Non-pinched, minimum energy distillation designs

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Abstract

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

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

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

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

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1. Introduction

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

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

In a recent paper, Lucia et al. (2007) give a comprehensive treatment of a new unifying principle in energy efficient process design—the shortest stripping line distance approach. This new approach states that the most energy efficient designs for processes in which distillation is involved correspond to the shortest stripping line distance for the distillation(s). Of course, the implicit assumption in this approach is that distillation is the largest energy consumer in many multi-unit processes and, for the most part, this is a very good assumption. Lucia et al. (2007) also presented a rigorous Mixed Integer Nonlinear Programming (MINLP) formulation for the shortest stripping line distance approach, along with an algorithm for implementing this MINLP formulation. This MINLP formulation is a two-level methodology that alternates between an NLP problem to find the minimum boil-up ratio and an Integer Program (IP) problem for finding the number of stages in a column such that stripping line distance is
shortest. Many examples for processes with up to six components were used to support the novel idea of shortest stripping line distance in energy efficient design including single distillation columns with feed, saddle, and tangent pinch points, non-pinched distillations, and hybrid separations such as extraction followed by distillation and reactive distillation.

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

2. Motivating example

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

2.1. The non-pinched distillation example of Koehler et al. revisited

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

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

Table 2 – Stripping line distance vs. boil-up ratio for problem from Koehler et al. (1995)

<table>
<thead>
<tr>
<th>Boil-up ratio</th>
<th>Distance</th>
<th>Liquid compositiona</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.46293rmin</td>
<td>0.290707822 (Dmin)</td>
<td>(0.5904986, 0.0567577) pinned</td>
</tr>
</tbody>
</table>
is, liquid compositions \( x_{209} \) to \( x_{299} \) are unstable pinch point compositions. Again, look carefully at Fig. 1. The important observation, however, is that the compositions for the pinched design on trays 209–299 correspond to a higher value of boil-up (and reflux) ratio than the corresponding pinched design. For example, the non-pinched design shown in Table 2 corresponds to \( s_{\text{min}} = 2.46293 \) and has a liquid composition on stage 209 (i.e., \( x_{209} = (0.5267737, 0.1015876) \)) that is equal to the unstable pinch point composition, \( x_{\text{PP}} = (0.5267737, 0.1015876) \) to seven significant digits. On the other hand, the actual boil-up ratio (and reflux ratio) that corresponds to this unstable pinch point is \( s = 1.987 \) and is far too low to give a feasible pinched, minimum energy design. What this implies is that there are many non-pinched, minimum energy designs for the column specifications given in Table 1—each with a different number of stripping and rectifying stages. However, the ‘best’ design in our opinion is the one with the shortest stripping line distance and defined by the NLP problem

\[
\min D_s = \sum_{j=1}^{N_s} ||x_j'|| = ||x_{j+1} - x_j|| \quad (1)
\]

subject to

\[
x_j' = x_{j+1} - x_j = \left[ \frac{s}{s+1} \right] y_j - x_j + \left[ \frac{1}{s+1} \right] x_B, \quad j = 1, \ldots, N_s \quad (2)
\]

\[
x_1 = x_B \quad (3)
\]

\[
r = (s - q + 1) \frac{(x_{j+1} - x_D)}{(x_{j+1} - x_{j})} - q \quad (4)
\]

\[
x_j' = x_{j+1} - x_j = \left[ \frac{r+1}{r} \right] y_j - x_j - \left[ \frac{1}{r} \right] x_D, \quad j = N_s + 1, \ldots, N \quad (5)
\]

\[
||x_D,\text{calc} - x_D,\text{spec}|| \leq \zeta \quad (6)
\]

\[
c(x_k) = 0 \quad \text{for some} \ K \in [1, N] \quad (7)
\]

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

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

3. Methods and materials: a summary of the shortest stripping line distance approach

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

3.1. Nonlinear programming

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

\[
\min D_s = \sum_{j=1}^{N_s} ||x_j'|| = ||x_{j+1} - x_j|| \quad (1)
\]

subject to

\[
x_j' = x_{j+1} - x_j = \left[ \frac{s}{s+1} \right] y_j - x_j + \left[ \frac{1}{s+1} \right] x_B, \quad j = 1, \ldots, N_s \quad (2)
\]

\[
x_1 = x_B \quad (3)
\]

\[
r = (s - q + 1) \frac{(x_{j+1} - x_D)}{(x_{j+1} - x_{j})} - q \quad (4)
\]

\[
x_j' = x_{j+1} - x_j = \left[ \frac{r+1}{r} \right] y_j - x_j - \left[ \frac{1}{r} \right] x_D, \quad j = N_s + 1, \ldots, N \quad (5)
\]

\[
||x_D,\text{calc} - x_D,\text{spec}|| \leq \zeta \quad (6)
\]

\[
c(x_k) = 0 \quad \text{for some} \ K \in [1, N] \quad (7)
\]
3.2. Integer programming

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

$$\min_{N_s} D_s = \sum_{j=1}^{N_s} ||x_j|| = ||x_{j+1} - x_j||$$  \hspace{1cm} (8)

subject to

$$x_j = x_{j+1} - \left[ \frac{s}{s+1} \right] y_j + \left[ \frac{1}{s+1} \right] x_0, \hspace{1cm} j = 1, \ldots, N_s \hspace{1cm} (9)$$

$$x_1 = x_0$$  \hspace{1cm} (10)

$$s = s_{\text{min}}$$  \hspace{1cm} (11)

$$r = (s - q + 1) \left( \frac{s_1 - x_0}{s_1 - x_1} \right) - q$$  \hspace{1cm} (12)

$$x_j = x_{j+1} - \left[ \frac{r + 1}{r} \right] y_j - \left( \frac{1}{r} \right) x_0, \hspace{1cm} j = N_s + 1, \ldots, N \hspace{1cm} (13)$$

$$||x_{\text{D,calc}} - x_{\text{D,spec}}|| \leq \zeta$$  \hspace{1cm} (14)

$$c(x_0) = 0 \text{ for some } K \in [1, N]$$  \hspace{1cm} (15)

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

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

4. Optimization algorithm and implementation

Lucia et al. also give an optimization algorithm that alternates between solving the NLP and IP sub-problems, where the NLP problem is solved using the terrain method and integer bisection is used to solve the IP sub-problem. Alternation between the NLP and IP sub-problems can be repeated as many times as necessary. We refer the reader to the paper by Lucia et al. (2007) for the details of the optimization algorithm.
constraints that restrict the feed to the distillation help define minimum energy demands that are not pinched.

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

(3) There are situations that we have encountered where the stripping and/or rectifying line trajectory passes near each other well away from any pinch point curve. More specifically, for the illustrative example that we provide for this situation, rectifying lines (including the one for minimum reflux ratio) loop around and pass very near stripping lines before converging to their respective pinch points. It is the looping structure of the rectifying and stripping line trajectories that gives rise to non-pinched designs and one in particular that uses minimum energy!

5. Results and analyses

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

5.1. Example 1

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

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

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

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

For column 1 in region 1, the pinch point curve that originates at B1. There are two stable disjoint branches, denoted by $B_1P_1$ and $P_2P_3$, and each branch lies in a different distillation region. These two branches are the upper two branches shown in Fig. 2 and, as in Koehler et al. (1995), we use the symbol $P_i$ to denote a liquid pinch point composition. Moreover, these two stable branches of the stripping pinch point curve are connected by an unstable branch, $P_1P_2$, which is shown as the solid curve in Fig. 2. It is interesting to observe that stripping trajectories that correspond to the last pinch points on each of the stable branches $P_1$ and $P_2$ trace out the unstable branch of the stripping pinch point curve.

For column 2 in region 2, the curve that originates at $B_2$ represents the stripping pinch point curve for the set of column specifications given on the right of Table 3. Note that this pinch point curve shows very similar behavior to the stripping pinch point curve for column 1. That is, the curves $B_2P_4$ and $P_5P_6$ are
Table 4 presents detailed numerical results for various distillation designs for this example. All distillations are considered feasible if they satisfy the condition $||y_D - y_{Dspec}|| \leq 0.05$. Note that there are non-pinched designs for both columns—as indicated by fewer than 300 stripping stages.

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

For column 2, which is depicted in Fig. 4, the minimum value of reboil ratio needed to find a feasible design is $s_{min} = 3.75544$. Again, this minimum boil-up ratio was determined by solving the shortest stripping line distance NLP defined by Eqs. (1)–(6). The stripping line distance for this pinched, minimum energy design is $D_s = 0.402642$. On the other hand, there is a non-pinched, minimum energy design with 72 stripping stages and a corresponding minimum stripping line distance of $D_s = 0.354424$, which can be easily determined by solving the IP sub-problem defined by Eqs. (8)–(14). Again, after one pass through the NLP and IP, no further reduction in the boil-up ratio or number of stages can be found.

Fig. 3 – First non-pinched minimum energy solution for formic acid/acetic acid/water distillation.

Fig. 4 – Second non-pinched minimum energy solution for formic acid/acetic acid/water distillation.
As in the motivating example, the pinched solution for column 1 with \( s_{\text{min}} = 6.6157 \) (with corresponding \( r_{\text{min}} = 18.818739 \)) and the pinched design for column 2 with \( s_{\text{min}} = 3.75544 \) (with corresponding \( r_{\text{min}} = 4.583277 \)) each follow a portion of the unstable branch of the stripping pinch point curve in the appropriate distillation region. See the solid curves shown in Fig. 2. Thus liquid compositions on the upper stages in the stripping section of the pinched designs actually have values that are unstable pinch point compositions. Moreover, these stage compositions in these non-pinched designs occur at higher values of boil-up (and reflux) ratio.

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

Note, as in earlier example, the behavior of the liquid composition trajectories near \( s_{\text{min}} \) is quite similar to the behavior of residue curves near boundaries in that they are essentially coincident until they reach the unstable branch of the stripping pinch point curve, at which they split or bifurcate, each converging to a pinch point on a separate branch of the stable stripping pinch point curve. Moreover, the portions of these trajectories between the point that they split and the two stable pinch points they converge to actually trace out the unstable branch of the appropriate stripping pinch point curve! Note that for column 1 with \( s = 6.6156 \), the stripping pinch point is \( P_4 = (0.540513, 0.450967) \) is clearly in a different distillation region than pinch point \( P_5 = (0.172905, 6.324402) \) for \( s = 3.75543 \), which is slightly less than \( s_{\text{min}} \), the resulting pinch point \( P_5 = (0.172905, 6.324402 \times 10^{-2}) \) is on the different stable pinch point curve, and hence in a different distillation region, than the pinch point \( P_3 = (0.819092, 7.404520 \times 10^{-2}) \), which corresponds to \( s_{\text{min}} = 3.75544 \).

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

### 5.2. Example 2

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

\[
K_i = \exp \left[ \ln \left( \frac{p_{ci}}{p} \right) + 5.37(1 + a_i) \left( 1 - \frac{T_c}{T} \right) \right]
\]

where \( p_{ci}, T_c, a_i \) are the critical pressure, critical temperature, and acentric factor for the ith component. For this example, we have used critical properties given in Elliott and Lira (1999).

The feed to the column is a mixture of n-butane (n-C4), iso-pentane (i-C5), n-pentane (n-C5) and n-hexane (n-C6) and is saturated liquid. The column specifications are given in Table 5. In our approach, the feed and bottoms compositions are fixed and the distillation is considered feasible if \( |y_0 - y_D| \) (calc) \( \leq 0.06 \). Note that the light and heavy key components for this separation are i-pentane and n-pentane, respectively, and that both the bottoms and distillate products lie on different faces of the tetrahedral feasible region.

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

Fig. 5 shows the minimum energy design for the distillation specifications given in Table 5. Unlike the mixture in the first example, this hydrocarbon mixture does not form any azeotropes and no distillation boundaries are present in the system. Moreover, the stripping and rectifying pinch point curves, which are shown as the blue dot-dashed curves in Fig. 5, lie on different faces of the tetrahedron and do not show

### Table 6 – Specifications for a quaternary hydrocarbon distillation

<table>
<thead>
<tr>
<th>Component</th>
<th>Distillate</th>
<th>Feed</th>
<th>Bottoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Butane</td>
<td>0.42742</td>
<td>0.25</td>
<td>9.1 ( \times 10^{-21} )</td>
</tr>
<tr>
<td>i-Pentane</td>
<td>0.50419</td>
<td>0.30</td>
<td>0.01228</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>0.06839</td>
<td>0.20</td>
<td>0.38544</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>10^{-10}</td>
<td>0.25</td>
<td>0.60227</td>
</tr>
</tbody>
</table>

* a Stripping line distance, \( D_s \), is measured from \( x_0 \) to stripping pinch point curve.
* b Stripping line distance, \( D_w \), measured from \( x_0 \) to stage \( s_i \).
* c Feasible if \( |y_0 - y_D| \) (calc) \( \leq 0.06 \).
any bifurcation behavior. They simply start at their respective product compositions and go directly toward the n-butane and n-hexane vertices without any branching or the presence of unstable pinch points. Also note that the stripping trajectory shown in Fig. 5 shows that the stripping section of the column lies in the iso-pentane/n-pentane/n-hexane face of the tetrahedron and effectively performs a sequence of binary separations—first separating n-pentane and n-hexane and then separating iso-pentane and n-pentane.

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

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

Key observation #2: Non-pinched solutions to this distillation exist because the boil-up and reflux ratios are sufficiently high enough to force the operating lines far enough into the feasible region and away from their respective pinch point curves so that they form loops and both loops effectively form a bridge between the pinch point curves—in much the same way that unstable branches of a pinch point curve connect stable branches in azetotropic mixtures.

5.2.1. Analysis

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

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

(1) The reasons for the existence of non-pinched, minimum energy designs for the hydrocarbon distillation given here also explain the results for the six-component non-pinched example presented in Lucia et al. (2007). In that case, n-butane is the light key component and goes through a maximum in composition and thus forms a loop in the stripping section.

(2) In this example there is no pinched design that uses minimum energy from which to find a non-pinched minimum energy design. However, this present no computational difficulties for the shortest stripping line distance approach. This type of non-pinched design can be determined in exactly the same manner that designs with rectifying pinch points are determined (see Lucia et al., 2007). Starting from the bottoms composition, one simply determines the transition (or feed) stage that gives a feasible design and then continues by reducing the boil-up ratio and determining the number of stages in each section of the column needed to maintain feasibility.

(3) Using both our own in-house version of Underwood’s method, we calculated values of minimum reflux ratio and

![Fig. 5 – Non-pinched minimum energy solution for quaternary hydrocarbon mixture.](image-url)
Table 8 – Specifications for distillation of four-component azeotropic mixture

<table>
<thead>
<tr>
<th>Component</th>
<th>Distillate</th>
<th>Feed*</th>
<th>Bottoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon tetrachloride</td>
<td>0.005</td>
<td>0.0928</td>
<td>0.140</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.990</td>
<td>0.6713</td>
<td>0.500</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.003</td>
<td>0.0921</td>
<td>0.140</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.002</td>
<td>0.1438</td>
<td>0.220</td>
</tr>
</tbody>
</table>

* Saturated liquid (q = 1).

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

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

5.3. Example 3

The last example in this article involves the separation of chloroform, acetone, carbon tetrachloride, and benzene at atmospheric pressure. The UNIQUAC equation of Prausnitz et al.\(^3\) was used to model the liquid phase and the vapor phase at atmospheric pressure. The UNIQUAC equation of Prausnitz et al.\(^3\) was used to model the liquid phase and the vapor phase at atmospheric pressure.

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

5.3.1. Analysis

Note that the pinched solution for $s_{\text{min}} = 4.3666$, with a corresponding minimum reflux ratio of $r_{\text{min}} = 7.12262$, follows a portion of the unstable branch of the stripping pinch point curve in Fig. 7. Thus liquid compositions on the upper stages of the stripping section of the pinched design actually have values that are unstable pinch point compositions. That is, the non-pinched design shown in Table 9 with $s_{\text{min}} = 4.3666$ has a liquid composition on stage 136, $x_{136} = (0.11010, 0.67905, 0.12814)$, that is equal to the unstable pinch point composition for a lower boil-up ratio of $s = 4.2801$. Since the composition for

Table 9 – Numerical results for four-component azeotropic mixture

<table>
<thead>
<tr>
<th>s²</th>
<th>$N_s$ **</th>
<th>$N_p$</th>
<th>$D_s$</th>
<th>Feasible</th>
<th>$x_{y_0}$ *</th>
<th>$y_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.360</td>
<td>300</td>
<td>0.6146</td>
<td>No</td>
<td>(0.1378, 0.2076, 0.5614)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.366</td>
<td>300</td>
<td>13</td>
<td>0.3313</td>
<td>Yes</td>
<td>(0.0871, 0.7610, 0.0763)</td>
<td></td>
</tr>
<tr>
<td>4.366</td>
<td>136</td>
<td>30</td>
<td>0.2315</td>
<td>Yes</td>
<td>(0.1101, 0.6790, 0.1281)</td>
<td></td>
</tr>
<tr>
<td>4.380</td>
<td>300</td>
<td>12</td>
<td>0.3321</td>
<td>Yes</td>
<td>(0.0869, 0.7617, 0.0760)</td>
<td></td>
</tr>
</tbody>
</table>

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

Fig. 6 – Branches of pinch point curves for four component azeotropic mixture.
stage 136 corresponds to unstable pinch point but occurs at a higher value of boil-up ratio (and reflux ratio), it is possible to reduce the number of stripping stages in the pinched design and find many non-pinched, minimum energy designs for the desired separation. The best design, in our opinion, is the one that we report.

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

5.4. Example 4

Here we briefly re-visit the non-pinched, minimum energy design for the six-component hydrocarbon separation recently studied by Lucia et al. (2007). The purpose of this discussion is to show that the non-pinched, minimum energy design for this six-component hydrocarbon example has

### Table 10 – Column specifications for a six-component hydrocarbon distillation

<table>
<thead>
<tr>
<th>Component</th>
<th>Distillate $^a$</th>
<th>Feed $^b$</th>
<th>Bottoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propane</td>
<td>0.3000</td>
<td>0.15</td>
<td>$1 \times 10^{-12}$</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.3900</td>
<td>0.20</td>
<td>0.0040</td>
</tr>
<tr>
<td>iso-Butane</td>
<td>0.3000</td>
<td>0.15</td>
<td>0.000014</td>
</tr>
<tr>
<td>iso-Pentane</td>
<td>0.0001</td>
<td>0.20</td>
<td>0.3990</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>0.0001</td>
<td>0.15</td>
<td>0.3000</td>
</tr>
<tr>
<td>n-Octane</td>
<td>0.0038</td>
<td>0.15</td>
<td>0.3010</td>
</tr>
</tbody>
</table>

$^a$ Feasible if $|y_D - y_D^{spec}| \leq 0.03$.

$^b$ Saturated liquid ($q = 1$).
trajectories that exhibit the same loping structure described in Section 5.2—even though the desired separation is closer to a direct split. In this example, the phase equilibrium is modeled using the K-value correlation of Wilson (1968), where the critical properties have been taken from Elliott and Lira (1999). Table 10 gives the column specifications for this separation.

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

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

Note that n-C4, which was designated as the light key component in this example, goes through a maximum in composition on tray 15 in the stripping section and that i-C4 exhibits a maximum in composition on stage 26, which is at the top of the rectifying section. These composition maxima are characteristic signatures of the looping structure of the trajectories in non-pinched designs.

6. Comparisons with rigorous column simulations

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

Notice that the shapes of the composition profiles for both approaches are qualitatively similar. The quantitative differences are due to differences between the Aspen Plus thermodynamics and our thermodynamics—even though both approaches use the UNIQUAC equation to model the liquid phase and the Hayden–O’Connell equation for the vapor. We have verified these differences by comparing residue curve maps for our version of UNIQUAC-HOC with that from Aspen Plus and have observed differences in the location of the formic acid/acetic acid/water ternary azeotrope and thus the distillation boundaries. The specific numerical values for each method are given in Table 12.

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

These comparisons clearly show that the shortest stripping line approach can provide very reliable initial estimates

<table>
<thead>
<tr>
<th>Acid–water column 1</th>
<th>Boil-up ratio</th>
<th>$N_s$</th>
<th>$N_r$</th>
<th>$x_b = (x_{FA}, x_{AA})$</th>
<th>$y_b (\text{calc}) = (y_{FA}, y_{AA})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSLDA$^b$</td>
<td>6.6157</td>
<td>72</td>
<td>8</td>
<td>(0.0717, 0.8800)</td>
<td>(1.730 × 10$^{-5}$, 0.0298)</td>
</tr>
<tr>
<td>RADFRAC</td>
<td>6.6430</td>
<td>75</td>
<td>10</td>
<td>(0.0757, 0.9144)</td>
<td>(1.710 × 10$^{-5}$, 0.04607)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Quaternary hydrocarbon column</th>
<th>Boil-up ratio</th>
<th>$N_s$</th>
<th>$N_r$</th>
<th>$x_b = (x_{C_4}, x_{C_5}, x_{C_6})$</th>
<th>$y_b (\text{calc}) = (y_{C_4}, y_{C_5}, y_{C_6})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSLDA$^b$</td>
<td>9.9254</td>
<td>65</td>
<td>16</td>
<td>(9.1 × 10$^{-21}$, 0.01228, 0.38544)</td>
<td>(0.433311, 0.535717, 0.030972)</td>
</tr>
<tr>
<td>RADFRAC</td>
<td>9.9420</td>
<td>69</td>
<td>20</td>
<td>(6.7 × 10$^{-21}$, 0.01599, 0.37425)</td>
<td>(0.423729, 0.497361, 0.078910)</td>
</tr>
</tbody>
</table>

Table 12 – Comparisons of non-pinched, minimum energy designs for the shortest stripping line approach & rigorous aspen plus simulations$^a$.

$^a$ Design specifications for RADFRAC were B/F and boil-up ratio.

$^b$ SSLDA: shortest stripping line distance approach.
7. Discussions and conclusions

In this paper, it was shown that the shortest stripping line distance approach represents a rigorous and systematic procedure for determining non-pinched, minimum energy distillation designs. In addition, several reasons that underlie the existence of non-pinched, minimum energy distillation designs were identified and discussed. These reasons include:

1. The combination of certain product specifications and ancillary conditions, as in hybrid separation processes such as reactive distillation and extraction-distillation.
2. Azeotropic separations that contains:
   (a) A maximum boiling azeotrope.
   (b) A stripping pinch point curve with stable and unstable branches.
   (c) A product composition that lies near a distillation boundary.
3. Separations that have stripping and rectifying trajectories that exhibit looping and intersect on their way to their respective pinch point curves, where the trajectory in at least one section of the column shows reverse separation of one of the key components.

We close this article with a discussion of two issues associated with non-pinched, minimum energy designs that we believe are important. First, in cases where pinched, minimum energy designs exist alongside non-pinched, minimum energy designs, the non-pinched designs offer the advantage of not having to necessarily use conventional rules of thumb to determine the rough size of a column necessary to make the desired separation. Typical design protocols often find pinched designs and then use rules of thumb to estimate the number of actual stages (or packing height) required to make the desired separation at modest energy consumption. It is common, for example, to take the minimum boil-up (or reflux) ratio, multiply it by a factor between 1.1 and 1.5 (see Koehler et al., 1995) to give an operating boil-up or reflux ratio, and then determine the number of stages required by trial and error. When non-pinched, minimum energy designs exist, there is no need to increase the minimum boil-up ratio, if the number of stages needed for the separation is small enough to represent a column that can be built—since it would only result in a column that unnecessarily uses more energy than needed. In addition, note that the existence of non-pinched, minimum energy designs also show that increasing the number of stages beyond that predicted by the non-pinched solutions does not necessarily result in any better separation. In fact, this practice could lead to wasted capital investment costs.

Second, and perhaps more important, are cases where there is no pinched, minimum energy distillation design. In these cases, it is clear that the shortest stripping line distance approach provides design solutions that no other methodology can. More specifically, if one treats the problem at hand in a manner similar to the rectifying pinch case described in Lucia et al. (2007), then it is clear that the shortest stripping line distance approach can reliably and systematically find non-pinched, minimum energy designs.

Acknowledgement

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