Synthesis and Design of Ternary Heterogeneous Azeotropic Distillation Processes Including Advanced Complex Column Configurations

Citation for published version (APA):
Prayoonyong, P. (2009). *Synthesis and Design of Ternary Heterogeneous Azeotropic Distillation Processes Including Advanced Complex Column Configurations*. University of Manchester.

SYNTHESIS AND DESIGN OF TERNARY HETEROGENEOUS AZEOTROPIC DISTILLATION PROCESSES INCLUDING ADVANCED COMPLEX COLUMN CONFIGURATIONS

A thesis submitted to The University of Manchester for the degree of
Doctor of Philosophy
in the Faculty of Engineering and Physical Sciences

2009

Paritta Prayoonyong

Under the supervision of
Dr. Megan Jobson

Centre for Process Integration
School of Chemical Engineering and Analytical Science
The University of Manchester

Table of Contents

Final word count: 51,324

List of Figures

List of Tables

Abstract

This thesis presents a novel methodology for synthesis of sequences separating ternary heterogeneous azeotropic mixtures employing distillation columns and decanters. Column design methods developed for assessing feasibility of proposed separations and for identifying economically attractive designs of columns in sequences.

Design methods for advanced and complex configurations of heterogeneous azeotropic columns exploit the boundary value method. The methods can be used for establishing product feasibility in a column and evaluating a column design on a basis of cost. A new design method is developed for columns with integrated decanters, in which the existence of two liquid phases is not limited to the decanter. For a column with multiple heterogeneous stages, multiple feasible designs can be generated, corresponding to different numbers of heterogeneous stages and various ratios of two liquid phases on the heterogeneous stages. The resulting feasible designs have different total numbers of stages and feed locations for a given set of product specifications and reflux ratio. The new design method is extended further for double-feed columns and columns with intermediate decanters.

A systematic approach for synthesising separation sequences for ternary heterogeneous azeotropic mixtures is developed. The synthesis procedure of Tao et al. (2003) and Vanage (2005), which considers only simple single-feed columns, decanters, and columns with integrated decanters, is extended to include more industrially relevant and novel options. The approach systematically assesses opportunities to employ double-feed columns and columns with intermediate decanters. The option of introducing a heterogeneous liquid stream directly to a column is also systematically considered. With these advanced column configurations included in the synthesis method, a wider range of sequences may be considered, allowing sequences that are more attractive than conventional designs to be identified. The feasibility of a separation proposed for an individual column in a sequence may be assessed using the new column design method. As the column design method allows a column to be evaluated in terms of cost, separation sequences can be evaluated and the most economic sequences can be identified.

Case studies are presented to demonstrate the applicability of the sequence synthesis approach and column design methods. The case studies indicate that the presence of heterogeneous liquid in columns considerably improves the economic performance in some cases. The economic performance is also affected by the number of heterogeneous stages. The number of heterogeneous stages that leads to near-optimal designs can be determined using the new column design methods. For some mixtures, employing complex column configurations makes the separation feasible and provides significant cost savings. For other mixtures, the complex columns may not be as attractive as single-feed columns with integrated decanters. Column design details and other results from the column design methods are used successfully to initialise rigorous simulations and to facilitate simulation convergence.

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 university or other institution of learning.

Paritta Prayoonyong

Copyright statement

i. The author of this thesis (including any appendices and/or schedules to this thesis) owns any copyright in it (the “Copyright”) and she has given The University of Manchester the right to use such Copyright for any administrative, promotional, educational and/or teaching purposes.

ii. Copies of this thesis, either in full or in extracts, may be made only in accordance with the regulations of the John Rylands University Library of Manchester. Details of these regulations may be obtained from the Librarian. This page must form part of any such copies made.

iii. The ownership of any patents, designs, trade marks and any and all other intellectual property rights except for the Copyright (the “Intellectual Property Rights”) and any reproductions of copyright works, for example graphs and tables (“Reproductions”), which may be described in this thesis, may not be owned by the author and may be owned by third parties. Such Intellectual Property Rights and Reproductions cannot and must not be made available for use without the prior written permission of the owner(s) of the relevant Intellectual Property Rights and/or Reproductions.

iv. Further information on the conditions under which disclosure, publication and exploitation of this thesis, the Copyright and any Intellectual Property Rights and/or Reproductions described in it may take place is available from the Head of School of Chemical Engineering and Analytical Science.

Acknowledgements

I would like to express my gratitude to my supervisor, Dr. Megan Jobson, whose encouragement and guidance enabled me to develop an understanding of the subject. Without her help, support and patience, this thesis would not have been possible.

I gratefully acknowledge the financial support from Royal Thai Government. I should like to express my thanks to all staff at the Office of Educational Affairs for their support in a number of ways.

I am appreciative of help from all staff of the Centre for Process Integration. I would also like to express my appreciation of academic and technical support from all CEAS staff.

I am also thankful to Bostjan, Ankur, Sourabh, Imran, Yannis, Michael, Rameshwar, Anestis, Yu Rong, Yuhang, Priti and all students at Centre for Process Integration for providing me with a cherish memory. I should like to express my gratitude to Fernan Mateos-Salvador for his help in the programming. I am thankful to Suwimol, Orawan, Weerakanya and Chaiwat for making my life in Manchester enjoyable.

Last, but by no means least, I am especially grateful to my family for their love and support throughout my life.

Nomenclature

B	flow rate of a bottom product
D	flow rate of top product
F	feed flow rate
h	molar enthalpy
I	organic liquid phase
II	aqueous liquid phase
L	liquid flow rate in a column
N	number of stages
Q	heat duty
q	feed condition
r	reflux ratio, = L/D
S	flow rate of a sidestream
s	reboil ratio, = V/B
V	vapour flow rate in a column
x	mole fraction in liquid phase
$\mathbf{x}$	vector of liquid composition
y	mole fraction in vapour phase
$\mathbf{y}$	vector of vapour composition

Greek Letter

ε	error in energy balance
ϕ	liquid phase ratio, $L^{II}/(L^{I}+L^{II})$

Subscripts

B	bottom product
C	condenser
D	top product
F	feed
FL	lower feed

FU	upper feed
H	number of heterogeneous stage in the rectifying section
i	index of component
L	lower feed
n	stage number in the rectifying section
m	stage number in the stripping section
M	lower feed stage or draw stage
R	reboiler
S	sidestream
U	upper feed

Superscripts

I	organic liquid phase
II	aqueous liquid phase
L	liquid phase
M	middle section
R	rectifying section
S	stripping section
V	vapour phase

Chapter 1

Introduction

1.1 Motivation

Heterogeneous azeotropic distillation is a technique to separate mixtures using liquid immiscibility to overcome the presence of azeotropes or tangent pinches (Doherty and Malone, 2001). The liquid immiscibility may already be present in the mixture or it may be induced by adding an entrainer. This separation technology is characterised by the use of distillation columns coupled with decanters in which the entrainer can be easily recovered. A well known example of the heterogeneous azeotropic distillation is the separation of ethanol and water using cyclohexane or benzene as an entrainer (Ryan and Doherty, 1989). Other examples of the heterogeneous azeotropic distillation are dehydration of sec-butyl alcohol using di-sec-butyl ether in a methyl-ethyl-ketone plant (Kovach and Seider, 1987b); dehydration of acetic acid using ethyl actetate or n-butyl acetate (Chien et al., 2004); recovery of hydrocarbon from acid and oxygenate by using binary entrainer (Diamond et al., 2004); separation of a mixture containing glycerine, methylesters and methanol (Schneider et al., 1997); separation of a mixture containing acetone, water and n-butanol (Pucci et al., 1986).

Synthesising separation sequences for a heterogeneous azeotropic mixture is a challenging task due to the large number of alternative sequences. The number of alternative solutions increases with the number of components and alternative flowsheet structures taken into account. Heterogeneous azeotropic distillation flowsheets include distillation columns and decanters: they can be interconnected in various ways. For example, a column may be coupled with an ‘integrated’ decanter at the top allowing two liquid phases to be separated and providing reflux for the column. Alternatively, a decanter may be connected to a stage in a column, allowing a liquid phase to be withdrawn as a product. Further, a column may have more than one feed stream. To apply such structural alternatives in a sequence, the separation feasibility needs to be established. In addition, there may be many recycling options in a sequence to choose from but not all options will lead to technically-feasible, economically-attractive sequences.

Design by simulation is a common practice in separation sequence and column design (Widagdo and Seider, 1996; Wasylkiewicz et al., 2003; Marquardt et al., 2008). This design technique is applicable to mixtures with any number of components and any column configurations. However, sequence synthesis by this approach does not guarantee that most promising sequences will be identified since sequences are not generated systematically. Separation sequences are usually generated based on heuristics, experience, intuition, or solutions of similar problems (Marquardt et al., 2008). Column configurations and/or column design parameters, e.g. number of stages, feed location, and heat duties, in the sequences are then changed iteratively until feasible and attractive designs are found. In addition, design by simulation is tedious and time-consuming (Wasylkiewicz et al., 2000) since heterogeneous azeotropic columns are usually difficult to converge without a good initial guess of the column design parameters. Furthermore, the simulation of a column may converge to a solution different from the desired products due to the existence of multiple solutions which is commonly found in the simulation of heterogeneous azeotropic columns (Kovach and Seider, 1987a,b; Gani and Jørgensen, 1994; Müller and Marquardt, 1997; Gaubert et al., 2001). Therefore, sequence synthesis by simulation is not suitable at the conceptual design step.

Another sequencing approach is to employ a systematic method to identify feasible and economic sequences. The sequencing method should take into account various alternative flowsheet structures while feasible sequences are identified with little time and effort. Also, it should allow potential recycling options to be identified. Once potential sequences are identified, they can be studied in more detail using a process simulator. To date, systematic approaches for heterogeneous azeotropic mixtures are scarce. A synthesis procedure has been introduced by Wahnschafft et al. (1993) but it requires repetitive process simulations to search for feasible sequences. The synthesis procedure of Tao et al. (2003) and its extension proposed by Vanage (2005) take into account only a few column configurations.

In general, sequence synthesis is divided into two main tasks, i.e. to generate feasible sequences, and to evaluate the sequences in terms of an economic measure so that the most attractive sequences can be identified. In the first task, the separation feasibility of individual columns in the sequence needs to be established. For the latter task, individual columns in the sequence need to be designed allowing the columns and sequence to be evaluated on a basis of an indicator, such as total vapour load or total annualised cost. Thus, a tool for assessing the separation feasibility and evaluating columns in sequences is required.

The separation feasibility and economic performance of a column can be evaluated by column design methods. The design methods allow the infeasible and uneconomic designs to be screened out rapidly. Moreover, the results from column design methods can be used to initialise a rigorous simulation and facilitate simulation convergence.

At present, there are two graphically-based design methods for heterogeneous azeotropic distillation. The first method is the boundary value method developed by Pham et al. (1989). The second method is the continuous distillation region based method proposed by Urdaneta et al. (2002). The boundary value method of Pham et al. (1989) is simple but is restricted to columns containing only one heterogeneous stage in the decanter. The continuous distillation region based method is computationally intensive but, unlike the boundary value method, does not restrict the two liquid phases to appear only in the decanter. The continuous distillation region based method can be used for estimating the minimum energy requirement of a column but it does not give the column design details, e.g. number of stages, feed location. On the other hand, the boundary value method can estimate the minimum energy requirement and provide design details of the column. There remains a need for a more comprehensive design method that can address separation feasibility and column design for a less restricted set of operating scenarios and for a wide range of column configurations.

1.2 Aims and scope

The main objective of this work is to develop a methodology for synthesis and evaluation of distillation sequences separating heterogeneous azeotropic mixtures. The goal of sequence synthesis is to identify feasible and economically attractive sequences of separation units that satisfy product purity requirements. Various types and configurations of column will be taken into account. Recycle opportunities will be considered. In this work, the synthesis procedure of Tao et al. (2003) is extended to include more column configurations as options. Double-feed columns, columns with intermediate decanters and columns separating heterogeneous feeds are incorporated into the synthesis procedure as they may allow a separation of a mixture be feasible and they may provide saving in costs.

In synthesising separation sequences, it is desirable that the separation feasibility and performance of individual columns in a sequence can be assessed rapidly. These two tasks can be done by using a column design method. In this work, a design method based on the boundary value method is developed for single and double-feed columns with integrated decanters and columns with intermediate decanters. The boundary value method is chosen to be developed further because it allows the product feasibility in a column to be assessed and it also provides column design details for evaluating columns. In addition, the calculations required for the method are not computationally intensive, compared to the continuous distillation region based method introduced by Urdaneta et al. (2002).

The design method presented in this work can be applied to columns in which heterogeneous liquid is not limited to the decanters. In fact, the boundary value method of Pham et al. (1989) has been extended by Urdaneta et al. (2002) for the same purpose. The boundary value method of Urdaneta et al. (2002) requires the number of heterogeneous stages to be specified. However, the number of heterogeneous stages is not known during the setting up of column specifications. In addition, the method of Urdaneta et al. (2002) aims to determine the minimum reflux ratio. In this work, the boundary value method is developed further for assessing the product feasibility and identifying feasible column designs. The column designs can then be evaluated in terms of total annualised cost, allowing columns having different numbers of stages, heat duties and column configurations to be compared.

The column design and sequence synthesis methods presented in this work are developed for ternary mixtures. However, the proposed methods can, in principle, be extended to multicomponent mixtures. The column design method requires liquid composition profiles of all column sections to be generated and these composition profiles need to be tested for their intersection. The calculation method of liquid composition profiles can be applied to mixtures with any number of components. However, it is difficult to search for intersection between composition profiles in the composition space of a multicomponent mixture.

Entrainer selection is not explicitly addressed in this work. The proposed sequencing method is applied after an entrainer is selected. However, the sequencing method allows the sequences with different entrainers to be generated and compared based on their costs.

It is assumed that the vapour-liquid-(liquid) equilibrium is achieved on every stage and the pressure drop over the column is zero. The impact of the two liquid phases on the rates of mass transfer and tray efficiency are not considered.

1.3 Thesis outline

Chapter 2 reviews relevant column design and sequence synthesis methods for azeotropic mixtures. Chapter 3 presents a new design method for single-feed columns with integrated decanters, together with the separation feasibility assessment and column design evaluation. The existence of multiple column designs for a set of product specifications is discussed. Chapters 4 and 5 describe the extension of the design method presented in Chapter 3 for double-feed columns with integrated decanters and columns with intermediate decanters, respectively. In Chapter 6, a systematic methodology for synthesising separation sequences for ternary heterogeneous azeotropic mixtures is presented. The proposed sequencing method takes into account various column configurations: single/double-feed columns with integrated decanters, columns with intermediate decanters. Also, a heterogeneous liquid stream may be fed directly to a column or separated in a decanter. Finally, Chapter 7 provides conclusions from this research work. Its limitations and future work are also discussed.

Chapter 2

Literature review

2.1 Introduction

The synthesis of separation sequences generally consists of two main tasks (Fien and Liu, 1994). The first task is to identify feasible sequences. In this task, a method to systematically generate sequences is required together with a tool for testing the separation feasibility in each individual column. The second task is to design each separation unit so that the sequence can be evaluated in terms of an economic measure allowing the sequence to be compared with other separation options. In the latter task, a column design method is needed. Methodologies for sequence synthesis and column design have been developed to carry out those two tasks. In this chapter, relevant column and sequence design methods for azeotropic mixtures are reviewed. To begin, a brief description of residue curve maps is given as the residue curve map is useful for preliminary design of distillation sequences for ternary systems (Fien and Liu, 1994; Widagdo and Seider, 1996).

2.2 Residue curve maps

For a ternary mixture, a triangular diagram is a useful tool for understanding and designing distillation processes since it can be used to graphically represent azeotropes, residue curves, distillation boundaries and two-liquid phase regions.

A residue curve is a trajectory plotted in composition space of the liquid composition of a mixture that changes with time in a single-stage batch distillation (Doherty and

Perkins, 1978). A residue curve also represents the liquid composition profile of a packed column operating at a total reflux (Van Dongen and Doherty, 1985). Different curves can be obtained from different starting compositions. The collection of residue curves for a mixture is called a residue curve map. For a staged column, it is generally assumed that residue curves are an approximation of liquid composition profiles at total reflux (Van Dongen and Doherty, 1985; Widagdo and Seider, 1996).

The presence of an azeotrope in a mixture may induce a simple distillation boundary which is a residue curve that passes the azeotrope. The distillation boundary divides the triangular diagram into regions. In each distillation region, all residue curves have a distinct pair of starting and ending points. The distillation boundary restricts the products of a simple distillation column (column with one feed and two products) to be in the same region (Doherty and Perkins, 1978). For homogeneous mixtures, the distillation boundaries may be crossed by a simple distillation column if they are highly curved (Laroche et al., 1992).

In a distillation region, residue curves start and end at singular points (Doherty and Perkins, 1978). The starting point of the residue curves is called an unstable node, which is the lowest-boiling component or azeotrope in the region. The residue curves end at a stable node which is the highest-boiling component or azeotrope. Other intermediate-boiling components or azeotropes are called saddle points where the residue curves move toward and away from the point. All residue curves in a distillation region start at the same unstable node and end at the same stable node, but they may approach different saddle points. In such case, the distillation region is divided further into regions called compartments (Thong and Jobson, 2001a). The compartments are divided by a compartment boundary which can be linearly approximated. Product compositions in adjacent compartments may be obtained using double-feed columns (Thong and Jobsons, 2001a).

For a mixture in which some components are partially immiscible, its liquid-liquid equilibrium can be represented by a two-liquid phase region (also known as miscibility gaps) which is bounded by a liquid-liquid envelope (or binodal curve). A mixture with a composition inside the two-liquid phase region has two liquid phases. The compositions of the light and heavy liquid phases corresponding to the mixture are connected by a liquid-liquid tie line. If the mixture is at its boiling point, the two liquid phases are in equilibrium with a vapour phase. The locus of all equilibrium vapour compositions corresponding to all liquid compositions inside the two-liquid phase region is called the vapour line (Doherty and Malone, 2001).

For example, Figure 2.1 illustrates a residue curve map of the 1-propanol/water/1-butanol system at 1 atm. The phase equilibrium of the mixture is obtained from HYSYS 2004.1 using UNIQUAC-ideal gas property package. The UNIQUAC interaction parameters are estimated using UNIFAC-VLE model. The validation of phase equilibrium model and parameters are presented in Appendix C.

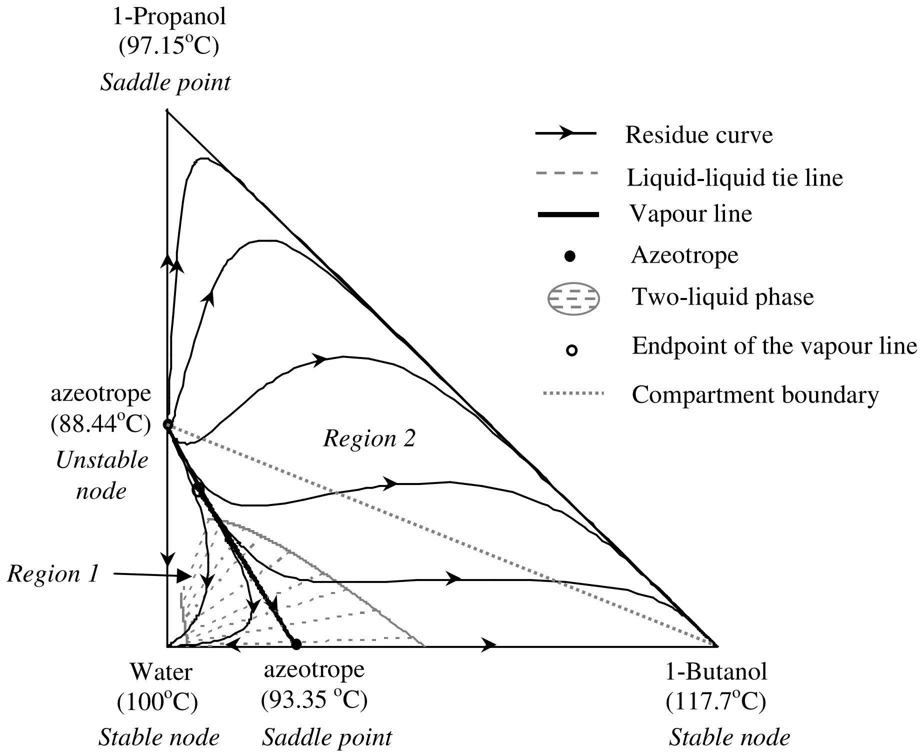


Figure 2.1. Residue curve map and two-liquid phase region at boiling points of 1-propanol/water/1-butanol mixture at 1 atm.

The mixture has a minimum-boiling azeotrope of 1-propanol and water, and a minimum-boiling heterogeneous azeotrope of water and 1-butanol. The existence of the two azeotropes divides the ternary diagram into two distillation regions. Distillation region 2 has two compartments because of the two saddle points in the region. Water and 1-butanol are partially immiscible. Figure 2.1 also shows a two-liquid phase region at boiling points and a vapour line representing all vapour compositions in equilibrium with liquid compositions inside the two-liquid phase region.

2.3 Column design methods

This section summarises the available column design methods for ternary heterogeneous azeotropic columns. A few column design methods have been developed for heterogeneous azeotropic columns separating ternary mixtures. They are graphical methods which are extended from the design methods for homogeneous azeotropic columns.

2.3.1 Boundary value method

The boundary value design method was introduced by Levy et al. (1985) for designing columns separating ternary ideal and homogeneous azeotropic mixtures. This design method is developed based on the assumption of constant molar overflow (the molar liquid and vapour flow rates are constant in each section). For a column with one feed and two products, this design method requires the specification of feed and product compositions and a feed condition. At a given reflux (or reboil) ratio, the liquid composition profiles of the rectifying and stripping sections are calculated using the material balance equations over each column section and vapour liquid equilibrium. The composition profiles are calculated starting from the fully specified product compositions. The specified product compositions are identified as feasible if the two composition profiles intersect each other. The number of theoretical stages can be counted from the composition profiles and the feed location is indicated from the intersection between the two composition profiles. A set of the product specifications is infeasible if the two compositions profiles do not intersect for any reflux ratio.

Pham et al. (1989) extended the boundary value design method for ternary heterogeneous azeotropic distillation columns, assuming constant molar overflow. In particular, the design method is developed for a column coupled with an integrated decanter in which liquid phase separation takes place before some of the liquid is refluxed into the column. The boundary value method proposed by Pham et al. (1989) restricts the two liquid phases to appear only in the top decanter, limiting the liquid in the column to be homogeneous. Apart from the feed and bottom product compositions and feed condition, the design method requires the composition of the vapour entering the condenser to be specified. The liquid composition profile of the rectifying section starts from the composition of reflux stream. Pham et al. (1989) suggested that the top vapour composition should not be located on the vapour line. As a result, only homogeneous liquid appears in the column. However, heterogeneous liquid usually occurs in industrial columns (Pucci et al., 1986; Kovach and Seider, 1987a,b; Repke and Wozny, 2002). Further, columns with multiple stages with heterogeneous liquid may be economically advantageous (Urdaneta et al., 2002).

Wasylkiewicz et al. (2000) and Wasylkiewicz et al. (2003) presented the application of the boundary value method for heterogeneous azeotropic columns with integrated decanters. In addition, they extended the boundary value method to double-feed columns with integrated decanters. Their results show that two liquid phases are not restricted to the top decanter. However, no explanation of how to model the column with multiple heterogeneous stages was presented.

Urdaneta et al. (2002) extended the boundary value method so that it is applicable to columns with multiple heterogeneous stages, without the constant molar overflow assumption (energy balances over column sections are included). Instead of the top vapour composition, the method of Urdaneta et al. (2002) requires two other degrees of freedom to be specified, i.e. the number of heterogeneous stages and the phase split ratio of the final stage where heterogeneous liquid appears in the rectifying section. However, the number of heterogeneous stages is not known when setting up the column specifications.

The boundary value design method allows column designs to be generated and evaluated in terms of their costs as the method provides column design parameters, e.g. the number of theoretical stages, feed location, and heat duties. The minimum reflux ratio, which can be used as an indicator for comparing column designs (Koehler et al., 1995), can also be determined by varying the reflux ratio until the two composition profiles just touch each other. However, this method is not practically applicable to multicomponent mixtures due to the small chances of composition profiles intersecting in multi-dimensional space (Thong and Jobson, 2001b). This is because liquid composition profiles are very sensitive to trace impurities in product compositions (Marquardt et al., 2008).

2.3.2 Rectification body method

Bausa et al. (1998) proposed the rectification body method for determining the minimum reflux ratio and assessing the product feasibility in columns separating homogeneous azeotropic mixtures, without the assumption of constant molar overflow. The design method of Bausa et al. (1998) requires rectification bodies of column sections to be constructed. For a simple single-feed column, rectification bodies of rectifying and stripping sections are generated by determining all pinch points of each column section at a given reflux ratio and fully specified product compositions. (A pinch point is a zone of a large number of stages for which the composition is essentially constant because the meeting vapour and liquid streams approach equilibrium (Doherty and Malone, 2001)). Then, all pinch points of each column section are connected with straight lines. A rectification body can be considered as a linear approximation of a region containing all possible liquid composition profiles of a column section at a given reflux ratio and product compositions. The intersection between the rectification bodies of the two sections indicates product feasibility. The smallest value of reflux ratio that makes the intersection of the two rectification bodies is the minimum reflux ratio.

The rectification body method is applicable to mixtures with any number of components. Although fully specified product compositions are needed, the method is not as sensitive to the mole fraction of trace components in the specified products as the boundary value method (Thong and Jobson, 2001a). No details of the column design, e.g. number of stages and heat duties, are obtained from this method. In addition, this method may incorrectly predict a feasible split as infeasible, or vice versa (Thong and Jobson, 2001a). The inaccuracy of the method arises because the rectification body is a linear approximation of a curved set of composition profiles. Hence, the method is most inaccurate for composition profiles having a strong curvature, which is common for heterogeneous mixtures (Urdaneta et al., 2002).

2.3.3 Continuous distillation region based method

Responding to the weakness of the rectification body method, Urdaneta et al. (2002) introduced the continuous distillation region based method for determining the minimum energy demand and testing the product feasibility in ternary heterogeneous azeotropic distillation columns. This method requires the continuous distillation regions of column sections to be constructed. A continuous distillation region is the region comprising all possible liquid composition profiles at a given reflux ratio and a given set of fully specified product compositions. For a column section, the continuous distillation region is constructed by determining all pinch points of the section at a particular reflux ratio. Then, all pinch points are connected with lines generated by stage-by-stage calculations. For a column section, there may be more than one continuous distillation region. The overlap of continuous distillation regions of the two column sections indicates product feasibility. The minimum reflux ratio is determined by finding the smallest reflux ratio that makes the continuous distillation regions of the two column sections intersect with minimal overlap.

This method can be applied to columns in which two liquid phases are not restricted only to the top decanters. Further, the continuous distillation region based method was extended to double-feed columns and columns with intermediate decanters (Urdaneta, 2005). However, this method is computationally intensive in determining all pinch points. The pinch points at a reflux ratio is determined by solving a set of nonlinear algebraic equations of material and energy balances, summations of mole fractions and phase equilibrium (Koehler et al., 1995). Solving the set of nonlinear algebraic equations may fail to find all pinch points unless a very good guess is provided (Fidkowski et al., 1991). To find all pinch points, a continuation method may be carried out to track locations of pinch points starting from total reflux to a specified reflux ratio (Fidkowski et al., 1991).

The continuous distillation region based method can be used as a product feasibility test. However, it does not explicitly provide details of a feasible column design, e.g. number of stages, heat duties. To determine the number of stages, after the product feasibility is established, liquid composition profile needs to be calculated starting from the bottom product composition at a particular reflux ratio. The upward stage-by-stage calculation continues until the composition profile intersects with the continuous distillation region of the rectifying section. Taking the intersection point as the feed location, the composition profile is calculated continuing from the feed location until it intersects with the decanter tie line. If the column profile does not intersect with the decanter tie line, a stage in the stripping section located inside the continuous distillation region of the rectifying section will be selected as a new feed location. Once the intersection of the column profile and decanter tie tine is found, the total number of stages can be counted.

2.3.4 Shortcut design method of Vanage (2005)

Vanage (2005) proposed a shortcut design method based on the Underwood's method for determining the minimum reflux ratio in columns separating ternary heterogeneous azeotropic mixtures. The method is applicable to columns with and without integrated decanters. It can be applied only to sharp direct and indirect splits (Vanage, 2005).

The shortcut design method of Vanage (2005) requires a controlling fixed point to be identified. For a column without a decanter, a controlling fixed point is a zone of a large number of stages with nearly constant composition, which is relatively invariant with reflux ratio. For a column with an integrated decanter, the composition of the reflux stream is taken to be a controlling fixed point. A controlling fixed point of a column is identified by generating the rectifying and stripping profiles at an arbitrary reflux ratio. The minimum reflux ratio is then determined from the material balance between the controlling fixed point and the top or bottom product depending on which column section the controlling fixed point is in.

The shortcut design method of Vanage (2005) is not highly iterative but it requires a good initial value of the fixed point composition in order to obtain an accurate minimum reflux ratio. This is because the controlling fixed point slightly changes within a narrow range of compositions over a wide range of reflux ratio. Thus, it is difficult to select the fixed point composition that closely corresponds to the minimum reflux ratio.

2.4 Synthesis of separation sequences

2.4.1 Distillation sequence synthesis for ideal mixtures and homogeneous azeotropic mixtures

Many sequence synthesis methods for the separation of ideal mixtures into nearly pure component products by simple columns have been proposed (Widagdo and Seider, 1996; Sargent, 1998). A challenge in distillation sequencing for ideal mixtures is that there is a large number of feasible sequences when the number of products increases; the number of different sequences for N components is equal to $(2(N\text{-}1)!)/(N!(N\text{-}1)!)$ (King, 1980). The number of sequences can be decreased by using heuristics as guidelines to eliminate alternatives with minimum effort (Barnicki and Siirola, 1997). Then, shortcut design methods, such as the Underwood method, may be used to evaluate sequences with respect to a cost indicator, e.g. total vapour load, to screen out uneconomic flowsheets (Malone et al., 1985).

Synthesis of distillation sequences for homogeneous azeotropic mixtures is challenging due to the existence of azeotropes resulting in distillation boundaries and/or compartments. Sequence synthesis for homogeneous azeotropic mixtures is complicated since the product compositions of a column depend upon the distillation region where the feed composition lies (Widagdo and Seider, 1996). For ternary azeotropic mixtures, distillation sequence synthesis may be carried out using residue curve maps, e.g. Doherty and Caldarola (1985). Assuming distillation boundaries are linear, product compositions of a column are confined to the same distillation region as the feed composition (Doherty and Caldarola, 1985). The problem in sequencing is thus to find a way to cross distillation boundaries, e.g. recycling, so that the desired products can be recovered (Doherty and Caldarola, 1985).

Systematic approaches have been proposed for generating distillation sequences separating homogeneous azeotropic mixtures, e.g. Wahnschafft et al. (1993), Castillo et al. (1998b), Rooks et al. (1998), Thong and Jobson (2001c) and Liu (2003). Among these methods, only the systematic approach of Wahnschafft et al. (1993) can be applied to heterogeneous azeotropic mixtures, which is described in Section 2.4.2.2.

Castillo et al. (1998b) proposed a sequence design procedure for ternary homogeneous azeotropic mixtures. The feasibility of separation is established by the overlap of product operation leaves; a product operation leaf is defined as the region containing all liquid composition profiles at any reflux or reboil ratio for a given product composition (Castillo et al., 1998a). In the synthesis procedure, column sequences are generated based on the synthesis of column sections instead of whole columns (Castillo et al., 1998b). Recycling is also considered; however, trial-and-error is required to identify potential recycle options.

Rooks et al. (1998) presented algorithms for synthesising distillation sequences separating multicomponent homogeneous azeotropic mixtures. Feasible splits are determined using the common saddle criterion, i.e. a set of product compositions is feasible if the rectifying and stripping profiles approach the same saddle at large reflux. However, the common saddle criterion is a sufficient, not a necessary, condition for split feasibility (Doherty and Malone, 2001). As a result, some feasible splits may be excluded (Thong and Jobson, 2001c). Further, the approach of Rooks et al. (1998) does not include separation methods for heterogeneous liquid mixtures and recycling options are not considered (Tao et al., 2003).

Thong and Jobson (2001c) developed an algorithm for generating distillation sequences separating multicomponent homogeneous azeotropic mixtures. Firstly, classes of feasible splits are identified using the feasibility test proposed by Thong and Jobson (2001a). Then, all possible distillation sequences are generated by recursive searching (Thong and Jobson, 2001c). A distillation sequence is accepted if it can recover all desired components. A set of recycle heuristics is proposed to screen out recycle options. In the synthesis approach of Thong and Jobson (2001c), distillation boundaries are assumed to be linear. Liu (2003) extended the approach of Thong and Jobson (2001c) for non-linear approximation of distillation boundaries and additional recycle heuristics are proposed to screen out uneconomic sequences.

For homogeneous azeotropic mixtures, systematic synthesis methods and product feasibility tests have been developed. Those methods cannot be applied in a straightforward way to heterogeneous azeotropic mixtures since the separation method involving liquid-liquid separation is not taken into account.

2.4.2 Distillation sequence synthesis for heterogeneous azeotropic mixtures

Synthesising separation sequences for a heterogeneous azeotropic mixture is a challenging task due to the large number of alternative sequences. The number of alternative solutions increases with the number of components and alternative flowsheet structures taken into account. Separation sequences for heterogeneous azeotropic distillation include distillation columns and decanters which can be interconnected in various ways. Also, there may be many recycling options in a sequence to choose from but not all options will lead to feasible and economically attractive sequences.

Design by simulation is a commonly applied approach to separation sequence synthesis design (Wasylkiewicz et al., 2003; Marquardt et al., 2008). Although this design approach is applicable to mixtures with any number of components and any column configurations, it is not suitable for heterogeneous azeotropic mixtures at the conceptual design step for the following reasons. Firstly, sequence synthesis by this approach is iterative as sequences are usually proposed based on heuristics, intuition, or solutions of similar problems (Marquardt et al., 2008). Column configurations and/or column design parameters, e.g. number of stages, feed location, and heat duties, in the sequences are then changed iteratively until feasible and attractive designs are found. Secondly, design by simulation is tedious and time-consuming (Wasylkiewicz et al., 2000). Even for an individual heterogeneous azeotropic column, the rigorous simulation is difficult to converge to a solution without a good initial guess of column design parameters (Seader and Henley, 1998; Wasylkiewicz et al., 2000; HYSYS 2004.1 User Guide). In addition, the simulation of a column may converge to a solution different from the desired products due to the existence of multiple solutions which is commonly found in the simulation of heterogeneous azeotropic columns (e.g. Kovach and Seider, 1987a,b; Gani and Jørgensen, 1994; Müller and Marquardt, 1997; Gaubert et al., 2001). Thus, by using the simulation-based design approach, the most promising sequences may not be identified (Marquardt et al., 2008).

Little work has been devoted to the synthesis of heterogeneous azeotropic distillation sequences. Some sequencing approaches for heterogeneous mixtures are summarised below.

2.4.2.1 Sequencing by residue curve map analysis

In the literature, separation sequences for heterogeneous azeotropic mixtures have been developed based on the residue curve map analysis (e.g. Stichlmair et al., 1989; Pham and Doherty, 1990; Westerberg et al., 2000; Wasylkiewicz et al., 2003).

Stichlmair et al. (1989) and Westerberg et al. (2000) proposed separation sequences for the dehydration of ethanol using toluene as an entrainer and the separation of a pyridine/toluene/water mixture, respectively, based on residue curve map analysis. In their sequences, only simple single-feed columns and stand-alone decanters are taken into account. The products of a simple single-feed column are confined to the same distillation region as its feed composition. The key for sequencing is to employ stand-alone decanters to cross distillation boundaries. Mixing and recycling are also considered so that desired products in different distillation regions can be recovered.

Pham and Doherty (1990) and Wasylkiewicz et al. (2003) studied the synthesis of separation sequences for ethanol/water/benzene mixture and other mixtures having similar residue curve map topologies. The sequencing involves using columns with integrated decanters to recover products in different distillation regions. The key for sequencing is to specify the vapour composition at the top of the column with an integrated decanter to be in the same distillation region as the bottom product of the column and to be close to the minimum-boiling heterogeneous azeotrope.

Separation sequence synthesis by residue curve map analysis relies on visual inspection, thus limiting the approach to ternary mixtures (Marquardt et al., 2008). For mixtures with more components, feasible products are more difficult to predict since the residue curve map becomes more complex (Widagdo and Seider, 1996). Moreover, this sequencing approach does not generalise to the synthesis of arbitrary mixtures.

2.4.2.2 Systematic synthesis approaches

Another sequencing approach is to employ a systematic method to identify feasible and economic sequences. A systematic approach allows separation sequences to be generated from a range of alternative structures in a systematic manner until a given feed is separated into target compositions (Barnicki and Siirola, 1997). Sequencing using a systematic approach also limits the number of sequence alternatives since only feasible sequences are generated within a range of alternative structures taken into account (Barnicki and Siirola, 1997).

Wahnschafft et al. (1993) introduced a systematic synthesis method for homogeneous and heterogeneous azeotropic mixtures. This method uses repeated process simulations to sequentially identify all feasible sequences for a given feed stream. A recycle stream may be assigned in a sequence for two purposes, i.e. to supply a separation agent to a column, and to avoid the duplication of separation units. If a recycle is assigned, the sequence needs to be simulated again until the process simulation converges since the recycle affects the mass balances and product feasibility of columns within the recycle loop. In principle, this method can be applied to mixtures with any number of components and any type of separation methods (Thong and Jobson, 2001c). However, the simulation of a heterogeneous azeotropic distillation column is tedious and time-consuming as it is difficult to converge to a solution (Seader and Henley, 1998; Wasylkiewicz et al., 2000). Thus, optimal columns and sequences may be unexplored.

Tao et al. (2003) proposed a synthesis method for systematically generating separation sequences for heterogeneous azeotropic mixtures. This method is applicable to mixtures with any number of components. Two types of separation units considered in the algorithm of Tao et al. (2003) are simple single-feed columns (having one feed and two products), and decanters. Separation sequences are sequentially generated using either columns or decanters depending on whether the liquid stream to be separated is heterogeneous or homogeneous. Feasible products of a column are identified using the common saddle criterion of Rooks et al. (1998). Tao et al. (2003) also proposed sets of mixing rules and recycle heuristics for modifying separation sequences for streams that cannot be separated by distillation and decanting. Vanage (2005) extended the synthesis method of Tao et al. (2003) to include single-feed columns with integrated decanters as an option. Vanage (2005) introduced further heuristic recycle rules to screen out uneconomic recycle options. The synthesis approaches of Tao et al. (2003) and Vanage (2005) consider only direct and indirect splits. In addition, the approaches do not take into account complex column configurations, e.g. double-feed columns with integrated decanters, columns with intermediate decanters, which may be a promising option to separate a mixture.

Moussa and Jiménez (2006) classified residue curve map topologies of ternary heterogeneous azeotropic mixtures to aid the sequence synthesis. A single-feed column with an integrated decanter is proposed when there are a saddle or a stable node of a pure component and an unstable node of a minimum-boiling heterogeneous azeotrope in the same distillation region. The pure component is recovered as a bottom product whereas the minimum-boiling heterogeneous azeotrope is obtained as a top vapour. If a pure component and a minimum-boiling heterogeneous azeotrope are nonadjacent saddle points in the same region, a double-feed column with an integrated decanter is considered. The saddle point of a minimum-boiling heterogeneous azeotrope will be recovered as the top vapour of the double-feed column while the saddle point of the pure component is recovered in another single-feed column without a decanter. The synthesis approach of Moussa and Jiménez (2006) aims to generate sequences for separating binary mixtures using an entrainer. In sequences resulting from the approach of Moussa and Jiménez (2006), only two components to be separated are recovered whereas entrainer rich streams are recycled. Thus, this method is not suitable for separation problems that require separating mixtures into their all constituents.

It can be seen that there is a lack of synthesis methods for heterogeneous azeotropic mixtures. Sequences in the literature were generally proposed based on residue curve map analysis. The synthesis method of Moussa and Jiménez (2006) can be used for the synthesis of sequences separating a binary mixture using an entrainer. The systematic methods proposed by Wahnschafft et al. (1993) and Tao et al. (2003) can be applied for generating sequences separating heterogeneous azeotropic mixtures into nearly pure components. However, the method of Wahnschafft et al. (1993) requires repetitive simulations which are not suitable for heterogeneous azeotropic distillation. The method of Tao et al. (2003) and its extension proposed by Vanage (2005) takes into account only direct and indirect splits, simple single-feed columns, stand-alone decanters and columns with integrated decanters.

2.5 Conclusions

Three column design methods can be applied to ternary heterogeneous azeotropic columns. The continuous region based method of Urdaneta et al. (2002) and the shortcut design method of Vanage (2005) focus on determining the minimum reflux ratio of a column as it can be used as an indicator for comparing column designs. However, determining the minimum reflux ratio by the continuous region based method is iterative as the reflux ratio needs to be repeatedly changed until the minimal overlap between the continuous regions of the column sections is found. The shortcut method of Vanage (2005), although not highly iterative, requires a good initial guess to obtain an accurate minimum reflux ratio. While the boundary value design method can also be used to determine the minimum reflux ratio, it also allows product feasibility to be established and column designs to be evaluated in terms of costs. Moreover, the calculations required for the boundary value method are not as computationally intensive as those of the continuous distillation region based method. Therefore, in this work, the boundary value method will be used as a tool for assessing product feasibility and evaluating column designs. The boundary value method will be extended to double-feed columns with integrated decanters and columns with intermediate decanters.

Little work has been devoted to the synthesis of heterogeneous azeotropic distillation sequences. Only the synthesis methods of Wahnschafft et al. (1993) and Tao et al. (2003) have been developed for heterogeneous azeotropic mixtures. However, the method of Wahnschafft et al. (1993) relies on process simulations, which are tedious and time-consuming. In this work, a synthesis method for identifying feasible and economic sequences is presented. It extends the synthesis methods of Tao et al. (2003) and Vanage (2005) to include various column configurations, such as double-feed columns and columns with integrated decanters. As more options are taken into account, more promising sequences may be identified.

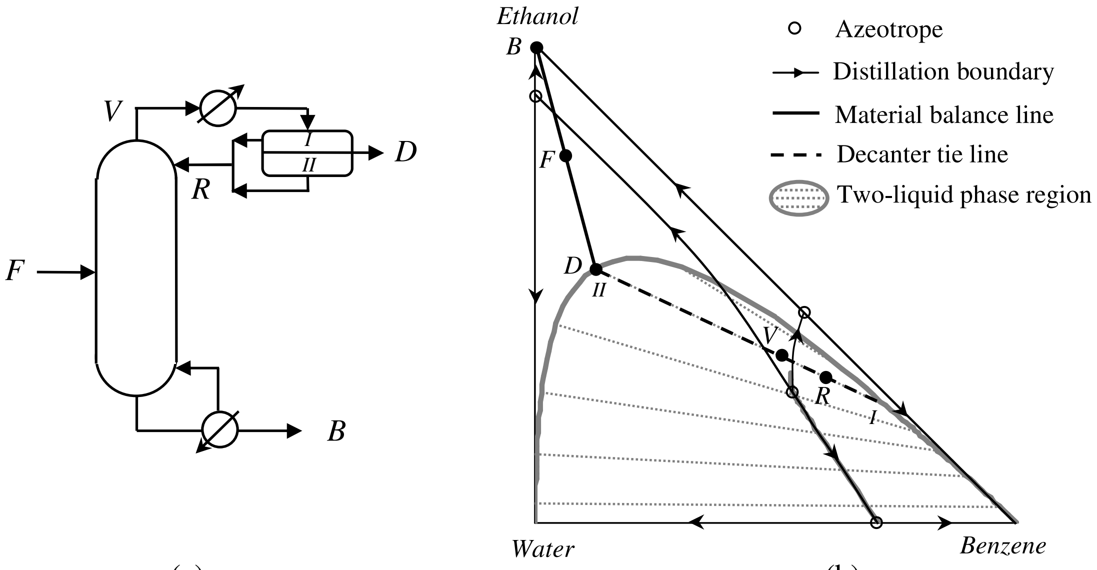
Chapter 3

Design method for single-feed heterogeneous azeotropic columns with integrated decanters

3.1 Introduction

Heterogeneous azeotropic distillation is a technique to separate close-boiling or azeotropic mixtures by employing an entrainer that induces liquid immiscibility to facilitate the distillation (Seader and Henley, 1998; Doherty and Malone, 2001). A column configuration commonly used in heterogeneous azeotropic distillation is a column with an integrated decanter as shown in Figure 3.1(a). The mass balance over the column comprises a feed stream and top and bottom products. At the top of the column, the top vapour is condensed and two liquid phases form in the decanter. The proportion of the two liquid phases from the decanter can be manipulated before being refluxed back into the column. As a result, the compositions of the top product and reflux stream are different from each other and from the top vapour. That the column is coupled with a decanter at the top allows its top and bottom products to be in different distillation regions, for example, in the separation of an ethanol/water/benzene mixture as discussed below.

A well known example of heterogeneous azeotropic distillation is the dehydration of ethanol (Ryan and Doherty, 1989; Pham and Doherty, 1990). The minimum-boiling azeotrope of water and ethanol can be overcome by adding benzene or cyclohexane as an entrainer to induce liquid immiscibility. Figure 3.1(b) shows the residue curve map and two-liquid phase region of the mixture. Using a column with an integrated decanter, the distillation boundary can be crossed allowing a highly pure ethanol to be obtained in the bottom product.



(a) (b)

Figure 3.1. (a) Schematic representation of a column with an integrated decanter, (b) Residue curve map and heterogeneous boiling envelope of the ethanol/water/benzene mixture showing column and decanter mass balances.

The design of a heterogeneous azeotropic column is challenging due to the highly nonideal system. Furthermore, having an integrated decanter at the top of a column, the proportion of heavy and light liquid phases being refluxed back into the column can be manipulated. Thus, the proportion of heavy and light liquid phases in the reflux stream is a degree of freedom which influences the feasibility of separations and cost of columns. In addition, multiple solutions for the same design problem are usually encountered (Wasylkiewicz et al., 2000).

A heterogeneous azeotropic column can be designed by simulation. However, design by simulation is a tedious and time-consuming method (Wasylkiewicz et al., 2000). This design technique involves selecting column designs parameters: the number of stages, feed location, feed thermal condition, and reflux ratio. Some of these parameters may need to be repeatedly changed until the simulation converges and the desired separation is achieved. Typically, simulation of a heterogeneous azeotropic column is difficult to converge without a good initial guess of the column design parameters (HYSYS 2004.1 User Guide) and the location where heterogeneous liquid appears in the column. Moreover, the simulation may converge to a solution different from the desired separation. Multiple solutions, or multiple steady states, in heterogeneous azeotropic columns are commonly encountered in simulation (Kovach and Seider, 1987a,b; Gani and Jørgensen, 1994; Müller and Marquardt, 1997; Gaubert et al., 2001). In addition, design by simulation requires an exhaustive search in order to identify the best designs.

A shortcut design method has been proposed by Vanage (2005). The method is developed based on the Underwood method for determining the minimum reflux ratio in columns separating ternary heterogeneous azeotropic mixtures. This design method proposed by Vanage (2005) is not iterative but it requires a good initial guess to obtain an accurate minimum reflux ratio and it can be applied only to sharp direct and indirect splits.

Two graphical design methods for heterogeneous azeotropic columns with integrated decanters are available: the boundary value method (Pham et al., 1989) and the continuous distillation region based method (Urdaneta et al., 2002). The two design methods are summarised below.

Pham et al. (1989) developed a column design method based on the boundary value method introduced by Levy et al. (1985) for the design of heterogeneous azeotropic columns with integrated decanters. The method requires liquid composition profiles of each column section to be calculated for a given product compositions, a reflux ratio, and a vapour composition feeding to the condenser. The intersection between composition profiles of each column section indicates the feasibility of proposed column specifications. The method provides column design parameters, e.g. number of stages, feed location and energy requirement, which allows the column design to be evaluated in terms of its cost. A limitation of the boundary value method proposed by Pham et al.

(1989) is that liquid phase splitting is restricted to occur only in the decanter. However, two liquid phases commonly appear in columns in industry (Pucci et al., 1986; Kovach and Seider, 1987a,b; Repke and Wozny, 2002), and they may provide economically advantageous designs (Urdaneta et al., 2002).

Wasylkiewicz et al. (2000) and Wasylkiewicz et al. (2003) presented the use of the boundary value method for heterogeneous azeotropic columns with integrated decanter. Their results show that two liquid phases are not limited to the top decanter. However, no explanation of how to model the column with multiple heterogeneous stages is given.

Urdaneta et al. (2002) extended the boundary value method such that the multiple heterogeneous stages appear in the column. In contrast to the method of Pham et al. (1989), Wasylkiewicz et al. (2000) and Wasylkiewicz et al. (2003), the top vapour composition is no longer a degree of freedom. Rather, the number of heterogeneous stages and the liquid phase split ratio of the final heterogeneous stage are additional degrees of freedom. However, the number of heterogeneous stages is not known when setting the column specifications. Moreover, having the phase split ratio of the final heterogeneous stage is a degree of freedom seems to imply that the proportion of two liquid phases on that stage can be manipulated in the same way as that of the reflux stream.

Urdaneta et al. (2002) introduced a graphical design method called continuous distillation region based method. The method requires the continuous distillation regions of each column section to be constructed; a continuous distillation region contains all possible liquid composition profiles for a given reflux ratio and product specifications. The construction of the continuous distillation region requires the determination of all pinch points at the given reflux ratio and stage-by-stage calculation starting from each pinch point. An overlap between continuous distillation regions of each column section indicates the feasibility of the proposed separation. This method is not restricted to the column containing two liquid phases only in the decanter. However, the method is computationally intensive, particularly in determining all pinch points. In addition, the method does not directly give the column design parameters, e.g. number of stages, feed location. To determine column design details for a feasible column design, stage-by-stage calculation needs to be carried out.

Between the two graphical design methods described above, the boundary value method is chosen to be developed further for column and flowsheet design. The boundary value method requires only the calculation of composition profiles, while the continuous distillation region based method requires the calculation of both composition profiles and pinch points. Moreover, the details of feasible column designs are more straightforward to obtain by using the boundary value method.

This chapter presents a conceptual design method based on the boundary value method for single-feed columns with integrated decanters, in which heterogeneous liquid is not limited to the decanter. The column design procedure is described using an illustrative example. The calculation of liquid composition profiles for each column section is presented. The method for the composition profile calculation developed in this work is similar to that of Urdaneta et al. (2002). A difference is that the number of heterogeneous stages in the rectifying section and the liquid phase split ratio of the last heterogeneous stage are not degrees of freedom. Instead, the phase split ratio of the reflux stream is a degree of freedom. Additionally, preliminary tests are developed for checking the possibility of a heterogeneous liquid to appear on a stage. Case studies are presented to show the application of the design method and its application to the separation sequence synthesis.

3.2 Design method for single-feed columns with integrated decanters

This section presents the boundary value design method for single-feed columns with integrated decanters. The calculation required for column design has been written in MATLAB 7.0 interfaced with HYSYS 2004.1 for phase equilibrium and enthalpy calculation (see Appendix D). To demonstrate the column design procedure, a separation of an acetic acid/water/n-butyl acetate mixture is taken as an example.

The dehydration of acetic acid using a conventional column is impractical (Chien et al., 2004). As the mixture of water and acetic acid has a tangent pinch close to pure water, a large number of stages are required to separate the mixture in a conventional column. This mixture is usually separated in a heterogeneous azeotropic column where n-butyl acetate is used as an entrainer.

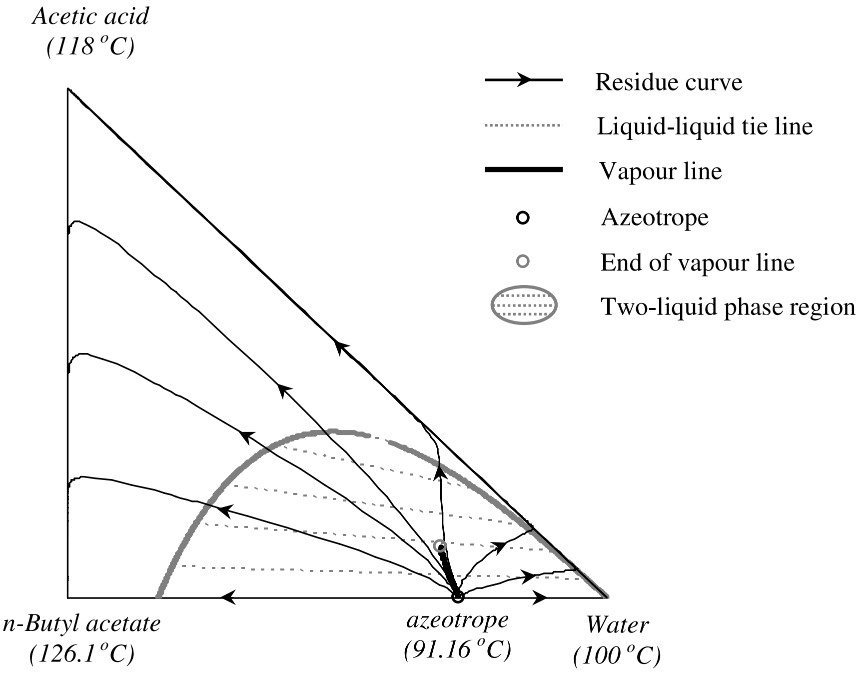


Figure 3.2. Residue curve map for water/acetic acid/n-butyl acetate mixture and heterogeneous boiling envelope at 1 atm

The residue curve map and heterogeneous boiling envelope for the mixture of acetic acid, water and n-butyl acetate is presented in Figure 3.2. The vapour line shown in Figure 3.2 is a line made up of vapour compositions which are in equilibrium with their corresponding light and heavy liquid compositions. The vapour-liquid-liquid equilibrium of this mixture is calculated using UNIQUAC-Virial model in HYSYS 2004.1 as the dimerisation of acetic acid occurs in the vapour phase. (See Appendix C for the validation of phase equilibrium model and parameters.) There is a minimum-boiling heterogeneous azeotrope between water and n-butyl acetate and one distillation region. The composition of the aqueous liquid phase associated with the heterogeneous azeotrope is 99.85 mol% water.

3.2.1 Model development

This section describes the column design procedure based on the boundary value method for single-feed columns with integrated decanter. The first step in column design is to set all specifications of the columns as discussed in Section 3.2.1.1. Next, liquid composition profiles for each column section are calculated from material and energy balances along with phase equilibrium. Then, the feasibility of the proposed separation is assessed. If a feasible design is identified, the corresponding column design details will be obtained and can be used for column cost estimation.

In this work, liquid composition profiles are calculated without an assumption of constant molar overflow (energy balance is included in the profile calculation) as such assumption is inadequate for a highly non-ideal system. The vapour-liquid-(liquid) equilibrium is assumed on every stage. The pressure drop over the column is zero. The same assumptions will be used throughout this thesis.

3.2.1.1 Specifications

For a single-feed column with an integrated decanter, the specifications of the boundary value method are: column pressure, which is assumed constant throughout the column; feed composition and flow rate; top and bottom product compositions and flow rates; reflux ratio; phase split ratio of reflux (defined below); either reboil ratio or feed condition. The product specifications are given such that the product purity requirement and material balance over the column are satisfied (equations 3.1 and 3.2)

$$F = D + B \tag{3.1}$$

$$\mathbf{x}_F F = \mathbf{x}_D D + \mathbf{x}_B B \tag{3.2}$$

The phase split ratio of the reflux stream (ϕ_1) is defined as the ratio of heavy liquid flow rate to total liquid in the reflux stream:

$$\phi_1 = \frac{L_1^{II}}{L_1} \tag{3.3}$$

where $L_1 = L_1^I + L_1^{II}$, L_1 is the total liquid flow rate of the reflux stream, L_1^I and L_1^{II} are the flow rates of light and heavy liquid phases in the reflux, respectively.

The value of reflux phase split ratio ranges from 0 to 1. $\phi_1 = 0$ means that only the light liquid phase is refluxed back to the column, whereas $\phi_1 = 1$ means that there is only the heavy liquid phase in the reflux stream.

If the reboil ratio (s) is specified, the feed condition (q) is calculated from its definition shown in equation (3.4), (Doherty and Malone, 2001):

$$q = \left(\frac{h_F^{V,sat} - h_F}{h_F^{V,sat} - h_F^{L,sat}} \right) \tag{3.4}$$

where h_F is calculated from the energy balance over the column, i.e.:

$$h_F = \frac{1}{F}\left(Dh_D + Bh_B + Q_C - Q_R\right) \tag{3.5}$$

The condenser and reboiler duties (Q_C and Q_R) are calculated from energy balances around the condenser and reboiler, respectively. The specified reflux and reboil ratios will be discarded if the corresponding feed condition is not realisable with available utilities, for instance a very low feed temperature.

If the feed condition is specified, the reboil ratio is calculated from the energy balance over the reboiler as shown in equation (3.6).

$$s = \frac{1}{\left(h_2^{S,L} - h_1^{S,V}\right)}\left(h_B - h_2^{S,L} - \frac{Q_R}{B} \right) \tag{3.6}$$

where $h_1^{S,V}$ and $h_2^{S,L}$ are the molar enthalpies of the vapour phase from the reboiler and the liquid phase entering the reboiler, respectively. The reboiler duty (Q_R) is determined from the energy balance over the column:

$$Q_R = Dh_D + Bh_B - Fh_F + Q_C \tag{3.7}$$

For example, Table 3.1 shows the specifications of a column separating a mixture of acetic acid, water, and n-butyl acetate. The column is operated at 1 atm. The feed is a saturated liquid homogeneous mixture. The bottom product is specified such that a highly pure acetic acid is achieved. The top product is specified so that a highly pure water (99.85 mol%) is obtained from the decanter. Note that only three out of six mole fractions of the top and bottom product compositions (at least one for each stream) are specified according to the desired product purities. The remaining mole fractions are determined from the material balance over the column. Figure 3.3 shows a mass balance line representing the mass balance of the column and the decanter tie line which is the tie line corresponding to the top product composition.

Table 3.1. Specifications of a column separating a water/acetic acid/n-butyl acetate mixture

	Feed, *F*	Distillate, *D*	Bottoms, *B*
Composition (mole fraction)			
Water	0.4499 [a]	0.8177	0.0019
Acetic acid	0.4501 [a]	0.0003 [a]	0.9980 [a]
n-Butyl acetate	0.1000	0.1820	0.0001 [a]
Feed condition (*q*)	1 [a]		
Flow rate (kmol/h)	100 [a]	54.91	45.09
Reflux ratio		1.45	
Phase split ratio of reflux	Case (i): $\phi_1 \neq \phi_1^o$	0.3	
	Case (ii): $\phi_1 = \phi_1^o$	0.5890	

[a] Specified values,

ϕ_1^o = Phase split ratio of the reflux that may cause the liquid leaving the stage next to the decanter ($\mathbf{x}_2^R$) to be heterogeneous

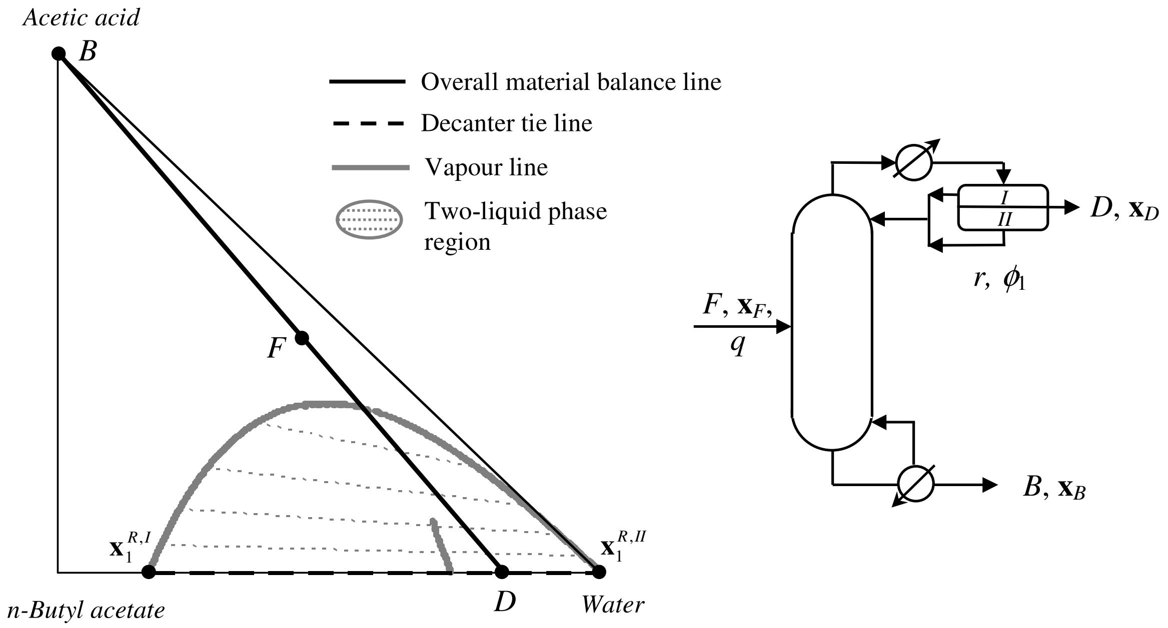


Figure 3.3. Material balance line and decanter tie line of the column

In general, the specifications for the column with an integrated decanter are the same as for a column without a decanter. The phase split ratio of reflux stream (ϕ_1) is an additional degree of freedom since the proportion of heavy to light liquid phases in the reflux can be manipulated. As a result, the compositions of the reflux stream and top product are different.

For a column with an integrated decanter, the top product composition must be chosen such that it is in the two-liquid phase region and a part of its liquid-liquid tie line is in the same distillation region as the bottom product. This is because for a column to be feasible, the top vapour composition must be in the same distillation region as the bottom product composition (Pham et al., 1989; Ryan and Doherty, 1989; Wasylkiewicz et al., 2000; Wasylkiewicz et al., 2003). According to the material balance over the top decanter (Figure 3.4), the compositions of the top product ($\mathbf{x}_D$), reflux stream ($\mathbf{x}_1^R$) and top vapour ($\mathbf{y}_2^R$) are located on the same tie line. To ensure that the top vapour composition will be in the same region as the bottom product, a part of the decanter tie line must be in the same distillation region as the bottom product.

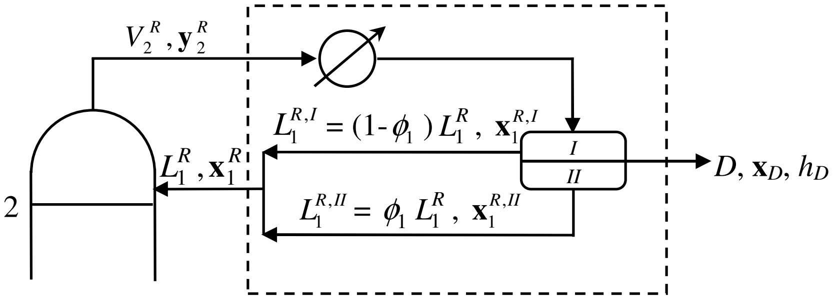


Figure 3.4. Schematic representation of top decanter mass balance (decanter is stage 1)

For the illustrative example, the top product can be chosen such that it is located on a liquid-liquid tie line close to the water/n-butyl acetate edge as no distillation boundary is present in the residue curve map shown in Figure 3.2. Thus, the top vapour composition will be located in the same distillation region as the bottom product.

In the rectifying section of a column, two liquid phases may appear on stages below the decanter. The appearance of two liquid phases in the rectifying section is dependent on how the phase split ratio of reflux (ϕ_1) is specified. If the decanter tie line crosses the vapour line (see Figure 3.3), there is a value of reflux phase split ratio that causes the top vapour composition to be on the vapour line, denoted by ϕ_1^o. Having the top vapour composition on the vapour line causes the two liquid phases, which are in equilibrium with the top vapour, to appear on the top stage of the column (stage 2). By fixing the top vapour composition ($\mathbf{y}_2^R$) to lie on the vapour line, the overall liquid composition of reflux ($\mathbf{x}_1^R$) can be determined from the mass balance over the decanter, equation (3.8), and the phase split ratio of the reflux ϕ_1^o can thus be calculated from lever rule, equation (3.9). If the calculated phase split ratio ϕ_1^o is out of the range, that is $\phi_1^o < 0$ or $\phi_1^o > 1$, it is physically meaningless because it causes the reflux composition ($\mathbf{x}_1^R$) to lie outside the two-liquid phase region. This indicates that the liquid on stage 2 cannot be heterogeneous at the specified reflux ratio.

$$\mathbf{x}_1^R = \frac{r+1}{r}\mathbf{y}_2^R - \frac{1}{r}\mathbf{x}_D \tag{3.8}$$

$$\phi_1^o = \frac{x_{1,i}^R - x_{1,i}^{R,I}}{x_{1,i}^{R,II} - x_{1,i}^{R,I}} = \frac{L_1^{R,II}}{L_1^R} \qquad \text{for } i = 1, 2 \text{ or } 3 \tag{3.9}$$

For the example in Table 3.1, the decanter tie line and the vapour line intersect each other. Therefore, the liquid leaving the top stage of the column ($\mathbf{x}_2^R$) can be either homogeneous or heterogeneous depending on the given reflux phase split ratio. To demonstrate, the composition profile of the rectifying section will be generated for both cases: (i) the liquid leaving the top stage of the column is homogeneous ($\phi_1 \neq \phi_1^o$), and (ii) the liquid leaving the top stage of the column is heterogeneous ($\phi_1 = \phi_1^o$). For the given reflux ratio and top product, the reflux phase split ratio that causes the top vapour composition to lie on the vapour line is 0.5890.

3.2.1.2 Composition profile of the rectifying section

The liquid compositions on each stage are calculated by solving material and energy balances simultaneously along with phase equilibrium. As the liquid on a stage in the rectifying section may be heterogeneous or homogeneous, material and energy balance equations for each case are different. Equations (3.10) and (3.11) are the material and energy balances for the rectifying section with a homogeneous liquid on stage *n*, respectively (cf. Figure 3.5a). Equations (3.12) and (3.13) are the material and energy balances for the rectifying section with a heterogeneous liquid on stage *n* (cf. Figure 3.5b).

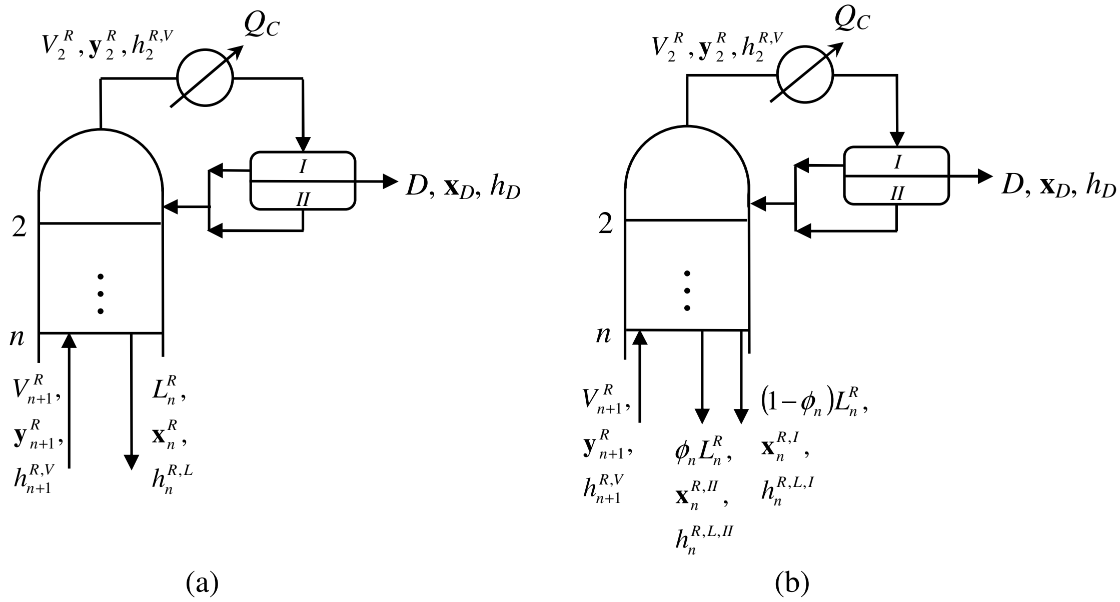


Figure 3.5. Schematic representation of rectifying sections with (a) homogeneous liquid on stage *n*, (b) heterogeneous liquid on stage *n*

$$\left(L_n^R + D\right)\mathbf{y}_{\mathrm{n}+1}^R - L_n^R\mathbf{x}_n^R - D\mathbf{x}_D = \mathbf{0} \tag{3.10}$$

$$\left(L_n^R + D\right)h_{n+1}^{R,V} - L_n^R h_n^{R,L} - Dh_D + Q_C = 0 \tag{3.11}$$

where Q_C is determined from equation (3.14).

$$\left(L_n^R + D\right)\mathbf{y}_{n+1}^R - L_n^R\left(\left(1-\phi_n\right)\mathbf{x}_{\mathrm{n}}^{R,I} + \phi_n\mathbf{x}_{\mathrm{n}}^{R,II}\right) - D\mathbf{x}_D = \mathbf{0} \tag{3.12}$$

$$\left(L_n^R + D\right)h_{n+1}^{R,V} - L_n^R\left(\left(1-\phi_n\right)h_n^{R,L,I} + \phi_n h_n^{R,L,II}\right) - Dh_D + Q_C = 0 \tag{3.13}$$

where Q_C is determined from equation (3.14).

$$Q_C = \left(\left(r+1\right)h_2^{R,V} - r\left(\left(1-\phi_1\right)h_1^{R,L,I} + \phi_1 h_1^{R,L,II}\right) - h_D\right)D \tag{3.14}$$

For a given top product composition ($\mathbf{x}_D$), reflux phase split ratio (ϕ_1), and reflux ratio (r), the rectifying liquid composition profile is calculated recursively starting from the reflux composition ($\mathbf{x}_1^R$) using either the set of equations (3.10) to (3.11) or the set of equations (3.12) to (3.13) and vapour-(liquid)-liquid equilibrium. The calculation depends on how the phase split ratio of reflux ϕ_1 is specified. The overall procedure for calculating the rectifying profile is shown in Figure 3.6. The rectifying profile calculation is explained in detail below.

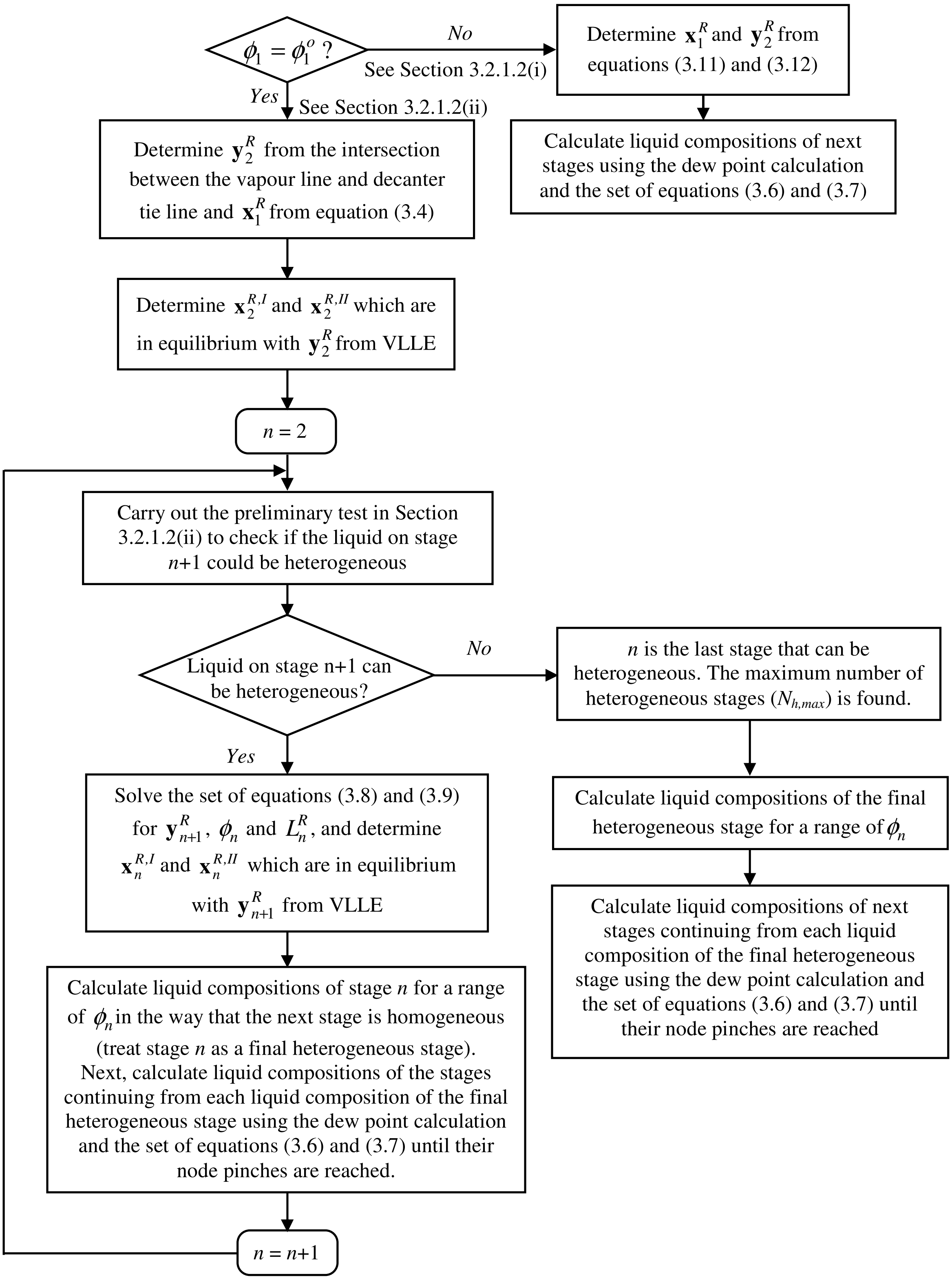


Figure 3.6. Flowchart showing the procedure in generating the rectifying profile

i. The phase split ratio of reflux is specified such that the top vapour composition is not on the vapour line ($\phi_1 \neq \phi_1^o$)

Figure 3.7 shows the rectifying profile of the column separating a mixture of acetic acid, water and n-butyl acetate according to the specifications in Table 3.1 when $\phi_1 = 0.3$. The rectifying profile is calculated as follows.

Assuming that liquid-liquid equilibrium is achieved in the decanter operating at boiling temperature, light and heavy liquid compositions ($\mathbf{x}_1^{R,I}$ and $\mathbf{x}_1^{R,II}$) in equilibrium with the top product will be formed in the decanter. For a given reflux phase split ratio (ϕ_1), the overall liquid composition of the reflux stream ($\mathbf{x}_1^R$) is calculated from equation (3.15). The top vapour composition ($\mathbf{y}_2^R$) is determined from the material balance over the decanter, equation (3.16) (see Figure 3.4). According to the material balance over the decanter, the compositions of the top product ($\mathbf{x}_D$), top vapour ($\mathbf{y}_2^R$), and reflux stream ($\mathbf{x}_1^R$) lie on a straight line, i.e. decanter tie line, as shown in Figure 3.7.

$$\mathbf{x}_1^R = (1-\phi_1)\mathbf{x}_1^{R,I} + \phi_1 \mathbf{x}_1^{R,II} \tag{3.15}$$

$$\mathbf{y}_2^R = \frac{r}{r+1}\left[(1-\phi_1)\mathbf{x}_1^{R,I} + \phi_1 \mathbf{x}_1^{R,II}\right] + \frac{1}{r+1}\mathbf{x}_D \tag{3.16}$$

The liquid composition on stage 2 ($\mathbf{x}_2^R$) in equilibrium with the top vapour ($\mathbf{y}_2^R$) is next determined from dew point calculation. Because the top vapour composition ($\mathbf{y}_2^R$) is not located on the vapour line, the liquid on stage 2 is homogeneous and its composition lies outside the two-liquid phase region.

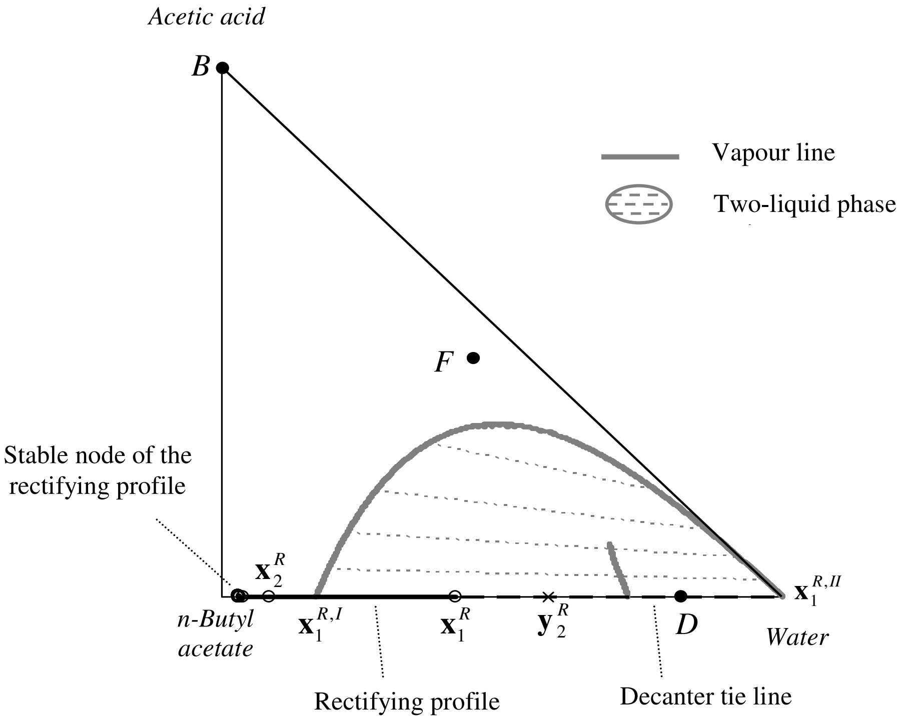


Figure 3.7. Rectifying profile of the column separating a mixture of acetic acid, water and n-butyl acetate according to the specifications in Table 3.1 at the phase split ratio of reflux (ϕ_1) of 0.3.

The calculation is continued to the next stages down the column by solving material and energy balances (equation 3.10 and 3.11), for $\mathbf{y}_{n+1}^R$ and L_n^R, simultaneously with vapour-liquid equilibrium, for $\mathbf{x}_{n+1}^R$. The calculation is stopped when the composition profile reaches its stable node pinch where there is no change in composition from one stage to the next. In Figure 3.7, the rectifying profile ends at a stable node close to the pure n-butyl acetate vertex.

ii. The phase split ratio of reflux is specified such that the top vapour composition is on the vapour line ($\phi_1 = \phi_1^o$)

In case that $\phi_1 = \phi_1^o$ is specified, more than one liquid composition profiles can be generated for the rectifying section. Figure 3.8 shows examples of the rectifying profiles of the column with the specifications in Table 3.1 when $\phi_1 = \phi_1^o = 0.5890$. The rectifying profile starts from the reflux composition to the composition of stage 9 and branches off, for example, into six profiles. The calculation of the rectifying profile is as follows.

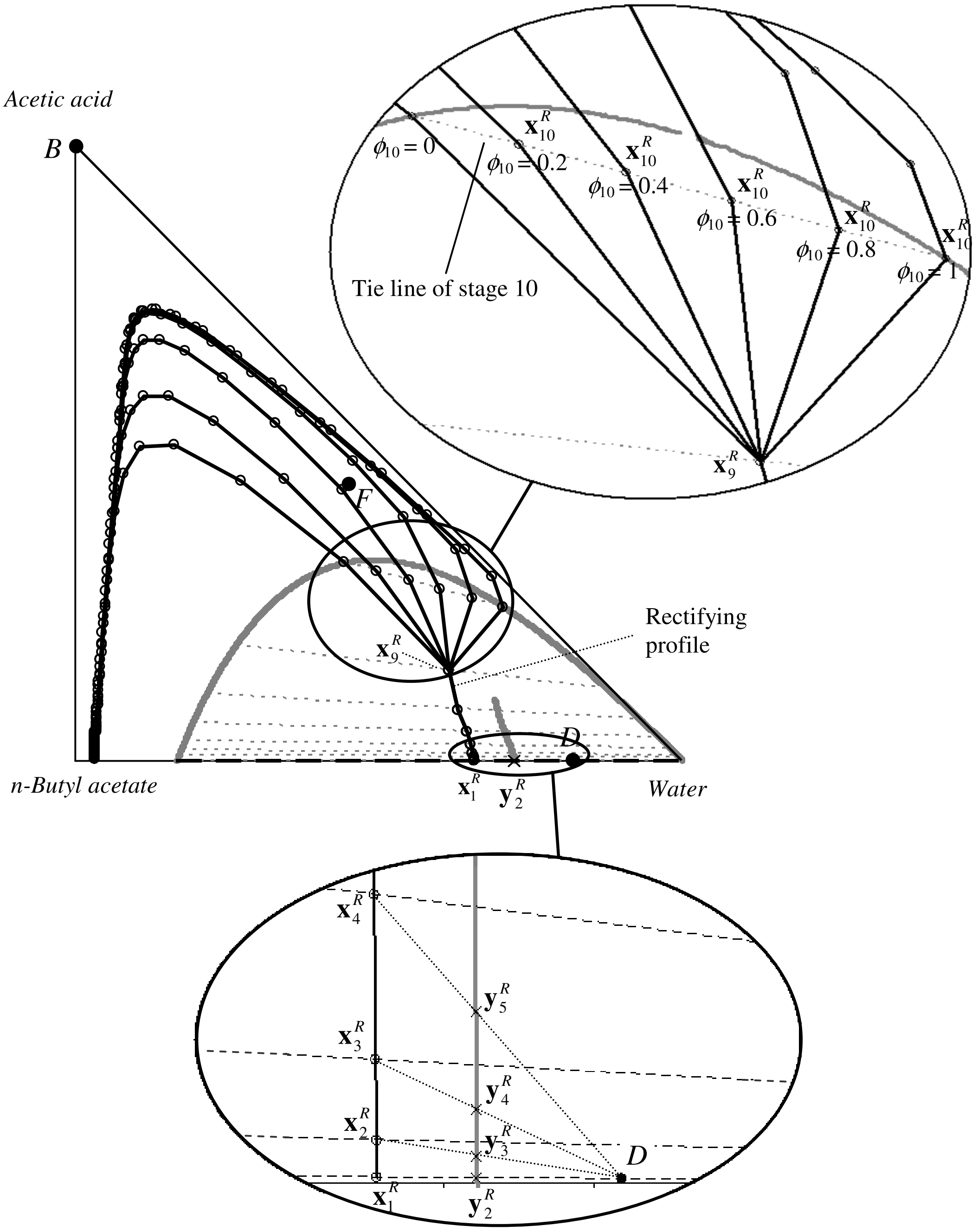


Figure 3.8. Rectifying profiles of the column separating a mixture of acetic acid, water and n-butyl acetate according to the specifications in Table 3.1 at the reflux phase split ratio (ϕ_1) of 0.5890. The profiles are calculated for ϕ_{10} = 0, 0.2, 0.4, 0.6, 0.8 and 1.

Because the phase split ratio of reflux is specified such that $\phi_1 = \phi_1^o$, the top vapour composition ($\mathbf{y}_2^R$) is located on the vapour line, and two liquid phases in equilibrium with the top vapour appear on stage 2. From the dew point calculation, the light and heavy liquid compositions ($\mathbf{x}_2^{R,I}$ and $\mathbf{x}_2^{R,II}$) are obtained.

Before the calculation of rectifying profile is continued, preliminary tests should be carried out to check if the liquid on the next stage below ($\mathbf{x}_{n+1}^R$) could be heterogeneous. For the liquid on the next stage ($\mathbf{x}_{n+1}^R$) to be heterogeneous, the vapour composition of the next stage ($\mathbf{y}_{n+1}^R$) must be on the vapour line while satisfying the material and energy balances, equations (3.12) and (3.13).

Preliminary tests

a. Test if there will be a vapour composition of the next stage ($\mathbf{y}_{n+1}^R$) located on the vapour line that can satisfy the material balance, equation (3.12).

- *a.1 Determine the light and heavy liquid compositions of stage n ($\mathbf{x}_n^{R,I}$ and $\mathbf{x}_n^{R,II}$), which are in equilibrium with the vapour composition of stage n ($\mathbf{y}_n^R$), from the dew point calculation.*
- *a.2 Check whether a line connecting $\boldsymbol{x}_D$ and $\mathbf{x}_n^{R,I}$ or a line connecting $\boldsymbol{x}_D$ and $\mathbf{x}_n^{R,II}$ crosses the vapour line by using a line intersection search algorithm developed by Hölz (2006).*
- *a.3 If one of the lines crosses the vapour line, the liquid on the next stage ($\mathbf{x}_{n+1}^R$) may be heterogeneous. Go to step b. Otherwise, stage n is the last stage that heterogeneous liquid could appear on.*

This test is developed from the fact that the material balance over the rectifying section requires that the liquid composition of stage *n* ($\mathbf{x}_n^R$), the vapour composition of the next stage ($\mathbf{y}_{n+1}^{R}$) and the top product composition ($\mathbf{x}_D$) must lie on a straight line in composition space. In addition, for the liquid on the next stage n+1 to be heterogeneous the vapour composition of the next stage must be on the vapour line. If an intersection exists, the top vapour composition ($\mathbf{y}_{n+1}^{R}$) can be on the vapour line and cause two liquid phases to appear on the stage n+1. The liquid on the next stage will be heterogeneous if the following test is satisfied.

b. If the previous test is satisfied, then test if there will be a vapour composition of the next stage ($\mathbf{y}_{n+1}^{R}$) located on the vapour line that can satisfy the energy balance, equation (3.13).

- *b.1 If an intersection is found in step a, determine the minimum and maximum of the phase split ratios of stage n ($\phi_{n,min}$ and $\phi_{n,max}$) that cause the intersection between the vapour line and the line connecting $\mathbf{x}_D$ and $\mathbf{x}_n^R$ (see Appendix A).*
- *b.2 Determine the vapour compositions of the next stage ($\mathbf{y}_{n+1}^{R}$) lying on the vapour line and their enthalpies ($h_{n+1}^{R,V}$) corresponding to the minimum and maximum phase split ratios of stage n.*
- *b.3 Calculate ε, which is the error in the energy balance, from equation (3.17), for both $\phi_{n,min}$ and $\phi_{n,max}$.*
- *b.4 If one of ε is negative, there is a value of ϕ_n between $\phi_{n,min}$ and $\phi_{n,max}$ that satisfies the energy balance. Thus, the next stage n+1 can be heterogeneous (for details, see Appendix A).*

$$\varepsilon = \left(L_n^R + D\right)h_{n+1}^{R,V} - L_n^R\left(\left(1-\phi_n\right)h_n^{R,L,I} + \phi_n h_n^{R,L,II}\right) - Dh_D + Q_C \tag{3.17}$$

If the tests are satisfied, the material and energy balances, equations (3.12) and (3.13), are solved simultaneously for $\mathbf{y}_{n+1}^{R}$, ϕ_n and L_n^R together with vapour-liquid-liquid equilibrium for $\mathbf{x}_{n+1}^{R,I}$ and $\mathbf{x}_{n+1}^{R,II}$. The overall liquid composition of stage n ($\mathbf{x}_n^R$) is then calculated from equation (3.18).

$$\mathbf{x}_n^R \;=\; (1-\phi_n)\mathbf{x}_n^{R,I} + \phi_n \mathbf{x}_n^{R,II} \tag{3.18}$$

In Figure 3.8, the rectifying profile is calculated starting from the reflux composition ($\mathbf{x}_1^R$). Because the top vapour composition ($\mathbf{y}_2^R$) is on the vapour line, two liquid phases occur on stage 2. The preliminary testing indicates that there is a vapour composition of the next stage ($\mathbf{y}_3^R$) lying on the vapour line while also satisfying both material and energy balances over the rectifying section. The vapour composition of stage 3 ($\mathbf{y}_3^R$), phase split ratio of stage 2 (ϕ_2), liquid flow rate on stage 2 (L_2^R), and overall liquid composition of stage 2 ($\mathbf{x}_2^R$) are calculated from the set of equations (3.12) to (3.13) and equation (3.18). The light and heavy liquid compositions of stage 3 ($\mathbf{x}_3^{R,I}$ and $\mathbf{x}_3^{R,II}$) are obtained from dew point calculation.

The calculation is continued down the column by solving the set of equations (3.12) and (3.13) together with the vapour-liquid-liquid equilibrium until stage 10 is reached. Two liquid phases appear on stages continuing from the decanter to stage 10 as shown in Figure 3.8. The dew point calculation of the vapour composition of stage 10 ($\mathbf{y}_{10}^R$) gives the light and heavy liquid compositions on stage 10 ($\mathbf{x}_{10}^{R,I}$ and $\mathbf{x}_{10}^{R,II}$). Performing the first test indicates that there is no liquid composition on the tie line of this stage that leads to the intersection between the vapour line and a line made up of $\mathbf{x}_D$ and $\mathbf{x}_{10}^R$. As a result, the calculation cannot be continued further in the same way.

If the preliminary tests are not satisfied, stage n (e.g. stage 10 in Figure 3.8) will be the final stage on which a heterogeneous liquid appears. The set of material and energy balances, equations (3.12) and (3.13), cannot be solved together with the vapour-liquid-liquid equilibrium as before. This is because there is no vapour composition of stage n+1

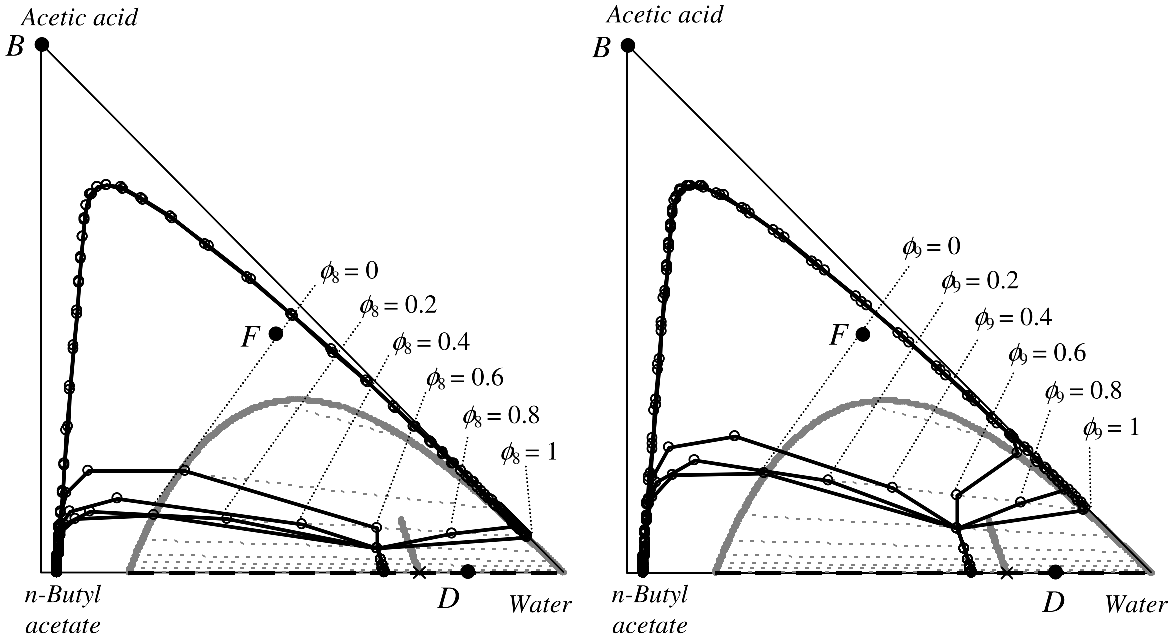
($\mathbf{y}_{n+1}^{R}$) that lies on the vapour line and satisfies the set of equations. However, there are an infinite number of vapour compositions of stage n+1 ($\mathbf{y}_{n+1}^{R}$) that satisfy the set of equations but they are not located on the vapour line (See Appendix A.2). Those vapour compositions ($\mathbf{y}_{n+1}^{R}$) corresponds to the entire range of phase split ratios of the final heterogeneous stage ($0 \leq \phi_n \leq 1$).

When the calculation reaches the final heterogeneous stage, there are three unknowns in the set of equations (3.12) and (3.13), i.e. vapour composition of the next stage ($\mathbf{y}_{n+1}^{R}$), phase split ratio (ϕ_n), and liquid flow rate (L_n^R). Note that only the light and heavy liquid compositions on stage n ($\mathbf{x}_n^{R,I}$ and $\mathbf{x}_n^{R,II}$), i.e. not the amounts of light and heavy liquid ($L_n^{R,I}$ and $L_n^{R,II}$), are obtained from vapour-liquid-liquid equilibrium. If one of those variables is specified, one of the multiple solutions can then be obtained.

Among those three unknown variables, it is most convenient to give the set of equations the phase split ratio (ϕ_n) since the phase split ratio has a minimum and a maximum value. Once ϕ_n is given, $\mathbf{x}_n^R$ is thus calculated from equation (3.18). Then, $\mathbf{y}_{n+1}^{R}$ and L_n^R can be determined from the set of equations (3.10) and (3.11) simultaneously with vapour-liquid equilibrium. The calculation of the rectifying profile can thus be continued down the column using the set of equations (3.10) to (3.11) and vapour-liquid equilibrium until the stable node of the profile is reached. Since multiple solutions are expected, the overall liquid composition on stage n can be calculated at various values of phase split ratio ranging from 0 to 1. A number of rectifying profiles are then generated downward from the liquid compositions corresponding to various phase split ratios of the final heterogeneous stage (ϕ_n). Although having to specify a variable at the final heterogeneous stage is counter-intuitive, it is consistent with the well-known phenomenon of multiple steady states in heterogeneous azeotropic distillation, as will be discussed in Section 3.2.1.5.

In Figure 3.8, stage 10 is the final heterogeneous stage where liquid compositions of stage 10 are calculated for ϕ_{10} = 0, 0.2, 0.4, 0.6, 0.8 and 1. The rectifying profiles are generated further from each liquid composition on stage 10 until their node pinches are reached near the pure n-butyl acetate vertex.

The rectifying profile in Figure 3.8 is calculated in such a way that heterogeneous liquid is allowed to occur on as many stages as possible. However, the rectifying profile may leave the two-liquid region and enter the homogeneous region after fewer heterogeneous stages since the number of heterogeneous stages cannot be controlled. For example, when the rectifying profile is calculated until stage 9 is reached, stage 10 can be homogeneous or heterogeneous. By treating stage 9 as the final heterogeneous stage, the calculation of rectifying profiles is continued downward from liquid compositions of stage 9 corresponding to a range of phase split ratios (ϕ_9). Figures 3.9(a) and (b) present the rectifying profiles having eight and nine heterogeneous stages continuing from the decanter, respectively. The liquid compositions of the final heterogeneous stage are calculated for ϕ_H = 0, 0.2, 0.4, 0.6, 0.8 and 1, where subscript H refers to the final heterogeneous stage. Some of these rectifying profiles having heterogeneous stages fewer than the maximum may lead to feasible designs as will be discussed in Section 3.2.1.4. An example will be provided (Section 3.3.2) to illustrate that some stages may be either heterogeneous or homogeneous.



(a) Eight heterogeneous stages (b) Nine heterogeneous stages

Figure 3.9. Rectifying profiles according to the specifications in Table 3.1 at the phase split ratio of reflux (ϕ_1) of 0.5890. (a) Stage 8 is the final heterogeneous stage; (b) stage 9 is the final heterogeneous stages. The profiles are calculated for ϕ_H = 0, 0.2, 0.4, 0.6, 0.8 and 1.

The calculation of the rectifying profile: Summary

For a given top product composition and reflux ratio, the calculation of a rectifying profile depends on a specified reflux phase split ratio. At a given reflux ratio, there is only one reflux phase split ratio (within the range of 0 to1) that causes two liquid phases to appear on stages below stage 2 ($\phi_1 = \phi_1^o$). The value of the reflux phase split ratio that causes two liquid phases to appear in the column can be calculated from equation (3.9).

If the reflux phase split ratio is specified such that $\phi_1 \neq \phi_1^o$, only one rectifying profile is calculated using the set of equations (3.10) and (3.11) (See Section 3.2.1.2(i)). The rectifying profile starts from the reflux composition and leaves the two-liquid phase region at stage 2.

If the reflux phase split ratio is specified such that $\phi_1 = \phi_1^o$, multiple rectifying profiles are calculated following the method in Section 3.2.1.2(ii). The rectifying profile is firstly calculated starting from the reflux composition in such a way that two liquid phases appear on as many stages as possible. The preliminary tests are applied to check whether the liquid on the next stage below could be heterogeneous. When the calculation reaches the last stage that could be heterogeneous, the tests indicate that there is no solution that satisfies the material and energy balances and the vapour-liquid-liquid equilibrium. Hence, a method for solving the set of nonlinear algebraic equations will not be carried out unnecessarily. Then, multiple rectifying profiles are generated for various phase split ratios of the final heterogeneous stage ranging from 0 to 1. Once the maximum number of heterogeneous stage is known, multiple rectifying profiles having fewer heterogeneous stages are generated further. By treating each heterogeneous stage as the final heterogeneous stage, the rectifying profiles are calculated for a range of phase split ratios of that final heterogeneous stage.

3.2.1.3 Composition profile of the stripping section

Figure 3.10 represents the balance envelope in the stripping section of a column. Equations (3.19) and (3.20) are material and energy balances of the stripping section. These equations can be applied to both homogeneous and heterogeneous stages.

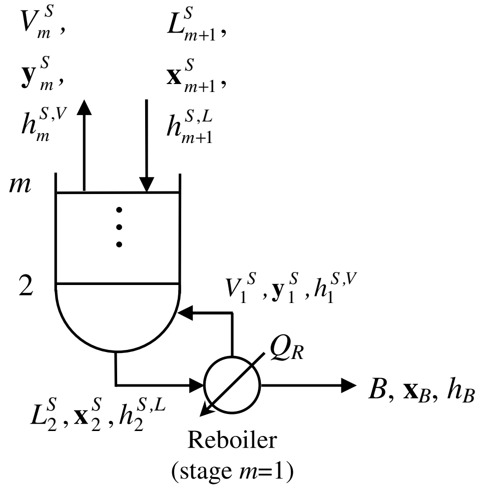


Figure 3.10. Schematic representation of the stripping section of a column

$$\left(V_m^S + B\right)\mathbf{x}_{\mathrm{m+1}}^S - V_m^S \mathbf{y}_{\mathrm{m}} - B\mathbf{x}_{\mathrm{B}} = \mathbf{0} \tag{3.19}$$

$$\left(V_m^S + B\right)h_{m+1}^{S,L} - V_m^S h_m^{S,V} - Bh_B + Q_R = 0 \tag{3.20}$$

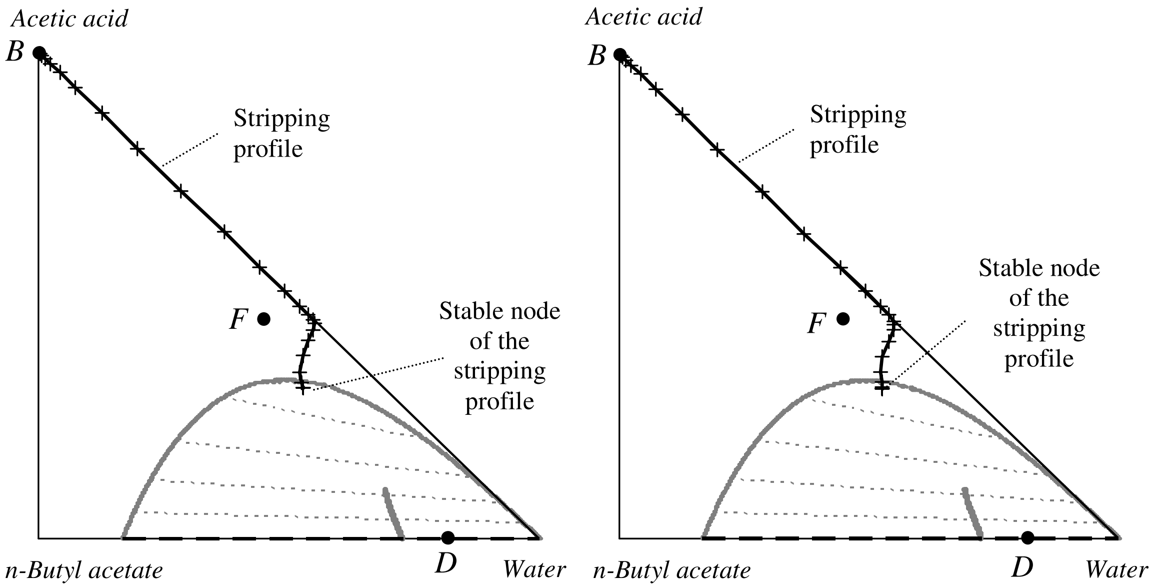
where $Q_R = \left(sh_1^{S,V} - (s+1)h_2^{S,L} + h_B\right)B$ when $s = V_1^S / B$ is specified, or

$Q_R = Dh_D + Bh_B - Fh_F + Q_C$ when the feed condition is specified.

For a given bottom product composition ($\mathbf{x}_B$) and a reboil ratio (s), the liquid composition profile of the stripping section is calculated recursively starting from the bottom product composition. The vapour composition from the reboiler ($\mathbf{y}_1^S$) in equilibrium with the bottom product is determined from the bubble point calculation. The liquid composition entering the reboiler ($\mathbf{x}_2^S$) is then calculated from the set of equations (3.19) and (3.20). The calculation is continued to the next stage up the column by solving the material and energy balances (equations 3.19 and 3.20), for $\mathbf{x}_{m+1}^S$ and V_m^S, together with vapour-liquid-liquid equilibrium for $\mathbf{y}_m^S$. The calculation is continued until the node pinch of the stripping profile is reached.

The generation of the stripping profile is carried out in the way discussed above even if a heterogeneous stage is encountered during the calculation. The calculation can be carried out in the same way for both heterogeneous and homogeneous stages since a result from the set of equations (3.19) and (3.20) is the overall liquid composition of the stage ($\mathbf{x}_{m+1}^S$), not the light and heavy liquid compositions ($\mathbf{x}_{m+1}^{S,I}$ and $\mathbf{x}_{m+1}^{S,II}$). The coexisting light and heavy liquid compositions ($\mathbf{x}_{m+1}^{S,I}$ and $\mathbf{x}_{m+1}^{S,II}$) and the vapour composition ($\mathbf{y}_{m+1}^S$) in equilibrium with $\mathbf{x}_{m+1}^S$ can be determined from the vapour-liquid-liquid equilibrium.

The stripping profiles for the two cases of the illustrative example in Table 3.1 are shown in Figure 3.11. For case (ii), $\phi_1 = \phi_1^o$ = 0.5890, unlike the rectifying section, the stripping section has only one liquid composition profile as shown in Figure 3.11(b). The stripping profiles of the two cases are slightly different because the two cases have different reboil duties resulting from their reflux phase split ratios. For a given feed condition and reflux ratio, a reboil duty is determined from the energy balance over the column (equation 3.7). In equation 3.7, the condenser duty depends on the specified reflux phase split ratio according to the energy balance over the decanter (equation 3.14). Thus, the reboil duty is dependent on the specified reflux phase split ratio. As a result, the stripping section for case (ii) has only one stripping profile and it is different from the stripping profile of case (i).



(a) Case (i): ϕ_1= 0.3

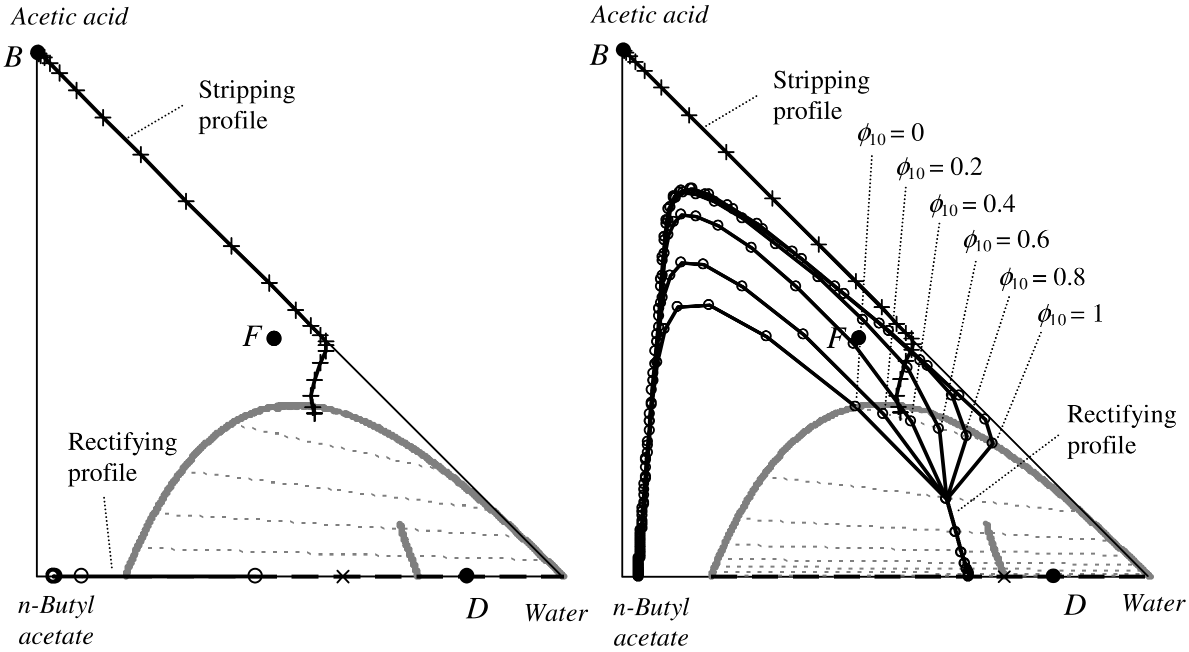
(b) Case (ii): $\phi_1 = \phi_1^o = 0.5890$

Figure 3.11. Stripping profile of the column separating a mixture of acetic acid, water and n-butyl acetate according to the specifications in Table 3.1

3.2.1.4 Feasibility assessment and column design evaluation

After all rectifying and stripping profiles are calculated corresponding to the column specifications, the feasibility of the proposed separation can be assessed and feasible designs can be evaluated. The intersection between a rectifying and stripping profile indicates the feasibility of the proposed separation. The intersection between the profiles can be identified using the line intersection search algorithm developed by Hölz (2006). For an intersection between the rectifying and stripping profiles, details of a column design can be determined. The intersection point of the profiles indicates the feed location (Pham et al., 1989). The number of stages required for the column can then be counted. For a column with many heterogeneous stages in the rectifying section, a number of feasible designs may be identified since the rectifying profiles are generated for different numbers of heterogeneous stages and for various phase split ratios of heterogeneous stages. Once the details of each column design are known, the design can be evaluated in terms of total annualised cost, allowing the design to be compared with other designs or separation processes.

Figure 3.12(a) presents the rectifying and stripping profiles according to the product specifications in Table 3.1 and reflux phase split ratio of 0.3 (case i). That the rectifying and stripping profiles do not intersect each other indicates that the proposed separation is not feasible at the reflux phase split ratio of 0.3.



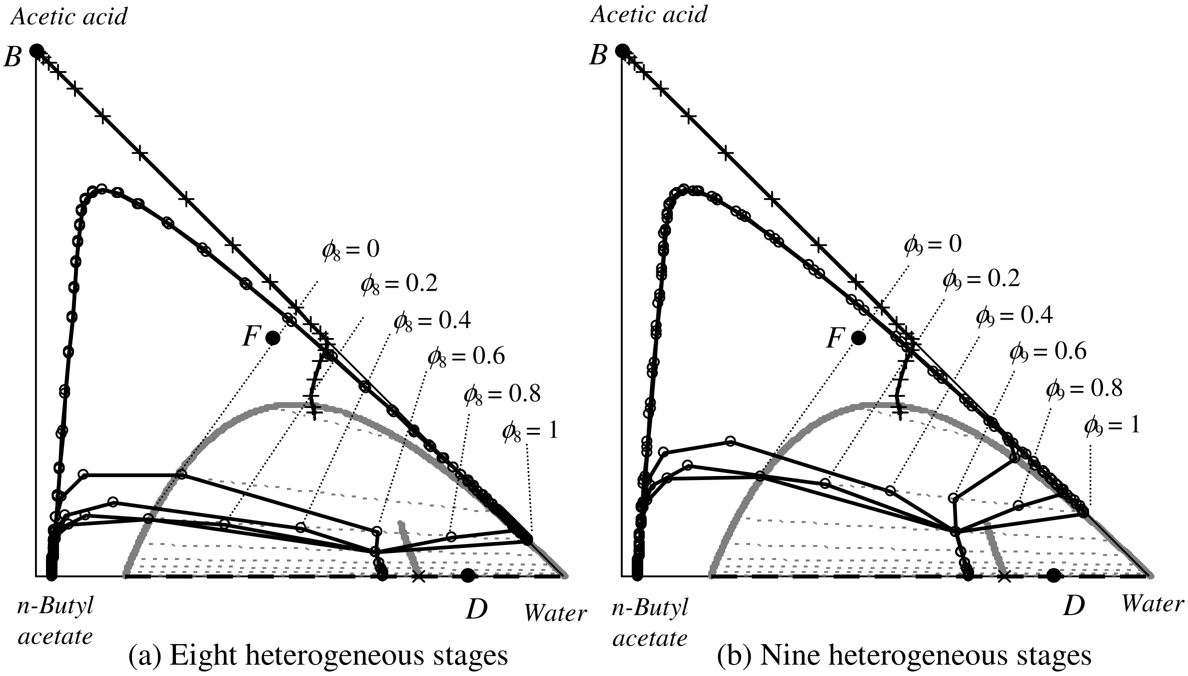
(a) Case (i): $\phi_1 = 0.3$

(b) Case (ii): $\phi_1 = \phi_1^o = 0.5890$.

Figure 3.12. Rectifying and stripping profiles of the column according to the specifications in Table 3.1. (a) Case (i): the liquid leaving the top stage of the column is homogeneous ($\phi_1 = 0.3$), (b) Case (ii): the liquid leaving the top stage of the column is heterogeneous ($\phi_1 = \phi_1^o = 0.5890$).

Figure 3.12(b) shows the rectifying and stripping profiles according to the product specifications in Table 3.1 and the reflux phase split ratio of 0.5890 (case ii). In this case, the rectifying profiles are calculated so that heterogeneous liquid appears on as many stages as possible, i.e. ten stages. Six rectifying profiles are generated for ϕ_{10} = 0, 0.2, 0.4, 0.6, 0.8 and 1. As shown in Figure 3.12(b), the rectifying profiles for ϕ_{10} = 0.4, 0.6, 0.8 and 1 intersect the stripping profile, resulting in four feasible designs. For each feasible design, the number of stages is counted and the feed location is identified, as shown in Table 3.2.

The numbers of stages for the rectifying and stripping sections (N_R and N_S) are counted from the top decanter and the reboiler, respectively, up to the intersection point. The total number of stages (N_{Total}) is N_R+N_S-1 since the intersection point is included in both N_R and N_S. In Table 3.2, the numbers of stages for both sections are reported in real numbers to show that the rectifying and stripping profiles do not coincide at the intersection point. The number of stages in real values is rounded when the design is taken to initialise a rigorous simulation.



(a) Eight heterogeneous stages

(b) Nine heterogeneous stages

Figure 3.13. Rectifying and stripping profiles according to the specifications in Table 3.1 at the reflux phase split ratio (ϕ_1) of 0.5890. (a) Eight heterogeneous stages in the rectifying section; (b) Nine heterogeneous stages in the rectifying section.

Feasible designs are also found for the rectifying profiles having heterogeneous stages fewer than the maximum. Figure 3.13 presents the stripping and rectifying profiles with eight and nine heterogeneous stages calculated for ϕ_H = 0, 0.2, 0.4, 0.6, 0.8 and 1. In Figure 3.13, the stripping profile intersects the rectifying profiles with ϕ_8 = 0.8 and 1, and ϕ_9 = 0.6, 0.8 and 1, leading to five feasible designs as listed in Table 3.2.

All feasible designs can be evaluated in terms of their total annualised costs so that they can be compared and the most attractive designs can be identified. In Table 3.2, the total annualised costs of column designs are estimated using the cost function in Appendix B based on a three-year repayment period and a 5% interest rate.

Table 3.2. Column designs for the proposed separation in Table 3.1

N_H	ϕ_H	N_R	N_S	N_{Total}	Total annualised cost* (£/year)
10	0.6	11.1	19.2	29.3	1,252,300
	0.8	12.3	18.2	29.5	1,267,400
	1	13.4	18.0	30.4	1,282,500
	0.4	10.2	21.8	31.0	1,297,600
9	0.6	14.7	18.0	31.7	1,312,600
	0.8	20.6	18.0	37.6	1,432,500
	1	26.9	18.0	43.9	1,566,000
8	0.8	37.1	18.0	54.1	1,786,000
	1	44.2	18.0	61.2	1,931,200
Condenser duty (kW)					1501
Reboiler duty (kW)					1508

* 3-year period, 5% interest rate

N_H = number of heterogeneous stages in the rectifying profile (including the decanter)
ϕ_H = phase split ratio of final heterogeneous stage
N_R = number of stages in the rectifying section, or feed location counted from the top (including the decanter)
N_S = number of stages in the stripping section (including the reboiler)
N_{Total} = total number of stages

All column designs in Table 3.2 satisfy the product specifications and have the same energy requirement but different numbers of stages and feed locations. Thus, the costs of the designs in Table 3.2 are different only in their capital costs. The most attractive design is the design with ten heterogeneous stages in the rectifying section and $\phi_{10} = 0.6$ as it requires the fewest stages.

Compared to the designs with fewer heterogeneous stages, the designs with the maximum number of heterogeneous stages are more attractive in terms of costs. The designs with eight and nine heterogeneous stages need more stages than those with the maximum number of heterogeneous stages, particularly in the rectifying section. As shown in Figure 3.13, the rectifying profiles that intersect the stripping profile need a large number of stages after the profiles leave the two-liquid phase region to the homogeneous region close to the water/acetic acid edge. Many stages are required due to the tangent pinch between water and acetic acid close to pure water.

The rectifying profiles having fewer than eight heterogeneous stages also lead to feasible designs (not shown in Table 3.2). Those designs are not as attractive as the designs in Table 3.2. As the number of heterogeneous stages decreases, the designs require many more stages in the rectifying section since their rectifying profiles leave the two-phase region nearer to the pure water vertex. As a result, more stages are required to pass the tangent pinch.

To illustrate that the column design method can be validated, a rigorous simulation of the first design in Table 3.2 is carried out in HYSYS. The UNIQUAC-Virial model is selected to predict the phase equilibrium behaviour as used in the design method. The column consists of 29 stages including the decanter and reboiler. The saturated liquid feed having a composition shown in Table 3.1 is added to the column at stage 11 from the top. The pressure of condenser and reboiler is 1 atm. The reflux ratio is 1.45. Additional column specifications given to HYSYS are listed in Table 3.3. The results from the design method, e.g. the liquid composition and temperature of each stage, the location where two liquid phases present in the column, are also given to HYSYS as an initial guess to facilitate the convergence.

The results and liquid composition profile of the first design from HYSYS are shown in Table 3.3 and Figure 3.14, respectively. The results of product streams from HYSYS are in excellent agreement with the product specifications of the design method. In HYSYS, two liquid phases appear on ten stages ranging from the top decanter to stage 9. Figure 3.14 also shows a good agreement of the composition profiles from simulation and the design method. In Figure 3.14, the rectifying profile from the design method deviates slightly from the profile predicted by HYSYS around the final heterogeneous stage (stage 10), resulting in the difference of the phase split ratios of this stage from the two methods. This small discrepancy occurs because the liquid composition of this final heterogeneous stage is close to the plait point of the heterogeneous boiling envelope. Calculating vapour-liquid-liquid equilibrium with high accuracy near the plait point is particularly difficult.

The simulation results from HYSYS and those of the design method for the first design in Table 3.2 can be seen to be in good agreement: the stripping and rectifying profiles coincide near the intersection point which corresponds to the feed stage (see Figure 3.12b). In Table 3.2, the numbers of stages for some designs are fractional numbers, for example the designs with ϕ_{10} = 0.8 and 1. For the designs with fractional numbers of stages, the results of their rigorous simulations may be different from those of the design method. Nonetheless, the design method provides column design parameters for initialising rigourous simulations. To make the simulation results consistent with those of the design method, some input variables, e.g. reflux ratio and feed condition, may be manually adjusted in either HYSYS or the design method. Alternatively, the product specifications may be revised. In addition, the deviation of the results from HYSYS and the design method may occur due to the existence of the multiple steady states.

Table 3.3. Column specifications given to HYSYS and simulation results from HYSYS based on the first column design in Table 3.2

Column specifications given to HYSYS

Reflux ratio	1.45
Temperature of the reboiler (^{o}C)	117.7
Mole fraction of n-butyl acetate in the bottoms	0.0001

Simulation results from HYSYS compared with design specifications for the boundary value method (BVM)

	BVM		HYSYS	
	Distillate, *D*	Bottoms, *B*	Distillate, *D*	Bottoms, *B*
Composition (Mole fraction)				
Water	0.8177	0.0019	0.8177	0.0019
Acetic acid	0.0003 [a]	0.9980 [a]	0.0003	0.9980
n-Butyl acetate	0.1820	0.0001 [a]	0.1820	0.0001 [a]
Flow rate (kmol/h)	54.91	45.09	54.91	45.09
Condenser duty (kW)	1501		1501	
Reboiler duty (kW)	1508		1508	
Number of heterogeneous stages	10		10	
Phase split ratio of the final heterogeneous stage	0.6		0.73	

[a] Specified values

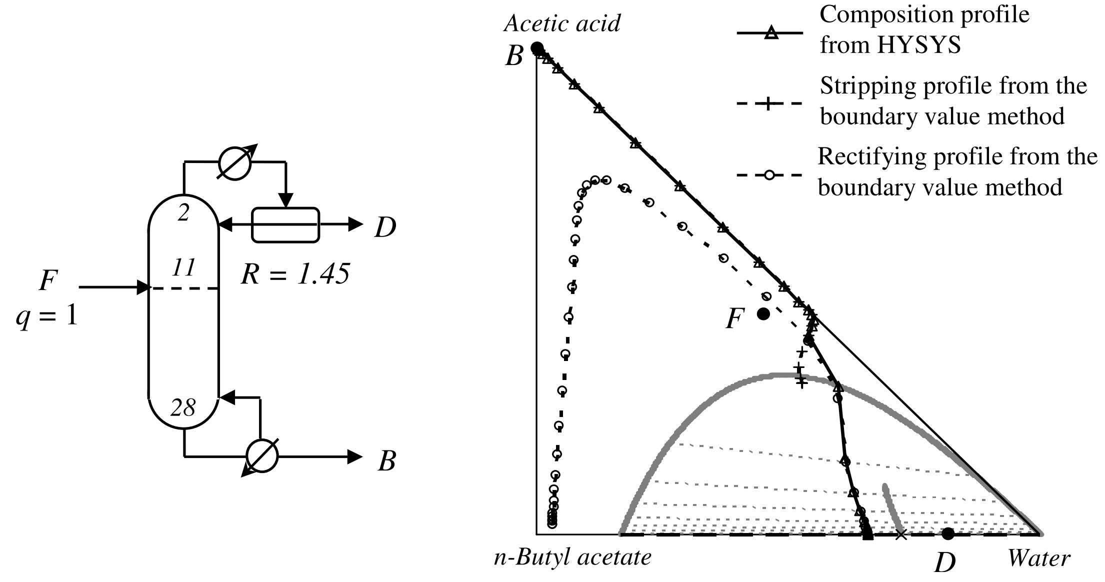


Figure 3.14. The first column design in Table 3.2 and its liquid composition profile from HYSYS compared with the profiles from the design method.

3.2.1.5 Validation of multiplicities

As shown in Table 3.2, in the case that the reflux phase split ratio is specified such that two liquid phases appear in the column, there are multiple column designs that satisfy the product compositions. All of the designs have the same heat duties but are different with respect to number of stages and feed location. These multiple solutions result from different numbers of heterogeneous stages in the rectifying section and phase split ratios of the final heterogeneous stages.

To validate the existence of multiple column designs, a rigorous simulation of the fourth design in Table 3.2 (the design with $\phi_{10} = 0.4$) is carried out in HYSYS. The column has 31 stages and its feed location is stage 10. The condenser and reboiler pressure is 1 atm and the reflux ratio is 1.45. Additional column specifications are listed in Table 3.4. The resulting product compositions and heat duties from HYSYS (Table 3.4) are identical to those of the first design (Table 3.3). In HYSYS, the column is also found to have ten heterogeneous stages. The liquid composition profile for the column with $\phi_{10} = 0.4$ predicted by HYSYS agrees well with the composition profiles from the design method (see Figure 3.15). The composition profiles of the designs with $\phi_{10} = 0.4$ and $\phi_{10} = 0.6$ predicted by HYSYS are different from each other at stage 10 from the top whereas their compositions of the reflux and the other nine stages below the decanter are identical.

Other designs shown in Table 3.2 with fewer than ten heterogeneous stages have been taken to initialise the rigorous simulation in HYSYS. However, none of their rigorous simulations successfully converge, which is maybe because of the existence of the tangent pinch. The results of rigorous simulations for columns with fewer than the maximum number of heterogeneous stages will be presented for another mixture in Section 3.3.2.

Table 3.4. Column specifications given to HYSYS and simulation results from HYSYS based on the fourth column design in Table 3.2

Column specifications given to HYSYS

Reflux ratio	1.45
Temperature of the reboiler (^{o}C)	117.7
Mole fraction of n-butyl acetate in the bottoms	0.0001

Simulation results from HYSYS compared with design specifications for the boundary value method (BVM)

	BVM		HYSYS	
	Distillate, *D*	Bottoms, *B*	Distillate, *D*	Bottoms, *B*
Composition (Mole fraction)				
Water	0.8177	0.0019	0.8177	0.0019
Acetic acid	0.0003 ^{a}	0.9980 ^{a}	0.0003	0.9980
n-Butyl acetate	0.1820	0.0001 ^{a}	0.1820	0.0001 ^{a}
Flow rate (kmol/h)	54.91	45.09	54.91	45.09
Condenser duty (kW)	1501		1501	
Reboiler duty (kW)	1508		1508	
Number of heterogeneous stages	10		10	
Phase split ratio of the final heterogeneous stage	0.4		0.26	

^{a} Specified values

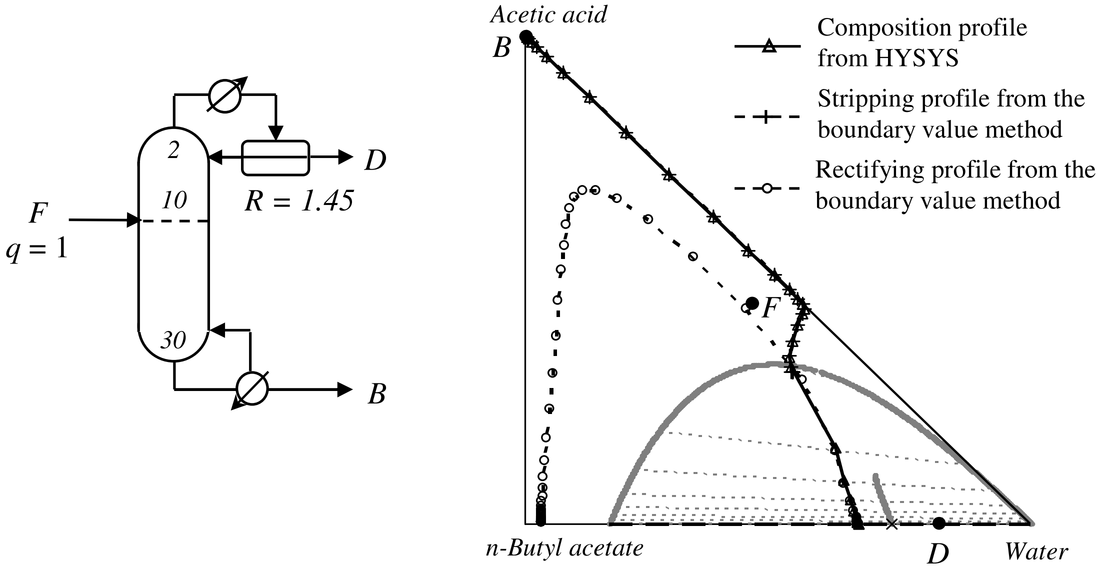


Figure 3.15. The fourth column design in Table 3.2 and its liquid composition profile from HYSYS compared with the profiles from the design method.

For heterogeneous azeotropic distillation, multiple solutions are commonly found in both simulation and operation (Kovach and Seider, 1987a,b; Widagdo et al., 1989; Gani and Jørgensen, 1994; Bekiaris et al., 1996; Müller and Marquardt, 1997; Gaubert et al., 2001). Most of the multiplicities reported in the literature are output multiplicities, that is, more than one sets of output variables (product compositions and flow rates, and compositions profiles) are obtained from the same set of input variables (the number of stages, feed location, and reflux ratio). Conversely, for the multiplicity resulting from the design method, more than one sub-sets of simulation input variables (the numbers of stages and feed locations) result in the same sub-set of simulation output variables (product compositions and flow rates). This type of multiplicity is called an input multiplicity, as defined by Gani and Jørgensen (1994). Input multiplicities are infrequently discussed in the literature. A reason for this is that different sets of input variables leading to the same set of output variables are difficult to find using conventional simulation calculations, as a column with a set of input variables is difficult to converge even to one solution (Seader and Henley, 1998), let alone to many solutions.

Column design by simulation is difficult because of the existence of output multiplicities. By using the proposed column design method, the difficulty in column design due to output multiplicity can be avoided. Furthermore, the new design method explicitly searches for multiple solutions.

Once economically attractive designs are identified, these can be assessed based on the issues of operability and controllability. These issues cannot be considered directly from the design method. For a column with multiple heterogeneous stages, the multiple designs identified from the design method result from the appearance of heterogeneous liquid on stages below the top decanter. Thus, a strategy to control the number of heterogeneous stages should be developed in order to ensure that the specified products are achieved. For example, the temperature front at the interface between heterogeneous and homogeneous stages should be maintained.

3.2.2 Column design procedure: summary

The column design procedure for a column with an integrated decanter is summarised below:

1. Calculate the vapour-liquid-liquid equilibrium of the mixture at a specified operating pressure to generate the heterogeneous boiling envelope and vapour line.
2. Set the compositions and flow rates of the feed and products. The compositions and flow rates of products are specified so that the product purity requirement and the overall material balance of the column are satisfied. Specify a reflux ratio and a reflux phase split ratio. (See Section 3.2.1.1)
3. Specify either the reboil ratio or the feed condition. If the reboil ratio is specified, the feed condition is calculated from Equation (3.4). If the feed condition is specified, the reboil ratio is calculated from Equation (3.6).
4. Calculate the composition profile of the rectifying section (See Section 3.2.1.2). If multiple heterogeneous stages appear in the rectifying section, generate multiple rectifying profiles for various phase split ratios of each heterogeneous stage.
5. Calculate the composition profile of the stripping section (See Section 3.2.1.3).
6. Search for feasible designs from the intersections between the rectifying and stripping profiles. If an intersection is found, count the number of theoretical stages. Find the feed location from the intersection point.
7. Calculate the total annualised costs of the designs (See Appendix B) and rank them.

The above column design procedure can be carried out to identify feasible column designs for given product specifications and a combination of two design variables between a reflux ratio, a reboil ratio and a feed condition. For a set of the design variables, multiple column designs may be found if the reflux phase split ratio is specified such that heterogeneous liquid is present on stages below the decanter. Those column designs can be evaluated and compared with each other in terms of their total annualised costs. Also, the designs can be compared with other designs with different values of the design variables or with other separation flowsheets. However, the most attractive designs found from the design method are identified based on process economics. The attractive designs need to be evaluated further based on other issues, such as operability and controllability.

3.3 Case studies

3.3.1 Water/acetic acid/n-butyl acetate mixture: Two liquid phases only in the decanter

Pham et al. (1989) proposed the boundary value design method for a column with an integrated decanter in which the liquid phase splitting is limited to the top decanter. This case study shows the results of applying this condition to the separation of the water/acetic acid/n-butyl acetate mixture used as the illustrative example in the previous section.

For the same feed and product specifications in Table 3.1, liquid composition profiles are generated at the reflux ratio of 1.45 and a range of reflux phase split ratios (ϕ_1) from 0 to 1 (step size of 0.1). Feasible column designs are identified and listed in Table 3.5.

Table 3.5. Column designs for the acetic acid/water/n-butyl acetate mixture corresponding to the specifications in Table 3.1 when two liquid phases appear only in the decanter

ϕ_1	N_R	N_S	N_{Total}	Q_C (kW)	Q_R (kW)	Total annualised cost* (£/year)
1	58.1	17.8	74.9	1537	1544	2,234,800
0.9	59.8	17.8	76.6	1529	1537	2,273,900
0.8	61.9	17.9	78.8	1521	1529	2,308,800
0.7	64.8	18.0	81.8	1512	1520	2,357,000

* 3-year period, 5% interest rate

As shown in Table 3.5, the proposed separation is feasible when the reflux phase split ratios ranging from 0.7 to 1 are specified. In fact, other reflux phase split ratios less than 0.7 also lead to feasible designs. The minimum reflux phase split ratio that gives rise to the feasible design is 0.5890 which is the value that causes multiple heterogeneous stages in the column. Unlike case (i) in the previous section ($\phi_1 = 0.3$), the rectifying profiles that lead to feasible designs leave the two-liquid phase region to the water vertex and moves along the acetic acid/water edge. For example, the composition profiles for the column with $\phi_1 = 0.7$ are presented in Figure 3.16. The designs in Table 3.5 require a large number of stages, particularly in the rectifying section because of the tangent pinch near the pure water vertex as discussed in Section 3.2.1.4. In addition, the column has greater heat duties when less organic liquid phase (entrainer) is refluxed into the column.

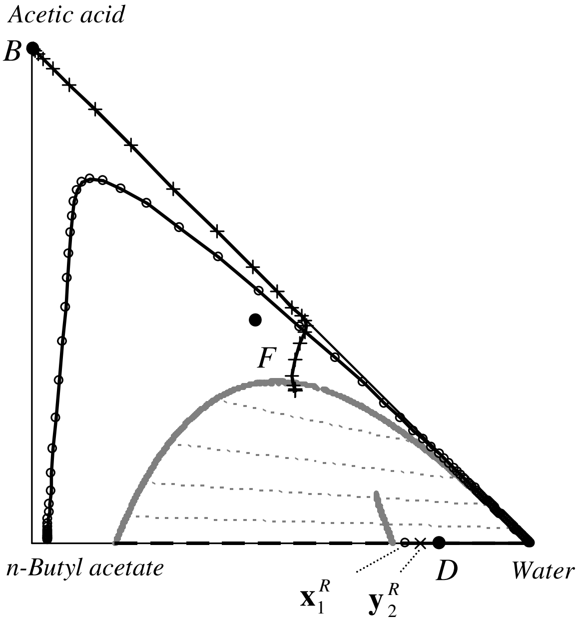


Figure 3.16. Liquid composition profiles for the product specifications in Table 3.1 corresponding to $r = 1.45$ and $\phi_1 = 0.7$.

Compared with the column in which liquid phase splitting is restricted to the decanter, the column designs with multiple heterogeneous stages (Table 3.2) are economically more attractive since they require significantly fewer stages. This is because the rectifying profiles with multiple heterogeneous stages move away from the tangent pinch. In addition, the designs in Table 3.2 require less heating and cooling duties than the designs in Table 3.5. Hence, a column with multiple heterogeneous stages is more economically and energetically attractive for the separation of this mixture.

3.3.2 Ethyl acetate/water/n-butyl acetate mixture

This section presents the application of the proposed column design method to a column separating an ethyl acetate/water/n-butyl acetate mixture in a separation sequence generated in a case study in Chapter 6 (column *C*-1 in Figure 6.14).

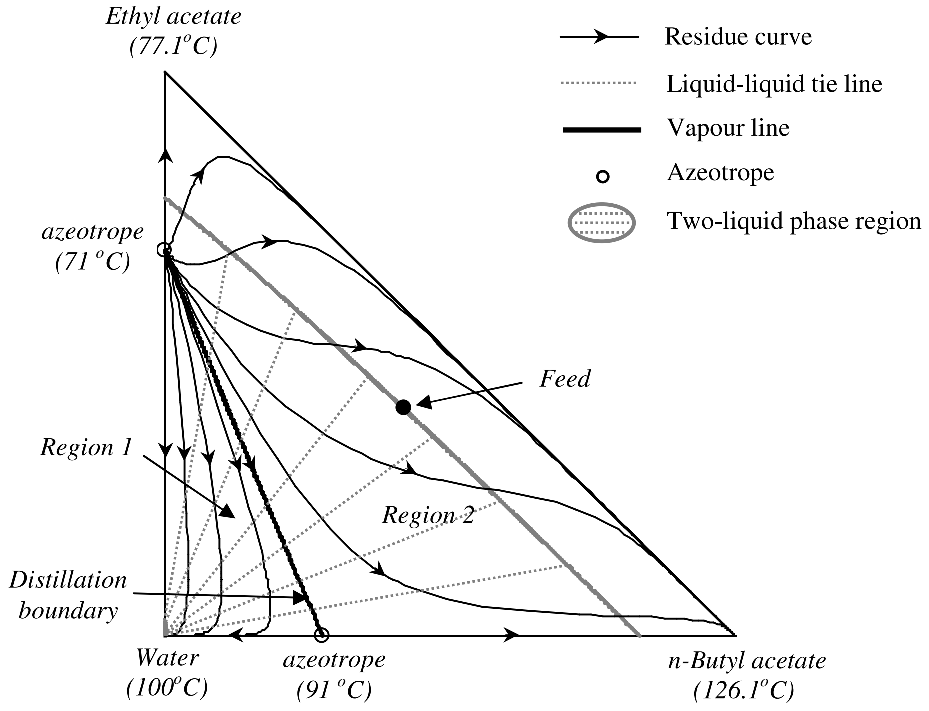


Figure 3.17. Residue curve map and heterogeneous boiling envelope of the mixture of ethyl acetate, water and n-butyl acetate mixture at 1 atm.

Figure 3.17 shows the residue curve map of the ethyl acetate/water/n-butyl acetate mixture calculated using UNIQUAC-ideal gas property package in HYSYS. The residue curve map features two distillation regions because of the presence of two minimum-boiling heterogeneous azeotropes of ethyl acetate/water and n-butyl acetate/water. The heterogeneous azeotrope of ethyl acetate/water is an unstable node whereas the azeotrope of water/n-butyl acetate is a saddle in the residue curve map. A vapour line corresponding to the heterogeneous boiling envelope is located very close to the distillation boundary. In addition, the residue curve map features a compartment boundary in distillation region 2 as two saddle points (ethyl acetate and water/n-butyl acetate azeotrope) exist in region 2.

The feed mixture is a saturated liquid at 1 atm. The feed is a homogeneous liquid in distillation region 2. The specifications of the column are shown in Table 3.6. The bottom product is specified such that a high purity of n-butyl acetate is achieved. The decanter tie line is located close to the ethyl acetate/water edge, part of which lies in the same region as the bottom product. The top product is at the intersection between the mass balance line and decanter tie line as shown in Figure 3.18. The composition of the aqueous phase obtained from the top decanter is 97.5 mol% water.

Table 3.6. Specifications of a column separating an ethyl acetate, water and n-butyl acetate mixture

	Feed, F	Distillate, D	Bottoms, B
Composition (mole fraction)			
Ethyl acetate	0.4026[a]	0.6907	0.0104
Water	0.1784[a]	0.3092	0.0002[a]
n-Butyl acetate	0.4190	0.0001[a]	0.9894[a]
Feed condition	1		
Flow rate (kmol/h)	35.66[a]	20.56	15.10
Reflux ratio		1.15	
Phase split ratio of reflux		0.1292 ($\phi_1 = \phi_1^o$)	

[a] Specified values

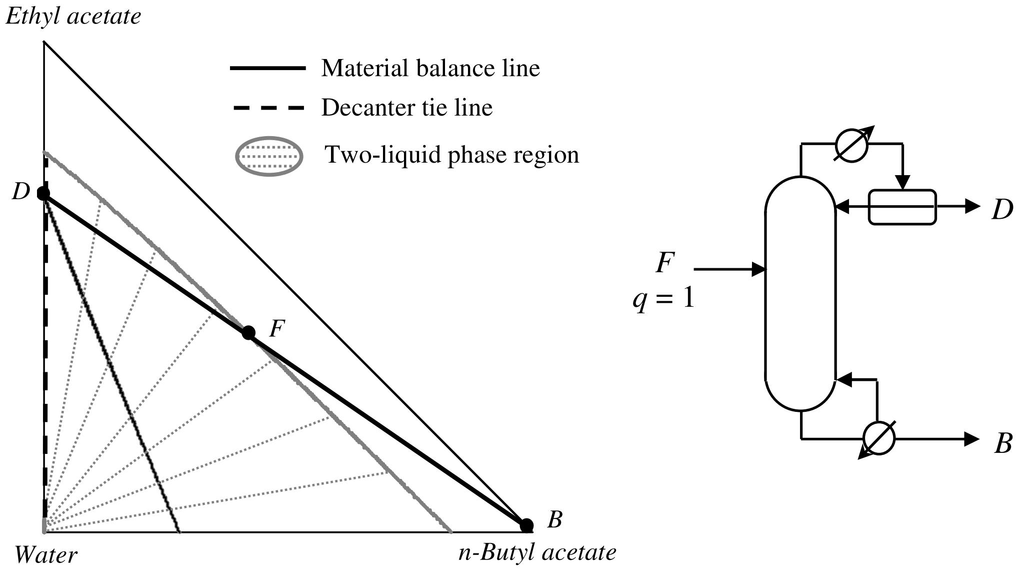


Figure 3.18. Material balance line and decanter tie line of a column separating an ethyl acetate/water/n-butyl acetate mixture

Using the line intersection search algorithm of Hölz (2006), multiple column designs are identified. The rectifying profiles having 10 to 21 heterogeneous stages give rise to feasible designs. Some lowest cost designs are shown in Table 3.7. In this case, the designs having the maximum number of heterogeneous stages (21 stages) are not as attractive as the designs with fewer heterogeneous stages ($N_H < N_{H,max}$) since they need more theoretical stages.

Table 3.7. Some lowest cost column designs for the proposed separation in Table 3.6

N_H	ϕ_H	N_R	N_S	N_{Total}	Total annualised cost* (£/year)
11	0.2	11.0	12.1	22.2	187,200
14	0.2	14.0	8.8	21.8	187,200
15	0.0	14.6	8.8	22.4	187,200
15	0.4	15.4	7.8	22.2	187,200
15	0.2	15.0	8.8	22.7	189,300
16	0.0	15.6	8.8	23.4	191,400
16	0.2	16.0	8.8	23.7	191,400
16	0.4	16.4	7.8	23.2	191,400
17	0.0	16.6	8.7	24.4	193,400
17	0.4	17.4	7.8	24.2	193,400
Condenser duty (kW)					437
Reboiler duty (kW)					477

* 3-year period, 5% interest rate

N_H = number of heterogeneous stages in the rectifying profile

ϕ_H = phase split ratio of final heterogeneous stage

The column designs with ϕ_{11} and ϕ_{14} of 0.2 in Table 3.7 are taken to initialise rigorous simulations in HYSYS to show that the two column designs with $N_H < N_{H,max}$ can be validated. The two designs have the same number of stages but different feed locations. The results and liquid composition profiles from HYSYS for the design with $\phi_{11} = 0.2$ are shown in Table 3.8 and Figure 3.19. For $\phi_{14} = 0.2$, the results and composition profile from HYSYS are shown in Table 3.9 and Figure 3.20.

Table 3.8. Column specifications given to HYSYS and simulation results from HYSYS based on the column design with ϕ_{11} of 0.2 in Table 3.7

Column specifications given to HYSYS

Reflux ratio	1.15
Mole fraction of n-butyl acetate in the organic phase of the distillate	1.13×10^{-4}
Mole fraction of water in the bottoms	0.0002

Simulation results from HYSYS compared with design specifications for the boundary value method (BVM)

	BVM		HYSYS	
	Distillate, *D*	Bottoms, *B*	Distillate, *D*	Bottoms, *B*
Composition (Mole fraction)				
Ethyl acetate	0.6907	0.0104	0.6903	0.0121
Water	0.3092	0.0002[a]	0.3096	0.0002[a]
n-Butyl acetate	0.0001[a]	0.9894[a]	0.0001	0.9877
Flow rate (kmol/h)	20.56	15.10	20.53	15.13
Condenser duty (kW)	437		437	
Reboiler duty (kW)	477		476	
Number of heterogeneous stages (including in the stripping section)	19		19	
Phase split ratio of the final heterogeneous stage in the rectifying section	0.2		0.19	

[a] Specified values

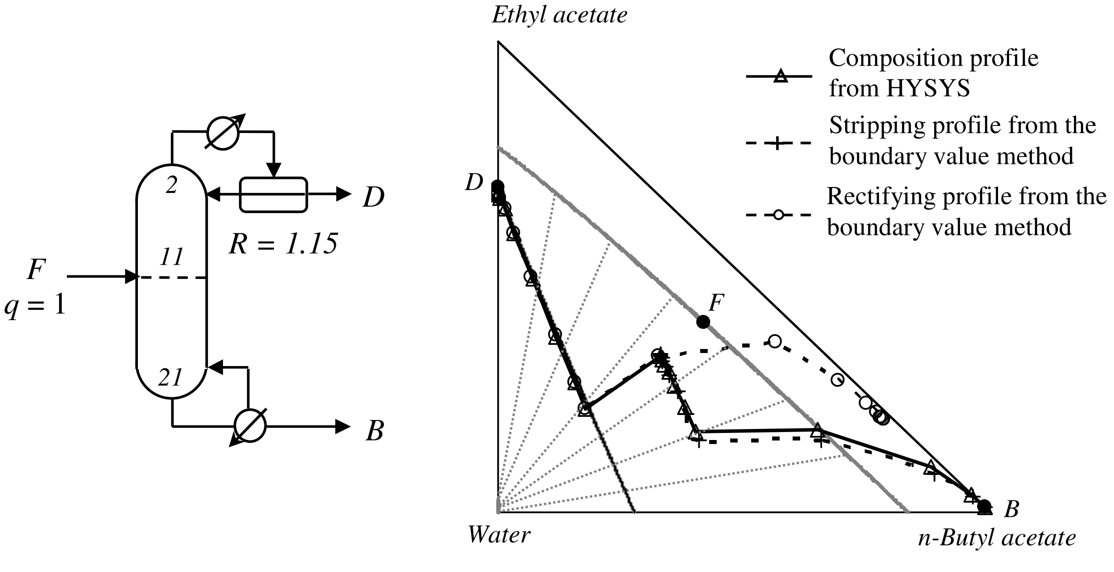


Figure 3.19. The column design with ϕ_{11} of 0.2 and its liquid composition profile from HYSYS.

Table 3.9. Column specifications given to HYSYS and simulation results from HYSYS based on a column design with ϕ_{14} of 0.2 in Table 3.7

Column specifications given to HYSYS

Reflux ratio	1.15
Mole fraction of n-butyl acetate in the organic phase of the distillate	1.13×10^{-4}
Mole fraction of water in the bottoms	0.0002

Simulation results from HYSYS compared with design specifications for the boundary value method (BVM)

	BVM		HYSYS	
	Distillate, *D*	Bottoms, *B*	Distillate, *D*	Bottoms, *B*
Composition (Mole fraction)				
Ethyl acetate	0.6907	0.0104	0.6910	0.0092
Water	0.3092	0.0002[a]	0.3089	0.0002
n-Butyl acetate	0.0001[a]	0.9894[a]	0.0001	0.9906
Flow rate (kmol/h)	20.56	15.10	20.58	15.08
Condenser duty (kW)	437		437	
Reboiler duty (kW)	477		477	
Number of heterogeneous stages (including in the stripping section)	19		19	
Phase split ratio of the final heterogeneous stage in the rectifying section	0.2		0.21	

[a] Specified values

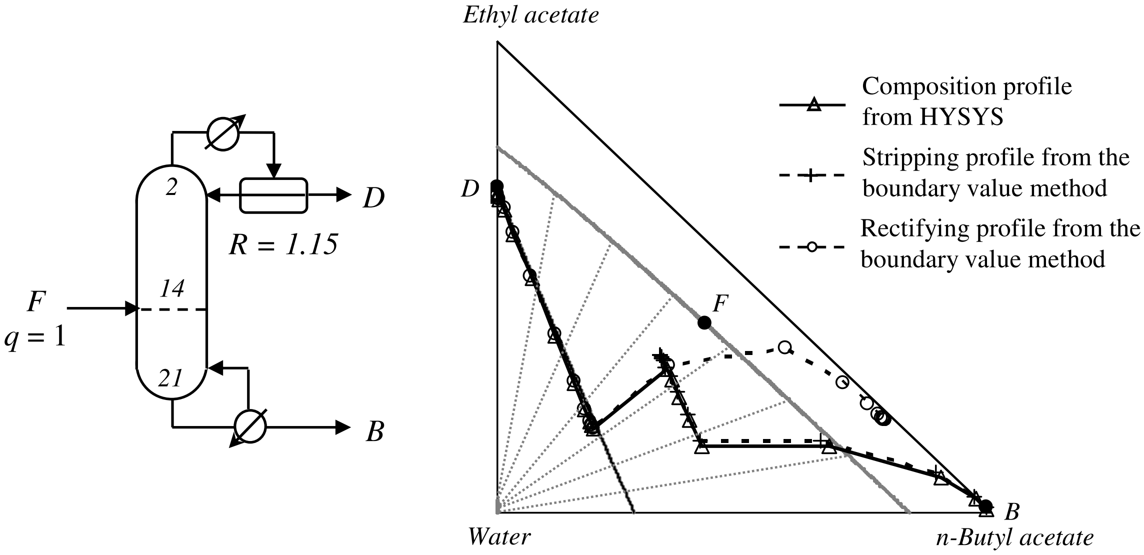


Figure 3.20. The column design with and ϕ_{14} of 0.2 and its liquid composition profile from HYSYS.

This example shows that the rectifying profiles leaving the two-liquid phase region before the last stage that could be heterogeneous is reached also lead to feasible designs and can be validated by rigorous simulation in HYSYS. As shown in Figures 3.19 and 3.20, the liquid composition profiles from HYSYS agree well with the profiles from the design method, particularly the profiles in the rectifying section. In the rectifying sections of the two columns in HYSYS, heterogeneous liquid appears on many stages, the same number as in the rectifying profiles from the design method. Moreover, in Figures 3.19 and 3.20, the liquid compositions of the reflux and the ten stages below the decanter predicted by HYSYS are identical with each other and with those from the design method. Although the top product compositions of the two columns in HYSYS are slightly different from the specified top product composition, they are located on the same tie line as the specified top product composition.

3.4 Application of the column design method in separation sequence synthesis

The synthesis of separation sequences includes identifying the configurations and operating conditions of separation units that satisfy the separation requirement. In synthesising separation sequences, a tool for assessing separation feasibility and evaluating sequences is required. It should screen out infeasible and unattractive designs with minimum time and effort. The proposed column design method presented in Section 3.2 can be used for assessing the feasibility of a separation in a column with an integrated decanter. Moreover, the results from the design method, e.g. number of stages, heat duties, allow column designs to be evaluated with respect to their costs. Thus, attractive column and flowsheet designs can be identified. This section presents an example of using the boundary value design method for identifying near-optimal designs of a column in a separation sequence.

The design method can be used for searching for attractive designs by generating multiple column designs for a range of one or more design variable(s). Given the column pressure, compositions and flow rates of feed and products, the design variables of a column with an integrated decanter are the feed condition, reflux ratio, reflux phase split ratio, and reboil ratio. Between the feed condition, reflux ratio, and reboil ratio, two of them are chosen to be the degrees of freedom, and the remaining variable can be determined from the energy balance of the column, as discussed in Section 3.2.1.1. Once column specifications are given, the design procedure in Section 3.2.2 is carried out to generate column designs for a range of one or two of the chosen degree(s) of freedom and a range of reflux phase split ratios.

For instance, if the feed condition is specified, feasible designs are searched for over a range of reflux phase split ratios and a range of reflux or reboil ratios. To illustrate, the separation of the ethyl acetate/water/n-butyl acetate mixture in Section 3.3.2 (cf. column C-1 in Figure 6.14) is taken as an example. With the feed and product specifications in Table 3.6, column designs are searched for a range of reflux ratios and reflux phase split ratios: r = 1, 1.05, 1.08, 1.13, 1.15, 1.17, 1.2, 1.25, and 1.3; ϕ_1 = 0 to 1 (step size of 0.2) and $\phi_1 = \phi_1^o$. Table 3.10 shows some feasible designs ranked by their total annualised costs. Thus, the proposed separation in Table 3.6 is feasible and its near-optimal designs are identified. When near-optimal designs of all columns in its associated sequence are identified, the sequence can then be compared with other sequence options.

Table 3.10. Near-optimal column designs for the separation of ethyl acetate/water/n-butyl acetate mixture in Table 3.6 generated for a range of reflux ratios and reflux phase split ratios: r = 1, 1.05, 1.08, 1.13, 1.15, 1.17, 1.2, 1.25, and 1.3; ϕ_1 = 0 to 1 (step size of 0.2) and $\phi_1 = \phi_1^o$

r	ϕ_1	s	N_H	ϕ_H	N_R	N_S	N_{Total}	Q_C (kW)	Q_R (kW)	TAC (£/year)
1.08	0.1297	3.01	13	0.4	13.4	9.4	21.8	423	463	183,100
1.08	0.1297	3.01	14	0.4	14.4	9.2	22.6	423	463	185,100
1.05	0.1299	2.97	13	0.4	13.4	10.9	23.3	417	457	185,400
1.13	0.1293	3.07	12	0.0	11.6	11.2	21.8	433	473	186,000
1.13	0.1293	3.07	14	0.0	13.6	9.5	22.1	433	473	186,000
1.13	0.1293	3.07	14	0.2	14.0	9.4	22.4	433	473	186,000
1.17	0.1291	3.12	14	0.0	13.6	8.5	21.1	441	481	186,200
1.17	0.1290	3.12	14	0.2	13.9	8.4	21.3	441	481	186,200
1.15	0.1292	3.10	15	0.0	14.6	8.8	22.4	437	477	187,100
1.15	0.1292	3.10	11	0.2	11.0	12.1	22.1	437	477	187,100
1.15	0.1292	3.10	14	0.2	14.0	8.8	21.8	437	477	187,100
1.15	0.1292	3.10	15	0.4	15.4	7.8	22.2	437	477	187,100

TAC = Total annualised cost (3-year period and 5% interest rate)

The iterative application of the boundary value method described above allows near-optimal designs to be identified; exhaustive optimisation is not appropriate or necessary during the conceptual design step. Unattractive column and flowsheet designs can then be screened out rapidly.

3.5 Conclusions

This chapter presents a column design method extending the boundary value method for the design of columns with integrated decanters. A new development is that the design method can be applied to columns in which heterogeneous liquid is not limited to the top decanter. The column design procedure includes setting column specifications, generating liquid composition profiles, identifying feasible column designs, and evaluating the designs in terms of their total annualised costs.

For a column with an integrated decanter, a reflux phase split ratio is a degree of freedom that may be specified such that a heterogeneous liquid appears on stages below the top decanter. For calculating a composition profile of a rectifying section in which the heterogeneous liquid is not limited to the decanter, a set of preliminary tests should be carried out for checking if the last stage that could be heterogeneous is reached. At the last stage that could be heterogeneous, the tests indicate that there is no solution that satisfies the set of material and energy balances and the vapour-liquid-liquid equilibrium. From the last stage that could be heterogeneous, the calculation is continued by generating multiple rectifying profiles corresponding to various phase split ratios of the last heterogeneous stage. Additionally, rectifying profiles are generated for various phase split ratios of other heterogeneous stages. Some of the multiple rectifying profiles may give rise to multiple feasible designs which have the same heat duties but different numbers of stages and feed locations. The column design method and the existence of multiple designs have been validated by simulation in HYSYS.

The new design approach allows the advantages of a column with multiple heterogeneous stages to be exploited. For example, in the separation of a water/acetic acid/n-butyl acetate mixture, it was shown that a column with multiple heterogeneous stages requires considerably fewer stages than a column in which the two liquid phases are limited to the decanter. In addition, a column with fewer heterogeneous stages may be more attractive than the column with the maximum number of heterogeneous stages, for instance in the separation of ethyl acetate/water/n-butyl acetate mixture.

The column design method is valuable as it can be applied in the synthesis of separation sequences. The design method can be used for assessing the feasibility of a separation in columns with integrated decanters in a sequence. Furthermore, the design method can be used to identify economically near-optimal designs of a column in a sequence by generating column designs for a range of design variable(s). Thus, separation sequences can be evaluated, allowing unattractive sequences to be screened out.

The proposed design method for columns with integrated decanters has been developed based on ternary mixtures. In principle, this method is not limited to the ternary mixtures since liquid composition profiles can be calculated for mixtures with any number of components. However, in practice, an intersection between the composition profiles of a multicomponent mixture is difficult to identify in higher-dimensional composition space. The reason is that a composition profile of a multicomponent mixture is very sensitive to the amount of trace components in the associated products. Nevertheless, this design method may provide a basis for developing a design method for multicomponent mixtures.

The proposed design method presented in this chapter may be extended for the design of complex columns. In particular, the extension of the boundary value design method for double-feed columns with integrated decanters and columns with intermediate decanters is presented in Chapters 4 and 5.

Chapter 4

Design method for double-feed heterogeneous azeotropic columns with integrated decanters

4.1 Introduction

A double-feed column may be an ideal option for separating a mixture. It is commonly used in extractive distillations in which a heavy boiling entrainer is added to facilitate the separation of a minimum boiling azeotropic mixture. Similarly to homogeneous azeotropic mixtures, the separation of some heterogeneous azeotropic mixtures that cannot be achieved in a single-feed column can be accomplished in a double-feed column. To promote the separation, a high boiling entrainer stream is usually added to the extractive distillation column near the top in order to alter the thermodynamic behaviour of the mixture in the middle section of the column. For heterogeneous extractive distillation, an entrainer is usually a heavy boiling compound that is partly immiscible with the original mixture, and commonly added to a double-feed column as an upper feed stream. In addition, a double-feed column may be more economic than a single-feed column since the double-feed column may require fewer theoretical stages than the single-feed column (Wasylkiewicz et al., 2000).

Typically, a double-feed column separating a heterogeneous azeotropic mixture would be designed by simulation. This technique may allow an exhaustive search but it is tedious and time-consuming since it involves selecting column design parameters, such as the number of stages, feed locations, feed condition and reflux ratio. These design parameters need to be guessed and repeatedly changed until convergence is achieved and the separation requirement is satisfied. The convergence of a heterogeneous azeotropic distillation column is usually difficult to achieve without a good initial guess. Moreover, an exhaustive search is needed for identifying the most promising designs.

Two graphical design methods for double-feed column design are available. The first method is the boundary value method extended to double-feed columns with integrated decanters by Wasylkiewicz et al. (2000). This method is based on the stage-by-stage calculation of liquid composition profiles of all column sections. However, how a composition profile for a rectifying section with multiple heterogeneous stages is accounted for is not described.

The second graphical design method is the continuous distillation region based method developed by Urdaneta (2005). The method requires continuous distillation regions of all column sections to be calculated; a continuous distillation region contains all possible liquid composition profiles of the section for a given reflux ratio and product specifications (Urdaneta et al., 2002). As discussed in Section 3.1, this method is computationally intensive as it requires the calculation of pinch points and composition profiles. In addition, the design method of Urdaneta (2005) does not directly provide column design details, e.g. number of stages and feed locations. To determine the column design details, stage-by-stage calculation needs to be carried out.

This chapter presents a conceptual design method for double-feed columns with integrated decanters based on the boundary value method described in Chapter 3. The column design procedure is discussed along with an illustrative example. The new design method can be used for assessing the feasibility of a proposed separation and evaluating the resulting column designs. The design procedure provides column design details, e.g. the number of stages, upper and lower feed locations for a given combination between two design variables of reflux ratio, reboil ratio, and upper feed condition. The column design details resulting from the design method allow the column cost to be estimated and they can be used as initial values for a rigorous simulation. Furthermore, the design method is an essential tool in separation sequence synthesis as it allows a double-feed column in a separation sequence to be assessed for its feasibility and evaluated with respect to cost. The separation flowsheet can then be evaluated and compared with other alternatives.

4.2 Design method for double-feed columns with integrated decanters

This section describes the extension of the boundary value method to double-feed columns with integrated decanters. The calculation procedure has been written in MATLAB 7.0 interfaced with HYSYS 2004.1 for phase equilibrium and enthalpy calculation (see Appendix D). To demonstrate the column design procedure, a dehydration of 1-propanol using 1-butanol as an entrainer is taken as an example.

Illustrative example

The phase equilibrium of 1-propanol/water/1-butanol mixture is obtained from HYSYS using the UNIQUAC model for the liquid phase and the ideal gas law for the vapour phase. The UNIFAC-VLE model provided in HYSYS is used to estimate the UNIQUAC parameters (see Appendix C for validation of phase equilibrium model and parameters).

The residue curve map and heterogeneous boiling envelope of the mixture is presented in Figure 4.1. Water and 1-butanol are partially immiscible: the composition of the aqueous liquid phase is 96.3 mol% water. The mixture has two azeotropes. One is the homogeneous azeotrope of 1-propanol and water, an unstable node. The other is a saddle, the heterogeneous azeotrope of water and 1-butanol. The composition space is divided into two distillation regions by a distillation boundary running from the unstable node, through the two-liquid phase region, to the heterogeneous azeotrope. A vapour line originates from the heterogeneous azeotrope of water and 1-butanol, as it must; it is located very close to the distillation boundary, ending before the 1-propanol/water azeotrope. In distillation region 2, the residue curve map features two compartments where all residue curves in a compartment share a common saddle (Thong and Jobson, 2001a). The compartments are divided by a compartment boundary which can be linearly approximated as shown in Figure 4.1. 1-propanol is a saddle point in one compartment whereas the heterogeneous azeotrope of water and 1-butanol is a saddle point in another compartment.

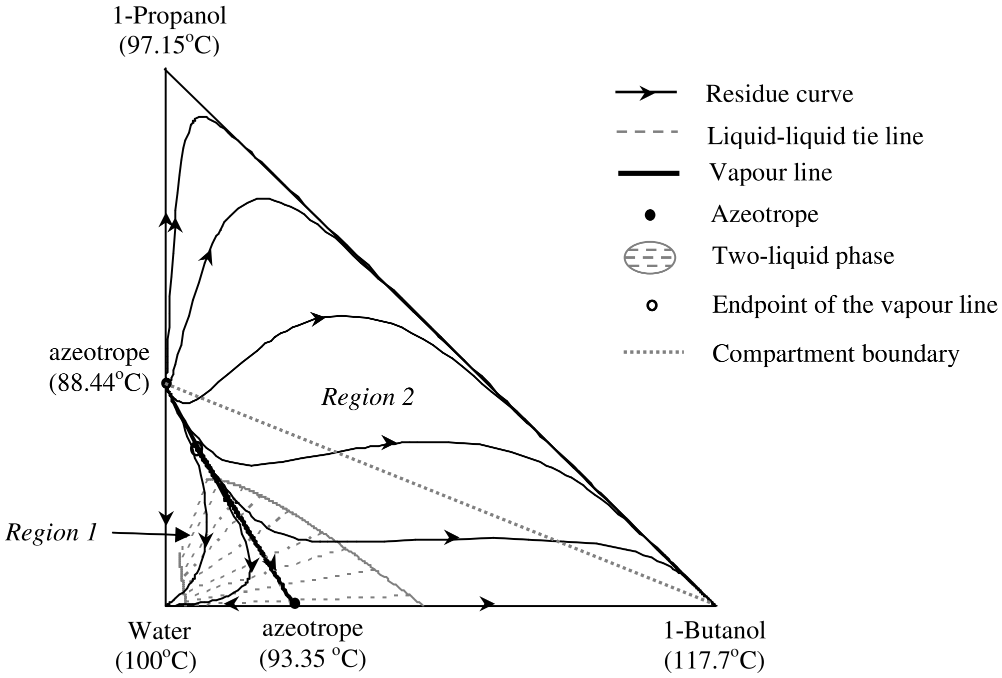


Figure 4.1. Residue curve map and heterogeneous boiling envelope of 1-propanol/water/1-butanol mixture at 1 atm.

The example for demonstrating the column design procedure is the separation of an equimolar mixture of 1-propanol and water, which is located in distillation region 2, using 1-butanol as an entrainer. Because of the existence of the distillation boundary and the compartments shown in Figure 4.1, the separation cannot be accomplished using single-feed columns. However, the separation of 1-propanol/water/1-butanol mixture can be achieved in a sequence including a double-feed column as will be discussed below.

The separation of the 1-propanol/water mixture using 1-butanol can be carried out in a similar way to homogeneous extractive distillation (Moussa and Jiménez, 2006). A well-known example of homogeneous extractive distillation is the dehydration of ethanol using ethylene glycol as an entrainer. Distillation region 2 in the residue curve map of 1-propanol/water/1-butanol mixture has two nonadjacent saddle points, i.e. 1-propanol and the heterogeneous azeotrope of water and 1-butanol. Similarly, in the residue curve map of ethanol/water/ethylene glycol mixture, water and ethanol are saddle points, which are nonadjacent, resulting in two distillation compartments. For the extractive distillation of ethanol/water/ethylene glycol mixture, ethanol, which is one of the saddle points, is recovered as a top product of a double-feed column in which ethylene glycol is introduced as an upper feed. Water, which is another saddle, is obtained from an entrainer recovery column (Doherty and Malone, 2001).

The dehydration of 1-propanol can be carried out in a column sequence, as shown in Figure 4.2, which is similar to the sequence for the extractive distillation of ethanol/water/ethylene glycol mixture (Moussa and Jiménez, 2006). (A systematic approach to employ double-feed columns in a separation sequence is presented in Chapter 6.) The column sequence shown in Figure 4.2 consists of a double-feed column with an integrated decanter and an entrainer recovery column. In the double-feed column, the 1-propanol/water mixture (F_L) is fed as a lower feed while a 1-butanol stream (F_U) is added as an upper feed. At the top, vapour having a composition close to the saddle heterogeneous azeotrope is condensed into two liquid phases in the top decanter. The aqueous liquid phase from the top decanter can be recovered as a product (D_1). At the bottom, a binary mixture of 1-propanol and 1-butanol (B_1) is separated further in another column.

The new column design method will be applied to the double-feed column in the sequence represented in Figure 4.2. How to generate the sequence and determine the sequence mass balance is described in Chapter 6.

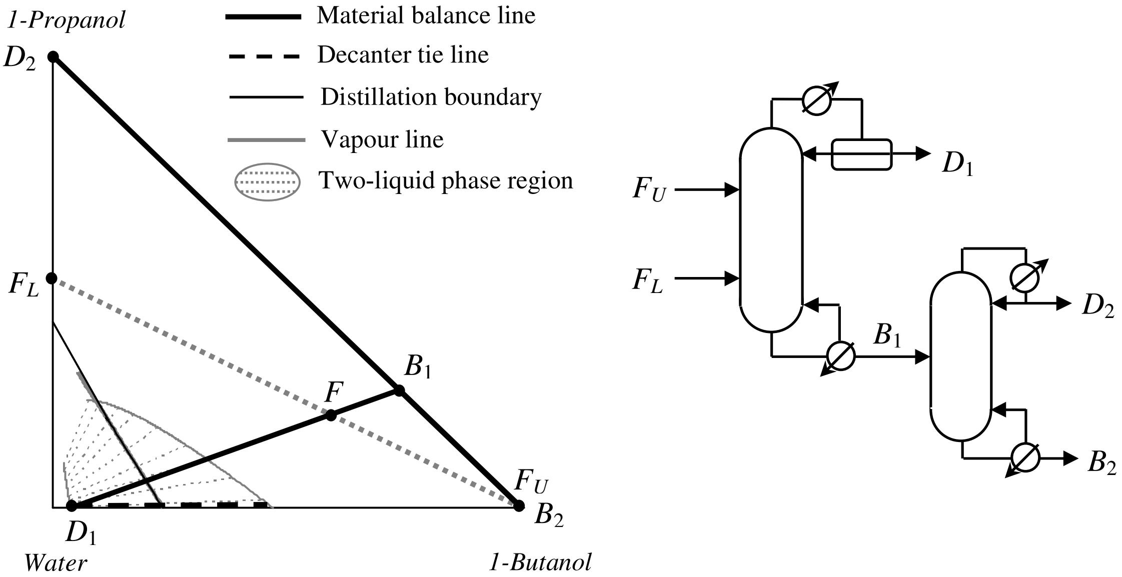


Figure 4.2. A separation sequence with a double-feed column and its mass balance lines for the separation of a 1-propanol/water/1-butanol mixture (adapted from Moussa and Jiménez, 2006). The column specifications are shown in Table 4.1.

4.2.1 Model development

This section provides a detailed discussion of the boundary value method for double-feed columns separating heterogeneous azeotropic mixtures. To design a double-feed column, all specifications of the column are firstly proposed as discussed in Section 4.2.1.1. The composition profiles of all column sections are then generated according to the column specifications using material and energy balances along with phase equilibrium. (Constant molar overflow is not assumed.) The feasibility of the proposed separation is then identified from the intersection of composition profiles. If the proposed separation is feasible, the column design parameters, such as the number of theoretical stages, feed stages, and feed conditions, are obtained. The column design can then be evaluated and compared to other flowsheet alternatives according to their costs.

4.2.1.1 Specifications

For a double-feed column integrated with a decanter at the top, the specifications of the boundary value method are: column pressure, which is assumed constant throughout the column; upper and lower feed compositions and flow rates; top and bottom product compositions and flow rates; lower feed condition; phase split ratio of reflux stream; reflux ratio; either reboil ratio or upper feed condition. The product specifications are chosen to satisfy the product purity requirement and material balance over the column (equations 4.1 and 4.2).

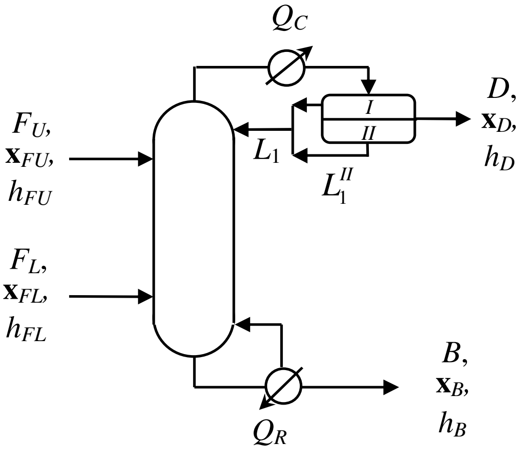


Figure 4.3. Schematic representation of a double-feed column with an integrated decanter

$$F_U + F_L = D + B \tag{4.1}$$

$$\mathbf{x}_{FU}F_U + \mathbf{x}_{FL}F_L = \mathbf{x}_D D + \mathbf{x}_B B \tag{4.2}$$

The phase split ratio of reflux (ϕ_1) is defined as the ratio of heavy liquid reflux flow rate, L_1^{II}, to total reflux flow rate, L_1,:

$$\phi_1 = \frac{L_1^{II}}{L_1} \tag{4.3}$$

where $L_1 = L_1^I + L_1^{II}$, L_1 is the total liquid flow rate of the reflux stream, L_1^I and L_1^{II} are the flow rates of light and heavy liquid phases in the reflux, respectively.

The value of the phase split ratio of the reflux ranges from 0 to 1. The ratio can be specified so that liquid phase splitting occurs only in the top decanter, or so that two liquid phases appear in the column. (See Section 3.2.1.1 for how the phase split ratio of reflux is specified.)

As noted above, one of the specifications of the double-feed column is either reboil ratio or upper feed condition. If the reboil ratio (s) is specified, the upper feed condition (q_{FU}) is determined from:

$$q_{FU} = \left(\frac{h_{FU}^{V,sat} - h_{FU}}{h_{FU}^{V,sat} - h_{FU}^{L,sat}} \right) \tag{4.4}$$

where h_{FU} is calculated from the energy balance over the column:

$$h_{FU} = \frac{1}{F_U} \left(D h_D + B h_B - F_L h_{FL} + Q_C - Q_R \right) \tag{4.5}$$

The condenser and reboiler duties (Q_C and Q_R) are calculated from energy balances around the condenser and reboiler, respectively. The specified reflux and reboil ratios will be discarded if the resulting feed condition is not realisable with available utilities, for example a very low feed temperature.

If the upper feed condition is specified, the reboil ratio is calculated from the energy balance over the reboiler:

$$s = \frac{1}{\left(h_2^{S,L} - h_1^{S,V} \right)} \left(h_B - h_2^{S,L} - \frac{Q_R}{B} \right) \tag{4.6}$$

where $h_1^{S,V}$ and $h_2^{S,L}$ are the molar enthalpies of the vapour phase from the reboiler and the liquid phase entering the reboiler, respectively. The reboiler duty (Q_R) is determined from the energy balance over the column:

$$Q_R = D h_D + B h_B - F_U h_{FU} - F_L h_{FL} + Q_C \tag{4.7}$$

In Table 4.1, the specifications of a double-feed column separating a mixture of 1-propanol and water using 1-butanol as an entrainer are given as an example for describing the calculation procedure. The pressure in the column, condenser and reboiler is 1 atm. The lower feed is a binary mixture of 1-butanol and water located in distillation region 2 (see Figure 4.2). The entrainer, 1-butanol, is added to the column as an upper feed as a saturated liquid. The top product is chosen such that it is in the two-liquid phase region. According to the mass balance of the column, the binary mixture of 1-propanol and 1-butanol is withdrawn as a bottom product, which can be separated further in another simple column (see Figure 4.2). Figure 4.2 shows the mass balance line of the double-feed column and the decanter tie line, which is a liquid-liquid tie line corresponding to the top product composition.

Table 4.1. Specifications of a double-feed column separating a mixture of 1-propanol, water and 1-butanol

	Upper feed, F_U	Lower feed, F_L	Distillate, D_1	Bottoms, B_1
Composition (mole fraction)				
1-propanol	0^a	0.5^a	0.0001^a	0.2159
water	0	0.5	0.9599	0.0150^a
1-butanol	1^a	0.0^a	0.0400^a	0.7691
Feed condition	1^a	1^a		
Flow rate (kmol/h)	72^a	40^a	19.39	92.61
Reflux ratio			5	
Phase split ratio of reflux	Case (i): $\phi_1 \neq \phi_1^o$		0.25	
	Case (ii): $\phi_1 = \phi_1^o$		0.45	

^{a} Specified values,

ϕ_1^o = Phase split ratio of the reflux that may cause the liquid leaving the stage next to the decanter ($\mathbf{x}_2^R$) to be heterogeneous

Similarly to the design of a single-feed column, the top product composition of a double-feed column with an integrated decanter is specified so that it is in the heterogeneous region, and a part of its corresponding tie line is in the same distillation region as the bottom product. In this example, the top product is chosen to be the aqueous phase from the top decanter (see Figure 4.2).

As shown in Figure 4.2, the decanter tie line corresponding to the specified top product crosses the vapour line. As a result, the heterogeneous liquid may appear on stages of the rectifying section next to the decanter according to how the phase split ratio of the reflux is specified. The liquid leaving the stage next to the decanter (stage 2) will be heterogeneous if the reflux phase split ratio is chosen such that the top vapour composition is located on the vapour line. Such a reflux phase split ratio, that causes the liquid leaving stage 2 to be heterogeneous, denoted by ϕ_1^o, can be determined from equation (3.9), (see Section 3.2.2.1 for details). For the illustrative example, the composition profile of the rectifying section will be generated for the following cases: (i) the liquid leaving the top stage of the column is homogeneous ($\phi_1 \neq \phi_1^o$), and (ii) the liquid leaving the top stage of the column is heterogeneous ($\phi_1 = \phi_1^o$).

4.2.1.2 Composition profiles

Once all specifications of the double-feed column are given, the rectifying, stripping and middle section profiles of the column are calculated using material and energy balances and phase equilibrium of the mixture. The liquid composition profiles are calculated without an assumption of constant molar overflow. The rectifying and stripping profiles for the double-feed column are generated in the same way as for the single-feed column (see Sections 3.2.1.2 and 3.2.1.3). After the calculation of the stripping profile is completed, a middle section profile is calculated starting from a specified stage of the stripping section.

Rectifying and stripping profiles

As described in Section 3.2.1.2, the rectifying profile calculation of a column integrated with a decanter at the top depends on how the phase split ratio of reflux (ϕ_1) is specified. For case (i) in Table 4.1, ϕ_1 = 0.25 is specified. Because $\phi_1 \neq \phi_1^o$, the presence of two liquid phases in the rectifying section occurs only in the top decanter. As shown in Figure 4.4(a), the rectifying profile starts at the reflux composition inside the heterogeneous boiling envelope in distillation region 2 and then leaves the two-liquid phase region moving toward 1-butanol vertex.

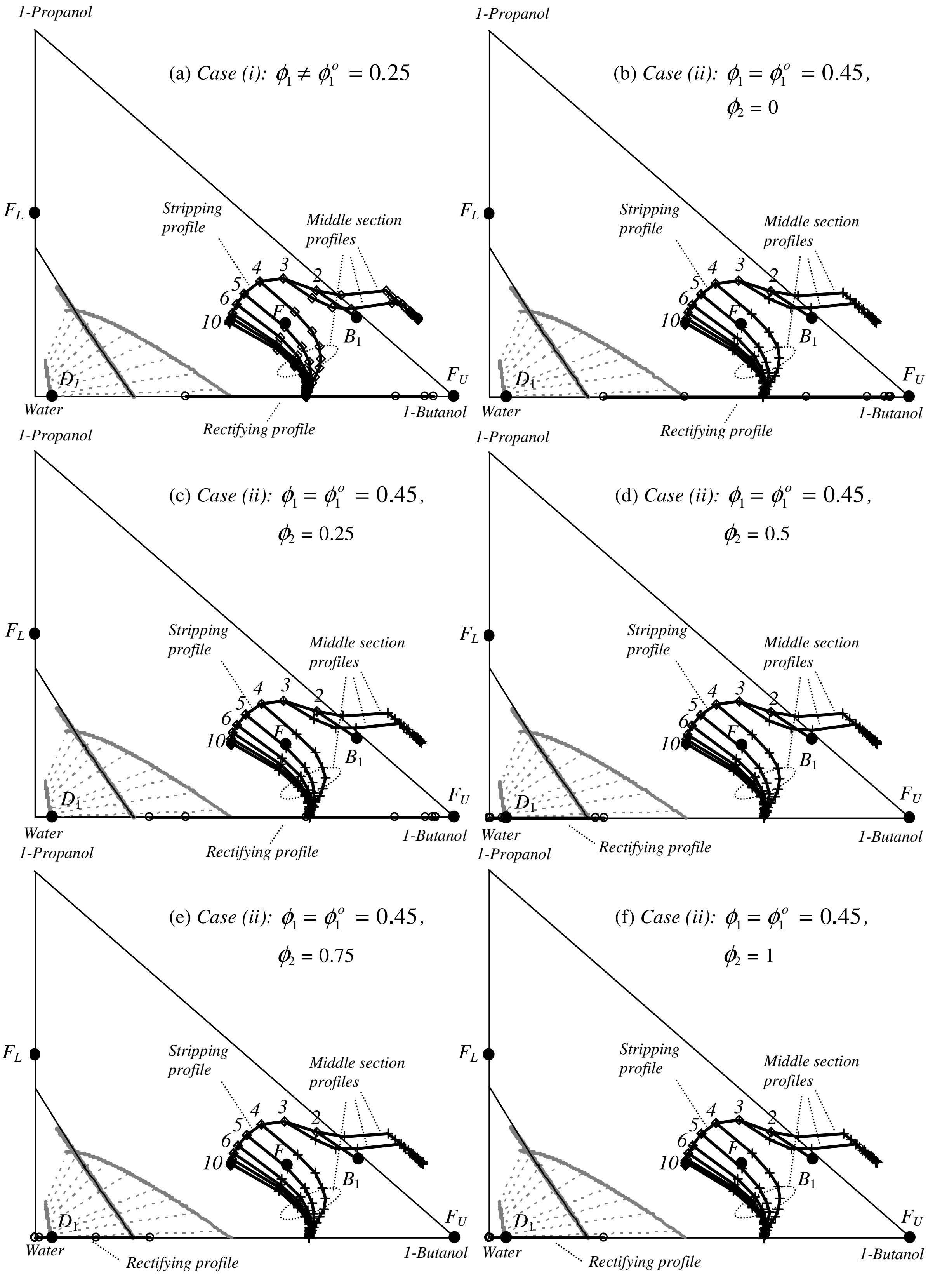


Figure 4.4. Composition profiles of the double-feed column separating a mixture of 1-propanol, water, and 1-butanol according to the specifications in Table 4.1.

For case (ii) in Table 4.1, $\phi_1 = \phi_1^o = 0.45$ is specified. Two liquid phases thus appear on the stage next to the decanter and possibly on some stages below. Using the calculation method described in Section 3.2.1.2 (ii), the maximum number of stages in the rectifying section that heterogeneous liquid can appear on, at the given reflux ratio and top product composition, is ten for this example. Multiple rectifying profiles can be generated based on various phase split ratios of stage 10. All profiles start from the same reflux composition to the composition of stage 9 before they diverge into several profiles according to various phase split ratios of stage 10. In addition, multiple rectifying profiles can be generated in a way that heterogeneous liquid appears on fewer stages than ten. Figures 4.4(b) to (f) show the rectifying profiles having two heterogeneous stages computed according to the following phase split ratios of stage 2, ϕ_2 = 0, 0.25, 0.5, 0.75 and 1. For more heterogeneous stages, their rectifying profiles according to ϕ_H = 0, 0.25, 0.5, 0.75 and 1, where H is the number of heterogeneous stages, look very similar to the rectifying profiles shown in Figure 4.4(b) to (f) as the compositions from the reflux stream to stage H-1 are very close to each other.

The stripping profile of the double-feed column is calculated using the method described in Section 3.2.1.3. The stripping profile for case (i) is shown in Figure 4.4(a) whereas the stripping profile of case (ii) is shown in Figure 4.4(b) to (f). Note that the stripping profiles in Figure 4.4(b) to (f) are identical. For case (ii), the stripping profile does not deviate according to different phase split ratios of stage 2 since the heat duty does not vary with phase split ratio of stage $H > 1$, as discussed in Section 3.2.1.3. The stripping profiles for the two cases are slightly different because of the difference in their reboil duties resulting from their reflux phase split ratios. For a given reflux ratio and feed condition, a reboil duty is calculated from the energy balance over the column (equation 4.7). The condenser duty in equation 4.7 depends on the specified reflux phase split ratio according to the energy balance over the decanter (equation 3.14). The reboil duty thus depends on the reflux phase split ratio. Therefore, the stripping profile for case (ii) has only one stripping profile and it is different from the stripping profile for case (i).

Middle section profile

After the rectifying and stripping profiles of the column are generated, the middle section profile is calculated. The calculation of the profile can be started either from a stage of the rectifying or stripping section. However, the calculation upward from a stage of the stripping section is more convenient as it is similar to the calculation of the stripping section which is simple since the phase split ratio is not a degree of freedom. As the middle section profile is calculated upward, it may be generated starting from any stage of the stripping section. The stage of the stripping section from which the middle section profile started, the lower feed location, is another degree of freedom.

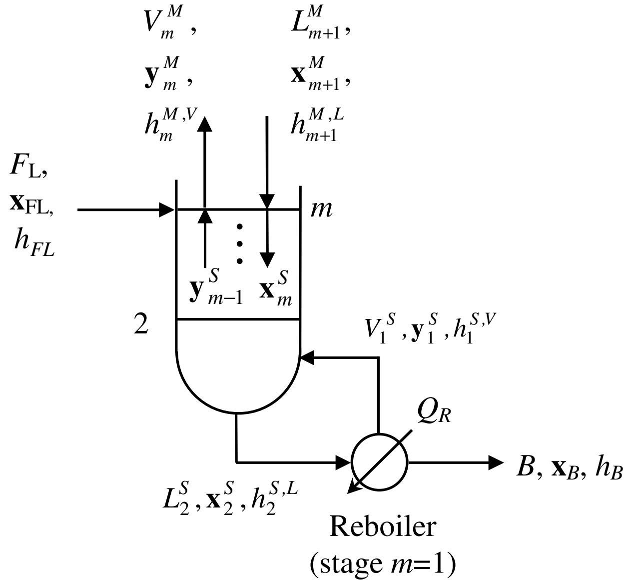


Figure 4.5. Schematic presentation of the stripping section including a lower feed

The calculation of a middle section profile can be carried out in the following procedure:

i. Choose a stage of the stripping section as the lower feed location, e.g. stage m of the stripping section in Figure 4.5.

ii. Determine the vapour composition of stage m ($\mathbf{y}^M_m$) which is in equilibrium with the liquid composition of stage m ($\mathbf{x}^S_m$) using bubble point calculation. Note that the composition, flow rate and enthalpy of the liquid leaving stage m is known from the stripping section profile.

iii. Calculate the liquid composition of the next stage m+1 ($\mathbf{x}_{m+1}^{M}$) from the material and energy balances (the set of equations 4.8 and 4.9).

iv. Continue the calculation in the next stages by solving the set of equations (4.8) and (4.9) together with vapour-liquid-(liquid) equilibrium until the stable node pinch of the profile is reached.

$$\left(V_m^M + B - F_L\right)\mathbf{x}_{m+1}^M - V_m^M \mathbf{y}_m^M - B\mathbf{x}_B - F_L\mathbf{x}_{FL} = \mathbf{0} \tag{4.8}$$

$$\left(V_m^M + B - F_L\right)h_{m+1}^{M,L} - V_m^M h_m^{M,V} - Bh_B + F_L h_{FL} + Q_R = 0 \tag{4.9}$$

where $Q_R = \left(sh_1^{S,V} - (s+1)h_2^{S,L} + h_B\right)B$ if $s = V_1^S / B$ is specified, or,

$Q_R = Dh_D + Bh_B - F_U h_{FU} - F_L h_{FL} + Q_C$ if the upper feed condition is specified.

Because the lower feed location is a degree of freedom, middle section profiles can be calculated from different stages of the stripping section using the procedure described above. Figure 4.4 shows the rectifying and stripping profiles together with middle section profiles which are calculated starting from stage 2 to 10 of the stripping section. As shown in Figure 4.4, adding the lower feed to the column at stage 2 and 3 of the stripping section does not lead to feasible designs because the middle section profiles started from those stages move away from the composition space. A liquid composition with a negative mole fraction can be plotted outside the composition space because two out of three mole fractions which are positive are used for plotting.

4.2.1.3 Feasibility assessment and column design evaluation

After the liquid composition profiles of all column sections are generated at the given reflux ratio, the feasibility of the proposed column can be assessed and feasible column designs can be evaluated. A feasible design of the proposed double-feed column is identified from the intersection between rectifying and middle section profiles. The intersection point indicates the upper feed location, and the stage of the stripping profile from which the middle section profile begins is the lower feed location. Next, the required number of theoretical stages of the column can be counted. The column design can then be evaluated and compared with other feasible designs or separation options in terms of their total annualised costs.

For the illustrative example, multiple feasible designs are found as several middle section profiles are calculated from various lower feed locations. Moreover, multiple rectifying profiles are generated in case (ii). Each feasible design is identified from the intersection between a rectifying profile and a middle section profile using a line-line intersection search algorithm developed by Hölz (2006). The total annualised cost of a feasible design is then estimated using the cost function in Appendix B based on a repayment period of three years and an interest rate of 5%. Some feasible designs and their total annualised costs are shown in Table 4.2.

Listed in Table 4.2(a) are the feasible designs for case (i). For $\phi_1 = 0.25$, the middle section profiles calculated upwards starting from stages 4 to 10 from the bottom intersect with the rectifying profile as shown in Figure 4.4(a). These designs all have the same energy requirement but they are different in terms of the numbers of theoretical stages and lower feed locations. All designs require the stream of 1-butanol to be added to the column as the upper feed at the stage below the decanter. The middle section profiles starting from below stage 4 from the reboiler lead to infeasible designs as they move out of the composition space. The most attractive designs require 23 stages, which are the designs having lower feed locations at stages 4, 5, 6 and 7 from the reboiler. More theoretical stages are required if the lower feed is added at the stages above stage 7. To minimise the column cost for a given reflux ratio, the lower feed location should be chosen such that the minimum number of stages is required.

For case (ii): $\phi_1 = 0.45$, Table 4.2(b) shows feasible column designs having two heterogeneous stages in the rectifying section. The middle section profiles generated starting from stages 4 to 10 intersect with the rectifying profiles calculated according to $\phi_2 = 0$ and 0.25, as shown in Figure 4.4(b) and (c). For $\phi_2 = 0.5$, 0.75 and 1, the rectifying profiles move toward the pure water edge and do not intersect with any middle section profiles. The columns require at least 24 stages for $\phi_2 = 0$ and 25 stages for $\phi_2 = 0.25$.

Table 4.2. Column designs for the double-feed column with the specifications in Table 4.1

(a) Case (i): $\phi_1 = 0.25$

Lower feed location (from the reboiler)	Upper feed location (from the decanter)	N_M	N_{Total}	Total annualised cost* (£/year)
4	2	18.9	22.9	378,300
5	2	17.5	22.5	378,300
6	2	16.7	22.7	378,300
7	2	16.2	23.2	378,300
8	2	16.0	24.0	383,700
9	2	15.9	24.9	386,400
10	2	15.8	25.8	389,100
Condenser duty (kW)		1375		
Reboiler duty (kW)		1367		

(b) Case (ii): $\phi_1 = \phi_1^o = 0.45$

	Lower feed location (from the reboiler)	Upper feed location (from the decanter)	N_M	N_{Total}	Total annualised cost* (£/year)
$\phi_2 = 0$	4	2.6	19.7	24.4	381,900
	5	2.6	18.1	23.7	381,900
	6	2.6	17.4	24.0	381,900
	7	2.6	16.9	24.6	384,600
	8	2.6	16.7	25.4	384,600
	9	2.6	16.6	26.2	389,900
	10	2.6	16.5	27.2	392,600
$\phi_2 = 0.25$	4	3	20.2	25.2	384,600
	5	3	18.6	24.6	384,600
	6	3	17.8	24.9	384,600
	7	3	17.4	25.5	389,900
	8	3	17.2	26.2	389,900
	9	3	17.0	27.0	392,600
	10	3	17.0	28.0	395,300
Condenser duty (kW)			1358		
Reboiler duty (kW)			1350		

* 3-year period, 5% interest rate

N_M = number of stages in the middle section (including the upper and lower feed stages)

Comparing the two cases, the columns in which liquid phase splitting only occurs in the decanter are more attractive. Although the energy requirement of the columns with ϕ_1 = 0.25 is slightly higher than that of the columns with ϕ_1 = 0.45, the columns with ϕ_1 = 0.25 require fewer theoretical stages than the columns with ϕ_1 = 0.45. As shown in Table

4.2, the lowest cost designs are the columns with $\phi_1 = 0.25$ and lower feed locations at stages 4 to 7.

Column designs with up to ten heterogeneous stages in the rectifying section are also found. However, those designs are not as attractive as the columns in which the heterogeneous liquid appears only in the top decanter because those designs need more theoretical stages. For more heterogeneous stages, the rectifying profiles calculated according to $\phi_H = 0$, 0.25, 0.5, 0.75 and 1 are very similar to the profiles with two heterogeneous stages calculated at the same values of phase split ratios shown in Figures 4.4(b) to (f). In the rectifying section with more than two heterogeneous stages, the liquid compositions from the reflux stream to stage H-1 are very close to each other. Therefore, more theoretical stages are required in the rectifying profiles.

The first design in Table 4.2(a), the column with the lower feed at stage 4 from the bottom, is taken to initialise a rigorous simulation in HYSYS. The column consists of 23 stages including the decanter and reboiler. The upper and lower feeds given in Table 4.1 are added to the column at stage 2 and 20 from the top of the column, respectively. The reflux ratio is 5 and the column pressure is 1 atm. Additional column specifications given to HYSYS are listed in Table 4.3. The liquid composition profile of the column obtained using HYSYS agrees with the composition profiles from the boundary value method (Figure 4.6). Also, the product compositions and flow rates as well as the energy requirement from HYSYS (Table 4.3) and from the boundary value method agree well with each other.

As discussed in Chapter 3, the results of rigorous simulation from HYSYS may be different from those of the design method. The discrepancy between the results from HYSYS and the specifications for the design method may arise due to the existence of multiple steady states. The results from the boundary value method, e.g. temperatures and compositions on particular stages, may be used as initial values for initialising a rigorous simulation to facilitate the HYSYS algorithm to converge to the specified separation. In addition, the simulation results from HYSYS may diverge from the design specifications in case that the column designs resulting from the boundary value method have fractional numbers of stages. The design specifications, e.g. reflux ratio, the amount of trace components in products, may be revised so that feasible designs with integral numbers of stages are found.

Table 4.3. Column specifications given to HYSYS and simulation results from HYSYS based on the first column design in Table 4.2(a)

Column specifications given to HYSYS

Reflux ratio	5
Mole fraction of water in the bottom stream	0.0150
Flow rate of heavy liquid phase in the distillate (kmol/h)	19.25

Simulation results from HYSYS compared with design specifications for the boundary value method (BVM)

	BVM		HYSYS	
	Distillate, D_1	Bottoms, B_1	Distillate, D_1	Bottoms, B_1
Composition (mole fraction)				
1-Propanol	0.0001 [a]	0.2159	0.0001	0.2159
Water	0.9599	0.0150 [a]	0.9599	0.0150 [a]
1-Butanol	0.0400 [a]	0.7691	0.0400	0.7691
Flow rate (kmol/h)	19.39	92.61	19.39	92.61
Condenser duty (kW)	1375		1375	
Reboiler duty (kW)	1367		1367	
Number of heterogeneous stages	1		1	
Phase split ratio of reflux	0.25		0.25	

[a] Specified values

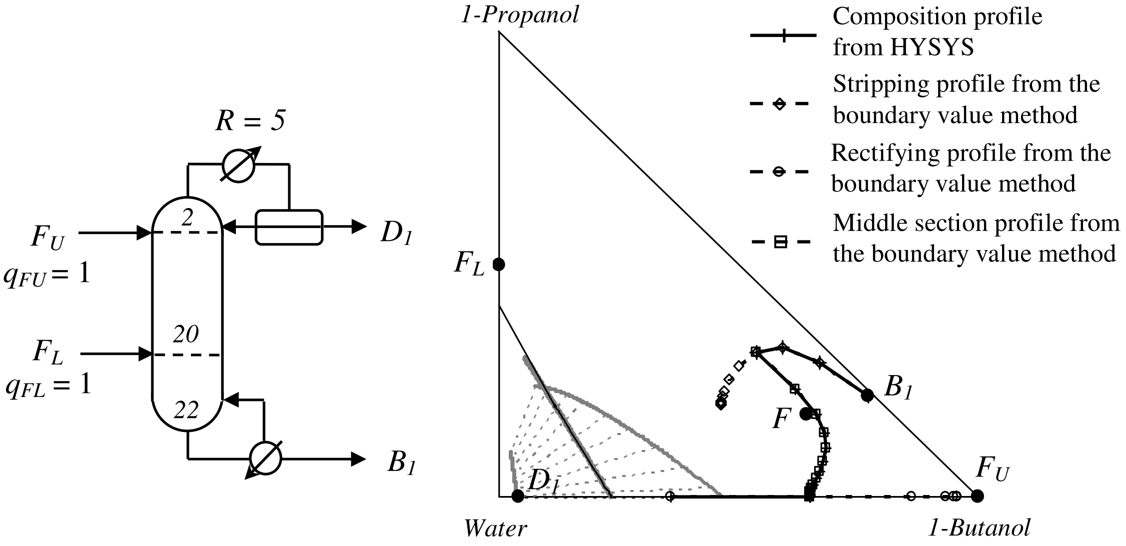


Figure 4.6. The first column design in Table 4.2(a) and its liquid composition profile from HYSYS.

4.2.2 Column design procedure: Summary

The column design procedure for a double-feed column with an integrated decanter is summarised as follows:

1. Calculate vapour-liquid-liquid equilibrium at a specified operating pressure to generate the heterogeneous boiling envelope and vapour line.
2. Set the compositions and flow rates of all feeds and products as well as the lower feed condition. The compositions and flow rates of products are specified to satisfy the product purity requirement and the overall material balance of the column. Also, specify a reflux ratio and a phase split ratio of reflux stream. (See Section 4.2.1.1)
3. Specify either the reboil ratio or the upper feed condition. If the reboil ratio is specified, the upper feed condition is calculated from Equation (4.4). If the upper feed condition is specified, the reboil ratio is determined from Equation (4.6).
4. Calculate the composition profile of the rectifying section. (See Section 3.2.1.2) If multiple heterogeneous stages appear in the rectifying section, generate multiple rectifying profiles for various phase split ratios of each heterogeneous stage.
5. Calculate the composition profile of the stripping section. (See Section 3.2.1.3)
6. Calculate the middle section profiles starting from various stages of the stripping section. (See Section 4.2.1.2)
7. Search for feasible designs from the intersections between the rectifying and middle section profiles. If an intersection is found, count the number of theoretical stages. Find the upper feed location from the intersection point.
8. Calculate the total annualised costs of the designs (see Appendix B) and rank them.

The proposed column design procedure described above can be used for generating feasible column designs for given product specifications and a combination of two design variables between a reflux ratio, a reboil ratio and a feed condition. For a given set of the design variables, multiple column designs may be identified in case that the reflux phase split ratio is specified so that two liquid phases appear on stages below the decanter. Multiple column designs may also be found as the lower feed location is a degree of freedom. Those column designs can be evaluated in terms of their total annualised costs as the proposed design method provides column design details, e.g. the number of stages and heat duties, which are necessary for column cost estimation. The resulting design details from the design method can also be used for initialising rigorous simulations. The economically attractive designs found from the design method should be evaluated further based on the issues of operability and controllability.

4.3 Economically near-optimal column designs

The goal of column and flowsheet design at the conceptual design step is generally to identify the configuration and operating conditions of columns and flowsheets that satisfy the separation requirement and that are economically attractive. In the previous section, the extension of the boundary value design method for feasibility assessment and performance evaluation of double-feed columns is described. In this section, the use of the developed boundary value method in searching for economically near-optimal designs is discussed.

In general, the cost of a column depends on its design. The boundary value method can be used to search for economically attractive column designs by generating multiple column designs for a range of one or more design variable(s). Those column designs are then evaluated according to their total annualised costs and near-optimal designs are thus identified. Given all feed and product compositions and flow rates, the design variables of a double-feed column include the thermal conditions of upper and lower feeds, reflux ratio, phase split ratio of reflux, reboil ratio, and upper-to-lower feed rate ratio. To apply the column design procedure in Section 4.2, the lower feed condition must be specified; otherwise the middle section profile cannot be calculated continuing from the stripping section of the column. The design procedure in Section 4.2 also requires the upper-to-lower feed rate ratio to be specified. As a result, there are four variables remaining, which are reflux ratio, phase split ratio of reflux, reboil ratio and upper feed condition.

Between reflux ratio, reboil ratio and upper feed condition, two degrees of freedom are chosen and the other variable is calculated from the overall energy balance of the column. The boundary value design method can be applied to generate column designs for a range of one or both of the chosen degree(s) of freedom and a range of phase split ratios of reflux.

For example, if the upper feed condition is specified, feasible column designs can be generated for a range of reflux or reboil ratios and a range of reflux phase split ratios. Once all column designs are generated, the most attractive designs can be identified from their costs. To illustrate, column designs with the specifications in Table 4.1, in which the upper feed is a saturated liquid, are generated for a range of reflux ratios; r = 3.5 to 18, and a range of reflux phase split ratios; $\phi_1 = 0$ to 1. The design procedure in Section 4.2.2 is applied. The liquid composition profiles of all column sections are calculated at the given reflux ratios and phase split ratios of reflux. Table 4.4 shows some feasible column designs ranked by their total annualised costs. The minimum reflux ratio is 3.5. Near-optimal designs are the column with the reflux ratio of 3.68, reflux phase split ratio of 0 and lower feed added at stage 7 or 8 from the reboiler. For a homogeneous extractive distillation, there exists a maximum reflux ratio above which the proposed column is infeasible (Knapp and Doherty, 1994; Brüggemann and Marquardt, 2004). For the double-feed column of heterogeneous azeotropic distillation, the maximum reflux ratio is also found. For this example, the maximum reflux ratio is 14.

Table 4.4. Near-optimal column designs for the separation of 1-propanol/water/1-butanol mixture in Table 4.1 generated for a range of reflux ratio and phase split ratio of reflux; r = 3.5, 3.68, 3.85, 4.03, 4.2, 5.25, 6.3, 8, 10, 12, 14, 16 and 18; ϕ_1 = 0 to 1 (step size of 0.25) and $\phi_1 = \phi_1^o$

r	ϕ_1	s	N_H	N_R	N_S	N_M	N_{Total}	Q_C (kW)	Q_R (kW)	TAC (£/year)
3.68	0	0.95	1	2.2	7	20.0	27.2	1086	1078	327,600
3.68	0	0.95	1	2.2	8	19.1	27.3	1086	1078	327,600
3.85	0	0.99	1	2.0	6	18.9	25.0	1126	1118	329,300
3.85	0	0.99	1	2.0	7	17.9	24.9	1126	1118	329,300
3.85	0	0.99	1	2.0	8	17.4	25.4	1126	1118	329,300
3.68	0	0.95	1	2.2	9	18.7	28.0	1086	1078	330,000
3.85	0.25	0.97	1	2.6	6	20.8	27.4	1109	1101	334,000
3.85	0.25	0.97	1	2.6	7	19.3	27.0	1109	1101	334,000
3.85	0.25	0.97	1	2.6	8	18.7	27.4	1109	1101	334,000
3.85	0	0.99	1	2.0	9	17.1	26.2	1126	1118	334,300
3.68	0.25	0.94	1	2.8	8	21.3	30.1	1070	1062	334,600
3.68	0.25	0.94	1	2.8	9	20.7	30.5	1070	1062	334,600

N_H = Number of heterogeneous stages in the rectifying section,
TAC = Total annualised cost (3-year period and 5% interest rate)

If the constraint of specified upper feed condition is relaxed, the reflux and reboil ratios can then be specified independently. The corresponding upper feed condition for the given reflux and reboil ratios is determined from the overall energy balance of the column if the column is feasible. The number of feasible designs will increase further if a range of reflux and reboil ratios is specified.

Near-optimal column designs for the illustrative example with the specifications in Table 4.1 can be found from a range of reflux and reboil ratios given that the upper feed condition is not fixed. Column designs are searched for the following ranges of reflux and reboil ratios; r = 3.1 to 4.9, and s = 0.9 to 1.9, and a range of phase split ratios of reflux; ϕ_1 = 0 to 1. Exploiting the boundary value design method, multiple column designs are found; the most economically attractive designs are shown in Table 4.5. They differ in terms of number of stages, operating conditions, and upper feed thermal conditions. The designs that require a very low upper feed temperature can be discarded. The lowest cost column designs in Table 4.5 are the columns requiring low reflux and reboil ratios. As almost all of the designs in Table 4.5 require 25 theoretical stages, their capital costs are slightly different only in their condenser costs. Consequently, the operating cost plays a significant role on the overall column cost.

Table 4.5. Near-optimal column designs for the separation of 1-propanol/water/1-butanol mixture in Table 4.1 generated for ranges of reflux, reboil ratios and reflux phase split ratios; r = 3.1, 3.4, 3.7, 4, 4.3, 4.6 and 4.9; s = 0.9, 1, 1.1, 1.2, 1.5, 1.7 and 1.9; $\phi_1 = 0$ to 1 (step size of 0.25) and $\phi_1 = \phi_1^o$

r	s	ϕ_1	q_{FU}	N_H	N_R	N_S	N_M	N_{Total}	Q_C (kW)	Q_R (kW)	TAC (£/year)
3.1	1	0	1.22	1	2.1	6	18.6	24.7	949	1132	327,100
3.1	1	0	1.22	1	2.1	7	17.7	24.8	949	1132	327,100
3.1	1	0	1.22	1	2.1	8	17.2	25.3	949	1132	327,100
3.4	1	0	1.14	1	2.0	6	18.5	24.5	1020	1132	329,100
3.4	1	0	1.14	1	2.0	7	17.6	24.6	1020	1132	329,100
3.4	1	0	1.14	1	2.0	8	17.1	25.2	1020	1132	329,100
3.7	1	0	1.06	1	2.0	6	18.5	24.5	1091	1132	331,000
3.7	1	0	1.06	1	2.0	7	17.5	24.5	1091	1132	331,000
3.7	1	0	1.06	1	2.0	8	17.1	25.1	1091	1132	331,000
3.1	1	0	1.22	1	2.1	9	17.0	26.1	949	1132	332,000
4.0	1	0	0.97	1	2.0	6	18.4	24.4	1162	1132	333,000
4.0	1	0	0.97	1	2.0	7	17.5	24.5	1162	1132	333,000

N_H = Number of heterogeneous stages in the rectifying section (including the decanter)
TAC = Total annualised cost (3-year period and 5% interest rate)

Another design variable for double-feed column design is the upper-to-lower feed rate ratio. Using the feed and product compositions, feed conditions and lower feed flow rate in Table 4.1, column designs are generated for a range of reflux ratios and phase split ratios of reflux, at various upper-to-lower feed ratios. Figure 4.7 shows the minimum and maximum reflux ratio as a function of upper-to-lower feed rate ratio; the minimum feed rate ratio for this example is 0.56. As shown in Figure 4.7, there exists a minimum and maximum reflux ratio for an upper-to-lower feed rate ratio. Moreover, the range of feasible reflux ratios reduces as the feed rate ratio decreases. The existence of a minimum feed rate ratio and minimum and maximum reflux ratios for a feed rate ratio is also found in homogeneous extractive distillation (Knapp and Doherty, 1994; Brüggemann and Marquardt, 2004).

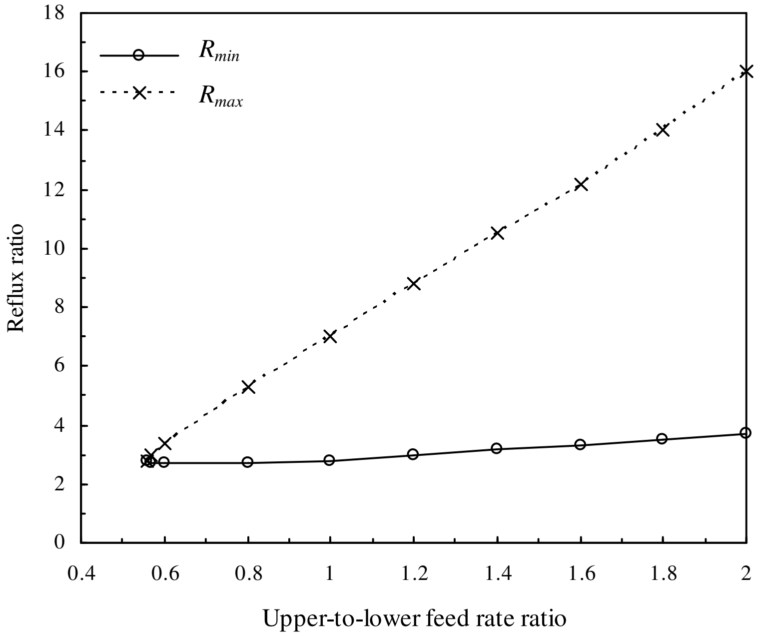


Figure 4.7. Minimum and maximum reflux ratios as a function of the upper-to-lower feed rate ratio for the separation of 1-propanol/water/1-butanol mixture in Table 4.1.

Not only does the upper-to-lower feed rate ratio influence the feasibility of the column but it also affects the cost of the column. Table 4.6 shows the most attractive designs for the illustrative example in Table 4.1 when the upper-to-lower feed rate ratio is a design variable. The optimal feed rate ratio is between 1.2 and 1.6. The columns with the feed rate ratio close to the minimum feed rate ratio are more expensive as they need more theoretical stages. On the other hand, adding a large amount of entrainer results in higher costs as a higher reflux ratio is needed and it also leads to more expensive entrainer recovery column.

Table 4.6. Some lowest cost designs for the column in Table 4.1 when the upper-to-lower feed rate ratio is a design variable (F_U/F_L = 0.56, 0.57, 0.6, 0.8, 1, 1.2, 1.4, 1.6, 1.8 and 2)

F_U/F_L	r	ϕ_1	s	N_H	N_R	N_S	N_M	N_{Total}	Q_C (kW)	Q_R (kW)	TAC (£/year)
1.4	3.36	0	1.1	1	1.9	7	22.5	29.5	1024	1018	320,500
1.4	3.36	0	1.1	1	1.9	8	21.6	29.6	1024	1018	322,900
1.4	3.36	0	1.1	1	1.9	9	21.2	30.1	1024	1018	322,900
1.2	3.15	0	1.18	1	1.9	7	26.2	33.1	980	976	324,100
1.2	3.15	0	1.18	1	1.9	8	24.8	32.7	980	976	324,100
1.2	3.15	0	1.18	1	1.9	9	24.2	33.1	980	976	324,100
1.4	3.52	0	1.14	1	1.9	6	22.0	27.8	1062	1057	324,600
1.4	3.52	0	1.14	1	1.9	7	20.8	27.6	1062	1057	324,600
1.4	3.52	0	1.14	1	1.9	8	20.2	28.0	1062	1057	324,600
1.6	3.65	0	1.05	1	2	7	19.3	26.3	1087	1080	325,300
1.2	3.3	0	1.22	1	1.8	6	25.7	31.4	1016	1012	325,800
1.2	3.3	0	1.22	1	1.8	7	23.8	30.5	1016	1012	325,800

N_H = Number of heterogeneous stages in the rectifying section,
TAC = Total annualised cost (3-year period and 5% interest rate)

In summary, this section describes the iterative application of the new column design method for identifying economically near-optimal designs of a double-feed column over a range of design variables, e.g. reflux phase split ratio, reflux ratio, reboil ratio and upper-to-lower feed ratio. By using the iterative application of the boundary value method, unattractive column and flowsheet designs can be screened out rapidly and near-optimal designs can be identified without exhaustive optimisation.

4.4 Conclusions

This chapter presents the extension of the boundary value method described in Chapter 3 for double-feed columns with integrated decanters. The proposed design method can be used to test the feasibility of a proposed separation, and to identify and evaluate feasible designs. The proposed design procedure includes setting column specifications, calculating liquid composition profiles of all column sections, assessing product feasibility and evaluating feasible designs in terms of their total annualised costs. The feasibility of a proposed separation is indicated from the intersection between a rectifying profile and a middle section profile.

For a given set of feed conditions, product compositions and reflux ratio, multiple column designs may be identified using the new design procedure. Similarly to a single-feed column with an integrated decanter, multiple column designs for a double-feed column with an integrated decanter may be generated if a specified reflux phase split ratio gives rise to the presence of two liquid phases on stages below the decanter. Multiple designs may also be found as the lower feed location is a degree of freedom.

The proposed column design method allows rigorous simulations of double-feed columns to be carried out without trial-and-error. A rigorous simulation of a double-feed column can be initialised using the resulting column design details from the column design method, e.g. total number of stages, feed locations and reflux ratio. Other results from the design method, such as the location of heterogeneous stages and temperatures and compositions on stages, can be used as initial values for facilitating simulation convergence.

The application of the new boundary value method for a double-feed column with an integrated decanter is demonstrated with the dehydration of 1-propanol using 1-butanol as an entrainer. For this mixture, the designs with multiple heterogeneous stages are not as attractive as the column in which heterogeneous liquid is restricted to the top decanter.

The iterative application of the boundary value method allows the identification of economically near-optimal designs over a range of design variables. For a given set of product specifications and upper-to-lower feed rate ratio, feasible designs can be sought for a range of reflux phase split ratios and a range of one or two design variables of reflux ratio, reboil ratio or upper feed condition. Feed rate ratios that lead to near-optimal designs can also be determined by applying the iterative design approach over a range of feed rate ratios.

The design method for double-feed columns with integrated decanters is developed for ternary mixtures. The design procedure may be applied for multicomponent mixtures; however searching for an intersection between composition profiles in a multi-dimensional composition space is difficult. This is because the liquid composition profiles are very sensitive to the trace components in the associated products. Nevertheless, the design method may be a basis for developing a design method for multicomponent mixtures.

Chapter 5

Design method for columns with intermediate decanters

5.1 Introduction

Columns with intermediate decanters are normally used to recover a component, typically water, as a sidestream from a stage where two liquid phases occur (Figure 5.1(a)). At a draw stage, a heterogeneous liquid is withdrawn and split into a decanter. From the decanter, a liquid phase, usually aqueous phase, is recovered as a sidestream product while the other liquid phase is returned to the column at one stage below the draw stage (Schneider et al., 1997). Alternatively, the column may contain a built-in donut decanter tray on the draw stage (Pucci et al., 1986; Ciric et al., 2000): such a tray collects the liquid from the above tray and allows phase splitting. With the aid of a liquid interfacial level controller in the decanter tray, aqueous phase can be removed as a sidestream and the organic phase will flow to the next tray below.

Columns with intermediate decanters can be used for separating mixtures of which residue curve map topologies are similar to those shown in Figure 5.1(b) (Ciric et al., 2000). Opportunities to employ this type of column in a flowsheet can be systematically identified using the distillation sequence synthesis method presented in Chapter 6. In Figure 5.1(b), the lowest-boiling component *A*, is recovered in a top product. Water and component *C* are partially immiscible and form a minimum-boiling heterogeneous azeotrope. Since the heterogeneous azeotrope of water and component *C* is a saddle point in the residue curve map, water can be recovered from the intermediate decanter in a sidestream and component *C* can be obtained at the bottom. Note that component *A* may form a maximum-boiling azeotrope with water or component *C*. Examples of mixtures that can be separated using columns with intermediate decanters are a mixture of acetone, water and 1-butanol (Pucci et al., 1986), a mixture of glycerine, methylesters and methanol (Schneider et al., 1997), and a mixture containing five components of some oxygenated organic compounds and water (Ciric et al., 2000).

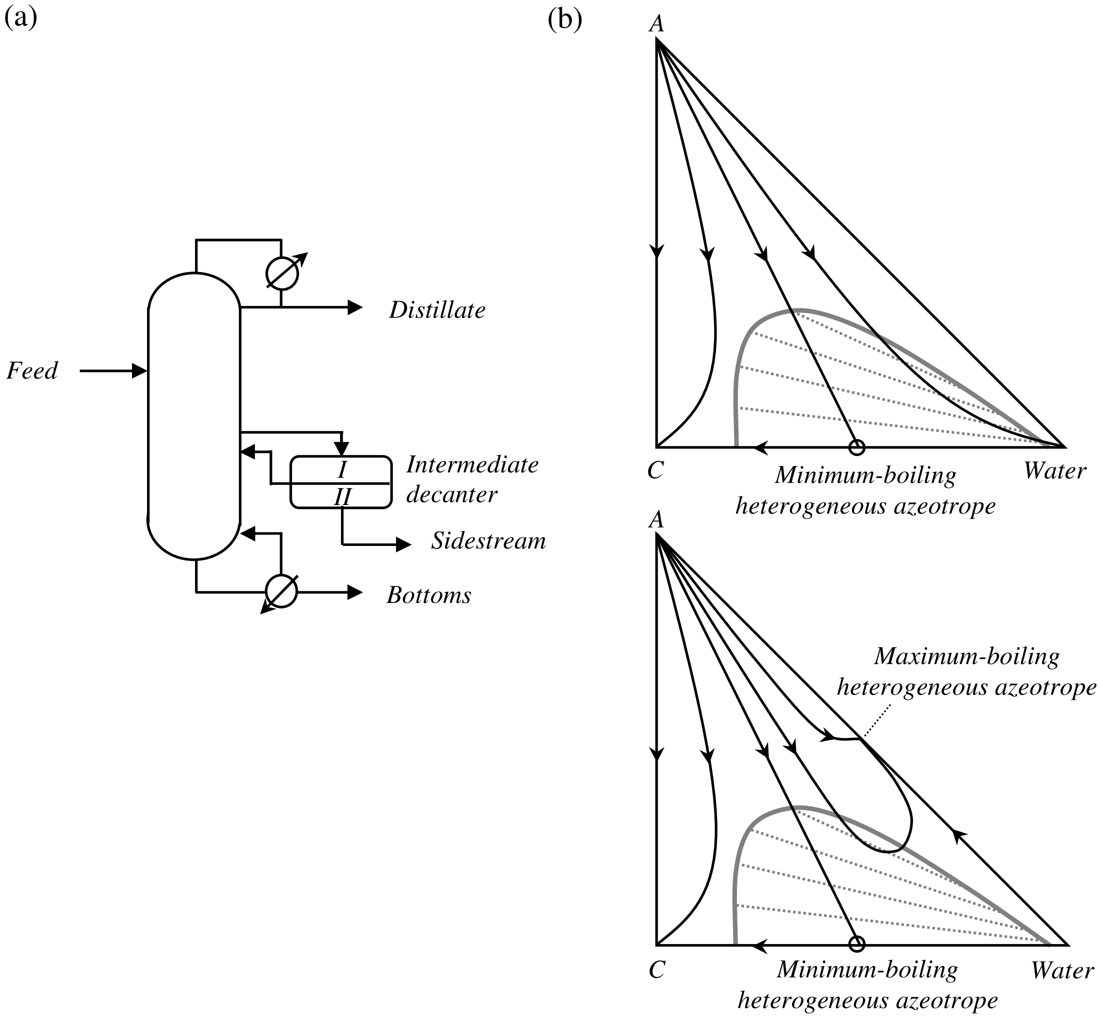


Figure 5.1. (a) Column with an intermediate decanter (b) Typical residue curve maps of mixtures that can be separated in columns with intermediate decanters according to Ciric et al. (2000)

A column with an intermediate decanter may be an attractive option in separating a mixture (Stichlmair and Fair, 1998). In general, to separate a ternary component mixture, two simple columns (a simple column is a column with a single feed and two products) are required to recover all components. On the other hand, it may be possible to recover the components in a column with an intermediate decanter using only one column and one decanter.

The design of a column with an intermediate decanter is challenging. Generally, the column design can be carried out by simulation. Design by simulation requires a great deal of time and effort as the convergence of column is typically difficult to achieve without a good initial guess of column design parameters. The design parameters of a column with an intermediate decanter are the number of stages, feed location and thermal condition, reflux ratio, and side draw location. In addition, predicting the stages at which two liquid phases appear in the column is essential in order to facilitate convergence of the simulation to the specified separation. Furthermore, exhaustive searching for the most promising designs by this technique is needed.

Another method to design the column is using the continuous distillation region based design method proposed by Urdaneta (2005). For a given reflux ratio and product specifications, a continuous distillation region contains all possible liquid composition profiles of a column section (Urdaneta et al., 2002). The region is produced by connecting all pinch points of a column section with lines generated from stage-by-stage calculations. This method allows the feasibility of a given separation to be assessed. However, the determination of pinch points is computationally intensive. Moreover, column design details, such as the number of the stages, feed and side draw locations, are not straightforward to obtain. The column details can be determined after the demanding calculation of continuous distillation regions by calculating liquid composition profiles.

This chapter presents a conceptual design method based on the boundary value method for columns with intermediate decanters. The design method can be applied for assessing the feasibility of a proposed separation. For a feasible column design, the design procedure provides column design details such as the number of theoretical stages, feed and side draw locations at a given combination between two design variables of reflux ratio, reboil ratio, and feed condition. The location of heterogeneous liquid stages in the column is also found from the design procedure. From the design results, a column design can be evaluated in terms of its total annualised cost. Economically near-optimal designs can thus be identified. Separation flowsheets with this type of column can also be evaluated and compared with other separation options.

5.2 Design method for column with intermediate decanter

This section describes the extension of the boundary value design method to columns with intermediate decanters. The calculation required for the boundary value method has been written in MATLAB 7.0 interfaced with HYSYS 2004.1 for phase equilibrium and enthalpy calculation. A separation of acetone/water/1-butanol mixture is taken as an example to demonstrate the column design procedure.

Illustrative example

Butanol, which is an alternative biofuel, can be produced from the acetone-butanol fermentation of biomass. The solvent recovery and product separation after the fermentation can be accomplished by distillation (Jones and Woods, 1986).

Figure 5.2 shows the residue curve map and heterogeneous boiling envelope of the mixture of acetone, water and 1-butanol. The phase equilibrium of the mixture is obtained from HYSYS using the NRTL-ideal gas property package (see Appendix C for the validation of thermodynamic medel and parameters). Water and 1-butanol are partially immiscible: the composition of the aqueous liquid phase is 98.8 mol% water. The ternary mixture has a saddle heterogeneous azeotrope of water and 1-butanol. The residue curve map features a distillation boundary running from the acetone vertex to the heterogeneous azeotrope. A vapour line begins at the heterogeneous azeotrope and it is located close to the distillation boundary.

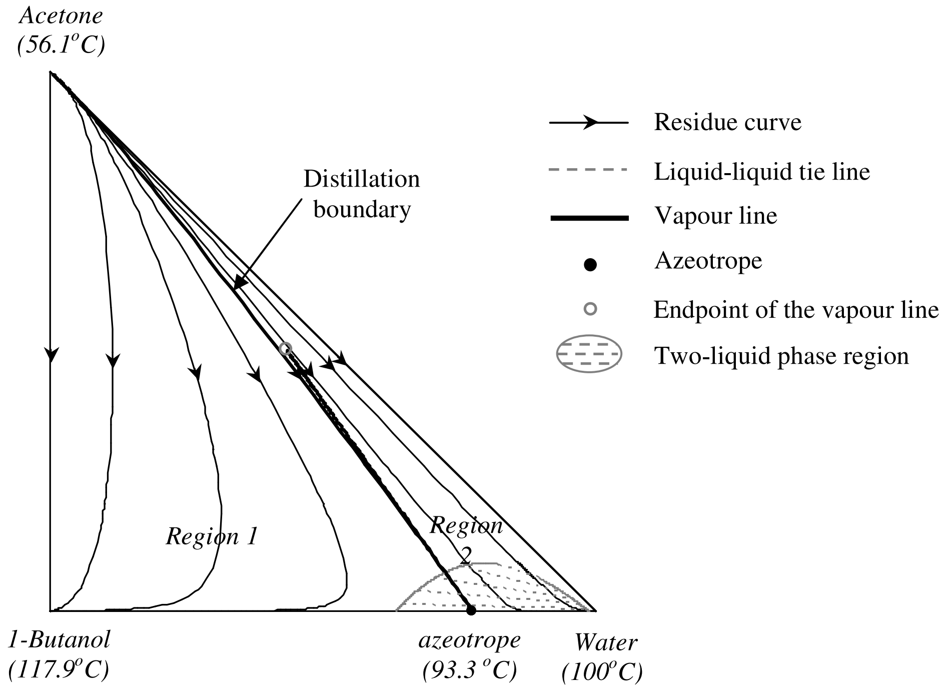


Figure 5.2. Residue curve map and heterogeneous boiling envelope of the acetone/water/1-butanol mixture at 1 atm.

5.2.1 Model development

In this section, the boundary value design method developed for columns with intermediate decanters is discussed in detail. To design a column with an intermediate decanter, the first step is to set all specifications of the column as discussed in Section 5.2.1.1. Next, liquid composition profiles of all column sections are calculated from material and energy balances together with phase equilibrium (the constant molar overflow is not assumed). The feasibility of the proposed separation is then indicated by the intersection of the composition profiles. The column design parameters are next obtained and used for the column cost estimation.

5.2.1.1 Specifications

The specifications of the boundary value design method for a column with an intermediate decanter are: column pressure, which is assumed constant throughout the column; feed composition and flow rate; top and bottom product compositions and flow rates; reflux ratio; either reboil ratio or feed condition. The product specifications are chosen to satisfy the product purity requirement and material balance over the column (equations 5.1 and 5.2).

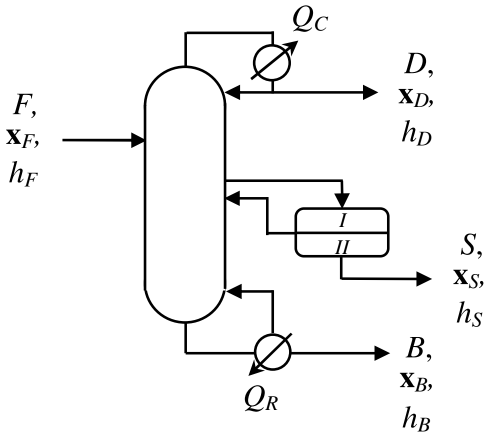


Figure 5.3. Schematic representation of a column with an intermediate decanter.

$$F = D + S + B \tag{5.1}$$

$$\mathbf{x}_F F = \mathbf{x}_D D + \mathbf{x}_S S + \mathbf{x}_B B \tag{5.2}$$

If the reboil ratio (s) is specified, the feed condition (q_F) is determined from:

$$q_F = \left(\frac{h_F^{V,sat} - h_F}{h_F^{V,sat} - h_F^{L,sat}} \right) \tag{5.3}$$

where h_F is calculated from the energy balance over the column:

$$h_F = \frac{1}{F}\left(Dh_D + Sh_S + Bh_B + Q_C - Q_R\right) \tag{5.4}$$

The condenser and reboiler duties (Q_C and Q_R) are calculated from energy balances around the condenser and reboiler, respectively. The specified reflux and reboil ratios will be rejected if the corresponding feed condition is not realisable with available utilities, for instance a very low feed temperature.

If the feed condition is given, the reboil ratio is calculated from the energy balance over the reboiler:

$$s = \frac{1}{\left(h_2^{S,L} - h_1^{S,V}\right)}\left(h_B - h_2^{S,L} - \frac{Q_R}{B}\right) \tag{5.5}$$

where $h_1^{S,V}$ and $h_2^{S,L}$ is the molar enthalpies of the vapour phase from the reboiler and the liquid phase entering the reboiler, respectively. The reboiler duty (Q_R) is determined from the energy balance over the column:

$$Q_R = Dh_D + Sh_S + Bh_B - Fh_F + Q_C \tag{5.6}$$

Table 5.1 shows the specifications of a column with an intermediate decanter separating a mixture of acetone, water and 1-butanol. The feed stream is a saturated liquid. The pressure of the feed stream and the pressure in the column, condenser and reboiler are 1 atm. The top and bottom products are relatively pure acetone and 1-butanol, respectively. The sidestream is the aqueous phase from the intermediate decanter. To specify the sidestream composition, the decanter tie line is firstly chosen and the composition of aqueous phase of the decanter tie line is the sidestream composition. The flow rates of all products are then determined from the set of equations 5.1 and 5.2.

Table 5.1. Specifications of a column with an intermediate decanter separating a mixture of acetone, water and 1-butanol

	Feed, F	Distillate, D	Sidestream, S	Bottoms, B
Composition (mole fraction)				
acetone	0.0995 [a]	0.9724 [a]	0.0016 [a]	1×10^{-6} [a]
water	0.7859 [a]	0.0276	0.9855 [a]	0.0024
1-butanol	0.1146	7×10^{-8} [a]	0.0129	0.9976 [a]
Feed condition	1 [a]			
Flow rate (kmol/h)	100 [a]	10.10	79.44	10.46
Reflux ratio		20		

[a] Specified values

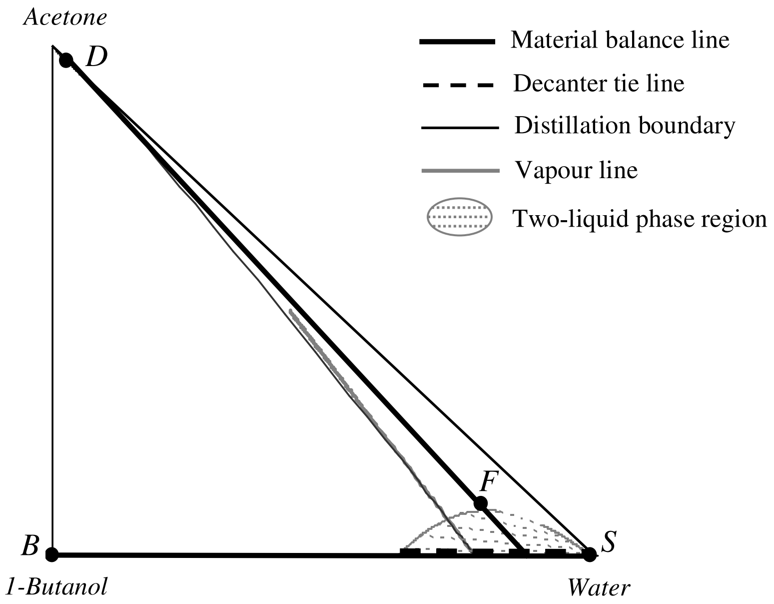


Figure 5.4. Material balance line and decanter tie line of the column with an intermediate decanter according to the specifications in Table 5.1

5.2.1.2 Calculation of composition profiles

After all specifications of the column are proposed, the calculation of rectifying, stripping and middle section profiles of the column is carried out using material and energy balances along with phase equilibrium of the mixture.

Rectifying profile

For the illustrative example, the proposed column has no liquid phase splitting at the top of the column (Figure 5.5). For such a rectifying section, the model for the rectifying profile calculation has been introduced by Levy et al. (1985). However, the model proposed by Levy et al. (1985) is developed based on the assumption of constant molar overflow which is inadequate for a highly non-ideal system.

The rectifying profile calculation can be carried out using the material and energy balance equations (3.10) and (3.11) for a rectifying section having only homogeneous liquid as discussed in Section 3.2.1.2. However, the condenser duty is determined from equation (5.7). For the rectifying section with no (integrated) decanter, the reflux stream has the same composition as the top product. For a given top product composition and reflux ratio, the rectifying profile starts from the top product composition ($\mathbf{x}_D$). It is then calculated recursively from stage to stage down the column using the set of equations (3.10) and (3.11) together with vapour liquid equilibrium of the mixture.

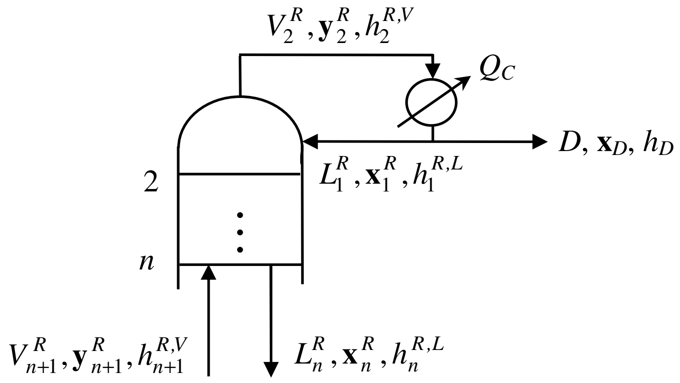


Figure 5.5. Schematic representation of a rectifying section with no (integrated) decanter

$$Q_C = \left((r+1)h_2^{R,V} - rh_1^{R,L} - h_D\right)D \tag{5.7}$$

For the given top product and reflux ratio in Table 5.1, the column has a single rectifying profile since there is no (integrated) decanter at the top. The rectifying profile of the column is shown in Figure 5.6. Note that the rectifying profiles in Figure 5.6(a) to (f) are identical. The profile starts from the top product composition near the pure acetone vertex. It continues in distillation region 2 and then moves towards the pure water vertex.

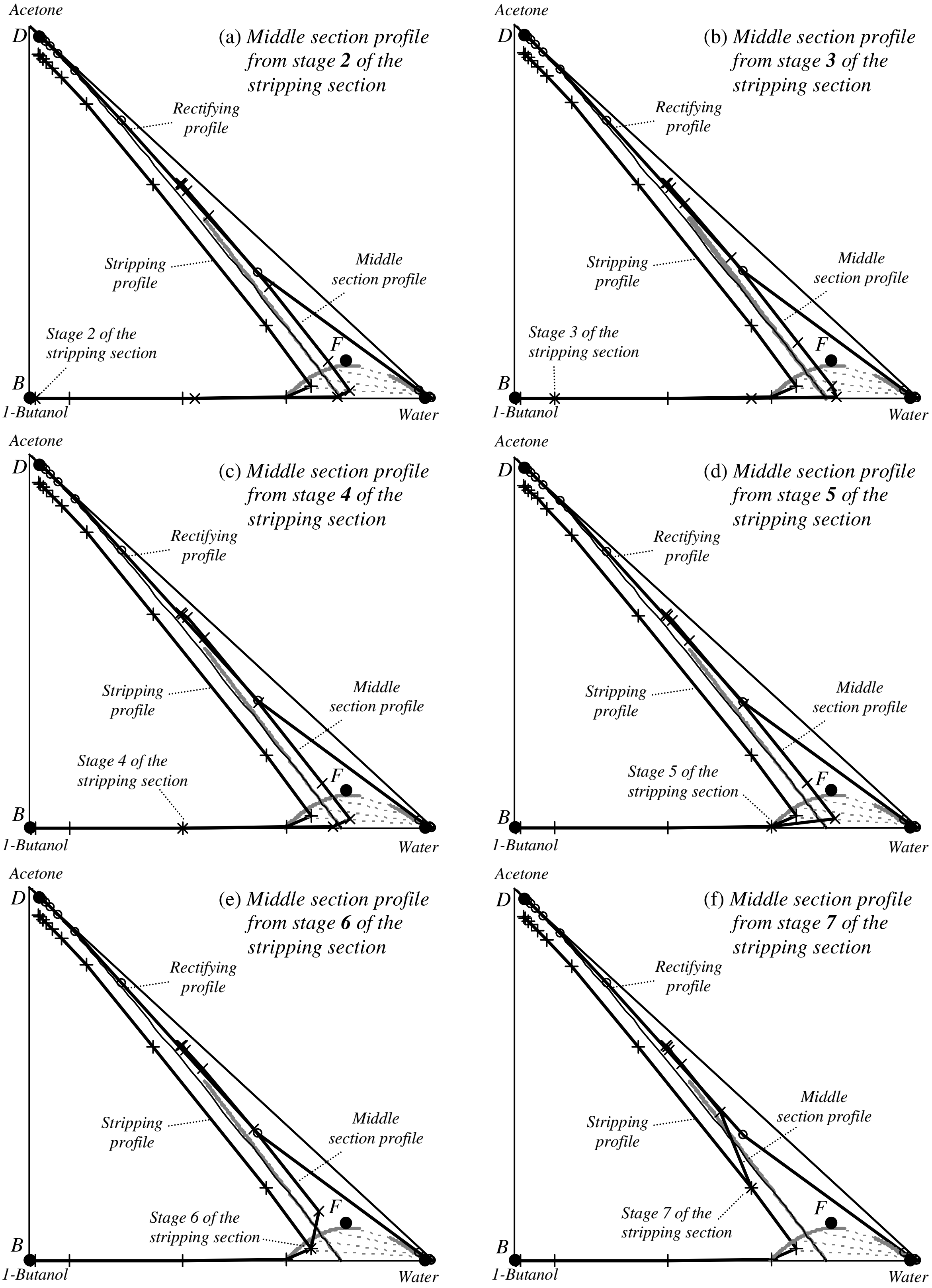


Figure 5.6. Composition profiles of the proposed column with an intermediate decanter separating a mixture of acetone, water and 1-butanol according to the specifications in Table 5.1.

Stripping profile

The stripping profile of the column is calculated using the method described in Section 3.2.1.3. For the illustrative example, the stripping profile presented in Figure 5.6 starts from the bottom product composition ($\mathbf{x}_B$). The profile moves along the 1-butanol/water edge before it continues into distillation region 1 and ends near the acetone vertex.

Middle section profile

Once the stripping profile calculation is complete, the middle section profile can be calculated starting from a specified stage of the stripping section. The stage of the stripping section from which the middle section profile begins is a degree of freedom. Assuming that the organic liquid phase from the intermediate decanter is returned to the column at the stage below the decanter draw stream, the draw stage is the stage next to the starting point of the middle section profile. For instance, a middle section profile is started from stage *m* of a stripping section in Figure 5.7. The draw stage is thus stage *m*+1.

The calculation of a middle section profile starting from stage *m* of the stripping section can be carried out in the following procedure:

i. Choose a stage from the stripping section as the stage at which the organic liquid phase from the intermediate decanter returns to, e.g. stage *m* in Figure 5.7. Thus, stage *m*+1 is the draw stage.

ii. Determine the vapour composition of stage *m* ($\mathbf{y}_m^M$) from the liquid composition of stage *m* ($\mathbf{x}_m^S$) using bubble point calculation. Note that the composition, flow rate and enthalpy of the liquid leaving stage *m* is known from the stripping section profile.

iii. Calculate the overall liquid composition of the next stage *m*+1 ($\mathbf{x}_{m+1}^M$) from the material and energy balances (the set of equations 5.8 and 5.9).

iv. Continue the calculation of the next stages in the middle section by solving the set of equations (5.8) and (5.9) together with vapour-liquid-(liquid) equilibrium.

v. Check if the liquid composition at the draw stage ($\mathbf{x}_{m+1}^{M}$) is a heterogeneous liquid. If not, discard that choice of start stage of the middle section profile.

$$\left(V_m^M + S + B\right)\mathbf{x}_{m+1}^M - V_m^M \mathbf{y}_m^M - S\mathbf{x}_S - B\mathbf{x}_B = \mathbf{0} \tag{5.8}$$

$$\left(V_m^M + S + B\right)h_{m+1}^{M,L} - V_m^M h_m^{M,V} - Sh_S - Bh_B + Q_R = 0 \tag{5.9}$$

where $Q_R = \left(sh_1^{S,V} - (s+1)h_2^{S,L} + h_B\right)B$ if $s = V_1^S / B$ is specified, or

$Q_R = Dh_D + Sh_S + Bh_B - Fh_F + Q_C$ if the feed condition is specified.

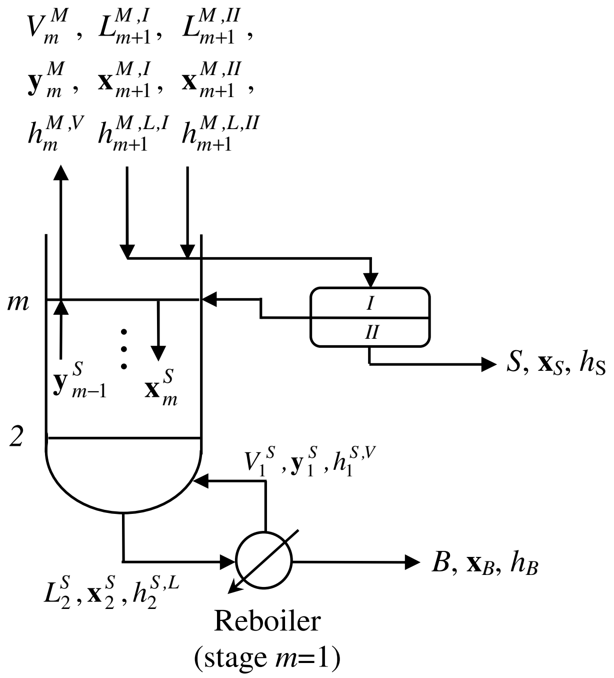


Figure 5.7. Schematic presentation of a stripping section including an intermediate decanter

Using the procedure described above, middle section profiles can be produced from different stages of the stripping section since the side draw location is a degree of freedom. However, a middle section profile may lead to feasible design only if (i) the middle section and rectifying profiles intersect, and (ii) its corresponding composition of the liquid stream entering the decanter is located inside the heterogeneous boiling envelope.

For the illustrative example, the middle section profiles calculated starting from stage 2 to 7 of the stripping section (corresponding to draw stage 3 to 8) are shown in Figure 5.6(a) to (f). As shown in Figure 5.6, only the columns with side draw location at stage 5 and 6 from the bottom (the middle section profiles start from stage 4 and 5 from the bottom, respectively) may lead to feasible designs because their liquid compositions lie at the draw stages in the two-phase region (see Figure 5.6(c) and (d)). As can be concluded from Figure 5.6, the feasibility criteria are rather stringent, leading to a relatively small number of feasible designs. The scarcity of feasible designs provides evidence of the need for a design method that does not rely purely on simulation.

5.2.1.3 Feasibility assessment and column design evaluation

Once the liquid composition profiles of all column sections are calculated at the given reflux ratio, the feasibility of the proposed separation can be assessed and feasible column designs can be evaluated. The proposed separation is feasible if (i) the rectifying and middle section profiles intersect each other, and (ii) the liquid stream feeding the intermediate decanter is a heterogeneous liquid. The intersection point corresponds to the feed location. The stage above the starting point of the middle section profile is the draw stage. The required number of theoretical stages of the column can then be counted. Afterwards, the column design can be evaluated and compared with other feasible designs according to its total annualised cost.

Using a line intersection search algorithm developed by Hölz (2006), all middle section profiles with the side draw locations from stage 3 to 8 from the bottom intersect with the rectifying profile as shown in Figure 5.6. However, not all of the middle section profiles lead to feasible designs. Only the columns with their draw stages at stage 5 and 6 from the bottom are feasible as the liquid compositions at those draw stages lie inside the two-liquid phase region. The liquid composition profiles of these feasible designs are shown in Figure 5.6(c) and (d). On the other hand, the columns with draw stage at stages 3, 4, 7 and 8 are infeasible designs because the liquid compositions at those draw stages are not located inside the two-liquid region.

Two feasible column designs of the illustrative example are listed in Table 5.2. The total annualised costs of the designs are estimated using the cost function in Appendix B based on a repayment period of 3 years and an interest rate of 5%. The cost of the decanter is estimated assuming that the decanter is externally coupled to the column. Those two designs have the same energy requirement and the same number of theoretical stages. As a result, their total annualised costs are equal. The designs are different in only their side draw location. Therefore, no design in Table 5.2 is more attractive than another.

Table 5.2. Column designs for the column with an intermediate decanter specified in Table 5.1.

Draw stage (from the reboiler)	N_R	N_M	N_{Total}	Total annualised cost* (£/year)
5	7.9	4.3	15.2	474,400
6	7.9	3.3	15.2	474,400
Condenser duty (kW)			1739	
Reboiler duty (kW)			1779	

* 3-year period, 5% interest rate

The first design in Table 5.2, the column with draw stage at stage 5 from bottom, is taken to initialise a rigorous simulation in HYSYS to show that the designs can be validated. The column has 15 stages including the condenser and reboiler. The feed given in Table 5.1 is added to the column at stage 8 from the top. The liquid stream at stage 11 from the top is removed to the intermediate decanter for liquid phase splitting and an aqueous liquid phase from the decanter is withdrawn as a sidestream product (Figure 5.8). The reflux ratio is 20 and the column pressure is 1 atm. The liquid composition profile of the column from HYSYS is shown in Figure 5.8. The results from HYSYS are in an excellent agreement with the design specifications for the boundary value method as shown in Table 5.3.

Table 5.3. Column specifications given to HYSYS and simulation results from HYSYS based on the first column design in Table 5.2

Column specifications given to HYSYS

Reflux ratio	20
Flow rate of the top product (kmol/h)	10.10

Simulation results from HYSYS compared with design specifications for the boundary value method (BVM)

	BVM			HYSYS		
	Distillate, *D*	Side stream, *S*	Bottoms, *B*	Distillate, *D*	Side stream, *S*	Bottoms, *B*
Composition (Mole fraction)						
Acetone	0.9724 [a]	0.0016 [a]	1×10^{-6} [a]	0.9724	0.0016	1×10^{-6}
Water	0.0276	0.9855 [a]	0.0024	0.0276	0.9855	0.0024
1-Butanol	7×10^{-8} [a]	0.0129	0.9976 [a]	7×10^{-8}	0.0129	0.9976
Flow rate (kmol/h)	10.10	79.44	10.46	10.10	79.44	10.46
Condenser duty (kW)		1739			1739	
Reboiler duty (kW)		1779			1779	

[a] Specified values

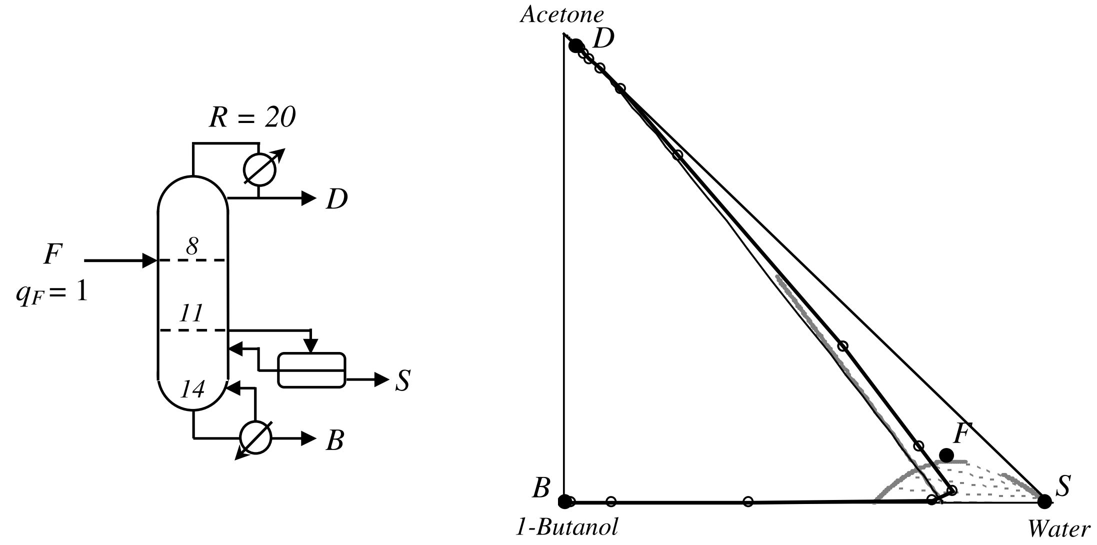


Figure 5.8. The column with an intermediate decanter at stage 11 from the top (the first column design in Table 5.2) and its liquid composition profile from HYSYS.

It can be seen that there is no discrepancy between the product compositions and flow rates, and heat duties predicted by HYSYS and those specified for the design method.

The good agreement is because the number of theoretical stages obtained from the boundary value method is close to an integer value. Also, as shown Figure 5.6(c), the middle section and rectifying profiles coincide near the intersection point which corresponds to the feed stage. The results from HYSYS may diverge from those of the design method if the intersection does not result from an overlap between the rectifying and middle section profiles. The variation between the results from HYSYS and the specifications for the design method may also arise from the existence of multiple steady states which are commonly found in heterogeneous azeotropic distillation (Ciric et al., 2000). The results from the boundary value method, such as the location of heterogeneous stages in the column, compositions and temperatures along the column, can be used as initial guesses to help the HYSYS algorithm converge to the required separation.

5.2.2 Column design procedure: Summary

The column design procedure for a column with an intermediate decanter is summarised below:

1. Calculate the vapour-liquid-liquid equilibrium of the mixture at a specified operating pressure to generate the two-liquid phase region and vapour line.
2. Set the feed composition and flow rate. Choose a decanter tie line and set the composition of the sidestream from the composition of the aqueous phase of the chosen tie line. Set the compositions of top and bottom products according to the product purity requirements and determine the flow rates of all products from the overall material balance of the column. Also, specify a reflux ratio. (See Section 5.2.1.1)
3. Specify either the reboil ratio or the feed condition. If the reboil ratio is specified, the feed condition is calculated from Equation (5.3). If the feed condition is specified, the reboil ratio is calculated from Equation (5.5).
4. Calculate the composition profile of the rectifying section based on its configuration. If a decanter is coupled at the top of the column as illustrated in Figure 3.4, the rectifying profile is calculated using the method in Section 3.2.1.2. If the column consists of a total condenser without a decanter at the

top (Figure 5.5), the rectifying profile is calculated using the method in Section 5.2.1.2.

5. Calculate the composition profile of the stripping section. (See Section 3.2.1.3)
6. Calculate the middle section profiles starting from various stages of the stripping section. (See Section 5.2.1.2) Discard the middle section profiles where their draw stage compositions are not located in the two-liquid phase region.
7. Search for feasible designs from the intersections between the rectifying and middle section profiles. If an intersection is found, count the number of theoretical stages. Find the feed location from the intersection point. The side draw location is the stage after the start point of the middle section profile.
8. Calculate the total annualised costs of the designs (see Appendix B) and rank them.

In summary, the proposed column design procedure above is developed for generating feasible column designs for given product specifications and a combination of two design variables between a reflux ratio, a reboil ratio and a feed condition. For a set of the design variables, multiple column designs may be found as the side draw location is a degree of freedom. Those column designs can be evaluated according to their total annualised costs. Therefore, the column designs can be compared with other column designs with different values of design variables or with other separation flowsheets. However, the decision in choosing among feasible columns must also be based on the issues of operability and controllability. These issues cannot be considered directly using the boundary value design method.

5.3 Case study

This case study compares a column with an intermediate decanter and a sequence of simple columns to separate an acetone/water/1-butanol mixture. The columns are designed using the proposed boundary value method presented in Section 5.2.2 and

Chapter 3. The feed mixture is a saturated liquid with the same composition as the feed in Table 5.1.

***Option 1:** Column with an intermediate decanter*

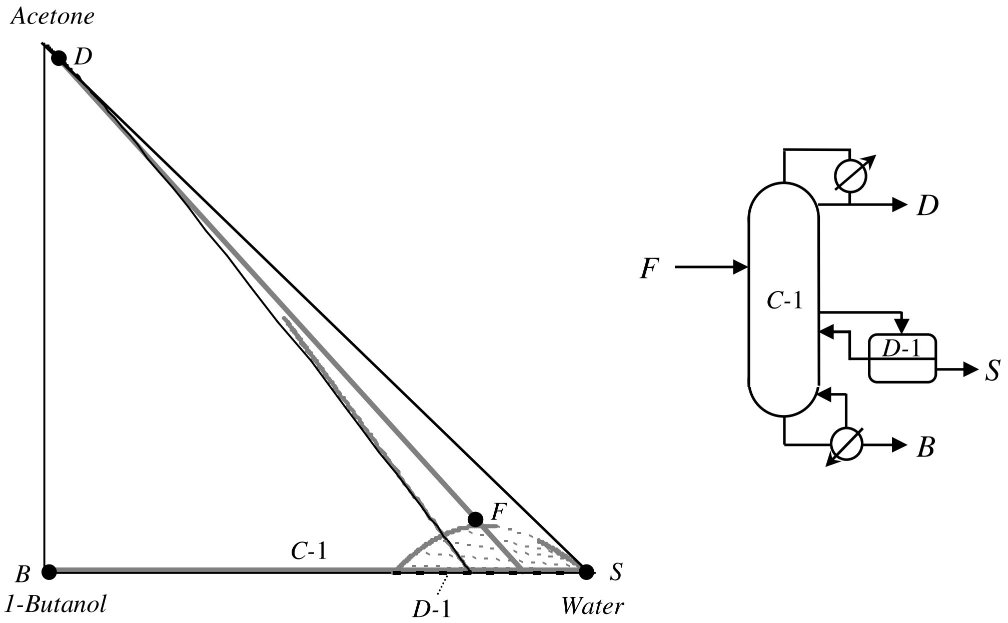


Figure 5.9. Column with an intermediate decanter for separating a mixture of acetone, water and 1-butanol with the specifications in Table 5.4.

The proposed boundary value method for a column with an intermediate decanter in Section 5.2.2 is applied. In Figure 5.9, using the column with an intermediate decanter (*C*-1 and *D*-1), acetone and 1-butanol are achieved in the top and bottom products (*D* and *B*), respectively, whereas water is withdrawn from the intermediate decanter as the sidestream product (*S*). The specifications of the column are shown in Table 5.4. For the given specifications, liquid composition profiles are generated for a range of reflux ratios; $r = 18.90$ to 24.57. Some feasible column designs ranked by their costs are shown in Table 5.5.

Table 5.4. Specifications and product compositions of the column with an intermediate decanter separating a mixture of acetone, water and 1-butanol in Figure 5.10

	F	*D*	*S*	*B*
Composition (mole fraction)				
acetone	0.0995 ^{a}	0.9700 ^{a}	0.0002 ^{a}	$1\times10^{-8\,a}$
water	0.7859 ^{a}	0.0300	0.9873 ^{a}	0.0101
1-butanol	0.1146	$2.4\times10^{-7\,a}$	0.0125	0.9899 ^{a}
Feed condition	1			
Flow rate (kmol/h)	100 ^{a}	10.25	79.18	10.57

^{a} Specified values

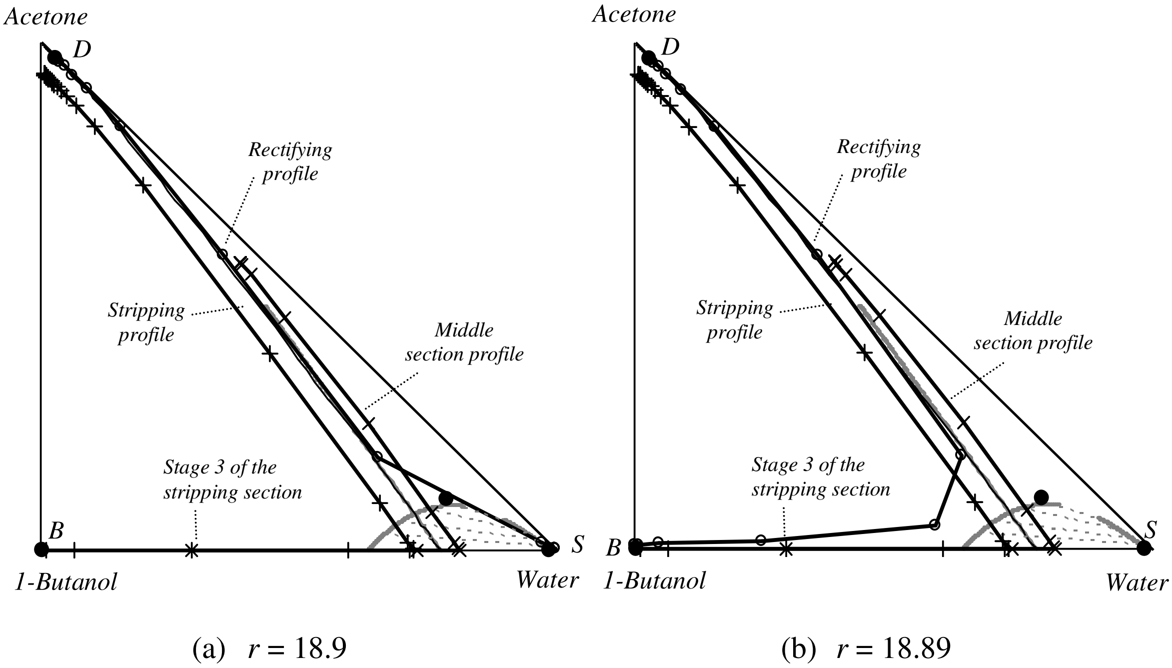
The lowest cost designs in Table 5.5 are the columns with the reflux ratio of 18.9, which is a minimum reflux ratio. The minimum reflux ratio is determined by changing the reflux ratio until the smallest value that causes the intersection between the rectifying and middle section profiles is found. Figure 5.10(a) shows the liquid composition profiles at $r = 18.9$ and side draw location at stage 4 from the bottom. For $r < 18.9$, the rectifying profile will not intersect with a middle section profile as it moves into distillation region 1 as shown in Figure 5.10(b).

Table 5.5. Near-optimal column designs for column *C*-1 in the column with an intermediate decanter (Figure 5.9) generated for a range of reflux ratios: r = 18.90, 19.37, 19.85, 20.32, 20.79, 21.26, 21.74, 22.21, 22.68, 23.63 and 24.57

r	s	N_R	N_S	N_M	N_{Total}	Q_C (kW)	Q_R (kW)	*TAC* (£/year)
18.90	13.05	8.2	3	6.5	15.7	1674	1714	461,700
18.90	13.05	8.2	8	2.6	16.7	1674	1714	464,400
18.90	13.05	8.2	4	6.3	16.4	1674	1714	466,300
18.90	13.05	8.2	5	5.7	16.8	1674	1714	469,600
18.90	13.05	8.2	6	4.7	16.9	1674	1714	469,600
18.90	13.05	8.2	7	3.7	16.8	1674	1714	469,600
19.37	13.35	8.1	3	6.5	15.6	1713	1754	470,700
19.37	13.35	8.1	8	2.6	16.7	1713	1754	473,400

TAC = Total annualised cost (3-year period and 5% interest rate)

The designs with r = 18.9 in Table 5.5 have slightly different costs because they have different numbers of stages in the stripping and middle sections. In addition, the difference in the side draw locations results in slight differences in the size of the decanter. The total annualised cost of the column depends strongly on the operating cost as all feasible designs within the specified range of reflux ratios require about 16 to 17 theoretical stages. The capital costs also increase with column diameter which increases with reflux ratio.



(a) $r = 18.9$ (b) $r = 18.89$

Figure 5.10. Liquid composition profiles of the proposed separation in Table 5.4 at (a) $r = 18.9$ and (b) $r = 18.89$, (side draw location at stage 4 from the bottom).

Typically, an optimal reflux ratio of columns for ideal mixtures is approximately 1.1 times the minimum reflux ratio (Smith, 2005). However, the lowest cost designs for the column with an intermediate decanter in this case study are operated at the minimum reflux ratio. This is because infinite number of theoretical stages is not found at the minimum reflux ratio as found in columns for ideal mixtures. Nonetheless, the designs with r = 18.9 may not be attractive because they can easily become infeasible with a small change of operating conditions. Operating a column with a higher reflux ratio may be more reliable.

Option2: *Simple-column sequence*

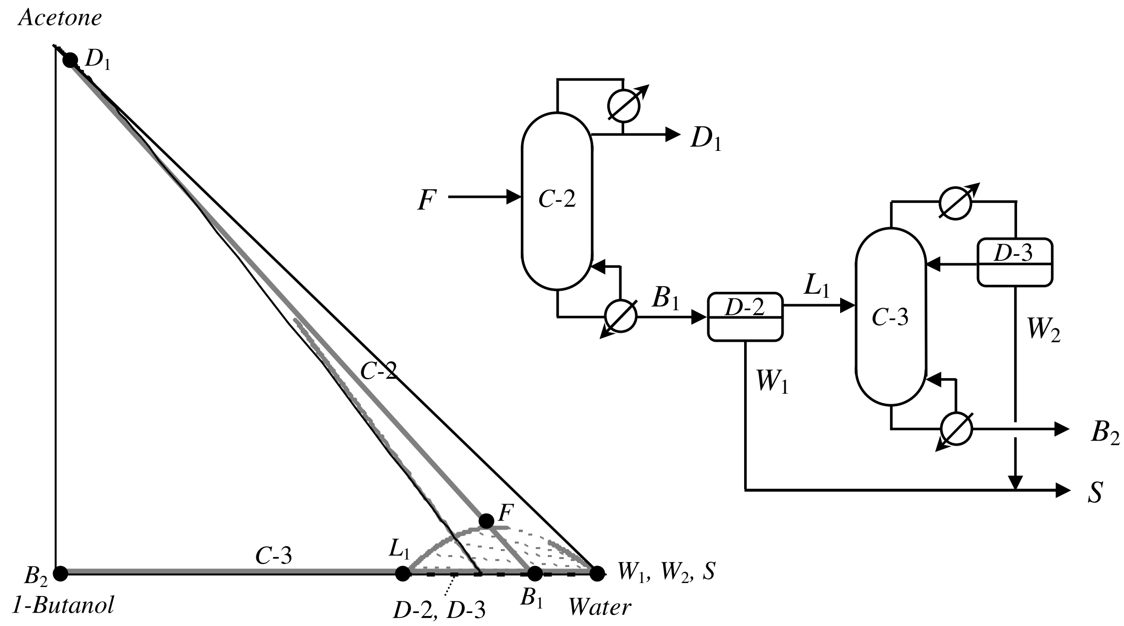


Figure 5.11. Simple column sequence for separating a mixture of acetone, water and 1-butanol with the specifications in Table 5.6.

An option to separate the mixture is the separation sequence in Figure 5.11. This sequence has been proposed using the distillation sequence synthesis algorithm developed by Tao et al. (2003) and Vanage (2005) (see Chapter 6 for details of sequence synthesis). The sequence consists of two single-feed columns and two decanters. The feed stream is first separated in a simple column *C*-2, which is a column with a single feed and two products, to recover acetone in the distillate (D_1). The binary heterogeneous mixture of water and 1-butanol is recovered at the bottom (B_1). The liquid phase splitting of the bottom product from column *C-2* is carried out in a decanter *D-2*, where relatively pure water is obtained (W_1). The other liquid phase from the decanter is the mixture of water and 1-butanol in distillation region 2 (L_1). This organic liquid phase is separated in another simple column *C*-3 with an integrated decanter *D*-3. With a decanter integrated at the top of the column, the distillation boundary can be crossed. Thus, the top product (W_2) can be chosen to be an aqueous liquid phase from the top decanter *D*-3. A high recovery of 1-butanol is achieved at the bottom of the column (B_2).

The mass balance of the system is shown in Table 5.6: the overall mass balance is almost identical to that presented in Table 5.4 for the complex column configuration.

Table 5.6. Mass balance of the simple-column sequence separating a mixture of acetone, water and 1-butanol in Figure 5.11

	F	D_1	B_1	L_1
Composition (mole fraction)				
acetone	0.0995 [a]	0.9700 [a]	5×10^{-5} [a]	0.0001
water	0.7859 [a]	0.0300	0.8723	0.6341
1-butanol	0.1146	2.4×10^{-7} [a]	0.1277	0.3658
Feed condition	1			
Flow rate (kmol/h)	100 [a]	10.25	89.75	29.26
	W_1	W_2	B_2	S
Composition (mole fraction)				
acetone	2.7×10^{-5}	0.0002	1×10^{-8} [a]	0.0001
water	0.9875	0.9873 [a]	0.0101	0.9874
1-butanol	0.0125	0.0125	0.9899 [a]	0.0125
Flow rate (kmol/h)	60.49	18.69	10.57	79.18

[a] Specified values

For each column in the sequence, the boundary value method for single-feed columns in Chapter 3 is applied to assess the feasibility of the proposed separation and search for economically near-optimal column designs. Note that the rectifying profile of column *C*-2 is calculated using the method in Section 5.2.1.2 since there is no integrated decanter at the top of the column. For the specifications in Table 5.6, liquid composition profiles of the columns are generated for a range of reflux ratios; r = 18.9 to 22.21 for column *C*-2 and r = 1.55 to 2.01 for column *C*-3, and a range of phase split ratios of reflux; $\phi_1 = 0$ to 1 for column *C*-3. Feasible designs for each column are then identified and ranked according to their costs. Near-optimal designs for each column are listed in Table 5.7. The total cost of the simple-column sequence corresponding to the lowest cost designs of the two columns is summarised in Table 5.8.

Table 5.7. Near-optimal column designs for column *C*-2, and column *C*-3 in the simple-column sequence (Figure 5.11) generated for a range of reflux ratios: r = 18.9, 19.37, 19.85, 20.32, 20.79, 21.26, 21.74 and 22.21 (for column *C*-2) and r = 1.55, 1.59, 1.63, 1.67, 1.71, 1.74, 1.78, 1.82, 1.86 and 2.01 (for column *C*-3)

a. Column designs for column C-2

r	s	N_R	N_S	N_{Total}	Q_C (kW)	Q_R (kW)	TAC (£/year)
19.37	1.66	8.1	5.3	12.4	1715	1740	439,500
19.85	1.70	8.1	5.3	12.4	1754	1780	448,100
18.90	1.62	8.2	5.3	12.5	1675	1700	453,400
20.32	1.74	8.1	5.3	12.4	1794	1819	456,700
20.79	1.78	8.0	5.3	12.3	1834	1859	465,200
21.26	1.81	7.9	5.4	12.3	1874	1899	473,800
22.21	1.89	7.5	6.2	12.7	1953	1979	494,400
21.74	1.85	7.6	5.9	12.5	1913	1939	500,700

b. Column designs for column C-3

r	ϕ_1	ϕ_H	s	N_H	N_R	N_S	N_{Total}	Q_C (kW)	Q_R (kW)	TAC (£/year)
1.59	0	0	4.41	1	3.4	4.5	6.9	564	580	167,200
1.55	0	0	4.34	1	4.4	4.4	7.8	556	571	170,900
1.63	0.026	0	4.47	2	4.2	4.3	7.5	573	588	171,900
1.59	0.017	0	4.41	2	4.6	4.3	7.9	564	579	172,800
1.71	0.043	0	4.60	2	3.6	4.4	7.0	590	604	172,900
1.55	0.007	0	4.34	2	5.3	4.3	8.6	556	571	173,700
1.67	0.035	0	4.53	2	3.9	4.3	7.2	581	596	173,800
1.74	0.050	0	4.66	2	3.4	4.5	6.9	598	613	174,800

ϕ_H = Phase split ratio of the final heterogeneous stage,
N_H = Number of heterogeneous stages in the rectifying section,
TAC = Total annualised cost (3-year period and 5% interest rate)

Comparing the products of the two options, the products recovered from the two options are slightly different only in the composition of the water rich stream (*S*). This is because the sidestream composition of the column with an intermediate decanter is a product of a single decanter. The composition of the water rich stream product from the simple-column sequence is the result from the mixing between the aqueous phase liquid streams from the two decanters in the sequence.

Table 5.8. A comparison between the costs of the column with an intermediate decanter (Figure 5.9) and the simple-column sequence (Figure 5.11)

Option	Separation unit	Cost of separation unit (£/year)	Total cost of the option (£/year)
Column with an intermediate decanter (Figure 5.9)	*C*-1 & *D*-1	461,700	461,700
Simple-column sequence (Figure 5.11)	*C*-2	439,500	611,900
	D-2	5,200	
	C-3 & *D*-3	167,200	

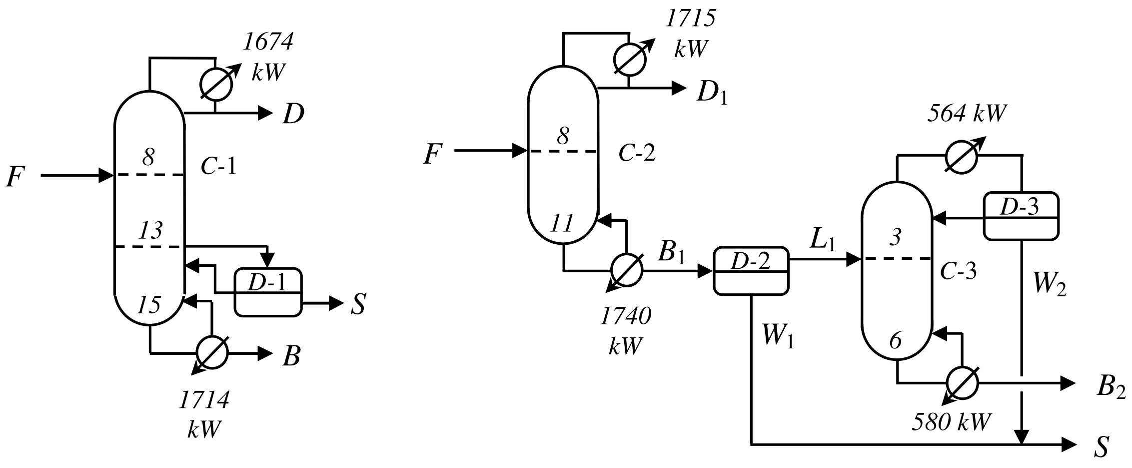


Figure 5.12. Lowest cost designs for the simple-column sequence (left) and the column with an intermediate decanter (right).

As shown in Table 5.8, the column with an intermediate decanter is significantly cheaper than the simple-column sequence. Using the column with an intermediate decanter, only one column, one condenser, one reboiler and one decanter are needed. Thus, less capital expenditure is required. Moreover, the energy requirement of the column with an intermediate decanter is close to that of the first column in the simple-column sequence (Figure 5.12). Therefore, the operating cost of the column with an intermediate decanter is much less than that of the simple-column sequence. In short, the column with an intermediate decanter can be used to separate the feed mixture for about the cost of the first column in the simple-column sequence.

In summary, this case study has shown the application of the proposed boundary value method in the design of the column with an intermediate decanter and the single-feed columns in the simple-column sequence. The design method is used for assessing the feasibility of the separations and generating column designs for ranges of reflux ratios. The feasible designs for each column are evaluated and the lowest cost designs are identified. As a result, the two proposed separation options can be evaluated and compared with each other. Compared with the two-simple column sequence, the column with an intermediate decanter is obviously more attractive in terms of cost, for separating the feed mixture.

5.4 Conclusions

This chapter describes the boundary value design method developed for columns with intermediate decanters. The design method can be used to assess the feasibility of a proposed separation, generate column designs and evaluate them. It also allows a distillation flowsheet to be evaluated with respect to its total annualised cost. Therefore, a proposed distillation flowsheet can be compared with other separation options.

The proposed design procedure includes setting up the specifications of the column, generating liquid composition profiles, assessing the feasibility of the column and evaluating the feasible designs in terms of their total annualised costs. The feasibility criteria for the column are that the middle section profile intersects with the rectifying profile and that the corresponding liquid composition at the draw stage must be located in the two-liquid phase region. For a given reflux ratio and feed condition, multiple column designs may be found as the side draw location is a degree of freedom. From the design procedure, column design details, such as the number of theoretical stages, feed and side draw locations, are obtained. The location of heterogeneous stages in the column is also known. Based on the costs, the best designs can be identified for further analysis or comparison with other separation options.

The results from the boundary value method, that is, the column details, can be used for initialising a rigorous simulation. Other results from the design method, such as the compositions and temperatures on stages, can be used as initial values for simulation algorithms to promote convergence. Although fractional numbers of theoretical stages may be obtained from the design procedure, operating conditions, such as reflux ratio, or the amount of trace components in a product, can be changed until the feasible design with an approximately integral number of stages is found.

The application of the boundary value method for a column with an intermediate decanter has been illustrated with the design of a column separating a mixture of acetone, water and 1-butanol. For a given set of product specifications, the most cost-effective designs were found for a range of reflux ratios. Compared with a column sequence separating the same mixture using only single-feed columns, the column with an intermediate decanter is considerably cost effective since only one column and one decanter are used and a significantly less heat requirement is required.

The proposed boundary value method for columns with intermediate decanters has been developed for ternary mixtures. There is no simple graphical representation for mixtures with more than four components. Moreover, a liquid composition profile is very sensitive to the amount of trace components in the associated product. As a result, it is difficult to find an intersection between liquid composition profiles in the composition space of a mixture containing more than three components. Despite the fact that the boundary value method is limited to ternary mixture in practice, the method provides valuable insight into a column with an intermediate decanter for heterogeneous azeotropic mixtures. This knowledge may motivate and facilitate the development of a design method for multicomponent mixtures.

Chapter 6

Synthesis of separation sequences for ternary heterogeneous azeotropic mixtures

6.1 Introduction

Highly nonideal mixtures commonly exhibit some thermodynamic nonidealities, such as azeotropes, distillation boundaries and regions, close boiling temperatures, distillation compartments, and liquid immiscibility. Using only simple columns (a simple column is a column with a single feed and two products), it may not be possible to separate the nonideal mixtures into their constituent components. Strategies for handling those thermodynamic nonidelities are needed for separating such nonideal mixtures (Siirola, 1996). Examples of strategies for separating nonideal mixture are exploiting liquid phase splitting in a decanter, employing complex column configurations, mixing, recycling, etc.

Separation sequence synthesis for heterogeneous azeotropic mixtures is challenging due to the large number of alternative flowsheet structures to choose from. Examples of alternative flowsheet structures are the number of feeds to a column; classes of splits: direct splits, indirect splits and saddle-type product splits; types of decanters: stand-alone decanters, integrated decanters, and intermediate decanters. Moreover, recycles are often encountered in the separation of nonideal mixtures, and may have many destinations to choose from in a sequence. Therefore, an approach for systematically generating separation sequences is necessary. The systematic approach should take into account various flowsheet structures so that the most promising structures are not overlooked.

The synthesis of separation sequences for heterogeneous azeotropic mixtures is traditionally based on the residue curve map analysis (e.g. Pham and Doherty, 1990; Wasylkiewicz et al., 2003). This synthesis approach does not lend itself to automation (Wahnschafft et al., 1993) as it relies on examining the residue curve map of the mixture. This approach is thus limited to ternary mixtures (Marquardt et al., 2008).

Tao et al. (2003) developed an approach for systematically generating separation sequences for separating heterogeneous azeotropic mixtures. Separation methods involved in this approach are simple single-feed columns and stand-alone decanters. The approach of Tao et al. (2003) was extended to account for single-feed columns with integrated decanters by Vanage (2005). Tao et al. (2003) also proposed mixing rules and recycle heuristics used for modifying separation sequences for generating high-purity and high-recovery sequences. The approach of Tao et al. (2003) does not take into account complex column configurations, such as double-feed columns, columns with intermediate decanters, which may make the separation of a mixture feasible and provide cost savings.

This chapter presents the extension of the algorithms of Tao et al. (2003) and Vanage (2005) to systematically identify double-feed columns with integrated decanters and columns with intermediate decanters in a separation sequence. Moreover, a heterogeneous liquid feed with its corresponding liquid compositions in different regions is not restricted to be separated only in a decanter. In the following section, the sequence synthesis approach of Tao et al. (2003) and its extension proposed by Vanage (2005) is summarised. A case study will be presented to demonstrate the application of the extended synthesis algorithm in generating separation sequences with complex column configurations.

6.2 Sequence synthesis approach of Tao et al. (2003) and Vanage (2005)

The first step in separation sequence synthesis is to define the problem. Firstly, the feed composition and flow rate, and desired product purities are specified. Then, the mixture is characterised in terms of residue curve map structure by determining azeotropes, distillation boundaries, distillation compartment boundaries, and heterogeneous boiling envelope at a specified pressure. The two-liquid phase region may be calculated at a subcooled temperature, but this option is not considered here. Once the specifications of the problem are addressed, separation sequences can be generated following the synthesis approach of Tao et al. (2003) and Vanage (2005).

The existing sequence synthesis approach (Tao et al., 2003; Vanage, 2005) consists of three algorithms and some heuristics for generating separation sequences with high purities and high recoveries. The sequence synthesis begins with the algorithm presented in Section 6.2.1. The first algorithm generates separation sequences based on the use of simple single-feed columns and decanters. The second algorithm in Section 6.2.2 proposed by Vanage (2005) is then employed to generate sequences utilising columns with integrated decanters. The resulting separation sequences that do not satisfy the desired product purities will be modified, if possible, based on the third algorithm, presented in Section 6.2.3. Finally, some heuristics, presented in Section 6.2.4, are used for identifying potential recycle destinations of a non-product stream in a separation sequence.

6.2.1 Algorithm of Tao et al. (2003) to generate sequences using simple single-feed columns and decanters

For a given feed composition and flow rate, and desired product purities, the synthesis of separation sequences starts with the following procedure proposed by Tao et al. (2003).

Algorithm 1: **Sequences using simple single-feed columns and decanters (Tao et al., 2003)**

1. Begin with a stream in a sequence. For the first sequence, start with the given feed stream.
2. Check if the current stream satisfies the desired product purities. If so, go to step 6. Otherwise, proceed to step 3.

3. Check if the stream being considered is a heterogeneous liquid with its corresponding liquid compositions in different distillation regions to each other. If not, continue to step 4. Otherwise, use a decanter to separate the stream, generate two new streams, and go to step 6.
4. Check if the stream being considered is a homogeneous liquid or a heterogeneous liquid with its corresponding liquid and heavy liquid compositions in the same distillation region. Test whether feasible direct and/or indirect split(s) exist for separating the current stream. An available feasibility test method is the common saddle test method of Rooks et al. (1998). If no feasible product exists, go to step 5. On the other hand, if a set of feasible products is identified, use a simple single-feed distillation column to separate the current stream. Two product streams are thus generated from the column.

   At this step, a new sequence may be generated if the current stream can be separated by both direct and indirect splits. In other words, a column exploiting a feasible split is added to the current sequence, whereas a column performing another feasible split is added to a new sequence. Next, go to step 6.
5. If the current stream cannot be separated using either a distillation column or a decanter, classify the stream as a non-product stream. The non-product stream is usually a homogeneous stream with a composition of an azeotrope or a composition at a distillation boundary. Continue to step 6.
6. If there is a stream that is not yet considered in the current sequence, repeat from step 2. Stop if all streams are considered. Otherwise, repeat the procedure for other sequences.

The above synthesis procedure can be summarised in Figure 6.1. This procedure allows separation sequences to be generated sequentially. In the synthesis procedure, only two types of separation units, i.e. simple single-feed columns and decanters, are involved. For a stream to be separated in a column, only direct and indirect splits are taken into accounted.

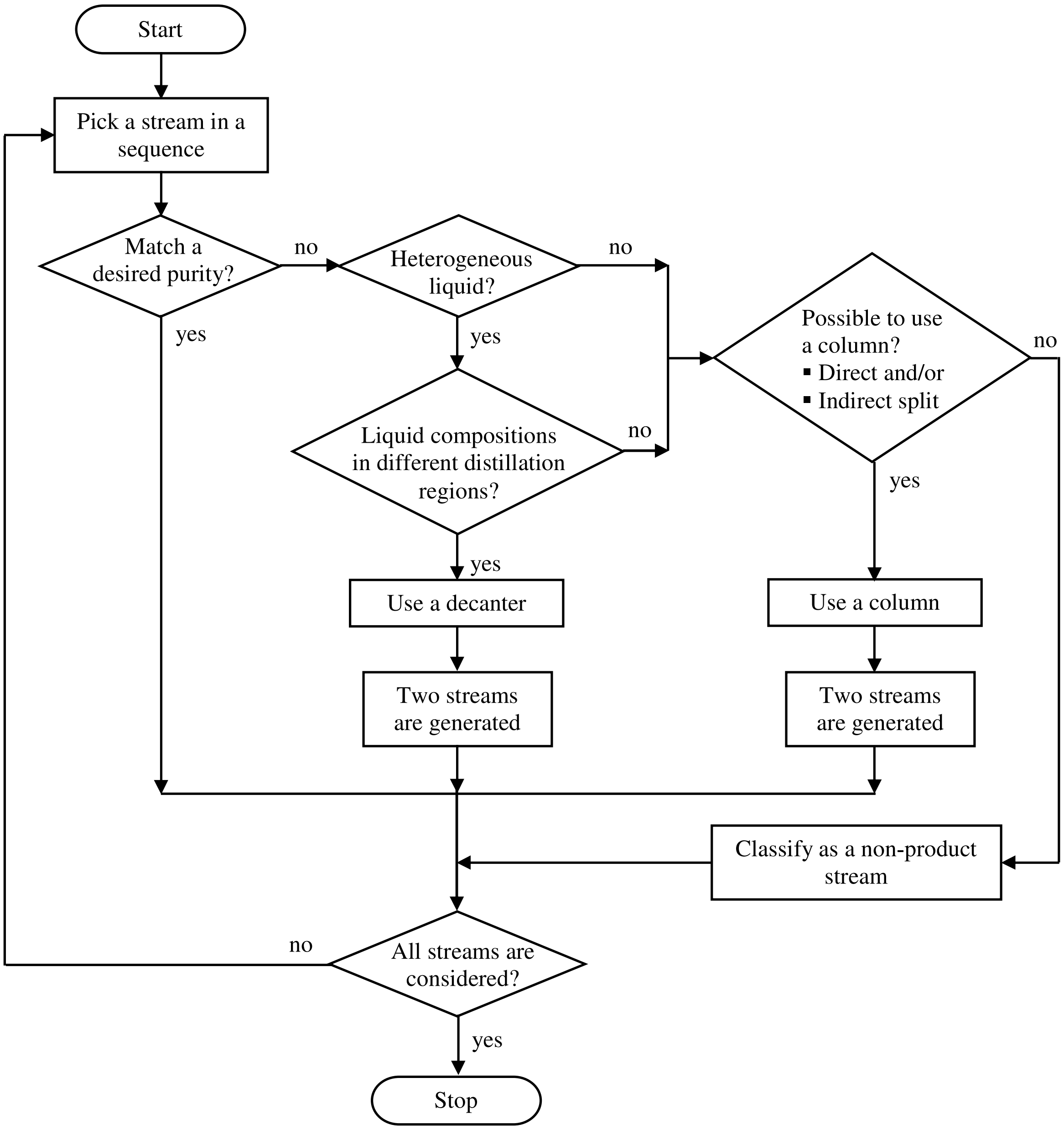


Figure 6.1. Synthesis procedure of Tao et al. (2003) for generating sequences using simple single-feed columns and decanters (Algorithm 1), (adapted from Tao et al. (2003).

Following the above procedure, one or more separation sequences will be generated. Some of those sequences may need to be modified if they cannot separate the mixture into pure components, or they are feasible sequences but have a non-product stream that cannot be separated in either a simple column or a decanter. The sequences that do not satisfy the desired purities may be modified by mixing the non-product streams together following the procedure in Section 6.2.3. For a feasible sequence with a non-product stream, it may be modified by recycling the non-product stream based on the heuristics in Section 6.2.4 so that high recoveries are achieved.

6.2.2 Algorithm of Vanage (2005) to generate sequences using columns with integrated decanters

In Algorithm 1, only stand-alone simple columns and decanters are involved. Columns with integrated decanters, which are an industrially relevant option, are not considered. The column with an integrated decanter is an essential configuration in sequence synthesis as it allows the distillation boundary to be crossed. Consequently, high purity products in different distillation regions may be achieved.

Vanage (2005) extended the synthesis algorithm of Tao et al. (2003) to include columns with integrated decanters as an option. The algorithm of Vanage (2005) is applied after all possible sequences are generated from Algorithm 1 in Section 6.2.1. Having the integrated column-decanter configuration as an option, additional separation sequences may be introduced. The algorithm of Vanage (2005) to identify a column with an integrated decanter consists of three steps below.

Algorithm 2: **Sequences using columns with integrated decanters (Vanage, 2005)**

1. For each generated sequence resulting from Algorithm 1, search for a column where its top product is fed to a decanter. Such a column usually has a minimum-boiling heterogeneous azeotrope in the top product which is subsequently separated into two liquid phases in the decanter. If such a column is found, continue to the next step.
2. Assume that the column followed by a stand-alone decanter identified in the previous step is replaced with a column with an integrated decanter. The liquid-liquid tie line of the integrated decanter is assumed to be that

of the stand-alone decanter. This tie line represents the range of possible top product compositions achievable from the column with the integrated decanter. Next, examine the residue curve map of the mixture to determine a range of bottom product compositions that can be obtained by drawing mass balance lines through the feed composition and various top product compositions throughout the tie line. As the column with an integrated decanter is used, the distillation boundary can be crossed. Therefore, the bottom product compositions can be in a different distillation region from the top product but they must be in a distillation region that contains a part of the decanter tie line.

3. Generate a new sequence using a column with an integrated decanter. Select a highly pure bottom product from the range of achievable bottom product compositions found in the previous step. Next, determine the top product composition which is at the intersection point between the mass balance line and the decanter tie line. Two new streams are produced from the column. Go to Algorithm 1 to complete the new sequence.

6.2.3 Modifying separation sequences to recover pure components by mixing

From Algorithms 1 and 2, some separation sequences that do not recover all pure components may be generated. Those infeasible sequences may be modified by mixing two or more non-product streams in the sequence together to create an opportunity for the resulting stream to be separated by distillation or decantation. A procedure for modifying a sequence to recover all components based on mixing streams is proposed by Tao et al. (2003). The general principle of this procedure is to create a new stream to be located in a two-phase region or in a different distillation region from the mixing streams. As a result, the new stream can be separated further in a decanter or a column. The procedure is summarised below.

Algorithm 3: **Sequences from mixing (Tao et al., 2003)**

1. Begin with a sequence having a stream that does not satisfy the product purity requirement. Count the number of non-product streams in the current sequence. If only one non-product stream is found, go to step 4. Otherwise, continue to the next step.
2. Test if the mixing of two or more non-product streams lead to a new stream with a composition in a two-phase region or a different distillation region from the streams being mixed. If such a new stream is found by mixing, continue to step 3. Otherwise, go to step 4.
3. Add a mixer to the sequence to create a new stream from the mixing of the two or more non-product streams found in step 2. Apply Algorithms 1 and 2 to identify separation tasks for the new stream and continue the algorithms until all streams in the sequence being considered are treated.
4. For a sequence with one or more non-product streams that does not meet the condition in step 2, test if the mixing of any non-product stream and a portion of one or more product streams results in a new stream in a two-phase region. The portion of the product stream mixed with a non-product stream is initially guessed. If the current stream can be mixed with a portion of a product stream to create a mixed stream in a two-phase region, use a decanter to separate the mixed stream. Apply Algorithms 1 and 2 to treat two new streams from the decanter. Otherwise, search for potential recycle destinations based on the recycle heuristics in Section 6.2.1.4.
5. Repeat from step 2 if there remains a sequence that does not meet the product purity requirement. Otherwise, terminate this algorithm. In case that no sequence recovering all components is identified, try using a new column pressure or relaxing the purity requirement. Alternately, try other different separation technology.

After applying Algorithms 1 to 3, feasible sequences that separate the feed mixture into all pure components may be identified. However, they may still have some non-product streams that cannot be separated in a column or a decanter. These non-product streams will be considered for recycling so that high recovery sequences are achieved. For a separation of a mixture, if no feasible sequence that recovers all pure components is identified from the above algorithms, the mixture should be separated by another separation technology (Tao et al., 2003).

6.2.4 Modifying separation sequences using recycles for high recoveries

A feasible sequence resulting from the algorithms in the preceding sections may have a stream that does not meet the desired purities. This non-product stream, which cannot be separated in a simple column or a decanter, is usually a homogeneous mixture with a composition close to an azeotrope or a distillation boundary. The non-product stream can be treated by recycling it to a separation unit in the sequence.

In general, recycling is a powerful alternative to performing additional processing (Barnicki and Siirola, 1997). In particular, a recycle stream containing a component functioning as an entrainer may aid the separation in the recycle loop (Wahnschafft et al., 1993). Recycling a non-product stream to a point upstream may also decrease the number of separation units needed (Wahnschafft et al., 1993). In addition, recycling a stream may allow high recoveries of components in the sequence (Tao et al., 2003).

Selecting the destinations for a recycle stream is a design challenge because recycling affects both feasibility and performance of the separation units (such as heat duties and number of stages of a column) in the recycle loop (Liu et al., 2005). In a separation sequence, there may be many recycle destinations but not all have potential to make the sequence feasible. Introducing a recycle may cause a separation in a separation unit within the recycle loop to become infeasible since the recycle affects the flow rates and compositions of streams in the recycle loop. For instance, the recycle may cause the composition of a stream to a column to move into a different distillation region in which the proposed separation is infeasible (Siirola, 1996; Tao et al., 2003). The recycle may also cause the composition of a stream to a decanter to become a homogeneous liquid (Tao et al., 2003). As a result, liquid phase splitting will no longer occur in the decanter.

Moreover, the recycle may cause infinite build-up of a component if there is no exit point for the component from the recycle loop (Barnicki and Siirola, 1997).

A strategy for systematically selecting potential destinations for a recycling stream is needed to screen out infeasible recycle destinations based on heuristics (Tao et al., 2003). The following heuristics are proposed by Siirola (1996), Thong and Jobson (2001c), Tao et al. (2003) and Vanage (2005) for screening out some infeasible and uneconomic recycle destinations. Thus, the number of recycle destinations remained for closed-loop material balances will decrease.

Heuristic 1: Recycle origin (Thong and Jobson, 2001c)

Do not recycle a stream to the unit that originally produces it if that unit is a single-feed, two-product separation unit. Otherwise, the mass balance over that unit will be violated

Heuristic 2: Recycle reachability (Tao et al., 2003)

For feasibility, there must be an exit point for each component not only for the entire process system, but also within each recycle loop.

Heuristic 3: Recycle composition (Tao et al., 2003)

Recycle only to intermediate streams that contain all components in the recycling stream.

For example, a stream consisting of components *A*, *B*, and *C* should not be recycled to an intermediate stream consisting of components *A*, *B* and *D*.

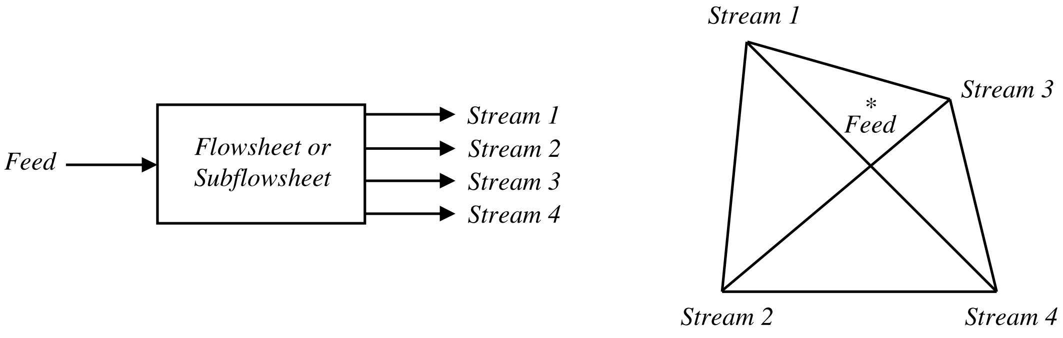
Heuristic 4: Recycle flow rate (Tao et al., 2003)

Do not recycle a stream having a very small flow rate compared to the feed flow rate. Instead, it should be treated an exit stream for waste treatment, fuel byproducts, etc.

Heuristic 5: Lever rule feasibility test (Tao et al., 2003)

The feed composition of a flowsheet or subflowsheet must be located inside a polygon formed by the output stream compositions of that associated flowsheet or subsflowsheet.

For example, if a flowsheet or subflowsheet has four output streams as in Figure 6.2, recycling one of these output streams to any internal destination will be feasible only if the feed composition of that flowsheet/subflowsheet lies inside the triangle formed by the compositions of other three output streams. Hence, only the recycling of streams 2 or 4 satisfies this rule whereas recycling of streams 1 or 3 is infeasible.



Recycle of Stream 1 only is infeasible;
Recycle of Stream 2 only is feasible;
Recycle of Stream 3 only is infeasible;
Recycle of Stream 4 only is feasible.

Figure 6.2. The lever rule feasibility test for a ternary composition space (Tao et al., 2003)

Heuristic 6: Duplication of separation units (Siirola, 1996)

If a stream requires to be separated in a unit or a set of units performing a separation that has already been created in the sequence, recycle the stream to that unit or set of units. This heuristic avoids the duplication of separation units, thus reducing the number of separation units.

Heuristic 7: Recycle effect on product flow rates (Vanage, 2005)

Recycle a stream to a column only if the recycle stream changes the flow rates of both products of the column.

6.2.5 Summary: Sequence synthesis approach of Tao et al. (2003) and Vanage (2005)

The complete sequence synthesis procedure consisting of the algorithms proposed by Tao et al. (2003) and Vanage (2005) is presented in Figure 6.3. For a given feed, Algorithm 1 (Section 6.2.1) is first applied to generate feasible separation sequences. The separation units considered in the algorithm are simple columns (a column with a single feed and two products), and stand-alone decanters. Two classes of splits are considered: direct and indirect splits.

Based on Algorithm 2, separation sequences utilising columns with integrated decanters can be generated. Once Algorithm 1 is completed, each resulting sequence will be searched for a column followed by a stand-alone decanter at the top. A new sequence using a column with an integrated decanter will be proposed if a column followed by a decanter at the top is identified.

After Algorithms 1 and 2 are completed, feasible sequences that satisfy the desired purities may be identified. However, some of the infeasible sequences may also be generated. These infeasible sequences may be modified by mixing the non-product streams together or recycling a portion of a pure component in order to create a new stream in a two-phase region or a different distillation region (Algorithm 3). Therefore, the new stream can be separated in a decanter or a column. If no feasible sequences are found using the synthesis procedure, separation sequences will need to be generated based on a new operating pressure, by relaxing purity requirement, or by using another separation technology. For a feasible sequence from Algorithms 1 to 3, some of the streams may not meet the product purity requirements as they cannot be separated by either distillation or decantation. The non-product streams may be treated by recycling to a separation unit upstream in the sequence. Some infeasible and uneconomic recycle destinations for a recycling stream can be screened out based on the recycle heuristics presented in Section 6.2.4.

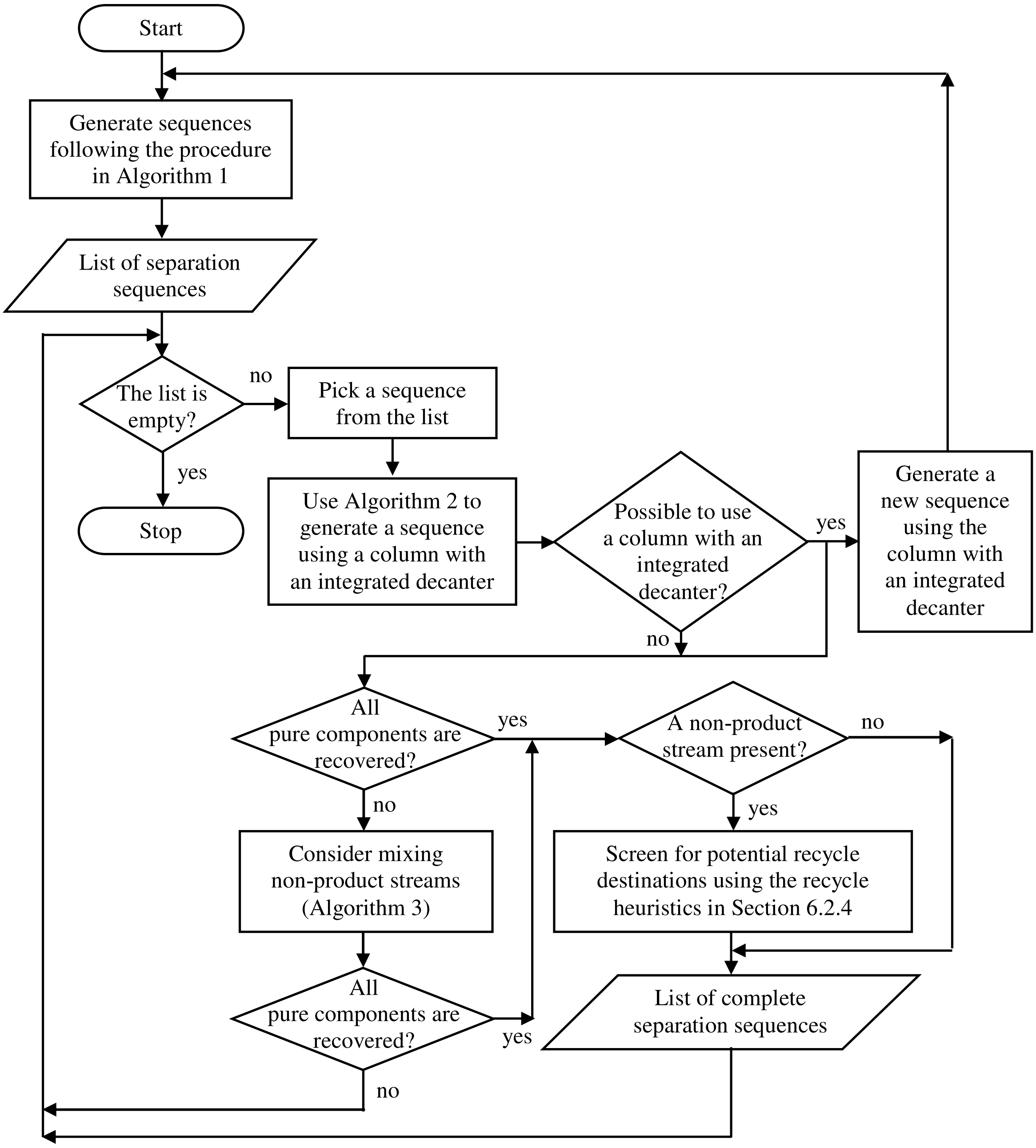


Figure 6.3. The synthesis procedure of Tao et al. (2003) and Vanage (2005) for generating high-purity and high-recovery separation sequences (adapted from Tao et al. (2003) and Vanage (2005))

In summary, the algorithms and recycle heuristics of Tao et al. (2003) and Vanage (2005) take into account simple columns performing either direct or indirect splits, stand-alone decanters, and columns with integrated decanters. Heterogeneous liquid streams will be separated in a decanter if their corresponding liquid compositions are in different distillation regions from one another. Non-product streams are treated by mixing and recycling, if possible. Infeasible and uneconomic recycle destinations are screened out so that less feasible sequences are left for closed-loop mass balances.

In separating a heterogeneous azeotropic mixture, the separation process involving a complex column configuration, e.g. a double-feed column or a column with an intermediate decanter, may be more attractive than using only simple single-feed columns. Those complex column configurations are not considered in the synthesis approaches of Tao et al. (2003) and Vanage (2005). How the synthesis approach can be extended to include such complex column configurations will be described in the next section.

6.3 Extension of the sequence synthesis approach of Tao et al. (2003) and Vanage (2005)

This section presents the extension of the synthesis approach of Tao et al. (2003) and Vanage (2005) to include three new features. The synthesis algorithm of Tao et al. (2003) in Section 6.2.1 (Algorithm 1) is revised to allow a heterogeneous feed with its coexisting liquid compositions in different distillation regions to be separated in a column. Algorithm 1 is also revised to include double-feed columns with integrated decanters as an option. Finally, a new algorithm for synthesising separation sequences employing columns with intermediate decanters is proposed.

6.3.1 Revised synthesis algorithm for distillation of heterogeneous streams

According to Algorithm 1, a heterogeneous liquid stream with its corresponding liquid compositions in different distillation regions from one another is always split in a decanter even if it may be separated in a column. That a column is not considered as an option for such a heterogeneous stream may cause some attractive separation options to be overlooked. A noteworthy example for separating such a stream in a column will be shown in a case study in Section 6.5. The example will show that separating such a stream in a column will lead to a sequence using a column with an intermediate decanter.

To include a simple column as an option for separating a heterogeneous liquid stream the tie line of which crosses a distillation boundary in the algorithm of Tao et al. (2003), Step 3 in Algorithm 1 is revised as follows (indicated by italic script).

3. Check if the stream being considered is a heterogeneous liquid with its corresponding liquid compositions in different distillation regions from one another. If not, continue to step 4. Otherwise, *(a) use a decanter to separate the stream, generate two new streams, and go to step 6, and (b) go to step 4 to test if the current heterogeneous stream can be separated in a column.*

6.3.2 Revised synthesis algorithm to include double-feed columns with integrated decanters

In separating nonideal mixtures, some thermodynamic nonidealities, such as distillation boundaries, distillation compartments, and liquid immiscibility, might be encountered. The separation of the mixtures exhibiting those features may not be accomplished in a sequence of simple single-feed columns. Alternatively, sequences including complex column configurations may be more favourable for separating those nonideal mixtures. For instance, a pure component which is a saddle in a distillation region cannot be recovered from a simple column at high purity (Siirola, 1996). The recovery of the saddle-type product can be obtained by using a double-feed column which is widely applied in extractive distillation flowsheets, as will be discussed below.

A synthesis methodology involving double-feed columns for heterogeneous azeotropic mixtures is based on residue curve map analysis. A strategic approach to generate a sequence consisting of a double-feed column was proposed by Moussa and Jiménez (2006). To generate a double-feed column, the residue curve map of a given mixture is examined. If the residue curve map of the mixture is similar to the typical residue curve map topology shown in Figure 6.4, a separation sequence with a double-feed column, as in Figure 6.5, will be generated. In Figure 6.4, distillation region 2 of the residue curve map has two distillation compartments because of the nonadjacent saddle points of heterogeneous azeotrope and pure component *A*.

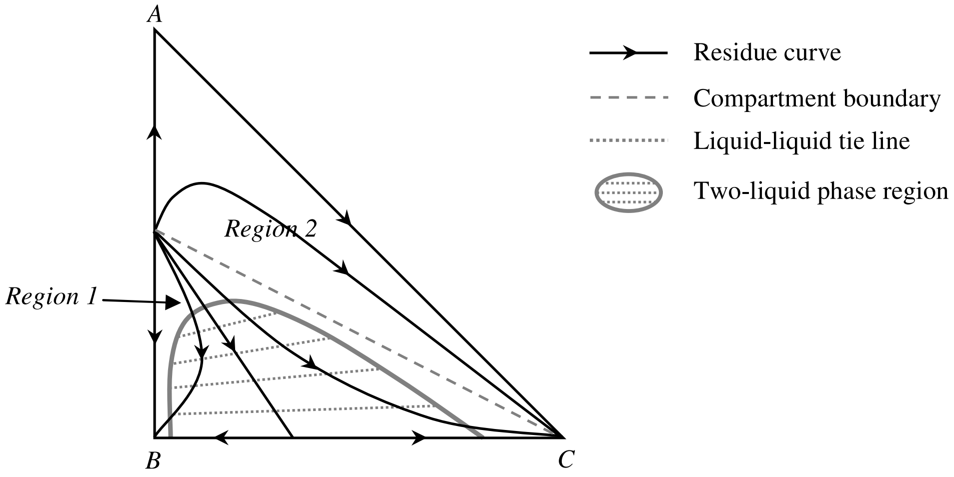


Figure 6.4. A typical residue curve map of mixtures that can be separated in double-feed columns

The class of split exploited in the sequence in Figure 6.5 is called saddle-type split (or called saddle-saddle split by Moussa and Jiménez (2006)) since two saddle-type products is obtained. As shown in Figure 6.4, the residue curve map features two saddles within a distillation region. One of the saddle points is the heterogeneous azeotrope of *B* and *C* while the other is the pure component *A*. Separating a mixture in the sequence in Figure 6.5, the saddle points are obtained in separate columns. The saddle heterogeneous azeotrope, or a product with nearly this composition, is obtained as the top vapour of the double-feed column. Having such a vapour at the top of the column, liquid phase splitting will occur in the top decanter allowing a relatively pure component *B* to be recovered. For the other saddle, the pure component *A* is separated from component *C* in the simple single-feed column following the double-feed column.

By analogy with extractive distillation, component *C* in Figure 6.4 acts as an entrainer. In the sequence in Figure 6.5, the entrainer stream B_2 and the entrainer rich phase *L* from the decanter at the top of the double-feed column can analogously be recycled to the double-feed column as an upper feed.

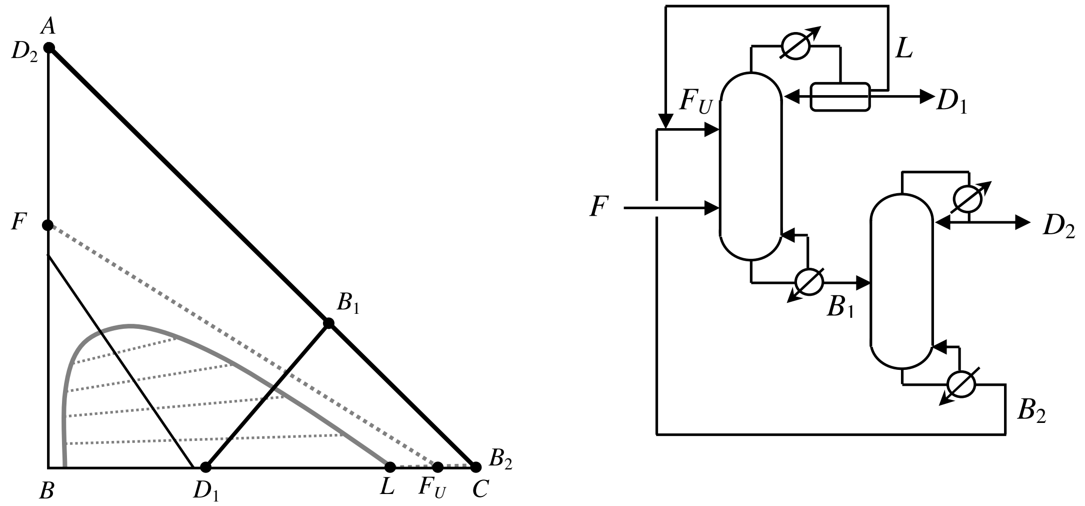


Figure 6.5. A separation sequence with a double-feed column and its mass balance lines (adapted from Moussa and Jiménez, 2006).

The synthesis approaches of Tao et al. (2003) and Vanage (2005) do not include opportunities to use double-feed columns. In this work, Algorithm 1 in Section 6.2.1 is extended to include double-feed columns. The new approach exploits the nature of the procedure in which opportunistic decisions are made on how each intermediate stream is separated.

In Algorithm 1 in Section 6.2.1, a decision is made for each non-product stream whether it will be separated by distillation during step 4. Originally in step 4, only simple single-feed columns performing either direct and/or indirect splits are considered. Opportunities to use double-feed columns generating saddle-type splits will be incorporated into the algorithm at this point. Step 4 in Algorithm 1 is revised as follows (indicated by italic script):

4. Check if the stream being considered is a homogeneous liquid, or, if a heterogeneous liquid whether its liquid tie line crosses a distillation boundary,

   (a) test whether feasible direct and/or indirect split(s) exist for separating the current stream using a feasibility test, e.g. the feasibility test method of Rooks et al. (1998), and

   (b) test whether the current stream can be separated in a double-feed column with an integrated decanter generating a saddle-type split using the feasibility test in Section 6.3.2.1.

   If no feasible product exists, go to step 5 (in Section 6.2.1). On the other hand, if a set of feasible products is found, use a (single- or double-feed) distillation column performing the feasible split identified to separate the current stream. Two feasible product streams are generated from the column.

   If the current stream can be separated by more than one type of split (direct, indirect, and *saddle-type*) add a column performing one such feasible split to the current flowsheet, and generate additional sequences for columns performing all other types of feasible splits. Next, go to step 6 (in Section 6.2.1).

The new, revised synthesis algorithm, extended from that of Tao et al. (2003) (Section 6.2.1) is presented in Figure 6.6.

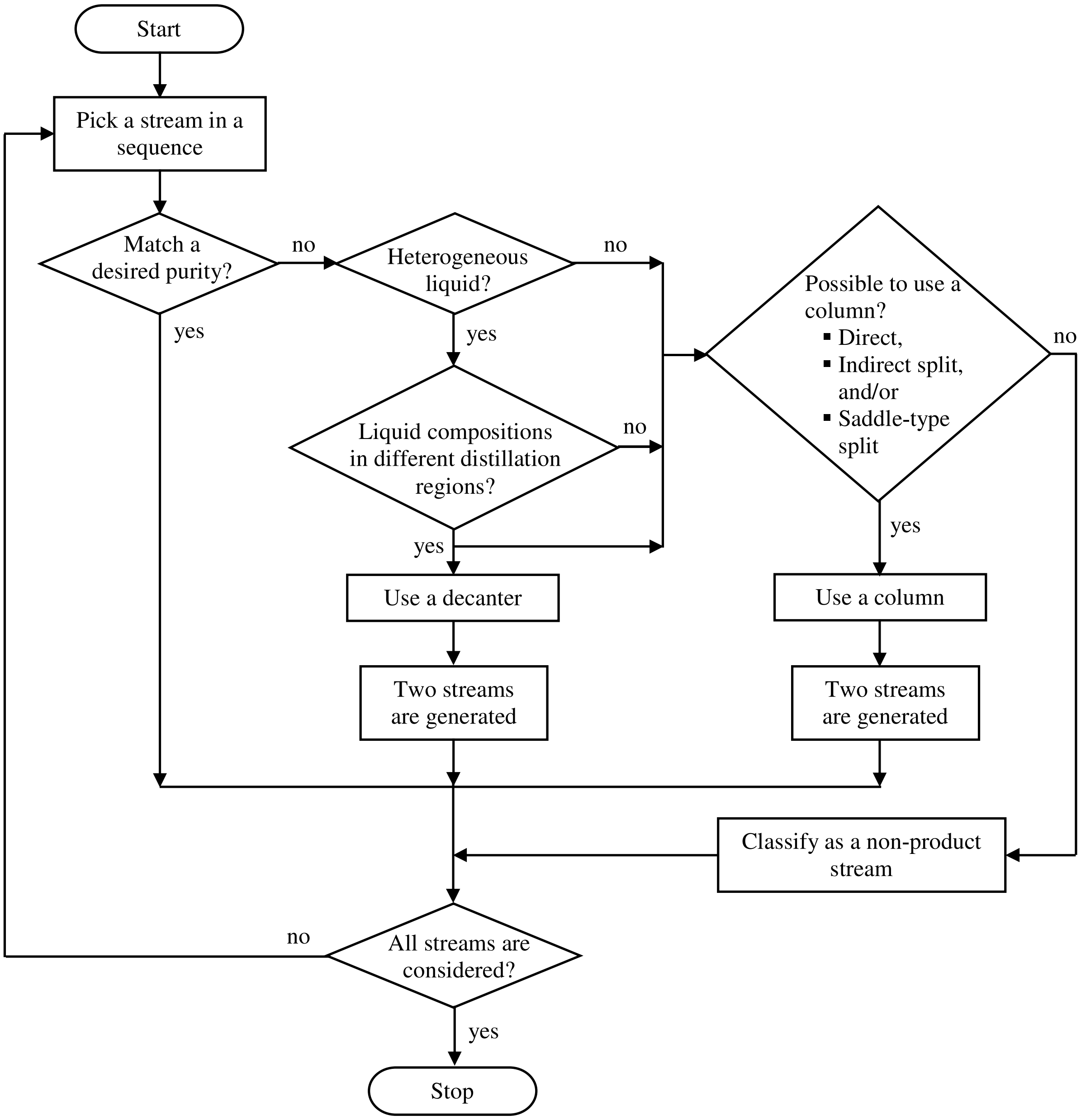


Figure 6.6. Revised Algorithm 1 to include a double-feed column (saddle-type split) and a separation of a heterogeneous stream with its liquid compositions in different distillation regions by distillation.

6.3.2.1 Feasibility test for a double-feed column with an integrated decanter

In step 4(b) of the Revised Algorithm 1, the separation feasibility in a double-feed column can be assessed using the boundary value method presented in Chapter 4. To apply the boundary value method for assessing the feasibility of a separation, the fully specified product compositions must be given. However, the upper feed is not known during step 4(b). Thus, it will initially be assumed. In extractive distillation, an entrainer, which is usually the heaviest component in the mixture, is commonly added to the double-feed column as an upper feed. Likewise, during step 4(b) in the synthesis algorithm, the upper feed is taken to be an entrainer, or the heaviest component in the mixture. Once the upper feed is assumed, the sequence synthesis of the current sequence can continue until all pure components are recovered. Afterwards, one or more streams from downstream will be recycled to replace the assumed upper feed stream. Then, the boundary value method is applied to assess the separation feasibility of the double-feed column.

A procedure for testing if the mixture can be separated in a double-feed column with an integrated decanter is presented below. The test consists of two main steps. The first step involves assuming an upper feed stream and sequencing the current sequence accordingly until all components are recovered. The second step is to allocate a recycle as the upper feed of the proposed double-feed column. Then, the boundary value method is applied to assess the feasibility of the separation in the proposed double-feed column.

Preliminary step:

1. Propose a double-feed column and assume a new stream of a pure component to be an upper feed. The pure component could be the entrainer, or the heaviest component of the mixture being considered.
2. Choose an upper-to-lower feed rate ratio. Specify the top product of the column such that it is on the liquid-liquid tie line passing through the saddle heterogeneous azeotrope. Determine the bottom product composition and flow rate from the mass balance over the column.

3. Continue synthesising the current sequence using Revised Algorithm 1 until all components are recovered.

Closing step:

1. Recycle the following streams to the double-feed column as the upper feed to replace the assumed stream: all organic phase from the integrated decanter of the double-feed column, and a part of a product stream consisting of the pure component in the assumed stream, i.e. the entrainer or the heaviest component. The amount of the product stream being recycled depends on the chosen upper-to-lower feed rate ratio in the next step.
2. Choose the upper-to-lower feed rate ratio (or use the value chosen at step 2 in the preliminary step)
3. Specify the top products of the two columns. Perform the mass balance calculation to determine the compositions and flow rates of all streams in the sequence.
4. Apply the boundary value method in Chapter 4 to search for feasible designs of the proposed double-feed column over ranges of reflux ratios and reflux phase split ratios. If a feasible design is found, stop and return to step 4 in Revised Algorithm 1. Otherwise, proceed to the next step.
5. Change the composition of top product of the double-feed column and repeat steps 3 and 4. Note that the top product composition of the double-feed column can lie somewhere along the decanter tie line. If no feasible design is found, even if the top product composition is varied throughout the tie line, go to the next step.
6. Vary the upper-to-lower feed rate ratio and repeat steps 3 to 5 until a feasible design is found. Note that there may be no feasible design of the double-feed column even for a range of feed rate ratios. Return to step 4 in Revised Algorithm 1.

Illustrative example

To demonstrate the feasibility test, the separation of a 1-propanol/water/1-butanol mixture in the illustrative example in Chapter 4 (Section 4.2) is revisited. The residue curve map of the mixture is presented in Figure 4.1. The residue curve map of the mixture is similar to that in Figure 6.4. In distillation region 2, the residue curve map features two compartments associated with the saddle heterogeneous azeotrope and the saddle point at the 1-propanol vertex, respectively. The feed mixture is a binary mixture of 1-butanol and water in distillation region 2 (see Table 4.1). Applying Algorithm 1 in Section 6.2.1, the mixture cannot be separated into all pure components using only simple columns because of the minimum-boiling azeotrope of water and 1-propanol. The feed is then tested if it can be separated in a double-feed column following the testing procedure above.

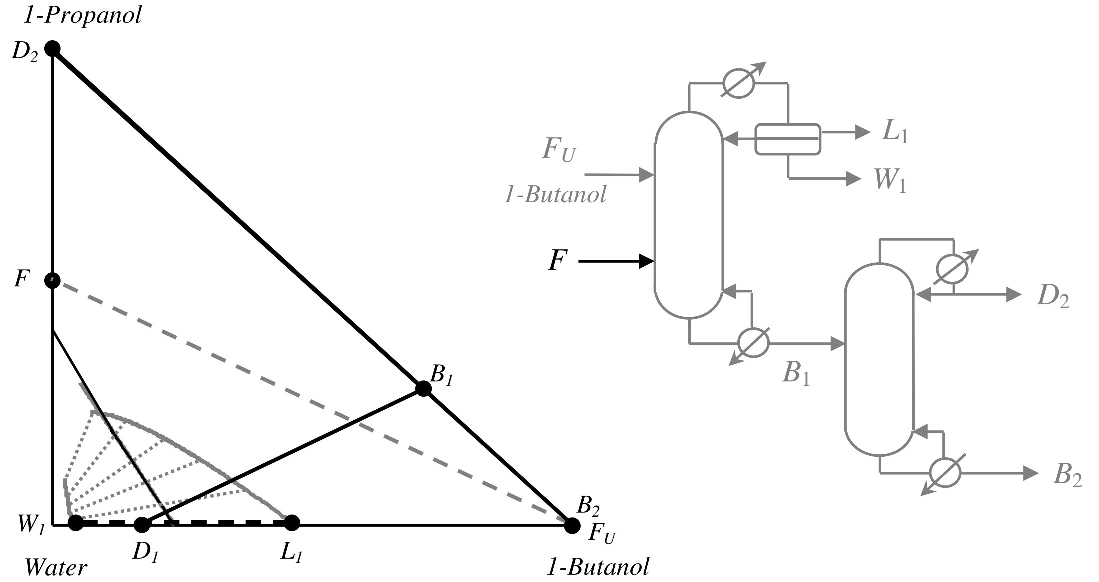


Figure 6.7. A sequence using a double-feed column proposed in the preliminary step.

For the illustrative example, the given binary feed F (see Figure 6.7) is tested if it can be separated in a double-feed column as follows. A stream of 1-butanol is taken to be an upper feed (F_U) of the double-feed column. The feed rate ratio is guessed and the top product is specified to be on a tie line associated with the saddle heterogeneous azeotrope of 1-butanol and water. The top product can be located in either of the two distillation regions. Once the top product is given, the bottom product composition and flow rate can be determined from the mass balance over the column. The bottom product of the double-feed column, which is a binary mixture of the 1-propanol and 1-butanol, is separated further in a simple single-feed column. Now that all components in the mixture are recovered, the sequence in Figure 6.7 will be completed with the closing step of the test.

To complete the sequence shown in Figure 6.7 and to test the feasibility of the proposed separation in the double-feed column, the closing step of the test is carried out. The organic phase from the top decanter (L_1) and a portion of 1-butanol from the bottom product of the second column (B_2) are recycled to the preceding double-feed column as the upper feed replacing the assumed stream. Given an upper-to-lower feed rate ratio and product compositions, the overall mass balance is calculated. The complete sequence using the double-feed column is shown in Figure 6.8. The boundary value method proposed in Chapter 4 can then be applied to assess the feasibility of the separation in the double-feed column over ranges of reflux ratios and phase split ratios. The top product composition of the double-feed column and/or the feed rate ratio is varied if no feasible designs are found for the assumed feed rate ratio and the specified top product. If a feasible design of the double-feed column is found, the double-feed column can thus be added to the current sequence.

The procedure for testing whether a stream can be separated in a double-feed column may be time-consuming due to the fact that the boundary value method used for the feasibility assessment requires full product specifications. Also, feasible designs are searched for ranges of reflux ratios and reflux phase split ratios. In addition, the top product and feed rate ratio of the double-feed column may need to be varied in order to search for a feasible design. The testing will be faster if a feasibility test method without full product specifications and varying the feed rate ratio is available.

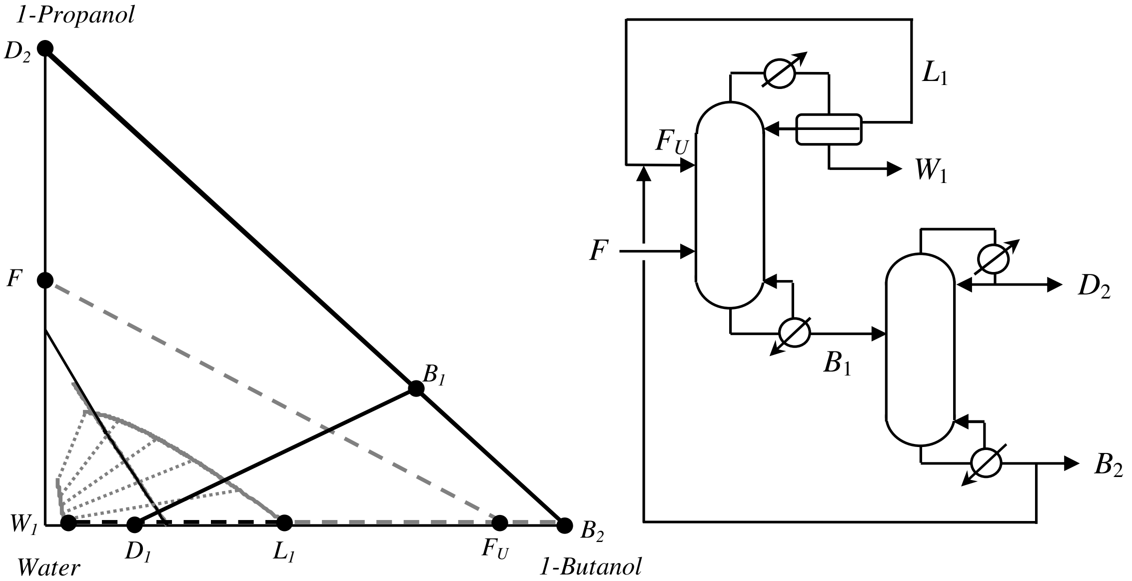


Figure 6.8. A complete sequence utilising a double-feed column with an integrated decanter for separating the mixture of 1-propanol/water/1-butanol.

6.3.3 Synthesis of separation sequences utilising columns with intermediate decanters

A column with an intermediate decanter is a column in which a heterogeneous liquid on a stage is removed to a decanter where a liquid phase is recovered as a product while the other liquid phase is returned to the column at one stage below the side draw location. This type of column is commonly used to recover a component, typically water, as a sidestream product (Ciric et al., 2000). A column with an intermediate decanter (and a condenser and a reboiler) can substitute a sequence of simple columns, each with a condenser and a reboiler – the complex configuration can offer significant benefits in terms of energy requirement and capital cost (Stichlmair and Fair, 1998). For example, the separation of an acetone/water/1-butanol mixture can be carried out in either a two-simple column or a column with an intermediate decanter as discussed in the case study in Chapter 5 (Figure 5.12). Comparing those two options, the column with an intermediate decanter has significantly lower operating and capital costs than the simple-column sequence.

An approach to employ a column with an intermediate decanter in a sequence is by examining the residue curve map of the mixture. A separation sequence using a column with an intermediate decanter may be proposed if the mixture has a residue curve map similar to the typical residue curve maps in Figure 5.1(b). In this section, the synthesis approach of Tao et al. (2003) is extended for systematically generating sequences using columns with intermediate decanters.

Consider the separation of an acetone/water/1-butanol mixture in the case study in Chapter 5. Following the synthesis algorithms of Tao et al. (2003) and Vanage (2005), a sequence of two simple single-feed columns and two decanters presented in Figure 6.9 is identified. At the bottom of the first column *C*-1, the bottom product B_1 is separated in the decanter *D*-1 from which a water-rich phase is removed as a product W_1. The organic liquid phase L_1 is then separated in a column with an integrated decanter (*C*-2 and *D*-2).

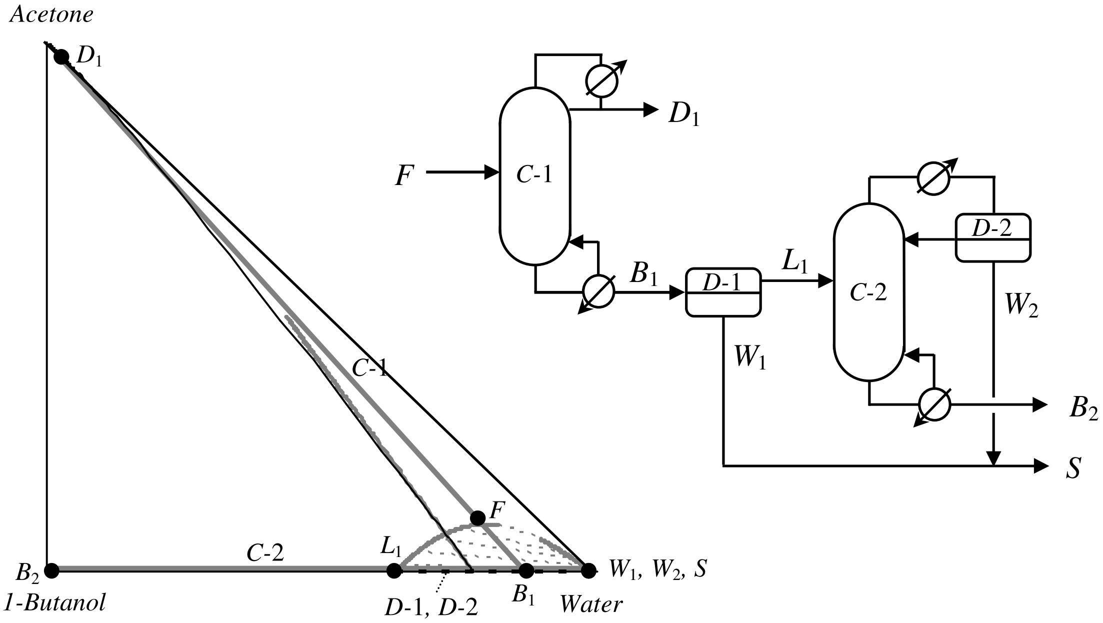


Figure 6.9. Simple column sequence for separating a mixture of acetone, water and 1-butanol

The sequence in Figure 6.9 can be simplified as the two columns in Figure 6.9 can be designed such that the tie lines of the two decanters are close to each other. In other words, the compositions of the light and heavy phases from both decanters can be approximately the same. Both decanters thus perform a similar function. According to a recycle heuristic proposed by Siirola (1996), (Heuristic 6 in Section 6.2.4), one of the decanters can be eliminated to avoid the duplication of separation units. As a result, the separation sequence becomes the one shown in Figure 6.10(a). In Figure 6.10(a), the bottom product of the first column *C*-1 is directly added to the integrated decanter of the second column *C*-2.

The separation sequence in Figure 6.10(a) can be simplified further. That the tie lines of the two decanters in Figure 6.9 are close to each other also implies that the vapour from the reboiler of the first column *C*-1 has approximately the same composition (composition of the heterogeneous azeotrope) as the top vapour of the second column *C*-2. In other words, the tie line corresponding to the bottom product B_1 is very close to that associated with the top vapour of the second column *C*-2. Therefore, the two columns in Figure 6.10(a) can be combined (Umeda et al., 1979; Stichlmair and Fair, 1998). Consequently, the sequence in Figure 6.10(a) can be replaced by the column with an intermediate decanter shown in Figure 6.10(b).

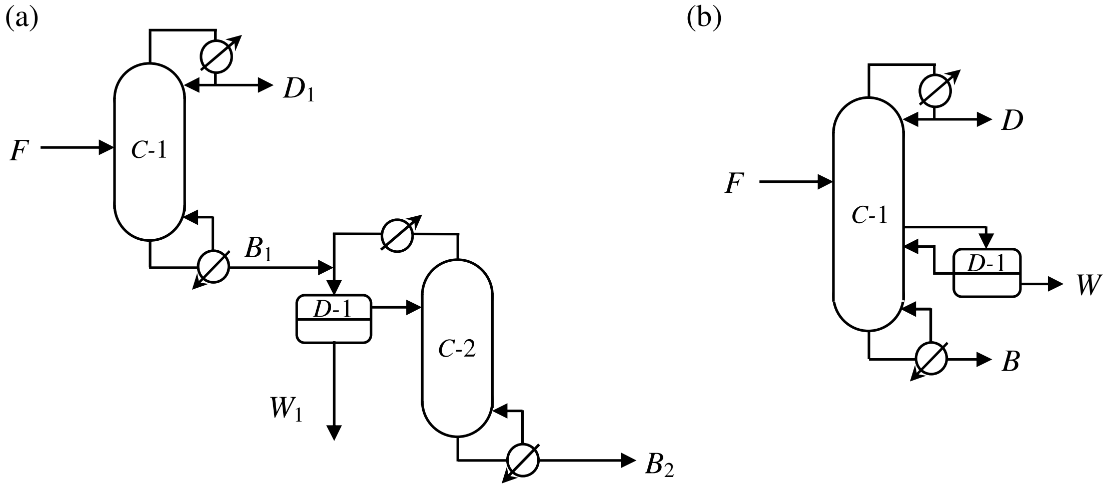


Figure 6.10. (a) Sequence with two-simple columns and a decanter, (b) column with an intermediate decanter

To identify a column with an intermediate decanter in a separation sequence, the following procedure is carried out after the synthesis algorithms of Tao et al. (2003) and Vanage (2005) in Sections 6.2.1 and 6.2.2 are complete.

Algorithm 4: **Sequences using columns with intermediate decanters**

1. For each sequence resulting from the algorithms of Tao et al. (2003) and Vanage (2005), search for a column where its bottom product followed by a decanter and that decanter is followed a column with an integrated decanter.
2. Test if the tie line of the decanter at the bottom of the preceding column is located very close to that of the integrated decanter of the subsequent column.
3. If such a sequence is found, a new flowsheet is generated using a column with an intermediate decanter to replace the two columns and decanters.

The complete synthesis approach of Tao et al. (2003) and Vanage (2005) as shown in Figure 6.3 is modified to include the new algorithm for generating columns with intermediate decanters as presented in Figure 6.11.

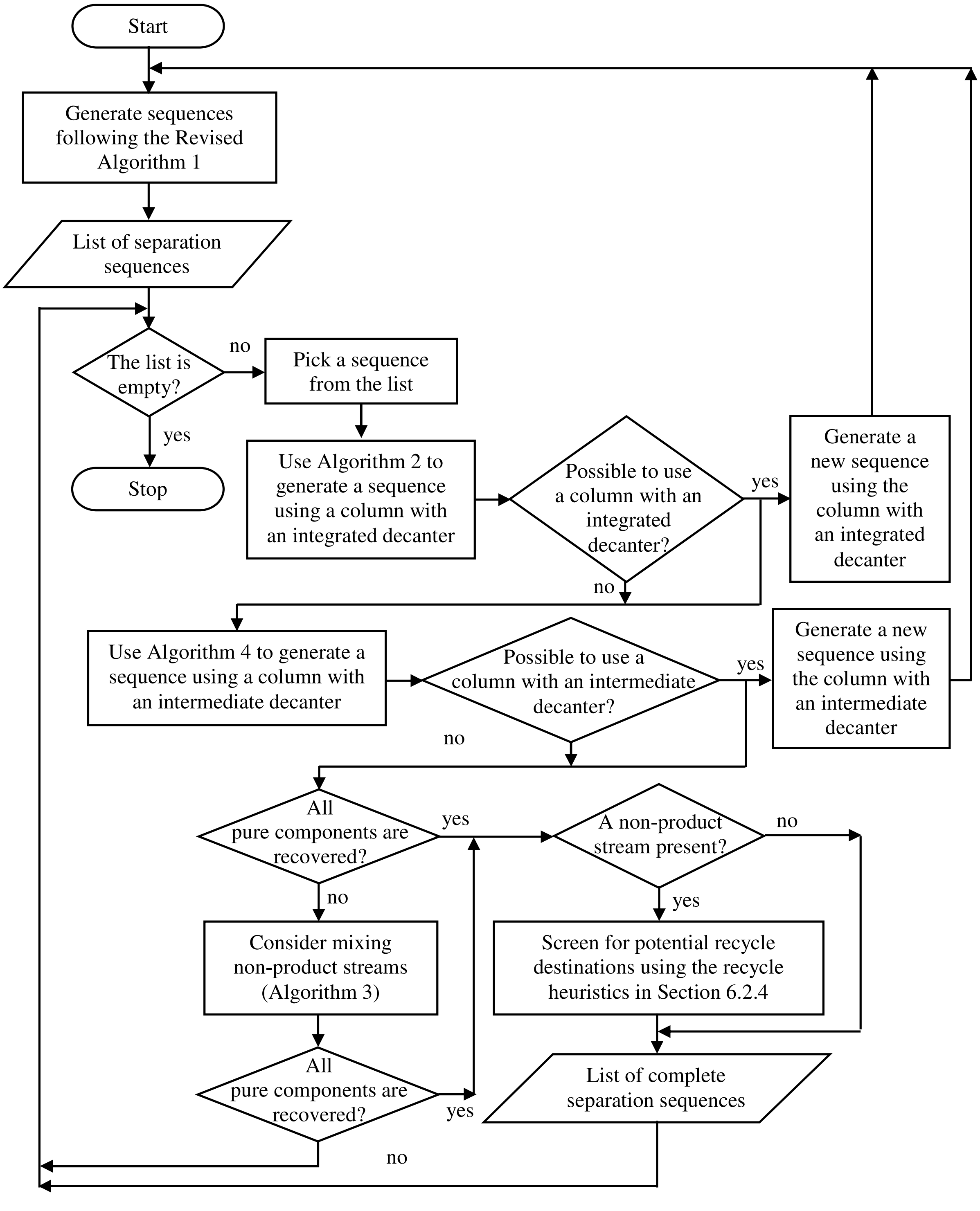


Figure 6.11. The extended synthesis approach of Tao et al. (2003) and Vanage (2005) including a column with an intermediate decanter as an option

6.4 Separation sequence evaluation

Applying the synthesis approach of Tao et al. (2003) and Vanage (2005), a number of feasible sequences that separate a mixture into (nearly) pure components will be generated. Further, with the extended algorithms in Sections 6.3.1 to 6.3.3, additional sequences may be identified as more column structural alternatives are incorporated in the approach. In order to choose the most attractive sequences, those sequences require to be quantitatively evaluated, such as, in terms of their economic performance. An indicator for ranking the sequences is the total annualised cost.

For the purpose of sequence evaluation, the total annualised cost of a sequence is the sum of total annualised costs of all separation units in the sequence. The total annualised cost of a separation unit is estimated based on the size, capacity, heat duties, materials of construction, etc. The details of total annualised cost estimation can be found in Appendix B. For the cost estimation of a column, column design parameters, such as the number of stages, heat duties, pressure and flows, are needed. These column details can be obtained from a design method, such as the boundary value method in Chapters 3 to 5.

Before a column can be designed individually, the mass balance of the sequence must be calculated so that the flow rates and compositions of all streams in the sequence are known. For the mass balance of a column, some of the mole fractions of the products need to be specified. The rest of the product mole fractions are then determined from the mass balance over the column. For example, for a single-feed column with an integrated decanter performing an indirect split of a known feed, the mole fractions of two components in the bottom product, one of which may be the heaviest component, may be specified together with the mole fraction of one component in the top product. (For the specifications of other types of columns, see Chapters 3 to 5.)

For a sequence without a recycle loop, the mass balance calculation is straightforward as the mass balance of each unit can be solved sequentially starting from the first unit following the given feed and continuing unit-by-unit. In contrast, the mass balance calculation for the sequence with a recycle loop may be complicated since the flow rate and composition of the recycle are not known at the beginning.

An approach for solving the mass balance of a sequence with a recycle loop is breaking (or tearing) the recycle stream (Schad, 1994; Turton et al., 2003). The composition and flow rate of the recycle stream are then determined by trial-and-error. In other words, the composition and flow rate of the recycle stream to the destination unit (tear stream) are first guessed. The mass balances of the subsequent units within the recycle loop can then be carried out. Once the composition and flow rate of the recycle from where it originates have been determined, the resulting values at the origin of the recycle are compared with the guessed values of the tear stream. The composition and flow rate of the tear stream are repeatedly changed until the values at the origin and the destination are very close within a desired tolerance. For a better update of the tear stream, a numerical method can be used. A method commonly used for the recycle loop convergence is Newton-Raphson method (Turton et al., 2003) as the calculation involves a set of nonlinear algebraic equations. For a quicker loop convergence, a good initial guess for the tear stream should be provided, e.g. for the composition and flow rate of the stream to be recycled before closing the loop (Vanage, 2005).

A recycle stream may cause the separation in a column or a decanter to become impossible. For example, the recycle stream may cause a feed stream of a column to move into a different distillation region. The recycle stream may also cause a heterogeneous feed stream of a decanter to become a homogeneous liquid. Therefore, once the mass balance of the flowsheet is solved, the feasibility of each column must be assessed and each feed stream to a decanter must be tested if it is a heterogeneous liquid (Tao et al., 2003). In addition, all streams in the sequence are checked if their flow rates are positive, and their mole fractions are nonnegative and sum to unity (Tao et al., 2003).

Once the mass balance of a flowsheet is complete, each column in the sequence can be independently designed using the boundary value method in Chapters 3 to 5 as appropriate to the type of column. The results from the boundary value method allow the total annualised cost of the column to be estimated. For each column, the column design variable(s) can be varied so that the economically near-optimal design is identified. For example, the near-optimal design of a column with an integrated decanter can be found by searching for feasible designs over ranges of reflux ratios and reflux phase split ratios, for a given feed condition. For the double-feed column, the upper-to-lower feed rate ratio is another degree of freedom that affects the feasibility and the cost of the proposed column.

Evaluating flowsheets using the boundary value method may be time-consuming. This is because the column design method is iterative as the column design variable(s) are varied in order to generate feasible designs and to search for the nearly cheapest design of the column.

6.5 Case study

This section describes the synthesis of separation sequences for the separation of an ethyl acetate/water/n-butyl acetate mixture. The mixture can be encountered in the co-production of ethyl acetate and n-butyl acetate (Van Acker et al., 2000). The sequences are generated using the synthesis algorithms of Tao et al. (2003) and Vanage (2005) in Section 6.2 and the extended algorithms in Section 6.3 for generating sequences utilising new features: a double-feed column, a column with an intermediate decanter, and a column with a heterogeneous feed where its coexisting liquid compositions are in different distillation regions. Once the feasible sequences are generated, they are evaluated on the basis of their total annualised cost and compared, to allow the most attractive sequence to be identified.

6.5.1 Problem definition

The first step in separation sequence synthesis is to specify the composition and flow rate of the feed stream. In this work, the pressure of the separation units is fixed at the outset. The desired product purities are then specified. Afterwards, the properties of the mixture are examined. For a ternary mixture, a useful thermodynamic representation of the mixture is a residue curve map (Barnicki and Siirola, 1997). To construct a residue curve map, all azeotropes and their stabilities are determined at a given pressure. Distillation boundaries and compartments can thus be identified. For a heterogeneous liquid, a heterogeneous boiling envelope and its associated vapour line can also be displayed in the residue curve map.

In this case study, the feed to be separated is a saturated liquid at 1 atm. It consists of 15 mol% ethyl acetate, 70 mol% water, and 15 mol% n-butyl acetate. The feed flow rate is 100 kmol/h. All separation units to separate the feed stream will be operated at 1 atm. Separation sequences will be generated to recover all components in the mixture with 97 mol% minimum purity.

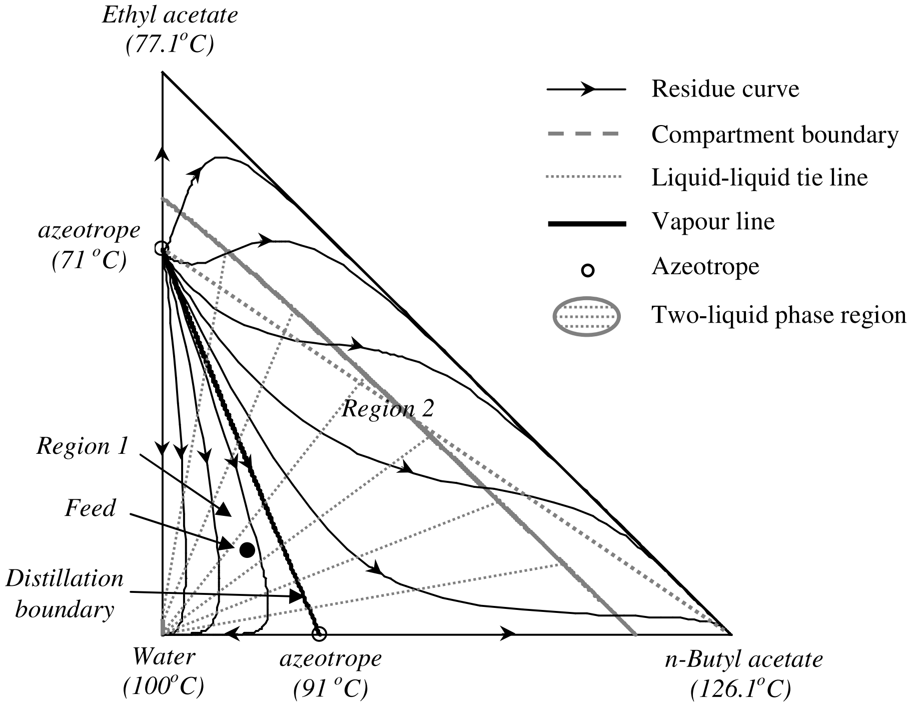


Figure 6.12. Residue curve map and heterogeneous boiling envelope of the mixture of ethyl acetate, water and n-butyl acetate mixture at 1 atm.

Figure 6.12 shows the residue curve map of the ethyl acetate/water/n-butyl acetate mixture calculated using UNIQUAC-ideal gas property package in HYSYS. (The validation of phase equilibrium model and parameters are presented in Appendix C.) Both ethyl acetate and n-butyl acetate form minimum-boiling heterogeneous azeotropes with water, inducing a heterogeneous boiling envelope. The shape of the two-phase region in Figure 6.12 is called a band-type binodal curve (Francis and Smith, 1969). The heterogeneous azeotrope of ethyl acetate and water is an unstable node in the residue curve map whereas the water/n-butyl acetate azeotrope is a saddle. A distillation boundary runs from the unstable heterogeneous azeotrope of ethyl acetate and water towards the saddle heterogeneous azeotrope of water and n-butyl acetate. The vapour line is located very close to the distillation boundary. The residue curve map also features a compartment boundary in the distillation region 2 since two saddle points (ethyl acetate and water/n-butyl acetate azeotrope) exist in the region. The feed composition is in the distillation region 1 and lies in the two-liquid phase region.

6.5.2 Separation sequence generation

Based on the synthesis algorithms of Tao et al. (2003) and Vanage (2005) in Section 6.2 and the extended algorithms in Section 6.3, several separation sequences can be generated. However, only five sequences will be shown and compared in this case study.

Option 1: A simple-column sequence resulting from the algorithms of Tao et al. (2003) and Vanage (2005)

The first option is a sequence resulting from the original algorithms of Tao et al. (2003) and Vanage (2005) in Section 6.2. Since the given feed *F* is a heterogeneous liquid and its coexisting liquid compositions are in different distillation regions, a decanter *D*-1 (see Figure 6.13) is firstly used to separate the feed stream, according to step 3 in Algorithm 1 in Section 6.2.1. Two streams (L_1 and W_1) are generated from the first decanter *D*-1. Stream W_1 is relatively pure water which satisfies the water product purity constraint. The other stream L_1 is an organic liquid phase which needs to be separated further.

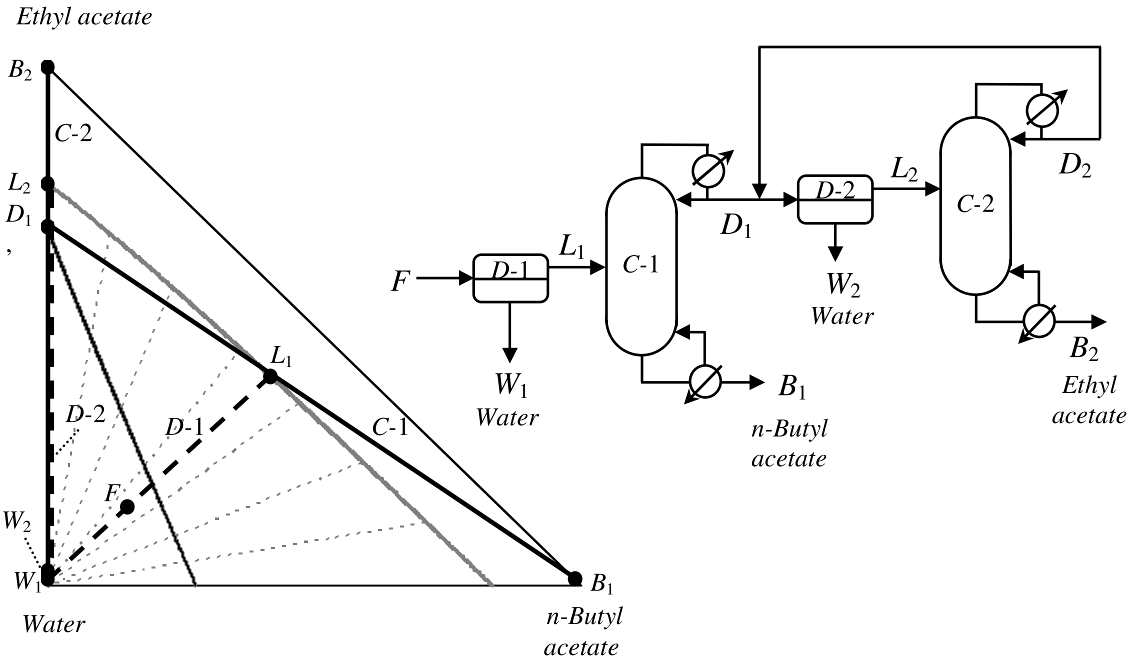


Figure 6.13. A simple-column sequence using stand-alone column-decanter configuration

According to step 4 in Algorithm 1 in Section 6.2.1, the homogeneous liquid stream L_1 is tested if it can be separated in a stand-alone single-feed column. Tested by the common saddle test method of Rooks et al. (1998), the stream L_1 can be separated by either direct or indirect split. Here, the indirect split is chosen. (Note that a sequence using a direct-split column can be generated but not shown here since it will end up using three columns and two decanters, which is not as attractive as the considered sequence.) Hence, a column performing an indirect split (C-1) is introduced into the current sequence. From the column C-1, the heaviest component, which is n-butyl acetate, is recovered at the bottom (B_1) whereas the top product (D_1) is a heterogeneous liquid mixture of ethyl acetate and water.

Since the top product stream D_1 is a heterogeneous liquid which has coexisting liquid compositions in different distillation regions, a decanter D-2 is used to separate the stream D_1. A relatively pure water (W_2) is taken out as a product. For the organic phase (L_2), it is separated in another simple single-feed column C-2. Ethyl acetate is recovered at the bottom (B_2). As the top product D_2 is a heterogeneous liquid, it may be separated in another decanter. However, the products from the new decanter will be the same as those from the previous decanter *D*-2. According to the recycle Heuristic 6 in Section 6.2.4, the top product D_2 should be recycled to the decanter *D*-2 to avoid the duplication of separation units performing the same function.

According to Algorithm 2 proposed by Vanage (2005) in Section 6.2.2, the stand-alone column-decanter configuration in Figure 6.13 can be replaced with the industrially relevant integrated column-decanter configuration. In the sequence in Figure 6.13, the column *C*-1 is followed by a stand-alone decanter *D*-2 and the top product is a composition near to the minimum boiling heterogeneous azeotrope. Thus, a column with an integrated decanter can replace the column *C*-1 followed by the stand-alone decanter *D*-2 according to Algorithm 2 of Vanage (2005) (Section 6.2.2). The column *C*-2 is also followed by a decanter since the top product D_2 is recycled to the decanter *D*-2. Consequently, the column *C*-2 can be replaced by a column with an integrated decanter. The new column sequence using columns with integrated decanters is shown in Figure 6.14. The mass balance of this sequence is shown in Table 6.1.

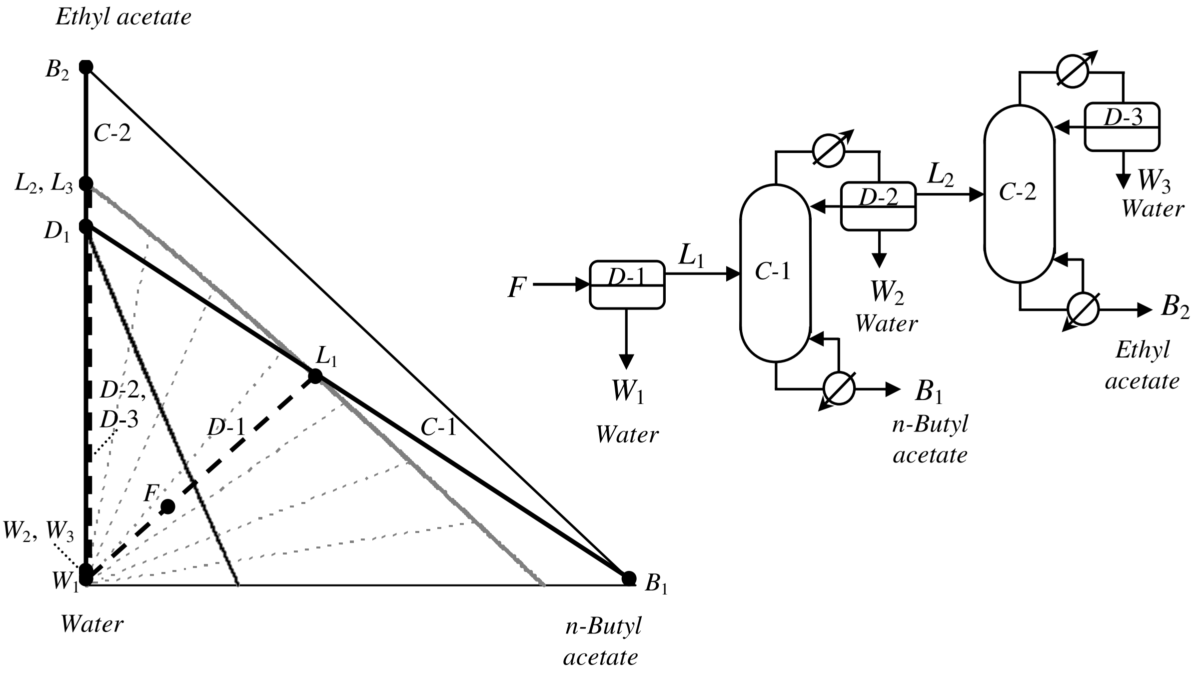


Figure 6.14. Option 1: a simple-column sequence using columns with integrated decanters

Table 6.1. Mass balance of the sequence using simple single-feed columns as shown in Figure 6.14

	F	L_1	W_1	B_1	D_1
Composition (mole fraction)					
ethyl acetate	0.1500	0.4026	0.0099	0.0104	0.6907
water	0.7000	0.1784	0.9891	0.0002[a]	0.3092
n-butyl acetate	0.1500	0.4190	0.0010	0.9894[a]	0.0001[a]
Feed condition	1				
Flow rate (kmol/h)	100	35.66	64.34	15.10	20.56
	L_2	W_2	B_2	W_3	
Composition (mole fraction)					
ethyl acetate	0.7753	0.0247	0.9989	0.0280	
water	0.2246	0.9753	0.0010[a]	0.9720	
n-butyl acetate	0.0001	3.4×10^{-7}	0.0001[a]	1×10^{-7} [a]	
Flow rate (kmol/h)	18.24	2.32	14.04	4.20	

[a] Specified values

Option 2: A sequence using a double-feed column in which the lower feed is a homogeneous liquid

The second option is a sequence consisting of a double-feed column identified from the extended synthesis approach in Section 6.3. In this sequence (Figure 6.15), the heterogeneous feed is first separated in a decanter *D*-1, as in the first option. According to step 4 in the Revised Algorithm 1 (Section 6.3.2), besides direct and indirect splits, a saddle-type split is also considered for the separation of the organic liquid stream L_1. In the first option, the organic liquid stream L_1 is separated in an indirect split column. In this option, a saddle-type split is considered.

To check if the organic liquid stream L_1 can be separated in the double-feed column (*C*-1), the testing procedure in Section 6.3.2.1 is applied. A stream of n-butyl acetate, which is the heaviest component, is assumed to be an upper feed (F_U). The upper-to-lower feed rate ratio is proposed so that the product compositions of the column can be estimated. In this case, the feed rate ratio of 1.8 is proposed. As the integrated decanter is used, the top product of the double-feed column performing a saddle-type split can lie on the liquid-liquid tie line of the heterogeneous azeotrope of water and n-butyl acetate. Once the top product D_1 is specified, the bottom product of the double-feed column B_1, which is a mixture of ethyl acetate and n-butyl acetate, can be calculated from the mass balance over the column. The sequence synthesis is continued until all components are recovered as shown in Figure 6.15.

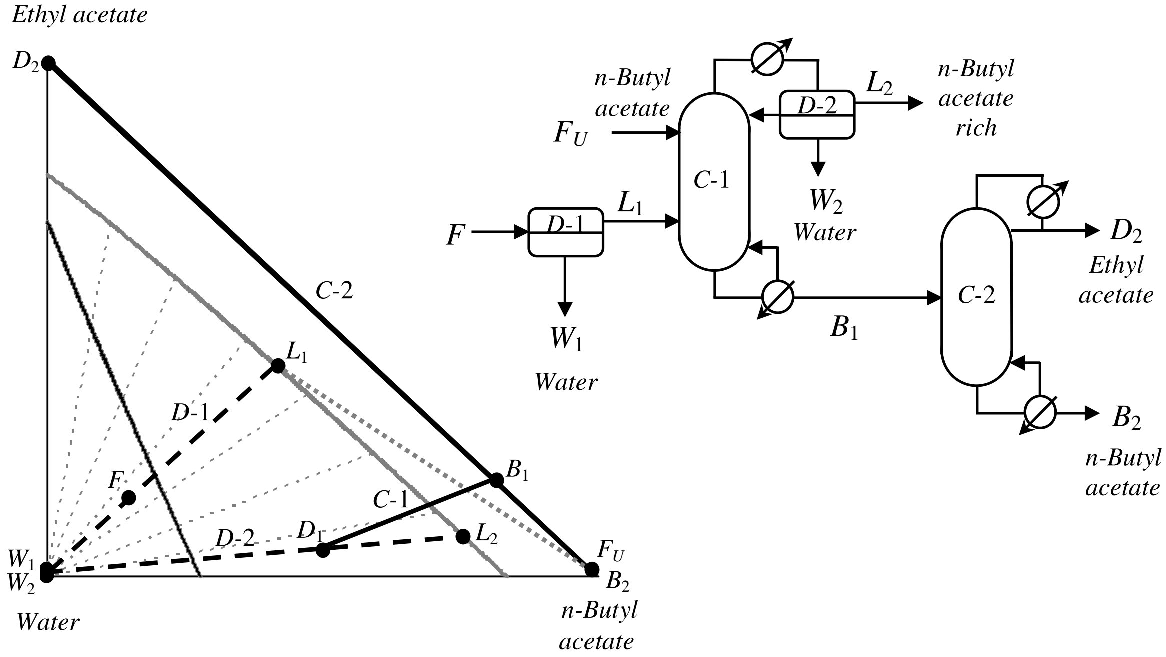


Figure 6.15. A sequence using a double-feed column assuming a stream containing n-butyl acetate to be an upper feed.

To complete the sequence, a part of the n-butyl acetate stream B_2 and the n-butyl acetate-rich stream L_2 are recycled to the double-feed column to replace the assumed upper feed as shown in Figure 6.16. Given the upper-to-lower feed rate ratio of 1.8 as before, the mass balances of the double-feed column and the next column can be updated using Newton's convergence method in Excel. The feasibility of the separation in the double-feed column is assessed using the boundary value method presented in Chapter 4. For the given feed rate ratio, feasible column designs are found for range of reflux ratios and reflux phase split ratio. Therefore, the double-feed column can be introduced into the current sequence. The complete sequence for option 2 is shown in Figure 6.16 and the converged mass balance is presented in Table 6.2.

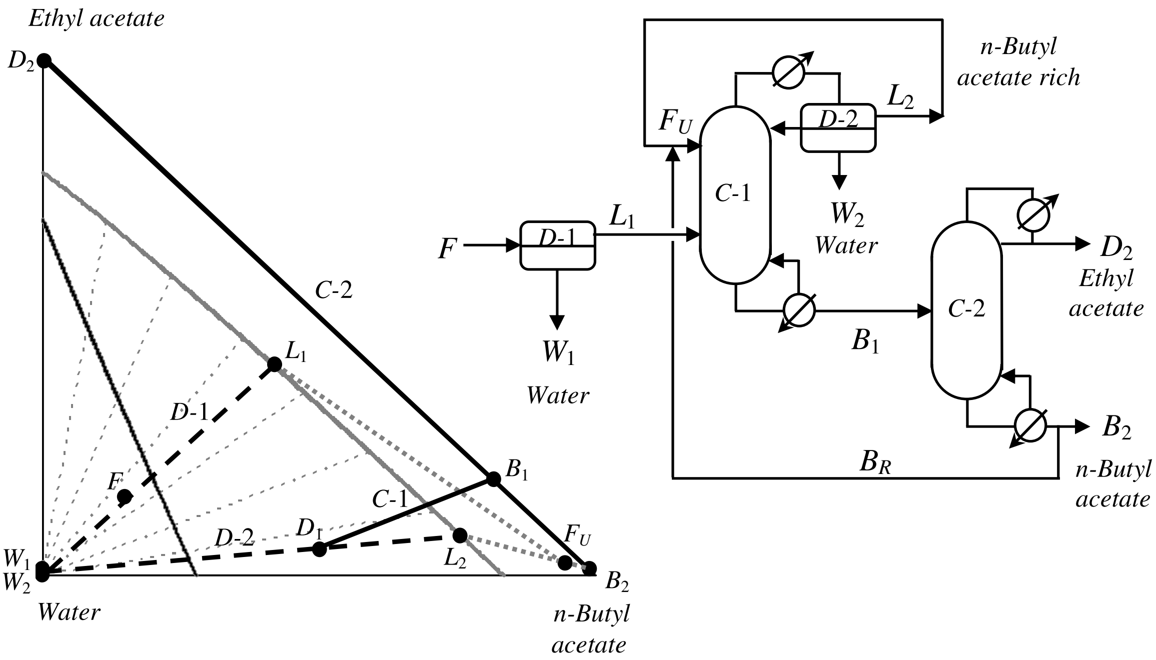


Figure 6.16. Option 2: a complete sequence using a double-feed column in which the lower feed is a homogeneous liquid

Table 6.2. Mass balance of the sequence using a double-feed column as shown in Figure 6.16

	F	W_1	L_1	F_U	B_1	D_1
Composition (mole fraction)						
ethyl acetate	0.1500	0.0099	0.4026	0.0224	0.1828	0.0500[a]
water	0.7000	0.9891	0.1784	0.0320	0.0010[a]	0.4500
n-butyl acetate	0.1500	0.0010	0.4190	0.9457	0.8162	0.5000[a]
Feed condition	1					
Flow rate (kmol/h)	100	64.34	35.66	64.19	81.33	18.51
	L_2	W_2	B_2	D_2	B_R	
Composition (mole fraction)						
ethyl acetate	0.0749	0.0016	0.0100	0.9899[a]	0.0100	
water	0.1680	0.9970	1×10^{-9} [a]	0.0057	1×10^{-9}	
n-butyl acetate	0.7571	0.0014	0.9900[a]	0.0044	0.9900	
Flow rate (kmol/h)	12.22	6.30	15.02	14.34	51.97	
Upper-to-lower feed rate ratio of the double-feed column C-1			1.8[a]			

[a] Specified values

Option 3: A sequence using a double-feed column in which the lower feed is a heterogeneous liquid

The third option (Figure 6.17) is similar to the second option (Figure 6.16) except the heterogeneous feed *F* is not first separated in a decanter but it is directly added to the double-feed column *C*-1 as a lower feed. This option is included in the Revised Algorithm 1 (Section 6.3.1). The sequence is then generated in a similar way as the sequence in Option 2. The upper-to-lower feed rate ratio of 1.8 is assumed for assessing the feasibility of the separation in the double-feed column. The mass balance of the sequence according to the given feed rate ratio and product specifications is shown in Table 6.3.

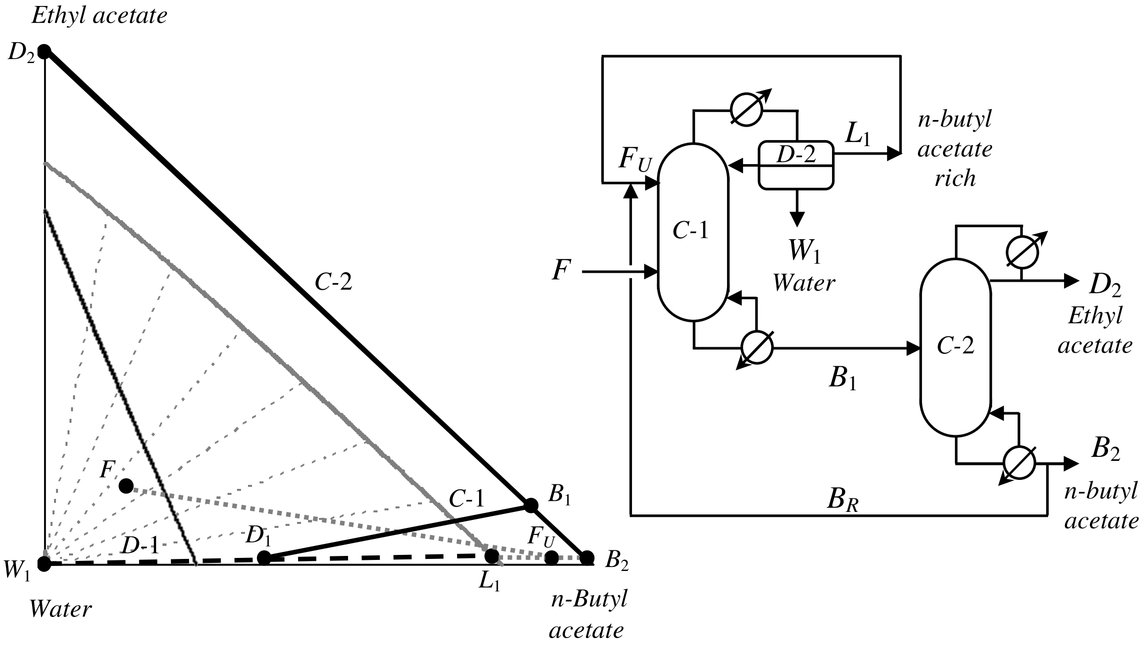


Figure 6.17. Option 3: a sequence using a double-feed column in which the lower feed is a heterogeneous liquid.

Table 6.3. Mass balance of the sequence using a double-feed column in which the lower feed is a heterogeneous liquid as shown in Figure 6.17

	F	F_U	D_1	L_1	W_1
Composition (mole fraction)					
ethyl acetate	0.1500	0.0123	0.0100[a]	0.0161	0.0004
water	0.7000	0.0625	0.5900	0.1673	0.9981
n-butyl acetate	0.1500	0.9252	0.4000[a]	0.8166	0.0015
Feed condition	1				
Flow rate (kmol/h)	100	180	137.46	67.21	70.25
	B_1	B_2	D_2	B_R	
Composition (mole fraction)					
ethyl acetate	0.1111	0.0100	0.9899[a]	0.0100	
water	0.0010[a]	1×10^{-9}[a]	0.0097	1×10^{-9}	
n-butyl acetate	0.8879	0.9900[a]	0.0004	0.9900	
Flow rate (kmol/h)	142.54	15.04	14.71	112.79	
Upper-to-lower feed rate ratio of the double-feed column C-1			1.8[a]		

[a] Specified values

For the given feed rate ratio and product compositions, the boundary value method presented in Chapter 4 is applied for assessing the feasibility of the proposed separation in the double-feed column. After searching for ranges of reflux ratios and reflux phase split ratios, no feasible designs are found even though the top product composition is varied throughout the decanter tie line. The feed rate ratio is thus varied, but still no feasible design found. As a result, the sequence in Figure 6.17 is rejected.

Option 4: A sequence in which the heterogeneous feed is separated in a column and uses only single-feed columns with integrated decanters

The fourth option is a sequence in which the heterogeneous feed F is directly separated in a single-feed column with an integrated decanter using the Revised Algorithm 1 (Section 6.3.1).

According to Algorithm 1 proposed by Tao et al. (2003) in Section 6.2.1, the heterogeneous feed F with its coexisting liquid compositions in different distillation regions will be separated in a decanter as shown in options 1 and 2. However, in this option, the heterogeneous feed *F* is not separated in the decanter but it is separated in a column according to the Revised Algorithm 1 in Section 6.3.1.

In Figure 6.18, the column *C*-1 is chosen to perform a direct split (the top vapour composition of the column is that of the heterogeneous azeotrope of ethyl acetate and water). As the column *C*-1 is coupled with an integrated decanter, the top product must be located somewhere on a tie line near the ethyl acetate/water azeotrope. A given top product shown in Table 6.4 lies in distillation region 2 whereas the resulting bottom product is located in distillation region 1. From the decanter *D*-1, relatively pure water W_1 is removed as a product while the ethyl acetate-rich stream (L_1) is separated in another column with an integrated decanter (*C*-2 and *D*-2).

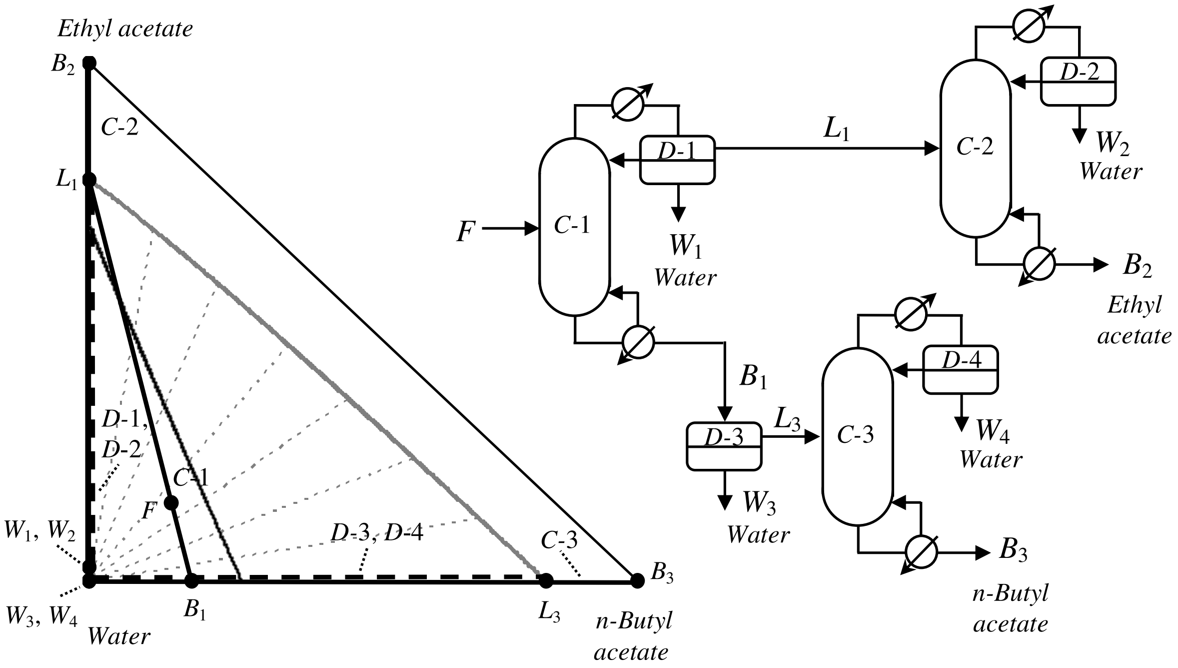


Figure 6.18. Option 4: A sequence in which the heterogeneous feed is separated in a column and uses only single-feed columns with integrated decanters

At the bottom of the first column *C*-1, the bottom product stream B_1, which is a binary heterogeneous mixture of water and n-butyl acetate, is separated in a decanter *D*-3. A water-rich phase W_2 is obtained from the decanter *D*-3. The n-butyl acetate-rich stream L_2 is separated in another column with an integrated decanter (*C*-3 and *D*-4). The mass balance of the sequence is shown in Table 6.4.

Table 6.4. Mass balance of the sequence in which the heterogeneous feed is separated in a column and uses only single-feed columns as shown in Figure 6.18

	F	D_1	B_1	L_1	W_1	
Composition (mole fraction)						
ethyl acetate	0.1500	0.7740^a	0.0001^a	0.7753	0.0247	
water	0.7000	0.2260	0.8139	0.2246	0.9753	
n-butyl acetate	0.1500	$1\times10^{-6\,a}$	0.1860	0.0001	3×10^{-7}	
Feed condition	1					
Flow rate (kmol/h)	100	19.37	80.63	19.33	0.03	
	B_2	W_2	L_3	W_3	B_3	W_4
Composition (mole fraction)						
ethyl acetate	0.9989^a	0.0280	0.0004	9×10^{-6}	0.0005	0.0002^a
water	0.0010	0.9720^a	0.1672	0.9985	0.0006	0.9982
n-butyl acetate	0.0001	$1\times10^{-7\,a}$	0.8324	0.0015	0.9989^a	0.0016^a
Flow rate (kmol/h)	14.88	4.44	17.90	62.73	14.92	2.99

^{a} Specified values

Option 5: A sequence using a column with an intermediate decanter

This option is the sequence modified from the sequence in option 4 using Revised Algorithm 4 in Section 6.3.3. In the sequence in Figure 6.18, the bottom product of the column *C*-1 is followed by the decanter *D*-3 after which the column with an intermediate decanter (*C*-3 and *D*-4) is placed. Moreover, the tie lines of the decanter at the bottom of the first column (*D*-3) and the decanter at the top of column *C*-3 (*D*-4) are very close to each other. According to the new algorithm in Section 6.3.3, such a sequence can be replaced by a column with an intermediate decanter. Therefore, one column and one decanter in Figure 6.18 can be eliminated. The resulting sequence is shown in Figure 6.19. The converged mass balance of the sequence in Figure 6.19 is shown in Table 6.5.

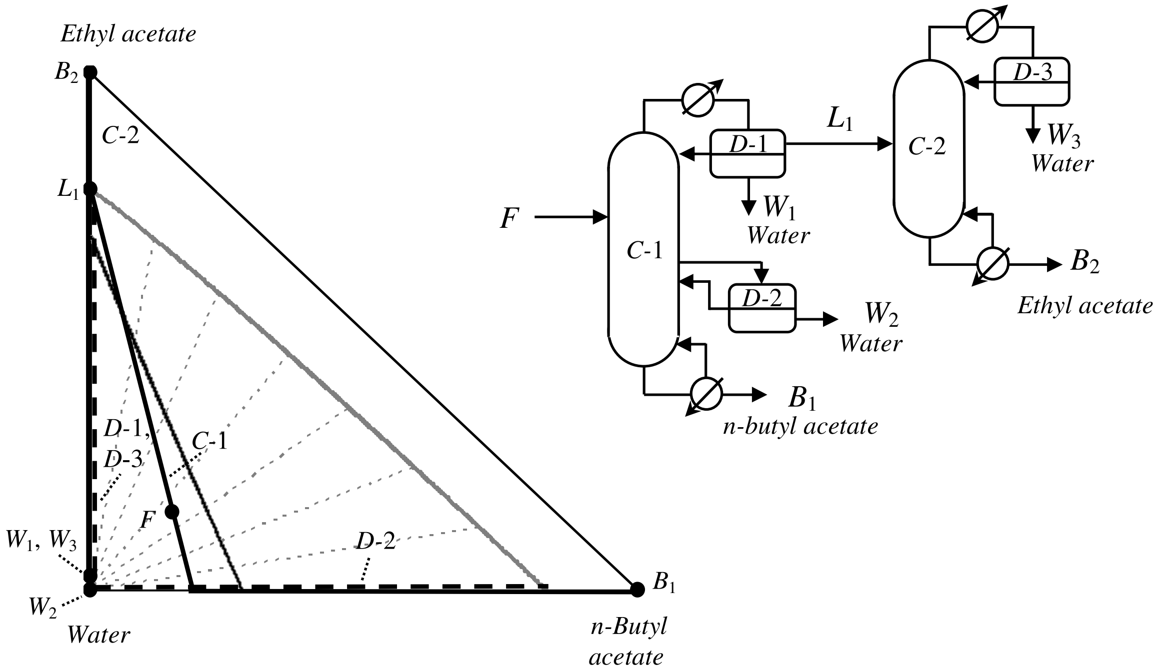


Figure 6.19. Option 5: a sequence using a column with an intermediate decanter.

Table 6.5. Mass balance of the sequence using a column with an intermediate decanter as shown in Figure 6.19

	F	D_1	B_1	L_1
Composition (mole fraction)				
ethyl acetate	0.1500	0.7740	1×10^{-6} [a]	0.7753
water	0.7000	0.2259	0.0013	0.2246
n-butyl acetate	0.1500	0.0001	0.9987	0.0001
Feed condition	1			
Flow rate (kmol/h)	100	19.38	14.92	19.35
	W_1	W_2	B_2	W_3
Composition (mole fraction)				
ethyl acetate	0.0247	1.4×10^{-7}	0.9989 [a]	0.0280
water	0.9753	0.9985	0.0010	0.9720 [a]
n-butyl acetate	3×10^{-7}	0.0015	0.0001	1×10^{-7} [a]
Flow rate (kmol/h)	0.03	65.70	14.04	4.20

[a] Specified values

In summary, the synthesis algorithms of Tao et al. (2003) and Vanage (2005) and the extended algorithms in Section 6.3 allow several sequences for separating the ethyl acetate/water/n-butyl acetate mixture to be generated. Only five sequences are presented. The first option consisting of only simple single-feed columns is generated from the algorithms of Tao et al. (2003) and Vanage (2005). The other four options are sequences utilising new features in the synthesis approach. The four options are identified from the extended approach in Sections 6.3.1 to 6.3.3. Option 3 in Figure 6.17 is eliminated because there is no feasible design for the double-feed column found. As a result, only four options remain for sequence evaluation.

6.5.3 Sequence evaluation

To select the most economically attractive sequences, the four options in the previous section are evaluated with respect to their total annualised costs. Hence, each separation unit in a sequence is individually designed and evaluated for a range of values of relevant design variables so that its total near-minimum annualised cost can be estimated. The cost of a decanter is a function of the size of the decanter which in turn depends on the feed flow rate of the decanter. The cost of a column is estimated based on the column design details such as number of stages, heat duties, product compositions and flow rates. (The cost estimation of decanters and columns is described in Appendix B.) Each column in a sequence is designed using the boundary value method in Chapters 3 to 5 as appropriate to the type of the column.

For each column in a sequence, the boundary value method is carried out to generate feasible column designs for a range of one or more design variable(s). Based on the total annualised cost, the economically near-optimal design of the column can thus be identified. An example illustrating the application of the boundary value method for identifying the near-optimal design is presented in Section 3.4 for column C-1 in Option 1 (Figure 6.14). For every column in this case study, feasible column designs are searched for a range of reflux ratios. They are also searched for a range of reflux phase split ratios in case that the column is coupled with an integrated decanter. For the double-feed column in Option 2 (Figure 6.16), column designs are also generated for a range of upper-to-lower feed rate ratios. The near-optimal design of the double-feed in Option 2 is found at the upper-to-lower feed rate ratio of 1.65. The mass balance of Option 2 for the new feed rate ratio shown in Table 6.6 is calculated using the Newton's convergence method in Excel.

Table 6.6. Mass balance of the sequence using a double-feed column as shown in Figure 6.16 (upper-to-lower feed rate ratio is 1.65)

	F	W_1	L_1	F_U	B_1	D_1
Composition (mole fraction)						
ethyl acetate	0.1500	0.0099	0.4026	0.0235	0.1950	0.0500^a
water	0.7000	0.9891	0.1784	0.0349	0.0010^a	0.4500
n-butyl acetate	0.1500	0.0010	0.4190	0.9416	0.8040	0.5000^a
Feed condition	1					
Flow rate (kmol/h)	100	64.34	35.66	58.84	75.97	18.53
	L_2	W_2	B_2	D_2	B_R	
Composition (mole fraction)						
ethyl acetate	0.0749	0.0016	0.0100	0.9899^a	0.0100	
water	0.1680	0.9970	$1\times10^{-9\,a}$	0.0053	1×10^{-9}	
n-butyl acetate	0.7571	0.0014	0.9900^a	0.0048	0.9900	
Flow rate (kmol/h)	12.2	6.30	15.02	14.34	46.61	
Upper-to-lower feed rate ratio of the double-feed column *C*-1			1.65^a			

[a] Specified values

Table 6.7 shows the near-optimal design and total annualised cost of each separation unit and the total annualised costs of the sequences. Among the four feasible options, the cheapest sequence is the first option (Figure 6.14) in which only two simple single-feed columns with integrated decanters are used. The first option is only about 4% less than that of the sequence consisting of a double-feed column placed after a decanter (Option 2). Compared with the sequences in which the heterogeneous feed is first separated in a column (Options 4 and 5), Options 1 and 2 (a decanter is first used) are considerably more attractive as they are approximately 13-17% cheaper. This is because about 65% of the feed is simply removed as nearly pure water by using the decanter. Having some of the feed removed substantially reduces the mass load in the subsequent columns. In addition, comparing Options 4 and 5, Option 5 which is generated by modifying the sequence in Option 4, has a very similar cost to Option 4. In this case, the column with an intermediate decanter in Option 5 does not provide cost savings even though Option 5 requires fewer columns and decanters than Option 4.

Note that the total annualised costs for the sequences in Table 6.7 are only estimated for main equipment, i.e. columns and decanters. The costs for piping, pumps and controllers are not included. If the costs for those pieces of equipment are included, the costs of sequences having similar costs in Table 6.7 (Options 4 and 5) may become different.

Table 6.7. Total annualised costs of options

Option	Separation unit	N_R	N_S	N_{Total}	Q_C (kW)	Q_R (kW)	*TAC* (£/year)	Total cost (£/year)
Option 1 (Figure 6.14)	*D*-1	-	-	-	-	-	5,000	318,700
	C-1, *D*-2	14	9	22	423	463	183,100	
	C-2, *D*-3	2	11	12	356	360	130,600	
Option 2 (Figure 6.16)	*D*-1	-	-	-	-	-	5,000	330,500
	C-1, *D*-2	2	6	18	348	385	154,500	
	C-2	8	8	15	421	464	171,000	
Option 3 (Figure 6.17)	*C*-1, *D*-2	-	-	-	-	-	-	-
	C-2	-	-	-	-	-	-	
Option 4 (Figure 6.18)	*C*-1, *D*-1	10	18	27	458	477	183,600	375,200
	C-2, *D*-2	2	11	12	377	382	136,400	
	D-3	-	-	-	-	-	5,000	
	C-3, *D*-4	3	5	7	55	92	50,200	
Option 5 (Figure 6.19)	*C*-1, *D*-1, *D*-2	11	20	32	484	540	236,400	372,800
	C-2, *D*-3	2	11	12	378	382	136,400	

TAC = Total annualised cost (3-year period and 5% interest rate)

6.5.4 Case study: Conclusions

The extended synthesis approach allows additional sequences utilising new features to be generated. By using the extended approach, a double-feed column and a column with an intermediate decanter can be identified. However, in the case study, the complex column configurations are not economically attractive as the simple-column sequence.

Following the extended algorithm, the given heterogeneous liquid feed with its liquid compositions in different distillation regions is allowed to be separated in a column. For this case study, the separation of the given feed in a double-feed column is infeasible. In contrast, the separations of the given feed in a single-feed column and a column with an intermediate decanter are feasible though they do not lead to economically favourable sequences.

In the case study, the sequences using a double-feed column and a column with an intermediate decanter are not as attractive as the simple-column sequence. Nonetheless, including those complex column configurations are still essential in sequence synthesis because the configurations may make a separation of a mixture feasible and they may be an economic option. For example, a double-feed column allows the separation of a 1-propanol/water/1-butanol mixture to be possible as discussed in Chapter 4. The case study in Chapter 5 shows that a column with an intermediate decanter is significantly cheaper than a simple-column sequence in separating an acetone/water/1-butanol mixture.

6.6 Conclusions

This chapter presents a methodology for synthesising sequences separating ternary heterogeneous azeotropic mixtures. The methodology is an extension of the synthesis approach of Tao et al. (2003) and Vanage (2005). Originally, the synthesis approach of Tao et al. (2003) and Vanage (2005) consists of three algorithms and some heuristics. Their approaches generate separation sequences using simple single-feed columns, decanters, and columns with integrated decanters. The classes of splits considered are direct and indirect splits. An algorithm of Tao et al. (2003) has been revised to include two more options: heterogeneous liquid streams with their liquid compositions in different distillation regions may be separated in either a decanter or a column; and double-feed columns with an integrated decanter can perform a saddle-type split. A new algorithm has been proposed and included in the synthesis approach of Tao et al. (2003) for synthesising sequences employing columns with intermediate decanters. The new features in the synthesis approach will lead to the increase in the number of separation sequences. As the new column configurations are explored, more attractive sequences may be found.

Separation sequences generated from the proposed synthesis approach can be evaluated using the iterative application of boundary value method presented in Chapters 3 to 5. For each column in a sequence, the boundary value method in Chapters 3 to 5 is used for generating feasible designs for a range of one or more design variable(s), e.g., reflux ratios, phase reflux ratios, and upper-to-lower feed rate ratios. The total annualised cost of a column design can be estimated based on the column design details obtained from the boundary value method, such as the number of stages, heat duties. The economically near-optimal design for a column can be thus identified. The cost of the sequence can then be estimated and compared with other sequences.

The application of the proposed synthesis approach in this chapter has been illustrated with the synthesis of separation sequences for separating a mixture of ethyl acetate/water/n-butyl acetate. The extended approach allows generation of separation sequences that includes complex column configurations: double-feed column with an integrated decanter, and column with an intermediate decanter. Each column in all sequences is designed using the boundary value method according to the type of the column, feed and product compositions and flow rates. Separation units and sequences are evaluated with respect to their total annualised costs. In this case study, the complex column configurations do not lead to the economically favourable sequences.

While the feasibility of the separation in a simple single-feed column is evaluated using the common saddle test proposed by Rooks et al. (1998), the feasibility in a double-feed column is checked using the boundary value method presented in Chapter 4. Assessing the separation feasibility using the boundary value method requires full product specifications. To test if a double-feed column can be used for separating a stream may be time-consuming because the column design variables, such as the feed rate ratio, top product composition, reflux ratio, reflux phase split ratio, may need to be varied until a feasible column design is found. The test will be faster if there is a feasibility test method available for assessing the feasibility of the separation in a double-feed column without full product specifications and exhaustive search for feasible designs.

The extension of synthesis approach of Tao et al. (2003) and Vanage (2005) in this chapter focuses on sequence synthesis for ternary heterogeneous azeotropic mixtures. The effect of pressure on the residue curve map and the effect of temperature on the two-liquid phase region are not considered. The proposed synthesis approach may be readily extended to consider these effects. The method may also, in principle, be extended to consider the separation of multicomponent mixtures. Other complex columns and separation options, e.g., subcooled decanter, pressure-swing flowsheet, hybrid distillation-membrane separation options, may be included in the approach if the feasibility of the separation in those options can be established.

Chapter 7

Conclusions and Future work

7.1 Conclusions

The main objective of this research work is to develop an improved methodology for synthesising separation sequences for heterogeneous azeotropic mixtures. This work presents a systematic approach for generation of feasible separation sequences employing distillation columns and decanters. The approach is an extension of the approaches of Tao et al. (2003) and Vanage (2005). Originally, the synthesis algorithms of Tao et al. (2003) and Vanage (2005) considers only simple single-feed columns, decanters, and columns with integrated decanters; two classes of split included in their synthesis approaches are direct and indirect splits. In this work, the synthesis algorithms of Tao et al. (2003) and Vanage (2005) are extended to include more design options, i.e. double-feed columns, columns with intermediate decanters, and columns with heterogeneous liquid feeds having coexisting liquid compositions in different distillation regions. The new options in the synthesis approach may give rise to increased numbers of separation sequences for a given design problem. Consequently, more economically attractive sequences may be identified.

The proposed sequence synthesis method requires separation feasibility and economic performance of individual columns in sequences to be assessed. This thesis presents a column design method exploiting the boundary value method for establishing separation feasibility and for identifying economically attractive designs of columns in sequences. The new design method is applicable to single- and double-feed columns with integrated decanters, and to columns with intermediate decanters. The design method allows column design details, e.g. number of stages, feed locations and heat duties, to be obtained so that the costs of columns can be estimated. A separation sequence resulting from the synthesis approach can be evaluated using iterative application of the new boundary value method. For an individual column in a sequence, feasible column designs are sought for a range of one or more design variables, such as reflux ratio, reflux phase split ratio, and upper-to-lower feed rate ratio. Economically near-optimal designs for a column can be then identified. The cost of the sequence can then be estimated and compared with that of other sequences. This iterative application of the design method allows infeasible separations and uneconomic column and sequence designs to be screened out rapidly. Promising designs can then be selected for studying in more detail.

The calculations required in the new column design method are not computationally intensive, compared to the continuous distillation region based method introduced by Urdaneta et al. (2002). The boundary value method needs only liquid composition profiles to be calculated, whereas the continuous distillation region based method requires the composition profile calculations and pinch point determination. Unlike the continuous distillation region based method, the boundary value method provides column design details necessary for column cost estimation and for initialising more rigorous simulations.

The new boundary value method is developed to overcome limitations of the boundary value method developed by other authors. The new design approach does not restrict two liquid phases only to the top decanter, as with the boundary value method of Pham et al. (1998) and Wasylkiewicz et al. (2000). Unlike the boundary value method proposed by Pham et al. (1989), Wasylkiewicz et al. (2000) and Urdaneta et al. (2002), the new design method has a reflux phase split ratio as a degree of freedom for the design of a column with an integrated decanter. In addition, the new design approach does not need as an input the maximum number of heterogeneous stages, which is unknown when setting column specifications, unlike the boundary value method of Urdaneta et al. (2002).

For a column with an integrated decanter, a reflux phase split ratio may be specified such that two liquid phases appear on stages below the top decanter. For the composition profile calculation of a rectifying section having multiple heterogeneous stages, a set of preliminary tests is introduced for checking whether the liquid on a particular stage in the rectifying section could be heterogeneous. Applying the new column design procedure, multiple rectifying profiles may be generated for various phase split ratios of every heterogeneous stage if two liquid phases occur on stages in the rectifying section. Some of the multiple rectifying profiles may give rise to multiple feasible designs having the same heat duties but different numbers of stages and feed locations for a given set of product specifications and reflux ratio. Such multiplicities are equivalent to ‘input multiplicities’ reported in the literature (Gani and Jørgensen, 1994). By using the new boundary value method, existence of input multiplicities for a given set of column specifications can be identified. The proposed design method and the existence of multiple column designs are verified by simulation in HYSYS.

Based on the design method for single-feed columns with integrated decanters, the new design method is extended to double-feed columns with integrated decanters and columns with intermediate decanters. Using the proposed design method, multiple feasible designs may be identified, corresponding to different lower feed locations and different sidestream locations, for double-feed columns and for columns with intermediate decanters, respectively.

With the proposed column and sequence design methods, synthesis of separation sequences using simulation-based methods, which is a common practice, can be avoided. Synthesising sequences using simulation-based methods is intuitive and iterative. Moreover, column design by simulation is tedious and time-consuming as even feasible separations in heterogeneous azeotropic columns are usually difficult to converge. Thus, design by simulation requires a great deal of time and effort to identify feasible and near-optimal designs. The column and sequence design methods presented in this thesis allow feasible and economic separation sequences for heterogeneous azeotropic mixtures to be identified systematically without an exhaustive search as is required by simulation-based methods. The potential sequences resulting from the synthesis approach can be studied further using a process simulator. Additionally, the new column design method provides column design details which can be used for initialising rigorous simulations. The simulation of a column may be facilitated by using other results from the design method, e.g. the location of heterogeneous stages, the compositions and temperatures on particular stages, as initial values.

Case studies are presented to illustrate the applicability of the sequence synthesis approach and the column design method. For the separation of an acetic acid/water/n-butyl acetate mixture in a column with an integrated decanter, the presence of two liquid phases in the column significantly improves economic performance. For this case, multiple-heterogeneous stage columns require fewer theoretical stages than columns in which two liquid phases are restricted to the decanter. This is because the column with multiple heterogeneous stages requires fewer heterogeneous stages and it is designed to be away from the tangent pinch of water and acetic acid.

The applicability of the new boundary value method to a double-feed column with an integrated decanter is demonstrated with the separation of 1-propanol/water/1-butanol mixture which cannot be separated into relatively pure components using the simple columns. In this case, the appearance of heterogeneous liquid in the column does not bring benefits in terms of cost. The new boundary value method allows the feed locations and a range of upper-to-lower feed rate that lead to feasible and economically attractive designs to be identified.

A separation of an acetone/water/1-butanol mixture can be carried out in a column with an intermediate decanter. The results from the design method show that the column with intermediate decanter is more economically attractive than a sequence using only simple single-feed columns. For this case, the column with an intermediate decanter provides significant saving in capital cost and it requires considerably smaller heat duties.

In case studies, column design details and other results from the design method are used to initialise rigorous simulations of columns and to facilitate simulation convergence. The simulation results are in good agreement with the column specifications given to the column design method. The existence of multiple solutions corresponding to the numbers of heterogeneous stages and phase split ratios of the heterogeneous stages is also verified by rigorous simulations. The simulation of a heterogeneous azeotropic column may still be difficult to converge even with the initial values from the column design method. For example, a successful simulation of an acetic acid/water/n-butyl acetate column with fewer heterogeneous stages than the maximum cannot be found, which may be because of the existence of the tangent pinch.

The sequence synthesis method is applied to the separation of ethyl acetate/water/n-butyl acetate mixture. By applying the original synthesis approaches of Tao et al. (2003) and Vanage (2005), only sequences using single-feed columns with and without integrated decanters are generated. The extended synthesis algorithms of Tao et al. (2003) and Vanage (2005) presented in this work allows the generation of sequences consisting of complex column configurations, i.e. double-feed column with integrated decanter and column with an intermediate decanter. Applying the column design method to the sequences resulting from the synthesis approach indicates that sequences consisting of complex columns are not economically attractive as the sequence using only single-feed columns with integrated decanters for this case. The results from the column design method also shows that the economic performance is also affected by the number of heterogeneous stages. For this case, columns with fewer heterogeneous stages than the maximum are more attractive.

7.2 Limitations

The column and sequencing design methods presented in the work has been developed for ternary heterogeneous azeotropic mixtures. In principle, the design method can be applied to multicomponent mixtures. Due to the limitations of graphical representation, the column design method is directly applicable only to ternary mixtures. In practice, it is difficult to identify an intersection between liquid composition profiles in higher-dimensional composition space. Furthermore, the liquid composition profiles of multicomponent mixtures are very sensitive to the amount of trace components in the associated products. Nevertheless, the design method may be a basis for developing a design method for multicomponent mixtures.

The synthesis approach of Tao et al. (2003) is applicable to multicomponent mixtures. However, in this work, the extended synthesis approach for generating sequences using double-feed columns and columns with intermediate decanters are proposed for ternary mixtures. The reason for this limitation is that the feasibility test and column design method for those column configurations are only available for ternary mixtures. The proposed synthesis method may be readily extended to multicomponent mixtures if the separation feasibility in those column configurations for multicomponent mixtures can be assessed.

The synthesis of separation sequences employing double-feed columns may be time-consuming. The product feasibility in a double-feed column is evaluated using the boundary value method presented in Chapter 4 which requires fully specified product compositions. Further, some column design variables, e.g. feed rate ratio, top product composition, reflux ratio, reflux phase split ratio, may need to be varied to search for a feasible design. Generating sequences may be faster if there is a feasibility test method for establishing the product feasibility in a double-feed column without fully specified products and exhaustive search for feasible designs.

7.3 Future work

Multicomponent heterogeneous azeotropic mixtures are commonly encountered in industrial separations. For example, waste streams from printing and pharmaceutical factories usually contain acetone, ethyl acetate, ethanol, isopropanol, methyl-ethyl-ketone, isopropyl acetate, heptane, and water (Szanyi et al., 2005). The column design method developed for ternary mixtures in this work may facilitate the development of a design method for multicomponent mixtures. The sequence synthesis method presented in this thesis may be extended for the separation of multicomponent mixtures to include double-feed columns and columns with intermediate decanters if the separation feasibility in those column configurations can be evaluated.

The proposed synthesis approach may be extended to include other complex column configurations and options. In this work, the effect of temperature on the two-liquid phase region is not considered. The temperature has an effect on the solubility of heterogeneous mixtures. The two-liquid phase region may be amplified by decreasing the liquid temperature. In addition, the effect of pressure on the residue curve map is not included in the synthesis approach. The operating pressure of a column affects the existence and composition of azeotropes, as well as component volatilities, and hence the separation feasibility and economic performance of the column, in turn affecting the performance of separation sequences.

References

Barnicki, S.D. and Siirola, J.J., 1997, Separations process synthesis, *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th Ed., JohnWiley & Sons, New York.

Bausa, J., Watzdorf, R.V., Marquart, W., 1998, Shortcut methods for nonideal multicomponent distillation: 1. Simple columns, *AIChE J.,* **44**(10), 2181.

Bekiaris, N., Meski, G.A. and Morari, M., 1996, Mulitple steady states in heterogeneous azeotropic distillation, *Ind. Eng. Chem. Res.*, **35**(1), 207-227.

Berg, L. and Yeh, A.I., 1986, The breaking of ternary acetate-alcohol-water azeotropes by extractive distillation, *Chem. Eng. Commun.*, **48**, 93-101.

Biegler, L.T., Grossmann, I.E. and Westerberg, A.W., 1997, Systematic Methods of Chemical Process Design, Prentice Hall, New Jersey.

Brüggemann, S. and Marquardt, W., 2004, Shortcut methods for nonideal multicomponent distillation: 3. Extractive distillation columns, *AIChE J.*, **50**(6), 1129-1149.

Castillo, F.J.L., Thong, D.Y.-C. and Towler, G.P., 1998, Homogeneous azeotropic distillation. 1. Design procedure for single-feed columns at nontotal reflux, *Ind. Eng. Chem. Res.*, **37**(3), 987-997.

Castillo, F.J.L., Thong, D.Y.-C. and Towler, G.P., 1998, Homogeneous azeotropic distillation. 2. Design procedure for sequences of columns, *Ind. Eng. Chem. Res.*, **37**(3), 998-1008.

Chien, I.L., Zeng, K.-L., Chao, H.-Y. and Liu, J.H., 2004, Design and control of acetic acid dehydration system via heterogeneous azeotropic distillation, *Chem. Eng. Sci.*, **59**(21), 4547-4567.

Chronis, J.H. and Amrhein, M., 1980, Vapour-liquid equilibrium model for a partially miscible multicomponent system: isopropanol-acetone-ethanol-n-butnol-water, Oak Ridge National Laboratory.

Ciric, A.R., Mumtaz, H.S., Corbett, G., Reagan, M., Seider, W.D., Fabiano, L.A., Kolesar, D.M. and Widagdo, S., 2000, Azeotropic distillation with an internal decanter, *Comput. Chem. Eng.*, **24**(11), 2435-2446.

DETHERM database, 2007, Thermophysical properties of pure substances and mixtures, DECHEMA e.V., Frankfurt am Main, FIZ CHEMIE Berlin.

Diamond, D., Hahn, T., Becker, H. and Patterson, G., 2004, Improving the understanding of a novel complex azeotropic distillation process using a simplified graphical model and simulation, *Chem. Eng. Proc.* **43**(3), 483–493.

Doherty, M.F., and Caldarola, G.A., 1985, Design and synthesis of homogeneous azeotropic distillations. 3. The sequencing of columns for azeotropic and extractive distillations, *Ind. Eng. Chem. Fundam.,* **24**(4), 474-485.

Doherty, M.F. and Malone, M.F., 2001, Conceptual design of distillation systems, McGraw-Hill, International edition, Singapore.

Doherty, M.F. and Perkins, J.D., 1978, On the dynamics of distillation processes – I. The simple distillation of multicomponent non-reacting, homogeneous liquid mixtures, *Chem. Eng. Sci.*, **33**(3), 281-301.

Douglas, J.M., 1988, Conceptual Design of Chemical Processes, McGraw-Hill, International edition, Singapore.

Fidkowski, Z.T., Malone, M.F., and Doherty, M.F., 1991, Nonideal multicomponent distillation: Use of bifurcation theory for design, *AIChE J.,* **37**(12), 1761.

Fien, G.-J.A.F. and Liu, Y.A., 1994, Heuristic synthesis and shortcut design of separation processes using residue curve maps: a review, *Ind. Eng. Chem. Res.*, **33**(11), 2505-2522.

Francis, A.W. and Smith, N.O., 1969, Ternary liquid systems, *J. Chem. Educ.*, **46**(12), 815-820.

Gani, R. and Jørgensen, S.B., 1994, Multiplicity in numerical solution of non-linear models: separation processes, *Comput. Chem. Eng. (Suppl.)*, **18**, S55-S61.

Gaubert, M.A., Gerbaud, V., Joulia, X., Peyrigain, P.S. and Pons, M., 2001, Analysis and multiple steady states of an industrial heterogeneous azeotropic distillation, *Ind. Eng. Chem. Res.*, **40**(13), 2914-2924.

Gerrard, A.M., 2000, Guide to capital cost estimating, 4th Ed, Institution of Chemical Engineers, Warwickshire, UK.

Gomis, V., Ruiz, F. and Asensi, J.C., 2000, The application of ultrasound in the determination of isobaric vapour-liquid-liquid equilibrium data, *Fluid Phase Equilib.*, **200**, 245-259.

Hölz, S., 2006, Curve intersect, http://www.mathworks.co.uk/matlabcentral/fileexchange/8908.

Hooper, W.B. and Jacobs, L.J., 1979, Decantation, Handbook of Separation Techniques for Chemical Engineers, McGraw-Hill, New York.

HYSYS 2004.1, 2005, Aspen Technology, Inc., Cambridge, USA.

Jones, D.T. and Woods, D.R., 1986, Acetone-butanol fermentation revisited, *Microbiol. Rev.*, **50**(4), 484-524.

King, C.J., 1980, *Separation processes*, Chemical engineering series, McGraw-Hill, 2nd edition, New York.

Knapp, J.P. and Doherty, M.F., 1994, Minimum entrainer flows for extractive distillation: a bifurcation theoretic approach, *AIChE J.*, **40**(2), 243-268.

Koehler, J., Poellmann, P., and Blass, E., 1995, A review on minimum energy calculations for ideal and nonideal distillations, *Ind. Eng. Chem. Res.*, **34**(4), 1003-1020.

Kovach, J.W., III and Seider, W.D., 1987a, Heterogeneous azeotropic distillation – Homotopy-continuation methods, *Comput. Chem. Eng.*, **11**(6), 593-605.

Kovach, J.W., III and Seider, W.D., 1987b, Heterogeneous azeotropic distillation: Experimental and simulation results, *AIChE J.*, **33**(8), 1300-1314.

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

Lee, L.S., Chen, W.C. and Huang, J.F., 1996, Experiments and correlations of phase equilibria of ethanol-ethyl acetate-water ternary mixture, *J. Chem. Eng. Jpn.*, **29**(3), 427-438.

Lee, L.-S. and Shen, H.-C., 2003, Azeotropic behaviour of a water+n-propanol+ cyclohexane mixture using cyclohexane as an entrainer for separating the water+ n-propanol mixture at 760 mmHg, *Ind. Eng. Chem. Res.*, **42**(23), 5905-5914.

Levy, S.G., Van Dongen, D.B., Doherty, M.F., 1985, Design and synthesis of homogeneous azeotropic distillations. 2. Minimum reflux calculations for nonideal and azeotropic columns, *Ind. Eng. Chem. Fundam.,* **24**(4), 463.

Liu, G., 2003, Synthesis of multicomponent azeotropic separation sequences, PhD Thesis, UMIST, Manchester.

Liu, G., Jobson, M., Smith, R. and Wahnschafft, O.M., 2005, Recycle selection for homogeneous azeotropic distillation sequences, *Ind. Eng. Chem. Res.*, **44**(13), 4641-4655.

Malone, M.F., Marquez, F.E., Douglas, J.M., and Glinos, K., 1985, Simple, analytical criteria for the sequencing of distillation columns, *AIChE J.*, **31**(4), 683-689.

Marquardt, W., Kossack, S. and Kraemer, K., 2008, A framework for the systematic design of hybrid separation processes, *Chin. J. Chem. Eng.*, **16**(3), 333-342.

Müller, D. and Marquardt, W., 1997, Experimental verification of multiple steady states in heterogeneous azeotropic distillation, *Ind. Eng. Chem. Res.*, **36**(12), 5410-5418.

Moussa, A.S. and Jiménez, L., 2006, Entrainer selection and systematic design of heterogeneous azeotropic distillation flowsheets, *Ind. Eng. Chem. Res.*, **45**(12), 4304-4315.

Newsham, D.M.T. and Vahdat, N., 1977, Prediction of vapour-liquid-liquid equilibria from liquid-liquid equilibria. Part I: Experimental results for the systems methanol-water-n-butanol, ethanol-water-n-butanol and n-propanol-water-n-butanol, *Chem. Eng. J.*, **13**, 27-31.

Ou-yang, F., Wang, G. and Gao, W., 1985, Determination and correlation of liquid-liquid equilibrium data for the ternary systems water-ethyl acetate-acetic acid and water-butyl acetate-acetic acid, *Huagong Xuebao*, **36**(1), 110-118.

Perry, R.H., Green, D.W. and Maloney, J.O., 1984, Perry's Chemical Engineers's Handbook, 6th ed., McGraw-Hill, New York.

Peters, M.S., Timmerhaus, K.D. and West, R.E., 2003, Plant Design and Economics for Chemical Engineers, 5th Ed., McGraw-Hill, New York.

Pham, H.N., Ryan, P.J., Doherty, M.F., 1989, Design and minimum reflux for heterogeneous azeotropic distillation columns, *AIChE J.*, **35**(10), 1585.

Pham, H.N., and Doherty, M.F., 1990, Design and synthesis of heterogeneous azeotropic distillations-III. Column sequences, *Chem. Eng. Sci.*, **45**(7), 1845-1854.

Pucci, A., Mikitenko, P. and Asselineau, L., 1986, Three-phase distillation. Simulation and application to the separation of fermentation products, *Chem. Eng. Sci.*, **41**(3), 485-494.

Repke, J.U. and Wozny, G., 2002, Experimental investigations of three-phase distillation in a packed column, *Chem. Eng. Technol.*, **25**(5), 513-519.

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.

Ryan, P.J. and Doherty, M.F., 1989, Design/Optimization of ternary heterogeneous azeotropic distillation sequences, *AIChE J.*, **35**(10), 1382.

Sargent, R.W.H., 1998, A functional approach to process synthesis and its application to distillation systems, *Comput. Chem. Eng.*, **22**, 31-45.

Schad, R.C., 1994, Don't let recycle streams stymie your simulations, *Chem. Eng. Prog.*, **90**(12), 68-76.

Schneider, R., Wozny, G. and Fieg, G., 1997, Optimization of an Industrial Three Phase Distillation Column Train with Experimental Verification, *Comput. Chem. Eng. (Suppl.)*, **21**, S1131-S1136.

Seader, J.D. and Henley, E.J., 1998, Separation process principles, John Wiley & Sons, USA.

Siirola, J.J., 1996, Strategic process synthesis: Advances in the hierarchical approach, *Comput. Chem. Eng. (Suppl.)*, **20**, S1637-S1643.

Sinnott, R.K., 1993, Coulson & Richardson's Chemical Engineering, 2nd ed., Butterworth-Heinemann, Oxford.

Smith, R. 2005, Chemical Process Design and Integraion, John Wiley & Sons, UK.

Stichlmair, J.G., Fair, J.R. and Bravo, J.L., 1989, Separation of azeotropic mixtures via enhanced distillation, *Chem. Eng. Prog.*, **85**(1), 63-69.

Stichlmair, J.G. and Fair, J.R., 1998, Distillation: principles and practice, Wiley-VCH, New York.

Szanyi, A., Mizsey, P., and Fonyo, Z., 2005, Separation of highly non-ideal quaternary mixtures with extractive heterogeneous-azeotropic distillation, *Chem. Biochem. Eng.*, **19**(2), 111.

Tao, L., Malone, M.F. and Doherty, M.F., 2003, Synthesis of azeotropic distillation systems with recycles, *Ind. Eng. Chem. Res.*, **42**(8), 1783-1794.

Thong, D.Y.-C. and Jobson, M., 2001a, Multicomponent homogeneous azeotropic distillation 1. Assessing product feasibility, *Chem. Eng. Sci.*, **56**(14), 4369-4391.

Thong, D.Y.-C. and Jobson, M., 2001b, Multicomponent homogeneous azeotropic distillation 2. Column design, *Chem. Eng. Sci.*, **56**(14), 4393-4416.

Thong, D.Y.-C. and Jobson, M., 2001c, Multicomponent homogeneous azeotropic distillation 3. Column sequence synthesis, *Chem. Eng. Sci.*, **56**(14), 4417-4432.

Thong, D.Y.-C., Liu, G., Jobson, M. and Smith, R., 2004, Synthesis of distillation sequences for separating multicomponent azeotropic mixtures, *Chem. Eng. Process.*, **43**, 239-250.

Triantafyllou, C. and Smith, R., 1992, The design and optimisation of fully thermally coupled distillation columns, *Trans IChemE*, **70**, 118-132.

Turton, R., Bailie, R.C., Whiting, W.B. and Shaeiwitz, J.A., 2003, Analysis, synthesis, and design of chemical processes, 2^{nd} Ed., Prentice Hall, New Jersey.

Ulrich, G.D. and Vasudevan, P.T., 2006, How to Estimate Utility Costs, *Chemical Engineering*, **113**(4), 66-69.

Umeda, T.K., Niida, K. and Shiroko, K., 1979, A thermodynamic approach to heat integration in distillation systems, *AIChE J.*, **25**(3), 423-429.

Urdaneta, R.Y., Bausa, J., Bruggemann, S. and Marquardt, W., 2002, Analysis and conceptual design of ternary heterogeneous distillation processes, *Ind. Eng. Chem. Res.*, **41**(16), 3849-3866.

Urdaneta, R.Y., 2005, Targeting and conceptual design of heteroazotropic distillation processes, PhD Thesis, Process Systems Engineering, RWTH Aachen University, Aachen, Germany.

Van Acker, P.E., Mathieu, O., Milner, R.J. and Pacynko, W.F. 2000, Ester co-production, US patent 6,093,845.

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**(4), 454-463.

Vanage, P. V., 2005, Synthesis of ternary heterogeneous azeotropic reaction-separation systems, PhD Thesis, University of Manchester, Manchester, UK.

Wahnschafft, O.M., Le Rudulier, 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**(6), 1121-1141.

Wasylkiewicz, S.K., Kobylka, L.C. and Castillo, F.J.L., 2000, Optimal design of complex azeotropic distillation columns, *Chem. Eng. J.*, **79**, 219.

Wasylkiewicz, S.K., Kobylka, L.C. and Castillo, F.J.L., 2003, Synthesis and design of heterogeneous separation systems with recycle streams, *Chem. Eng. J.*, **92**(1-3), 201-208.

Westerberg, A.W., Lee, J.W. and Hauan, S., 2000, Synthesis of distillation-based processes for non-ideal mixtures, *Comput. Chem. Eng.*, **24**, 2043-2054.

Widagdo, S., Seider, W.D. and Sebastian, D.H., 1989, Bifurcation analysis in heterogeneous azeotropic distillation, *AIChE J.*, **35**(9), 1457-1472.

Widagdo, S. and Seider, W.D., 1996, Azeotropic distillation, *AIChE J.*, **42**(1), 96-130.

Appendix A

Calculation of rectifying profiles having multiple heterogeneous stages

This appendix describes the calculation of rectifying profiles having multiple heterogeneous stages in a column with an integrated decanter. Section A.1 presents the application of preliminary tests described in Chapter 3 for calculating a rectifying profile in a way that two liquid phases appear on many stages as possible. Section A.2 discusses the existence of multiple solutions of a heterogeneous stage in the rectifying section.

A.1 Preliminary tests

In this section, the preliminary tests presented in Chapter 3 are described in detail to demonstrate how to apply them for generating a rectifying profile having heterogeneous liquid on many stages as possible.

In a column with an integrated decanter, a reflux phase split ratio is a degree of freedom in column design as described in Chapter 3. The reflux phase split ratio may be specified such that the composition of a vapour entering the condenser lies on the vapour line ($\phi_1 = \phi_1^o$). Consequently, two liquid phases may appear on stages below the top stage of the column.

Liquid compositions on each stage of a rectifying section are calculated by solving material and energy balances simultaneously, using Newton's method, along with phase equilibrium. For a homogeneous liquid on stage n, the material and energy balances for the rectifying section are calculated by using Equations (A.1) and (A.2) (equations 3.10 and 3.11), respectively. Likewise, Equations (A.3) and (A.4) (equations 3.12 and 3.13) are used for a heterogeneous liquid.

$$\left(L_n^R + D\right)\mathbf{y}_{\mathrm{n+1}}^R - L_n^R\mathbf{x}_n^R - D\mathbf{x}_D = \mathbf{0} \tag{A.1}$$

$$\left(L_n^R + D\right)h_{n+1}^{R,V} - L_n^R h_n^{R,L} - Dh_D + Q_C = 0 \tag{A.2}$$

$$\left(L_n^R + D\right)\mathbf{y}_{n+1}^R - L_n^R\left(\left(1-\phi_n\right)\mathbf{x}_{\mathrm{n}}^{R,I} + \phi_n\mathbf{x}_{\mathrm{n}}^{R,II}\right) - D\mathbf{x}_D = \mathbf{0} \tag{A.3}$$

$$\left(L_n^R + D\right)h_{n+1}^{R,V} - L_n^R\left(\left(1-\phi_n\right)h_n^{R,L,I} + \phi_n h_n^{R,L,II}\right) - Dh_D + Q_C = 0 \tag{A.4}$$

As discussed in Section 3.2.1.2, for $\phi_1 = \phi_1^o$, the rectifying profile is firstly generated in such a way that two liquid phases appear on many stages as possible. The rectifying profile is calculated starting from the reflux composition until reaching the last stage where two liquid phases could appear. At the last heterogeneous stage, a number of liquid compositions are calculated for a range of phase split ratios of that stage. A number of rectifying profiles are then calculated continuing from the liquid compositions of the last heterogeneous stage until reaching their node pinches. Once the maximum number of heterogeneous stages is found, multiple rectifying profiles are generated further for ranges of phase split ratios of each heterogeneous stage.

To generate a rectifying profile having the maximum number of heterogeneous stages, the liquid compositions of the heterogeneous stages from stage 2 to a stage above the last stage that could be heterogeneous are calculated using the set of equations (A.3) and (A.4) together with the vapour-liquid-liquid equilibrium. When the rectifying profile calculation reaches the last stage that could be heterogeneous, the set of equations (A.3) and (A.4) cannot be solved along with the vapour-liquid-liquid equilibrium. The reason is that there is no vapour composition of stage n+1 ($\mathbf{y}_{n+1}^R$) lying on the vapour line while also satisfying material and energy balances (equations A.3 and A.4). Thus, the preliminary tests for checking whether the last heterogeneous stage is reached should be carried out before solving the set of equations (A.3) and (A.4). Otherwise, the Newton's method will be carried out unnecessarily as the set of equations (A.3) and (A.4) cannot be solved along with the vapour-liquid-liquid equilibrium.

The preliminary tests employ simple calculations to indicate that there is no solution for the set of equations (A.3) and (A.4) and the vapour-liquid-liquid equilibrium at the last heterogeneous stage. The tests consist of two main steps below. If two steps of the tests are satisfied, the next stage n+1 can be heterogeneous. Otherwise, stage n is the last stage where two liquid phases could appear, and the liquid composition of stage n+1 will lie outside the two-phase region.

Procedure of the preliminary tests

The algorithm is presented below, followed by a detailed discussion of its application and rationale.

a. Test if there will be a vapour composition of the next stage ($\mathbf{y}_{n+1}^{R}$) located on the vapour line that can satisfy the material balance, equation (A.3) or (3.12).

- *a.1 Determine the light and heavy liquid compositions of stage n ($\mathbf{x}_n^{R,I}$ and $\mathbf{x}_n^{R,II}$), which are in equilibrium with the vapour composition of stage n ($\mathbf{y}_n^{R}$), from the dew point calculation.*
- *a.2 Check whether a line connecting $\boldsymbol{x}_D$ and $\mathbf{x}_n^{R,I}$ or a line connecting $\boldsymbol{x}_D$ and $\mathbf{x}_n^{R,II}$ crosses the vapour line by using a line intersection search algorithm developed by Hölz (2006).*
- *a.3 If one of the lines crosses the vapour line, the liquid on the next stage ($\mathbf{x}_{n+1}^{R}$) may be heterogeneous. Go to step b. Otherwise, stage n is the last stage that heterogeneous liquid could appear on.*

b. If the previous test is satisfied, then test if there will be a vapour composition of the next stage ($\mathbf{y}_{n+1}^{R}$) located on the vapour line that can satisfy the energy balance, equation (A.4) or (3.13).

b.1 *If an intersection is found in step a, determine the minimum and maximum of the phase split ratios of stage n ($\phi_{n,min}$ and $\phi_{n,max}$) that cause the intersection between the vapour line and the line connecting $\mathbf{x}_D$ and $\mathbf{x}_n^R$.*

b.2 *determine the vapour compositions of the next stage ($\mathbf{y}_{n+1}^R$) lying on the vapour line and their enthalpies (h_{n+1}^V) corresponding to $\phi_{n,min}$ and $\phi_{n,max}$.*

b.3 *calculate ε, which is the error in the energy balance, from equation (A.5) or (3.17), for $\phi_{n,min}$ and $\phi_{n,max}$.*

b.4 *If one of ε is negative, the next stage n+1 can be heterogeneous because one positive and one negative value of ε implies that there is a value of ϕ_n for which ε is zero, and the energy balance is satisfied.*

$$\varepsilon = \left(L_n^R + D\right)h_{n+1}^{R,V} - L_n^R\left(\left(1-\phi_n\right)h_n^{R,L,I} + \phi_n h_n^{R,L,II}\right) - Dh_D + Q_C \tag{A.5}$$

To demonstrate the application of the preliminary tests, the separation of an acetic acid/water/n-butyl acetate mixture with the specifications in Table 3.1, when $\phi_1 = \phi_1^o = 0.5890$, is revisited. Here, the calculation of the rectifying profile at stage 2 from the top is described. The complete rectifying profiles with ten (maximum) heterogeneous stages are presented in Figure 3.8.

For the given top product and reflux ratio shown in Table 3.1, and $\phi_1 = \phi_1^o$, the rectifying profile starting from the reflux composition to stage 2 is calculated as follows. As $\phi_1 = \phi_1^o$, the top vapour composition ($\mathbf{y}_2^R$) is located on the vapour line as shown in Figure A.1. As a result, the liquid of stage 2 is heterogeneous. The coexisting light and heavy liquid compositions ($\mathbf{x}_2^{R,I}$ and $\mathbf{x}_2^{R,II}$), which are in equilibrium with $\mathbf{y}_2^R$, can be obtained from the vapour-liquid-liquid equilibrium. Before solving material and energy balances (equations A.3 and A.4) and the vapour-liquid-liquid equilibrium, the preliminary tests are carried out to check whether the liquid of stage 3 could be heterogeneous. If stage 3 could be heterogeneous, the set of equations (A.3) and (A.4) are solved together with the vapour-liquid-liquid equilibrium for $\mathbf{x}_2^R$, $\mathbf{y}_3^R$, L_2^R, and

$\mathbf{x}_3^{R,I}$ and $\mathbf{x}_3^{R,II}$. On the other hand, if the liquid of stage 3 cannot be homogeneous, stage 2 will be the last stage on which two liquid phases could appear, and multiple rectifying profiles will be generated from stage 2.

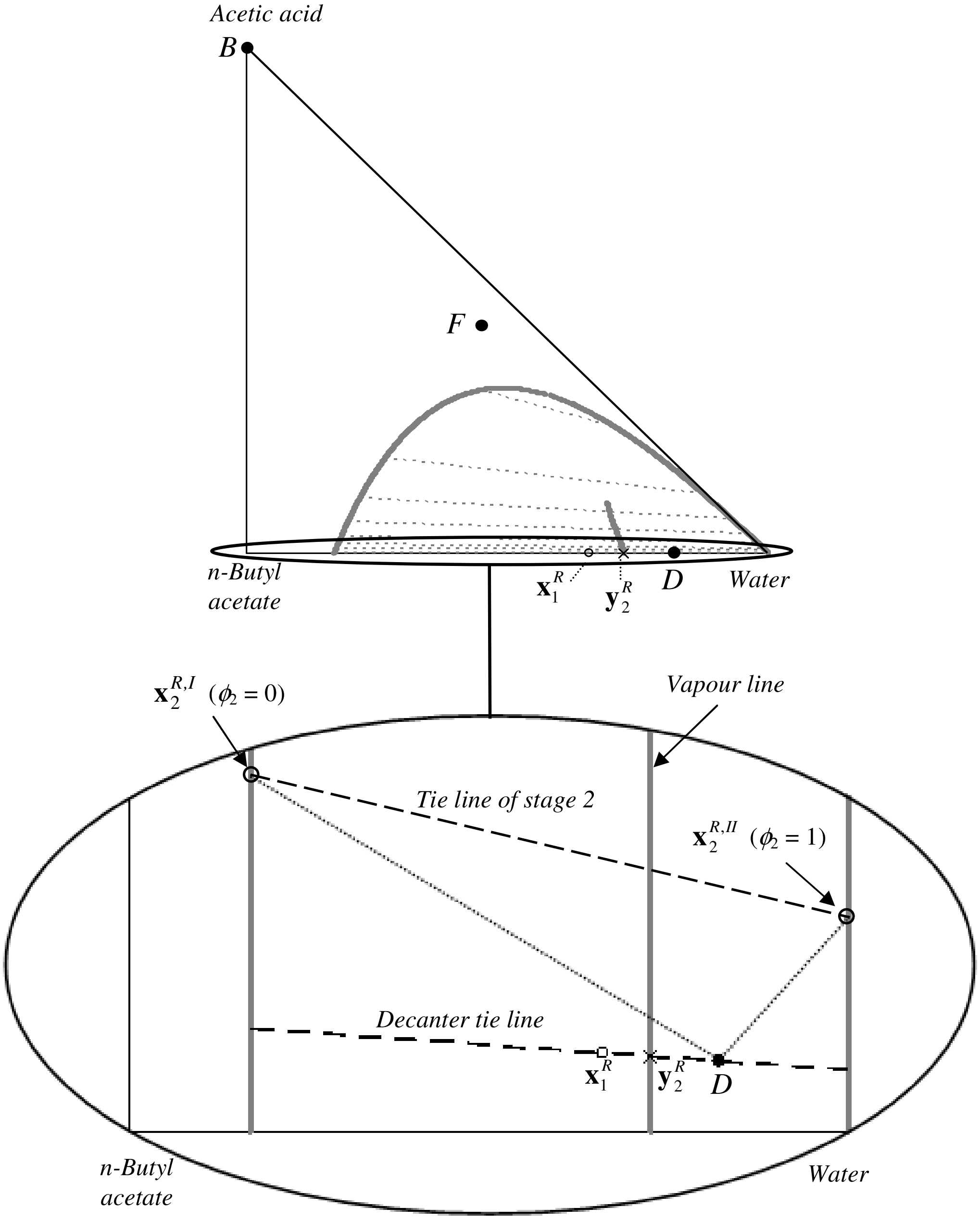


Figure A.1. Step *a* of the preliminary tests for the calculation of stage 2 from the top of the column with the specifications in Table 3.1 at $\phi_1 = \phi_1^o = 0.5890$.

The preliminary tests are carried out to check whether stage 3 could be heterogeneous as follows. For step *a.1*, the coexisting light and heavy liquid compositions ($\mathbf{x}_2^{R,I}$ and $\mathbf{x}_2^{R,II}$) in equilibrium with $\mathbf{y}_2^R$ are obtained from the vapour-liquid-liquid equilibrium. For step *a.2*, the top product composition ($\mathbf{x}_D$) is connected with $\mathbf{x}_2^{R,I}$ and $\mathbf{x}_2^{R,II}$ with straight lines as presented in Figure A.1. The line made up of $\mathbf{x}_D$ and $\mathbf{x}_2^{R,I}$ crosses the vapour line whereas the line connecting $\mathbf{x}_D$ and $\mathbf{x}_2^{R,II}$ does not. Having one of the lines crossing the vapour line indicates that there is a vapour composition of stage 3 ($\mathbf{y}_3^R$) locating on the vapour line that satisfies the material balance (A.3).

Step *a* of the tests is developed from the fact that the material balance over the rectifying section requires that the liquid composition of stage *n* ($\mathbf{x}_n^R$), the vapour composition of the next stage ($\mathbf{y}_{n+1}^R$) and the top product composition ($\mathbf{x}_D$) must lie on a straight line. Moreover, the vapour composition of the next stage ($\mathbf{y}_{n+1}^R$) must be on the vapour line for the liquid on the next stage *n*+1 to be heterogeneous. If an intersection is found in step *a*, the top vapour composition ($\mathbf{y}_{n+1}^R$) can be located on the vapour line, causing two liquid phases to appear on the stage *n*+1.

The procedure in step *b* of the tests is carried out as follows. Firstly, the minimum and maximum of the phase split ratios of stage 2 ($\phi_{2,min}$ and $\phi_{2,max}$) that give rise to the intersection between the vapour line and the line connecting $\mathbf{x}_D$ and $\mathbf{x}_2^R$ are determined. As shown in Figure A.1, the vapour line is crossed by the line connecting $\mathbf{x}_D$ and $\mathbf{x}_2^{R,I}$, the minimum phase split ratio ($\phi_{2,min}$) that causes the intersection is $\phi_2 = 0$. The maximum phase split ratio of stage 2 ($\phi_{2,max}$) is at the point where the tie line of stage 2 crosses the vapour line (see Figure A.2). Using the line intersection search algorithm developed by Hölz (2006), the liquid composition on the tie line of stage 2 at $\phi_{2,max}$ is obtained. The phase split ratio ($\phi_{2,max}$) corresponding to the liquid composition ($\mathbf{x}_2^R$) found from the intersection between the vapour line and the tie line of stage 2 is calculated from equation (A.6), which is $\phi_2 = 0.6682$ for this case.

$$\phi_n = \frac{x_{n,i}^{R} - x_{n,i}^{R,I}}{x_{n,i}^{R,II} - x_{n,i}^{R,I}} \qquad \text{for } i = 1, 2 \text{ or } 3 \qquad (A.6)$$

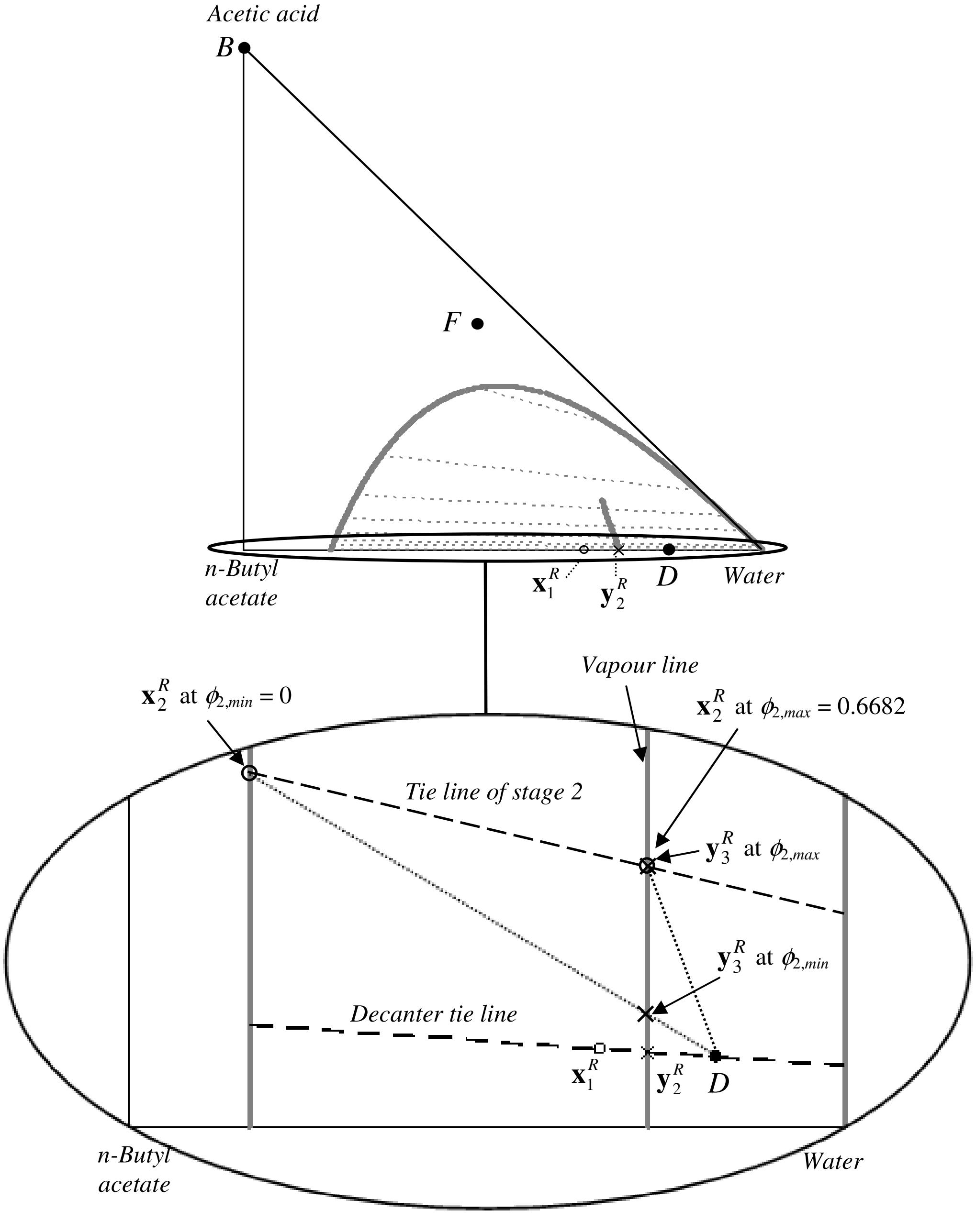


Figure A.2. Step *b*.1 of the preliminary tests for the calculation of stage 2 from the top of the column with the specifications in Table 3.1 at $\phi_1 = \phi_1^o = 0.5890$.

Once $\phi_{2,min}$ and $\phi_{2,max}$ are known, the next step (*b.2*) is to determine the vapour compositions of stage 3 ($\mathbf{y}_3^R$) locating on the vapour line and their enthalpies (h_3^V) corresponding to $\phi_{2,min}$ and $\phi_{2,max}$. The vapour compositions of stage 3 ($\mathbf{y}_3^R$) corresponding to $\phi_{2,min}$ and $\phi_{2,max}$ can be found from the intersection between the vapour line and the lines connecting $\mathbf{x}_D$ and $\mathbf{x}_2^R$ at $\phi_{2,min}$ and $\phi_{2,max}$ (see Figure A.2).

In step *b.3*, ε at $\phi_{2,min}$ and $\phi_{2,max}$, where ε is a deviation from zero in the energy balance, are calculated from equation (A.5), or (3.17). If one of ε is negative, there is a value of ϕ_2 and a vapour composition of stage 3 ($\mathbf{y}_3^R$) locating on the vapour line that satisfies the energy balance and stage 3 could be heterogeneous.

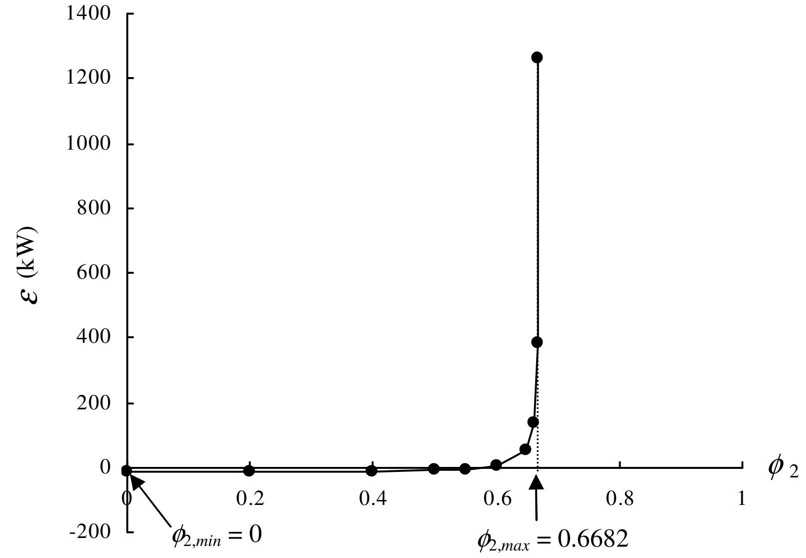


Figure A.3. The deviation from zero in the energy balance (equation A.4) at $\phi_{2,min} = 0$ and $\phi_{2,max} = 0.6682$, and at other ϕ_2.

Figure A.3 shows a plot of ε at $\phi_{2,min} = 0$ and $\phi_{2,max} = 0.6682$, and other values in between. The value of ε at $\phi_{2,min} = 0$ is negative whereas the value of ε at $\phi_{2,min} = 0.6682$ is positive. Having one of ε is negative indicates that there is a value of ϕ_2 leading to $\varepsilon =$

0. In other words, there is a value of ϕ_2 between $\phi_{2,min}$ and $\phi_{2,max}$ that causes vapour composition of stage 3 ($\mathbf{y}_3^R$) to be located on the vapour line while the energy balance (equation A.4) is satisfied. Therefore, stage 3 can be heterogeneous.

As the two steps of the tests are satisfied, the material and energy balances for the heterogeneous stage (equations A.3 and A.4, or 3.12 and 3.13) are solved simultaneously along with the vapour-liquid-liquid equilibrium. The solutions include $\mathbf{y}_3^R$, ϕ_2, L_2^R, $\mathbf{x}_3^{R,I}$ and $\mathbf{x}_3^{R,II}$. Once ϕ_2 is known, the overall liquid composition of stage 2 ($\mathbf{x}_2^R$) can be determined from equation (A.7), or (3.18).

$$\mathbf{x}_n^R \;=\; (1-\phi_n)\mathbf{x}_n^{R,I} + \phi_n\mathbf{x}_n^{R,II} \tag{A.7}$$

Note that, in step *b.1*, the $\phi_{2,max}$ is determined from the intersection between the vapour line and the tie line of stage 2 (Figure A.2). In case that the tie line of stage *n* does not cross the vapour line, the $\phi_{n,max}$ (or $\phi_{n,min}$) is determined in the following way. For instance, Figure A.4 shows the rectifying profile of the illustrative example described above is calculated until stage 9 from the top is reached. In this case, the vapour line does not cross the tie line of stage 9. In Figure A.4, the minimum phase split ratio of stage 9 ($\phi_{9,min}$) that causes the intersection between the vapour line and the $\mathbf{x}_D$- $\mathbf{x}_9^R$ line is $\phi_9 = 0$. The liquid composition ($\mathbf{x}_9^R$) corresponding to the maximum phase split ratio ($\phi_{9,max}$) is determined by extending the line connecting $\mathbf{x}_D$ and the end point of the vapour line until the line touches the tie line. The maximum phase split ratio ($\phi_{9,max}$) is then calculated from equation (A.6).

In summary, this section describes in detail the procedure of the preliminary tests carried out before solving the material and energy balances and the vapour-liquid-liquid equilibrium of a heterogeneous stage in the rectifying section. The preliminary tests are fast and use simple calculations to assess whether there is a solution for the material and energy balances (equations A.3 and A.4) and the vapour-liquid-liquid equilibrium.

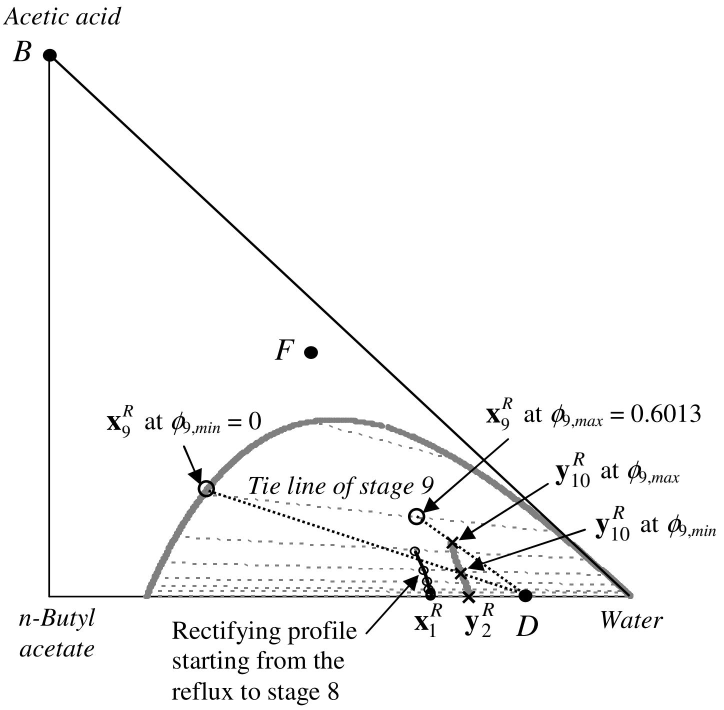


Figure A.4. Determining $\phi_{9,min}$ and $\phi_{9,max}$ that cause the intersection between $\mathbf{x}_D$ and $\mathbf{x}_9^R$ (step *b*.1) for the calculation of stage 9 from the top of the column with the specifications in Table 3.1 at $\phi_1 = \phi_1^o = 0.5890$.

A.2 Multiple solutions of a heterogeneous stage

When the rectifying profile is calculated starting from the reflux composition until the preliminary tests are no longer satisfied, this indicates that the last stage that could be heterogeneous is reached. At that stage, a number of rectifying profiles can be generated for a range of phase split ratios of that final heterogeneous stage, as will be discussed below.

For example, Figure A.5 shows the rectifying profile of the illustrative example discussed in Section A.1 calculated until stage 10 is reached. Carrying out the preliminary tests indicates that there is no liquid composition on the tie line of stage 10 ($\mathbf{x}_{10}^R$) that gives rise to an intersection between the vapour line and the $\mathbf{x}_D$-$\mathbf{x}_{10}^R$ line as presented in Figure A.5. Hence, stage 10 is the last stage on which a heterogeneous liquid can appear.

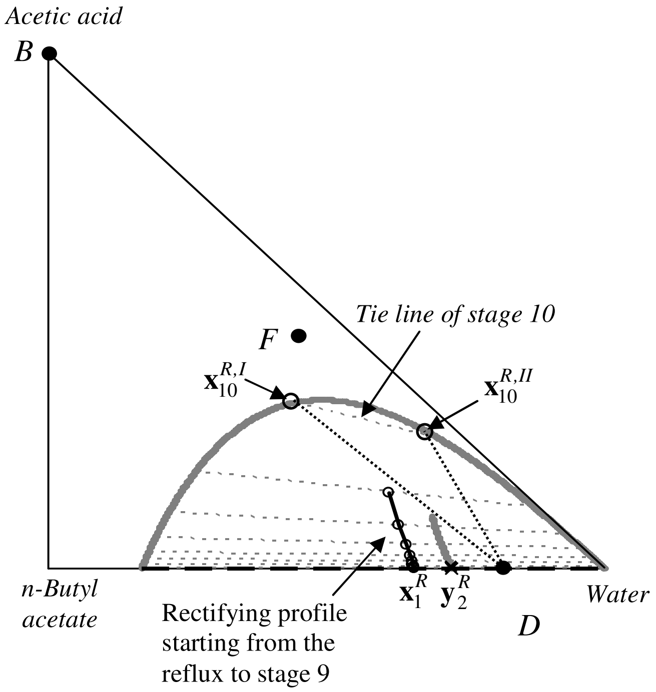


Figure A.5. The calculation at stage 10 from the top of the column with the specifications in Table 3.1 at $\phi_1 = \phi_1^o = 0.5890$.

For the last stage that could be heterogeneous, the set of equations (A.3) and (A.4) cannot be solved together with the vapour-liquid-liquid equilibrium. In other words, at the last stage, there is no vapour composition of stage 11 ($\mathbf{y}_{11}^R$) lying on the vapour line that satisfies the material and energy balances. However, there are several vapour compositions of stage 11 that satisfy the material and energy balances (equations A.3 and A.4) but they are not located on the vapour line, as will be illustrated below. Those vapour compositions ($\mathbf{y}_{11}^R$) can be determined by solving the set of equations (A.3) and (A.4) for various values of phase split ratios of stage 10 ranging from 0 to 1. The overall liquid composition of stage 10 ($\mathbf{x}_{10}^R$) corresponding to a value of ϕ_{10} can be calculated from equation (A.7). The tie line of stage 10 is thus the entire range of possible liquid compositions of stage 10.

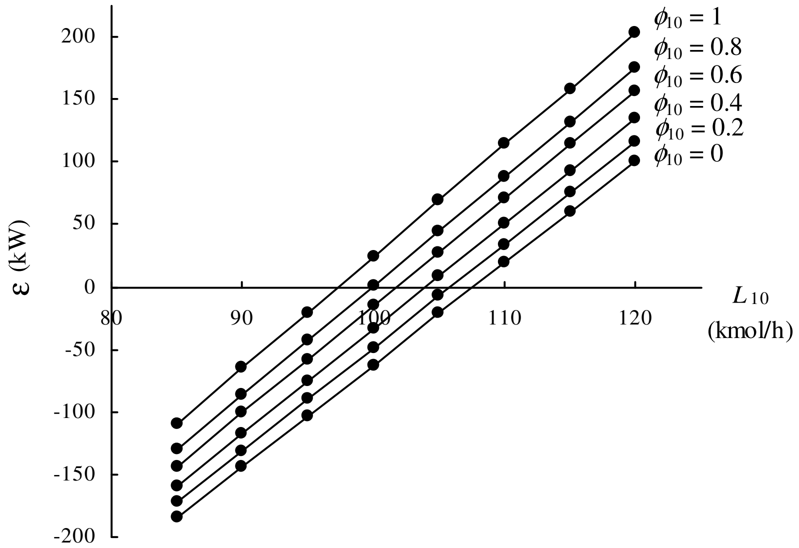


Figure A.6. The deviation from zero in the energy balance (equation A.5) at various ϕ_{10} ranging from 0 to 1

Figure A.6 shows the deviations from zero in the energy balance (equation A.5) at ϕ_{10} = 0 to 1 (step size of 0.2) corresponding to various values of $\mathbf{y}_{11}^{R}$ which are not located on the vapour line. The values of ε are calculated from equation (A.5) by guessing the liquid flow rate of stage 10 (L_{10}^{R}). As shown in Figure A.6, the energy balance (A.5) is satisfied, i.e. $\varepsilon = 0$, for the range of ϕ_{10} from 0 to 1. Multiple rectifying profiles can then be generated for the range of ϕ_{10} as shown in Figure 3.8.

As discussed in Section 3.2.1.2, liquid compositions of stage 10 ($\mathbf{x}_{10}^{R}$) are calculated for various values of ϕ_{10} using equation (A.7), or (3.18). For a value of ϕ_{10}, the vapour composition of stage 11 ($\mathbf{y}_{11}^{R}$), and the liquid rate of stage 10 (L_{10}^{R}) can be determined from material and energy balances (equations A.3 and A.4). The vapour composition of stage 11 ($\mathbf{y}_{11}^{R}$) satisfies the material and energy balances but it is not located on the vapour line, causing the liquid on stage 11 to be homogeneous.

For a rectifying profile with fewer heterogeneous stages, the phase split ratios of every heterogeneous stage ranging from 0 to 1 can also be the solutions of the material and energy balances (equations A.3 and A.4). For example, when the rectifying profile has nine heterogeneous stages as shown in Figure 3.9(b), the phase split ratios of stage 9 (ϕ_9) ranging from 0 to 1 can be the solutions of equations A.3 and A.4. However, there is only one value of ϕ_9 that causes the vapour compositions below stage 9 ($\mathbf{y}_{10}^{R}$) to lie on the vapour line and causes the liquid on stage 10 to be heterogeneous.

Although multiple rectifying profiles are generated for various phase split ratios of each heterogeneous stage, only the rectifying profiles that intersect with the stripping profile give rise to feasible column designs. The resulting column designs will have different numbers of heterogeneous stages and phase split ratios in the final heterogeneous stages. The existence of multiple column designs has been validated and presented in Sections 3.2.1.5 and 3.3.2.

Appendix B

Equipment cost estimation

The equipment cost estimation is carried out in two steps (Biegler et al., 1997): equipment sizing and costing. Once the equipment is sized, the capital cost can be estimated using correlations or cost data from literature as appropriate. The operating cost is calculated according to the energy requirement.

This section describes the method for estimating the capital and operating costs. It also presents the method for sizing columns, heat exchangers and decanters. After the capital and operating costs are calculated, the total annualised costs of separation units can be determined from the sum of annualised capital cost and operating cost. The total annualised cost can then be used as an indicator for screening design options.

B.1 Capital cost

The installed cost of a unit (C) is the cost of the equipment (C_{equip}) and the cost of installing the unit (Gerrard, 2000), as presented in equation B.1. The equipment cost data for each item of equipment (C_{equip}), which is a function of equipment size, material, and operating condition, can be found in the literature. The installed cost (C) is given by:

$$C = (1+F_{install})\, C_{equip} \tag{B.1}$$

where $F_{install}$ is overall installation factor given by equation B.2. The overall installation factor can be broken down into sub-factors (f_i) accounting for various engineering activities, e.g., piping, structural supports, instruments, electrical, insulation (Douglas, 1988).

$$F_{install} = f_{erection} + f_{piping} + f_{instruments} + f_{electrical} + f_{civil} + f_{structures\ and\ buildings} + f_{lagging} \quad \text{(B.2)}$$

Gerrard (2000) reported the values of these installation sub-factors (f_i) based on carbon steel equipment.

The cost data from the literature can be updated to the present year, for example using Equation B.3 where the Chemical Engineering Plant Cost Index (*CEPCI*) published in *Chemical Engineering* magazine is used (Smith, 2005). In this work, the cost data are taken from *Guide to Capital Cost Estimating* (Gerrard, 2000). The cost data for year 2000 are updated to year 2007 using the *CEPCI* of 394.1 and 525.4 for years 2000 and 2007, respectively.

$$\frac{Cost_{Year1}}{Cost_{Year2}} = \frac{Cost\ Index_{Year1}}{Cost\ Index_{Year2}} \quad \text{(B.3)}$$

B.1.1 Capital cost of a column (excluding heat exchanger)

The capital cost of a column is the sum of the costs of the column shell and trays (Peters et al., 2003). The cost of shell is proportional to the weight of column which is a function of column diameter, height, material, and operation condition. The cost of trays is a function of column diameter, the actual number of stages, and column internals. In this work, sieve trays are assumed. The cost data of carbon steel shell and trays is taken from *Guide to Capital Cost Estimating* (Gerrard, 2000). To estimate the capital cost of a column, the column is sized as follows.

The height of a column is estimated based on the actual number of stages. The height of the column (H) is given by Equation B.4 (Peters et al., 2003).

$$H = (N_{act} - 1)H_S + \Delta H \quad \text{(B.4)}$$

where N_{act} is the actual number of stages, H_S is the tray spacing, and ΔH is the additional height for vapour and liquid disengagement at the top and bottom of the column. The column height calculation is based on the overall tray efficiency of 70%, tray spacing of 0.46 m (18 in), and additional height of 4 m for phase disengagement (Triantafyllou and Smith, 1992).

The diameter of a column (D) is estimated by determining the vapour velocities at both ends of the column. Then, the vapour velocity that leads to the maximum diameter is selected. Assuming that the downcomer occupies 15% of the cross sectional area of column, the diameter of the column is calculated from Equation B.5 (Sinnott, 1993):

$$D = \sqrt{\frac{4V}{\pi(0.85u)}} \tag{B.5}$$

where V is the volumetric vapour flow rate, and u is the vapour velocity. The vapour velocity (u) is assumed to be 80% of flooding velocity (u_f) in the column. The flooding velocity (u_f) is calculated from Equation B.6 (Sinnott, 1993):

$$u_f = K_1\sqrt{\frac{\rho_L - \rho_V}{\rho_V}} \tag{B.6}$$

$$F_{LV} = \frac{L'}{V'}\sqrt{\frac{\rho_V}{\rho_L}} \tag{B.7}$$

where ρ_L is the density of liquid, ρ_V is the density of vapour, K_1 is a coefficient, L' is mass liquid flow rate, V' is mass vapour flow rate, and F_{LV} is a liquid-vapour flow factor. For $F_{LV} < 0.2$, K_1 is taken to be 0.75 for the tray spacing of 0.46 m (Biegler et al., 1997).

B.1.2 Capital costs of a heat exchanger

The capital cost of a heat exchanger is a function of total heat transfer area. The cost data of the heat exchanger is taken from *Guide to Capital Cost Estimating* (Gerrard, 2000).

The total heat transfer area (A) of a heat exchanger is given by:

$$A = \frac{Q}{U\, \Delta T_{LM}} \tag{B.8}$$

where Q is a heat duty of condenser or reboiler, ΔT_{LM} is the log mean temperature calculated from Equation (B.9).

$$\Delta T_{LM} = \frac{\left(T_{in}^{hot} - T_{out}^{cold}\right) - \left(T_{out}^{hot} - T_{in}^{cold}\right)}{ln\frac{\left(T_{in}^{hot} - T_{out}^{cold}\right)}{\left(T_{out}^{hot} - T_{in}^{cold}\right)}} \tag{B.9}$$

For the condenser,

$$\Delta T_{LM} = \frac{\left(T_D - T_{out}^{CW}\right) - \left(T_D - T_{in}^{CW}\right)}{ln\frac{\left(T_D - T_{out}^{CW}\right)}{\left(T_D - T_{in}^{CW}\right)}} \tag{B.10}$$

where T_D is the temperature of the top product, T_{in}^{CW} and T_{out}^{CW} are the inlet and outlet temperatures of the cooling water, respectively.

For the reboiler,

$$\Delta T_{LM} = T_{steam} - T_B \tag{B.11}$$

where T_B is the temperature of the bottom product, and T_{steam} is the steam temperature.

For condensers, the temperature of cooling water is taken to be 25^{o}C. A minimum temperature difference of 10^{o}C is assumed. The overall heat transfer coefficient (U) is estimated to be 600 W/m^2 K for a horizontal heat exchanger with the cooling water in the tube side and an organic vapour in the shell side (Perry et al., 1984).

For reboilers, steam at 446, 1135 and 3204 kPa (64.7, 164.7, and 464.7 psi) is assumed to be available for hot utility. A minimum temperature difference of 20^{o}C is assumed. The overall heat transfer coefficient (U) is assumed to be 1136 W/m^2 K for a heat exchanger with the steam in the tube side and an organic liquid in the shell side (Perry et al., 1984).

B.1.3 Capital cost of a decanter

The cost model of carbon steel horizontal pressure vessel (Equation B.12) is used for estimating the cost of a decanter (Peters et al., 2003). The decanter cost is proportional to the decanter weight which is a function of the diameter and length of the vessel.

$$Cost = 73\ weight^{-0.34} \tag{B.12}$$

where the cost is in US dollar and the weight of vessel is in kg.

The sizing of a decanter is carried out based on the method of Hooper and Jacobs (1979). The first step in decanter sizing is to predict which liquid phase is continuous and which phase is dispersed. The dispersed phase can be identified using a correlation in Equation (B.13) (Hooper and Jacobs, 1979):

$$\theta = \frac{q_L}{q_H}\left(\frac{\rho_L \mu_H}{\rho_H \mu_L}\right)^{0.3} \tag{B.13}$$

where q is volumetric flow rate, ρ is density, and μ is viscosity of light phase (L) and heavy phase (H). If $\theta < 0.5$, the light phase is the dispersed phase. If $\theta > 2$, the heavy phase is the dispersed phase. If $0.5 < \theta < 2$, a phase inversion is probable (Hooper and Jacobs, 1979).

The decanter will be designed such that the velocity of continuous phase is less than settling velocity of the droplets of dispersed phase. The settling velocity of droplets (u_D) is calculated from Equation B.14 derived from Stoke's law:

$$u_D = \frac{g d_D^2 (\rho_D - \rho_C)}{18 \mu_C} \tag{B.14}$$

where d is droplet diameter, g is gravitational acceleration, and subscripts C and D refer to the continuous and dispersed phase, respectively. A recommended design droplet diameter is 150 μm (Hooper and Jacobs, 1979).

The decanter diameter is then determined from Equation B.15, and the length of a decanter vessel is taken to be 5 times the diameter (Hooper and Jacobs, 1979).

$$D_{decanter} = \frac{1}{2}\sqrt{\frac{q_C}{u_D}} \tag{B.15}$$

B.1.4 Annualised capital cost

The capital cost is annualised over a fixed period at a fixed rate of interest by Equation B.16.

$$annualised\ capital\ cost = capital\,cost \times \frac{i\,(1+i)^n}{(1+i)^n - 1} \tag{B.16}$$

where *n* is the number of years, and *i* is an interest rate per year. A period of three years and an interest rate of 5% are used in calculating the annualised capital costs.

B.2 Operating cost

B.2.1 Steam cost

Steam at 446, 1135 and 3204 kPa (64.7, 164.7, and 464.7 psi) is assumed to be available for heating. The cost of the steam is calculated based on steam generation in a boiler using natural gas as a fuel. The boiler is assumed to have an efficiency of steam generation of 85% and distribution losses of 10% (Smith, 2005). Boiler feed water is available at 100^{o}C. The costs of steam at each pressure determined from Equation (B.17) (Smith, 2005) are shown in Table B.1. The average cost of the natural gas in 2007 is £0.13/m^3 (from *U.S. Energy Information Administration*, www.eia.doe.gov).

$$\begin{matrix}\text{Cost of}\\\text{steam}\end{matrix} = \begin{matrix}\text{Fuel}\\\text{cost}\end{matrix} \times \left(\begin{matrix}\text{Enthalpy}\\\text{of}\\\text{steam}\end{matrix} - \begin{matrix}\text{Enthalpy of}\\\text{boiler}\\\text{feedwater}\end{matrix}\right) \times \begin{matrix}\text{Overall}\\\text{boiler}\\\text{efficiency}\end{matrix} \tag{B.17}$$

Table B.1. Costs of steam at 446, 1135 and 3204 kPa (64.7, 164.7, and 464.7 psi)

Steam	Pressure (kPa)	Pressure (psi)	Cost	
			£/tonne	£/kW yr
LP	446	64.7	10.72	160
MP	1135	164.7	10.90	173
HP	3204	464.7	11.00	196

B.2.2 Cooling water cost

Cooling utility is assumed to be cooling water at 25°C. The unit cost of cooling water is taken to be 1% of the cost of power (Smith, 2005). The cost of electricity is calculated from Equation (B.18), (Ulrich and Vasudevan, 2006).

$$C_{S,elec} = a(CEPCI) + b(C_{S,f}) \tag{B.18}$$

where, $C_{S,elec}$ is the price of electricity in \$/kWh, a and b are the cost coefficients, *CEPCI* is the Chemical Engineering Plant Cost Index, and $C_{S,f}$ is the cost of fuel in \$/GJ. For the electricity purchased from outside the plant, a = 0.00013 and b = 0.010.

Based on the cost of natural gas of £0.13/m^3 and *CEPCI* of 252.4 in 2007, the cost of electricity calculated from equation (B.18) is £0.07/kWh. The cost of cooling water based on the electricity cost is £0.04/m^3 (£6.10/kW yr).

Appendix C

Validation of physical property models

C.1 Physical property models

This section presents the UNIQUAC and NRTL models, as applied in HYSYS 2004.1, used for predicting activity coefficients of the mixtures in case studies.

UNIQUAC (HYSYS 2004.1 user guide)

$$\begin{aligned} \ln\gamma_i = {} & \ln\left(\frac{\Phi_i}{x_i}\right) + 0.5Zq_i\ln\left(\frac{\theta_i}{\Phi_i}\right) + L_i - \left(\frac{\theta_i}{\Phi_i}\right)\sum_{j=1}^{n}L_jx_j \\ & + q_i\left(1-\ln\sum_{j=1}^{n}\theta_j\tau_{ji}\right) - q_i\sum_{j=1}^{n}\left(\frac{\theta_j\tau_{ij}}{\sum\limits_{k=1}^{n}\theta_k\tau_{kj}}\right) \end{aligned} \tag{C.1}$$

where $L_j = 0.5Z(r_j - q_j) - r_j + 1$

$$\theta_i = \frac{q_ix_i}{\sum\limits_j q_jx_j}$$

$$\tau_{ij} = exp-\left(\frac{a_{ij}+b_{ij}T}{RT}\right)$$

$$\Phi_i = \frac{r_ix_i}{\sum\limits_j r_jx_j}$$

γ_i = activity coefficient of component *i*

x_i = mole fraction of component *i*

T = temperature (K)

n = number of components

a_{ij} = non-temperature dependent energy parameter between components i and j (cal/mol)

b_{ij} = temperature dependent energy parameter between components i and j (cal/mol K)

q_i = van der Waals area parameter ($A_{w,i}/2.5e9$)

A_w = van der Waals area

r_i = van der Waals volume parameter ($V_{w,i}/15.17$)

V_w = van der Waals volume

NRTL (HYSYS 2004.1 user guide)

$$ln\,\gamma_i = \frac{\sum_{j=1}^{n}\tau_{ij}x_jG_{ji}}{\sum_{k=1}^{n}x_kG_{ki}} + \sum_{j=1}^{n}\frac{x_jG_{ji}}{\sum_{k=1}^{n}x_kG_{kj}}\left(\tau_{ij} - \frac{\sum_{m=1}^{n}x_m\tau_{mj}G_{mj}}{\sum_{k=1}^{n}x_kG_{kj}}\right) \tag{C.2}$$

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

$$\tau_{ij} = \frac{a_{ij} + b_{ij}T}{RT}$$

γ_i = activity coefficient of component i

x_i = mole fraction of component i

T = temperature (K)

n = number of components

a_{ij} = non-temperature dependent energy parameter between components i and j (cal/mol)

b_{ij} = temperature dependent energy parameter between component i and j (cal/mol K)

α_{ij} = NRTL non-randomness constant

C.2 Interaction parameters

This section presents interaction parameters for calculating activity coefficients in the models shown in Section C.1. All parameters are taken from HYSYS 2004.1 database.

C.2.1 Water/acetic acid/n-butyl acetate mixture

UNIQUAC-virial property package in HYSYS 2004.1 is used to predict the phase equilibrium of the water/acetic acid/n-butyl acetate mixture. The virial equation is selected for the vapour phase model as dimerisation of acetic acid occurs in the vapour phase. The binary parameters a_{ij} are listed in Table C.1. The binary parameters b_{ij} are all zero.

Table C.1. UNIQUAC interaction parameters (a_{ij}) for water/acetic acid/n-butyl acetate mixture from HYSYS 2004.1 (components in row and column representing component *i* and *j*, respectively)

Component	Water	Acetic acid	n-Butyl acetate
Water	-	427.741	738.169
Acetic acid	-305.452	-	712.235
n-Butyl acetate	398.290	-298.434	-

C.2.2 1-Propanol/water/1-butanol mixture

The phase equilibrium of 1-propanol/water/1-butanol mixture is predicted using UNIQUAC-ideal gas property package in HYSYS 2004.1. The UNIFAC-VLE model is used to estimate the UNIQUAC parameters (see Section C.3.2). The binary parameters a_{ij} are shown in Table C.2. The binary parameters b_{ij} are all zero.

Table C.2. UNIQUAC interaction parameters estimated by UNIFAC-VLE (a_{ij}) for 1-propanol/water/1-butanol mixture from HYSYS 2004.1 (components in row and column representing component *i* and *j*, respectively)

Component	1-Propanol	Water	1-Butanol
1-Propanol	-	414.781	9.289
Water	26.845	-	134.218
1-Butanol	-2.927	402.753	-

C.2.3 Acetone/water/1-butanol mixture

NRTL-ideal gas property package in HYSYS 2004.1 is used to predict phase equilibrium of acetone/water/1-butanol mixture. The interaction parameters a_{ij} and α_{ij} for the NTRL model are listed in Table C.3 and C.4, respectively. The interaction parameters b_{ij} are all zero.

Table C.3. NRTL interaction parameters (a_{ij}) for acetone/water/1-butanol mixture from HYSYS 2004.1 (components in row and column representing component *i* and *j*, respectively)

Component	Acetone	Water	1-Butanol
Acetone	-	1299.395	594.609
Water	750.318	-	570.136
1-Butanol	-85.730	2794.666	-

Table C.4. NRTL interaction parameters (α_{ij}) for acetone/water/1-butanol mixture from HYSYS 2004.1 (components in row and column representing component *i* and *j*, respectively)

Component	Acetone	Water	1-Butanol
Acetone	-	0.586	0.300
Water	0.586	-	0.470
1-Butanol	0.300	0.470	-

C.2.4 Ethyl acetate/water/n-butyl acetate mixture

UNIQUAC-ideal gas property package in HYSYS 2004.1 is used to predict the phase equilibrium of ethyl acetate/water/n-butyl acetate mixture. The interaction parameters a_{ij} are listed in Table C.5. The interaction parameters b_{ij} are all zero.

Table C.5. UNIQUAC interaction parameters (a_{ij}) for ethyl acetate/water/n-butyl acetate mixture from HYSYS 2004.1 (components in row and column representing component *i* and *j*, respectively)

Component	Ethyl acetate	Water	n-Butyl acetate
Ethyl acetate	-	151.642	49.355
Water	757.585	-	738.169
n-Butyl acetate	-36.183	398.290	-

C.3 Validation of phase equilibrium models

This section compares the phase equilibrium behaviour of mixtures predicted using thermodynamic models with published experimental data. DETHERM (thermophysical properties database system) is used to search for the experimental data of the mixtures at 1 atm. In this work, adjusting the interaction parameters to fit the experimental data is not attempted.

C.3.1 Water/acetic acid/n-butyl acetate mixture

The phase equilibrium of the water/acetic acid/n-butyl acetate mixture is predicted using UNIQUAC-virial property package and the interaction parameters in HYSYS 2004.1. This mixture has a heterogeneous azeotrope of water and n-butyl acetate. The composition and temperature of the azeotrope resulting from the UNIQUAC-virial model and the azeotropic data from experiment are presented in Table C.6. The compositions of vapour and two liquid phases corresponding to the heterogeneous azeotrope of water and n-butyl acetate are shown in Table C.7. Since no experimental vapour-liquid-liquid equilibrium data of the ternary mixture at 1 atm is reported, the liquid-liquid equilibrium at 50°C calculated using the thermodynamic model is compared with the experimental data, as shown in Figure C.1. Comparing with the experimental data, the UNIQUAC-virial model sufficiently predicts the phase equilibrium behaviour of the water/acetic acid/n-butyl acetate mixture.

Table C.6. Azeotropic data for the mixture of water (1), acetic acid (2) and n-butyl acetate (3)

	UNIQUAC-virial				Experimental data[a]			
	x_1	x_2	x_3	T (°C)	x_1	x_2	x_3	T (°C)
Water+n-butyl acetate	0.7225	-	0.2775	91.16	0.7220	-	0.2780	90.5

[a] Gomis et al. (2000)

Table C.7. Vapour-liquid-liquid equilibrium in binary systems for the mixture of water (1) and n-butyl acetate (3)

	UNIQUAC-virial			Experimental data[a]		
	x_1 or y_1	x_2 or y_2	x_3 or y_3	x_1 or y_1	x_2 or y_2	x_3 or y_3
Water+n-butyl acetate						
Organic phase	0.1671	-	0.8329	0.1760	-	0.8240
Aqueous phase	0.9985	-	0.0015	0.9990	-	0.0010
Vapour phase	0.7225	-	0.2775	0.7220	-	0.2780

[a] Gomis et al. (2000)

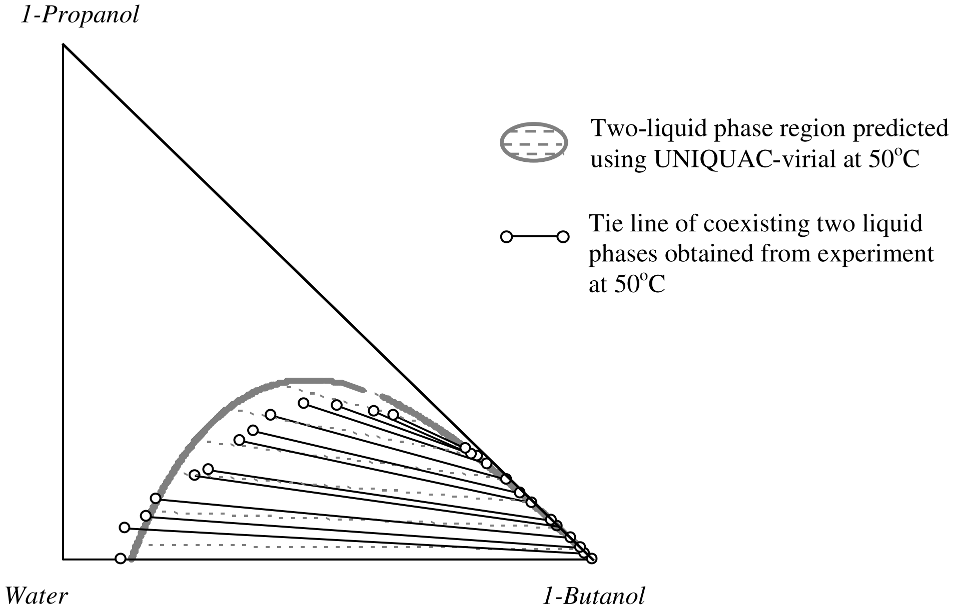


Figure C.1. Comparison of liquid-liquid equilibrium predicted using UNIQUAC-virial model and experimental liquid-liquid equilibrium data of Ou-yang et al. (1985) at 50°C

C.3.2 1-Propanol/water/1-butanol mixture

The phase equilibrium of the 1-propanol/water/-1-butanol mixture is predicted using UNIQUAC-ideal gas model and the interaction parameters estimated using UNIFAC-VLE model in HYSYS 2004.1. This mixture exhibits two binary azeotropes as listed in Table C.8 together with their compositions and temperatures calculated using the model and the azeotropic data from experiment. Figure C.2 presents the comparison of the vapour-liquid-liquid equilibrium resulting from the thermodynamic model and the experimental vapour-liquid-liquid equilibrium data.

Table C.8. Azeotropic data for the mixture of 1-propanol (1), water (2) and 1-butanol (3)

	UNIFAC-VLE				Experimental data			
	x_1	x_2	x_3	T (°C)	x_1	x_2	x_3	T (°C)
1-Propanol + water	0.4111	0.5889	-	88.44	0.427[a]	0.573[a]	-	87.5[a]
Water +1-Butanol	-	0.7662	0.2335	93.35	-	0.767[b]	0.233[b]	93.0[b]

[a] Lee and Shen (2003)
[b] Berg and Yeh (1986)

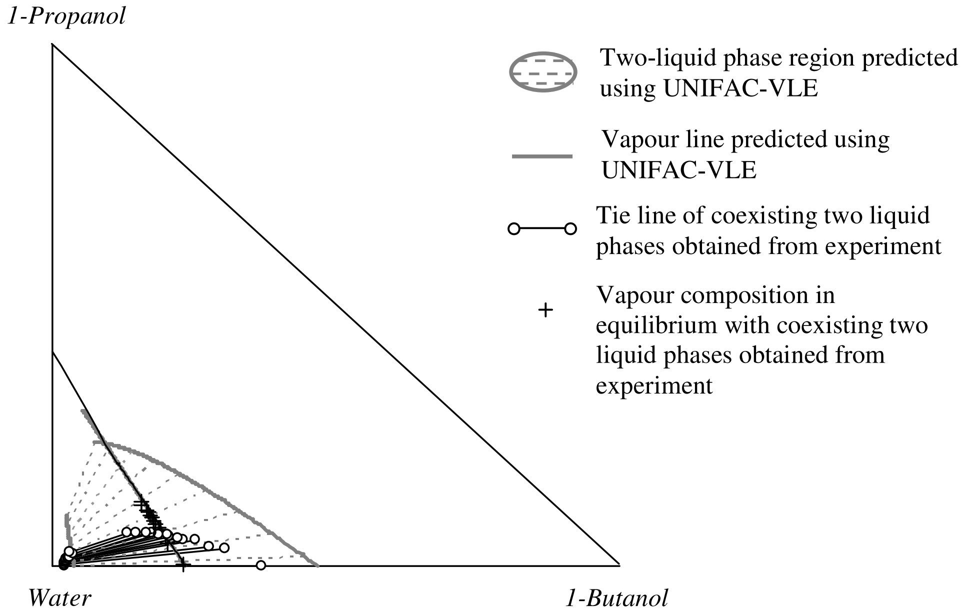


Figure C.2. Comparison of vapour-liquid-liquid equilibrium predicted using UNIFAC-VLE model and experimental vapour-liquid-liquid equilibrium data of Newsham and Vahdat (1997)

For this mixture, no other thermodynamic model with its default interactive parameters in HYSYS (e.g. NRTL, UNIQUAC) predicts the vapour-liquid-liquid equilibrium behaviour more accurately than the UNIQUAC model with the parameters estimated using UNIFAC-VLE. If the NRTL and UNIQUAC models with their default interaction parameters in HYSYS database are used, the binary mixture of 1-propanol and water is found to be partially miscible. If UNIFAC-LLE model is used to estimate the interaction parameters, the boiling heterogeneous envelope is found to be similar to the one shown in Figure C.2; however, the vapour line is poorly predicted comparing to the vapour line resulting from UNIFAC-VLE as shown in Figure C.2.

The UNIQUAC-ideal model together with the interaction parameters from UNIFAC-VLE is selected to predict the phase equilibrium behaviour of this mixture even though this model poorly predict the boiling heterogeneous envelope as shown in Figure C.2. The phase equilibrium behaviour may be predicted more accurately by adjusting the binary interaction parameters. Adjusting the interaction parameters is not attempted in this work since the mixture is taken only for demonstrating the column design procedure.

C.3.3 Acetone/water/1-butanol mixture

The phase equilibrium of the acetone/water/1-butanol mixture is predicted using NRTL-ideal gas model and the interaction parameters in HYSYS 2004.1. This mixture has a heterogeneous azeotrope of water and 1-butanol. The composition and temperature of the azeotrope predicted using the phase equilibrium model and the experimental data are presented in Table C.9. Figure C.3 shows the comparison of the vapour-liquid-liquid equilibrium resulting from the NRTL-ideal gas model and experimental equilibrium data. The vapour-liquid-liquid equilibrium of this mixture is adequately represented using the NRTL-ideal gas model.

Table C.9. Azeotropic data for the mixture of acetone (1), water (2) and 1-butanol (3)

	NRTL-ideal gas				Experimental data[a]			
	x_1	x_2	x_3	T (°C)	x_1	x_2	x_3	T (°C)
Water +1-Butanol	-	0.7745	0.2254	93.3	-	0.767	0.233	93.0

[a] Berg and Yeh (1986)

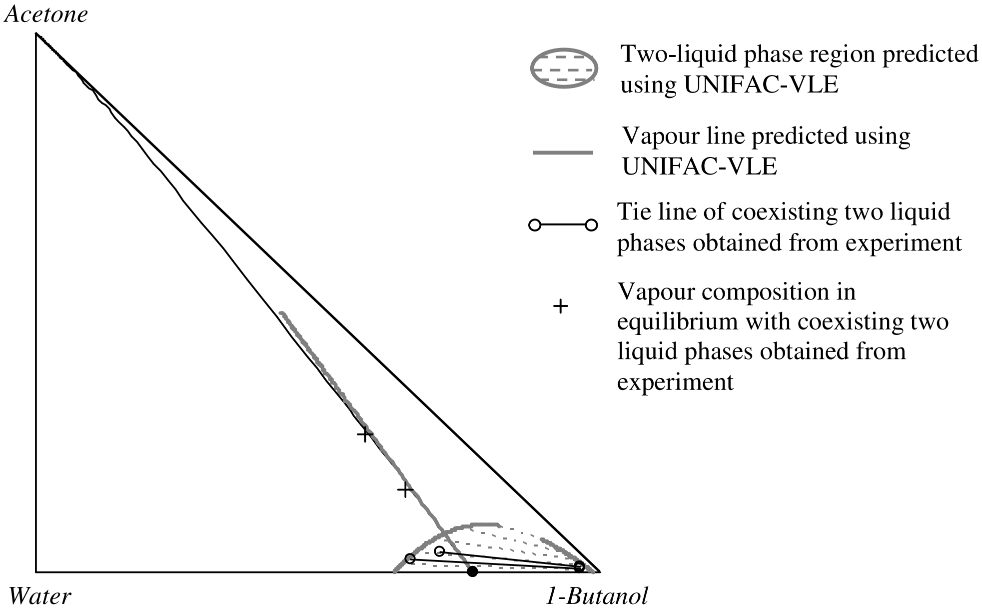


Figure C.3. Comparison of vapour-liquid-liquid equilibrium predicted using NRTL model and experimental vapour-liquid-liquid equilibrium data of Chronis and Amrhein (1980)

C.3.4 Ethyl acetate/water/n-butyl acetate mixture

The phase equilibrium of the ethyl acetate/water/n-butyl acetate mixture is predicted using UNIQUAC-ideal gas property package and the interaction parameters in HYSYS 2004.1. This mixture exhibits two heterogeneous azeotropes. The compositions and temperatures of the azeotropes resulting from the thermodynamic model and the azeotropic data from experiment are presented in Table C.10. The compositions of vapour and two liquid phases corresponding to the two heterogeneous azeotropes are shown in Table C.11. For this mixture, no experimental vapour-liquid-liquid equilibrium data of ternary system at 1 atm is reported. The liquid-liquid envelope at 35°C calculated using the model is compared with the experimental data at the same temperature, as shown in Figure C.4. Comparing with the experimental data, the UNIQUAC-ideal gas model sufficiently predicts the phase equilibrium of the ethyl acetate/water/n-butyl acetate mixture.

Table C.10. Azeotropic data for the mixture of ethyl acetate (1), water (2) and n-butyl acetate (3)

	UNIQUAC-ideal gas				Experimental data			
	x_1	x_2	x_3	T (^{o}C)	x_1	x_2	x_3	T (^{o}C)
Ethyl acetate + water	0.6844	0.3156	-	71.04	0.6870[a]	0.3130[a]	-	71.0[a]
Water + n-Butyl acetate	-	0.7231	0.2769	91.19	-	0.7220[b]	0.2780[b]	90.5[b]

[a] Lee et al. (1996)
[b] Gomis et al. (2000)

Table C.11. Vapour-liquid-liquid equilibrium in binary systems for the mixture of ethyl acetate (1), water (2) and n-butyl acetate (3)

	UNIQUAC-ideal gas			Experimental data		
	x_1 or y_1	x_2 or y_2	x_3 or y_3	x_1 or y_1	x_2 or y_2	x_3 or y_3
Ethyl acetate+water						
Organic phase	0.7754	0.2246	-	0.7760[a]	0.2240[a]	-
Aqueous phase	0.0247	0.9753	-	0.0120[a]	0.9980[a]	-
Vapour phase	0.6844	0.3156	-	0.6870[a]	0.3130[a]	-
n-Butyl acetate+water						
Organic phase	-	0.1672	0.8328	-	0.1760[b]	0.8240[b]
Aqueous phase	-	0.9985	0.0015	-	0.9990[b]	0.0010[b]
Vapour phase	-	0.7231	0.2769	-	0.7220[b]	0.2780[b]

[a] Lee et al. (1996)
[b] Gomis et al. (2000)

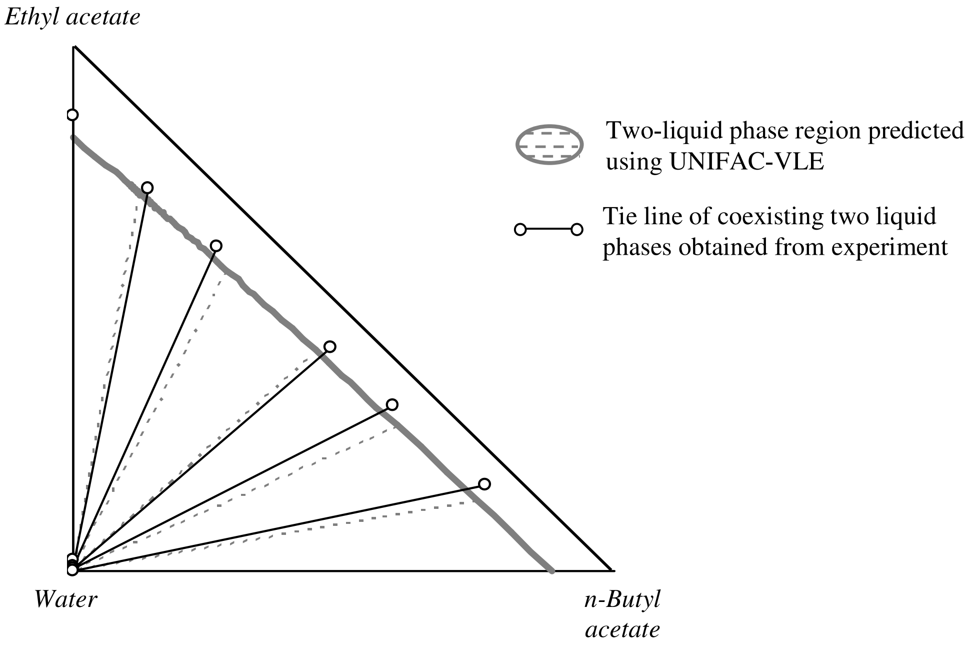


Figure C.4. Comparison of liquid-liquid equilibrium predicted using UNIQUAC-ideal gas model and experimental liquid-liquid equilibrium data of Berg and Yeh (1986) at 35^{o}C

Appendix D

MATLAB-HYSYS Interface for generating process stream data

HYSYS can be accessed from external software, such as Visual Basic and Excel, using a method called automation (HYSYS 2004.1 User Guide). By writing code in the external software, information of a stream or unit operation can be sent to and received from HYSYS.

HYSYS can also be accessed from MATLAB. However, the procedure to link MATLAB and HYSYS is not provided in HYSYS 2004.1 User Guide. An example to demonstrate the interface between MATLAB and HYSYS is described below.

Example: Bubble point calculation of a saturated liquid mixture having 50 mol% water, 10 mol% acetic acid and 40 mol% n-butyl acetate at 1 atm. (Property package: UNIQUAC-Virial model)

In HYSYS,

1. Specify components, i.e. water (1), acetic acid (2) and n-butyl acetate (3). Choose fluid property package, i.e. UNIQUAC-Virial model.
2. Create a material stream (named 'STREAM'). The pressure, vapour fraction, temperature, flow rate and composition of the stream can be given from MATLAB.
3. Create a spreadsheet (named 'SPRDSHT-STREAM'). This spreadsheet is used for receiving mole fractions of the stream from MATLAB and sending them to the material stream created in the previous step.

3.1 The mole fractions of the stream sent from MATLAB will be stored in cells A1 (for water), A2 (for acetic acid) and A3 (for n-butyl acetate).

3.2 Define the values in cells B1, B2 and B3 to be equal to those in cells A1, A2 and A3, respectively.

3.3 Make connections between cells B1, B2 and B3 and mole fractions of the material stream created in step 2 using 'Exported Variables' in 'Connections' tap of the spreadsheet.

4. Keep HYSYS open with only one active file and flowsheet.

MATLAB code

```
% Specify mole fractions of the ternary mixture
      xf = [0.5,0.1,0.4];

% Invoke MATLAB-HYSYS communication
      h = actxserver('HYSYS.Application');
% Active the HYSYS document and the flowsheet being opened in HYSYS
      hActive = h.ActiveDocument;
      hFlowsheet = hActive.Flowsheet;

% Connect to HYSYS Solver
      hSolver = hActive.Solver;

% Link to the material stream 'STREAM'
      hSTREAM = hFlowsheet.Streams.Item('STREAM');
% Link to the spreadsheet 'SPRDSHT-STREAM'
      hSprd = hFlowsheet.Operations.Item('SPRDSHT-STREAM');
% Link to cell A1 in 'SPRDSHT-STREAM'
      hCellA1 = hSprd.Cell('A1');
% Link to cell A2 in 'SPRDSHT-STREAM'
      hCellA2 = hSprd.Cell('A2');
% Link to cell A3 in 'SPRDSHT-STREAM'
      hCellA3 = hSprd.Cell('A3');

% Set the pressure of 'STREAM' to be 1 atm
      hSTREAM.Pressure.SetValue(1, 'atm');
% Set the vapour fraction of 'STREAM' as saturated liquid
      hSTREAM.VapourFraction.SetValue(0);
% Turn HYSYS Solver off
      hSolver.CanSolve = 0;
% Delete the current value in cell A1 in 'SPRDSHT-STREAM'
      hCellA1.Erase;
% Delete the current value in cell A2 in 'SPRDSHT-STREAM'
      hCellA2.Erase;
% Delete the current value in cell A3 in 'SPRDSHT-STREAM'
      hCellA3.Erase;
% Set the mole fraction of component 1 (water) in cell A1 in
'SPRDSHT-STREAM'
      hCellA1.CellValue = xf(1);
% Set the mole fraction of component 2 (acetic acid) in cell A2 in
```

```
'SPRDSHT-STREAM'
      hCellA2.CellValue = xf(2);
% Set the mole fraction of component 3 (n-butyl acetate) in cell A3 in
'SPRDSHT-STREAM'
      hCellA3.CellValue = xf(3);

% Turn HYSYS Solver on (HYSYS automatically determines phase
equilibrium)
      hSolver.CanSolve = 1;

% Define 'hDplSTREAM' to use for retrieving phase equilibrium data
      hDplSTREAM = hSTREAM.DuplicateFluid;
% Get the composition of light liquid phase in equilibrium with xf
      LL = hDplSTREAM.LightLiquidPhase.MolarFractionsValue;
% Get the composition of heavy liquid phase in equilibrium with xf
      HL = hDplSTREAM.HeavyLiquidPhase.MolarFractionsValue;
% Get the composition of vapour phase in equilibrium with xf
      V = hDplSTREAM.VapourPhase.MolarFractionsValue;
% Get the boiling temperature (°C)
      Temp = hDplSTREAM.TemperatureValue;
% Get the molar enthalpy of light liquid phase (kJ/kmol)
      H_LL = hDplSTREAM.LightLiquidPhase.MolarEnthalpyValue;
% Get the molar enthalpy of heavy liquid phase (kJ/kmol)
      H_HL = hDplSTREAM.HeavyLiquidPhase.MolarEnthalpyValue;
% Get the molar enthalpy of vapour phase (kJ/kmol)
      H_V = hDplSTREAM.VapourPhase.MolarEnthalpyValue;
```

Results:

	Overall liquid	Light liquid phase	Heavy liquid phase	Vapour phase
Composition (mole fraction)				
Water	0.5	0.2211	0.9224	0.7117
Acetic acid	0.1	0.1181	0.0727	0.0311
n-Butyl acetate	0.4	0.6609	0.0050	0.2572
Molar enthalpy (kJ/kmol)		-4.5462×10^5	-2.9360×10^5	-3.0594×10^5
Boiling temperature (^{o}C)	92.64			