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NEW APPROACH TO THE DESIGN AND OPTIMIZATION OF ENERGY EFFICIENT CHEMICAL PROCESSES

BY

AMIT AMALE

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
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IN
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DOCTOR OF PHILOSOPHY DISSERTATION

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DEAN OF THE GRADUATE SCHOOL

UNIVERSITY OF RHODE ISLAND
2008

ABSTRACT

Energy use in many process industries is dominated by separation processes. As energy costs are rising rapidly, there is a renewed interest in better methodologies for the synthesis, design and/or retrofitting of separation processes. In this thesis, a novel method for determining energy efficient process designs based on finding the separation with the shortest stripping line distance is proposed. A problem formulation based on mixed integer nonlinear programming (MINLP) is given and a global optimization algorithm is presented for determining energy efficient process designs. A variety of examples of separations involving ideal, non-ideal, azeotropic and reactive mixtures are used to demonstrate the versatility and advantages of the shortest stripping line distance approach over available methods in literature. One of the major advantages of the proposed methodology is that it can be used to identify minimum energy requirement for multi-unit processes such as hybrid separations involving extraction followed by distillation and reaction/separation/recycle processes.

The proposed shortest stripping line distance method is extended and a two-level distillation design procedure is developed for finding portfolios of minimum energy designs when specifications are given in terms of key component recoveries. It is shown that the proposed two-level design procedure is flexible and can find minimum energy designs for both zeotropic and azeotropic distillations. It is also shown that the two-level design method encompasses Underwood's solution, when it exists, and can find minimum energy designs when Underwood's method is not applicable. This two-

level design approach also overcomes the well-know limitation of distillation line methods of sensitivity of column profiles to the product compositions.

Non-pinched, minimum energy distillation designs are an important and often overlooked class of distillation designs that provided added economic advantages in practice. All current methods for designing distillation columns available in literature are based on the concept of pinch points and are incapable of finding non-pinched, minimum energy solutions. In contrast, it is demonstrated that shortest stripping line distance approach is capable of systematically and reliably finding non-pinched, minimum energy distillation designs as well as providing insights into the reasons for the existence of non-pinched, minimum energy design. These reasons include trajectories that follow unstable branches of a pinch point curve in azeotropic systems, the inherent looping structure of trajectories in hydrocarbon separations, and the presence of ancillary constraints in multi-unit processes like extraction/distillation.

Several examples are studied and many numerical results and geometric illustrations are presented in each section show that the shortest stripping line distance methodology is indeed a powerful and versatile tool for designing energy efficient processes and can be considered as a next generation method for conceptual design of energy efficient chemical processes.

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PREFACE

This thesis is written in the manuscript format. Chapter 1 is published in Computers and Chemical Engineering in 2008. The basic formulation of a novel method for designing energy efficient separation processes based on finding the shortest separation (stripping) line and the algorithm to implement this method is the subject of this chapter.

Chapter 2 has already been published in Industrial Engineering and Chemistry Research in 2006. Chapter 2 focuses on the use of the shortest stripping line approach for designing energy efficient multi-unit processes. In particular, the synthesis of hybrid separation process for purification of acetic acid from water –acetic acid mixtures using extraction with ethyl acetate followed by distillation is discussed.

Chapter 3 has been submitted to AIChE Journal and is under review. In this chapter, the concept of shortest stripping line is extended to develop a novel two-level design method for generating portfolios of promising energy efficient designs that meet required criteria on key component recoveries. A detailed algorithm for implementing this two-level design approach and its advantages over conventional methods are discussed with the help of various examples in this chapter.

Chapter 4 is in press in Chemical Engineering Research and Design (doi:10.1016/j.cherd.2008.02.017). This chapter discusses the use of the shortest

stripping line method for identifying non-pinched, minimum energy designs-an important class of minimum energy designs that is poorly understood in the literature. A detailed description of how the shortest stripping line distance methodology can be used to systematically and intelligently find these non-pinched, minimum energy designs and more importantly, to understand the reasons behind there existence is given in this manuscript.

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INTRODUCTION

Separation processes play an important role in chemical, petrochemical, pharmaceutical and related industries. Distillation is the most important and versatile separation process available to date and will continue to be so in the near future. With the rapid increase in global energy costs, it is not only critical to design distillation and other separation processes in energy efficient ways but also to develop newer and less energy intensive ways to perform separation tasks. Hybrid processes such as extraction/distillation appear to be one promising alternative as they have the ability to handle both the throughput and product purities of distillation processes and, at the same time, reduce processing cost significantly.

There are an estimated 40,000 distillation columns in the U.S. Rough estimates put the energy consumed by distillation alone around 6% of the total energy in the U.S. Many of the existing distillation columns are more than 20-30 years old and were designed using methods that were developed when energy was far less expensive. Retrofitting these columns to save energy and designing newer replacements will be an on-going task in the process industry as energy costs continue to rise.

Shortcut design methods play an important role in conceptual process design, especially for separation processes. Conceptual or shortcut methods are often used for screening promising alternatives among a larger set of possible designs. They are also used to get quick estimates of capital and operating costs. A good shortcut design method can save time and effort and also lead to more innovative, creative and effective design solutions.

Attempts to design distillation columns in a systematic way started in the early 1900s. McCabe and Thiele (1925) developed a method for the conceptual design of distillation columns for binary mixtures. Underwood, on the other hand, developed a shortcut method in 1932 for finding minimum energy requirements for the distillation of multi-component mixtures. As separation processes are energy intensive, the rise in the cost of energy has spawned renewed interest in methods for designing energy efficient chemical processes.

Motivation

As mentioned earlier, methods for conceptual process design were available as early as 1925. Underwood's method, which first appeared in 1932, is perhaps the most famous and widely used shortcut design method and specifically addresses the issue of energy consumption. This method is presently included in most commercially available simulation programs (e.g., Aspen Plus, ProII, etc.). In addition to Underwood's method, there are several other methods that have been developed in recent years that are capable of finding minimum energy requirements for separating a multi-component mixture by distillation. These methods include the boundary value methods of Doherty and co-workers, the rectifying body method, and V_{min} diagrams. A detailed survey of these methods is included in the chapters to follow.

Though there are several methods for finding minimum energy requirements for separation processes, most of them have serious limitations. For example, Underwood's method is really only applicable when phase behavior of the system can be well approximated by constant relative volatilities; thus it can not be used for azeotropic mixtures. In addition, the performance of a given separation unit often depends on an upstream process such as a reactor or an extractor. In these cases, one needs to consider the reactor-separator configuration or the extraction unit simultaneously when designing a process with overall energy efficiency. It is rather surprising that there are no shortcut methods in the literature that allow one to find minimum energy requirements and corresponding operating conditions for these multi-unit processes. Hence, there is a need for a design methodology that will both unify all existing methods for finding minimum energy requirement in chemical processes and overcome the limitations of existing shortcut methods with regard to their inherent reliance on pinch points, their sensitivity to product compositions, and their inability to handle multi-unit processes. The main objective of this research project was to develop a versatile shortcut method for conceptual design of separation and other chemical processes that will fulfill these needs.

Background

Residue curve maps have long been used during the early stages of synthesis and design to provide insight into feasibility and limitations of separation by distillation, particularly for azeotropic mixtures. Residue curve maps were first proposed by Ostwald[1,2] and independently by Schreinemakers [3]. The concept of a residue curve is simple. If one places a liquid mixture of known composition in a single stage batch vessel without reflux (i.e., simple distillation), adds heat to keep the liquid boiling, removes the vapor produced immediately and plots the composition of the liquid residue as a function of time until the last drop of liquid is vaporized, then the resulting trajectory of liquid compositions is called a residue curve. Analytically, a residue curve is a trajectory that represents the solution to the set of ordinary differential mass balance and algebraic phase equilibrium equations that model a simple distillation. The collection of all residue curves for different starting compositions is called a residue curve map. See Figure 1.

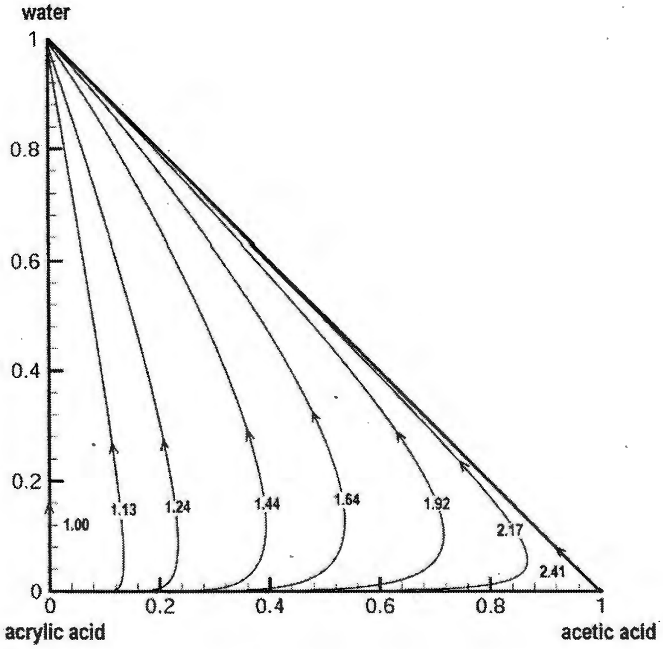

Figure 1: Residue Curve Map and Line Integrals for Acetic Acid/ Water/ Acrylic Acid

Though derived from the analysis of simple distillation, residue curve maps provide good approximations to liquid composition profiles in continuous distillation at total reflux. This approximation is often good enough for analysis at the conceptual design stage. For azeotropic systems, residue curve maps also help to identify different distillation regions or boundaries for a given mixture.

While the first papers on residue curve maps appeared at the beginning of the 19th century, they have received renewed attention in the last 20 years or so. There are several recent review papers on residue curve maps – for example, the paper by Pollmann and Blass[7] and the work of Kiva et al.[8]

Recently, Lucia and Taylor[9] have shown that exact distillation boundaries correspond to residue curves with locally longest line integral that connect the unstable and stable node in a particular distillation region. See Fig. 1. This has helped to develop a method that can precisely locate distillation boundaries. More importantly, the work of Lucia and Taylor has clearly shown that this geometrical principle of measuring line integrals readily extends to mixtures with more than three components. For example, Bellows and Lucia[10] have demonstrated that for four-component mixtures a boundary corresponds to a local maximum in surface area while for more than four components the boundary is a maximum in volume. Taylor et al.[11] have shown that same concept of locally maximum line integrals defines a distillation boundary in reacting mixtures as well.

Since a distillation boundary represents, in some sense, a limiting case in terms of the degree of difficulty of separation, it is reasonable to draw an intuitive connection between the length of distillation lines and energy consumed. Specifically the locally longest residue curve or distillation line at total reflux obviously corresponds to a separation that uses the most energy. Intuitively then, one might imagine that the shortest residue curve or distillation line should provide some information regarding the easiest or most energy efficient separation. This key observation forms the fundamental idea behind this dissertation research. In the chapters that follow it will be shown that this connection between distillation line length and energy consumption is in fact true for any kind of mixture. Moreover, it will be quantified and exploited to develop a novel shortcut methodology for designing energy efficient chemical processes.

Layout of the Thesis

This thesis is written in the manuscript format and is organized in following way. This introduction is followed by chapter 1, in which the basic formulation of the proposed methodology for energy efficient process design is discussed. A detailed literature survey is given at the start of the chapter to summarize the methods currently available in the literature for finding minimum energy requirement in separation processes, highlighting the advantages and disadvantages of each.

Governing equations used in this entire work, the basic philosophy and principles behind the shortest stripping line distance approach are subsequently discussed. Problem formulations that take the general form of nonlinear programming (NLP) and mixed integer nonlinear programming (MINLP) problems are presented. A detailed two-step algorithm based on global optimization is presented for implementing this MINLP formulation in order to obtain energy efficient process designs. This two-step algorithm consists of an NLP stage and an Integer Programming (IP) stage. Various algorithmic issues involved in using the proposed two-step algorithm for different types of pinch points and algorithm modifications for handling multi-unit processes are also discussed at length. Examples of multi-component separations involving mixtures of varying degrees of non-ideality, reactive mixtures, and multi-unit processes are used to illustrate key concepts and the robustness of the shortest stripping line methodology. Chapter 1 is published in Computers and Chemical Engineering in year 2008.

Chapter 2 focuses on the use of the shortest stripping distance line approach for designing energy efficient multi-unit processes. In particular, the synthesis of a hybrid separation process for purification of acetic acid from an acetic acid solution using extraction with ethyl acetate followed by distillation is discussed. It is shown that the shortest stripping line approach correctly finds the extract target composition that connects extractor to the distillation column, corresponding to the most energy efficient design for both low and high purity acetic acid. Chapter 2 was published in Industrial Engineering and Chemistry Research in 2006.

In Chapter 3, the concept of shortest stripping line distance is extended to develop a novel two-level design method for generating portfolios of promising energy efficient designs that meet required criteria for key component recoveries. A detailed algorithm for implementing this two-level design approach and its advantages over conventional methods are discussed with the help of various examples. It is shown that design portfolios frequently encompass Underwood's solution, when it exists, and that the two-level approach readily extends to cases where Underwood's method fails. This chapter has been submitted to AIChE Journal for publication and is under review.

Chapter 4 discusses the use of the shortest stripping line method for identifying non-pinched, minimum energy designs. Non-pinched, minimum energy designs are an important class of minimum energy designs that are poorly understood. A detailed description of how the shortest stripping line distance methodology can be used to systematically and intelligently find these non-pinched, minimum energy designs and, more importantly, to understand the reasons behind there existence is given in this chapter. The key concepts involved are illustrated with the help of different numerical examples of separations involving azeotropic and hydrocarbon mixtures. Comparisons of results obtained using the shortest stripping line method with a rigorous simulation method in Aspen Plus (i.e., RADFRAC) towards the end of this chapter show the usefulness of the proposed method for finding non-pinched, minimum energy solutions. This chapter has been accepted for publication in Chemical Engineering Research and Design and can be found using doi:10.1016/j.cherd.2008.02.017.

Chapter 4 is followed by a conclusions chapter that summarizes the major contributions made by this research project.

Summary

Newer ways of designing energy efficient chemical process are needed due to continuously increasing costs of energy. Residue curve maps are traditionally used for gaining insight regarding distillation regions and distillation boundaries, especially for azeotropic mixtures. Recent investigations by Lucia and Taylor[9] have shed new light on the analysis of residue curve maps and have uncovered a fundamental underlying geometric principle that defines distillation boundaries in a precise way. In the chapters of this dissertation, we use a second fundamental geometric principle – that energy consumption can be described by the concepts of longest and shortest distillation line – to develop a novel method for designing energy efficient chemical processes.

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MANUSCRIPT I

Distillation Pinch Points and More

This chapter is the manuscript entitled, Distillation Pinch Points and More, that was published in Computers and Chemical Engineering in 2008.

Abstract

Rising energy costs have spawned renewed interest in improving methodologies for the synthesis, design and/or retrofitting of separation processes. It is well known that energy use in many process industries is dominated by separation tasks – particularly distillation. In this work, the shortest stripping line approach recently proposed by Lucia and co-workers[1] is used to find minimum energy requirements in distillation. The new aspects of this work show that this shortest stripping line approach can find minimum energy requirements for

1) Distillations with feed pinch, saddle pinch, and tangent pinch points.
2) Distillations for which the minimum energy solutions do not correspond to a pinch point.
3) Processes with multiple units (e.g., reactive distillation, extraction/distillation, etc.).

Other novel features of this work also shows that the shortest stripping line approach

4) Can be used to identify correct processing targets in multi-unit processes.
5) Encompasses longstanding methods for finding minimum energy requirements including the McCabe-Thiele method and boundary value methods.

A back-to-front design approach based on shortest stripping lines is used so that correct processing targets can be identified so that all tasks in can be synthesized simultaneously in such a way that the most energy efficient designs are achieved. New problem formulations that take the general form of nonlinear programming (NLP) and mixed integer nonlinear programming (MINLP) problems are given and a novel global optimization algorithm is presented for obtaining energy efficient process designs. A variety of ideal and nonideal distillations, including examples with four or more components, are used to demonstrate the efficacy of the shortest stripping line approach. The examples with more than three components are particularly significant because they clearly illustrate that the proposed approach can be readily used to find minimum energy requirements for distillation problems involving any number of components. Many geometric illustrations are used to highlight the key ideas of the method where appropriate.

Keywords

pinch point and non-pinch solutions, shortest stripping lines, energy efficiency.

I.1 Introduction

The primary motivation for this work is the current rapidly rising costs of energy. As a result of recent significant increases in global energy demands, and every indication that demand will remain high, it has become increasingly important to consider ways, perhaps unconventional ways, of designing new processes and/or retrofitting existing ones so that they are energy efficient. To do this – to allow engineers to find creative and energy efficient solutions to processing challenges – new methodologies are needed to support synthesis and design efforts. Separation and energy use in many industries is dominated by distillation. There are an estimated 40,000 distillation columns in the U.S. that consume approximately 18% of all of the energy in the manufacturing sector (see the recent DOE workshop study spearheaded by Eldridge et al.[2]). Because distillation is such a large energy user and because it will continue to be used to address a wide variety of separation needs, any new synthesis and design methodologies for overall energy efficiency should, in our opinion, include and/or extend techniques for finding minimum energy requirements in distillation. This is the approach we have adopted in this work.

This paper addresses energy efficiency in the design and optimization of separation processes. The particular design and optimization approach proposed in this work is based on the novel concept of shortest separation (stripping) lines, and is a direct outgrowth of recent results by Lucia and Taylor[3], and subsequently Taylor et al.[4], that shed new light on residue curves and distillation lines (i.e., that separation boundaries are defined by *longest* residue curves or distillation lines). Through new global optimization formulations based on shortest separation lines, the proposed methodology

1) Encompasses all existing methodologies for finding minimum flows and minimum energy requirements in distillation in the presence of feed, saddle or tangent pinch points.
2) Is unaffected by the number of components or the presence of reverse separation.
3) Uses a back-to-front philosophy to identify correct processing targets for processes with multiple units (e.g., reactors, other separators) such that overall energy consumption is minimized.
4) Can easily find minimum energy solutions that do not correspond to separation pinch points.
5) Can be readily combined with other synthesis methods such as the attainable regions approach for the simultaneous design of multi-unit processes.
6) Can solve synthesis and design problems other methods cannot solve.
7) Can provide starting values for more detailed process optimization studies.
8) Can be used to establish that *longest and shortest paths are unifying geometric principles* for the design of energy efficient chemical processes.
9) Provides a new methodology for the teaching and practice of various aspects of energy efficiency in process design that can be easily understood by the general public.

The focus of this manuscript is to show that *the key synthesis or design idea of the concept of shortest stripping lines readily applies to conventional distillation processes as well as the synthesis, design or retrofitting of processes such as* [redacted]*tor/separator/recycle (RSR) processes and hybrid separation schemes.* Problem formulations that take the general form of nonlinear programming (NLP) and mixed integer nonlinear programming (MINLP) problems are presented and a global optimization algorithm is presented for obtaining energy efficient process designs.

I.2 Literature Survey

Many papers on minimum flows and minimum energy use in distillation have been published beginning with the work of Underwood[5] for the case of constant relative volatility. This includes papers on regular columns, columns with side-streams, extractive distillation, azeotropic distillation, reactive distillation, Petlyuk and other multiple column configurations. For single columns, it is well known that minimum energy requirements generally correspond to minimum reflux and/or boil-up ratios and an infinite number of equilibrium stages so that the column just performs the desired separation (or exhibits one or more pinch points). Most methods for determining minimum energy requirements in this case are based on either methods for directly finding pinch points or rigorous column simulations. See, for example, Vogelpohl[6], Hausen[7], Doherty and co-workers[8, 9, 10, 11], Koehler et al.[12], and Urdaneta et al.[13] for methods based on finding pinch points, and Brown and Holcomb[14], Murdoch and Holland[15] and Acrivos and Amundson[16], Shiras et al.[17], Bachelor[18], and Holland and co-workers[19, 20, 21] for methods based on rigorous column simulation. Koehler et al.[22] give a good survey of methods for determining minimum energy requirements for single and multiple column configurations up to 1995 and show that many of the pinch point techniques are related to the original method of Underwood – some more strongly than others. They also give an example of a minimum energy column that does not correspond to a pinch point. More recent work by Gani and Bek-Pedersen[23] shows that a simple graphical algorithm based on a maximum in the separation driving force defined as $|y_{LK} - x_{LK}|$, where the subscript LK denotes the light key component, can be used to determine near minimum (or minimum) energy requirements for conventional distillations. The graphical approach of V_{min} diagrams by Halvorsen and Skogestad[24] also is related to the work of Underwood while that of the rectification body method (RBM) of Urdaneta et al.[13] for reactive distillation and Kim[25] for thermally coupled columns are both based on the use pinch points and residue curves. Finally, the paper by Alstad et al.[26] gives an example of energy savings in complex column configurations using over-fractionation. There are also many other papers on synthesis and design of single and multiple separator configurations. However, these papers do not specifically address minimum energy requirements and therefore they have not been included in this literature survey.

I.3 Some Details of Existing Methods for Finding Separation Pinch Points

Current methods for finding pinch points and minimum energy requirements in distillation include boundary value methods, reversible distillation models, eigenvalue methods, separation driving force methods, the rectification body approach, and V_{min} diagrams.

I.3.1 Boundary Value Method

Over the last twenty years, Doherty and co-workers[8-11, 27-29] have published several papers and a variety of numerical methods for addressing minimum energy requirement in azeotropic multicomponent distillation, heterogeneous azeotropic distillation and reactive distillation. Most of these methods are based on finite difference approximations of column profiles in ordinary differential equation form under the assumption of constant molar overflow (CMO). Conditions such as minimum reflux are determined using a boundary value method, in which the rectifying profile for the liquid compositions is integrated from top to the feed stage while the stripping profile is integrated from bottom to the feed stage. Thus a feasible column configuration is one in which the rectifying and stripping profiles intersect and the reflux ratio for which these profiles just touch each other corresponds to minimum reflux. When only one pinch occurs at minimum reflux it is designated as a feed pinch. This procedure for finding minimum reflux requires calculating column profiles several times.

A second type of pinch point, called a saddle pinch, can also appear in a column profile if a saddle point 'attracts' part of the profile. Using the boundary value approach, Doherty and co-workers show that a saddle pinch is characterized by a co-linearity condition – that is, the saddle pinch, feed pinch point, and feed composition are co-linear. The reflux ratio that makes the saddle pinch, feed pinch point, and feed composition co-linear is the minimum reflux ratio, is exact only for ideal mixtures, and is considered a good approximation for non-ideal mixtures. The boundary value approach was initially proposed for homogeneous mixtures, and later extended to heterogeneous azeotropic distillation by incorporating vapor-liquid-liquid equilibrium in the decanter during the initialization of the rectifying profile calculations. On the other hand, the co-linearity method is not useful for calculating minimum reflux for heterogeneous azeotropic distillations because a saddle pinch may not appear in the case of heterogeneous azeotropic distillation. Barbosa and Doherty[27] have extended the boundary value approach to calculate minimum reflux for reactive distillation using a set of reaction invariant transformed composition variables while Zhang and Linninger[30] propose a boundary value method based on a bubble point distance criterion for finding feasible designs, pinch points and minimum reflux conditions.

A closely related algebraic method, called the zero volume method, is given by Julka and Doherty[28] and Fidkowski et al.[10]. This zero volume method uses a continuation method to find pinch points of the operating lines in either the rectifying or stripping sections of a column. These fixed points are used to construct a set of special vectors and the value of reflux that makes the (oriented) volume of these vectors zero corresponds to minimum reflux. For feed pinch points the zero volume method is straightforward. Tangent pinch points, on the other hand, correspond to turning points of the volume with respect to reflux ratio and require a bit more care in computing because of the singularity condition that accompanies any turning point.

I.3.2 Reversible Distillation Models

The method of Koehler et al.[12] is based on a reversible distillation model. This reversible distillation model assumes that heat can be transferred to and from a column at zero temperature difference and that no contact of non-equilibrium liquid and vapor streams is allowed. Reversible distillation path equations are derived by rearranging the column material balances as well as the equilibrium relationships for the most and least volatile components. The solution of this reduced set of equations requires that the flow rates of the most and least volatile components be specified at the feed plate. Koehler et al. show that a reversible distillation path is generated by adding heat continuously along the length of column and consists of exactly all pinch points of an adiabatic (CMO) calculation. The concentration reached in a reversible distillation column section for any given amount of continuously introduced energy exactly corresponds to the stationary concentration that is obtained in an adiabatic (CMO) section, provided the same amount of energy is introduced only at the ends (through condenser or reboiler). This value of energy represents the minimum energy requirement for the section. The reversible distillation model approach has also been used to determine tangent pinch points based on a maximum energy criterion. Here a tangent pinch appears if there is a local maximum in the reversible energy profile between the distillate and the computed pinch point composition, provided the energy demand at this maximum exceeds the energy demand at the tangent pinch point. Numerical methods based on any reversible distillation model require knowledge of the products that can be achieved by the distillation before starting the computations for finding the minimum reflux.

I.3.3 Eigenvalue Methods

Poellmann et al.[31] proposed a method based on eigenvalue theory. Their eigenvalue method makes use of the fact that any nonlinear liquid composition profile can be accurately linearized near a pinch point because the change in composition from one stage to next is very small. As a result, the method of Poellmann et al. is independent of the number of components in the feed mixture as well as the extent of non-ideality. However, the claims in this paper are not supported by numerical examples.

I.3.4 Separation Driving Force Method

Gani and Bek-Pedersen[23] proposed a simple graphical method based on driving force for separation. Here the separation driving force is defined as $F_{Di} = |y_i - x_i|$, where the subscript i = LK denotes the light key component. Gani and Bek-Pedersen demonstrate that minimum or near minimum energy requirements generally correspond to $dF_{Di} / dx_i = 0$ or a maximum in the driving force, where the correct expression for x_i at the maximum is $x_i = [(\alpha_{ij})^{1/2} - 1] / [\alpha_{ij} - 1]$, where α_{ij} is the relative volatility of the light key. The proposed method is quite simple and applies to two product distillations with N stages. The authors demonstrate their claims with examples that include a multi-component mixture, which is handled using a pseudo-binary approximation by specifying light and heavy key components. They also suggest that their approach is applicable to rate-based processes and multi-feed and/or solvent-based distillation operations but provide no examples of these applications.

I.3.5 Rectification Body Methods

Bausa et al.[32] proposed a method called the rectification body method (RBM) for the determination of minimum energy demands for multi-component distillations. This method is based on triangular rectification body approximations of the liquid composition profiles, which are constructed from the pinch points of the rectifying and stripping sections of the column. Here minimum reflux corresponds to the case when the triangles for the stripping and rectifying sections just intersect. Minimum energy requirements are determined using procedure very similar to the boundary value method of Doherty and co-workers. Bausa et al. state that the RBM method is analogous to Underwood's method as interpreted by Franklin and Forsyth[33]. In our opinion, this method is more closely related to a combination of the eigenvalue method by Poellmann et al.[32] and the boundary value method of Doherty and co-workers. Moreover, because the rectification bodies are only a linear approximation of the curved concentration profiles, their accuracy can be low in cases where the profiles show strong curvature. Urdaneta et al.[13] have recently extended the RBM to the case of minimum energy requirements for reactive distillation.

I.3.6 V_{min} Diagrams

Halvorsen and Skogestad[24] have recently introduced the concept of V_{min} (minimum vapor flow) diagram for determining minimum energy consumption in distillation and use Underwood's equations to develop a procedure to construct V_{min} diagrams. Analytical expressions are derived for ideal mixtures under CMO and constant relative volatility. Subsequently the concept was extended to complex columns (Petlyuk arrangements) for ideal mixtures. While this work can be viewed as new approach based on Underwood's method, for multi-component, non-ideal mixtures, construction of V_{min} diagrams requires the use of rigorous simulation techniques. Moreover, all of the examples presented in these papers involve ideal mixtures. While the authors conclude that their technique can be applied to non-ideal mixtures, this claim is not supported by rigorous examples involving non-ideal mixtures.

I.4 The Concept of Shortest Separation (or Stripping) Lines

The starting point for the novel aspects of this paper is the recent work by Lucia and Taylor[3] who show that exact separation boundaries for ternary mixtures are given by the set of locally longest residue curves (or distillation lines at infinite reflux) from any given unstable node to any reachable stable node. See Figure I.1.

We then began with the intuitive belief that following the longest residue curve must somehow be related to the highest energy costs associated with performing a given separation. Furthermore, if the longest residue curve is the most costly separation, then the shortest curve should result in the use of the least amount of energy required for the given separation.

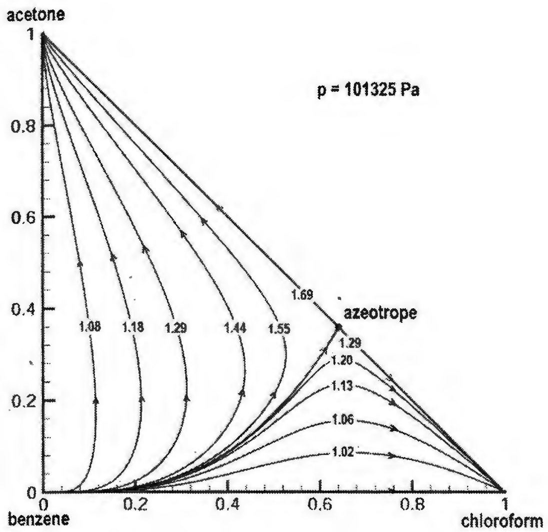


Figure I.1: Residue Curve Map and Line Integrals for Chloroform / Acetone / Benzene

I.4.1 Governing Equations

The equations used in this work to determine distillation lines under infinite or finite reflux ratio and/or number of stages can be found in Fidkowski et al.[10], are easily derived, and given by

$$x_j' = [(r+1)/r]y_j - x_j - (1/r)x_D \qquad (I.1)$$

$$x_j' = [(s)/(s+1)]y_j - x_j + [1/(s+1)]x_B \qquad (I.2)$$

Here x_j denotes a vector of c-1 liquid compositions and y_j is a vector of c-1 vapor compositions on stage j, where c is the number of components in the mixture. Also x_D and x_B are the distillate and bottoms compositions respectively, r = L/D is the reflux ratio, s = V'/B is the boil-up ratio, L is the reflux rate, V' denotes boil-up rate, and D and B are the distillate and bottoms flow rates respectively. Moreover, j is a stage index, and the stages are numbered from bottom to top. Equation I.2 is easily modified for a partial condenser by replacing x_D with y_D. Note that only one of the variables r or s can be chosen independently since the overall mass and energy balances can be combined to give the relationship

$$s = (r + q)[(x_F - x_B)/(x_D - x_F)] + q - 1 \tag{I.3}$$

where q represents thermal conditions of the feed. Equations I.1 and I.2 are equivalent to the rectifying and stripping profile in a CMO column, provided we define $x_j' = (x_{j+1} - x_j)/\Delta$ where $\Delta = 1$. To see this, let $\Delta = 1$ and use $x_j' = x_{j+1} - x_j$ in Eq. 1. This gives

$$x_{j+1} = [(r+1)/r]y_j - (1/r)x_D \tag{I.4}$$

Solving Eq. 4 for y_j yields

$$y_j = [r/(r+1)]x_{j+1} + [1/(r+1)]x_D = (L/V)x_{j+1} + (D/V)x_D \tag{I.5}$$

which is a component mass balance or operating line for the rectifying section of a staged column under CMO conditions. Here V = L + D is the vapor flow leaving the top equilibrium stage in the column. Equation I.5 applies to a column with a total condenser. Again the modifications required for a column equipped with a partial condenser, where y_D replaces x_D, are straightforward. In a similar way, it is easy to show that Equation I.2 is equivalent to a component mass balance (or operating line) for the stripping section of a CMO column. Finally, note that at infinite reflux and boil-up ratios, these equations reduce to the c-1 residue curve equations given by the differential equation $x' = y - x$.

I.4.2 Remark

In simulating the behavior of any staged column using the differential equations defined by Equations I.1 and I.2 and phase equilibrium, it is important to recognize that the integration step size, h, must be set to $h = \Delta = 1$ and that forward Euler integration must be used. Moreover, one must also be careful of the direction of integration because of stage indexing and the direction of vapor and liquid flow. For columns with finite stages, integration must always proceed from the bottom up. Thus in the rectifying section, we integrate from the feed stage to the condenser and in the stripping section, integration takes place from the reboiler to the feed stage. Without these precautions the representation of the component mass balances for a staged column defined by Equations. I.4 and I.5 is not exact.

I.4.3 Pinch Points, Minimum Flows and Energy Efficiency

For infinite s, it is easy to show that Equation I.2 reduces to $x_j' = y_j - x_j$, which has a stable fixed point or pinch point at $y_j = x_j$. In theory, this pinch point occurs when j = infinity. In practice $j \geq N$ will suffice, where N is some large positive integer. For fixed x_B, as s is reduced, this stable fixed point or pinch point changes and is defined by solving the (c-1) algebraic equations

$$0 = sy_N - (s+1)x_N + x_B = s(K_N x_N) - (s+1)x_N + x_B \tag{I.6}$$

for the (c-1) unknowns x_N, where the K_N in Equation I.6 is a vector of (c-1) K-values and N is some sufficiently large positive integer. Vapor compositions can be back calculated using $y_N = K_N x_N$ once Equation I.6 is solved. In our work, pinch points are important in that they help establish the correct interpretation of shortest stripping lines, which in turn can be related to minimum reflux and boil-up ratios, and thus minimum energy use.

I.5 Optimization Formulations and Algorithm

In this section we outline a MINLP formulation and suggest a methodology for finding energy efficient process designs. The overall strategy for determining minimum energy requirements proceeds in two stages – an NLP stage in which minimum boil-up ratio is determined followed by an integer programming (IP) stage in which the smallest number of stages at fixed minimum boil-up ratio is determined. One of the key features of the formulations given in this section is that they apply to mixtures with any number of components and are not restricted to just ternary mixtures.

I.5.1 Nonlinear Programming

The determination of the most energy efficient design with a pinch is equivalent to finding the shortest stripping line and defined by the NLP problem

$$\min_{s} \quad D_s = \sum_{j=1}^{N_s} \| x_j' \| = \|x_{j+1} - x_j\| \qquad \text{(I.7)}$$

subject to

$$x_j' = x_{j+1} - x_j = [(s)/(s+1)]y_j - x_j + [1/(s+1)]x_B, \; j = 1,\ldots, N_s \quad \text{(stripping line)} \qquad \text{(I.8)}$$

$$x_1 = x_B \qquad \text{(bottoms specification)} \qquad \text{(I.9)}$$

$$r = (s - q + 1)[x_{Fi} - x_{Di}]/[x_{Bi} - x_{Fi}] - q \qquad \text{(I.10)}$$

$$x_j' = x_{j+1} - x_j = [(r+1)/r]y_j - x_j - (1/r)x_D, \quad j = N_s+1,\ldots, N \quad \text{(rectifying line)} \qquad \text{(I.11)}$$

$$x_{D,i} \leq \text{specified } x_{D,i} \qquad \text{(distillate specifications)} \qquad \text{(I.12)}$$

$$c(x_K) = 0 \text{ for some } K \,\varepsilon\, [1, N] \qquad \text{(auxiliary constraint)} \qquad \text{(I.13)}$$

where D_s represents a distance function along a discrete stripping trajectory, $\| \cdot \|$ denotes the two-norm, and $c(x_K)$ is some constraint function that defines any auxiliary conditions that must be met to make the design both structurally and/or operationally feasible. It is important to note that Equation I.12 is an illustration of one type of distillate specification for defining feasibility; there are others that can and will also be used, as shown in the examples section of this paper. Also, the significance of the ancillary constraints will be explained in the section on multi-unit processes. Note that the unknown optimization variable for the problem defined by Equation I.7 to I.13

is the boil-up ratio, s, and the optimal trajectory is actually a sequence of liquid compositions denoted by $\{x_j\}^*$ that is assumed to be piece-wise linear. We typically use $N_s = 300$ in Equation I.7 to approximate an infinite number of stages in the stripping section, which are numbered from bottom to top.

I.5.2 Integer Programming

To further look for solutions that do not correspond to pinch points, we use a simple integer programming strategy to determine if it is possible to reduce the number of stripping stages from infinity to some reasonable finite number without increasing the boil-up and reflux ratios by solving the following problem

$$\min_{N_s} \quad D_s = \sum_{j=1}^{N_s} \| x_j' \| = \|x_{j+1} - x_j\| \qquad \text{(I.14)}$$

subject to

$$x_j' = x_{j+1} - x_j = [(s)/(s+1)]y_j - x_j + [1/(s+1)]x_B, \quad j = 1,\ldots, N_s \text{ (stripping line)} \qquad \text{(I.15)}$$

$$x_1 = x_B \qquad \text{(bottoms specification)} \qquad \text{(I.16)}$$

$$s = s_{min} \qquad \text{(fixed boil-up from NLP)} \qquad \text{(I.17)}$$

Note that the only the unknown optimization variable in this IP problem formulation is the number of stages, N_s. Moreover, the solution from the previously solved NLP problem is used as a constraint (i.e., Equation I.17) to fix the boil-up ratio. The foregoing problem formulation assumes the column in question is a stripping column. For columns with both a rectifying and stripping section, one would again add the rectifying line equation (Equation I.11), the equation relating stripping ratio and reflux ratio (Equation I.10), and any specifications on the distillate product (e.g., Equation I.12).

I.5.3 Optimization Algorithm

In this section, a two-level MINLP algorithm for finding the shortest stripping line based on the NLP and IP formulations (Equations. I.7 to I.12 and Equations. I.14 to I.17 respectively) is described. Algorithmic steps are presented for the case of a direct split, where a feed pinch occurs on the stripping pinch point curve, since it is somewhat easier to understand. Modifications of the algorithm for a feed pinch point in the rectifying section, and for situations such as hybrid separation by extraction/distillation and reactive distillation that involve ancillary constraints (i.e., Equation I.13) are also discussed.

<u>Nonlinear Programming</u>

1) Specify the feed conditions (i.e., F, x_F, and q), the bottoms composition, x_B, the desired distillate composition, x_D (or y_D), the number of stripping stages, $N_s = 300$, $x_1 = x_B$, and $D_0 = 0$. Set a small tolerance value, $\varepsilon = 10^{-12}$.
2) Initialize the boil-up ratio, s.
3) For stages j = 1 to N_s, calculate x_j' using Eq. 8, $x_{j+1} = x_j + x_j'$, and calculate $D_j = D_{j-1} + ||x_{j+1} - x_j||$. Set $D_s = D_{Ns}$ and k = 0.

4) If the column has a rectifying section, then calculate r using Eq. 10 and set k = 1. Else go to step 6.

5) If necessary, set $j = N_s+k$, calculate x_j' from Eq. 11 and $x_{j+1} = x_j + x_j'$.

6) Set $x_D(\text{calc}) = x_{Ns+k}$ (or $y_D(\text{calc}) = y_{Ns+k}$ if no rectifying section) and check if all constraints for the specified distillate product are satisfied. If so, set $N_r = k$ and go to step 7. Else check the following

   a) If $x_D(\text{calc})$ is outside the feasible region, go to step 2.

   b) If $x_D(\text{calc})$ has converged to a point that is not the desired distillate, then go to step 2.

   c) If $x_D(\text{calc})$ is inside the feasible region and has not converged, then set $k = k+1$ and go to step 5.

7) Form the Lagrangian function $\Lambda = D + \Sigma\ \mu^T c_D$, where μ is a vector of Kuhn-Tucker multipliers and c_D is a vector of distillate specification constraints. Check the Kuhn-Tucker conditions (i.e., $d\Lambda/ds = 0$, $\mu^T c_D = 0$, $\mu > 0$) for optimality. If $N_s = 300$ and optimality is satisfied, set $D_{min} = D_s$, $s_{min} = s$ and go to step 8. Else reduce the reboil ratio, s, using an optimization method of choice and go to step 2.

Integer Programming

8) Set an initial upper bound on the number of stripping stages $N_U = N_s$. Set the feed, bottoms and distillate conditions as in step 1. Also fix $s = s_{min}$.

9) Find a lower bound on the number of stripping stages, N_L, such that the design is infeasible.

10) If $(N_U - N_L) \leq 1$, stop. Else set $N_s = (N_L + N_U)/2 + \text{mod}\,[(N_L + N_U)/2]$ using integer bisection.

11) Use the distillation model equations (i.e., Equations. I.8 to I.12) with fixed $s = s_{min}$ and determine if the design is feasible or infeasible for the current value of N_s.

    a) If the design is feasible, calculate $D_s = D_{Ns}$ and set $N_U = N_s$ and go to step 10.

    b) If the design is infeasible, set $N_L = N_s$ and go to step 10.

Nonlinear Programming Algorithm

Step 1 specifies the feed, bottoms, and desired distillate conditions while step 2 simply initializes the boil-up ratio. Step 3 of the algorithm generates the liquid composition profile for the stripping section of the column to the stripping pinch point curve and, along the way, calculates the cumulative distance of the stripping line. Step 4 calculates the reflux ratio from the feed, bottoms, and desired distillate compositions and the current value of the reboil ratio. The liquid composition for each stage of the rectifying section is determined one stage at a time in steps 5 and 6 of the algorithm, where step 6 checks that all constraints for the desired distillate are satisfied. Note that it is a simple matter to use y_D(calc) in place of x_D(calc) for stripping columns or columns with partial condensers. If the desired distillate constraints are satisfied, the separation is feasible for the current value of reboil ratio and the number of rectifying stages is determined. If not, then three outcomes are possible a) The calculated distillate composition, x_D(calc), can leave the feasible region, b) The rectifying profile can converge to a point other than the desired distillate, and c) the current rectifying profile has not converged. If the rectifying profile leaves the feasible region, then the separation is clearly infeasible for the current value of reboil ratio. This is step 6a of the algorithm. On the other hand, if the calculated distillate composition has converges to a different distillate product composition, then the separation is also infeasible. Convergence to a different distillate composition in step 6b can be easily checked by checking the condition ||x'|| < ε at the calculated distillate composition. Convergence is characterized by a very small value of ||x'|| and some care must be exercised to avoid identifying rectifying saddle pinches as converged distillate compositions. If the current calculated distillate composition is feasible and has not converged, as indicated in step 6c, then the number of rectifying stages is incremented by one and the next rectifying stage liquid composition is calculated by returning to step 5. Optimality with respect to reboil ratio is checked in step 7 of the algorithm. If optimality conditions are satisfied, then the methodology has determined the shortest stripping line from the given bottoms composition to the stripping pinch point curve. If not, the reboil ratio is reduced using an optimization algorithm and the whole process (i.e. steps 2 to 7 of the algorithm) is repeated. If, on the other hand, the NLP has reached optimality, then the minimum reboil ratio and minimum stripping line distance are determined and the algorithm goes to step 8, where it begins the integer programming calculations.

[illegible]eger Programming Algorithm

The integer programming problem has special structure that can be exploited. For example, once the boil-up ratio that gives the minimum stripping line distance from the bottoms composition to the stripping pinch point curve has been determined, we know that N_s is to be reduced. Remember s remains fixed at s_{min} (and therefore r is fixed). The only things that change are the number of stripping stages, the number of rectifying stages, and the rectifying composition profile. One could use enumeration – reducing the number of stripping stages by one and determining if the resulting stripping plus rectifying line still results in a feasible column. However, there is a better way. Integer bisection, which repeatedly finds the number of stages half way between a current infeasible and current feasible column design for $s = s_{min}$ is both straightforward and computationally tractable. By integer bisection we simply mean repeatedly testing column designs with $N_s = (N_L + N_U)/2 + \text{mod}\ [(N_L + N_U)/2]$, where N_L and N_U are the current estimates of the lower and upper bounds on the number of stripping stages that define an infeasible and feasible design respectively. To do this, step 8 simply sets $s = s_{min}$ and the initial estimate of an upper bound on the number of stripping stages for a feasible design to $N_U = N_s$. Step 9, on the other hand, determines a lower bound on the number of stripping stages for an infeasible design. In the absence of any knowledge, one can simply set $N_L = 1$. If the difference between the upper and lower bounds on the number of stripping stages has been narrowed to 1, then the integer programming method terminates with N_U equal to the minimum number of stripping stages for which the design is feasible for the given feed, bottoms, and distillate specifications with $s = s_{min}$. This value of $N_s = N_U$ could correspond to either a pinched or non-pinched design. Step 10 uses simple integer bisection and selects the number of stripping stages as the average of N_L and N_U plus the remainder of that average. Step 11 tests the design with this estimate of the number of stripping stages for feasibility or infeasibility and resets either the upper bound, N_U, in step 11a or the lower bound, N_L, in step 11b before returning to integer bisection. Note that this integer bisection approach is guaranteed to find either find a non-pinched solution or return with a pinched solution (if no non-pinched solution exists) in at most nine integer iterations!

I.5.4 Algorithm Modifications for Feed Pinch Points on the Rectifying Pinch Point Curve

For indirect splits, there is often a feed pinch on the rectifying pinch point curve. In this case, the stripping line does not exhibit a feed pinch and therefore some modification of the algorithm is required. Remember, one must still calculate the distance to the stripping pinch point curve to provide a meaningful distance measurement. However, the point (or stage) at which there is a switch from the stripping section to the rectifying section (i.e., the feed tray) is not on the stripping pinch point curve. Therefore, one must determine the feed tray by determining the stripping tray number at which to make the switch and, at the same time, ensure that the distillate specifications are met. The most straightforward way to do this is use the feed composition as a target. By this we mean find the stripping profile that passes through the feed point, locate the intersection of this stripping line with the rectifying pinch point curve, identify the corresponding reflux ratio from the rectifying pinch point curve, and count the number of stripping stages needed to get from x_B to the rectifying pinch point curve. A detailed example of this is given in the section entitled Rectifying Feed Pinch Points and the Concept of Processing Targets.

I.5.5 Algorithm Modifications for Handling Targets in Multi-Unit Processes

For hybrid separations like extraction plus distillation and reactive distillation there are often additional constraints that must be considered. For example, in an extraction/distillation process the feed must lie on the binodal (or liquid-liquid equilibrium) curve. This type of processing target requires that conditions in the form of the ancillary constraints given by Equation I.13 be enforced. Here, as in the case of the indirect split, feasible solutions do not show a pinch on the stripping pinch point curve. In fact, most feasible solutions for these multi-unit processes, including the one corresponding to minimum energy requirements, are often non-pinched solutions. Handling processing targets requires that the ancillary constraints be included in the NLP. We recommend solving this type of NLP using a penalty or barrier function approach by including only the ancillary constraints in the penalty or barrier function term. See Lucia et al.[1] for an illustration of this.

I.6 Distillation Examples

The next section presents a number of distillation examples that illustrate the use of the shortest stripping lines approach for calculating minimum energy requirements. These problems include examples of feed, saddle, and tangent pinch points for ideal and non-ideal mixtures as well as problems whose solutions are <u>not</u> pinch points. In all cases, the liquid phase is modeled by the UNIQUAC equation, unless otherwise specified. All interaction parameters can be found in the appendix. In all case where a pinched solution is reported, we solved the Nonlinear Programming (NLP) problem defined by Equations I.7 to I.12. In all cases where a non-pinched solution is reported we solved the NLP and then the integer programming problem defined by Equations I.14 to I.17 plus Equations I.10 to I.12. For the multi-unit process examples an NLP defined by Equations I.7 to I.13 was solved. However, we remark the reader must keep in mind that configuration must be accounted for correctly. That is, a column with stripping and rectifying sections obviously involves a different set of equations that, for example, a stripping column. All heat duties were determined using energy balance calculations around the reboiler and condenser. Finally, calculations were performed on a Pentium III with a Lahey F77/EM32 compiler, a Pentium IV equipped with a Lahey-Fijitsu LF95 compiler, and using Maple.

I.6.1 Binary Mixtures

Binary mixtures can exhibit both feed and tangent pinch points but not saddle pinch points. However, before discussing any ternary examples it is important to define what we mean by feasibility.

Recall the remarks made at the end of section 4 regarding our decisions to integrate both column sections from the bottom up. From a mathematical perspective, it is possible to completely specify the bottoms product composition since this simply corresponds to specifying the initial conditions for a nonlinear dynamical system –

regardless of the number of components in the mixture. As a result, the corresponding column trajectory will be unique provided the energy balance is used to define the reflux ratio and the appropriate liquid composition in the stripping section is used to initialize the rectifying profile. For each specified bottoms composition, there will be one and only one resulting distillate composition for each choice of boil-up ratio. Consequently we define feasibility based on whether the calculated distillate composition satisfies desired distillate compositions constraints and typically use one or more inequalities to define this condition.

Feed Pinch Points

Consider the separation of n-pentane and n-heptane by distillation. The feed, distillate, and bottoms compositions for this example are summarized in Table I.1. The single feed is assumed to be saturated liquid, the liquid and vapor phases are treated as ideal mixtures, and the column is equipped with a total condenser. The distillation is considered feasible if $x_D(n\text{-}C_5) > 0.99$.

Table I.1: Feed and Product Compositions for n-Pentane /n-Heptane Distillation

[redacted]ent	Distillate$^+$	Feed*	Bottoms
n-Pentane (n-C_5)	0.9900	0.3200	0.0100
n-Heptane (n-C_7)	0.0100	0.6800	0.9900

[redacted]

+ Feasible if $x_D(n\text{-}C_5) > 0.99$; * Saturated liquid ($q = 1$).

Figure I.2 shows the distillation lines and stripping line distances for the liquid composition profile for three different values of boil-up ratio, where the stripping line distance is simply the stripping line measured from the bottoms composition to the pinch point on the equilibrium curve along the x-axis. Reflux ratios that satisfy overall energy balance for the column are also given in Figure. I.2.

The stripping line distance of 0.1932 corresponds to a boil-up ratio of s = 0.4750 and represents a case where the reboil ratio is less than the minimum required. This is because the resulting rectifying line has a reflux ratio of r = 0.0266 and does not produce the desired overhead product. Therefore the desired separation is infeasible for s = 0.4750. On the other hand, the middle column profile, which is shown in red, corresponds to the minimum boil-up ratio for which the desired separation is feasible. The stripping line distance for a boil-up ratio of s = 0.7055 in this case is 0.3100, r = 0.5248, and the corresponding rectifying profile a distillate product with a composition of x_D = 0.99863 – clearly greater than the specified value of x_D. Moreover, for all reboil ratios greater than s_{min} = 0.7055, the separation is always feasible and the distance of the stripping line is always greater that 0.3100 – as shown for the case of s = 1.0500, for which the reflux ratio is r = 1.2693, x_D = 0.99943, and the stripping distance is 0.4311. These results are tabulated in Table I.2 and easily show that *the determination of shortest feasible stripping line correctly identifies the minimum boil-up (and reflux) ratio and thus minimum energy requirements for this distillation.*

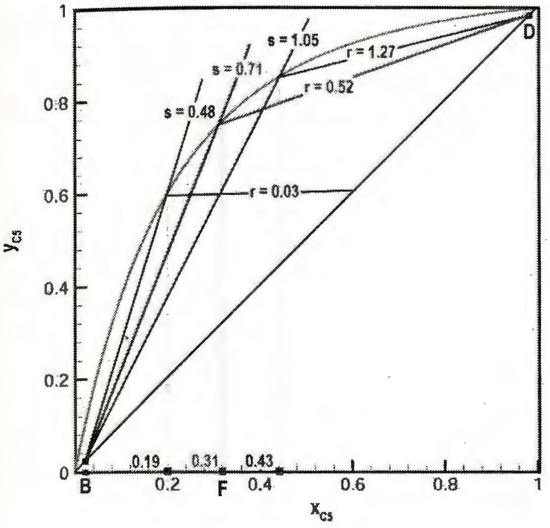


Figure I.2: Feed Pinch Determined by Shortest Stripping Line for n-C_5 /n-C_7

Table I.2: Summary of Boil-up and Stripping Line Distances for n-Pentane /n-Heptane Distillation

BR	Distance (D_s)	Feasible	xD(n-C_5)	Q_R*	Q_C*
0.4750	0.1932	no			
0.7055	0.3100	yes	0.99863	$1.594\text{x}10^4$	$4.625\text{x}10^3$
1.0500	0.4311	yes	0.99943	$1.916\text{x}10^4$	$5.053\text{x}10^3$

* Duties in units of Btu/h per lbmol/h of feed.

Tangent Pinch Points

Consider the distillation of acetone (A) and water (W) at 1 atm. The equilibrium curve for acetone and water shows an inflection and hence can give rise to a tangent pinch point that determines the minimum boil-up ratio for this distillation. The feed, approximate distillate, and bottoms compositions for this distillation are given in Table I.3, where the feed is saturated liquid and the vapor phase is assumed to be ideal. The distillation is feasible if x_D (A) > 0.96.

Table I.3: Column Compositions for Acetone/Water Distillation

Component	Distillate[+]	Feed*	Bottoms
Acetone	0.9600	0.2000	0.0100
Water	0.0400	0.8000	0.9900

+ Feasible if x_D (A) > 0.96; * Saturated liquid ($q = 1$)

In this example, the NLP defined by Eqs. 7 to 12 was solved. Figure I.3 shows three sets of operating lines at different values of reboil ratio. The stripping profile for a boil-up ratio of $s = 0.3268$ results in a stripping line distance is 0.1909. However, the corresponding reflux ratio predicted by overall energy balance, $r = 0.3072$, is too low and the resulting rectifying profile intersects the equilibrium curve at xD (A) = 0.66000. Thus the desired separation is infeasible.

If, on the other hand, the boil-up ratio is increased to $s = 0.4822$, the stripping line pinches at $x = 0.2661$. The corresponding rectifying profile becomes tangent to the equilibrium curve and the tangent pinch is $x_{TP} = 0.89475$. For $s = 0.4823$, the stripping line distance is 0.2561, the corresponding reflux ratio is $r = 0.9292$, and the resulting distillate composition is x_D (A) = 0.98428 – well above the specified value of 0.96. This particular curve is shown in red in Figure. I.3.

For all boil-up ratios greater than s_{min} = 0.4823 the separation is feasible and the associated stripping line distance is always greater than 0.2561. For example, for s = 0.6900, the stripping line distance is 0.3257, the corresponding reflux ratio is 1.7600, and the distillate composition is x_D (A) = 0.99335. These results are summarized in Table I.4, where it is evident that the minimum boil-up and reflux ratios, as well as minimum reboiler and condenser duties, correspond to the shortest stripping line for which the desired separation is feasible. Note that this example illustrates that pinch points in the rectifying section of a column can still be determined by the shortest stripping line distance – by paying careful attention to separation specifications.

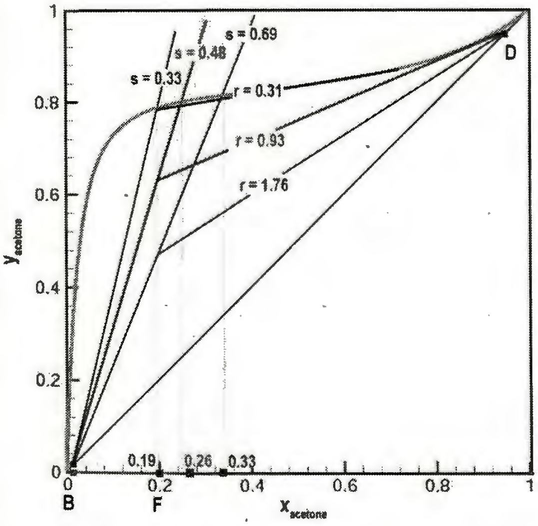


Figure I.3: Tangent Pinch Determined by Shortest Stripping Line for Acetone / Water

Table I.4: Summary of Results for Acetone /Water Distillation

[redacted]	Distance(D_s)	Feasible	x_D (A)	Q_R*	Q_C*
0.3268	0.1909	no	0.66000		
0.4823	0.2560	yes	0.98428	2.07564×10^4	4.9808×10^3
0.6900	0.3257	yes	0.99335	2.36640×10^4	7.1260×10^3

* Heat duties in units of Btu/h per lbmol/h of feed

Results for the two binary distillation examples clearly show that the concept of shortest stripping line applies equally well to feed and tangent pinch points. They also provide a shortest stripping line interpretation of the McCabe-Thiele method. Moreover, for the case of constant relative volatility and constant molar overflow, it is easily seen that the shortest stripping line approach becomes equivalent to Underwood's method for conventional columns. Remember, for binary mixtures, the stripping line distance is measured from the desired bottoms composition to the pinch point on the equilibrium curve along the x-axis.

I.6.2 Ternary Mixtures

Ternary mixtures can exhibit feed, saddle, and tangent pinch points. Saddle pinch points arise from azeotropes that are saddle point nodes of the governing differential equations. All pinch solutions to the distillation examples in this section were determined by solving the NLP defined by Equations. I.7 to I.12. This includes all ternary, the quaternary, the five-component, and the six-component examples.

Feed Pinch Points

A clear illustration of the application of the shortest stripping line approach to a feed pinch in ternary mixtures has been studied by Lucia et al.[1] and the details of that example can be found in that paper. What is different here is the distillate specifications have been changed so that the overhead product is closer to the ethyl acetate-water azeotropic composition and we have provided heat duty requirements for all feasible distillations. The mixture of interest is acetic acid (AA), water (W) and ethyl acetate (EAc) at atmospheric pressure and the column is equipped with a partial condenser. The feed, distillate, and bottoms compositions for this distillation are given in Table I.5 and the separation is considered feasible if the calculated distillate composition is near the ethyl acetate-water azeotrope and satisfies the conditions x_D (AA) $\leq 1 \times 10^{-4}$ and x_D (EAc) ≤ 0.6300.

Table I.5: Column Specifications for the Distillation of Acetic Acid/Ethyl Acetate/ Water

Component	Distillate[+]	Feed*	Bottoms
Acetic Acid	1×10^{-4}	0.5000	0.9999
Ethyl Acetate	0.6300	0.3150	5×10^{-5}
Water	0.3699	0.1850	5×10^{-5}

+ Feasible if x_D (AA) $\leq 1 \times 10^{-4}$ and x_D (EAc) ≤ 0.6300; * $q = 1$.

Figure I.4 shows several column profiles with their corresponding stripping line distances (measured to the stripping pinch point curve) as well as the liquid-liquid equilibrium (or binodal) curve while Table I.6 summarizes the numerical results.

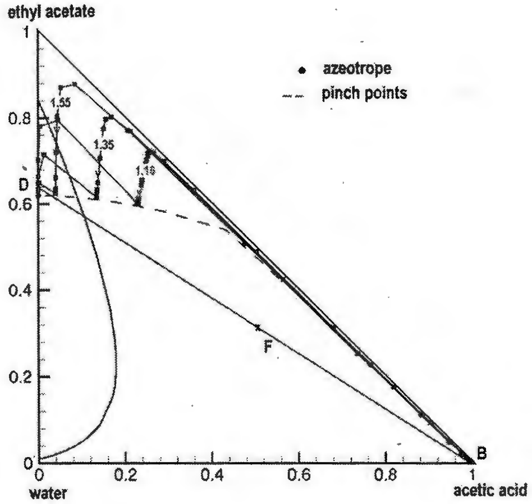


Figure I.4: Distillation Lines for the Separation of Acetic Acid / Ethyl Acetate / Water

Table I.6: Summary of Results for Acetic Acid /Ethyl Acetate/Water Distillation

	Distance(D_s)	Feasible	xD (AA, EAc)	Q_R*	Q_C*
3.933	1.161	yes	(4.21519 x 10^{-5}, 0.62998)	2.29146x10^4	2.84566x10^4
7.0	1.3511	yes	(7.82468 x 10^{-5}, 0.62740)	4.17264x10^4	5.88884x10^4
25	1.5465	no	(1.7090 x 10^{-4}, 0.62692)		

* Heat duties in units of Btu/h per lbmol/h of feed

Saddle Pinch Points

It is well established that the presence of a saddle pinch point can often determine minimum energy requirements in distillation. Therefore, consider the separation of a mixture of chloroform (C), acetone (A) and benzene (B) at atmospheric pressure, as described in Koehler et al.[22], where the vapor phase is assumed to be ideal. This separation is defined by the feed, approximate distillate and bottoms compositions, as shown in Table I.7. This separation is considered feasible if the acetone composition in the distillate product satisfies the inequality $x_D(A) \geq 0.99$.

Table I.7: Column Specifications for the Distillation of Chloroform/Acetone/Benzene

Component	Distillate$^+$	Feed*	Bottoms
Chloroform	6.666×10^{-4}	0.1100	0.13266
Acetone	0.9900	0.1700	1×10^{-10}
Benzene	0.0093	0.7200	0.86734

+ Feasible if $x_D(A) \geq 0.99$; * Saturated liquid feed ($q = 1$)

Table I.8 and Figure. I.5 give a summary of the numerical results for three different column profiles, two of which meet the desired column specifications. As shown in Figure I.5, the rectifying profile furthest to the right exhibits a saddle pinch point, has the shortest associated stripping line distance, and therefore corresponds to a minimum boil-up ratio of $s_{min} = 1.159295$. There is also a feed pinch in the stripping section that occurs at $x_{FP} = (x_C, x_A) = (0.1299970, 0.18713213)$. The reflux ratio corresponding to s_{min} is $r = 4.59189353$ and the distillate composition is $x_D(A) = 0.994044$; clearly feasible.

Table I.8: Summary of Numerical Results for Chloroform/Acetone/Benzene Distillation

[redacted]	ance (D_s)	Feasible	x_D (A)	Q_R*	Q_C*
1.159295	0.3271525	yes	0.994044	1.383686×10^4	1.221046×10^4
1.159300	0.327155	yes	0.991663	1.383690×10^4	1.221052×10^4
1.159400	0.327206	no	0.984250		

[redacted]

* Heat duties in Btu/h per lbmol/h of feed

For all boil-up ratios less than s_{min}, the separation is infeasible because it does not meet the desired acetone purity in the distillate. The reflux ratio and distillate composition for the middle profile in Figure I.5 are r = 4.59191765 and x_D (A) = 0.991663 respectively. There is also an upper bound on boil-up ratio as is clearly indicated by the fact that for s = 1.1594, the separation is also infeasible since the resulting reflux and distillate composition are r = 4.5940000328 and x_D (A) = 0.984250. Thus there is a narrow window of boil-up ratio that meets the desired separation. Nevertheless, the shortest stripping line identifies the minimum boil-up ratio and hence minimum energy requirements for this separation.

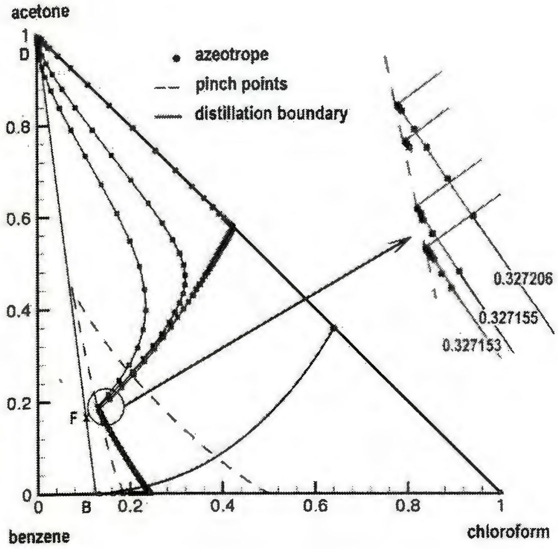


Figure I.5: Feed and Saddle Pinch Determined by Shortest Stripping Line

This example also illustrates a number of important points regarding the shortest stripping line approach. First, it shows that the shortest stripping line can find minimum energy solutions corresponding to both a feed and saddle pinch. Second, it clearly shows that it is the shortest stripping line that is important in finding minimum energy requirements – not the distance of the stripping plus rectifying line. Finally, it illustrates that the shortest stripping line approach is unaffected by reverse separation and narrow windows of feasibility (see the inset in Figure I.5 or Table I.8). By reverse separation we mean that lower values of boil-up (and reflux) ratio result in higher acetone purity. Thus less energy is required to produce an overhead product that is higher in acetone than one lower in acetone, as identified by Wanschafft et al.[34].

Tangent Pinch Points

Tangent pinch points can also determine minimum energy consumption in distillation. The recovery of acrylic acid from a mixture of acrylic acid (AcA), water (W), and acetic acid (AA) at atmospheric pressure provides an example of a tangent pinch. Here the liquid is modeled using the UNIQUAC equation and the vapor is modeled by the Hayden-O'Connell (HOC) equation since both acetic acid and acrylic acid show strong vapor phase dimerization. Table I.9 gives the feed, approximate distillate, and bottoms composition. Separation feasibility is defined by the purity of acrylic acid in the overhead product and for this illustration, $x_D(AcA) \geq 0.99$ was used.

Table I.9: Column Specifications for the Distillation of Acetic Acid/Water/Acrylic Acid

Component	Distillate	Feed	Bottoms
Acetic Acid	1×10^{-11}	0.0495	0.1000
Water	0.9900	0.5000	1×10^{-10}
Acrylic Acid	0.0100	0.4505	0.9000

+ Feasible if $x_D(AcA) \geq 0.99$; * Saturated liquid (q = 1)

Figure I.6 and Table I.10 give numerical results for the column specifications given in Table I.9.

Table I.10: Summary of Numerical Results for Acrylic Acid/Water/Acetic Acid Distillation

BR	Distance(Ds)	Feasible	x_D(AcA)	Q_R*	Q_C*
2.1428	0.9253	no	0.94267		
2.2592	1.0305	yes	0.99733	$2.225987x10^4$	$1.949458x10^4$
2.6530	1.1943	yes	0.99844	$2.494946x10^4$	$2.289267x10^4$

* Heat duties in Btu/h per lbmol/h of feed

For the desired separation, the rectifying section shows a tangent pinch in addition to a feed pinch in the stripping section. At the point of tangency, a small change in the boil-up ratio shifts the observed distillate composition by a significant amount. For a stripping ratio of s_{min} = 2.1428, the acrylic acid composition in the overhead is 0.94267. For slightly higher values of s, the acrylic acid composition in the distillate jumps to greater than 0.99. We remark that Levy and Doherty[29] have reported this abrupt shift in product composition accompanying a tangent pinch point.

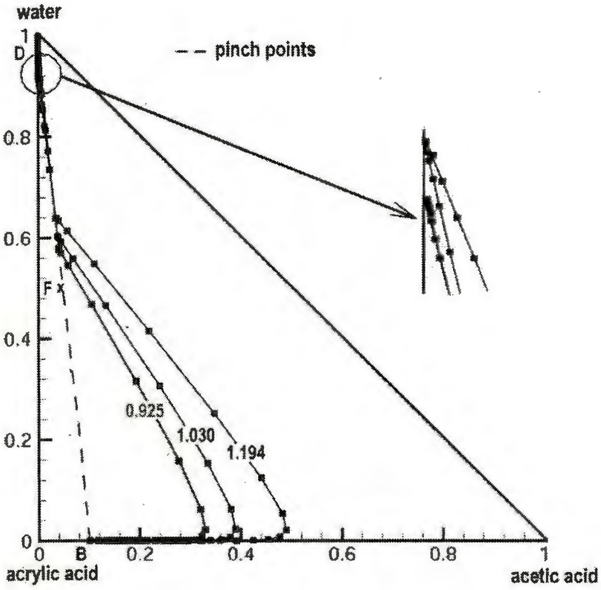


Figure I.6: Tangent Pinch Determined by Shortest Stripping Line

I.6.3 Quaternary Mixtures

Quaternary mixtures still afford a pictorial representation and can also exhibit feed, saddle, and tangent pinch points. In this section, an example of a feed pinch in a quaternary distillation determined by the shortest stripping line approach is illustrated.

Consider the atmospheric distillation of a quaternary mixture of acetic acid (AA), ethanol (E), ethyl acetate (EAc) and water (W) in which the feed is saturated liquid. This distillation is an example of a split whose overhead product is close to the ethanol/ethyl acetate/water azeotrope and a bottoms stream is an acetic acid product that contains small amounts of the other components. The ternary azeotrope for ethanol/ethyl acetate/ water is x_{Az} = (0.13511, 0.55462, 0.31027), where the components are in the order ethanol, ethyl acetate, and water. The specific feed, bottoms, and approximate distillate compositions are given in Table I.11. The distillation is considered feasible if the overhead product is 'near' the ethanol/ethyl acetate/water azeotrope. Thus separation feasibility is defined by a top product that is within an ε-sphere about the ternary azeotrope. Here $\varepsilon = 0.1$ and again, the vapor phase is modeled by the HOC equation in order to account for vapor phase dimerization of acetic acid.

Table I.11: Column Specifications for the Distillation of Acid/Ethanol/Ethyl Acetate/Water

Component	Distillate$^+$	Feed*	Bottoms
Acetic Acid	1×10^{-10}	0.5000	0.9950
Ethanol	0.1400	0.0697	0.00025
Ethyl Acetate	0.5600	0.2800	0.0030
Water	0.3000	0.1527	1.75×10^{-3}

+ Feasible if $\|x_D(\text{calc}) - x_{Az}\| < 0.1$; * Saturated liquid ($q = 1$)

For this quaternary mixture, there are no separation boundaries internal to the tetrahedral composition space. The only distillation boundaries present are those present in the ethanol, ethyl acetate, water face of the tetrahedron shown in Figure. I.7 and these boundaries are one-dimensional curves. Figure I.7 also shows three column profiles with corresponding stripping line distances for which two profiles are feasible and one is not.

For this example, the minimum boil-up ratio that gives the desired separation is s_{min} = 6.263, the stripping line distance is 1.31397, and there is a feed pinch that occurs at the point x_{FP} = (0.14850, 0.13635, 0.55189). The corresponding reflux ratio is r = 4.9279661 and the resulting distillate product is $x_D = (1.88 \times 10^{-12}, 0.21360, 0.53467)$, where the components are in the order acetic acid, ethanol, and ethyl acetate. Note that minimum boil-up places the distillate composition very close to but inside the boundary of the ε-sphere since $\| x_D - x_{Az} \| = 0.09992 < 0.1 = \varepsilon$, where the component order is ethanol, ethyl acetate, and water. For s = 9, the separation is also feasible since $\| x_D - x_{Az} \| = 0.0498 < 0.1$. However, for this value of boil-up ratio the stripping line distance is 1.391917, the corresponding reflux ratio is r = 7.5185527, and $x_D = (1.12 \times 10^{-13}, 0.17315, 0.54807)$. For s = 3.5, the separation is infeasible, as shown in Figure I.7, since $\| x_D - x_{Az} \| = 0.5250 > 0.1$.

Note that for a very wide range of boil-up ratios, the stripping sections of many distillations follow virtually the same residue curve. The significant differences between different distillations are with respect to their rectifying sections – as shown in Figure I.7. The liquid profile that corresponds to the minimum boil-up ratio has part of the stripping section and the entire rectifying section shown in red. Numerical results for this example are summarized in Table I.12 and show that the shortest stripping line distance corresponds to minimum boil-up ratio among all feasible profiles.

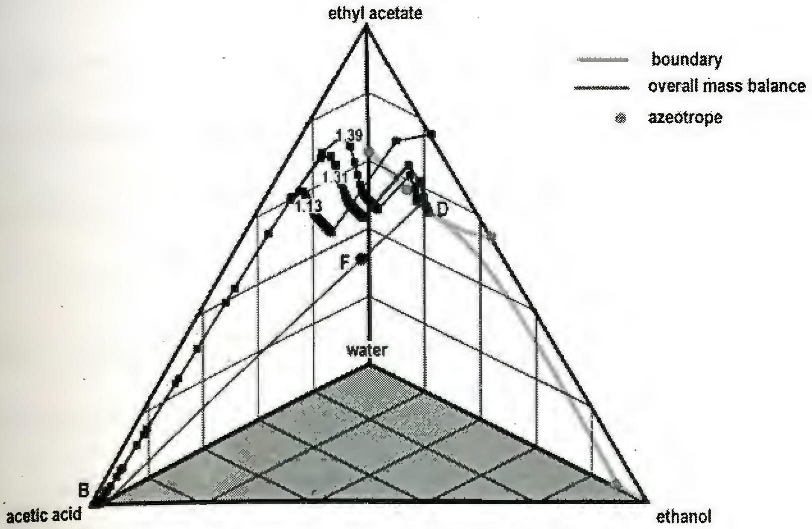


Figure I.7: Feed Pinch Determined by Shortest Stripping Line for Quaternary Mixture

Table I.12: Summary of Numerical Results for Acetic Acid/Ethanol/Ethyl Acetate/Water Distillation

BR	Distance(D_s)	Feasible	$\| x_D - x_{Az} \|$	Q_R*	Q_C*
3.5	1.13242	no	0.5250		
6.263	1.31397	yes	0.0999	$3.79318\text{x}10^4$	$9.05092\text{x}10^4$
9.0	1.39192	yes	0.0498	$5.44187\text{x}10^4$	$1.30296\text{x}10^5$

* Heat duties in Btu/h per lbmol/h of feed

I.6.4 A Five-Component Mixture

Consider the non-sharp atmospheric distillation of a five-component mixture consisting of methanol (M), acetic acid (AA), ethanol (E), ethyl acetate (EAc), and water (W), where the feed is saturated liquid and the column is equipped with a total condenser. Here the primary purpose of the separation is to produce an overhead product that is largely a mixture of methanol and ethyl acetate since the low boiling mixture is the methanol-ethyl acetate azeotrope at $x_{Az} = (x_M, x_{EAc}) = (0.69410, 0.30590)$. The feed, approximate distillate, and bottoms product compositions are given in Table I.13. Separation feasibility, in this example, is defined by the condition $\| x_D - x_{D,spec} \| \leq 0.02$, where $x_{D,spec}$ is the distillate composition given in Table I.13. Vapor phase behavior is modeled using the HOC equation.

Table I.13: Column Specifications for Five-Component Distillation

Component	Distillate$^+$	Feed*	Bottoms
Methanol	0.6900	0.4150	5.1343×10^{-2}
Acetic Acid	1×10^{-10}	0.3538	0.8217
Ethanol	1.5×10^{-3}	0.01167	2.5113×10^{-2}
Ethyl Acetate	0.3000	0.1873	3.8292×10^{-2}
Water	8.5×10^{-3}	0.03223	0.06355

$^+$ Feasible if $\| x_D(\text{calc}) - x_{D,spec} \| \leq 0.02$; Saturated liquid ($q = 1$)

The shortest stripping line distance for this example is 0.94241 for a minimum boil-up ratio of $s_{min} = 4.459$. The feed pinch point is $x_{FP} = (x_M, x_{AA}, x_E, x_{EAc}) = (0.53510, 0.15819, 0.011261, 0.26924)$. The resulting reflux ratio is $r = 2.371927$ and the calculated distillate composition is $x_D = = (0.68129, 1.23 \text{ x } 10^{-11}, 7.350 \text{ x } 10^{-4}, 0.31798,)$, which is very close to the boundary of the hyper-sphere of radius 0.02 about the specified distillate composition. Boil-up ratios less than s_{min} do not satisfy the condition $\| x_D - x_{D,spec} \| \leq 0.02$ while those greater than s_{min} do. Numerical results are summarized in Table I.14.

I.6.5 A Six-Component Petroleum Refinery Mixture

This example is adapted from Holland[35] and involves the distillation of a six-component mixture of light paraffins at 400 psia. The feed to the column is a mixture of propane (nC_3), n-butane (nC_4), isobutene (iC_4), iso-pentane (iC_5), n-pentane (nC_5) and n-octane (nC_8), is saturated liquid, the column has a partial condenser, and the liquid and vapor phases were assumed to be ideal and modeled using a correlation given by Wilson[36]. This correlation estimates K-values based on critical properties and is given by the relationship $K_i = \exp[\ln(p_{c,i}/p) + 5.37(1 + \omega_i)(1 - T_{c,i}/T)]$, where $p_{c,i}$, $T_{c,i}$, and ω_i are the critical pressure, critical temperature and acentric factor for the ith component. We used critical properties in Elliott and Lira[37].

Table I.14: Numerical Results for a Five-Component Distillation

Boil-up Ratio	Distance(D_s)	Feasible	$\lVert x_D - x_{D,spec} \rVert$	Q_R*	Q_C*
4.0	0.91561	no	0.030210		
4.458	0.94097	no	0.020011		
4.459	0.94102	yes	0.019998	2.70456×10^4	2.99045×10^4
5.0	0.96585	yes	0.014996	2.97259×10^4	3.35328×10^4
6.0	1.00141	yes	0.011058	3.46804×10^4	4.02394×10^4

* Heat duties in Btu/h per lbmol/h of feed

The problem studied here is a direct split that takes the light component, n-propane, as the overhead product. The feed, bottoms, and approximate distillate compositions for this direct split are given in Table I.15. The distillation is considered to be feasible if the condition $\lVert y_D - y_{D,spec} \rVert \leq 0.01$ is satisfied. Thus the calculated distillate product must lie within a small hyper-sphere about the specified distillate composition.

The shortest stripping line distance of 1.37254 corresponds to a minimum boil-up ratio of 3.0132. The corresponding reflux ratio is $r = 15.8538$ and the feed pinch in the stripping section is at $x_{FP} = (x_{nC3}, x_{nC4}, x_{iC4}, x_{iC5}, x_{nC5}) = (0.670377, 0.087849, 0.078203, 0.069014, 0.050096)$. The rather high value of the minimum reflux ratio is due to the need to remove substantial amounts of the heavier components in the rectifying section of this column, which actually contains only three stages.

Table I.15: Column Specifications for a Six-Component Distillation

Component	Distillate+	Feed*	Bottoms
Propane	0.989	0.15	1×10^{-10}
n-Butane	0.0031	0.20	0.2352
iso-Butane	0.0023	0.15	0.1764
iso-Pentane	0.0031	0.20	0.2352
n-Pentane	0.0023	0.15	0.1764
n-Octane	0.0002	0.15	0.1768

+ Feasible if $\|y_D - y_{D,spec}\| \leq 0.01$; * Saturated liquid (q = 1)

Table I.16 summarizes the numerical results for this example.

Table I.16: Numerical Results for a Sharp Separation of a Six-Component Mixture

BR	Distance(Ds)	Feasible	$\| y_D - y_{D,spec} \|$	Q_R*	Q_C*
2.5	1.23793	no	0.015026		
3.0130	1.37249	no	0.010001		
3.1032	1.37254	yes	0.009999	4.77049×10^4	2.25389×10^4
4.0	1.56608	yes	0.006071	5.81314×10^4	3.30484×10^4
4.5	1.64113	yes	0.005603	6.39446×10^4	3.71794×10^4

* Heat duties in Btu/h per lbmol/h of feed

I.6.6 Examples of Non-Pinched Minimum Energy Solutions

Here we show that the concept of shortest stripping line can determine minimum energy in cases where the minimum energy solution does not lie at a pinch point. For both illustrative examples in this section, non-pinched solutions were determined by first solving the NLP problem defined by Eqs. 7 to 12 and subsequently solving the IP problem defined by Eqs. 14 to 17 together with Eqs. 10 to 12 since these non-pinched examples have both stripping and rectifying sections in the columns using integer bisection.

A Non-Pinched Minimum Energy Solution for a Ternary Mixture

Koehler et al.[22] provide an example where minimum energy consumption does not correspond to a pinch point and that it is possible to construct a finite column that uses minimum energy. Consider the separation of a mixture of chloroform, acetone and benzene at atmospheric pressure where the vapor phase is assumed to be ideal. Feed, bottoms, and approximate distillate compositions for this example are shown in Table I.17. The primary objective of this separation is to produce a chloroform-rich distillate such that $x_D(C) \geq 0.945$.

Distillations with minimum energy solutions that do not lie at a pinch point can be solved using a two-step approach based on the concept of shortest stripping line – as described in section 5. First, the shortest stripping line that gives a pinch for the desired separation is determined by solving the NLP defined by Eqs. 7 to 12.

Table I.17: Column Specifications for Chloroform/Acetone/Water Distillation with No Pinch

Component	Distillate$^+$	Feed*	Bottoms
Chloroform	0.9450	0.4395	0.3297
Acetone	0.0330	0.0330	0.0330
Benzene	0.0210	0.5275	0.6373

+ Feasible if $x_D(C) \geq 0.945$; *Saturated liquid ($q = 1$)

For the example under consideration, there is a feed pinch at $x_{FP} = (x_C, x_A) = (0.590498, 0.056757)$ corresponding to $s_{min} = 2.46293$, where the stripping line distance to the pinch point curve is 0.2920, as shown in Figure I.8. The reflux ratio is $r = 10.33889904$ and the resulting distillate composition is $x_D(C) = 0.99962$ and easily meets the purity specification for chloroform. Using this value of s_{min}, and integer programming (see section 5), the number of stripping stages, N_s, is determined that still gives the desired separation. This reduction in stripping stages obviously results in a smaller value of stripping line distance. For this example, the number of stages is reduced from 300 (considered infinite) to 209, for which the corresponding feed tray composition is $x = (x_C, x_A) = (0.526774, 0.101588)$ in 9 integer bisection iterations. Note that this feed tray composition is very close to the stripping pinch point curve. This results in a reduction in stripping line distance from $D_s = 0.2920$ to $D_s = 0.2141$ and a distillate composition of $x_D(C) = 0.99842$, which also easily meets the desired purity specification for chloroform. However, it is important to note that the numerical calculations for this example are very sensitive. Slight changes in boil-up ratio and feed tray composition can result in a significantly different pinch point and an acetone-rich distillate product respectively. Thus different computers may give different results close to the pinch point curve.

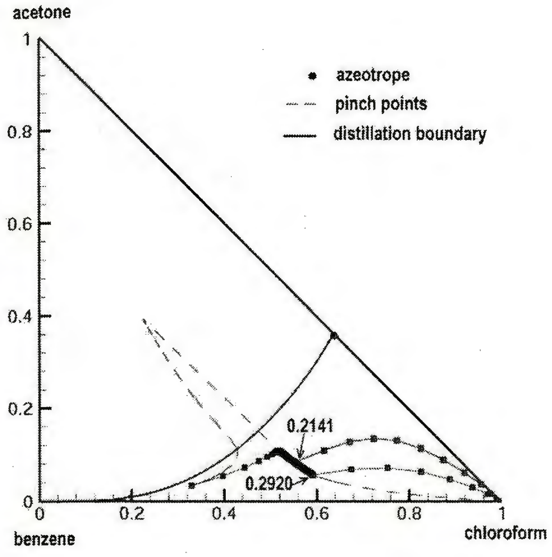


Figure I.8: Minimum Energy Requirements for a Column with No Pinch

A Non-Pinched Minimum Energy Solution for a Six-Component Refinery Mixture

Consider the feed mixture shown in Table I.15 and let the desired separation be a split between the C_4's and C_5's as shown in Table I.18. The liquid and vapor phases for this example are assumed to be ideal solutions where the K-values are given by the method in Wilson[36]. The distillation is considered feasible if the condition $|| y_D - y_{D,spec} || \leq 0.03$ is satisfied, where $y_{D,spec}$ is given in Table I.18. Surprisingly, this distillation is a more difficult separation than one might imagine because of the relatively volatilities of the components involved. Normal butane distributes more readily than expected. Nonetheless, Table I.19 gives results for two non-pinched solutions for the desired separation.

Table I.18: Column Specifications for a Six-Component Distillation

Component	Distillate+	Feed*	Bottoms
Propane	0.3000	0.15	1×10^{-12}
n-Butane	0.3960	0.20	0.0040
iso-Butane	0.3000	0.15	0.000014
iso-Pentane	0.0001	0.20	0.3990
n-Pentane	0.0001	0.15	0.3000
n-Octane	0.0038	0.15	0.3010

+ Feasible if $\| y_D - y_{D,spec} \| \leq 0.03$; * Saturated liquid ($q = 1$)

As shown in Table I.19, the minimum boil-up ratio for this distillation is $s_{min} = 12.669$ and corresponds to the shortest stripping line distance of 2.66343. However, it is also important to note that this minimum energy solution is not pinched. It is a non-pinched solution that has only 20 stripping stages and 6 rectifying stages and a corresponding minimum reflux ratio of $r_{min} = 11.669$. Moreover, each of the solutions in Table I.19 defines a neighborhood of boil-up ratios for which the desired separation is feasible. That is, all boil-up ratios in the ranges given by [12.669, 12.776] and [13.961, 14.402] actually meet the desired separation defined by the condition $\| y_D - y_{D,spec} \| \leq 0.03$.

Table I.19: Numerical Results for an Indirect Split of a Six-Component Mixture

BR	Distance(D_s)	Feasible*	$\|\| y_D - y_{D,spec} \|\|$	Q_R*	Q_C*
12.669	2.66343	yes	0.029989	1.041031×10^5	6.95585×10^4
13.961	2.69320	yes	0.029998	1.139429×10^5	7.66521×10^4

* Heat duties in Btu/h per lbmol/h of feed

We explain the non-pinched nature of the minimum energy solution to this problem in the following way. For this indirect split, the overall energy balance for the column dictates that the boil-up ratio cannot go below s = 1 otherwise the corresponding reflux ratio would be less than zero. However, even at slightly greater than one, the stripping feed pinch point is x_{FP} = (0.43039, 0.00312, 0.00001, 0.24100, 0.17500) where the compositions are in the order propane, n-butane, isobutene, iso-pentane, and n-pentane. At this stripping feed pinch point the composition of propane is already higher than the specified propane composition in the distillate in Table I.18. Since any rectification only increases the propane concentration in the distillate, it is clear that there is not a stripping feed pinch in this column. On the other hand, the rectifying pinch points that are relevant to this separation are severely limited. For a feed rectifying pinch point to occur, both the composition on some tray for the stripping profile and reflux ratio calculated by overall energy balance for a given value of s must match a composition and reflux ratio on the rectifying pinch point curve.

However, in this distillation, at relatively low values of reflux ratio the rectifying pinch point curve moves rapidly to the n-octane corner and we have a similar situation to that described for the top of the column. That is, at low values of reflux ratio the rectifying pinch point composition is greater than the specified n-octane concentration in the bottoms is 0.3010. Thus, there is no rectifying feed pinch for this column and the only alternative is a non-pinched minimum energy solution.

We compared the results in Table I.19 with those predicted by Underwood's method as implemented in the Aspen Plus program DSTWU, which uses constant relative volatility to describe the phase equilibrium. For the Underwood method we assumed that nC_4 and iC_5 were the light and heavy key components respectively, the recoveries for the light and heavy keys in the distillate were 0.9999 and 0.00025 respectively, and the column was equipped with a partial condenser. Also simple mass balance shows that $D/F = 0.5$ if the goal is to separate the C_4's and C_5's. The results predicted by Underwood's method differed substantially from those predicted by the shortest stripping line approach when Wilson's method[36] was used to describe the phase equilibrium. DSTWU predicts a minimum reflux ratio of $r = 1.3388$ and a minimum boil-up ratio of $s = 2.3388$.

To understand these marked differences we did several things.

1) Attempted to simulate the column using the minimum reflux and boil-up results from DSTWU and our shortest stripping line approach with Wilson's method[36] to describe the phase equilibrium.

2) Estimated constant relative volatilities and used those values to model the vapor-liquid equilibrium within our programs to determine minimum boil-up ratio based on the shortest stripping line distance.

3) Tried other examples using DSTWU and compared them to results using the shortest stripping line approach.

In the first case, where s = 1.3388 was used in our shortest stripping line approach, the propane composition at the stripping pinch point is well above the desired propane composition in the distillate product. Further rectification only makes matters worse and it is not possible to meet the desired specifications shown in Table I.18 at the top and bottom of the column with the minimum boil-up and reflux ratios predicted by Underwood's method. In the second case, we used constant relative volatilities of 4.9501, 1.9470, 2.4210, 1, 0.8522, and 0.1042 for propane, n-butane, i-butane, i-pentane, n-pentane, and n-octane respectively and our shortest stripping line approach. The minimum boil-up ratio calculated using the shortest stripping line approach and a constant relative volatility model matched the results in Table I.19 – not those given by DSTWU. Finally, we used DSTWU to determine minimum reflux and boil-up ratios for two other problems – the direct split of this six-component mixture whose results are described in Table I.16 and an indirect split of the ternary mixture described in the next section. Minimum reflux and boil-up ratios predicted by Underwood's method and the shortest stripping line approach agree quite well for the direct split of the six-component refinery mixture. On the other hand, for the indirect split of the ternary mixture described in the next section, DSTWU fails and thus provides no values for the minimum reflux or boil-up ratio.

I.6.7 Rectifying Feed Pinch Points and the Concept of Processing Targets

Most of the numerical results that we have presented thus far involve solutions that are derived directly or indirectly from pinch points on the stripping line equation (i.e., Eq. 6). In this section we show that the shortest stripping line approach can also easily find feed pinch points in the rectifying section as well as multiple pinch points. It is well known that indirect splits often give rise to rectifying feed pinch points and/or combinations of feed and saddle pinch points. For this illustration we consider a problem from Doherty and Malone[38]. This separation involves an indirect split of the ternary mixture of methanol (M), ethanol (E) and n-propanol (P), where the phase equilibrium is modeled assuming constant relative volatility. The relative volatilities for this example are $\alpha_{MP} = 3.25$, $\alpha_{EP} = 1.90$ and $\alpha_{PP} = 1.0$. Feed, bottoms, and approximate distillate compositions are shown in Table I.20. The distillation is considered to be feasible if the condition $||y_D - y_{D,spec}|| \leq 0.01$ is satisfied or when the calculated distillate product lies within a small hyper-sphere about the specified distillate composition.

Table I.20: Column Specifications for Indirect Split of Methanol/Ethanol/n-Propanol

Component	Distillate	Feed	Bottoms
Methanol	0.55	0.30	$5. \times 10^{-11}$
Ethanol	0.44	0.25	0.022
n-Propanol	0.01	0.45	0.978

+ Feasible if $||y_D - y_{D,spec}|| \leq 0.01$; * Saturated liquid (q = 1)

For this example we solved the NLP problem defined by Eqs. 7 to 12 with the modifications described for finding a rectifying pinch point as given in the algorithm section. Figure I.9 shows the results for two separate profiles that make the desired separation given in Table I.18. The column with the rectifying profile shown in red has a feed pinch in the rectifying section of the column and a saddle point pinch in the stripping section. It also corresponds to the shortest stripping line distance, measured to the stripping pinch point curve, for all feasible separations (i.e., 1.25003) and minimum energy requirements for this separation. The approximate feed pinch point is $x_{FP} = (x_M, x_E) = (0.171425, 0.357352)$ and the corresponding minimum boil-up and reflux ratios are $s_{min} = 2.965326689$ and $r_{min} = 1.47110557457$ respectively.

Doherty and Malone report a minimum reflux of r = 1.35, which we believe is wrong since their approach does not satisfy mass balance around the feed stage! To see this, note that the rectifying line in Figure 20b in Doherty and Malone pinches between two discrete stripping stages. The vapor composition from bubble point calculations for either of these stripping stages in their stripping profile near the rectifying stage that pinches will not match the vapor composition predicted by mass balance (and dew point calculations). Thus there will be component mass balances errors around the feed point.

The second, and longer column profile in Figure I.9 corresponds to a boil-up ratio of s = 20.28. This column has a stripping line distance of 2.17599, a near saddle pinch in the stripping section, but does not pinch in the rectifying section. In fact, this second solution can easily be considered a non-pinched solution since it has 34 stages in the stripping section and only 4 rectifying stages. Table I.21 gives other feasible solutions for this indirect split.

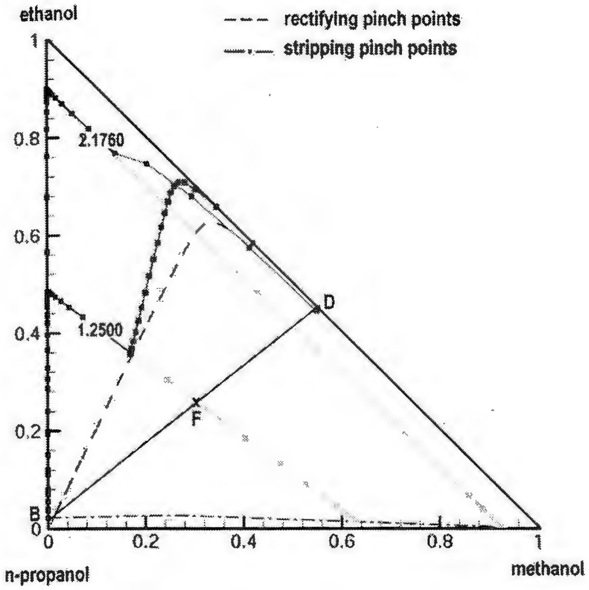


Figure I.9: Rectifying Feed Pinch Determined by Shortest Stripping Line

Table I.21: Numerical Results for the Indirect Split of Methanol/Ethanol/n-Propanol

[redacted]	(D_s)	Stages$^+$	Feasible	$\|\| y_D - y_{D,spec} \|\|$	Q_R*	Q_C*
2.9678968	1.25003	37(21)	yes	0.007614	3.22738×10^4	2.13544×10^4
20.28	2.17599	34(4)	yes	0.009972	1.73085×10^5	1.45917×10^5
32.62	2.25514	33(5)	yes	0.009999	2.73456×10^5	2.34706×10^5
55.16	2.30993	32(6)	yes	0.009971	4.56790×10^5	3.96884×10^5
93.47	2.34311	31(7)	yes	0.009992	7.68393×10^5	7.97748×10^5

[redacted]

+ Stripping stages (rectifying stages); * Heat duties in Btu/h for lbmol/h feed

This example also illustrates a number of important points regarding the shortest stripping line approach. First, the correct way to measure stripping line distance is always from the bottoms composition to the stripping pinch point curve – even though the pinch may occur in the rectifying section. Note that we have included the complete stripping profiles to the stripping pinch point curve in light gray in Figure 9 for clarity. Second, it again clearly shows that it is the shortest stripping line that is important in finding minimum energy requirements – not the distance of the stripping line plus rectifying line. Third, this example illustrates that there is a very simple way of deciding whether there is a potential feed pinch in the rectifying or stripping section and how to find a good approximation of the feed pinch point. Notice that the stripping profiles cross the rectifying pinch point curve before they cross the stripping pinch point curve. This, we believe, clearly suggests that there is a potential feed pinch in the rectifying section and not in the stripping section. Moreover, note that the extended stripping line corresponding to minimum boil-up ratio passes through the feed point. Thus, the intersection of this actual stripping profile with the rectifying pinch point curve represents a useful processing target for the amount of separation that needs to be accomplished (or the number of stages) in the stripping section of the column design that gives a rectifying feed pinch. Thus all one needs to do is find the stripping profile that passes through the feed point, locate the intersection of this stripping line with the rectifying pinch point curve, say x_{FP}, identify the corresponding reflux ratio from the rectifying pinch point curve, say r_{FP}, and count the number of stripping stages needed to get from x_B to x_{FP}. If there is a feed pinch point in the rectifying section, then the reflux ratio, r, calculated from overall energy balance (i.e., Equation I.10) should match closely with the value of r_{FP}. As in the case of the six-component refinery example, each non-pinched solution shown in Table I.21 defines a range of boil-up ratios that meet the desired separation for the given number of stripping and rectifying stages. For example, for <u>all</u> s = [20.28, 23.19], a column configured with 34 stripping stages and 4 rectifying stages easily makes the desired separation given in Table I.20. Finally, despite all of these problem characteristics, the shortest stripping line approach easily identifies the minimum boil-up ratio and hence minimum energy requirements for this separation.

I.7 Minimum Energy Requirement for Multi-Unit Process

One of the key features of the concept of shortest stripping line is its ability to find minimum energy requirements for multi-unit processes. In doing so, it provides correct processing targets so that the overall process uses minimum energy. Two examples of multi-unit processes – a hybrid extraction/distillation process and reaction/separation/recycle system – are given. In each case the NLP problem defined by Equations I.7 to I.13, which include ancillary constraints, was solved. The reason these additional constraints are required is to define correct processing targets that are constrained to lie on surfaces defined by liquid-liquid equilibrium curves or reaction equilibrium curves.

I.7.1 Hybrid Separation of Acetic Acid and Water

Lucia et al.[1] have recently analyzed the energy consumption of a hybrid separation scheme for the production of acetic acid. Here we briefly summarize the results and provide some additional energy requirement information. The process flow diagram for producing acid by extraction and distillation is shown in Figure 10. To correctly determine minimum energy use, it is necessary to determine the extent of extraction that results in the subsequent distillation processes using minimum energy such that the acetic acid specifications in the bottoms stream of the acid recovery column are still met. To do this, careful attention must be paid to the fact that the feed to the acetic acid recovery column must lie on the binodal curve. Thus there is a correct processing target (i.e., extract composition) that results in minimum energy use.

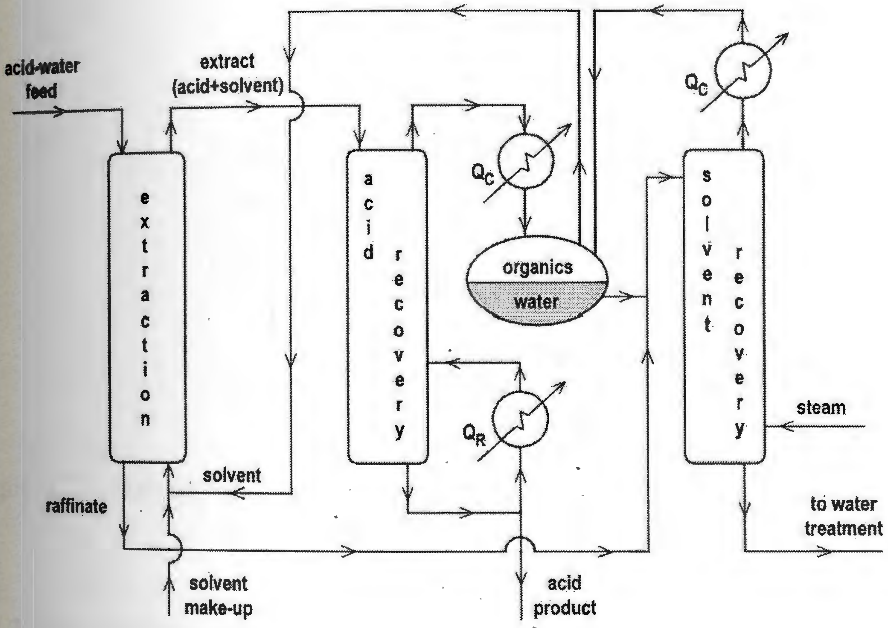


Figure I.10: Hybrid Separation Process for Acetic Acid

Feasible and infeasible acid recovery columns are shown in Figure 11 while boil-up ratios, target extract compositions, and energy requirements are tabulated in Table I.22. The most energy efficient solution to the acid recovery column is a stripping column with 17 stages and is clearly not pinched, has a stripping line distance of D_s = 1.3659 and corresponds to the minimum boil-up ratio of $s_{min} = 9.10$. It is also worth noting that the reason for the differences in energy requirements for the two feasible stripping columns is not the difference in the boil-up ratios but rather the difference in throughput to the acetic acid recovery column, which in turn, is due to the significant difference in the extent of extraction.

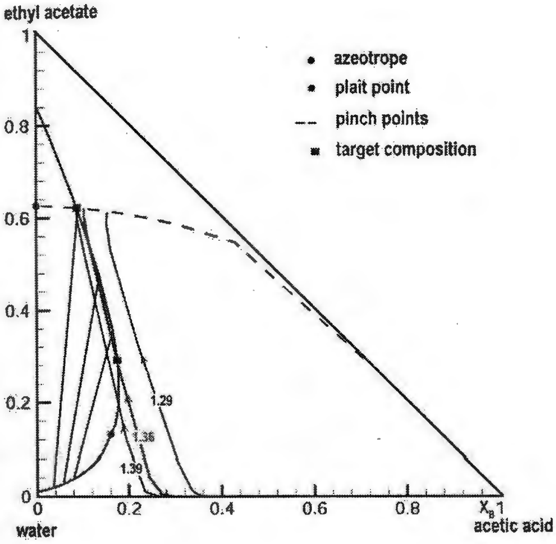


Figure I.11: Hybrid Separation of Lower Purity Acetic Acid

I.7.2 Reaction/Separation/Recycle Versus Reactive Distillation

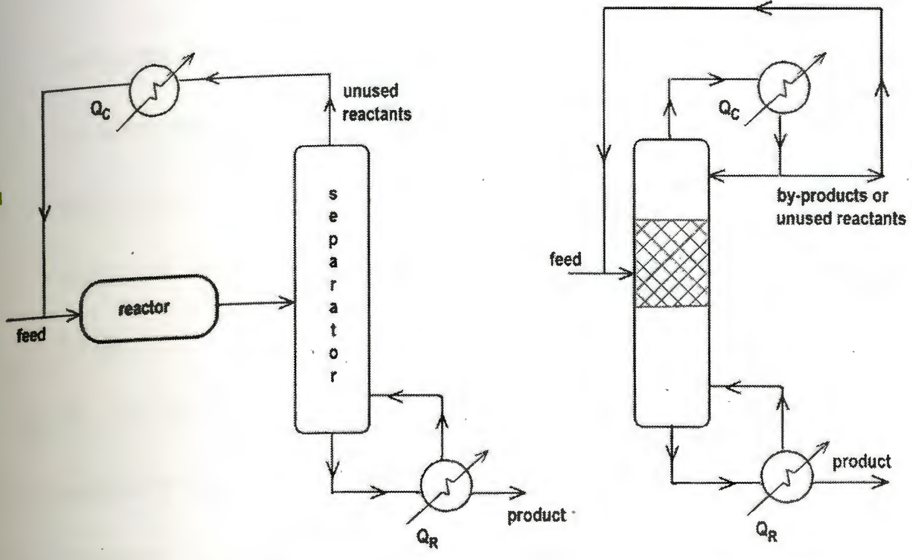
In this section we compare two processes for producing Methyl Tertiary Butyl Ether (MTBE) – reaction/separation/recycle (RSR) and reactive distillation – as shown in Figure 12. In both cases, we show that the concept of shortest stripping line correctly determines minimum energy requirements.

Table I.22: Summary of Stripping Lines and Boil-up Ratios for Acetic Acid Recovery Column+

BR	(D_s)	Feasible	Target (Feed)	Distillate	Q_R*	Q_C*
10.89	1.3908	yes	(0.0888, 0.6199)	(0.0056, 0.6769)	9.5542×10^3	1.5332×10^4
9.10	1.3659	yes	(0.1764, 0.2807)	(0.0864, 0.3115)	9.3988×10^3	1.4904×10^4
6.0	1.2923	no	(0.0152, 0.7135)			

+ x_B(AA, EAc) = (0.9950, 1×10^{-10}); * Heat duties in Btu/h per lbmol/h of extract (i.e., feed to acid recovery column)

The production of MTBE from isobutene and methanol at slightly elevated pressure has been studied extensively in the literature [39,40,41]. For definiteness, consider the production of MTBE (3) from isobutene (1) and methanol (2), in which inerts such as n-butane are not considered. In order to compare the RSR and RD processes, the MTBE flow rate and composition were specified to be 1 kmol/time unit and $x_B = (10^{-12}, 10^{-8}, 1)$ respectively. The pressure was assumed to be the same in both processes and, following Nisoli et al.[39], was specified to be 8 atm. In both processes we assume reaction equilibrium in the reactor effluent of the RSR process and on each stage in the reactive section of the RD process.



reaction /separation /recycle

reactive distillation

Figure I.12: Reaction/Separation/Recycle and Reactive Distillation Processes

Reaction equilibrium is represented by

$$x_1 \gamma_1 x_2 \gamma_2 K - x_3 \gamma_3 = 0 \tag{I.18}$$

where K is a reaction equilibrium constant. Liquid phase activity coefficients were calculated from the Wilson equation while the vapor phase was assumed to be ideal. Vapor pressures needed in the vapor-liquid equilibrium calculations for the stripping column in the RSR process as well as those in the RD column were obtained from Antoine's equation. Parameters for all models used to estimate thermodynamic properties are given by Nisoli et al.[39].

One notes immediately from Figure 7 in Nisoli et al. that

1) For the case of no reaction (i.e., Figure 7a), the separation boundary for isobutene, methanol, and MTBE at 8 atm. is the longest path and can be found by computing the longest residue curve or distillation line from methanol-isobutene azeotrope through the methanol-MTBE azeotrope to both the methanol and MTBE vertices using the procedure described in Lucia and Taylor[3].
2) For the case of reactive separation at high Damkohler number, the separation boundary changes significantly as shown in Figure 7b in Nisoli et al. However, Taylor et al.[4] have shown that this separation boundary is actually the longest path (i.e., reactive residue curve or distillation line) that runs from the isobutene vertex to the methanol vertex. The longest path corresponds to the chemical equilibrium curve.

A Reaction/Separation/Recycle System

The objective of this RSR process is to produce pure MTBE. However, producing pure isobutene at the top of the column in the RSR process is not a concern as it is in reactive distillation because the overhead product in the RSR process can be recycled to the reactor. Figure I.13 shows various stripping lines for the mixture isobutene (I), methanol (M) and MTBE at 8 atm, for the production of high purity MTBE. Also shown in Figure 13 are the chemical equilibrium curve (under the assumption that the Damkohler number is high enough to drive the reaction to equilibrium), the distillation boundary for the case of no reaction, the attainable region for PFR's for a range of isobutene and methanol feeds, and the distances of various stripping lines.

The feasible stripping columns for the production of pure MTBE that are shown in Figure 13 assume that the reactor effluent is on the chemical equilibrium line. We note that in Figure 13, as in other figures in this manuscript, the stripping line distance is measured from the bottoms composition to the stripping pinch point curve and only the stripping line at the very bottom of the triangular region is infeasible. However, it is clear from Figure 13 that the (back-to-front) approach to synthesis and design based on the concept of shortest separation line easily identifies the correct PFR reactor effluent target composition so that the RSR process uses minimum energy. This reactor effluent target, in turn, identifies the overall feed (fresh feed plus recycle) to the reactor by following the appropriate PFR trajectory in the attainable region toward the hypotenuse.

The net result of this is that if minimum energy is the objective, then the overall feed to the reactor should not consist of a stoichiometric (or 1:1) ratio of isobutene and methanol but should be a mixture of 58-mol% isobutene and 42-mol% methanol. This ratio of reactants to the column is easily determined by extrapolating the PFR trajectory back to the hypotenuse. On the other hand, the overall feed to the process is equimolar mixture of isobutene and methanol and is fixed by overall mass balance to the RSR process. Numerical results for this RSR process are summarized in Table I.23.

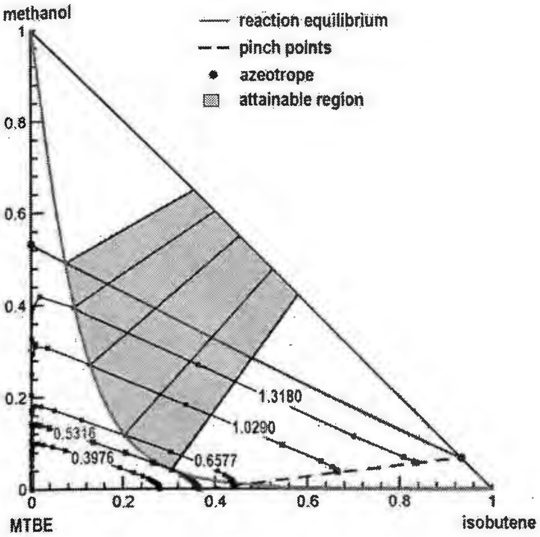


Figure I.13: Minimum Energy Requirements for a Reaction /Separation /Recycle Process

Note with regard to this illustration

1) It is important to know the location of the distillation boundary shown in Figure I.13 because it shows that without sufficient reaction, the reactor effluent would lie in the distillation region at the top and recovery of a high purity MTBE product would not be possible.
2) Due to the presence of the distillation boundary, little is gained by rectification and therefore separation can be achieved using a stripping column, in which the overhead product is recycled back to the reactor.
3) The energy of any PFR increases as conversion approaches the chemical equilibrium line. However, these energy requirements are insignificant compared to the energy requirements for separation.

4) As in the case of the hybrid separation scheme, the proposed back-to-front approach based on the concept of shortest separation lines clearly identifies the correct reactor effluent target for the desired MTBE product. Moreover, this effluent target does not lie at a pinch point for the stripping column.

5) The stripping column design that uses minimum energy corresponds to the shortest stripping line distance of 0.5316, $s_{min} = 0.917$, and has 37 stages. It is clear from Figure 13 that this design is not pinched.

6) The reactor effluent target determined from the shortest stripping line distance shows that minimum energy consumption requires a reactor feed of 58 mol% isobutene and 42 mol% methanol.

Table I.23: Summary of Stripping Lines and Boil-up Ratios for Recovery of Pure MTBE Using an RSR Process

	Distance(D_s)	Feasible	$x_T^{\#}$	$x_F^{\#}$	Q_R*
10.01	1.3180	yes	(0.0949, 0.3953)	(0.4005, 0.5995)	203.55
3.036	1.0290	yes	(0.1283, 0.2714)	(0.4553, 0.5447)	61.70
1.204	0.6577	yes	(0.2031, 0.1174)	(0.5225, 0.4745)	24.47
0.917	0.5316	yes	(0.3056, 0.0415)	(0.5799, 0.4201)	18.64
0.7000	0.3976	no			

mole fractions of isobutene and methanol respectively; * Reboiler duty in Btu/h per lbmol/h of MTBE.

ctive Distillation

The design of a column to accomplish both reaction and separation simultaneously can be more complicated than the design of a non-reactive distillation column since there are more things to consider. For definiteness we adopt a column configuration considered by Lee and Westerberg[40] in which there is no reaction in the stripping section of the column, in the condenser, or in the reboiler. The single feed to the column is to the first stage in the rectifying section. Heat effects such as differences in latent heats, non-CMO behavior, and heat of reaction are ignored. The bottoms composition is specified exactly as in the RSR process while the distillate specification defining feasibility is $x_D(iC_4) \geq 0.998$.

Governing Equations

The equations used to determine distillation lines for the reactive distillation processes differ in format from Equations I.1 to I.6 and are, therefore, summarized here. The total and component material balances are given by

$$F - D - B = -\nu\varepsilon_T \tag{I.19}$$

$$Fz_i - Dx_{i,D} - Bx_{i,B} = -\nu_i\varepsilon_T \tag{I.20}$$

where ν_i is the stoichiometric coefficient for the ith component and the unsubscripted variable, ν, in Equation I.19 is the stoichiometric coefficient for the overall reaction and has the value of -1 for the production of MTBE from isobutene and methanol. The variable, ε_T, in Equation I.19 and I.20 denotes the extent of reaction for the entire column and signifies that the number of degrees of freedom is one higher than that for a conventional distillation. Thus for the three component mixture under consideration we can specify two mole fractions in both the distillate and bottoms streams. The overall and component material balances together with the mole fraction summation equations may then be solved for the flow ratios, F/B and D/B, as well as the overall extent of reaction that is needed to achieve the specified product purities.

The model equations for the jth stage in an RD column include the overall and component material balances

$$F_j + L_{j+1} + V_{j-1} - V_j - L_j = -\nu\,\varepsilon_j \tag{I.21}$$

$$F_j z_{i,j} + L_{j+1}x_{i,j+1} + V_{j-1}\,y_{i,j-1} - V_j\,y_{i,j} - L_j x_{i,j} = -\nu_i\varepsilon_j \tag{I.22}$$

where ε_j is the extent of reaction on the jth stage. To these equations we add the familiar equations of phase equilibrium, mole fraction summation, and the stage energy balance, which in the assumed absence of heat effects simplifies to $V_j = V_{j-1}$.

Calculation of the composition profile and associated stripping line distance begins by solving the equations for the reboiler. This is a special case of Equations I.21 and I.22 in which $V_0 = 0$ and $V_1 / B = s$ and provides the composition of the vapor leaving the reboiler, the composition of the liquid entering the reboiler, the temperature, and the unknown flows. Moving from the reboiler to each stage in the stripping section, we continue the calculations in a similar manner until we reach the pinch at the end of the stripping line. However, these stage-to-stage calculations in the stripping section require that Equations I.21 and I.22 be augmented by the simple equation $\varepsilon_j = 0$, which expresses the condition of no reaction in the stripping section.

We must now search for the feed stage and continue the stage-to-stage calculations up the rectifying section of the column. Remember, in this case, reaction equilibrium constrains the composition of the liquid *leaving* the feed stage and all stages in the rectifying section. Thus, to find the feed stage we must search for a stage composition that lies on the reaction equilibrium line. Each of the stripping profiles shown in Figure I.13 has a stage composition that lies on the reaction equilibrium line. However, not all of these stripping lines are candidates for the stripping section of a reactive distillation column to make MTBE with the specified composition. Other stripping ratios intermediate between those shown given in Table I.23 will lead to profiles that do not have a stage composition on the reaction equilibrium line.

Once we have located a feasible feed stage composition we can continue to solve the model equations for the stages in the reactive rectifying section. The model for the feed stage and all higher stages necessarily includes the reaction equilibrium equation for the composition of the liquid entering the feed stage from the stage above together with the equations of phase equilibrium for the stage above because it is these equations that determine the temperature at which the activity coefficients in Equation I.18 are to be evaluated. For the stages with reaction, the extent of reaction is found as part of the solution.

The composition profile for the reactive section of all feasible column configurations follows the reaction equilibrium line and terminates in the isobutene corner of the composition triangle shown in Figure I.13. This fact makes matching or surpassing the desired distillate purity simpler than that for any of the other cases considered in this paper.

Because the stripping section of the RD column carries out exactly the same separation as the stripping column in the RSR process it follows that the RD column with the lowest energy demand is the same as that in the RSR process and corresponds to the shortest stripping line distance. Numerical results for this RD process are shown in Table I.24 and Figure I.13. However, it is important to note that only the two shortest stripping profiles in Figure I.13 are able to serve as the stripping section of a feasible reactive distillation column. The other columns either encounter the stripping pinch point curve before reaching the reaction equilibrium line or miss the reaction equilibrium line altogether. Our calculations show that column design that satisfies the specified bottoms composition, reaches the desired distillate purity of $x_D(iC_4) \geq 0.998$, and uses the least energy has 37 stripping stages and 6 rectifying stages. This minimum energy design corresponds to the shortest stripping line distance of 0.5316 and a minimum boil-up ratio of $s_{min} = 0.917$.

Table I.24: Summary of Stripping Lines and Boil-up Ratios for Recovery of Pure MTBE Using an RD Process

BR	(D_s)	Feasible	x_T#	x_F#	Q_R*
10.01	1.3180	no	(0.0949, 0.3953)	(0.4005, 0.5995)	
3.036	1.0290	no	(0.1283, 0.2714)	(0.4553, 0.5447)	
1.204	0.6577	yes	(0.2031, 0.1174)	(0.5225, 0.4745)	24.47
0.917	0.5316	yes	(0.3056,0.0415)	(0.5799, 0.4201)	18.64
0.700	0.3976	no			

mole fractions of isobutene and methanol respectively; * Reboiler duty in Btu/h per lbmol/h of MTBE.

It is also important to note that the feed composition plays an important role in design and operation of MTBE reactive distillation columns. For example, if the feed composition approaches equal parts isobutene and methanol, then the reflux ratio must increase significantly in order to ensure that there is sufficient liquid to return to the column and it actually operates as a (reactive) distillation column. In the example of Lee and Westerberg[40], the feed is 60% isobutene, the reflux ratio is 14 and there are 16 stripping stages and 3 reactive stages in the rectifying section including the feed stage. Figure I.13 clearly shows that the design of Lee and Westerberg is not a minimum energy design. Moreover, the MTBE purity in this design is “only” 99.2%. In practice the production of MTBE via reactive distillation is normally carried out in the presence of an inert such as n-butane. See, for example, Chen et al.[41]. Moreover, there may also be other compounds present in the feed, which among other things, guarantees that there is sufficient liquid to return to the column as reflux.

In retrospect it is not surprising that the minimum energy stripping section is the same for the RSR and RD processes given the vessel configurations and recycle stream shown in Figure I.12. The volatilities of the compounds involved in this process are such that the reaction should take place above the feed; thus, the same non-reactive stripping line suffices for both processes. However, one should be cautious about generalizing this result since there is a wide variety of possible reactive distillation column configurations[39]. We also note here that for columns that attain reaction equilibrium on each stage the material balances can be written in form of transformed composition variables[27,39] and it is easy to show that the lowest energy design corresponds to that with the shortest stripping line when expressed in terms of these transformed composition variables.

Finally we remark that if distillate product is actually drawn from the RD process, this will alter the overall mass balance for the RD process and change, perhaps significantly, the design that uses minimum energy. Nevertheless, our back-to-front approach based on shortest stripping line can be used to find minimum energy designs for this case as well.

I.8 Conclusions

The concept of shortest stripping lines was used to find minimum energy requirements in distillation, reactive distillation, hybrid separation processes, and [redacted]/separation/recycle systems. Optimization formulations of the shortest stripping line approach were presented and a variety of examples involving binary and multi-component mixtures were studied – including examples with five and six components. It was shown that the shortest stripping line successfully determines minimum energy requirements for distillation and reactive distillation processes regardless of the underlying thermodynamic models. Illustrative examples show that our approach can find feed, saddle, and tangent pinch points as well as minimum energy solutions that do not correspond to a pinch. Moreover, it was shown that the shortest stripping line approach finds correct processing targets in multi-unit processes so that the overall process consumes minimum energy. Results for two examples of multi-unit processes – an extraction/distillation process for the separation of acetic acid and water and MTBE production using reactive distillation and a reactor-separation-recycle process – were presented to support these claims.

Finally, we close with the remark that the concept of shortest stripping line is a fundamental principle in separations that encompasses many approaches to minimum energy consumption in distillation processes. For example, in this paper we have demonstrated that both McCabe-Thiele method and the boundary value methods of Doherty and co-workers have shortest stripping line interpretations when they are used to determine minimum energy requirements. In more recent work, Amale and Lucia[42] have shown that Underwood's method also has a shortest stripping line interpretation and represents a global minimum in energy consumption for a specified set of light and heavy key component recovery fractions.

Nomenclature

B	bottoms product molar flow rate
c, $c(x)$, c_D	number of components, constraint function, distillate constraint
D, D_s	distillate molar flow rate, stripping line distance
F, F_{Di}	feed molar flow rate, driving force function
HK	heavy key component
K, K	vector of equilibrium ratios, reaction equilibrium constant
L	liquid molar flow rate in rectifying section
LK	light key component
Ns, N	number of stripping stages, number of total stages
N_L, N_U	lower and upper bounds on the number of stripping stages
p, p_c	pressure, critical pressure
q	thermal quality of feed stream
Q_R, Q_C	reboiler duty, condenser duty
r	reflux ratio
s	boil-up or stripping ratio
T, T_c	temperature, critical temperature
V, V'	rectifying section vapor molar flow rate, stripping section vapor molar flow rate
x_i, x_i'	liquid molar composition of ith component, derivative of x_i with respect to independent variable
x, x_B, x_D	vector of liquid mole fractions, bottoms composition, liquid distillate

	composition
x_T, x_F	extract target composition, feed composition
x_{PP}, x_{TP}, x_{FP}	pinch point composition, tangent pinch composition, feed pinch composition
y_i	vapor molar composition of ith component
y, y_D	vector of vapor mole fractions, vapor distillate composition

Greek symbols

α	relative volatility
$\varepsilon, \varepsilon_T$	convergence tolerance, extent of reaction
γ	vector of activity coefficients
Λ	Lagrangian function
ν_i, ν	ith component stoichiometric coefficient, overall stoichiometric coefficient
μ	vector of Kuhn-Tucker multiplier
ω	acentric factor

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Appendix I.1

In this appendix, the relevant physical property data for the examples studied in this paper consist of binary interaction parameters for the UNIQUAC activity coefficient model and the constants required to compute standard state fugacities for each component in the liquid phase.

Table I.A1: Pure Component Constants for Extended Antoine Equation

Component	c_1	c_2	c_3	c_4	c_5	c_6
chloroform	174.24	-8140.0	0	0.065975	-29.011	-3.0001×10^{-5}
methanol	333.87	-12679.0	0	0.13671	-57.722	-5.9496×10^{-5}
acetic acid	386.98	-15091.0	0	0.16774	-67.642	-7.2738×10^{-5}
ethanol	-90.91	-3465.9	0	-0.062301	20.486	2.0664×10^{-5}
acetone	-230.66	686.03	0	-0.14358	46.384	6.3961×10^{-5}
ethyl acetate	-129.13	-2259.9	0	-0.096853	28.02	4.3325×10^{-5}
n-pentane	69.020	-5362.5	0	0.0099221	-9.4897	-3.8363×10^{-5}
benzene	97.209	-6976.1	0	0.019082	-14.212	-6.7182×10^{-6}
n-heptane	-17.613	-4669.8	0	-0.035093	6.9580	1.4503×10^{-5}
water	57.042	-7004.8	0	0.0035888	-6.6689	-8.5054×10^{-7}
acrylic acid	13.200	-5489.7	0	0	0	0

The standard state liquid phase component fugacities can be expressed using an extended Antoine equation of the form

$$\ln f_i^0 = c_{i,1} + c_{i,2}/(T + c_{i,3}) + c_{i,4}T + c_{i,5}\ln(T) + c_{i,6}T^2 \qquad \text{(I.A1)}$$

where has units of bar. Table I.A1 gives the numerical values of the pure component constants in Eq. I.A1.

Table I.A2: Binary Interaction Parameters for the UNIQUAC Equation

[redacted]	Component j	a_{ij} (K)	a_{ji} (K)
chloroform	acetone	93.96	-171.71
chloroform	benzene	4.98	-50.53
methanol	acetic acid	-20.50	-25.69
methanol	ethanol	660.19	-292.39
methanol	ethyl acetate	-107.54	579.61
methanol	water	-50.82	148.27
acetic acid	ethanol	244.67	-210.53
acetic acid	ethyl acetate	-214.39	426.54
acetic acid	water	-173.64	196.41
acetic acid	acrylic acid	-119.22	166.65
ethanol	ethyl acetate	-167.61	571.73
ethanol	water	-64.56	380.68
acetone	water	530.99	-100.71
acetone	benzene	-108.79	174.0
ethyl acetate	water	569.86	80.91
water	acrylic acid	-170.98	292.67

The temperature-dependent interaction terms, τ_{ij}, for the UNIQUAC equation of Prausnitz et al.[34] are expressed in the form

$$\tau_{ij} = \exp(-a_{ij}/T) \qquad \text{(I.A2)}$$

where the a_{ij}'s are binary interaction parameters. Table I.A2 gives the binary interaction parameters for the UNIQUAC equation for the chemical species used in this paper.

MANUSCRIPT II

Energy Efficient Hybrid Separation Processes

This chapter is the manuscript entitled, Energy Efficient Separation Processes, that was published in Industrial Engineering and Chemistry Research in 2006.

Abstract

Distillation accounts for a large percentage of the energy used in the manufacturing industry. As energy costs rise, hybrid separation strategies – strategies that combine one or more separation techniques with distillation – are attracting attention as a means of saving energy. Examples of hybrid separation schemes include extraction followed by distillation, reactive distillation, adsorption/distillation, and others. In this work, the energy efficiency of hybrid separation schemes is studied using the novel concept of shortest separation lines. Hybrid separation of acetic acid and water using extraction/distillation is used to show that shortest separation lines correctly define target extract compositions for the extractor and lead to the most energy efficient hybrid separations. A global optimization strategy, which uses a mixture of feasible and infeasible subsets of constraints to avoid the discrete nature of the feasible region, is presented for directly computing the most energy efficient hybrid separation schemes.

Keywords

Shortest separation lines, energy efficiency, hybrid separations, discrete feasible region.

II.1 Introduction

Batch and continuous distillation and crystallization have been the workhorses for separations in the petroleum, chemical, pharmaceutical, and other industries for many years, and this is unlikely to change. These unit operations, as well as others, will remain the primary means of separation in many industries for the foreseeable future. Other separation techniques like chromatography and membrane separation simply cannot provide the purity and volume to be competitive. However, distillation consumes significant amounts of energy. While some believe that these unit operations are mature technologies and that there is little to be gained from research in separations like distillation and crystallization, we disagree with this viewpoint for two reasons. First, with the recent significant increase in global energy demands and every indication that demand will remain high, it is important to consider ways of designing new separation processes and retrofitting existing ones so they are energy efficient. *Hybrid separations such as extraction followed by distillation and reactive distillation can often be used to reduce the energy costs of conventional distillation alone.* Second, the approach taken in this work is a direct outgrowth of recent results that shed new light on residue curves and distillation lines and it is unlikely that we would have uncovered the proposed characterization of energy efficient separations without our initial results.

Lucia and Taylor[1] have recently presented a geometric methodology for finding exact boundaries in separation processes and show that for ternary mixtures all separation boundaries are given by locally longest residue curves that run from a given unstable node to all reachable stable nodes. See Fig. II.1 – in which the numbers associated with each residue curve represent the distance from any unstable node to all reachable stable nodes. For this illustration of ethanol/ethyl acetate/water at 1 atm, the liquid phase was modeled by the UNIQUAC equation and the vapor phase was assumed to be ideal. The associated binary interaction parameters for the UNIQUAC model can be found in the Appendix.

For four-component mixtures, boundaries are local maxima in surface areas while for five or more components boundaries correspond to local maxima in volumes. This geometric theory has led to an efficient feasible path optimization algorithm for computing exact separation boundaries for a wide variety of batch or continuous separations. Moreover, rigorous proof and a number of challenging numerical illustrations have been used to validate the theory.

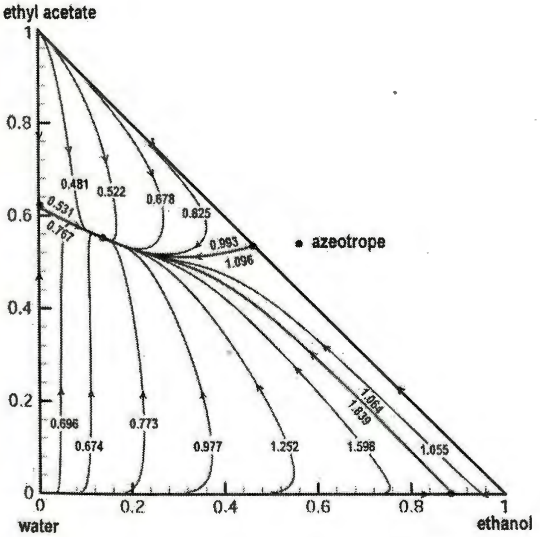

Figure II.1: Residue Curve Map and Line Integrals for Ethanol / Ethyl Acetate/Water

Motivation and Overview of This Work

Recent increases in the demand for energy on the world market have resulted in serious concern over the high-energy costs associated with distillation. Hybrid separation schemes (i.e., extraction/distillation, reactive distillation, adsorption/distillation, and so on) represent one way of reducing the energy costs of distillation alone. The motivation for this work comes from our fundamental belief that there is a connection between the length of residue curves (or distillation lines) and the energy needed to perform a given separation. In particular, we began with the intuitive belief that following the longest residue curve must somehow be related to the highest energy costs associated with performing a given separation. Furthermore, if the longest residue curve is the most costly separation, then the shortest curve should result in the use of the least amount of energy required for the given separation given task. Because we are interested in finite designs (i.e., finite stages and finite internal flows), we use distillation lines, which are equivalent to component mass balances (or operating lines) for finite separators under Constant Molar Overflow (CMO). Figure II.2 shows distillation lines for the ethanol/ethyl acetate/water mixture. Note the strong similarities between Figs. II.1 and II.2. All distillation regions in Figs. II.1 and II.2 contain shortest paths internal to these separation regions and longest paths that define the separation boundaries. Moreover, the shortest paths in each figure occur at roughly the same location, their corresponding lengths have approximately the same numerical values, and the longest paths define the exact same separation boundaries.

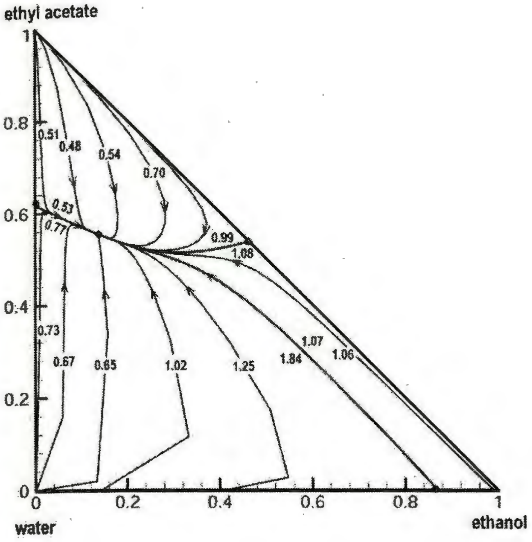

Figure II.2: Distillation Lines and Line Integrals for Families of Sharp Separations

The main contribution of this manuscript shows that *shortest separation lines give information regarding numbers of stages and minimum reflux or boil-up ratios, which in turn permit energy efficient separation process designs.* As a result, they provide definitive guidance for capital investment and operating costs associated with the synthesis, design, and retrofitting of finite separators for energy efficiency!

This paper is organized in the following way. Section 2 gives a brief survey of methodologies for the synthesis and design of energy efficient separations. The governing equations for distillation lines and their relationship to pinch point curves are presented in section 3. Section 4 provides an illustrative example of a hybrid extraction/distillation separation scheme. It is shown that the most energy efficient designs are the ones that correspond to shortest separation lines and that shortest separation lines can be used effectively to define correct target extract compositions.

It is also shown that the extraction/distillation synthesis problem has some unique characteristics that make it quite challenging from a mathematical perspective. In particular, the feasible region is not compact but comprised of a finite set of disjoint distillation lines. In addition, the extract stream that couples the extractor to the primary recovery column changes so the column synthesis is different than that which is usually studied in distillation. In section 5, the basic ideas – shortest separation lines defined on either continuous or disjoint feasible regions – are formalized. More specifically, a constrained nonlinear programming formulation is given that can be used to directly find energy efficient separation schemes. Conclusions and remarks are presented in section 6.

II.2 Brief Literature Survey

The literature on minimum flows and minimum energy use in distillation is quite large and dates back to the work of Underwood[2] for the case of constant relative volatility – including columns with complex configurations. It is well known that minimum energy requirements correspond to minimum reflux and/or boil-up ratios and an infinite number of equilibrium stages so that the column just performs the desired separation (or exhibits one or more pinch points). Most methods for determining minimum energy requirements are based on either methods for directly finding pinch points or rigorous column simulations.

The method of Underwood is straightforward and for the most part applies to ideal mixtures, although extensions to binary azeotropic mixtures and heat effects have been proposed. See Vogelpohl[3] and Hausen[4], respectively. For non-ideal multicomponent mixtures, and particularly those that exhibit azeotropes, methodologies for finding minimum reflux and boil-up ratios are more complicated. Perhaps foremost of those among these methods is the work of Doherty and co-workers[5, 6, 7, 8], who have developed techniques for non-azeotropic separations as well as homogeneous and heterogeneous azeotropic distillations. The approach of Doherty and co-workers relies heavily on the concept of pinch points, which are fixed points of the differential form of the operating line equations in the rectifying and stripping sections of a column (see the equations in the next section). In general, three types of pinch points are recognized – feed pinch points, saddle pinches, and tangent pinch points. A feed pinch point is easily recognized and corresponds to a pinch point composition equal to the feed composition. Saddle pinches, on the other hand, often occur at compositions that are not feed or product compositions and are generally the result of the attraction of an intermediate boiling azeotrope (i.e., a saddle point of the associated residue curve map). See Koehler et al.[9] for an illustration of a saddle pinch for the mixture chloroform, acetone and benzene. Doherty and co-workers also show that minimum energy requirements result when a saddle pinch in one section of the column is collinear to a feed pinch and an end pinch in the other section of the column. A tangent pinch point occurs when the algebraic form of any operating line equation exhibits a turning point. Physically, this corresponds to a point were the operating line is tangent to the phase equilibrium surface.

Pinch points can be determined by either algebraic or differential methods and most techniques for doing this are based on a Constant Molar Overflow (CMO) assumption – although some procedures do attempt to incorporate energy balance effects. Algebraic methods use the steady state form of column model equations, which are referred to as pinch point equations. These pinch point equations can be solved directly by Newton-like or other equation-solving methods to determine pinch point compositions. For example, Fidkowski et al.[7] illustrate the use of a continuation method for finding pinch points of the operating lines in either rectifying or stripping sections of a column. For feed pinch points the method of Fidkowski et al.[7] is straightforward. Tangent pinch points, on the other hand, correspond to turning points of the pinch point equations and require a bit more care in computing because of the singularity condition that accompanies any turning point. Koehler et al.[10] also present a method for finding tangent pinch points.

Rigorous simulation methods have also been used to determine minimum reflux (and energy) requirements for a variety of column configurations and many of these methods date back to the 1940's and 1950's. One of the first papers for finding minimum reflux was the work of Brown and Holcomb[11], who used the tray-by-tray method of Lewis-Matheson for column simulation. Other approaches by Murdoch and Holland[12] and Acrivos and Amundson[13] were based on CMO assumption and constant relative volatilities. The methodologies of Shiras et al.[14] and Bachelor[15], on the other hand, are based on the tray-to-tray approach of Thiele-Geddes and thus permit energy balances to be included in the determination of minimum reflux.

Holland and co-workers[16, 17,1 8] also present a method for computing minimum reflux for conventional and complex column configurations that is based on their θ-method. The θ-method is also a tray-by-tray approach closely related to the Thiele-Geddes method. While these methods are considered more rigorous than techniques that solve pinch point equations, because they can incorporate energy tray effects, they are also more laborious since they involve energy as well as mass balance equations. Finally, pinch points can also be determined in a reliable manner by integrating the differential form of the operating line equations presented in the next section and can be considered a rigorous simulation approach very similar to the Lewis-Matheson method.

II.3 Governing Equations

The equations used in this work to determine distillation lines under infinite or finite reflux ratio and/or number of stages can be found in Fidkowski et al.[7], are easily derived, and given by

$$x_j' = [(r+1)/r]y_j - x_j - (1/r)x_D \qquad (II.1)$$

$$x_j' = [(s)/(s+1)]y_j - x_j + [1/(s+1)]x_B \qquad (II.2)$$

Here x_j denotes a vector of c-1 liquid compositions and y_j is a vector of c-1 vapor compositions on stage j, where c is the number of components in the mixture. Also x_D and x_B are the distillate and bottoms compositions respectively, r = L/D is the reflux ratio, s = V'/B is the boil-up ratio, L is the reflux rate, V' denotes boil-up rate, and D and B are the distillate and bottoms flow rates respectively. Moreover, j is a stage index, and the stages are numbered from bottom to top. Equation II.2 is easily modified for a partial condenser by replacing x_D with y_D.

Equations II.1 and II.2 are equivalent to the rectifying and stripping profile in a CMO column, provided we define $x_j' = (x_{j+1} - x_j)/\Delta$ where $\Delta = 1$. To see this, let $\Delta = 1$ and use $x_j' = x_{j+1} - x_j$ in Eq. 1. This gives

$$x_{j+1} = [(r+1)/r]y_j - (1/r)x_D \tag{II.3}$$

Solving Eq. 3 for y_j yields

$$y_j = [r/(r+1)]x_{j+1} + [1/(r+1)]x_D = (L/V)x_{j+1} + (D/V)x_D \tag{II.4}$$

which is a component mass balance or operating line for the rectifying section of a staged column under CMO conditions. Here $V = L + D$ is the vapor flow leaving the top equilibrium stage in the column. Equation II.4 applies to a column with a total condenser. Again the modifications required for a column equipped with a partial condenser, where y_D replaces x_D, are straightforward. In a similar way, it is easy to show that Eq. 2 is equivalent to a component mass balance (or operating line) for the stripping section of a CMO column. Finally, note that at infinite reflux and boil-up ratios, these equations reduce to the c-1 residue curve equations given by the differential equation x' = y - x.

II.3.1 Remark

In simulating the behavior of any staged column using the differential equations defined by Eqs. II.1 and II.2 and phase equilibrium, it is important to recognize that the integration step size, h, must be set to $h = \Delta = 1$ and that forward Euler integration must be used. Moreover, one must also be careful of the direction of integration because of stage indexing and the direction of vapor and liquid flow. For columns with finite stages, integration must always proceed from the bottom up. Thus in the rectifying section, we integrate from the feed stage to the condenser and in the stripping section, integration takes place from the reboiler to the feed stage. Without these precautions the representation of the component mass balances for a staged column defined by Eqs. 3 and 4 is not exact.

II.3.2 Pinch Points, Minimum Flows and Energy Efficiency

Consider Eq. 2. For infinite s, it is easy to show that Eq. 2 reduces to $x_j' = y_j - x_j$, which has a stable fixed point or pinch point at $y_j = x_j$. In theory, this pinch point occurs when j = infinity. In practice $j \geq N$ will suffice, where N is some large positive integer. For fixed x_B, as s is reduced, this stable fixed point or pinch point changes and is defined by solving the (c-1) equations

$$0 = sy_N - (s+1)x_N + x_B = s(K_N x_N) - (s+1)x_N + x_B \qquad \text{(II.5)}$$

for the (c-1) unknowns x_N, where the K_N in Eq. 5 is a vector of (c-1) K-values and N is some sufficiently large positive integer. Vapor compositions can be back calculated using $y_N = K_N x_N$ once Eq. 5 is solved. In our work, pinch points are important in that they help establish the correct interpretation of shortest separation lines, which in turn can be related to minimum reflux and boil-up ratios, and thus minimum energy use.

II.4 A Methodology for Energy Efficient Hybrid Separations

The remainder of this paper presents a methodology for determining minimum energy requirements for a given separation based on the concept of shortest separation lines. To make the methodology clear, the separation of acetic acid and water is used. Acetic acid is an important chemical commodity because many intermediates (e.g., vinyl acetate monomer, terphthalic acid, acid anhydride, and various solvents) are manufactured from low water-content acetic acid. The separation of acetic acid and water by conventional distillation is known to be energy intensive and does not represent best industrial practice. For dilute solutions of acetic acid in water (i.e., at or below 30 wt% = 11.5 mol% acetic acid) hybrid separation using liquid-liquid extraction followed by distillation is often used. Throughout the remainder of this paper, we model liquid and vapor phases using the UNIQUAC equation and Hayden-O'Connell equation respectively as given in Prausnitz et al.[19]. Binary interaction parameters for the UNIQUAC model can be found in the Appendix.

II.4.1 Conventional Distillation of Acetic Acid and Water

The reason that conventional distillation of acetic acid and water is energy intensive, and not used in practice, is because acetic acid is the heavy component and thus forces large amounts of water to be condensed overhead, only to be re-vaporized internally in the column. Conventional distillation of acetic acid and water also requires high boil-up ratios for high purity acetic acid. To see this, consider a saturated liquid acetic acid-water feed of 11.5-mol% acetic acid. Also let the bottoms composition be high purity acetic acid with $x_B = (0.9999, 1 \times 10^{-4})$ and the distillate composition be $x_D = (1 \times 10^{-3}, 0.999)$. Let the total feed flow rate be 10,000 lb/h or 438.89 lbmol/h. For this feed and the given product compositions, the distillate and bottoms flow rates are D = 388.80 lbmol/h and B = 50.09 lbmol/h, respectively. It is also straightforward to determine the minimum reflux and boil-up ratios, either computationally or by using a McCabe-Thiele diagram. The minimum boil-up ratio that gives a feed pinch for this illustration is $s_{min} = 20.96$. The corresponding minimum reflux ratio is $r_{min} = 2.70$. The minimum boil-up ratio together with the bottoms flow rate determines approximate energy requirements. In particular, the vapor boil-up, $V' = s_{min}B = 20.96(50.09 \text{ lbmol/h}) = 1049.89 \text{ lbmol/h}$, which in turn gives a reboiler duty, $Q_R = V'\lambda_{AA} = (1049.89 \text{ lbmol/h})(10431.6 \text{Btu/lbmol}) = 10.952 \text{ MBtu/h}$, where ΔH^{vap} is approximated by λ_{AA}, the latent heat for pure acetic acid. Similarly, the duty for a total condenser is $Q_C = D(r_{min} + 1)\lambda_W = 3.70(388.80 \text{ lbmol/h})(17465.22 \text{ Btu/lbmol}) = 25.125 \text{ MBtu/h}$, where here ΔH^{vap} is approximated by λ_W, the latent heat of vaporization of water. The minimum total heat requirement for the separation of acetic acid and water by conventional distillation is simply $Q_R = 10.952$ MBtu/h. A conventional distillation with s = $1.1s_{min}$ requires 38 stages to operate near minimum energy requirements.

II.4.2 Hybrid Separation

The hybrid separation schemes studied in this work consist of liquid-liquid extraction followed by two distillations – an acetic acid recovery column and a solvent recovery column – with and without solvent recycle. See Fig. II.3. Hybrid separation is one way that acetic acid and water are separated in industry and thus represents current practice. The primary purpose of extraction is to first remove large amounts of water by phase separation. Moreover, solvent is usually chosen so that the relative volatility of solvent-acetic acid is much higher than that of water-acetic acid so the internal flows in the subsequent distillations are smaller. For a proposed hybrid separation scheme, some of the important synthesis and design questions include

1) How many stages are required for the extraction column?
2) What is the number of stages for the subsequent distillations?
3) How much extraction should be performed so that the subsequent distillations use a minimum amount of energy and still produce the desired acetic acid composition?

In reality these questions are strongly interrelated. Moreover, the synthesis and design of the distillations require comparisons of columns that have different feeds because they depend on the separation performed by the extraction column. This is more challenging than the problems studied by Fidkowski[7] or those presented in the review paper of Koehler et al.[9] where the feed under consideration remains fixed. In our case, we must be careful to make meaningful comparisons of all of the separations involved. We begin with the acetic acid recovery column, which dominates the energy consumption for this process, and investigate both high and lower purity acetic acid production.

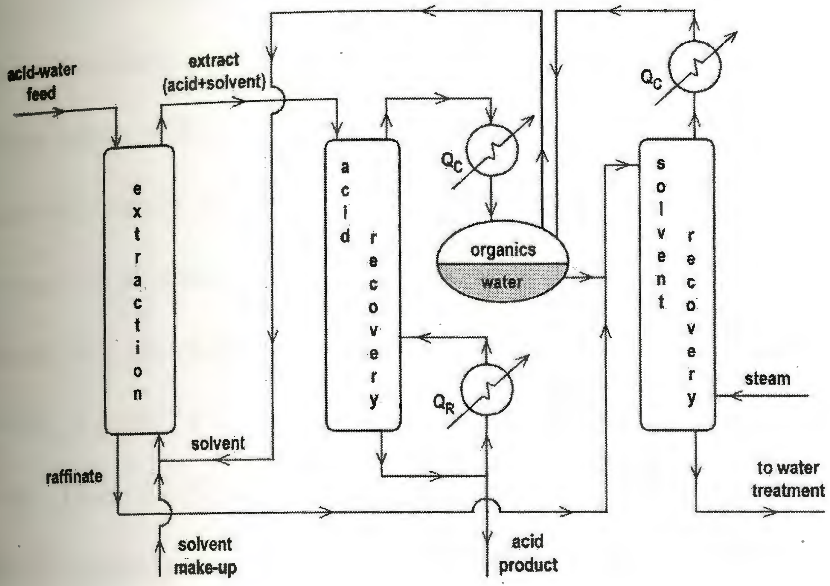

Figure II.3: Hybrid Separation Process for Acid Production

Case 1: High Purity Acetic Acid, No Solvent Recycle

Consider the use of a stripping column to recover acetic acid from a feed that is the extract from a liquid-liquid extraction column. Let ethyl acetate be the solvent used to extract acetic acid from a water solution of 11.5-mol% acetic acid. Let the desired bottoms composition be high purity acetic acid with $x_B = (0.9999, 5 \times 10^{-5}, 5 \times 10^{-5})$, where the components are ordered acetic acid(1), ethyl acetate(2) and water(3). We emphasize that no solvent recycle is considered in the analysis at first; solvent recycle is addressed later in the paper. Note also that there are no separation boundaries internal to the triangular region for this ternary mixture. The boundaries are simply the edges of the feasible region and this is correctly predicted by the geometric theory of Lucia and Taylor[1].

[illegible]c Acid Recovery Column

Figure II.4 shows a few of the distillation lines for the given bottoms composition for various values of the stripping ratio, which all end at different points on the stripping pinch point curve. In addition, the binodal curve at 298.15 K and a few liquid-liquid tie lines are also shown in Fig. II.4. It is important to note that desired separation requires that the stripping column not only have a bottoms composition of $x_B = (0.9999, 5 \times 10^{-5}, 5 \times 10^{-5})$, but also have a feed that lies somewhere on the binodal curve. Thus, the distillation line that intersects the pinch point curve farthest to the right is infeasible. Moreover, the remaining three distillation lines in Fig. II.4 are the only distillation lines that result in feasible extractor/acetic acid recovery column configurations since these distillation lines have a liquid tray composition that lands exactly on the binodal curve.

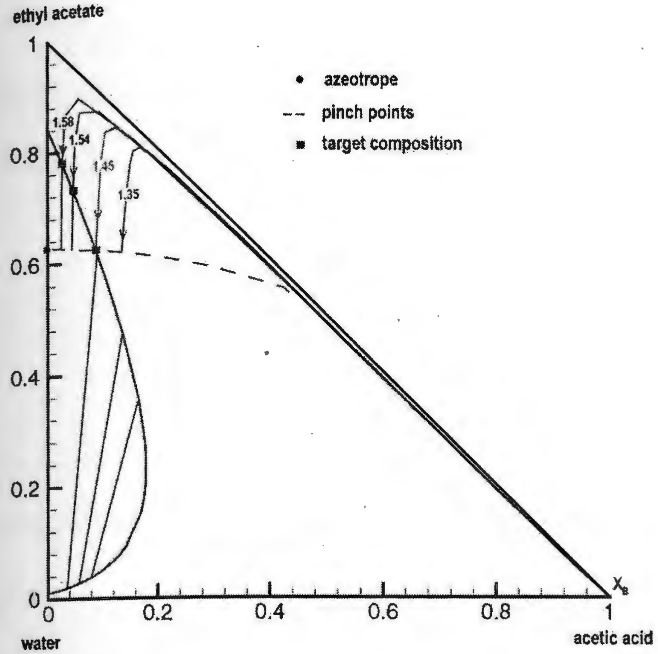

Figure II.4: Hybrid Separation of Acetic Acid and Water

A closer look at Figure II.4 shows that the smallest feasible boil-up ratio that results in a stripping pinch point that is on the binodal curve and produces the desired bottoms composition is s = 10.92. The pinch point for this minimum boil-up ratio is x_T = (0.0890, 0.6204, 0.2906). *What is actually more interesting is that this minimum boil-up ratio corresponds to the shortest stripping line from the desired acetic acid bottoms composition to the pinch point curve such that the liquid composition for some tray lies on the binodal curve.* Other feasible distillation lines from the same exact bottoms composition are either feasible (and longer in length) or they are infeasible. Table II.1 summarizes these results.

Table II.1: Summary of Stripping Lines and Boil-up Ratios for Acetic Acid Recovery Column

Bottoms Comp.*	Distance	Feasible	BR+	x_T*	y_D*
(0.9999, 0.00005)	1.5808	yes	40.23	(0.0274, 0.7790)	(0.0032, 0.7984)
	1.5385	yes	22.24	(0.0473, 0.7301)	(0.0045, 0.7630)
	1.4473	yes	10.92	(0.0890, 0.6204)	(0.0056, 0.6771)
	1.3521	no	7	(0.0117, 0.7032)	

---

* mole fractions of acetic acid and ethyl acetate

\+ Boil-up ratio

The energy requirements for the acetic acid recovery column that correspond to the shortest stripping line in Fig. II.4 are as follows. The extract stream from the extractor, which feeds the acetic acid recovery column, has a flow of 567.036 lbmol/h with a composition of x_T = (0.0890, 0.6204, 0.2906). The corresponding vapor overhead composition leaving the top stage is y_D = (0.0056, 0.6771, 0.3173). Material balance gives bottoms and distillate flows of B = 47.562 lbmol/h and D = 519.474 lbmol/h. Note that this stripping column recovers about 95-mol% of the acetic acid in the extract. The minimum reboiler duty is $Q_R = sB\lambda_{AA}$ = (10.92)(47.562 lbmol/h)(10,431.60 Btu/lbmol) = 5.418 MBtu/h. Condensing the overhead vapor requires $Q_C = D\lambda_D$ = (519.474 lbmol/h)(16,740.91 Btu/h) = 8.696 MBtu/h, where λ_D is the heat of vaporization of the overhead stream and determined from the weighted average $\lambda_D = \Sigma\ y_{Di}\lambda_i$. Thus the minimum energy requirement for the acetic acid recovery column is Q_R = 5.418 MBtu/h, which is half of the 10.952 MBtu/h required for conventional distillation.

Acetic Acid Recovery Column Decanter

The vapor overhead stream from the acetic acid recovery column will phase separate when condensed. Often times this liquid is sub-cooled to enhance phase separation. Table II.2 shows the compositions of all streams associated with the overhead decanter where the liquid is sub-cooled to 298.15 K.

Table II.2: Phase Separation Molar Compositions for the Acetic Acid Recovery Column Decanter

	Overhead Vapor	Organic Phase	Water Phase
Acetic acid (AA)	0.0056	0.0063	0.0027
Ethyl acetate (EAc)	0.6771	0.8291	0.0120
Water (W)	0.3173	0.1646	0.9863

The flow rates of the organic (S_1) and water phases (S_2) are $S_1 = 422.840$ lbmol/h and $S_2 = 96.634$ lbmol/h respectively. The water phase can be combined with the raffinate stream from the extractor and sent to a solvent recovery column. Again, recycling of the organic phase (S_1) is considered later in this paper.

Liquid-Liquid Extraction Column

Analysis from the acetic acid recovery column using shortest separation lines defines the extractor design since it defines the target extract composition, x_T. For 10,000 lb/h of acetic acid-water feed of 11.5 mol% acetic acid, a 15-stage extraction column requires 31,218.25 lb/h of ethyl acetate to meet a target extract of x_T. In all comparisons in this paper, we use a liquid-liquid extraction column with 15 stages. Moreover, the raffinate molar flow rate and composition can be calculated from knowledge of all other streams entering or leaving the extractor since the feed is given, the solvent is pure ethyl acetate (assuming no recycle) and the extract is known. Extraction column stream molar flow rates and compositions are summarized in Table II.3.

Table II.3: Extraction Column Stream Flow Rates and Molar Compositions

	Feed	Solvent	Extract	Raffinate
Flow rate (lbmol/hr)	438.89	354.310	567.036	226.167
x_{AA}	0.115	0	0.0890	0.0001
x_{Eac}	0.885	1	0.6204	0.0111
x_W	0	0	0.2906	0.9888

Solvent Recovery

Combining the raffinate with the water phase from the acetic acid recovery column decanter gives a feed to the solvent stripping column that has a total flow rate of F = 322.301 lbmol/h and a composition of x_F = (0.0008, 0.0114, 0.9878), where the components are ordered acetic acid, ethyl acetate and water. This stream contains only 0.261 lbmol/h of acetic acid and 4.512 lbmol/h of ethyl acetate. Furthermore, since water is the primary component of this feed, sparged steam is used to avoid the equipment costs associated with a reboiler. The energy requirements for solvent recovery are easily computed. A feed pinch, in which the overhead vapor is in equilibrium with $x_F = (0.0007, 0.0114, 0.9879)$, gives $y_D = (0.0012, 0.6421, 0.3578)$. Assuming the water stream leaving the bottom of this column has a composition of $x_B = (0.0005, 0.0005, 0.999)$, the distillate and bottoms flow rates are D = V = 5.479 lbmol/h and B = 322.801 lbmol/h. Note that the sparged steam flow rate is also V = 5.479 lbmol/h. Moreover, these CMO conditions easily give a minimum boil-up ratio s = V/B = 0.0173. The corresponding reboiler and condenser duties are $Q_R = sB\lambda_W$ = (0.0173)(322.301 lbmol/h)(17,465.22 Btu/h) = 0.097 MBtu/h and $Q_C = D\lambda_D$ = (5.479 lbmol/h)(16,825.09 Btu/lbmol) = 0.092 MBtu/h. Thus the energy requirements for the solvent recovery column are quite small – Q_R = 0.097 MBtu/h. The molar compositions and flow rates for the solvent recovery column are summarized in Table II.4.

Table II.4: Solvent Recovery Column Stream Flow Rates and Molar Compositions

	Feed	Steam	Bottoms	Overhead
Flow rate (lbmol/hr)	322.301	5.479	322.301	5.479
x_{AA}	0.0008	0	0.0005	0.0012
x_{Eac}	0.0114	0	0.0005	0.6421
x_W	0.9878	1	0.999	0.3578

Energy Requirements

The net energy requirements and column equilibrium stage requirements for all feasible hybrid separation schemes for high purity acetic acid are summarized in Table II.5. Table II.5 clearly shows that *the shortest stripping line from the desired acetic acid bottoms composition to the pinch point curve such that the liquid composition for some tray lies on the binodal curve corresponds to the minimum boil-up ratio for the acetic acid recovery column and the minimum energy requirements for the hybrid separation configuration shown in Fig. II.3*, under the condition of no recycle.

Table II.5: Summary of Energy Requirements for Feasible Hybrid Separation of Acetic Acid-Water Separation

Distance	Extraction*	BR$^+$	Acid* Recovery	BR^{++}	Solvent* Recovery	Energy (MBtu/h)
1.5808	15	40.23	16	0.017	18	18.724
1.5385	15	22.24	17	0.016	18	10.694
1.4473	15	10.92	28	0.017	14	5.515

---

* number of equilibrium stages, + boil-up ratio of acid recovery column, ++ boil-up ratio for solvent recovery column.

Case 2: Lower Purity Acetic Acid

Note that we do not really need the concept of shortest stripping line to determine the minimum energy requirements for the previous illustration, although this is certainly possible. The correct target composition can be determined by simply finding the intersection of the pinch point and binodal curves in Fig. II.4. Using this target composition and CMO conditions, the boil-up ratios in both the acetic acid and solvent recovery columns can be determined by mass balance principles. *The purpose of this second example is to show that for lower purity acetic acid essentially devoid of solvent the correct target extract composition must be determined using the concept of shortest separation lines.* This is because the correct target composition occurs at a point on the binodal curve that is <u>not a pinch point</u>. This, in turn, provides strong evidence for the concept of shortest separation lines as a unifying principle for synthesizing and designing energy efficient separators.

<u>Acetic Acid Recovery Column</u>

For this example, let the desired bottoms composition be $x_B = (0.995, 1 \times 10^{-10}, 0.005)$. Figure II.5 shows the paths and lengths of several stripping lines from the desired bottoms composition. Note unlike Fig. II.4, here the stripping lines follow the acetic acid-water axis before turning toward the pinch point curve. Note also that the longest stripping line enters the liquid-liquid region and converges to a pinch point on the binodal curve. The second distillation line from the left in Fig. II.5, on the other hand, is 'almost tangent' to the binodal curve but converges to a pinch point in the single liquid region. By almost tangent, we mean that a specific stage liquid composition lands exactly on the binodal curve while stages above and below this stage are outside the two-liquid region. This can be confusing since it can give the appearance that the stripping line cuts through the liquid-liquid region. However, it is important to remember that these are discrete stages and the lines connecting them don't have

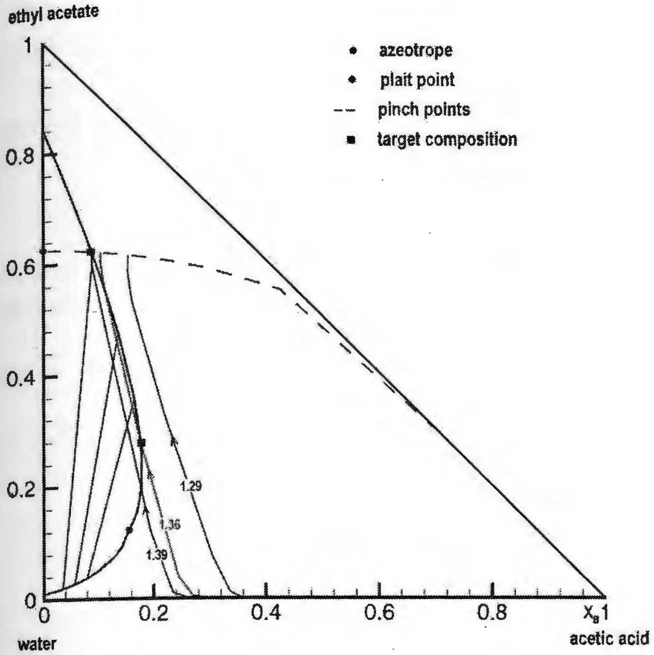

Figure II.5: Hybrid Separation of Lower Purity Acetic Acid

any real physical meaning. Finally, note that the stripping line furthest to the right in Fig. II.5 never enters the liquid-liquid region and is infeasible for the same reasons given in the previous case. These results are summarized in Table II.6.

Energy Requirements

What is important in this second illustration, with regard to energy requirements, is not the relatively small difference in boil-up ratio, but rather the large difference in throughput to the acetic acid and solvent recovery columns that results from markedly different performance of the extraction column. For the target extract composition located at the intersection of the pinch point and binodal curves, the resulting extract flow is 568.410 lbmol/h. On the other hand, for the target extract composition closest to the plait point the extract flow is only 281.771 lbmol/h. This large decrease in throughput to the acetic acid and solvent recovery columns results in a considerable reduction in energy demands.

Table II.6: Summary of Distillation Lines and Boil-up Ratios for Acetic Acid Recovery Column

Bottoms Comp.*	Distance	Feasible	BR	x_T*	y_D*
(0.995, 1 x 10^{-10})	1.3908	yes	10.89	(0.0888, 0.6199)	(0.0056, 0.6769)
	1.3659	yes	9.10	(0.1764, 0.2807)	(0.0864, 0.3115)
	1.2923	no	6	(0.0152, 0.7135)	

* mole fractions of acetic acid and ethyl acetate

Table II.7 summarizes the energy and stage requirements for both feasible hybrid separation schemes for lower purity acetic acid without solvent recycle.

Note again that Table II.7 clearly shows that *the shortest stripping line from the desired acetic acid bottoms composition to the pinch point curve such that the liquid composition for some tray lies on the binodal curve corresponds to the minimum boil-up ratio for the acetic acid recovery column and the minimum energy requirements for the hybrid separation configuration.* However, this second illustration also shows that for lower purity acetic acid knowledge of the intersection of the binodal and pinch point curves does not define the configuration of minimum energy. Rather, it is the concept of shortest separation lines that gives the minimum energy configuration.

Table II.7: Summary of Energy Requirements for Feasible Hybrid Separation of Acetic Acid-Water Separation

Distance	Extraction*	BR^+	Acid* Recovery	BR^{++}	Solvent* Recovery	Energy (MBtu/h)
1.3908	15	10.89	24	0.017	18	5.518
1.3659	15	9.10	18	0.025	19	2.795

* number of equilibrium stages, + boil-up ratio of acid recovery column, ++ boil-up ratio for solvent recovery column.

Coda. For both high and lower purity acetic acid separations, energy requirements for all feasible hybrid separation schemes are dominated by acetic acid removal. For high purity acetic acid, minimum energy requirements correspond to a feed pinch in the acetic acid removal column. On the other hand, for lower purity acetic acid the distillation line corresponding to minimum energy is 'almost tangent' to the binodal curve and has exactly one liquid tray composition on the binodal curve. In either case, minimum energy requirements correspond to *the shortest stripping line from the desired acetic acid bottoms composition to the pinch point curve such that the liquid composition for some tray lies on the binodal curve*, and this, in our opinion, provides strong support for the concept of shortest separation lines as a unifying principle in determining minimum energy requirements.

[redacted] Heat Effects, Material Recycle and Heat Integration

Both energy efficiency and overall process economics can be strongly influenced by sensible heat effects, material recycle, and heat integration. For the illustrative examples, the sensible heat effects that come from sub-cooled feeds to the acetic acid recovery and solvent columns have been determined to be small compared to the latent heat effects of boiling and condensing. Thus their impact on minimum energy requirements has been neglected in this analysis. On the other hand, if desired, the bottoms stream of the solvent recovery column, which is saturated water at 1 atm., can be used to partially pre-heat the feed to the acetic acid recovery column.

Solvent Recycle

Recycling material from the acetic acid column decanter and the solvent recovery column, on the other hand, can significantly reduce the need for fresh solvent. Figure II.6 provides numerical results for a converged process flow diagram for the high purity acetic acid hybrid separation scheme with solvent recycle where the component molar flow rates are given in lbmol/h and all mass balances are satisfied. However, in checking these results the reader may find slight errors in the mass balances due to rounding because we have reported results to only three and four significant differences.

Solvent recycle greatly reduces the need for fresh solvent as indicated by the small solvent make-up flow rate of 0.42 lbmol/h. However, while solvent recycle is important for overall hybrid separation process economics, it does not change the target extract composition or boil-up ratios in either column to any great extent and thus does not have a large effect on the energy requirements for the overall process. Without solvent recycle the total energy requirements were calculated to be 5.515 MBtu/h. With solvent recycle, there are increases in the throughputs to the acetic acid recovery and solvent recovery columns because the recycle streams also contain acetic acid and water. In particular, the throughput to the acetic acid recovery column increases from 567.036 lbmol/h to 589.477 lbmol/h, which results an increase in the bottoms flow rate from 47.562 to 49.453 lbmol/h. However, the bottoms purity and the boil-up ratio remain fixed at $x_{AA} = 0.9999$ and 10.92 respectively. As a result, reboiler duty for the acetic acid recovery column increases by approximately 4 % - from 5.418 to 5.633 MBtu/h. There are also slight changes to the solvent recovery column due to recycling. The feed to the solvent recovery column also increases from 322.801 lbmol/h to 397.958 lbmol/h from both increases in the raffinate flow rate and the flow rate of the water phase from the decanter. This, in turn, changes the sparged steam requirement from 5.479 to 8.098 lbmol/h and results in an increase in the required energy for the solvent recovery column from 0.097 to 0.141 MBtu/h. As a result, the boil-up ratio for the solvent recovery column increases from 0.017 to 0.020 since more organics enter this column from the raffinate stream and the water phase from the decanter. Thus, solvent recycle slightly increases the total energy requirements for the hybrid separation scheme from 5.515 MBtu/h without solvent recycle to 5.774 MBtu/h with solvent recycle.

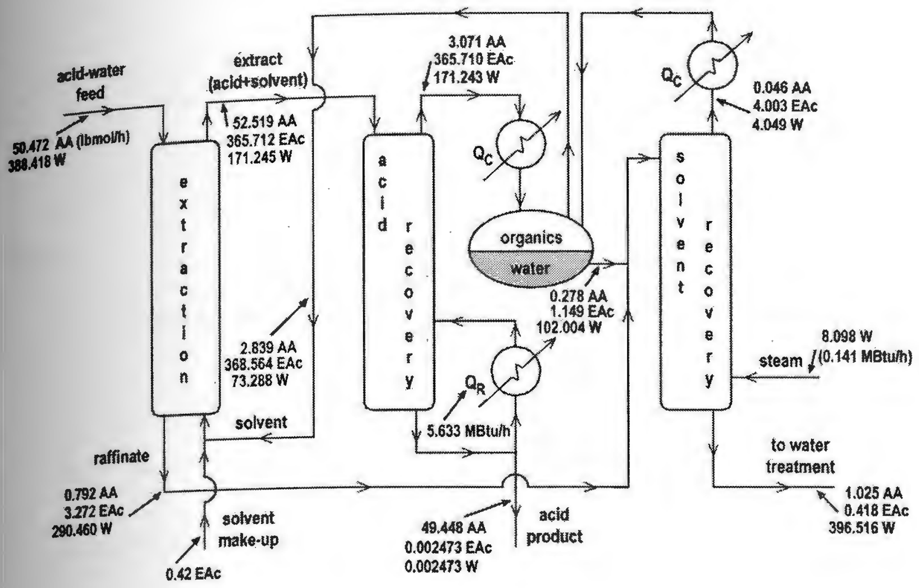

Figure II.6: Hybrid Separation Process of Acid Production with Solvent Recycle

II.5 The Theory of Shortest Separation Lines

In this section a mathematical formulation of the concept of shortest separation lines is presented. Generalized formulations and algorithmic issues are also discussed.

II.5.1 Formulation

Calculation of the shortest separation line can formulated as a constrained optimization problem that is similar in some ways to the nonlinear programming problem given in Lucia and Taylor[1] for finding separation boundaries. We illustrate this for the hybrid separation scheme for acetic acid recovery for which the shortest separation line, say $\{x_j\}^*$, is given by the solution of the nonlinearly constrained optimization problem

$$\min_{s} \quad D = \sum_{j=1}^{N_s} \| x_j' \| \qquad \text{(II.6)}$$

subject to

$$x_j' = [(s)/(s+1)]y_j - x_j + [1/(s+1)]x_B \qquad \text{(stripping line)} \qquad \text{(II.7)}$$

$$x_1 = x_B \qquad \text{(bottoms specification)} \qquad \text{(II.8)}$$

$$c(x_K) = \|x_K - x^b_K\| = 0 \text{ for some } K \in [1, N] \qquad \text{(auxiliary constraint)} \qquad \text{(II.9)}$$

where D represents a distance function along a discrete trajectory, $\| \, . \, \|$ denotes the two-norm, x_j and y_j represent the liquid and vapor compositions on stage j, x_B is the bottoms composition, and $c(x_K)$ is some constraint function that defines any auxiliary conditions that must be met to make the design feasible. For example, for the illustrative example, $c(x_K) = 0$ can be viewed as a constraint that forces the liquid composition on tray K, x_K, for the acetic acid recovery column to lie at some point, x^b_K, on the binodal curve. Note here that the unknown optimization variable is the boil-up ratio and the optimal trajectory is actually a sequence of liquid compositions denoted by $\{x_j\}^*$ that is assumed to be piece-wise linear. Also remember, for discrete stages the integration step size is $h = 1$; thus the upper limit on the summation in Equation II.6 represents some large number of stages. We typically use $N_s = 300$ as an approximation for the number of stripping stages.

II.5.2 Algorithmic Issues

In our opinion, any optimization algorithm for finding the shortest separation line subject to operating line, specification, and auxiliary constraints should:

1) Be a global optimization method as opposed to a local optimizer,
2) Enforce feasibility on the operating line and specification constraints at each iteration, and
3) Handle auxiliary constraints through the use of a penalty or barrier function approach.

Because the ancillary constraints can give rise to a feasible region that is a disjoint set of distillation lines, as illustrated in the hybrid separation of acetic acid and water, enforcing auxiliary constraint satisfaction from one optimization iteration to the next would require the optimizer to jump from one feasible distillation line to another. This is not practical and precludes the use of Newton-based methods, which rely on derivative information. On the other hand, if infeasibility in the auxiliary constraints is permitted through the use of a penalty or barrier function, then there is a smoother transition between feasible solutions since now the modified objective function has the form

$$f = D + P[c(x)] \tag{II.10}$$

where P is some penalty parameter and c(x) is a shorthand notation for any auxiliary constraints. Note that the modified objective function is still a function of boil-up ratio but is now differentiable. However, the use of penalty or barrier functions can introduce multiple minima in the modified objective function as shown in Fig. II.7 for the hybrid separation of high purity acetic acid presented earlier. Note that the minimum energy configuration corresponds to the global minimum of the modified objective function in Fig. II.7 and thus clearly shows that a global optimization algorithm is required to find the shortest distillation line or most energy efficient separation scheme.

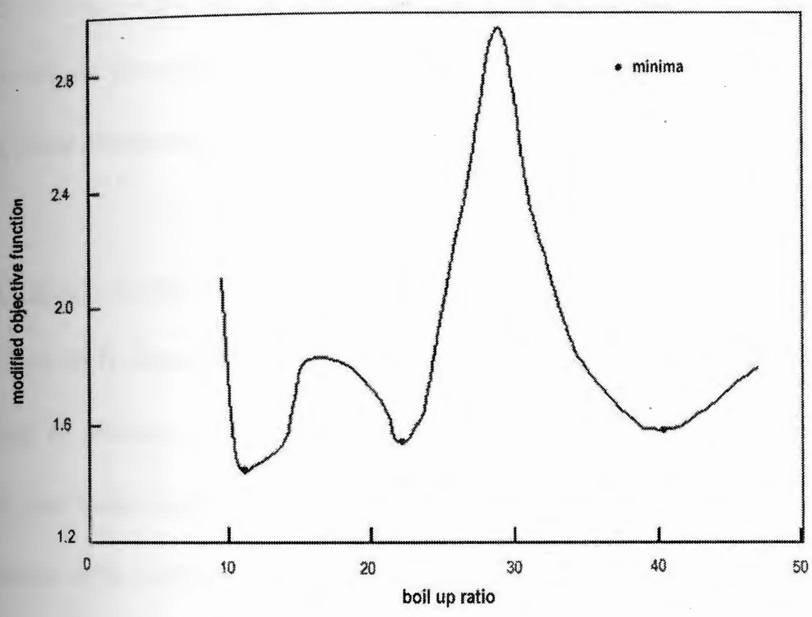

Figure II.7: Multiple Minima for Hybrid Separation of Acetic Acid and Water

II.5.3 Generalizations and Other Formulations

The nonlinear programming problem defined by Equations II.6 through II.9 can be further generalized by using any appropriate set of constraint functions that define feasibility. Other formulations for more conventional separation problems are also possible within the theory of shortest separation lines.

Constraints

It is, in our opinion, straightforward to imagine conditions similar to Eq. 9 for other hybrid separation system configurations. The primary requirement of these more general auxiliary constraints is that they define a feasible region in some meaningful way. Given that, the auxiliary constraints can be written in the general form $c(x_1, x_2, \ldots, x_N, y_1, y_2, \ldots, y_N) = 0$, where now c is some vector function of the liquid and vapor compositions throughout the separator. Since phase equilibrium implies that $y_j = y_j(x_j)$, these constraints can actually be written in the compact form as simply $c(x) = 0$.

Conventional Separator Designs

Here we shift focus by considering single column designs and showing how the concept of shortest separation lines readily extends to more traditional settings in which the feed is specified, a prescribed separation is demanded, and conventional separators with rectifying and stripping sections are considered as design alternatives. One important difference between this type of synthesis problem and the synthesis of hybrid separation schemes is that the feed to the primary recovery column is not fixed in the latter.

For the purpose of illustration, the use of both rectification and stripping in the acetic acid recovery column to achieve essentially the same desired high purity acetic acid separation is considered. Consider Fig. II.4 and assume that the desired separation is the one defined by the stripping column with a feed pinch on the binodal curve. Thus the desired high purity acetic acid separation consists of a feed stream with a flow rate of F = 567.036 lbmol/h and composition of $x_T = x_F = (0.0890, 0.6204, 0.2906)$, a bottoms composition of $x_B = (0.9999, 5 \times 10^{-5}, 5 \times 10^{-5})$, and an overhead vapor composition close to $y_D = (0.0056, 0.6771, 0.3173)$. By close, we mean that the overhead vapor composition must be within some half open ball about y_D. It is important for the reader to understand that is not possible to specify all compositions x_F, x_B and y_D exactly when discrete stages are used. This is easily seen from any McCabe-Thiele diagram for specified reflux and boil-up ratios. Given specific values of x_F, x_B and y_D, operating lines for any reflux and related boil-up ratio can be drawn. However, this is simply a necessary synthesis tactic. When stages are actually stepped off starting from x_B, the end point of the top stage is unlikely to occur exactly at y_D. The same is true for ternary and other multi-component mixtures.

The extension of the concept of shortest separation lines is quite straightforward, even for conventional separators. In particular, we still use the distance of the stripping line from the desired bottoms composition to the stripping pinch point curve as the correct measure of energy requirements – even though the separator has a rectifying section. To see why this is correct, consider an alternative separator with both a rectifying and stripping section for making the same separation that the optimal stripping column for high purity acetic acid recovery does. See Table II.1. In particular, let the stripping section for the alternative separator correspond to the feasible solution with s = 22.24 as shown in Fig. II.4. Once the boil-up ratio has been selected, the energy requirements are fixed. Moreover, the reflux ratio is fixed by overall energy balance, which gives the relationship

$$r = s[x_{Fi} - y_{Di}]/[x_{Bi} - x_{Fi}] - 1 \qquad \text{(II.11)}$$

For s = 22.24 the corresponding reflux ratio is r = 1.0365. Moreover, the transition between the rectifying and stripping section can, in principle, occur at any tray in the stripping section. While this does not guarantee optimal placement of the feed, it does provide a large number of alternative feasible designs. However, all of this has no effect on the reboiler duty and thus does not change the energy requirements for the column even though it has a rectifying section. For example, select the stripping tray that lies on the binodal curve as the transition point between stripping and rectification. See again Table II.1 or Fig. II.4. As a result, only one rectifying stage is needed to produce the desired overhead vapor within a half open ball around the specified y_D. However, the reboiler duty for s = 22.24 remains the same as before. Thus the shortest stripping line from the desired bottoms composition to the stripping pinch point curve is still the correct measure of minimum energy requirements – even for conventional separators. Figure II.8 clearly illustrates this concept for two alternate separators (s = 22.24 and s = 40.23). Both alternate separators have 16 stripping stages and 1 rectifying stage.

In this figure, actual stage compositions are indicated by the filled squares and for clarity, no tie lines have been shown in the liquid-liquid region. Of course it is rather obvious that these alternate column designs will not result in a lower energy requirement than the stripping column determined previously because the boil-up ratio is significantly higher than minimum boil-up. See also Table II.1 and Fig. II.4.

Feasibility

Relaxing the condition of exactly fixing y_D expands the feasible region to all distillation lines above the distillation line labeled 1.4473. See the shaded region in Fig. II.8. Thus it is possible to consider all conventional column designs that have a boil-up ratio of $s \geq 10.92$, and corresponding reflux ratios calculated from Eq. 11. The resulting calculations clearly show that the shortest stripping line from the desired bottoms composition to the stripping pinch point curve corresponds to the minimum energy requirement for the desired separation.

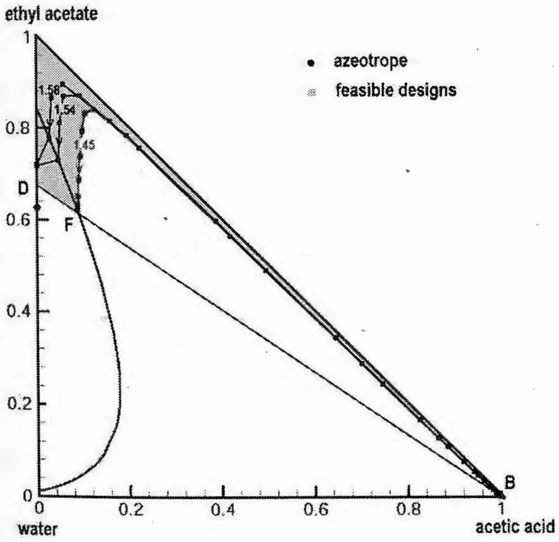

Figure II.8: Distillation Lines for Various Acetic Acid Recovery Column Designs

ional Column Formulation

The global optimization formulation for minimum energy requirements based on the concept of shortest separation lines is very similar to that given by Eqs. 6 to 9. We still minimize the stripping line distance with respect to the boil-up ratio – only here rectifying equations, the overall energy balance equation, and relaxed separation constraints are included. This gives the following nonlinear programming problem

$$\min_{s} \quad D = \sum_{j=1}^{N_s} \| x_j' \| \qquad \text{(II.12)}$$

subject to

$$x_j' = [(s)/(s+1)]y_j - x_j + [1/(s+1)]x_B \qquad \text{(stripping line)} \qquad \text{(II.13)}$$

$$x_j' = [(r+1)/r]y_j - x_j - (1/r)y_D \qquad \text{(rectifying line)} \qquad \text{(II.14)}$$

$$r = s[x_{Fi} - y_{Di}]/[x_{Bi} - x_{Fi}] - 1 \qquad \text{(energy balance)} \qquad \text{(II.15)}$$

$$x_1 = x_B \qquad \text{(bottoms specification)} \qquad \text{(II.16)}$$

$$y_D \; X \; B(y_D, \varepsilon) \qquad \text{(overhead specification)} \qquad \text{(II.17)}$$

where N_s still denotes the total number of stripping stages and the last constraint implies that the calculated value of the overhead vapor composition must lie within some half open ball around the specified overhead vapor composition.

II.6 Conclusions

The synthesis and design of energy efficient hybrid extraction/distillation separation schemes was studied. The novel concept of shortest separation lines was introduced. It was shown that the shortest separation line identifies the correct target extract composition and provides a rigorous methodology for finding the most energy efficient design. The hybrid separation of high and lower purity acetic acid by extraction with ethyl acetate was used as an example to illustrate key concepts and identify important numerical characteristics of this class of synthesis problems. It was shown that the interpretation of shortest separation line requires careful wording with respect to the correct measure of distance and that extraction/distillation problems can lead to feasible regions that are comprised of discrete (and disconnected) sets of distillation lines. It was also shown that in some cases the most energy efficient hybrid separation scheme design does not coincide with a pinch point. A global optimization formulation, in which constraints are divided into feasible and infeasible subsets, was presented for directly finding the most energy efficient hybrid separation designs. The approach of shortest separation lines was generalized to conventional separators and was shown to represent a unifying principle for generating separation process designs that are energy efficient.

Other Applications

We have also applied the concept of shortest separation lines to a variety of single distillation columns that exhibit feed, saddle point, or tangent pinch points, reactive distillation columns, and columns that have minimum energy requirements that do not occur at a pinch point. These results are the subject of a separate paper on the principle of shortest separation lines. In addition, we have applied the concept of shortest separation lines to multi-unit reaction/separation/recycle (RSR) processes such as the production of MTBE from isobutene and methanol. In all cases, we have been able to illustrate that minimum energy requirements correspond to the shortest separation line.

Nomenclature

B	bottoms product molar flow rate
c, c(x)	number of components, constraint function
D	distillate molar flow rate, distance
F, f	feed molar flow rate, modified objective function
K	equilibrium ratio
L	liquid molar flow rate
N_s	number of stripping stages
P	penalty function parameter
Q, Q_R, Q_C	heat duty, reboiler duty, condenser duty
r	reflux ratio
s	boil-up or stripping ratio
V, V'	rectifying section vapor molar flow rate, stripping section vapor molar flow rate
x, x_B, x_D	vector of liquid mole fractions, bottoms composition, liquid distillate composition
x_T, x_F	extract target composition, feed composition
y, y_D	vector of vapor mole fractions, vapor distillate composition
λ	heat of vaporization

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Appendix II.1

In this appendix, the relevant physical property data for the examples studied in this paper are the binary interaction parameters for the UNIQUAC activity coefficient model and the constants required to compute standard state fugacities for each component in the liquid phase.

The standard state liquid phase component fugacities can be expressed using an extended Antoine equation of the form

$$\ln f_i^0 = c_{i,1} + c_{i,2}/(T + c_{i,3}) + c_{i,4}T + c_{i,5}\ln(T) + c_{i,6}T^2 \qquad \text{(II.A1)}$$

where has units of bar. Table II.A1 gives the numerical values of the pure component constants in Equation II.A1.

Table II.A1: Pure Component Constants for Extended Antoine Equation

Component	c_1	c_2	c_3	c_4	c_5	c_6
ethanol	-90.91	-3465.9	0.	-0.062301	20.486	2.0664×10^{-5}
ethyl acetate	-129.13	-2259.9	0.	-0.096853	28.02	4.3325×10^{-5}
water	57.042	-7004.8	0.	0.0035888	-6.6689	-8.5054×10^{-7}
acetic acid	386.98	-15091.	0.	0.16774	-67.642	-7.2738×10^{-5}

The [redacted]perature-dependent interaction terms, τ_{ij}, for the UNIQUAC equation of Prausnitz et al.[19] are expressed in the form

$$\tau_{ij} = \exp(-a_{ij}/T) \tag{II.A2}$$

where the a_{ij}'s are binary interaction parameters. Table II.A2 gives the binary interaction parameters for the UNIQUAC equation for the chemical species used in this paper.

Table II.A2: Binary Interaction Parameters for the UNIQUAC Equation

Component i	Component j	a_{ij} (K)	a_{ji} (K)
ethanol	ethyl acetate	-167.61	571.73
ethanol	water	-64.56	380.68
ethyl acetate	water	569.86	80.91
acetic acid	ethyl acetate	-214.39	426.54
acetic acid	water	-173.64	196.41

MANUSCRIPT III

A Two-Level Distillation Design Method

This chapter is the manuscript entitled, A Two-Level Distillation Design Method submitted to AIChE Journal and is under review.

Abstract

Recently, Lucia and co-workers have used a distillation line approach to develop the concept of shortest stripping line distance approach to minimum energy designs of distillation columns and multi-unit processes. It is well known that distillation line methods can be very sensitive to specified product compositions. A two-level distillation design procedure is proposed for finding portfolios of minimum energy designs when specifications are given in terms of key component recoveries. Thus product compositions are not specified but calculated. It is shown that the proposed two-level design procedure is flexible and can find minimum energy designs for both zeotropic and azeotropic distillations. It is also shown that the two-level design method encompasses Underwood's solution but can find minimum energy designs when Underwood's method fails. Numerical results for several distillation examples involving ternary and quaternary mixtures are presented to support these claims and geometric illustrations are used to elucidate key points.

Keywords

shortest stripping line distance, two-level design methodology, global minimum, portfolio of minimum energy designs, Underwood's method

III.1 Introduction

Underwood's method[1,2] and its variations have long been used to determine minimum energy requirements for distillations. Practitioners find these and other group or shortcut methods quite useful in the early stages of design, despite their limitations, and most commercial chemical process simulators offer their own implementation of Underwood's method to their customers. For example, the Aspen Plus simulator has a block known as DSTWU, which is an implementation of the Winn-Underwood method. The recent development of V_{min} diagrams by Halvorsen and Skogestad[3,4] for finding minimum energy consumption in single and multiple columns is strongly rooted in Underwood's method.

Because Underwood's method is based on a constant relative volatility assumption, it is somewhat limited. Thus other methods like the boundary value methods of Doherty and co-workers[5] have emerged. In particular, Doherty and co-workers use distillation lines or stage-to-stage calculations at constant molar overflow (CMO) and allow more rigorous thermodynamics models to find minimum energy requirements for distillation columns. They classify the types of column design problems as direct, indirect, and transition splits based on the resulting pinch point – stripping pinch, rectifying pinch, or double feed pinch. A transition split is equivalent to Underwood's method for problems in which all components distribute. Direct and indirect split correspond to cases in Underwood's method where not all components distribute and there are components that are heavier than the heavy key and components lighter than the light key respectively.

More recently, Lucia et al.[6] have developed a novel and comprehensive approach to minimum energy requirements in distillations as well as multi-unit processes based on the concept of shortest stripping line distance. This work clearly shows that minimum energy requirements for all types of processes, distillations, hybrid separations like extraction/distillation, and reaction, separation, recycle processes, can be determined in a straightforward geometric and intuitive manner by finding the shortest stripping line distance for the problem at hand. This new approach is quite general, encompasses many existing methods for finding minimum energy requirements, and is also capable of finding minimum energy requirements that do not correspond to pinch points – something the other methods cannot do.

It is well known that any methodology based on distillation lines can be very sensitive to specified product compositions. Small variations in product compositions can result in very large changes in minimum energy demands! Moreover, there are cases in which numerical difficulties arise in generating stripping and/or rectifying profiles that meet product specifications – even though these profiles are in theory possible. These numerical difficulties are often due to rounding and truncation errors. The main purpose of this paper is to present a two-level distillation design methodology that addresses the sensitivity of distillation line methods to specified product compositions and design feasibility. The inner loop of our two-level design method is comprised of the shortest stripping line approach, which determines minimum energy requirements for fixed bottoms composition. The outer loop, on the other hand, is a Gauss-Newton strategy that is used to adjust the bottoms composition. In addition, the numerical analysis that comes from the outer loop provides a straightforward way of understanding the sensitivity of distillation line trajectories to bottoms product composition. We also show that our two-level methodology encompasses Underwood's method as a special case of the shortest stripping line approach (Lucia et al.[6]) by demonstrating that the minimum boil-up ratio determined by Underwood's method with vapor-liquid equilibrium given by constant relative volatilities corresponds to the minimum of all shortest stripping line distances for a given set of key component recovery fractions. Finally, we show that Underwood's method often fails to find even a feasible design for problems involving mixtures that form azeotropes but that the proposed two-level design approach easily finds a portfolio of minimum energy designs in these cases.

Accordingly this paper is organized in the following way. First a very brief summary of Underwood's method is presented. This is followed by a description of a two-level algorithm for design and optimization based on processing target. The description of the inner loop, which is the shortest stripping line approach of Lucia et al.[6], includes for the first time all of the equations and derivative expressions necessary to determine minimum boil-up ratios for fixed values of bottoms composition. Next the details of the outer loop are described. Here we also provide all of the equations and sensitivity information required to adjust bottoms composition under fixed boil-up ratio to locate a specific processing target. Several numerical examples are presented to illustrate the effectiveness of our two-level design methodology. Three examples show that

Underwood's method has a shortest stripping line distance interpretation and represents a global minimum in energy demands for a given set of key component recoveries. *Two additional examples involving mixtures that form azeotropes and/or create distillation boundaries are presented to show that Underwood's method often fails to find a feasible design while the proposed two-level design method easily finds a portfolio of feasible minimum energy designs.* In all cases, geometric figures are used to illustrate key points. Finally, we discuss the engineering value of our proposed two-level design approach and show that it enables the practicing engineer to get a geometric picture of the effects of bottoms composition on minimum energy demands and span a number of relevant energy efficient scenarios during the synthesis and design process.

III.1.1 A Brief Summary of Underwood's Method

Underwood's original method Underwood[1] for finding minimum reflux ratios is well known and several modifications and extensions (e.g., Shiras, et al.[7]; Barnes et al.[8]) have been developed over the years. The original method of Underwood considers vapor-liquid equilibrium described by constant relative volatilities and is suitable for class 1 separations. In class 1 separations all components in the multicomponent mixture under consideration distribute between the bottoms and distillate products. Shiras, et al.[7] extended the method of Underwood to class 2 separations – that is mixtures for which some components do not distribute. The equations of Underwood are well known and do not need repeating here, except in a limited sense. We refer the reader to the original papers by Underwood or one of the many descriptions of

Underwood's method that can be found in the literature (e.g., Shiras, et al.[7]; Henley and Seader[9]; Halvorsen and Skogestad[3,4]).

Class 1 separations correspond to a double feed pinch point and the resulting expression for minimum reflux ratio, r_{min}, is given by

$$r_{min} = [(x_{D,LK}/x_{P,LK}) - (\alpha_{LK})_P x_{D,HK}/x_{P,HK}]/[(\alpha_{LK})_P - 1] \qquad \text{(III.1)}$$

where it is assumed that the feed is saturated liquid with a composition of x_F, x_P is a pinch point, x_D is the distillate composition, α is the relative volatility, and where the subscripts LK and HK denote the light and heavy key components respectively. For class 1 separations $x_P = x_F$ and Eq. III.1 is easily applied.

For class 2 separations Eq. III.1 still applies. However, there is either a rectifying or stripping pinch but not both. Thus x_P is not known and iteration is required. Different cases must be considered depending on which components are suspected of distributing. Class 2 separations require root finding to determine the root or roots, θ, that satisfy

$$(\alpha_{i,r})_P x_{F,i}/[(\alpha_{i,r})_P - \theta] = 1 - q \qquad \text{(III.2)}$$

where q is the thermal quality of the feed and where the subscript r denotes a reference component such as the heavy key.

One of the great appeals of Underwood's method is that is simple to program and easy to use. It also finds pinch points without regard for column composition profiles. Thus the convergence difficulties experienced by, for example, boundary value methods (i.e., trajectories that do not meet) are irrelevant in Underwood's method. However, it does have some disadvantages. Underwood's method is based constant relative volatility and on recovery fractions of key components in the product streams, which can be satisfied by a range of product compositions. Product compositions cannot be specified directly in Underwood's method. Consequently if certain product compositions are required, something in addition to Underwood's method is needed. Moreover, Underwood's method can fail on problems involving azeotropic mixtures – as we demonstrate in the Numerical Examples section of this article.

III.2 A Design & Optimization Methodology for Hitting Processing Targets

In this section, we describe a two-level design and optimization algorithm for finding or getting as close as possible to specific processing target compositions. The inner loop of this algorithm is the shortest stripping line approach, in which minimum energy requirements are determined for fixed bottoms composition. In most distillation design problems the bottoms composition is often not known a priori. While the designer is usually at liberty to specify something about the bottoms composition in response to desired recovery fractions, when there are distributed non-key components present in the mixture under consideration, it is generally not possible to specify the bottoms product composition completely. Some component compositions must be 'guessed' in the absence of additional knowledge and this can create unforeseen numerical difficulties.

Since small changes in product compositions can make very big differences in minimum energy requirements, the uncertainty about non-key component compositions can dramatically affect the energy efficiency of the resulting design. To address this issue, we propose an outer loop that is a Gauss-Newton method for finding bottoms composition for fixed boil-up ratio and study the effect of bottoms composition on minimum energy requirements.

III.2.1 The Inner Problem

The inner problem is the following.

$$\min_{s} D = \sum_{k=1}^{N_s} \| \Delta x_j \| = \|x_{j+1} - x_j\| \qquad \text{(III.3)}$$

subject to

$$x_{j+1}' = [s/(s+1)]y_j - x_j + [1/(s+1)]x_B, \qquad j = 1,\ldots, N_s \qquad \text{(III.4)}$$

$$x_B = x_{B,\,spec} \qquad \text{(III.5)}$$

$$r = (s - q + 1)\,[x_{Fi} - x_{Di}]/[x_{Bi} - x_{Fi}] - q \qquad \text{(III.6)}$$

$$x_{j+1}' = [(r+1)/r]y_j - x_j - [1/r]x_D, \qquad j = N_s+1,\ldots, N \qquad \text{(III.7)}$$

$$f(x_N, x_{D,spec}) \leq \zeta \qquad \text{(III.8)}$$

where D is stripping line distance, $x_B = x_1$ is a fixed value of bottoms composition, x_D is a nominal value of the distillate composition, and $f(x_N, x_{D,spec})$ denotes some measure of feasibility for the distillate product (e.g., $f(x_N, x_{D,spec}) = \| x_N - x_{D,spec} \| \leq \zeta$). The theoretical motivation for the shortest stripping line approach comes from the fact that longest residue curves or distillation lines correspond to separation boundaries and are calculated at infinite boil-up and use the most energy. Therefore, it stands to reason that if the longest stripping line distances correspond to the most energy consumption, the shortest stripping line distances should correspond to the least energy consumption or most energy efficient distillations. Our computational experience with many types of distillations shows that this is in fact the case and that the inner problem always has a unique minimum. For the details of the shortest stripping line distance approach,. including the integer formulation for non-pinched minimum energy designs, we refer the reader to the paper by Lucia et al.[6].

Sensitivity Information for the Inner Problem

In order to actually compute the minimum stripping line distance with respect to boil-up ratio using a Newton-based optimization method, sensitivity or partial derivative information quantifying the change in trajectory with respect to boil-up ratio is required. This information can be computed efficiently using the implicit function theorem to generate recursion formulae for the partial derivatives and actually calculating this partial derivative information during the process of generating a trajectory. Here the goal is to find expressions for the changes in x_j and y_j with respect to boil-up ratio since these derivatives are, in turn, needed to compute dD/ds and d^2D/ds^2.

Consider the stripping line equation for the jth stage (i.e., Eq. III.4) written in the form

$$F(s, y_j(x_j), x_j, x_{j+1}) = x_{j+1}' - [s/(s+1)]y_j + x_j - [1/(s+1)]x_1 \qquad \text{(III.9)}$$

where $x_1 = x_B$. By the implicit function theorem,

$$\Delta x_{j+1} = [s/(s+1)]J_{yx}\Delta x_j + [1/(s+1)]I\Delta x_1 + [1/(s+1)^2](y_j - x_1)\Delta s \qquad \text{(III.10)}$$

which reduces to

$$\Delta x_{j+1} = [s/(s+1)]J_{yx}\Delta x_j + [1/(s+1)^2](y_j - x_1)\Delta s \qquad \text{(III.11)}$$

for fixed bottoms composition. Remember the inner problem is always solved with the bottoms composition fixed! Also J_{yx} is the (c-1) x (c-1) matrix of partial derivatives of y_j with respect to x_j that include any implicit temperature derivatives and account for the summation equations for x_j and y_j. The expressions for J_{yx} are given in the Appendix.

It is straightforward to develop the following recursion formulae by applying Eq. III.11 for j = 2, …, N_s.

$$\Delta x_j = J_{j-1}\Delta s \qquad \text{for } j = 1, \ldots, N_s \qquad \text{(III.12)}$$

$$J_{j-1} = \{[s/(s+1)]\, J_{yx}J_{j-2} + [1/(s+1)^2](y_j - x_1)\Delta s \qquad \text{for } j = 2, \ldots, N_s \qquad \text{(III.13)}$$

where $J_0 = 0$. Note that J_{j-1} is the matrix of partial derivatives of x_j with respect to boil-up ratio. Note that similar sensitivity equations can be generated for the rectifying line equation (i.e., Eq. III.7).

Partial Derivatives of the Distance Function

To use any Newton-based optimization method like the terrain method of Lucia and co-workers (Lucia and Feng[10]), first and second derivatives of distance with respect to boil-up ratio are required. These derivatives depend on the sensitivities J_{j-1} for j = 1, …, N_s. To begin, note that the distance along any stripping line trajectory in going from tray j to tray j+1 is given by

$$\Delta_j = x_{j+1} - x_j \qquad \text{(III.14)}$$

By the implicit function theorem

$$\Delta(\Delta_j) = \Delta x_{j+1} - \Delta x_j \qquad \text{(III.15)}$$

Use of Eq. III.12 gives

$$\Delta(\Delta_j) = J_j\Delta s - J_{j-1}\Delta s \tag{III.16}$$

Using the recursion relationship for J (Eq. III.13) in Eq. III.16 yields

$$\Delta(\Delta_j) = \{[s/(s+1)]J_{yx}J_{j-1} + [1/(s+1)^2](y_j - x_1)\}\Delta s - J_{j-1}\Delta s \tag{III.17}$$

$$= \{([s/(s+1)]J_{yx} - I)J_{j-1} + [1/(s+1)^2](y_j - x_1)\}\Delta s = J_{\Delta j}\Delta s \tag{III.18}$$

Since $D = \Sigma \|\Delta_j\| = \Sigma (\Delta_j^T\Delta_j)^{1/2}$, for $j = 1, \ldots, N_s$ it follows that

$$\Delta_j^+ = \Delta_j + J_{\Delta j}\Delta s \tag{III.19}$$

and therefore

$$(D^+)^2 = \Sigma (\Delta_j^T\Delta_j)^+ = (\Delta_j + J_{\Delta j}\Delta s)^T(\Delta_j + J_{\Delta j}\Delta s) \tag{III.20}$$

$$= (\Delta_j^T\Delta_j) + 2(\Delta_j^TJ_{\Delta j})\Delta s + (J_{\Delta j}^TJ_{\Delta j})\Delta s^2 \tag{III.21}$$

$$= D^2 + 2(\Delta_j^TJ_{\Delta j})\Delta s + (J_{\Delta j}^TJ_{\Delta j})\Delta s^2 \tag{III.22}$$

which gives a local quadratic approximation to the distance squared $(D^+)^2$. Consequently,

$$dD^2/ds = 2\Sigma(\Delta_j{}^T J_{\Delta j}) \qquad \text{(III.23)}$$

$$d^2D^2/ds^2 = \Sigma J_{\Delta j}{}^T J_{\Delta j} \qquad \text{(III.24)}$$

Note that the quantities in Eqs. III.23 and III.24 are both scalar quantities since $\Delta_j{}^T$ is 1 x (c-1) and $J_{\Delta j}$ is (c-1) x 1! Also note that

$$dD^2/ds = 2D(dD/ds) \qquad \text{(III.25)}$$

and therefore

$$dD/ds = \Sigma(\Delta_j{}^T J_{\Delta j})/D \qquad \text{(III.26)}$$

Moreover, since $d^2D/ds^2 = d/ds(dD/ds)$, it follows that

$$d^2D/ds^2 = d/ds[dD^2/ds/2D] = [D(d^2D^2/ds^2) - dD^2/ds]/D^2 \qquad \text{(III.27)}$$

which gives

$$d^2D/ds^2 = \tfrac{1}{2}\,[D(\Sigma J_{\Delta j}{}^T J_{\Delta j}) - 2(\Sigma \Delta_j{}^T J_{\Delta j})]/D^2 \qquad \text{(III.28)}$$

These quantities, dD/ds and d^2D/ds^2, are of course scalar quantities and are needed for applying any full Newton-based optimization method to the inner problem.

III.2.2 The Outer Problem

For N_s very large (say $N_s \geq 300$) and each value of x_B, there is a stripping line trajectory $x[\alpha(x_B)]$ that terminates on the stripping pinch point curve. Here α represents a parameterization of the trajectory and should not be confused with the symbol for constant relative volatility. However, stripping line trajectories for real distillation columns may or may not end at the stripping pinch point curve. This depends on the type of pinch. Nonetheless, all stripping lines have a terminus, $x_{Ns}(x_B)$, and the difference between this point and a processing target composition, x_T, defines the implicit vector function

$$F(x_B) = [x_T - x_{Ns}(x_B)] \qquad \text{(III.29)}$$

Application of the implicit function theorem to Eq. III.29 yields

$$\Delta x_B = -J^{-1}[x_T - x_{Ns}(x_B)] \qquad \text{(III.30)}$$

overy Fractions

To draw a close analogy to Underwood's method, it is useful to re-formulate Eq. III.30 in terms of recovery fractions for all components. It is easily seen that the bottoms composition can be expressed in terms of recovery fractions using the equation

$$x_{B,k} = [r_k f_k]/[\sum_{j=1}^{c} r_j f_j], \qquad k = 1,\ldots, c\text{-}1 \qquad \text{(III.31)}$$

where r denotes recovery fraction, f is a molar flow rate, and the subscripts j and k denote component indices. Equation III.31 clearly implies that c-1 x_B's are a function of c recovery fractions. This functionality can be written as $x_B = F(r)$. Thus Eq. III.29 is

$$F(r) = [x_T - x_{N_s}(x_B(r))] \qquad \text{(III.32)}$$

Application of the implicit function theorem gives

$$\Delta x_{B,k} = \Sigma\ (\partial x_{B,k} /\partial r_j)\Delta r_j, \qquad k = 1,\ldots, c\text{-}1 \qquad \text{(III.33)}$$

where

$$\Delta x_B = J_r \Delta r \qquad \text{(III.34)}$$

where J_r is a (c-1) x c matrix of partial derivatives of bottoms composition with respect to recovery fractions. Thus the terms in Eq. III.33 are summed from 1 to c. Since the light and heavy key component recovery fractions in both product streams are fixed in Underwood's method, the matrix J_r is actually (c-1) x (c-2) and the vector Δr is dimension c-2. A first order Taylor series expansion and the chain rule applied to Eq. III.32 gives

$$\Delta r = -(J_r^T[J^TJ]J_r)^{-1} J_r^T J^T[x_T - x_{Ns}(x_B(r))] = -(J_r^T[J^TJ]J_r)^{-1} g \qquad \text{(III.35)}$$

where $g = g(r) = J_r^T J^T[x_T - x_{Ns}(x_B(r))]$ is the gradient of ½ $F(r)^T F(r)$. Equation III.35 defines a straightforward Gauss-Newton strategy to calculate iterative changes in recovery fractions of non-key components. Iterative corrections to all bottoms compositions can be back calculated from Eq. III.34.

<u>Partial Derivative Information</u>

To use Eqs. III.30 to III.35 to adjust x_B and move $x_{Ns}(x_B)$ toward the target composition, x_T, we require sensitivity information in the form of the partial derivatives in J and J_r. The partial derivatives in J_r are easily calculated and given by

$$[J_r]_{ik} = \{\delta_{ik} [\Sigma\, r_j f_j] f_k - [r_k f_k] f_k\}/[\Sigma\, r_j f_j]^2 \qquad i = 1,\ldots, c-1;\ k = 1,\ldots,c-2 \quad \text{(III.36)}$$

where δ is the Kronecker delta function and ik denotes the matrix element in the ith row and kth column of J_r.

It is important that the reader recognize that there is a domino effect to changes in bottoms composition. That is, changing $x_1 = x_B$ changes y_1 and, in turn changes x_2. Subsequently changing x_2 changes y_2 and then x_3; and so on all the way to the pinch if necessary. The effects of these changes, which are measured by the product of partial derivatives times an appropriate perturbation, recur at each stage and therefore can be accumulated as one proceeds up the column. Thus the sensitivity information in J can be accumulated while integrating the stripping line equation by making use of the implicit function theorem and recursion. To see this, note that for fixed boil-up ratio, s, the stripping line equation reduces to the implicit function

$$F(x_{j+1}, x_j, x_1) = x_{j+1} - [s/(s+1)]y_j - [1/(s+1)]x_1 \qquad \text{(III.37)}$$

Remember $x_1 = x_B$. Since $y_j = f(x_j, T_j)$, application of the implicit function theorem gives

$$\Delta x_{j+1} = [s/(s+1)]J_{yx}\Delta x_j + [1/(s+1)]I\Delta x_1 \qquad \text{(III.38)}$$

Stage-to-stage application of this last equation leads to the recursion formulae

$$\Delta x_j = J_{j-1}\Delta x_1, \qquad \text{for } j = 2,\ldots, N_s \qquad \text{(III.39)}$$

$$J_{j-1} = \{[s/(s+1)]\, J_{yx}J_{j-2} + [1/(s+1)]I, \qquad \text{for } j = 2,\ldots, N_s \qquad \text{(III.40)}$$

and where $J_0 = I$.

If we set

$$J = J_{Ns-1} \tag{III.41}$$

then it is a simple matter to use J and J_r to calculate changes in non-key component recovery fractions from Eq. III.35 and changes in bottoms compositions from Eq. III.34. These values in turn give a new value of x_B, from which the boil-up ratio that minimizes the stripping line distance to the stripping pinch point curve can be found by resolving the inner problem.

III.3 A Two-Level Algorithm for Energy Efficient Design and Optimization

The overall algorithm is very simple.

1) Given key component recovery fractions and a target composition, x_T, guess x_B.
2) Solve the inner problem for $s_{min}(x_B)$.
3) Measure $\| x_T - x_{Ns}(x_B(r)) \| < \varepsilon$, stop. Else go to step 4.
4) Using $s_{min}(x_B)$ from step 2, use the outer algorithm to calculate $x_{B,new}(s_{min})$.
5) Set $x_B = x_{B,new}(s_{min})$ and return to step 2.

Step 2 of the algorithm involves the application of the shortest stripping line methodology. It is very important to understand that the bottoms composition is held fixed in solving the inner nonlinear programming sub-problems defined by Eqs. III.3 to III.8. To use any Newton-based methodology to solve the inner sub-problems, the recursion formulae for calculating the changes in trajectory with respect to boil-up ratio (i.e., Eqs. III.12 and III.13) and the recursion formulae for determining the partial derivatives of distance function with respect to boil-up ratio (i.e., Eqs. III.26 and III.28) are needed. Step 3 defines a simple measure of closeness to the desired target. Step 4 is the outer sub-problem, which updates the recovery fractions of the <u>non-key</u> components and is solved by the Gauss-Newton strategy (i.e., Eq. III.35). The necessary partial derivatives for solving the outer sub-problem by a Gauss-Newton method are given by Eq. III.36 and Eqs. III.39 to III.41. In our opinion, a Gauss-Newton method is appropriate for solving the outer problem because we are not <u>necessarily</u> interested in fast convergence. Rather, we are interested in a methodology that is robust, generates a number (or portfolio) of different minimum energy designs, and shows how these minimum energy designs are related to Underwood's method for a variety of situations.

III.3.1 Advantages of the Proposed Two-Level Approach

The proposed two-level approach has several advantages because it

1) Permits many minimum energy designs to be investigated in one sweep.
2) Allows for the investigation of direct, indirect and transitions splits in one sweep.

3) Can handle bounds on lighter than light and heavier than heavy key recovery fractions to be included.

4) Finds feasible minimum energy designs that Underwood's method cannot find.

1) Investigating Portfolios of Minimum Energy Designs

The outer problem formulation given in the last section allows the practicing design engineer to investigate a range of minimum energy designs (in the spirit of Underwood) in a very straightforward way. In particular, it is a simple matter to modify Eq. III.35 to include a line search parameter, say β, which gives

$$\Delta r = -\beta(J_r^T[J^TJ]J_r)^{-1} J_r^T J^T[x_T - x_{Ns}(x_B(r))] \qquad \text{(III.42)}$$

For β =1, full Gauss-Newton steps are taken. However, by selecting smaller value of β it is possible to use the set of outer problem equations (i.e., Eqs. III.31 to III.41) to investigate any number of desired minimum energy designs en route to the target. For example, if β = 1 results in five minimum energy designs, then β = 0.25 will give result in approximately twenty minimum energy designs – provided one uses a fixed value of β and does not use automatic step size adjustment. This is important because Underwood's method does not always result in minimum energy solutions that correspond to desired product purity specifications. However, our portfolio idea gives the engineer the opportunity to view a set of minimum energy designs and screen those designs with respect to additional desired solution characteristics.

[redacted]ning Direct, Indirect & Transition Splits

The proposed two-level design approach can be initialized using a direct or indirect split. Depending on the problem specifications, one or both initializations will converge to the transition split – if it exists. Note that if the target composition is selected as the feed composition (i.e., $x_T = x_F$), then the two-level algorithm asymptotically approaches a transition split (or double feed pinch point) for class 1 separations. Also note that the primary difference between direct and indirect splits in the context of Underwood's method is the choice of light and heavy key components. Thus the proposed two-level algorithm is readily applied to either case by simply varying the choice of light and heavy key components. This process of spanning direct and indirect splits provides a convenient way to understand the effect of the recovery fractions of non-key components.

3) Bounds on Recovery Fraction

For class 2 separations, where there are lighter than light (LLK) and heavier than heavy key (HHK) components, there are usually physical bounds on the recovery fractions of the LLK and HHK components. The recovery fraction of any LLK component in the bottoms cannot be greater than the recovery fraction of the light key and the recovery fraction of any HHK components cannot be less than the heavy key component. This gives the bounds

$$r_{LLK} \leq r_{LK} \qquad \text{(III.43)}$$

$$r_{HHK} \geq r_{HK} \tag{III.44}$$

These bounds are easily included in the two-level design algorithm (i.e., Eqs. III.31 to III.42).

4) Determines Feasible Designs that Underwood's Method Cannot Find

For mixtures that form azeotropes, it is well known that Underwood's method can have difficulties and fail to find a feasible design regardless of whether one of the distillation product compositions is azeotropic or not. Difficulties arise because the concept of light and heavy key component can be skewed for azeotropic mixtures, making the Underwood equations ill-defined. In contrast, the two-level design approach has no difficulties whatsoever in finding feasible minimum energy designs for distillations involving mixtures that form azeotropes.

III.4 Numerical Examples

In this section, we illustrate two-level design and optimization methodology for a number of multicomponent mixtures and consider direct, indirect, and transition splits. In all cases, the calculations were performed in double precision arithmetic using a Pentium IV personal computer with the Lahey-Fujitsu compiler (LF95).

III.4.1 Example 1

The primary purpose of this first example is to present the details of the two-level design method for a very simple case. This example was adapted from Doherty and

Malone[5] (p.124, 2001) and involves the separation of a mixture of methanol (1) ethanol (2) and propanol (3) at atmospheric pressure, The phase equilibrium is modeled using a constant relative volatility model with relative volatilities of α_{13}=3.25, α_{23}=1.90, and α_{33}=1, as given in Doherty and Malone. Methods based on distillation lines generally fix the bottoms and top compositions in the problem definition and are not easily compared to Underwood's method. Therefore, the column specifications were changed slightly, as shown in Table III.1, and given in terms of recoveries so a more direct comparison between the two-level design methodology proposed in this paper and the work of Underwood can be made.

Table III.1: Feed Composition & Recoveries for Methanol/Ethanol/Propanol Separation.

Component	Feed Composition$^+$	HK/LK *	Recovery Fraction in Top Product
Methanol	0.3	LK	1 - 7.576×10^{-11}
Ethanol	0.25		
Propanol	0.45	HK	0.012

* HK: Heavy Key, LK: Light Key

\+ Feed is saturated liquid

Ethanol, which is an intermediate boiler, is designated as the non-key component and thus the separation corresponds to a class 1 separation according to classification of Shiras et al. (1950). In the material that follows, we show that for all class 1 separations when the processing target is set to the feed composition (i.e. $x_T = x_F$), the two-level design methodology converges to the Underwood's solution, which in this case is a double-feed pinch (or transition split). We also discuss other advantages offered by our two-level design methodology.

Evolution of Direct Splits

One way to initialize our two-level design methodology is to set the ethanol recovery fraction, r_E, in the top product such that the separation is a direct split (e.g., $r_E = 0.96$). This choice of recovery fraction is arbitrary and other appropriate initial guesses are equally useful and will result in convergence to Underwood's solution. Ideally, the initial guess should be away from the transition split so that the recovery fraction (or composition) iterates sample an appropriate range of the feasible range. Once the recoveries of all components are specified, the composition of the bottom and top products can be easily calculated. From this, the two-level design methodology alternates between the shortest stripping line approach to find the corresponding minimum energy requirement for the column and the outer loop to update values of the recovery fractions, as described by the equations from the previous section.

Table III.2: Two-Level Iterations Initialized Using a Direct Split

iteration	r_E*	$x_B = (x_M, x_E)$	s_{min}	r_{min}	D**
1	0.9600	$(3.319893\text{x}10^{-11}, 0.350569)$	1.694100	2.67710	0.67851
2	0.7654	$(3.573908\text{x}10^{-11}, 0.300880)$	1.552300	1.711570	0.64200
3	0.6803	$(3.697570\text{x}10^{-11}, 0.276689)$	1.48340	1.366320	0.62083
4	0.6386	$(3.761357\text{x}10^{-11}, 0.264211)$	1.44790	1.210716	0.60896
5	0.6172	$(3.795017\text{x}10^{-11}, 0.257626)$	1.429110	1.133780	0.60239
6	0.6058	$(3.813030\text{x}10^{-11}, 0.254103)$	1.419100	1.094050	0.59881
7	0.5998	$(3.822685\text{x}10^{-11}, 0.252214)$	1.413710	1.073100	0.59686
8	0.5966	$(3.827895\text{x}10^{-11}, 0.251195)$	1.410808	1.061920	0.59580
9	0.5948	$(3.830707\text{x}10^{-11}, 0.250645)$	1.4092433	1.05591	0.59523
10	0.5939	$(3.832223\text{x}10^{-11}, 0.250348)$	1.4084490	1.052759	0.59495
11	0.5934	$(3.832990\text{x}10^{-11}, 0.250198)$	1.40797184	1.0510536	0.59477

Results from Underwood's Method

-	0.5929	$(3.83400\text{x}10^{-11}, 0.250000)$	1.407407	1.048898	-

* Recovery fraction of non-key (ethanol) in bottom product

** Stripping line distance measured from x_B to stripping pinch point curve

Table III.2 shows the minimum boil-up, reflux ratios, and stripping line distances for the recovery fraction iterates given by the outer loop, starting from the direct split with

$r_E = 0.96$. The solution for Underwood's method is also shown in Table III.2. For all inner loop (or shortest stripping line) problems, the solution is considered feasible if the distillate product satisfies the condition $\|y_D - y_{D,spec}\| \leq 0.05$, where $y_{D,spec}$ changes from one outer loop iteration to the next but can be calculated from the given values of x_B, x_F, and the set of recoveries.

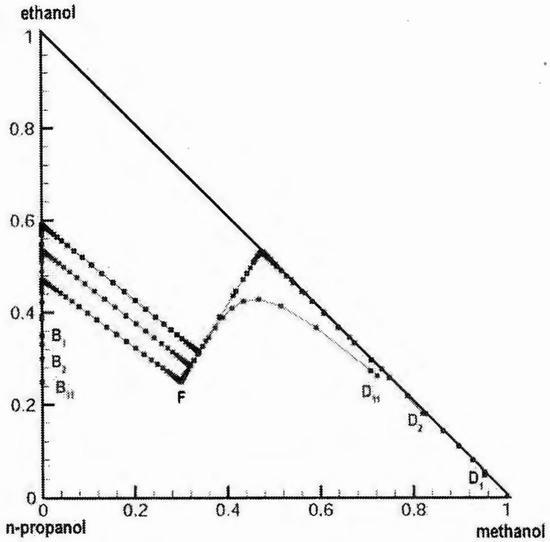

Figure III.1: Evolution of Minimum Energy Solutions to Underwood's Solution from Direct Split

The results in Table III.2 provide a portfolio of minimum energy designs with varying bottoms compositions that converge to the double-feed pinch predicted by Underwood's method. In fact, one can easily interpret the results of Underwood's method for the case of a double-feed pinch in the context of the shortest stripping line approach. Underwood's solution for class 1 separations corresponds to the minimum shortest stripping line distance (or the global minimum stripping line distance) and thus the global minimum energy design for fixed key component recovery fractions –

provided it is understood that the composition of the resulting product streams is not a consideration in deciding what is optimal.

Table III.3: Additional Information for Two-Level Design Procedure*

iteration	$\|\|[x_T - x_{Ns}(x_B(r))]\|\|$	N_s	N_r	$y_D(calc) = (y_M, y_E)$
1	$5.48785x10^{-3}$	300	41	(0.95237866, 0.04762133)
2	$1.56436x10^{-3}$	300	23	(0.81964444, 0.18035555)
3	$4.5462x10^{-4}$	300	18	(0.78771593, 0.21228407)
4	$1.3270x10^{-4}$	300	15	(0.77303875, 0.22696124)
5	$3.8790x10^{-5}$	300	18	(0.76993168, 0.23006831)
6	$1.1327x10^{-5}$	300	14	(0.74772180, 0.23632936)
7	$3.3115x10^{-6}$	300	16	(0.73205885, 0.25098788)
8	$9.6690x10^{-7}$	300	18	(0.70529179, 0.27662011)
9	$2.8208x10^{-7}$	300	20	(0.72619436, 0.25630616)
10	$8.4269x10^{-8}$	300	20	(0.71684277, 0.24732092)
11	$2.6627x10^{-8}$	300	24	(0.72263855, 0.26162361)

*Initialized with direct split

Table III.3, on the other hand, gives additional details regarding the two-level design procedure and the resulting designs, including the number of stripping stages (N_s), the number of rectifying stages (N_r), the calculated distillate product (y_D), and the norm of the targeting function, $[x_T - x_{Ns}(x_B(r))]$. The number of rectifying stages is determined automatically by ensuring that the distillate specifications are made. Figure III.1 gives distillation line representations of several of the minimum energy designs in Table III.2.

Note that the norm of the targeting function decreases monotonically as the two-level design procedure approaches the Underwood solution, and that fast convergence of the outer loop is not necessarily desirable if the goal of the engineering investigation is to generate a portfolio of minimum energy designs.

Evolution of Indirect Splits

It is important to note that any physically meaningful value of r_E is possible but it is often easiest to initialize the two-level method and find an initial feasible design with either an approximate direct or indirect split. Here we initialize the proposed two-level algorithm with a starting guess for the recovery of the non-key component that corresponds to an indirect split. To explore various designs starting from the indirect split, the ethanol recovery fraction in the bottom product was initialized to $r_E = 0.04$. Table III.4 shows the iterations given by the two-level approach starting from the indirect split. Here we use a line search parameter value of $\beta = r_{min}/2s_{min}$.

Note again that the two-level approach converges to the solution given by Underwood's method – this time from the indirect split – and provides a portfolio of minimum energy designs. Moreover, the same shortest stripping line interpretation of

Underwood's method is valid here. That is, Underwood's solution for class 1 separations corresponds to the <u>minimum</u> shortest stripping line distance (or the global minimum stripping line distance) and thus the global minimum energy design. Finally, note that the norm of the targeting function decreases monotonically as the two-level design procedure converges to Underwood's solution.

Table III.4: Two-Level iterations Initialized Using an Indirect Split

iteration	r_E*	$x_B = (x_M, x_E)$	s_{min}	r_{min}	D**
1	0.040	$(5.0 \times 10^{-11}, 0.02200)$	2.9653267	1.4711056	1.25003
2	0.2815	$(4.413380 \times 10^{-11}, 0.136664)$	2.16093600	1.29441000	0.96395
3	0.4643	$(4.053628 \times 10^{-11}, 0.207037)$	1.69082290	1.15792000	0.75006
4	0.5580	$(3.891064 \times 10^{-11}, 0.238838)$	1.48424800	1.08457000	0.63900
5	0.5869	$(3.843566 \times 10^{-11}, 0.248129)$	1.42731627	1.06523400	0.60581
6	0.5935	$(3.832847 \times 10^{-11}, 0.250226)$	1.40805163	1.05213570	0.59479

* Recovery fraction of non-key (ethanol) in bottom product

** Stripping line distance measured from x_B to stripping pinch point curve

Figure III.2 gives a number of liquid composition profiles for the results shown in Table III.3. Table III.5 provides additional information about the design portfolio shown in Table III.4.

Figure III.3, summarizes all of the calculations given in Tables III.2, III.3, III.4 and III.5. In particular, it shows a family of curves of F^TF versus recovery fraction of the non-key component in the bottoms, where F is defined by Eq. III.29. Each curve in this figure was obtained using the boil-up ratio found by solving the corresponding inner loop (or shortest stripping line) problem. The lines that move from one point to another on a given curve depict the outer loop calculation while the vertical lines represent the transition from the outer loop to inner loop and the subsequent determination of a new corresponding minimum boil-up ratio.

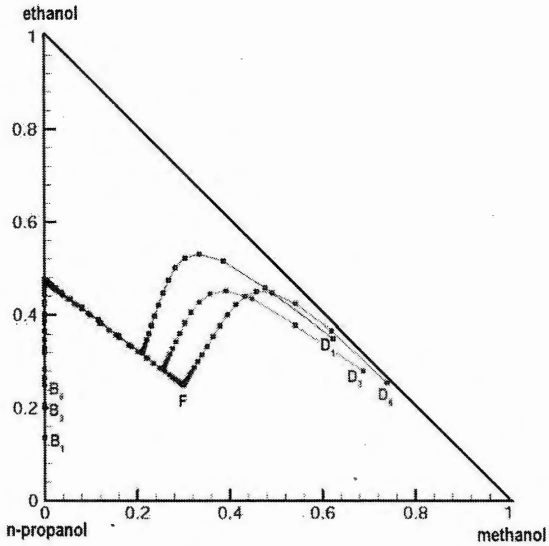

Figure III.2: Evolution of Minimum Energy Solutions to Underwood's Solution from Indirect Split

It is also interesting to note that the new estimate predicted by solving the outer loop problem often lands very close to the minimum of each curve for the case of the direct split but that the minima for the curves corresponding to indirect splits can be outside the feasible region – except specifically for the curve that gives Underwood's solution.

This is why it is often a good idea to use a line search parameter $\beta < 1$ for the two-level design procedure when it is initialized using the indirect split.

Remarks

The slight difference between Underwood's solution and the final solutions shown in Tables III.2 and III.4 can be attributed to fundamental differences between the two methods and numerical inaccuracies. Underwood's method is a group method while the shortest stripping line is a tray to tray method, which always goes from bottom to top. Since the final solution in this case is a double-feed pinch, the integration of the rectifying section should start exactly at the pinch point. In practice

Table III.5: Additional Information for Two-Level Design Procedure*

iteration	$\|\|[x_T - x_{N_s}(x_B(r))]\|\|$	N_s	N_r	$y_D(\text{calc}) = (y_M, y_E)$
1	$1.65156\text{x}10^{-1}$	37	20	(0.55902450, 0.44097540)
2	$6.18529\text{x}10^{-2}$	49	18	(0.61545038, 0.37431627)
3	$1.21346\text{x}10^{-2}$	63	18	(0.68766355, 0.28107372)
4	$1.01895\text{x}10^{-3}$	77	21	(0.69291668, 0.29426556)
5	$5.72960\text{x}10^{-5}$	86	25	(0.73610970, 0.26389029)
6	$3.46877\text{x}10^{-8}$	300	25	(0.73942885, 0.25569592)

* Initialized with indirect split

the integration usually starts 'close to' but not exactly at the pinch point. However, the solutions in Tables III.2 and III.4 are close enough to the Underwood's solution to be useful in practice.

The biggest advantage of our two-level design methodology is that it offers a systematic way of using distillation line methods to explore a portfolio of feasible minimum energy designs that encompass Underwood's solution.

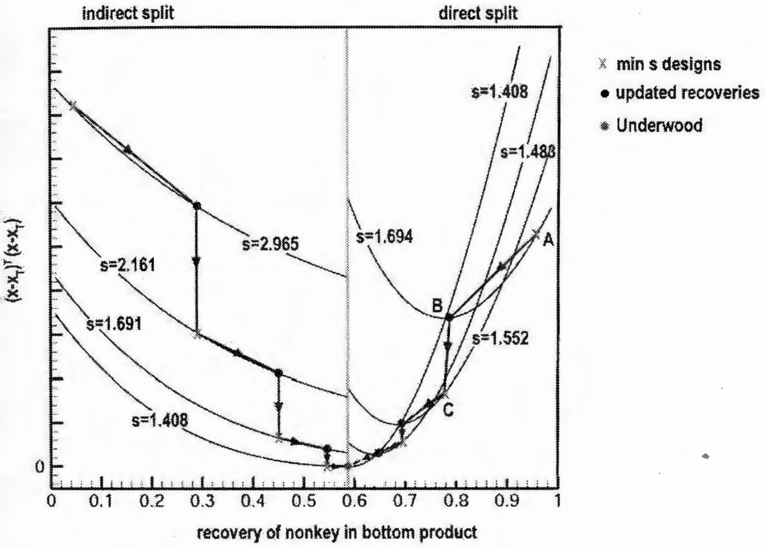

Figure III.3: Underwood's Method and Shortest Stripping Line Approach for Double Feed Pinch

In our opinion, one of the major disadvantages of distillation line methods is the way in which specifications are made (i.e., in terms of product concentrations). This requires fixing the recoveries of key as well as non-key components. It is well known that the results of distillation line methods are very sensitive to product compositions, especially trace compositions of non-key components. Our two-level algorithm easily overcomes this limitation and offers a novel way to explore a range of minimum energy designs for different non-key component recoveries with fixed key components and recoveries. Note that all of the designs in Tables III.2 to III.5 satisfy the recovery constraints for the key components and each solution is a minimum energy design for a particular non-key recovery fraction. The resulting designs span the entire range of non-key component recoveries and converge to Underwood's solution. Moreover, each of these minimum energy designs is obtained by using the shortest stripping line method for the corresponding inner loop problem.

III.4.2 Example 2

The second example involves the separation of the quaternary hydrocarbon mixture at 400 psia. The specific feed composition and recovery fractions are shown in Table III.6.

Table III.6: Feed Composition & Recoveries for a Quaternary Hydrocarbon Mixture

Component	Feed Composition+	HK/LK *	Recovery Fraction in Top Product
n-Butane	0.2	LK	0.990
iso-Pentane	0.3		
n-Pentane	0.2		
Hexane	0.3	HK	0.010

* HK: Heavy Key, LK: Light Key

\+ Feed is saturated liquid.

The purpose of this second example is to show that the proposed two-level design methodology is independent of the number of components or the number of non-key components present in the mixture. For this example the liquid and vapor phases are considered ideal solutions and the vapor-liquid equilibrium is modeled by using the correlation given in Wilson[11]. This correlation estimates K-values based on critical properties from the simple relationship

$$K_i = \exp[\ln(p_{c,i}/p) + 5.37(1 + \omega_i)(1 - T_{c,i}/T)] \qquad \text{(III.45)}$$

where $p_{c,i}$, $T_{c,i}$, and ω_i are the critical pressure, critical temperature and acentric factor for the ith component. We used critical properties given in Elliott and Lira[12]. Relative volatilities for this mixture vary over a moderate temperature range and both iso-pentane and n-pentane are intermediate boilers. Thus there are two distributing non-key components for this separation. As in the first example, when the processing target is set to the feed composition (i.e. $x_T = x_F$), the two-level design methodology produces several minimum energy designs and ultimately converges to Underwood's solution.

Direct Split

The two-level design methodology is initialized to a direct split by setting the non-key recoveries of iso-pentane (r_{IP}) and n-pentane (r_{NP}) to 0.98. Using these non-key recoveries and the key component recoveries in Table III.6, the compositions of the bottom and top products are calculated.

Table III.7: Two-Level Iterations for Four-Component Hydrocarbon Separation (Direct)

iter$^+$	(r_{IP}*, r_{NP}*)	$x_B = (x_{n\text{-}C4}, x_{i\text{-}C5}, x_{n\text{-}C5})$	s_{min}	r_{min}	D**
1	(0.98000, 0.98000)	(0.002535, 0.372624, 0.248416)	1.250655	3.676622	0.3830
2	(0.90001, 0.97291)	(0.002619, 0.353627, 0.254816)	1.189712	2.843316	0.3571
3	(0.81247, 0.91120)	(0.002759, 0.336204, 0.251371)	1.162155	2.063580	0.3521
4	(0.69638, 0.81010)	(0.002985, 0.311844, 0.241845)	1.117530	1.268698	0.3435
5	(0.64788, 0.74947)	(0.003109, 0.302156, 0.233023)	1.095743	0.975778	0.3399
6	(0.62427, 0.72139)	(0.003172, 0.297009, 0.228809)	1.084468	0.850968	0.3378
7	(0.61209, 0.70683)	(0.003205, 0.294276, 0.226552)	1.078479	0.789764	0.3367
8	(0.60885, 0.70299)	(0.003214, 0.293540, 0.225948)	1.076875	0.773912	0.3364

Results from Underwood's Method (for relative volatilities at feed conditions)

iter$^+$	(r_{IP}*, r_{NP}*)	$x_B = (x_{n\text{-}C4}, x_{i\text{-}C5}, x_{n\text{-}C5})$	s_{min}	r_{min}	D**
-	(0.59915, 0.69111)	(0.003241, 0.291335, 0.224036)	1.070436	0.724196	-

$^+$ Outer loop iteration number

* Recovery fraction of non-key components (i-pentane, n-pentane) in bottom product

** Stripping line distance measured from x_B to stripping pinch point curve

As in the case of example 1, the two-level design methodology generates a portfolio of minimum energy designs as it alternates between inner and outer loops. This portfolio of minimum energy designs is summarized in Table III.7, along with Underwood's solution obtained by using relative volatilities calculated at the feed composition given in Table III.6.

It can be seen that the outer loop converges monotonically to a solution very close to the Underwood solution. Also, for all inner loop (or shortest stripping line) problems, the solution is considered feasible if the distillate product satisfies the condition $||y_D - y_{D,spec}|| \leq 0.05$. It is important to remember that in this example the K-Wilson model (i.e., Eq. III.45) was used to describe vapor-liquid equilibrium instead of assuming constant relative volatilities. Hence the final solution shown in Table III.7, as expected, differs to greater extent from Underwood's solution than the results for example 1. However, this example illustrates two important aspects regarding the proposed methodology.

1) It is independent of the number of non-key components and thus is applicable to mixtures with any number of components.
2) Any thermodynamic model can be used to describe vapor–liquid equilibrium, provided the necessary derivative information is obtained properly.

Table III.8: Additional Information for Four-Component Hydrocarbon Separation*

iteration	$\|[x_T - x_{N_s}(x_B(r))]\|$	N_s	N_r	$y_D(calc) = (y_{n\text{-}C4}, y_{i\text{-}C5}, y_{n\text{-}C5})$
1	3.81760×10^{-3}	300	14	(0.92467419, 0.07172481, 0.00360114)
2	2.29453×10^{-3}	300	18	(0.82873078, 0.16893228, 0.00233783)
3	1.20000×10^{-3}	300	11	(0.72150668, 0.24332863, 0.03516468)
4	3.44901×10^{-4}	300	14	(0.59809138, 0.31333183, 0.08857769)
5	9.68878×10^{-5}	300	8	(0.52229352, 0.33324994, 0.13834291)
6	2.82425×10^{-5}	300	8	(0.50630602, 0.33622185, 0.13661996)
7	8.29321×10^{-6}	300	8	(0.50971007, 0.31583263, 0.13363540)
8	4.94050×10^{-6}	300	8	(0.51468095, 0.30232592, 0.13335395)

* Initialized with direct split

Table III.7 also shows the minimum boil-up ratios, reflux ratios, and minimum stripping line distances corresponding to the recovery fraction iterates given by the outer loop. Note that the minimum stripping line distance for the eighth solution is the smallest of all minimum stripping line distances and again easily demonstrates that Underwood's solution is the global minimum in stripping line distance (or global minimum in energy demands) for the given set of key component recoveries. As canbe seen in Table III.7, this final shortest stripping line solution gives the smallest reflux and smallest reboil ratio and hence requires the least amount of energy of all other solutions in Table III.7. Table III.8, on the other hand, gives additional information regarding these minimum energy designs.

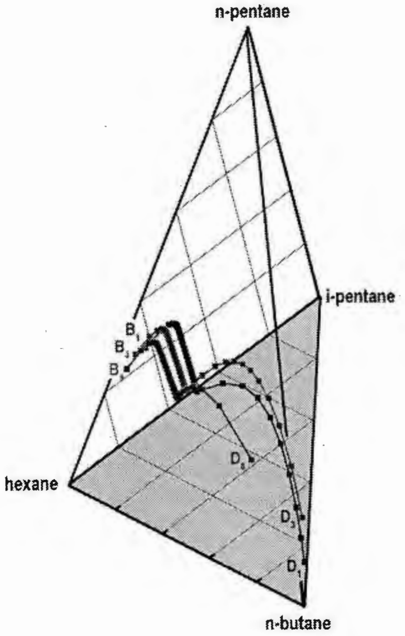

Figure III.4: Minimum Energy Design Portfolio for an N-Alkane Distillation

Figure III.4 shows a few of the distillation line trajectories and thus the evolution of the designs from a direct split to the Underwood solution, where the column section profiles for the last design (in red) show an approximate double pinch at feed.

Indirect Splits

As in the first example, it is possible to initialize the two-level design algorithm with a starting guess for the recoveries of the non-key component that corresponds to an indirect split. Thus to explore various designs starting from the indirect split, the recoveries of iso-pentane (r_{IP}) and n-pentane (r_{NP}) in bottom product were set to 0.02

and 0.05 respectively. Table III.9 shows the iteration history for the two-level design approach starting from the indirect split. For all inner loop (or shortest stripping line distance) problems, the solution is considered feasible if the distillate product satisfies the condition $\|y_D - y_{D,spec}\| \leq 0.05$. Table III.10 provides additional information regarding the two-level design portfolio shown in Table III.9.

Table III.9: Two-Level Iterations for Four-Component Hydrocarbon Separation (Indirect)

it^{+}	(r_{IP}^{*}, r_{NP}^{*})	$x_B = (x_{n\text{-}C4}, x_{i\text{-}C5}, x_{n\text{-}C5})$	s_{min}	r_{min}	D**
1	(0.02000, 0.05000)	(0.006349, 0.019048, 0.031746)	5.045085	1.320000	0.845450
2	(0.09289, 0.20717)	(0.005430, 0.075665, 0.112500)	3.411450	0.989000	0.892531
3	(0.29218, 0.41676)	(0.004255, 0.186495, 0.177342)	2.139120	0.897000	0.755017
4	(0.39979, 0.52059)	(0.003824, 0.229263, 0.199069)	1.677050	0.839000	0.622294
5	(0.46534, 0.58034)	(0.003606, 0.251683, 0.209257)	1.447500	0.803000	0.532224
6	(0.50722, 0.61690)	(0.003481, 0.264847, 0.214743)	1.319300	0.781700	0.472788

\+ Outer loop iteration number

* Recovery fraction of non-key components (i-pentane, n-pentane) in bottom product

** Stripping line distance measured from x_B to stripping pinch point curve

Similar to the direct split, when initialized from an indirect split, the two-level design approach converges to a solution close to that given by Underwood's method and generates a portfolio of minimum energy designs. Thus the same shortest stripping line interpretation that Underwood's solution corresponds to the global minimum in stripping line distances, requires minimum reboil and reflux ratio and thus represent a global minimum energy design is valid here.

Also note that the norm of the targeting function decreases monotonically as the two-level design procedure converges to Underwood's solution. Figure III.5 gives several liquid composition profiles for the results shown in Table III.9.

Table III.10: Additional Information for Two-Level Design Procedure*

iter	$\|\|[x_T - x_{N_s}(x_B(r))]\|\|$	N_s	N_r	$y_D(calc) = (y_{n\text{-}C4}, y_{i\text{-}C5}, y_{n\text{-}C5})$
1	1.95100×10^{-2}	6	300	(0.297112, 0.427774, 0.270657)
2	1.34494×10^{-2}	7	300	(0.327074, 0.425886, 0.242129)
3	7.56045×10^{-3}	6	300	(0.355773, 0.421546, 0.217252)
4	4.17299×10^{-3}	6	300	(0.392375, 0.382588, 0.183176)
5	2.23239×10^{-3}	6	300	(0.431439, 0.372574, 0.166707)
6	1.17117×10^{-3}	5	300	(0.449459, 0.341253, 0.198987)

* Initialized with indirect split

We remark that the final solution to which the two-level design methodology converges from indirect split is not as close as the one reached from the direct split.

This is due to the numerical difficulties associated with finding a design with a double feed pinch.

While this difficulty will vary depending on the specific example, it is always possible to find a solution which is close enough to Underwood's solution for engineering use. Figure III.6 shows the variation of non-key component recoveries for the entire design portfolio (Tables III.7 and III.9) for this example. Note the design portfolio spans the entire range of non-key component recoveries and gives a design that is very close to Underwood's solution.

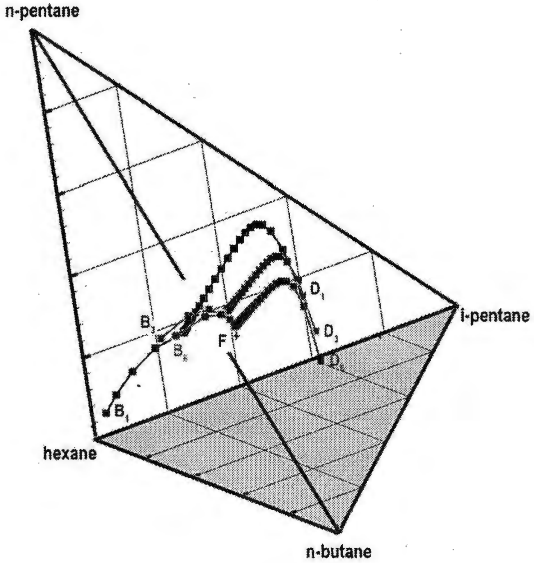

Figure III.5: Design Portfolio for an N-Alkane Distillation from Indirect Split

III.4.3 Example 3

The third example involves the separation of a mixture of chloroform (C), benzene (B) and toluene (T) at atmospheric pressure. *Unlike the first two examples, this* *mixture is strongly non-ideal and the purpose of including it is twofold – to show that the two-level design methodology is flexible and allows any phase equilibrium model to be used and to show that not all problem specifications admit feasible designs from both the direct and indirect splits.* Here the liquid phase is modeled by the UNIQUAC equation and the vapor phase is considered as ideal. Table III.11 lists the feed composition, key components, and their recoveries. Benzene, which is intermediate boiler, is the only non-key component for this example.

Direct Split

As in the earlier examples, the processing target for this example is set to the feed composition. To initialize the two-level design methodology, the non-key recovery was first set to a value ($r_B = 0.98$) that makes the separation a direct split.

Table III.11: Feed Composition & Recoveries for Chloroform/Benzene/Toluene Separation

Component	Feed Composition$^+$	HK/LK *	Recovery Fraction in Top Product
Chloroform	0.3	LK	0.95
Benzene	0.3		
Toluene	0.4	HK	0.01

* HK: Heavy Key, LK: Light Key

$+$ Feed is saturated liquid

Using this initialization, the two-level design methodology alternates between the inner and outer loops, producing several minimum energy designs. Table III.12 gives minimum reboil ratios, reflux ratios, non-key recovery fractions, and stripping line distances for these minimum energy designs. For all inner loop (or shortest stripping line) problems, the solution was considered feasible if the distillate product satisfies the condition $||y_D - y_{D,spec}|| \leq 0.05$, where $y_{D,spec}$ changes from one outer loop iteration to the next but can be computed from the given values of x_B, x_F, and the set of recoveries. Underwood's solution, obtained by using relative volatilities calculated at feed conditions, is also listed in Table III.12. For a meaningful comparison to Underwood's method, K-values used for calculating relative volatilities were obtained using the UNIQUAC equation and an ideal vapor phase.

From Table III.12, it can be seen that the two-level design methodology converges to final solution (i.e., design 16) which is close to Underwood's solution. Like earlier examples, the shortest stripping line distance for this final solution in the portfolio is the smallest of all minimum stripping line distances and thus Underwood's solution can be interpreted as the global minimum in stripping line distance.

III.12: Two-Level Iterations for Chloroform/Benzene/Toluene Distillation$^+$

iteration	r_B*	$x_B = (x_C, x_B)$	s_{min}	r_{min}	D**
1	0.9800	(0.021277, 0.417021)	1.787000	3.270627	0.607543
2	0.8479	(0.022544, 0.382287)	1.703100	2.386217	0.592473
3	0.7602	(0.023471, 0.356883)	1.640100	1.904059	0.578696
4	0.6982	(0.024176, 0.337588)	1.591000	1.600916	0.566302
5	0.6521	(0.024727, 0.322487)	1.553000	1.394939	0.556360
6	0.6178	(0.025153, 0.310796)	1.522900	1.249831	0.547731
7	0.5914	(0.025492, 0.301519)	1.499000	1.143060	0.540633
8	0.5710	(0.025760, 0.294178)	1.480000	1.063213	0.534791
9	0.5551	(0.025973, 0.288349)	1.464000	1.001334	0.529274
10	0.5420	(0.026151, 0.283473)	1.451000	0.951905	0.524916
11	0.5315	(0.026295, 0.279516)	1.440300	0.912743	0.521204
12	0.5229	(0.026414, 0.276243)	1.431600	0.881293	0.518233
13	0.5160	(0.026511, 0.273595)	1.424400	0.856118	0.515666
14	0.5103	(0.026592, 0.271393)	1.418500	0.835614	0.513594
15	0.5057	(0.026657, 0.269606)	1.413700	0.819164	0.511893
16	0.5020	(0.026709, 0.268162)	1.409800	0.805983	0.510493
Results from Underwood's Method					
-	0.48466	(0.026963, 0.261216)	1.390780	0.743863	-

\+ Initialized from direct split; * Recovery fraction of non-key (benzene) in bottom product

** Stripping line distance measured from x_B to stripping pinch point curve

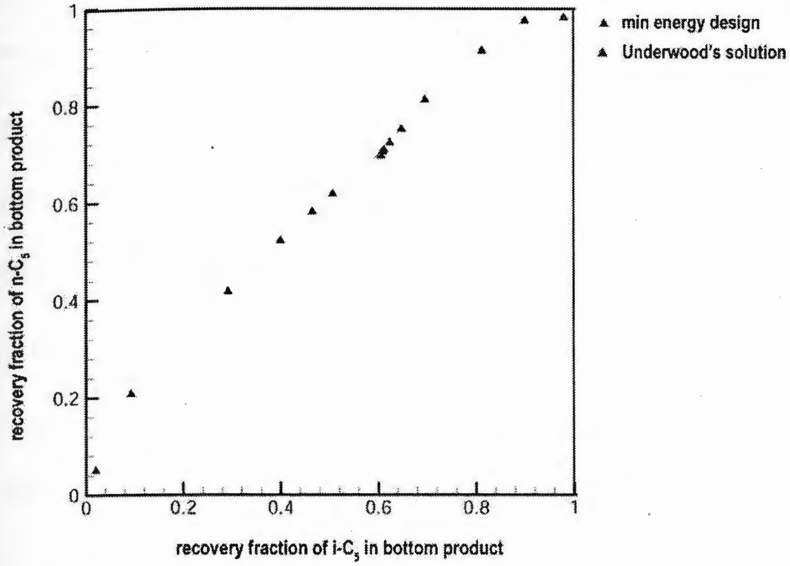

Figure III.6: Design Portfolio for Quaternary Alkane Mixture

This final solution from the two-level design methodology also has the smallest reflux ratio and smallest reboil ratio; hence it is also a global minimum in energy demands for the given set of key component recoveries. However, because of the non-ideal nature of the mixture, relative volatilities vary over a wide range and thus the final solution from the two-level design methodology differs from Underwood's solution to a greater extent than the final converged solutions for the first two examples.

Table III.13: Additional Information for Chloroform/Benzene/Toluene Distillation*

iteration	$\|\|[x_T - x_{N_s}(x_B(r))]\|\|$	N_s	N_r	$y_D(calc) = (y_C, y_B)$
1	$1.1525\text{x}10^{-2}$	300	24	(0.995053, 0049467)
2	$7.4888\text{x}10^{-3}$	300	14	(0.831891, 0.168109)
3	$4.9500\text{x}10^{-3}$	300	12	(0.784644, 0.215356)
4	$3.3063\text{x}10^{-3}$	300	14	(0.726750, 0.273251)
5	$2.1986\text{x}10^{-3}$	300	10	(0.759190, 0.240811)
6	$1.4796\text{x}10^{-3}$	300	9	(0.723509, 0.276491)
7	$9.9771\text{x}10^{-4}$	300	8	(0.721417, 0.278584)
8	$6.7761\text{x}10^{-4}$	300	7	(0.695999, 0.304002)
9	$4.6800\text{x}10^{-4}$	300	8	(0.677751, 0.322250)
10	$3.1879\text{x}10^{-4}$	300	8	(0.669309, 0.330691)
11	$2.1798\text{x}10^{-4}$	300	10	(0.682568, 0.317432)
12	$1.4800\text{x}10^{-4}$	300	8	(0.641245, 0.357751)
13	$1.0122\text{x}10^{-4}$	300	12	(0.636909, 0.363091)
14	$6.8723\text{x}10^{-5}$	300	9	(0.692601, 0.307258)
15	$4.6855\text{x}10^{-5}$	300	8	(0.671810, 0.320832)
16	$3.2200\text{x}10^{-5}$	300	7	(0.609782, 0.363747)

* Initialized with direct split

Table III.13, on the other hand, gives additional information regarding this portfolio of minimum energy designs. Figure III.7 gives the distillation line trajectories of several of the minimum energy designs in Tables III.12 and III.13.

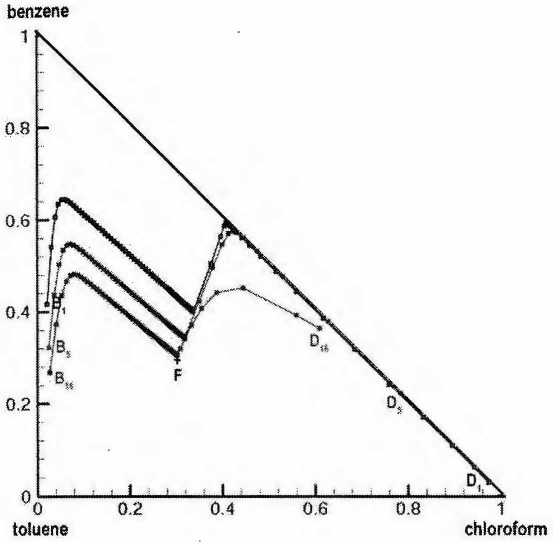

Figure III.7: Minimum Energy Design Portfolio for Chloroform/Benzene/Toluene Distillation

To re-emphasize, this example demonstrates that the two-level design methodology can be applied to any non-ideal vapor-liquid mixtures using suitable phase models, simple or complicated. Moreover, this flexibility is useful when volatilities change over a wide range due to the non-ideal nature of mixture under consideration and where Underwood's method, which is based on assumption of constant relative volatilities, is expected to have greater error in calculating minimum energy requirements. However, what is advantageous is that for the proposed two-level design methodology, the design problem can be specified in a way that is analogous to Underwood's method using only two key component recoveries. Finally, this example illustrates that for the specific set of key component recoveries used here, it is not possible to initialize the two-level design methodology by setting the non-key component (benzene) recovery to a value which will make the split close to an indirect split. This is due to the fact that it is not possible to find a feasible minimum energy design with a rectifying pinch that satisfies the constraints for the given key component recoveries. Thus the design portfolio for this example covers designs from direct split to the approximate transition split.

III.4.4 Example 4

This fourth example involves the separation of a four-component azeotropic mixture at atmospheric pressure, where the liquid phase is modeled by the UNIQUAC equation and the vapor phase is ideal. *The purpose of this example is to show that Underwood's method fails while illustrating the applicability of the two-level design methodology to azeotropic systems*. Table III.14 shows the feed composition, the heavy and light key components, and the desired recoveries for this separation.

This particular mixture has two binary azeotropes at atmospheric pressure – a methanol/acetone azeotrope, $(x_M, x_A) = (0.2343, 0.7657)$, and an ethanol/water azeotrope $(x_E, x_W) = (0.8874, 0.1126)$. The methanol/acetone azeotrope is minimum boiling and is the only stable node for this system. Bellows and Lucia[13] show that there are two simple distillation regions for this mixture.

Table III.14: Feed Composition & Recoveries for Methanol/Ethanol/Acetone/Water Still

Component	Feed Composition^{+}	HK/LK *	Recovery Fraction in Top Product
Methanol (M)	0.25		
Ethanol (E)	0.20		
Acetone (A)	0.35	LK	0.99
Water (W)	0.20	HK	0.01

* HK: Heavy Key, LK: Light Key

\+ Feed is saturated liquid

In this specific distillation, the majority of acetone is taken overhead while the majority of the water is recovered in the bottom product. There are, of course, constraints defined by the key component recoveries. In addition, since the methanol/acetone azeotrope is the only stable node in the system, the top product must lie near the methanol/acetone azeotrope to ensure feasibility. Because of this last condition, one expects the design portfolio to contain fewer alternatives than earlier examples.

Table III.15: Two-Level Iterations for Methanol/Ethanol/Acetone/Water Distillation

iter$^+$ (r_M*, r_E*)	$x_B = (x_{n\text{-}C4}, x_{i\text{-}C5}, x_{n\text{-}C5})$	s_{min}	r_{min}	D**
1 (0.6100, 0.8400)	(0.292146, 0.321839, 0.006705)	2.1500	1.34794	0.62364
2 (0.6333, 0.8868)	(0.294731, 0.330166, 0.006515)	2.0900	1.42585	0.61413
3 (0.6524, 0.9262)	(0.296632, 0.336898, 0.006365)	2.1670	1.64691	0.62776
4 (0.6746, 0.9705)	(0.298898, 0.343985, 0.006203)	2.4110	2.12192	0.66682

\+ Outer loop iteration number

* Recovery fraction of non-key components (methanol, ethanol) in bottom product

** Stripping line distance measured from x_B to stripping pinch point curve

To initialize the two-level design methodology, one needs to find a feasible, minimum energy design. Choosing initial guesses for the non-key component recoveries for this example requires careful consideration, which is an inherent difficulty for separations involving azeotropic mixtures. For this particular example, since the top product must lie near the methanol/acetone azeotrope in any feasible design, guidelines available in the literature such as those given by Fidkowski et al.[14] can be useful for picking reasonable starting values for the non-key component recoveries. Once initialized properly, the two-level design methodology simply alternates between the inner and outer loops and produces the portfolio of minimum energy designs shown in Table III.15. *Also note that we did not report a solution for Underwood's method as in other tables in this article. This is obviously because constant relative volatility and the* *concept of light and heavy key component are moot assumptions in azeotropic mixtures; there is no Underwood solution!*

Table III.16: Additional Information for Methanol/Ethanol/Acetone/Water Distillation

iteration	$\|[x_T - x_{Ns}(x_B(r))]\|$	N_s	N_r	$y_D(calc) = (y_M, y_E, y_A)$
1	4.95093×10^{-3}	300	3	(0.210127, 0.032512, 0.703323)
2	3.57830×10^{-3}	300	5	(0.236180, 0.006213, 0.733900)
3	4.03500×10^{-3}	300	5	(0.228018 0.019966, 0.722671)
4	8.18694×10^{-3}	300	6	(0.222414, 0.01811, 0.742572)

Table III.16, on the other hand, gives additional information regarding this portfolio of minimum energy designs. Note that the design portfolio for this azeotropic mixture is analogous to a direct split because the distillate products are in the neighborhood of the minimum boiling methanol/acetone azeotrope.

As expected, the design portfolio spans a smaller range of non-key component recoveries than designs in earlier examples. Also, note that the norm of the targeting function in Table III.16 and the reboil ratios does not decrease monotonically over the outer loop iterations. In fact, both the norm and the reboil ratio decrease on the first iteration and then increase thereafter. Figure III.8 gives the distillation line trajectories for first (black), second (red) and fourth (blue) solution in Tables III.15 and III.16.

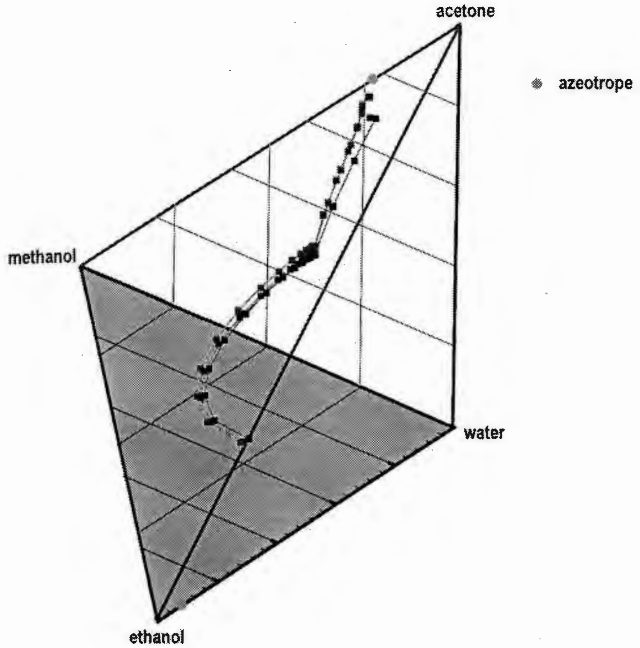

Figure III.8: Minimum Energy Design Portfolio for Methanol/Ethanol/Acetone/Water Distillation

If one compares the results for this example to those shown in Fig. 3, we can draw some analogies. For example, the curved lines for each outer loop problem in Fig. 3 are one-dimensional curves because the mixture under consideration is a three component mixture. For this example and any other four-component mixture, the correct geometric representation would consist of a family of two-dimensional surfaces. Moreover, the global minimum for earlier examples corresponds to a zero-valued minimum in norm. Here, however, the iterations pass though a minimum value of reboil ratio that is <u>bounded away from zero</u>. Despite these differences, the outer loop provides a convenient way of exploring alternate minimum energy designs.

Moreover it shows that the design with the global minimum stripping line distance is the one which consumes the least amount of energy.

III.4.5 Example 5

The purpose of this final example is to show that Underwood's method fails to predict a feasible design for an azeotropic mixture with a distillation boundary where neither product composition is anywhere near azeotropic whereas the two-level design method finds a minimum energy design portfolio that includes some non-pinched designs. The mixture used in this example is formic acid (FA), acetic acid (AA) and water (W), where the liquid and vapor were modeled by the UNIQUAC equation Hayden-O'Connell equation respectively. The specifications for this atmospheric distillation are given in Table III.17 and is considered feasible if $||y_D - y_{D,spec}|| \leq 0.065$.

Table III.17: Feed Composition & Recoveries for Formic Acid/Acetic Acid/Water Distillation

Component	Feed Composition$^+$	HK/LK *	Recovery Fraction in Top Product
Formic Acid (FA)	0.09	LK	0.01
Acetic Acid (AA)	0.58	HK	0.01
Water (W)	0.33		

* HK: Heavy Key, LK: Light Key

\+ Feed is saturated liquid

This example contains a distillation boundary that runs from the formic acid-water azeotrope to the acetic acid vertex and divides the feasible triangular region into two distinct distillation regions, as shown in Figure III.9. Note that the specifications given in Table III.17 correspond to a distillation in the left hand side of Fig. 9, where the distillate product is a cleaner water stream (i.e., cleaner than the feed) and where formic acid is designated as the light key component and acetic acid is the heavy key component. Water is the non-key component in this illustration.

Table III.18: Two-Level Iterations for Formic Acid/Acetic Acid/Water Distillation

iter$^+$	r_W*	$x_B = (x_{FA}, x_{AA})$	s_{min}	r_{min}	D**
1	0.8500	(0.094405, 0.608392)	0.4660	6.8258	0.04916
2	0.7608	(0.097443, 0.627968)	0.8810	8.4082	0.10302
3	0.5248	(0.106515, 0.686431)	1.8600	8.5162	0.23934
4	0.2673	(0.118559, 0.764047)	2.8636	7.6610	0.37283
5	0.1856	(0.122971, 0.792482)	4.4746	10.7706	0.55831
6$^\&$	0.1856	(0.122971, 0.792482)	4.4746	10.7706	0.54080

\+ Outer loop iteration number

* Recovery fraction of non-key component (water) in bottom product

** Stripping line distance measured from x_B to stripping pinch point curve

& Non-pinched design

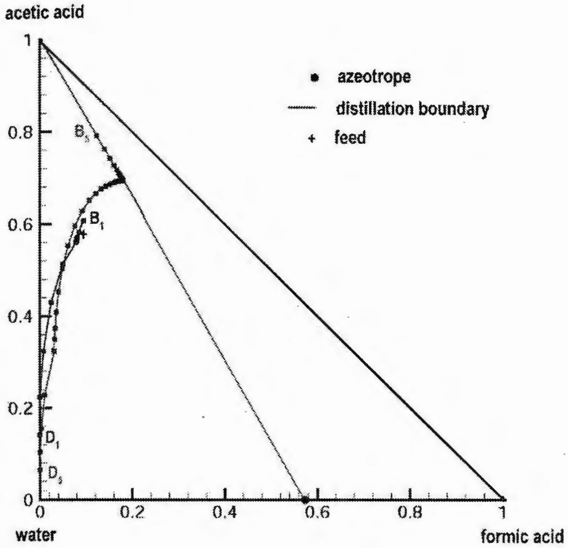

Figure III.9: Minimum Energy Design Portfolio for Formic Acid/Acetic Acid/Water Distillation

Table III.18 gives a minimum energy portfolio that corresponds to the specifications given in Table III.17. In particular, there are six minimum energy designs in this portfolio, over which the recovery fraction of water varies from 0.185 to 0.85. We note that one of the minimum energy designs is a non-pinched design. The distillate product composition in this minimum energy portfolio varies from approximately 86 mol % to 93 mol %. As can be seen from Table III.18 the corresponding minimum boil-up ratio varies significantly from roughly $s_{min} = 0.466$ to $s_{min} = 4.475$. Moreover, even at the high end of water purity in the distillate there is a significant change in the required minimum boil-up ratio. Table III.19 gives additional information associated with the minimum energy portfolio presented in Table III.18. Figure III.9 shows the trajectories for two of the minimum energy designs.

We tried using Underwood's method for this distillation. In particular, we used both our own in-house computer program of Underwood's method and DSTWU from Aspen Plus with the specified key components. Both versions failed to find even a feasible solution for this distillation – no less a minimum energy design! We have explored all other combinations of key components and still find that Underwood's method fails to find a feasible design.

Table III.19: Additional Information for Formic Acid/Acetic Acid/Water Distillation

iteration	$\|\|[x_T - x_{N_s}(x_B(r))]\|\|$	N_s	N_r	$y_D(\text{calc}) = (y_{FA}, y_{AA})$
1	$4.536506\text{x}10^{-4}$	300	5	(0.000117, 0.143603)
2	$3.026425\text{x}10^{-3}$	300	5	(0.000067, 0.110705)
3	$1.726122\text{x}10^{-2}$	300	4	(0.000002, 0.080367)
4	$3.217711\text{x}10^{-2}$	300	5	(0.000000, 0.070668)
5	$7.795300\text{x}10^{-2}$	300	4	(0.000233, 0.062121)
$6^{\&}$	$6.800500\text{x}10^{-2}$	82	4	(0.000246, 0.068456)

& Non-pinched design

III.5 Conclusions

A novel two-level distillation design methodology was proposed for generating portfolios of minimum energy designs where separation specifications are given in terms of key component recovery fractions. The inner loop of this design methodology is based on the concept of shortest stripping line distance while the outer loop is a Gauss-Newton method that adjusts product compositions. Moreover, our results clearly demonstrate that stripping line distances for different distillation configurations can be compared – even though the bottoms composition for each separation in the portfolio is different – and that meaningful comparisons can be made – *provided the key component recoveries are the same.* Five example problems involving ternary and quaternary mixtures were presented to illustrate that the proposed two-level approach easily finds portfolios of minimum energy distillation designs. For zeotropic mixtures, it was also shown that Underwood's method has a shortest stripping line interpretation and that the proposed two-level design procedure converges to that solution when the feed composition is used as the processing target. On the other hand, for azeotropic mixtures, it was shown that Underwood's method fails to find a feasible design whereas the two-level design procedure provides a correct interpretation of minimum energy requirements in terms of a non-zero valued, global minimum in the norm of the targeting function. Finally, the mathematical machinery needed to implement the two-level design methodology was presented in detail.

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Appendix III.1

This appendix provides an implicit theorem analysis of phase equilibrium equations. The main result is the definition of the (c-1) x (c-1) matrix of partial derivatives of y with respect to x, J_{yx}, which accounts for summation equations for both liquid and vapor phases as well as the implicit dependence of temperature.

For any system of phase equilibrium equation involving c components, we have

$$F_j(y_j, x_1, x_2, .., x_c) = y_j(x_1, x_2, .., x_c, T(x_1, x_2, .., x_c)) - x_j = 0, \quad j = 1,\dots, c \qquad \text{(III.A1)}$$

where T denotes absolute temperature and F_j is an implicit function. By the implicit function theorem, it follows that

$$\Delta y_j = (\partial y_j/\partial x_1)\Delta x_1 + \dots + (\partial y_j/\partial x_c)\Delta x_c + (\partial y_j/\partial T)\Delta T \qquad \text{(III.A2)}$$

Since $\Sigma\, x_k = 1$, it follows that

$$\Delta x_c = - \sum_{k=1}^{c-1} \Delta x_k \qquad \text{(III.A3)}$$

Use of Eq. III.A3 in Eq. III.A2 gives

$$\Delta y_j = [(\partial y_j/\partial x_1) - (\partial y_j/\partial x_c)]\Delta x_1 + \dots + [(\partial y_j/\partial x_{c-1}) - (\partial y_j/\partial x_c)]\Delta x_{c-1}$$

$$+ (\partial y_j/\partial T)\Delta T \qquad j = 1,\dots,c \qquad \text{(III.A4)}$$

Summing the Δy's and noting that $\Sigma\ \Delta y_j = 0$ because of the summation equation for y gives

$$\Sigma\ [(\partial y_j/\partial x_1) - (\partial y_j/\partial x_c)]\Delta x_1 + \ldots + \Sigma\ [(\partial y_j/\partial x_{c-1}) - (\partial y_j/\partial x_c)]\Delta x_{c-1}$$

$$+ \Sigma\ (\partial y_j/\partial T)\Delta T \qquad \text{(III.A5)}$$

Equation III.A5 can be solved for ΔT and yields

$$\Delta T = -\{\Sigma\ [(\partial y_j/\partial x_1) - (\partial y_j/\partial x_c)]\ /\ \Sigma\ (\partial y_j/\partial T)\}\Delta x_1 - \ \ldots$$

$$- \ \{\Sigma\ [(\partial y_j/\partial x_{c-1}) - (\partial y_j/\partial x_c)]\ /\ \Sigma\ (\partial y_j/\partial T)\}\Delta x_{c-1} \qquad \text{(III.A6)}$$

This expression for ΔT can be used in Eq. III.A4 resulting in

$$\Delta y_j = \{[(\partial y_j/\partial x_1) - (\partial y_j/\partial x_c)]$$

$$- (\partial y_j/\partial T)[\ \Sigma\ [(\partial y_k/\partial x_1) - (\partial y_k/\partial x_c)]\ /\ \Sigma\ (\partial y_k/\partial T)]\}\Delta x_1$$

$$+ \ \ldots + \{[(\partial y_j/\partial x_{c-1}) - (\partial y_j/\partial x_c)]$$

$$- (\partial y_j/\partial T)[\ \Sigma\ [(\partial y_k/\partial x_{c-1}) - (\partial y_k/\partial x_c)]\ /\ \Sigma\ (\partial y_k/\partial T)]\}\Delta x_{c-1} \qquad \text{(III.A7)}$$

Equation III.A7 applies to c-1 vapor compositions and gives the (c-1) x (c-1) Jacobian matrix, J_{yx}, where the (j,k) element of J_{yx} is

$$[J_{yx}]_{jk} = \{[(\partial y_j/\partial x_k) - (\partial y_j/\partial x_c)]$$

$$- (\partial y_j/\partial T)[\ \Sigma\ [(\partial y_k/\partial x_k) - (\partial y_k/\partial x_c)]\ /\ \Sigma \partial y_k/\partial T)]\} \qquad \text{(III.A8)}$$

MANUSCRIPT IV

Non-Pinched, Minimum Energy Distillation Design

This chapter is the manuscript entitled, Non-Pinched, Minimum Energy Distillation Design that has been accepted for publication in Chemical Engineering Research and Design and can be found using doi:10.1016/j.cherd.2008.02.017.

Abstract

Non-pinched, minimum energy solutions are important class of distillation designs that offer the potential advantage of a better trade-off between capital investment and operating costs. In this paper, two important tasks associated with non-pinched distillation designs are studied. Thus the novel contributions of this work to the literature are

1) A comprehensive methodology for finding non-pinched minimum energy designs.

2) Understanding of the reasons for the existence of non-pinched distillation designs.

It is shown that the recent shortest stripping line distance approach of Lucia et al. (2007) is capable of systematically and reliably finding non-pinched, minimum energy distillation designs. In addition, we provide an understanding of the reasons behind the existence of non-pinched designs, which include trajectories that follow unstable branches of a pinch point curve in azeotropic systems, the inherent looping structure of trajectories in hydrocarbon separations, and the presence of ancillary constraints in multi-unit processes like extraction/distillation. Several distillation examples are studied and many numerical results and geometric illustrations are presented that show the shortest stripping line distance methodology is indeed a powerful and systematic tool for computing non-pinched, minimum energy designs and that support the underlying reason we provide for the existence of non-pinched designs.

Keywords

Distillation design, non-pinched solutions, minimum energy designs, pinch point curves, looping structure, ancillary constraints.

IV.1 Introduction

In their review paper, Koehler et al. (1995) summarize the state of the art as it relates to finding minimum energy designs for distillation columns. They give a very good overview of methods available for finding minimum energy designs that correspond to pinch points and clearly point to the need for a systematic methodology for finding non-pinched, minimum energy designs with the following quote on page 1016 of their paper: "This special case of a minimum energy throughput without a pinch will not be handled by any of the published approximation procedures. Exact column simulations are here unavoidable."

Unfortunately, there was no progress in finding a systematic methodology for finding non-pinched, minimum energy distillation designs until the work of Lucia et al. (2007).

In a recent paper, Lucia et al. (2007) give a comprehensive treatment of a new unifying principle in energy efficient process design – the shortest stripping line distance approach. This new approach states that the most energy efficient designs for processes in which distillation is involved correspond to the shortest stripping line distance for the distillation(s). Of course, the implicit assumption in this approach is that distillation is the largest energy consumer in many multi-unit processes and, for the most part, this is a very good assumption. Lucia et al. (2007) also presented a rigorous Mixed Integer Nonlinear Programming (MINLP) formulation for the shortest stripping line distance approach, along with an algorithm for implementing this

MINLP formulation. This MINLP formulation is a two-level methodology that alternates between an NLP problem to find the minimum boil-up ratio and an Integer Program (IP) problem for finding the number of stages in a column such that stripping line distance is shortest. Many examples for processes with up to six components were used to support the novel idea of shortest stripping line distance in energy efficient design including single distillation columns with feed, saddle, and tangent pinch points, non-pinched distillations, and hybrid separations such as extraction followed by distillation and reactive distillation.

The purpose of this paper is to provide a more detailed description of how the shortest stripping line distance methodology can be used to systematically and intelligently find non-pinched, minimum energy process designs and to address the broader question – what give rise to non-pinched designs? Accordingly, this paper is organized in the following way. A motivating example is presented first. Next the shortest stripping line distance approach of Lucia et al. (2007) is summarized. This is followed by an analysis of the conditions that give rise to non-pinched designs for single columns and multi-unit processes that involve distillation. Next a number of example problems are presented to support our analysis. This article ends with some conclusions regarding the findings of this work.

IV.2 Motivating Example

In this section, we present a non-pinched, minimum energy distillation design taken from the open literature that gives a modest savings in capital investment costs.

The Non-Pinched Distillation Example of Koehler et al. Revisited

Consider a column design given in Koehler et al. (1995) that was studied by Lucia et al. (2007). The specifications for this distillation are shown in Table IV.1. The feed pinched, minimum energy design for this column has an infinite (300 in practice) stripping stages and 6 rectifying stages. However the number of stripping stages can be reduced to 209 using the integer bisection algorithm given in Lucia et al. While this reduction in stripping stages results in a larger rectifying section with 18 stages, now there is no feed pinch point in either section of the column. *Thus the minimum energy design corresponds to a column with 209 stripping stages and 18 rectifying stages – and is clearly <u>not</u> a pinched solution!*

Table IV.1: Specifications for Chloroform/Acetone/Water Distillation from Koehler et al. (1995)

Component	Distillate$^+$	Feed*	Bottoms
Chloroform	0.9450	0.4395	0.3297
Acetone	0.0330	0.0330	0.0330
Benzene	0.0210	0.5275	0.6373

+ Feasible if $x_D(C) \geq 0.945$; *Saturated liquid ($q = 1$)

Table IV.2 clearly shows that the stripping line distance versus boil-up ratio for this example behaves monotonically in the neighborhood of minimum boil-up ratio and thus this non-pinched, minimum energy distillation design corresponds to the minimum stripping line distance.

Table IV.2: Stripping Line Distance v. Boil-up Ratio for Problem from Koehler et al. (1995)

Boil-up Ratio	Distance	Liquid Composition*
2.471	0.295663549	
2.470	0.295478380	
2.469	0.295293515	
2.468	0.295109067	
2.467	0.294925182	
2.466	0.294742043	
2.465	0.294559798	
2.464	0.294437754	
2.463	0.294003499	
2.46293 (s_{min})	0.290707822 (D_{min})	(0.5904986, 0.0567577) pinched
2.46292	0.611694926	(0.2256828, 0.3912509) pinched$^+$
2.46293 (s_{min})	0.214714193(D_{min})	(0.5267737, 0.1015876)non-pinched

---

* $x = (x_C, x_A)$; + infeasible because resulting distillate is acetone-rich

Figure IV.1, which was reproduced from Lucia et al. (2007), shows the pinched and non-pinched column designs for the example defined in Table IV.1. Note that the results shown here are slightly different than those in Lucia et al. simply because a different computer and a compiler (LF77/90-EM32) with fewer significant digits was used to generate the results in this paper. Nonetheless, the behavior is clearly qualitatively the same as that given in Lucia et al. (2007). The important thing to notice is that the pinched solution for s_{min} = 2.46293 (r_{min} = 10.338899) follows a portion an unstable branch of the stripping pinch point curve (shown as a dot-dashed curve in Fig. IV.1). That is, liquid compositions x_{209} to x_{299} are unstable pinch point compositions. Again, look carefully at Fig. IV.1. The important observation, however, is that the compositions for the pinched design on trays 209 to 299 correspond to a higher value of boil-up (and reflux) ratio than the corresponding pinched design.

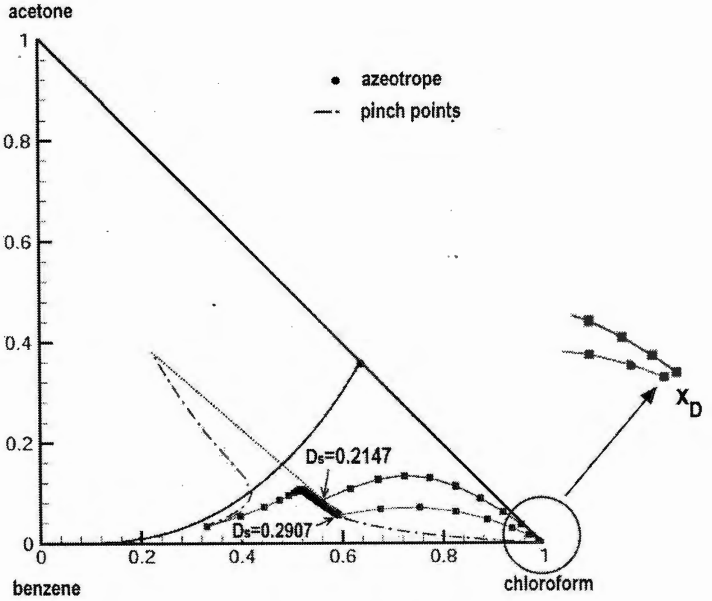

Figure IV.1: Minimum Energy Requirements for a Column with No Pinch

For example, the non-pinched design shown in Table IV.2 corresponds to s_{min} = 2.46293 and has a liquid composition on stage 209 (i.e., x_{209} = (0.5267737, 0.1015876)) that is equal to the unstable pinch point composition, x_{PP} = (0.5267737, 0.1015876) to seven significant digits. On the other hand, the actual boil-up ratio (and reflux ratio) that corresponds to this unstable pinch point is s = 1.987 and is far too low to give a feasible pinched, minimum energy design. What this implies is that there are many non-pinched, minimum energy designs for the column specifications given in Table IV.1 – each with a different number of stripping and rectifying stages. However, the 'best' design in our opinion is the one with the shortest stripping line distance of D_s = 0.2147, 209 stripping stages, and 18 rectifying stages since it uses minimum energy and has the lowest capital investment costs.

Note also that the stripping pinch point composition 'jumps' to a very different composition (or stable branch) for a very small change in boil-up ratio near s_{min} and that the resulting distillate is acetone-rich instead of chloroform-rich, making the column design infeasible. For example, for s = 2.46292 < s_{min}, the resulting pinch point is x_{PP} = (0.2256828, 0.3912509), which is significantly different than the pinch point (0.5904986, 0.0567577) for s = 2.46293 = s_{min}. In fact, the behavior of the liquid composition trajectories for s = 2.46292 and 2.46293 is quite similar to the behavior of residue curves near boundaries (see, Lucia and Taylor, 2006). That is, these trajectories for s = 2.46292 and 2.46293 are essentially coincident until they reach the unstable branch of the stripping pinch point curve, at which they split or bifurcate, each converging to a pinch point on a separate branch of the stable stripping pinch point curve. Moreover, the portions of these trajectories between the point that they split and the two stable pinch points actually trace out the unstable branch of the stripping pinch point curve!

Key Observation #1:

The reason non-pinched solutions to this separation exist is because a portion of the liquid composition profile of the stripping section of the column follows an unstable branch of the stripping pinch point curve and these compositions when coupled with the 'higher' boil-up ratio (and reflux ratio) from a stable pinched design make it possible to reach the desired distillate product with fewer stripping stages than is required by the associated pinched design.

IV.3 Methods and Materials: A Summary of the Shortest Stripping Line Distance Approach

In this section we briefly summarize the nonlinear programming (NLP) and integer (IP) formulations that comprise the shortest stripping line distance approach.

IV.3.1 Nonlinear Programming

The determination of the most energy efficient design with a pinch is equivalent to finding the shortest stripping line distance and defined by the NLP problem

$$\min_{s} \quad D_s = \sum_{j=1}^{N_s} \| x_j' \| = \|x_{j+1} - x_j\| \qquad \text{(IV.1)}$$

subject to

$$x_j' = x_{j+1} - x_j = [(s)/(s+1)]y_j - x_j + [1/(s+1)]x_B, \quad j = 1,\ldots, N_s \qquad \text{(IV.2)}$$

$$x_1 = x_B \qquad \text{(IV.3)}$$

$$r = (s - q + 1)[x_{Fi} - x_{Di}]/[x_{Bi} - x_{Fi}] - q \qquad \text{(IV.4)}$$

$$x_j' = x_{j+1} - x_j = [(r+1)/r]y_j - x_j - (1/r)x_D, \qquad j = N_s+1,\ldots, N \qquad \text{(IV.5)}$$

$$||x_{D,calc} - x_{D,spec}|| \leq \zeta \qquad \text{(IV.6)}$$

$$c(x_K) = 0 \text{ for some } K \, \varepsilon \, [1, N] \qquad \text{(IV.7)}$$

where s is the boil-up ratio, D_s represents an objective function or the cumulative distance along a discrete stripping trajectory, || . || denotes the two-norm, x_j denotes liquid composition on stage j, and N_s is the number of stripping stages. Equation IV.2 is the operating line for the stripping section of the column, where y_j is the vapor in equilibrium with x_j. Equation IV.3 is the bottoms composition specification while Eq. IV.4 relates the reflux ratio to the boil-up ratio and the feed, bottoms, and distillate compositions. Equation IV.5, on the other hand, is a differential form of the operating line for the rectifying section of the column, where N is the total number of stages in the entire column, and Eq. IV.6 is one of many forms for specifying distillate specifications and defining feasibility, where ζ is some small number. Equation IV.7 provides for ancillary constraints such as requiring a liquid stage composition to lie on a binodal curve, where the integer K denotes the stage index for which the ancillary constraint is satisfied. See Lucia et al. (2007) for other distillate specifications and a discussion of ancillary constraints.

Note that the unknown optimization variable for the problem defined by Eqs. IV.1 to IV.7 is the boil-up ratio, s, and the optimal trajectory is actually a sequence of liquid compositions denoted by $\{x_j\}^*$ that is assumed to be piece-wise linear. We typically use $N_s = 300$ in Eq. IV.1 to approximate an infinite number of stages in the stripping section, which are numbered from bottom to top.

IV.3.2 Integer Programming

To look for solutions that do not correspond to pinch points, we use a simple integer programming strategy to determine if it is possible to reduce the number of stripping stages from infinity to some reasonable finite number without increasing the boil-up and reflux ratios by solving the following problem

$$\min_{N_s} \quad D_s = \sum_{j=1}^{N_s} \| x_j' \| = \|x_{j+1} - x_j\| \tag{IV.8}$$

subject to

$$x_j' = x_{j+1} - x_j = [(s)/(s+1)]y_j - x_j + [1/(s+1)]x_B, \quad j = 1,\ldots, N_s \tag{IV.9}$$

$$x_1 = x_B \tag{IV.10}$$

$$s = s_{min} \tag{IV.11}$$

$$r = (s - q + 1)[x_{Fi} - x_{Di}]/[x_{Bi} - x_{Fi}] - q \quad \text{(IV.12)}$$

$$x_j' = x_{j+1} - x_j = [(r+1)/r]y_j - x_j - (1/r)x_D, \quad j = N_s+1, \ldots, N \quad \text{(IV.13)}$$

$$\|x_{D,calc} - x_{D,spec}\| \leq \zeta \quad \text{(IV.14)}$$

$$c(x_K) = 0 \text{ for some } K \, \varepsilon \, [1, N] \quad \text{(IV.15)}$$

Note that the only the unknown optimization variable in this IP problem formulation is the number of stages, N_s. Moreover, the boil-up from the NLP problem is used as a constraint to fix the boil-up ratio in the integer program.

Alternation between the NLP and IP can be performed as many times as needed. For example, suppose the initial NLP with 300 stages yields a solution, $s_{min} = 2$, and then the IP results in a reduction in the number of stripping and rectifying stages to $N_s = 75$ and $N_r = 10$. One could then return to the NLP with $N_s = 75$ and $N_r = 10$ and attempt to reduce the boil-up ratio below the initial calculated value of $s_{min} = 2$. If no further reduction in boil-up ratio is determined, then the algorithm terminates. If, on the other hand, the boil-up can be reduced, then the algorithm would return to the IP to try and further reduce the number of stages. This procedure, as stated, can be repeated as many times as needed until no further reduction in either boil-up ratio or number of stages occurs at which point the algorithm terminates.

IV.3.3 Optimization Algorithm & Implementation

Lucia et al. also give an optimization algorithm that alternates between solving the NLP and IP sub-problems, where the NLP problem is solved using the terrain method and integer bisection is used to solve the IP sub-problem. Alternation between the NLP and IP sub-problems can be repeated as many times as necessary. We refer the reader to the paper by Lucia et al (2007) for the details of the optimization algorithm.

IV.4 What Gives Rise to Low Energy, Non-Pinched Solutions?

In our opinion, this is a very important question simply because there is absolutely no understanding of non-pinched, minimum energy designs described in the open literature. We gave some indication of what can cause the existence of non-pinched, minimum energy designs for a single distillation column involving an azeotropic mixture in the introduction. However, from our experience, we know the situation is more complicated than this. There are several ways in which non-pinched, minimum energy process designs can occur. Specifically, non-pinched, minimum energy solutions can exist when

1) Certain product specifications and ancillary conditions, as in hybrid separation processes such as reactive distillation and extraction-distillation, must be satisfied.
2) The separation under consideration contains
   a) A maximum boiling azeotrope.
   b) A stripping pinch point curve with unstable branches.
   c) A product composition that lies near a distillation boundary.

3) The separation under consideration has stripping and rectifying trajectories that exhibit looping and intersect on their way to their respective pinch point curves and the trajectory in at least one section of the column shows reverse separation of one of the key components.

In all cases, the common thread seems to be the complicated interplay between the distillation line profiles and the pinch point curves.

1) Lucia et al. (2007) have clearly demonstrated that hybrid separations like extraction-distillation systems and reactive distillations often have non-pinched, minimum energy solutions because the feed to the distillation must lie on a binodal or chemical equilibrium curve and because low energy distillation line trajectories, which have pinch points outside the liquid-liquid region, fortuitously have a liquid stage composition that lands on the binodal or equilibrium curve! For example, in the hybrid separation of acetic acid and water using ethyl acetate as the solvent that was studied by Lucia et al. (2007) the extract from the liquid-liquid extraction column, which is the feed to the primary acid recovery column, must lie on the binodal curve. Thus the feed to the primary column is constrained. For a relatively low purity acetic acid bottoms product ($x_{AA} \leq 0.995$), several low energy distillation line trajectories have a liquid stage composition that lands on the binodal curve well before reaching their corresponding pinch points, which lie in the single liquid region. Thus the path of the trajectories combined with a feed that must lie on the liquid-liquid equilibrium curve forces the design to be non-pinched. Similarly, in the reactive distillation

example, the stream leaving the bottom stage of the reactive rectifying section of the reactive column lies on the chemical equilibrium curve. Here again there is a liquid stage composition for some of the low energy distillation lines that lands on the chemical equilibrium curve long before ever reaching the stripping pinch point curve. Again, see Lucia et al. (2007). Thus in both hybrid separation examples, problem specifications and ancillary constraints that restrict the feed to the distillation help define minimum energy demands that are not pinched.

2) In the case of single distillation columns, there can be a variety of reasons for the existence of non-pinched, minimum energy designs. For zeotropic mixtures, the pinch point curves generally show no bifurcation behavior. However, the existence of a non-pinched design is tightly tied to the relationship between the actual distillation line trajectory (i.e., the liquid composition profile and the corresponding boil-up and reflux ratios), the pinch points, and the boil-up ratios associated with the pinch points. Mixtures that can form azeotropes, on the other hand, can have pinch point curves that exhibit bifurcations. Non-pinched designs for columns separating azeotropic mixtures exist whenever part of the liquid composition profile follows an unstable branch of the pinch point curve so that tray compositions correspond to unstable pinch point compositions. In addition, the boil-up ratio for the actual column must be greater than the boil-up ratio for any given unstable pinch point.

3) There are situations that we have encountered where the stripping and/or rectifying line trajectory passes near each other well away from any pinch point curves. More

specifically, for the illustrative example that we provide for this situation, rectifying lines (including the one for minimum reflux ratio) loop around and pass very near stripping lines before converging to their respective pinch points. It is the looping structure of the rectifying and stripping line trajectories that gives rise to non-pinched designs and one in particular that uses minimum energy!

IV.5 Results and Analyses

In this section, we present a number of examples that have non-pinched minimum energy solutions and describe in detail how we use the concept of shortest stripping line distance to find these non-pinched, minimum energy designs. All numerical calculations were done in double precision arithmetic using a Pentium IV computer with the Lahey-Fujitsu (LF95) compiler.

IV.5.1 Example 1

This first example involves the separation of acetic acid, formic acid and water at atmospheric pressure, where the UNIQUAC equation of Prausnitz et al. (1980) was used to model the liquid phase and the vapor phase was modeled by the Hayden-O'Connell (HOC) equation to account for hydrogen bonding (i.e., vapor phase dimerization of acetic acid and formic acid). The purpose of this example is twofold.

1) To show that the non-pinched design example of Koehler et al. (1995) is not an isolated case but there appears to be a well defined set of characteristics which give rise to this behavior.

2) To show that pinched, minimum energy distillation profiles that follow unstable branches of a pinch point curve give rise to non-pinched designs for the same boil-up ratio.

Two different separations are discussed. Feed, distillate, and bottoms compositions for each separation are given in Table IV.3. Figure IV.2 shows that there are four distinct distillation regions separated by a (linear) boundary that runs from the maximum boiling formic acid-water azeotrope through the ternary azeotrope, branch, and continue to the acetic acid , water and formic acid vertices and the stripping pinch point curves for the columns defined in Table IV.3.

Table IV.3: Feed Composition & Recoveries for Two Formic Acid/Acetic Acid/Water Separations

	Distillation Region 1			Distillation Region 2		
Component	Feed+	Distillate	Bottoms	Feed+	Distillate	Bottoms
Formic acid	0.05377	0.0005	0.0717	0.7000	0.9900	0.5050
Acetic acid	0.6600	0.0005	0.8800	0.1216	0.0050	0.2000
Water	0.28623	0.9990	0.0483	0.1784	0.0050	0.2950

+ Feed is saturated liquid (q=1)

For column 1 in region 1, the pinch point curve that originates at B_1. There are two stable disjoint branches, denoted by B_1P_1 and P_2P_3, and each branch lies in a different distillation region. These two branches are the upper two branches shown in Fig. IV.2

and, as in Koehler et al. (1995), we use the symbol P_i to denote a liquid pinch point composition. Moreover, these two stable branches of the stripping pinch point curve are connected by an <u>unstable</u> branch, P_1P_2, which is shown as the solid curve in Fig. IV.2. It is interesting to observe that stripping trajectories that correspond to the last pinch points on each of the stable branches P_1 and P_2 trace out the unstable branch of the stripping pinch point curve.

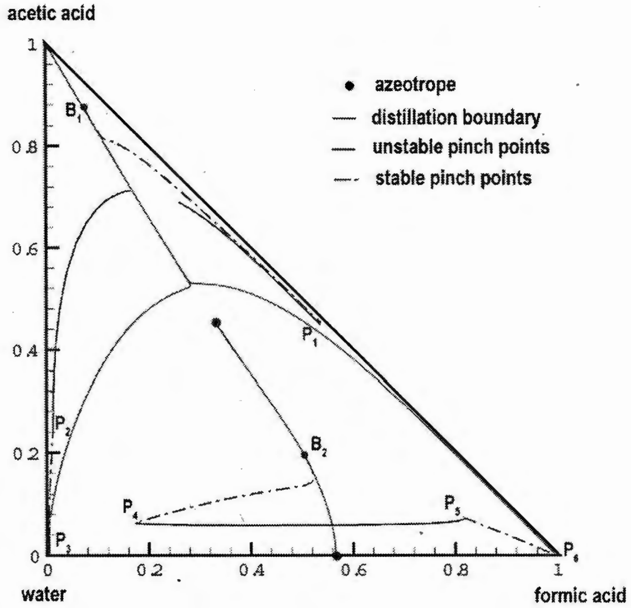

Figure IV.2: Branches of Pinch Point Curves for Formic Acid/Acetic Acid/Water Distillation

For column 2 in region 2, the curve that originates at B_2 represents the stripping pinch point curve for the set of column specifications given on the right of Table IV.3. Note that this pinch point curve shows very similar behavior to the stripping pinch point curve for column 1. That is, the curves B_2P_4 and P_5P_6 are stable branches that are connected by an unstable branch of the stripping pinch point curve, P_4P_5, and the trajectories that end at P_4 and P_5 trace out the unstable branch.

Table IV.4 presents detailed numerical results for various distillation designs for this example. All distillations are considered feasible if they satisfy the condition $\|y_D - y_{D,spec}\| \leq 0.05$. Note that there are non-pinched designs for both columns – as indicated by fewer than 300 stripping stages.

Table IV.4: Numerical Results for Formic Acid/Acetic Acid/Water Distillations

Column 1

BR	N_s*	N_r	D_s	Feasible	x_{Ns}^+	$y_D(calc) = (y_{FA}, y_{AA})$
6.61	300		0.658060	No	(0.5388, 0.4526)	
6.6157	300	5	0.708223	Yes	(1.269×10^{-2}, 0.2574)	(3.372×10^{-5}, 3.027×10^{-2})
6.6157	72	8	0.382132	Yes	(0.0479, 0.5805)	(1.730×10^{-5}, 2.982×10^{-2})
6.63	300	5	0.708231	Yes	(1.2668×10^{-2}, 0.2569)	(3.371×10^{-5}, 3.020×10^{-2})

Column 2

BR	N_s*	N_r	D_s	Feasible	x_{Ns}^+	$y_D(calc) = (y_{FA}, y_{AA})$
3.75	300		0.56208	No	(0.1731, 6.330×10^{-2})	
3.75544	300	5	0.402642	Yes	(0.8191, 7.402×10^{-2})	(0.9836, 7.176×10^{-3})
3.75544	72	5	0.354424	Yes	(0.7736, 6.365×10^{-2})	(0.9655, 6.586×10^{-5})
3.77	300	4	0.403071	Yes	(0.8197, 7.382×10^{-2})	(0.9837, 7.153×10^{-3})

---

* Design is considered pinched if $N_s = 300$; + liquid composition on feed (transition) stage

For column 1, the minimum reboil ratio that gives a feasible pinched design is s_{min} = 6.6157 for which the corresponding stripping line distance is D_s = 0.708223 – as determined by solving the shortest stripping line distance NLP (i.e., Eqs. IV.1 to IV.6 with y_D in place of x_D in Eq. IV.6 in this case). However, when the integer programming part of our MINLP shortest stripping line algorithm is used, the number of stripping stages is reduced to 72 (i.e., by solving the IP defined by Eqs. IV.8 to IV.14). That is, the results of solving the IP show that a feasible column design with 72 stripping stages can be found and that the corresponding stripping line distance for this non-pinched, minimum energy design, D_s = 0.382132, is truly the shortest stripping line distance. The associated rectifying section of this non-pinched design is shown in red in Fig. IV.3 and has 8 stages. No further reduction in boil-up ratio or number of stages is possible.

For column 2, which is depicted in Fig. IV.4, the minimum value of reboil ratio needed to find a feasible design is s_{min} = 3.75544. Again, this minimum boil-up ratio was determined by solving the shortest stripping line distance NLP defined by Eqs. IV.1 to IV.6. The stripping line distance for this pinched, minimum energy design is D_s = 0.402642. On the other hand, there is a non-pinched, minimum energy design with 72 stripping stages and a corresponding minimum stripping line distance of D_s = 0.355309, which can be easily determined by solving the IP sub-problem defined by Eqs. IV.8 through IV.14. Again, after one pass through the NLP and IP, no further reduction in the boil-up ratio or number of stages can be found.

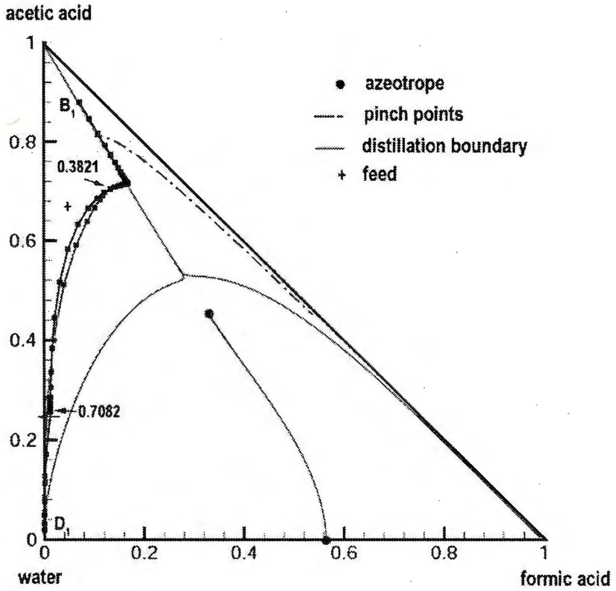

Figure IV.3: First Non-Pinched Minimum Energy Solution for Formic Acid/Acetic Acid/Water Distillation

<u>Analysis</u>

The behavior of the column profiles and stripping pinch point curves for both non-pinched solutions shown in Table IV.4 are similar and also similar to the behavior of the motivating example in the following way. *Portions of the liquid composition profiles of the stripping sections of these columns follow an <u>unstable</u> branch of the stripping pinch point curve and these compositions when coupled with the <u>'higher' boil-up ratio</u> (and reflux ratio) from a pinched design make it possible to reach the desired distillate product with fewer stages than is required for the corresponding pinched design.*

As in the motivating example, the pinched solution for column 1 with $s_{min} = 6.6157$ (with corresponding $r_{min} = 18.818739$) and the pinched design for column 2 with $s_{min} =$

3.75544 (with corresponding r_{min} = 4.583277) each follow a portion of the unstable branch of the stripping pinch point curve in the appropriate distillation region. See the solid curves shown in Fig. IV.2. Thus liquid compositions on the upper stages in the stripping section of the pinched designs actually have values that are unstable pinch point compositions. Moreover, these stage compositions in these non-pinched designs occur at higher values of boil-up (and reflux) ratio.

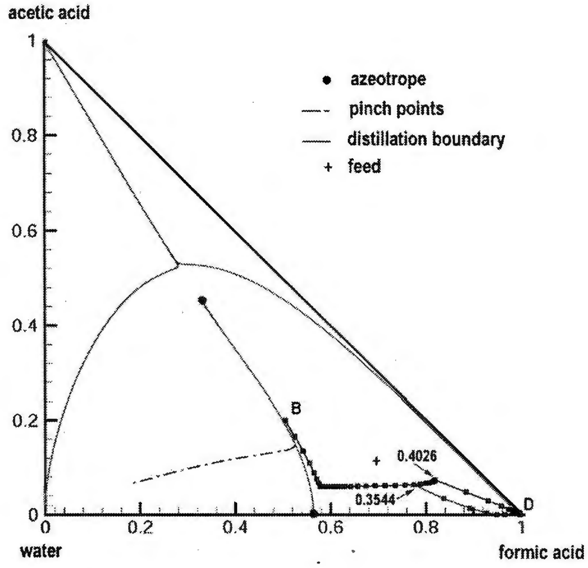

Figure IV.4: Second Non-Pinched Minimum Energy Solution for Formic Acid/Acetic Acid /Water Distillation

That is, the non-pinched design for column 1 shown in Table IV.4 with s_{min} = 6.6157 has a liquid composition on stage 72, x_{72} = (0.0479, 0.5805), that is equal to the unstable pinch point composition that corresponds to a lower boil-up ratio of s = 2.70209. Similarly for column 2, liquid composition x_{72}= (0.7736, 0.06365) in the non-pinched design with s_{min} = 3.75544 actually corresponds to an unstable pinch point composition for s = 2.38409. Consequently these stage compositions, x_{72} in column 1 and x_{72} in column 2, which correspond to unstable pinch points at higher values of reboil ratio (and reflux ratio) make it possible to reduce the number of stripping stages, which in turn results in non-pinched, minimum energy designs for these separations. Actually there are many non-pinched designs for these separations since all compositions x_{72} to x_{299} in columns 1 and 2 correspond to unstable pinch points at higher boil-up ratio.

Note, as in earlier example, the behavior of the liquid composition trajectories near s_{min} is quite similar to the behavior of residue curves near boundaries in that they are essentially coincident until they reach the unstable branch of the stripping pinch point curve, at which they split or bifurcate, each converging to a pinch point on a separate branch of the stable stripping pinch point curve. Moreover, the portions of these trajectories between the point that they split and the two stable pinch points they converge to actually trace out the unstable branch of the appropriate stripping pinch point curve! Note that for column 1 with s = 6.6156, the stripping pinch point is $P_1 = (0.540513, 0.450967)$ is clearly in a different distillation region than pinch point $P_2 = (1.263809\text{x}10^{-2}, 0.256353)$ for $s = s_{min} = 6.6157$. For column 2 with s = 3.75543, which is slightly less than s_{min}, the resulting pinch point $P_4 = (0.172905, 6.324402\text{x}10^{-2})$ is on the different stable pinch point curve, and hence in a different distillation region, than the pinch point $P_5 = (0.819092, 7.404520\text{x}10^{-2})$, which corresponds to $s_{min} = 3.75544$.

Thus we generalize our key observation #1 by stating that *for separations involving pinch point curves with stable and unstable branches, non-pinched solutions exist because a portion of the liquid composition profile of the stripping section of the column follows an unstable branch of the stripping pinch point curve and these compositions when coupled with the 'higher' boil-up ratio (and reflux ratio) from a stable pinched design make it possible to reach the desired distillate product with fewer stripping stages than is required by the associated pinched design.*

IV.5.2 Example 2

The second example involves the separation of a four-component hydrocarbon mixture at 2.7572×10^6 Pa (400 psia). The purpose of this example is to illustrate that mixtures with pinch point curves that do not bifurcate can still exhibit non-pinched, minimum energy solutions. The phase equilibrium model is the K-Wilson method, where the liquid and vapor are modeled using a correlation given by Wilson (1968). This correlation estimates K-values based on critical properties and is given by the relationship

$$K_i = \exp[\ln(p_{c,i}/p) + 5.37(1 + \omega_i)(1 - T_{c,i}/T)]$$

where $p_{c,i}$, $T_{c,i}$, and ω_i are the critical pressure, critical temperature and acentric factor for the i^th component. For this example, we have used critical properties given in Elliott and Lira (1999).

The feed to the column is a mixture of n-butane (n-C_4), iso-pentane (i-C_5), n-pentane (n-C_5) and n-hexane (n-C_6) and is saturated liquid. The column specifications are given in Table IV.5. In our approach, the feed and bottoms compositions are fixed and the distillation is considered feasible if $\|y_D - y_D\text{ (calc)}| \leq 0.06$. Note that the light and heavy key components for this separation are i-pentane and n-pentane respectively and that both the bottoms and distillate products lie on different faces of the tetrahedral feasible region.

Table IV.5: Specifications for a Quaternary Hydrocarbon Distillation+

Component	Distillate	Feed*	Bottoms
n-butane	0.42742	0.25	$9.1\text{x}10^{-21}$
i-pentane	0.50419	0.30	0.01228
n-pentane	0.06839	0.20	0.38544
n-hexane	10^{-10}	0.25	0.60227

+ Pressure = $2.7572 \text{ x } 10^6$ Pa

* Saturated liquid (q = 1)

Table IV.6 shows a number of very similar non-pinched designs – including the minimum energy design.

Table IV.6: Numerical Results for Quaternary Hydrocarbon Distillation

BR	N_s	N_r	D_s^{+}	D_{NP}^{*}	y_D (calc) = ($y_{n\text{-}C4}$, $y_{i\text{-}C5}$, $y_{n\text{-}C5}$)$^{\&}$
12.020	65	4	2.46140	1.41684	(0.383596, 0.505468, 0.108441)
10.014	65	8	2.32544	1.30399	(0.384100, 0.509655, 0.106077)
9.9254	65	16	2.31784	1.29799	(0.433311, 0.535717, 0.030972)

+ Stripping line distance, D_s, is measured from x_B to stripping pinch point curve

* Stripping line distance, D_{NP}, measured from x_B to stage N_s

& Feasible if $||y_D - y_D \text{ (calc)}| \leq 0.06$

Figure IV.5 shows the minimum energy design for the distillation specifications given in Table IV.5. Unlike the mixture in the first example, this hydrocarbon mixture does not form any azeotropes and no distillation boundaries are present in the system. Moreover, the stripping and rectifying pinch point curves, which are shown as the blue dot-dashed curves in Fig. IV.5, lie on different faces of the tetrahedron and do not show any bifurcation behavior. They simply start at their respective product compositions and go directly toward the n-butane and n-hexane vertices without any branching or the presence of unstable pinch points. Also note that the stripping trajectory shown in Fig. IV.5 shows that the stripping section of the column lies in the iso-pentane/ n-pentane/n-hexane face of the tetrahedron and effectively performs a sequence of binary separations – first separating n-pentane and n-hexane and then separating iso-pentane and n-pentane.

So what gives rise to non-pinched designs in this situation? In our opinion, there are both simple and complicated reasons for the existence of non-pinched designs for this separation. The simple and obvious answer is that the rectifying and stripping lines intersect well before they reach their respective pinch point curves. The difficult part of this analysis is determining the real reasons that underlie this intersecting behavior. To understand this we first rule out what cannot occur. The specifications for this column are such that the column cannot have a double feed pinch point because the rectifying and stripping pinch point curves do not intersect; they lie in completely different faces of the feasible tetrahedron. A stripping or a rectifying feed pinch is also unlikely because the feed composition is well away from either pinch point curve and because the specifications do not correspond to either a direct or indirect split of the feed.

The reason that there are non-pinched solutions for this separation is because the pinch point curves lie in different faces of the tetrahedron but the feed contains all components in significant amount. Thus it follows that the rectifying and stripping lines, when extended to their respective pinch point curves, must each form a loop in the appropriate face of the tetrahedron. The key question is – why do these loops intersect?

Key Observation #2:

Non-pinched solutions to ***this*** *distillation exist because the boil-up and reflux ratios are sufficiently high enough to force the operating lines far enough into the feasible region and away from their respective pinch point curves so that they form loops and both loops effectively form a bridge between the pinch point curves – in much the same way that unstable branches of a pinch point curve connect stable branches in azeotropic mixtures.*

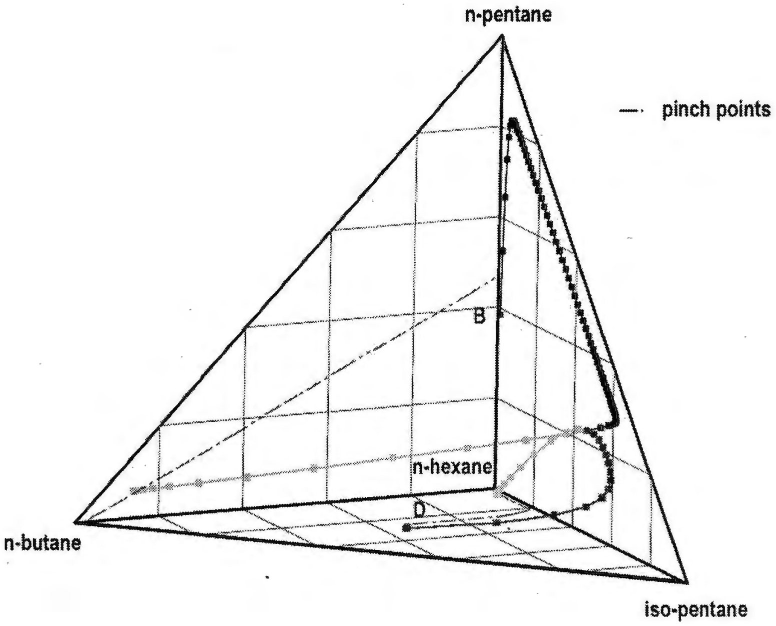

Figure IV.5: Non-Pinched Minimum Energy Solution for Quaternary Hydrocarbon Mixture

Analysis

The stripping profile loop in Fig. IV.2 causes the composition of the light key component, iso-pentane, to necessarily go through a maximum value and then decrease while the loop in the rectifying section causes n-pentane, the heavy key, to also go through a maximum in composition. These composition loops are sufficient to give rise to the potential for the stripping and rectifying trajectories to intersect – provided the boil-up ratio and corresponding reflux ratio are large enough. Table IV.7 shows the liquid compositions for the top of the stripping section and bottom of the rectifying section for the minimum energy distillation design, which has 81 total stages, and clearly shows there is no feed pinch. Note that the iso-pentane composition increases, as it should, then decreases – which indicates that iso-pentane is not being stripped from the liquid.

Remarks

There are several additional remarks that are relevant to this hydrocarbon distillation example.

1) The reasons for the existence of non-pinched, minimum energy designs for the hydrocarbon distillation given here also explain the results for the six-component non-pinched example presented in Lucia et al. (2007). In that case, n-butane is the light key component and goes through a maximum in composition and thus forms a loop in the stripping section.
2) In this example there is no pinched design that uses minimum energy from which to find a non-pinched minimum energy design. However, this present no computational difficulties for the shortest stripping line distance approach. This type of non-pinched design can be determined in exactly the same manner that designs with rectifying pinch points are determined (see, Lucia et al., 2007). Starting from the bottoms composition, one simply determines the

transition (or feed) stage that gives a feasible design and then continues by reducing the boil-up ratio and determining the number of stages in each section of the column needed to maintain feasibility.

3) Using both our own in-house version of Underwood's method, we calculated values of minimum reflux ratio and minimum boil-up ratio of $r_{min} = 4.17611$ and $s_{min} = 7.29344$ for this example for relative volatilities calculated at feed conditions. DSTWU in Aspen Plus also gives very similar results. However, the values of reflux ratio and boil-up ratio given by Underwood's method do not yield a feasible column design!

4) Rigorous simulations with RADFRAC also re-verified the validity of the design given by the shortest stripping line distance approach and the failure of Underwood's method to yield anything useful in this case. That is, for the column specifications given in Table IV.5 and the calculated boil-up ratio, reflux ratio, and number of stages calculated by the shortest stripping line approach, calculations using RADFRAC converged to a non-pinched column design very close to the one shown in Fig. IV.5. On the other hand, using a large number of stages and the minimum reflux ratio predicted by Underwood's method, RADFRAC could not find a feasible column design.

Table IV.7: Liquid Compositions for Top of Stripping and Bottom of Rectifying Sections

Stage Number	Liquid Composition			
	n-butane	iso-pentane	n-pentane	n-hexane
Stripping section				
55	0.000124	0.607884	0.295439	0.096553
56	0.000231	0.611136	0.292135	0.096498
57	0.000430	0.614024	0.289101	0.096445
58	0.000800	0.616516	0.286294	0.096390
59	0.001487	0.618529	0.283654	0.096330
60	0.002761	0.619892	0.281095	0.096252
61	0.005117	0.620266	0.278474	0.096143
62	0.009463	0.619016	0.275551	0.095970
63	0.017428	0.614979	0.271912	0.095681
64	0.031868	0.606101	0.266851	0.095180
65	0.057532	0.588945	0.259211	0.094312
Rectifying section				
66	0.059593	0.631379	0.260643	0.048385
67	0.060814	0.661101	0.254086	0.023999
68	0.061574	0.683643	0.243103	0.011680
69	0.062121	0.702480	0.229776	0.005623
70	0.062608	0.719500	0.215202	0.002690

IV.5.3 Example 3

The last example in this article involves the separation of chloroform, acetone, carbon tetrachloride, and benzene at atmospheric pressure. The UNIQUAC equation of Prausnitz et al. (1980) was used to model the liquid phase and the vapor phase was assumed to be ideal. The purpose of this example is to show that non-pinched designs can arise in mixtures with any number of components and that the proposed shortest stripping line methodology for finding these non-pinched designs is unaffected by the number of components. Table IV.8 shows the column specifications for this example.

Table IV.8: Specifications for Distillation of Four-Component Azeotropic Mixture

Component	Distillate	Feed*	Bottoms
Carbon tetrachloride	0.005	0.0928	0.140
Chloroform	0.990	0.6713	0.500
Acetone	0.003	0.0921	0.140
Benzene	0.002	0.1438	0.220

* Saturated liquid (q = 1)

Figure IV.6 shows the distillation regions for this four component mixture where the methodology of Bellows and Lucia (2007) was used to generate the boundary, which is a surface.

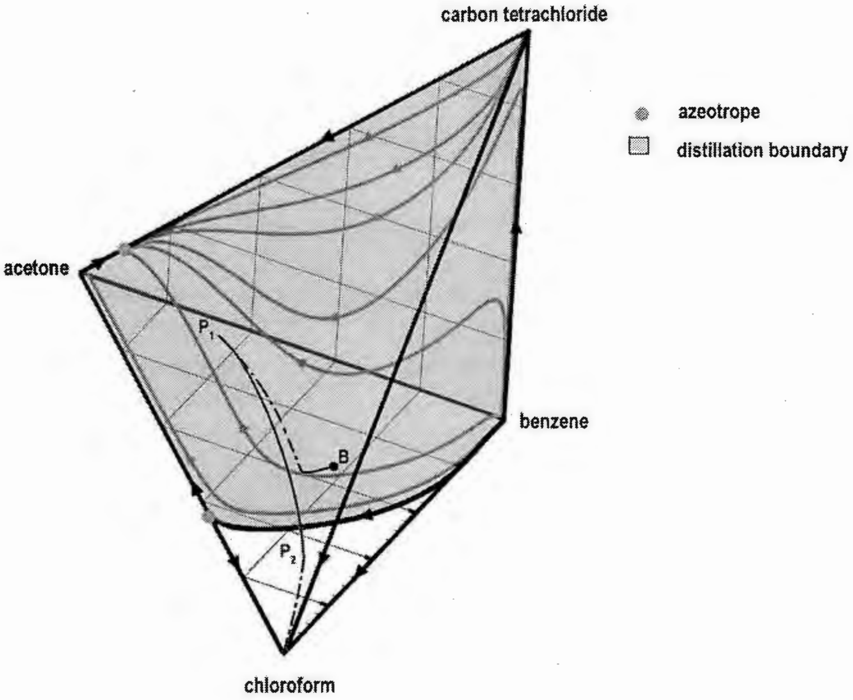

Figure IV.6: Branches of Pinch Point Curves for Four Component Azeotropic Mixture

Note that there are two distinct distillations regions which are separated by the boundary shown by shaded region in Fig. IV.6. Also note that the behavior of the stripping pinch point curve is similar to the one for the three-component azeotropic mixture described in Example 1. That is, there are two stable disjoint branches of the pinch point curve, denoted by BP_1 and P_2P_3, and each branch lies in a different distillation region. These two stable branches of the stripping pinch point curve are connected by an unstable branch, P_1P_2, which is shown by the solid curve in Fig. IV.6.

Table IV.9 shows numerical results for the column specifications given in Table IV.8. Note that the minimum boil-up ratio that gives a feasible pinched design is $s_{min} = 4.3666$ and that the corresponding stripping line distance obtained by solving the NLP is D_s = 0.331267. However, when the integer programming part of our MINLP algorithm is used, the number of stripping stages is reduced from 300 to 136, with 30 stages in rectifying section. Thus, as in the earlier examples, solving the IP provides a minimum energy design that has a finite number of stages and clearly shows that the corresponding stripping line distance for this non-pinched, minimum energy design, D_{NP} = 0.231482, is actually the shortest stripping line distance. Figure IV.7 shows liquid composition profiles for both the pinched and non-pinched, minimum energy design for this column and are shown in black and green respectively.

Table IV.9: Numerical Results for Four-Component Azeotropic Mixture

s	N_s	N_r	D_s	Feasible	x_{Ns}^{+}	y_D
4.360	300		0.6146	no	(0.1378, 0.2076, 0.5614)	
4.3666	300	13	0.3313	yes	(0.0871, 0.7610, 0.0763)	(0.0118, 0.9880, 6.8798×10^{-5})
4.3666	136	30	0.2315	yes	(0.1101, 0.6790, 0.1281)	(0.0169, 0.9828, 1.9021×10^{-4})
4.380	300	12	0.3321	yes	(0.0869, 0.7617, 0.0760)	(0.0116, 0.9882, 5.5978×10^{-5})

* Boil-up ratio
** Design is considered pinched if $N_s = 300$
\+ Liquid composition on feed (transition) stage

Analysis

Note that the pinched solution for s_{min} = 4.36660, with a corresponding minimum reflux ratio of r_{min} = 7.12262, follows a portion of the unstable branch of the stripping pinch point curve in Fig. IV.7. Thus liquid compositions on the upper stages of the stripping section of the pinched design actually have values that are unstable pinch point compositions. That is, the non-pinched design shown in Table IV.9 with s_{min} = 4.3666 has a liquid composition on stage 136, x_{136} = (0.11010, 0.67905, 0.12814), that is equal to the unstable pinch point composition for a lower boil-up ratio of s = 4.2801. Since the composition for stage 136 corresponds to unstable pinch point but occurs at a higher value of boil-up ratio (and reflux ratio), it is possible to reduce the number of stripping stages in the pinched design and find many non-pinched, minimum energy designs for the desired separation. The best design, in our opinion, is the one that we report.

Note that this example demonstrates that non-pinched, minimum energy solutions can occur in a mixture with any number of components and is independent of the nature of the boundary. Thus for azeotropic mixtures with any number of components, if the pinch point curve corresponding to the desired bottom composition has stable and unstable branches, *then there is a possibility that the minimum energy design is non-pinched solution. Moreover, for azeotropic mixtures, the existence of such solutions is independent of number of components and the reason these non-pinched designs exist is because a portion of the liquid composition profile of the stripping section of the column follows an unstable branch of the stripping pinch point curve and these compositions, when coupled with the 'higher' boil-up ratio (and reflux ratio) from a stable pinched design, make it possible to reach the desired distillate product with fewer stripping stages than is required by the associated pinched design.*

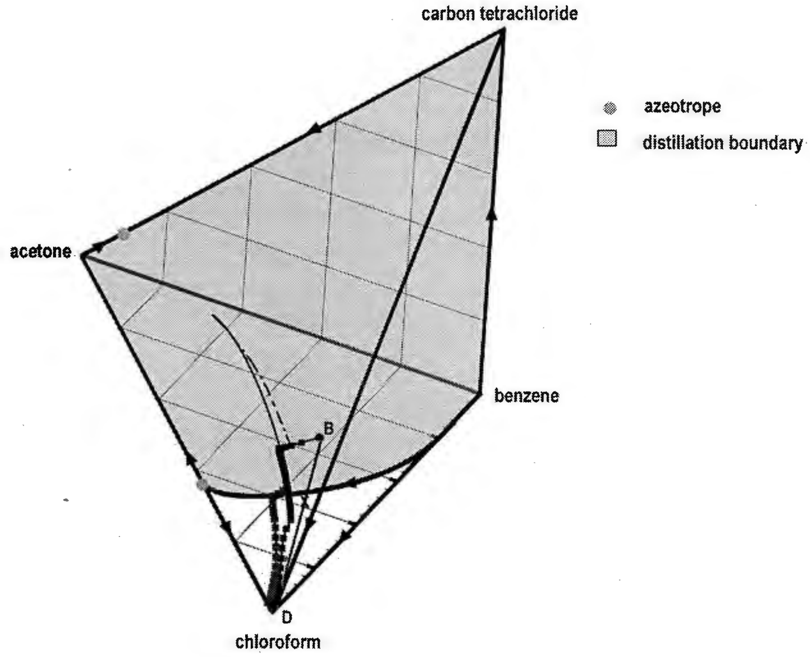

Figure IV.7: Non-Pinched Minimum Energy Solution for Four Component Azeotropic Mixture

IV.5.4 Example 4

Here we briefly re-visit the non-pinched, minimum energy design for the six component hydrocarbon separation recently studied by Lucia et al. (2007). The purpose of this discussion is to show that the non-pinched, minimum energy design for this six component hydrocarbon example has trajectories that exhibit the same loping structure described in Example 2 – even though the desired separation is closer to a direct split. In this example, the phase equilibrium is modeled using the K-value correlation of Wilson (1968), where the critical properties have been taken from Elliott and Lira (1999). Table IV.10 gives the column specifications for this separation.

Lucia et al. (2007) report a non-pinched, minimum energy design for this separation that has a minimum boil-up ratio of s_{min} = 12.669 that corresponds to the shortest stripping line distance of 2.66343. This minimum energy design has 20 stripping stages, 6 rectifying stages, and a corresponding minimum reflux ratio of $r_{min} = 11.669$. Underwood's method, on the other hand, predicts a minimum reflux ratio of $r = 1.3388$ and a minimum boil-up ratio of $s = 2.3388$ and does not provide a feasible solution for this separation.

Table IV.10: Column Specifications for a Six-Component Hydrocarbon Distillation

Component	Distillate$^+$	Feed*	Bottoms
Propane	0.3000	0.15	1×10^{-12}
n-Butane	0.3960	0.20	0.0040
iso-Butane	0.3000	0.15	0.000014
iso-Pentane	0.0001	0.20	0.3990
n-Pentane	0.0001	0.15	0.3000
n-Octane	0.0038	0.15	0.3010

+ Feasible if $\| y_D - y_{D,spec} \| \leq 0.03$; * Saturated liquid ($q = 1$)

Table IV.11 gives the liquid composition profile for this non-pinched, minimum energy solution. This numerical data is actual computer output from our shortest stripping line distance program.

Table IV.11: Liquid Composition Profile for 6-Component Non-Pinched, Minimum Energy Design

Stage #	C_3	n-C_4	i-C_4	i-C_5	n-C_5
1	0.1000D-011	0.4000D-002	0.1400D-004	0.3990	0.3000
2	0.5438D-011	0.9747D-002	0.4070D-004	0.5513	0.3653
3	0.2453D-010	0.1896D-001	0.9555D-004	0.5999	0.3499
4	0.1062D-009	0.3500D-001	0.2135D-003	0.6194	0.3199
5	0.4517D-009	0.6299D-001	0.4664D-003	0.6242	0.2877
6	0.1876D-008	0.1101	0.9918D-003	0.6109	0.2535
7	0.7531D-008	0.1844	0.2026D-002	0.5728	0.2164
8	0.2869D-007	0.2903	0.3905D-002	0.5051	0.1766
9	0.1020D-006	0.4207	0.6960D-002	0.4120	0.1366
10	0.3347D-006	0.5539	0.1133D-001	0.3098	0.1014
11	0.1016D-005	0.6652	0.1690D-001	0.2197	0.7496D-001
12	0.2902D-005	0.7419	0.2351D-001	0.1536	0.5792D-001
13	0.7936D-005	0.7864	0.3117D-001	0.1113	0.4815D-001
14	0.2113D-004	0.8074	0.4009D-001	0.8669D-01	0.4295D-001
15	0.5537D-004	0.8132	0.5064D-001	0.7300D-001	0.4026D-001
16	0.1436D-003	0.8093	0.6324D-001	0.6559D-001	0.3888D-001
17	0.3700D-003	0.7987	0.7836D-001	0.6159D-001	0.3814D-001
18	0.9474D-003	0.7827	0.9644D-001	0.5938D-001	0.3771D-001
19	0.2411D-002	0.7615	0.1178	0.5805D-001	0.3739D-001
20	0.6089D-002	0.7341	0.1428	0.5713D-001	0.3710D-001
21	0.1520D-001	0.6982	0.1708	0.5627D-001	0.3675D-001
22	0.1790D-001	0.7256	0.2084	0.3044D-001	0.1672D-001
23	0.2315D-001	0.7101	0.2444	0.1541D-001	0.7100D-002
24	0.3586D-001	0.6720	0.2819	0.7534D-002	0.2903D-002
25	0.6688D-001	0.6111	0.3175	0.3537D-002	0.1135D-002
26	0.1387	0.5194	0.3401	0.1551D-002	0.4093D-003
27	0.2851	0.3872	0.3272	0.5964D-003	0.1240D-003
27	0.2862	0.3879	0.3250	0.5573D-003	0.1221D-03 (y_D)

Note that n-C_4, which was designated as the light key component in this example, goes through a maximum in composition on tray 15 in the stripping section and that i-C_4 exhibits a maximum in composition on stage 26, which is at the top of the rectifying section. These composition maxima are characteristic signatures of the looping structure of the trajectories in non-pinched designs.

IV.6 Comparisons with Rigorous Column Simulations

In order to provide some assessment of the quality of the non-pinched, minimum energy designs computed using the shortest stripping line distance approach, we compared our designs with non-pinched, minimum energy solutions determined using the Aspen Plus program RADFRAC. In particular, Fig. IV.8 shows that for the formic acid/acetic acid/water separation in distillation region 1 of Fig. IV.3, the non-pinched, minimum energy designs determined by the shortest stripping line distance approach and RADFRAC are in good qualitative agreement.

Notice that the shapes of the composition profiles for both approaches are qualitatively similar. The quantitative differences are due to differences between the Aspen Plus thermodynamics and our thermodynamics – even though both approaches use the UNIQUAC equation to model the liquid phase and the Hayden-O'Connell (HOC) equation for the vapor. We have verified these differences by comparing residue curve maps for our version of UNIQUAC-HOC with that from Aspen Plus and have observed differences in the location of the formic acid/acetic acid/water ternary

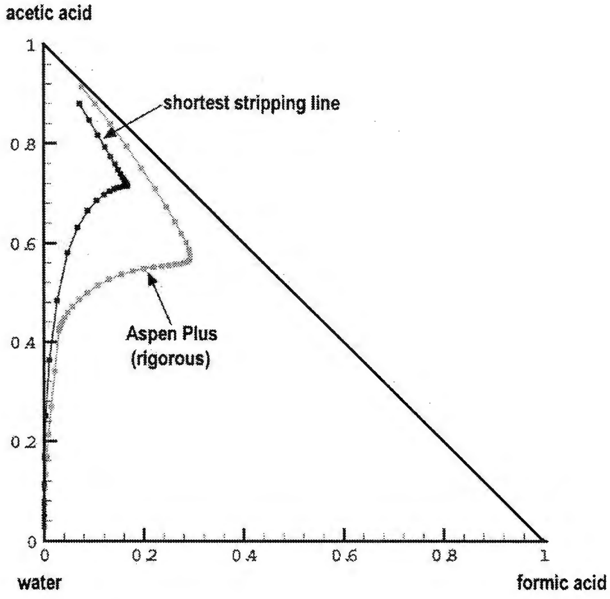

Figure IV.8: Approximate & Rigorous Non-Pinched, Minimum Energy Designs for Acid-Water Distillation

azeotrope and thus the distillation boundaries. The specific numerical values for each method are given in Table IV.12.

Figure IV.9 and Table IV.12 show a similar comparison for the quaternary hydrocarbon distillation. Here the agreement is very good both qualitatively and quantitatively since there are no distillation boundaries and the thermodynamic models are ideal. Here any differences can be attributed to the fact that component boiling points and heats of vaporization vary significantly, making the assumption in the shortest stripping line approach only approximate and differences in the calculation procedures. Nonetheless, we think the reader will agree that the liquid composition profiles, minimum boil-up ratio, and required number of stripping and rectifying

Table IV.12: Comparisons of Non-Pinched, Minimum Energy Designs for the Shortest Stripping Line Approach & Rigorous Aspen Plus Simulations*

Acid-Water Column 1

	BR	N_s	N_r	$x_B = (x_{FA}, x_{AA})$	y_D(calc) $= (y_{FA}, y_{AA})$
SSLDA$^+$	6.6157	72	8	(0.0717, 0.8800)	($1.730\text{x}10^{-5}$, 0.02982)
RADFRAC	6.6430	75	10	(0.0757, 0.9144)	($1.710\text{x}10^{-5}$, 0.04007)

Quaternary Hydrocarbon Column

	BR	N_s	N_r	$x_B = (x_{n\text{-}C4}, x_{i\text{-}C5}, x_{n\text{-}C5})$	y_D (calc) $= (y_{n\text{-}C4}, y_{i\text{-}C5}, y_{n\text{-}C5})$
SSLDA$^+$	9.9254	65	16	($9.1\text{x}10^{-21}$, 0.01228, 0.38544)	(0.433311, 0.535717, 0.030972)
RADFRAC	9.9420	69	20	($6.7\text{x}10^{-21}$, 0.01599, 0.37425)	(0.423729, 0.497361, 0.078910)

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* Design specifications for RADFRAC were B/F and boil-up ratio

\+ SSLDA = shortest stripping line distance approach

stages for the shortest stripping line distance approach and RADFRAC are virtually the same.

These comparisons clearly show that the shortest stripping line approach can provide very reliable initial estimates of non-pinched, minimum energy designs for more rigorous simulations!

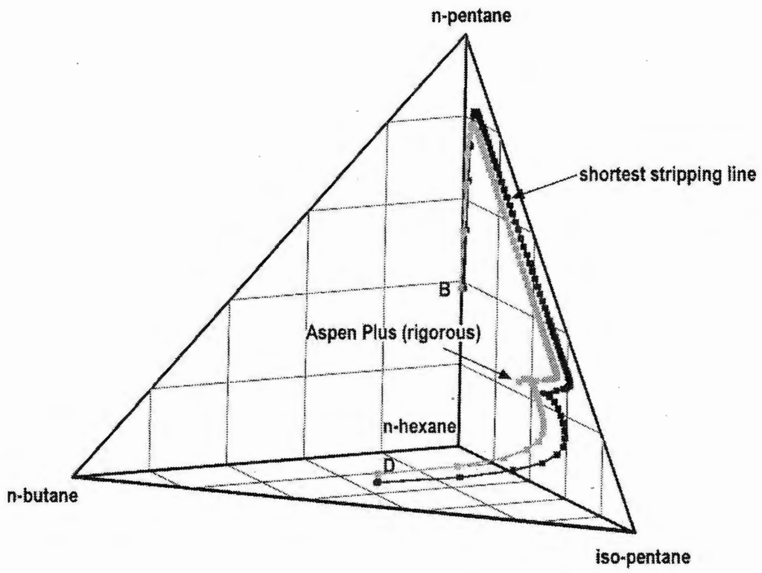

Figure IV.9: Approximate & Rigorous Non-Pinched, Minimum Energy Designs for Hydrocarbon Distillation

IV.7 Discussions and Conclusions

In this paper, it was shown that the shortest stripping line distance approach represents a rigorous and systematic procedure for determining non-pinched, minimum energy distillation designs. In addition, several reasons that underlie the existence of non-pinched, minimum energy distillation designs were identified and discussed. These reasons include

1) The combination of certain product specifications and ancillary conditions, as in hybrid separation processes such as reactive distillation and extraction-distillation.
2) Azeotropic separations that contains
    a) A maximum boiling azeotrope.
    b) A stripping pinch point curve with stable and unstable branches.

    c) A product composition that lies near a distillation boundary.

3) Separations that have stripping and rectifying trajectories that exhibit looping and intersect on their way to their respective pinch point curves, where the trajectory in at least one section of the column shows reverse separation of one of the key components.

We close this article with a discussion of two issues associated with non-pinched, minimum energy designs that we believe are important. First, in cases where pinched, minimum energy designs exist alongside non-pinched, minimum energy designs, the non-pinched designs offer the advantage of not having to necessarily use conventional rules of thumb to determine the rough size of a column necessary to make the desired separation. Typical design protocols often find pinched designs and then use rules of thumb to estimate the number of actual stages (or packing height) required to make the desired separation at modest energy consumption. It is common, for example, to take the minimum boil-up (or reflux) ratio, multiply it by a factor between 1.1 and 1.5 (see Koehler et al., 1995) to give an operating boil-up or reflux ratio, and then determine the number of stages required by trial and error. When non-pinched, minimum energy designs exist, there is no need to increase the minimum boil-up ratio, if the number of stages needed for the separation is small enough to represent a column that can be built – since it would only result in a column that unnecessarily uses more energy than needed. In addition, note that the existence of non-pinched, minimum energy designs also show that increasing the number of stages beyond that predicted by the non-pinched solutions does not necessarily result in any better separation. In fact, this practice could lead to wasted capital investment costs.

Second, and perhaps more important, are cases where there is no pinched, minimum energy distillation design. In these cases, it is clear that the shortest stripping line distance approach provides design solutions that no other methodology can. More specifically, if one treats the problem at hand in a manner similar to the rectifying pinch case described in Lucia et al. (2007), then it is clear that the shortest stripping line distance approach can reliably and systematically find non-pinched, minimum energy designs.

Nomenclature

B	bottoms flow
c, c(x)	number of components, constraint function
D_s, D_{NP}	stripping line distance, non-pinched stripping line distance
F	feed flow rate
K	vector of equilibrium ratios, index stage in ancillary constraint
N_s, N_r, N	number of stripping stages, number of rectifying stages, number of total stages
p, p_c	pressure, critical pressure
P	pinch point
q	thermal quality of feed stream
r	reflux ratio
s	boil-up or stripping ratio
T, T_c	temperature, critical temperature
x_j, x_j'	liquid molar composition of j^{th} component, derivative of x_i with respect to independent variable
x, x_B, x_D	vector of liquid mole fractions, bottoms composition, liquid distillate composition
x_F, x_{PP}	feed composition, pinch point composition
y_j	vapor molar composition of j^{th} component
y, y_D	vector of vapor mole fractions, vapor distillate composition

Greek symbols

ω	acentric factor
ζ	feasibility tolerance

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CONCLUSIONS

A novel methodology to find minimum energy requirement in separation processes based on the shortest stripping line distance was proposed in this work. It was shown that the most energy efficient separation corresponds to one that has the shortest stripping line distance among all feasible solutions. A systematic optimization approach was developed to find this separation with the shortest stripping line distance and it was demonstrated that this methodology overcomes several limitations in existing methods and extends to cases where currently available methodologies in literature for finding minimum energy requirements do not apply.

The formulation for the shortest stripping line distance approach is a global optimization MINLP formulation, which involves both a non-linear programming (NLP) problem followed by an integer programming (IP) problem. This optimization based formulation makes the methodology quite robust and, as a result, it can be used to identify minimum energy requirements for any kind of separation involving ideal, non-ideal or azeotropic mixtures. A variety of examples were solved using the proposed methodology and clearly show its applicability to determining minimum energy requirements regardless of number of components or the thermodynamic models used to describe phase behavior. Examples in manuscript I show that shortest stripping line approach can find minimum energy requirements in the presence of feed, saddle and/or tangent pinch points and easily extends to separations with reactive mixtures. Thus the shortest stripping line approach overcomes the limitation of having to use different techniques depending on the nature of mixture or number of components and represents a general purpose shortcut method for providing a good conceptual design of any kind of separation process.

Moreover, it was shown that the shortest stripping line approach finds correct processing targets in multi-unit processes so that the overall process consumes minimum energy. Hybrid separation of high and lower purity acetic acid by extraction with ethyl acetate followed by distillation, the production of MTBE using reactive distillation and a reactor-separation-recycle process were used as examples to illustrate key concepts and identify important numerical characteristics of this class of synthesis problems. At the present time, there is no shortcut method other than the shortest stripping line distance approach that can handle this type of multi-unit synthesis problem.

In manuscript III, the shortest stripping line approach was further extended to develop a novel two-level distillation design methodology for generating portfolios of promising minimum energy designs where separation specifications are given in terms of key component recovery fractions. The inner loop of this two-level design methodology is based on the concept of shortest stripping line distance while the outer loop is a Gauss-Newton method that adjusts product compositions. It was shown that these minimum energy portfolios contain Underwood's solution, when it exists, and thus Underwood's method has a shortest stripping line interpretation. In fact, Underwood's solution corresponds to the smallest of all shortest stripping line distances or the global minimum stripping line distance.

Unlike Underwood's method, the proposed two-level design methodology based on shortest stripping line distance readily extends to azeotropic systems or cases where the phase behavior is described by more complex thermodynamic models. This two-level design method automatically generates several promising process alternatives and can be used to understand the effect of product compositions on energy requirements for a given separation in a systematic way in the presence of required key component recoveries.

Non-pinched, minimum energy designs are an important but poorly understood type of separation design that can result in savings in energy as well as capital costs. Thus understanding the reasons behind the existence of non-pinched, minimum energy designs represents a significant contribution of this research project. In manuscript IV, the reasons behind the existence of non-pinched, minimum energy distillation designs were studied in detail. It was demonstrated that the non-pinched, minimum energy solutions can exist in azeotropic mixtures, hydrocarbon mixtures, and in hybrid separation process such as extraction-distillation. In the case of azeotropic separation non-pinched, minimum energy designs exists because a portion of the liquid composition profile for the stripping section of the column follows an unstable branch of the stripping pinch point curve whereas for hydrocarbon mixtures the inherent looping structures in the column profiles are responsible for non-pinched, minimum energy solutions. It was shown that the integer programming (IP) part of the shortest stripping line approach correctly identifies these non-pinched, minimum energy solutions when they exist. No other design methodology in the literature is capable of finding non-pinched, minimum energy designs.

In summary, the shortest stripping line distance approach is a fundamental geometric design concept that provides a unified, versatile, and rigorous shortcut methodology for the design, synthesis and retrofitting of energy efficient chemical processes. It overcomes many of the limitations of available design methods and readily extends to situations where no other method is applicable. Thus the shortest stripping line methodology represents a powerful next generation shortcut technique for energy efficient process design.

APPENDIX

List of all publications and conference presentations

Publications

1. Amale, A.; Lucia, A. A Two-Level Distillation Design Method, American Institute of Chemical Engineers Journal, submitted.
2. Amale, A.; Lucia, A. Non-Pinched, Minimum Energy Distillation Design, Chemical Engineering Research and Design, in press (doi:10.1016/j.cherd.2008.02.017)
3. Lucia, A; Amale, A, Taylor, R. Distillation Pinch Points and More. Computers and Chemical Engineering, In press and available on-line (doi:10.1016/j.compchemeng.2007.06.019)
4. Lucia, A.; Amale A.; Taylor, R. Energy Efficient Hybrid Separation Processes. Industrial and Engineering Chemistry Research, 2006, 45, 8319.
5. Lucia, A.; Amale, A.; Taylor R., Synthesis, Design and Retrofitting of Energy Efficient Separation Processes. Distillation-Absorption 2006, E. Sorenson, Ed., Institution of Chemical Engineers, 2006, 63.

Conference presentations

1. Amale A.; Lucia, A. Fresh Look at Underwood's Method. AIChE Spring Meeting, Houston, TX, April 2007.
2. Lucia, A.; Amale, A.; Taylor, R.; Energy Efficient Separation Processes. AIChE Spring Meeting, Orlando, FL, April 2006.
3. Lucia, A.; Amale, A.; Taylor, R.; Synthesis, Design and Retrofitting of Energy Efficient Separation Processes. Distillation-Absorption 2006, London, UK, September 2006.
4. Lucia, A.; Amale, A.; Taylor, R. New Approach to Energy Efficient Process Design. AIChE Annual Meeting, San Francisco, CA, November 2006.
5. Lucia, A; Amale, A. A New Approach to the Synthesis & Optimization of Energy Efficient Chemical Processes, Second International Conference on Continuous Optimization, Hamilton, Ontario, Canada August 2007.

6. Lucia, A.; Amale, A.; Taylor, R. A New Approach to Energy Efficient Chemical Process Design. European Congress of Chemical Engineering, Copenhagen, Denmark, September 2007.

7. Amale A.; Taylor, R.; Lucia, A.; Non-Pinched Minimum Energy Solutions in Distillation. AIChE Annual Meeting, Salt Lake City, UT, November 2007.

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