

Distillation pinch points and more

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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, Amale, & Taylor (2006) 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 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.

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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, Seibert, & Robinson, 2005). Because

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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
N_s, 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 i 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_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 i th component
y, y_D	vector of vapor mole fractions, vapor distillate composition
<i>Greek symbols</i>	
α	relative volatility
$\varepsilon, \varepsilon_T$	convergence tolerance, extent of reaction
γ	vector of activity coefficients
Λ	Lagrangian function
ν_i, ν	i th component stoichiometric coefficient, overall stoichiometric coefficient
μ	vector of Kuhn-Tucker multiplier
ω	acentric factor

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 (2006), and subsequently Taylor, Miller, and Lucia (2006), 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 reactor/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.

2. Literature survey

Many papers on minimum flows and minimum energy use in distillation have been published beginning with the work of Underwood (1948) 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, 1974, Hausen, 1935, Levy, Van Dongen, & Doherty, 1985; Pham, Ryan, & Doherty, 1989; Fidkowski, Malone, & Doherty, 1991; Fidkowski, Doherty, & Malone, 1993, Koehler, Aguirre, & Blass, 1991; and Urdaneta, Bausa, & Marquardt, 2004; for methods based on finding pinch points, and Brown & Holcomb, 1940; Murdoch & Holland, 1952; Acrivos & Amundson, 1955; Shiras, Hanson, & Gibson, 1950; Bachelor, 1957; and McDonough, Holland, & Bauni, 1961; McDonough & Holland, 1962a; McDonough & Holland, 1962b; for methods based on rigorous column simulation). Koehler, Poellmann, & Blass, 1995 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 & Bek-Pedersen (2000) 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 (2003) also is related to the work of Underwood while that of the rectification body method (RBM) of Urdaneta et al. (2004) for reactive distillation and Kim (2006) for thermally coupled columns are both based on the use of pinch points and residue curves. Finally, the paper by Alstad, Halvorsen, and Skogestad (2004) 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.

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.

3.1. Boundary value methods

Over the last 20 years, Doherty and co-workers (Barbosa & Doherty, 1988; Julka & Doherty, 1990; Levy & Doherty, 1986) 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 recti-

fying 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 (1988) 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 (2004) 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 (1990) and Fidkowski et al. (1991). 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.

3.2. Reversible distillation models

The method of Koehler et al. (1991) 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 the 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 the 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.

3.3. Eigenvalue methods

Poellmann, Glanz, and Blass (1994) 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.

3.4. Separation driving force method

Gani and Bek-Pedersen (2000) 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 $i = \text{LK}$ 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.

3.5. Rectification body methods

Bausa, Watzdorf, and Marquardt (1998) 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 a 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 (1953). In our opinion, this method is more closely related to a combination of the eigenvalue method by Poellmann et al. (1994) 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. (2004) have recently extended the RBM to the case of minimum energy requirements for reactive distillation.

3.6. V_{\min} diagrams

Halvorsen and Skogestad (2003) have recently introduced the concept of V_{\min} (minimum vapor flow) diagrams 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.

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 (2006) 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 Fig. 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.

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. (1991), are easily derived, and given

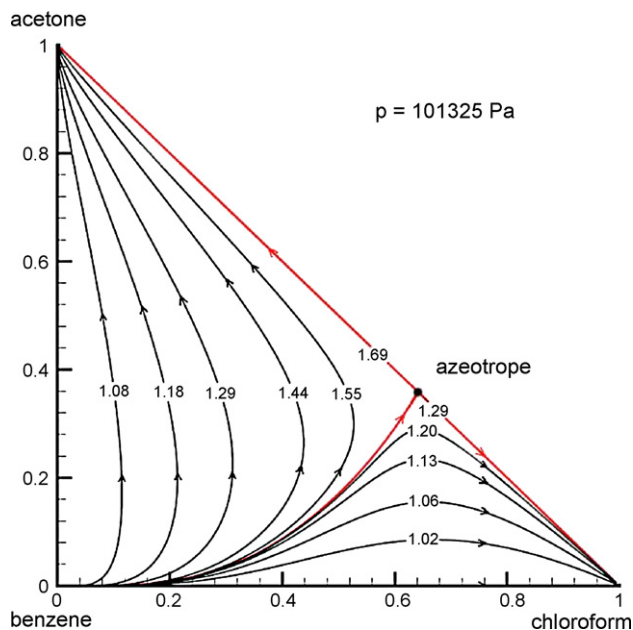


Fig. 1. Residue curve map and line integrals for chloroform/acetone/benzene.

by

$$x'_j = \left[\frac{r+1}{r} \right] y_j - x_j - \left(\frac{1}{r} \right) x_D \quad (1)$$

$$x'_j = \left[\frac{s}{s+1} \right] y_j - x_j + \left[\frac{1}{s+1} \right] x_B \quad (2)$$

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. Eq. (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

$$s = (r+q) \left[\frac{(x_F - x_B)}{(x_D - x_F)} \right] + q - 1 \quad (3)$$

where q represents thermal conditions of the feed. Eqs. (1) and (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

$$x_{j+1} = \left[\frac{r+1}{r} \right] y_j - \left(\frac{1}{r} \right) x_D \quad (4)$$

Solving Eq. (4) for y_j yields

$$y_j = \left[\frac{r}{r+1} \right] x_{j+1} + \left[\frac{1}{r+1} \right] x_D = \left(\frac{L}{V} \right) x_{j+1} + \left(\frac{D}{V} \right) x_D \quad (5)$$

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. Eq. (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 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 $x' = y - x$.

4.2. Remark

In simulating the behavior of any staged column using the differential equations defined by Eqs. (1) and (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. (4) and (5) is not exact.

4.3. Pinch points, minimum flows and energy efficiency

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 $j = \text{infinity}$. 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

$$0 = s y_N - (s+1) x_N + x_B = s(K_N x_N) - (s+1) x_N + x_B \quad (6)$$

for the $(c-1)$ unknowns x_N , where the K_N in Eq. (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 Eq. (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.

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.

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

$$\min_s D_s = \sum_{j=1}^{N_s} \|x'_j\| = \|x_{j+1} - x_j\| \quad (7)$$

subject to

$$x'_j = x_{j+1} - x_j = \left[\frac{s}{s+1} \right] y_j - x_j + \left[\frac{1}{s+1} \right] x_B, \quad j = 1, \dots, N_s \quad (\text{stripping line}) \quad (8)$$

$$x_1 = x_B \quad (\text{bottoms specification}) \quad (9)$$

$$r = (s - q + 1) \frac{[x_{Fi} - x_{Di}]}{[x_{Bi} - x_{Fi}]} - q \quad (10)$$

$$x'_j = x_{j+1} - x_j = [(r + 1)/r]y_j - x_j - \left(\frac{1}{r}\right)x_D, \quad j = N_s + 1, \dots, N \quad (\text{rectifying line}) \quad (11)$$

$$x_{D,i} < \text{specified } x_{D,i} \quad (\text{distillate specifications}) \quad (12)$$

$$c(x_K) = 0 \text{ for some } K \in [1, N] \quad (\text{auxiliary constraint}) \quad (13)$$

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 Eq. (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 Eqs. (7)–(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 Eq. (7) to approximate an infinite number of stages in the stripping section, which are numbered from bottom to top.

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 increas-

ing the boil-up and reflux ratios by solving the following problem

$$\min_{N_s} D_s = \sum_{j=1}^{N_s} \|x'_j\| = \|x_{j+1} - x_j\| \quad (14)$$

subject to

$$x'_j = x_{j+1} - x_j = \left[\frac{s}{s+1} \right] y_j - x_j + \left[\frac{1}{s+1} \right] x_B, \quad j = 1, \dots, N_s \quad (\text{stripping line}) \quad (15)$$

$$x_1 = x_B \quad (\text{bottoms specification}) \quad (16)$$

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

Note that the only 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., Eq. (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 (Eq. (11)), the equation relating stripping ratio and reflux ratio (Eq. (10)), and any specifications on the distillate product (e.g., Eq. (12)).

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 (Eqs. (7)–(12) and (14)–(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., Eq. (13)) are also discussed.

• Nonlinear Programming

- (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 $j = 1$ through 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 $D_s = D_{N_s}$ 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 $x_D(\text{calc}) = x_{N_s+k}$ (or $y_D(\text{calc}) = y_{N_s+k}$ 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 $\Lambda = D + \sum \mu^T c_D$, 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., Eqs. (8)–(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 $D_s = D_{N_s}$ 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.

5.4. 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 $y_D(\text{calc})$ in place of $x_D(\text{calc})$ 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, $x_D(\text{calc})$, 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 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 $\|x'\| < \epsilon$

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 2–7 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.

5.5. Integer 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 a non-pinched

solution or return with a pinched solution (if no non-pinched solution exists) in at most nine integer iterations!

5.6. 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 Section 6.14.

5.7. 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 Eq. (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. (2006) for an illustration of this.

6. Distillation examples

The next section presents a number of distillation examples that illustrate the use of the shortest stripping line 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 not pinch points. In all cases, the liquid phase is modeled by the UNIQUAC equation, unless otherwise specified. All interaction parameters can be found in Appendix A. In all case where a pinched solution is reported, we solved the nonlinear program-

ming (NLP) problem defined by Eqs. (7)–(12). In all cases where a non-pinched solution is reported we solved the NLP and then the integer programming problem defined by Eqs. (14)–(17) plus Eqs. (10)–(12). For the multi-unit process examples an NLP defined by Eqs. (7)–(13) was solved. However, we remark the reader must keep in mind that the column configuration must be accounted for correctly. That is, a column with stripping and rectifying sections obviously involves a different set of equations than, 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.

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.

6.2. 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 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 $x_D(n-C_5) > 0.99$.

Fig. 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

Table 1
Feed and product compositions for n -pentane/ n -heptane distillation

Component	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

⁺ Feasible if $x_D(n-C_5) > 0.99$.

^{*} Saturated liquid ($q = 1$).

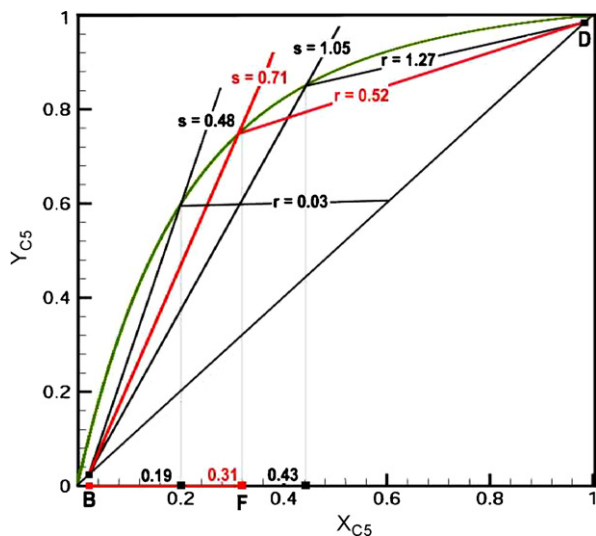


Fig. 2. Feed pinch determined by shortest stripping line for $n\text{-C}_5/n\text{-C}_7$.

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 Fig. 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 has 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 than 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 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.

6.3. Tangent pinch points

Consider the distillation of acetone (A) and water (W) at 1 atm. The equilibrium curve for acetone and water shows an

Table 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 ($q=1$).

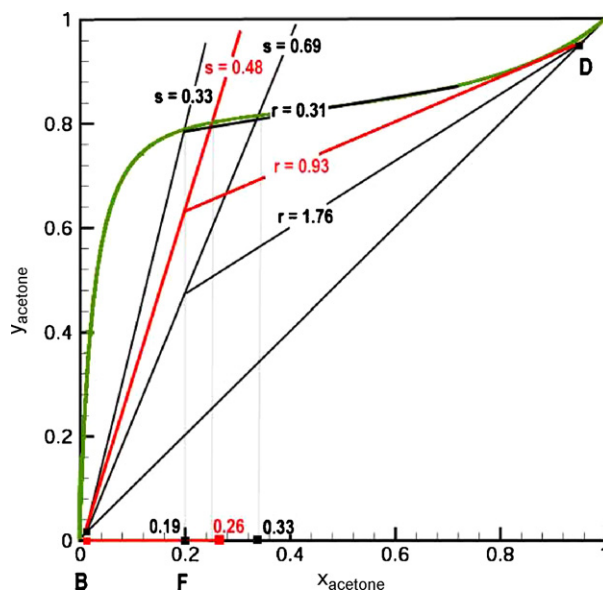


Fig. 3. Tangent pinch determined by shortest stripping line for acetone/water.

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 3, where the feed is saturated liquid and the vapor phase is assumed to be ideal. The distillation is feasible if $x_D(A) > 0.96$.

In this example, the NLP defined by Eqs. (7)–(12) was solved. Fig. 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 of 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 $x_D(A)=0.66000$. 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

Table 2
Summary of boil-up and stripping line distances for $n\text{-pentane}/n\text{-heptane}$ distillation

Boil-up ratio	Distance (D_s)	Feasible	$x_D(n\text{-C}_5)$	Q_R^a	Q_C^a
0.4750	0.1932	No			
0.7055	0.3100	Yes	0.99863	1.594×10^4	4.625×10^3
1.0500	0.4311	Yes	0.99943	1.916×10^4	5.053×10^3

^a Duties in units of Btu/h per lbmol/h of feed.

Table 4
Summary of results for acetone/water distillation

Boil-up ratio	Distance (D_s)	Feasible	$x_D(A)$	Q_R^a	Q_C^a
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

^a Heat duties in units of Btu/h per lbmol/h of feed.

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 Fig. 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 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.

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.

6.4. Ternary mixtures

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

6.5. 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. (2006) 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, distil-

Table 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 $x_D(EAc) \leq 0.6300$.

^{*} Saturated liquid ($q=1$).

late, and bottoms compositions for this distillation are given in Table 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 $x_D(EAc) \leq 0.6300$.

Fig. 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 6 summarizes the numerical results.

6.6. 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. (1995), where the vapor phase is assumed to be ideal. This separation is defined by the feed, approximate distillate and bottoms compositions, as shown

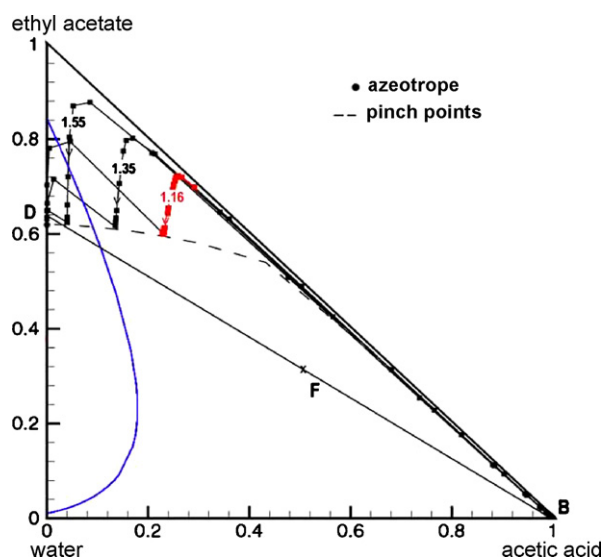


Fig. 4. Distillation lines for the separation of acetic acid/ethyl acetate/water.

Table 6
Summary of results for acetic acid/ethyl acetate/water distillation

Reboil ratio	Distance (D_s)	Feasible	$x_D(\text{AA, EAc})$	Q_R^a	Q_C^a
3.933	1.1611	Yes	$(4.21519 \times 10^{-5}, 0.62998)$	2.29146×10^4	2.84566×10^4
7.0	1.3511	Yes	$(7.82468 \times 10^{-5}, 0.62740)$	4.17264×10^4	5.88884×10^4
25	1.5465	No	$(1.7090 \times 10^{-4}, 0.62692)$		

^a Heat duties in units of Btu/h per lbmol/h of feed.

Table 7
Column specifications for the distillation of chloroform/acetone/benzene

Component	Distillate ⁺	Feed [*]	Bottoms
Chloroform	6.666×10^{-4}	0.1100	0.13266 8
Acetone	0.9900	0.1700	1×10^{-10} 8
Benzene	0.0093	0.7200	0.86734 8

⁺ Feasible if $x_D(A) \geq 0.99$.

^{*} Saturated liquid feed ($q = 1$).

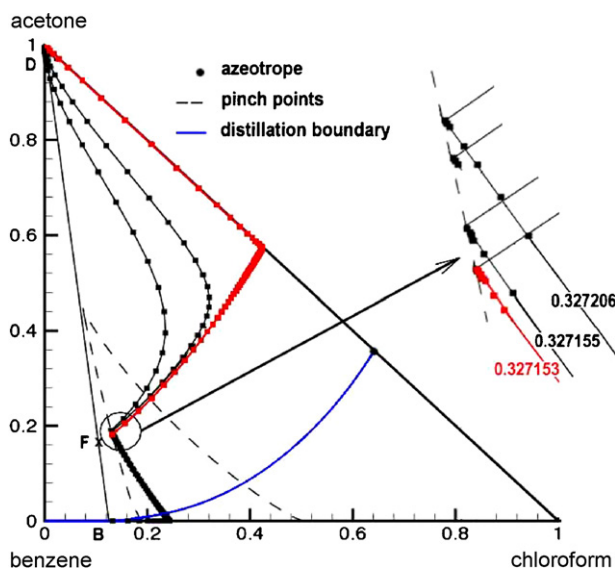


Fig. 5. Feed and saddle pinch determined by shortest stripping line.

in Table 7. This separation is considered feasible if the acetone composition in the distillate product satisfies the inequality $x_D(A) \geq 0.99$.

Table 8 and Fig. 5 give a summary of the numerical results for three different column profiles, two of which meet the desired column specifications.

As shown in Fig. 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

Table 8
Summary of numerical results for chloroform/acetone/benzene distillation

Boil-up ratio	Distance (D_s)	Feasible	$x_D(A)$	Q_R^a	Q_C^a
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		

^a Heat duties in Btu/h per lbmol/h of feed.

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. 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 Fig. 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.

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 Fig. 5 or Table 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 Wanschaff, Koehler, and Westerberg (1994).

6.7. 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

Table 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 $x_D(\text{AcA}) \geq 0.99$.

^{*} Saturated liquid ($q = 1$).

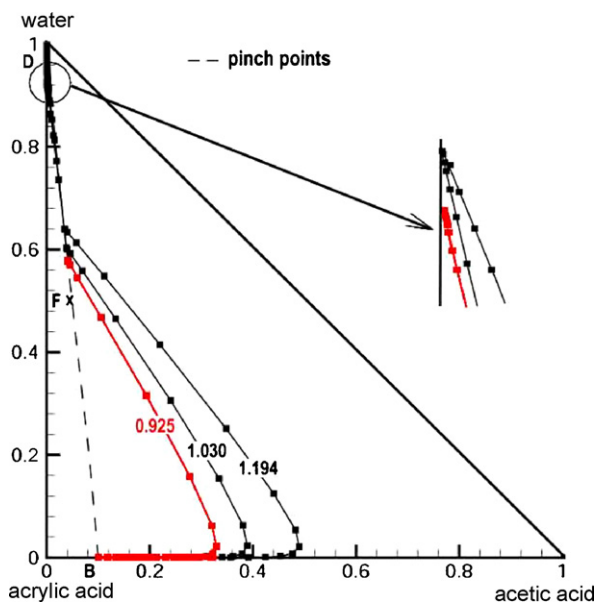


Fig. 6. Tangent pinch determined by shortest stripping line.

since both acetic acid and acrylic acid show strong vapor phase dimerization. Table 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, $x_D(\text{AcA}) \geq 0.99$ was used.

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

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 (1986) have reported this abrupt shift in product composition accompanying a tangent pinch point.

Table 10
Summary of numerical results for acrylic acid/water/acetic acid distillation

Boil-up ratio	Distance (D_s)	Feasible	$x_D(\text{AcA})$	Q_R^a	Q_C^a
2.1428	0.9253	No	0.94267		
2.2592	1.0305	Yes	0.99733	2.225987×10^4	1.949458×10^4
2.6530	1.1943	Yes	0.99844	2.494946×10^4	2.289267×10^4

^a Heat duties in Btu/h per lbmol/h of feed.

Table 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 ($q = 1$).

6.8. 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 that 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 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.

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 Fig. 7 and these boundaries are one-dimensional curves. Fig. 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

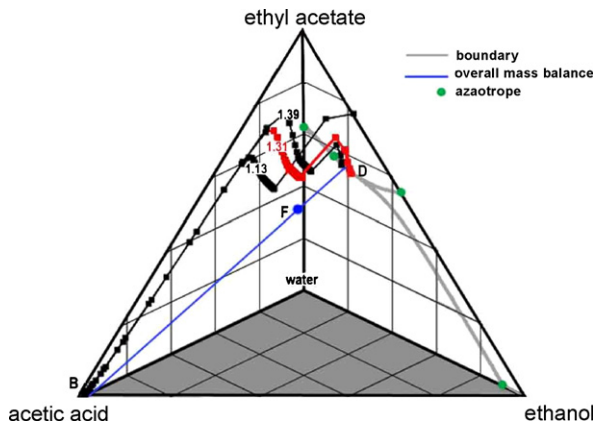


Fig. 7. Feed pinch determined by shortest stripping line for quaternary mixture.

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 Fig. 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 Fig. 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 12 and show that the shortest stripping line distance corresponds to minimum boil-up ratio among all feasible profiles.

6.9. 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 (EA_c), 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 $x_{Az} = (x_M, x_{EA_c}) = (0.69410, 0.30590)$. The feed, approximate distillate, and bottoms product compositions are given in Table 13. Separation feasibility, in this example, is defined by the condition $\|x_D - x_{D,spec}\| \leq 0.02$,

Table 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 ($q=1$).

where $x_{D,spec}$ is the distillate composition given in Table 13. Vapor phase behavior is modeled using the HOC equation.

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 $x_{FP} = (x_M, x_{AA}, x_E, x_{EA_c}) = (0.53510, 0.15819, 0.011261, 0.26924)$. The resulting reflux ratio is $r=2.371927$ and the calculated distillate composition is $x_D = (0.68129, 1.23 \times 10^{-11}, 7.350 \times 10^{-4}, 0.31798)$, 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 14.

6.10. A six-component petroleum refinery mixture

This example is adapted from Holland (1964) and involves the distillation of a six-component mixture of light paraffins at 400 psi. 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 (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. We used critical properties in Elliott and Lira (1999).

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 15. The distillation is considered to be feasible if the condition $\|y_D - y_{D,spec}\| \leq 0.01$ 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

Table 12

Summary of numerical results for acetic acid/ethanol/ethyl acetate/water distillation

Boil-up ratio	Distance (D_s)	Feasible	$\ x_D - x_{Az}\ $	Q_R^a	Q_C^a
3.5	1.13242	No	0.5250		
6.263	1.31397	Yes	0.0999	3.79318×10^4	9.05092×10^4
9.0	1.39192	Yes	0.0498	5.44187×10^4	1.30296×10^5

^a Heat duties in Btu/h per lbmol/h of feed.

Table 14
Numerical results for a five-component distillation

Boil-up ratio	Distance (D_s)	Feasible	$\ x_D - x_{D,spec}\ $	Q_R^a	Q_C^a
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

^a Heat duties in Btu/h per lbmol/h of feed.

Table 15
Column specifications for a six-component distillation

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

⁺ Feasible if $\|y_D - y_{D,spec}\| \leq 0.01$.

^{*} Saturated liquid ($q = 1$).

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 16 summarizes the numerical results for this example.

6.11. Examples of non-pinch 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-pinch solutions were determined by first solving the NLP problem defined by Eqs. (7)–(12) and subsequently solving the IP problem defined by Eqs. (14)–(17) together with Eqs. (10)–(12) since these non-pinch examples have both stripping and rectifying sections in the columns using integer bisection.

6.12. A non-pinch minimum energy solution for a ternary mixture

Koehler et al. (1995) provide an example where minimum energy consumption does not correspond to a pinch point and

Table 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 ($q = 1$).

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 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)–(12). 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 Fig. 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 $D_s = 0.2920$

Table 16
Numerical results for a sharp separation of a six-component mixture

Boil-up ratio	Distance (D_s)	Feasible	$\ y_D - y_{D,spec}\ $	Q_R^a	Q_C^a
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

^a Heat duties in Btu/h per lbmol/h of feed.

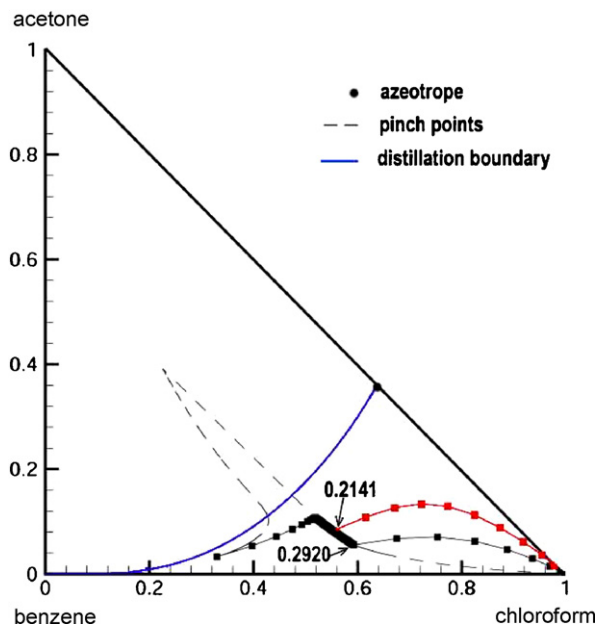


Fig. 8. Minimum energy requirements for a column with no pinch.

Table 18
Column specifications for a six-component distillation

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

⁺ Feasible if $\|y_D - y_{D,spec}\| \leq 0.03$.

^{*} Saturated liquid ($q = 1$).

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.

6.13. A non-pinch minimum energy solution for a six-component refinery mixture

Consider the feed mixture shown in Table 15 and let the desired separation be a split between the C_4 's and C_3 's as shown in Table 18. The liquid and vapor phases for this example are

Table 19
Numerical results for an indirect split of a six-component mixture

Boil-up ratio	Distance (D_s)	Feasible ^a	$\ y_D - y_{D,spec}\ $	Q_R^a	Q_C^a
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

^a Heat duties in Btu/h per lbmol/h of feed.

assumed to be ideal solutions where the K -values are given by the method in Wilson (1968). 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 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 19 gives results for two non-pinch solutions for the desired separation.

As shown in Table 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-pinch 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 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 $\|y_D - y_{D,spec}\| \leq 0.03$.

We explain the non-pinch 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 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-pinch minimum energy solution.

We compared the results in Table 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 (Wilson, 1968) 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 (Wilson, 1968) 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 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 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 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.

6.14. 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

Table 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 ($q = 1$).

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 (2001). 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 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.

For this example we solved the NLP problem defined by Eqs. (7)–(12) with the modifications described for finding a rectifying pinch point as given in the algorithm section. Fig. 9 shows the results for two separate profiles that make the desired separation given in Table 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 $x_{FP} = (x_M, x_E) = (0.171425, 0.357352)$

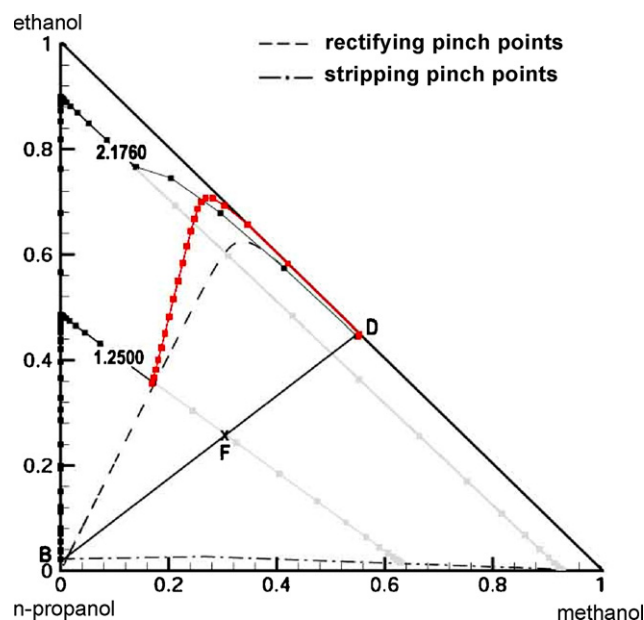


Fig. 9. Rectifying feed pinch determined by shortest stripping line.

Table 21
Numerical results for the indirect split of methanol/ethanol/*n*-propanol

Boil-up ratio	Distance (D_s)	No. 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

⁺ Stripping stages (rectifying stages).

^{*} Heat duties in Btu/h for lbmol/h feed.

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 Fig. 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 Fig. 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 21 gives other feasible solutions for this indirect split.

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 Fig. 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., Eq. (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 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 all $s = [20.28, 23.19]$, a column configured with 34 stripping stages and 4 rectifying stages easily makes the desired separation given in Table 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.

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 Eqs. (7)–(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.

7.1. Hybrid separation of acetic acid and water

Lucia et al. (2006) 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 Fig. 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.

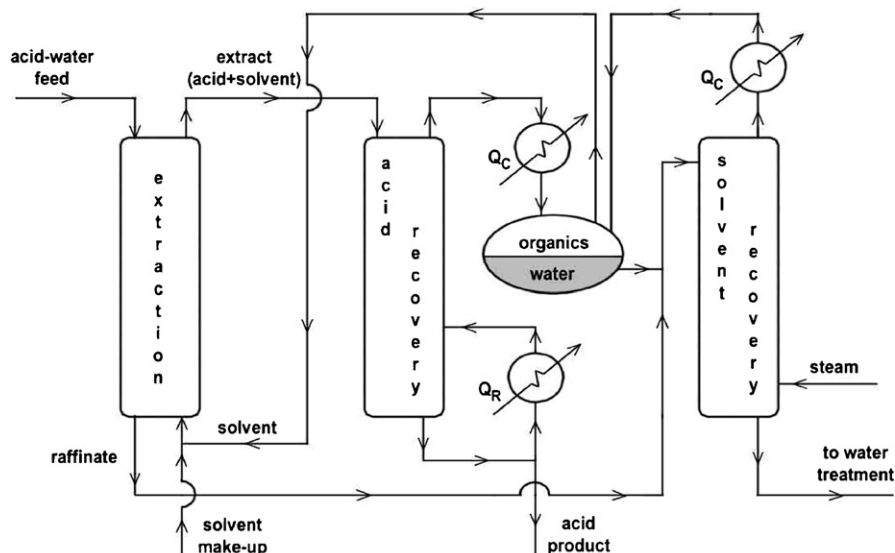


Fig. 10. Hybrid separation process for acetic acid.

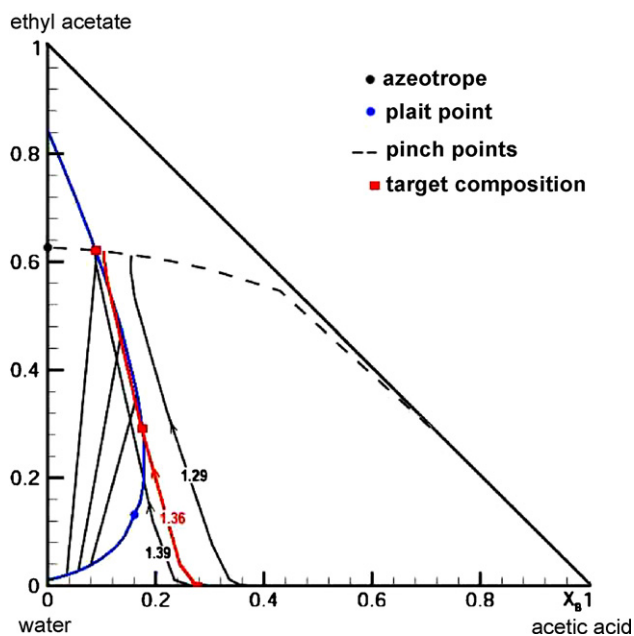


Fig. 11. Hybrid separation of lower purity acetic acid.

Feasible and infeasible acid recovery columns are shown in Fig. 11 while boil-up ratios, target extract compositions, and energy requirements are tabulated in Table 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.

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 Fig. 12. In both cases, we show that the concept of shortest stripping line correctly determines minimum energy requirements.

The production of MTBE from isobutene and methanol at slightly elevated pressure has been studied extensively in the literature (Nisoli, Malone, & Doherty, 1997; Lee & Westerberg, 2001; Chen, Huss, Malone, & Doherty, 2000). 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. (1997), was specified to be 8 atm. In both processes we assume reaction equilibrium in the reactor effluent of the RSR

Table 22
Summary of stripping lines and boil-up ratios for acetic acid recovery column⁺

Boil-up ratio	Distance (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)			

⁺ $x_B(\text{AA, EAc}) = (0.9950, 1 \times 10^{-10})$.

* Heat duties in Btu/h per lbmol/h of extract (i.e., feed to acid recovery column).

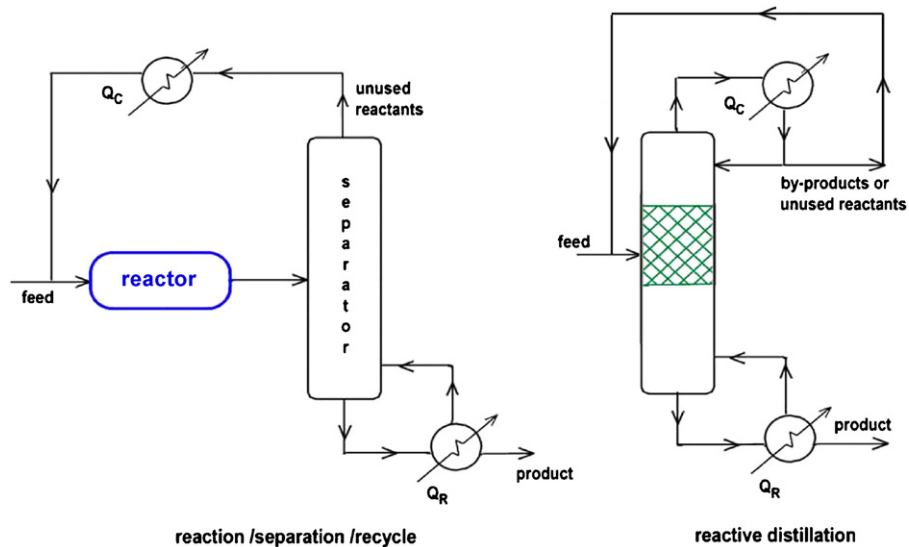


Fig. 12. Reaction/separation/recycle and reactive distillation processes.

process and on each stage in the reactive section of the RD process.

Reaction equilibrium is represented by

$$x_1\gamma_1x_2\gamma_2K - x_3\gamma_3 = 0 \quad (18)$$

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. (1997).

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

- (1) For the case of no reaction (i.e., Fig. 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 (2006).
- (2) For the case of reactive separation at high Damkohler number, the separation boundary changes significantly as shown in Fig. 7b in Nisoli et al. However, Taylor et al. (2006) 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.

7.3. 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. Fig. 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 Fig. 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 Fig. 13 assume that the reactor effluent is on the chemical equilibrium line. We note that in Fig. 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

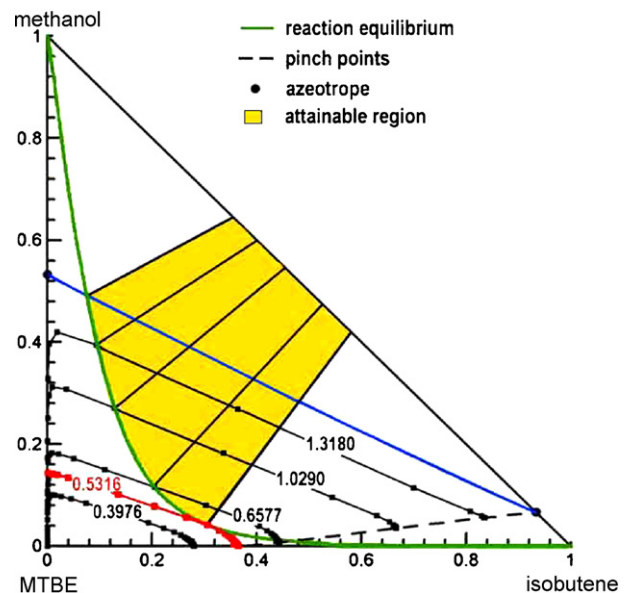


Fig. 13. Minimum energy requirements for a reaction/separation/recycle process.

Table 23
Summary of stripping lines and boil-up ratios for recovery of pure MTBE using an RSR process

Boil-up ratio	Distance (D_s)	Feasible	$x_T^\#$	$x_B^\#$	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.

of the triangular region is infeasible. However, it is clear from Fig. 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 23.

Note with regard to this illustration

- (1) It is important to know the location of the distillation boundary shown in Fig. 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 Fig. 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.

7.4. Reactive 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 (2001) 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 $x_D(iC_4) \geq 0.998$.

7.5. Governing equations

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

$$F - D - B = -v\varepsilon_T \quad (19)$$

$$Fz_i - Dx_{i,D} - Bx_{i,B} = -v_i\varepsilon_T \quad (20)$$

where v_i is the stoichiometric coefficient for the i th component and the unsubscripted variable, v , in Eq. (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 Eqs. (19) and (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 j th stage in an RD column include the overall and component material balances

$$F_j + L_{j+1} + V_{j-1} - V_j - L_j = -v\varepsilon_j \quad (21)$$

$$F_j z_{i,j} + L_{j+1} x_{i,j+1} + V_{j-1} y_{i,j-1} - V_j y_{i,j} - L_j x_{i,j} = -v_i \varepsilon_j \quad (22)$$

where ε_j is the extent of reaction on the j th 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 Eqs. (21) and (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 Eqs. (21) and (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 Fig. 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 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 Eq. (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 Fig. 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 24 and Fig. 13. However, it is important to note that only the two shortest stripping profiles in Fig. 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 $x_D(iC_4) \geq 0.998$, uses the least energy, and 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 $s_{\min} = 0.917$.

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 (2001), the feed is 60% isobutene, the reflux ratio is 14 and there are 16 stripping stages and three reactive stages in the rectifying section including the feed stage. Fig. 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. (2000). 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 Fig. 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 (Nisoli et al., 1997). We also note here that for columns that attain reaction equilibrium on each stage the

Table 24
Summary of stripping lines and boil-up ratios for recovery of pure MTBE using an RD process

Boil-up ratio	Distance (D_s)	Feasible	$x_F^{\#}$	$x_F^{\#}$	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
0.7000	0.3976	No			

[#] Mole fractions of isobutene and methanol, respectively.

^{*} Reboiler duty in Btu/h per lbmol/h of MTBE.

Table A1
Pure component constants for extended antoine equation

Component	Component					
	c_1	c_2	c_3	c_4	c_5	c_6
Chloroform	174.24	−8140.0	0	0.065975	−29.011	$−3.0001 \times 10^{-5}$
Methanol	333.87	−12679.0	0	0.13671	−57.722	$−5.9496 \times 10^{-5}$
Acetic acid	386.98	−15091.0	0	0.16774	−67.642	$−7.2738 \times 10^{-5}$
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}
<i>n</i> -Pentane	69.020	−5362.5	0	0.0099221	−9.4897	$−3.8363 \times 10^{-5}$
Benzene	97.209	−6976.1	0	0.019082	−14.212	$−6.7182 \times 10^{-6}$
<i>n</i> -Heptane	−17.613	−4669.8	0	−0.035093	6.9580	1.4503×10^{-5}
Water	57.042	−7004.8	0	0.0035888	−6.6689	$−8.5054 \times 10^{-7}$
Acrylic acid	13.200	−5489.7	0	0	0	0

material balances can be written in form of transformed composition variables (Barbosa & Doherty, 1988; Nisoli et al., 1997) 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.

8. Conclusions

The concept of shortest stripping lines was used to find minimum energy requirements in distillation, reactive distillation, hybrid separation processes, and reaction/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 (submitted for publication) 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.

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Appendix A

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 for computing 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

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

Table A2
Binary interaction parameters for the UNIQUAC equation

Component <i>i</i>	Component <i>j</i>	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

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

The temperature-dependent interaction terms, τ_{ij} , for the UNIQUAC equation of Prausnitz et al. (1980) are expressed in the form

$$\tau_{ij} = \exp\left(\frac{-a_{ij}}{T}\right) \quad (\text{A2})$$

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

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