

Energy Efficient Hybrid Separation Processes

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

1. Introduction

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

Lucia and Taylor¹ have recently presented a geometric methodology for finding exact boundaries in separation processes and shown that for ternary mixtures all separation boundaries are given by the locally longest residue curves that run from a given unstable node to all reachable stable nodes. See Figure 1—in which the numbers associated with each residue curve represent the distance from any unstable node to all reachable stable nodes. For this illustration of ethanol/ethyl acetate/water at 1 atm, the liquid phase was modeled by the UNIQUAC equation and the vapor phase was assumed to be ideal. The associated binary interaction parameters for the UNIQUAC model can be found in the Appendix.

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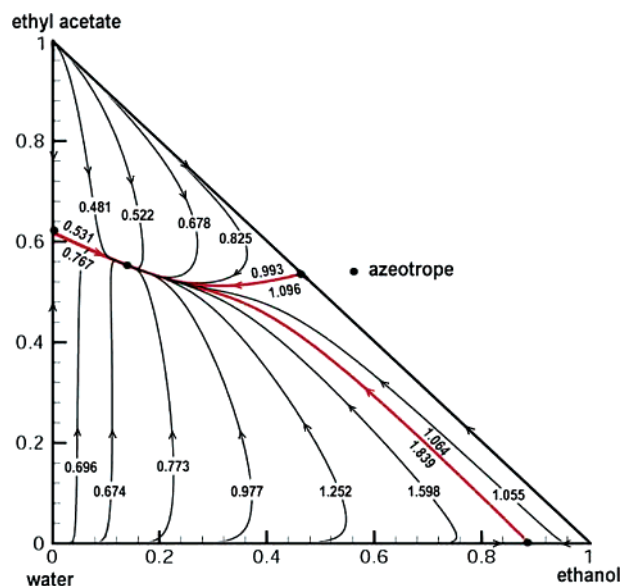


Figure 1. Residue curve map and line integrals for ethanol/ethyl acetate/water.

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

Motivation and Overview of this Work. Recent increases in the demand for energy on the world market have resulted in serious concern over the high energy costs associated with distillation. Hybrid separation schemes (i.e., extraction/distillation, reactive distillation, adsorption/distillation, and so on) represent one way of reducing the energy costs of distillation alone. The motivation for this work comes from our fundamental belief that there is a connection between the length of residue curves (or distillation lines) and the energy needed to perform a given separation. In particular, we began with the intuitive

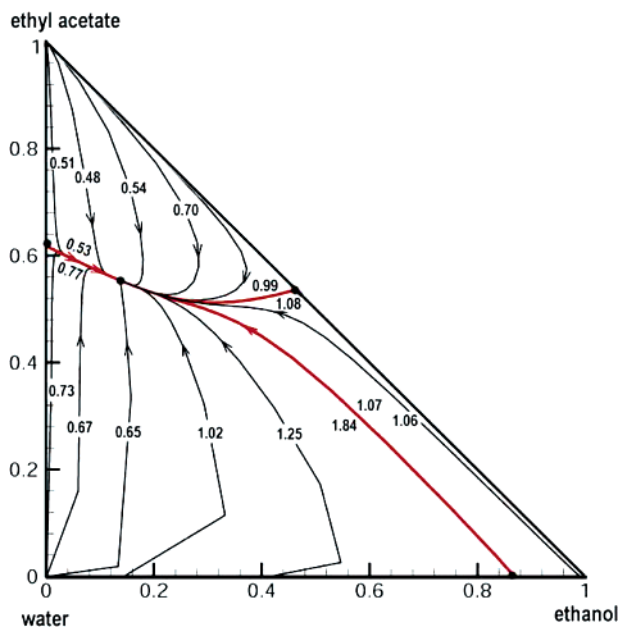


Figure 2. Distillation lines and line integrals for families of sharp separations.

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 task. Because we are interested in finite designs (i.e., finite stages and finite internal flows), we use distillation lines, which are equivalent to component mass balances (or operating lines) for finite separators under constant molar overflow (CMO). Figure 2 shows distillation lines for the ethanol/ethyl acetate/water mixture. Note the strong similarities between Figures 1 and 2. All distillation regions in Figures 1 and 2 contain the shortest paths internal to these separation regions and the longest paths that define the separation boundaries. Moreover, the shortest paths in each figure occur at roughly the same location, their corresponding lengths have approximately the same numerical values, and the longest paths define exactly the same separation boundaries.

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

This paper is organized in the following way. Section 2 gives a brief survey of methodologies for the synthesis and design of energy efficient separations. The governing equations for distillation lines and their relationship to pinch point curves are presented in section 3. Section 4 provides an illustrative example of a hybrid extraction/distillation separation scheme. It is shown that the most energy efficient designs are the ones that correspond to the shortest separation lines and that the shortest separation lines can be used effectively to define the correct target extract compositions. It is also shown that the extraction/distillation synthesis problem has some unique characteristics that make it quite challenging from a mathematical perspective. In particular, the feasible region is not compact but is comprised of a finite set of disjoint distillation lines. In addition, the extract stream that couples the extractor to the primary recovery column changes so the column synthesis is different than that which is

usually studied in distillation. In section 5, the basic ideas—shortest separation lines defined on either continuous or disjoint feasible regions—are formalized. More specifically, a constrained nonlinear programming formulation is given that can be used to directly find energy efficient separation schemes. Conclusions and remarks are presented in section 6.

2. Brief Literature Survey

The literature on minimum flows and minimum energy use in distillation is quite large and dates back to the work of Underwood² for the case of constant relative volatility—including columns with complex configurations. It is well-known that minimum energy requirements correspond to minimum reflux and/or boil-up ratios and an infinite number of equilibrium stages so that the column just performs the desired separation (or exhibits one or more pinch points). Most methods for determining minimum energy requirements are based on either methods for directly finding pinch points or rigorous column simulations.

The method of Underwood is straightforward and, for the most part, applies to ideal mixtures, although extensions to binary azeotropic mixtures and heat effects have been proposed. See the work of Vogelpohl³ and Hausen,⁴ respectively. For nonideal multicomponent mixtures, and particularly those that exhibit azeotropes, methodologies for finding minimum reflux and boil-up ratios are more complicated. Perhaps foremost of those among these methods is the work of Doherty and co-workers,^{5–8} who have developed techniques for nonazeotropic separations as well as homogeneous and heterogeneous azeotropic distillations. The approach of Doherty and co-workers relies heavily on the concept of pinch points, which are fixed points of the differential form of the operating line equations in the rectifying and stripping sections of a column (see the equations in the next section). In general, three types of pinch points are recognized: feed pinch points, saddle pinches, and tangent pinch points. A feed pinch point is easily recognized and corresponds to a pinch point composition equal to the feed composition. Saddle pinches, on the other hand, often occur at compositions that are not feed or product compositions and are generally the result of the attraction of an intermediate boiling azeotrope (i.e., a saddle point of the associated residue curve map). See Koehler et al.⁹ for an illustration of a saddle pinch for a mixture of chloroform, acetone, and benzene. Doherty and co-workers also show that minimum energy requirements result when a saddle pinch in one section of the column is collinear to a feed pinch and an end pinch in the other section of the column. A tangent pinch point occurs when the algebraic form of any operating line equation exhibits a turning point. Physically, this corresponds to a point where the operating line is tangent to the phase equilibrium surface.

Pinch points can be determined by either algebraic or differential methods and most techniques for doing this are based on a constant molar overflow (CMO) assumption—although some procedures do attempt to incorporate energy balance effects. Algebraic methods use the steady state form of column model equations, which are referred to as pinch point equations. These pinch point equations can be solved directly by Newton-like or other equation-solving methods to determine pinch point compositions. For example, Fidkowski et al.⁷ illustrate the use of a continuation method for finding pinch points of the operating lines in either the rectifying or stripping sections of a column. For feed pinch points, the method of Fidkowski et al.⁷ is straightforward. Tangent pinch points, on the other hand, correspond to turning points of the pinch point equations and

require a bit more care in computing because of the singularity condition that accompanies any turning point. Koehler et al.¹⁰ also present a method for finding tangent pinch points, while Zhang and Linninger¹¹ propose a bubble point distance criterion for finding feasible designs, pinch points, and minimum reflux conditions.

Rigorous simulation methods have also been used to determine minimum reflux (and energy) requirements for a variety of column configurations, and many of these methods date back to the 1940s and 1950s. One of the first papers for finding minimum reflux was the work of Brown and Holcomb,¹² who used the tray-by-tray method of Lewis–Matheson for column simulation. Other approaches by Murdoch and Holland¹³ and Acrivos and Amundson¹⁴ were based on the CMO assumption and constant relative volatilities. The methodologies of Shiras et al.¹⁵ and Bachelor,¹⁶ on the other hand, are based on the tray-to-tray approach of Thiele–Geddes and thus permit energy balances to be included in the determination of minimum reflux. Holland and co-workers^{17–19} also present a method for computing minimum reflux for conventional and complex column configurations that is based on their θ -method. The θ -method is also a tray-by-tray approach closely related to the Thiele–Geddes method. While these methods are considered more rigorous than techniques that solve pinch point equations, because they can incorporate energy tray effects, they are also more laborious since they involve energy as well as mass balance equations. Finally, pinch points can also be determined in a reliable manner by integrating the differential form of the operating line equations presented in the next section, and this manner can be considered a rigorous simulation approach very similar to the Lewis–Matheson method.

3. Governing Equations

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

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

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

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 the 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 2 is easily modified for a partial condenser by replacing x_D with y_D .

Equations 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

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

Solving eq 3 for y_j yields

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

which is a component mass balance or operating line for the

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

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 3 and 4 is not exact.

Pinch Points, Minimum Flows, and Energy Efficiency. Consider eq 2. For infinite s , it is easy to show that eq 2 reduces to $x_j' = y_j - x_j$, which has a stable fixed point or pinch point at $y_j = x_j$. In theory, this pinch point occurs when $j = \text{infinity}$. 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 $(c - 1)$ equations

$$0 = sy_N - (s + 1)x_N + x_B = s(K_N x_N) - (s + 1)x_N + x_B \quad (5)$$

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

4. Methodology for Energy Efficient Hybrid Separations

The remainder of this paper presents a methodology for determining minimum energy requirements for a given separation based on the concept of shortest separation lines. To make the methodology clear, the separation of acetic acid and water is used. Acetic acid is an important chemical commodity because many intermediates (e.g., vinyl acetate monomer, terephthalic acid, acid anhydride, and various solvents) are manufactured from low water-content acetic acid. The separation of acetic acid and water by conventional distillation is known to be energy intensive and does not represent the best industrial practice. For dilute solutions of acetic acid in water (i.e., at or below 30 wt % = 11.5 mol % acetic acid), hybrid separation using liquid–liquid extraction followed by distillation is often used. Throughout the remainder of this paper, we model liquid and vapor phases using the UNIQUAC equation and the Hayden–O'Connell equation, respectively, as given in the work of Prausnitz et al.²⁰ Binary interaction parameters for the UNIQUAC model can be found in the Appendix.

Conventional Distillation of Acetic Acid and Water. The reason that the conventional distillation of acetic acid and water

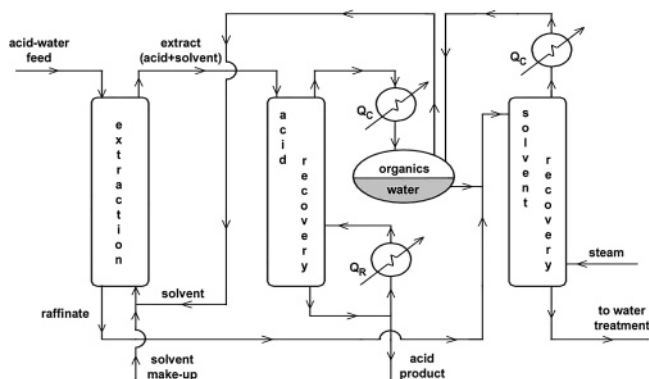


Figure 3. Hybrid separation process for acid production.

is energy intensive, and not used in practice, is because acetic acid is the heavy component and thus forces large amounts of water to be condensed overhead, only to be revaporized internally in the column. The conventional distillation of acetic acid and water also requires high boil-up ratios for high purity acetic acid. To see this, consider a saturated liquid acetic acid–water feed of 11.5-mol % acetic acid. Also, let the bottoms composition be high purity acetic acid with $x_B = (0.9999, 1 \times 10^{-4})$ and the distillate composition be $x_D = (1 \times 10^{-3}, 0.999)$. Let the total feed flow rate be 10 000 lb/h or 438.89 lbmol/h. For this feed and the given product compositions, the distillate and bottoms flow rates are $D = 388.80$ lbmol/h and $B = 50.09$ lbmol/h, respectively. It is also straightforward to determine the minimum reflux and boil-up ratios, either computationally or by using a McCabe–Thiele diagram. The minimum boil-up ratio that gives a feed pinch for this illustration is $s_{\min} = 20.96$. The corresponding minimum reflux ratio is $r_{\min} = 2.70$. The minimum boil-up ratio together with the bottoms flow rate determines the approximate energy requirements. In particular, the vapor boil-up $V' = s_{\min}B = 20.96(50.09 \text{ lbmol/h}) = 1049.89$ lbmol/h, which in turn gives a reboiler duty $Q_R = V'\lambda_{AA} = (1049.89 \text{ lbmol/h})(10431.6 \text{ Btu/lbmol}) = 10.952$ MBtu/h, where ΔH^{vap} is approximated by λ_{AA} , the latent heat for pure acetic acid. Similarly, the duty for a total condenser is $Q_C = D(r_{\min} + 1)\lambda_W = 3.70(388.80 \text{ lbmol/h})(17\,465.22 \text{ Btu/lbmol}) = 25.125$ MBtu/h, where ΔH^{vap} is approximated by λ_W , the latent heat of vaporization of water. The minimum total *heat* requirement for the separation of acetic acid and water by conventional distillation is simply $Q_R = 10.952$ MBtu/h. A conventional distillation with $s = 1.1s_{\min}$ requires 38 stages to operate near the minimum energy requirements.

Hybrid Separation. The hybrid separation schemes studied in this work consist of liquid–liquid extraction followed by two distillations—an acetic acid recovery column and a solvent recovery column—with and without solvent recycle. See Figure 3. Hybrid separation is one way that acetic acid and water are separated in industry and thus represents current practice. The primary purpose of extraction is to first remove large amounts of water by phase separation. Moreover, the solvent is usually chosen so that the relative volatility of solvent–acetic acid is much higher than that of water–acetic acid so the internal flows in the subsequent distillations are smaller. For a proposed hybrid separation scheme, some of the important synthesis and design questions include the following: (1) How many stages are required for the extraction column? (2) What is the number of stages for the subsequent distillations? (3) How much extraction should be performed so that the subsequent distillations use a minimum amount of energy and still produce the desired acetic acid composition? In reality, these questions are strongly interrelated. Moreover, the synthesis and design of the distil-

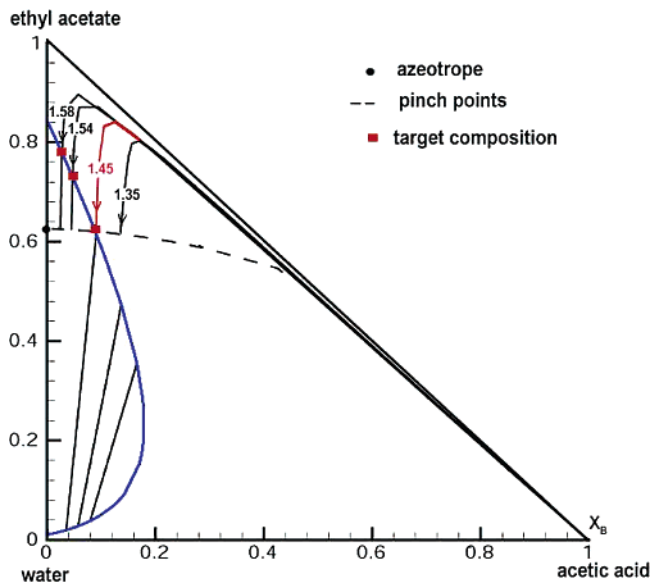


Figure 4. Hybrid separation of acetic acid and water.

lations require comparisons of columns that have different feeds because they depend on the separation performed by the extraction column. This is more challenging than the problems studied by Fidkowski⁷ or those presented in the review paper of Koehler et al.⁹ where the feed under consideration remains fixed. In our case, we must be careful to make meaningful comparisons of all of the separations involved. We begin with the acetic acid recovery column, *which dominates the energy consumption for this process*, and investigate high and lower purity acetic acid production.

Case 1: High Purity Acetic Acid, No Solvent Recycle.

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

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

A closer look at Figure 4 shows that the smallest feasible boil-up ratio that results in a stripping pinch point that is on the binodal curve and produces the desired bottoms composition is $s = 10.92$. The pinch point for this minimum boil-up ratio is

Table 1. Summary of Stripping Lines and Boil-Up Ratios for the Acetic Acid Recovery Column

bottoms comp ^a	dis- tance	feas- ible	boil-up ratio	x_T^a	y_D^a
(0.9999, 0.00005)	1.5808	yes	40.23	(0.0274, 0.7790)	(0.0032, 0.7984)
	1.5385	yes	22.24	(0.0473, 0.7301)	(0.0045, 0.7630)
	1.4473	yes	10.92	(0.0890, 0.6204)	(0.0056, 0.6771)
	1.3521	no	7		(0.0117, 0.7032)

^a Mole fractions of acetic acid and ethyl acetate.

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

	overhead vapor	organic phase	water phase
acetic acid (AA)	0.0056	0.0063	0.0027
ethyl acetate (Eac)	0.6771	0.8291	0.0120
water (W)	0.3173	0.1646	0.9863

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

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

Acetic Acid Recovery Column Decanter. The vapor overhead stream from the acetic acid recovery column will phase separate when condensed. Oftentimes, this liquid is subcooled to enhance phase separation. Table 2 shows the compositions of all streams associated with the overhead decanter where the liquid is subcooled to 298.15 K.

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

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

Table 3. Extraction Column Stream Flow Rates and Molar Compositions

	feed	solvent	extract	raffinate
flow rate (lbmol/hr)	438.89	354.310	567.036	226.167
x_{AA}	0.115	0	0.0890	0.0001
x_{Eac}	0.885	1	0.6204	0.0111
x_W	0	0	0.2906	0.9888

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

	feed	steam	bottoms	overhead
flow rate (lbmol/hr)	322.301	5.479	322.301	5.479
x_{AA}	0.0008	0	0.0005	0.0012
x_{Eac}	0.0114	0	0.0005	0.6421
x_W	0.9878	1	0.999	0.3578

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

distance	extraction ^a	boil-up ratio	acid recovery ^a	boil-up ratio	solvent recovery ^a	energy (MBtu/h)
1.5808	15	40.23	16	0.017	18	18.724
1.5385	15	22.24	17	0.016	18	10.694
1.4473	15	10.92	28	0.017	14	5.515

^a Number of equilibrium stages.

extract is known. Extraction column stream molar flow rates and compositions are summarized in Table 3.

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

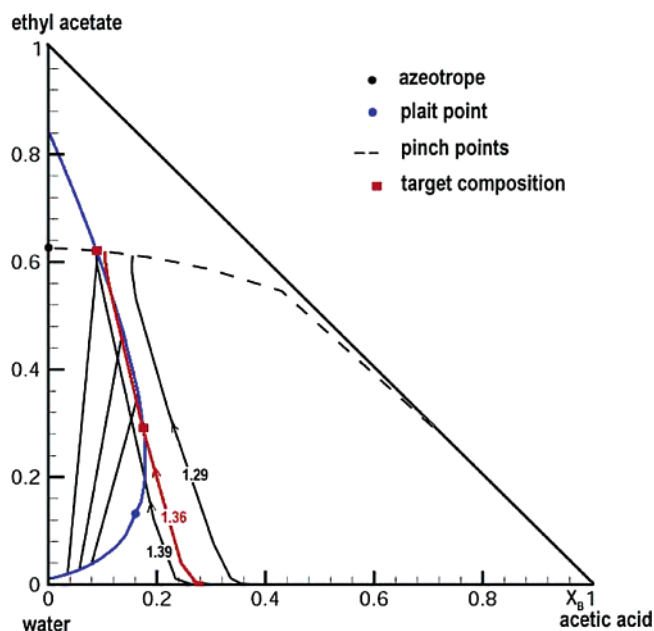
Energy Requirements. The net energy requirements and column equilibrium stage requirements for all feasible hybrid separation schemes for high purity acetic acid are summarized in Table 5. Table 5 clearly shows that *the shortest stripping line from the desired acetic acid bottoms composition to the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

Case 2: Lower Purity Acetic Acid. Note that we do not really need the concept of shortest stripping line to determine the minimum energy requirements for the previous illustration, although this is certainly possible. The correct target composition can be determined by simply finding the intersection of the pinch

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

bottoms comp. ^a	distance	feasible	boil-up ratio	x_T^a	y_D^a
(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)

^a Mole fractions of acetic acid and ethyl acetate.

**Figure 5.** Hybrid separation of lower purity acetic acid.**Table 7. Summary of Energy Requirements for Feasible Hybrid Separation of Acetic Acid–Water**

distance	extraction ^a	boil-up ratio	acid recovery ^a	boil-up ratio	solvent recovery ^a	energy (MBtu/h)
1.3908	15	10.89	24	0.017	18	5.518
1.3659	15	9.10	18	0.025	19	2.795

^a Number of equilibrium stages.

point and binodal curves in Figure 4. Using this target composition and CMO conditions, the boil-up ratios in both the acetic acid and solvent recovery columns can be determined by mass balance principles. *The purpose of this second example is to show that for lower purity acetic acid essentially devoid of solvent the correct target extract composition must be determined using the concept of shortest separation lines.* This is because the correct target composition occurs at a point on the binodal curve that is *not a pinch point*. This, in turn, provides strong evidence for the concept of shortest separation lines as a unifying principle for synthesizing and designing energy efficient separators.

Acetic Acid Recovery Column. For this example, let the desired bottoms composition be $x_B = (0.995, 1 \times 10^{-10}, 0.005)$. Figure 5 shows the paths and lengths of several stripping lines from the desired bottoms composition. Note that, unlike Figure 4, here the stripping lines follow the acetic acid–water axis before turning toward the pinch point curve. Note also that the longest stripping line enters the liquid–liquid region and converges to a pinch point on the binodal curve. The second distillation line from the left in Figure 5, on the other hand, is “almost tangent” to the binodal curve but converges to a pinch point in the single liquid region. By almost tangent, we mean that a specific stage liquid composition lands exactly on the binodal curve while stages above and below this stage are outside the two-liquid region. This can be confusing since it can give the appearance that the stripping line cuts through the liquid–liquid

region. However, it is important to remember that these are discrete stages and the lines connecting them do not have any real physical meaning. Also note that there is no pinch at the composition that lands on the binodal curve. Finally, note that the stripping line furthest to the right in Figure 5 never enters the liquid–liquid region and is infeasible for the same reasons given in the previous case. These results are summarized in Table 6.

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

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

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

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

Sensible Heat Effects, Material Recycle, and Heat Integration. Both energy efficiency and overall process economics can be strongly influenced by sensible heat effects, material recycle, and heat integration. For the illustrative examples, the sensible heat effects that come from subcooled feeds to the acetic acid recovery and solvent columns have been determined to be small compared to the latent heat effects of boiling and condensing. Thus, their impact on the minimum energy require-

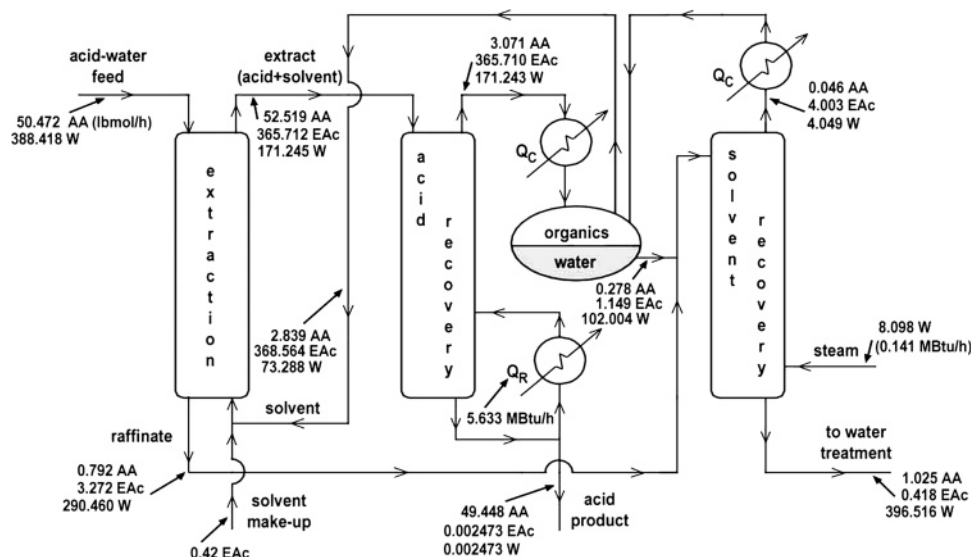


Figure 6. Hybrid separation process of acid production with solvent recycle.

ments has been neglected in this analysis. On the other hand, if desired, the bottoms stream of the solvent recovery column, which is saturated water at 1 atm, can be used to partially preheat the feed to the acetic acid recovery column.

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

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

increases the total energy requirements for the hybrid separation scheme from 5.515 MBtu/h without solvent recycle to 5.774 MBtu/h with solvent recycle.

5. Theory of Shortest Separation Lines

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

Formulation. Calculation of the shortest separation line can be formulated as a constrained optimization problem that is similar in some ways to the nonlinear programming problem given in Lucia and Taylor¹ for finding separation boundaries. We illustrate this for the hybrid separation scheme for acetic acid recovery for which the shortest separation line, say $\{x_j\}^*$, is given by the solution of the nonlinearly constrained optimization problem

$$\min_s D = \sum_{j=1}^{N_s} \|x_j'\| \quad (6)$$

subject to

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

$$x_1 = x_B \quad (\text{bottoms specification}) \quad (8)$$

$$c(x_K) = \|x_K - x_K^b\| = 0 \quad \text{for some } K \in [1, N] \quad (\text{auxiliary constraint}) \quad (9)$$

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

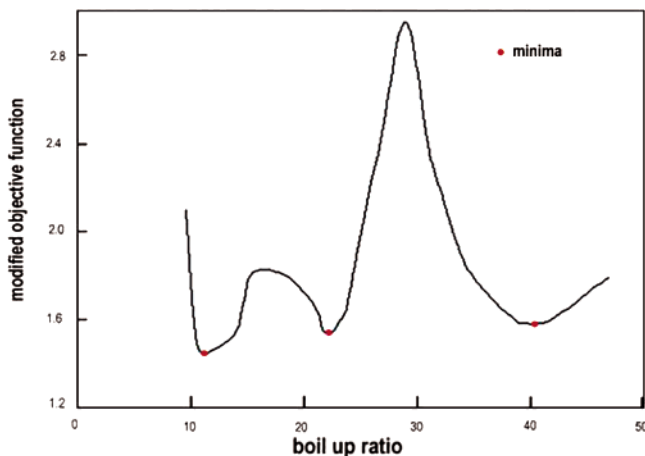


Figure 7. Multiple minima for hybrid separation of acetic acid and water.

number of stages. We typically use $N_s = 300$ as an approximation for the number of stripping stages.

Algorithmic Issues. In our opinion, any optimization algorithm for finding the shortest separation line subject to operating line, specification, and auxiliary constraints should: (1) be a global optimization method as opposed to a local optimizer, (2) enforce feasibility on the operating line and specification constraints at each iteration, and (3) handle auxiliary constraints through the use of a penalty or barrier function approach. Because the ancillary constraints can give rise to a feasible region that is a disjoint set of distillation lines, as illustrated in the hybrid separation of acetic acid and water, enforcing auxiliary constraint satisfaction from one optimization iteration to the next would require the optimizer to jump from one feasible distillation line to another. This is not practical and precludes the use of Newton-based methods, which rely on derivative information. On the other hand, if infeasibility in the auxiliary constraints is permitted through the use of a penalty or barrier function, then there is a smoother transition between feasible solutions since now the modified objective function has the form

$$f = D + P[c(x)] \quad (10)$$

where P is some penalty parameter and $c(x)$ is 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 7 for the hybrid separation of high purity acetic acid presented earlier. Note that the minimum energy configuration corresponds to the global minimum of the modified objective function in Figure 7 and thus clearly shows that a global optimization algorithm is required to find the shortest distillation line or most energy efficient separation scheme.

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

Constraints. It is, in our opinion, straightforward to imagine conditions similar to eq 9 for other hybrid separation system configurations. The primary requirement of these more general auxiliary constraints is that they define a feasible region in some meaningful way. Given that, the auxiliary constraints can be written in the general form $c(x_1, x_2, \dots, x_N, y_1, y_2, \dots, y_N) = 0$, where now c is some vector function of the liquid and vapor

compositions throughout the separator. Since phase equilibrium implies that $y_j = y_j(x_j)$, these constraints can actually be written in the compact form as simply $c(x) = 0$.

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

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

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

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

For $s = 22.24$, the corresponding reflux ratio is $r = 1.0365$. Moreover, the transition between the rectifying and the stripping section can, in principle, occur at any tray in the stripping section. While this does not guarantee optimal placement of the feed, it does provide a large number of alternative feasible designs. However, all of this has no effect on the reboiler duty and thus does not change the energy requirements for the column even though there is a rectifying section. For example, select the stripping tray that lies on the binodal curve as the transition point between stripping and rectification. See again Table 1 or Figure 4. As a result, only one rectifying stage is needed to produce the desired overhead vapor within a half open ball around the specified y_D . However, the stripping line distance to the pinch point curve and the reboiler duty for $s = 22.24$

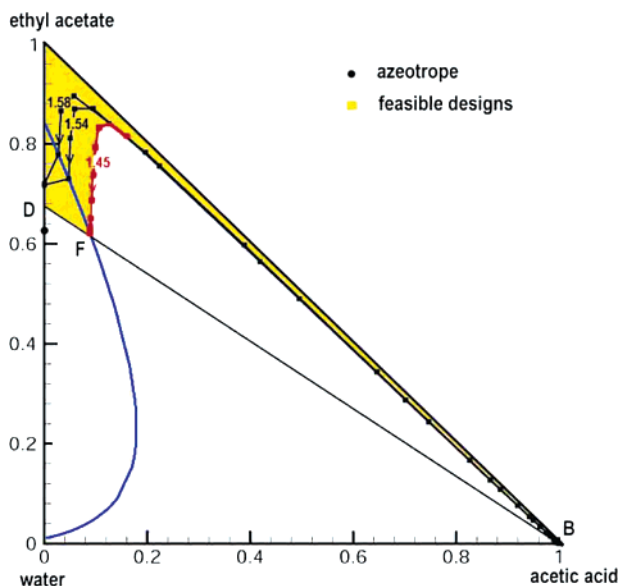


Figure 8. Distillation lines for various acetic acid recovery column designs.

remains the same as before. Thus, the shortest stripping line from the desired bottoms composition to the stripping pinch point curve is still the correct measure of minimum energy requirements—even for conventional separators. Figure 8 clearly illustrates this concept for two alternate separators ($s = 22.24$ and $s = 40.23$) where both alternate separators have 16 stripping stages and 1 rectifying stage.

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

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

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

$$\min_s D = \sum_{j=1}^{j=1} \|x_j'\| \quad (12)$$

subject to

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

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

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

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

$$y_D \times B(y_D, \epsilon) \quad (\text{overhead specification}) \quad (17)$$

where N_s denotes the total number of stripping stages and the last constraint implies that the calculated value of the overhead vapor composition must lie within some half open ball around the specified overhead vapor composition. We treat the distillate constraint using a penalty function similar to eq 10.

6. Conclusions

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

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

Appendix

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

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

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

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

Table A1. Pure Component Constants for the Extended Antoine Equation

component	c_1	c_2	c_3	c_4	c_5	c_6
ethanol	-90.91	-3 465.9	0	-0.062 301	20.486	$2.066 4 \times 10^{-5}$
ethyl acetate	-129.13	-2 259.9	0	-0.096 853	28.02	$4.335 2 \times 10^{-5}$
water	57.042	-7 004.8	0	0.005 388 8	-6.668 9	$-8.505 4 \times 10^{-7}$
acetic acid	386.98	-15 091.	0	0.167 74	-67.642	$-7.273 8 \times 10^{-5}$

Table A2. Binary Interaction Parameters for the UNIQUAC Equation

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

The temperature-dependent interaction terms, τ_{ij} , for the UNIQUAC equation of Prausnitz et al.²⁰ are expressed in the form

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

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

Nomenclature

B = bottoms product molar flow rate

c , $c(x)$ = number of components, constraint function

D = distillate molar flow rate, distance

F , f = feed molar flow rate, modified objective function

K = equilibrium ratio

L = liquid molar flow rate

N_s = number of stripping stages

P = penalty function parameter

Q , Q_R , Q_C = heat duty, reboiler duty, condenser duty

r = reflux ratio

s = boil-up or stripping ratio

V , V' = rectifying section vapor molar flow rate, stripping section vapor molar flow rate

x , x_B , x_D = vector of liquid mole fractions, bottoms composition, liquid distillate composition

x_T , x_F = extract target composition, feed composition

y , y_D = vector of vapor mole fractions, vapor distillate composition

λ = heat of vaporization

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