# SYNTHESIS OF MULTICOMPONENT AZEOTROPIC DISTILLATION SEQUENCES

A thesis submitted to the

# University of Manchester Institute of Science and Technology

for the degree of

## **Doctor of Philosophy**

by

## **Guilian Liu**

Under the supervision of

Dr Megan Jobson and Prof. Robin Smith

Department of Process Integration, UMIST Manchester, United Kingdom 2003

## Declaration

No portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other universities, or other institution of learning.

> Guilian Liu Manchester, October 2003

### Abstract

A large number of distillation sequences can be generated to separate a multicomponent azeotropic mixture. However, there is no systematic and efficient method for synthesising promising sequences, which also consider recycle connections and flowrates. In this work, a systematic procedure is developed for synthesising economically promising distillation sequences separating multicomponent homogeneous azeotropic mixtures. The procedure uses spherically approximated distillation boundaries, a shortcut column design method, and allows recycle and sequence alternatives to be screened. Both feasibility and design are addressed.

Approximation of a distillation boundary as a spherical surface is a simple nonlinear, yet more accurate representation of the actual boundary than a linear approximation. For shortcut column design, azeotropes are treated as pseudo components and the relative volatilities of all singular points of the system are characterised, based on the transformation of vapour-liquid equilibrium behaviour in terms of pure components into that in terms of singular points. Once the relative volatilities of singular points are obtained, the classical Fenske-Underwood-Gilliland method can be used to design columns separating azeotropic mixtures. This method is extremely computationally efficient and can be applied to homogeneous azeotropic mixtures with any number of components; the results are useful for initialising rigorous simulations using commercial software and for assessing feasibility of proposed splits. Together with the spherical approximation of distillation boundaries, this shortcut method provides a basis for evaluating distillation sequences with recycles.

Analysis of feasibility requirements of splits, component recovery requirements and the effects of recycles on the performance of proposed splits allows rules and procedures for selecting recycles to be proposed. Recycles with compositions of either singular points or mixtures of singular points are identified that are beneficial to the feasibility of sequences and the recovery of components. The principles are applicable to azeotropic mixtures with any

iii

number of components; using these procedures, recycle structures can be generated and are much simpler than the superstructures of recycle alternatives.

The sequence synthesis procedure of Thong and Jobson (2001c) allows all potentially feasible sequences to be generated. To screen among these sequences, a split feasibility test and a two-step screening procedure are proposed. In the first step, feasibility of splits is tested efficiently and sequences containing either infeasible or sloppy splits are eliminated. In the second step, sequences containing sloppy splits are generated, based on the evaluation of sequences containing only feasible sharp splits. Using this procedure, the number of distillation sequences identified using the procedure of Thong and Jobson (2001c) can be significantly reduced.

A systematic methodology is proposed for the synthesis and evaluation of multicomponent homogeneous azeotropic distillation sequences. The methodology is computationally efficient. It is demonstrated through a case study, the synthesis of distillation sequences separating a five-component mixture, in which two homogeneous azeotropes are formed, and for which over 5000 sequences producing pure component products can be generated. Using this methodology, only ten sequences are evaluated to identify three promising sequences. The evaluation of each sequence using the shortcut column design method is extremely efficient compared with that using the boundary value method.

iv

## Acknowledgements

I would like to express my gratitude to my supervisor, Dr Megan Jobson, for her dedication and guidance throughout the course of this research. Her vision, advice, consistent supports were very important to me. Her kindness and consideration outside the academic world are also appreciated. In particular, I am much indebted to her hard work over the past few weeks reading and re-reading my incoherent paragraphs.

I also would like to thank Prof. Robin Smith for his encouragement, understanding and helpful advice. Parts of this work are indirect results of his advice and helpful comments.

Appreciation is due to Prof. Oliver M. Wahnschafft for his enthusiasm and contributions to this work. The discussion with him is always helpful. His ideas and suggestions result in parts of this work.

Many thanks to Chris Sutton who is always so patient in explaining and dealing with the problems I brought to his attention. Thanks also to the administrative staff and computing staff for providing such a pleasant work environment.

Thanks is also given to all the postgraduate students of the department, in particular my senior colleagues, Dennis, Sutijan, and my current colleague Ramona and Jiaona, for the discussions, support, help and ideas shared with me.

I am grateful for the financial support from the Process Integration Research Consortium and the Overseas Research Students Awards Scheme.

Many thanks to Prof. Xiao Feng for her encouragement and support. Without her support, I would not decide to pursue a PhD degree. Thanks are also given to all my friends here and in China for their support and the happy time.

Finally, I would like to express my appreciation to my parents, my brothers and my sister for their support and encouragement through out this research.

# Table of contents

Chapter 1	Introduction	1
1.1. Bac	kground	1
1.2. Aim	s and scope	2
1.3. Vap	our-liquid equilibrium models and assumptions	4
1.4. App	lication of computational tools	4
1.5. Out	line of the thesis	5
Chapter 2	Literature review	6
2.1. Intro	oduction	6
2.2. Vap	oour-liquid equilibrium characteristics of azeotropic mixtures	7
2.2.1.	Effect of azeotropes on volatility order	7
2.2.2.	Residue curve maps and distillation line maps	8
2.2.3.	Distillation regions and compartments	9
2.2.4.	Simplified representation of azeotropic systems1	1
2.3. Dist	tillation of non-azeotropic mixtures1	4
2.3.1.	Synthesis of distillation sequences 1	4
2.3.2.	Shortcut design method for columns separating non-azeotropic	
mixture	s1	6
2.3.2.	1. Fenske equation – minimum number of stages 1	7
2.3.2.	2. Underwood equations — Minimum reflux ratio 1	7
2.3.2.	3. Gilliland correlation 1	9
2.4. Dist	tillation of ternary azeotropic mixtures 2	0
2.4.1.	Sequence design and recycle selection2	0
2.4.2.	Assessing column feasibility2	2
2.5. Dist	tillation of multicomponent azeotropic mixtures	5
2.5.1.	Synthesis of distillation sequences with recycles 2	5
2.5.1.	1. Sequential methodology of Wahnschafft (1993) 2	5
2.5.1.	2. Superstructure-based method of Bauer and Stichlmair (1998). 2	6
2.5.1.	3. The synthesis method of Rooks et al. (1998) 2	6
2.5.1.	4. The algorithmic method of Thong and Jobson (2001c) 2	7

2.5.2.	Calculation of minimum reflux ratio and column design	30
2.6. Co	nclusions	34
Chapter 3	Shortcut method for column design and sequence evaluation	
	·····	37
3.1. Inti	roduction	37
3.2. No	n-linear approximation of distillation boundaries	38
3.2.1.	The necessity to characterise a distillation boundary	38
3.2.2.	Non-linear approximation of distillation boundary	39
3.2.3.	Identifying the distillation region that a composition point lies in using	ng
a sphe	rically approximated distillation boundary	46
3.3. Re	presentation of the vapour-liquid equilibrium (VLE) behaviour in terr	ns
of singul	ar points	50
3.3.1.	Compartments as subsystems in the composition space	51
3.3.2.	Transformation of compositions	53
3.3.3.	Calculation of relative volatilities of singular points	57
3.4. Sh	ortcut method for column design	59
3.4.1.	Calculation of minimum reflux ratio and minimum energy cost using	g
Under	wood method	60
3.4.2.	Calculating minimum number of stages by Fenske equation	63
3.4.3.	Gilliland correlation can be used to calculate operation reflux ratio	
and nu	mber of equilibrium stages	66
3.4.4.	Identifying infeasible and very difficult splits using the shortcut	
metho	d	67
3.4.5.	Estimating the distribution of non-key components	68
3.5. Ev	aluation of distillation sequences with recycles specified	70
3.5.1.	Evaluation procedure with shortcut method and spherically	
approx	kimated distillation boundary	70
3.5.2.	Application of the evaluation procedure to four-column sequence.	73
3.6. Co	nclusions	76
Chapter 4	Recycle selection for azeotropic distillation sequences	79
4.1. Int	roduction	79

4.2. Background concept79
4.3. Characteristics of recycles in distillation sequence
4.4. Recycles with singular point compositions
4.4.1. Distillation-boundary crossing (DBC) Splits
4.4.1.1. Characteristics of distillation-boundary crossing (DBC) splits 85
4.4.1.2. Effect of recycles recycled to the feed of the DBC split
4.4.1.3. Effect of recycles recycled to the feed of the upstream of DBC
split 95
4.4.1.4. Discussion
4.4.2. Type A splits 102
4.4.3. Type B splits 104
4.4.4. Type C splits 109
4.4.5. Effect of different type of recycles on the performance of splits 113
4.4.6. Procedure for screening singular recycles
4.5. Recycles with the compositions of mixtures of several singular points122
4.6. Conclusions
Chapter 5 Reducing the number of sequence alternatives 127
5.1 Introduction 127
5.2 Preliminary screening of distillation sequences 128
5.2.1 Eliminating distillation sequences including infeasible splits 128
5.2.1.1 Feasibility characteristics of different types of splits 129
5.2.1.2 Feasibility test for Type C splits 130
5.2.2.2. Eliminating sequences containing sloppy splits
5.3. Identification of promising sequences containing sloppy splits
5.3.1. Promising sequences can be identified based on the evaluation of
sequences containing only sharp splits
5.3.1.1. Identifying appropriate sloppy splits
5.3.1.2. Identifying appropriate sharp splits
5.3.2. Procedure for identifying promising distillation sequences including
sloppy splits
5.4 Conclusions 155

Chapte	er 6 Overview and application of sequence synthesis methodolog	gy
		156
6.1.	Introduction	156
6.2.	Systematic procedure for the synthesis of distillation sequences	
sepa	rating multicomponent azeotropic mixtures	156
6.3.	Case study	159
6.4.	Conclusions	175
Chapte	er 7 Conclusions and Future Work	177
7.1.	Summary	177
7.2.	Limitations	180
7.3.	Future work	181
Notatio	on	183
Refere	ences	186
Appen	ndix A Operating and Capital Cost Estimation	193
A.1.	Cost Estimation	193
A.2.	Steam and Cooling Water Cost	194
A.3.	Capital Cost	194
A.3	3.1.Column Cost	195
A.3	3.2. Heat exchanger cost	196
A.4.	Total Annualised Cost	197
Appen	ndix B Derivation of the effect of recycles using the Underwood	
	equations	198
Appen	ndix C Potentially feasible sequences for the case study of Chapt	er
	6	201

# List of figures

Fig. 2.1	Volatility behaviour of a non-azeotropic and an azeotropic binary mixture.Summary
Fig.2.2	Adjacency and reachability matrix of a quaternary mixture with three azeotropes. One distillation boundary and one compartment boundary are shown by shaded surfaces
Fig. 2.3	A binary system, ethanol (A) – benzene (B), with one azeotrope can be transformed into two subsystems with the azeotrope treated as a pseudo component (Vogelpohl, 1974)
Fig. 2.4	Residue curve map of ternary system of acetone, chloroform and methanol
Fig. 2.5	Synthesis of distillation sequence separating a binary azeotropic mixture with recycles (A, B and C are pure components, D and E are azeotropes) (Doherty and Caldarola, 1985)
Fig. 2.6	Operation leaves for two sets of feasible product compositions that do not satisfy the common saddle criterion (Thong and Jobson, 2001a)
Fig. 2.7	A feasible ternary split with two section profiles intersected
Fig. 2.8	Branches of the pinch point curves for two product compositions and rectification bodies at a particular value of reflux ratio (Bausa <i>et al.</i> , 1998)
Fig. 3.1	Ternary system with distillation boundary linearly approximated 40
Fig. 3.2	Comparison of spherically approximated distillation boundary of a ternary system with the actual boundary
Fig. 3.3	Comparison of elliptically and spherically approximated distillation boundary of a ternary system

Fig. 3.4	In ternary system, identifying which distillation boundary contains point E
Fig. 3.5	In quaternary system, identifying which distillation boundary contains point E
Fig. 3.6	A ternary azeotropic system of methyl acetate, methanol and ethanol. The composition space is separated into two compartments, 1-2-4 and 1-3-4
Fig. 3.7	A ternary system of methyl acetate, methanol and ethanol, with singular point compositions expressed in terms of pure components
Fig. 3.8	Ternary system with one minimum boiling azeotrope. The whole composition space is a compartment. It is impossible to transform the composition in terms of pure components into composition in terms of singular points
Fig. 3.9	Ternary azeotropic system with curved distillation boundary, which is also compartment boundary
Fig. 3.10	Vapour-liquid equilibrium relationships in terms of pure components can be transformed into vapour-liquid equilibrium relationships in terms of singular points
Fig. 3.11	Separations of quaternary azeotropic mixtures (details given in Table 3.2)
Fig. 3.12	Relative volatility profiles (in terms of singular points) for the separations simulated using HYSYS (2001) at the minimum reflux ratio and with feed and product compositions shown in Table 3.2Volatility behaviour of a non-azeotropic and an azeotropic binary mixture
Fig. 3.13	Four-column distillation sequence separating the quaternary mixture of acetone, chloroform, benzene and toluene shown in Fig. 3.11(a)

Fig. 3.14	Compartment boundary crossing split in the ternary system of benzene, 1-propanol and toluene
Fig. 3.15	Optimisation procedure of the sequence using shortcut method 72
Fig. 3.16	Four-column distillation sequence with recycles (results as well as recycle structure)
Fig. 4.1	In quaternary system of acetone, chloroform, benzene and toluene, split 1/3-4-5 is a sharp split that breaks the azeotrope between acetone and chloroform
Fig. 4.2	Effects of the same recycle stream with different destinations: the feed of upstream split and the feed of non-upstream split
Fig. 4.3	In a ternary azeotropic system, a distillation boundary limits the product composition and flowrates of a distillation column
Fig. 4.4	A ternary azeotropic system with a distillation boundary. The actual distillation boundary and the linearly approximated distillation boundary bound the region of feasible feed compositions for DBC splits
Fig. 4.5	The effect of RB and RP types of recycles on the feed composition (P) of a DBC split. The recycles are to be mixed with this feed 89
Fig. 4.6	The effect of RP type recycle on the feasibility of a DBC split. The recycle is to be mixed with the feed of this DBC split, which lies inside the region of feasible feed compositions
Fig. 4.7	Four-column distillation sequence with RP type recycle
Fig. 4.8	The effect of RP type recycle to the feasibility of a DBC split. The feed of this DBC split is the destination of the RP type recycle and lies outside the region of feasible feed compositions
Fig. 4.9	A four-column sequence with a DBC split. Recycles may be recycled to the feed of the upstream splits of the DBC split (column C3). All possible recycle connections of the downstream products of column C3 are shown

Fig. 4.10	A RB type recycle recycled to the feed of the upstream split (split	
	breaking the azeotrope) of the DBC split of interest can enhance the	ne
	recovery of a constituent of the azeotrope giving rise to the	
	distillation boundary	98

Fig. 4.11	The effect of a RP type recycle when it is recycled to the feed of an
	upstream split of the DBC split reduces recovery of a constituent of
	the azeotrope giving rise to the distillation boundary

- Fig. 4.12 A four-column distillation sequence with recycles: (a) simple recycle structure identified using the rules introduced above; (b) recycle superstructure considering only singular recycles. F=100kmol/h.. 103

- Fig. 4.17 A split with two downstream recycles. The two recycles have the singular point compositions of HK (R3) and HHK (R5) ...... 117

Fig. 5.1	Quaternary system of Methyl acetate, Methanol, Ethanol and 2- Propanol. The composition space is separated into two compartments by compartment boundary 1-4-5 (Thong and Jobson, 2001c)
Fig. 5.2	46 potential sequences that can separate the quaternary mixture shown in Fig. 5.1 into pure components (Thong and Jobson, 2001c). Shaded splits are infeasible
Fig. 5.3	Simplified connection between Type C split 1-2/3-4-5 and its downstream products
Fig. 5.4	20 feasible sequences that can separate the quaternary mixture shown in Fig. 5.1 into pure components. Shaded splits are sloppy splits
Fig. 5.5	Examples of a sharp split (Split I) and sloppy split (Split II). A, B and C denote singular points
Fig. 5.6	Two flowsheets that can be used to separate quaternary mixture of acetone, chloroform, benzene and toluene. Sequence <i>a</i> contains only sharp splits; Sequence <i>b</i> contains sloppy splits
Fig. 5.7	All sequences containing only feasible sharp splits, that can separate the quaternary mixture shown in Fig. 5.1 into pure components
Fig. 5.8	In quaternary system of methyl acetate, methanol, ethanol and 2- propanol, different types of sloppy splits can be obtained with different singular points distributed between the two products of sharp Type A split 1-3-4/5
Fig. 5.9	A sharp Type C split (1-3/2-4-5) lying in quaternary system of methyl acetate, methanol, ethanol and 2-propanol
Fig. 5.10	Distillation sequences that can be used to separate quaternary mixture of methyl acetate, methanol, ethanol and 2-propanol. (a) Distillation sequence contains only sharp splits; (b) Distillation

- Fig. 6.1 A distillation sequence identified using the method of Thong and Jobson (2001c) for the separation of five-component azeotropic mixture of acetone, benzene, 1-propanol, toluene and styrene .... 161

# List of tables

Table 2.1	Distillation regions, distillation boundaries, compartments and
	compartment boundaries in the quaternary system shown in Fig. 2.2
Table 3.1	Comparison of the compositions of points lying on the actual
	boundary, and spherical and elliptical approximations of distillation
	boundary45
Table 3.2	Minimum reflux ratios calculated rigorously and using the
	Underwood equations61
Table 3.3	Comparison of minimum energy demand determined with Aspen
	Plus boundary value method rectification body method and
	Linderwood method
Table 3.4	Comparison of the results of shortcut design and rigorous simulation
	of a distillation sequence (ACBT system)
Table 3.5	Shortcut design results of each column shown in Fig. 3.16
Table 3.6	Design results of each column shown in Fig. 3.16 by rigorous
	simulation using HYSYS76
Table 4 1	The design results of each column shown in Fig. 4.6 using HYSYS
	92
Table 4.2	Effects of RB and RP type recycle destination for a sequence 97
Table 4.3	The effects of different recycles on the feasibility of the DBC split of
	interest and the recovery of the azeotrope constituents 101
Table 4.4	Design parameters for columns shown in Fig. 4.12
Table 4.5	Distribution of intermediate-boiling singular points, HDSP and LDSP,
	in products affects feasibility of Type B splits 106
Table 4.6	Effects of different recycles on the feasibility of the Type B split

1-3-4/3-4-5shown in Fig.	4.14	108
--------------------------	------	-----

Table 4.7 Effect of HK and HHK recycles on the split shown in Fig. 4.17..... 118

- Table 5.2 Results of the evaluation of flowsheets shown in Fig. 5.12....... 152

Table 6.1Singular points in the five-component azeotropic mixture of acetone,benzene, 1-propanol, toluene and styrene160

 Table 6.2
 Feasibility of Type C splits included in the sequences separating a five-component azeotropic mixture

 162

- Table A.1 Steam cost as a function of steam pressure
   194
- Table A.2 Values of installation sub-factor for columns (IChemE A Guide to<br/>Capital Cost Estimating, 1988)196
- Table A.3 Values of installation sub-factor for heat exchangers (IChemE AGuide to Capital Cost estimating, 1988)197

## Chapter 1

## Introduction

#### 1.1. Background

Homogeneous distillation (including extractive distillation), in which there is only one liquid phase, or heterogeneous azeotropic distillation, in which there are two liquid phases, or pressure swing distillation can be used to separate azeotropic mixtures. To recover all components of an azeotropic mixture, distillation sequences are always needed. In comparison to non-azeotropic distillation, the column design and synthesis of distillation sequences separating azeotropic mixtures are more complicated and poorly understood. The complexity increases with the increase of the number of components included in azeotropic mixtures.

In recent years, much attention has been paid on the separation of ternary azeotropic mixtures (Doherty and Caldarola, 1985; Knapp and Doherty, 1992; Manan et al., 2001; Sutijan, 2002). Graphical tools, such as residue curve maps (Doherty and Perkins, 1979) and operation leaves (Wahnschafft *et al.*, 1992; Castillo, 1997), and graphically based methods have been developed for column design and sequence synthesis. However, these tools and methods are only applicable for ternary azeotropic mixtures, since the composition space cannot be visualised for azeotropic mixtures with more than four components.

A large number of distillation sequences can be used to separate a multicomponent azeotropic mixture. The number will increase when phase splitting and pressure swing are considered. Synthesis of distillation sequences separating multicomponent azeotropic mixtures is a very difficult problem as no graphical tools are available. To date, all proposed column design methods are computationally intensive, as they are based on either pinch point calculation or

stage-by-stage equilibrium and mass balance calculation (Julka and Doherty, 1990, 1993; Köhler et al., 1991; Pöllmann et al., 1994; Bausa et al., 1998); no efficient method for the design of columns separating multicomponent homogeneous azeotropic mixtures is available. Although several algorithmic proposed for synthesising methodologies are distillation sequences (Wahnschafft, 1993; Bauer and Stichlmair, 1998; Rooks et al., 1998; and Thong and Jobson, 2001c), these methods cannot guarantee the best sequence to be found. There is still no systematic and efficient method for identifying recycles and synthesising distillation sequences separating multicomponent homogeneous azeotropic mixtures.

#### 1.2. Aims and scope

Using the procedure of Thong and Jobson (2001c), all potentially feasible sequences can be generated for separating a multicomponent azeotropic mixture. However, too many sequences can be generated and it is necessary to screen out a few promising sequences. The aim of this work is to develop a systematic and efficient methodology for synthesising distillation sequences separating multicomponent azeotropic mixtures. This work builds on the work of Thong and Jobson (2001c) and considers the separation of homogeneous mixtures using single-feed columns. Each column can perform either a sloppy or a sharp split, in which, at least one pair of 'components' (singular points) does not distribute between its two products. Desired products of the sequence are streams with nearly pure component compositions. Pressure swing, which can help break pressure-sensitive azeotropes, is not considered in this work.

In a distillation sequence, distillation boundaries always constraint the product compositions and thus affect the feasibility of splits and the sequence. Therefore, it is necessary to identify the distillation region in which its products lie, so that the feasibility of proposed splits can be preliminarily tested in the synthesis of distillation sequences. Residue curves or linearly approximated distillation boundaries (Doherty and Caldarola, 1985) can be used to identify the

distillation region in which a composition or product lies. However, the former approach will make the sequence synthesis (an iterative process) timeconsuming and the latter method cannot represent the actual distillation boundaries well, so will introduce big errors. This work aims to overcome these shortcomings by developing a simple non-linear approximation of the distillation boundaries in multicomponent composition space.

For multicomponent azeotropic mixtures, existing column design methods are computationally intensive and mainly concentrate on the calculation of minimum reflux ratios. The evaluation of distillation sequences with recycles is computationally inefficient when these methods are applied. Also, there is no efficient method for estimating the number of stages and feed stage. An aim of this work is to develop a simplified approach for assessing feasibility and column design for the purpose of evaluation of flowsheets including distillation columns and recycles.

Using existing methods for sequence synthesis, only recycle superstructures can be generated. However, the evaluation of all such flowsheet alternatives is computationally expensive because of the number of all possible recycles. Each recycle option makes the evaluation procedure iterative. To efficiently evaluate each sequence, a simpler recycle structure needs to be generated. This work aims to develop systematic approach for generating simplified recycle structures that incorporates insights into the effect of different types of recycles on separation feasibility and flowsheet performance.

The large number of sequences identified using the procedure of Thong and Jobson (2001c) are only potentially feasible. Through evaluating each sequence, promising sequences among them can be identified. However, such an evaluation is extremely time-consuming. This work aims to develop a screening procedure for these distillation sequences to allow economically promising sequences containing both sharp and sloppy splits to be identified.

Finally, this work aims to illustrate how the new methodology may be applied to a relatively difficult separation problem.

## 1.3. Vapour-liquid equilibrium models and assumptions

To account for the liquid-phase non-ideality of azeotropic mixtures, the Wilson model is used in all the calculations presented in this work, unless stated otherwise. Since the calculation is carried out at atmospheric pressure, the ideal gas model is used for the vapour phase. The pure-component vapour pressure is calculated using the Reid-Prausnitz-Polling equation (Reid *et al.*, 1987). The parameters used for calculating activity coefficient, enthalpy and density are obtained from Reid *et al.* (1987) and HYSYS 2.1 (AspenTech., Calgary, Canada).

In this work, the following conditions are assumed to be valid:

- (1) Constant molar flow within the column.
- (2) Pressure drop over the column is zero.
- (3) Liquid and vapour phases are in equilibrium on all stages of the column.
- (4) In the liquid phase, no phase splitting occurs.
- (5) Vapour-liquid equilibrium and activity coefficient models and parameters are valid.

## **1.4.** Application of computational tools

The numerous iterations and complex calculations performed in this work are coded using Fortran 77, incorporated into a software package, COLOM 1.7a (Sutton *et al.*, 2003). Unless stated otherwise, all the results presented in this work are calculated using COLOM. The results of the proposed method are validated using commercial software package HYSYS 2.1 (AspenTech., Calgary, Canada). Distil 5.0 (AspenTech., Calgary, Canada) is used to calculate the adjacency and reachability matrices. All calculations in this work are carried out on an AMDXP 2000+ machine.

#### 1.5. Outline of the thesis

Chapter 2 reviews characteristics of azeotropic mixtures, and existing methods for assessing column feasibility and column design, and for flowsheet synthesis for ternary and multicomponent azeotropic mixtures. In Chapter 3, the nonlinear approximation of distillation boundaries and shortcut column design method are proposed, together with the procedure for sequence evaluation. Chapter 4 discusses rules and procedures for selecting recycle structures. Screening of distillation sequences identified using the procedure of Thong and Jobson (2001c) is studied in Chapter 5. Based on these methods, a systematic procedure for synthesising and evaluating promising distillation sequences is developed and demonstrated in Chapter 6. Finally, Chapter 7 concludes this work and presents directions for future work.

## Chapter 2

## Literature review

#### 2.1. Introduction

In this chapter, relevant work from the literature is reviewed. For a nonazeotropic mixture, the volatility order of components is constant and can be used to identify distillation sequences; the column of each sequence can be designed using the classical Fenske–Underwood–Gilliland method, which assumes constant relative volatility. However, the composition space of an azeotropic mixture is always divided into distillation regions and compartments, and volatility order is different in different distillation regions and compartments. Therefore, the methods applicable for non-azeotropic mixtures cannot be directly applied to azeotropic mixtures.

Many graphical tools, such as residue curve maps and operation leaves method, have been proposed for azeotropic mixtures. These tools can be used to identify distillation regions and feasible splits, and to synthesise distillation sequences with recycles. Since only three-dimensional composition space can be visualised, such representations are not applicable for multicomponent mixtures. For multicomponent azeotropic mixtures, algorithm-based methodologies are proposed for identification of distillation regions and compartments, column design and sequence synthesis. These methods focus on homogeneous azeotropic distillation, as reviewed below.

# 2.2. Vapour-liquid equilibrium characteristics of azeotropic mixtures

#### 2.2.1. Effect of azeotropes on volatility order

In a non-azeotropic mixture, the volatility order of constituents does not change. Relative volatility between two components *i* and *j*,  $\alpha_{ij}$ , defined by Equation (2.1), is either larger or smaller than unity.

$$\alpha_{ij} = \frac{\frac{y_i}{x_i}}{\frac{y_j}{x_i}}$$
(2.1)

where, y and x represent the mole fraction of a component in the vapour and liquid phases in equilibrium, respectively.

In an azeotropic mixture, the volatility order of components changes with the composition. At the azeotrope, the vapour and liquid in equilibrium have the same composition, and the volatilities (relative to same reference component of the system) of the azeotropic components are equal.



Fig. 2.1 Volatility behaviour of a non-azeotropic and an azeotropic binary mixture.

For example, in the acetone (1) – benzene (2) system shown in Fig. 2.1 (a), no azeotrope forms and the relative volatility between these two components is always larger than unity ( $\alpha_{12} > 1$ ) through the whole composition space. In the

binary system of acetone (1) and chloroform (2), an azeotrope forms; the relative volatility between these two components is less than unity ( $\alpha_{12} < 1$ ) for  $x_1 < x_{az}$ , and larger than the unity ( $\alpha_{12} > 1$ ) on the other side of the azeotrope, as shown in Fig. 2.1 (b).

#### 2.2.2. Residue curve maps and distillation line maps

A residue curve is defined as the trajectory of the liquid composition of a mixture during a simple distillation process (Schreinemakers, 1901). Van Dongen and Doherty (1985) proved that residue curves represent the liquid composition profiles of packed columns operated at total reflux. A group of residue curves form a residue curve map, in which all pure component vertices and azeotropes are defined as singular points (Doherty and Perkins, 1979). A singular point is a stable node if residue curves only converge to it. A singular point is an unstable node if residue curves only diverge from it. A singular point with residue curves moving towards it and away from it, is a saddle. This work employs the convention (Knight and Doherty, 1990) that the singular points are numbered in the order of increasing boiling temperature.

A residue curve map is useful for assessing the feasibility of distillation columns and column sequences, especially for azeotropic mixtures. At total reflux, the proposed column is feasible if: (a) the top and bottom product compositions belong to the same residue curve, and, (b) products and feed are located at the straight line in the composition diagram, which means that they satisfy the mass balance (Van Dongen and Doherty, 1985; Laroche *et al.*, 1992b).

A distillation line, defined as the composition of the liquid phase on each plate of a staged column operated at total reflux (Stichlmair, 1987), represents the liquid composition profile of staged column operated at total reflux ratio. Unlike residue curves, distillation lines are not smooth curves and the points on a distillation line are joined by tie lines that assist visualisation but have no physical meaning. A group of distillation lines form a distillation line map.

Although residue curves and distillation lines represent profiles of packed and staged columns, respectively, they are qualitatively identical (Widagdo and Seider, 1996). Therefore, distillation line maps can be used in the same way as residue curve maps, which are more popular.

#### 2.2.3. Distillation regions and compartments

Azeotropes will result in the formation of either compartments or distillation regions. Within a distillation region, all residue curves have the same pair of initial and terminal singular points. Residue curves in different distillation regions have different stable or unstable nodes (Doherty and Perkins, 1979). Two adjacent distillation regions are separated by a distillation boundary, which imposes limitations on product compositions (and composition profiles) of distillation columns. At total reflux, a feasible split must have two products that lie in the same distillation region (Van Dongen and Doherty, 1985). A split, with products lie in one region and a feed in another, may also be feasible if the feed lies on the concave side of the distillation boundary. Such a split crosses the distillation boundary and is called distillation-boundary crossing (DBC) split in this work.

Within a distillation region, although all residue curves begin at the same unstable node and end at the same stable node, sometimes they may approach (move towards and away from) different saddle points. In this case, the distillation region is generally separated into several 'continuous distillation regions' (Safrit and Westerberg, 1997) or 'compartments' (Thong and Jobson, 2001a). In each compartment, all residue curves start from the unstable node, approach saddle points one by one in order of increasing boiling temperature, and end at the stable node. Within a compartment, residue curves can approach all the saddle points that appear in it (Thong and Jobson, 2001a). This behaviour is analogous to that in the composition space of non-azeotropic mixtures. The difference between two neighbouring compartments, which lie in the same distillation region, is that they have different saddle points. Two

adjacent compartments are separated by a compartment boundary, which is termed as 'continuous distillation boundary' by Safrit and Westerberg (1997) and can be linearly approximated by connecting the common singular points of the two compartments using straight lines (Thong and Jobson, 2001a). Single-feed columns can sometimes cross a compartment boundary (*i.e.* the two products lie in adjacent compartments), and two-feed columns can further facilitate such a split (Thong and Jobson, 2001a).

Residue curve maps can visually indicate distillation regions and compartments. However, for multicomponent azeotropic mixtures, the topology of the composition space (existence and location of distillation regions and compartments and their boundaries) cannot be visualised. Fortunately, the approach of Knight and Doherty (1990) allows a mathematical representation of the topology. For a multicomponent azeotropic mixture, with singular points numbered in the order of increasing boiling temperature, an adjacency matrix, A, and a reachability matrix, R, can be defined (Knight and Doherty, 1990). The adjacency matrix is defined by  $a_{i,j} = 1$  if a residue curve joins *i* to *j*; otherwise,  $a_{i,i} = 0$ . The reachability matrix is defined by  $r_{i,i} = 1$  if there is any path from i to *j*; otherwise,  $r_{i,j} = 0$ . Rooks *et al.* (1998) developed a general procedure for computing the adjacency and reachability matrices for n-component homogeneous mixtures. Based on this, algorithmic procedures for identifying the distillation regions and compartments are proposed by Rooks et al. (1998) and Thong and Jobson (2001a), respectively, without relying on visualisation tools. Distillation boundaries are assumed to be linear in the procedure of Rooks et al. (1998) and compartment boundaries are linearly approximated in that of Thong and Jobson (2001a).

Fig. 2.2 illustrates the adjacency and reachability matrices of a quaternary mixture with three azeotropes. Using the procedures of Rooks *et al.* (1998), it can be determined that the whole composition space is separated into two distillation regions by distillation boundary 1-2-3-5. Two compartments in distillation region 1-2-3-5-6 and three in region 1-2-3-4-5-7 can be identified

using the procedure of Thong and Jobson (2001a). The distillation regions, compartments and corresponding boundaries are listed in Table 2.1 (2001a).



Fig.2.2 Adjacency and reachability matrix of a quaternary mixture with three azeotropes. One distillation boundary and one compartment boundary are shown by shaded surfaces.

Table 2.1 Distillation regions, distillation boundaries, compartments and compartmentboundaries in the quaternary system shown in Fig. 2.2.

Distillation regions	1-2-3-5-6	1-2-3-4-5-7
Compartments	1-2-5-6 1-3-5-6	1-2-5-7
		1-3-5-7
		1-3-4-7
Compartment boundaries	1-5-6	1-5-7
		1-3-7
		1-7
Distillation boundary	1-2-3-5	

## 2.2.4. Simplified representation of azeotropic systems

Vogelpohl (1974) showed that, in distillation, an azeotrope behaves like a pure component and a binary azeotropic system can be simplified into two ideal

systems by treating the azeotrope as a pseudo component. For example, with the minimum azeotrope between ethanol (A) and benzene (B) treated as a pseudo pure component, the binary (A-B) system, shown in Fig. 2.3, can be transformed into two ideal systems, system 3 and system 33 (Vogelpohl, 1974). When the mole fraction of A is less than  $x_{az, A}$ , the mixture can be treated as the ideal system of the azeotrope and B in system 3 On the other side of the azeotrope, the mixture can be taken as the ideal system of the azeotrope and A in system 33



Fig. 2.3 A binary system, ethanol (A) – benzene (B), with one azeotrope can be transformed into two subsystems with the azeotrope treated as a pseudo component (Vogelpohl, 1974).

As shown in Fig. 2.3, each system can be treated as an independent system, and the composition of any mixture can be transformed to the new coordinate system. In the transformed system, the relative volatility of the pseudo component (pure component or azeotrope) can be calculated according to the transformed composition. For example, in transformed system 33 the relative volatility between the azeotrope and A can be calculated using Equation (2.2). For the mixture of ethanol (A) and benzene (B) at 1 bar, it was shown that the relative volatility  $\alpha_{az,A}$  has an almost constant value (4.32±0.32), and this transformed system can be treated as an ideal system (Vogelpohl, 1974). The

other transformed system can also be treated as an ideal system as the relative volatility between B and the azeotrope is also approximately constant (Vogelpohl, 1974).

$$\alpha_{az,A} = \frac{\eta_{azeotrope} (1 - \xi_{azeotrope})}{\xi_{azeotrope} (1 - \eta_{azeotrope})}$$
(2.2)

Vogelpohl (2002) recently extended this work for ternary systems. However, his claims that the method is generally applicable for multicomponent systems (Vogelpohl, 2002) have not been substantiated. In this method, with azeotropes treated as pseudo components, a ternary azeotropic system with *A* azeotropes can be treated as an enlarged system with (3+*A*) components. The enlarged system can be separated into several approximately ideal subsystems. For example, there are four azeotropes in the ternary system of acetone, chloroform and methanol, as shown in Fig. 2.4. Vogelpohl (2002) proposed that the composition space could be treated as a seven-component system with three 'quaternary' ideal subsystems, 1-4-5-6, 1-2-4-7 and 2-3-4-6. In each subsystem, the relative volatilities of pure components and azeotropes are assumed to be constant and can be calculated using Equation (2.3) (Vogelpohl, 2002).

$$\alpha_{ik} = \frac{\gamma_i \boldsymbol{p}_i^0}{\gamma_k \boldsymbol{p}_k^0} \tag{2.3}$$

With  $\gamma_i$  the activity coefficient, and  $p_i^0$  the vapour pressure,  $\gamma_i p_i^0$  and  $\gamma_k p_k^0$  are evaluated for any pure component or azeotrope *i* and *k*, respectively (Vogelpohl, 2002).

Applying the distillation theory of ideal systems and Equation (2.3) to calculate the relative volatility of the pure components and azeotropes, the distillation lines regarding to the subsystems may be calculated, and an approximate model of the real system can be obtained (Vogelpohl, 2002). For a simple system, such as a ternary system with only one azeotrope, distillation lines calculated using this method are in good agreement with those calculated rigorously. For a complex system, such as the ternary system shown in Fig. 2.4,

the deviation between the distillation lines calculated using this method and those calculated rigorously is large (Vogelpohl, 2002).



Fig. 2.4 Residue curve map of ternary system of acetone, chloroform and methanol.

Another problem with this method is that there is no clear definition of what constitutes a subsystem. For the example shown in Fig. 2.4, subsystem 1-2-4-7 contains two distillation regions, 1-4-7 and 2-4-7, while subsystem 1-4-5-6 corresponds to a distillation region. Therefore, this method cannot be systematically applied.

#### 2.3. Distillation of non-azeotropic mixtures

#### 2.3.1. Synthesis of distillation sequences

To recover the constituents of an *n*-component non-azeotropic mixture using simple columns that have one feed and two products, a distillation sequence is needed. The larger the number of components, the more columns there are in the sequence. The large number of alternative sequences that can be used to separate a multicomponent non-azeotropic mixture can be identified according

to the volatility order. These sequences can be represented by a superstructure, such as a tree superstructure (Hendry and Hughes, 1972) and a network superstructure (Andrecovich and Westerberg, 1985). The minimum number of possible sequences can be calculated by Equation 2.4 (Thompson and King, 1972).

$$S_R = \frac{(2(n-1))!}{n!(n-1)!}$$
(2.4)

Here, *n* is the number of components, and  $S_R$  is the minimum number of possible sequences with simple columns making sharp splits. A split, for which there is no distribution of any components between the two products is said to perform a sharp split. Otherwise the split is sloppy.

The number of sequences increases significantly with the increase of the number of components. For example, the number of sequences separating a quaternary mixture is 5, but the number of sequences to separate a tencomponent mixture is 4862. If sloppy splits are considered, the number of possible sequences will become unmanageably large. The problem arising now is how to efficiently identify the best few sequences among the enormous number of alternatives.

Based on case studies, heuristics were developed (Lockhart, 1947; Harbert, 1957; Heaven, 1969) that can be used to quickly identify reasonable sequences that will prove to be close to the best sequences. Seader and Westerberg (1977) ranked a reasonable set of heuristics as follows (Westerberg, 1985):

- (Most important) Separate first where the adjacent relative volatilities are large.
- (2) Separate out plentiful components early
- (3) Use the "direct sequence" of separating out the most volatile component first, then the second most volatile and so forth.

Instead of using heuristics, many algorithmic approaches were proposed to identify promising sequences. In 1970s, many branch-and-bound algorithms, were proposed for solving mixed integer nonlinear problems (Thompson and King, 1972; Westerberg and Stephanopoulos, 1975; Rodrigo and Seader, 1975; Gomez and Seader, 1976). These methods are also called MINLP methods; together with NLP, and MILP methods, they were widely used for synthesis and optimisation (Andrecovich and Westerberg, 1985; Floudas and Paules IV, 1988; Aggarwal and Floudas, 1990; Yeomans and Grossmann, 2000). All these methods are based on the superstructure and shortcut or rigorous column design, none of them addressed mixtures with significantly non-ideal behaviour, such as azeotrope-forming mixtures.

## 2.3.2. Shortcut design method for columns separating nonazeotropic mixtures

For design of columns separating non-azeotropic mixtures, the Fenske-Underwood-Gilliland (FUG) method is the most widely used shortcut method. This method employs the Fenske equation (Fenske, 1932), the Underwood equations (Underwood, 1945, 1946a, 1946b, 1948) and the Gilliland correlation (Gilliland, 1940) in an analytical form (e.g. Eduljee, 1975) to calculate the minimum number of stages, the minimum reflux ratio, and the operating reflux ratio or number of theoretical stages, respectively. The FUG method needs the separation between two components, the light key (LK) and the heavy key (HK) component, to be specified. The light key component has a specified maximum recovery in the bottom product, while the recovery or mole fraction of the heavy key component in the top product is specified. The underlying theory and limitation of the Fenske equation, Underwood equations and Gilliland correlation are discussed in the following sections.

#### 2.3.2.1. Fenske equation – minimum number of stages

When operated at total reflux ratio, a column can achieve the desired separation with the minimum number of stages. If a column is used to separate a binary mixture with components A and B, at total reflux, where the volatility of component A relative to component *B*,  $\alpha_{AB}$ , is constant, it can be derived (Fenske, 1932):

$$N_{\min} = \frac{\log\left[\left(\frac{x_A}{x_B}\right)_D / \left(\frac{x_A}{x_B}\right)_B\right]}{\log(\alpha_{AB})}$$
(2.5)

where, *D* and *B* denote the distillate and bottom product, respectively, and  $N_{min}$  is the minimum number of stages.

Equation (2.5) is known as the Fenske equation (Fenske, 1932). The minimum number of equilibrium stages includes the reboiler and partial condenser, but not a total condenser. In the derivation of the Fenske equation, there are no assumptions limiting the number of components in the system. Therefore, it can be used for mixtures with any number of components. From Equation (2.5), it can be seen that the minimum number of stages depends only on the separation requirement of the two key components. For a column separating a multicomponent mixture, once the minimum number of stages is obtained, the Fenske equation can be used to calculate the distribution of non-key components at total reflux (King, 1971).

#### 2.3.2.2. Underwood equations — Minimum reflux ratio

Based on the constant molar overflow (CMO) and constant relative volatility (CRV) assumptions, Underwood developed a well-known algebraic procedure to calculate the minimum reflux ratio (Underwood, 1945, 1946a, 1946b, 1948). For the rectifying section, he defined a quantity  $\phi$ :

$$V_{\min} = \sum_{i=1}^{n} \frac{\alpha_i D x_{i,D}}{\alpha_i - \phi}$$
(2.6)

where *n* is the number of components,  $\alpha_i$ , *D*,  $x_{i,D}$ , and  $V_{min}$  are the relative volatility of component *i* (*i*=1, 2, ..., *n*), the distillate flowrate, the mole fraction of *i* in the distillate and the minimum vapour flowrate, respectively. The minimum vapour flowrate corresponds to the vapour flow at minimum reflux. Similarly, for the stripping section, he defined a quantity  $\phi N$ 

$$-V_{\min} = \sum_{i=1}^{n} \frac{\alpha_i B x_{i,B}}{\alpha_i - \phi'}$$
(2.7)

where, *B* and  $x_{i,B}$  are the bottom product flowrate, and the mole fraction of *i* in the bottom product, respectively. It is apparent that there are as many values of  $\phi$  and  $\phi$ N satisfying Equations (2.6) and (2.7) as there are components. If components are numbered in the order of increasing normal boiling temperature, these solutions obey:

$$\alpha_{1} > \phi_{1} > \alpha_{2} > \phi_{2} > \alpha_{3} > \dots > \alpha_{n} > \phi_{n}$$
  
$$\phi'_{1} > \alpha_{1} > \phi'_{2} > \alpha_{2} > \phi'_{3} > \dots \phi'_{n} > \alpha_{n}$$
(2.8)

As shown by Underwood (1946b), at minimum vapour flowrate, some roots of  $\phi$  and  $\phi$ /Vare identical, *i.e.*,  $\phi_i = \phi'_{i+1}$ . Generally,  $\theta$  is used to denote the common root of Equations (2.6) and (2.7). When the CMO assumption holds, the difference between the vapour flows of the top and bottom sections is (1-q)F. From Equations (2.6) and (2.7), it follows:

$$1 - q = \sum_{i=1}^{n} \frac{\alpha_i x_{i,F}}{\alpha_i - \theta}$$
(2.9)

$$R_{\min} + 1 = \sum_{i=1}^{n} \frac{\alpha_i x_{i,D}}{\alpha_i - \theta}$$
(2.10)

where,  $x_{i,F}$  and  $R_{min}$  are the feed composition of component *i* and the minimum reflux ratio, respectively; *q* is the feed thermal condition, which is equal to the

liquid fraction of the feed when  $0 \le q \le 1$ . The Underwood equations can be used for mixtures with any number of components and are insensitive to the distribution of impurities (non-key components) in the products (King, 1971).

When the two key components are adjacent to each other in volatility, there is only one solution for  $\theta$ , which lies between  $\alpha_{LK}$  and  $\alpha_{HK}$ . Otherwise, there are several solutions for  $\theta$  lying between  $\alpha_{LK}$  and  $\alpha_{HK}$ . In this case, it is difficult to decide which  $\theta$  value allows Equation (2.10) to give a good prediction of the minimum reflux ratio. In practice, Underwood equations are used for such cases with arbitrarily selected  $\theta$  value but inaccurate result. The iterative procedure employed to solve for the value of  $\theta$  should be highly accurate (King, 1971). However, if the denominator ( $\alpha_i - \theta$ ) (for any *i*) is very small, the Underwood equations may give inaccurate predictions, even if  $x_i$  is also small.

#### 2.3.2.3. Gilliland correlation

Once the minimum reflux ratio and minimum number of stages are known, the Gilliland correlation can be used to determine the number of equilibrium stages as a function of selected values of operating reflux ratio (Gilliland, 1940). This correlation, which is based on stage-by-stage calculations for over 50 binary and multicomponent distillations, was first developed as a plot (Gilliland, 1940). Many attempts have been made to represent Gilliland's correlation analytically (Liddle, 1968; Molokanov *et al.*, 1972; Eduljee, 1975; Rusche, 1999). Equation (2.11) is the correlation of Eduljee (1975):

$$\frac{N - N_{\min}}{N + 1} = 0.75 \left[ 1 - \left(\frac{R - R_{\min}}{R + 1}\right)^{0.566} \right]$$
(2.11)

Equation (2.11) is commonly applied in two ways. One approach is to specify the ratio between operating reflux and minimum reflux, and then calculate the number of equilibrium stages. The other is to specify the ratio between the
number of equilibrium stages and the minimum number of stages, and then determine the operating reflux ratio.

In the FUG method, both the Underwood and Fenske equations are based on the CRV assumption. However, relative volatilities generally vary through the column and the average value needs to be found. Different ways can be used to calculate the mean relative volatilities of a column. Generally, the geometric mean value of relative volatility at the top and the bottom of the column is used (Humphrey and Keller, 1997). When the relative volatilities along the column change significantly (e.g. non-azeotropic binary column separating acetone from benzene), this method cannot give good results (King, 1971). For a column separating an azeotropic mixture, the relative volatility generally changes significantly along the column and sometimes even the volatility order will change. The FUG method cannot be used directly to design columns for such mixtures.

#### 2.4. Distillation of ternary azeotropic mixtures

#### 2.4.1. Sequence design and recycle selection

The objective of distillation sequence synthesis for azeotropic mixtures is to identify sequences of separation tasks and the associated set of recycle streams that will achieve a given separation objective (Thong *et al.*, 2003). The basic difference between the design of sequences for non-azeotropic and azeotropic mixtures is that, for the latter, the component distribution between the products of a column depends upon the distillation region in which the feed composition lies. Furthermore, as the number of species increases, the composition space becomes more complex, and the product compositions become more difficult to predict (Widagdo and Seider, 1996). For ternary mixtures, as residue curve maps and distillation line maps can be visualised, synthesising distillation sequences is simplified considerably. These graphical tools are reviewed below.

Doherty and Caldarola (1985) assume that the distillation boundaries are linear and employ residue curve maps to synthesis feasible distillation sequences. The key for sequence synthesis is to find a way to cross the distillation boundaries so that the desired products can be obtained. For the distillation sequence shown in Fig. 2.5 (b), every column is feasible in terms of mass balance, as shown in Fig. 2.5(a). However, the sequence is infeasible (Doherty and Caldarola, 1985) because the subsystem formed by column C2 and C3, as shown in Fig. 2.5 (b), does not satisfy the mass balance. Therefore, it is concluded that linear distillation boundary can never be crossed by distillation (Doherty and Caldarola, 1985).



Fig. 2.5 Synthesis of distillation sequence separating a binary azeotropic mixture with recycles (A, B and C are pure components, D and E are azeotropes) (Doherty and Caldarola, 1985).

A curved distillation boundary can be crossed provided it has enough curvature (Laroche *et al.*, 1992a). Also columns operating at finite reflux can cross a curved distillation boundary (Wahnschafft *et al.*, 1992; Stichlmair and Herguijuela, 1992; Pöllmann and Blass, 1994; Castillo, 1997, Li *et al.*, 1999). Pressure swing can also be used to cross a distillation boundary (Knapp and Doherty, 1992) that is sensitive to pressure. Thong (2000) showed that a curved distillation boundary can be crossed by mixing two streams lying in different side of the boundary. In this work, only simple columns with products lying in

one region and a feed in another are used to cross a curved distillation boundary.

The composition profiles of a packed-column section will be bounded by the product residue curve, which represents the total reflux bound, and the product pinch point curve, which represents the minimum reflux bound (Wahnschafft *et al.*, 1992). This region is named an "operation leaf" (Castillo, 1997).

Castillo (1997) defined the product operation leaf as the region of all possible liquid composition profiles at any reflux or reboil ratio leading to the specified product composition. Based on this, a sequence design procedure for ternary azeotropic mixtures was proposed (Castillo, 1997). Trial-and-error is needed for establishing potential recycle compositions. A systematic procedure for generating a set of the most promising separation sequences for ternary azeotropic mixtures without boundary crossing is proposed by Manan and Banares-Alcantara (2001). Ternary azeotropic systems are classified on the basis of the type of entrainer used to break the azeotrope; feasible sequences for each class of ternary azeotropic system are generated. These sequences are screened using a set of heuristics developed based on graphical analysis, as well as some well-established sequencing heuristics, to give most promising sequences for each class of azeotropic system. Sutijan (2002) proposed a general flowsheet synthesis procedure for ternary azeotropic mixtures. Sequences can be automatically identified, and recycle streams and good initial values for recycle variables can be identified using graphically based method. Graphical tools are employed in all these methods. Some algorithmic methods (Wahnschafft et al., 1993; Rooks, et al., 1998; Bauer and Stichlmair, 1998; Thong and Jobson, 2001c) proposed for multicomponent azeotropic mixtures can also be applied for ternary systems. These will be introduced later.

#### 2.4.2. Assessing column feasibility

At total reflux, residue curve maps or distillation line maps can be used to assess the feasibility of columns separating ternary azeotropic mixtures. A proposed column is feasible if: (a) the top and bottom product compositions belong to the same residue curve, and, (b) products and feed satisfy the mass balance (Van Dongen and Doherty, 1985; Laroche *et al.*, 1992).

A split, which is infeasible at total reflux, is sometimes feasible at finite reflux (Wahnschafft *et al.*, 1992; Stichlmair and Herguijuela, 1992; Pöllmann and Blass, 1994; Castillo, 1997, Li *et al.*, 1999). The boundary value method, operation leaves and stage composition lines can be used to test the feasibility of proposed splits at total reflux and with finite reflux (Levy *et al.*, 1985; Wahnschafft *et al.*, 1992; Castillo, 1997).

The boundary value method, proposed by Levy *et al.* (1985), can be used to determine the minimum reflux ratio and feasible design parameters of a column separating a ternary homogeneous azeotropic mixture. This method requires fully specified product compositions, feed composition and quality. Once these specifications have been made, only one degree of freedom remains between the reflux and boil-up ratios. With a specified reflux (or boil-up) ratio, liquid composition profiles for rectifying and stripping sections can be calculated from the fully specified products. The intersection of these two profiles indicates feasibility and provides design parameters, *i.e.* number of stages and feed stage location of this split. The minimum reflux ratio can be found through repeated calculation for different reflux ratios.

Operation leaves (Wahnschafft *et al.*, 1992; Castillo, 1997) and stage composition lines (Castillo, 1997) can also be used to test the feasibility of a proposed split. An operation leaf, the region bounded by product residue curve, which represents the total reflux bound, and the product pinch point curve, which corresponds to the minimum reflux, contains all the composition profiles of a packed-column section. The intersection of the operation leaves of the rectifying and stripping sections of a column indicates the feasibility of this split. Although this method is not iterative, it is computationally intensive because of the calculation of product pinch point curve.

The stage composition line is a smooth line formed by connecting liquid composition points on a certain stage when the reflux/boil-up ratio is varied (Castillo, 1997). Stage composition lines are essentially a different way organising the information calculated in the liquid composition profiles for a column section. Intersection between the stage composition lines of two sections of a column indicates the column feasibility and column design parameters, including stage number in each section, feed stage, and reflux and reboil ratio. This method is not iterative. However, since many column section composition profiles at different reflux and reboil ratios need to be calculated to construct stage composition lines, this method is computationally demanding.



Fig. 2.6 Operation leaves for two sets of feasible product compositions that do not satisfy the common saddle criterion (Thong and Jobson, 2001a).

Feasible splits can also be identified by applying the "common saddle criterion", which requires the rectifying and stripping composition profiles of a feasible column to approach the same saddle at high reflux (Rooks *et al.*, 1998). This criterion is only a sufficient condition for identifying feasible split. A split that does not satisfy this criterion may be feasible (Thong and Jobson, 2001a). Therefore, not all feasible splits can be identified using this criterion. For example, in the ternary system of acetone, chloroform, and methanol, shown in

Fig. 2.6, a split with the distillate, d', and bottom product, b', does not satisfy the common saddle criterion. However, this split is feasible with the stripping and rectifying operation leaves intersect (Thong and Jobson, 2001a). Similarly, b'' and d'' are a pair of feasible product compositions that do not satisfy the common saddle criterion.

#### 2.5. Distillation of multicomponent azeotropic mixtures

#### 2.5.1. Synthesis of distillation sequences with recycles

For multicomponent azeotropic mixtures, graphical tools are not available, so sequence synthesis methods for ternary azeotropic mixtures cannot be applied. Several algorithmic methodologies that are not based on graphic tools have been proposed, and are reviewed below.

#### 2.5.1.1. Sequential methodology of Wahnschafft (1993)

A methodology for sequence synthesis for multicomponent mixtures is presented by Wahnschafft *et al.* (1993). Repeated process simulations are employed to identify all possible column sequences for a given feed composition. Then, for the identified sequences, splits are combined according to the stream compositions and recycle streams are assigned. Because recycles affect the feed compositions to proposed separations, the sequences are resimulated until the flowsheet simulation converges. This methodology is sequential in nature and needs repeated simulation. In principle, it is applicable to the separation of *n*-component mixtures. Unfortunately, obtaining the appropriate recycle compositions becomes difficult for multicomponent mixtures, and it is difficult to converge the simulation. Since simulation at high reflux ratios is used to check feasibility of proposed splits, this approach can miss separations only possible at lower reflux ratios.

## 2.5.1.2. Superstructure-based method of Bauer and Stichlmair (1998)

Bauer and Stichlmair (1998) proposed a superstructure-based method for synthesising distillation sequences separating multicomponent azeotropic mixtures. In this method, 'preferred separations' (*i.e.* distillations with minimum energy input) are generated sequentially from a fully specified feed composition and form the sequence superstructure. The superstructure is optimised using mixed integer non-linear programming (MINLP) after recycles are assigned. Ternary and quaternary residue curve maps are employed to aid the selection of suitable recycling options for three and four-component mixtures. A systematic approach for selecting recycles is not proposed for multicomponent mixtures, therefore, it is difficult to apply this method to mixtures with more than four components.

Since each column is supposed to perform a sharp split at minimum reflux, the generated superstructure does not embed all feasible separations, such as sloppy splits, and therefore, this method cannot guarantee to find the best sequence. The application of the computationally intensive MINLP routine to complex superstructures separating *n*-component azeotropic mixtures, is a further limitation of this method. To overcome this limitation, the authors simplified the superstructures by combining some splits in the complex superstructure. Although this simplification reduces the size of the problem, there is no guarantee of the solution quality, as clear guidelines for combining splits do not exist.

#### 2.5.1.3. The synthesis method of Rooks et al. (1998)

Based on the common saddle criterion for identifying feasible splits, Rooks *et al.* (1998) proposed a method, using the reachability matrix, to identify feasible sequences within a distillation region. Splits crossing a distillation boundary are not accounted for. Recycling is not systematically accommodated and column

designs are not obtained during sequence selection. Since the common saddle criterion is a sufficient, but not necessary condition for split feasibility, this approach will exclude some feasible splits, and therefore some feasible column sequences may be missed by this method.

#### 2.5.1.4. The algorithmic method of Thong and Jobson (2001c)

Thong and Jobson (2001c) proposed an algorithmic procedure for generating distillation sequences separating *C*-component azeotropic mixtures. This procedure exploits the fact that internal recycle streams allow the manipulation of the feed composition to any column in the sequence. Product regions are employed to specify product compositions instead of exact compositions. A product region is the set of product compositions that satisfies a certain topological constraint. For example, in Fig. 2.6, the (1-4) product region is the set of mixtures lying on the binary edge between the singular points **1** and **4**. Recycles can change the product compositions in corresponding product regions. Three sequential steps are included in this procedure: problem specification, preliminary screening of column sequences and generating recycle options for a sequence of column. Since the work of this thesis is a further develop of the method of Thong and Jobson (2001c), this method will be introduced in more detail below.

#### **Problem specification**

In this step, feed and desired product compositions are specified. For a given feed mixture, all the azeotropes that may occur can be found (e.g. Fidkowski *et al.*, 1993), and the adjacency and reachability matrices can be calculated (Knight and Doherty, 1990). The distillation regions, distillation boundaries, compartments and compartment boundaries are identified using the procedure proposed by Rookes *et al.* (1998) and Thong and Jobson (2001a). For a given set of desired products, it can then be determined whether the feed and

products lie in the same or different distillation regions (Thong and Jobson, 2001c; Thong et al., 2003).

#### Preliminary screening of column sequences

After specifying the problem, all possible sequences can be identified. In this step, the adjacency and reachability matrices are used to identify feasible and potentially feasible splits (Thong and Jobson, 2001a). Compositions of the feed and product of these splits are represented by product region. Once all the splits have been identified, all possible column sequences are generated by recursive searching and are represented by a tree superstructure (Hendry and Hughes, 1972). Each sequence starts with (*C*-1)-dimensional splits. Only column sequences that recover all the desired components are accepted. No recycling is considered at this stage. The full algorithm for generating feasible column sequences is presented in Thong and Jobson (2001c).

In the generated sequences, the potentially feasible splits are classified as Type A, B and C (Thong and Jobson, 2001a, 2001c); these three types of splits have different characteristics. Type A splits satisfy the common saddle criterion and are feasible for any pair of product compositions in the corresponding product regions. Type B splits do not satisfy the common saddle criterion and are only feasible for part of product compositions in the corresponding product regions. Type A and Type B splits do not cross compartment boundaries, but both type may cross a distillation boundary. Like Type B splits, Type C splits do not satisfy the common saddle criterion Type B splits is that a Type C split cross a compartment boundary. Type C splits are potentially feasible (Thong and Jobson, 2001a), further checks are needed to confirm their feasibility. Because these Type C splits are not definitely feasible, not all sequences containing Type C splits are feasible. A sequence containing an infeasible split is of course infeasible (Note: the work of Thong and Jobson (2001c) does not explicitly address this issue).

#### Generating recycle options for a sequence of column

In this step, suitable recycling options can be identified using a simple procedure. First, a superstructure of recycling options is constructed for a given sequence (Thong and Jobson, 2001c). Every product of a column (pure component, azeotrope or a stream with no desired components) is a potential recycle stream. Every feed to a column is a potential destination for every recycle stream. The size of this superstructure is then reduced using a set of rules, which are as follows (Thong and Jobson, 2001c):

- 1. Azeotropes can either be recovered, partially recovered, or recycled completely.
- 2. Never recycle a stream to the column that produces it.
- Never mix a recycle stream with a feed to a column performing a split where the recycle stream contains one or more components that are not present in either product stream.
- 4. Never mix streams with compositions in different compartments. The exception to this is recycle streams to columns performing Type C splits; these streams can lie in either compartment that the split traverses.

These rules do not account for the effects of recycles on the performance of each split and the recovery of azeotropic components. There are many recycle options in each generated recycle superstructure, and the appropriate recycle options can only be finalised after the stream compositions have been determined. Thong and Jobson (2001c) proposed an iterative procedure for determining product compositions of each column. Once all stream compositions have been identified, appropriate recycle options are determined using a material balance across every column (Thong and Jobson, 2001c). The procedure for closing the mass balance was not systematic. And the resulting sequence may be uneconomic as the product compositions of each column are arbitrarily specified.

Using the three-step procedure of Thong and Jobson (2001 a, c), all feasible and potentially feasible sequences can be identified, and a recycle superstructure can also be determined for each sequence. Enormous varieties of alternative sequences can be used to separate a *C*-component azeotropic mixtures. For example, 5001 possible sequences can be used to separate a five-component mixture of acetone, benzene, 1-propanol, toluene and styrene with molar composition as  $[0.2 \ 0.16 \ 0.17 \ 0.27 \ 0.2]^T$ . As for the separation of non-azeotropic mixtures, the problem arising now is how to identify the promising sequences efficiently. Selecting suitable recycle connections and flowrates is an additional issue for azeotropic systems as recycles introduce new iterations within the sequence.

#### 2.5.2. Calculation of minimum reflux ratio and column design

Based on geometrical analysis, Julka and Doherty (1990) introduced the zerovolume criterion to determine the minimum energy requirements for direct and indirect splits. For example, for a quaternary system, four fixed points  $(\hat{x}_1^r, \hat{x}_2^r, \hat{x}_3^r, \hat{x}_1^s)$  are computed, all of which lie in the same plane. Each of these fixed points and the feed composition,  $x_F$ , define a vector. At minimum reflux ratio, these four vectors lie in the same plan, and the volume spanned by these vectors is zero. Julka and Doherty (1993) later extended this procedure for column design at finite reflux with a dimensionless parameter introduced to represent operation away from minimum reflux condition. Although this method can be applied to columns separating multicomponent azeotropic mixtures, it is computationally intensive and difficult to implement. In addition, they provide an exact solution only when the relative volatilities of the species are constant throughout the column (Widagdo and Seider, 1996).

The boundary value method (Levy *et al.*, 1985) reviewed in Section 2.4.2 was extended by Julka and Doherty (1990) to multicomponent mixtures for column design and minimum reflux ratio calculation. Instead of checking the intersection

of rectifying and stripping composition profiles, as shown in Fig. 2.7, a feasible split is indicated when two stages, which lie on the composition profiles of two different sections, have the same liquid compositions. However, in columns separating multicomponent azeotropic mixtures, section composition profiles are very sensitive to impurity concentrations in the product and it is difficult to find exact intersections between the rectifying and stripping profiles. The feasibility criterion of Julka and Doherty (1990) may be relaxed, by defining a maximum allowable distance,  $\varepsilon$ , between two stages. If the liquid compositions of stage *i* of rectifying section and stage *k* of stripping section,  $\sum_{i} (x_{l,i}^{R} - x_{k,i}^{S})^{2} \leq \varepsilon$ , the rectifying and stripping section profiles intersect (Amminudin, 1999; Kusardi, 2001). Fully specified product compositions are needed, but no rational basis available (analogy to Hengstebeck-Geddes method or Fenske method) for calculating the distribution of non-key components. The accuracy of the results then depends on the specified maximum allowable difference. Suitable maximum allowable distances are different for different azeotropic mixtures, and cannot easily be specified a priori.



Fig. 2.7 A feasible ternary split with two section profiles intersected.

The boundary value method can also be used to test the feasibility of splits. For an infeasible split, the two section profiles will not intersect or approach each other within the tolerance (maximum allowable distance) for any reflux ratio. This feasibility test is iterative in nature and therefore computationally timeconsuming.

Köhler *et al.* (1991) proposed the minimum angle criterion, which requires the minimisation of the angle spanned by the feed composition and pinch points in both column sections at minimum reflux. When applied to an ideal mixture, the angle is zero and the method is identical to the Underwood method (Thong, 2000). Non-zero angles at minimum reflux are the results of non-ideal behaviour. The minimum angle criterion should, in principle, apply to any type of split. There are, however, many pinch points in an *n*-dimensional split and it is impossible to identify the active pinch point (Thong, 2000).

The eigenvalue criterion, developed by Pöllmann *et al.* (1994), is similar to the minimum angle criterion. This criterion requires the composition profiles close to the pinch points in both column sections to be calculated and checked for intersection. This criterion cannot be applied to multicomponent azeotropic mixtures for the same reason as for the minimum angle criterion – it is impossible to identify the controlling pinch points in both column sections.

Bausa *et al.* (1998) proposed the rectification body method (RBM) for the determination of minimum energy requirements of a specified split. For a fully specified product composition, branches of the pinch point curves can be found. Rectification bodies can be constructed by joining points on the branches of pinch point curves with straight lines, as shown in Fig. 2.8. For either section of a column, a rectification body can be constructed; its size and position depend on the corresponding reflux or boil-up ratio. The intersection of rectification bodies of two sections of a column indicates its feasibility. The minimum reflux ratio can be obtained through iterative search of the intersection of rectification bodies corresponding to different reflux ratios. Since this method utilises only the pinch point curves to construct rectification bodies, it may, in principle, easily be applied to mixtures with any number of components. Although the method requires the complete specification of both product compositions, it is not as

sensitive to impurity concentrations as the boundary value method (Levy *et al.*, 1985). Furthermore, the intersection (in higher dimension) between linear 'edges' or 'surfaces' can be easily assessed, using algebraic equations or geometric relations.





The rectification body method can be used to calculate the minimum reflux ratio and minimum energy cost, and to test the feasibility of a split. Because faces on rectification bodies are linearly approximated by joining branches of pinch point curves using straight lines, this method cannot guarantee to give accurate results. The minimum reflux ratio may be inaccurately predicted, or feasible splits may be incorrectly identified as infeasible. No information about column design (number of stages and operating reflux ratio) is obtained from the RBM. The calculation of pinch point curves has considerable computational requirements.

Thong and Jobson (2001b) proposed a column design method using manifolds. Instead of fully specifying product compositions, only the mole fractions of principal components and the sum of the mole fractions of the impurities are specified in this method. A product specified in this way is known as a product region. Several representative compositions are chosen to represent the

specified product region, and composition manifolds, analogous to points on a composition profile, can be linearly approximated according to the section profiles calculated from these representative compositions (Thong and Jobson, 2001b). The intersection of a pair of rectifying and stripping manifolds indicates feasible column design parameters, including the reflux (and boil-up) ratio, total number of stages and feed stage. The linear approximation of manifolds, which are actually surfaces, introduces error.

The methods of Bausa *et al.* (1998) and Thong and Jobson (2001b) overcome the limitations of the boundary value method by eliminating the requirement of fully specified product compositions. However, the method of Thong and Jobson (2001b) is more computationally intensive than the boundary value method, especially for multicomponent mixtures: to build two sets of section manifolds at a certain reflux (or reboil) ratio, many profiles need to be calculated for each pair of product regions.

#### 2.6. Conclusions

For non-azeotropic mixtures, volatility order is constant and can be used to synthesise distillation sequences. Heuristic rules have been proposed, based on case studies, for the identification of promising sequences. Efficient shortcut methods, such as the classical Fenske-Underwood-Gilliland method (Fenske, 1932; Underwood, 1945, 1946a, 1946b, 1948; Gilliland, 1940), can be used to design columns and hence to evaluate alternative sequences.

Compared with non-azeotropic mixtures, sequence synthesis for homogeneous azeotropic mixtures is a much more complex task. For an azeotropic mixture, volatilities of components within a column change significantly and the volatility order may even change. Because of the existence of azeotropes, the composition space is generally divided into several distillation regions and compartments by distillation boundaries and compartment boundaries, respectively. These boundaries restrict feasibility for distillation. Methods

applicable to non-azeotropic mixtures cannot be directly applied to azeotropic mixtures.

Many graphical tools have been proposed for the synthesis of distillation sequences and for testing the feasibility of columns separating ternary azeotropic mixtures. Several feasibility test methods can also be used to determine minimum reflux ratios. These graphical methods are convenient. However, these methods can only be used for ternary, and to a certain extent, quaternary, azeotropic mixtures, since multicomponent mixtures cannot be visualised.

Some algorithmic methods are proposed for sequence synthesis for multicomponent azeotropic mixtures. The sequential methodology of Wahnschafft (1993), superstructure-based method of Bauer and Stichlmair (1998), and the synthesis method of Rooks et al. (1998) can in principle be used to identify sequences separating multicomponent azeotropic distillation sequences. However, these methods cannot guarantee the best sequence to be found. The algorithmic method of Thong and Jobson (2001c) can be used to identify all potentially feasible distillation sequences separating multicomponent azeotropic mixtures. The problem with this method is that too many sequences can be generated and there is still no efficient way to identify promising distillation sequences with recycles (select connections and flowrates for economic performance). Methods for column design and minimum reflux calculation are also proposed. These methods are based on either pinch point calculation or stage-by-stage equilibrium and mass balance calculation. Some of them, such as the boundary value method, even need iterative calculation to obtain the desired results. Because of this, these methods are computationally inefficient when applied to evaluate sequences with recycles.

To date, no efficient method for the design of columns separating multicomponent homogeneous azeotropic mixtures is available in the literature. Existing methods are based on either pinch point calculation or stage-by-stage equilibrium and mass balance calculation. There is still no systematic and

efficient method for identifying recycles and synthesising distillation sequences separating multicomponent homogeneous azeotropic mixtures.

Methods for shortcut column design, evaluation of distillation sequences, and screening of recycles and sequences will be developed in this work. The proposed methods will enable the systematic synthesis of sequences with recycles for the separation of multicomponent homogeneous azeotropic mixtures, and will build on the work of Thong and Jobson (2001 a, b, c) and Rooks *et al.* (1998).

## Shortcut method for column design and sequence evaluation

#### 3.1. Introduction

For non-azeotropic mixtures, effective methods exist for the shortcut design of columns. Several design methods for columns separating azeotropic mixtures have been proposed with many of them concentrating on the calculation of minimum reflux ratios. The methods are computationally intensive and therefore cannot conveniently be used to solve larger problems, such as synthesis and evaluation of distillation flowsheet alternatives. Furthermore, there is still no reliable method for calculating the minimum number of stages for a column separating an azeotropic mixture.

In this chapter, a spherically approximated distillation boundary, which can be easily obtained and can give a good representation of the actual distillation boundary, is proposed. With such an approximated distillation boundary, the distillation region in which a composition point lies can be easily identified.

A shortcut method for the design of columns separating azeotropic mixtures is also proposed in this chapter. In this method, azeotropes are treated as pseudo-components, and the relative volatilities of singular points can be characterised. This allows the classic Fenske-Underwood-Gilliland method to be used to design columns. This method is computationally efficient and can be applied to azeotropic mixtures with any number of components. Satisfactory column design parameters can be easily obtained using this method.

With this shortcut column design method and employing a non-linear approximation of the distillation boundary, a procedure for the evaluation of

distillation sequences with recycles is proposed. This procedure can efficiently identify the best set of recycle flowrates that correspond to the minimum total cost of the sequences and the associated column design parameters. A four-column sequence with four recycle streams is evaluated using this procedure.

#### 3.2. Non-linear approximation of distillation boundaries

#### 3.2.1. The necessity to characterise a distillation boundary

A distillation boundary, which separates two neighbouring distillation regions in composition space, limits the feasibility and product compositions of a split. At total reflux, the necessary condition for a split to be feasible is that, its distillate and bottom products lie in the same distillation region. To preliminarily test the feasibility of a column, it is necessary to identify the distillation region that its products lie in.

For a given mixture, the residue curve passing through the point representing its composition can be obtained by integration. Through identifying the stable and unstable node connected by this residue curve, the distillation region in which this mixture lies can be identified. However, this method is time-consuming because of the integration calculation, especially when applied to sequence evaluation, which needs many such tests because of the existence of recycles. Among two neighbouring distillation regions, an ideal method to identify which one that a composition lies in is through identifying the relative location of the composition to the distillation boundary separating these two distillation regions. To use this method, it is necessary to identify the distillation boundary.

However, a distillation boundary does not have a regular geometric shape and cannot be obtained analytically. Only through testing the terminal points of residue curves passing through many compositions, can the exact distillation boundary (shape and location) be identified. For ternary mixtures, the distillation boundary can be identified this way without excessive calculations. The 2-

dimensional residue curve map, together with the identified distillation boundaries, can be used to identify the location of a composition point. This is the method widely used in the literature. However, as the number of components increases, the shape and location of distillation boundaries became increasingly complex and the number of calculations needed to identify a distillation boundary increases significantly. Even with the exact distillation boundary known, there is still no method that can be used to identify which region a composition belongs to except through testing the terminal singular points of the residue curve passing through this point. The reason is that, distillation boundaries do not have a regular shape and cannot be visualised for multicomponent systems.

Therefore, although it is necessary to identify the distillation boundary, it is impractical to identify the exact distillation boundary. In any case, the location of the boundary may vary with the liquid phase model (parameters) used for the mixture; in other words, there may be a significant amount of uncertainty associated with a boundary's location, however carefully it is calculated.

#### 3.2.2. Non-linear approximation of distillation boundary

In an azeotropic system, all distillation boundaries, each of which is characterised by the singular points lying on it, can be easily identified (Rooks *et al.*, 1998). Since it is necessary but impractical to identify the exact distillation boundary, approximating a distillation boundary by a regular geometrical shape is desirable. Such an approximation allows its shape and location to be easily characterised using analytical expressions. A suitable geometrical shape that can be used to approximate distillation boundary should be chosen.

A distillation boundary can be linearly approximated according to the singular points lying on it (Doherty and Caldarola, 1985). For a *C*-component system, which lies in (C-1)-dimensional composition space, (C-1) points are needed to linearly approximate a distillation boundary. However, a linearly approximated distillation boundary generally does not give a good representation of the actual

boundary, and cannot be crossed by a simple column. When a curved distillation boundary is linearly approximated, a feasible split may look infeasible. For example, Fig. 3.1 illustrates both the curved distillation boundary and the linear approximation for the ternary system of acetone, chloroform and benzene. It can be clearly seen from this figure that there is a big deviation, which is shown by the shaded region between the actual and linearly approximated distillation boundaries. A feasible split, with distillate, bottom, and feed composition as D, B, and F, respectively, looks infeasible at total reflux because of the linear approximation of the distillation boundary.



Fig. 3.1 Ternary system with distillation boundary linearly approximated.

To improve the accuracy, the distillation boundary can be approximated by a spherical shape (part of a circle or a sphere), the simplest non-linear geometrical shape. In a *C*-component azeotropic system, which lies in (*C*-1) dimensional space, Equation (3.1) can be used to describe the sphere that the spherically approximated boundary lies in.

$$\sum_{i=1}^{C-1} (x_{j,i} - x_{o,i})^2 = R^2$$
(3.1)

where, *R* is the radius of the sphere, *o* is the centre of the sphere, and *j* corresponds to a point lying on the distillation boundary. To characterise a sphere described by Equation (3.1), *C* variables, which are *R* and  $x_{o,i}$  (*i*=1, 2, ...,

C-1), need to be determined. Therefore, C composition points lying on the distillation boundary need to be identified, so that Equation (3.1) has a unique solution.

Singular points lying on a distillation boundary are the most important points to characterise the distillation boundary, and should be used to approximate the boundary. To make the approximated distillation boundary give a good representation to the actual one, the additional points used to derive R and  $X_o$  should be approximately evenly distributed on the distillation boundary. The compositions of singular points in terms of pure components are known. The compositions of the points distributed between them need to be determined through calculation. The procedure for selecting these composition points is as follows:

- 1. Identify the azeotropic system and specify the distillation boundary that needs to be approximated by a spherical shape.
- 2. Linearly approximate this distillation boundary according to the singular points lying on it.
- 3. Select compositions distributed evenly between the singular points lying on the linearly approximated distillation boundary. The total number of points including the singular points lying on the boundary, should be equal to *C*, the total number of components of this system.
- Select a singular point that is not on the boundary as reference point, X<sub>R</sub>. This singular point should lie only in one of the two distillation regions separated by the specified distillation boundary.
- 5. Select one of the compositions identified in step 3,  $X_M$ , and connect it with the reference point by a straight line. The composition of point, N, lying on the straight line can be expressed as:

$$x_{N,i} = x_{R,i} + \gamma (x_{M,i} - x_{R,i})$$
(3.2)

here, *i* (*i*=1, 2, ..., *C*-1) corresponding to pure component, M and R represent the composition point lying on the linearly approximated distillation boundary and the reference point, respectively.

- 6. Calculate the residue curve passing through  $X_N$ .
- 7. Search along the straight line (*i.e.* vary  $\gamma$ ), until the point, for which a slight change of composition will result in the residue curve passing through it lying in a different distillation region, is found. This point is the point lying on the actual distillation boundary and can be used to approximate the specified distillation boundary.
- Repeat steps 5, 6 and 7 for the other composition points identified in step 3.

Once the *C* points that will be used to approximate the distillation boundary are identified, Newton's method can be used to solve Equation (3.1), so that the centre point of the sphere and radius can be determined. Then, the locus of compositions lying on the distillation boundary can be characterised as:

$$\sum_{i=1}^{C-1} (x_i - x_{o,i})^2 = R^2$$
  

$$x_C = 1 - \sum_{i=1}^{C-1} x_i$$
  

$$0 \le x_i \le 1, \quad i = (1, 2, ..., C)$$
  
(3.3)

That is, the part of the sphere that lies outside of the composition space of interest, is excluded.

A distillation boundary may curve away from either of the distillation regions separated by it. For the specified distillation boundary in step 1, the curvature can be identified from the composition points identified in step 7. According to Equation (3.2), each point found to lie on the boundary in step 7 corresponds to a  $\gamma$  value. If all the  $\gamma$  values are larger than 1, the distillation boundary curves away from the region in which the reference point lies. Otherwise, it curves away from the other region. If some  $\gamma$  values are larger than 1, the others are smaller than 1, the curvature of the distillation boundary is significantly irregular, and the boundary cannot be well represented by a spherical shape. This kind of situation will not be accounted for in this work.



Fig. 3.2 Comparison of spherically approximated distillation boundary of a ternary system with the actual boundary.

Using the above procedure, a distillation boundary lying in ternary system will be approximated by a segment of a circle (a 2-dimentional sphere). For the ternary system shown in Fig. 3.1, it is identified that the composition space is separated into two distillation regions, 1-3-4 and 2-3-4, by the distillation boundary 3-4. Singular points **3** and **4** lie on the distillation boundary. As shown in Fig. 3.2, the distillation boundary can be approximated by the straight line joining singular points 3 and 4. To spherically approximate the distillation boundary, one additional point, lying half way along this line can be used. Point **M** can be selected. Taking singular point **1** as the reference point,  $X_R$ , an expression for the straight line connecting points 1 and M can be formulated. Searching along the straight line, point N, which lies on the actual distillation boundary, is found. Point  $X_N$  lies beyond the linear approximation of the boundary ( $\gamma$ =1.14). Therefore, the distillation boundary curves away from the distillation region, 1-3-4, which the reference point, singular point 1, lies in. Spherical approximation of the distillation boundary includes points **3**, **4** and **N**. Solving Equation (3.1), the centre of the circle and its radius can be determined. The composition of point lying on the spherically approximated distillation boundary can be expressed by the equation shown in Fig. 3.2. Fig. 3.2 compares the actual distillation boundary, calculated using Distil 5.0 (Wilson

activity model at 1 atm), with the spherically approximated distillation boundary. It can be concluded that the segment of the circle provides a good approximation of the actual distillation boundary. Similar results have been obtained for other ternary, quaternary mixtures.

To further improve accuracy, the distillation boundary can be approximated by part of an ellipse. In a *C*-component system, the ellipse that the elliptically approximated distillation boundary lies in can be described by Equation (3.4).

$$\sum_{i=1}^{C-1} \frac{(x_{j,i} - x_{o,i})^2}{a_i} = 1$$
(3.4)
  
 $j = 1, 2, ..., 2C - 2$ 

Here, point *o* is the centre of the elliptical shape approximating the distillation boundary, where, *i* corresponds to a pure component and *j* is a composition lying on the distillation boundary. Since there are (2*C*-2) variables ( $X_{o,i}$  and  $a_i$ ), (2*C*-2) points lying on the actual distillation boundary are needed for a unique solution to be found.





Since elliptical approximation has more adjustable parameters than a spherical approximation, it is, in principal, more accurate. For example, for the same ternary system shown in Fig. 3.2, the distillation boundary is elliptically

approximated based on the four points shown in Fig. 3.3. The equation for an ellipse that can be used to describe the approximated distillation boundary is also shown in Fig. 3.3. The compositions of ten points lying evenly on the elliptically approximated boundary are calculated using this equation, and are compared with those lying on the actual boundary (calculated using DISTIL5.0) and spherically approximated boundary (calculated using the equation shown in Fig. 3.2) in Table 3.1. It can be seen that elliptically approximated distillation boundary can give a better representation to the actual distillation boundary than the spherically approximated boundary can.

However, to elliptically approximate a distillation boundary, both the number of points on the boundary that need to be found and the number of variables need to be determined are (C-2) more than those needed to spherically approximate a distillation boundary. For ternary or quaternary mixtures, the difference between the numbers of variables is small (1 or 2). For multicomponent mixtures, the difference can become significant. In this case, it can be difficult to find a solution for Equation (3.4). The distillation boundary will be approximated by part of a sphere in this work.

Table 3.1 Comparison of the compositions of points lying on the actual boundary, and spherical and elliptical approximations of distillation boundary.

X <sub>1</sub>	X <sub>2</sub>			$(\Delta x_2)^2$	
	Actual	Spherical	Elliptical	Spherical	Elliptical
0.0308	0.2996	0.2713	0.3152	0.000801	0.000243
0.0616	0.3671	0.3530	0.3735	0.000197	4.11E-05
0.0924	0.4194	0.4122	0.4206	5.13E-05	1.38E-06
0.1232	0.4625	0.4597	0.4610	7.73E-06	2.27E-06
0.154	0.4998	0.4995	0.4969	6.83E-08	8.54E-06
0.1848	0.5330	0.5337	0.5294	5.5E-07	1.29E-05
0.2156	0.5630	0.5635	0.5593	2.87E-07	1.36E-05
0.2464	0.5906	0.5897	0.5871	8.07E-07	1.24E-05
0.2772	0.6159	0.6128	0.6131	9.73E-06	7.87E-06
0.308	0.6396	0.6332	0.6376	4.14E-05	4.02E-06
$\Sigma(\Delta x_2)^2$				0.00111	0.000348

# 3.2.3. Identifying the distillation region that a composition point lies in using a spherically approximated distillation boundary

For an azeotropic system, with distillation boundaries spherically approximated, the distillation region in which a given composition lies can be easily identified. The procedure is similar to that for identifying the point lying on the actual distillation boundary. A straight line connects a reference point (a singular point) and the composition of interest (Point **E**). The whole procedure, as presented below, works by the process of elimination, and is illustrated by examples shown in Fig. 3.4 and Fig. 3.5.

- Identify the azeotropic system the point lies in, calculate all azeotropes (Fidkowski et al., 1993), and identify all distillation regions and distillation boundaries (Rooks et al., 1998).
- 2. Select a distillation boundary (which has not been tested), and identify which two distillation regions are separated by it.
- 3. Spherically approximate the selected distillation boundary using the method introduced in Section 3.2.2 and Equation (3.3).
- 4. Select a singular point, **R**, which lies in only one of the two distillation regions separated by the distillation boundary as the reference point.
- Connect the composition E with the reference point, R, using a straight line. The composition of point N lying on the straight line can be expressed as:

$$x_{N,i} = x_{R,i} + \gamma (x_{E,i} - x_{R,i})$$
(3.5)

where, *i*=1, 2, ..., C-1 and  $0 \le x_{N,i} \le 1$ .

6. Solve Equations (3.3) and (3.5) to obtain the composition of the intersection between the straight line and the spherical approximation of distillation boundary, together with the corresponding value of  $\gamma$ .

- 7. According to the value of  $\gamma$ , the distillation region in which point **E** does not appear can be identified. If  $\gamma < 1$ , **E** does not lie in the region in which the reference point, **R**, appear, go to step 8. If  $\gamma > 1$ , point **E** does not lie in the distillation region in which the reference point **R** does not appear, go to step 8. If  $\gamma=1$ , point **E** lies on this distillation boundary, stop.
- If there are still some distillation boundaries that have not been tested, go to step 2. Otherwise, according to the information in step 7, the distillation regions that point E does not lie in can be omitted, and the remaining one is the distillation region that composition point E lies in.





For a ternary system, the distillation region containing a composition of interest can be easily obtained from the residue curve map. For example, the ternary system shown in Fig. 3.4 is separated into three distillation regions, 1-2-5, 1-2-3-4, and 1-3-6. From this figure, the distillation region containing point **E** can be identified to be distillation region 1-2-5. To illustrate the above procedure, it will be determined according to the spherically approximated distillation boundary.

As shown in Fig. 3.4, two distillation boundaries, 1-2 and 1-3, exist in this ternary system. Boundary 1-2 separates distillation regions 1-2-5 and 1-2-3-4; boundary 1-3 separates distillation regions 1-3-6 and 1-2-3-4. Using the procedure proposed in Section 3.2.2, two points, points A and B lying approximately in the middle of these two boundaries, respectively, and the curvatures of these two boundary can be identified. Distillation boundary curves

away from distillation region 1-2-5, and, boundary 1-3 curves away from distillation region 1-3-6. These two boundaries are approximated according to point 1, 2, A, and, 1, 3, B, respectively. The spheres that the approximated boundaries lie in can be expressed as:

Boundary 1-2: 
$$(x_1 - 0.1106)^2 + (x_2 - 0.5613)^2 = 5.1134^2$$
 (3.6)

Boundary 1-3: 
$$(x_1 - 0.0453)^2 + (x_2 + 0.369)^2 = 0.8194^2$$
 (3.7)

First, distillation boundary 1-3 is tested. This boundary separates distillation regions 1-3-6 and 1-2-3-4. If singular point **6** is the reference point, for each point lying on the straight line connecting singular point **6** and composition point **E**, its composition ( $x_1$ ,  $x_2$ ,  $x_3$ ) satisfies the line equations:

$$x_1 = 0.20 - \gamma$$
  

$$x_2 = 0.6\gamma$$
  

$$x_3 = 1 - \gamma$$
(3.8)

Solving the quadratic Equation (3.7) and linear Equation (3.8), the intersection of the straight line through points **6** and **E** and the spherically approximated distillation boundary 1-3 is point **N**<sub>1</sub>, whose composition is (0.1480, 0.4439, 0.4081). The corresponding  $\gamma$  value is 0.7398. Since  $\gamma$ <1, therefore, composition point **E** does not lie in the distillation region 1-3-6, in which the reference point, singular point **6**, lies.

At this stage, the distillation region containing point E is still unknown. Then, distillation boundary 1-2 is tested. This boundary separates distillation regions 1-2-5 and 1-2-3-4. If singular point **4** is the reference point, for each point lying on the straight line connecting singular point **4** and composition point **E**, its composition ( $x_1$ ,  $x_2$ ,  $x_3$ ) satisfy the line equations:

$$x_{1} = 1 + (0.20 - 1)\gamma$$
  

$$x_{2} = 0.6\gamma$$
  

$$x_{3} = 0.2\gamma$$
  
(3.9)

Solving the quaternary Equation (3.6) and linear Equation (3.9), the intersection of the straight line through points **4** and **E** and the spherically approximated distillation boundary 1-2 is point  $N_2$ , whose composition is (0.3924, 0.4557,

0.1519). The corresponding  $\gamma$  value is 0.7594. Since  $\gamma$ <1, therefore, composition point **E** does not lie in the distillation region 1-2-3-4. Since point E lies in neither distillation region 1-3-6 and 1-2-3-4, it can only lies in region 1-2-5. When DISTIL5.0 is used to calculate the residue curve passing through **E**, the same result is obtained

Sometime, the straight line connecting the reference point and the composition point to be tested does not intersect the distillation boundary. To avoid this, it is better to select the singular point, lying on the concave side of the to be tested distillation boundary, as reference point. For example, when testing the distillation boundary 1-3 shown in Fig. 3.4, if singular point **4** is selected as the reference point, no intersection point will be found between the straight line connecting point **E** and point **4**, and the spherically approximated distillation boundary 1-3, as shown in Fig. 3.4.





In the quaternary system shown in Fig. 3.5, the distillation region containing point **E**, with composition (0.05, 0.35, 0.24, 0.36), needs to be identified. The composition space is found to have two distillation regions, 1-3-4-5 and 2-3-4-5, separated by distillation boundary 3-4-5. Using the method proposed in Section 3.2.2, the distillation boundary is spherically approximated according to composition points **3**, **4**, **5** and **3** The points lying on the spherically approximated distillation boundary satisfy the equation:

$$(x_1 - 1.7721)^2 + (x_2 - 0.4964)^2 + (x_3 - 0.4995)^2 = 1.9076^2$$
(3.10)

If singular point **1** is the reference point, for each point lying on the straight line connecting singular point **1** and composition point **E**, its composition ( $x_1$ ,  $x_2$ ,  $x_3$ ,  $x_4$ ) satisfy the linear equations:

$$x_{1} = 1 + (0.05 - 1)\gamma$$

$$x_{2} = 0.35\gamma$$

$$x_{3} = 0.24\gamma$$

$$x_{4} = 0.36\gamma$$
(3.11)

Solving the quadratic Equation (3.10) and linear Equation (3.11), the intersection of the straight line through points **1** and **E** and the spherically approximated distillation boundary is point **N**, whose composition is (0.0783, 0.3396, 0.2328, 0.3492). The corresponding  $\gamma$  value is 0.9702. Since  $\gamma$ <1, therefore, composition point **E** does not lie in the same distillation region as the reference point, singular point **1**, but lies in distillation region 2-3-4-5. The same result is obtained when DISTIL5.0 is used to calculate the residue curve passing through **E**.

### 3.3. Representation of the vapour-liquid equilibrium (VLE) behaviour in terms of singular points

Relative volatility is a key driving force in distillation. Only when the relative volatility between two components differs from unity, can they be separated by distillation. The more the relative volatility differs from unity, the easier the separation. Azeotropes, which cannot be separated in an equilibrium flash stage, behave like pure components in distillation (Vogelpohl, 1974; Vogelpohl, 2002). This means that an azeotrope will affect the design of column as an individual component would, rather than its constituents would.

In this work, azeotropes will be treated as pseudo components, and a Ccomponent system with A azeotropes will be treated as an enlarged (C+A)component system, where all singular points constitute its components. Vapour–liquid equilibrium compositions in terms of pure components can be transformed into vapour-liquid equilibrium compositions in terms of singular points. This allows the relative volatility of the azeotropes to be characterised.

#### 3.3.1. Compartments as subsystems in the composition space

A compartment is the largest subsystem of composition space required to consistently treat azeotropic mixtures as non-azeotropic mixtures of pseudo components. First, it is necessary to identify compartment boundaries. In a distillation region, by testing the saddle points approached (*i.e.* singular points moved towards and away from) by residue curves passing through different compositions, the compartments that these compositions belong to can be identified in principle, as can compartment boundaries. However, it is not a straightforward matter to identify which saddle points are approached by a given residue curve. In particular, inflections in residue curves may indicate that saddle points lying in two different compartments are 'approached'.

In this work, the compartment boundary is linearly approximated by connecting all singular points that appear in two neighbouring compartments by straight lines. Since the feasibility of splits crossing a compartment boundary does not depend on its curvature (Thong and Jobson, 2001a), the linear approximation of the compartment boundary is not a limiting assumption.

In a compartment, residue curves behave analogously to those in the composition space of a non-azeotropic mixture (thong and Jobson, 2001a). With the compartment boundary linearly approximated, residue curves in a compartment generally start from the unstable node, approach the saddle points that appear in the compartment one by one in the order of increasing temperature, and end at the stable node, as illustrated in Fig. 3.6. In this ternary system of methyl acetate, methanol and ethanol, there is one minimum azeotrope (1) between methyl acetate (2) and methanol (3), and the whole composition space is separated into two compartments 1-2-4 and 1-3-4. The saddle point 2 can only appear in compartment 1-2-4, while saddle point 3 can

only appear in compartment 1-3-4. The linearly approximated compartment boundary is the straight line connecting the stable node **4** and the unstable node **1**. Although there are residue curves, such as residue curves **3**V, and **V**, that approach both saddle points **2** and **3**, residue curves generally approach only one saddle point. In compartment 1-2-4, residue curves, such as residue curves **3** 33 and 333 start from unstable node **1**, approach saddle point **2**, and end at stable node **4**. The behaviour of this compartment is analogous to that of the non-azeotropic system with singular points **1**, **2**, and **4**. Similarly, the behaviour of compartment 1-3-4 is analogous to that of the non-azeotropic system with singular points **1**, **3**, and **4**.





In this work, an azeotropic system will be treated as an enlarged system with all singular points as the constituents. In this respect, the work is like that of Volgelpohl (1974; 2002). In this approach, however, compartments, which may be rigorously defined, and linearly approximated, are defined as the subsystems that are treated as non-azeotropic composition regions. In each compartment, an azeotrope acts as a pure component, and any mixture can be treated as a mixture of the singular points that appear in this compartment. A systematic

approach for expressing compositions in terms of singular points, rather than in terms of pure components, is presented below.

#### 3.3.2. Transformation of compositions

In an azeotropic system, the composition of each singular point, either pure component or azeotrope, can be expressed in terms of pure components using a  $C \times (C + A)$  matrix, which is defined as the transformation matrix. Each column of a transformation matrix represents the composition of a singular point, while each row represents a pure component. The pure components are ordered with respect to boiling temperature at the system pressure, as are the singular points. For example, in the methyl acetate, methanol, and ethanol system shown in Fig. 3.7,  $X_1$ ,  $X_3$  can be used to express the molar compositions of singular points **1** and **3**, respectively, in terms of pure components. All the singular point compositions can be expressed in the  $3 \times 4$ -dimensional transformation matrix *M*.



Fig. 3.7 A ternary system of methyl acetate, methanol and ethanol, with singular point compositions expressed in terms of pure components.

In the enlarged system with all singular points as its constituents, the composition of a point can be expressed in terms of these singular points. As mentioned previously, a compartment behaves as the non-azeotropic mixture of

the singular points it contains. Singular points that are not included in the compartment are inactive, or irrelevant to the VLE behaviour of the compartment. Therefore, when the composition of a point lying in a compartment is expressed in terms of all singular points, the mole fraction of singular points that do not appear in the compartment of interest can be set to zero. The transformation matrix allows compositions expressed in terms of pure components to be expressed in terms of all singular points. The matrix, together with *C*-dimensional and (C+A)-dimensional composition vectors, form a set of linear equations. The procedure for setting up and solving these equations is illustrated by example.

For a stream with composition vector **P**, shown in Fig. 3.7

1. The molar composition, in terms of pure components, is

$$X = \begin{bmatrix} 0.33 & 0.33 & 0.34 \end{bmatrix}^T$$

2. The composition in terms of all singular points is

$$\mathbf{S} = \begin{bmatrix} \mathbf{s}_1 & \mathbf{s}_2 & \mathbf{s}_3 & \mathbf{s}_4 \end{bmatrix}^T$$

where,  $s_i$  (*i*=1, 2, 3, or 4) represents the mole fraction of singular point *i*.

- 3. Since point **P** lies in compartment 1-3-4, and singular point **2** does not appear in this compartment, set  $s_2 = 0$
- 4. The linear equations to be solved are:

$$X = M \cdot S \tag{3.12}$$

where, *M* is shown in Fig. 3.7. Hence, the composition of vector  $\mathbf{P}$ , in terms of all singular points, is

$$S = \begin{bmatrix} 0.5020 & 0 & 0.1580 & 0.34 \end{bmatrix}^T$$

Note that a composition can only be expressed as a mixture of the singular points lying in the same compartment. For example, the point **P**, shown in Fig. 3.7, lies in compartment 1-3-4, and can be taken as the mixture of singular points **1**, **3** and **4**, but not as a mixture of singular points **1**, **2** and **4**.

A restriction of this method is that, in a *C*-component azeotropic system, the number of singular points that lie in the compartment of interest must be equal to *C*. When the number of singular points lying in the compartment of interest is not equal to *C*, there is no solution for the set of linear equations  $X = M \cdot S$ . For example, in the ternary system shown in Fig. 3.8, there is a minimum azeotrope (1) between the lightest component, acetone (2), and the heaviest component, n-heptane (4). The whole composition space is a compartment, as can be seen in the residue curve map. In this three-component compartment, the number of singular points is 4 and compositions in terms of pure components cannot be transformed into compositions in terms of singular points using the introduced procedure.



Fig. 3.8 Ternary system with one minimum boiling azeotrope. The whole composition space is a compartment. It is impossible to transform the composition in terms of pure components into composition in terms of singular points.
In a multicomponent azeotropic system, the compartment in which a given composition lies can be determined by identifying which saddle point is approached by the residue curve containing this composition. Since the compositions of points lying on the residue curve are expressed in terms of pure components, it is difficult to identify which saddle point is approached by the residue curve. With the composition transformation procedure, this problem can be easily solved, through searching different compartments; calculation of the residue curve is not necessary. For a given composition, we may assume it lies in one of the compartments identified using the procedure of Rooks *et al.* (1998) and Thong *et al.* (2001a); if we try to transform its composition in terms of pure components into composition in terms of singular points using the transformation procedure and there is a solution, it can be concluded that this assumption is correct. The candidate compartments (within a given distillation region) must be tested in turn until a solution to Equation (3.12) is obtained.

The assumption that compartment boundaries are linear restricts the applicability of this transformation procedure. In a composition space with several distillation regions, a distillation boundary is also a compartment boundary. To transform a composition in terms of pure components into a composition in terms of singular points, such a distillation boundary sometimes needs to be linearly approximated. In this case, compositions lying on the concave side of a curved distillation boundary will be assigned to the wrong compartment.

For example, for the ternary system presented in Fig. 3.9, the composition space is separated into two distillation regions, 1-3-4 and 2-3-4. Each distillation region is equivalent to a compartment and the distillation boundary is also a compartment boundary. As shown in Fig. 3.9, the compositions lying in the shaded region belong to distillation region 1-3-4. To transform compositions in terms of pure components into compositions in terms of singular points, the distillation boundary is linearly approximated, and compositions lying in the shaded region will be classified as lying in distillation region 2-3-4.



Fig. 3.9 Ternary azeotropic system with curved distillation boundary, which is also compartment boundary.

### 3.3.3. Calculation of relative volatilities of singular points



Fig. 3.10 Vapour-liquid equilibrium relationships in terms of pure components can be transformed into vapour-liquid equilibrium relationships in terms of singular points.

For an azeotropic mixture, vapour-liquid equilibrium behaviour in terms of pure components can be calculated using suitable liquid-phase models. Compositions of the equilibrium vapour and liquid, in terms of pure components, can then be transformed into compositions in terms of singular points. The transformed vapour and liquid compositions still represent an equilibrium pair. This claim can be supported as follows. The transformation procedure is based on the principle that each compartment behaves like a non-azeotropic mixture of the singular points appearing in it, and will not distort the vapour-liquid equilibrium relations within the compartment. In Fig. 3.10, points  $P_1$  and  $P_2$ correspond to equilibrium liquid and vapour compositions, respectively. Their compositions in terms of pure components, which are represented by  $(x_1, x_2, x_3)$ and  $(y_1, y_2, y_3)$ , respectively, are known, and can be transformed into corresponding compositions in terms of singular points. After transformation, points  $P_1$  and  $P_2$ , with transformed compositions  $(s_1, s_2, s_3, s_4)$  and  $(s'_1, s'_2, s'_3, s'_4)$ , respectively, are still in equilibrium with each other.

Since a compartment behaves like a non-azeotropic mixture of the singular points that appear in it, the equilibrium vapour and liquid compositions generally lie in the same compartment. In this case, both the vapour and liquid can be taken as the mixture of the singular points lying in the compartment of interest. After the composition transformation, the relative volatilities of these singular points can be calculated according to the definition of relative volatility, which is shown in Equation (3.13).

$$\alpha_{i,H} = \frac{\frac{\mathbf{s'}_i}{\mathbf{s}_i}}{\frac{\mathbf{s}_i}{\mathbf{s}_H}}$$
(3.13)

*i*: singular point

#### H: the heaviest singular point

The relative volatility of singular point *j* lying outside the compartment of interest can be represented by that of the singular point *k*, which lies in the compartment of interest and has the most similar composition to it. For example, in the ternary system shown in Fig. 3.10, singular point **2** does not appear in compartment 1-3-4, therefore, its relative volatility in this compartment can be set to be equal to that of singular point **1**, the azeotrope containing it. Similarly, in compartment 1-2-4, the relative volatility of singular point **3**, lying outside this compartment, is set to equal to that of singular point **1**.

When a pair of equilibrium vapour and liquid compositions lie in two different compartments, the vapour and liquid behave like the mixtures of two different sets of singular points. Singular points lying on the compartment boundary between these two compartments are active in both phases; their mole fractions are not zero in the transformed compositions of the vapour and liquid, and their relative volatilities can be calculated according to Equation (3.13). For the singular points that are active only in one of these two compartments, their mole fractions are zero in either the vapour or the liquid phase, their relative volatilities cannot be calculated according to Equation (3.13). Nor can suitable values be set to the relative volatilities of these singular points.

While Vogelpohl's method (2002) treats each subsystem as an ideal (*i.e.* with constant relative volatilities) system of the singular points that appear in it, this method treats each compartment as a non-azeotropic mixture of the singular points that appear in it, for which the VLE behaviour is rigorously calculated in terms of pure components. As a result, the relative volatilities calculated using this method are more reliable than those used in the method of Vogelpohl (2002). Furthermore, in this work, a systematic approach to identify compartments is used. Since no visual tools are needed, this method can be applied to azeotropic mixtures with any number of components, as long as the number of singular points in a given compartment is equal to the number of components present.

### 3.4. Shortcut method for column design

With azeotropes treated as pseudo components and a *C*-component system with *A* azeotropes treated as a (*C*+*A*)-component system, a column separating a *C*-component azeotropic mixture can be treated as a column separating a (*C*+*A*)-component non-azeotropic mixture. Based on the assumption of constant molar overflow, the classical Fenske-Underwood-Gilliland method can be used to design the column on condition that relative volatilities, in terms of singular points, do not change significantly along the column.

## 3.4.1. Calculation of minimum reflux ratio and minimum energy cost using Underwood method

When the relative volatilities, expressed in terms of singular points, do not change significantly along a column separating an azeotropic mixture, it will be shown that Underwood equations can be used to calculate the minimum reflux ratio and the minimum energy cost. A characteristic set of mean relative volatilities in terms of singular points will be used in the Underwood equations. Different ways of calculating these mean relative volatilities will give more or less satisfactory results.



Fig. 3.11 Separations of quaternary azeotropic mixtures (details given in Table 3.2).

The two quaternary systems shown in Fig. 3.11 provide examples. The first split (Fig. 3.11 (a)) lies within a single compartment that is bounded by a simple distillation boundary. In the second split (Fig. 3.11 (b)), the two products lie in different compartments. The minimum reflux ratios of these two splits are calculated rigorously using HYSYS 2.1 (AspenTech., Calgary, Canada) (for a column with 90 stages); details of the feeds and design results (including product compositions and minimum reflux ratio) are presented in Table 3.2. With the same feed composition and the product compositions specified as

shown in Table 3.2, the minimum reflux ratio is calculated using the Underwood method, where the mean relative volatility is calculated in three different ways. It can be seen in Table 3.2 that minimum reflux ratios based on the geometric mean relative volatility are in good agreement with those calculated by rigorous simulation. The Underwood prediction of  $R_{min}$  is within 26% deviation of the rigorously calculated value in both cases. Results based on the relative volatility of the feed have the biggest deviation from the rigorous simulation results. Numerous other examples studied gave the same general result.

System and split		Compos	Minimum reflux ratio, $R_{\min}$						
			Distillate	Bottom	D/F	Underwood			Exact
		Feed				$lpha_{ ext{geom}}$	$\alpha_{\mathrm{alg}}$	$\alpha_{f}$	HYSYS
ACBT	Acetone	0.2261	0.99	0.06		5.79	3.53	2.37	6.26
	Chloroform	0.2743	0.009	0.332	0.179				
	Benzene	0.1784	0.001	0.217					
	Toluene	0.3212	1.0E-7	0.391					
MMEI	Methyl acetate	0.1282	0.7889	1.0E-7		3.33	2.50	6.24	2.65
	Methanol	0.0968	0.2111	0.0746	0 162				
	Ethanol	0.0625	1.0E-7	0.0746					
	2-propanol	0.7125	1.0E-7	0.8507					
* For all singular points their mean relative volatilities are: $\alpha = \sqrt{\alpha \alpha}$									

Table 3.2 Minimum reflux ratios calculated rigorously and using the Underwood equations.

\* For all singular points, their mean relative volatilities are:  $\alpha_{geom} = \sqrt{\alpha_D \alpha_B}$ ,  $\alpha_{alg} = (\alpha_D + \alpha_B)/2$ ,  $\alpha_f = \alpha_{feed}$ . Feed and products are liquids at 1 atm.

Fig. 3.12 presents details of the relative volatility behaviour in the columns simulated using HYSYS 2.1 (AspenTech., Calgary, Canada) at the minimum reflux ratio. From this figure, it can be seen that the relative volatilities in terms of singular points change significantly at the feed stage. This is most pronounced for the specified separation of the MMEI mixture. The change in volatility order seen in the ACBT system is related to the linear approximation of compartment boundary. In the remainder of this paper, the geometric mean relative volatility will be used in the Underwood and Fenske equations.



Fig. 3.12 Relative volatility profiles (in terms of singular points) for the separations simulated using HYSYS 2.1 (AspenTech., Calgary, Canada) at the minimum reflux ratio and with feed and product compositions shown in Table 3.2.

For different splits in different systems, Table 3.3 compares the minimum energy demand calculated using the Underwood equations with that determined by other rigorous or semi-rigorous methods, including the rectification body method (RBM) (Bausa *et al.*, 1998), boundary value method (BVM) (Levy *et al.*, 1985) and rigorous simulation using Aspen Plus (1996). It can be seen that the Underwood method gives a good approximation of the minimum energy demand, with deviations of up to 12%. While the accuracy of the Underwood method is poorer than that of the rectification body method and the boundary value method, the Underwood method is much more computationally efficient. It may be concluded that Underwood method can be used to estimate the minimum reflux ratio and the minimum energy cost of a column separating an azeotropic mixture.

The Underwood method assumes constant relative volatility in the columns and is most reliable in cases that relative volatilities (in terms of singular points) are relatively constant. The results of Underwood equations are also affected by the accuracy with which relative volatility is calculated. In particular, when one or both product compositions of a column lie near a non-linear distillation boundary

or compartment boundary, this approach will lead to a poor approximation of VLE behaviour of the non-ideal mixture. In these cases, the minimum reflux ratio calculated using Underwood equations would be less accurate.

System	Fe com	eed and pro	duct moland flow rat	ir tios	Q <sub>B,min</sub> /F(10 <sup>6</sup> J/kmol)*			
System	Feed	Distillate	Bottom	D/F	Aspen Plus	BVM	RBM	Underwood
Acetone	0.35	0.7	1.0E-7					
Methanol	0.15	0.3	1.0E-7	0.5	47.0	46.0	46.8	50.4
Ethanol	0.5	1.0E-7	1.0					
Acetone	0.46	1.0	1.0E-7					
Chloroform	0.1026	1.0E-7	0.19	0.46	44.5	44.4	44.4	49.6
Benzene	0.4374	1.0E-7	0.81					
Acetone	0.3	0.4958	1.5E-6					
Chloroform	0.3	0.4876	0.0127	0.005	74 5	67.0	67.6	62.0
Benzene	0.2	0.0165	0.4810	0.605	71.5	07.8	67.6	62.9
Toluene	0.2	1.0E-7	0.5063					

Table 3.3 Comparison of minimum energy demand determined with Aspen Plus, boundary value method, rectification body method, and Underwood method.

\* The separation specifications and Aspen Plus, BVM and RBM results are taken from the work of Bausa *et al.* (1998). Feed and products are saturated liquids at 1 atm.

# 3.4.2. Calculating minimum number of stages by Fenske equation

With a column separating a C-component azeotropic mixture treated as a column separating a (C+A)-component non-azeotropic mixture, the Fenske equation can be used to calculate the minimum number of stages, assuming that the relative volatilities of singular points are constant through the column. The minimum number of stages depends only on the separation of the two key

components, or in this case, pseudo components (singular points). The geometric mean of the distillate and bottom relative volatilities can be used to represent the relative volatility of the column.



Fig. 3.13 Four-column distillation sequence separating the quaternary mixture of acetone, chloroform, benzene and toluene shown in Fig. 3.11(a).

For the four-column sequence shown in Fig. 3.13, the Fenske equation is used to calculate the minimum number of stages. In Table 3.4, the results are compared with those calculated by rigorous simulation using HYSYS 2.1 (AspenTech., Calgary, Canada). Except for a small difference in impurity concentrations, the product compositions calculated by rigorous simulation using HYSYS 2.1 (AspenTech., Calgary, Canada), which are shown in Table 3.4, are almost same as the specified values used in the shortcut method. From Table 3.4, it can be seen that, column 33 has the biggest error in the prediction of the minimum number of stages. This column crosses the curved distillation boundary shown in Fig. 3.11(a); as a result, the relative volatilities of the singular points are far from constant in the column and the linear approximation of the compartment boundary is an oversimplification. For other columns, the predictions for  $N_{min}$  are up to 3 stages different to the rigorously simulated values. The Fenske equation may thus be seen to be very good for this sequence. Furthermore, the calculation of  $N_{min}$  is extremely quick and simple, especially when compared to other available methods, such as the boundary

value method (Levy *et al.*, 1985) or the use of manifolds Thong and Jobson, 2001b).

		Splits											
		Column 3(1/3-4-5)		Column 33(2-3/4-5)			Column 333(2/3)			Column 3/ (4/5)			
		X <sub>F</sub>	x <sub>D</sub>	x <sub>B</sub>	X <sub>F</sub>	x <sub>D</sub>	X <sub>B</sub>	X <sub>F</sub>	x <sub>D</sub>	x <sub>B</sub>	X <sub>F</sub>	x <sub>D</sub>	x <sub>B</sub>
Aceto	ne	0.26	0.93	0.09	0.09	0.16	0	0.16	0	0.31	0	0	0
Chloroform		0.32	0.04	0.39	0.39	0.83	0.02	0.83	1	0.67	0.02	0.02	0
Benzene		0.21	0.03	0.26	0.26	0.01	0.48	0.01	0	0.02	0.48	0.98	0
Tolue	ne	0.21	0	0.26	0.26	0	0.50	0	0	0	0.50	0	1.0
V <sub>F</sub>			1		1		1			1			
V <sub>D</sub>		0		0		0			0				
V <sub>B</sub>		0		0		0			0				
D/F		0.21		0.47		0.41			0.5				
	$R_{\min}$	5.12			1.95		5.35		2.29				
Shortcut	$N_{\min}$	25			26		23			11			
method	R	6.14		2.34		6.42		2.75					
	Ν	53		58		48			25				
	$R_{\min}$	6.06		2.5		4.5			2.12				
	$N_{\min}$	28		20		20		9					
птото	R		6.3		3.1		7.26			2.96			
	Ν	53		58		48			25				
	$R_{\min}$	-16%		-22%		+19%			+8%				
Error	$N_{\min}$	-11% (-3)		+30% (+6)		+15% (+3)			+22% (+2)				
	R	+2%		-24%			-12%			-7%			

Table 3.4 Comparison of the results of shortcut design and rigorous simulation of a distillation sequence (ACBT system).

\*  $v_F$ ,  $v_D$  and  $v_B$  are the vapour fraction of feed, distillate and bottom, respectively. Mole fractions less than 10<sup>-6</sup>, are shown as 0 in the table.

## 3.4.3. Gilliland correlation can be used to calculate operation reflux ratio and number of equilibrium stages

Once the minimum reflux ratio and minimum number of stages of a column separating a multicomponent azeotropic mixture have been determined, the Gilliland correlation can be used to calculate the operating reflux ratio and number of equilibrium stages. Either the ratio between the actual and minimum reflux ratios is specified, and the number of equilibrium stages is calculated using the Gilliland correlation, or the ratio between the number of equilibrium stages and the minimum number of stages is specified and the operating reflux ratio is calculated.

For each of the splits shown in Table 3.4, the ratio between the operating reflux and the minimum reflux, as calculated by the Underwood equations, is set to be 1.2, and the number of equilibrium stages is calculated using the equation of Eduljee (1975) to represent the Gilliland correlation. In the rigorous simulation of each column using HYSYS, the number of stages of each column is chosen to be the same as that calculated by the Gilliland correlation, and the operating reflux ratio is determined.

From the design results, which are shown in Table 3.4, it can be seen that, the reflux ratios determined by the FUG shortcut method and rigorous simulation are in good agreement. Except for column 33 the error in the reflux ratio obtained by the FUG method is less than 12%. Since column 33 crosses a curved distillation boundary, both its products lie near the boundary. As discussed previously, the shortcut method proposed in this work is least accurate for such splits.

Other expressions of Gilliland correlation have been used for estimating the number of stages but give inferior results in this case. The methods of Molokonov (1972) and Rusche (1999) predict numbers of stages that are almost the same as the minimum predicted by the Fenske equation. The method of Liddle (1968) predicts between 6 and 15 stages less than that of

Eduljee (1975), which would widen further the difference between shortcut predictions of the reflux ratio and rigorous simulation results.

The shortcut method developed in this work employs the Fenske equation, Underwood equations and the Gilliland correlation to design columns separating azeotropic mixtures. Before the classical FUG method can be applied to azeotropic mixtures, vapour-liquid equilibrium compositions in terms of pure components need to be transformed into vapour-liquid equilibrium compositions in terms of singular points. Since only linear equations need to be solved to perform this transformation, applying the FUG shortcut method to azeotropic distillation is as computationally efficient as for non-azeotropic mixtures. As for non-azeotropic mixtures, the FUG method can be used to initialise rigorous simulation using commercial software, such as HYSYS.

## 3.4.4. Identifying infeasible and very difficult splits using the shortcut method

It can be inferred from the Fenske equation when a proposed split will be very difficult or even infeasible. When the relative volatilities between two components is near unity, or the relative volatility between these two key components of a column will be nearly unity, the value of  $log(\alpha_{LK/HK})$  will be nearly zero. The minimum number of stages,  $N_{min}$ , which is inversely proportional to  $log(\alpha_{LK/HK})$  in the Fenske equation, will become very large. The number of equilibrium stages, N, determined by the Gilliland correlation, will be even larger. Therefore, the Fenske-Underwood-Gilliland shortcut design method can easily identify such splits. Compared with other feasibility tests, such as the boundary value and rectification body methods, this method is much more computationally efficient.

For example, the ternary split, with feed and product compositions shown in Fig. 3.14, crosses a compartment boundary. For a saturated liquid feed and the ratio  $R/R_{min}$  taken to be 1.2, the shortcut design method gives the reflux ratio and

number of stages as 0.16 and 2841, respectively. It can be concluded that this separation is either infeasible or very difficult. With the same product specifications, both the boundary value method and rigorous simulation using HYSYS (specifying D/F and mole fraction of benzene in the bottom product) indicate that this separation is infeasible.



Fig. 3.14 Compartment boundary crossing split in the ternary system of benzene, 1propanol and toluene.

## 3.4.5. Estimating the distribution of non-key components

For a column separating a non-azeotropic mixture, the Fenske equation can be used to estimate the distribution of non-key components in the distillate and the bottom at total reflux. This is based on the mass balance of the products and the feed. For a split that does not cross a boundary (a distillation boundary or a compartment boundary), its feed and two products lies in the same compartment, and can be taken as mixtures of the same set of singular points. The products and the feed of this split are in mass balance in terms of singular points, as are in terms of pure components. In this case, the Fenske equation can be used to estimate the distribution of non-key components (singular points) between the distillate and the bottom, as can be used in non-azotropic mixture. While for a split crossing a boundary (distillation boundary or compartment boundary), the products and the feed do not appear in the same compartment, the two products of a split crossing a compartment boundary lie in two different compartments. For a split crossing a distillation boundary, its feed lies in a compartment (distillation region) different from the one in which its products lie. In such case, the products and the feed can be taken as mixtures of different sets of singular points, and do not satisfy the mass balance in terms of singular points, and the Fenske equation cannot be used to the estimate the distribution of singular points in the distillate and the bottom. For example, the feasible split shown in Fig. 3.11(b) cross the compartment boundary 1-4-5. The distillate lies in compartment 1-2-4-5, and can be taken as the mixture of singular points 1, 2, 4, and 5. Based on this, its composition in terms of pure components (shown in Table 3.2) can be transformed into composition in terms of singular points, which is  $S_D = [0.6162, 0.3838, 0, 0, 0]^T$ . The bottom product and the feed lie in compartment 1-3-4-5. Their compositions in terms of singular points can also be obtained through transformation and are  $S_{B}=[0.0, 0.0, 0.0746, 0.0746, 0.8507]^{T}$ and  $S_{F}=[0.1950, 0.0, 0.03, 0.0625, 0.7125]^{T}$ , respectively. With the distillate to feed ratio as 0.162 (shown in Table 3.2), it can be seen that the two products and the feed do not satisfy mass balance in terms of singular points. No solution can be obtained if the Fenske equation is used to estimate the distribution of non-key singular points.

For a split that does not cross a boundary (distillation or compartment boundary), if its feed or one of its products lies near the curved distillation boundary on the concave side, the Fenske equation cannot be used to estimate the distribution of singular points, either. The reason is that, the distillation region in which this product lies may be missed treated with linearly approximated distillation boundary, as analysed in Section 3.3.2.

### 3.5. Evaluation of distillation sequences with recycles specified

Many sequence alternatives can be used to separate a multicomponent homogeneous azeotropic mixture and thus recover all pure or nearly pure constituents. The algorithmic procedure proposed by Thong and Jobson (2001c) can be used to identify all potentially feasible sequences with only product regions specified for each column. Recycles are needed by the sequence; their compositions and flowrates can change each product composition in the corresponding product region, and thus affect the feasibility of each split and the cost of the sequence, as will be introduced in Chapter 4.

With recycle streams specified for each potentially feasible sequence, it is necessary to evaluate this sequence, so that the best set of recycle flowrates, which corresponds to the minimum total cost of the sequence, can be found. In the evaluation process, the shortcut method proposed in the previous section can be used to design each column instead of a more rigorous method, such as the boundary value method (Levy *et al.*, 1985), thus sequences can be computationally efficiently evaluated. The evaluation procedure is iterative because of the existence of recycle streams.

## 3.5.1. Evaluation procedure with shortcut method and spherically approximated distillation boundary

The distillate and bottom products of a feasible column generally lie in the same distillation region. However, in a distillation sequence, the change of recycle flowrates will change the compositions of the distillates, bottoms or feeds of some, even all columns, and thus will change the location of these streams. Therefore, during the evaluation process of a fixed distillation sequence, it is necessary to test the distillation region that product streams, which can be either final product streams or intermediate streams, lie in. In this kind of iterative evaluation procedure, it is time consuming to identify the distillation regions that streams lie in through calculating residue curves. This problem can

be solved with distillation boundaries spherically approximated and the procedure introduced in Section 3.2 employed to identify the distillation regions that streams located in.

To calculate the capital cost and operating cost of each column during the evaluation of a distillation sequence, column design parameters, such as number of stages and reflux ratio, need to be calculated. Rigorous or semirigorous column design methods, such as boundary value method, are iterative and need stage-by-stage calculation at different reflux ratios, and are therefore not suitable for sequence evaluation. The shortcut column design method developed in this work is computationally efficient, so is very well suited to sequence evaluation.

The evaluation procedure, using spherically approximated distillation boundaries and the shortcut column design method, is shown in Fig. 3.15. Starting with the fully specified final products (compositions and flowrates), for each set of recycle flowrates, the mass balance of the sequence can be closed backward. Feed compositions of columns with both products as final products of the sequence can be calculated at the beginning. These feed streams generally are the product streams of other columns. Therefore, the product compositions of some intermediate columns are known, and the feed compositions of these columns can be calculated. Sequentially, the mass balance of the whole sequence can be closed.

Once the mass balance of the sequence is closed, the shortcut method is used to calculate the reflux ratio and number of stages of each column if the products of the column lie in the same distillation region. Then, the energy and capital cost of each column and the sequence can be calculated according to the costing correlation and parameters given in Appendix A. Trial and error (*i.e.* an exhaustive search) is employed to search for the best set of recycle flowrates (resulting in the minimum total annualised cost). The result of the evaluation is the best among the search range. To spherically approximate the distillation boundary, the compositions on the boundary should be specified or identified before the sequence is evaluated.



Fig. 3.15 Optimisation procedure of the sequence using shortcut method.

The efficiency can be improved with a more elegant optimisation method, such as SQP (Successive Quadratic Programming) method and MINLP (Mixed Integer non-linear programming) method, rather than the trial and error. However, these methods cannot guarantee that the best solution can be found.

## 3.5.2. Application of the evaluation procedure to four-column sequence

In this section, the sequence evaluation procedure shown in Fig. 3.15 will be used to evaluate the four-column distillation sequence shown in Fig. 3.16. This sequence is used to separate the four-component mixture shown in Fig. 3.5.



Fig. 3.16 Four-column distillation sequence with recycles (results as well as recycle structure).

Using the procedure proposed by Rooks *et al.* (1998) and Thong *et al.* (2001), it can be identified that the whole composition space of this system is separated

into two distillation regions, 1-3-4-5 and 2-3-4-5. The distillation boundary that separates these two distillation regions is 3-4-5. Each of these distillation regions is a compartment. Using the composition transformation procedure introduced in Section 3.4.1, it can be identified that the equimolar mixture to be separated, lies in compartment or distillation region 1-3-4-5. The flowrate of each recycle stream shown in Fig. 3.16 is varied in a wide range, from 0 to 3F, where, *F* is the molar flowrate of the mixture to be separated (100 kmol/h).

Four recycle streams are specified for this sequence (rules for screening beneficial recycles will be introduced in Chapter 4); all mixed with the process feed. Different recycle streams with different flowrates will have different effect on feasibility and design parameters of the columns and hence on the total cost of this sequence. Therefore, the evaluation procedure searches the whole range of possible recycle flowrates, so that the best set of recycle flowrates, corresponding to the minimum total annualised cost, can be found.

In the evaluation procedure, distillation boundary 3-4-5 is spherically approximated as shown in Fig. 3.5. Although trial and error is used, the optimisation is relatively computationally efficient because of the application of the shortcut method. With the search step size of each recycle flowrate as 0.2*F*, the results can be obtained in less than 15 minutes (AMDXP 2000+, 512MB RAM). The best set of recycle flowrates are shown in Fig. 3.16, and the design parameters, together with the feed and product compositions are shown in Table 3.5. As shown in Fig. 3.16, only one recycle stream (stream **3**, the acetone-chloroform azeotrope) is recycled; its flowrate is 0.2*F*. Using the same computer and same procedure, and replacing the shortcut method by the boundary value method, it takes about 30 hours to get the results, which are same as those obtained using the shortcut method. It can be seen that the efficiency of sequence evaluation can be significantly improved by the shortcut method.

Colu	imn	C1	C2	C3	C4
R	2	6.14	2.34	6.42	1.56
N		53	57	48	26
Reboiler du	ty, 10 <sup>6</sup> kJ/h	5.35	4.77	5.35	2.11
Feed	Acetone	0.2638	0.0727	0.1534	0.0
composition	Chloroform	0.3217	0.4037	0.8439	0.0075
and flowrate.	Benzene	0.2071	0.2071 0.2616		0.4950
kmol/h	Toluene	0.2075	0.2621	0.0004	0.4975
	Flowrate	120	95	45	50
Distillate	Acetone	0.99	0.1534	0.01	0.0
composition	Chloroform	0.01	0.8439	0.99	0.015
and flowrate,	Benzene	0.0	0.0022	0.0	0.98
kmol/h	Toluene	0.0	0.0004	0.0	0.005
	Flowrate	25	45	25	25
Bottom	Acetone	0.0727	0.0	0.3327	0.0
composition	Chloroform	0.4037	0.0075	0.6613	0.0
and flowrate,	Benzene	0.2616	0.4950	0.0050	0.01
kmol/h	Toluene	0.2621	0.4975	0.001	0.99
	Flowrate	95	50	20	25

Table 3.5 Shortcut design results of each column shown in Fig. 3.16.

Taking the recycle flowrates and the design parameters of each column (N, R and distillate flowrate) as the initial values for the rigorous simulation of this sequence using HYSYS, the results are shown in Table 3.6. In the rigorous simulation, the stage number of each column is taken to be that obtained by the shortcut method. The flowsheet, including recycles, is converged. Comparing Tables 3.5 and 3.6, it can be seen that, except for column C2, there are small deviations between the results of rigorous simulation and those of shortcut design. Given that C2 crosses a distillation boundary, larger derivations are to be expected. In particular, except for column C2, rigorously calculated reflux ratios are within 15% of those obtained by the shortcut method, and mole fractions of the key components (singular points), in the column products are within 4% of those assumed in the shortcut method. The entire flowsheet, method proved very useful for initialising the HYSYS simulation: the entire flowsheet, so the entire flowsheet, and the shortcut method is the shortcut method.

given column specifications (stage number, reflux ratio, product flowrate *et al*.), converged easily and quickly with little help from the user.

Colu	ımn	C1	C2	C3	C4	
R	ł	7.09	4.12	5.63	1.50	
N	*	53	57	48	26	
Reboiler du	ty, 10 <sup>⁰</sup> kJ/h	6.073	6.792	4.851	1.971	
Feed	Acetone	0.2623	0.0812	0.1714	0.0	
composition	Chloroform	0.3171	0.3915	0.8179	0.0077	
and flowrate,	Benzene	0.2123	0.2641	0.0107	0.4926	
kmol/h	Toluene	0.2083	0.2632	0.0	0.5001	
	Flowrate	120	95	45	50	
Distillate	Acetone	0.9501	0.1714	0.0490	0.0	
composition	Chloroform	0.0344	0.8179	0.9509	0.0154	
and flowrate.	Benzene	0.0155	0.0107	0.0001	0.9746	
kmol/h	Toluene	0.0	0.0	0.0	0.01	
	Flowrate*	25	45	25	25	
Bottom	Acetone	0.0812	0.0	0.3243	0.0	
composition	Chloroform	0.3915	0.0077	0.6517	0.0	
and flowrate.	Benzene	0.2641	0.4922	0.0240	0.0097	
kmol/h	Toluene	0.2632	0.5001	0.0	0.9903	
	Flowrate	95	50	20	25	

Table 3.6 Design results of each column shown in Fig. 3.16 by rigorous simulation using HYSYS.

\* Specified values

## 3.6. Conclusions

The spherically approximated distillation boundary proposed in this work can give a good representation of the actual distillation boundary in a multicomponent azeotropic mixture and can be quickly and easily obtained. The approximation of the distillation boundary allows the distillation region in which a composition lies to be easily identified, only through solving linear and quadratic equations. A distillation compartment behaves like a non-azeotropic mixture of the singular points appearing in it. Based on this observation, a shortcut method is developed for the design of columns separating homogeneous multicomponent azeotropic mixtures. In this method, azeotropes are treated as pseudo components, and a *C*-component system with *A* azeotropes is treated as an enlarged (*C*+*A*)-component non-azeotropic system.

In each compartment, with the compartment boundary linearly approximated, a transformation relates vapour-liquid equilibrium behaviour in terms of pure components to that in terms of singular points. The transformation requires a set of linear equations to be solved and allows the relative volatility of all singular points to be calculated. Since this calculation is based on rigorous models of equilibrium behaviour, satisfactory results can be obtained. However, when the mixture composition is near to a compartment or distillation boundary, its relative volatility will be poorly approximated, because of the linear approximation of compartment and distillation boundaries. Nevertheless, such separations, even separations crossing a curved distillation boundary, may be modelled approximately by this method. Once the relative volatilities of singular points are obtained, the classical Fenske-Underwood-Gilliland method can be used to design columns separating azeotropic mixtures.

This shortcut method can be applied to homogeneous azeotropic mixtures with any number of components. While this method is less accurate than more rigorous approaches, such as the boundary value method, the error is within a tolerable range. As there is no need to calculate pinch point curves, nor stageby-stage mass balance and equilibrium relationships, this method is extremely computationally efficient. The absence of efficient methods for estimating the reflux ratio and number of stages of a column separating an azeotropic mixture makes this shortcut method highly attractive. The method can give satisfy results with simple calculation, although for columns near a distillation boundary or compartment boundary, errors increase.

It is the first systematic and efficient method for estimating the reflux ratio and number of stages of a column separating an azeotropic mixture. In multicomponent azeotropic systems, for which the composition space cannot be visualised, the composition transformation procedure can also be used to identify the compartment in which a given composition point lies. In addition to column design, the shortcut method is valuable in that it allows one to identify very difficult and infeasible splits through simple calculations.

With this shortcut column design method and non-linearly approximated distillation boundary, a procedure for the evaluation of a distillation sequence with candidate recycles is proposed. Even using trial and error, this procedure can efficiently identify the best set of recycle flowrates, which corresponds to the minimum total cost of the sequence, together with the associated column design parameters. The results of this shortcut design can be used to initialise rigorous simulations (e.g. using commercial software, such as HYSYS). This was demonstrated for the evaluation of a four-column sequence with four candidate recycle streams.

## **Recycle selection for azeotropic distillation sequences**

## 4.1. Introduction

Compared with sequences separating non-azeotropic mixtures, sequences separating azeotropic mixtures always need recycles because of the constraint of distillation and compartment boundaries on product distributions. In a distillation sequence, there are two kinds of recycles, recycles with compositions close to those of singular points (*i.e.* pure components and azeotropes) and recycles with the compositions of mixtures of singular points. In this chapter, systemic procedures are developed for evaluating these two kinds of recycles and for selecting suitable recycle connections for a given sequence and separation objective.

Recycles with singular point compositions are analysed first from two aspects, the feasibility requirement of different types of splits and the effect of recycles on the performance of splits. Based on this analysis, a set of rules and a systematic procedure for selecting recycles with singular point compositions is developed. A second procedure is proposed for identifying promising recycles with the compositions of mixtures of singular points. The two procedures are applicable to distillation sequence separating azeotropic mixtures with any number of components.

## 4.2. Background concept

Considering distillation sequences separating azeotropic mixtures, azeotropes can be taken as pseudo components. Thus, a distillation sequence separating a

*C*-component mixture with *A* azeotropes can be treated as a distillation sequence separating a (C+A)-component non-azeotropic mixture. In this chapter, the components separated by a column or a distillation sequence refer to singular points, which include pure components and azeotropes.

In a distillation sequence, each column performs a specific split; the split performed by column ( $C_i$ ) can be called split  $C_i$ . The splits in a distillation sequence are interconnected since the product of one split may feed another column or is mixed with recycles and then feed another split. The concept of upstream and downstream are defined as follows. If the feed of split  $C_i$  is the distillate (or bottom) or part of the distillate (or bottom) of split  $C_j$ , split  $C_i$  is downstream of split  $C_j$ , while split  $C_j$  is the upstream of split  $C_i$ . The products of split  $C_i$  are called downstream products of split  $C_j$ , or downstream products of the distillate (or bottom) of split  $C_j$ .

With azeotropes treated as pseudo components, each column of a sequence performs a sharp or sloppy split in terms of singular points. Unlike column separating a non-azeotropic mixture, the key components of a column separating an azeotropic mixture are singular points. The light key component has a specified maximum recovery in the bottom product, while the recovery or mole fraction of the heavy key component in the top product is specified.

A split is a sharp split between two singular points, which do not coexist in the two products and the corresponding downstream products of this split. Otherwise, the split is a sloppy split between these two singular points. A split, in which there is no overlap between its two products and the corresponding downstream products in terms of any pair of singular points, is a sharp split. Otherwise, it is a sloppy split. A sharp split between the constituents of an azeotrope is said to be the split breaking this azeotrope.

For example, in the distillation sequence shown in Fig. 4.1, split 1/3-4-5 in column C1 can separate a quaternary mixture of acetone, chloroform, benzene and toluene, into distillate 1 (product region) and bottom product 3-4-5 (product region). The distillate contains only singular point **1**, so cannot be further

separated. Bottom product 3-4-5 can be further separated into downstream products, namely the four singular points, **2**, **3**, **4** and **5**. For column C1, the distillate has no singular points in common with the bottom and the downstream products of the bottom, so split 1/3-4-5 performed by column C1 is a sharp split. Since the azeotrope constituents acetone (**1**) and chloroform (**2**) only appear in the distillate and the downstream product of the bottom product, respectively, this split breaks the azeotrope (**3**) between acetone and chloroform.



Fig. 4.1 In quaternary system of acetone, chloroform, benzene and toluene, split 1/3-4-5 is a sharp split that breaks the azeotrope between acetone and chloroform.

### 4.3. Characteristics of recycles in distillation sequence

In a distillation sequence separating an azeotropic mixture, recycles are always necessary. Without recycles, a distillation sequence cannot recover all pure components of the azeotropic mixture of interest. Each recycle stream, together with all the columns, whose feed or product composition is affected by this recycle, forms a corresponding recycle loop.

There are three aims of using recycles in a distillation sequence. The first one is to avoid repeated separation between the same two key components. For example, to avoid repeated separation, streams with the composition of the azeotrope are always recycled to the column that breaks this azeotrope. The second aim is to help break the azeotrope so that all azeotropic constituents can be recovered. Recycle streams with the compositions of the components that can act as mass separation agents always have this effect. The third aim is to adjust a product's composition and flowrate, and thus adjust the feasibility of a split and the component recovery. These three aims are not completely independent. A recycle stream can help break the azeotrope and adjust product compositions at the same time.

In the recycle superstructure of a distillation sequence (Thong, 2000), all product streams are taken as possible recycles, and all feeds of columns are possible destinations of recycles. A recycle superstructure can be constructed with all these possibilities accounted for. However, such a recycle superstructure contains too many recycles, and, its evaluation is extremely time-consuming. To reduce the size of the recycle superstructure, Thong (2000) proposed the following four general rules:

- 1. Azeotropes can be recovered, partially recovered, or recycled completely.
- 2. Never recycle a stream to the column that produces it.
- Never mix a recycle stream with a feed to a column performing a split where the recycle stream contains one or more components that are not present in either product stream.
- 4. Never mix streams with compositions in different compartments. The exception to this is recycle streams to columns performing Type C splits (splits crossing compartment boundary); these streams can lie in either compartment that the split traverses.

From rule 2 and rule 3, it can be seen that, in a distillation sequence, for a sharp split, only its downstream products can be recycled to its feed. No such a conclusion can be obtained for a sloppy split. When the product of a sharp or sloppy split,  $C_i$ , is recycled to the feed of its upstream split,  $C_j$ , the splits contained in the recycle loop formed by this recycle are the upstream splits of split  $C_i$  lying between split  $C_i$  and  $C_j$  in the sequence. For the sequence shown

in Fig. 4.1, if the bottom product of column C3 is recycled to the feed of column C2, the recycle loop formed by this recycle contains column C2 and C3, as shown in Fig. 4.2 (a). However, when the product stream is recycled to the feed of the split, which is not an upstream split, a bigger recycle loop will be formed by this recycle. This recycle loop not only contains all the upstream splits of this recycle, but also the split whose feed is the destination of this recycle, and its downstream splits. This can be seen from Fig. 4.2 (b), if the bottom product of column C3 is recycled to the feed of column C4, which is not its upstream, instead of the feed of column C2, the whole sequence will be affected by this recycle. Such a kind of recycle will significantly increase the vapour flowrate of the sequence of interest and should be avoided. In this work, streams are only recycled to the feed of a column upstream of the recycle.



Fig. 4.2 Effects of the same recycle stream with different destinations: the feed of upstream split and the feed of non-upstream split.

In a distillation sequence, recycle streams can be classified according to compositions into two types, singular recycles and mixed recycles. Singular recycles have the compositions close to those of singular points; mixed recycles have compositions of mixtures of singular points. A singular recycle cannot be further separated and thus must be the final product of a distillation sequence. Since the main component of this kind of recycle is simple and known, it is easy to analyse whether recycling will benefit a split. A mixed recycle is generally an intermediate stream of the distillation sequence of interest. The composition of

such a recycle is complex and might change with flowrate and composition of another recycle. It is difficult to directly analyse whether such a recycle stream is necessary.

In the following section, the requirement of different types of splits (Type A, Type B and Type C splits) on singular recycles will be analysed from two aspects, split feasibility and component recovery. The effects of different singular recycles on the performance of splits will also be analysed. Based on this, the necessary mixed recycles will be analysed and selected.

### 4.4. Recycles with singular point compositions

Type A, Type B and Type C splits have different feasibility characteristics and need different recycles to adjust their feasibility. For a distillation sequence separating an azeotropic mixture, the feasibility of each split and the recovery of constituents of an azeotrope need to be considered first. Therefore, the requirement of each type of split on singular recycles can be analysed from these two aspects. The split with feed on one side of a distillation boundary producing products lying on the other side of the same distillation boundary crosses a distillation boundary and is called a distillation-boundary crossing (DBC) split in this work. Since a DBC split can be either Type A or Type B split, and has special characteristics and thus has special requirements on recycles, it will be analysed separately. Different recycle streams have different effects on the performance of the column. In this section, singular recycles will be analysed from these two aspects, the requirement of splits (feasibility and recovery of azeotropic constituents) and the effects of recycles.

## 4.4.1. Distillation-boundary crossing (DBC) Splits

## 4.4.1.1. Characteristics of distillation-boundary crossing (DBC) splits



Fig. 4.3 In a ternary azeotropic system, a distillation boundary limits the product composition and flowrates of a distillation column.

An azeotrope, especially a maximum-boiling azeotrope, may introduce a distillation boundary into the composition space. The azeotrope always lies on the distillation boundary caused by it, while its constituents lie on different sides of this boundary. A distillation boundary always limits the product compositions and flowrates of a feasible column, and thus limits the recovery of the constituents of the azeotrope. The ternary azeotropic system of acetone, chloroform and benzene shown in Fig. 4.3 has a distillation boundary caused by the maximum azeotrope between acetone and chloroform. For a mixture with composition  $P_1$ , if there were no distillation boundary, a column could fully recover acetone in the distillate D. The corresponding bottom product B is the mixture of chloroform and benzene. However, because of the existence and limitation of the distillation boundary, the split that a column can perform with the biggest recovery of acetone corresponds to the distillate D and bottom product  $B_1$ , which lies on the distillation boundary. No further increase in

recovery is possible, even though there is still some acetone included in bottom product  $B_1$ .

To recover all the pure constituents of an azeotrope, which introduces a distillation boundary into the composition space, crossing the distillation boundary is always necessary. Doherty and Cadarola (1985) concluded that a linear distillation boundary could not be crossed. Only if the boundary is curved, can it be crossed by a simple column from its concave side. The greater the curvature of a distillation boundary, the easier it is to cross the distillation boundary. A DBC split can be either Type A or Type B split, and its feed and products lie on the concave and convex side of the distillation boundary it crosses, respectively.

A distillation boundary can be linearly approximated by connecting the neighbouring singular points, which lie on this distillation boundary, with straight lines. Although the linearly approximated distillation boundary can only roughly represent the actual distillation boundary, together with the actual distillation boundary, they clearly outline the region of feasible feed compositions for DBC splits. Only when the feed of a DBC split lies in the region of feasible feed compositions, the region between the linearly approximated distillation boundary and the actual curved distillation boundary, can this split be feasible.

In Fig. 4.4, feed composition  $P_1$  lies in the region of feasible feed compositions. A DBC split with this feed composition has feasible product regions in the neighbouring distillation region and is feasible. On the other hand, for feed composition  $P_2$ , which lies outside the region of feasible feed compositions, the feasible product regions lie in the same distillation region as  $P_2$ . That is,  $P_2$  is not a feasible feed for a DBC split.

A DBC split can only produce products that lie in the different distillation region with its feed. Since distillation boundary can only be crossed in one direction, from its concave side to its convex side, the products of the DBC split of interest cannot be further separated into products that lie in the same distillation region with the feed of this DBC split. Therefore, a DBC split does not have any

products or downstream products that lie in the same distillation region with its feed.



Fig. 4.4 A ternary azeotropic system with a distillation boundary. The actual distillation boundary and the linearly approximated distillation boundary bound the region of feasible feed compositions for DBC splits.

For a DBC split, all its products and downstream products can be recycled. When these streams are recycled to its feed or the feeds of its upstream splits, the compositions of its feed and products will be affected, as well split feasibility. Doherty and Cadarola (1985) concluded that crossing a linear distillation boundary through introducing a recycle loop is infeasible. For a curved distillation boundary, a recycle may facilitate boundary crossing (Thong, 2000). Different singular recycles have different effects on the feasibility of a DBC split. Some recycles can move the feed composition into the region of feasible feed compositions, or move the feed composition towards the distillation boundary, thus will increase the feasibility of the DBC split or make it easier. Some other recycles will have the opposite effect, decreasing the feasibility of the split. All possible singular recycle streams, which are the products or downstream products of the DBC split of interest, can be classified into two types according to composition:

RP type recycles: Recycles with the composition of singular points lying on the convex side of the distillation boundary crossed by the DBC split.

RB type recycles: Recycles with the composition of singular points lying on the distillation boundary crossed by the DBC split.

For each DBC split, the products and downstream products can be classified in this way.

## 4.4.1.2. Effect of recycles recycled to the feed of the DBC split

The necessary condition for a DBC split to be feasible is that its feed composition lies in the region of feasible feed compositions. For a given DBC split, only its downstream products can be recycled to its feed as either RB type or RP type recycles. These two types of recycles have different effects on the feed and product compositions and on the feasibility of this split, as will be discussed below.

### (1) RB type recycles

For a DBC split, its RB type recycles that can be recycled to its feed are its downstream products with the compositions of singular points lying on the distillation boundary crossed by it. With this type of recycles, its feed will move towards the singular points, which are contained in these recycles and lie on the distillation boundary crossed by the DBC split of interest. Since singular points lying on the distillation boundary form the linearly approximated distillation boundary, with a RB type recycle, the feed composition of the DBC split of interest will move towards the linearly approximated distillation boundary, but

can never cross it. Whether the feed composition moves towards the actual curved distillation boundary depends on the original location of the feed of the DBC split.

Consider the feed of a DBC split that lies in the region of feasible feed compositions, such as point  $P_1$  shown in Fig. 4.5 (a), with the RB type recycle with the composition of the azeotrope, the feed composition  $P_1$  will move along the straight line **RB**- $P_1$  towards the linearly approximated distillation boundary, for example. If the DBC split of interest is a Type A split, which is feasible for all pairs of product compositions in its corresponding product regions, the RB type recycles will not improve its feasibility. For a Type B split, which is not feasible for all pairs of product compositions in its product regions, RB type recycles can adjust its product compositions and thus change its feasibility. The characteristics of Type A and Type B splits will be introduced in detail in Sections 4.4.2 and 4.4.3, respectively.



Fig. 4.5 The effect of RB and RP types of recycles on the feed composition (P) of a DBC split. The recycles are to be mixed with this feed.

If the feed of a DBC split lies outside the corresponding region of feasible feed compositions, such as composition point  $P_2$  shown in Fig. 4.5 (a), this DBC split is infeasible. With RB type recycles mixed with it, the feed composition will move towards the linearly approximated distillation boundary, but cannot cross it. For example, it can move from  $P_2$  to  $P_2$ '. The furthest the feed composition

can move is to the azeotrope point that lies on the distillation boundary. Therefore, RB type recycles can never move the feed of a DBC split from the outside of the region of feasible feed compositions to the inside. That means, RB type recycles cannot make an infeasible DBC split become feasible.

From this analysis, it can be concluded that, only when a DBC split is a Type B split with the feed that lies in the region of feasible feed compositions, can RB type recycles recycled to its feed possibly improve its feasibility.

#### (2) RP type recycles

For a DBC split, its RP type recycles are its downstream products with compositions of singular points that do not lie in the same distillation region with its feed. When a RP type recycle is recycled to the feed of this DBC split, the mix between the recycle and the feed of the DBC split is the mix of streams lying in two different distillation regions. Therefore, the feed composition of this DBC split will move towards, even cross the corresponding distillation boundary. With only feasibility considered, this type of recycles certainly can increase the feasibility of this DBC split or make this kind of splits easier, such as shown in Fig. 4.5 (b). However, from the point of component recovery, this type of recycle is not always feasible. The effect of a RP type recycle to the DBC split depends on the location of the feed of the DBC split, which may or may not lie in the region of feasible feed compositions.

Fig 4.6 shows a feasible DBC split, for which the feed,  $P_1$ , lies in the region of feasible feed compositions. Its distillate and bottom products are  $D_1$  and  $B_1$ , respectively. With the RP type recycle shown in this figure, the feed composition  $P_1$  will move along the straight line  $RP-P_1$ , towards both the recycle composition and the actual distillation boundary. If the recycle flowrate is great enough, the feed of the DBC split can even cross the distillation boundary and move to composition point  $P_1$ '. The composition of the bottom product, pure benzene, is not affected by this recycle. Therefore, when the feed composition is moved to  $P_1$ ', the corresponding distillate product will move to  $D_1$ ', which in terms of mass

balance is the mixture of **RP** and **D**<sub>1</sub>. **D**<sub>1</sub>' lies in the same distillation region as **RP** and **D**<sub>1</sub>, and, therefore, can be further separated into streams with the composition of **RP** and **D**<sub>1</sub>, respectively. This means that such a RP type recycle can be produced and recycled to the feed of the DBC split of interest. Since the original feed of DBC split, **P**<sub>1</sub>, is lying in the region of feasible feed compositions, the RP type recycle will not change the feasibility of this split. As the feed composition move towards the curved distillation boundary, the DBC split will become easier.



Fig. 4.6 The effect of RP type recycle on the feasibility of a DBC split. The recycle is to be mixed with the feed of this DBC split, which lies inside the region of feasible feed compositions.

For example, in the feasible four-column sequence shown in Fig. 3.16, column C2 performs a DBC split and crosses the distillation boundary 3-4-5, which is shown in Fig. 4.7. The feed of column C2 lies in the region of feasible feed compositions. The distillate of column C3 is the downstream product of column C2, which can be recycled to the feed of the column C2. Since the recycle has the composition of chloroform, which appears in a distillation region different from that of the feed of column C2, it is a RP type recycle. In Fig. 3.16, only the bottom product of column C3 is used and the DBC split C2 and the sequence are feasible. If the distillate of column C3 is recycled to the feed of column C2 (RP type recycle) with flowrate as 0.15F, the distillation sequence will be the
one shown in Fig. 4.7. The number of stages in each column is kept to be the same value as that shown in Table 3.5, and this sequence is simulated using HYSYS. The simulation results are shown in Table 4.1.



Fig. 4.7 Four-column distillation sequence with RP type recycle.

Column		C1	C2	C3	C4
R		7.16	3.47	1.71	1.50
N	I	53	57	48	26
Feed flowra	ate, kmol/h	120	110	60	50
Distillate flow	/rate, kmol/h	25	60	40	25
Reboiler du	ıty, 10 <sup>⁰</sup> kJ/h	6.127	7.90	3.177	1.971
	Acetone	0.2614	0.0767	0.1406	0.0
Feed	Chloroform	0.3169	0.4666	0.8487	0.0079
composition	Benzene	0.2134	0.2294	0.0107	0.4919
	Toluene	0.2083	0.2273	0.0	0.5001
	Acetone	0.9482	0.1406	0.0520	0.0
Distillate	Chloroform	0.0363	0.8487	0.9471	0.0159
composition	Benzene	0.01525	0.0107	0.0010	0.9741
	Toluene	0.0	0.0	0.0	0.010
	Acetone	0.0806	0.0	0.3177	0.0
Bottom	Chloroform	0.3907	0.0079	0.6521	0.0
composition	Benzene	0.2655	0.4919	0.0302	0.0094
	Toluene	0.2632	0.5001	0.0	0.9906

Table 4.1 The design results of each	column shown in Fig.	4.6 using HYSYS.
--------------------------------------	----------------------	------------------

The simulation shows that, with this RP type recycle, column C2 together with the sequence are still feasible. Same as the sequence shown in Fig. 3.16, all products can be obtained with desired flowrates and compositions. Compare the results shown in Table 4.1 with those shown in Table 3.5, it can be seen that, with the RP type recycle, the operating reflux ratio of the DBC split decreases from 4.12 to 3.47. This example illustrates that the RP type recycle can ease the DBC split, for which the feed lies in the region of feasible feed compositions. Without this RP recycle, the feed of the DBC split (column C2) lies in distillation region 1-3-4-5. Using Distil, it is found that, with this RP recycle, the feed of column C2 moves to distillation region 2-3-4-5. This means that, with this recycle, the feed and products of column C2 lies on the same side of the distillation boundary and column C2 does not cross this boundary anymore. This sequence crosses the distillation boundary by mixing.



Fig. 4.8 The effect of RP type recycle to the feasibility of a DBC split. The feed of this DBC split is the destination of the RP type recycle and lies outside the region of feasible feed compositions.

On the other hand, when the feed of a DBC split lying *outside* the region of feasible feed compositions, the effect of RP recycles is different. Fig. 4.8 provides an illustrative example. As shown in Fig. 4.8, the split with feed composition  $P_2$  cannot cross the distillation boundary. If the bottom product is set to be  $B_2$ , benzene, which lies on the distillation boundary, the distillate

corresponding to the maximum recovery of benzene can only be  $D_2$ , which lies in the same distillation region as feed  $P_2$ .

With the RP type recycle shown in Fig. 4.8 recycled to  $P_2$ , the feed composition of the split of interest will move along the straight line **RP**-**P**<sub>2</sub>, towards the distillation boundary. If the flowrate of the RP type recycle is large enough, the feed composition can be moved into the region of feasible feed compositions, and thus the DBC split become feasible. For example, the feed composition can move from **P**<sub>2</sub> to **P**<sub>2</sub>', as shown in Fig. 4.8. The split with feed composition as **P**<sub>2</sub>' can cross the distillation boundary.

An RP type recycle lying across the distillation boundary can make an infeasible DBC split feasible. However, unless the DBC split is already feasible, the RP type recycle cannot be produced downstream of the DBC split. Therefore, RP type recycles cannot be used to overcome the infeasibility of a DBC split. This clearly shown by the example shown in Fig. 4.8.

In Fig. 4.8,  $P_2$ ' is the mixture of  $P_2$  and RP, and  $D_2$ ' is the mixture of  $D_2$  and RP. In principal, the **RP** recycle should be the downstream product of the distillate  $D_2$ '. Therefore, if  $D_2$ ' can be separated into **RP** and other products, which mixed together as  $D_2$ , the downstream splits will produce the **RP** stream. However, from Fig. 4.7, it can be seen that, because of the existence of the azeotrope and the distillation boundary, which can only be crossed from the concave side,  $D_2$ ' does not lie in the same distillation region with  $D_2$ , and, can never be further separated into RP and other products, which can be mixed as  $D_2$ . Therefore, recycling this RP type recycle to the feed  $P_2$  of a DBC split is infeasible.

From this analysis, it can be concluded that only when the feed of a DBC split lies in the region of feasible feed compositions, can an RP type recycle benefit this split. Since the region of feasible feed compositions of a DBC split is bounded by the linearly approximated distillation boundary and the actual distillation boundary, it follows that recycles can be recycled to a column with the feed lying in the other side of the actual curved distillation boundary, but cannot be recycled to a column with the feed lying beyond the linearly approximated distillation boundary. This conclusion is in good agreement with both the work of Doherty and Caldarola (1985) and the work of Thong and Jobson (2001c).

## 4.4.1.3. Effect of recycles recycled to the feed of the upstream of DBC split

The feed of a DBC split is produced by its upstream splits. When the products or downstream products of a DBC split are recycled to the feed of its upstream split, the feed composition of the DBC split is also affected. This kind of recycles therefore also deserve analysis.



Fig. 4.9 A four-column sequence with a DBC split. Recycles may be recycled to the feed of the upstream splits of the DBC split (column C3). All possible recycle connections of the downstream products of column C3 are shown.

For a DBC split, when its downstream products are recycled to the feed of its upstream split, the effect of these recycles to the DBC split is same as that of recycling them directly to the feed of this DBC split. For example, the four-column sequence shown in Fig. 4.9(b) can be used to recover all pure components of the quaternary feed mixture shown in Fig. 4.9 (a). Split C3

crosses the distillation boundary 3-4-5 and is a DBC split, while splits C1 and C2 are its upstream splits. RB and RP type recycles can be recycled to the feed of columns C1, C2, and C3. No matter which column they are recycled to, these recycles have the same effect on the feed and product compositions of column C3. Furthermore, these recycles also will change the product compositions of the up-stream splits included in the corresponding loops.

The products of the DBC split of interest can also be recycled to the feed of its upstream split. For the DBC split of interest, recycling its products to the feed of its upstream split will not affect its product composition, but will affect its feed composition. The effect of such a recycle depends on its type. For a given DBC split, a RB (or RP) type recycle, which is its product and is recycled to the feed of its upstream split, has the same effect on this split as other RB (or RP) type recycles, which are its downstream products and are recycled to its feed. Such recycles also affect the upstream splits included in the corresponding loops.

Therefore, for a DBC split of interest, it is necessary to analyse the effect of its RB and RP type recycles, which include its products and the downstream products and are recycled to the feed of its upstream split.

A DBC split of interest may have several upstream splits, and it is impossible to take account of recycling streams to all these possible destinations. Therefore, it is necessary to decide the best destination. Recycles to this best destination will have the best effect on the sequence. A RB or RP type recycle has the same effect on the DBC split of interest (in terms of mass balance), whichever upstream split it is recycled to. Therefore, the best destination does not depend on the effect of recycles on the DBC split, but depend on the effect on the upstream splits of the DBC split.

Each constituent of an azeotrope, which gives rise to the distillation boundary crossed by the DBC split, only appears in one of the two distillation regions separated by this distillation boundary. A sharp split between the constituents of an azeotrope is breaking this azeotrope. Since the products and downstream products of the DBC split can only lie on the convex side of the distillation

96

boundary, this DBC split does not break the azeotrope, giving rise to this distillation boundary. To recover all the constituents of an azeotrope which causes a distillation boundary, the DBC split must have an upstream split breaking this azeotrope.

In a distillation sequence separating an azeotropic mixture, as well as adjusting the feed composition of a DBC split, RB and RP type recycles can also work as mass separation agents for breaking an azeotrope. Upstream of the DBC split of interest, there is a split breaking the azeotrope, which introduce the distillation boundary crossed by the DBC split. Recycles should be recycled to the feed of the upstream split breaking azeotrope by reasoning shown in Table 4.2. For example, in the sequence shown in Fig. 4.9 (b), column C2 breaks the azeotrope, so, candidate recycles should mix with the feed of column C2. Recycles mixed with the feed of column C1 will increase total cost of the sequence without improving the performance of column C2.

Recycle destination	Consequence	Conclusion
To the feed of azeotrope-breaking split	Recycle can help breaking the azeotrope	Accept
Upstream of azeotrope- breaking split	Recycle can help breaking the azeotrope, upstream flows increased without benefit to feasibility	Reject
Downstream of azeotrope-breaking split	Recycle cannot help breaking the azeotrope	Reject

Table 4.2 Effects of RB and RP type recycle destination for a sequence.

Note: all splits is the upstream splits of the DBC split of interest, and the azeotrope refer to the one causing the distillation boundary crossed by the DBC split.

Only if a RB or RP type recycle can help this upstream split to break the azeotrope, can the recovery of the azeotrope constituents be improved. The effects of RB type and RP type of recycles are different and will be analysed with the illustrative splits in a quaternary system of acetone, chloroform, benzene and toluene.

Fig. 4.10 illustrates the effect of a RB type recycle. Split C1, which separates  $F_1$ , into distillate  $D_1$ , and bottom product,  $B_1$ , breaks the azeotrope between acetone and chloroform.  $B_1$  is on the curved distillation boundary and can be further separated by a DBC split and its downstream splits into four products with the compositions of singular points 2, 3, 4 and 5. One downstream product of  $B_1$  has the composition of the azeotrope (3), which lies on the distillation boundary, and can be recycled to  $F_1$  as a RB type recycle. With this recycle, the feed composition of split C1 can move to  $F_2$ . If the composition and flowrate of the distillate  $D_1$  do not change, the bottom product of split C1 will change to  $B_2$ , which is the mixture of  $B_1$  and the RB recycle.  $B_2$  is not on the curved distillation boundary, but lies in the region of feasible feed compositions of the DBC split. Therefore, the DBC split with feed  $B_2$  is still feasible, and the feed composition is the same as if **3** was recycled directly to the DBC split. That is, the RB type recycle to the feed of an upstream split does not affect the feasibility of the DBC split.





However, the RB type recycle moves the bottom product composition of split C1 away from the curved distillation boundary, as shown in Fig. 4.10. The bottom product can be moved back onto the curved distillation boundary, and the recovery of azeotropic components can be increased as well. For example, the bottom product composition of split C1 can be moved from  $B_2$  to  $B_3$ , which lies

on the curved distillation boundary. As the bottom product moves from  $B_2$  to  $B_3$ , the flowrate of the distillate product, acetone, will increase.

From this example, it can be concluded that, for a DBC split, recycling an RB type recycle to the feed of the upstream split breaking the azeotrope causing the distillation boundary, can improve the recovery of a constituent of the azeotrope.

For the same splits (split C1 and the DBC split shown in Fig. 4.10), Fig. 4.11 shows the effects of a RP recycle, which is recycled to the feed of split C1,  $F_1$ . This RP type recycle is a downstream product of  $B_1$  with the composition of singular point 2. For a given recycle flowrate, the feed composition of split C1 will move along the straight line  $F_1$ -RP to  $F_2$ , as shown in Fig. 4.11. If the composition and flowrate of the distillate  $D_1$  do not change, the bottom product of split C1 will change to  $B_2$ , which does not lie in the same region as distillate  $D_1$ . Split C1, therefore, is infeasible, unless its bottom product is moved along the mass balance line to at least point  $B_3$ , which lies on the distillation boundary. The recovery of acetone corresponding to bottom product  $B_3$  is less than that corresponding to bottom product  $B_1$ . This means that recycling the RP type recycles to the feed of an upstream split cannot benefit the recovery of acetorepe constituents.



Fig. 4.11 The effect of a RP type recycle when it is recycled to the feed of an upstream split of the DBC split reduces recovery of a constituent of the azeotrope giving rise to the distillation boundary.

#### 4.4.1.4. Discussion

From the above analysis, it can be seen that the feasibility of a DBC split depends on one or more of its upstream splits to produce the feed lying in the region of feasible feed compositions. If the feed of the DBC split lies outside the region of feasible feed compositions, which is bounded by the linearly approximated distillation boundary and the curved distillation boundary, the DBC split is infeasible, and no recycles to its feed can change that. If the feed composition of the DBC split of interest lies within this region, recycling RP type recycle can make the split easier, while recycling RB type recycles to its feed will not benefit its feasibility, unless the DBC split of interest is a Type B split.

The products or downstream products of the DBC split of interest can be recycled to the feed of an upstream split. The best possible destination for these recycles is the feed of the upstream split, which breaks the azeotrope associated with the distillation boundary crossed. For the DBC split of interest, recycling a RB type recycle to the feed of its upstream split, which breaks the azeotrope causing the distillation boundary crossed by it, can improve the recovery of the azeotrope constituents. The effect of this RB type recycle to the DBC split is same as that of directly recycling it to the feed of the DBC split. For the DBC split of interest, recycling a RP type recycle to the feed of its upstream split, will decrease the recovery of the azeotrope constituents. Therefore, RP type recycles could not be recycled to the feed of the upstream split of the DBC split of the precise could not be recycled to the feed of the upstream split of the DBC split of the DBC split of the DBC split of the precise could not be recycled to the feed of the upstream split of the DBC split of the precise could not be recycled to the feed of the upstream split of the DBC split of

For a DBC split of interest, the effects of recycling different recycles to its feed and the feed of its upstream split are analysed from two aspects, feasibility and component recovery, and are summarised in Table 4.3. It can be seen that,

 A RB type recycle can be recycled to the feed of a DBC split, which is a Type B split with feed composition lies in the region of feasible feed compositions.

- For a DBC split, a RB type recycle can also be recycled to the feed of an upstream split which breaks the azeotrope causing the distillation boundary crossed by it.
- A RP type recycle can be recycled to the feed of the DBC split of interest when its feed composition lies in the region of feasible feed compositions.

Table 4.3 The effects of different recycles on the feasibility of the DBC split of interestand the recovery of the azeotrope constituents.

Destination	Type of	Effect on the feasibility of the	Effect on the recovery of the
of recycle	recycle	DBC split of interest	azeotrope constituents
The feed of	RB	Only benefit the feasibility of the Type B split, whose feed lies in the region of feasible feed compositions. Cannot make	No benefit
DBC split of			Reduce the recovery of
interest	RP	Can make feasible an infeasible DBC split, or make a feasible DBC split easier	azeotrope constituents when the feed of DBC split lies outside the region of feasible feed compositions
The feed of the upstream split	RB	Same as recycling this type of recycle to the feed of the DBC	Increase the recovery of the azeotrope constituents
	RP	split of interest	Decrease the recovery of the azeotrope constituents

Therefore, criteria for evaluating candidate recycles consider the feasibility of each split and the recovery of desired components. The economic evaluation of recycle alternatives can only be carried out after feasibility and recovery criteria have been met.

#### 4.4.2. Type A splits

Now that recycle options for DBC splits have been evaluated, we address the much simpler issue of recycle option for Type A split.

The two products of a Type A split lie in the same compartment. Since a compartment behaves like a well-behaved distillation region, the distribution of singular points in the two products of a Type A split depends on the relative volatility order of singular points, just like that of a non-azeotropic mixture. This means that nearly all the lighter than light key singular components are recovered to the distillate, all the heavier than heavy key singular points are recovered to the bottom, and the singular points with relatilities between those of the light and heavy key components distribute between the distillate and bottom products.

Type A splits satisfy the common saddle criterion, which requires both rectifying and stripping profiles to approach the same saddle point, and are always feasible. Therefore, the feasibility of a Type A split does not need to be adjusted through recycling streams to its feed. Nevertheless, Type A splits sometimes need recycles to improve component (or singular point) recoveries.

As analysed in Section 4.4.1, for a DBC split, recycling its RB type recycles to the feed of its upstream split, which breaks the azeotrope causing the distillation boundary crossed by it, can improve the recovery of azeotrope constituent. Therefore, when a Type A split is upstream of a DBC split and breaks the azeotrope causing the distillation boundary crossed by this DBC split, RB type recycles can be recycled to the feed of this Type A split. This allows the desired recovery of azeotrope constituents to be achieved.

In the distillation sequence shown in Fig. 4.9, all splits are Type A splits. Split 2-3/4, which is performed by column C3, crosses the distillation boundary, while its upstream split 1/3-4, which is performed by column C2, breaks the azeotrope. The azeotrope broken by split 1/3-4 causes the distillation boundary crossed by split 2-3/4. Based on the above analysis, RP type recycle can be recycled to the feed of split 2-3/4, while a RB type recycle can be recycled to the feed of split 1/3-4. The resulting recycle structure of this sequence is shown in Fig. 4.12 (a) and is much simpler than the recycle superstructure shown in Fig. 4.12 (b), where only singular recycles are considered. Using the evaluation procedure introduced in Section 3.5.1, both recycle structures shown in Fig. 4.12 are evaluated. The same best set of recycle flowrates, as shown in Fig. 4.12, is obtained, and the corresponding design parameters of each column are shown in Table 4.4.





Fig. 4.12 A four-column distillation sequence with recycles: (a) simple recycle structure identified using the rules introduced above; (b) recycle superstructure considering only singular recycles. F=100kmol/h.

Column		C1	C2	C3	C4
Reflux ratio		1.21	6.14	2.33	6.42
Sta	je No.	24	55	53	49
Energy C	Cost, £/year	220 457	205 648	180 677	210 036
Capita	al cost, £	286 936	396 376	379 689	374 126
Total co	ost, £/year	316 102	337 773	307 240	334 745
Total cost of the	sequence, £/year		1 29	5 861	
	Acetone	0.2550	0.3332	0.0986	0.1534
Feed mole	Chloroform	0.2513	0.4063	0.5479	0.8439
composition and flowrate	Benzene	0.2425	0.2592	0.3514	0.0022
kmol/h	Toluene	0.2513	0.0015	0.0021	0.0004
	Flowrate	100	95	70	45
Distillate mole	Acetone	0.3400	0.99	0.1534	0.01
	Chloroform	0.3350	0.01	0.8439	0.99
composition and flowrate.	Benzene	0.3200	0.001	0.022	0
kmol/h	Toluene	0.0050	0	0.0004	0
	Flowrate	75	25	45	25
	Acetone	0	0.0986	0	0.3327
Bottom mole	Chloroform	0	0.5479	0.015	0.6613
composition and flowrate.	Benzene	0.01	0.3514	0.980	0.005
kmol/h	Toluene	0.99	0.0021	0.005	0.001
	Flowrate	25	70	25	20

Table 4.4 Design parameters for columns shown in Fig. 4.12.

#### 4.4.3. Type B splits

Type B splits are different from Type A splits in that they do not satisfy the common saddle criterion: the stripping and rectifying section profiles approach two different saddle points which lie in the same compartment. In this work, these two saddle points are defined as difference saddle points of the Type B split; LDSP and HDSP will be used to represent the lighter and heavier difference saddle points, respectively. For a Type B split, its rectifying section profile and stripping section profile approach the HDSP and the LDSP, respectively. The HDSP must appear in the distillate, otherwise, both section profiles of this split will approach the LDSP, and the Split will not be a Type B

split. Similarly, the LDSP must appear in the bottom product, or both section profiles will approach the HDSP.



Fig. 4.13 A Type B split is not feasible for all pairs of product compositions lying in the corresponding product regions.

A Type B split is feasible, but not for all pairs of product compositions lying in the corresponding product regions. For example, split 1-3-4/3-4-5 shown in Fig. 4.13 is a Type B split. Composition **B** lies in bottom product region 3-4-5, and compositions  $D_1$  and  $D_2$  both lie in distillate product region 1-3-4. For each product composition, Fig. 4.13 shows the corresponding section profile at total reflux. It can be seen that the rectifying section profiles approach saddle point **4**, while the stripping section profile approach saddle point **3**. Using boundary value method, it is found that  $D_1$  and **B** are a pair of feasible products, but  $D_2$  and **B** are not. Therefore, in a distillation sequence, to make a Type B split feasible, recycles to its feed are needed.

Like for Type A splits, the two products of a Type B split lie in the same compartment and the distribution of the singular points in the two products, depends only on the volatility order of the singular points. Lighter than light key singular components and heavier than heavy key singular points are recovered almost entirely to the distillate and bottom product, respectively, while singular points with volatilities between those of the light and heavy key components distribute between the distillate and bottom product. In particular, the two difference saddle points, LDSP and HDSP, must distribute between the distillate and the bottom products.

The singular points appear in a product and the corresponding concentrations determine the shape of the corresponding section profile. LDSP and HDSP and their concentrations are the key to the feasibility of a Type B split, affecting the likelihood the rectifying and stripping profiles intersection. The feasibility a Type B split can be adjusted by adjusting the mole fractions of HDSP and LDSP, in the distillate and bottoms by recycles.

For a Type B split, if the mole fraction of HDSP is decreased or the mole fraction of LDSP is increased in its distillate, the distillate will move away from the HDSP, and the corresponding rectifying profile will moves towards the LDSP and the stripping profile, which approaches the LDSP. In this way, the possibility of these two section profiles intersection will increase, as will the feasibility of the split. The converses are also true, as summarised in Table 4.5.

Droduoto	Mole frection of UDSD	Male fraction of LDSD	Improve feasibility of	
Products		Mole fraction of LDSP	Type B split?	
Distillato	Decrease	Increase	Yes	
Distillate	Increase	Decrease	No	
Pottom	Increase	Decrease	Yes	
DOLLOIN	Decrease	Increase	No	

Table 4.5 Distribution of intermediate-boiling singular points, HDSP and LDSP, in products affects feasibility of Type B splits.

When a downstream product of the distillate with the composition of non-HDSP singular point, is recycled to the feed of Type B split, the mole fraction of the HDSP in the distillate of the Type B split will decrease and the feasibility of this split will increase. If the recycled downstream product of the distillate has the composition of LDSP, the mole fraction of LDSP in the distillate will increase while that of the HDSP decreases, and can significantly increase the feasibility of the Type B split. Conversely, a downstream product of the distillate with the composition of the HDSP will decrease the feasibility of the split.

Similarly, only a downstream product of the bottom that does not have the composition of the LDSP, recycled to the feed of a Type B split, will increase the feasibility of this Type B split.

Therefore, for a Type B split, among all the possible recycles, recycling the downstream product of the distillate with the composition of LDSP or recycling the downstream product of the bottom product with the composition of HDSP can significantly increase the feasibility of the Type B split of interest.



	Distillate 1-3-4	DOILOITI 3-4-3	reeu
Acetone	0.3907	0.1905	0.2812
Chloroform	0.4386	0.3789	0.4060
Benzene	0.17	0.1457	0.1567
Acetone	0.001	0.2849	0.16
Flowrate	72.5kmol/h	87.5kmol/h	160kmol/h

Fig. 4.14 A Type B split with all possible recycles.

In the acetone, chloroform, benzene and toluene system shown in Fig. 4.13, the distillation sequence shown in Fig. 4.14 can be used to separate the feed mixture into its pure components. Split 1-3-4/3-4-5 is a Type B split. Its HDSP and LDSP are singular points **4** and **3**, respectively. As shown in Fig. 4.14, distillate 1-3-4 can be further separated into four streams with the compositions of singular points **1**, **2**, **3**, and **4**, respectively. Bottom product 3-4-5 can be

further separated into streams with composition of singular points **3**, **4** and **5**, respectively. This Type B split is feasible with the product compositions shown in Fig. 4.14. To analyse the effect of different recycles on this split, all the possible downstream recycles with singular point compositions (shown in a simplified form in Fig. 4.14) are evaluated using the boundary value method. The result is shown in Table 4.6.

	Only recyc	nly recycle downstream product of distillate 1-3-4			Comments
Recycle	F1	F2	F3		
Singular point	3	1	4 (HDSP)		
Base case	0	0	0	$\checkmark$	
	0	0	0.1F to1.5F	Х	Recycling downstream
Recycle	0.0F to1.5F	0	0	$\checkmark$	the composition of
flowrate F4=0	0	0.1F to1.5F	0	$\checkmark$	HDSP will reduce feasibility
F5=0	0	0.9F to1.5F	0.1F	$\checkmark$	Recycling downstream
F6=0	0.5F to1.5F	0	0.1F	$\checkmark$	product of distillate with
	0	1.4F to1.5F	0.2F	$\checkmark$	HDSP will increase
	0.9F to1.5F	0	0.1F	$\checkmark$	feasibility
	Only recyc bot	le down stream tom product 3-4	product of 4-5	Feasible?	Comments
Recycle	F4	F5	F6		
Singular point	<b>3</b> (LDSP)	4	5		
Base case	0	0	0	$\checkmark$	
	0.0F to1.5F	0	0	Х	Recycling downstream
Recycle	0	0.1F to 0.4 F	0	$\checkmark$	the composition of
F1=0	0	0	0.0F to1.5F	$\checkmark$	LDSP will reduce feasibility
F2=0	0.1F	0.1F to 0.6F	0	$\checkmark$	Recycling downstream
F3=0	0.1F	0	0.3F to1.5F	$\checkmark$	product of bottom with
	0.2F	0.1F to1.5F	0	$\checkmark$	LDSP will increase
	0.2F	0	0.7F to1.5F	$\checkmark$	feasibility

Table 4.6 Effects of different recycles on the feasibility of the Type B split	
1-3-4/3-4-5shown in Fig. 4.14*.	

\*Maximum recycle flowrate investigated =1.5F

Table 4.6 shows that recycling the downstream product of the distillate with the composition of HDSP or recycling the downstream product of the bottom product with the composition of LDSP will reduce the feasibility of this Type B split, and recycling another downstream product of distillate or another downstream product of bottom product will increase the feasibility. These results are in good agreement with the above analysis. From Table 4.6, it can also be seen that recycling the downstream product of the distillate with the composition of LDSP is better than recycling the other downstream product swith the composition of non-HDSP, and recycling the downstream product of the bottom product with the composition of HDSP is better than recycling the downstream product of the bottom product with the composition of HDSP, and recycling the downstream product of the bottom product with the composition of non-HDSP, which is also as expected.

If a Type B split is upstream of a DBC split and breaks the azeotrope causing the distillation boundary crossed by the DBC split, RB type recycles of the DBC split can also be recycled to the Type B split, as discussed in Section 4.4.1.3.

#### 4.4.4. Type C splits

Unlike Type A and Type B splits, Type C splits cross compartment boundaries. The distillate and bottom products of a Type C split lie in two neighbouring compartments, and the distribution of the singular points in the two products does not depend on the volatility order of the singular points. For a Type C split, the lighter singular points can appear in the bottom, and the heavier can appear in the distillate. The two section profiles of a Type C split lie in two different compartments and approach different saddle points lying in these two compartments. Therefore, Type C splits do not satisfy the common saddle criterion and may or may not be feasible. Even for a feasible Type C split, not all pairs of product compositions in its corresponding product regions are feasible.

Recycling downstream products of a Type C split can therefore enhance its feasibility. While all the downstream products can be recycled to adjust the

distillate and bottom product compositions, not all these recycles will benefit its feasibility.

The products of a Type C split lie in two neighbouring compartments, which have same pair of stable and unstable nodes and different saddle points. The singular points lying on the compartment boundary include a pair of stable and unstable nodes, and sometimes the saddle points common to the two compartments separated by the boundary. The singular points that only appear in one of the two neighbouring compartments (and not on the compartment boundary between them) are the difference saddle points of the Type C split.

All possible recycles, which are downstream products of the Type C split of interest and have the composition of singular points, can be classified into two types, RBC type and RNBC type. Recycles with the compositions of singular points lying on the compartment boundary crossed by the Type C split of interest are RBC type recycles. Recycles with the composition of singular points not lying on this compartment boundary are RNBC type recycles.

The rectifying and stripping operation leaves of a Type C split, each of which bounds all possible section profiles, generally lie in different compartments and approach the difference saddle points of this split. Therefore, the rectifying operation leaf cannot cross the compartment boundary by very much and nor can the stripping operation leaf. Any intersection between the two operation leaves is generally near the corresponding compartment boundary.

For example, the ternary system shown in Fig. 4.15 is separated into two compartments, compartment 1-3-4 and compartment 1-2-4.  $B_1$ ,  $B_2$ ,  $B_3$  and  $B_4$  are possible bottom products of Type C split 1-2/3-4: their corresponding stripping operation leaves lie in compartment 1-3-4 and approach saddle point **3**. Both rectifying operation leaves, corresponding to proposed distillate products,  $D_1$  and  $D_2$ , lie mainly in compartment 1-2-4, and approach the saddle point **2**. The rectifying operation leaf corresponding to  $D_1$  crosses compartment boundary, and intersects the stripping operation leaf corresponding to  $B_4$  near the compartment boundary.

110



Fig. 4.15 Operation leaves corresponding to the possible distillate and bottom products of Type C split 1-2/3-4.  $B_1$ ,  $B_2$ ,  $B_3$ , and  $B_4$  are proposed bottom products, while  $D_1$  and  $D_2$  are proposed distillates.

The location of operation leaves depends on the product compositions. The nearer the product composition to the compartment boundary crossed by the Type C split, the nearer the corresponding operation leaf is to the compartment boundary. This is common for azeotropic mixtures with any number of components, and can be seen clearly by comparing the operation leaves of  $B_1$ ,  $B_2$ ,  $B_3$ , and  $B_4$  and the operation leaves corresponding to  $D_1$  and  $D_2$ , shown in Fig. 4.15. Therefore, to increase the feasibility of Type C splits, the composition of the two products should be moved towards the compartment boundary by recycles.

The RBC type recycles of a Type C split lie on the compartment boundary. Therefore, recycling these recycles to the feed will move the products towards the compartment boundary. If a RBC type recycle is a downstream product of the distillate of this Type C split, the distillate will move towards the compartment boundary. If the RBC type recycle is a downstream product of the bottom product, the bottom product will move towards the compartment boundary. RNBC type recycles, which do not lie on the compartment boundary,

will move the product compositions away from the compartment boundary. Therefore, to increase the feasibility of a Type C split, RBC type recycles should be recycled to its feed.

For the sharp Type C split 1-2/3-4 shown in Fig. 4.15, with the bottom product composition specified as  $B_4$ , and feed  $F_1$ , the distillate composition is  $D_1$  which is to be further separated into products 1 and 2. However, there is no intersection between the operation leaves corresponding to  $B_4$  and  $D_1$ , so the split is infeasible.

If Type C split 1-2/3-4 were feasible, it would have a downstream product with composition of singular point **1**, which lies on the compartment boundary. This downstream product could be recycled to the feed of the Type C split as a RBC type recycle and would move the composition of the distillate towards the compartment boundary. The distillate composition could be moved to  $D_2$  without the bottom product composition being affected. There would be intersection between the two operation leaves corresponding to  $B_4$  and  $D_2$ , and the split would be feasible. The RBC type recycle with composition of singular point **1** could be produced through further separation of the distillate  $D_2$ . In this case, the RBC type recycle could make feasible an infeasible Type C split.

Fig. 4.16 shows the effect of a RNBC type recycle on a Type C split in the ternary system of butanol, butyl acetate and 1-propanol. The Type C split with distillate **D** and bottom product **B** is feasible, as shown in Fig. 4.16 (a). If two RNBC type recycles with the composition of butyl acetate and butanol, respectively, are recycled to the feed of this Type C split, the distillate and bottom products of this split will change to  $D_1$  and  $B_1$ , separately. As shown in Fig. 4.16 (b), there is no intersection between the operation leaves corresponding to this pair of products. This example demonstrates how a RNBC type recycle can reduce the feasibility of a Type C split.



Fig. 4.16 With RNBC type recycle, the feasibility of Type C split will be reduced.

# 4.4.5. Effect of different type of recycles on the performance of splits

A recycle stream will form a recycle loop. The product compositions and the performance of all the columns involved in the loop are affected by this recycle. Different recycles change the product compositions of a column in different ways and thus have different effects on the performance of this column. The effect of a recycle on the performance of a column is indicated by the change of its vapour flowrate, which is directly proportional to the duty of both the reboiler and a total condenser (King, 1980).

In chapter 3, it has been demonstrated that the Underwood method can be used to calculate the minimum reflux ratios and the minimum vapour flowrates of columns separating azeotropic mixtures. Therefore, the Underwood equations can be used to analyse the effects of different singular recycles (with singular point compositions) on column performances. For a column separating a C-component mixture with A azeotropes, the Underwood equations for the calculation of minimum vapour flowrate can be written as Equations (4.1), (4.2), and (4.3).

$$1 - q = \sum_{i=1}^{C+A} \frac{\alpha_i x_{F,i}}{\alpha_i - \theta}$$
(4.1)

$$V_{\min} = \sum_{i=1}^{C+A} \frac{\alpha_i D x_{D,i}}{\alpha_i - \theta}$$
(4.2)

$$-V_{\min} = \sum_{i=1}^{C+A} \frac{\alpha_i B x_{B,i}}{\alpha_i - \theta}$$
(4.3)

where,  $\alpha_i$  is the relative volatility of singular point *i*,  $x_{F,i}$ ,  $x_{D,i}$ , and  $x_{B,i}$  correspond to the mole fraction of singular point *i* in the feed, distillate and bottom, respectively; *F*, *D* and *B* represent the molar flowrate of the feed, distillate and bottom; *q* and  $V_{min}$  represent the feed quality (the feed thermal condition) and minimum molar vapour flowrate, respectively.

To analyse the effect of recycle composition on minimum vapour flow, we assume that the relative volatilities of all pure components and azeotropes will not change significantly with the introduction of small amount of recycle. Recycles will affect the flowrates and compositions of the feed and products and the vapour flowrate of the column of interest. With  $F_i$ ,  $D_i$  and  $B_i$  to represent the molar flowrate of singular point *i*, the effect of the recycle stream with the composition of singular point *a* can be analysed. From Equation (4.1), it can be derived (Appendix B illustrates the detailed derivation):

$$\frac{d\theta}{dF_{f,a}} = \frac{\sum_{i=1}^{C+A} \frac{\alpha_i}{F_i} - \frac{F_i}{F_i^2}}{\sum_{i=1}^{C+A} \frac{\alpha_i}{F_i} - \frac{\alpha_a}{F(\alpha_a - \theta)}}{\sum_{i=1}^{C+A} \frac{\alpha_i}{F_i} - \frac{G_i}{F(\alpha_i - \theta)^2}}$$
(4.4)

where  $F_{f,a}$  is the molar flow of singular point *a* in the feed and volatilities are with respect to the same reference component (singular point).

If singular point a is a heavy key (HK) component or heavier than heavy key (HHK) component, it appears only in the bottom product of the column carrying out a sharp split. Therefore, its flowrate in the feed will not affect the composition and flowrate of the distillate. From Equation (4.2), it can be derived:

$$\frac{dV_{\min,a}}{dF_a} = D \sum_{i=1}^{C+A} \frac{\alpha_i \frac{D_i}{D} \frac{d\theta}{dF_a}}{(\alpha_i - \theta)^2}$$
(4.5)

Substituting  $\frac{d\theta}{dF_{f,a}}$  by Equation (4.4), it can be obtained:

$$\frac{dV_{\min,a}}{dF_{a}} = D\sum_{i=1}^{C+A} \left( \frac{\alpha_{i} \frac{D_{i}}{D}}{(\alpha_{i} - \theta)^{2}} \frac{\sum_{i=1}^{C+A} \frac{\alpha_{i} \frac{-F_{i}}{F^{2}}}{\alpha_{i} - \theta} - \frac{\alpha_{a}}{F(\alpha_{a} - \theta)}}{\sum_{i=1}^{C+A} \frac{\alpha_{i}F_{i}}{F(\alpha_{i} - \theta)^{2}}} \right)$$
(4.6)

According to Equation (4.6), the effect of recycle with the composition of another HK or HHK component, component **b**, can be written as:

$$\frac{dV_{\min,b}}{dF_{b}} = D\sum_{i=1}^{C+A} \left( \frac{\alpha_{i} \frac{D_{i}}{D}}{(\alpha_{i} - \theta)^{2}} \frac{\sum_{i=1}^{C+A} \frac{\alpha_{i} \frac{-F_{i}}{F^{2}}}{\alpha_{i} - \theta} - \frac{\alpha_{b}}{F(\alpha_{b} - \theta)}}{\sum_{i=1}^{C+A} \frac{\alpha_{i}F_{i}}{F(\alpha_{i} - \theta)^{2}}} \right)$$
(4.7)

Assume the flowrate change of the two recycles are same,  $dF_a = dF_b$ , from Equations (4.6) and (4.7), it can be derived:

$$\frac{dV_{\min,a} - dV_{\min,b}}{dF_b} = D\sum_{i=1}^{C+A} \left( \frac{\alpha_i \frac{D_i}{D}}{(\alpha_i - \theta)^2} \frac{\frac{(\alpha_a - \alpha_b)\theta}{F(\alpha_a - \theta)(\alpha_b - \theta)}}{\sum_{i=1}^{C+A} \frac{\alpha_i F_i}{F(\alpha_i - \theta)^2}} \right)$$
(4.8)

From Equation (4.8), it can be seen that, when  $\alpha_a > \alpha_b$ ,  $dV_{\min,a} > dV_{\min,b}$ . Otherwise, if  $\alpha_a < \alpha_b$ , then  $dV_{\min,a} < dV_{\min,b}$ . This means that recycling a HHK component is better than recycling a HK component, *i.e.* the heavier the recycled component, the better. Where, a component can be either a pure component or an azeotrope.

If component a is a light key (LK) component or lighter than light key (LLK) component, it only appears in the distillate and will not affect the composition and flowrate of the bottom product. From Equations (4.3) and (4.4), it can be derived:

$$-\frac{dV_{\min,a}}{dF_{a}} = B\sum_{i=1}^{C+A} \left( \frac{\alpha_{i} \frac{B_{i}}{B}}{(\alpha_{i} - \theta)^{2}} \frac{\sum_{i=1}^{C+A} \frac{\alpha_{i} \frac{-F_{i}}{F^{2}}}{\alpha_{i} - \theta} - \frac{\alpha_{a}}{F(\alpha_{a} - \theta)}}{\sum_{i=1}^{C+A} \frac{\alpha_{i}F_{i}}{F(\alpha_{i} - \theta)^{2}}} \right)$$
(4.9)

To compare the effect of this recycle stream with that of another recycle stream, which has the same recycle flowrate and the composition of singular point  $\boldsymbol{b}$ , another LK or LLK singular point, Equation (4.10) can be obtained:

$$-\frac{dV_{\min,a} - dV_{\min,b}}{dF_{b}} = B\sum_{i=1}^{C+A} \left( \frac{\alpha_{i} \frac{B_{i}}{B}}{(\alpha_{i} - \theta)^{2}} \frac{\frac{(\alpha_{a} - \alpha_{b})\theta}{F(\alpha_{a} - \theta)(\alpha_{b} - \theta)}}{\sum_{i=1}^{C+A} \frac{\alpha_{i}F_{i}}{F(\alpha_{i} - \theta)^{2}}} \right)$$
(4.10)

From Equation (4.10), it can be seen that, when  $\alpha_a > \alpha_b$ ,  $dV_{\min,a} < dV_{\min,b}$ . Otherwise, if  $\alpha_a < \alpha_b$ , then  $dV_{\min,a} > dV_{\min,b}$ . This means that recycling a LLK component is better than recycling a LK component, and the lighter the recycled component, the better.



Fig. 4.17 A split with two downstream recycles. The two recycles have the singular point compositions of HK (R3) and HHK (R5).

For the Type A split 1/3-4-5 shown in Fig. 4.17, the effects of two different recycles will be analysed. This split is used to separate a quaternary mixture of acetone, chloroform, benzene and toluene; its LK and HK components are singular points **1** and **3**, respectively. The bottom product, which lies in product region 3-4-5, can be further separated into downstream products with compositions of singular points **2**, **3**, **4** and **5**. As shown in Fig. 4.17, the two downstream products with compositions of singular point **3** (HK) and singular point **5** (HHK), are recycled to the feed of this split. Since these two recycles are the downstream products of the bottom, the distillate flowrate, which is the ratio between the minimum reflux ratio and the minimum vapour flowrate, is not affected by these two recycles. Therefore, the minimum reflux ratio is proportional to the minimum vapour flowrate.

When both flowrates of these two recycles, which are represented by R3 and R5, are equal to 0, split 1/3-4-5 is feasible. Its minimum reflux ratio is 5.93 calculated using Underwood equations or 6.27 using HYSYS. If R5, the flowrate of recycle with the composition of singular point **5**, is increased to 20kmol/h, the minimum reflux ratio of this split decreases, while if R3, the flowrate of recycle with the composition of singular point **3**, is increased to 20kmol/h, the minimum

reflux ratio increases, as shown in Table 4.7. These results are in good agreement with the previous analysis.

	Rectycle		Mole fra	R <sub>min</sub>			
Case	flowrate, kmol/h	Component	Feed	Distillate	Bottom	Underwood*	HYSYS
	D2-0	Acetone	0.2270	0.9901	0.0610		
Base	R3=0	Chloroform	0.2730	0.0027	0.3318	5 93	6 27
case	R5=0	Benzene	0.1786	0.0072	0.2159	0.00	0.27
		Toluene	0.3214	0.0	0.3913		
		Acetone	0.2409	0.9901	0.1023		
Increase	R3=20	Chloroform	0.3216	0.0046	0.3802	6 69	7 68
R3	R5=0	Benzene	0.1562	0.0053	0.1842	0.03	7.00
		Toluene	0.2812	0	0.3333		
		Acetone	0.1986	0.9901	0.0520		
Increase	R3=0	Chloroform	0.2389	0.0025	0.2827	5 15	5 89
R5	R5=20	Benzene	0.1562	0.0014	0.1838	5.15	0.09
		Toluene	0.4062	0	0.4815		

Table 4.7 Effect of HK and HHK recycles on the split shown in Fig. 4.17.

\* Relative volatilities recalculated for each case.

The effect of recycles on the performance of a column is analysed in terms of the minimum vapour flowrate. However, in a distillation sequence, a recycle will affect all the columns included in the loop formed by it. The singular point contained in a recycle may be the LLK component of one of these columns, but the LK, HK or HHK component of another column. Therefore, a recycle can have different effects on the columns involved in the recycle loop formed by it. In a distillation sequence, to identify the effect of a recycle stream, all the columns included in the corresponding loop formed by this recycle need to be analysed. However, it is impossible to carry out this analysis for an unknown recycle flowrate. Therefore, recycles cannot be evaluated without quantifying their effect on the performance of the sequence.

For a distillation sequence, in which there are a few columns, or sometimes only one column, which have much higher energy demand than the others, the effect of a recycle on this sequence can be reflected by its effect on these columns.

#### 4.4.6. Procedure for screening singular recycles

In Section 4.4.5, the effect of recycles on the performance of columns is analysed. However, the effect of recycles on the distillation sequence depends on the effect on the performance of all the columns included in the recycle loop, as well as on the flowrate.

In Section 4.4, the requirements of different types of splits on recycles are analysed from two aspects, feasibility and component recovery. According to these analysis, the following rules, which can be used to guide the selection of recycles in distillation sequences, can be derived:

- For a DBC split with feed composition lying in the region of feasible feed compositions, RP type recycles can be recycled to its feed. If it is a Type B split, RB type recycles can also be recycled to its feed.
- For a Type A split, upstream of a DBC split, which breaks the azeotrope that causes the distillation boundary crossed by this DBC split, RB type recycles of this DBC split can be recycled to its feed. Otherwise, no recycles to its feed are needed.
- 3. For a Type B split, the downstream products of its distillate with compositions of non-HDSP and the downstream products of its bottom product with compositions of non-LDSP can be recycled to its feed. If the Type B split is upstream of a DBC split and breaks the azeotrope that causes the distillation boundary crossed by this DBC split, RB type recycles of this DBC split can be recycled to its feed.
- 4. For a Type C split, RBC type recycles, which have the compositions of singular points lying on the compartment boundary crossed by it, can increase its feasibility. If the Type C split is upstream of a DBC split and breaks the azeotrope that causes the distillation boundary crossed by this DBC split, RB type recycles can be recycled to its feed.

These four rules account for the requirements of DBC splits, Type A splits, Type B splits and Type C splits. DBC splits are either Type A or Type B splits with the special characteristics that they cross a distillation boundary. For a distillation sequence, beneficial recycles with singular point compositions can be screened according to these four rules. With recycles selected in this way, each column and the whole sequence have the greatest possibility to be feasible.

According to these rules, a systematic procedure for screening singular recycles (recycles with singular point compositions) for a distillation sequence can be generated. This procedure is as follows:

- 1. Specify the distillation sequence.
- 2. Select a split from the sequence.
- Identify if the selected split is the final split or not. If yes, no recycles to its feed are needed, go to 9. Otherwise, classify this split (Type A, B, or C, DBC split) (Thong, 2001a) and go to 4.
- If it is a DBC split, identify its RB and RP type recycles. If it is a Type A split, recycle its RP type recycles to its feed. Otherwise, recycle both RB and RP type recycles to its feed. Then go to 9.
- 5. If it is a Type A split, no recycles to its feed are needed, go to 8.
- If it is a Type B split, identify the corresponding LDSP and HDSP. Recycle the downstream products of its distillate with the composition of non-HDSP singular points and the downstream products of its bottom product with the composition of non-LDSP singular points to its feed. Then go to 8.
- 7. If it is a Type C split, recycle its RBC type recycles (which have the composition of singular points lying on the compartment boundary crossed by it) to its feed. Go to 8.
- If the split is upstream of a DBC split and breaks the azeotrope that causes the distillation boundary crossed by this DBC split, recycle RB type recycles of this DBC split to its feed.

9. If not all splits in the sequence have been analysed, select an unanalysed split and go to 3.

10. Finish this screening procedure.





This procedure is applied to a distillation sequence separating the quaternary mixture of acetone, chloroform, benzene and toluene. The resulting recycle structure is shown in Fig. 4.18 (a). Compared with the corresponding recycle superstructure (Thong, 2000) shown in Fig. 4.18 (b), which has only recycles with singular point compositions, the simplified recycle structure has fewer recycle streams.

### 4.5. Recycles with the compositions of mixtures of several singular points

In Section 4.4, only singular recycles (recycles with the composition of singular points) are studied. Mixed recycles (recycles with the compositions of the mixtures of singular points) can also be used in a distillation sequence. These recycles are generally intermediate streams, rather than final products, of a distillation sequence. For a sequence, if a mixed recycle is recycled to the feed of a split instead of several singular recycles, the cost of the sequence can possibly be reduced. The reason is that fewer columns can be included in the recycle loop than when only singular recycles are used.

In a distillation sequence, there are many potential mixed recycles and each candidate can be recycled to several destinations. Since each recycle is a mixture of several singular points, it is difficult to evaluate whether it will benefit a split.

Singular recycles in a distillation sequence separating an azeotropic mixture, can be screened using the procedure introduced in Section 4.4. These selected recycles indicate which singular points can benefit the feasibility or component recovery. Based on this, promising mixed recycles can be evaluated.

For a mixed stream (stream with the composition of a mixture of several singular points), if all its downstream final products (with the composition of each of the singular points included in it) can be recycled to the feed of a split, this stream can also be recycled to the feed of this split. This kind of recycle can possibly reduce the cost of a sequence. Otherwise, if there is at least one downstream final product that cannot be recycled to a split, the stream that is a mixer of these singular points should not be recycled, either. The reason is that, the singular points that cannot be recycled may reduce, or even completely counteract the benefit of recycling the other singular points.

Based on the recycle structure with only recycles with singular point compositions, a procedure for selecting mixed recycles is proposed as follows:

122

- 1. Select an intermediate product of the distillation sequence which is a mixture of several singular points.
- 2. Identify all the singular points included in this stream
- 3. Based on the simplified recycle structure (of Section 4.4) with only singular recycles, check whether there is a feed, to which all downstream final products of the stream selected in Step 1 can be recycles. Only if there is such a feed, can the stream selected in Step 1 be recycled to this feed.
- 4. If not all intermediate streams have been analysed, select another one, and go to 2
- 0.2F 0.2F 0.1F 2 2 0.0F 0.0F 2-3 2-3 C3 1-3-4-5 1-<u>3-4-5</u> റാ C F F 3 3 3-4-5 3-4-5 C2 C2 4 4 4-5 4-5 C4 0.0F 0.0F 5 5 0.0F 0.0F 0.0F 0.0F Total cost: 1 162 259£/year Total cost: 1 426 060 £/year (a) (b)
- 5. Finish the procedure

Fig. 4.19 A four-column sequence with recycles: (a) simple recycle structure identified using the procedure proposed above; (b) recycle structure with one unnecessary recycle.

For the sequence shown in Fig. 4.18(a), the bottom product of column C2, is the mixture of singular points **4** and **5**. Since products **4** and **5** can both be recycled to the feed of column C1, the bottom product of column C2 can be recycled to the same destination. On the other hand, the distillate of column C2 cannot be recycled to the feed of column C1. Since it contains singular point **2**, which

should not be recycled to the feed of column C1. Fig. 4.19(a) shows the simplified recycle structure of this sequence with beneficial singular and mixed recycles. Using the sequence evaluation procedure introduced in Chapter 3, the minimum cost and the corresponding recycle flowrates can be found, and are also shown in Fig. 4.19. The only recycle used in the simplified sequence is the stream with the composition of singular point **3** and a flowrate of 0.2F. The performance of the optimised sequence is, in this case, not affected by the option of the mixed recycle containing singular point **4** and **5**. If the distillate of column C2 is also recycled to the feed of column C1 (with a minimal flowrate of 0.1F), as shown in Fig. 4.19 (b), the minimum total cost of the sequence increases by around 23%.

#### 4.6. Conclusions

In a distillation sequence separating azeotropic mixture, recycles are always needed. According to compositions, recycles can be classified into two types, singular recycles and mixed recycles. Singular recycles have the compositions of singular points; mixed recycles are the mixtures of singular points. Recycles allow repeated separation tasks to be avoided. Recycle streams can also help to break azeotropes and adjust product and feed compositions of a column.

Singular recycles are easily evaluated. Three types of splits, Type A, Type B and Type C splits (Thong and Jobson, 2001a), can exist in a distillation sequence. These three types of splits have different characteristics and thus need different types of recycles. Since distillation-boundary crossing (DBC) splits, which can be either Type A or Type B splits, have special characteristic of crossing a distillation boundary, these splits need specific analysis.

The feasibility of a DBC split depends on one or several upstream splits to produce the feed lying in the region of feasible feed compositions. This region is bounded by the linearly approximated distillation boundary and the curved distillation boundary. For a DBC split with feed composition lying in the region of feasible feed compositions, an RP type recycle should be recycled to its feed. While its RB type recycles could be recycled to its feed only when it is a Type B split. If the feed composition of the DBC split does not lie in the region of feasible feed compositions, this DBC split is infeasible, which no recycles to its feed can change.

Type A splits are always feasible and do not need recycles to their feed to adjust feasibility. A Type B split is feasible, but not for all pairs of product compositions lying in the corresponding product regions. Therefore, recycles to its feed are needed. The rectifying and stripping section profiles of a Type B split approach two different saddle points, the HDSP and LDSP, respectively. Recycling the downstream products of its distillate with non-HDSP composition or the downstream products of its bottom product with non-LDSP compositions will increase its feasibility.

Type C splits cross compartment boundaries and are only potentially feasible. Even for a feasible Type C split, not all pairs of product compositions in the corresponding product regions are feasible. To increase the feasibility of a Type C split, RBC type recycles (which have the composition of singular points lying on the compartment boundary crossed by the split of interest) can be recycled to its feed.

When a split, either Type A, Type B or Type C split, is upstream of a DBC split and breaks the azeotrope that causes the distillation boundary crossed by this DBC split, RB type recycles can be recycled to its feed and could improve the recovery of the constituents of the azeotrope.

Different recycles also have different effect on splits. With azeotropes treated as pseudo components, the Underwood equations can be used to analyse the effect of different recycle options on the performance of column, in terms of the minimum vapour flowrate. It was found that recycling a heavier than heavy key (HHK) component is better than recycling a heavy key (HK) component, and the heavier the recycled component the better. Similarly, recycling a lighter than light key (LLK) component is better than recycling a light key (LK) component,

and the lighter the recycled component the better. Here, component can be either a pure component or an azeotrope. Since a recycle affects more than one column in a sequence, results cannot be used to selecting promising recycles for a distillation sequence.

Rules for screening mixed recycles are based on the analysis of singular recycles. All recycles that will benefit either the feasibility of splits or the recovery of azeotrope constituents can be systematically identified.

In this chapter, recycle options are only analysed from two aspects, the feasibility of the DBC split and the recovery of azeotrope constituents, but not the total cost. The recycle structure generated using the two screening procedures, may not lead to cost-optimal solutions. For a distillation sequence separating an azeotropic mixture, the feasibility of each split and the recovery of desired components are most important. Only when these two conditions are satisfied, can the total cost of a sequence be taken into account. Therefore, identifying recycles this way is reasonable. The screening procedures are applicable to distillation sequence separating homogeneous azeotropic mixtures with any number of components. Once the recycle structure of a distillation sequence has been generated, the total cost of the flowsheet can be minimised by optimising all recycle flowrates.

### Reducing the number of sequence alternatives

#### 5.1. Introduction

Many potential distillation sequences can be used to separate an azeotropic mixture; the number of these sequences increases as the number of components increases. In each sequence, there are many candidate recycle options, which make the sequence synthesis an iterative procedure. The synthesis of alternative sequences with recycles is an enormous task, especially for multicomponent azeotropic mixtures.

Using the procedure proposed by Thong and Jobson (2001c), all potential sequences that can be used to separate a multicomponent azeotropic mixture into its pure components can be identified. For each of these identified sequences, simple recycle structures can be determined using the procedure proposed in Chapter 4. However, too many potential sequences can be generated, for example, 46 sequences can be identified for an equimolar quaternary mixture of methyl acetate, methanol, ethanol and 2-propanol. It is time-consuming to identify one or a few promising sequences through evaluating all these sequences with recycles, even using the shortcut column design method proposed in Chapter 3. Therefore, it is necessary to eliminate the number of alternative sequences with promising ones remaining.

In this chapter, a two-step procedure is proposed for reducing the number of potential sequences with promising sequences screened out. The first step is preliminary screening. In this step, distillation sequences including infeasible or sloppy splits will be eliminated. Since not all sequences including sloppy splits are outperformed by sequences including only sharp splits, promising

127
sequences containing sloppy splits will be identified in the second step based on the evaluation of sequences containing only sharp splits. Using this two-step procedure, the number of distillation sequences can be significantly reduced with promising sequences screened out using simple calculations.

### 5.2. Preliminary screening of distillation sequences

In the distillation sequences identified using the procedure proposed by Thong and Jobson (2001c), not all splits are feasible. Since an infeasible split will result in the sequences including it being infeasible, it is necessary to identify infeasible splits, so that infeasible sequences including these splits can be eliminated without further investigation. Furthermore, many sloppy splits are included in the identified sequences. Sloppy splits will increase the number of columns and the complexity of a distillation sequence; sequences including sloppy splits are generally outperformed by those including only sharp splits, and are not preferred in practice. Therefore, sequences including either infeasible splits or sloppy splits will be eliminated in the first step.

## 5.2.1. Eliminating distillation sequences including infeasible splits

Three types of splits, Type A, Type B and Type C, are included in the distillation sequences generated by the procedure of Thong and Jobson (2001c). In this section, the feasibility characteristics of these three types of splits will be analysed. Then, an efficient feasibility test method is proposed, and the sequences including infeasible splits will be eliminated.

### 5.2.1.1. Feasibility characteristics of different types of splits

A Type A split satisfies the common saddle criterion of Rooks *et al.* (1998), as its two products lie in the same compartment and its two section profiles approach the same saddle point. In the potential sequences identified using the procedure of Thong and Jobson (2001c), only the product regions are known for each split. According to the work of Thong and Jobson (2001a), Type A splits are feasible for all pairs of product compositions in the corresponding product regions. Therefore, it is not necessary to test the feasibility of Type A splits.

Type B splits do not satisfy the common saddle criterion. The section profiles of a Type B split approach two different saddle points, heavy difference saddle point (HDSP) and light difference saddle point (LDSP). Because of this, Type B splits are feasible, but not for all pairs of product compositions in their product regions (Thong and Jobson, 2001a). In other words, there is at least one pair of feasible product compositions lying in its product regions. Therefore, for a Type B split in a distillation sequence, a feasible pair of product compositions can always be found with appropriate recycles. According to the analysis in Chapter 4, this can be achieved through recycling to the column feed the downstream products of its distillate with compositions of non-HDSP singular points and the downstream products of its bottom product with compositions of non-LDSP singular points. Therefore, the feasibility of Type B splits does not need to be tested either.

Unlike Type A and Type B splits, Type C splits cross compartment boundaries; their two products lie in two different compartments, which have same nodes, but different saddles. Type C splits do not satisfy the common saddle criterion and so are only potentially feasible. This means that a Type C split can be either feasible or infeasible, and it is necessary to test for the feasibility. The procedure for the feasibility test is described in the following section.

### 5.2.1.2. Feasibility test for Type C splits

In a distillation sequence, recycles can be used to adjust the product compositions of a Type C split and thus can adjust its feasibility. As discussed in Chapter 4, for a Type C split in a sequence, without taking into account the breaking of azeotropes or crossing distillation boundaries, recycling its downstream product to the feed of its upstream split will have the same effect on this Type C split as recycling the same stream to its feed. Therefore, to simplify the analysis of the effect of recycles on the feasibility of a Type C split, only recycles to the feed of a Type C split need to be accounted for. Another simplification is that only recycles with singular point compositions will be considered. Since several such recycles mixed together have the same effect as a recycle with the composition of a mixture of singular points, this simplification will not affect the feasibility analysis or test.

For a feasible Type C split, there is at least one pair of feasible product compositions. In a distillation sequence, this pair of feasible product compositions can be obtained using suitable recycles. On the other hand, for an infeasible Type C split, there is no feasible pair of product compositions in its product regions and no recycles can change that. According to this, the feasibility of Type C splits can be tested.

As discussed in Chapter 4, some recycles can increase the feasibility of Type C splits, while some others have the opposite effect. For a Type C split with recycles that can enhance its feasibility, if no feasible product compositions cannot be found for a certain range of recycle flowrates, this split is infeasible, otherwise, it is feasible.

Although a Type C split can appear in several identified distillation sequences, in different sequences, it, together with its downstream splits, can generally produce the same downstream products, some of which are desired products. The downstream recycles of a Type C split can be classified into two types, RBC type and RNBC type, according to their compositions. RBC type recycles have the compositions of singular points lying on the compartment boundary

crossed by the Type C split of interest, RNBC type recycles have the compositions of singular points and are not lying on this compartment boundary. Recycling RBC type recycles to the feed of a Type C split can make its product compositions move towards compartment boundary and enhance its feasibility. The bigger the flowrates of this type of recycles, the nearer the product compositions will lie to the compartment boundary and the more likely this Type C split is to be feasible. If the Type C split of interest is infeasible with a set of large RBC recycles, this Type C split must be infeasible for the specified range of recycle flowrates. Once an infeasible Type C is identified, all sequences containing this split can be eliminated.



Fig. 5.1 Quaternary system of Methyl acetate, Methanol, Ethanol and 2-Propanol. The composition space is separated into two compartments by compartment boundary 1-4-5 (Thong and Jobson, 2001c).

The quaternary system of methyl acetate, methanol, ethanol and 2-propanol shown in Fig. 5.1, serves as an illustrative example. This system is separated into compartments 1-3-4-5 and 1-2-4-5 by compartment boundary 1-4-5. To separate an equimolar feed into pure components, 46 sequences can be identified using the procedure proposed by Thong and Jobson (2001c) and are shown in Fig. 5.2. Six Type C splits, 1-3/2-4, 1-2/3-4, 1-3/2-4-5, 1-2/3-4-5, 1-3/2-5, 1-3/2-5, 1-

4/2-4-5 and 1-2-4/3-4-5 are contained in these sequences. In different sequences, each Type C split has same final products with singular point compositions.







For each of the Type C splits, the compositions of the downstream products, in terms of pure components, are known. The final product flowrates can be calculated by a mass balance over the sequences. With the flowrates of RBC type recycles taken as the maximum allowable values, e.g. 3F, where F is the molar flowrate of the feed, the product compositions of the Type C split of interest can be calculated according to the compositions and flowrates of its

downstream product compositions and downstream recycles. Then, the feasibility of this split can be tested using the boundary value method.



Final-product composition estimates								
	1	2	3	4	5			
Methyl acetate	0.66	0.98	0.02	0	0			
Methanol	0.34	0.02	0.98	0	0			
Ethanol	0	0	0	0.98	0.02			
2-propanol	0	0	0	0.02	0.98			

Fig. 5.3 Simplified connection between Type C split 1-2/3-4-5 and its downstream products.

Fig. 5.3 shows the simplified connection between Type C split 1-2/3-4-5 and its downstream products. The feed to be separated by split 1-2/3-4-5 is an equimolar mixture with flowrate *F*. The desired products are streams with composition of singular points **2**, **3**, **4** and **5**, and the purity of each product is 98%. With the volatility order as a guide, the desired product compositions can be specified, as shown in Fig. 5.3. Therefore, the desired product flowrates can be calculated by mass balance. Here, the flowrate of each desired product is 0.25*F*. Among the possible downstream products, streams with compositions of singular points **1**, **3** and **4** can be recycled as RBC type recycles. If we set the flowrate of these recycles at the upper bound, 3*F*, the product compositions of this Type C split can be calculated according to mass balance. With these recycle connections and flowrates, this Type C split is most likely to be feasible.

Using the boundary value method, the feasibility of this Type C split can be tested. The 1-2/3-4-5 split is found to be feasible.

The whole feasibility test procedure of Type C splits is as follows:

- 1. Specify a Type C split, its downstream product compositions, and the upper bounds of flowrates of possible recycles.
- 2. Identify the streams that can be recycled as RBC type recycles and recycle these streams to the feed of the Type C split.
- 3. Set the flowrates of selected recycle streams to the upper bounds and calculate the product compositions of the Type C split.
- 4. Use boundary value method to test the feasibility.
- 5. With these recycles, if the boundary value method shows this Type C split is feasible, then it is feasible. Otherwise, this Type C split is infeasible.

In step 4, other feasibility test methods such as the shortcut column design method proposed in Chapter 3 and the rectification body method (Bausa *et al.*, 1998), can also be used to test the feasibility of splits. If the shortcut method is used, the criteria by which a split is judge to be 'difficult' need to be specified. However, it is difficult to specify appropriate criteria. In this work, the boundary value method is used instead of the other two methods. The reason is that the boundary value method is a rigorous method and can give better results than the shortcut method, and the rectification body method. Since only one set of recycle flowrates needs to be tested in the above procedure, using the boundary value method is still computationally efficient.

If the test shows that the Type C split is infeasible, sequences including this Type C split can be eliminated. For the potential sequences shown in Fig. 5.2, the feasibility of the six Type C splits contained in these identified sequences is tested. The upper bound of the flowrate of each recycle is set to be 3F (where *F* is the feed flowrate). The feasibility tests show that Type C splits 1-2/3-4, 1-

2/3-4-5, 1-2-4/3-4-5 are feasible, while splits 1-3/2-4, 1-3/2-4-5, 1-3-4/2-4-5 are infeasible. Infeasible splits are shaded in Fig. 5.2. 26 sequences including one or two of these infeasible Type C splits are infeasible and are eliminated. After eliminating the infeasible sequences, the 20 sequences shown in Fig. 5.4 remain.



Fig. 5.4 20 feasible sequences that can separate the quaternary mixture shown in Fig. 5.1 into pure components. Shaded splits are sloppy splits.

#### 5.2.2. Eliminating sequences containing sloppy splits

With azeotropes treated as pseudo components, a column separating a *C*-component azeotropic mixture with *A* azeotropes can be taken as separating a (C+A)-component non-azeotropic mixture. Correspondingly, sharp and sloppy splits can be classified according to the distribution of pseudo components (singular points) rather than pure components. A split, in which no pair of singular points appears in both products is defined as a sharp split. This means that no singular point distributes between the distribute and the bottom product of a sharp split. Otherwise, the split is sloppy. Fig. 5.5 shows an example of a sharp and a sloppy split. In terms of singular points, there is no overlap between the two products of split I, which is a sharp split. Split I performs sharp separation between the distillate and bottom product, so this split is sloppy. Split II performs a sharp split between A and C but a sloppy split between A and B.



Fig. 5.5 Examples of a sharp split (Split I) and sloppy split (Split II). A, B and C denote singular points.

Among the distillation sequences identified using the procedure of Thong and Jobson (2001c), some sequences contain only sharp splits, while the others contain one or several sloppy splits. Since sequences containing sloppy splits includes more columns and are more complex than those containing only sharp splits, such sequences are generally outperformed by those containing only sharp splits and are not preferred. For example, the two distillation sequences shown in Fig. 5.6 can be used to separate the quaternary mixture of acetone (1), chloroform (2), benzene (4) and toluene (5) into its pure components. An

azeotrope (3) exists between acetone (1) and chloroform (2). All the splits included in Sequence *a* are sharp splits. When sharp split 1/3-4-5 of the Sequence *a* is replaced by the sloppy split 1-3/3-4-5, to recover all pure components, an additional split (1/3) is needed, giving Sequence *b*. Sequence *b* contains one more split than Sequence *a*. All possible recycles identified using the procedure proposed in Chapter 4, are also shown for both sequences in Fig. 5.6. Clearly, flowsheet *b* is more complex than flowsheet *a*, as Sequence *b* has one more column and one more recycle than Sequence *a*.



Sequence a



Fig. 5.6 Two flowsheets that can be used to separate quaternary mixture of acetone, chloroform, benzene and toluene. Sequence *a* contains only sharp splits; Sequence *b* contains sloppy splits.

Since distillation sequences including sloppy splits are seldom needed in industry, such sequences will be eliminated, so that the number of sequences identified using the procedure of Thong and Jobson (2001c) can be further reduced. For example, of the 20 sequences shown in Fig. 5.4, eliminates all the sequences including sloppy splits, which are shown in shade, only three sequences remain. These are shown in Fig. 5.7.



Fig. 5.7 All sequences containing only feasible sharp splits, that can separate the quaternary mixture shown in Fig. 5.1 into pure components.

With all sequences containing infeasible or sloppy splits eliminated, the number of sequences identified using the procedure of Thong and Jobson (2001c) is significantly reduced. However, it is expected that some sequences containing sloppy splits may outperform sequences containing only sharp splits. Therefore, it is necessary to identify promising sequences that contain sloppy splits, as discussed in the following section.

# 5.3. Identification of promising sequences containing sloppy splits

Some sequences containing feasible sloppy splits may outperform sequences containing only sharp splits. Such sequences can be identified through evaluating sequences containing feasible sloppy splits eliminated initially. However, because of the large number of possible sequences and recycles, the evaluation of these sequences, even using the shortcut column design method proposed in Chapter 3, is time-consuming. For example, it is time-consuming to evaluate the 17 sequences containing feasible sloppy splits shown in Fig. 5.4.

For sequences separating non-azeotropic mixtures, heuristics, derived from case studies (Lockhart, 1947; Harbert, 1957; Heaven, 1969), can be used to

quickly identify promising sequences, with low capital and operating costs. One of the proposed heuristics is that separations where the relative volatility of the key components is close to unity should be performed in the absence of nonkey components. Put in another way, it means that the most difficult separations should be reserved until last in a sequence (King, 1971). With azeotropes taken as pseudo components, this heuristic allows promising distillation sequences containing sloppy splits to be identified.

For a sharp split in a sequence, if the relative volatility between the two key components is near unity, this split is difficult. According to the heuristic mentioned above, this split should be reserved until last in a sequence. Therefore, if this difficult sharp split is not the final split of the sequence, a sloppy split between the two key components, together with one or several sharp splits, one of which perform sharp splits between the two key components, can be used to replace this difficult sharp split. Among all the splits used to replace a difficult sharp split, the sharp splits are downstream of the sloppy split. The introduction of the sloppy split allows the difficult split to be carried out in the absence of non-key components, thus the resulting sequence may require less energy. However, the resulting sequence contains more columns and potentially more recycles than the distillation sequence containing only sharp splits, and thus may need more capital investment. Therefore, the total annualised cost of the resulting sequence may or may not cost less than the sequence containing only sharp splits. If a difficult sharp split is a final split with no further separation of its products, there is no advantage to introduce a sloppy split into the sequence.

For example, in Fig. 5.6, sharp split 1/3-4-5 in Sequence **a** is a difficult split if the relative volatility between its two key components, singular points **1** and **3**, is near unity. To get a potentially more economic sequence, sloppy split 1-3/3-4-5 and sharp split 1/3 are used to replace this difficult sharp split, and Sequence **b** emerges. Sequence **b** contains more columns and more recycles than Sequence **a**. However, the energy cost, as well as the total annualised cost of Sequence **b** may be less than that of Sequence **a**, because the difficult split

140

between singular points **1** and **3** is performed in the absence of other singular points.

If a sloppy split, together with its downstream sharp splits, is used to replace an easy sharp split of a distillation sequence, the easy sharp split will be carried out later in the resulting sequence. This disobeys the heuristic and furthermore, the resulting sequence will contain more columns and possibly more recycles. Therefore, the resulting sequence is unlikely to be more economic than the sequence containing only sharp splits.

It can be concluded that, through replacing a difficult sharp split of a distillation sequence by a sloppy split and its downstream sharp splits, the sequence that contains sloppy splits may cost less. A systematic approach to identify promising sequences containing sloppy splits is discussed in the following section.

# 5.3.1. Promising sequences can be identified based on the evaluation of sequences containing only sharp splits

After the preliminary screening, only a small number of sequences remain. For example, for the quaternary mixture shown in Fig. 5.1, only the three sequences (shown in Fig. 5.7) of the initial 46 sequences (shown in Fig. 5.2) remain. For each of these remaining sequences, the corresponding recycle structure can be determined and evaluated using the procedures introduced in Chapter 4 and Chapter 3, respectively. Thus, the set of recycle flowrates, for which the sequence of interest has the minimum cost, can be found. Difficult splits can be identified as those requiring a large number of stages or a large reflux ratio.

The total cost of a sequence may be reduced when its easy splits are kept unchanged and only difficult split is replaced by an appropriate sloppy split and the downstream sharp splits of this sloppy split. According to this, promising sequences containing sloppy splits can be identified. With a difficult sharp split between two singular points replaced by a sloppy split between these two singular points and the downstream sharp splits, the resulting sequence contains sloppy split and potentially outperforms the original one. The problem is how to identify appropriate sloppy and sharp splits that can be used to replace the difficult sharp split. This will be discussed next.

### 5.3.1.1. Identifying appropriate sloppy splits

Since changes on easy sharp splits will not benefit a distillation sequence, such changes should be avoided when using a sloppy split and its downstream sharp splits to replace a difficult sharp split. To achieve this, the distillate (or bottom product) of the introduced sloppy split should lie in the same compartment as that of the difficult sharp split.

As discussed in Chapter 4, Type B splits are sloppy splits. Therefore, in a distillation sequence, difficult sharp splits can only be Type A and Type C splits. Since the distillate (or bottom product) of the sloppy split, which, together with its downstream sharp splits, can be used to replace the difficult sharp split, should lie in the same compartment as that of the difficult sharp split, the sloppy split that can be used as one of the splits to replace a difficult sharp Type A split can be either Type A or Type B split, but cannot be a Type C split. Similarly, the sloppy split that can be used as one of the splits to replace a difficult sharp Type C split can be used as one of the splits to replace a difficult sharp Type C split can be used as one of the splits to replace a difficult sharp Type C split can be used as one of the splits to replace a difficult sharp Type C split can only be Type C split. An appropriate sloppy split can be identified by distributing proper singular points between the distillate and bottom products of the difficult sharp split to be replaced, as will be discussed in the following paragraphes.

The two products of a sharp Type A split always lie in the same compartment. The distribution of singular points in the two products depends on the volatility order of singular points in this compartment. Also, the light key (LK) and heavy key (HK) components are next to each other in volatility order. To identify the suitable sloppy split, which can be used as one of the splits to replace a difficult sharp Type A split between two key components, at least one of the two key components should distribute between the two products of this sloppy split.



Fig. 5.8 In quaternary system of methyl acetate, methanol, ethanol and 2-propanol, different types of sloppy splits can be obtained with different singular points distributed between the two products of sharp Type A split 1-3-4/5.

If only one key component is distributed, this sloppy split is still a Type A split as its two products still lie in the same compartment and only one singular point is distributed between them. If one key component together with one or several other components, which can be either key or non-key components, are distributed between the distillate and bottom, the sloppy split is more likely a Type B split. For example, split 1-3-4/5 shown in Fig. 5.8 is a sharp Type A split. The two key components are singular points **4** and **5**. With light key component **4** distributed between the top and bottom products, this split will change to sloppy Type A split 1-3-4/4-5, with distillate, DN and bottom product, BN If both singular points **3** and **4** are distributed between the top and bottom product, by If both sharp Type A split 1-3-4/5 will change to Type B split 1-3-4/3-4-5, with distillate, DQ and bottom product, BQ The rectifying and stripping section composition profiles approach saddle points **4** and **3**, respectively. Both splits 1-3-4/4-5 and

1-3-4/3-4-5 are feasible, tested using the feasibility test procedure of Thong and Jobson (2001a).

The two products of a Type C split lie in two compartments, which are separated by a compartment boundary and share the singular points lying on the compartment boundary. The two section profiles approach the difference saddle points of this split, which lie in only one of these two compartments. For a Type C split, at least one difference saddle point must appear in exactly one of the product. Otherwise, this split will not be a Type C split.



Fig. 5.9 A sharp Type C split (1-3/2-4-5) lying in quaternary system of methyl acetate, methanol, ethanol and 2-propanol.

For example, in the quaternary system of methyl acetate, methanol, ethanol and 2-propanol, shown in Fig. 5.9, the Type C split 1-3/2-4-5 crosses the compartment boundary 1-4-5. Distillate 1-3 lies in compartment 1-3-4-5, while the bottom product 2-4-5 lies in compartment 1-2-4-5. The rectifying section profile approaches difference saddle point **3**, which only lies in compartment 1-3-4-5, while the stripping section profile approaches the difference saddle point **2**, which only appears in compartment 1-2-4-5. If singular point **3** disappears from the distillate, then the Type C split 1-3/2-4-5 will change to split 1/2-4-5, which is a Type A split and lies in compartment 1-2-4-5. Similarly, if singular point **2** disappears from the bottom product 2-4-5, the Type C split will change to split 1-3/4-5, which is a Type A split and product 2-4-5. If singular 1-3-4-5. If singular point **2** disappears from the bottom product 2-4-5, the Type C split will change to split 1-3/4-5, which is a Type A split product 2-4-5. If singular point **2** disappears from the bottom product 2-4-5. If singular point **2** disappears from the bottom product 2-4-5. If Type C split will change to split 1-3/4-5. If saddle point **2** disappears from the bottom product 2-4-5. If Type C split will change to split 1-3/4-5.

point **2** (or **3**) appears in both the distillate and bottom products, the Type C split will be 1-2-3/2-4-5 (1-3/2-3-4-5), which is not a feasible split for this system.

Since at least one difference saddle point must appear in exactly one product of a Type C split, identifying a suitable sloppy Type C split, which can be used as one of the set of splits to replace a difficult sharp Type C split between two key components, cannot be achieved by distributing its difference saddle points, but only by distributing the common singular points, which lie on the compartment boundary, between the two products. For example, to identify a suitable sloppy Type C split that can be used as one of a set of splits to replace the sharp Type C split 1-3/2-4-5, which is shown in Fig. 5.9, singular point **2** and **3**, the difference saddle points, cannot be distributed between the distillate and bottom products. Singular point **4**, which only appear in the bottom product of split 1-3/2-4-5, lies on the compartment boundary and can be distributed into the distillate; the resulting sloppy Type C split 1-3-4/2-4-5 can be used as one of the splits to replace the sharp split 1-3/2-4-5.

As an illustrative example, the distillation sequence illustrated in Fig. 5.10 (a), which contains only sharp splits, is used to separate the equimolar quaternary mixture shown in Fig. 5.9. Recycles were selected according to the rules proposed in Chapter 4. Using the evaluation procedure introduced in Section 3.5, this sequence is evaluated with the best set of recycle flowrates determined, as shown in Fig. 5.10 (a). Table 5.1 presents the corresponding column design and cost data for this sequence. From this table, it can be seen that split 1-3-4/5 is a difficult split, requiring 164 stages with a reflux ratio of 5.1. This column is a good candidate to be replaced by an appropriate set of sloppy and sharp splits. The light key and heavy key components of this split are singular points **4** and **5**, respectively. According to the above analysis, sloppy Type A split 1-3-4/4-5, with singular point **4** distributing, can be used as one of the set of splits to replace sharp split 1-3-4/5.



Fig. 5.10 Distillation sequences that can be used to separate quaternary mixture of methyl acetate, methanol, ethanol and 2-propanol. (a) Distillation sequence contains only sharp splits; (b) Distillation sequence contains a sloppy split (1-3-4/4-5).

	Split	1-3-4/5		1-2/3-4		1/2		3/4		
	Reflux ratio	5.1		2.94		3.42		3.30		
	No. of stages	164		118		64		44		
(a)	Energy Cost, £/year	684 287 606		606 8	)6 840 4		433 654		164 438	
	Capital cost, £	1 407 392	2	899 2	39	526 240		306 089		
	Total annualised cost, £/year	2 9		2 935	35 540					
	Splits	1-3-4/4-5	,	1-2/3-4	1/	2	3/4		4/5	
	Reflux ratio	4.58		2.47	3.42		2.45		17.66	
(b)	Stage No.	42		102	64		45		88	
(D)	Energy Cost, £/year	522 629	5	33 188	433 654		54 133 455		346 903	
	Capital cost, £	412 904	7	23 458	526	240	299 728	8	574 134	
	Total annualised cost, £/year	2 815 317								

Table 5.1 Design results for the two distillation sequences shown in Fig. 5.10.

#### 5.3.1.2. Identifying appropriate sharp splits

After the appropriate sloppy split is identified, the sharp splits, which are downstream of this sloppy split, can be identified, so that these splits together with the sloppy split can be used to replace the difficult sharp split of a sequence.

For example, if sloppy Type A split 1-3-4/4-5 is used as one of the splits to replace the sharp split 1-3-4/5 of the sequence shown in Fig. 5.10 (a), the sharp splits, which are downstream of the newly introduced sloppy split 1-3-4/4-5, need to be identified. Since sloppy split 1-3-4/4-5 has the same distillate as the sharp split 1-3-4/5 and the downstream splits of the distillate of split 1-3-4/5 are all easy, these downstream splits can be kept unchanged. On the other hand, the bottom product of the sloppy split 1-3-4/4-5 is a mixture of singular points 4 and 5, and so is different from that of sharp split 1-3-4/5. To recover 2-propanol (5), the bottom product, 4-5, needs to be further separated, using split 4/5. Therefore, the pair of sloppy split 1-3-4/4-5 and sharp split 4/5 can be used to replace difficult sharp split 1-3-4/5; the resulting sequence is shown in Fig. 5.10 (b). The recycle structure of this sequence is screened and evaluated using the rules proposed in Chapter 4 and procedure proposed in Chapter 3, respectively; the results are shown in Table 5.1. It can be seen that the sequence containing sloppy split is more economic than that containing only sharp splits, even through one additional column is required.

For an identified sloppy split, there may be more than one option of downstream sharp splits. Each option together with the sloppy split can be used to replace a difficult sharp split and corresponds to a distillation flowsheet. A method to compare the performance of these alternatives is needed. For example, in the sequence shown in Fig. 5.10(a), sharp split 1-3-4/5 can also be replaced by sloppy split 1-3-4/3-4-5, which is a Type B split. The distillate of split 1-3-4/3-4-5 is same as that of split 1-3-4/5 and the downstream splits of the distillate of split 1-3-4/5 are all easy. Therefore, these downstream splits do not need to be

changed. However, the bottom product, 3-4-5, needs to be further separated. The two different options to carry out this separation are shown in Fig. 5.11.



Fig. 5.11 The two options, each of which together with sloppy split 1-3-4/3-4-5 can be used to replace the sharp split 1-3-4/5 of the sequence shown in Fig. 5.10 (a).

Once the sloppy split that can be used as one of the splits to replace a difficult sharp split is identified, the heuristic that one should separate last the components for which the relative volatility is near unity can also be used to identify promising sharp-split options. To apply this heuristic, the difficulty of the separation difficulty between different pairs of singular points needs to be evaluated. Fortunately, such information can be obtained from the results of the evaluation of sequence containing only sharp splits. Consider, for example, the two options shown in Fig. 5.11. Table 5.1 in the previous section presents design information for the sequence containing only sharp splits. It can be seen that it is difficult to separate singular points **4** and **5**, but easy to separate

singular points **3** and **4**. It follows that singular points **4** and **5** should be separated after singular points **3** and **4** have been separated, *i.e.* Option 2 is more promising than Option 1.

The introduction of sloppy split affects the downstream separation of the sequence of interest. When there is more than one difficult sharp split in a distillation sequence, the difficult sharp split, for which the upstream splits are all relatively easy, should be replaced first.

# 5.3.2. Procedure for identifying promising distillation sequences including sloppy splits

A procedure for identifying promising distillation sequences including sloppy splits is proposed, based on the analysis presented in Section 5.3.1:

- 1. Select a sequence from the remaining distillation sequences which includes only feasible sharp splits.
- 2. Select the recycle structure, specify the upper bound of the flowrate of each recycle streams, and the final product compositions.
- 3. Evaluate the sequence using the procedure proposed in Section 3.5.
- 4. Identify difficult splits according to reflux ratio and number of stages required by each column.
- 5. Select one of these difficult splits, for which the upstream splits are all relatively easy.
- Identity the corresponding sloppy splits, which can be used as one of the splits to replace this difficult sharp split, by distributing appropriate singular points between the two products, as introduced in Section 5.3.1.1.
- 7. For each of the sloppy splits identified in step 6, identify all options of downstream sharp splits, which, together with the sloppy split, can be

used to replace the difficult sharp split selected in step 2. Identify the best option using heuristics, as introduced in Section 5.3.1.2.

- 8. Identify if there is any other difficult sharp split, for which the upstream splits are all easy. If there is, go to 6.
- 9. Evaluate the resulting sequence that including sloppy splits.

For example, Fig. 5.7 presents the three sequences that remain after sequences containing infeasible or sloppy splits have been eliminated. The possible recycle streams for these three remaining distillation sequences can be identified, by the procedures presented in Sections 4.4.6 and 4.5, as shown in Fig. 5.12. The recycle flowrates corresponding to the minimum total annualised cost for each sequence, and corresponding column design parameters, can be determined using the procedure for sequence evaluation proposed in Section 3.5. Table 5.2 shows the column design parameters of each sequence; corresponding recycle flowrates are shown in Fig. 5.12.

Table 5.2 shows that the sharp splits 1-3-4/5, 1-2/3-4-5, 1-2/3-4 and 4/5 are difficult. Each of these splits has either a large number of stages (>100) or a large reflux ratio (>10). Since split 4/5 is a binary split between two singular points without downstream splits, it does not need to be replaced by a set of sloppy and sharp split. Split 1-2/3-4 is a Type C split and there is no feasible sloppy Type C split that can be used as one of splits to replace it (feasibility of splits is tested using the procedure of Thong and Jobson (2001a)). Split 1-3-4/5 is a Type A split 1-3-4/3-4-5. The two resulting distillation sequences are shown in Fig. 5.13. Split 1-2/3-4-5 is a Type C split that can be replaced by sloppy Type C split 1-2-4/3-4-5. The two resulting sequences including sloppy split 1-2-4/3-4-5 5 are also shown in Fig. 5.13.





Sequence **b** 



Sequence *c* 

Fig. 5.12 Recycle structure of sequences shown in Fig. 5.7. All the splits contained in these sequences are feasible sharp splits.

	Splits	1-3-4/5	1-2/3-4	1/2	3/4		
	Reflux ratio	5.1	2.94	3.42	3.30		
Sequence	Stage No.	164	118	64	44		
а	Energy Cost, £/year	684 287	606 840	433 654	164 438		
-	Capital cost, £	1 407 392	899 239	526 240	306 089		
	Total cost, £/year	2 935 540					
	Splits	1-2/3-4-5	1/2	3-4/5	3/4		
	Reflux ratio	3.32	3.42	13.96	3.30		
Sequence	Stage No.	105	64	62	44		
b	Energy Cost, £/year	671 231	433 654	1 111 195	164 438		
	Capital cost, £	863 736	526 240	730 517	306 089		
	Total cost, £/year						
	Splits	1-2/3-4-5	1/2	3/4-5	4/5		
	Reflux ratio	2.34	3.42	4.43	12.56		
Sequence	Stage No.	110	64	39	89		
С	Energy Cost, £/year	919 329	867 308	205 721	506 048		
	Capital cost, £	983 365	711 052	303 834	664 187		
	Total cost, £/year	3 385 886					

Table 5.2 results of the evaluation of flowsheets shown in Fig. 5.12.



#### Sequence c

Sequence d

Fig. 5.13 Four possibly promising flowsheets containing sloppy splits derived from sequences presented in Fig. 5.12. Sequence *a*: split 1-3-4/4-5 is sloppy; Sequence *b*: Split 1-3-4/3-4-5 is sloppy; Sequence *c* and Sequence *d*: split 1-2-4/3-4-5 is sloppy.

The four sequences are evaluated using the evaluation procedure proposed in Chapter 3 and the results are shown in Table 5.3. Comparing these results with those shown in Table 5.2, it can be seen that the total cost of the sequence can be reduced by replacing difficult sharp splits by appropriate sets of sloppy and sharp splits. For example, the costs of Sequence *a* and *b* shown in Fig. 5.13 are both less than that of the Sequence *a* shown in Fig. 5.12.

-										
	Splits	1-3-4/4-5	1-2/3-4		1/2	2		3/4		4/5
	Reflux ratio	4.58	2.47	2.47		3.42		2.45		17.66
Sequence <i>a</i>	No. of stages	42	102		64		45			88
	Energy Cost, £/year	522 629	533 188		433 654		133 455			346 903
	Capital cost, £/year	412 904	723 458		526 240		299 728			574 134
	Total cost*, £/year				2 815	317				
	Splits	1-3-4/3-4-5	1-2/3-4		1/2	3/	4	3/4-5		4/5
	Reflux ratio	0.51	2.47		3.42	2.4	45	2.37		17.66
Sequence	No. of stages	26	102		64	4	5	20		88
b	Energy Cost, £/year	150 142	533 188	4	33 654	133	455	55 64 936		346 903
	Capital cost, £/year	245 615	723 458	526 240 299		728 166 107		7	574 134	
	Total cost*, £/year	2 507 372								
	Splits	1-2-4/3-4-5	1/2-4 3-4		3-4/	/5		3/4		2/4
	Reflux ratio	1.55	3.88		6.46		2	2.45		1.43
Sequence	No. of stages	55	58		81		44			35
с	Energy Cost, £/year	607 280	752 962		419 948		133 455			91 949
	Capital cost, £/year	489 008	608 428		580 558		299 728			269 709
	Total cost*, £/year	2 754 737								
	Splits	1-2-4/3-4-5	1/2-4		3/4-5		4/5			2/4
	Reflux ratio	1.55	3.88		4.44		23.51			1.43
Sequence	No. of stages	56	59		37		88			36
d	Energy Cost, £/year	608 115	752 962		205 561		454 662			91 949
	Capital cost, £/year	489 244	608 428		300 563		634 342			269 709
	Total cost*, £/year	2 880 678								

Table 5.3 Results of the evaluation of sequences shown in Fig. 5.13.

\*Total annualised cost.

#### 5.4. Conclusions

Many potential distillation sequences can be used to separate a multicomponent azeotropic mixture; these sequences can be identified using the procedure proposed by Thong and Jobson (2001c). However, too many potential sequences can be generated, an efficient method is needed to eliminate the number of alternatives with promising sequences remain.

In this chapter, a two-step procedure is proposed for reducing the number of sequences identified using the procedure of Thong and Jobson (2001c). This procedure can efficiently eliminate infeasible and uneconomic distillation sequences with low computational demand. The first step of this procedure is preliminary screening, in which sequences containing infeasible splits are eliminated. The feasibility of splits is tested by an efficient procedure, the boundary value method or other feasibility tests, including the shortcut column design procedure described in Chapter 3, may be employed. Sequences including sloppy splits are also eliminated because they contain more columns and have more complex recycle structures than those containing only sharp splits. The set of flowsheet alternatives that remain is much smaller than the original set of options, and may be evaluated and optimised with respect to the total annualised cost easily.

In the second step, potentially alternative sequences containing sloppy splits are identified. The identification is based on the evaluation of the sequences not eliminated during the first step. For each difficult sharp split in these sequences, appropriate sloppy splits are identified according to the characteristics of the Type of the difficult split; each sloppy split together with one or several sharp splits is used to replace this difficult split. The resulting sequences containing sloppy splits and are potentially more economic than the original ones.

Using this two-step procedure, the distillation sequences containing only sharp splits and the potentially attractive sequences containing sloppy splits are identified. The number of distillation sequences identified using the procedure of Thong and Jobson (2001c) can thus be significantly reduced.

155

# Overview and application of sequence synthesis methodology

### 6.1. Introduction

In the preceding chapters, shortcut column design method, rules and procedures for screening of recycles and distillation sequences are proposed, respectively. Based on these methods and procedures, a systematic procedure for synthesising distillation sequences separating multicomponent azeotropic mixtures is proposed in this chapter. The proposed procedure can be used to screen a few promising sequences from those identified using the procedure of Thong and Jobson (2001c) and corresponding recycles. The approach is demonstrated by a case study in which a five-component mixture with two azeotropes is separated into its pure component products.

# 6.2. Systematic procedure for the synthesis of distillation sequences separating multicomponent azeotropic mixtures

To separate a multicomponent azeotropic mixture, all potentially feasible sequences and corresponding recycle superstructures can be identified using the algorithm proposed by Thong and Jobson (2001c). In each of these sequences, products of each column are specified in terms of product regions; recycles can change the composition of each product within corresponding product region and thus affect the total cost of each sequence. However, promising sequences cannot be distinguished from the set of sequences, where only recycle superstructures and product regions of each column are known. To

screen for promising sequences, the best performance of each sequence, corresponding to the best set of recycle flowrates, has to be found. Only by evaluating each distillation flowsheet (sequence and recycles), can the best set of recycle flowrates, with the minimum total annualised cost, be found.

The recycle superstructure for each distillation sequence can be generated using the procedure of Thong (2000). However, it is time consuming to evaluate such a recycle superstructure, since too many recycles are included and each recycle will make the evaluation with iterative. The rules and procedures proposed in Chapter 4 can be used to screen recycle structure with beneficial recycles without calculation. The resulting recycle structure is much simpler than the original recycle superstructure of Thong (2000). The best performance of each sequence and the corresponding best set of recycle flowrates can be determined using the sequence evaluation procedure proposed in Chapter 3, which employs the shortcut column design method to design each column. With recycle structures of all sequences, which are identified using the procedure of Thong and Jobson (2001c), screened and evaluated, promising flowsheets can be identified.

However, too many possible sequences can be identified using the procedure of Thong and Jobson (2001c). For example, 46 sequences can be identified to separate the equimolar quaternary mixture of methyl acetate, methanol, ethanol and 2-propanol. Although a simple recycle structure for each sequence can be determined using the rules and procedures proposed in Chapter 4, evaluation of all resulting flowsheets is still time-consuming.

The two-step procedure proposed in Chapter 5 can be used to identify promising sequences without evaluating all sequences identified using the procedure of Thong and Jobson (2001c). In the first step, the preliminary screening step, the feasibility of splits is assessed and sequences containing either infeasible or sloppy splits are eliminated; the number of sequences can be significantly reduced, without defining the recycle structure or evaluating each sequence. This step can be used to reduce the number of sequences from those identified using the procedure of Thong and Jobson (2001c). The

157

remaining sequences contain only feasible sharp splits and their recycle structures can be screened and evaluated using the rules and procedures proposed in Chapters 3 and 4.

However, some of the eliminated sequences containing sloppy splits may be promising. Such sequences are identified in the second step of the two-step procedure proposed in Chapter 5. First, all sequences containing feasible sharp splits (the remaining sequences of the preliminary screening step), are evaluated after recycle structures are generated. The sets of sloppy and sharp splits that can be used instead of particularly difficult sharp splits are investigated.

The overall procedure for systematically screening and evaluating promising sequences among those identified using the procedure of Thong and Jobson (2001c) is as follows:

- 1. Distinguish all Type C splits included in the sequences identified using the procedure of Thong and Jobson (2001c).
- Test the feasibility of Type C splits using the procedure proposed in Section 5.2.1.2, and eliminate all sequences containing one or several infeasible Type C splits.
- 3. Among the remaining sequences, identify and eliminate sequences containing sloppy splits.
- 4. For each remaining sequence, identify recycles with compositions of singular points or mixtures thereof, according to the procedure proposed in Sections 4.4.6 and 4.5.
- Evaluate each sequence using the procedure proposed in Section 3.5.1 (the shortcut column design method); determine the best set of recycle flowrates, corresponding total annualised cost and column design parameters.
- 6. Identify the promising sequences containing sloppy splits using the procedure proposed in Section 5.3.2.

- 7. For each sequence identified in step (6), identify all recycles according to the procedure proposed in Sections 4.4.6 and 4.5.
- 8. Evaluate each sequence with recycles determined in step (7), and determine the best set of recycle flowrates, corresponding total cost and column design parameters.

Only the main steps are listed above. Each step needs to be performed by a set of sub-steps. Duplicated sub-steps of two consecutive main steps should be avoided. For example, in the procedure proposed in Section 5.3.2, each sequence containing only sharp splits needs to be evaluated. However, in the procedure proposed above, each sequence is evaluated in step (5). Therefore, when performing step (6) (or the procedure proposed in Section 5.3.2), sequences containing only sharp splits need not be re-evaluated.

#### 6.3. Case study

In this section, sequences that can be used to separate a five-component mixture of acetone, benzene, 1-propanol, toluene and styrene are systematically synthesised using the procedure summarised above. The aim of these sequences is to separate the mixture with molar composition  $X_F = [0.2 \ 0.16 \ 0.17 \ 0.27 \ 0.2]^T$  into pure component products (purities of 95% are specified for all products).

In this five-component homogeneous azeotropic system, two azeotropes are found using DISTIL 5.0, and the transformation matrix can be constructed. The transformation matrix and all singular points are listed in Table 6.1. Using the procedure proposed by Rooks *et al.* (1998) and Thong *et al.* (2001a), it can be determined that the whole composition space of this system is a single distillation region, which is separated into three compartments, namely compartments 1-2-3-6-7, 1-2-4-5-7 and 1-2-4-6-7.

Singular	Components or	Boiling point Transformation matrix						riv		
point	azeotropes	Bonnig point								
1	Acetone	55.68°C		۲1	0	0	0	0	0	07
2	Benzene-1-Propanol	75.28°C			0	0	0	0	0	0
_				0	0.7863	1	0	0	0	0
3	Benzene	78.32°C	<i>M</i> =	0	0.2137	0	0.6489	1	0	0
4	1-Propanol-Toluene	92.66°C		0	0	0	0.3511	0	1	0
5	1-Propanol	96.83°C		0	0	0	0	0	0	1]
6	Toluene	110.18°C								
7	Styrene	144.95°C								

Table 6.1 Singular points in the five-component azeotropic mixture of acetone, benzene, 1-propanol, toluene and styrene.

Using the composition transformation procedure proposed in Chapter 3, it can be identified that the mixture with composition  $X_F = [0.2 \ 0.16 \ 0.17 \ 0.27 \ 0.2]^T$ , lies in compartment 1-2-4-6-7. The algorithm of Thong and Jobson (2001c) (incorporated in COLOM Version 1.7a) generates 5001 potentially feasible sequences, as listed in Appendix C, which can be used to separate this mixture into nearly pure components. The systematic procedure proposed in the previous section is used to identify and evaluate promising flowsheet alternatives.

Before using the systematic procedure proposed in the previous section, the compositions and flowrates of final products (products that cannot be further separated) need to be specified. According to the composition and flowrate of the mixture to be separated and the desired products, the flowrate of each desired pure product can be estimated. In this case, the desired products are streams with compositions of singular points **1**, **3**, **5**, **6** and **7**, respectively; their flowrates are 0.2F, 0.16F, 0.17F, 0.27F and 0.2F, respectively, where *F* is the flowrate of the mixture to be separated (100kmol/h). However, final products in different sequences are produced by different splits, and may contain different impurities with different concentrations. No reliable method exists that can be used to estimate the distribution of impurity concentrations before rigorous

design of each column. No method can be used to reliably estimate the distribution of impurities in the intermediate products, either.

In this case study, for a split producing final products, only key components are assumed to distribute between its distillate and bottom products; the mole fraction of the heavier key component in the distillate and of the lighter key component in the bottom product is set to be 0.05. This way, the final product compositions can be estimated. This allows the mass balance of the sequence to be closed with the distribution of impurities ignored in the columns that do not produce a final product. Thus, the product compositions of each column can be estimated easily. Since the Underwood and Fenske equations are not sensitive to impurity concentrations, this assumption will not have a significant effect on the results of the synthesis results.



Fig. 6.1 A distillation sequence identified using the method of Thong and Jobson (2001c) for the separation of five-component azeotropic mixture of acetone, benzene, 1-propanol, toluene and styrene.

For example, one of the sequences identified using the procedure of Thong and Jobson (2001c) is shown in Fig. 6.1. Recycles are screened according to the rules and procedures proposed in Chapter 4. In this sequence, column C3 perform a 2/3 split; its distillate and bottom product compositions in terms of

singular points can be written as (0, 0.95, 0.05, 0, 0, 0, 0) and (0, 0.05, 0.95, 0, 0, 0, 0). These compositions can easily be transformed into compositions in terms of pure components (using the composition transformation procedure developed in Chapter 3). Similarly, product compositions of column C5 and column C6 in terms of pure components can be calculated. Thus, the mass balance of columns C3, C5 and C6, can be closed, to obtain their feed compositions and flowrates. This then allows the mass balance of column C4 to be closed, as the feeds of column C5 and C6 are the distillate and bottom product of column C4, respectively. The feed of column C4 is the mixture of the bottom product of column C2 and two recycle streams. For a set of specified recycle flowrates, the bottom product composition and flowrate of column C2 can be calculated according to mass balance. Sequentially, the mass balance of the whole sequence can be closed.

Table 6.2 Feasibility of Type C splits included in the sequences separating a five-							
component azeotropic mixture.							
Type C split	Feasible?	Type C split	Feasible?				

Type C split	Feasible?	Type C split	Feasible?
2-3/4-6-7		1-2-3/4-6	$\checkmark$
2-3-6/4-6-7		1-2-4/2-3-6	$\checkmark$
2-3/4-6		1-2-3/2-4-6	
2-4/3-6	√	1-2-3/4-6-7	
4-5/6-7	√	1-2-3/2-4-6-7	
4-6/5-7	X	1-2-4-6/4-5-7	X
2-4-6/5-7	X	1-2-4-6/5-7	X
2-4-6/4-5-7	x	1-2-4-6/2-4-5-7	X
1-2-4/3-6	$\checkmark$		

Once final product compositions are estimated, the distillation sequences generated using the procedure of Thong and Jobson (2001) can be synthesised. Firstly, 17 Type C splits included in the sequences are identified, as listed in Table 6.2. The feasibility of each Type C split is tested using the feasibility test proposed in Section 5.2.1.2. The boundary value method is employed in this procedure. Since only one set of recycle flowrates needs to be tested, the test is computationally efficient. For each Type C split, the reflux

ratio is varied between 0.2 and 14.7 with step length 0.5. In this test, the upper bound of the flowrate of each recycle is set to be 2F, where F is the molar flowrate of the mixture to be separated (100kmol/h). The maximum allowable distance between the two section profiles of a feasible split is set to be 0.005. For an infeasible split, the distance between its two section profiles is always larger than this value. It takes about one minute to test the feasibility of each split (AMDXP 2000+, 512MB RAM). The results are shown in Table 6.2. It can be seen that six of the 17 Type C splits are infeasible. Each infeasible Type C split can appear in many sequences. For example, Type C split 1-2-4-6/2-4-5-7 appears in 768 sequences and Type C split 1-2-4-6/4-5-7 appears in 102 sequences. Among the original set of 5001 sequences, 3986 sequences containing one or several of these infeasible Type C splits are infeasible and are eliminated. Thereafter, among the remaining sequences, another 1012 sequences containing one or several sloppy splits are eliminated. In total, 4998 sequences containing infeasible or sloppy splits are eliminated and only 3 sequences containing feasible sharp splits are left, as shown in Fig. 6.2.



Fig. 6.2 Feasible sequences that can be used to separate the five-component azeotropic mixture of acetone, benzene, 1-propanol, toluene and styrene. Only sharp splits are contained in these sequences.
For each sequence shown in Fig. 6.2, recycles beneficial to the sequence are screened according to the algorithm proposed in Sections 4.4.6 and 4.5, and the resulting recycle structure is shown in Fig. 6.3. The flowrate of each of the recycle streams shown in Fig. 6.3 varies from 0 to 2F, with step length 0.2*F*. Each sequence is evaluated using the shortcut column design method proposed in Chapter 3 to design each column. The aim of the evaluation procedure is to search for the best set of recycle flowrates, corresponding to the minimum total annualised cost of the flowsheet. The results are obtained in less than 30 minutes (AMDXP 2000+, 512MB RAM). The best sets of recycles are shown in Fig. 6.3, and the corresponding column design results are shown in Table 6.3.



#### Sequence A1





Fig. 6.3 Recycle structures of the sequences shown in Fig. 6.2. Streams lying in different compartment are shown with different type of lines.

Column of Sequence A1	C1	C2	C3	C4	C5	C6		
Split	1/2-4-6-7	2-3/4-6-7	2/3	4-5/6-7	4/5	6/7		
Reflux ratio	3.81	2.76	3.39	0.98	4.28	1.04		
Number of stages	28	1470	25	53	30	16		
Energy cost, £/year	134 268	761 388	650 381	179 950	328 601	80 587		
Capital cost, £	263 040	13 274 500	414 920	366 042	320 195	186 828		
Total cost, £/year		I	7 077 0	15				
Column of Sequence A2	C1	C2	C3	C4	C5	C6		
Split	1-2-3/4-6-7	1-2/3	1/2	4-5/6-7	4/5	6/7		
Reflux ratio	1.09	0.49	3.17	0.79	4.28	1.81		
Number of stages	1 481	22	25	48	31	17		
Energy cost, £/year	279 207	138 526	159 901	229 377	492 899	108 710		
Capital cost, £	9 313 040	248 048	266 058	360 001	365 409	210 953		
Total cost, £/year			4 996 4	56				
Column of Sequence A3	C1	C2	C3	C4	C5	C6		
Split	1-2-3/4-6-7	1/2-3	2/3	4-5/6-7	4/5	6/7		
Reflux ratio	1.06	2.97	2.13	1.0	4.28	3.06		
Number of stages	1446	27	30	44	31	17		
Energy cost, £/year	312560	201399	157 384	130 322	164 303	154 115		
Capital cost, £	9 340 940	282 522	287 907	304 527	283 098	232 130		
Total cost, £/year	4 697 126							

Table 6.3 Design results of each column shown in Fig. 6.3. Columns presented in boldfont are difficult splits.

From Table 6.3, it can be seen that, splits 2-3/4-6-7 and 1-2-3/4-6-7 are difficult splits. The former is performed by column C2 of sequence A1, and the latter is performed by column C1 of sequence A2 and sequence A3; all columns have more than 1400 stages. According to the algorithm proposed in Chapter 5, it can be identified that sloppy Type C split 2-3-6/4-6-7 together with sharp split 2-3/6 can be used to replace Type C split 2-3/4-6-7, and three different sets of splits can be used to replace Type C split 1-2-3/4-6-7. With these substitutions, 7 sequences containing sloppy splits are resulted, as shown in Fig. 6.4.



Fig. 6.4 Potentially promising sequences containing sloppy splits.

The algorithm developed in Chapter 4 allows the recycle structure of each sequence shown in Fig. 6.4 to be determined; these flowsheets are illustrated in Fig. 6.5. With the evaluation procedure proposed in Chapter 4 and each column

designed using the shortcut column design method, the best sets of recycles can be found; these are shown in Fig. 6.5. The corresponding column design results of each sequence are shown in Table 6.4.

Sequence B1 shown in Fig. 6.5 is derived from Sequence A1 when the difficult sharp Type C split 2-3/4-6-7 (shown in Fig. 6.3) is replaced by sloppy Type C split 2-3-6/4-6-7 and sharp split 2-3/6. Although Sequence B1 contains one more column than Sequence A1, the cost of Sequence B1 (2 555 601£/year) is much less than that of Sequence A1 (7 077 015£/year). The difficult sharp split 1-2-3/4-6-7, which appear in Sequences A2 and A3, can be replaced by three different sets of sloppy and sharp splits with greatly varying impact on the process costs. For Sequence A2, when split 1-2-3/4-6-7 is replaced by either of two different sets of splits including sloppy splits 1-2-3-6/4-6-7 and 1-2-3/2-4-6-7, respectively, the cost of the resulting sequences (Sequences B2 and B4) increases. The total annualised cost of Sequence B4 is nearly three times that of Sequence A2. In sequence B6, split 1-2-3/4-6-7 of Sequence A2 is replaced by the triple splits of 1-2-3-6/2-4-6-7, 1-2-3/6 and 2/4-6-7, by increasing the number of columns from 6 to 8. Nevertheless, the total annualised cost of Sequence B6 is 56% of that of Sequence A2. Similar results (Sequences A3, A5, A7) can be obtained when the difficult sharp split 1-2-3/4-6-7 of Sequence A3 is replaced by those three sets of sloppy and sharp splits.







Sequence B2



Sequence B4



Sequence B6



Fig. 6.5 Recycle structures of potentially promising sequences containing sloppy splits. Streams lying in different compartments are shown with different types of lines. The best set of recycle flowrates for each sequence is also shown.

Column of Sequence B1	C1	C2	C3	C4	C5	C6	C7
Split	1/2-4-6-7	2-3-6/4- 6-7	2-3/6	2/3	4-5/6-7	4/5	6/7
Reflux ratio	3.81	7.97	0.41	3.39	0.62	4.28	1.99
Number of stages	28	72	20	26	49	31	18
Energy cost, £/year	134 268	640 721	72 805	108 402	236 362	550 404	59 760
Capital cost, £	263 040	650 903	192 316	256 581	361 327	381 728	152 744
Total cost*, £/year				2 555 601			
Column of	C1	C2	63	C4	C5	66	C7
Sequence B2		02		04			0,
Split	1-2-3-6/4-6-7	1-2-3/6	1-2/3	1/2	4-5/6-7	4/5	6/7
Reflux ratio	2.15	0.02	0.69	4.05	0.75	4.28	1.99
Number of stages	1 497	39	23	25	53	31	17
Energy cost, £/year	427 185	119 362	132 971	128 152	109 226	164 303	59 760
Capital cost, £/year	10 849 213	295 112	246 572	255 937	333 788	283 098	152 744
Total cost*, £/year				5 279 781			
Column of Sequence B3	C1	C2	C3	C4	C5	C6	C7
Split	1-2-3-6/4-6-7	1-2-3/6	1/2-3	2/3	4-5/6-7	4/5	6/7
Reflux ratio	5.51	0.02	2.30	2.97	0.62	4.28	3.83
Number of stages	1460	50	28	29	41	31	16
Energy cost, £/year	870 064	119 645	167 957	98 603	107 797	164 303	94 585
Capital cost, £/year	13 751 967	332 550	280 425	262 632	288 845	283 098	195 230
Total cost*, £/year				6 754 536			1
Column of	C1	C2	C3	C4	C5	C6	C7
Split	1-2-3/2-4-6-7	1-2/3	1/2	2/4-6-7	4-5/6-7	4/5	6/7
Reflux ratio	1.6	0.49	3.17	133.11	0.81	4.28	2.47
Number of stages	1457	22	25	484	46	31	17
Energy cost, £/year	335 833	138 526	159 901	3 928 362	176 791	328 601	132 619
Capital cost, £/year	9 836 404	248 048	266 058	11 010 747	335 595	320 195	219 697
Total cost*, £/year				12 612 882			
Column of	C1	C2	C3	C4	C5	C6	C8
Sequence B5		02		04			
Split	1-2-3/2-4-6-7	1/2-3	2/3	2/4-6-7	4-5/6-7	4/5	6/7
Reflux ratio	0.95	6.53	1.52	132.57	1.06	4.28	1.81
Number of stages	1445	25	31	484	53	31	17
Energy cost, £/year	342 623	188 059	256 499	3 879 782	127 371	164 303	108 710
Capital cost, £/year	9 784 074	276 109	310 387	10 921 173	3 391 170	283 098	210 953
Total cost*, £/year		•	•	12 442 317	•	•	

Table 6.4 Design results of each column shown in Fig. 6.5.

Column of					_					
	C1	C2	C3	C4	C5	C6	C7	C8		
Sequence B6										
Split	1-2-3-6/2-4-	1-2-3/6	1-2/3	1/2	2/4-6-7	4-5/6-7	4/5	6/7		
Opin	6-7	120/0	12/0	172	214 0 1	+ 0/0 /	-1/0	0/1		
Reflux ratio	2.03	0.07	0.45	2.19	7.74	0.70	4.28	1.54		
Number of stages	206	24	21	26	52	51	31	17		
Energy cost, £/year	356 116	108 195	96 458	123 551	258 334	214 759	492 899	51 197		
Capital cost, £/year	1 335 157	237 230	216 513	257 214	382 030	362 568	365 409	153 151		
Total cost*, £/year		2 804 599								
Column of	C1	C2	C3	C4	C5	C6	C7	C8		
Sequence B7	•••			•			•			
Oralit	1-2-3-6/2-4-	4 0 0/0	4/0.0	0/0	0/4 0 7	4 5/0 7	A / E	0/7		
Split	6-7	1-2-3/0	1/2-3	2/3	2/4-0-7	4-5/6-7	4/5	6/7		
Reflux ratio	1.69	0.06	2.61	2.97	7.74	0.70	4.28	1.54		
Number of stages	206	24	28	29	52	51	31	17		
Energy cost, £/year	318 762	108 119	137 246	98 603	258 334	214 759	492 899	51 197		
Capital cost, £/year	1 282 883	241 460	266 533	262 632	382 030	362 568	365 409	153 151		
Total cost*, £/year	2 785 473									

Table 6.4 Design results of each column shown in Fig. 6.5 (Continued).

\* Total annualised cost

In this case study, 10 possibly promising sequences are efficiently screened from 5001 sequences. Comparing the sequence design results shown in Tables 6.3 and 6.4, it can be seen that the three most promising sequences are Sequences B1, B6 and B7, with total annualised costs of  $\pounds 2.6 \cdot 10^6$ /year,  $\pounds 2.8 \cdot 10^6$ /year and  $\pounds 2.8 \cdot 10^6$ /year, respectively. All of these sequences contain sloppy splits.

This case study demonstrates that the systematic procedure proposed in the previous section can be used to efficiently distinguish and evaluate promising distillation sequences among those identified using the procedure proposed by Thong and Jobson (2001c). Although the boundary value method is employed to identify infeasible splits, the feasibility test is efficient. Promising sequences can be determined without evaluating every sequence of the huge number of those identified using the procedure proposed by Thong and Jobson (2001c). For each promising sequence, a simple recycle structure with beneficial

recycles can be generated using the algorithm proposed in Chapter 4 and evaluated using the shortcut column design method proposed in Chapter 3.

#### 6.4. Conclusions

In this chapter, a systematic procedure for determining and evaluating promising distillation sequences is proposed based on the methods and algorithms proposed in Chapters 3, 4 and 5. Feasibility test, screening of distillation sequences and recycles, and sequence evaluation with the shortcut column design method are all embeded within this procedure. Among all the possible sequences identified using the procedure proposed by Thong and Jobson (2001c), promising sequences can be screened and evaluated, as demonstrated by the case study.

The preliminary screening can efficiently reduce the number of sequences by eliminating sequences containing either infeasible or sloppy splits. Only feasible sharp splits are included in the remaining sequences. A simple recycle structure with beneficial recycles can be screened using the rules and procedures for recycle selection. Once the recycle structure is identified, each sequence can be evaluated with the shortcut method to design each column and the best set of recycles can be identified. Potentially promising sequences containing sloppy splits can be screened according to the evaluation results of sequences containing only sharp splits, and then evaluated. Thereafter, one or more promising sequences can be determined. The whole procedure is computationally efficient and can be applied to azeotropic mixtures with any number of components.

In the case study, distillation sequences for separating a five-component azeotropic mixture with two azeotropes are synthesised. 5001 sequences are identified using the procedure of Thong and Jobson (2001c). The aim of these sequences is to separate the mixture into nearly pure components. Using the systematic procedure proposed in this Chapter, ten potentially promising

sequences are identified and evaluated, with recycle structures screened. Three of them contain only sharp splits, and the other seven sequences contain sloppy splits. The evaluation results shows that three sequences containing sloppy splits are more promising than the others.

## **Conclusions and Future Work**

### 7.1. Summary

To date, several procedures are proposed for the synthesis of distillation sequences separating multicomponent azeotropic mixtures. However, most of these methods cannot guarantee the best sequence to be generated; the number of components or the existence of distillation boundaries also limits their application. Although the procedure of Thong and Jobson (2001c) can be used to generate all potentially feasible sequences and corresponding recycle superstructures for separating a multicomponent azeotropic mixture, however, too many sequences can be generated and it is extremely time-consuming to evaluate all these recycle superstructures.

This work is based on the work of Thong and Jobson (2001c) and proposed a systematic synthesis procedure for screening and evaluating promising distillation sequences separating multicomponent homogeneous azeotropic mixtures into pure component products. New models and methods are proposed for non-linear approximation of distillation boundaries, shortcut column design, screening of beneficial recycles and promising sequences are all incorporated in this synthesis procedure.

In a C-component azeotropic system, a distillation boundary can be spherically approximated by part of a circle or sphere. Such an approximation allows the distillation region in which a composition lies easily identified by solving linear and quadratic equations. This new approach overcomes the shortcomings of existing methods as it require only a few residue curves to be generated and is relative accurate, compared to the linear approximation of distillation boundaries. The spherically approximated distillation boundary allows the

distillation region in which a composition lies to be easily identified by solving linear and quadratic equations.

In an azeotropic system, each compartment behaves like a non-azeotropic mixture of the singular points appearing in it. Based on this observation, a shortcut method is developed for the design of columns separating homogeneous multicomponent azeotropic mixtures. In this method, azeotropes are treated as pseudo components, and a *C*-component system with *A* azeotropes is treated as an enlarged (C+A)-component non-azeotropic system.

With compartment boundaries linearly approximated, a transformation relates vapour-liquid equilibrium behaviour in terms of pure components to that in terms of singular points in each compartment. The transformation requires a set of linear equations to be solved and allows the relative volatility of all singular points to be calculated. The transformation is based on rigorous models of equilibrium behaviour, so does not introduce significant inaccuracies in the representation of vapour-liquid equilibrium.

The classical Fenske-Underwood-Gilliland method can then be used to design columns separating azeotropic mixtures. This shortcut method is extremely computationally efficient and can be applied to homogeneous azeotropic mixtures with any number of components. The shortcut simulation results are in satisfactory agreement with rigorous simulation results, but require only simple calculation. The shortcut method is far better suited to flowsheet synthesis and optimisation than existing column design methods because of its simplicity. The shortcut method is also useful for assessing feasibility of proposed splits and for initialising rigorous simulation.

Employing the shortcut column design method and spherically approximated distillation boundary, a procedure is proposed for the evaluation of distillation sequences separating multicomponent azeotropic mixtures with recycles. This procedure is computationally efficient and can be used to determine the minimum total cost of the sequence, corresponding to the best set of recycle flowrates, and the associated column design parameters. No such

comprehensive approach to evaluation of distillation flowsheets including recycles have been proposed to date. In this work, trial and error is used to select recycle flowrates; in principle, more sophisticated search or optimisation algorithms, such as the SQP method, can also be employed. The results can be used to initialise rigorous simulations (e.g. using commercial software, such as HYSYS).

The requirements of different types of splits on recycles are analysed from two aspects, feasibility of splits and recovery of azeotropic components. The effect of recycles on the performance of splits is analysed using the Underwood equations. Based on these analyses, systemic rules and procedures are developed for selecting beneficial recycles for a given sequence and separation objective. The procedures can be applied to distillation sequences separating homogeneous azeotropic mixtures with any number of components. The recycle structure generated by this procedure is much simpler than the corresponding recycle superstructure.

A two-step procedure is proposed for screening promising sequences out of the sometime very large number of distillations sequences identified using the procedure of Thong and Jobson (2001c). In the first step, potentially feasible sequences are preliminary screened; those containing infeasible splits or sloppy splits are eliminated. Promising sequences containing sloppy splits are identified in the second step. Sequences identified as promising in the first step that contain only sharp splits are evaluated. Opportunities to replace each difficult sharp split by an appropriate set of sloppy and sharp splits can then be systematically explored. Using this two-step procedure, the number of distillation sequences identified using the procedure of Thong and Jobson (2001c) can be significantly reduced without evaluating every possible sequence.

By employing the spherical approximation of distillation boundaries, shortcut column design, screening procedures for distillation sequences and recycles, a systematic procedure is developed for the synthesis of promising distillation sequences separating multicomponent homogeneous azeotropic mixtures. This

systematic procedure is demonstrated by a case study, in which a fivecomponent mixture with two azeotropes is separated into its pure component products. Of the large number of potentially feasible sequences, only 10 need to be evaluated and only 17 Type C splits need to be tested for feasibility. The procedure proposed in this work thus allows a potentially unmanageable separation problem to be systematically and boundably solved.

### 7.2. Limitations

To transform compositions in terms of pure components into compositions in terms of pseudo components (pure components and azeotropes), compartment boundary and sometimes distillation boundaries are linearly approximated. Such an approximation restricts the applicability of this transformation procedure. For example, when a curved distillation boundary is linearly approximated, compositions lying on the concave side of this curved distillation boundary can be assigned to the wrong compartment and region. In this case, the relative volatilities of some singular points will be poorly approximated.

In a *C*-component azeotropic system, only when the number of singular points that lie in the compartment of interest equals to *C*, can compositions in terms of pure components be transformed into compositions in terms of singular points, and thus can the shortcut column design method be applied. Otherwise, the shortcut column design method cannot be used to design the column with one or both products lying in this compartment. For example, for the ternary system of acetone, benzene and n-heptane, its composition space is a compartment, in which four singular points appear. Because of this, composition transformation and the shortcut column design method cannot be applied.

The rules and procedures proposed for screening recycles are based on the analysis of the effects of recycles on the feasibility of splits and recovery of azeotropic components, but not on the total annualised cost (including capital cost and energy cost). Only recycles beneficial to the feasibility of splits or recovery of azeotropic components can be identified. Some recycles excluded by these rules and procedures may benefit the total annualised cost of the sequence. In such case, the generated recycle structure may not lead to costoptimal solutions.

In the two-step procedure for screening distillation sequences, promising sequences containing sloppy splits are identified through replacing each difficult sharp split (included in sequences containing only sharp splits) by a set of sloppy and sharp splits. The results depend on the criteria by which a split is judge to be 'difficult'. Promising sequences containing sloppy splits may be excluded by inappropriate judgement.

The spherical approximation of a distillation boundary can give a better representation than the linear approximation. However, when the actual distillation boundary is highly irregular, it cannot be well presented by part of a sphere (in higher-dimensional space). In such case, a composition may be classified as lying in a wrong distillation region according to spherically approximated distillation boundaries.

The application and results of the systematic synthesis procedure are also limited by the limitations of the spherical approximation of distillation boundary, shortcut column design method, screening of beneficial recycles and distillation sequences. For an azeotropic system, only when the number of singular points lying in each compartment equals to the number of the pure components of this system, can the synthesis procedure be applied. Using this procedure, promising sequences might be excluded and the identified promising sequences maybe are not the cost-optimal.

### 7.3. Future work

In this work, the shortcut column design method, the algorithm for selecting recycles and the screening procedure for sequence alternatives are based on

the analysis of quaternary mixtures, their application to more complex systems needs to be further studied, so does the synthesis procedure.

In this work, all columns in a distillation sequence are operated at atmospheric pressure. The operating pressure of a column affects its feasibility as well as total cost and thus affects the feasibility and performance of the distillation sequence it lies in. In a distillation sequence, each column has a corresponding best operation pressure that corresponding to the minimum cost of the sequence. Furthermore, when one or more of the azeotropes to be separated are pressure-sensitive, the location of distillation boundaries will change with operation pressure. Two columns operated at two different pressures can be used to cross such a distillation boundary. Therefore, operating pressure should be accounted for in the synthesis of distillation sequences. The quality of the feed of each column, which can affect the cost of the column and the sequence, should also be incorporated as another, but less significant, design variable in the synthesis of distillation sequences.

Heat integration always can benefit distillation sequences, especially when there is big difference in the boiling point temperatures of components to be separated. Sutijan (2002) has showed that heat integration has a great opportunity to reduce the cost of a sequence separating a ternary azeotropic mixture. Incorporating heat integration in the synthesis procedure may significantly benefit the total annualised cost of distillation sequences separating multicomponent azeotropic mixtures. An integrated approach to this problem will allow opportunities for heat recovery to be created during sequence synthesis, rather than treating flowsheet synthesis and heat recovery in a sequential fashion.

# Notation

A	Number of azeotropes
Α	Adjacency matrix of azeotropic system
В	Molar flowrate of bottom product
С	Number of pure components
D	Molar flowrate of distillate product
F	Molar flowrate of feed
М	Transformation matrix
n	Number of pure components
Ν	Number of stages in a column
$p_i^0$	Vapour pressure of pure component or azeotrope <i>i</i>
q	Feed quality (ratio of heat required to vaporise 1 mole of feed to molar latent heat of vaporisation)
Q	Energy demand of the reboiler
R	Reflux ratio
R	Reachability matrix of azeotropic system
s <sub>k</sub>	Mole fraction of singular point <i>k</i> in liquid phase
s <sub>k</sub>	Mole fraction of singular point <i>k</i> in vapour phase
S	Vector of mole fraction in terms of singular points (pure components and azeotropes)
S <sub>R</sub>	Minimum number of sequences
V	Vapour fraction of a mixture (molar)
V	Molar flowrate of vapour in the column
X <sub>i</sub>	Mole fraction of pure component <i>i</i> in liquid phase

X	Vector of mole fraction in terms of pure components
<b>y</b> <sub>i</sub>	Mole fraction of pure component <i>i</i> in vapour phase
$lpha_{ij}$	Relative volatility of singular point or pure component <i>i</i> with respect to <i>j</i>
$\phi$	Root of Underwood equation for the rectifying section, Equation (5)
φr	Root of Underwood equation for the stripping section, Equation (6)
$\gamma_i$	Activity coefficient of component or pseudo component <i>i</i>
$\eta_k$	Mole fraction of singular point <i>k</i> in vapour phase
θ	Common root of Underwood equation for both column sections
ξ <sub>k</sub>	Mole fraction of singular point <i>k</i> in liquid phase

### SUBSCRIPT

az	Azeotrope
F	Feed of the column
D, d	Distillate product
B, b	Bottom product
НК	heavy key component of a column
i	Singular point or pure component <i>i</i>
j	Singular point or pure component <i>j</i>
k	Singular point or pure component k
LK	Light key component of a column
min	Minimum value
Н	The heaviest singular point in an azeotropic system

#### ACRONYMS

- BVM Boundary value method
- CMO Constant molar overflow
- CRV Constant relative volatility
- FUG Fenske-Underwood-Gilliland method for column design
- RBM Rectification body method

### References

Aggarwal, A. and Floudas, C. A., 1990, Synthesis of general distillation sequences — Nonsharp separations. *Comput. Chem. Eng.*, 14, 631-653.

Amminudin, K. A., 1999, Design and optimisation of the dividing wall distillation column, PhD Thesis, UMIST, UK.

Andrecovich M. J. and A. W. Westerberg, 1985, An MINLP formulation for heat integrated distillation sequences synthesis, *AIChE J.*, 31, 1461-1474.

Aspen Plus. 1996, Release 9.3-1. Aspen Tech.: Cambridge, MA, USA.

Bauer, M.H. and Stichlmair, J., 1998, Design and economic optimisation of azeotropic distillation processes using mixed-integer nonlinear programming, *Comp. Chem. Engng.*, 22(9), 1271-1286.

Bausa, J., Von Watzdorf, R. and Marquardt, W., 1998, Minimum energy demand for nonideal multicomponent distillation: 1. Simple columns, *AIChE J.*, 44(10), 2181-2198.

Castillo, F.J.L., 1997, Synthesis of homogeneous azeotropic distillation sequences, PhD Thesis, UMIST, Manchester.

DISTIL 5.0., 2001, Aspen Tech.: Calgary, Alberta, Canada.

Doherty, M.F. and Caldarola, G.A., 1985, Design and synthesis of homogeneous azeotropic distillations. 3. The sequencing of columns for azeotropic and extractive distillation, *Ind. Eng. Chem. Fundam.*, 24, 474-485.

Doherty, M. F. and Perkins, J. D. 1979, On the dynamics of distillation process – III. The topological structure of ternary residue curve maps, *Chem. Eng. Sci.*, 34, 1401-1414.

Eduljee, H. E. 1975, Equations replace Gilliland plot, *Hydrocarbon Processing*. 54(9), 120-122.

Fenske, M. R., 1932, Fractionation of straight-run Pennsylvania gasoline, *Ind. Eng. Chem.*, 24, 482.

Fidkowski, Z.T., Malone, M.F. and Doherty, M.F., 1993, Computing azeotropes in multicomponent mixtures, *Comp. Chem, Engng*, 17(12), 1141-1155.

Floudas, C. A. and Paules 3/, G. E., 1988, A mixed-integer nonlinear programming formulation for the synthesis of heat integrated distillation sequences, *Comput. Chem. Eng.*, 12, 531-546.

Gilliland, E. R. 1940, Multicomponent rectification, Ind. Eng. Chem., 32, 1220.

Gomez, M. A. and Seader, J. D., 1976, Separator sequence synthesis by a predictor based ordered search, *AIChE J.*, 22, 970.

Harbert, V. D., 1957, Which tower goes where? Petrol. Refiner, 36, 169-174.

Heaven, D. L., 1969, Optimum sequencing of distillation columns in multicomponent fractionation, M. S. Thesis, University of California, Berkeley.

Hendry, J.E. and Hughes, R.R., 1972, Generating separation process flowsheets, *Chem. Eng. Prog.*, 68(6), 71-76.

Humphrey, J. L. and Keller, G. E., 1997, *Separation Process Technology*, McGraw-Hill, 26-37.

HYSYS 2.1, 1999, Aspen Tech.: Calgary, Alberta, Canada.

Julka, V. and Doherty, M.F., 1990, Geometric behaviour and minimum flows for nonideal multicomponent distillation, *Chem. Eng. Sci.*, 45, 1801-1822.

Julka, V. and Doherty, M.F., 1993, Geometric nonlinear analysis of multicomponent nonideal distillation: A Simple Computer-Aided Design Procedure, *Chem. Eng. Sci.*, 48(8), 1367-1391.

King, J. C., 1971, *Separation Processes*, McGraw-Hill Book Company: New York, 442-467.

Knapp, J.P. and Doherty, M.F., 1992, A new pressure-swing distillation process for separating homogeneous azeotropic distillation, *Ind. Eng. Chem. Res.*, 31, 346-357.

Knight, J. R. and Doherty, M. F., 1990, Systematic approaches to the synthesis of separation schemes for azeotropic mixtures, Foundations of Computer-Aided Process Design, Amsterdam, 417-433.

Köhler, J.W., Aguirre, P. and Blass, E., 1991, Minimum reflux calculations for nonideal mixtures using the reversible distillation model, *Chem. Eng. Sci.*, 46, 3007-3021.

Kusardi, T. W., 2001, Design and optimisation of reboiled absorption columns and flowsheet synthesis and optimisation of physical absorption processes. PhD Thesis, UMIST, UK.

Laroche, L., Bekiaris, N., Andersen, H.W. and Morari, M., 1992a, The curious behaviour of homogeneous azeotrope distillation: Implications for entrainer selection, *AIChE J.*, 38, 1309-1328.

Laroche, L., Bekiaris, N., Andersen, H.W. and Morari, M., 1992b, Homogeneous azeotropic distillation: Separability and flowsheet synthesis, *Ind. Eng. Chem. Res.*, 31, 2190-2209.

Levy, S.G., Van Dongen, D.B. and Doherty, M.F., 1985, Design and synthesis of homogeneous azeotropic distillation: 2. Minimum reflux calculations for nonideal and azeotropic columns, *Ind. Eng. Chem. Fund.*, 24, 463-474.

Li, Y., Chen, H. and Liu, J., 1999, Composition profile of an azeotropic continuous distillation with feed composition on a ridge or in a valley, *Ind. Eng. Chem. Res.*, 38, 2482-2484.

Liddle, C.J., 1968, Improved shortcut method for distillation calculations, *Chem. Eng.*, 22, Oct. 21, 137.

Lockhart, F. J., 1947, Multi-column distillation of natural gasoline, *Petrol. Refiner*, 26 (8), 104.

Manan, Z.A. and Banares-Alcantara, R., 2001, A new catalog of the most promising separation sequences for homogeneous azeotropic mixtures I. Systems without boundary crossing, *Ind. Eng. Chem. Res.*, 40, 5795-5809.

Molokanov, Y.K., Korablina, T.P., Mazurina, N.I. and Nikiforov, G.A., 1972, An approximation method for calculating the basic parameters of multicomponent fraction, *Int. Chem. Eng.*, 12(2), 209.

Peters, M.S. and Timmerhaus, K.D., 1991, *Plant Design and Economics for Chemical Engineers*, McGraw-Hill Book Company: New York, 617-815.

Pöllmann, P. and Blass, E., 1994, Best products of homogeneous azeotropic distillations, *Gas Separation and Purification*, 8(4), 194-228.

Reid, R.C., Prausnitz, J.M. and Poling, B.E., 1987, *The properties of gases and liquids,* 4th edition, McGraw-Hill, Inc., New York.

Ridrigo, B. F. R. and Seader, J. D., 1975, Synthesis of separation sequences by order branch search, *AIChE J.* 21, 885.

Rooks, R.E., Julka, V., Doherty, M.F. and Malone, M.F., 1998, Structure of distillation regions for multicomponent azeotropic mixtures, *AIChE J.*, 44(6), 1382-1391.

Rusche, F.A., 1999, Gilliland plot revisited, *Hydrocarbon Processing*, 78(2), 79.

Safrit, B.T. and Westerberg, A.W., 1997, Algorithm for generating the distillation regions for azeotropic multicomponent mixtures, *Ind. Eng. Chem. Res.*, 36, 1827-1840.

Schreinemakers, F.A.H., 1901, Dampfdrucke im system:wasser, aceton und phonel, *Z. Phys. Chem.*, 39, 440.

Seader, J. D. and Westerberg, A. W., 1977, A combined heuristic and evolutionary strategy for synthesis of simple separation sequences, *AIChE J.* 23, 951.

Stichlmair, J., 1988, Distillation and Rectification, Ullmann's Encyclopedia of Industrial Chemistry, VCH Verlagsgesellschaft: Weinheim, Germany, Vol. B3, pp. 4-1-4-94.

Stichlmair, J. and Herguijuela, J.R, 1992, Separation regions and processes of zeotropic and azeotropic ternary distillation, *AIChE J.*, 38, 1523-1535.

Sutijan, 2002, Synthesis and optimisation of ternary homogeneous azeotropic distillation flowsheets, PhD Thesis, UMIST, Manchester.

Sutton, C., 2003, COLOM v1.7a, Azeotropic Distillation Simulation Package, Department of Process Integration, UMIST.

Thompson R. W. and King, C. J., 1972, Systemic synthesis of separation schemes. *AIChE J.* 18, 941.

Thong, D.Y-C., Castillo, F.J.L. and Towler, G.P., 1999, Distillation design and retrofit using stage composition lines, *Chem. Eng. Sci.*, 55(3), 625-640.

Thong, D.Y.-C. and Jobson, M., 2001a, Multicomponent homogeneous azeotropic distillation. 1. Assessing product feasibility, *Chem. Eng. Sci.*, 56, 4369-4391.

Thong, D.Y.-C. and Jobson, M., 2001b, Multicomponent homogeneous azeotropic distillation. 2. Column design, *Chem. Eng. Sci.*, 56, 4392-4416.

Thong, D.Y.-C. and Jobson, M., 2001c, Multicomponent homogeneous azeotropic distillation. 3. Column sequence synthesis, *Chem. Eng. Sci.* 56, 4417-4432.

Thong, D.Y.-C., Liu, G., Jobson, M. and Smith, R., 2003, Synthesis of distillation sequences for separating multicomponent azeotropic mixtures, *Chem. Eng. Prog.* In press.

Underwood, A. J. V., *et al.*, 1945, Fractional distillation of ternary mixtures, Part I. *J. Inst. Pet.* 31, 111-118.

Underwood, A. J. V., *et al.*, 1946, Fractional distillation of ternary mixtures, Part II. *J. Inst. Pet.* 32, 598-613.

Underwood, A. J. V., 1946, Fractional distillation of multicomponent mixtures–Calculation of minimum reflux ratio, *J. Inst. Pet.*, 32, 614-626.

Underwood, A. J. V., 1948, Fractional distillation of multicomponent mixtures, *Chem. Eng. Prog.*, 44(8), 603.

Van Dongen, D.B. and Doherty, M.F., 1985, Design and synthesis of homogeneous azeotropic distillations. 1. Problem formulation for a single column, *Ind. Eng. Chem. Fundam.*, 24, 454-463.

Vatavuk, W.M., 2002, Updating the CE plant cost index, *Chemical Engineering*, 109(1), 62-70.

Vogelpohl, A., 1974, Die näherungsweise berechnung der rektifikation von gemischen mit binären azeotropen, *Chem. Ing. Tech.*, 46, 195.

Vogelpohl, A., 2002, On the relation between ideal and real mixtures in multicomponent distillation, *Chem. Eng. Technol.*, 25(9), 869-872.

Wahnschafft, O.M., Köhler, J.W., Blass, E. and Westerberg, A.W., 1992, The product composition regions of single-feed azeotropic distillation columns, *Ind. Eng. Chem. Res.*, 31, 2345-2362.

Wahnschafft, O.M. and Westerberg, A.W., 1992, The product composition regions of azeotropic distillation columns. 2. Separability in two-feed columns and entrainer selection, *Ind. Eng. Chem. Res.*, 32, 1108-1120.

Wahnschafft, O.M., Le Ruduilier, J. P. and Westerberg, A. W., 1993, A problem decomposition approach for the synthesis of complex separation processes with recycles, *Ind. Eng. Chem. Res.*, 32, 1121-1141.

Westerberg A. W., 1985, The synthesis of distillation based separation sequences, *Comp. Chem. Engng.*, 9, 421-429.

Westerberg, A. W. and Stephanopoulos, G., 1975, Studies in process synthesis – 3 Branch and bound strategy with list techniques for the synthesis of separation schemes, *Chem. Engen Sci.*, 30, 963.

Widagdo, S. and Seider, W.D., 1996, Azeotropic distillation, *AIChE J.*, 42, 96-130.

Yeomans, H. and Grossmann, I. E., 2000, Disjunctive programming models for the optimal design of distillation columns and separation sequences, *Ind. Eng. Chem. Res.*, 39, 1637-1648.

### Appendix A

### **Operating and Capital Cost Estimation**

This section illustrates the data and methods that are used in this work to calculate the capital costs of column and operation cost for utilities.

### A.1. Cost Estimation

In this work, the capital cost is calculated based on the costs in 1987 (Triantafyllou, 1991), the energy cost is based on the cost in 1990 (Peters and Timmerhaus, 1991). Then, the capital and operating costs are modified according to the Chemical Engineering Plant Cost Index (Vatavuk, 2002), which is shown in Fig. A.1.



Figure A.1 Chemical engineering plant cost index (Vatavuk, 2002).

Cost Indeces in 1987, 1990 and 2000 are 323.8, 357.6 and 394.1, respectively. Costs for 2000 are calculated using equation (Peters and Timmerhaus, 1991):

$$Cost_{2001,energy} = \frac{Cost \ Index_{2000}}{Cost \ Index_{1990}} Cost_{1990,energy}$$

$$Cost_{2001,equipment} = \frac{Cost \ Index_{2000}}{Cost \ Index_{1987}} Cost_{1987,equipment}$$
(A.1)

### A.2. Steam and Cooling Water Cost

Cost data for 1990 are taken from Peters and Timmerhaus (1991). Calculated according to Equation (A.1), cost of steam and cooling water in 2000 are as follows.

Steam Type	Pressure, 10⁵Pa	Temperature, °C	Cost, £/1000 kg
High pressure	34.5	240	6.326
Medium pressure	6.9	265	5.191
Low pressure	3.5	138	2.433

Table A.1 Steam cost as a function of steam pressure.

Cooling Water (20-25°C) =  $\pounds$ 0.382/ m<sup>3</sup>

### A.3. Capital Cost

The total capital cost includes the column cost and heat exchanger (reboiler and condenser) cost. The costs of the equipment in the current year is calculated by adding cost and heat exchanger costs and updating it using equation (A.1).

### A.3.1.Column Cost

The column cost consists of the shell and tray costs and the installation cost, as presented in Equation (A.2). The data and equations to calculate the capital cost are taken from Triantafyllou (1991).

$$Cost_{column} = (Cost_{Shell} + Cost_{Tray}) \cdot (1 + F_{Install})$$
(A.2)

where: 
$$Cost_{Shell} = W \cdot exp[2.98 - 0.88 \cdot ln(W) + 0.085(ln(W))^2]$$
 (A.3)

$$Cost_{Trav} = N \cdot \exp[5.97 + 1.5 \cdot \ln(D)] \tag{A.4}$$

$$F_{install} = F_{Er} + F_P + F_I + F_{El} + F_C + F_{SB} + F_{Lg}$$
(A.5)

- *W*: Weight of the shell (tonne) within the range of 3 to 100 tonnes
- *N:* Number of Stages
- *D:* Diameter of the column, within a range of 1 to 6 metres. For the Diameters up to 1 metre, use £570 for the cost per tray
- *F<sub>er</sub>:* Erection factor
- *F<sub>p</sub>:* Piping factor
- *F<sub>I</sub>:* Instruments and controllers factor
- *F<sub>EI</sub>:* Electrical Factor
- *F<sub>C</sub>*: Civil factor
- *F*<sub>SB</sub>: Structures and building factor
- *F*<sub>*lg*</sub>: Lagging factor

Note that the pressure correction factor has been accounted for in the calculation of the shell cost by calculating the weight of shell as the function of column height and shell thickness. The detailed value for the sub-factors used in the installation factor,  $F_{Install}$ , for each range of equipment costs can be obtained in the IChemE A Guide to Capital Cost Estimating (1988) and are listed in Table A.2.

		60 000	24 000	12 000	3 600	1 800	
Equipment cost	Over 180 000	to	to	to	to	to	Under 1 800
(~)	100 000	180 000	60 000	24 000	12 000	3 600	
Erection factor	0.3	0.38	0.45	0.56	0.67	0.77	1.13
Piping factor	0.2	0.33	0.49	0.78	1.11	1.58	1.94
Instruments and controllers factor	0.18	0.33	0.43	0.6	0.77	0.96	1.38
Electricity factor	0.19	0.25	0.34	0.46	0.6	0.74	1
Civil factor	0.15	0.21	0.31	0.4	0.5	0.6	0.85
Structures and building factor	0.14	0.24	0.31	0.41	0.5	0.59	0.74
Lagging factor	0.04	0.06	0.1	0.17	0.26	0.35	0.4

Table A.2 Values of installation sub-factor for columns (IChemE A Guide to Capital Cost Estimating, 1988).

### A.3.2. Heat exchanger cost

The capital cost of a heat exchanger contains the purchase cost and the installation cost. The exchanger cost, shown in Equation (A.6) (Triantafyllou, 1991) is derived from the cost correlation graph in the IChemE *A Guide to Capital Cost Estimating* (1988).

$$Cost_{Exchanger} = (5391 + 113.4A - 0.32A^{2} + 9.013 \cdot 10^{-4} \cdot A^{3} - 1.027 \cdot 10^{-6} \cdot A^{4} + 4.095 \cdot 10^{-10} \cdot A^{5}) \cdot (1 + F_{Install})$$
(A.6)

where A represents the area of the heat exchanger  $(m^2)$  within a range of 10 to  $1000m^2$ .

The values of the installation sub-factors for heat exchangers are listed in Table A.3.

Equipment cost	Over	60 000	24 000	12 000	3 600	1 800	
		to	to	to	to	to	Under 1 800
(~)	100 000	180 000	60 000	24 000	12 000	3 600	1 000
Erection factor	0.05	0.08	0.1	0.11	0.13	0.15	0.38
Piping factor	0.16	0.26	0.4	0.66	0.98	1.4	1.76
Instruments and controllers factor	0.09	0.13	0.22	0.34	0.49	0.65	1
Electricity factor	0.03	0.03	0.03	0.06	0.1	0.13	0.19
Civil factor	0.08	0.1	0.14	0.17	0.22	0.28	0.35
Structures and building factor	0.012	0.025	0.025	0.04	0.05	0.06	0.08
Lagging factor	0.03	0.04	0.08	0.14	0.21	0.31	0.38

Table A.3 Values of installation sub-factor for heat exchangers (IChemE A Guide to Capital Cost estimating, 1988).

### A.4. Total Annualised Cost

The total annualised cost of a column can be calculated by adding annulised capital cost to the operating cost, as shown in equation (A.7).

$$Cost_{total} = Cost_{operating} + a_{ann} \cdot (Cost_{column} + Cost_{reboiler} + Cost_{Condenser})$$
 (A.7)

where  $a_{ann}$  is the annualisation factor, which is taken to be 0.33 in this work.

# Derivation of the effect of recycles using the Underwood equations

With azeotropes taken as pseudo components, the Underwood equations for the calculation of minimum vapour flowrate can be written as Equations B.1, B.2, and B.3.

$$1 - q = \sum_{i=1}^{C+A} \frac{\alpha_i x_{F,i}}{\alpha_i - \theta}$$
(B.1)

$$V_{min} = \sum_{i=1}^{C+A} \frac{\alpha_i D x_{D,i}}{\alpha_i - \theta}$$
(B.2)

$$-V_{min} = \sum_{i=1}^{C+A} \frac{\alpha_i B x_{B,i}}{\alpha_i - \theta}$$
(B.3)

where,

- $\alpha_i$ : relative volatility of singular point *i*
- $x_{F,i}$ : mole fraction of singular point *i* in the feed
- $x_{D,i}$ : mole fraction of singular point *i* in the feed
- $x_{B,i}$ : mole fraction of singular point *i* bottom product;
- *F* : molar flowrate of the feed
- *D*: molar flowrate of distillate
- *B* : molar flowrate of bottom product
- q: feed quality

#### $V_{min}$ : minimum molar vapour flowrate

We assume that the relative volatilities of all pure components and azeotropes will not change significantly with the introduction of a small amount of recycle. With  $F_i$ ,  $D_i$  and  $B_i$  to represent the molar flowrate of singular point *i*, the effect of the recycle stream with the composition of singular point *a* can be analysed.

The feed flowrate can be written as:

$$F = \sum_{i \neq a} F_i + F_a \tag{B.4}$$

From Equation (B.1), it can be derived

$$\sum_{\substack{i=1\\i\neq a}}^{C+A} \frac{\alpha_i \frac{-F_i}{F^2} (\alpha_i - \theta) + \alpha_i \frac{F_i}{F} \frac{d\theta}{dF_a}}{(\alpha_i - \theta)^2} + \frac{\alpha_a \frac{-F_a}{F^2} (\alpha_a - \theta) + \alpha_a \frac{F_a}{F} \frac{d\theta}{dF_a}}{(\alpha_a - \theta)^2} = 0$$
(B.5)

Equation (B.5) can be simplified as Equation (B.6).

$$-\sum_{i=1}^{C+A} \frac{\alpha_i \frac{-F_i}{F^2}}{(\alpha_i - \theta)} + \sum_{i=1}^{C+A} \frac{\alpha_i F_i}{F(\alpha_i - \theta)^2} \frac{d\theta}{dF_a} + \frac{\alpha_a}{F(\alpha_a - \theta)} = 0$$
(B.6)

And,  $\frac{d\theta}{dF_a}$  can be derived as:

$$\frac{d\theta}{dF_{f,a}} = \frac{\sum_{i=1}^{C+A} \frac{\alpha_i}{\alpha_i} - \frac{F_i}{F^2}}{\sum_{i=1}^{C+A} \frac{\alpha_i}{F(\alpha_a - \theta)}} - \frac{\alpha_a}{F(\alpha_a - \theta)}}{\sum_{i=1}^{C+A} \frac{\alpha_i}{F(\alpha_i - \theta)^2}}$$
(B.7)

If singular point **a** is a heavy key (HK) component or heavier than heavy key (HHK) component, it will not affect  $D_i$ ,  $x_{D,i}$ . From Equation (B.2), it can be derived:
$$\frac{dV_{\min,a}}{dF_a} = D \sum_{i=1}^{C+A} \frac{\alpha_i}{D} \frac{\frac{D_i}{D}}{\frac{d\theta}{dF_a}}$$
(B.8)

Substituting  $\frac{d\theta}{dF_a}$  into Equation (B.8), it can be derived that

$$\frac{dV_{\min,a}}{dF_{a}} = D\sum_{i=1}^{C+A} \left( \frac{\alpha_{i} \frac{D_{i}}{D}}{(\alpha_{i} - \theta)^{2}} \frac{\sum_{i=1}^{C+A} \frac{\alpha_{i} \frac{-F_{i}}{F^{2}}}{\alpha_{i} - \theta} - \frac{\alpha_{a}}{F(\alpha_{a} - \theta)}}{\sum_{i=1}^{C+A} \frac{\alpha_{i}F_{i}}{F(\alpha_{i} - \theta)^{2}}} \right)$$
(B.9)

If component **a** is a light key (LK) component or lighter than light key (LLK) component, it will not affect  $B_i$ ,  $x_{B,i}$ . From Equation (B.3), it can be derived:

$$-\frac{dV_{min,a}}{dF_a} = B \sum_{i=1}^{C+A} \frac{\alpha_i}{\alpha_i} \frac{\frac{B_i}{B}}{\frac{d\theta}{dF_a}} \frac{d\theta}{dF_a}$$
(B.10)

$$-\frac{dV_{\min,a}}{dF_{a}} = B\sum_{i=1}^{C+A} \left( \frac{\alpha_{i} \frac{B_{i}}{B}}{(\alpha_{i} - \theta)^{2}} \frac{\sum_{i=1}^{C+A} \frac{\alpha_{i} \frac{-F_{i}}{F^{2}}}{\alpha_{i} - \theta} - \frac{\alpha_{a}}{F(\alpha_{a} - \theta)}}{\sum_{i=1}^{C+A} \frac{\alpha_{i}F_{i}}{F(\alpha_{i} - \theta)^{2}}} \right)$$
(B.11)

According to Equation (B.9), the effects of recycles with the composition of heavy key and heavier than heavy key components, on the performance of columns, can be evaluated and compared. For recycles with the composition of light key and lighter than light key components, their effects on the performance of columns can be analysed according to Equation (B.11).

## Potentially feasible sequences for the case study of Chapter 6

In this appendix, all potentially feasible sequences identified using the procedure of Thong and Jobson (2001c) for separating the five-component mixture studies in Section 6.2 are illustrated. Shaded splits are infeasible.































































































-A

-A

-A

-A

-A

-A

-A

-A

<u>4</u> 6

4

2 4

2 4

<u>4</u> 5 -A

4 5 -A

5

<u>6</u> 7 –A

5\_A

–A

-A

A