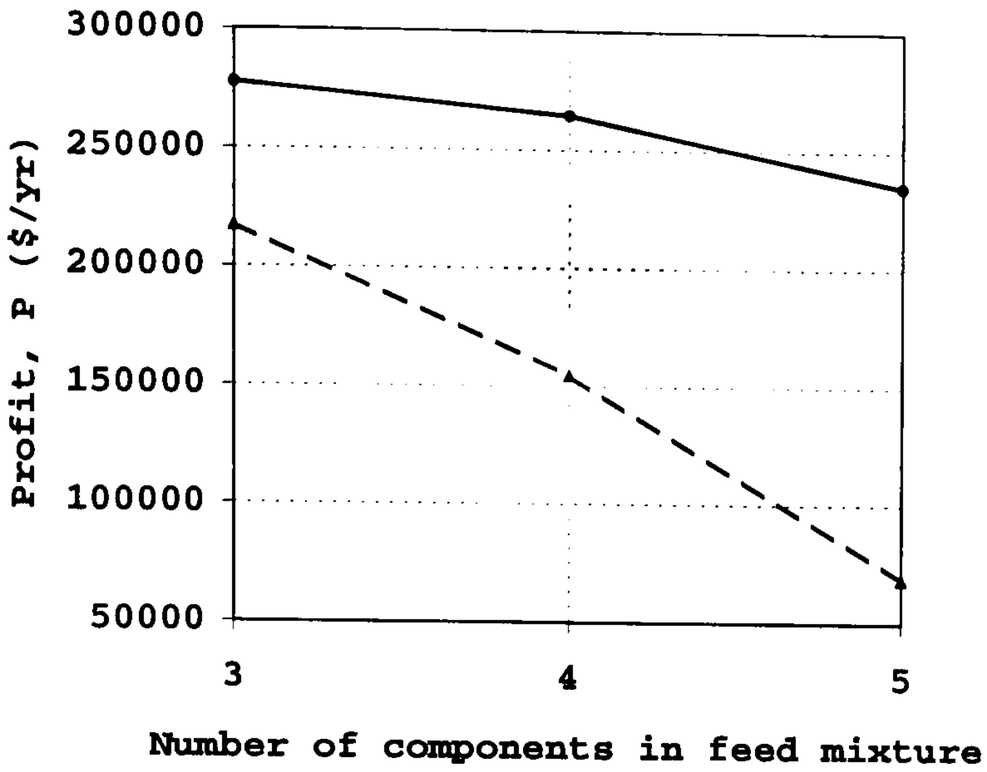
The results in Table 5.18 shows that the use of a multivessel system is significantly more profitable than that of a regular column even for the simplest case of a ternary mixture (case A). The multivessel system gave a 28% higher annual profit, *i.e.* 277 672 compared to 217 229 $\$/yr$ for the regular column. The multivessel system requires two column sections of 8 and 9 trays each, and fewer total number of trays than the regular column (17 compared to 20, respectively[3]). Furthermore, the multivessel system is able to reduce the batch processing time by about a quarter that of a regular column (1787 to 1350 s), which, for a 24 hr production plant, means a higher number of batches can be processed

[3]The optimal profit achieved for the regular column with 17 trays is 209 922 $\$/yr$. The revenue, capital cost and operating cost are 271 673, 60 817 and 933 $\$/yr$, respectively.

Distillation System	Regular System				Multivessel System			
Feed mixtures	*A*	*B*	*C*	*D*	*A*	*B*	*C*	D
Column section configuration	-	-	-	-	8:9	5:6	6:11:10	6:9:14:12
Total number of stages	20	5	15	12	17	11	27	41
Profit, P ($/yr$)	217 229	293 347	154 552	68 526	277 672	318 617	264 596	235 044
Batch time, t_f (s)	1787	1274	2584	3783	1350	1100	1300	1400
Vapour load, (mol/s)	1.40	1.40	1.57	1.60	1.48	1.41	1.60	1.56
Revenue ($/yr)	282 536	333 681	215 919	125 623	340 403	369 748	345 893	335 084
Operating cost ($/yr)	907	907	1011	1037	959	907	1037	1011
Capital cost ($/yr)	64 400	39 426	60 355	56 061	61 772	50 224	80 260	99 029
Constraints ($molfraction$)								
Purity 1	0.94	0.95	0.96	0.99	0.97	0.98	0.97	0.98
Purity 2	0.90*	0.93	0.94	0.92	0.90*	0.91†	0.91†	0.91†
Purity 3	0.91†	0.91†	0.90*	0.90*	0.95	0.95	0.90*	0.91†
Purity 4	-	-	0.93	0.94	-	-	0.95	0.90*
Purity 5	-	-	-	0.95	-	-	-	0.96

Purity constraints (0.90, 0.90, 0.90, 0.90)
* on or † near the lower bounds

Table 5.18: Summary of optimal results for both regular and multivessel columns for different feed mixtures



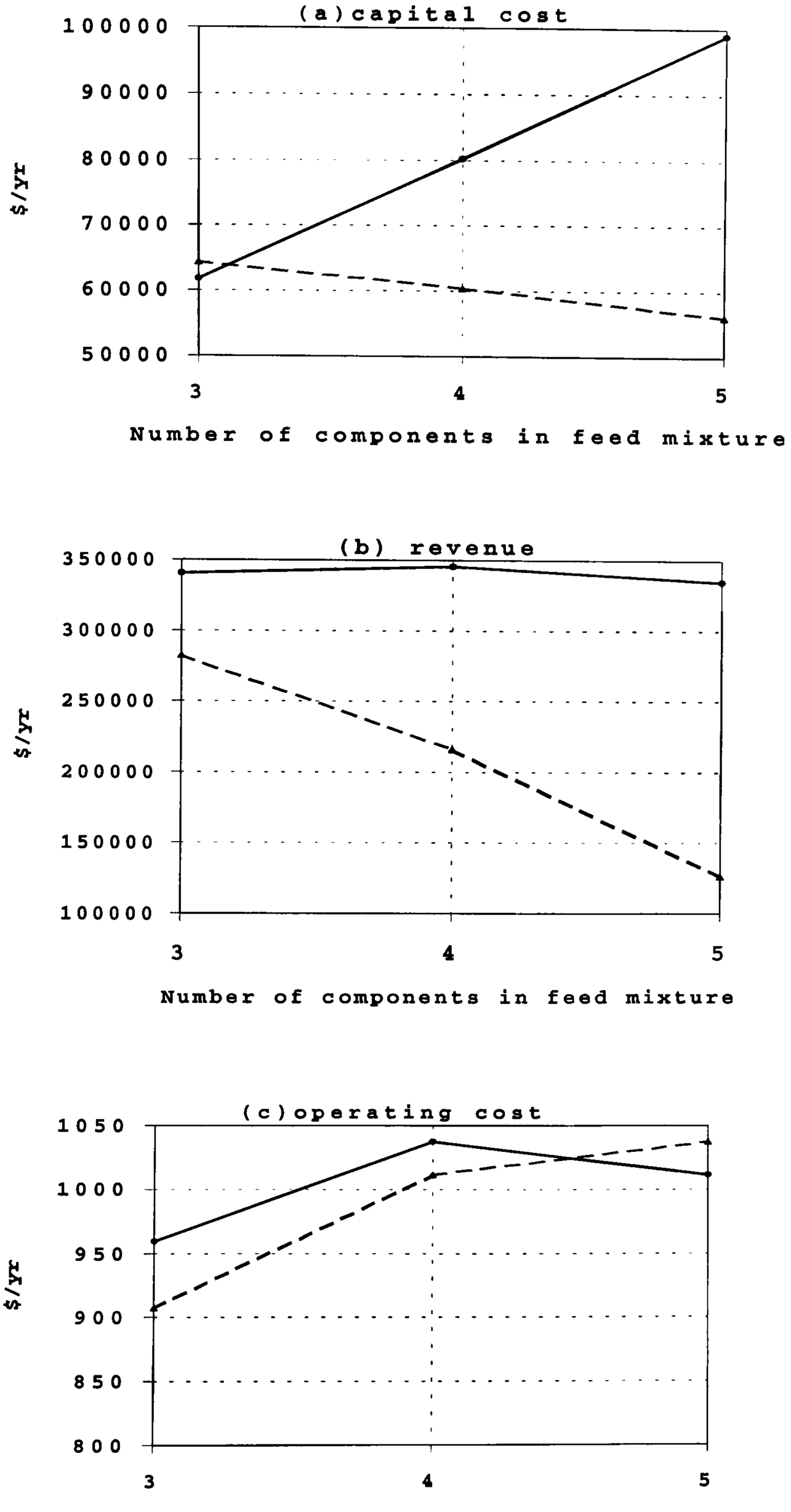
— multivessel system; - - - regular column

Figure 5.11: Profitability of regular and multivessel systems for different separation mixtures

per year. The combination of lower capital investment incurred by the multivessel system (61 772 compared to 64 400 $\$/yr$) and considerable increase in revenue (340 403 compared to 282 536 $\$/yr$) resulted in a net increase in profitability.

As expected, the number of trays required to separate an easier separation (case B) is fewer than what would be required for a harder separation (case A). The regular column needs 15 trays fewer whilst the multivessel system needs 6 fewer (configuration 5:6 instead of 8:9 in case A). Thus, both regular column and multivessel system optimally designed for the easier separation, incur lower capital costs. In terms of optimal operation, both systems have lower batch processing time and higher revenue. Although, as a result, both systems show higher profits for the easier separation, the increase is greater (35%) for the regular column than for the multivessel system (15%). This implies that, in other words, the economical benefit of using the multivessel system in favour of the conventional batch rectifier becomes more prominent when dealing with harder separations.

The results in Table 5.18 also shows that the economical benefit of adopting the multivessel system over the regular column becomes more apparent for separating mixtures with



—— multivessel system; - - - regular column

Figure 5.12: Cost index of regular and multivessel systems for different separation mixtures

higher number of components (compare cases A with C and D). In this case study, the multivessel system increasingly out performs the traditional regular column by about 30, 70 and 240% in terms of profit for the separation of a ternary, quaternary and five components hydrocarbon mixture, respectively. Although the profitability of both systems would diminish when used to separate mixtures with greater number of components, the performance index (profitability) of the multivessel system decreases only 5 and 11% compared to the higher decrement of 29 and 56% for the regular column (Figure 5.11).

This can be explained by considering the contribution of the individual costs as shown in Figure 5.12. For the multivessel system, the number of column sections and the total number of trays increase with the number of components (17, 27 and 41 trays of 8:9, 6:11:10 and 6:9:14:12 configurations, respectively). Conversely, the optimised regular column designs display an inverse trend whereby the optimal number of trays decrease (20 to 12 trays [4]) as the number of components to be separated increase. This translate into higher capital investment for the multivessel system or, in other words, the multivessel system becomes relatively more expensive compared to the regular column (Figure 5.12a). This economic aspect is thus the main drawback of the multivessel system. However, the main advantage of the multivessel system is its ability to maintain its revenue (Figure 5.12b) compared to the revenue of the regular column which deteriorates significantly as the number of components increase. This highlights the advantageous feature of the multivessel system which performs simultaneous separation regardless of the number of components in the mixture (see similar batch times for the multivessel system in Table 5.18). In contrast, the operation in the batch rectifier becomes more time consuming (1787 to 3783 s) as the number of product and offcuts increases.

Note that both systems operate optimally at high condenser vapour load, V. For a specified amount of distillate, the batch processing time is inversely proportional to V. Since the capital and utility costs increase with V by an economic factor of less than 1, columns would tend to have high vapour loading to favour higher production rate in the expense of capital and utility costs.

[4] As the number of operation intervals increase, the economical impetus towards reducing capital cost rather than increasing the revenue (since the greater number of offcut periods would not contribute to higher product yield) becomes more prominent.

Also note that in all the cases, only the minimum product purity was achieved for at least one or more of the components (on or close [5] to the lower bounds), indicating the governing task(s) for that particular optimal design and operation.

5.9 Conclusions

5.9.1 Optimal Batch Distillation System

In this chapter, the simultaneous optimal design and operating policies of the batch distillation system has been presented, for regular column with single and multiple separation duties, as well as for the novel multivessel system. The problem consists of a nonlinear annualised profit objective function that encapsulates the various trade-offs between the design and control decision variables, between the production revenue, capital and utility costs as well as between the different mixtures. By considering a comprehensive economics performance index which takes into account all capital and operational cost trade-offs, instead of focusing on a specific performance criterion such as batch time or energy efficiency, the benefit of the multivessel system can be elicited and compared to the regular column more conclusively.

Generally, this conceptual study indicates that the annual profitability achievable by adopting a multivessel system can be more than twice that of the traditional batch rectifier. When a mixture with many components is to be separated and for relatively more difficult separations, the economical benefit of using the multivessel system becomes more prominent.

5.9.2 Optimal Design Practice

The case studies highlighted the importance of considering all the design and operational degrees of freedom available in order to gain a comprehensive economical insight into the

[5] Due to the stochastic nature of the genetic algorithm, the accuracy of the final constraint values were dependent on the convergence setting. Therefore, before decimal round-off, some of the purities achieved could be reasonably interpreted as being on-specification, rather than distinctly overpurified.

batch distillation process as optimal column design and operating policies depend highly on the design scenario, *i.e.* production time, capital costs, mixture characteristics, process allocation *etc.* Furthermore, it has been shown that the design of the multivessel column section configuration, as well as the feed and product distribution, is strongly influenced by the separation duty, *i.e.* feed composition, relative volatilities and product specification. These decision variables should be optimised, and as a result of the optimisation, significant enhancement in the system performance can be achieved. The case studies in this work demonstrated significant reduction in batch time and energy consumption. This, in turn, means an increase in the number of batches per production period and a cut down on production cost per operation.

As a further note, in terms of operation, the flexibility of the multivessel system allows additional degrees of freedom in terms of varying vessel holdups during the separation process. Several optimal control studies have indicated that the performance of the multivessel system can be improved by allowing the vessel holdups to be optimised (11 to 43% in production rate, 12% in batch time and 21% in mean energy consumption have been claimed by Hasebe *et al.*, 1997; Noda *et al.*, 2000 and Furlonge *et al.*, 1999, respectively). However, in practice, the implementation of the optimal holdup policy, although feasible, involved a much more complicated on-line control system (*e.g.* such as that proposed by Noda *et al.*, 2000) than a simpler level controller needed for maintaining the holdup. This trade-off suggests that further comparative study should be conducted by the design engineer in order to evaluate whether a more complicated operating policy and its associated control system are indeed worthwhile; if the improvement is small, perhaps the constant holdup policy using level controller or the temperature controller proposed by Wittgens *et al.* (1996) would be more attractive.

5.9.3 Optimal Design Tool

The stochastic optimisation approach, genetic algorithm-penalty function framework, used in this work to solve the mixed integer dynamic optimisation problem was found to be a robust and viable way to solve the batch design problem and can be used with a range of models with different complexity. The proposed algorithm is found to be robust compared to other deterministic approaches as it does not rely heavily on information

from previous iterations for the search direction or on the topography of the search space. The genetic algorithm-based methodology is also more robust in absorbing infeasible solutions. However, the genetic algorithm parameters have to be selected appropriately in order to fulfil the problem constraints as well as to avoid premature convergence.

Chapter 6

Optimal Configuration Design of Batch Distillation

In this chapter, the automated determination of optimal batch distillation configuration, design and operation for a given separation duty is presented. The configuration design approach is based on a mixed integer dynamic optimisation formulation similar to that posed in chapter 5, but with additional discrete variables for configuration selection, which is again solved using the genetic algorithm-penalty function approach. The key features of utilising rigorous models and a profitability index are retained to obtain an overall optimal batch distillation system. The feasibility of the approach is demonstrated for both binary separation and multicomponent separation scenarios. In the binary separation case study, the effect of feed composition for different binary mixtures on the optimal configuration, i.e. regular versus inverted columns, is investigated. Generally, the regular column was found to be more profitable for feeds with a high fraction of the light component whilst the inverted column is optimal for heavier feeds. However, the optimality of a particular configuration over another is case study specific, depending on, for example, different feed mixtures. In the multicomponent separation case study, the results obtained reiterated the superiority of the multivessel configuration over the regular and inverted configurations as highlighted in chapter 5.

6.1 Introduction and Aims of This Work

Traditionally, the batch distillation configuration design problem is seldom posed because the design engineer typically starts off the batch distillation design process with a batch rectifier, *i.e.* with a regular column configuration, in mind. However, in recent years, motivated by the drive for greater process performance and efficiency, the fundamental configuration of the batch distillation process itself is being exploited, resulting in the emergence of new unconventional columns such as the inverted, middle vessel and multivessel columns. As a result, the design engineer is faced with the challenging task of determining the best configuration, design and operation for a given distillation duty.

The performance of alternative batch distillation configurations has been actively researched through many comparative studies where the process operation in different configurations are compared either through parametric simulation or optimal control studies based on various performance indices (*i.e.* Chiotti and Iribarren, 1991; Mujtaba and Macchietto, 1994; Davidyan *et al.*, 1994; Meski and Morari, 1995; Hasebe *et al.*, 1996; Sørensen and Skogestad, 1996; Noda *et al.*, 1999; Furlonge *et al.*, 1999 and Ruiz Ahón and de Medeiros, 2001) (details in chapter 2.4). Recently, Warter *et al.* (2002) compared the practicality of the competing configurations by conducting a pilot plant scale experimental study on the operations of the middle vessel and regular columns. In chapter 5, the simultaneous optimal design and operation of the multivessel and regular columns were compared for the first time, which provided a fairer and more conclusive comparison for batch distillation column configuration selection.

In their effort to aid batch distillation column configuration screening by means of providing insights into the behaviour of different column configurations, Kim and Diwekar (2000) performed the most comprehensive comparative studies to date where the performance of the column configurations, *i.e.* the regular, inverted and middle vesssel columns, based on various performance indices, were obtained via parametric simulations using statistical sampling of design and operation variables within specificed ranges. Due to the high number of simulations conducted in the study, a simplified model that assumes zero holdup in the column section, constant molal overflow and constant relative volatility

was used. Through an example, the work also demonstrated how the screening of column configurations could be elicited through a sort of heuristic analysis of the trade-off among the performances indices of the competing column configurations. Despite the vast quantity of data obtained, which in turn provided many insights into the column behaviour, ultimately any guideline drawn up were limited by the range of the sampled parameters and could not serve as a conclusive mean for batch distillation column configuration determination for other separation scenario cases.

As the number of possible batch distillation column configurations proposed in the literature continues to increase, it becomes important to be able to choose the best one among them in an automatic manner without the need for manually considering each one of them separately. The aim of this work is to propose a configuration design methodology based on a mixed discrete dynamic optimisation formulation that can automatically generate the optimal configuration, design and operation for a given separation duty. Again, the use of a rigorous model and an overall profitability index are the key characteristics of this study. In the next section, the formulation of the optimisation problem is presented followed by the description of the model and the optimisation solution technique. The feasibility of the approach is demonstrated for a number of case studies which include several binary separation scenarios and a multicomponent separation scenario. In the binary separation case studies, the effect of feed composition on the optimal configuration is also investigated.

6.2 The Batch Distillation Configuration Design Problem: Optimisation Formulation

The batch distillation configuration problem is more complicated than the decision-making involved in the batch distillation design trade-off problem illustrated in Figure 5.1 (chapter 5). That is, in addition to determining the set of design and operation variables which gives the optimal trade-off in capital and operational costs, the problem here is expanded to also explore configurational variables in an effort to further increase the profitability of a particular batch distillation process. Thus, the overall batch distillation can be based on the solution of a mixed integer dynamic optimisation problem. with a

profitability objective function similar to that defined in chapter 5.2.2.

In batch distillation, the configuration of the system is primarily characterised by the location of the initial feed charge and the location of product withdrawal, thus giving rise to alternative column configurations (Figure 6.1). There is also the choice of the number of column sections and holdup vessels in the case of multicomponent distillation, however, this configurational degree of freedom is proportional to the number of components, N_C, as discussed in chapter 5.7.2. Conceptually, the determination of the optimal configuration for a particular separation duty can be tackled by optimisation in the continuous domain, *i.e.* by optimising the initial feed holdup distribution, $M_j(t_0)$, and the reflux ratio profiles, $R_j(t_i)$, for all control intervals, Δt_i, at all potential output locations, j, on a dynamic superstructure model. The maximum and minimum bounds of these continuous variables, $M_j(t_0) \in [0, H_{feed}]$ and $R_j(t_i) \in [0, 1]$, correspond to the distinct column configurations known as the regular, inverted and multivessel columns as illustrated in Figure 6.1. However, the final solution would in all probability lie within the continuous range in between the bounds, and thus, despite offering the highest possible degrees of freedom, result in none of the straightforward distinct column configurations (Figure 6.1) but in less practical configurations with complicated implementation.

To obtain distinct structures, the configurational degrees of freedom must be treated in a discrete manner. For example, discrete decisions may be incorporated into the mathematical model as a set of time-invariant binary variables $y \in \{0, 1\}$, each representing the existence or non-existence of a particular connecting stream or a process unit (*e.g.* side vessels), or part thereof (*e.g.* accumulators at a particular task interval). Optimal streams between process units can easily be incorporated into the superstructure model by algebraic equations (see Sharif *et al.*, 1998). The development of the dynamic superstructure model is by no means a trivial task because it needs to encompass all the different options available. Furthermore, the mathematical superstructure model formulation may have a significant impact on the robustness and efficiency of the numerical integration and optimisation solution techniques. For these reasons, to quote Oldenburg *et al.* (2002) - "considerable effort may be spent in defining ways to build superstructure models that are generic to the extent possible and provide favourable properties in con-

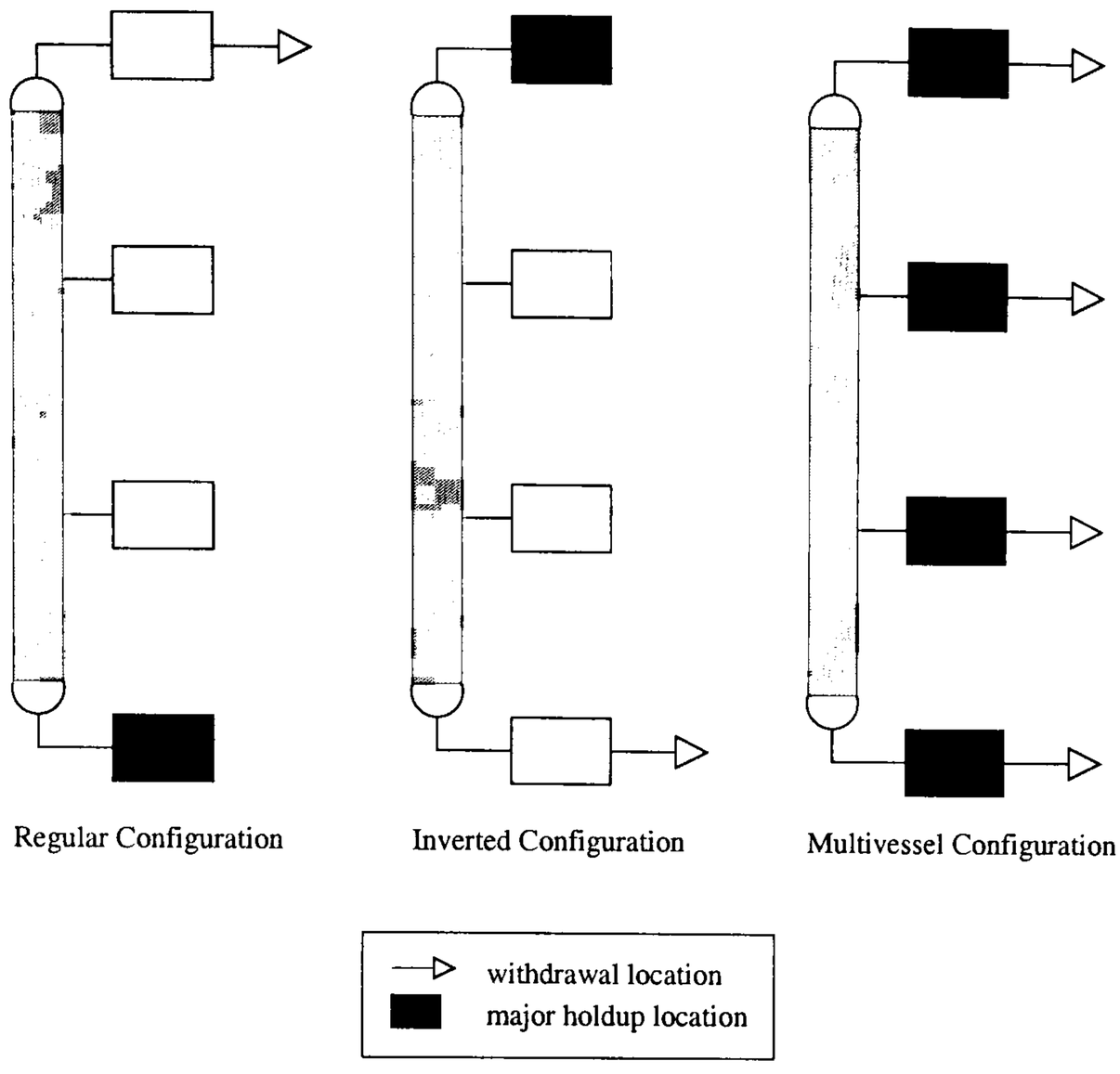


Figure 6.1: Schematic of different batch distillation column configurations

junction with especially designed numerical solution algorithms". In this work, the need for a superstructure model is avoided (see below and section 6.3).

In this work, the discrete decision is characterised by disjunctions, where a disjunction represents the discrete decision as to whether the batch distillation process is to be operated in the regular, inverted or multivessel mode. For example, this could be achieved by using the boolean type variable, $Y \in \{Regular,\ Inverted,\ Multivessel^{1}\}$, where a direct relationship is pre-established between the discrete boolean variable, Y, and the grouped configurational variables and conditions, *e.g.* top and bottom streams and initial holdups conditions:

$$\begin{bmatrix} Y = \{Regular\} \\ M_{bottom}(t_0) = H_{feed} \\ R_{LB} \leq R_{top}(t_i) \leq R_{UB} \\ R_{bottom} = 1 \end{bmatrix} \vee \begin{bmatrix} Y = \{Inverted\} \\ M_{top}(t_0) = H_{feed} \\ R_{top} = 1 \\ R_{LB} \leq R_{bottom}(t_i) \leq R_{UB} \end{bmatrix} \vee \begin{bmatrix} Y = \{Multivessel\} \\ M_i(t_0) = H_{feed}/N_C \\ R_j = 1 \\ \forall j \in \{top, sides, bottom\} \end{bmatrix} \tag{6.1}$$

[1] *Total reflux constant holdup* policy considered, $R_j = 1$ (see chapter 5.7.2).

In summary, the approach to batch distillation design in this work is based on a mixed integer dynamic optimisation problem, where the discrete aspect of the problem formulation includes the integer variable associated with the number of trays, N, and the logical boolean variable, Y, for the selection of distinct column configurations, in addition to the continuous variables like the time invariant boilup rate, V, and the reflux ratio profile, $R(t)$.

In mathematical terms, the optimisation problem is posed as follow:

$$max_{Y,u_d,u_o}\ P \tag{6.2}$$

subject to

$$f\left(\dot{x}, x, t, u\right) = 0 \tag{6.3}$$

$$x_i(t_f) \geq x_i^{\min} \qquad \forall\, i = 1, .., N_C \tag{6.4}$$

$$Y \in \{Regular, Inverted, Multivessel\} \tag{6.5}$$

$$u_d^{\min} \leq u_d \leq u_d^{\max} \tag{6.6}$$

$$u_o^{\min} \leq u_o \leq u_o^{\max} \tag{6.7}$$

where the objective is to maximise the annual profit function, P (defined in chapter 5.2.2), u_d is the set of design variables (*i.e.* $u_d = \{N\}$), u_o the set of operating control variables (*i.e.* $u_o = \{V, R(t_i)\}$), Equation 6.3 represents the batch distillation model, where x is the vector of state variables, u the vector of control variables and t is the process time.

6.3 Solution Methodology

Recently, Oldenburg *et al.* (2002) proposed a deterministic gradient-based solution method to solve a mixed logic dynamic optimisation (MLDO) problem for the separation of a ternary mixture using two sequential batch distillation units operated either in the regular or inverted mode. Note that the discrete aspect of their optimisation problem consisted only of boolean variables, namely $Y \in \{True, False\}$ signifying regular and inverted configurations, respectively. The number of trays in each column were specified *a priori*. Hence, the problem is of the MLDO type which did not contain any integer variables. The tailored logic-based solution approach proposed in their study was based on the familiar decomposition strategy which consists of a primal subproblem and a master subproblem. The primal problem was formed as an ordinary dynamic optimisation problem with the conditions and constraints in those disjunctions for which the corresponding boolean variable, Y, is fixed as $True$, whilst the variables and constraints related to the other disjunctions were removed from the primal subproblem. The master problem was then obtained by linearising the objective function and constraints at the optimal solution of the primal subproblem and tranforming it into a mixed integer linear programming (MILP) problem by a reformulation using Big-M constraints (Yeomans and Grossmann, 2000) which is then solved using a branch-and-bound method. However, the study did not tackle the design issue, *i.e.* optimal number of trays.

In this work, the mixed integer dynamic optimisation problem consists of continuous (*e.g.* boilup rate and reflux ratio profile), integer (*e.g.* the number of stages) and logical (*e.g.* column configuration) variables. The batch distillation DAE model and the profitability performance index are nonlinear with a nonconvex solution space. As in the work in chapter 5, here, the optimisation is solved by the stochastic method of steady state genetic algorithm-penalty function framework (see chapter 3.6). One of the key advantage of this approach is that the framework can easily accommodate the continuous, integer and logical variables within its genome set without any modification to the adaptive search procedure (see chapter 3.7.2). In terms of implementation, the framework can also be applied to handle the logical disjunctions in a simple manner whereby the genetic algorithm program performs a directed call to the specific model file that contains

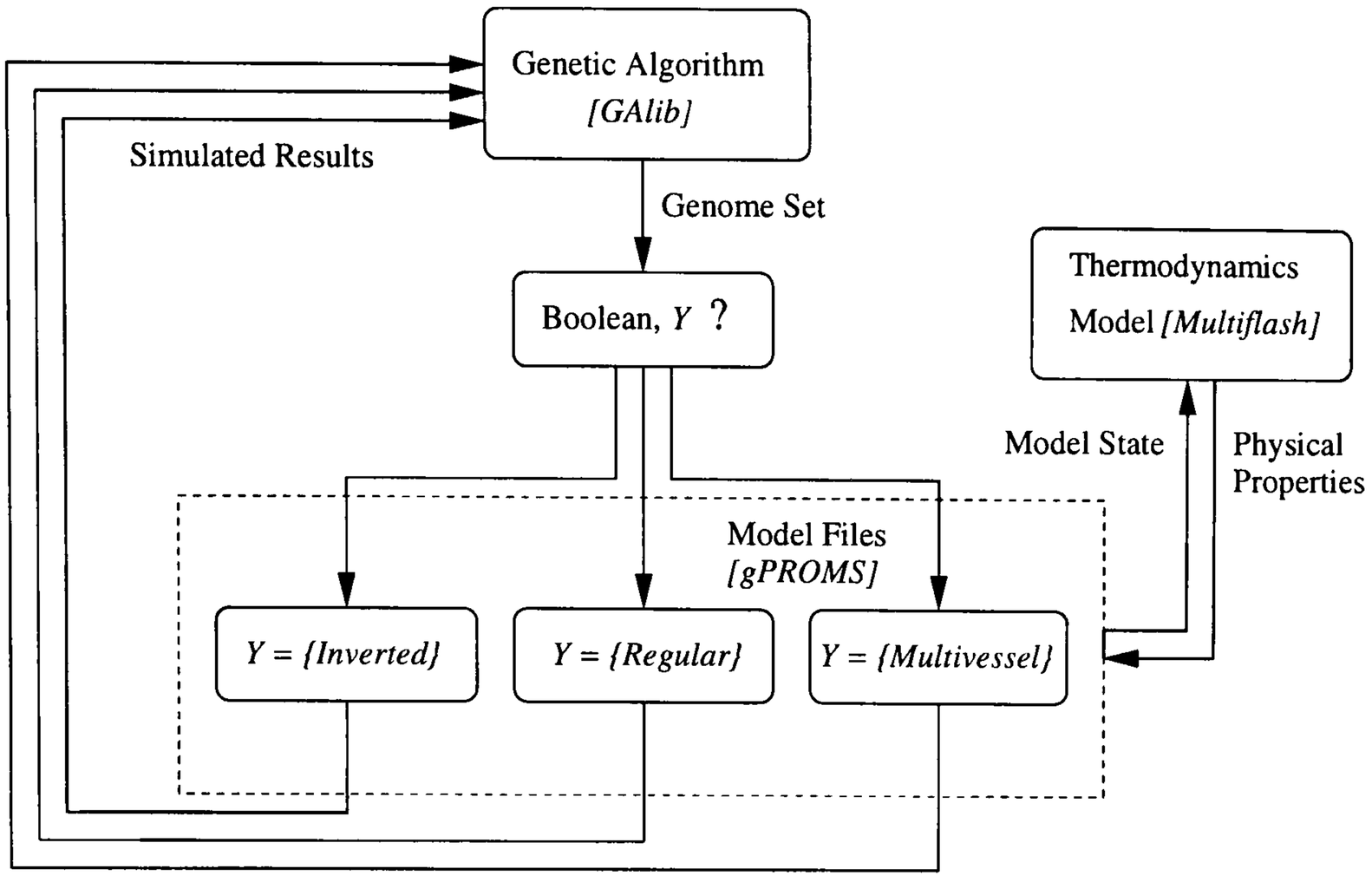


Figure 6.2: Schematic diagram of the batch distillation design optimisation implementation

the relevent conditions and constraints (Equation 6.1) that correspond to a particular genome's boolean variable, Y, *i.e.* regular, inverted or multivessel models (Figure 6.2). Hence, the need to develop a superstructure model is avoided.

6.4 Mathematical Models

The stochastic optimisation framework proposed in this study, can be utilised in conjunction with any level of model abstraction and the choice is dependent on the level of detail or accuracy required versus the computational cost. Although many previous batch distillation studies commonly utilised simple and semi-rigorous models, the batch distillation design work here is conducted using a rigorous model.

The models are constructed using the *gPROMS* modelling tool (Process Systems Enterprise Ltd., 2000). The model equations are presented in Appendix A. Thermophysical properties (including density, enthalpy and fugacity) required in the rigorous model are calculated using the *Multiflash* (Infochem Computer Services Ltd., 2000) physical properties package interfaced to *gPROMS*. The Soave-Redlich-Kwong (SRK) Equation of State is used for both the vapour and liquid phases.

Available annual production time, T_A $(h/year)$	8760
Batch set-up time, t_s (s)	1800
Operating pressure, P (Pa)	101325
Major holdup (batch size), H_{feed} (mol)	3000
Minor holdup, M_{rd} or M_{reb} (mol)	45
Tray holdup, H_{tray} (mol)	4.5
Feed composition, $x_{1,feed}$, $x_{2,feed}$ $(molfraction)$	
Cyclohexane, toluene	varied
Product purity specifications, $(molfraction)$	
First product, $x_1(t_f)$	0.99 of cyclohexane
Second product, $x_2(t_f)$	0.99 of toulene
Cost, C_i $(\$/mol)$	
Cyclohexane, C_1	0.034
Toluene, C_2	0.034
Feed, C_{feed}	0.002

Table 6.1: Specifications and operating conditions for the binary separation case study

6.5 Optimal Configuration for Binary Separation

In this section, the configurational design of optimal batch distillation processes is investigated for the case of binary mixture separation. Previous works, *e.g.* by Sørensen and Skogestad (1996), have indicated that the optimal configuration, *i.e.* either rectification or stripping mode, is dependent on the separation duty, for example, the composition of the feed. In this study, the optimal batch distillation configuration, column size and operation conditions, *i.e.* constant boilup rate and reflux ratio profiles, for a given feed composition and product purity requirement will be automatically generated via an optimisation program.

Separation of a binary mixture of cyclohexane and toluene is considered in this case study, and the effect of different feed compositions on the optimal solution is investigated. A summary of the column specifications and operating conditions is given in Table 6.1.

Decision Variables	Bounds
Y	{Regular , Inverted}
N	[4 , 30]
V $(kmol/hr)$	[0.6 , 6.0]
$R(t_{2,3})$	[0.4 , 1.0]
Δt_1 (s)	[0, 2000]
Δt_2 (s)	[0 , 10000]
Δt_3 (s)	until purity achieved

Table 6.2: Decision variables bounds for the binary separation case study

The 3000 *mol* major holdup corresponds to the batch size, and the decision on its initial location, *i.e.* either in the reflux drum or reboiler pot, is optimised through the boolean variable, Y. Accordingly, the minor holdup occupies the vessel at the opposite end of the column. The batch distillation operation is separated into three task intervals, starting with a total reflux period followed by a first product withdrawal period and finally, an offcut period to purify the other product. Again, whether cyclohexane or toluene is withdrawn first, from the top or bottom of the column, respectively, depends on the disjunction represented by Y. The minimum product purity specifications are set at 99.0 *mol%* for both cyclohxane and toluene. Similar to the case study in the previous chapter, the cost coefficients K_1, K_2 and K_3 of the objective function were set to the values of 1500, 9500 and 180, respectively (chapter 5).

The optimised decision variables are the column configuration, Y, number of trays, N, column constant boilup rate, V, and reflux ratio profile, *i.e.* the values of the normalised reflux ratio, $R(t_i)$ (except in the first task interval where $R(t_1)$ is set to 1 for total reflux), and the durations of each of the first two task intervals, Δt_1 and Δt_2. In the final task interval, the duration, Δt_3, is set corresponding to the minimum time needed to purify the remaining component (in either the reboiler pot or the reflux drum) to its required purity of 99.0 *mol%* (*i.e.* set as a termination condition during simulation). The bounds for each variable are given in Table 6.2.

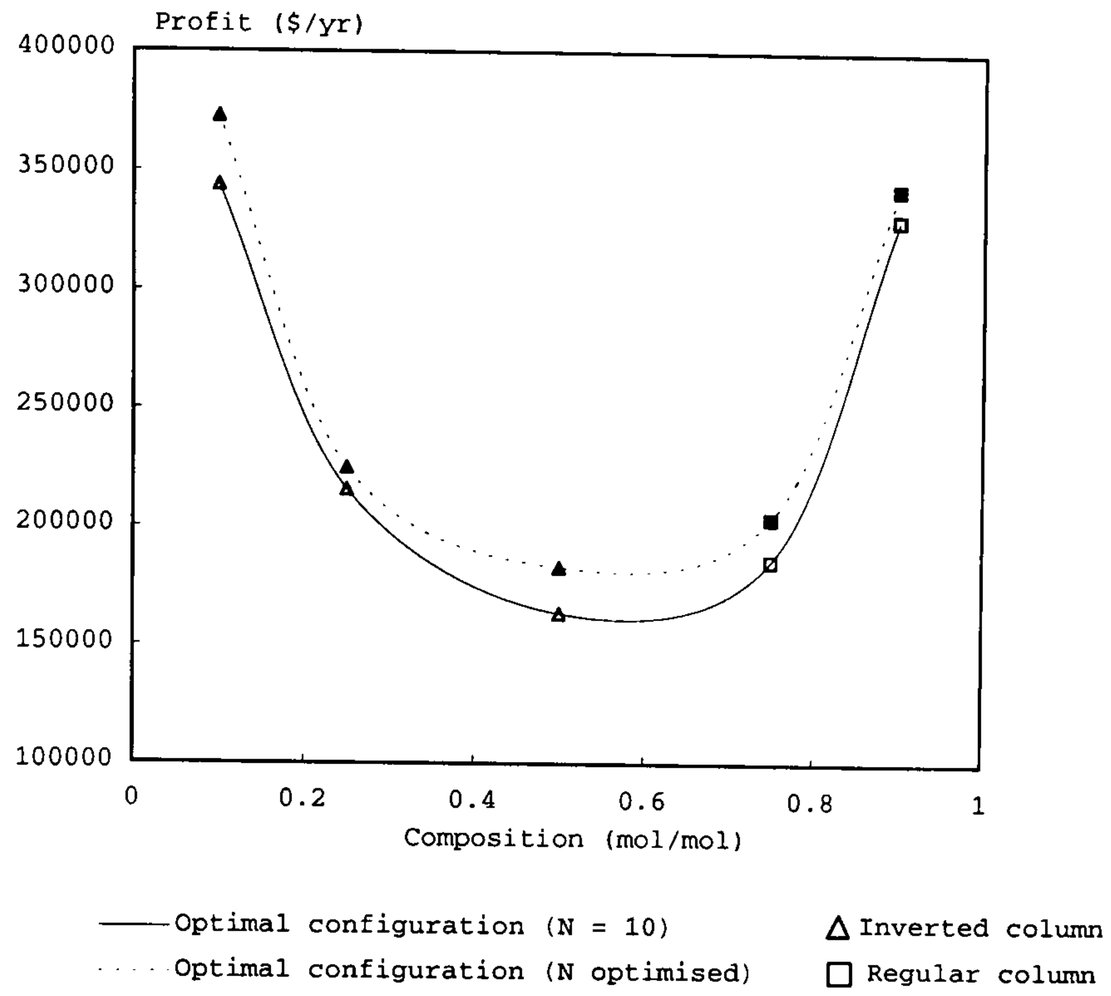
	Fixed Column Size ($N = 10$)		Optimal Column Size		
Feed Composition ($molfraction$)	Optimal Configuration	Profit ($/yr$)	Optimal Configuration	Optimal Size, N	Profit ($/yr$)
0.90, 0.10	Regular	330 063	Regular	22	342 989
0.75, 0.25	Regular	185 963	Regular	21	203 953
0.50, 0.50	Inverted	163 602	Inverted	16	183 078
0.25, 0.75	Inverted	215 719	Inverted	20	224 953
0.10, 0.90	Inverted	343 999	Inverted	23	372 788

Table 6.3: Summary of optimal results for the separation of the cyclohexane-toluene binary mixture

6.5.1 Case I: Effect of Different Feed Compositions

The optimal results for the cases of different feed compositions are summarised in Table 6.3. The results are illustrated in Figure 6.3 which highlights the optimal configurations and their associated objective function values for a range of feed compositions. The shape of the optimal profitability curve indicates that feeds with a relatively higher fraction of either component, *i.e.* towards both ends of the feed composition, achieved higher profitability. The figure clearly suggests that it is economically beneficial to consider alternative column configurations according to specific separation scenario. In this case study for example, the optimal column configuration varies, depending on the feed compositions. For a mixture with a higher fraction of the heavy component, the inverted column gave a higher profitability than the regular column, but the opposite is true for a mixture with a higher fraction of the light component.

The results are in agreement with the findings of Sørensen and Skogestad (1996) who proposed that the reason why the inverted column configuration is better than the regular column with small amounts of light component is that, when this light component is to be removed from the column at high purity, a very high reflux ratio must be used in order to meet the product specification in the conventional rectification mode. For

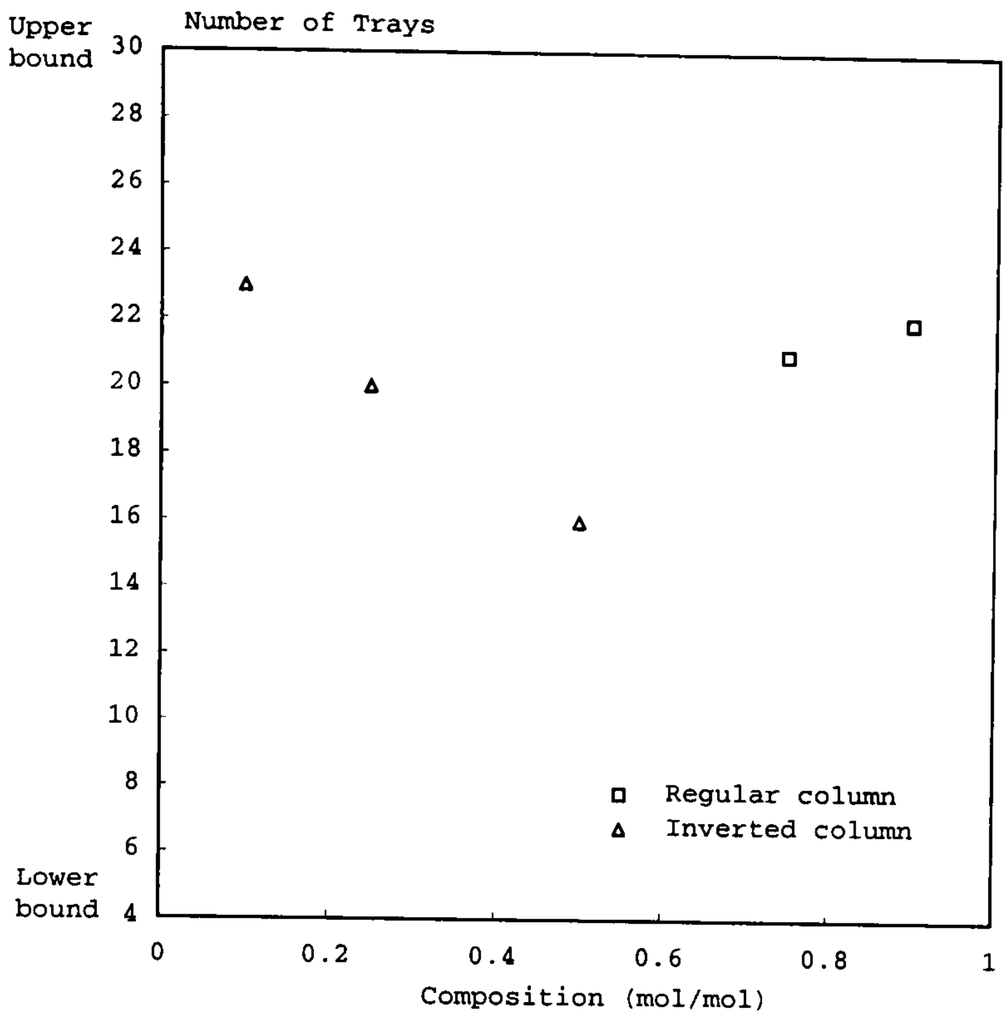


Cyclohexane-toluene mixture

Figure 6.3: Optimal profits and configurations for different feed compositions

the inverted configuration, however, a large amount of heavy component is withdrawn very quickly from the bottom using a low reboil ratio, thus resulting in a relatively lower operating time and higher profit value.

Figure 6.3 also displays the results for the cases where the column size, *i.e* number of trays, is fixed ($N = 10$) and where it is optimised. As expected, the profits were increased in all cases when the number of trays is optimised. The trend of the curve for the case where N is optimised matches the one obtained for fixed number of tray in terms of shape as well as the optimal configuration obtained for a particular feed composition. In Figure 6.4, it can be observed that the optimal number of trays for all the cases are above the previously fixed 10 trays, indicating that a favourable economic trade-off have been made whereby the performance gained from a bigger column, *i.e.* lower batch processing time, is worth the higher capital cost incurred. However, the magnitude of increase in the number of trays is not uniform across the cases, but appeared to establish a pattern. The optimal number of trays were 22 and 23 for feeds with 0.90 $molfraction$ of either components, and slightly lower at 20 and 21 trays for feeds with a 0.75 $molfraction$



Cyclohexane-toluene mixture

Figure 6.4: Optimal column sizes and configurations for different feed compositions

(refer Table 6.3). The lowest increment in the optimal number of trays occurred for the equimolar feed. This observation can be explained by the fact that the opportunity to increase performance through minimising reboil or reflux ratios, *i.e.* higher production per unit time or lower batch time per fixed product volume, is greater for the separation of a mixture with a more asymmetrical molar ratio than for an equimolar mixture.

To investigate the accuracy of the batch distillation design, the optimal results for fixed column configuration and column size ($N = 10$) were obtained for similar set of feed compositions (Table 6.4). The results are plotted in Figure 6.5 with the optimal configuration curve (dashed line) of Figure 6.3 (for $N = 10$) superimposed on it. For both the fixed regular and inverted column cases, it is demonstrated that the profitability curves were influenced to an unique extent for different feed compositions, and thereby there exists a point where the two curves intersect. This intersection at approximately 0.69 $molfraction$ of the light component for this study, is the location where the advantage of one configuration over the other is flipped. It can be seen in Figure 6.5 that the optimal configuration profitability curve was able to trace closely the optimal path,

	Fixed Column Size ($N = 10$)	
Feed Composition ($molfraction$)	Fixed Configuration	Profit ($/yr$)
0.90, 0.10	Regular	**329 113**
	Inverted	255 162
0.75, 0.25	Regular	**187 550**
	Inverted	178 902
0.50, 0.50	Regular	137 982
	Inverted	**162 164**
0.25, 0.75	Regular	148 111
	Inverted	**211 092**
0.10, 0.90	Regular	208 556
	Inverted	**336 176**

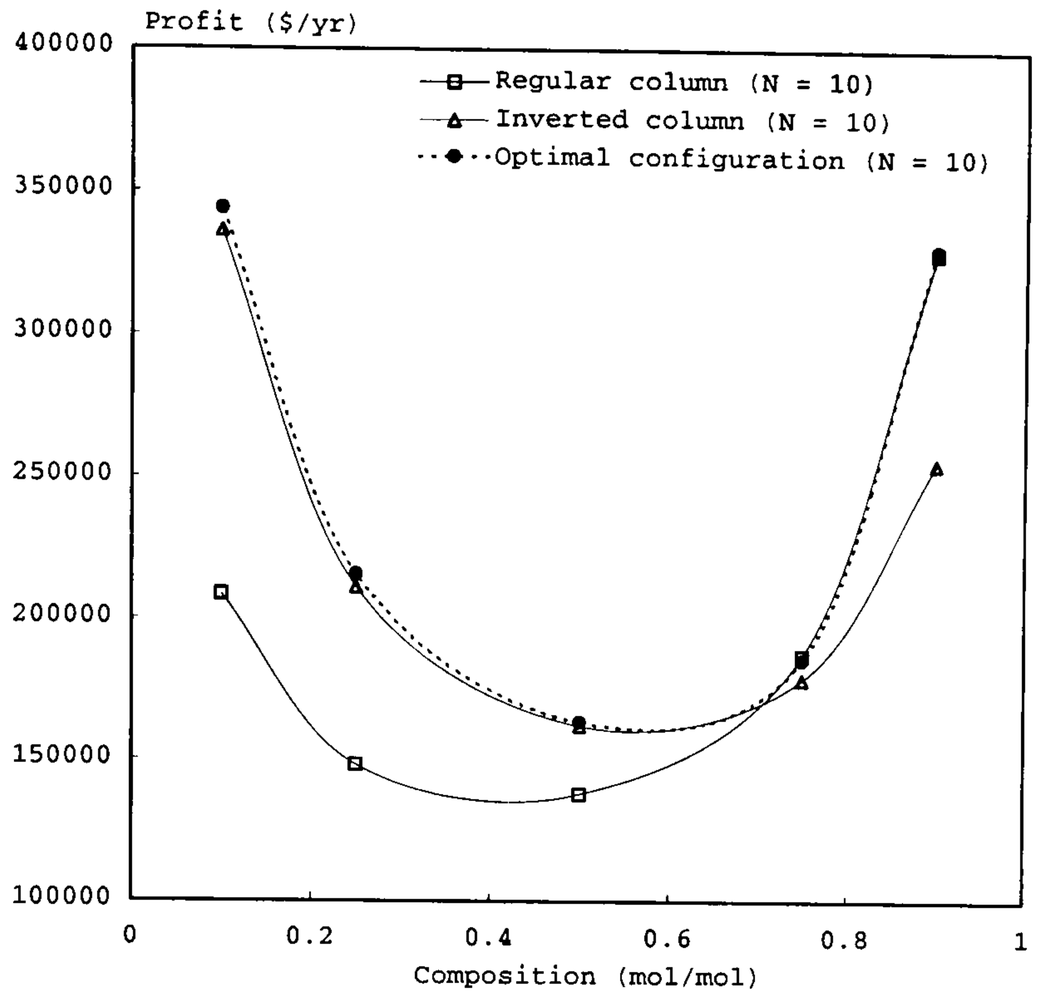
Table 6.4: Summary of optimal results for fixed column configurations and sizes

that is, it closely matches the profitability curve of the inverted column to the left of the flip point where the inverted column is superior, and then followed accordingly the profitability curve of the regular column to the right of the flip point to take advantage of the rectification configuration.

Location of The Flip Point

It is interesting to note that in Figure 6.5, the location of the flip point is not at the symmetrical separation ($x_{i,feed} = 0.50$). This phenomenon has also been observed by Sørensen and Skogestad (1996) who put forward the explanation that the inverted column is not the true inverse of the regular column since the feed and product are in liquid, and not vapour, phase. However, the optimal configuration for a particular separation is also determined by other factors depending on the feed mixture (see the following section 6.5.2) and product purity specification.

The exact location of the flip point can be estimated from the intersection of the profitability curves in Figure 6.5. Figures 6.6, 6.7, 6.8 and 6.9 show the percentage of the



Cyclohexane-toluene mixture

Figure 6.5: Optimal profits for different column configurations and feed compositions

Optimum Profit ($/yr$)	Optimal Genome Y, N, V, $R(t_1)$†, $R(t_2)$, $R(t_3)$, Δt_1, Δt_2, Δt_3‡
146 299	Inverted, 10, 1.667, 1, 0.91, 0.95, 250, 4100, -
146 091	Regular, 10, 1.667, 1, 0.81, 0.92, 150, 5200, -
145 814	Inverted, 10, 1.667, 1, 0.91, 0.95, 200, 4050, -
145 064	Inverted, 10, 1.667, 1, 0.91, 0.94, 200, 4100, -
144 413	Regular, 10, 1.667, 1, 0.81, 0.92, 250, 5200, -
144 192	Inverted, 10, 1.667, 1, 0.91, 0.94, 250, 4100, -
143 499	Regular, 10, 1.667, 1, 0.81, 0.93, 300, 5200, -
142 844	Inverted, 10, 1.667, 1, 0.91, 0.95, 150, 4300, -
141 369	Regular, 10, 1.667, 1, 0.84, 0.94, 0, 6350, -
141 154	Regular, 10, 1.667, 1, 0.83, 0.95, 200, 6100, -

† set as total reflux,

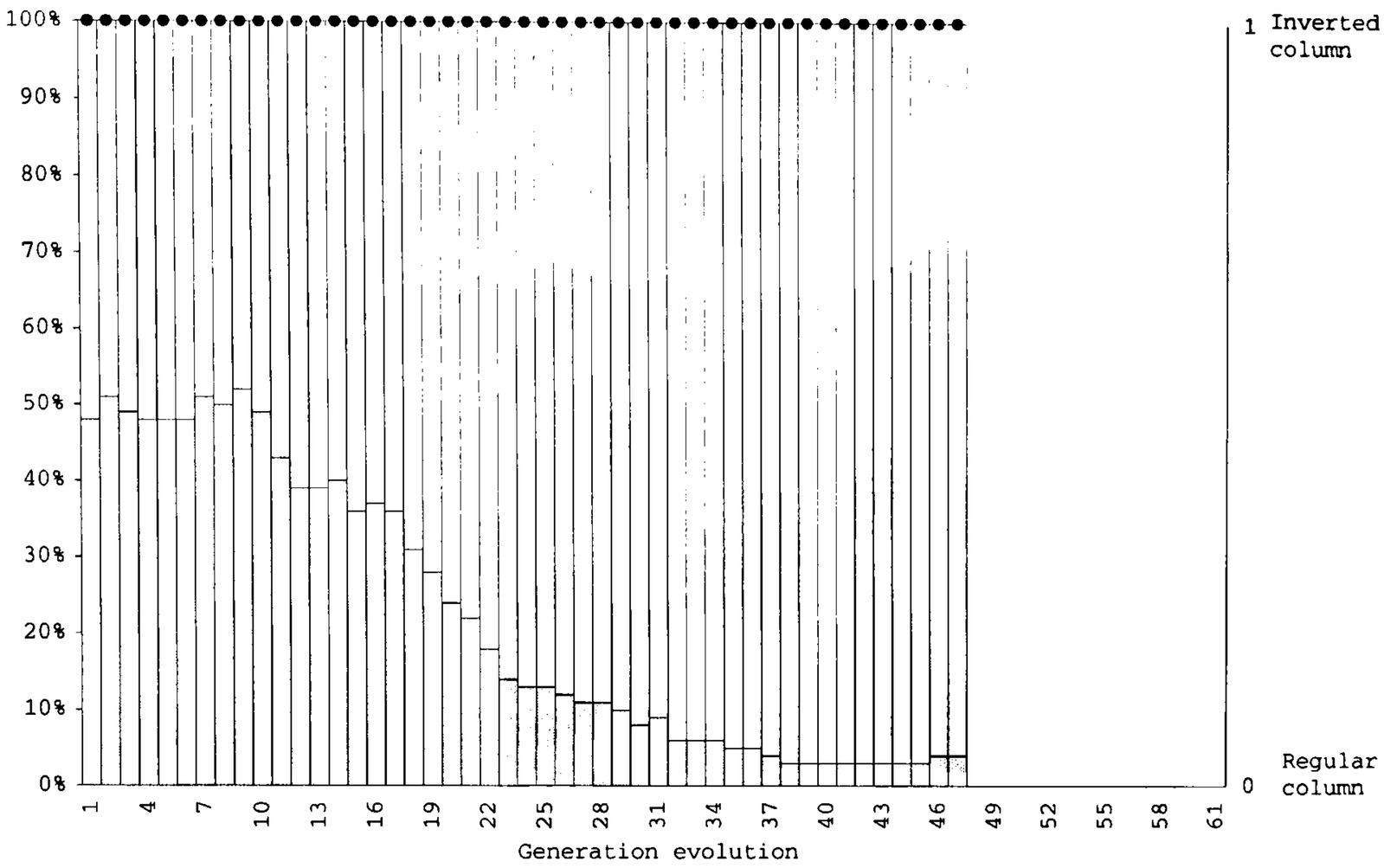
‡ minimum duration to achieve the required purity of the the remaining component

Table 6.5: Optimisation solution vectors for feed 69.2 *mol*% cyclohexane (top 20 genomes)

number of regular columns (white area) and inverted columns (shaded area) represented by all the genomes in each generation of the genetic algorithm for the cases of feed composition $x_{1,feed}$ = 69.0 *mol*%, 69.1 *mol*%, 69.2 *mol*% and 70.0 *mol*%, respectively. For the case of feed composition 69.0 *mol*% of cyclohexane, the population of the first generation (*i.e.* the one after the initial random population) consisted of an equal percentage of genomes representing the regular and inverted configurations, however, over the subsequent generations the genomes representing the inverted configuration began to steadily dominate the population of best solutions (Figure 6.6). In contrast, Figure 6.9 shows that for the case of feed composition 70.0 *mol*% of cyclohexane, genomes representing the regular configuration dominates the population quickly, and by the 13*th* generation it is already clear that the regular column would emerge as the optimal configuration. Therefore, it can be surmised that the flip point is located between the feed composition 69.0 *mol*% and 70.0 *mol*% of cyclohexane, which confirms the approximation obtained from the intersection of the curves in Figure 6.5. Figures 6.7 and 6.8 demonstrate the characteristic of the genetic algorithm search in the vicinity of this flip point. Note that, in the case of feed composition 69.2 *mol*% of cyclohexane, the best 100 solutions in every generation over the course of the evolution consisted of both configurations. The best solution in each generation also switched between the regular and the inverted configuration. In the final generation, the evolved population contained solutions for both configurations. Table 6.5 indicates that at the flip point, of 69.2 *mol*% cyclohexane, the regular and inverted column configurations give equal peformance (difference of 0.1%) in terms of economics, *i.e.* 146 091 and 146 299 $/yr$, respectively.

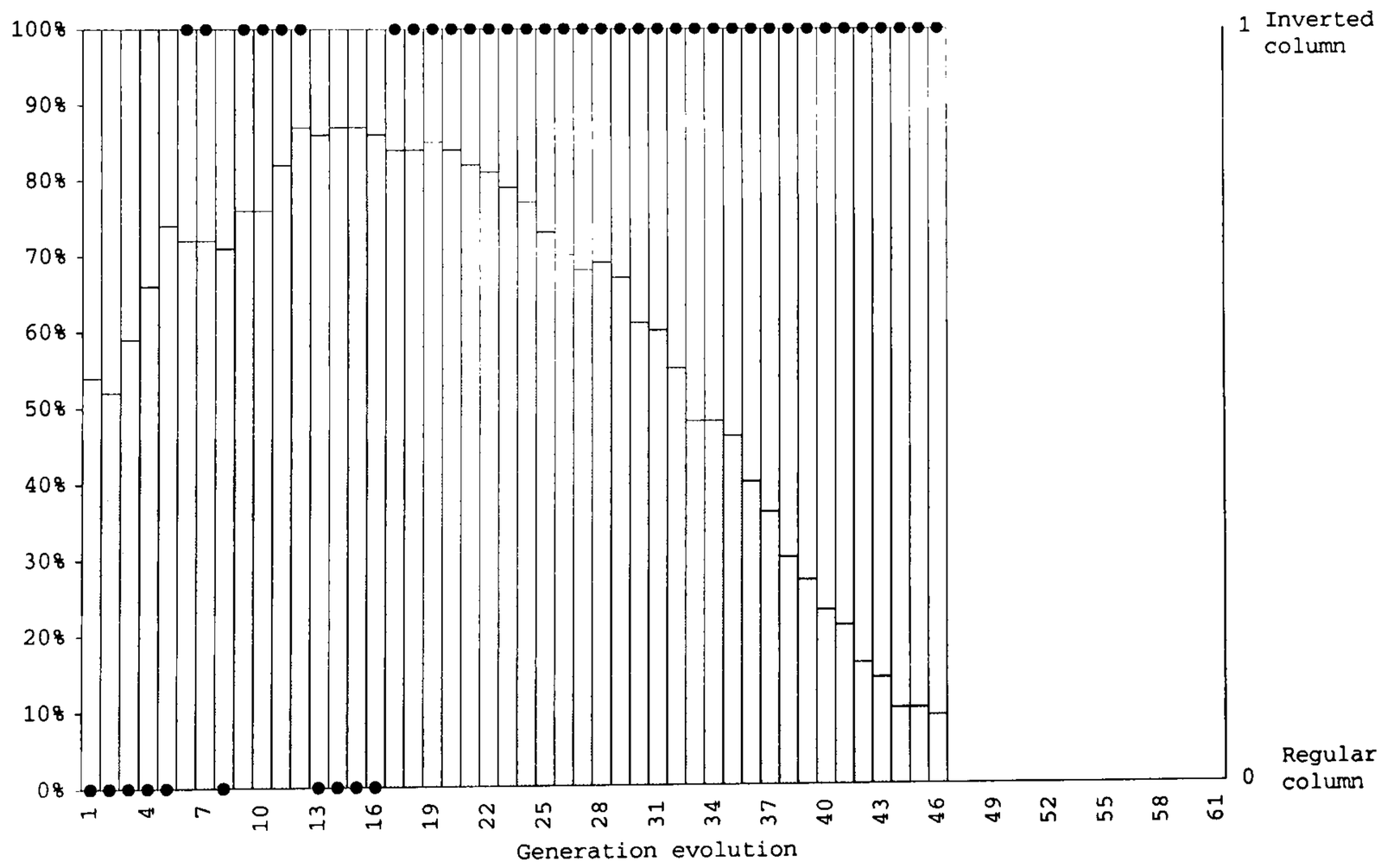
6.5.2 Case II: Different Scenario

In this case study, the optimal design is performed for another separation scenario, *i.e.* a different binary mixture of heptane and toluene, in order to investigate whether the mixture to be separated has any influence on the trend of results shown in case study I above (section 6.5.1). The vapour-liquid phase equilibrium relationships in Figure 6.10 suggest that the distillation of heptane-toluene is more difficult compared to the previous case of cyclohexane-toluene separation. The specifications and decision variable bounds are similar to those of the previous case (given in Tables 6.1 and 6.2, respectively) except for the product purities requirement, which was set at 95 *mol*% of cyclohexane and



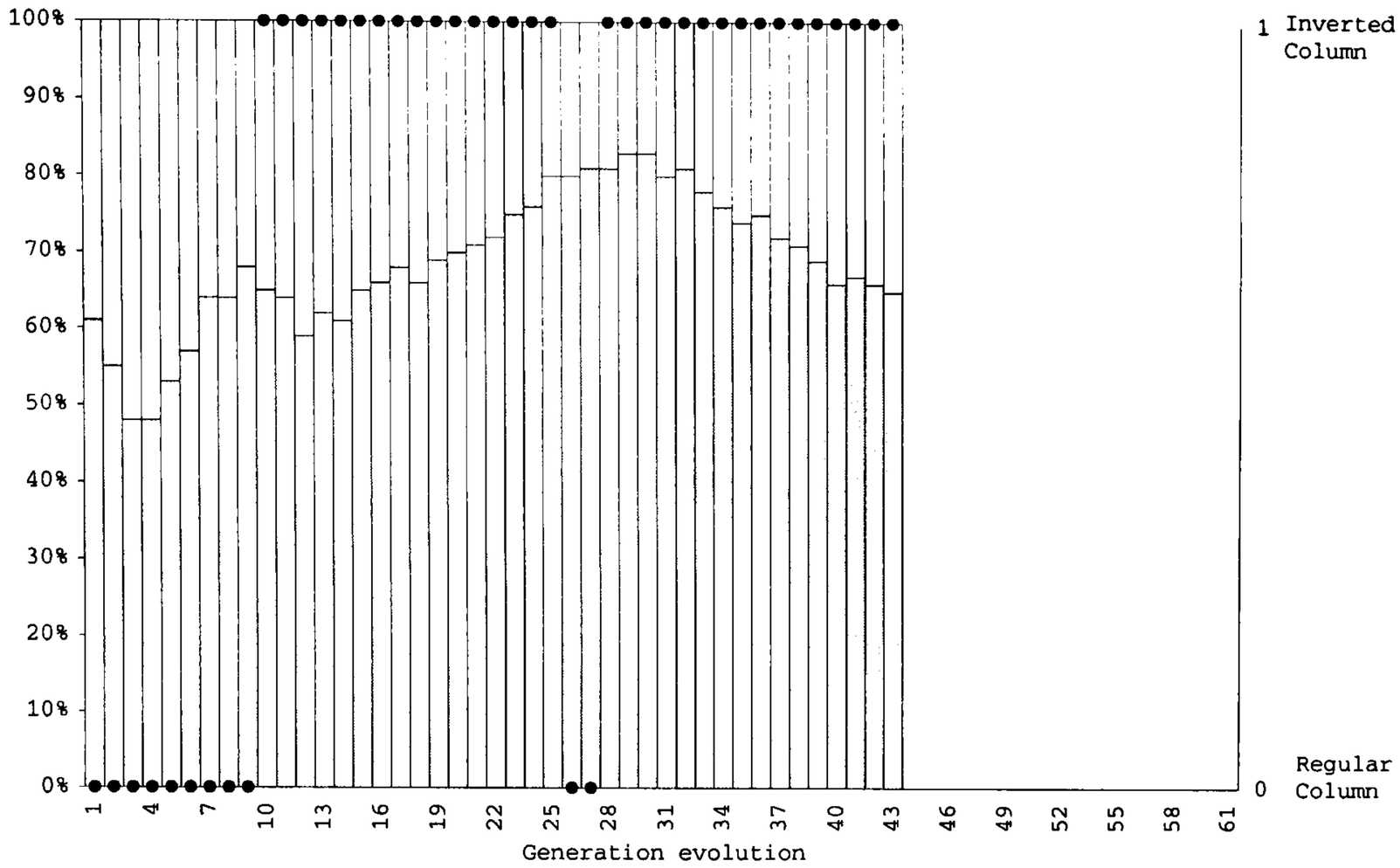
Based on top 100 genomes in each generation; • best configuration in each generation

Figure 6.6: Percentage of column configurations in each generation of the genetic algorithm (feed 69.0 *mol*% cyclohexane)



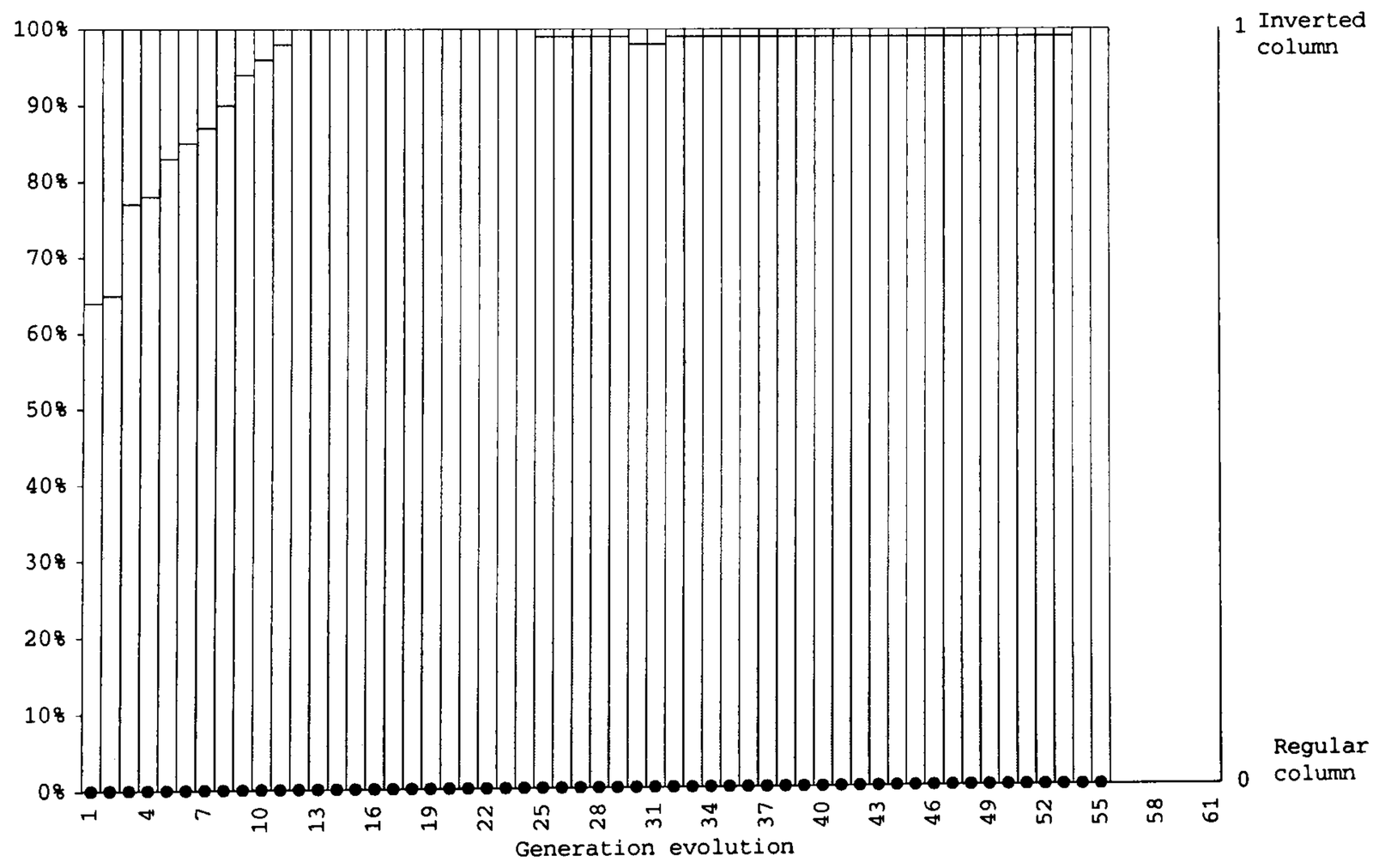
Based on top 100 genomes in each generation; • best configuration in each generation

Figure 6.7: Percentage of column configurations in each generation of the genetic algorithm (feed 69.1 *mol*% cyclohexane)



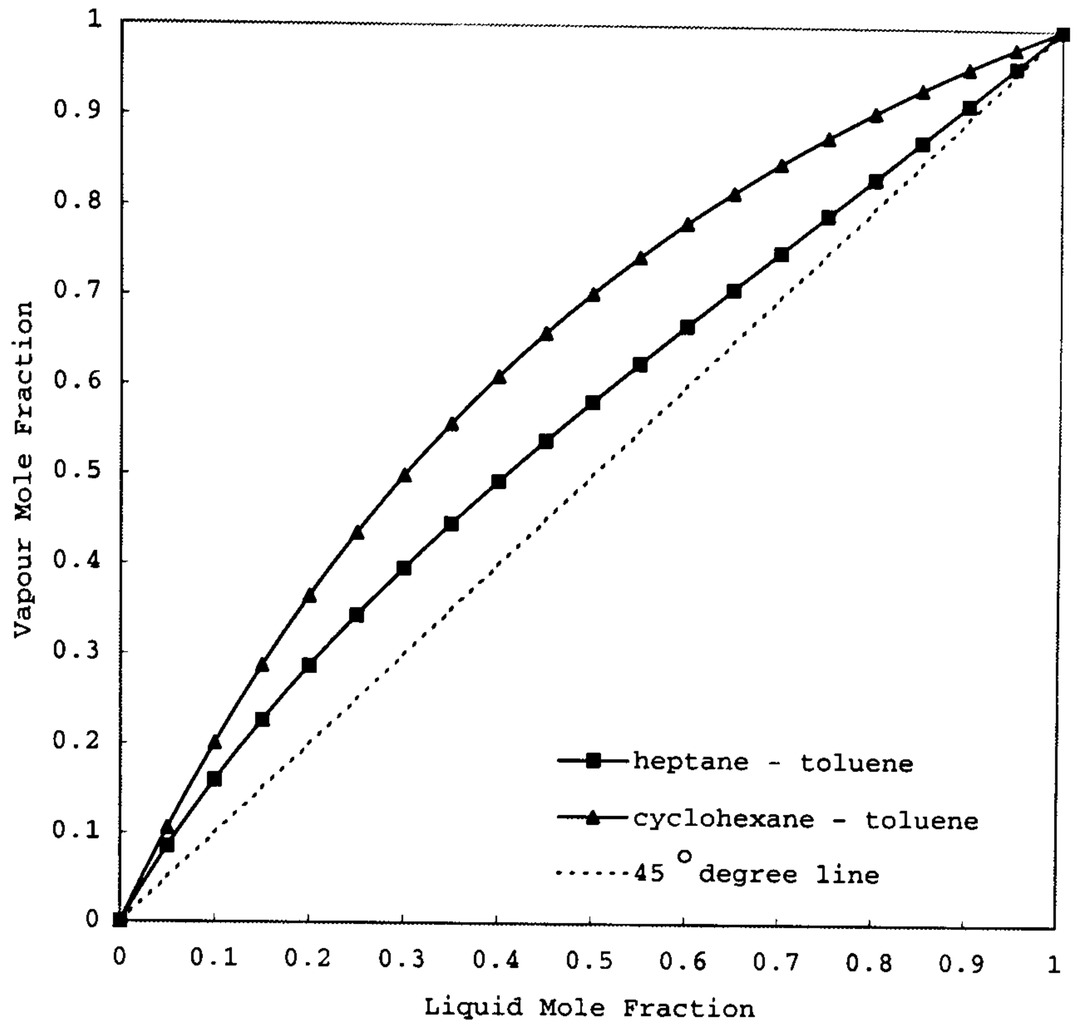
Based on top 100 genomes in each generation; • best configuration in each generation

Figure 6.8: Percentage of column configurations in each generation of the genetic algorithm (feed 69.2 *mol*% cyclohexane)



Based on top 100 genomes in each generation; • best configuration in each generation

Figure 6.9: Percentage of column configurations in each generation of the genetic algorithm (feed 70.0 *mol*% cyclohexane)



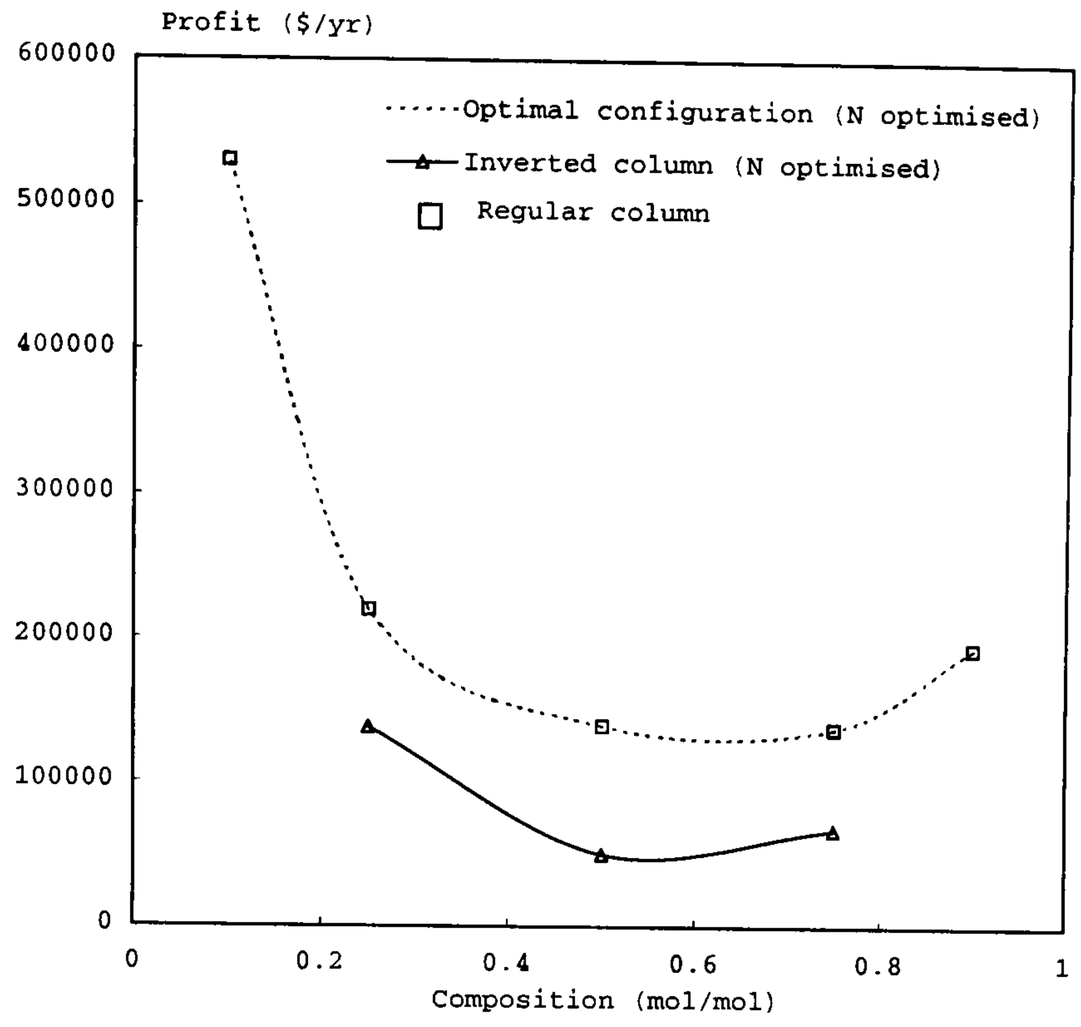
Generated by SRK method at 101.32 kPa (*Multiflash*)

Figure 6.10: Equilibrium diagram for binary systems

toluene. In addition, the upper bound for the number of trays variable, N, was raised to 40.

The optimal results for different feed compositions are presented in Table 6.6. For the range of feed compositions considered, the regular column configuration was found to be optimal in all cases. This is contrary to the previous case study (section 6.5.1) where the optimal column configuration changes at a flip point location. In this case study, there appeared to be no flip point. This is confirmed in Figure 6.11 where the results of the optimally designed fixed inverted configuration show lower profit values than those of the regular column configuration obtained from the configuration optimisation. The results obtained in this investigation highlight the complex dependence of the optimal economics and performance trade-offs on various factors such as feed composition, mixture type and product specification.

It is also interesting to note the contrast between how the optimal design and operation variables are affected by different separation scenarios. In the previous case study



Heptane-toluene mixture

Figure 6.11: Optimal profits and configurations for different feed compositions

with cyclohexane-toluene mixture, greater optimal column sizes were needed for feed mixtures with a higher deviation from equimolar composition. For this case study of heptane-toluene, the optimal number of trays for the symmetrical feed (50:50 $mol\%$) and for compositions with a higher disproportion (10:90, 90:10 $mol\%$) were similar ($N = 31$), whilst for the intermediate compositions (25:75, 75:25 $mol\%$), the optimal column sizes are greater at 37 and 38 trays (Table 6.7). This observation implies a shift in the weighting of the economics trade-off, for examples, between capital costs and batch time - *i.e.* the justification of higher capital cost by lowering batch time might have been altered moving towards the composition edges for the case of a more difficult separation such as the case of the heptane-toluene mixture.

A more detailed analysis of the configuration design outcome can be elicited by contrasting it with the results for the optimal inverted column configuration, *i.e.* fixed $Y = \{Inverted\}$, as given in Table 6.7. For the equimolar composition (50:50 $mol\%$), the more profitable configuration, *i.e.* regular column, had 1452 *mol* of heptane-rich product withdrawn with 1520 *mol* of toluene-rich product remaining in the reboiler pot. whilst

for the inverted configuration, the toluene-rich product withdrawn and the heptane-rich product in the reflux drum were 1170 *mol* and 1368 *mol*, respectively. This comparison revisits previous similar observations, *e.g.* obtained in the previous case study (case I) as well as by Sørensen and Skogestad (1996), that the regular configuration and its inverted form performed differently even at symmetrical feed composition, and goes on further to highlight that, for relatively more difficult separations, such as the heptane-toluene separation investigated here, the difference in performance could become more prominent (note the significant difference in total batch time, 17 192 *s* for the inverted compared to 11 295 *s* for the regular column) and unrecovered product (462 *mol* for inverted against 28 *mol* for regular). In the heavier feed scenario (*e.g.* 0.25:0.75 *mol*%) whereby the inverted configuration has generally been shown to be more favourable, a significantly smaller column (about half the size of the regular column) and lower reflux ratios resulted in lower capital cost and batch time (17 192 *s* to 8022 *s*). Despite a much lower capital cost and bigger percentage of reduction in batch time compared to the regular configuration (53% against 38%), the inverted configuration still performed worse in terms of the overall profitability objective function, with lower yield (1057 *mol* of offcut) being the main cause. Thus, this work serves as an indication that, although the general guideline of "regular column for light feeds and inverted column for heavier feeds" is true for some cases (as shown in case I), the exact location of the flip point is case specific and has to be determined. It is also dependent on factors like the mixture to be separated, as demonstrated here. In practice, although general heuristics gathered from this and previous works (*e.g.* heavier feeds for inverted column and vice versa *etc.*) can be used to predict the optimal configuration for a particular separation duty, the study highlights the need for a design methodology such as the one proposed in this work to analyse each case separately and in more detail.

6.6 Conclusions

In the preceding case studies, the simultaneous determination of optimal configuration. design and operation for different binary separation scenarios has been considered. The optimal configuration, *i.e.* regular versus inverted configurations, was found to be dependent on feed composition (section 6.5.1). Furthermore, in the second case study (section

Feed Composition ($molfraction$)	Optimal Configuration	Optimal Size, N	Profit ($/yr$)
0.90, 0.10	regular	31	195 041
0.75, 0.25	regular	38	138 306
0.50, 0.50	regular	31	139 673
0.25, 0.75	regular	37	220 218
0.10, 0.90	regular	31	530 457

Table 6.6: Summary of optimal results for the separation of the heptane-toluene binary mixture

Feed Composition ($molfraction$)	Optimal Size	Reflux Ratio		Task Duration (s)		Batch Time (s)	Separated Products (mol)		
	N	$R(t_2)$	$R(t_3)$	Δt_1	Δt_2	$\Delta t_1 + \Delta t_2 + \Delta t_3$	Heptane	Toluene	Offcut
0.90, 0.10	31	0.80	0.93	0	8750	8818	2935	57	8
0.75, 0.25	38	0.85	1.00	600	9450	10932	2403	597	0
	26	*0.97*	*0.98*	*300*	*10000*	*17008*	*2276*	*500*	*224*
0.50, 0.50	31	0.91	0.99	300	9400	11295	1452	1520	28
	28	*0.91*	*0.97*	*150*	*7800*	*17192*	*1368*	*1170*	*462*
0.25, 0.75	37	0.93	0.96	450	3750	7048	454	2349	197
	18	*0.80*	*0.70*	*50*	*5850*	*8022*	*1*	*1942*	*1057*
0.10, 0.90	31	0.98	0.96	1300	1550	3060	54	2931	15

Italicised: results for the inverted column, *i.e.* fixed $Y = \{Inverted\}$
Note: all product cuts were at the minimum purity of 95.0 $mol\%$

Table 6.7: Details of optimal results for the separation of the heptane-toluene binary mixture

6.5.2), it was shown that optimal column configuration is also dependent on conditions such as the difficulty of separation, *i.e.* the specific mixture to be separated. In short, it can be surmised that the choice of optimal column configuration is highly dependent on different separation scenarios. Thus, for different separation cases, it is important to determine the best configuration, design and operation for the most profitable performance, and the simultaneous approach proposed here could be used for doing so.

6.7 Optimal Configuration for Multicomponent Separation

In this final section, the optimal configurational design of a multicomponent batch distillation system is investigated. The distillation involves the separation of a quaternary mixture of pentane, hexane, heptane and octane. There is a choice to set-up the process in either the rectification, stripping or multivessel configurations. The latter option would consist of a system with three column sections and four major holdup vessels including the reflux drum, two side vessels and the reboiler pot (see chapter 5.7.2).

The case study specifications and operating conditions are listed in Table 6.8. The batch size or major holdup (600 *mol*) is charged wholly to either the reboiler pot or reflux drum in the cases of the regular and inverted configurations, respectively, or in the case of the multivessel configuration, the major holdup is equally distributed across the four vessels (150 *mol* in each)[2] - depending on the uptake of the optimised boolean decision variable, Y. The minimum product purity specifications were set at 90.0 *mol*% for all four pentane, hexane, heptane and octane-rich cuts. The cost coefficients, K_1, K_2 and K_3, of the objective function were set to similar values of the previous case study, *i.e.* 1500, 9500 and 180, respectively.

The optimised decision variables include the column configuration, Y, the number of trays in each column section, N_1, N_2 and N_3, the constant boilup rate, V, and the reflux ratio profile, *i.e.* the values of the normalised reflux ratio, $R(t_i)$ (except in the first task intervals where $R(t_1)$ is set to 1 for total reflux), and the durations of each of

[2]For the multivessel column, is it also possible to optimise the initial feed distribution on the vessels. Variable holdup and product withdrawal during the operation can also be considered. In this design study, the simplest *total reflux constant holdup* policy is considered , $R_j = 1$ (see chapter 5.7.2).

Available annual production time, T_A $(h/year)$	8760
Batch set-up time, t_s (s)	1800
Operating pressure, P (Pa)	101325
Major holdup (batch size), H_{feed} (mol)	600
Minor holdup, M_{rd} or M_{reb} (mol)	3.5
Tray holdup, H_{tray} (mol)	3.5
Feed composition, $x_{i,feed}$ $(molfraction)$	
Pentane, $x_{1,feed}$	0.25
Hexane, $x_{2,feed}$	0.25
Heptane, $x_{3,feed}$	0.25
Octane, $x_{4,feed}$	0.25
Product purity specifications, $(molfraction)$	
First product, $x_1(t_f)$	0.90 of pentane
Second product, $x_2(t_f)$	0.90 of hexane
Third product, $x_3(t_f)$	0.90 of heptane
Fourth product, $x_4(t_f)$	0.90 of octane
Cost, C_i $(\$/mol)$	
Pentane, C_1	0.035
Hexane, C_2	0.035
Heptane, C_3	0.035
Octane, C_4	0.035
Feed, C_{feed}	0.001

Table 6.8: Specifications and operating conditions for the multicomponent separation case study

Decision Variables	Bounds
Y	{Regular , Inverted , Multivessel}
N_1, N_2, N_3	[2 , 20]
V $(kmol/hr)$	[0.6 , 6.0]
$R(t_{2,3,4,5,6,7})$	[0.4 , 1.0]
Δt_i (s)	[0, 2000]

Table 6.9: Decision variables bounds for the multicomponent separation case study

the first six task intervals, $\Delta t_{1,2,3,4,5,6}$. Task intervals Δt_2, Δt_4 and Δt_6 represent the withdrawal period of the pentane, hexane and heptane-rich product cuts, respectively, with Δt_3 and Δt_5 representing the intermediate off-cuts. In the final task interval, the duration Δt_7 is set corresponding to the minimum time needed to purify the remaining component (in either the reboiler pot or reflux drum) to its required purity of 99.0 $mol\%$. The bounds for each variable are given in Table 6.9. The size of the single column in the regular and inverted configurations is taken as the sum of N_1, N_2 and N_3. For the multivessel configuration, the simple *total reflux constant holdup* policy (see chapter 5.7.2) is considered here, hence when the boolean variable $Y = \{multivessel\}$, the reflux ratios, $R(t_i)$, for the seven task intervals are ignored and set to total reflux, $R(t_i) = 1$.

6.7.1 Optimal Result

The result of the optimisation is presented in Table 6.10. In this case study, the optimal configuration was found to be the multivessel system with an optimal design structure of 7, 11 and 12 trays in the top, middle and bottom column sections, respectively. For comparison, optimisation were performed with fixed $Y = \{\text{Regular}\}$ and $Y = \{\text{Inverted}\}$, and it is evident from the results that the optimal profits of these two configurations, 45 339 and 50 489 $\$/yr$, respectively, are significantly lower than that of the multivessel configuration (169 588 $\$/yr$). The result obtained from the cconfiguration design optimisation is in agreement with earlier findings in the previous chapter (section 5.8) which demonstrated the superiority of the multivessel system compared to the regular column.

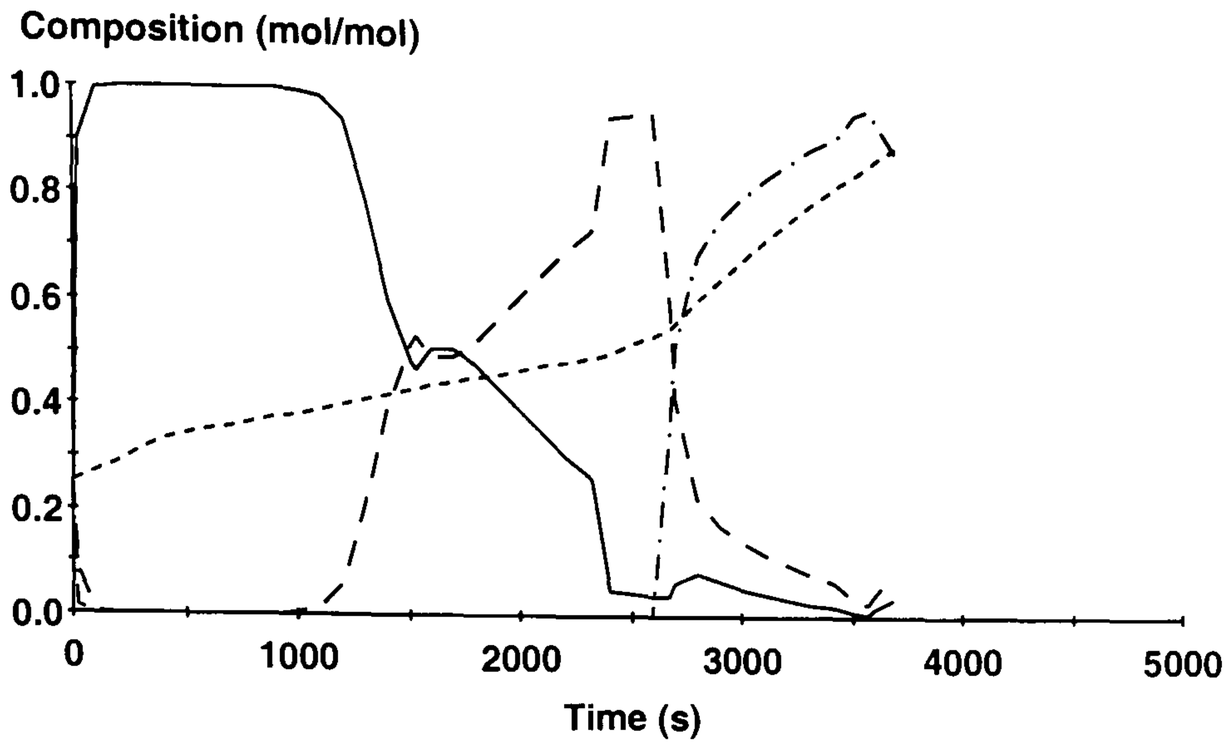
Note that, the optimal structure of the multivessel system (7:11:12 trays) is almost similar to the result obtained in section 5.8 (6:11:10 trays) for the same quaternary mixture

Optimum Profit ($/yr)	Optimal Configuration	Optimal Design	Optimal Operation
169 588	Y = {multivessel}	$N_1 = 7$ $N_2 = 11$ $N_3 = 12$ $N_T = 30$	$V = 6.0\ kmol/hr$ $R_i = 1.0$ ‡ $t_f = 701\ s$ § Product purities: (0.99, 0.90*, 0.91†, 0.96)

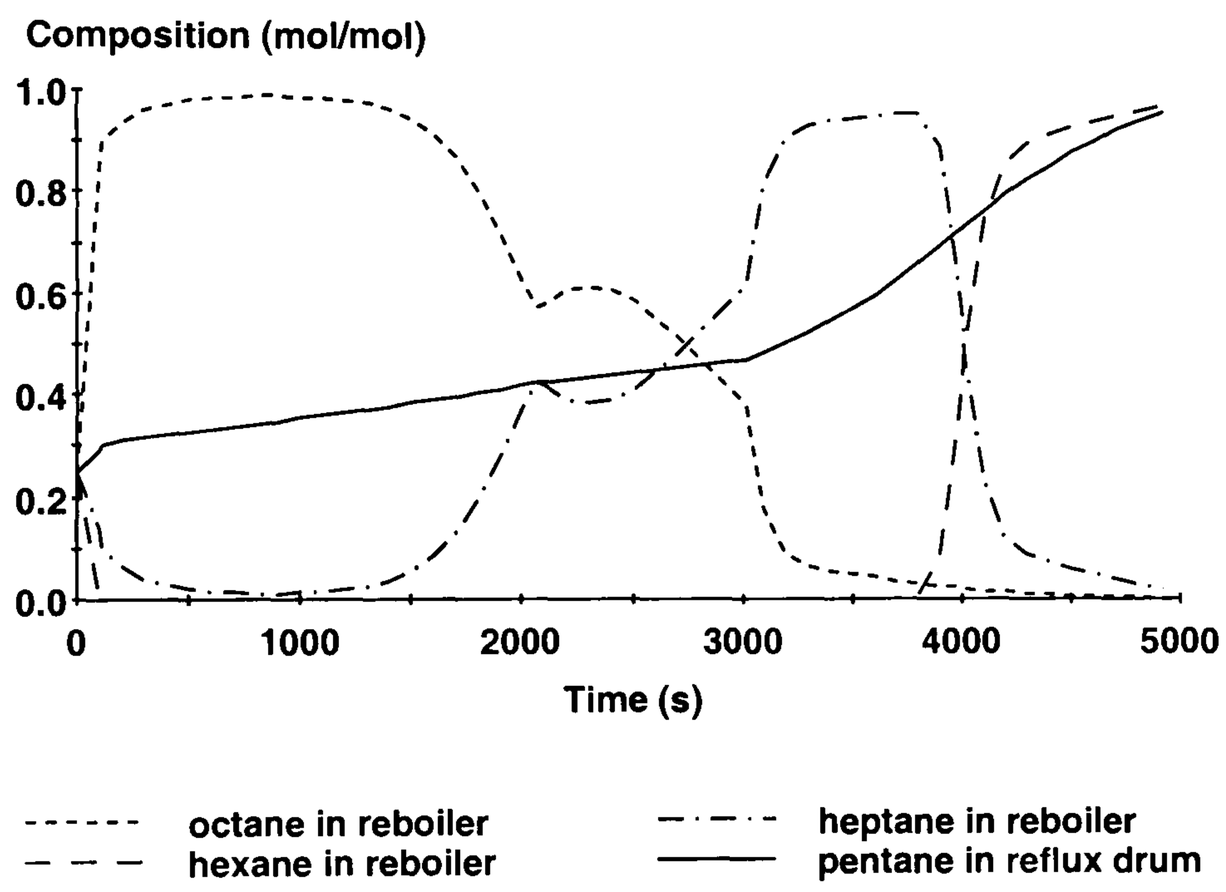
Optimum Profit ($/yr)	Configuration	Optimal Design	Optimal Operation
45 339	Y = {regular} (fixed)	$N = 20$	$V = 2.4\ kmol/hr$ $R_1 = 1.0$ ‡, $\Delta t_1 = 24\ s$ $R_2 = 0.87$, $\Delta t_2 = 1501\ s$ $R_3 = 0.91$, $\Delta t_3 = 800\ s$ $R_4 = 0.53$, $\Delta t_4 = 350\ s$ $R_5 = 0.83$, $\Delta t_5 = 748\ s$ $R_6 = 0.71$, $\Delta t_6 = 150\ s$ $R_7 = 1.0$, $\Delta t_7 = 117\ s$ $t_f = 3690\ s$ § Product purities: (0.93, 0.94, 0.96, 0.90*)
50 489	Y = {inverted} (fixed)	$N = 18$	$V = 2.0\ kmol/hr$ $R_1 = 1.0$ ‡, $\Delta t_1 = 929\ s$ $R_2 = 0.85$, $\Delta t_2 = 1950\ s$ $R_3 = 0.92$, $\Delta t_3 = 944\ s$ $R_4 = 0.72$, $\Delta t_4 = 952\ s$ $R_5 = 0.74$, $\Delta t_5 = 50\ s$ $R_6 = 0.73$, $\Delta t_6 = 94\ s$ $R_7 = 0.98$, $\Delta t_7 = 0\ s$ $t_f = 4919\ s$ § Product purities: (0.96, 0.90*, 0.91†, 0.92)

‡ pre-set in disjunction; § $t_f = \sum_{i=1}^{7} \Delta t_i$
* on or † near the lower bounds

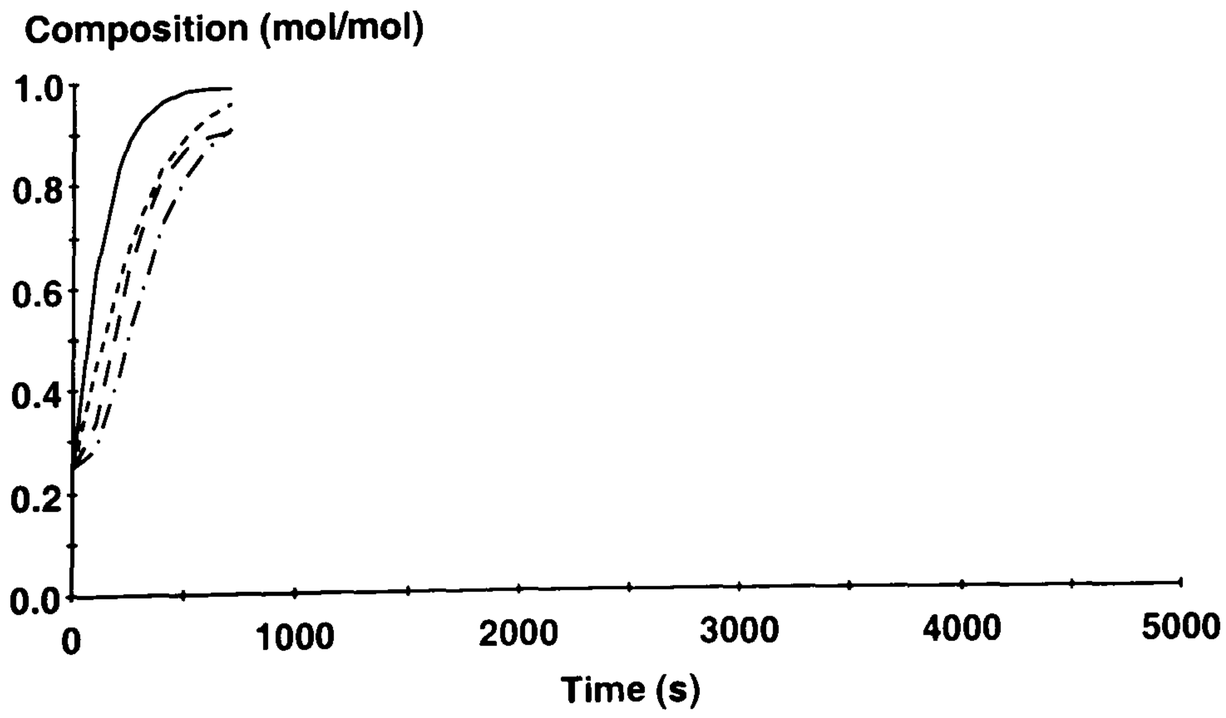
Table 6.10: Summary of optimal results for the multicomponent separation case study



(a) Regular column

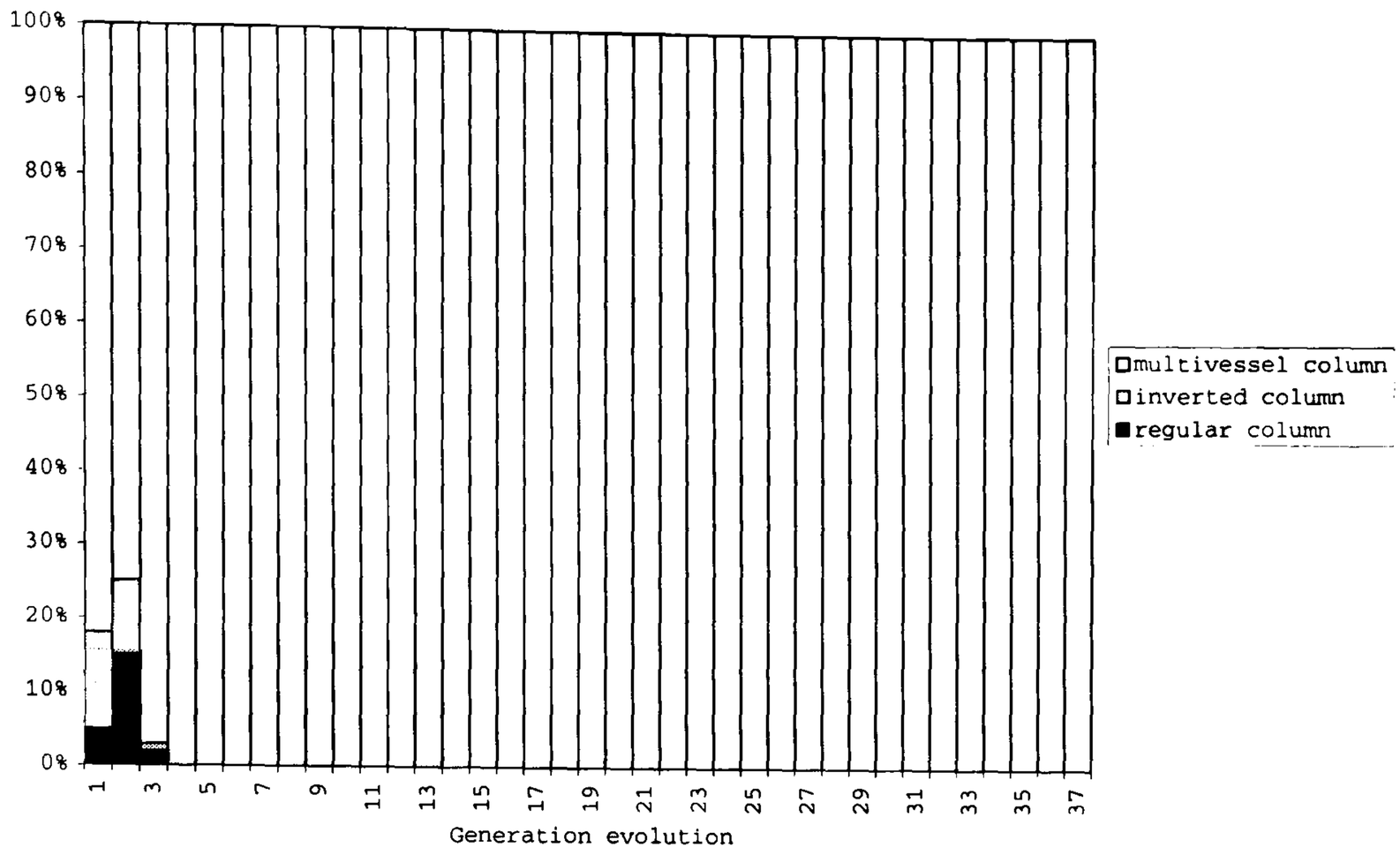


(b) Inverted column



(c) Multivessel column

Optimal composition profiles for different batch distillation configurations



Based on top 100 genomes in each generation

Figure 6.13: Percentage of column configurations in each generation of the genetic algorithm

of pentane, hexane, heptane and octane with the same feed composition and purity constraints (see case C, Table 5.18). The difference in the tray configurations may be attributed to the difference in the specifications in the two cases (*i.e.* feed amount and tray holdup) and/or the sensitivity of the optimisation itself.

The composition profiles of the four components in the regular, inverted and multivessel configurations are presented in Figure 6.12. Compared to the separation of the regular and inverted columns where each product is purified and withdrawn in sequence, the multivessel arrangement performs the separation tasks simultaneously (in parallel), resulting in a significant reduction in processing time.

The progress of the genetic algorithm search indicates that genomes bearing the gene, $Y = \{\text{multivessel}\}$, dominated the population from the first generation (Figure 6.13). In contrast, the total number of genomes representing the regular and inverted configurations were only 18, 25 and 3 out of the top 100 genomes in the first, second and third generations, respectively. By the fourth generation, the multivessel configuration occu-

pied all the best 100 solutions in the population. The termination criteria was fulfilled in 37 generations (see chapter 3.7.8).

6.8 Conclusions

In this chapter, the automated simultaneous determination of optimal batch distillation configuration, design and operation was presented. The design approach was based on the solution of a mixed discrete dynamic optimisation problem with logical, discrete and continuous decision variables using a genetic algorithm and penalty function framework. The design was based on a rigorous column model. A comprehensive economics performance index that takes into account production revenue, capital and operational costs was utilised as the basis of the design.

The separation of binary and multicomponent mixtures were considered. In the binary separation case study, the optimal configuration, *i.e.* regular versus inverted configurations, was found to be dependent on feed composition. The inverted column was found to be more profitable for feeds with high fraction of the light component whilst the regular column is optimal for heavier feeds, and for some separations, such as that investigated for the cyclohexane-toulene mixture, there exists a flip point where a switch in the most profitable configuration occurs. Through another case study, of a heptane-toluene mixture, it was shown that optimal column configuration is also dependent on conditions such as the difficulty of separation.

In conclusion, the choice of optimal column configuration is dependent on different separation scenarios, thus the configuration design approach presented in this chapter serves as useful tool in the determination of the most economical configuration, design and operation for specific separation cases.

The optimisation design procedure was also found to be feasible in the multicomponent separation scenario whereby the number of configurational, design and operational

decision variables are greater than that in the binary case. The configuration design result obtained provided a further demonstration of the superiority of the multivessel configuration over the regular and inverted configurations as highlighted in chapter 5.

Chapter 7

Conclusions and Directions for Future Research

This chapter summarises the main contributions and findings that have been presented in this thesis. In the final section, some possible directions for future research are outlined.

7.1 Main Contributions and Conclusions

This thesis is concerned with the determination of the *optimal* configuration, design and operation of batch distillation systems. The conceptual study in this project involves the development of batch distillation models and application of computer-aided optimisation techniques. The study also aims to determine the optimal batch distillation conditions under different separation scenarios, for both traditional and unconventional batch distillation systems, in order to gain further insights on their comparative performances that may serve as useful guidelines for batch distillation screening.

In general, the overall work presented in this thesis is characterised by several key features which distinguish it to various degrees from previous batch distillation optimisation studies. These features include the use of rigorous and detailed models, the exploration of more degrees of freedom and the consideration of economics performance measurements.

i.e. a profitability objective function. Over the course of this research project, three main areas of work have been conducted, namely, the optimal operation of extractive batch distillation for separating azeotropic mixtures, the simultaneous optimal design and operation for zeotropic mixtures, and finally, the optimal configuration design of the batch distillation system. A summary of the main contributions, findings and conclusions in these three areas are reviewed and discussed in the following sections.

7.1.1 Optimal Operation of Extractive Batch Distillation

The first major contribution of this thesis is the rigorous study of the optimal operation of the separation of an azeotropic system via extractive batch distillation (see chapter 4). The technology of solvent-enhanced extractive distillation in the batch mode has been an area of continuous research over the past decade, as highlighted in the literature review in chapter 2. The works ranged from initial feasibility studies to operational issues and lately, the potential of operation in alternative process configurations. The studies so far have mainly been focused on either graphical-based theoretical studies or sensitivity analysis via parametric simulations. Recently, the optimal operation of the extractive batch distillation process has begun to be investigated (see Mujtaba, 1999 and Ruiz Ahón and de Medeiros, 2001).

The work in this research was conducted in response to the need for a more rigorous and comprehensive optimisation study leading to further understanding on the optimal operation of this complex batch process. The use of approximate models can lead to different or suboptimal solutions when compared to the results obtained through a higher rigour of modelling (see Furlonge, 2000). For this reason, the use of simplified models was avoided and a detailed dynamic model that took into account variable vapour and liquid holdups, tray hydraulics and rigorous mass and energy balances were used as the basis for the study. The operations were optimised based on a profitability objective function and the dynamic optimisation problem was solved using a nonlinear programming technique based on control vector parameterisation. The work here provided the first comparison between extractive batch distillation operation in the regular and middle vessel configurations in different scenarios based on optimised performances. Furthermore, additional

degrees of freedom, such as feed distribution and liquid and vapour stream configurations at the middle section of the middle vessel column, were exploited via optimisation.

Several new insights were gained from the case studies. Reboiler-fed low-reflux operation was found to be a more economical procedure than the widely proposed middle vessel steering policy (*e.g.* Safrit *et al.*, 1995) where the whole feed is fed to the middle vessel and then steered towards the required product purity with concurrent high purity solvent recycling. Although this policy might be plausible from feasibility studies using simple models, it is not optimal due to a long processing time, as proven by the optimal results obtained in chapter 4. This finding has since been vindicated by newly published experimental works by Cui *et al.* (2002) and Warter *et al.* (2002) which also found long batch time as well as practical difficulties associated with high purity solvent recycling in the middle vessel configuration during the operation (this highlights the significance of using detailed models as advocated in this conceptual study).

The study here also shows that the performance of the middle vessel column varies considerably depending on the liquid and vapour stream configurations at the middle section. Chapter 4 also describes how the performance of the middle vessel column can be improved by allowing the stream configurations to vary during the course of the process itself. By exploiting this additional degree of freedom, the performance of the middle vessel column can be higher than that of the batch rectifier; however, the degree of advantage gained is found to be dependent on factors such as the feed composition.

7.1.2 Optimal Design and Operation of Batch Distillation

A major contribution of this work is the development of a new methodology for the simultaneous optimal design and operation of batch distillation systems (chapter 5). In this approach, a stochastic framework consisting of genetic algorithm and penalty function is used to solve the mixed integer dynamic optimisation problem. This is in contrast to previous works which attempted decomposed NLP and MINLP approaches. The approach here is found to be practical and easy-to-use, and good results as well as multiple

solutions were available following the optimisation. Another major advantage of this approach is that it can also tackle more complex problems like batch distillation configuration design (see the following section 7.1.3).

Using the proposed solution approach, a comprehensive study of the simultaneous optimal design and operation of batch distillation systems has been conducted. The key features of this work are again the use of rigorous models and the exploration of a wide range of degrees of freedom. The effect of different design scenarios, such as production time, capital costs, process allocation, objective function, product specification, relative volatility, number of components and feed composition, on the optimal designs and operations were investigated. The insights elicited from the results, as discussed in detail in chapter 5, constitute a significant contribution of this work. Furthermore, the optimal design of the unconventional multivessel system is studied here for the first time, and is compared to the regular column in a more conclusive manner. The multivessel system is found to offer higher efficiency than the batch rectifier. Insights on how the benefit is derived were obtained by analysing the individual component revenue and costs obtained.

7.1.3 Optimal Confuguration of Batch Distillation

In chapter 6, the problem of determining the best batch distillation configuration, design and operation simultaneously for a specific separation scenario in a single optimisation problem is solved for the first time. This work highlights the potential for the process design engineer to simultaneously and automatically perform the tasks of configuration screening, column sizing and operation condition determination based on an overall objective function instead of the traditional methods of heuristic, simulation and correlation. The configuration design methodology proposed in this work is based on the solution of a mixed integer dynamic optimisation problem using the stochastic genetic algorithm-penalty function framework. The discrete boolean variable and its associated set of disjunction conditions that represents the various options of batch distillation configurations were easily incorporated into the solution framework. This is due to the natural ability of the genetic algorithm to handle boolean variables in addition to integer and continuous variables within its genome set and the use of direct calls to specific

model files representing the different configurations. The approach, which again is based on rigorous models, is found to produce good results when applied to several case studies.

Several key findings were put forward from the case studies. In the binary separation case study, the location of the flip point (also found by Sørensen and Skogestad, 1996), where a switch in the optimal configuration occurs, depending on the initial feed composition, could be pin-pointed. The results also suggest that the optimal column configuration is highly dependent on other factors such as the difficulty of separation. Different mixtures also affect how the batch distillation column is optimally sized. In the multicomponent case study, the multivessel system was found, as expected, to dominate the population of solutions in the genetic algorithm from an early stage in the evolution, thereby re-iterating the economics superiority of this configuration over the regular and inverted configurations, as was also found to be the case in chapter 5.

7.1.4 Summary of Main Contributions

- The optimal operation of the complex extractive batch distillation based on overall profitability have been successfully determined using a detailed model with variable holdups. By considering all the important operational variables simultaneously during the optimisation, the operating policies for both single product and multiple products cases have been obtained for the solvent-aided separation of a binary azeotropic mixture. The problem was solved by applying a NLP approach based on control vector parameterisation.

- The optimal operating policy for the extractive distillation process in the middle vessel column has been studied for the first time. The results obtained suggest alternative operating procedures that are different to the middle vessel-steering policy commonly associated with this column. The thesis also explored the optimal performances of middle vessel columns with different liquid and vapour streams configuration between the column and middle vessel. By allowing the middle section stream configurations to vary optimally during the process, the economic performance of the process was shown to improve significantly.

- In this thesis, the performances of the extractive distillation process in the regular and middle vessel were rigorously compared for the first time. The comparison was made based on optimal operations and the work demonstrated how their relative performances change according to the separation scenarios, *i.e.* different feed compositions.

- A methodology for the optimal design of batch distillation processes has been proposed in this thesis. Due to the complexity of the dynamic optimisation problem which require the consideration of integer variables and nonlinear functions, a stochastic solution framework based on genetic algorithm and penalty function has been presented and implemented with satisfactory results.

- Optimal designs and operating policies have been determined simultaneously for the traditional regular column with single duty, multipurpose column as well as unconventional columns including the inverted and multivessel columns. Through a number of case studies, the study has demonstrated how factors such as production time, capital cost, mixture allocation, relative volatility and performance index have a significant effect on the optimal design and operating policies of batch distillation. This thesis also provided for the first time, specific insights on the optimal design of the multivessel system, for example how the structure (*i.e.* relative sizing of the column sections) adjusted itself optimally in accordance to different scenarios such as feed composition and product purity specification.

- Although the multivessel system has frequently been promoted by academic research as a more efficient alternative to the traditional batch rectifier, until now there has not been a more comprehensive comparison of the two configurations. In this thesis, the configurations are compared on the basis of their optimal design and operation for a number of separation scenarios. The study showed that when a mixture with many components is to be separated, the economical benefit of choosing the multivessel system becomes more prominent. The reason for this

was explained in this study by considering the individual costs of capital outlay, operation and revenue.

- A methodology to tackle the batch distillation configuration design problem has been presented by expanding the genetic algorithm-penalty function framework. Thus, the optimal configuration, design and operating policy of the batch distillation process have been obtained simultaneously and automatically for the first time.

- The automated configuration design methodology was successfully applied for both binary and multicomponent case studies. The case studies highlighted the influence of different separation scenarios like feed composition and ease of separation on the optimal configuration selection. In one case study, the configuration design results were verified by pin-pointing the location of the flip point where a switch in the optimal configuration occurs. In accordance to the comparative study conducted earlier, the optimisation also successfully identified the optimal configuration as being the multivessel system for the multicomponent case study.

7.2 Directions for Future Research

In this section, the limitations of this work and main recommendations for future work are discussed. Some broader future issues related to batch distillation research are also outlined.

7.2.1 Extending This Research

Batch distillation is a widely used separation unit operation in the fine and specialty chemical and biochemical processing industries, and is expected to remain a process of significant interest as long as these industries continue to expand. The overall scope of this research has demonstrated how advanced computer-aided modelling and optimisation tools can be utilised effectively to attain optimal performances and conceptual insights on such dynamic batch distillation processes. In this research, considerable progress has been made in the study of the optimal configuration, design and operating policy of

batch distillation processes in different separation scenarios. Nevertheless, there is scope for future work in the following aspects:

Greater Detail in Modelling

The conceptual studies reported in this thesis were mostly based on first principle rigorous equilibrium models that took into account dynamic mass and energy balances in the column cascade. In the study of the complex extractive batch distillation process, the use of a detailed model that incorporates variable vapour and liquid stage holdups resulted in a more realistic and practical optimal operation of the process. There is scope to achieve an even more rigorous investigation by taking into account effects such as mass transfer rates (non-equilibrium), entrainment (to check flooding), weeping and downcomer dynamics. Additional assumptions such as perfect mixing and adiabatic operation may also be relaxed. The abstraction of modelling required for a particular optimisation study is basically dependent on the accuracy required, computational cost, the availability of data and the purpose of the study. For example, in chapter 4, the purpose of the study was to conduct a detailed optimal study of the extractive distillation process in a more practical scenario, whereas in chapter 6, the study was more concerned with the broader aspect of deciding the overall best batch distillation configuration, design and operation where specific data like internal column dimensions are yet to be decided. Thus, the models used reflect the purposes. Nonetheless, as mentioned in section 7.1 above, one of the feature of this research is the use of rigorous models in favour of simplified models which tend to be used in the majority of previous studies. A recent work by Greaves *et al.* (2003) proposed the use of artificial neural network process model for the optimal operation of batch distillation. This is an alternative approach to first principle modelling and which may prove to be more advantageous in terms of computational effort.

Unexplored Degrees of Freedom

In this study, a wide range of degrees of freedom was considered, culminating in the simultaneous consideration of configurational, design and operation variables in chapter 6. For example, consideration of feed distribution and stream configuration in the middle vessel and multivessel systems led to greater insights into their performances. However,

certain possibilities still remain for further exploration. For instance, in the configuration design study in chapter 6, the option of withdrawal from the side vessels of the multivessel column may be explored (note that this is considered in the middle vessel column in chapter 4). In addition to the determination of the optimal number of stages, it would be interesting to optimise the volume (holdup) of those stages (see Diwekar, 1988; Mujtaba and Macchietto, 1998). Although offcuts were considered in the case studies, the *recycling* of the offcuts has not been considered in this study. It is possible to incorporate the economics of recycling into the optimisation problem (see Christensen and Jorgensen, 1987; Mujtaba and Macchietto, 1992 and 1993).

The optimal design and configuration case studies in this work have been confined to zeotropic batch distillation. Nevertheless, the general modelling and optimisation approach demonstrated in this study can also be applied to extractive, azeotropic or reactive batch distillation systems. The work in these areas are more challenging due to the more complicated thermodynamics and kinetics as well as the additional degrees of freedom to be considered like solvent feed and withdrawal locations. The use of unconventional column configurations for these hybrid systems to tackle complex azeotropic separations is currently an active area of research (*e.g.* Warter *et al.*, 2002, Skouras and Skogestad, 2002 and Rèv *et al.*, 2003). The development of an integrated approach to solvent selection and process design is one of the ultimate objectives of future work.

Alternative Solution Techniques

The optimal solutions presented in this thesis have been obtained using either the NLP (chapter 4) or genetic algorithm (chapters 5 and 6) techniques. However, it must be emphasised that these solution techniques cannot guarantee that the best solutions will be found. The NLP method used here has only local optimisation capability, and whilst the genetic algorithm approach has the potential for finding the global optimum, this can only be guaranteed when a very large population and a very tight convergence criterion is used. Nonetheless, from a practical point of view, if the solutions obtained are better that those that could be obtained using heuristic techniques, and can be generated automatically, for example in configuration design, then considerable progress has been made. However, as an extension of this work, it might be interesting to investigate the effect of

more complex genetic algorithm parameters tuning techniques (for example, parameter optimisation or adaptable parameters) on the computational efficiency, and quality of the solutions, of the algorithm. Furthermore, the *gPROMS* tool (Process System Enterprise Ltd., 2000) used in chapter 4 for dynamic optimisation has recently been extended to take into account discrete decisions using mixed integer dynamic optimisation (MIDO) (deterministic decomposition approach). By using this facility, it would be interesting (and easier) to conduct a comparative study on the two solution approaches in terms of computational performance and results obtained, with regards to the work in chapters 5 and 6.

The development of robust and efficient global optimisation techniques for mixed discrete dynamic systems is currently being pursued actively by various researchers (examples of published works include Smith and Pantelides, 1999; Adjiman *et al.*, 2000; Liberti and Pantelides, 2003 and Bjork *et al.*, 2003), thus there is a prospect of applying these emerging solution techniques to the batch distillation optimisation problem in the future.

7.2.2 Broader Recommendations

Experimental Work

Although the optimal performance of unconventional batch distillation systems, as well as fairly complex processes such as extractive batch distillation, can now be analysed using quite rigorous conceptual optimisation study as demonstrated in this thesis, there is always a need for more practical experimental work. Although the use of rigorous and detailed models would encourage greater confidence in the solutions obtained, experimental data are required for the purpose of model validation and to verify the feasibility of the so-called "optimal" solutions. For example, by using a more detailed model in chapter 4, the process and economics limitation of the previously proposed middle vessel operating steering policy was elicited and this limitation was then indirectly confirmed by observations seen in the recent experimental works by Cui *et al.* (2002) and Warter *et al.* (2002) (see section 7.1.1).

The results of this research point to the considerable benefits that can be achieved by

using unconventional configurations in cases whereby these systems are optimal. In addition to the conceptual optimisation work here, more pilot-plant studies on their practical implementation (*e.g.* Wittgens and Skogestad, 2000; Cui *et al.*, 2002 and Warter *et al.*, 2002) and on-line control system (*e.g.* Noda *et al.*, 2001) are needed in the effort to further encourage the industrial adoption of these novel configurations.

Integrated Design

In chapter 5, a case study of the optimal design of a multipurpose column based on overall economics was presented. This represents a way of tackling the issue of column flexibility in which the external uncertainty of changing product demand is taken into account. However, batch processes often encounter other internal operational uncertainties like disturbances caused by, for example, variability in feed composition or coolant flowrate, which must be controlled. Besides controllability, other operability issues include start-up and shutdown ability, safety concerns, environmental impact and maintenance. Therefore, it is desirable for future research to look into the integrated optimisation of batch distillation systems in an effort to realise not only economical, but also *operable*, processes. The integrated design of dynamic and nonlinear systems with both continuous and discrete variables such as batch distillation is a challenging milestone that requires sophisticated methodology and considerable computational power.

Synthesis

This thesis proposes a methodology for the simultaneous and optimal determination of batch distillation configuration, design and operating policy in single unit. If required, this may be expanded to consider a sequence of interconnnected units. The work by Sundaram and Evans (1993) appeared to be the only significant attempt on batch distillation sequencing, until recently when the problem was revisited by Oldenburg *et al.* (2002) who proposed a mixed logic nonlinear programming approach for solving the problem. The ultimate aim in this area is to achieve simultaneous consideration of columns sequencing, design and operation.

Batch Versus Continuous Mode

Although this thesis has been solely concerned with distillation processes in the batch mode, it is nonetheless acknowledged that the industry is also very much interested in the decision issues related to batch versus continuous operation. The choice of batch or continuous distillation should be made on both economics and plant operability (*e.g.* flexibility) grounds. Although the choice is naturally clear for certain plant capacities (*e.g.* continuous distillation for handling large volume in the oil refining sector, or a batch plant being suffice for processing less than 10 tons per year), there are situations whereby the choice should be determined case by case, based on economics. Hasebe *et al.* (1999) attempted the comparison of the batch (multivessel system) and continuous distillation system from an energy consumption perspective by using different performance indices for the multivessel system (production rate divided by vapour flowrate) and the continuous system (sum of product flowrates divided by the sum of vapour flowrates). However, it would be of interest for future work to consider a more comprehensive economics comparison (*i.e.* by including all the relevent revenue, capital and operating costs, similar to the case studies in this thesis) and expand the comparison of the different batch systems (the objective of this thesis) to include the continuous system.

List of Publications

[1] Low K.H. and E. Sørensen, Optimal operation of extractive distillation in different batch configurations, *AIChE Journal*, 48, 1034-1050, 2002. (chapter 4)

[2] Low K.H. and E. Sørensen, Simultaneous optimal design and operation of multi-purpose batch distillation columns, *International Conference on Distillation and Absorption*, Baden-Baden, Germany, 2002. (chapters 3 & 5)

[3] Low K.H. and E. Sørensen, Simultaneous optimal design and operation of multi-purpose batch distillation columns, *Chemical Engineering and Processing*, 2003, in press. (chapters 3 & 5)

[4] Low K.H. and E. Sørensen, Simultaneous optimal design and operation of multi-vessel batch distillation, *AIChE Journal*, 2003, in press. (chapter 5)

[5] Low K.H. and E. Sørensen, Simultaneous optimal configuration, design and operation of batch distillation, *AIChE Annual Meeting*, 2003, accepted. (chapter 6)

Bibliography

[1] Abram H.J., M.M. Miladi and T.F. Attarwala, Preferable alternatives to conventional batch distillation, *IChemE Symposium Series No.104*, United Kingdom, 1987.

[2] Allgor R.J. and P.I. Barton, Mixed-integer dynamic optimization I: problem formulation, *Computers & Chemical Engineering*, 23, 567-584, 1999.

[3] Al-Tuwaim M.S. and W.L. Luyben, Multicomponent batch distillation. 3. Shortcut design of batch distillation columns, *Industrial & Engineering Chemistry Research*, 30, 507-516, 1991.

[4] Avraam M.P., N. Shah and C.C. Pantelides, A decomposition algorithm for the optimisation of hybrid dynamic processes, *Computers & Chemical Engineering*, S23, S451-S454, 1999.

[5] Bäck T. and M. Schutz, Intelligent mutation rate control in canonical genetic algorithms, *Foundation of Intelligent Systems 9th International Symposium (ISMIS'96)*, Ras W. *et al.* (editors), Springer, Berlin, 158-167, 1996.

[6] Bansal V., V. Sakizlis, R. Ross, J.D. Perkins and E.N. Pistikopoulos. New algorithms for mixed-integer dynamic optimization, *Computers & Chemical Engineering*, 27, 647-668, 2003.

[7] Barolo M., G.B. Guarise, S.A. Rienzi, A. Trotta and S. Macchietto, Running batch distillation in a column with a middle vessel, *Industrial & Engineering Chemistry Research*, 35, 4612-4618, 1996.

[8] Bernot C., M.F. Doherty and M.F. Malone, Patterns of composition change in multicomponent batch distillation, *Chemical Engineering Science*, 45, 1207-1221, 1990.

[9] Bernot C., M.F. Doherty and M.F. Malone, Feasibility and separation sequencing in multicomponent batch distillation, *Chemical Engineering Science*, 46, 1311-1326, 1991.

[10] Bernot C., M.F. Doherty and M.F. Malone, Design and operating targets for non-ideal multicomponent batch distillation, *Industrial & Engineering Chemistry Research*, 32, 293-301, 1993.

[11] Bjork K.M., P.O. Lindberg and T. Westerlund, Some convexifications in global optimization of problems containing signomial terms, *Computers & Chemical Engineering*, 27, 669-679, 2003.

[12] Bogart M.J.P., The design of equipment for fractional batch distillation, Transactions of AIChE, 33, 139, 1937.

[13] Bosley J.R. and T.F. Edgar, An efficient dynamic model for batch distillation, *Journal Process Control*, 4, 195-204, 1994.

[14] Boston J.F., H.I. Britt, S. Jirapongphan and V.B. Shah, An advanced system for the simulation of batch distillation operations, *Foundations of Computer-Aided Process Design (FOCAPD'80)*, Volume II, Mah R.S.H. and W.D. Seider (editors), New York, 1980.

[15] Cheong W. and P.I. Barton, Azeotropic distillation in a middle vessel batch column. 1. model formulation and linear separation boundaries, *Industrial & Engineering Chemistry Research*, 38, 1504-1530, 1999a.

[16] Cheong W. and P.I. Barton, Azeotropic distillation in a middle vessel batch column. 2. nonlinear separation boundaries, *Industrial & Engineering Chemistry Research*. 38, 1531-1548, 1999b.

[17] Cheong W. and P.I. Barton, Azeotropic distillation in a middle vessel batch column. 3. model validation, *Industrial & Engineering Chemistry Research*, 38, 1549-1564, 1999c.

[18] Chiotti O.J. and O.A. Iribarren, Simplified models for binary batch distillation. *Computers & Chemical Engineering*, 15, 1-5, 1991.

[19] Christensen F.M. and S.B. Jorgensen, Optimal-control of binary batch distillation with recycled waste cut, *Chemical Engineering Journal* 34, 57-64, 1987.

[20] Coley D.A., An introduction to genetic algorithms for scientists and engineers, World Scientific Publishing, Singapore, 1st ed., 1999.

[21] Cui X.B., Z.C. Yang, Y.R. Zhai and Y.J. Pan, Batch extractive distillation in a column with a middle vessel, *Chinese Journal of Chemical Engineering*, 10, 529-534, 2002.

[22] Davidyan A.G., V.N. Kiva, G.A. Meski and M. Morari, Batch distillation in a column with a middle vessel, *Chemical Engineering Science*, 49, 3033-3051, 1994.

[23] Distefano G.P., Mathematical modelling and numerical integration of multicomponent batch distillation equations, *AIChE Journal*, 14, 190-199, 1968.

[24] Diwekar U.M., Simulation, design and optimisation of multicomponent batch distillation columns, PhD Thesis, Indian Institute of Technology, India, 1988.

[25] Diwekar U.M., K.P. Madhavan and R.E. Swaney, Optimization of multicomponent batch distillation columns, *Industrial & Engineering Chemistry Research*, 28, 1011-1017, 1989.

[26] Diwekar U.M. and K.P. Madhavan, Multicomponent batch distillation column design, *Industrial & Engineering Chemistry Research*, 30, 713-721, 1991.

[27] Diwekar U.M., Unified approach to solving optimal design-control problems in batch distillation, *AIChE Journal*, 38, 1551-1563, 1992.

[28] Diwekar U.M., How simple can it be? - a look at the models for batch distillation. *Computers & Chemical Engineering*, S18, S451-S457, 1994.

[29] Domenech S. and M. Enjalbert, Program for simulating batch rectification as a unit operation, *Computers & Chemical Engineering*, 5, 181-184, 1981.

[30] Douglas J.M., Conceptual design of chemical processes, McGraw-Hill Inc., New York, Int. ed., 1988.

[31] Duran M.A. and I.E. Grossmann, An outer-approximation algorithm for a class of mixed-integer nonlinear programs, *Mathematical Programming*, 36, 307-339, 1986.

[32] Düssel R. and J. Stichlmair, Separation of azeotropic mixtures by batch distillation using an entrainer, *Computers & Chemical Engineering*, S19, S113-S118, 1995.

[33] Fair J.R., Distillation - whither, not whether, *Chemical Engineering Research & Design*, 66, 363-370, 1988.

[34] Fair J.R., Encyclopedia of separation technology, Ruthven D.M. (editor), Wiley, New York, 1997.

[35] Fraga E.S. and T.R. Senos Matias, Synthesis and optimization of a nonideal distillation system using parallel genetic algorithm,*Computers & Chemical Engineering*, 20S, S76-S84, 1996.

[36] Furlonge H.I., C.C. Pantelides and E. Sørensen, Optimal operation of multivessel batch distillation columns, *AIChE Journal*, 45, 781-801, 1999.

[37] Furlonge H.I., Optimal operation of unconventional batch distillation columns, PhD Thesis, University of London, United Kingdom, 2000.

[38] Galindez H. and A. Fredenslund, Simulation of multicomponent batch distillation process, *Computers & Chemical Engineering*, 12, 281-288, 1988.

[39] Garrard A. and E.S Fraga, Mass exchange network synthesis using genetic algorithms, *Computers & Chemical Engineering*, 22, 1837-1850, 1998.

[40] Gear C.W., Simultaneous numerical solution of differential and algebraic equations, *IEEE Transaction Circuit Theory*, 18, 89-95, 1971.

[41] Geoffrion A.M., Generalized benders decomposition, *Journal of Optimization Theory and Application*, 10, 237-260, 1972.

[42] Gmehling J. and U. Onken, Vapour-liquid equilibrium data collection, *Chemistry data series*, *DECHEMA*, Frankfurt, 1977.

[43] Goldberg D.E., Genetic algorithms in search, optimisation and machine learning. Addison-Wesley, 1989.

[44] Greaves M.A., I.M. Mujtaba, M. Barolo, A. Trotta and M.A. Hussain. Neural-network approach to dynamic optimization of batch distillation - application to a middle-vessel column, *Chemical Engineering Research & Design*, 81, 393-401. 2003.

[45] Hanke M. and P. Li, Simulated annealing for the optimization of batch distillation processes, *Computers & Chemical Engineering*, 24, 1-8, 2000.

[46] Hasebe S., B.B. Abdul Aziz, I. Hashimoto and T. Watanebe, Optimal design and operation of complex batch distillation column, *Preprints of the IFAC Workshop on Interaction between Process Design and Process Control*, London, 177-182, 1992.

[47] Hasebe S., T. Kurooka and I. Hashimoto, Comparison of the separation performances of a multi-effect batch distillation system and a continuous distillation system, *Preprints of DYCORD+'95*, Helsingor, Denmark, 249-254, 1995.

[48] Hasebe S., T. Kurooka, B.B. Abdul Aziz, I. Hashimoto and T. Watanebe, Simultaneous separation of light and heavy impurities by a complex batch distillation column, *Journal of Chemical Engineering of Japan*, 29, 1000-1006, 1996.

[49] Hasebe S., M. Noda and I. Hashimoto, Optimal operation policy for multi-effect batch distillation system, *Computers & Chemical Engineering*, 21S, S1221-S1226, 1997.

[50] Hasebe S., M. Noda and I. Hashimoto, Optimal operation for total reflux and multi-effect batch distillation systems, *Computers & Chemical Engineering*, 23, 523-532, 1999.

[51] Huckaba C.E. and D.E. Danly, Calculation procedures for binary batch rectification, *AIChE Journal*, 6, 335-342, 1960.

[52] Infochem Computer Services Ltd., Multiflash command reference, London, 2000.

[53] Kim K.J. and U.M. Diwekar, Comparing batch column configurations: parametric study involving multiple objectives, *AIChE Journal*, 46, 2475-2488, 2000.

[54] Kim K.J. and U.M. Diwekar, New era in batch distillation: computer aided analysis, optimal design and control, *Reviews in Chemical Engineering*, 17, 111-164, 2001.

[55] Kim Y.H., Optimal design and operation of a multi-product batch distillation column using dynamic model, *Chemical Engineering and Processing*, 38, 61-72, 1999.

[56] Kreul L.U., A. Gorak and P.I. Barton, Dynamic rate-based model for multicomponent batch distillation, *AIChE Journal*, 45, 1953-1962, 1999.

[57] Lang P., H. Yatim, P. Moszkowicz and M. Otterbein, Batch extractive distillation under constant reflux ratio, *Computers & Chemical Engineering*, 18, 1057-1069. 1994.

[58] Lang P., Z. Lelkes, P. Moszkowicz, M. Otterbein and H. Yatim, Different operational policies for the batch extractive distillation, *Computers & Chemical Engineering*, S19, S645-S650, 1995.

[59] Lang P., G. Modla, B. Kotai, Z. Lelkes and P. Moszkowicz, Homoazeotropic distillation of maximum azoetropes in a batch rectifier with continuous entrainer feeding II. Rigorous simulation results, *Computers & Chemical Engineering*, 24, 1429-1435, 2000.

[60] Lelkes Z., P. Lang, P. Moszkowicz, B. Benadda and M. Otterbein, Batch extractive distillation: the process and the operational policies, *Chemical Engineering Science*, 53, 1331-1348, 1998a.

[61] Lelkes Z., P. Lang, P. Moszkowicz and B. Benadda, Feasibility of extractive distillation in a batch rectifier, *AIChE Journal*, 44, 810-822, 1998b.

[62] Lewin D.R., H. Wang and O. Shalev, A generalized method for HEN synthesis using stochastic optimization - 1. general framework and MER optimal synthesis,*Computers & Chemical Engineering*, 22, 1503-1513, 1998.

[63] Liberti L. and C.C. Pantelides, Convex envelopes of monomials of odd degree, *Journal of Global Optimization*, 25, 157-168, 2003.

[64] Llano-Restrepo M. and J. Aguilar-Arias, Modeling and simulation of saline extractive distillation columns for the production of absolute ethanol, *Computers & Chemical Engineering*, 27, 527-549, 2003.

[65] Logsdon J.S., U.M. Diwekar and L.T. Biegler, On the simultaneous optimal design and operation of batch distillation columns, *Transactions of IChemE*, 68, 434-444. 1990.

[66] Logsdon J.S. and L.T. Biegler, Accurate determination of optimal reflux policies for the maximum distillate problem in batch distillation, *Industrial & Engineering Chemistry Research*, 32, 692-700, 1993.

[67] Marriott J.I., E. Sørensen and I.D.L. Bogle, Rigorous optimal design of a pervaporation plant, *AIChE Symposium Series 323*, 96, 415-418, 2000.

[68] McCabe W.L. and E.W. Thiele, Graphic design of fractionating columns, *Journal of Industrial and Engineering Chemistry*, 17, 605-611, 1925.

[69] Meadows E.L., Multicomponent batch distillation calculations on a digital computer, *Chemical Engineering Progress Symposium Series*, 59, 48-55, 1963.

[70] Mehlhorn A., J.M. Nougues and L. Puigjaner, Using rate-based approach under consideration of different contacting regimes for multicomponent batch distillation simulation, *Computers & Chemical Engineering*, S22, S645-S648, 1998.

[71] Meski G.A. and M. Morari, Design and operation of a batch distillation column with a middle vessel, *Computers & Chemical Engineering*, S19, S597-S602, 1995.

[72] Milani S.M., Optimization of solvent feed rate for maximum recovery of high purity top product in batch extractive distillation, *Transactions of IChemE*, 77, 469-470, 1999.

[73] Mohideen M.J., J.D. Perkins and E.N. Pistikopoulos, Optimal design of dynamic systems under uncertainty, *AIChE Journal*, 42, 2251-2272, 1996.

[74] Mujtaba I.M. and S. Macchietto, An optimal recycle policy for multicomponent batch distillation, *Computers & Chemical Engineering*, S16, S273-S280, 1992.

[75] Mujtaba I.M. and S. Macchietto, Optimal operation of multicomponent batch distillation - multiperiod formulation and solution, *Computers & Chemical Engineering*, 17, 1191-1207, 1993.

[76] Mujtaba I.M. and S. Macchietto, Optimal operation of multicomponent batch distillation - a comparative study using conventional and unconventional columns, *Preprints Advanced Control of Chemical Processes (ADCHEM'94)*, Kyoto, Japan, 415-420, 1994.

[77] Mujtaba I.M. and S. Macchietto, Simultaneous optimization of design and operation of multicomponent batch distillation column - single and multiple separation duties, *Journal of Process Control*, 6, 27-36, 1996.

[78] Mujtaba I.M., Use of continuous distillation columns for batch separation, *Chemical Engineering Research & Design*, 75, 609-619, 1997.

[79] Mujtaba I.M. and S. Macchietto, Holdup issues in batch distillation - binary mixtures, *Chemical Engineering Science*, 53, 2519-2530, 1998.

[80] Mujtaba I.M., Optimization of batch extractive distillation processes for separating close boiling and azeotropic mixtures, *Transactions of IChemE*, 77, 588-596, 1999.

[81] Mukherjee S., R.K. Dahule, S.S. Tambe, D.D. Ravetkar and B.D. Kulkarni, Consider genetic algorithms to optimize batch distillation - alternative simulation tool calculates best reflux conditions to separate binary mixtures, *Hydrocarbon Processing*, 80, 59-66, 2001.

[82] Noda M., A. Kato, S. Hasebe and I. Hashimoto, Optimal structure of batch distillation column, *Computers & Chemical Engineering*, S23, S105-S108, 1999.

[83] Noda M., T. Chida, S. Hasebe and I. Hashimoto, On-line optimization system of pilot scale multi-effect batch distillation system, *Computers & Chemical Engineering*, 24, 1577-1583, 2000.

[84] Noda M., A. Kato, T. Chida, S. Hasebe and I. Hashimoto, Optimal structure and on-line optimal operation of batch distillation column, *Computers & Chemical Engineering*, 25, 109-117, 2001.

[85] Oldenburg J., W. Marquardt, D. Heinz and D. Leineweber, Mixed-logic dynamic optimization applied to configuration and sequencing of batch distillation processes, *European Symposium on Computer Aided Process Engineering (ESCAPE-12)*, The Hague, Netherlands, 283-288, 2002.

[86] Perry R.H. and D. Green, Perry's chemical engineers' handbook, McGraw-Hill Inc.. New York, 6th ed., 1984.

[87] Phimister J.R. and W.D. Seider, Semicontinuous, middle vessel distillation of ternary mxitures, *AIChE Journal*, 46, 1508-1520, 2000.

[88] Process Systems Enterprise Ltd., *gPROMS* advanced user's guide, London, 2000.

[89] Quesada I. and I.E. Grossmann, An LP/NLP based branch and bound algorithm for convex MINLP optimization problems, *Computers & Chemical Engineering*, 16, 937-947, 1992.

[90] Rayleigh L., On the distillation of binary mixtures, *Philosophical Magazine (vi)*, 4, 521, 1902.

[91] Rèv E., Z. Lelkes, V. Varga, C. Steger and Z. Fonyo, Separation of a minimum-boiling azeotrope in a batch extractive rectifier with an intermediate-boiling entrainer, *Industrial & Engineering Chemistry Research*, 42, 162-174, 2003.

[92] Robinson C.S. and E.R. Gilliland, Elements of fractional distillation, McGraw-Hill Inc., New York, 4th ed., 1950.

[93] Rose L.M., Distillation design in practice, Elsevier, New York, 1985.

[94] Ruiz Ahón V. and J.L. de Medeiros, Optimal programming of ideal and extractive batch distillation: single vessel operations, *Computers & Chemical Engineering*, 25, 1115-1140, 2001.

[95] Safrit B.T., A.W. Westerberg, U. Diwekar and O.M. Wahnschafft, Extending continuous conventional and extractive distillation feasibility insights to batch distillation, *Industrial & Engineering Chemistry Research*, 34, 3257-3264, 1995.

[96] Safrit B.T. and A.W. Westerberg, Improved operational policies for batch extractive distillation columns, *Industrial & Engineering Chemistry Research*, 36, 436-443, 1997.

[97] Salomone H.E., O.J. Chiotti and O.A. Iribarren, Short-cut design procedure for batch distillations, *Industrial & Engineering Chemistry Research*, 36, 130-136. 1997.

[98] Salomone H.E., Conceptual dynamic models for the design of batch distillations, *AIChE Symposium Series No.323*, 96, 342-345, 2000.

[99] Sarkar D. and J.M. Modak, Optimisation of fed-batch bioreactors using genetic algorithms, *Chemical Engineering Science*, 58, 2283-2292, 2003.

[100] Sharif M., N. Shah and C.C. Pantelides, On the design of multicomponent batch distillation columns, *Computers & Chemical Engineering*, S22, S69-S76, 1998.

[101] Sharif M., Design of integrated batch processes, PhD Thesis, University of London, United Kingdom, 1999.

[102] Skouras S. and S. Skogestad, Separation of ternary heteroazeotropic mixtures in the closed multivessel batch distillation column, *International Conference on Distillation and Absorption*, Baden-Baden, Germany, 2002.

[103] Silva C.M. and E.C. Biscaia, Genetic algorithm development for multi-objective optimization of batch free-radical polymerization reactors, *Computers & Chemical Engineering*, 27, 1329-1344, 2003.

[104] Sinnott R.K., Coulson and Richardson's Chemical Engineering, Volume 6, Pergamon Press Ltd., Oxford, 2nd ed., 1993.

[105] Skogestad S., B. Wittgens, R. Litto and E. Sørensen, Multivessel batch distillation, *AIChE Journal*, 43, 971-978, 1997.

[106] Smith E.M.B. and C.C. Pantelides, A symbolic reformulation/spatial branch-and-bound algorithm for the global optimisation of nonconvex MINLPs, *Computers & Chemical Engineering*, 23, 457-478, 1999.

[107] Smith R., Chemical process design, McGraw-Hill Inc., New York, 1995.

[108] Smoker E.H. and A. Rose, Graphical determination of batch distillation curves for binary mixtures, *Transactions of AIChE*, 36, 285-293, 1940.

[109] Sørensen E., A cyclic operating policy for batch distillation - theory and practice, *Computers & Chemical Engineering*, 23, 533-542, 1999.

[110] Sørensen E. and S. Skogestad, Comparison of regular and inverted batch distillation, *Chemical Engineering Science*, 51, 4949-4962, 1996.

[111] Sundaram S. and L.B. Evans, Synthesis of separations by batch distillation, *Industrial & Engineering Chemistry Research*, 32, 500-510, 1993.

[112] Tomazi K.G., Limitations and dynamics imposed on multicomponent batch distillation by tray hydraulics, *Industrial & Engineering Chemistry Research*, 36, 4273-4281, 1997.

[113] Vassiliadis V.S., R.W.H. Sargent and C.C. Pantelides, Solution of a class of multistage dynamic optimization problems. 1. problems without path constraints, *Industrial & Engineering Chemistry Research*, 33, 2111-2122, 1994a.

[114] Vassiliadis V.S., R.W.H. Sargent and C.C. Pantelides, Solution of a class of multistage dynamic optimization problems. 2. problems with path constraints, *Industrial & Engineering Chemistry Research*, 33, 2123-2133, 1994b.

[115] Viswanathan J. and I.E. Grossmann, A combined penalty-function and outer-approximation method for MINLP optimization, *Computers & Chemical Engineering*, 14, 769-782, 1990.

[116] Wahnschaff O.M. and A.W. Westerberg, The product composition regions of azeotropic distillation columns. 2. Separability in two-feed columns and entrainer selection, *Industrial & Engineering Chemistry Research*, 32, 1108-1120, 1993.

[117] Wall M., GAlib: C++ genetic algorithms library, Version 2.4.5, http://lancet.mit.edu/ga, 1999.

[118] Watson S., X. Joulia, S. Macchietto, J.M. Le Lann, G. Vayrette and J.J. Letourneau, Azeotropic batch distillation - new problems and some solutions, *Computers & Chemical Engineering*, S19, S589-S596, 1995.

[119] Warter M. and J. Stichlmair, Batchwise extractive distillation in a column with a middle vessel, *Computers & Chemical Engineering*, S23, S915-S918, 1999.

[120] Warter M., D. Demicoli and J. Stichlmair, Operation of a batch distillation column with a middle vessel: experimental results for the separation of zeotropic and azeotropic mixtures, *International Conference on Distillation and Absorption*, Baden-Baden, Germany, 2002.

[121] Wittgens B., R. Litto, E. Sørensen and S. Skogestad, Total reflux operation of multivessel batch distillation, *Computers & Chemical Engineering*, S20, S1041-S1046. 1996.

[122] Wittgens B. and S. Skogestad, Closed operation of multivessel batch distillation: experimental verification, *AIChE Journal*, 46, 1209-1217, 2000.

[123] Yatim H., P. Moszkowicz, O.A. Otterbein and P. Lang, Dynamic simulation of a batch extractive distillation process, *Computers & Chemical Engineering*, S17, S57-S62, 1993.

[124] Yeomans H. and I.E. Grossmann, Disjunctive programming models for the optimal design of distillation columns and separation sequences, *Industrial & Engineering Chemistry Research*, 39, 1637-1648, 2000.

[125] Zamar S.D., E. Salomone and O.A. Iribarren, Short-cut method for multiple task batch distillations, *Industrial & Engineering Chemistry Research*, 37, 4801-4807, 1998.

[126] Zhang Z., M. Mazzotti and M. Morbidelli, Multiobjective optimization of simulated moving bed and varicol processes using genetic algorithm, *Journal of Chromatography A*, 989, 95-108, 2003.

Nomenclature

A	cross-sectional area	m^2
A_{holes}	total area of holes on a tray	m^2
A_k	cross-sectional tray liquid catchment area	m^2
A_{reb}	cross-sectional area of reboiler drum	m^2
c	sigma multiplier	
C_{cap}	main capital cost	\$
C_{ex}	installed heat exchanger cost	\$
C_{feed}	unit cost of feed	$\$/mol$
C_i	selling price of product i	$\$/mol$
C_p	specific heat capacity	$J/molK$
C_Q	unit cost of heating	$\$/J$
C_{sh}	installed column shell cost	\$
C_{sol}	unit cost of solvent	$\$/mol$
C_{uty}	utilities cost	\$
D	column diameter	m
f	corrected fitness of genome	
f_{ave}	average fitness of population	
f^{σ}	population standard deviation	
f^{S}	scaled fitness of genome	
f_{sum}	total fitness of genome population	
F_{mv}	liquid withdrawal flowrate from middle vessel	mol/s
F_p	packing factor	

F_{reb}	liquid withdrawal flowrate from reboiler	mol/s
F_R^V	vapour flowrate leaving the reboiler drum	mol/s
F_{sol}	solvent feedrate	mol/s
F_w	wall correction factor	
F^W	product withdrawal flowrate	mol/s
g	acceleration due to gravity	m/s^2
h	specific molar enthalpy	J/mol
h_j	partial molar enthalpy of component j	J/mol
h^{vap}	specific latent heat of vaporisation	J/mol
h_{weir}	weir height	m
h'_{weir}	height of liquid above weir	m
H	liquid holdup	mol
$H_{A,i}$	amount of accumulated product i	mol
$H_{A,sol}$	amount of recovered solvent	mol
$H_{D,i}$	holdup in vessel i	mol
H_{feed}	amount of feed	mol
$H_{feed,i}$	amount of component i in feed	mol
H_{rd}	liquid holdup in reflux drum	mol
$H_{sol}^{make-up}$	amount of make-up solvent	mol
H_S	enthalpy difference between steam and liquid states	J/mol
H_{tray}	liquid holdup in tray	mol
K_1	column investment cost coefficient	
K_2	reboiler and condenser cost coefficient	
K_3	utility cost coefficient	
l	liquid level	m
l_{weir}	weir length	m
L	liquid flowrate	mol/s
L_i	reflux flowrate from vessel i	mol/s
L_{mv}	reflux flowrate from middle vessel	mol/s
L'_{mv}	effective flowrate from middle vessel	mol/s
M	liquid holdup	mol
M_{mv}	liquid holdup in middle vessel	mol

M_{reb}	liquid holdup in reboiler	mol
n_c	number of constraints	
N	number of trays	
N_b	number of batches	
N_C	number of components	
N_I	number of control intervals	
N_m	number of mixtures	
N_{pop}	number of genomes in one population	
N_S	number of column sections in multivessel system	
p	penalty function power coefficient	
P	pressure	Pa
P	profit/objective function	\$
P_A	annual profit	$\$/yr$
P_c	probability of crossover	%
P_m	probability of mutation	%
P_{ss}	percentage of population overlap	%
q	volumetric flowrate of liquid over weir	m^3/s
Q	rate of heat transfer	W
Q_C	rate of heat transfer in condenser	W
Q_{mv}	rate of heat transfer in middle vessel	W
Q_{reb}	reboiler heat duty	W
Q_T	total heat duty	W
R	internal reflux ratio	
R_B	reboil ratio	
R_c	random number generated for crossover operator	
R_{D2}	liquid stream split ratio	
R_{D3}	vapour stream split ratio	
R_m	random number generated for mutation operator	
R_s	random number generated for selection operator	
t	time	s
t	temperature	K
t_f	batch processing time	s

t_s	batch set-up time	s
T	temperature	K
T_A	total processing time per year	s
u	control variables	
u_d	set of design decision variables	
u_o	set of operation decision variables	
v	molar volume	m^3/mol
V	column vapour loading	mol/s
W_S	mass vaporisation rate	mol/s
x	liquid composition	mol/mol
x	differential variables	
$x_{A,i}$	mole fraction of main component in product i	mol/mol
$x_{A,sol}$	mole fraction of solvent in recovered solvent	mol/mol
$x_{feed,sol}$	mole fraction of solvent in solvent feed	mol/mol
$x_{D,i}$	mole fraction of main component in vessel i	mol/mol
y	algebraic variables	
Y	boolean variables	

Greek Letters

α	tray vapour flow coefficient	$mol/sPa^{0.5}$
β	aeration factor	
γ	condenser vapour flow coefficient	
κ	penalty function	
λ	Wilson interaction parameter	J/mol
μ	parameters of basis function	
ν	volume	m^3
Π	recovery	$mol\%$
ρ	molar density	mol/m^3
ϕ	fugacity coefficient	
ϕ_m	fraction of production time allocated to mixture m	s/s
φ	scale parameter	
Ψ	production sales revenue	\$

Ω	objective function

Subscripts

A	accumulator
b	batch
BC	base case
C	condenser
cap	capital
D	distillate/divider
ex	heat exchanger
f	final
$feed$	feed
i, j	component/control interval/constraint/product/column section/vessel
k	tray
LB	lower bound
m	mean
m, M	mixture
mv	middle vessel
Q	heating
rd	reflux drum
reb	reboiler
sh	column shell
sol	solvent
stm	steam
T	total
UB	upper bound
uty	utility

Superscripts

in	inlet stream
L	liquid
max	specified upper bound

min	specified lower bound
out	outlet stream
V	vapour
W	withdrawal

Appendix A

Batch Distillation Modelling and Implementation

The mathematical models used for the work as discussed in chapter 3 are presented. The submodels making up the batch distillation column include the reboiler, tray, condenser, pressure vessel, accumulator, divider and mixer (Figure A.1). Sections A.1.1 to A.1.7 list both the detailed (used in chapters 4 and 5) and rigorous (used in chapters 5 and 6) submodel equations. The connection of the submodels to form the overall batch distillation columns, as implemented in the *gPROMS* modelling tool (Process Systems Enterprise Ltd., 2000), is discussed in section A.2.

A.1 Submodels

A.1.1 Reboiler

Detailed model key assumptions

- Perfect mixing of both liquid and vapour phase
- Phase thermodynamic equilibrium
- Adiabatic
- No liquid entrainment in vapour stream

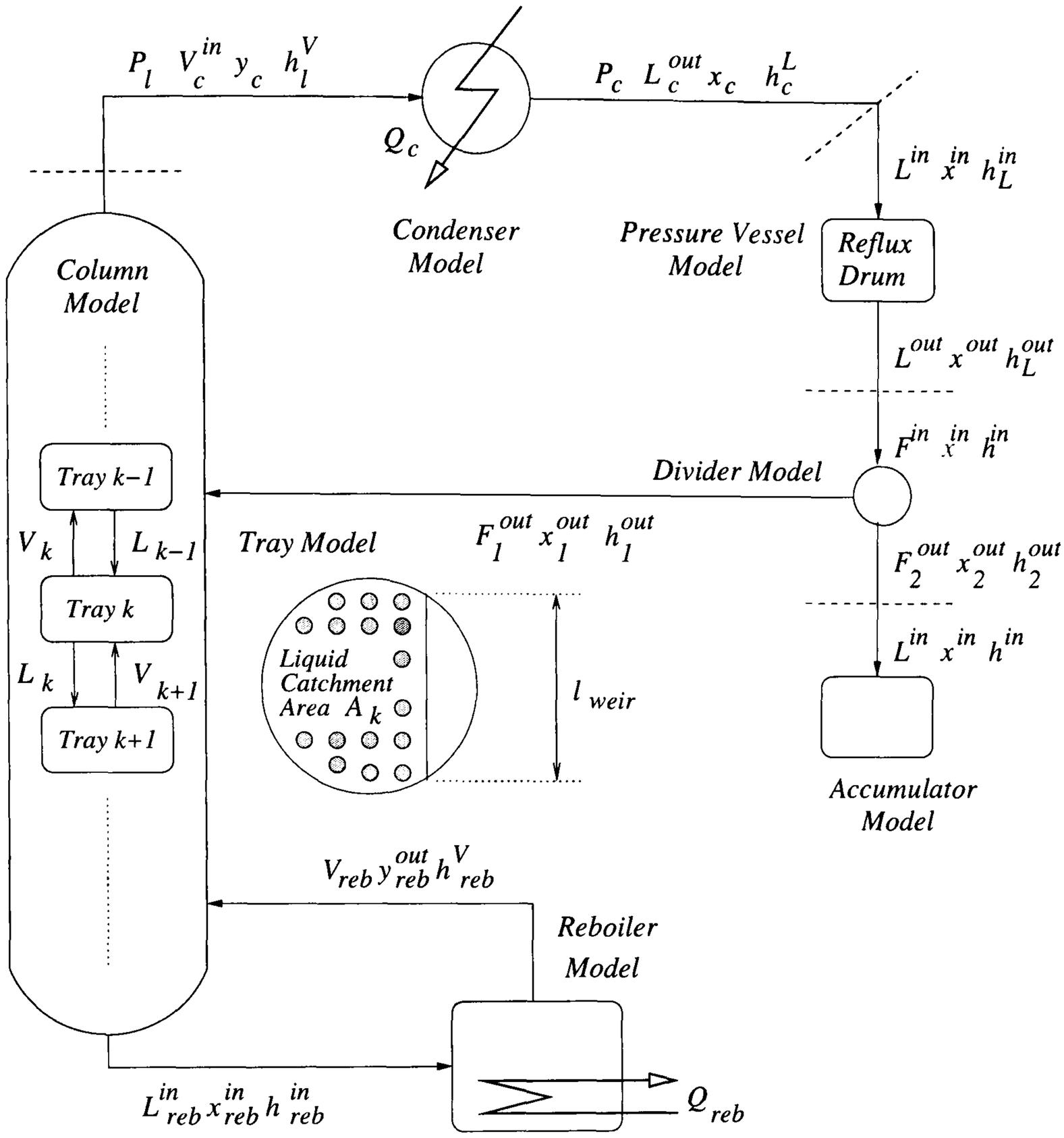


Figure A.1: Batch distillation model

Equations

Molar balance on component i:

$$\frac{dM_{i,reb}}{dt} = x_{i,reb}^{\text{in}} L_{reb}^{\text{in}} - y_{i,reb}^{\text{out}} V_{reb} \qquad i = 1, .., N_C \tag{A.1}$$

Energy balance:

$$\frac{dU_{reb}}{dt} = h_{reb}^{\text{in}} L_{reb}^{\text{in}} - h_{reb}^V V_R + Q_{reb} \tag{A.2}$$

Liquid and vapour contributions to component holdup:

$$M_{i,reb} = x_{i,reb} M_{reb}^L + y_{i,reb}^{\text{out}} M_R^V \qquad i = 1, .., N_C \tag{A.3}$$

Liquid and vapour contributions to total internal energy:

$$U_{reb} = h^L_{reb} M^L_{reb} + h^V_{reb} M^V_{reb} - P_{reb} v_{reb} \tag{A.4}$$

Height of liquid in the reboiler:

$$l_{reb} = \frac{M^L_{reb}}{\rho^L_R A_{reb}} \tag{A.5}$$

Total volume constraint:

$$v_{reb} = \frac{M^L_{reb}}{\rho^L_{reb}} + \frac{M^V_{reb}}{\rho^V_{reb}} \tag{A.6}$$

Equilibrium relationship:

$$\phi^V_{i,reb}\, y^{\text{out}}_{i,reb} = \phi^L_{i,reb}\, x_{i,reb} \qquad i = 1, .., N_C \tag{A.7}$$

Normalisation equations:

$$\sum_{i=1}^{N_C} x_{i,reb} = \sum_{i=1}^{N_C} y^{\text{out}}_{i,reb} = 1 \tag{A.8}$$

In cases with withdrawal, F_{reb} (chapter 4), was added to the balance equations accordingly:

Molar balance on component i:

$$\frac{dM_{i,reb}}{dt} = x^{\text{in}}_{i,reb} L^{\text{in}}_{reb} - y^{\text{out}}_{i,reb} V_{reb} - x_{i,reb} F_{reb} \qquad i = 1, .., N_C \tag{A.9}$$

Energy balance:

$$\frac{dU_{reb}}{dt} = h^{\text{in}}_{reb} L^{\text{in}}_{reb} - h^V_{reb} V_R + Q_{reb} - h^L_{reb} F_{reb} \tag{A.10}$$

Additional assumptions for the rigorous model

- Fast energy dynamics
- Negligible vapour holdup
- Constant liquid holdup

Equations

Molar balance on component i:

$$\frac{dM_{i,reb}}{dt} = x_{i,reb}^{\text{in}} L_{reb}^{\text{in}} - y_{i,reb}^{\text{out}} V_{reb} \qquad i = 1,..,N_C \tag{A.11}$$

Fast energy balance:

$$Q_{reb} = h_{reb}^{\text{in}} L_{reb}^{\text{in}} - h_{reb}^{V} V_{reb} \tag{A.12}$$

Liquid contributions to component holdup (negligible vapour contribution):

$$M_{i,reb} = x_{i,reb} M_{reb}^{L} \qquad i = 1,..,N_C \tag{A.13}$$

Equilibrium relationship:

$$\phi_{i,reb}^{V}\, y_{i,reb}^{\text{out}} = \phi_{i,reb}^{L}\, x_{i,reb} \qquad i = 1,..,N_C \tag{A.14}$$

Normalisation equations:

$$\sum_{i=1}^{N_C} x_{i,reb} = \sum_{i=1}^{N_C} y_{i,reb}^{\text{out}} = 1 \tag{A.15}$$

Usual specifications

- Connection of liquid inlet stream (L_{reb}^{in})
- Connection or flowrate of outlet stream (F_{reb} and V_{reb})
- Reboiler duty (Q_{reb}) (detailed model)
- Reboiler boilup rate (V_{reb}) (rigorous model, chapter 6)
- Operating pressure (P) (rigorous model)
- Initial temperature T on the reboiler (detailed model)
- Initial total liquid holdup (M_{reb}^{L})
- Initial mole fraction of ($N_C - 1$) component in the liquid phase ($x_{i,reb}$)

A.1.2 Sieve Tray

Detailed model key assumptions

- Both liquid and vapour phases exist in all times
- Perfect mixing of liquid and vapour
- Phase thermodynamic equilibrium (Murphree plate efficiency = 1)
- No entrainment of liquid or vapour phase
- No weeping
- The dynamics in the downcomer are neglected

Equations

Here, we consider the kth tray, counting downwards from the top of the column.

Molar balance on component i:

$$\frac{dM_{i,k}}{dt} = x_{i,k-1}L_{k-1} + y_{i,k+1}V_{k+1} - x_{i,k}L_k - y_{i,k}V_k \qquad i = 1,..,N_C \tag{A.16}$$

Energy balance:

$$\frac{dU_k}{dt} = h^L_{k-1}L_{k-1} + h^V_{k+1}V_{k+1} - h^L_k L_k - h^V_k V_k \tag{A.17}$$

Liquid and vapour contributions to component holdup:

$$M_{i,k} = x_{i,k}M^L_k + y_{i,k}M^V_k \qquad i = 1,..,N_C \tag{A.18}$$

Liquid and vapour contributions to total internal energy:

$$U_k = h^L_k M^L_k + h^V_k M^V_k - P_k v_k \tag{A.19}$$

Height of liquid in the tray:

$$l_k = \left(h_{weir} + h'_{weir,k}\right) = \frac{M^L_k}{\rho^k_R A_k} \tag{A.20}$$

Total volume constraint:

$$v_k = \frac{M_k^L}{\rho_k^L} + \frac{M_k^V}{\rho_k^V} \tag{A.21}$$

Equilibrium relationship:

$$\phi_{i,k}^V \, y_{i,k} = \phi_{i,k}^L \, x_{i,k} \qquad i = 1, .., N_C \tag{A.22}$$

Normalisation equations:

$$\sum_{i=1}^{N_C} x_{i,k} = \sum_{i=1}^{N_C} y_{i,k} = 1 \tag{A.23}$$

Liquid flowrate relationship using Francis weir formula (Perry and Green, 1984):

$$L_k = \frac{1.7764 \, l_{weir} \rho_k^L}{F_w^{1.5}} \left[\frac{\left(h_{weir} + h'_{weir,k} \right) - \beta h_{weir}}{\beta} \right]^{3/2} \tag{A.24}$$

where β is the aeration factor and F_w the wall correction factor.

Relationship between vapour flowrate and pressure drop across the tray (Perry and Green, 1984):

$$V_{k+1} = \overline{\rho}_{k+1}^V A_{holes} \left[\frac{P_{k+1} - P_k - g\varphi \overline{\rho}_k^L \left(h_{weir} + h'_{weir,k} \right)}{\alpha \rho_{k+1}^V} \right]^{1/2} \tag{A.25}$$

where α is the tray vapour flow coefficient and φ the scale parameter.

In the case of middle vessel and multivessel distillation models, the bottom tray and top tray submodel connected to the column sections (an array of tray submodels) requires extra terms in the balances to account for either the vapour and liquid flows, $F^{V/L}$, from the side vessels:

Molar balance on component i:

$$\frac{dM_{i,k}}{dt} = x_{i,k-1} L_{k-1} + y_{i,k+1} V_{k+1} - x_{i,k} L_k - y_{i,k} V_k - z^{V/L} F^{V/L} \qquad i = 1, .., N_C \tag{A.26}$$

Energy balance:

$$\frac{dU_k}{dt} = h^L_{k-1}L_{k-1} + h^V_{k+1}V_{k+1} - h^L_k L_k - h^V_k V_k - h^{V/L}F^{V/L} \qquad \text{(A.27)}$$

Additional assumptions for the rigorous model

- Fast energy dynamics
- Negligible vapour holdup
- Constant liquid holdup

Equations

Molar balance on component i:

$$\frac{dM_{i,k}}{dt} = x_{i,k-1}L_{k-1} + y_{i,k+1}V_{k+1} - x_{i,k}L_k - y_{i,k}V_k \qquad i = 1,..,N_C \qquad \text{(A.28)}$$

Fast energy balance:

$$h^L_{k-1}L_{k-1} + h^V_{k+1}V_{k+1} = h^L_k L_k + h^V_k V_k \qquad \text{(A.29)}$$

Liquid contributions to component holdup (negligible vapour contribution):

$$M_{i,k} = x_{i,k}M^L_k \qquad i = 1,..,N_C \qquad \text{(A.30)}$$

Flowrate balance:

$$L_{k-1} + V_{k+1} = L_k + V_k \qquad \text{(A.31)}$$

Equilibrium relationship:

$$\phi^V_{i,k}\, y_{i,k} = \phi^L_{i,k}\, x_{i,k} \qquad i = 1,..,N_C \qquad \text{(A.32)}$$

Normalisation equations:

$$\sum_{i=1}^{N_C} x_{i,k} = \sum_{i=1}^{N_C} y_{i,k} = 1 \qquad \text{(A.33)}$$

Usual specifications

- Tray geometry (v_k, h_{weir}, l_{weir}, A_k, A_{holes})
- Tray characteristics (φ, F_w, β, α)
- Connection or flowrates of two inlet streams (L_{k-1}, V_{k+1})
- Connection or flowrates of one outlet stream (V_k)
- Operating pressure (P) (rigorous model)
- Initial temperature T on the tray (detailed model)
- Initial total liquid holdup (M_k^L)
- Initial mole fraction of ($N_C - 1$) component in the liquid phase ($x_{i,k}$)

A.1.3 Condenser

Detailed model key assumptions

- Total condensation
- No pressure drop along the condenser
- No subcooling
- Molar balance

Equations

Molar balance on component i:

$$y_{i,C} = x_{i,C} \qquad i = 1, .., N_C \tag{A.34}$$

Molar balance:

$$V_C^{\text{in}} = L_C^{\text{out}} \tag{A.35}$$

Vapour flow relationship for a tray column (Perry and Green, 1984):

$$V_C^{\text{in}} = \gamma\sqrt{(P_1 - P_C)} \tag{A.36}$$

where γ is the condenser vapour flow coefficient.

Energy balance:

$$h_1^V V_C^{\text{in}} = h_C^L L_C^{\text{out}} + Q_C \tag{A.37}$$

Equilibrium relationship:

$$\phi_{i,C}^V \, \overline{y}_{i,C} = \phi_{i,C}^L \, x_{i,C} \qquad i = 1, .., N_C \tag{A.38}$$

Normalisation equation:

$$\sum_{i=1}^{N_C} \overline{y}_{i,C} = 1 \tag{A.39}$$

Rigorous model

The flowrate into the condenser, V_C^{in}, is a specified degree of freedom. Hence, the equations are similar to the detailed model above with Equation A.38 dropped.

Usual specifications

- Connection of the inlet stream (V_C^{in})
- Condenser vapour flow coefficient (γ) (detailed model)
- Condenser vapour loading (V_C^{in}) (rigorous model)
- Condenser pressure (P)

A.1.4 Pressure Vessel

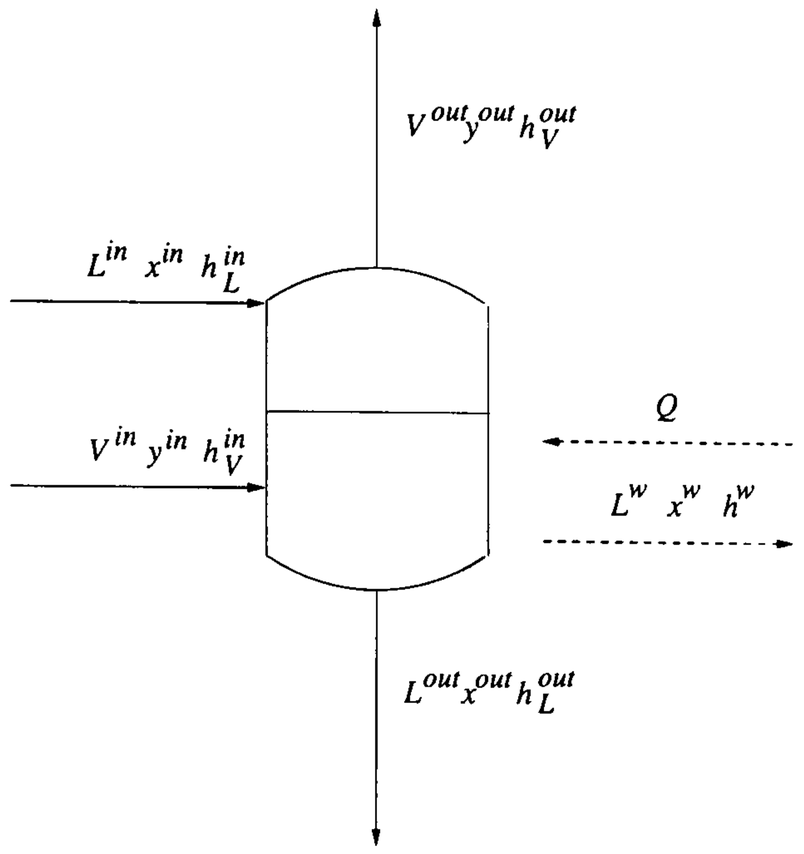


Figure A.2: Pressure vessel

Detailed model key assumptions

- Both phases are perfectly mixed
- Phase thermodynamic equilibrium
- Adiabatic

Equations

Molar balance on component i:

$$\frac{dM_i}{dt} = x_i^{\text{in}} L^{\text{in}} - x_i^{\text{out}} L^{\text{out}} + y_i^{\text{in}} V^{\text{in}} - y_i^{\text{out}} V^{\text{out}} \qquad i = 1, .., N_C \qquad \text{(A.40)}$$

Energy balance:

$$\frac{dU}{dt} = h_L^{\text{in}} L^{\text{in}} - h_L^{\text{out}} L^{\text{out}} + h_V^{\text{in}} V^{\text{in}} - h_V^{\text{out}} V^{\text{out}} \qquad \text{(A.41)}$$

Liquid and vapour contributions to component holdup:

$$M_i = x_i^{\text{out}} M^L + y_i^{\text{out}} M^V \qquad i = 1, .., N_C \qquad \text{(A.42)}$$

Liquid and vapour contributions to internal energy:

$$U = h_L^{\text{out}} M^L + h_V^{\text{out}} M^V - Pv \tag{A.43}$$

Total volume constraint:

$$v = \frac{M^L}{\rho^L} + \frac{M^V}{\rho^V} \tag{A.44}$$

Height of liquid in the vessel:

$$l = \frac{M^L}{\rho^L A} \tag{A.45}$$

Equilibrium relationship:

$$\phi_i^V \; y_i^{\text{out}} = \phi_i^L \; x_i^{\text{out}} \qquad i = 1, .., N_C \tag{A.46}$$

Normalisation equations:

$$\sum_{i=1}^{N_C} x_i^{\text{out}} = \sum_{i=1}^{N_C} y_i^{\text{out}} = 1 \tag{A.47}$$

This pressure vessel model is used for the middle vessel in chapter 4. It is also used for the reflux drum, in which case the vapour streams are dropped (V^{in} and V^{out}). In both the middle and reflux vessels, the outlet liquid flowrate is set equal to the inlet liquid flowrate ($L^{\text{in}} = L^{\text{out}}$).

In the case where an additional liquid withdrawal stream, L^{w}, and heating, Q, is included, these are added to the balance equations:

Molar balance on component i:

$$\frac{dM_i}{dt} = x_i^{\text{in}} L^{\text{in}} - x_i^{\text{out}} L^{\text{out}} + y_i^{\text{in}} V^{\text{in}} - y_i^{\text{out}} V^{\text{out}} - x_i^{\text{w}} L^{\text{w}} \qquad i = 1, .., N_C \tag{A.48}$$

Energy balance:

$$\frac{dU}{dt} = h_L^{\text{in}} L^{\text{in}} - h_L^{\text{out}} L^{\text{out}} + h_V^{\text{in}} V^{\text{in}} - h_V^{\text{out}} V^{\text{out}} - h^{\text{w}} L^{\text{w}} + Q \tag{A.49}$$

Additional assumptions for the rigorous model

- Fast energy dynamics
- Negligible vapour holdup
- Constant liquid holdup

Equations

Molar balance on component i:

$$\frac{dM_i}{dt} = x_i^{\text{in}} L^{\text{in}} - x_i^{\text{out}} L^{\text{out}} \qquad i = 1, .., N_C \tag{A.50}$$

Fast energy balance:

$$h_L^{\text{in}} L^{\text{in}} = h_L^{\text{out}} L^{\text{out}} \tag{A.51}$$

Liquid contributions to component holdup (negligible vapour contribution):

$$M_i = x_i^{\text{out}} M^L \qquad i = 1, .., N_C \tag{A.52}$$

Equilibrium relationship:

$$\phi_i^V \; y_i^{\text{out}} = \phi_i^L \; x_i^{\text{out}} \qquad i = 1, .., N_C \tag{A.53}$$

Normalisation equations:

$$\sum_{i=1}^{N_C} x_i^{\text{out}} = \sum_{i=1}^{N_C} y_i^{\text{out}} = 1 \tag{A.54}$$

The rigorous pressure vessel model is used for the reflux drum as well as the intermediate vessels in the multivessel column model. Again, the outlet liquid flowrate is set equal to the inlet liquid flowrate ($L^{\text{in}} = L^{\text{out}}$) for both cases.

Usual specifications

- Connection of the inlet streams (L^{in}, V^{in})

- Flowrate of outlet liquid (L^{in})
- Initial temperature T in the vessel (detailed model)
- Initial total liquid holdup (M^L)
- Initial mole fraction of $(N_C - 1)$ component in the liquid phase (x_i^{out})

A.1.5 Accumulator Model

The model of the accumulator is similar to that of the pressure vessel model, except that there is no flows leaving the unit, *i.e.* $L^{\text{out}} = V^{\text{out}} = 0$.

A.1.6 Stream Divider

Model key assumptions

- No change in temperature and composition
- No pressure drop through the divider

Equations

Molar balance:

$$F^{\text{in}} = F_1^{\text{out}} + F_2^{\text{out}} \tag{A.55}$$

Split ratio definition:

$$R = \frac{F_1^{\text{out}}}{F^{\text{in}}} \tag{A.56}$$

Inlet and outlet relationship:

$$P^{\text{in}} = P_1^{\text{out}} = P_2^{\text{out}} \tag{A.57}$$

$$T^{\text{in}} = T_1^{\text{out}} = T_2^{\text{out}} \tag{A.58}$$

$$h^{\text{in}} = h_1^{\text{out}} = h_2^{\text{out}} \tag{A.59}$$

$$x_j^{\text{in}} = x_{j,1}^{\text{out}} = x_{j,2}^{\text{out}} \qquad i = 1, .., N_C \tag{A.60}$$

Usual specifications

- Connection or specification of the inlet stream (F^{in}, P^{in}, T^{in}, x_j^{in})
- Split ratio (R)

A.1.7 Streams Mixer

This submodel is used to introduce solvent into the batch distillation column (chapter 4).

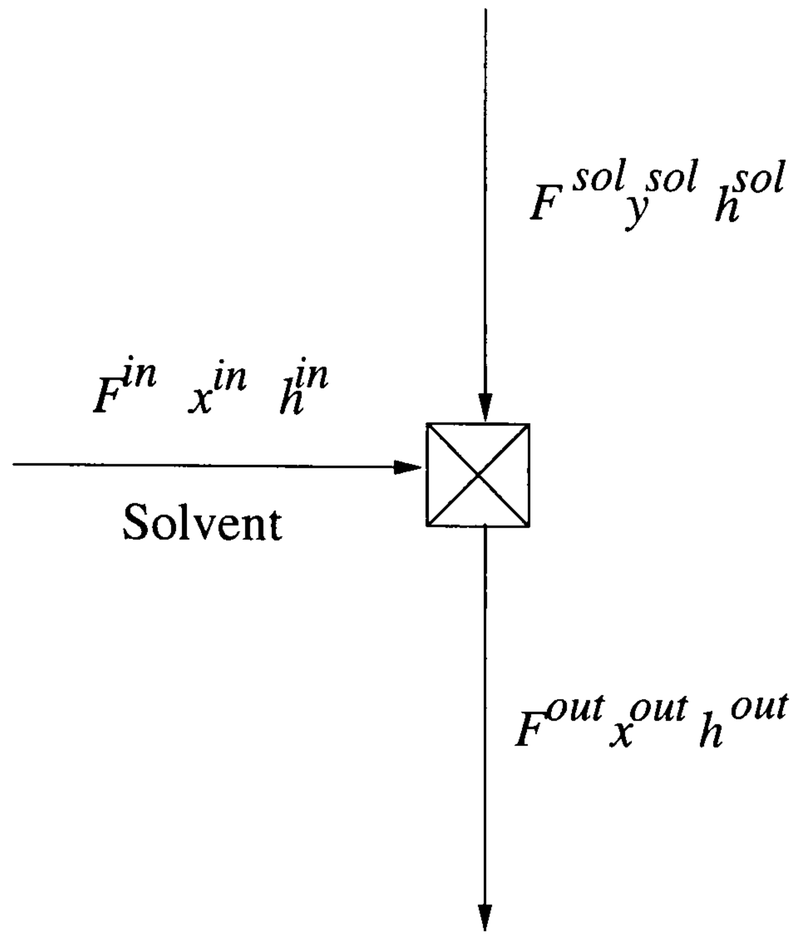


Figure A.3: Stream mixer

Model key assumptions

- Perfect mixing
- No pressure drop through the mixing

Equations

Molar balance:

$$F^{\text{out}} x_i^{\text{out}} = F^{\text{in}} x_i^{\text{in}} + F^{\text{sol}} x_i^{\text{sol}} \tag{A.61}$$

Energy balance:

$$F^{\text{out}} h^{\text{out}} = F^{\text{in}} h^{\text{in}} + F^{\text{sol}} h^{\text{sol}} \tag{A.62}$$

Normalisation equations:

$$\sum_{i=1}^{N_C} x_i^{out} = \sum_{i=1}^{N_C} x_i^{sol} = 1 \tag{A.63}$$

Outlet pressure:

$$P^{\text{out}} = P^{\text{in}} \tag{A.64}$$

Usual specifications

- Connection or specification of the inlet streams (F^{in}, P^{in}, T^{in}, x_j^{in}; F^{sol}, P^{sol}, T^{sol}, x_j^{sol})

A.2 Batch Distillation Model Development

The model is implemented using the *gPROMS* modelling tool (Process Systems Enterprise Ltd., 2000). The overall batch distillation column model is constructed by using the instances of the reboiler, tray, condenser, pressure vessel, accumulator, divider and mixer submodels and connected accordingly depending on the configuration needed. As an example, the schematic of the batch distillation model used in the study of extractive distillation in the middle vessel configuration in chapter 4 is shown in Figures A.2. The rectifying, extractive and stripping column sections are arrays of the tray submodel.

The mathematical model for a batch distillation column forms a set of ordinary differential and algebraic equations (DAEs). For integration of the DAE system, a consistent set of initial conditions is required. For each tray, reboiler, reflux drum and accumulator, there are $N_C + 1$ differential variables which arise from N_C dynamic component material balances plus a dynamic energy balance. By choosing an appropriate set of specifications, the resulting DAE system is of index 1, and the number of initial conditions must be $N_C + 1$ for each unit. A practical and consistent set of initial conditions includes initial values for the mole fractions of N_C - 1 components in the liquid phase, the total liquid holdup and the temperature in each unit. In the rigorous model, the dynamic energy balance is replaced with the simpler fast energy balance, thus, the need to specify as initial temperature in each unit is eliminated thus making the model independent of the sensitive variable and more robust during initialisation. The decision variables involved in batch distillation are discussed in section 1.3 (chapter 1).

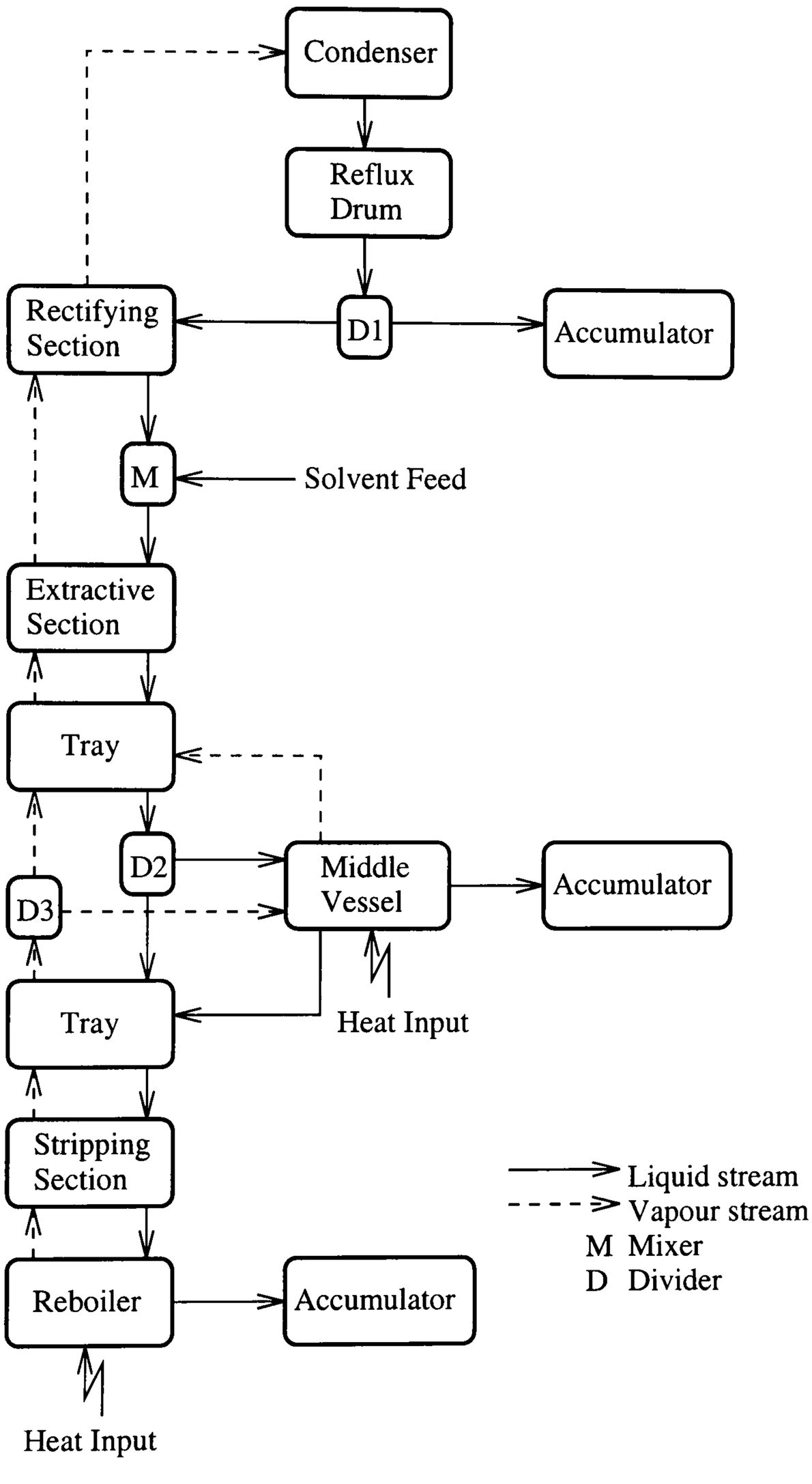


Figure A.4: Schematic of extractive batch distillation in a middle vessel column

Appendix B

General Dynamic Optimisation Problem Statement

The general form of the dynamic optimisation problem for batch distillation is outlined.

B.1 Model

The mathematical model describing batch distillation operations (section 3.1), and used for the purposes of optimisation, has the general form:

$$f(x(t), \dot{x}(t), y(t), u(t), v, t) = 0 \quad \forall\, t \in [0, t_f] \tag{B.1}$$

$x(t)$ and $y(t)$ are the *differential* and *algebraic* variables respectively, both of which are functions of time t. Typically, $x(t)$ represents component molar holdups and internal energy while $y(t)$ represents compositions, flowrate, temperature and pressure. The *control variables* $u(t)$ represent time-dependent decision variables (*e.g.* reflux ratio) while v are *time-invariant parameters* that may represent, for instance, reboiler heat duty if it is kept constant throughout the operation.

B.2 Initial Conditions

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

$$I(x(0), \dot{x}(0), y(0), u(0), v) = 0 \tag{B.2}$$

The values of the initial holdups, temperatures and compositions throughout the column may represent suitable initial conditions. All of these are algebraic variables in our case. Therefore, the initial conditions used are of the simpler form:

$$\hat{y}(0) - \hat{y}_0 = 0 \tag{B.3}$$

where $\hat{y}$ represents a subset of the algebraic variables y, and $\hat{y}_0$ are *given* initial values.

B.3 Constraints

There are usually different types of constraints which need to be satisfied. *Path constraints*, which hold at all times, may generally be represented as:

$$h(x(t), \dot{x}(t), y(t), u(t), v, t) \leq 0 \qquad \forall\, t \in [0, t_f] \tag{B.4}$$

For instance, the liquid holdup in the reboiler drum must not exceed the maximum level (to avoid over-filling) nor fall below a minimum level (for instance to prevent damage to a heating coil) at *any* time throughout the operation of the column (for example, Equation 4.9 in chapter 4).

Constraints which hold at a particular instant in time, t_λ, are referred to as *point constraints*, and these have the following general form:

$$g(x(t_\lambda), \dot{x}(t_\lambda), y(t_\lambda), u(t_\lambda), v, t_\lambda) \leq 0 \qquad \lambda = 1, 2, .. \tag{B.5}$$

Of particular interest are constraints that hold at the final time, t_f. (*"end-point"* constraints) such as specifications imposed on the purities and quantities of the products (for example, Equation 4.5 in chapter 4):

$$k(x(t_f), \dot{x}(t_f), y(t_f), u(t_f), v, t_f) \leq 0 \tag{B.6}$$

B.4 Bounds

There are also bounds on the control variables and on the time-invariant parameters, which define the optimisation search space:

$$u^{\min} \leq u(t) \leq u^{\max} \qquad \forall\, t \in [0, t_f] \tag{B.7}$$

$$v^{\min} \leq v \leq v^{\max} \tag{B.8}$$

For instance, the internal reflux ratio must lie between 0 and 1 ($0 \leq R(t) \leq 1$).

There may also be limitations on the batch processing time:

$$t_f^{\min} \leq t_f \leq t_f^{\max} \tag{B.9}$$

B.5 Objective Function

The *objective function* is generally of the form:

$$\min \Phi\,(x(t_f), \dot{x}(t_f), y(t_f), u(t_f), v, t_f) \tag{B.10}$$

Some problems of practical interest involve objective functions expressed in terms of integrals of the form:

$$\int_0^{t_f} \Psi(x(t), \dot{x}(t), y(t), u(t), v, t)dt \tag{B.11}$$

However, these can always be reduced to form (B.10) by defining a new variable $\omega(t)$ via the differential equation:

$$\dot{\omega} = \Psi(x(t), \dot{x}(t), y(t), u(t), v, t)\,;\ \omega(0) = 0 \tag{B.12}$$

which allows the above integral to be replaced by $\omega(t_f)$.

B.6 General Optimisation Problem Statement

The general dynamic optimisation problem formulation for batch distillation may be summarised as follows:

$$\min \Phi\left(x(t_f), \dot{x}(t_f), y(t_f), u(t_f), v, t_f\right) \tag{B.13}$$

subject to

$$f(x(t), \dot{x}(t), y(t), u(t), v, t) = 0 \qquad \forall\, t \in [0, t_f] \tag{B.14}$$

$$I(x(0), \dot{x}(0), y(0), u(0), v) = 0 \tag{B.15}$$

$$h(x(t), \dot{x}(t), y(t), u(t), v, t) \leq 0 \qquad \forall\, t \in [0, t_f] \tag{B.16}$$

$$g(x(t_\lambda), \dot{x}(t_\lambda), y(t_\lambda), u(t_\lambda), v, t_\lambda) \leq 0 \qquad \lambda = 1, 2, .. \tag{B.17}$$

$$k(x(t_f), \dot{x}(t_f), y(t_f), u(t_f), v, t_f) \leq 0 \tag{B.18}$$

$$u^{\min} \leq u(t) \leq u^{\max} \qquad \forall\, t \in [0, t_f] \tag{B.19}$$

$$v^{\min} \leq v \leq v^{\max} \tag{B.20}$$

$$t_f^{\min} \leq t_f \leq t_f^{\max} \tag{B.21}$$

Appendix C

Genetic Algorithm Parameters Tuning

C.1 Tuning Procedures

This appendix presents a sensitivity analysis in order to investigate the effect of different genetic algorithm parameters on the performance of the genetic algorithm-penalty function framework as used in the batch distillation optimisation in chapters 5 and 6, and shows how suitable values for these parameters can be obtained. The investigation of the parameters sensitivity below is based on design case study I (the details of the case study are presented in chapter 5.6.1).

One of the major drawbacks of genetic algorithm is the need to determine the algorithm parameters in order to obtain an acceptable performance, *i.e.* in terms of efficacy in obtaining better results, and efficiency for faster convergence. A survey of the open literature suggests that theoretical considerations have been carried out in order to link the population size with the number of variables of the optimisation problem, and a huge amount of experimental work has been done to better tune mutation and crossover rates. Nonetheless, the tuning operation cannot be made once and for all, but in principle it

needs to be conducted *ad hoc* for each specific problem at hand, *e.g.* the batch distillation design problem in this research where the genetic algorithm approach has not been applied before.

The general procedure is to firstly obtain good initial guesses for these parameters based on general heuristics and rules of thumb (Golberg, 1989), or from experience of similar chemical engineering applications (*e.g.* Marriott *et al.*, 2000 *etc.*). For example, most of the applications in various fields, including outside chemical engineering problems, points to high crossover rates and low mutation rates, *e.g.* above 70% and below 20%, respectively, which in a sense mimic the natural biological conditions from which the algorithm is based upon. This should be followed by proper tuning of the parameters and this process is conventionally achieved either through a sensitivity analysis, as presented in this study, or parametric optimisation, which is more complicated.

C.2 Population Size and Overlap Percentage

Lewin *et al.* (1998) found the genetic algorithm to be insensitive to the population size provided that it is not very small. Garrard and Fraga (1998) also studied the effect of population size and overlap percentage and for the range considered, $N_{pop} \in [10,100]$ and $P_{ss} \in [25\%,75\%]$, respectively, there was very little effect on the average of the best solutions based on a number of runs. The higher the population size and percentage overlap, the better is the standard deviation from the optimum solution value in each of the runs, but at a higher computer cost. Hence it can be concluded that the decision is basically a trade-off between the quality and reliability of the solution and the computer cost, so long that a critical mass of population size is established. Figure C.1 shows the effect of varying the population size with all the other parameters fixed (fixed at values given in Table C.2). The figure clearly indicates that for the batch distillation design problem, a *critical* population size is required to support the algorithm. A population size less than 100 will result in suboptimal solutions, *e.g.* the fitness function solution for a population size of 50 (33692 $\$/yr$) is around 60% lower than the optimal solutions obtained using population sizes 100 and 150. This is despite the fact that the same number of generations are needed for convergence (228, 237 and 232, respectively).

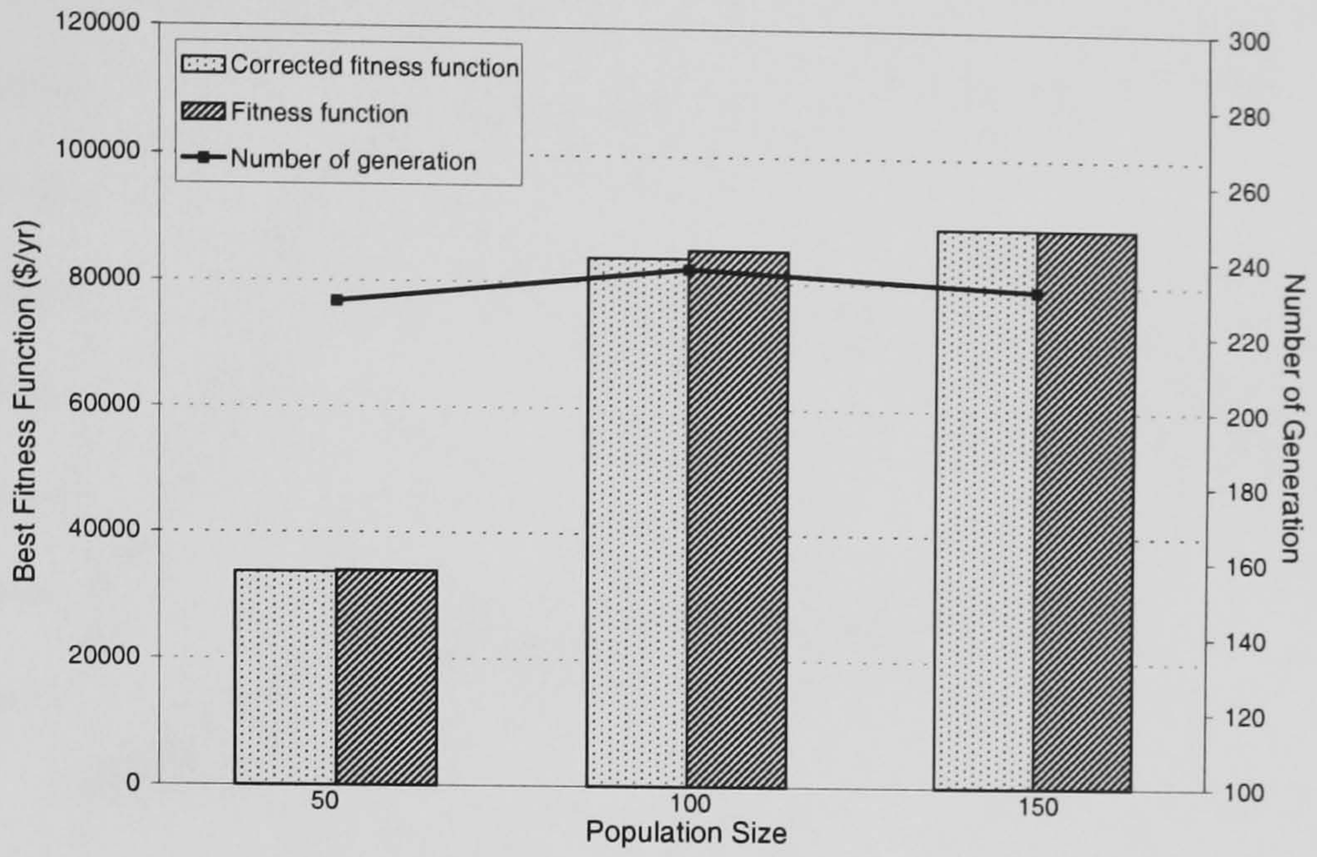


Figure C.1: Best fitness function and number of iteration for different population sizes

C.3 Penalty Function Coefficient

The penalty function is an approach used to handle constraints whereby the severity of the penalty placed on violated constraints has to be chosen a priori. Table C.1 and Figure C.2 show the effect of the penalty function coefficient, p_i, on the handling of the constraints. If the coefficient is set too low, the genetic algorithm produces a batch distillation design that does not statisfy the separation duty, *e.g.* a constraint violation of 44% when p_i is set to 1. The overall violation (taken as the sum of the constraints

Penalty Function Coefficient, p_i	Purity Achieved† (mole fraction)	Constraints Violation (%)	Overall Violation (%)	Generation Converged
1	[0.518] [0.855] [0.979]	[-42.1] [- 0.9] [- 1.1]	-44.1	279
6	[0.891] [0.857] [0.980]	[- 0.4] [- 0.7] [- 1.0]	-2.1	229
7	[0.895] [0.863] [0.989]	[0] [0] [- 0.1]	-0.1	228
8	[0.897] [0.863] [0.988]	[+ 0.2] [0] [- 0.2]	0	219
9	[0.898] [0.858] [0.990]	[+ 0.3] [- 0.6] [0]	-0.3	131
20	[0.894] [0.877] [0.992]	[- 0.1] [+ 1.6] [+ 0.2]	+1.7	124

† constraints specification [0.895,0.863,0.990]

Table C.1: Effect of penalty function coefficient on the handling of constraints

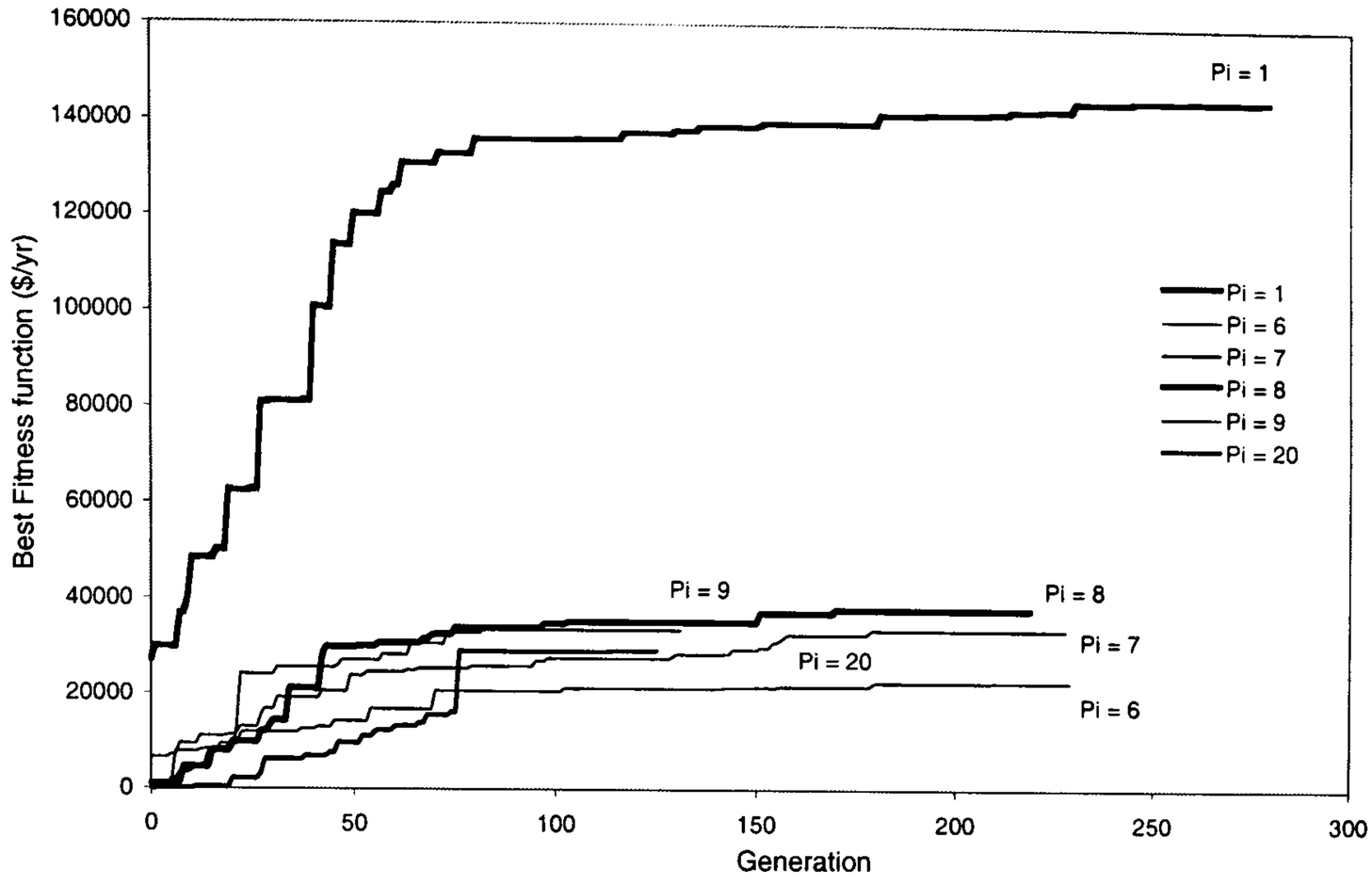


Figure C.2: Fitness function evolution for different penalty function coefficient values

violation) is reduced as the penalty function coefficient is increased. On the other hand, if the coefficient is set too high, the genetic algorithm converged prematurely on any feasible solution it can find, *e.g.* when p_i is set at 20, the algorithm converges prematurely at the $124th$ generation, compared to more than 200 generations for p_i set at 8 and lower. From this analysis (*i.e.* this case study problem), a coefficient of 8 is found to be the right balance for sufficient constraint checking and global solution.

C.4 Mutation and Crossover Rates

The fitness function evolution profiles of Figure C.3 clearly illustrate the effect of the mutation rate on the performance of the genetic algorithm for a fixed crossover rate of 75% (Lewin *et al.*, 1998 and Garrard and Fraga, 1998). High mutation rates (*e.g.* P_m = 90% or P_m = 100%) reduces the power of the algorithm and basically causes it to act like a random search. On the other side of the spectrum, a genetic algorithm with no exploration capability at all (*e.g.* P_m = 0%) causes it to be trapped in the local area of the best solution found and to converge early to a sub-optimal value. In this particular analysis (see Figure C.3), a mutation rate of 10% is found to give the best performance as

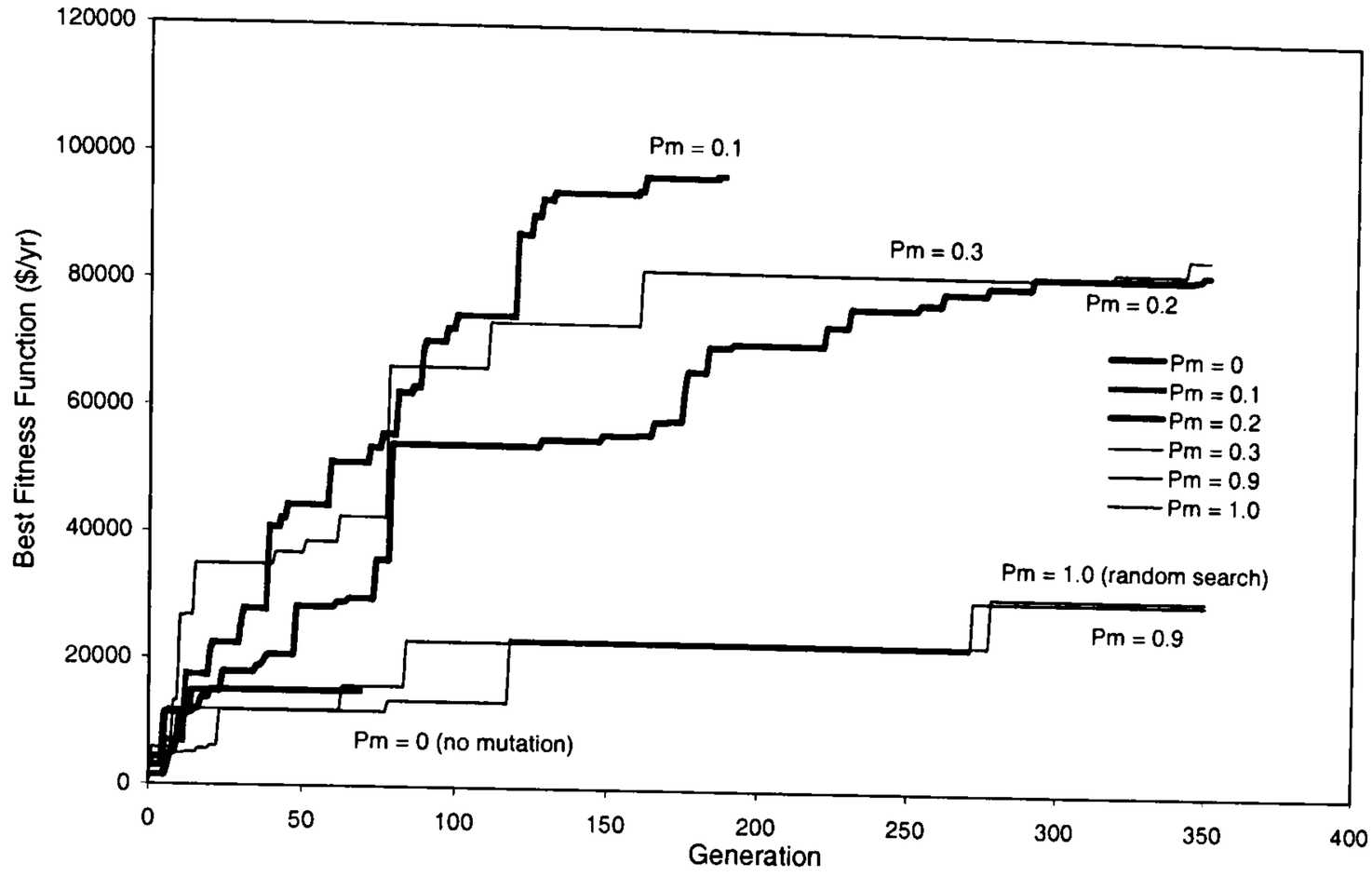


Figure C.3: Fitness function evolution for different mutation rates

it returns the highest fitness function value from a fewer number of population evolution (compared to mutation rates of 20% and 30%).

C.5 Conclusions

Based on the sensitivity studies presented above, a *general* guideline is now available for appropriate algorithm parameter values in batch distillation optimisation. The values of the parameters used in this work are as listed in Table C.2. Note that the sensitivity trials presented above were based on a single batch distillation problem (case study I of section 5.6.1), hence further parameter values adjustment may be needed when the size or complexity of the batch distillation problem itself varies widely from case to case. Nonetheless, of the six genetic algorithm parameters concerned, the population overlap, P_{ss}, mutation rate, P_m, crossover rate, P_c and termination criterion, $P_{converge}$, are relatively less critical in terms of fine-tuning compared to the population size, N_{pop} and penalty function coefficient, p_i. This is because the values of P_{ss}, P_m, P_c and $P_{converge}$, as listed in Table C.2, are typical values which have been used and shown to be effective in most genetic algorithm applications on a wide range of problems including those

Population size, N_{pop}	120, 150 (in chapter 5 and 6, respectively)
Population overlap, P_{ss}	70%
Penalty function power coefficient, p_i	8 to 15 (various cases)
Mutation probability, P_m	10%
Crossover probability, P_c	75%
Convergence percentage, $P_{converge}$	95% and 90%‡ (in chapter 5 and 6, respectively)

‡ to population average *and* to the population best of the previous 30 generations

Table C.2: Genetic algorithm parameters used in this work (chapters 5 and 6)

outside of the chemical engineering field. This has also been confirmed by the sensitivity analysis conducted in this study for the batch distillation problem. In contrast, the population size, N_{pop} and penalty function coefficient, p_i, parameters are more specific to a particular problem, and therefore should be specified more carefully. For example, the population size, N_{pop}, was increased to 150 (see Table C.2) in chapter 6 where the optimisation problem was enlarged to include configurational variables. The penalty function power coefficient, p_i, was adjusted accordingly for cases with a higher purity (hence, tighter) constraints specification. Therefore, in this study, some *ad hoc* decision-making is retained despite the sensitivity analysis. A simple guideline for obtaining the genetic algorithm parameters is given in Figure C.4.

As a suggestion for future work, a possible approach for more rigorous tuning of the algorithm parameters is to try to automate the adaptation of the parameters to the specific problem at hand and one of the approaches that have been proposed to this end, is self-adaptation (Bäck and Schutz, 1996). This self-adapting mechanism updates the parameters periodically over a fixed period of progress of the search.

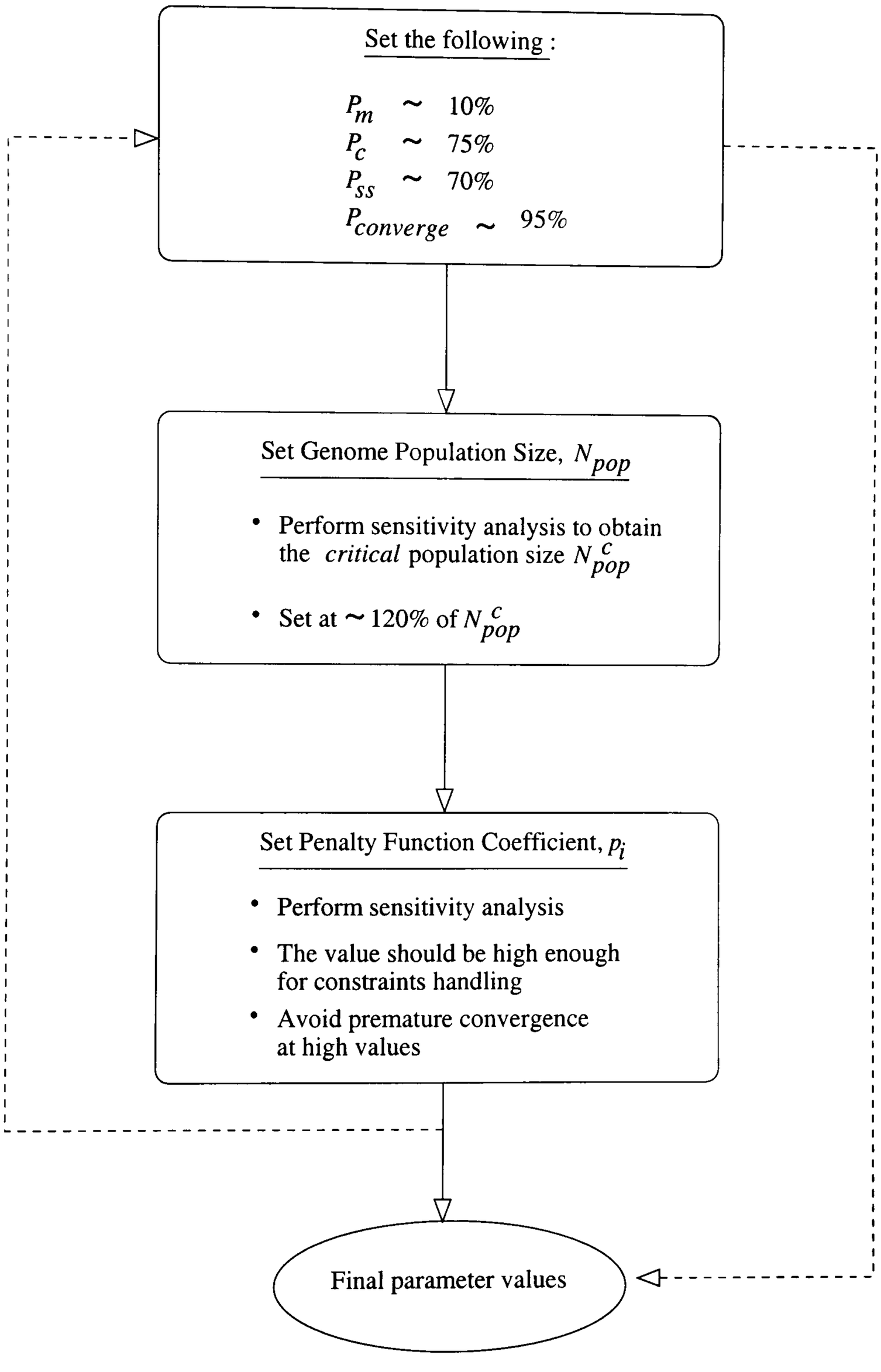


Figure C.4: General guideline for genetic algorithm parameters determination

Appendix D

Optimisation Computational Statistics

Here, a sample of computational statistics on the solution of some of the optimisation problems addressed in this thesis are presented. Both nonlinear programming and genetic algorithm data are considered. All the computations reported were performed on an IBM RISC System/6000 computer workstation with 128 Mb of RAM running under the AIX 4.3.3 operating system.

D.1 Nonlinear Programming Computational Considerations

The computational statistics for the optimisation runs in Case I of chapter 4 are summarised in Table D.1. The computational times required for the solution of this sample of optimisation runs is in the order of 1.5 *hrs* to 4 days. The difference in computational effort is due to the number of optimisation variables, the size of the underlying DAE model and the initial guesses of the decision variables supplied to the NLP algorithm at the start. Note that the statistics recorded in Table D.1 is for the final run of the optimisation - in cases where optimisation failure occurred, the optimisation is restarted using the last point before the failure as the initial guess for the new run and this is repeated until an optimal solution is reached. The total solution time may therefore in some cases be much longer.

Column	Regular	Middle Vessel		
Feed location	a	a	b	c
Number of Optimisation Iterations	53	511	42	7
Number of Line Search Steps	170	>999	204	19
% CPU Time Spent on State Integration	55.3	66.5	64.9	41.1
% CPU Time Spent on Sensitivity Integration	44.7	33.5	35.1	58.9
CPU Ratio of Sensitivity and State Integration/State Integration	3.6	3.9	3.7	5.5
Computational Time (hrs)	7.7	94.7	8.0	1.5

Table D.1: Sample summary of computational statistics for NLP optimisation cases

D.2 Genetic Algorithm Computational Considerations

Table D.2 shows the computational statistics for the stochastic optimisation run of the case study scenario I in chapter 5.6.1. Note that 188 generations with 15 912 function evaluations, *i.e.* model integrations, were required to achieve convergence. The mean fitness, *i.e.* the objective function, of the population increased from 61 239 ($/yr$ loss) to 97 230 ($/yr$ profit). Figure D.1 shows that the progress of the algorithm is rapid initially with both the best and mean fitness of the population climbing steeply. However, the progress became slow towards a steady state. The optimisation duration is about one week with the majority of the computation time spent on function evaluations.

In contrast, the optimisation duration for each run of case study scenario III in chapter 5.6.3 is less than one day on the same machine used in case study I. This is due to faster simulation associated with the simpler model as well as faster convergence (< 25 generations) compared to case study scenario I above.

Generally, the computational times for the genetic algorithm runs for all cases covered in chapters 5 and 6 is in the order of 1 to 7 days depending on the number of optimisation variables, the size of the underlying DAE model and the parameters used in the genetic algorithm (see Appendix C), in particular the population size and termination criterion. The CPU time spent on the genetic algorithm is negligible compared to the CPU time spent on the model integration, thus the size and complexity of the underlying DAE

Number of generations	188
Number of genome evaluations	15 912
Mean fitness in initial population	-61 239
Maximum fitness in initial population	3088
Mean fitness in final population	92 372
Maximum fitness in final population	97 230

Table D.2: Sample summary of computational statistics for a GA optimisation case

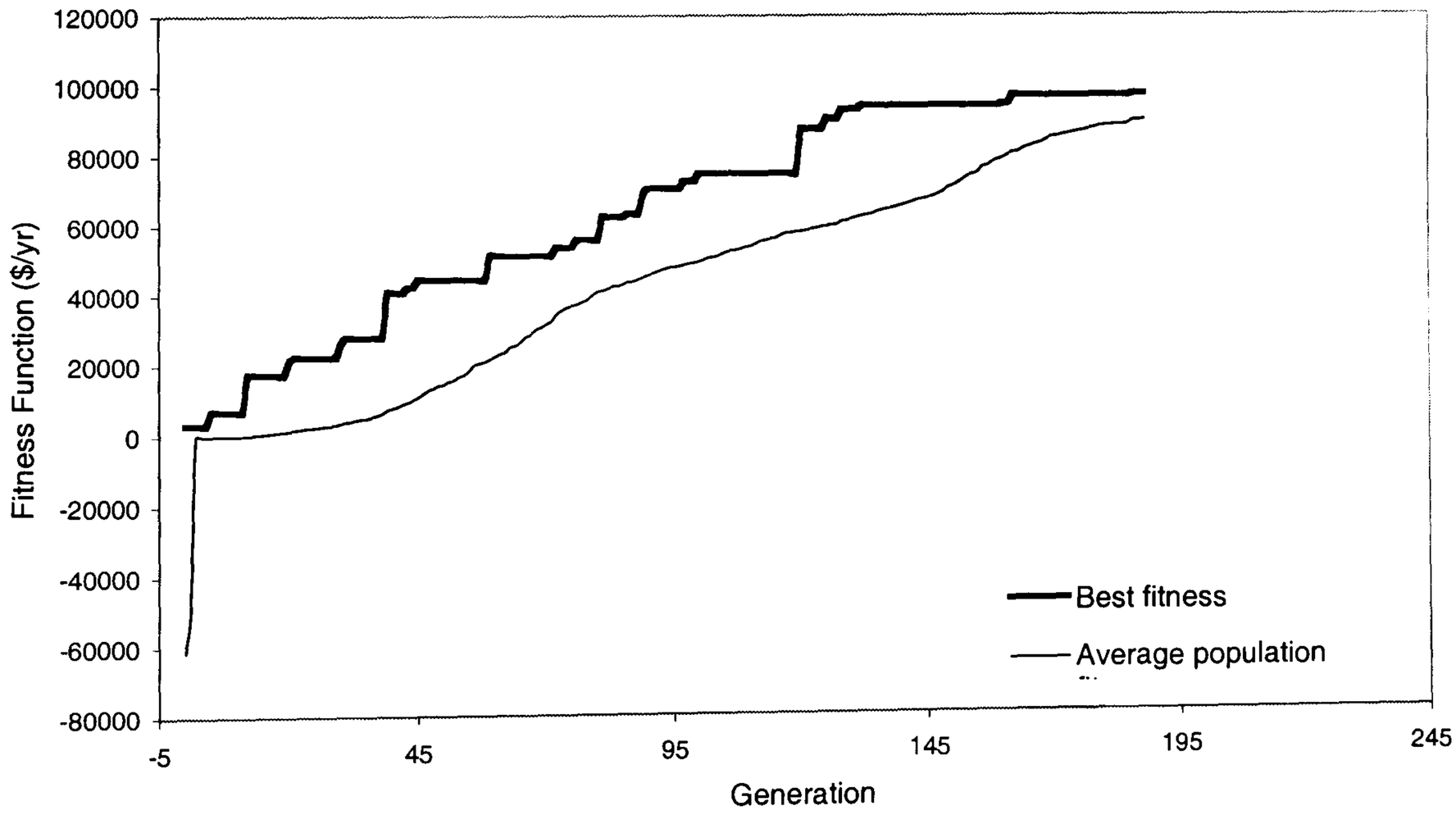


Figure D.1: Fitness function evolution

model is the predominant factor affecting computational cost. The genetic algorithm technique offers the opportunity for parallel processing to reduce computational time, however, this was not considered in this work.

Appendix E

Simulation of Extractive Batch Distillation

A simulation test of extractive distillation in a regular column with operation steps similar to the ones given by Lang *et al.* (1994) has been undertaken (see Table E.1 for the case study information):

1. Operation under total reflux ($R = 1$) without solvent feeding ($F_{sol} = 0$).

2. Operation under total reflux ($R = 1$) with solvent feeding ($F_{sol} = 0.05\ mol/s$).

3. Operation under finite reflux ($R = 0.9$) with solvent feeding ($F_{sol} = 0.05\ mol/s$). Acetone product cut is obtained overhead.

4. Operation under finite reflux ($R = 0.9$) without solvent feeding ($F_{sol} = 0$). Methanol-rich cut obtained overhead while the solvent is concentrated in the reboiler.

The first two steps were operated for a duration of 1000 s each. The third step was terminated when the acetone product purity fell below 0.95 $mol\%$. The operation is then stopped when the purity of the solvent in the reboiler drum reaches 0.99 $mol\%$. The reboiler duty was set at 5 kW and there was no subcooling in the condenser operating at atmospheric pressure.

	Lang *et al.* (1994) (Pilot Plant)	This Work (Simulation)
Column diameter	97 *mm*	50 *mm*[1]
Number of trays	32[2]	30[1]
Feed charge	9 $l \approx 150$ *mol**	100 *mol*
Solvent flowrate	2.0 $l/hr \approx 0.03$ *mol/s**	0.05 *mol/s*
Reboiler volume	12 $l \approx 0.012$ m^3*	0.015 m^3
Reboiler duty	1.5 *kW*	5 *kW*
Batch operation time (*hr*)	≈ 4	2.4
Acetone product purity (*mol*%)	96.0	95.0
Acetone product recovery (*mol*%)	82.0	92.3

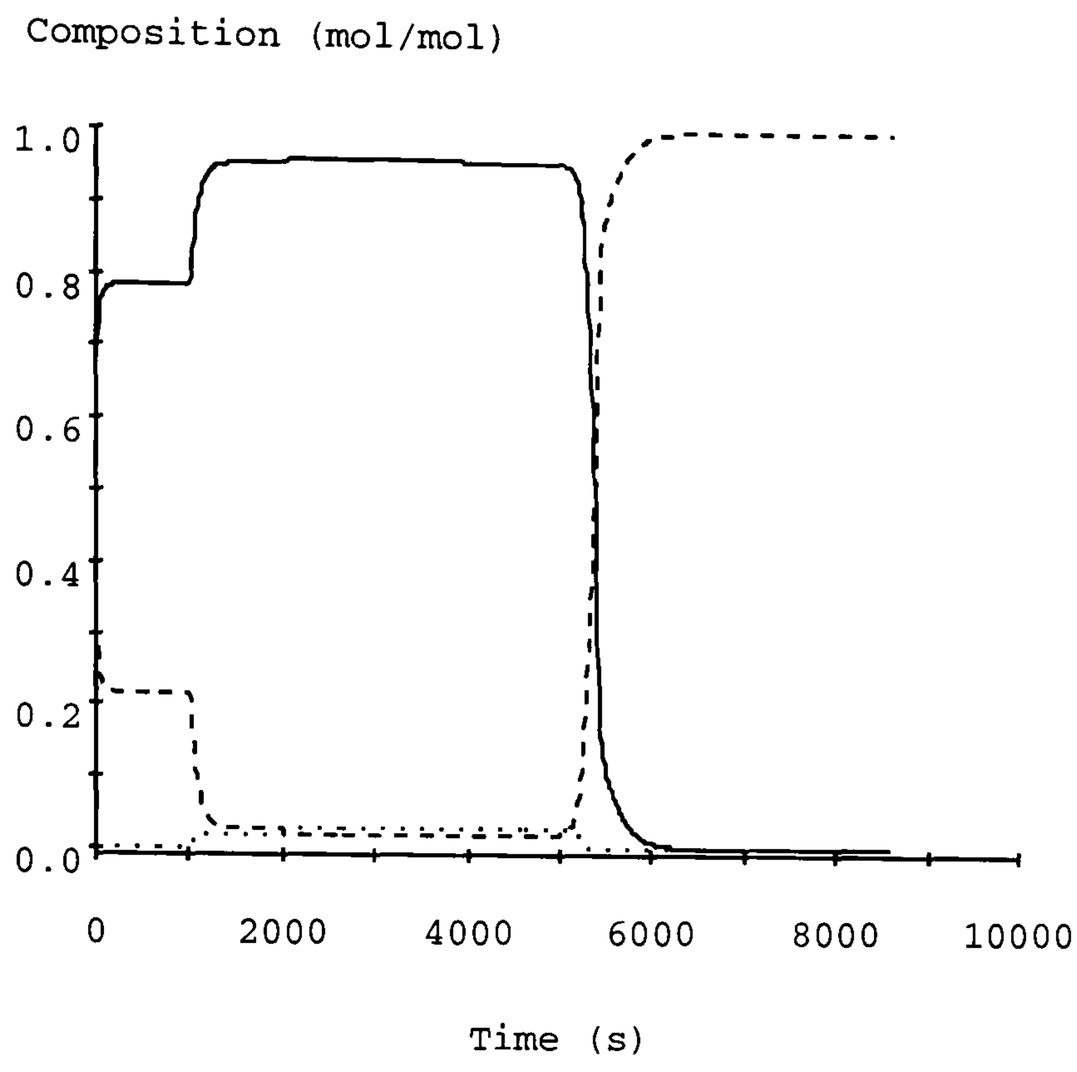
[1] based on our laboratory column; [2] bubble cap trays; * SI units estimations

Table E.1: Scale comparison of an experimental work and this work

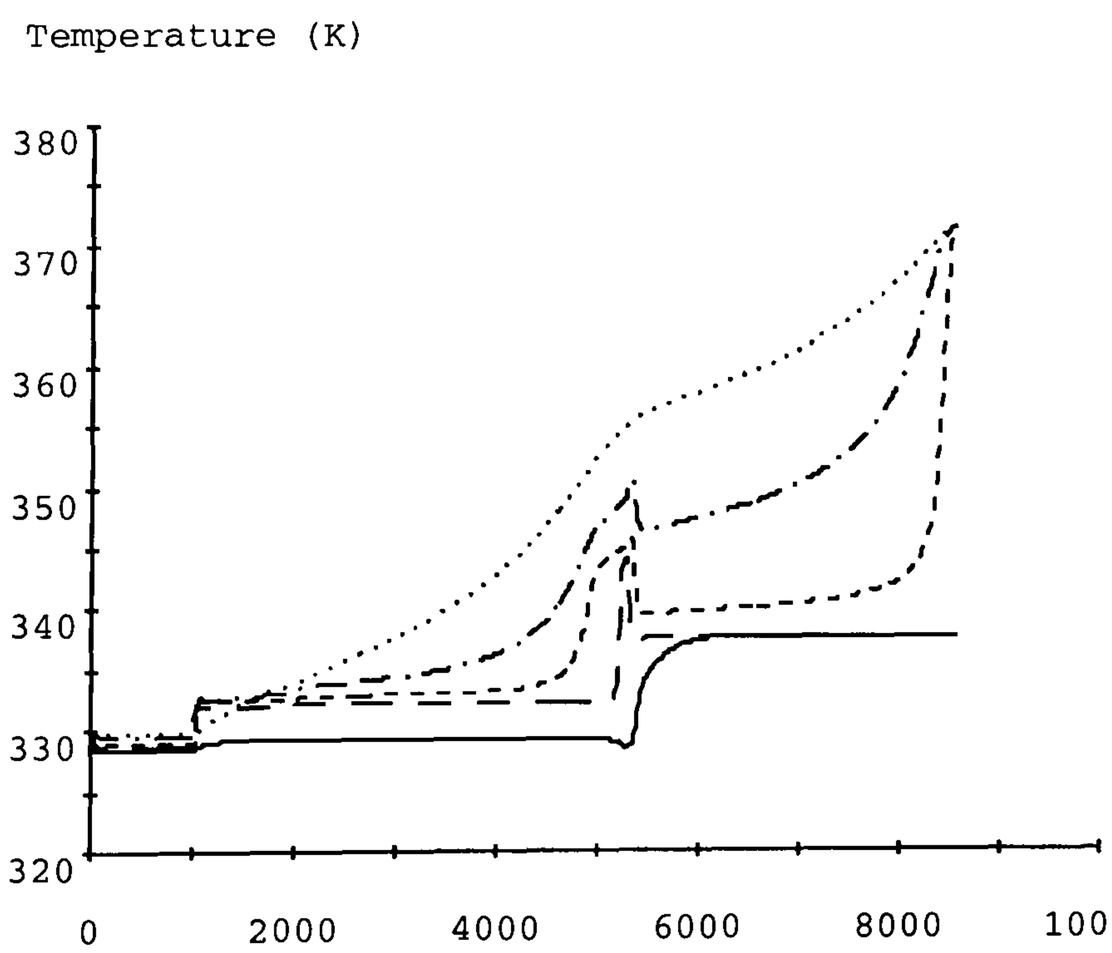
As can be seen in Figure E.1a (after 1000 s), by the end of the first total reflux step the distillate composition reaches that of the binary azeotrope (78 *mol*% of acetone). With the introduction of the solvent, the concentration of methanol decreases rapidly in the distillate composition due to the adsorptive effect of the water. At the end of this second step (1000-2000 s), the acetone purity reaches its maximal value (above 0.95 *mol*%). Collection of the high purity acetone is conducted during the third step (2000-5282 s). In the final step (5282-8574 s), methanol is withdrawn leaving high purity solvent in the reboiler.

The temperature profile of the column as shown in Figure E.1b is similar to the pilot plant observations of Lang *et al.* (1994). It can be seen that after the start of solvent feeding at the beginning of step two, the bottom temperature is lower than the temperature of the extractive trays. This is because as the solvent is introduced at the $6th$ tray, the concentration of solvent increases more rapidly on these trays as they are nearer to the solvent feed point and their holdups are much smaller than the holdup in the reboiler.

The switch from step 3 to step 4 (at 2000 s) of the operation is determined by the deterioration of the distillate quality (below 0.95 *mol*%). As can been seen, the approaching decrease of distillate quality is indicated in advance by the steep rise of the temperatures



(a) —– acetone; - - - methanol; . . . solvent



(b) —– top; – – 12th; - - - 28th; - . - 30th tray; . . . bottom

Figure E.1: Simulated distillate composition and column temperature profiles

of the extractive plates, firstly the tray at the bottom, followed by the 28th and 12th tray. This indication can be used for the prediction of the end of the third step production period, *e.g.* for control purposes.

In conclusion, the general behaviour of the column profiles (Figure E.1) and simulation results (Table E.1) is verified with the pilot-plant experimental observation by Lang *et al.* (1994) (a rigorous *validation* of the model against real process data is beyond the scope of this study).

Appendix F

Additional Results for Chapter 4

The product and solvent purities obtained for the different cases considered in chapter 4 are presented in the following tables:

Column	Regular	Middle Vessel		
Feed Location	a	a	b	c
Acetone	93.0	93.0	93.0	93.0
Solvent	99.0	99.0	99.0	99.0

Table F.1: Product purities ($mol\%$) obtained for case study I (see Table 4.7)

Column Configuration	Regular	Middle Vessel				
		A	B	C	D	Optimal
Acetone	93.0	93.0	93.0	93.0	93.0	93.0
Methanol	93.0	93.0	93.0	93.0	93.0	93.0
Solvent	99.0	99.0	99.0	99.0	99.0	99.0

Table F.2: Product purities ($mol\%$) obtained for case study II (see Table 4.8)

Column	Regular			Middle Vessel Simple Configuration			Middle Vessel Optimal Configuration		
Feed composition † ($molfraction$)	0.25, 0.75	0.50, 0.50	0.75, 0.25	0.25, 0.75	0.50, 0.50	0.75, 0.25	0.25, 0.75	0.50, 0.50	0.75, 0.25
Acetone	93.0	93.0	93.0	93.0	93.0	93.0	93.0	93.0	93.0
Methanol	93.0	93.0	93.0	93.0	93.0	93.0	93.0	93.0	93.0
Solvent	99.0	99.0	99.0	99.0	99.7†	99.0	99.0	99.0	99.0

†exceeds specification

Table F.3: Product purities ($mol\%$) obtained for case study III (see Table 4.9)

In almost all the cases, the results above indicate that optimal operations of extractive batch distillation involve the products and solvent being purified to just their required minimum specifications, *i.e.* 93 *mol*% for the products acetone and methanol and 99 *mol*% for the solvent (water). This is in concordance to economics expectation whereby, in order to maximise the profitability objective function, no operational effort (in terms of higher reflux or longer batch processing time) is wasted to produce products above the required minimum purities.

Appendix G

Derivation of Objective Function for Batch Distillation Design

Economical design is a trade-off between lower capital and operating costs against higher production revenue, thus the objective function must be formulated to encapsulate all of these costs.

In this work, the production sales revenue for each batch is given by:

$$\Psi = \sum_{i=1}^{N_C} C_i H_i(t_f) - C_{feed} H_{feed} \tag{G.1}$$

where C_i and C_{feed} represent the unit costs of product i and feed, respectively, and H_i and H_{feed} the quantity of on-specification of product i collected and feed, respectively. The revenue per unit time is obtained by dividing the batch processing time, t_f, plus the set-up time for each batch, t_s, as follows:

$$\Psi_t = \left(\frac{\sum_{i=1}^{N_C} C_i H_i(t_f) - C_{feed} H_{feed}}{t_f + t_s} \right) T_A \tag{G.2}$$

where T_A is the total time available for processing per year, thus Ψ_t is revenue per annum.

The total annual costs associated with a batch distillation column includes installed

equipment capital costs and operational utilities cost. Using Guthrie's correlations (Douglas, 1988), the installed cost of a distillation column shell can be written as:

$$C_{sh} = C_{sh,BC}\left(\frac{N}{N_{BC}}\right)^{0.862}\left(\frac{D}{D_{BC}}\right)^{1.066} \tag{G.3}$$

where N is the number of trays, D is the diameter of the column and BC represents the base case column from which the Guthrie's correlation is obtained. Assuming the column diameter varies as the square root of the column vapour loading, $D \propto \sqrt{V}$ (Douglas, 1988), Equation G.3 can be written as:

$$C_{sh} = C_{sh,BC}\left(\frac{N}{N_{BC}}\right)^{0.802}\left(\frac{V}{V_{BC}}\right)^{0.533} \tag{G.4}$$

Apart from the column shell, the column reboiler and condenser would also contribute significantly to the installed equipment cost of batch distillation.

Guthrie (Douglas, 1988) proposed that the annual installed costs of a heat exchanger be written as:

$$C_{ex} = C_{ex,BC}\left(\frac{A}{A_{BC}}\right)^{0.65} \tag{G.5}$$

whereby the heat exchanger area, A, can normally be calculated from the equation:

$$Q = VC_p\Delta t = UA\Delta T_m \tag{G.6}$$

where Δt is the temperature difference of the reboiler or condenser fluid and ΔT_m is the mean temperature difference across the heat exchanger apparatus. Assuming constant values of heat capacities, C_p, and overall heat transfer coefficient, U, substituting A in Equation G.5 with G.6 gives:

$$C_{ex} = C_{ex,BC}\left(\frac{V\Delta t\Delta T_{m,BC}}{V_{BC}\Delta t_{BC}\Delta T_m}\right)^{0.65} \tag{G.7}$$

If the stream temperatures are fixed, a simple model for the heat exchangers costs in terms of flows can be obtained:

$$C_{ex} = C_{ex,BC}\left(\frac{V}{V_{BC}}\right)^{0.65} \tag{G.8}$$

The main operating cost in batch distillation is utilities cost, *e.g.* steam for the reboiler and cooling water for the condenser. In the simplest case, the following correlation can be used:

$$C_{stm} = C_{stm,BC}\frac{W_S}{W_{S,BC}} \tag{G.9}$$

Then from a heat balance we find

$$Q = VC_p\Delta t = W_S\Delta H_S \tag{G.10}$$

where W_S is the mass vaporisation rate and ΔH_S is the enthalpy difference between the steam and liquid. Substituting G.10 into G.9 and similarly, for fixed temperatures:

$$C_{stm} = C_{stm,BC}\left(\frac{V}{V_{BC}}\right) \tag{G.11}$$

The cooling water utility cost, C_{cw} can be correlated is a similar way, and the total utility cost can be represented by:

$$C_{uty} = C_{uty,BC}\left(\frac{V}{V_{BC}}\right) \tag{G.12}$$

Equations G.4, G.8 and G.12 can be written respectively as:

$$C_{sh} = K_1 N^{0.802} V^{0.533} \tag{G.13}$$

$$C_{ex} = K_2 V^{0.65} \tag{G.14}$$

$$C_{uty} = K_3 V \tag{G.15}$$

where the value of the correlation coefficients K_1, K_2 and K_3 can be calculated according to a base case column:

$$K_1 = \frac{C_{sh,BC}}{N_{BC}^{0.802} V_{BC}^{0.533}} \tag{G.16}$$

$$K_2 = \frac{C_{ex,BC}}{V_{BC}^{0.65}} \tag{G.17}$$

$$K_3 = \frac{C_{uty,BC}}{V_{BC}} \tag{G.18}$$

The objective function of the simultaneous batch distillation design and operation problem is set up as profit per unit time, i.e. given by the production sales revenue minus the total capital cost and utility cost. Mathematically, the objective function can be written as:

$$P = \Psi_t - (C_{sh} + C_{ex}) - C_{uty} \tag{G.19}$$

Substituting Equations G.2, G.12, G.14 and G.15 into G.19:

$$P = \left(\frac{\sum_{i=1}^{N_C} C_i H_i(t_f) \; - \; C_{feed} H_{feed}}{t_f + t_s} \right) T_A - \left(K_1 N^{0.802} V^{0.533} + K_2 V^{0.65} \right) - K_3 V \tag{G.20}$$