

SYNTHESIS, DESIGN AND RETROFITTING OF ENERGY EFFICIENT SEPARATION PROCESSES

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A new methodology for the synthesis, design and retrofitting of energy efficient separation processes that is based on the concept of shortest separation lines is presented. The basic theory of shortest distillation lines, formulated as a nonlinear programming problem, is given. Two examples are presented that show that energy efficient separations correspond to shortest stripping lines – even when solutions that correspond to minimum energy consumption do not occur at pinch points.

KEYWORDS: shortest distillation lines, energy efficiency, hybrid separations

INTRODUCTION

Batch and continuous distillation remain the primary means of separation in many industries. Other separation techniques like chromatography and membrane separation simply cannot provide the combined purity and volume to be competitive. Thus distillation will continue to be used in some capacity as a principal physico-chemical separation technique for the foreseeable future. On the other hand, distillation consumes significant amounts of energy. With the recent significant increase in global energy demands and every indication that demand will remain high, it is important to consider ways of combining distillation with other separation methods to improve energy efficiency. Hybrid separations – such as extraction followed by distillation and reactive distillation – can often be used to reduce the energy costs of conventional distillation alone. One of the main contributions of this manuscript is the introduction of the novel concept of *shortest distillation lines*, which gives information regarding numbers of stages and minimum boil-up ratio, and in turn permits energy efficient hybrid separation process designs. The other main contribution of this paper shows that the concept shortest distillation lines is widely applicable and forms the basis of a general-purpose methodology for synthesizing, designing, and/or retrofitting all types of energy efficient finite separators!

GOVERNING EQUATIONS

The literature on minimum flows and minimum energy use in distillation is quite large and dates back to the work of Underwood¹. It is well known that minimum energy requirements often correspond to minimum reflux and/or boil-up ratios and an infinite number of equilibrium stages. This condition corresponds to a column that just performs the desired separation or exhibits one or more pinch points. Most methods for determining

minimum energy requirements are therefore based on either algebraic methods for directly finding pinch points or rigorous column simulation methods using algebraic or differential equations. Koehler et al.² give a good survey of methods presently available for finding minimum energy requirements in distillation and their corresponding limitations. However they do not address complex hybrid separations.

Some of the equations used in this work can be found in Fidkowski et al.³ and take the form of differential operating line (or distillation line) equations given by

$$x'_j = [(r + 1)/r]y_j - x_j - (1/r)x_D \quad (1)$$

$$x'_j = [(s)/(s + 1)]y_j - x_j + [1/(s + 1)]x_B \quad (2)$$

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. Equation 1 is easily modified for a partial condenser by replacing x_D with y_D .

A METHODOLOGY FOR ENERGY EFFICIENT HYBRID SEPARATIONS

This paper presents a general methodology for determining minimum energy requirements for a given separation based on the concept of shortest distillation lines. To make the methodology clear, the separation of acetic acid and water is used. For dilute solutions of acetic acid in water (i.e., at or below 30 wt% = 11.5 mol% acetic acid) hybrid separation is often used. In this study, liquid and vapor phases are modeled by the UNIQUAC equation and Hayden-O'Connell equation respectively as given in Prausnitz et al.⁴

The specific hybrid separation scheme studied in this work consist of liquid-liquid extraction followed by two distillations, is one way that acetic acid and water are separated in industry, and thus represents current practice. The primary purpose of extraction is to first remove large amounts of water by exploiting both the density difference between water and solvent and the preferential solubility of acetic acid in the solvent. An appropriate solvent is usually chosen so that the relative volatility of solvent-acetic acid is much higher than that of water-acetic acid so that the internal flows in the subsequent distillations are smaller. For any proposed hybrid separation scheme consisting of extraction followed by acetic acid recovery and then solvent recovery, some of the important synthesis and design questions include

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

It is important to note that in this example the synthesis and design of the distillations require comparisons of columns that have *different feeds* that lie on a liquid-liquid binodal curve because they depend on the separation performed by the extraction column. This is more challenging than the problems studied by Fidkowski³ or those presented in the review paper of Koehler et al.² where the feed under consideration remains fixed. Here, one must be careful to make meaningful comparisons of all of the separations involved. *The purpose of this example is to show that for low purity acetic acid essentially devoid of solvent the correct target extract composition must be determined using the concept of shortest distillation lines and that separators that lead to minimum energy requirements do not always correspond at pinch points.* This, in turn, provides strong evidence for the concept of shortest distillation lines as a unifying principle for synthesizing and designing energy efficient separators.

Let the feed to the extraction column be 10,000 lb/h and have a composition that is 30% acetic acid by weight. Assume that ethyl acetate is used as the solvent and that the desired bottoms composition for the acetic acid recovery column is $x_B = (0.995, 1 \times 10^{-10}, 0.005)$, where the components are in the order acetic acid (AA), ethyl acetate (EAc), and water (W). Moreover, assume that a stripping column is used for acetic acid recovery. Figure 1 shows the paths and lengths of several distillation lines

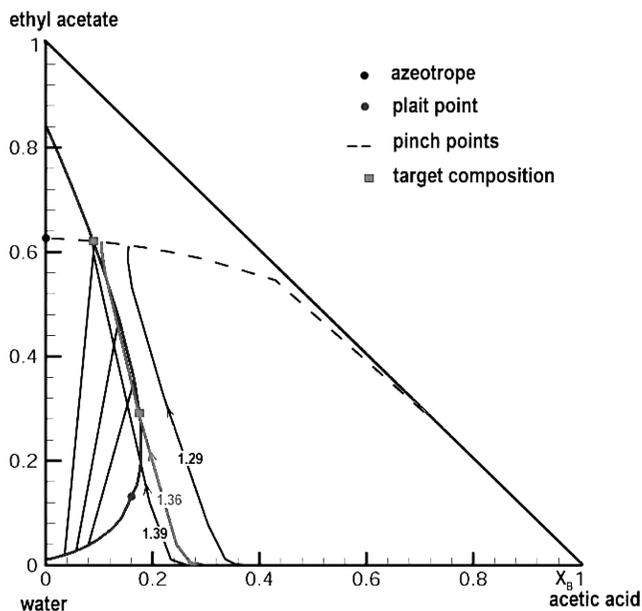


Figure 1. Hybrid separation of lower purity acetic acid

Table 1. Summary of distillation lines and boil-up ratios for acetic acid recovery column

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

*mole fractions of acetic acid and ethyl acetate

for a stripping column that meets the desired acetic acid bottoms composition. Also shown is the liquid-liquid equilibrium at 298 K along with a few liquid-liquid tie lines. Note that there are only two distillation lines that result in feasible stripping columns because the feed and vapor overhead product must simultaneously lie on the stripping line (i.e., equation 2) and the overall material balance line. The longest distillation line corresponds to a boil-up ratio of $s = 10.89$, enters the liquid-liquid region and converges to a pinch point on the binodal curve. The next distillation line from the left is “almost tangent” to the binodal curve at a point very near to the maximum acetic acid concentration, has a boil-up ratio of $s = 9.10$, but eventually converges to a pinch point in the single liquid region. By almost tangent, we mean that a specific stage liquid composition lands exactly on the binodal curve while stages above and below this stage are outside the two-liquid region. The important thing to note here is that the intersection of this distillation line and the binodal curve is not a pinch point.

The distillation line furthest to the right in Figure 1 never enters the liquid-liquid region and is infeasible because, as noted, the material balances for a stripping column cannot be satisfied for a boil-up ratio of $s = 6$. These results are summarized in Table 1.

ENERGY REQUIREMENTS

It turns out that the acetic acid recovery column dominates the overall energy requirements of the hybrid separation scheme for this example. However, it is not the relatively small difference in boil-up ratio that is important to overall energy consumption. Rather it is the large difference in throughput to the acetic acid and solvent recovery columns that results from markedly different performance of the extraction column that is important. For the target extract composition located at the intersection of the pinch point and binodal curves, 355.5 lbmol/h of solvent are required and the resulting extract flow is 568.410 lbmol/h. The reboiler and condenser duties for the acetic acid recovery column are 5.431 and 8.715 MBtu/h respectively while the solvent stripping column reboiler duty is 0.170 MBtu/h. On the other hand, for the target extract composition closest to the plait point in Figure 1, only 81.75 lbmol/h of solvent is required and the extract flow is 281.771 lbmol/h. This large decrease in throughput to the acetic acid and solvent recovery columns results in a considerable reduction in energy demands. In this case, the reboiler and condenser duties for this extract target composition are 2.648 and

Table 2. Summary of energy requirements for feasible hybrid separation of acetic acid-water separation

Distance	Extraction*	Boil-up Ratio	Acid* Recovery	Boil-up Ratio	Solvent* Recovery	Energy (MBtu/h)
1.3908	15	10.89	24	0.017	18	5.431
1.3659	15	9.10	18	0.025	18	2.648

*number of equilibrium stages

4.200 MBtu/h while those for the solvent stripper total to 0.289 MBtu/h. Table 2 summarizes the net energy and stage requirements for both feasible hybrid separation schemes for low purity acetic acid.

Note that Table 2 shows that *the shortest distillation line (i.e., stripping line) from the desired acetic acid bottoms composition to the pinch point curve such that the liquid composition for some tray lies on the binodal curve corresponds to the minimum boil-up ratio for the acetic acid recovery column and the minimum energy requirements for the hybrid separation.* However, this illustration also clearly shows that for low purity acetic acid recovery knowledge of the intersection of the binodal and pinch point curves alone is insufficient to define the design of minimum energy. This is because the most energy efficient separation scheme does not correspond to a pinch point for the acetic acid recovery column that lies on the binodal curve. Rather, it is the concept of shortest distillation lines that gives the minimum energy design.

THE THEORY OF SHORTEST DISTILLATION LINES

Calculation of the shortest distillation (stripping) line can be formulated as a constrained optimization problem that is similar in some ways to the nonlinear programming problem given in Lucia and Taylor⁵ for finding exact separation boundaries. This is illustrated for the acetic acid recovery column within the hybrid separation scheme for which the shortest distillation line, say $\{x_j\}^*$, is given by the solution of the nonlinearly constrained optimization problem

$$\min_s D = \sum_{j=1}^N \|x'_j\| \quad (3)$$

subject to

$$x'_j = [(s)/(s + 1)]y_j - x_j + [1/(s + 1)]x_B \quad (\text{stripping line}) \quad (4)$$

$$x_1 = x_B \quad (\text{bottoms specification}) \quad (5)$$

$$c(x_K) = \|x_K - x_K^b\| = 0 \text{ for some } K \in [1, N] \quad (\text{auxiliary constraint}) \quad (6)$$

where D represents a distance function along a discrete trajectory, $\| \cdot \|$ denotes the two-norm, and $c(x_K)$ is some constraint function that defines any ancillary conditions that must be met to make the design feasible. For example, $c(x_K) = 0$ can be viewed as a constraint that forces the liquid composition on tray K , x_K , for the acetic acid recovery column to lie at some point, x_K^b , on the binodal curve. Note that the unknown optimization variable 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 $N = 300$ in equation 3.

OPTIMIZATION

Note that auxiliary constraints can give rise to a feasible region that is a disjoint set of distillation lines, as illustrated in Figure 1. In our opinion, infeasibility in any auxiliary constraints should be permitted through the use of a penalty or barrier function of the form

$$f = D + P[\Sigma c_j(x)] \quad (7)$$

where P is some penalty parameter and $\Sigma c_j(x)$ is a shorthand notation for any auxiliary constraints. Note that the modified objective function is still a function of boil-up ratio but is now differentiable. However, the use of penalty or barrier functions can introduce multiple minima in the modified objective function as shown in Figure 2, where the minimum energy configuration corresponds to the global minimum of f and thus

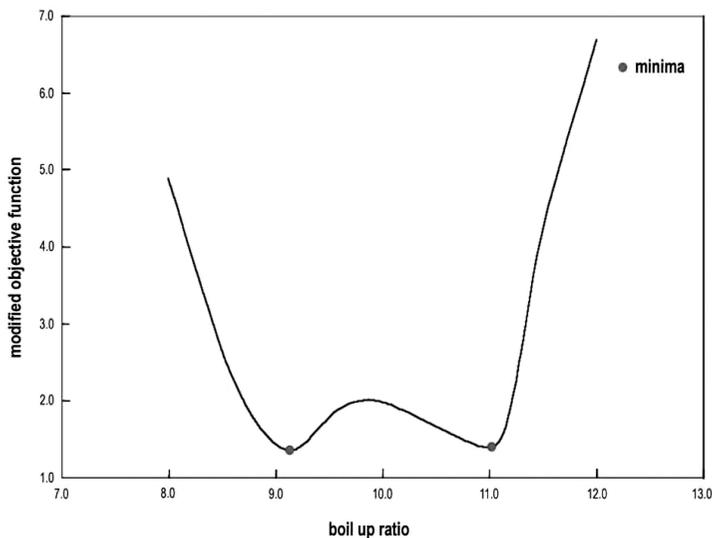


Figure 2. Multiple minima for hybrid separation of acetic acid and water

emphasizes the need for a global optimization algorithm to find the shortest distillation line or most energy efficient separation scheme.

CONVENTIONAL SEPARATORS AND ADDITIONAL SPECIFICATIONS

To show that the proposed synthesis methodology based on the concept of shortest distillation lines is generally applicable a more conventional distillation with a rectifying and stripping section and specifications at both ends of the column is studied. Let the feed be saturated liquid with a flow rate of 100 lbmol/h and let the feed, bottoms, and vapor distillate have compositions of $x_F = (0.5000, 0.3150)$, $x_B = (0.9999, 5 \times 10^{-5})$, and $y_D = \leq 1 \times 10^{-5}, 0.6300$, respectively. Moreover, a separator is considered feasible if $y_{D,AA} \leq 1 \times 10^{-5}$ and $y_{D,EAc} \leq 0.6300$.

Figure 3 shows distillation lines for the liquid composition profiles for several feasible columns along with the corresponding distances of the *stripping portion* of those distillation lines. Note that there are two liquid phases on some of the trays at the top of these columns and that, unlike the previous example, the feasible region is not discrete but comprised of a

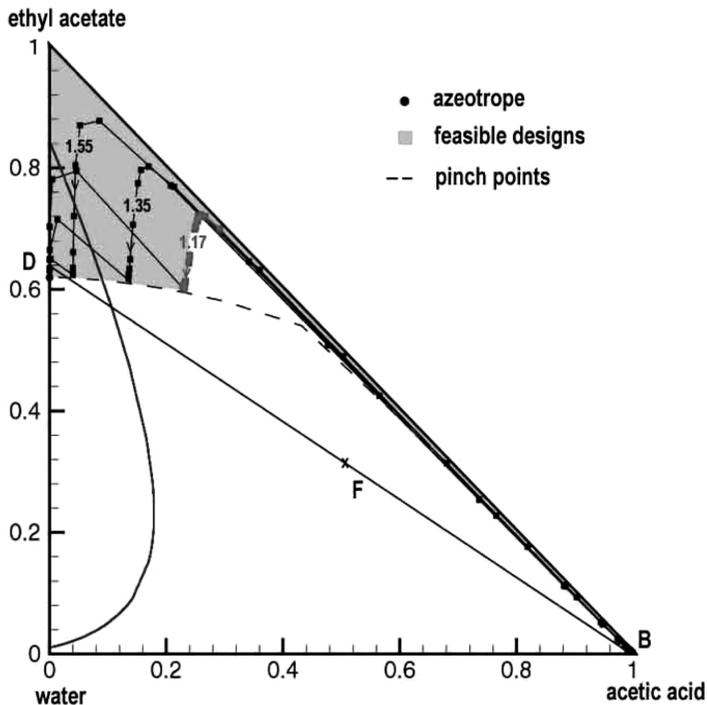


Figure 3. Distillation lines for the separation of acetic acid/ethyl acetate/water

continuous set of distillation lines. More importantly, the column design corresponding to minimum energy requirements is not the one with the smallest total distance (i.e., rectifying plus stripping sections). Rather *it is the column design with the shortest stripping line (and smallest boil-up ratio) that corresponds to the column that uses the least energy.* The reason for this is simple and due to the fact that the boil-up ratio and reflux ratio are coupled through the overall energy balance relationship

$$r = (s - q + 1)[x_{Fi} - y_{Di}]/[x_{Bi} - x_{Fi}] - q \quad (8)$$

where q is the thermal quality of the feed. In this example, $q = 1$ since the feed is saturated liquid. Clearly from equation 8 smaller values of boil-up ratio give smaller values of reflux ratio and correspondingly reduced energy requirements. Table 3 summarizes these results.

The results in Table 3 were determined assuming that a pinch would occur within 300 equilibrium stages. In reality, all pinch points were reached well before 300 stages. Also movement away from any pinch point to the liquid composition in equilibrium with y_D also required very few stages.

The column with minimum energy requirements can be determined from a non-linear programming problem very similar to the one defined by equations 3 to 6. In fact, all that is needed in this case is to add the rectifying line equations as equality constraints and replace the auxiliary constraint (i.e., equation 6) with inequality bounds that define feasibility in terms of the desired overhead product composition. That is, we still minimize the distance of the stripping line subject to equations 4, 5 and the constraints

$$x'_j = [(r + 1)/r]y_j - x_j - (1/r)y_D \quad (9)$$

$$y_{D,AA} \leq 1 \times 10^{-5} \quad (10)$$

$$y_{D,EAc} \leq 0.6300 \quad (11)$$

which guarantee that the rectifying section gives the desired overhead product. Note that in this example equations 10 and 11 can still be treated using a penalty or barrier function approach.

Table 3. Energy requirements for feasible separators for acetic acid/ethyl acetate/water distillation

Stripping Line Distance	Stripping* Stages	Boil-up Ratio	Reboiler Duty (MBtu/h)	Rectifying* Stages	Reflux Ratio	Condenser Duty (MBtu/h)
1.1671	40	3.933	2.051	4	2.933	2.465
1.3521	28	7	3.651	3	6	5.040
1.5479	23	25	13.039	2	24	20.166

*equilibrium stages.

In principle the transition between rectifying and stripping section can occur at any tray in the stripping section. Some choices of transition stage will give feasible columns, others will not. For those columns that are feasible, the number of equilibrium stages in each section and the feed location will change. However, the energy requirements will not change since the boil-up ratio and reflux ratio are related through equation 8. Thus, the results in Figure 3 and Table 3 remain valid irrespective of the choice of transition stage between stripping and rectifying section.

CONCLUSIONS

The synthesis and design of energy efficient distillation and hybrid extraction/distillation separation schemes was studied. The novel concept of shortest distillation lines was introduced. It was shown that the shortest distillation line identifies the correct target extract composition and provides a rigorous methodology for finding the most energy efficient hybrid separation system design. The hybrid separation of low purity acetic acid by extraction with ethyl acetate was used as an example to illustrate key concepts and identify important numerical characteristics of this class of synthesis problems. It was shown that the interpretation of shortest distillation line requires careful wording with respect to the correct measure of distance and that extraction/distillation problems lead to feasible regions that are comprised of discrete (and disconnected) sets of distillation lines. It was also shown that there are cases in which the most energy efficient hybrid separation scheme does not occur at a pinch point. A global optimization formulation, in which constraints are divided into feasible and infeasible subsets, was presented for directly finding the most energy efficient hybrid separation designs. The concept of shortest distillation lines was also applied to a conventional distillation column example. Here, as in the synthesis of the hybrid separation scheme, it was shown that the most energy efficient column design corresponds to the shortest stripping line from the desired bottoms composition to the stripping pinch point curve. In our opinion, these results help support the claim that the concept of shortest distillation lines is a unifying principle for generating energy efficient separation processes.

We close by stating that we have recently shown that the concept of shortest separation lines can be used to determine energy efficient process designs for separations that exhibit tangent and saddle pinch points, other hybrid separation strategies like reactive distillation, and reaction/separation/recycle processes. These results are the subject of a separate paper.

NOTE

Due to space limitations, process flow diagrams, UNIQUAC and Hayden-O'Connell model parameters, and detailed computations for all examples in this paper are available from A. Lucia.

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