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A Two-Level Distillation Design Method

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Recently, Lucia et al. have used a distillation line method to develop the concept of shortest stripping line distance approach to minimum energy designs of distillation columns and multiunit processes. It is well known that distillation line methods can be very sensitive to specified product compositions. A two-level distillation design procedure is proposed for finding portfolios of minimum energy designs when specifications are given in terms of key component recoveries. Thus, product compositions are not specified but calculated. It is shown that the proposed two-level design procedure is flexible and can find minimum energy designs for both zeotropic and azeotropic distillations. It is also shown that the two-level design method encompasses Underwood's solution but can find minimum energy designs when Underwood's method fails. Numerical results for several distillation examples involving ternary and quaternary mixtures are presented to support these claims, and geometric illustrations are used to elucidate key points. © 2008 American Institute of Chemical Engineers *AIChE J,* 54: 2888–2903, 2008
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Introduction

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

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

More recently, Lucia et al.[6] have developed a novel and comprehensive approach to minimum energy requirements in distillations as well as multiunit processes based on the concept of shortest stripping line distance. This work clearly shows that minimum energy requirements for all types of processes, distillations, hybrid separations like extraction/distillation, and reaction, separation, recycle processes, can be determined in a straightforward geometric and intuitive manner by finding the shortest stripping line distance for the problem at hand. This new approach is quite general, encompasses many existing methods for finding minimum energy requirements, and is also capable of finding minimum energy

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requirements that do not correspond to pinch points—something the other methods cannot do.

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

Accordingly, this article is organized in the following way. First, a very brief summary of Underwood's method is presented. This is followed by a description of a two-level algorithm for design and optimization based on processing target. The description of the inner loop, which is the shortest stripping line approach of Lucia et al.,[6] includes for the first time all of the equations and derivative expressions necessary to determine minimum boil-up ratios for fixed values of bottoms composition. Next, the details of the outer loop are described. Here, we also provide all of the equations and sensitivity information required to adjust bottoms composition under fixed boil-up ratio to locate a specific processing target. Several numerical examples are presented to illustrate the effectiveness of our two-level design methodology. Three examples show that Underwood's method has a shortest stripping line distance interpretation and represents a global minimum in energy demands for a given set of key component recoveries. Two additional examples involving mixtures that form azeotropes and/or have distillation boundaries are presented to show that Underwood's method often fails to find a feasible design, whereas the proposed two-level design method easily finds a portfolio of feasible minimum energy designs. In all cases, geometric figures are used to illustrate key points. Finally, we discuss the engineering value of our proposed two-level design approach and show that it enables the practicing engineer to get a geometric picture of the effects of bottoms composition on minimum energy demands and span a number of relevant energy efficient scenarios during the synthesis and design process.

A Brief Summary of Underwood's Method

Underwood's original method[1] for finding minimum reflux ratios is well known, and several modifications and extensions[7,8] have been developed over the years. The original method of Underwood considers vapor–liquid equilibrium described by constant relative volatilities and is suitable for Class-1 separations. In Class-1 separations, all components in the multicomponent mixture under consideration distribute between the bottoms and distillate products. Shiras et al.[7] extended the method of Underwood to Class-2 separations—that is mixtures for which some components do not distribute. The equations of Underwood are well known, and not repeated here, except in a limited sense. We refer the reader to the original articles by Underwood or one of the many descriptions of Underwood's method that can be found in the literature.[3,4,7,9]

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

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

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

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

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

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

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

A Design and Optimization Methodology for Hitting Processing Targets

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

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

The Inner Problem

The inner problem is as follows:

$$\min_{s} D = \sum_{j=1}^{N_s} \left\| \Delta x_j \right\| = \left\| x_{j+1} - x_j \right\| \qquad (3)$$

subject to

$$x'_{j+1} = [s/(s+1)]y_j - x_j + [1/(s+1)]x_{B,} \quad j = 1, ..., N_s \qquad (4)$$

$$x_B = x_{B,\mathrm{spec}} \qquad (5)$$

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

$$x'_{j+1} = [(r+1)/r]y_j - x_j - [1/r]x_{D,} \quad j = N_s + 1, ..., N \qquad (7)$$

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

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

Sensitivity information for the inner problem

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

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

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

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

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

which reduces to

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

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

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

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

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

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

Partial derivatives of the distance function

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

$$\Delta_j = x_{j+1} - x_j \tag{14}$$

By the implicit function theorem,

$$\Delta(\Delta_j) = \Delta x_{j+1} - \Delta x_j \tag{15}$$

Use of Eq. 12 gives

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

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

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

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

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

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

and therefore,

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

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

$$= D^2 + 2(\Delta_j^{\mathrm{T}}J_{\Delta j})\Delta s + (J_{\Delta j}^{\mathrm{T}}J_{\Delta j})\Delta s^2 \tag{22}$$

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

$$dD^2/ds = 2\Sigma(\Delta_j^{\mathrm{T}}J_{\Delta j}) \tag{23}$$

$$d^2D^2/ds^2 = \Sigma J_{\Delta j}^{\mathrm{T}}J_{\Delta j} \tag{24}$$

Note that the quantities in Eqs. 23 and 24 are both scalar quantities as Δ_j^{T} is $1 \times (c - 1)$ and $J_{\Delta j}$ is $(c - 1) \times 1$. Also, note that

$$dD^2/ds = 2D(dD/ds) \tag{25}$$

and therefore,

$$dD/ds = \Sigma(\Delta_j^{\mathrm{T}}J_{\Delta j})/D \tag{26}$$

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

$$d^2D/ds^2 = d/ds[dD^2/ds/2D] = [D(d^2D^2/ds^2) - dD^2/ds]/D^2 \tag{27}$$

which gives

$$d^2D/ds^2 = \tfrac{1}{2}[D(\Sigma J_{\Delta j}^{\mathrm{T}}J_{\Delta j}) - 2(\Sigma\Delta_j^{\mathrm{T}}J_{\Delta j})]/D^2 \tag{28}$$

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

The Outer Problem

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

$$F(x_{\mathrm{B}}) = [x_{\mathrm{T}} - x_{N_s}(x_{\mathrm{B}})] \tag{29}$$

Application of the implicit function theorem to Eq. 29 yields

$$\Delta x_{\mathrm{B}} = -J^{-1}[x_{\mathrm{T}} - x_{N_s}(x_{\mathrm{B}})] \tag{30}$$

Recovery fractions

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

$$x_{\mathrm{B},k} = [r_k f_k] / \left[\sum_{j=1}^{c} r_j f_j\right], \quad k = 1, \ldots, c-1 \tag{31}$$

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

$$F(r) = [x_{\mathrm{T}} - x_{N_s}(x_{\mathrm{B}}(r))] \tag{32}$$

Application of the implicit function theorem gives

$$\Delta x_{\mathrm{B},k} = \Sigma\,(\partial x_{\mathrm{B},k}/\partial r_j)\Delta r_j, \quad k = 1, \ldots, c-1 \tag{33}$$

where

$$\Delta x_{\mathrm{B}} = J_r \Delta r \tag{34}$$

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

$$\Delta r = -(J_r^{\mathrm{T}}[J^{\mathrm{T}}J]J_r)^{-1}J_r^{\mathrm{T}}J^{\mathrm{T}}[x_{\mathrm{T}} - x_{N_s}(x_{\mathrm{B}}(r))] = -(J_r^{\mathrm{T}}[J^{\mathrm{T}}J]J_r)^{-1}\mathrm{g} \tag{35}$$

where $g = g(r) = -J_r^{\mathrm{T}}J^{\mathrm{T}}[x_{\mathrm{T}} - x_{N_s}(x_{\mathrm{B}}(r))]$ is the gradient of [1/2] $F(r)^{\mathrm{T}}F(r)$. Equation 35 defines a straightforward Gauss-

Newton strategy to calculate iterative changes in recovery fractions of nonkey components. Iterative corrections to all bottoms compositions can be back calculated from Eq. 34.

Partial derivative information

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

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

where δ is the Kronecker delta function, and *ik* denotes the matrix element in the *i*th row and *k*th column of J_r.

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

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

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

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

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

$$\Delta x_j = J_{j-1}\Delta x_1, \quad \text{for} \quad j = 2, \ldots, N_s \tag{39}$$

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

and where $J_0 = I$.

If we set

$$J = J_{N_s - 1} \tag{41}$$

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

A Two-Level Algorithm for Energy Efficient Design and Optimization

The overall algorithm is very simple.

(1) Given key component recovery fractions and a target composition, x_T, guess x_B.

(2) Solve the inner problem for $s_{\min}(x_B)$.

(3) Measure $\|x_T - x_{N_s}(x_B(r))\| < \varepsilon$, stop. Else, go to Step 4.

(4) Using $s_{\min}(x_B)$ from Step 2, use the outer algorithm to calculate $x_{B,\text{new}}(s_{\min})$.

(5) Set $x_B = x_{B,\text{new}}(s_{\min})$ and return to Step 2.

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

Advantages of the Proposed Two-Level Approach

The proposed two-level approach has several advantages because it

(1) Permits many minimum energy designs to be investigated in one sweep.

(2) Allows for the investigation of direct, indirect, and transitions splits in one sweep.

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

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

Investigation of portfolios of minimum energy designs

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

$$\Delta r = \beta(J_r^{\mathrm{T}}[J^{\mathrm{T}}J]J_r)^{-1}J_r^{\mathrm{T}}J^T[x_T - x_{N_s}(x_B(r))] \tag{42}$$

For β =1, full Gauss-Newton steps are taken. However, by selecting smaller value of β, it is possible to use the set of outer problem equations (i.e., Eqs. 31–41) to investigate any number of desired minimum energy designs en route to the target. For example, if $\beta = 1$ results in five minimum energy designs, then $\beta = 0.25$ will give result in ~20 minimum energy designs—provided one uses a fixed value of β and does not use automatic step size adjustment. This is important because Underwood's method does not always result in minimum energy solutions that correspond to desired product purity specifications. However, our portfolio idea gives the engineer the opportunity to view a set of minimum energy designs and screen those designs with respect to additional desired solution characteristics.

Spanning of direct, indirect, and transition splits

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

Bounds on recovery fractions

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

$$r_{\mathrm{LLK}} \leq r_{\mathrm{LK}} \tag{43}$$

$$r_{\mathrm{HHK}} \geq r_{\mathrm{HK}} \tag{44}$$

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

Determination of feasible designs that Underwood's method cannot find

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

Table 1. Feed Composition and Recoveries for Methanol/Ethanol/Propanol Separation

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

*Feed is saturated liquid.
[†] HK, heavy key; LK, light key.

Numerical Examples

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

Example 1

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

Ethanol, which is an intermediate boiler, is designated as the nonkey component, and thus, the separation corresponds to a Class-1 separation according to classification of Shiras et al.[7] In the material that follows, we show that for all Class-1 separations when the processing target is set to the feed composition (i.e. $x_T = x_F$), the two-level design methodology converges to the Underwood's solution, which in this case is a double-feed pinch (or transition split). We also discuss other advantages offered by our two-level design methodology.

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

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

Iteration	r_E*	$x_B = (x_M, x_E)$	s_{min}	r_{min}	$D^{\dagger}$
1	0.9600	$(3.319893 \times 10^{-11}, 0.350569)$	1.694100	2.67710	0.67851
2	0.7654	$(3.573908 \times 10^{-11}, 0.300880)$	1.552300	1.711570	0.64200
3	0.6803	$(3.697570 \times 10^{-11}, 0.276689)$	1.48340	1.366320	0.62083
4	0.6386	$(3.761357 \times 10^{-11}, 0.264211)$	1.44790	1.210716	0.60896
5	0.6172	$(3.795017 \times 10^{-11}, 0.257626)$	1.429110	1.133780	0.60239
6	0.6058	$(3.813030 \times 10^{-11}, 0.254103)$	1.419100	1.094050	0.59881
7	0.5998	$(3.822685 \times 10^{-11}, 0.252214)$	1.413710	1.073100	0.59686
8	0.5966	$(3.827895 \times 10^{-11}, 0.251195)$	1.410808	1.061920	0.59580
9	0.5948	$(3.830707 \times 10^{-11}, 0.250645)$	1.4092433	1.05591	0.59523
10	0.5939	$(3.832223 \times 10^{-11}, 0.250348)$	1.4084490	1.052759	0.59495
11	0.5934	$(3.832990 \times 10^{-11}, 0.250198)$	1.40797184	1.0510536	0.59477
Results from Underwood's Method					
–	0.5929	$(3.83400 \times 10^{-11}, 0.250000)$	1.407407	1.048898	–

*Recovery fraction of nonkey (ethanol) in bottom product.
†Stripping line distance measured from x_B to stripping pinch point curve.

the outer loop to update values of the recovery fractions, as described by the equations from the previous section.

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

The results in Table 2 provide a portfolio of minimum energy designs with varying bottoms compositions that converge to the double-feed pinch predicted by Underwood's method. In fact, one can easily interpret the results of Underwood's method for the case of a double-feed pinch in the context of the shortest stripping line approach. Underwood's solution for Class-1 separations corresponds to the minimum shortest stripping line distance (or the global minimum stripping line distance) and thus the global minimum energy design for fixed key component recovery fractions—provided it is understood that the composition of the resulting product streams is not a consideration in deciding what is optimal.

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

Iteration	$\|[x_T - x_{N_s}(x_B(r))]\|$	N_s	N_r	y_D (calc) $= (y_M, y_E)$
1	5.48785×10^{-3}	300	41	(0.9523, 0.0476)
2	1.56436×10^{-3}	300	23	(0.8196, 0.1803)
3	4.5462×10^{-4}	300	18	(0.7877, 0.2122)
4	1.3270×10^{-4}	300	15	(0.7730, 0.2260)
5	3.8790×10^{-5}	300	18	(0.7699, 0.2300)
6	1.1327×10^{-5}	300	14	(0.7477, 0.2363)
7	3.3115×10^{-6}	300	16	(0.7320, 0.7052)
8	9.6690×10^{-7}	300	18	(0.7052, 0.2766)
9	2.8208×10^{-7}	300	20	(0.7261, 0.2563)
10	8.4269×10^{-8}	300	20	(0.7168, 0.2473)
11	2.6627×10^{-8}	300	24	(0.7226, 0.2616)

*Initialized with direct split.

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

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

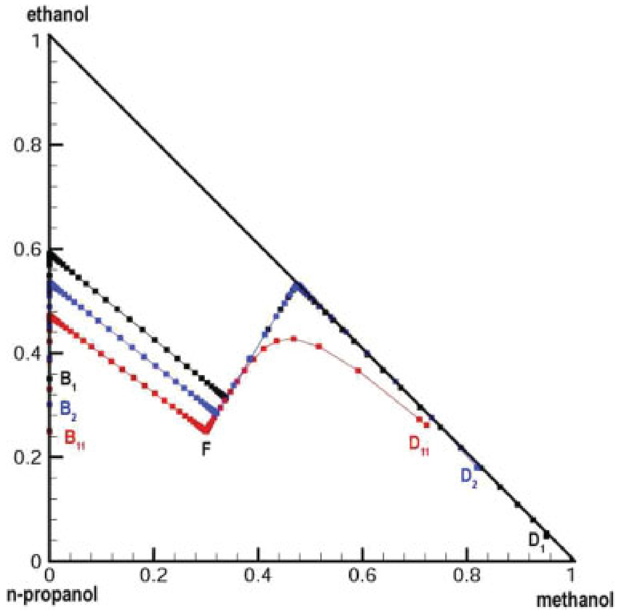

Figure 1. Evolution of minimum energy solutions to Underwood's solution from direct split.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table 4. Two-Level Iterations Initialized Using an Indirect Split

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

*Recovery fraction of nonkey (ethanol) in bottom product.

†Stripping line distance measured from x_B to stripping pinch point curve.

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

Note again that the two-level approach converges to the solution given by Underwood's method—this time from the indirect split—and provides a portfolio of minimum energy designs. Moreover, the same shortest stripping line interpretation of Underwood's method is valid here. That is, Underwood's solution for Class-1 separations corresponds to the minimum shortest stripping line distance (or the global minimum stripping line distance) and thus the global minimum energy design. Finally, note that the norm of the targeting function decreases monotonically as the two-level design procedure converges to Underwood's solution. Figure 2 gives a number of liquid composition profiles for the results shown in Table 3. Table 5 provides additional information about the design portfolio shown in Table 4.

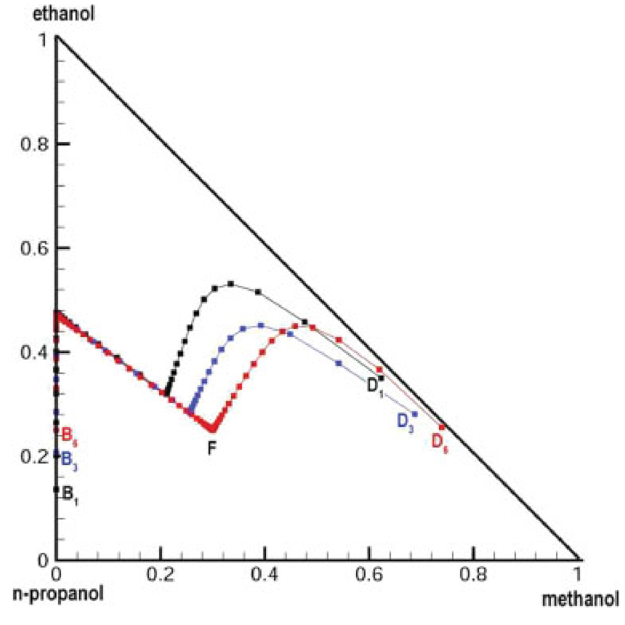

Figure 2. Evolution of minimum energy solutions to Underwood's solution from indirect split.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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

It is also interesting to note that the new estimate predicted by solving the outer loop problem often lands very close to the minimum of each curve for the case of the direct split but that the minima for the curves corresponding to indirect splits can be outside the feasible region—except specifically for the curve that gives Underwood's solution. This is why it is often a good idea to use a line-search parameter $\beta < 1$ for the two-level design procedure when it is initialized using the indirect split.

Remarks. The slight difference between Underwood's solution and the final solutions shown in Tables 2 and 4 can be attributed to fundamental differences between the two methods and numerical inaccuracies. Underwood's method is a group method, whereas the shortest stripping line is a tray to tray method, which always goes from bottom to top. As the final solution in this case is a double-feed pinch, the integra-

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

Iteration	$\|[x_T - x_{N_s}(x_B(r))]\|$	N_s	N_r	$y_D(\text{calc}) = (y_M, y_E)$
1	1.65156×10^{-1}	37	20	(0.5590, 0.4409)
2	6.18529×10^{-2}	49	18	(0.6154, 0.3743)
3	1.21346×10^{-2}	63	18	(0.6876, 0.2810)
4	1.01895×10^{-3}	77	21	(0.6929, 0.2942)
5	5.72960×10^{-5}	86	25	(0.7361, 0.2638)
6	3.46877×10^{-8}	300	25	(0.7394, 0.2556)

*Initialized with indirect split.

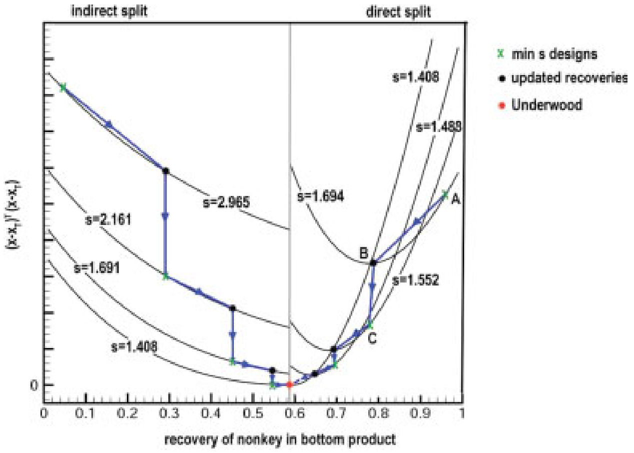

Figure 3. Underwood's method and shortest stripping line approach for double feed pinch.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tion of the rectifying section should start exactly at the pinch point. In practice, the integration usually starts "close to" but not exactly at the pinch point. However, the solutions in Tables 2 and 4 are close enough to the Underwood's solution to be useful in practice.

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

Example 2

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

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

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

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

Direct Splits. The two-level design methodology is initialized to a direct split by setting the nonkey recoveries of iso-pentane (r_{IP}) and n-pentane (r_{NP}) to 0.98. Using these nonkey recoveries and the key component recoveries in Table 6, the compositions of the bottom and top products are calculated. As in the case of Example 1, the two-level design methodology generates a portfolio of minimum energy designs as it alternates between inner and outer loops. This portfolio of minimum energy designs is summarized in Table 7, along with Underwood's solution obtained by using relative volatilities calculated at the feed composition given in Table 6. It can be seen that the outer loop converges monotonically to a solution very close to the Underwood solution. Also, for all inner loop (or shortest stripping line) problems, the solution is considered feasible if the distillate product satisfies the condition $\|y_D - y_{D,spec}\| \leq 0.05$.

It is important to remember that in this example the K-Wilson model (i.e., Eq. 45) was used to describe vapor–liquid equilibrium instead of assuming constant relative volatilities. Hence, the final solution shown in Table 7, as expected, differs to a greater extent from Underwood's solution than the results for example 1. However, this example illustrates two important aspects regarding the proposed methodology.

(1) It is independent of the number of nonkey components, and thus it is applicable to mixtures with any number of components.

(2) Any thermodynamic model can be used to describe vapor–liquid equilibrium, provided the necessary derivative information is obtained properly.

Table 7 also shows the minimum boil-up ratios, reflux ratios, and minimum stripping line distances corresponding

Table 6. Feed Composition and Recoveries for a Quaternary Hydrocarbon Mixture

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

*Feed is saturated liquid.
[†] HK, heavy key; LK, light key.

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

Iter* (r_{IP}†, r_{NP}†)	(x_B, x_{IP}, x_{NP})	s_{min}	r_{min}	D‡	
1	(0.98000, 0.98000)	(0.002535, 0.372624, 0.248416)	1.250655	3.676622	0.3830
2	(0.90001, 0.97291)	(0.002619, 0.353627, 0.254816)	1.189712	2.843316	0.3571
3	(0.81247, 0.91120)	(0.002759, 0.336204, 0.251371)	1.162155	2.063580	0.3521
4	(0.69638, 0.81010)	(0.002985, 0.311844, 0.241845)	1.117530	1.268698	0.3435
5	(0.64788, 0.74947)	(0.003109, 0.302156, 0.233023)	1.095743	0.975778	0.3399
6	(0.62427, 0.72139)	(0.003172, 0.297009, 0.228809)	1.084468	0.850968	0.3378
7	(0.61209, 0.70683)	(0.003205, 0.294276, 0.226552)	1.078479	0.789764	0.3367
8	(0.60885, 0.70299)	(0.003214, 0.293540, 0.225948)	1.076875	0.773912	0.3364
Results from Underwood's Method (For Relative Volatilities at Feed Conditions)					
–	(0.59915, 0.69111)	(0.003241, 0.291335, 0.224036)	1.070436	0.724196	–

*Outer loop iteration number.

†Recovery fraction of nonkey components (i-pentane, *n*-pentane) in bottom product.

‡Stripping line distance measured from x_B to stripping pinch point curve.

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

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

Indirect Splits. As in the first example, it is possible to initialize the two-level design algorithm with a starting guess for the recoveries of the nonkey component that corresponds to an indirect split. Thus, to explore various designs starting from the indirect split, the recoveries of iso-pentane (r_{IP}) and *n*-pentane (r_{NP}) in bottom product were set to 0.02 and 0.05, respectively. Table 9 shows the iteration history for the two-level design approach starting from the indirect split. For all inner loop (or shortest stripping line distance) problems, the solution is considered feasible if the distillate product satisfies the condition $\|y_D - y_{D,spec}\| \leq 0.05$. Table 10 provides additional information regarding the two-level design portfolio shown in Table 9.

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

Iteration	$\|[x_T - x_{N_s}(x_B(r))]\|$	N_s	N_r	y_D(calc) = y_B, y_{IP}, y_{NP}
1	3.81760×10^{-3}	300	14	(0.9246, 0.0717, 0.0036)
2	2.29453×10^{-3}	300	18	(0.8287, 0.1689, 0.0023)
3	1.20000×10^{-3}	300	11	(0.7215, 0.2433, 0.0351)
4	3.44901×10^{-4}	300	14	(0.5980, 0.3133, 0.0885)
5	9.68878×10^{-5}	300	8	(0.5222, 0.3332, 0.1383)
6	2.82425×10^{-5}	300	8	(0.5063, 0.3362, 0.1366)
7	8.29321×10^{-6}	300	8	(0.5097, 0.3158, 0.1336)
8	4.94050×10^{-6}	300	8	(0.5146, 0.3023, 0.1335)

*Initialized with direct split.

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

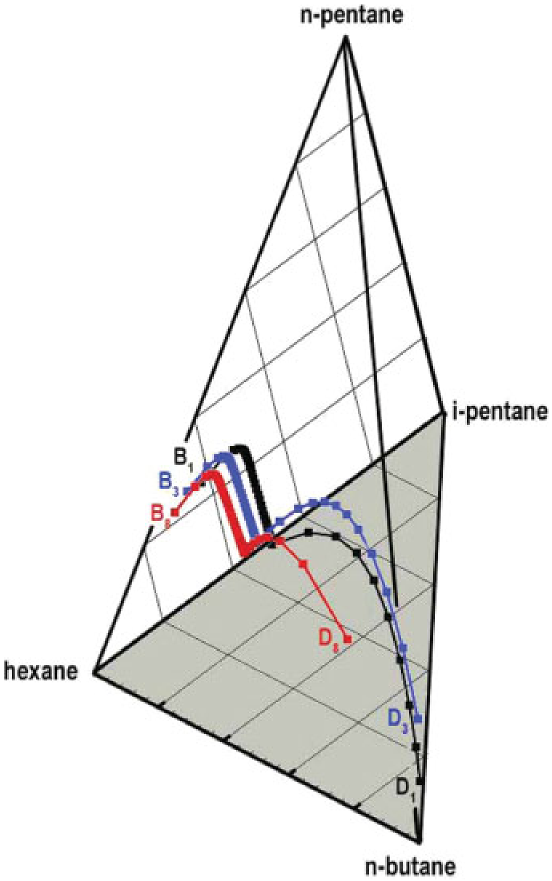

Figure 4. Minimum energy design portfolio for an *n*-alkane distillation.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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

Iter* (r_{IP}†, r_{NP}†)	$x_B = (x_n - C_4, x_i - C_5, x_n - C_5)$	s_{min}	r_{min}	D‡	
1	(0.02000, 0.05000)	(0.006349, 0.019048, 0.031746)	5.045085	1.320000	0.845450
2	(0.09289, 0.20717)	(0.005430, 0.075665, 0.112500)	3.411450	0.989000	0.892531
3	(0.29218, 0.41676)	(0.004255, 0.186495, 0.177342)	2.139120	0.897000	0.755017
4	(0.39979, 0.52059)	(0.003824, 0.229263, 0.199069)	1.677050	0.839000	0.622294
5	(0.46534, 0.58034)	(0.003606, 0.251683, 0.209257)	1.447500	0.803000	0.532224
6	(0.50722, 0.61690)	(0.003481, 0.264847, 0.214743)	1.319300	0.781700	0.472788

*Outer loop iteration number.
†Recovery fraction of nonkey components (i-pentane, n-pentane) in bottom product.
‡Stripping line distance measured from x_B to stripping pinch point curve.

ces, requires minimum reboil and reflux ratio and thus represent a global minimum energy design is valid here. Also, note that the norm of the targeting function decreases monotonically as the two-level design procedure converges to Underwood's solution. Figure 5 gives several liquid composition profiles for the results shown in Table 9.

We remark that the final solution to which the two-level design methodology converges from indirect split is not as close as the one reached from the direct split. This is due to the numerical difficulties associated with finding a design with a double feed pinch. Although this difficulty will vary depending on the specific example, it is always possible to find a solution which is close enough to Underwood's solution for engineering use. Figure 6 shows the variation of nonkey component recoveries for the entire design portfolio (Tables 7 and 9) for this example. Note the design portfolio spans the entire range of nonkey component recoveries and gives a design that is very close to Underwood's solution.

Example 3

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

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

Iteration	$\|[x_T - x_{N_s}(x_B(r))]\|$	N_s	N_r	y_D (calc) $= y_B, y_{IP}, y_{NP}$
1	1.95100×10^{-2}	6	300	(0.2971, 0.4277, 0.2706)
2	1.34494×10^{-2}	7	300	(0.3270, 0.4258, 0.2421)
3	7.56045×10^{-3}	6	300	(0.3555, 0.4215, 0.2172)
4	4.17299×10^{-3}	6	300	(0.3923, 0.3825, 0.1831)
5	2.23239×10^{-3}	6	300	(0.4314, 0.3725, 0.1667)
6	1.17117×10^{-3}	5	300	(0.4494, 0.3412, 0.1989)

*Initialized with indirect split.

Direct Splits. As in the earlier examples, the processing target for this example is set to the feed composition. To initialize the two-level design methodology, the nonkey recovery was first set to a value ($r_B = 0.98$) that makes the separation a direct split. Using this initialization, the two-level design methodology alternates between the inner and outer loops, producing several minimum energy designs. Table 12 gives minimum reboil ratios, reflux ratios, nonkey recovery fractions, and stripping line distances for these minimum energy designs. For all inner loop (or shortest stripping line) problems, the solution was considered feasible if the distillate product satisfies the condition $\|y_D - y_{D,spec}\| \leq 0.05$, where $y_{D,spec}$ changes from one outer loop iteration to the next but can be computed from the given values of x_B, x_F, and the set

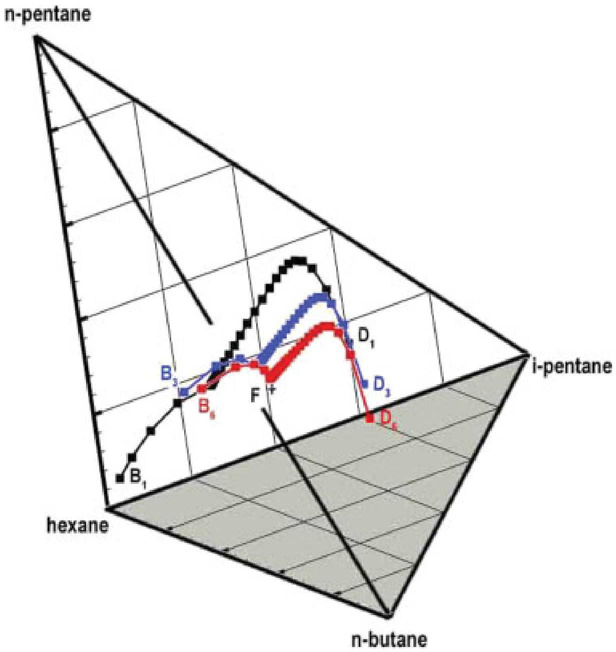

Figure 5. Design portfolio for an n-alkane distillation from indirect split.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

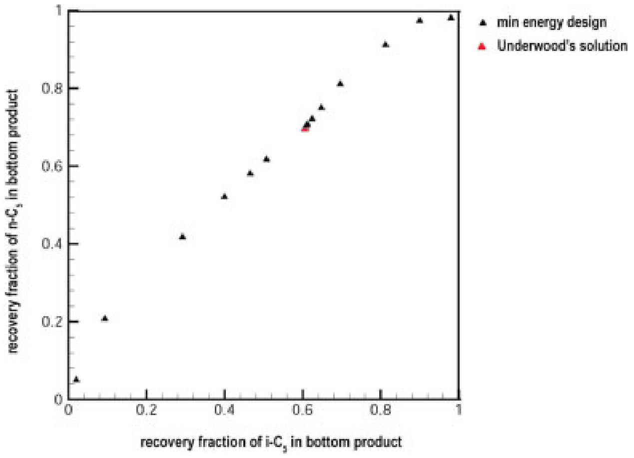

Figure 6. Design portfolio for quaternary alkane mixture.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of recoveries. Underwood's solution, obtained by using relative volatilities calculated at feed conditions, is also listed in Table 12. For a meaningful comparison to Underwood's method, K-values used for calculating relative volatilities were obtained using the UNIQUAC equation and an ideal vapor phase.

From Table 12, it can be seen that the two-level design methodology converges to a final solution (i.e., design 16) which is close to Underwood's solution. Like earlier examples, the shortest stripping line distance for this final solution in the portfolio is the smallest of all minimum stripping line distances, and thus, Underwood's solution can be interpreted as the global minimum in stripping line distance. This final solution from the two-level design methodology also has the smallest reflux ratio and smallest reboil ratio; hence, it is also a global minimum in energy demands for the given set of key component recoveries. However, because of the nonideal nature of the mixture, relative volatilities vary over a wide range, and thus, the final solution from the two-level design methodology differs from Underwood's solution to a greater extent than the final converged solutions for the first two examples.

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

Table 11. Feed Composition and Recoveries for Chloroform/Benzene/Toluene Separation

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

*HK, heavy key; LK, light key.
†Feed is saturated liquid.

Table 12. Two-Level Iterations for Chloroform/Benzene/Toluene Distillation*

Iteration	r_B†	$x_B = (x_C, x_B)$	s_{min}	r_{min}	D‡
1	0.9800	(0.0212, 0.4170)	1.787	3.270	0.6075
2	0.8479	(0.0222, 0.3822)	1.703	2.386	0.5924
3	0.7602	(0.023, 0.3568)	1.64	1.904	0.5786
4	0.6982	(0.0241, 0.3375)	1.591	1.600	0.5663
5	0.6521	(0.0247, 0.3224)	1.553	1.394	0.5563
6	0.6178	(0.0251, 0.3107)	1.522	1.249	0.5477
7	0.5914	(0.025, 0.3015)	1.499	1.143	0.5406
8	0.5710	(0.0257, 0.2941)	1.480	1.063	0.534
9	0.5551	(0.0259, 0.2884)	1.464	1.001	0.529
10	0.5420	(0.0261, 0.2834)	1.451	0.951	0.524
11	0.5315	(0.0262, 0.2795)	1.440	0.912	0.521
12	0.5229	(0.0264, 0.2762)	1.431	0.881	0.518
13	0.5160	(0.0265, 0.2735)	1.424	0.856	0.5156
14	0.5103	(0.0265, 0.2713)	1.418	0.835	0.5135
15	0.5057	(0.0266, 0.2696)	1.413	0.819	0.5118
16	0.5020	(0.0267, 0.2681)	1.409	0.805	0.5104
Results from Underwood's Method					
–	0.48466	(0.0269, 0.2612)	1.390	0.743	–

*Initialized from direct split.
†Recovery fraction of nonkey (benzene) in bottom product.
‡Stripping line distance measured from x_B to stripping pinch point curve.

To reemphasize, this example demonstrates that the two-level design methodology can be applied to any nonideal vapor–liquid mixtures using suitable phase models, simple, or complicated. Moreover, this flexibility is useful when volatilities change over a wide range due to the nonideal nature of the mixture under consideration and where Underwood's method, which is based on assumption of constant relative volatilities, is expected to have greater error in calculating minimum energy requirements. However, what is advantageous is that for the proposed two-level design methodology, the design problem can be specified in a way that is analogous to Underwood's method using only two key component recoveries. Finally, this example illustrates that for the specific set of key component recoveries used here, it is not possible to initialize the two-level design methodology by set-

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

Iteration	$\|[x_T - x_{N_s}(x_B(r))]\|$	N_s	N_r	$y_D(\text{calc}) = (y_C, y_B)$
1	1.1525×10^{-2}	300	24	(0.9950, 00494)
2	7.4888×10^{-3}	300	14	(0.8318, 0.1681)
3	4.9500×10^{-3}	300	12	(0.7846, 0.2153)
4	3.3063×10^{-3}	300	14	(0.7267, 0.2732)
5	2.1986×10^{-3}	300	10	(0.7591, 0.2408)
6	1.4796×10^{-3}	300	9	(0.7235, 0.2764)
7	9.9771×10^{-4}	300	8	(0.7214, 0.2785)
8	6.7761×10^{-4}	300	7	(0.6959, 0.3040)
9	4.6800×10^{-4}	300	8	(0.6777, 0.3222)
10	3.1879×10^{-4}	300	8	(0.6777, 0.3222)
11	2.1798×10^{-4}	300	10	(0.6825, 0.3174)
12	1.4800×10^{-4}	300	8	(0.6412, 0.3577)
13	1.0122×10^{-4}	300	12	(0.6369, 0.3630)
14	6.8723×10^{-5}	300	9	(0.6926, 0.3072)
15	4.6855×10^{-5}	300	8	(0.6718, 0.3208)
16	3.2200×10^{-5}	300	7	(0.6097, 0.3637)

*Initialized with direct split.

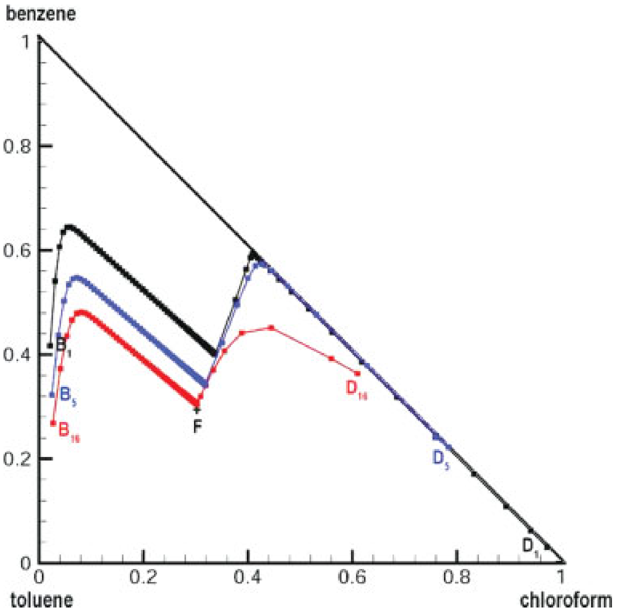

Figure 7. Minimum energy design portfolio for chloroform/benzene/toluene distillation.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ting the nonkey component (benzene) recovery to a value which will make the split close to an indirect split. This is due to the fact that it is not possible to find a feasible minimum energy design with a rectifying pinch that satisfies the constraints for the given key component recoveries. Thus, the design portfolio for this example covers designs from direct split to the approximate transition split.

Example 4

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

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

Table 14. Feed Composition and Recoveries for Methanol/Ethanol/Acetone/Water Still

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

*Feed is saturated liquid.
†HK, heavy key, LK, light key.

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

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

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

As expected, the design portfolio spans a smaller range of nonkey component recoveries than designs in earlier exam-

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

Iter*	$(r_M^\dagger, r_E^\dagger)$	(x_M, x_E, x_A)	s_{min}	r_{min}	$D^\ddagger$
1	(0.6100, 0.8400)	(0.292146, 0.321839, 0.006705)	2.1500	1.34794	0.62364
2	(0.6333, 0.8868)	(0.294731, 0.330166, 0.006515)	2.0900	1.42585	0.61413
3	(0.6524, 0.9262)	(0.296632, 0.336898, 0.006365)	2.1670	1.64691	0.62776
4	(0.6746, 0.9705)	(0.298898, 0.343985, 0.006203)	2.4110	2.12192	0.66682

*Outer loop iteration number.
†Recovery fraction of nonkey components (methanol, ethanol) in bottom product.
‡Stripping line distance measured from x_B to stripping pinch point curve.

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

Iteration	$\|[x_T - x_{N_s}(x_B(r))]\|$	N_s	N_r	y_D(calc) = (y_M, y_E, y_A)
1	4.95093×10^{-3}	300	3	(0.2101, 0.0325, 0.7033)
2	3.57830×10^{-3}	300	5	(0.2361, 0.0062, 0.7339)
3	4.03500×10^{-3}	300	5	(0.228 0.0199, 0.7226)
4	8.18694×10^{-3}	300	6	(0.2224, 0.01811, 0.7425)

ples. Also, note that the norm of the targeting function in Table 16 and the reboil ratios does not decrease monotonically over the outer loop iterations. In fact, both the norm and the reboil ratio decrease on the first iteration and then increase thereafter. Figure 8 gives the distillation line trajectories for first (black), second (red), and fourth (blue) solution in Tables 15 and 16.

If one compares the results for this example to those shown in Figure 3, we can draw some analogies. For example, the curved lines for each outer loop problem in Figure 3 are one-dimensional curves because the mixture under consideration is a three component mixture. For this example and any other four-component mixture, the correct geometric representation would consist of a family of two-dimensional surfaces. Moreover, the global minimum for earlier examples corresponds to a zero-valued minimum in norm. Here, however, the iterations pass through a minimum value of norm that is bounded away from zero. Despite these differences, the outer loop provides a convenient way of exploring alternate minimum energy designs. Moreover, it shows that the design with the global minimum stripping line distance is the one which consumes the least amount of energy.

Table 17. Feed Composition and Recoveries for Formic Acid/Acetic Acid/Water Distillation

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

*Feed is saturated liquid.
†HK, heavy key; LK, light key.

Example 5

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

This example contains four distillation regions, as shown in Figure 9. Note that the specifications given in Table 17 correspond to a distillation in the left hand side of Figure 9, where the distillate product is a cleaner water stream (i.e., cleaner than the feed), and FA is designated as the light key component, and AA is the heavy key component. Water is the nonkey component in this illustration.

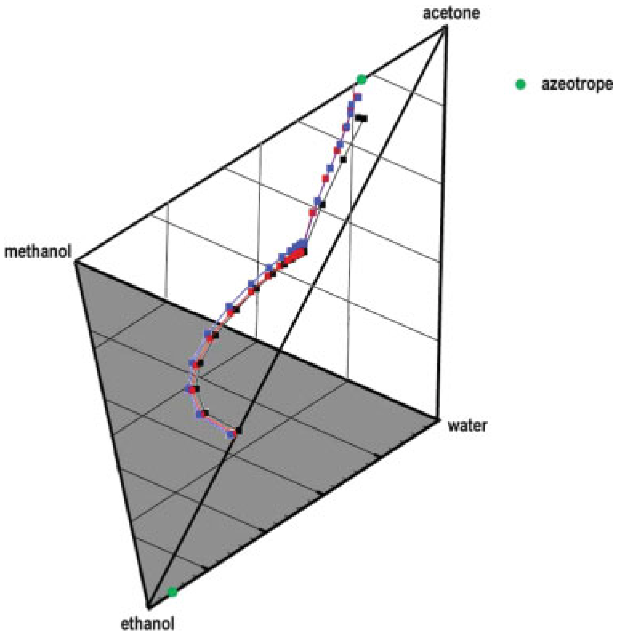

Figure 8. Minimum energy design portfolio for methanol/ethanol/acetone/water distillation.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

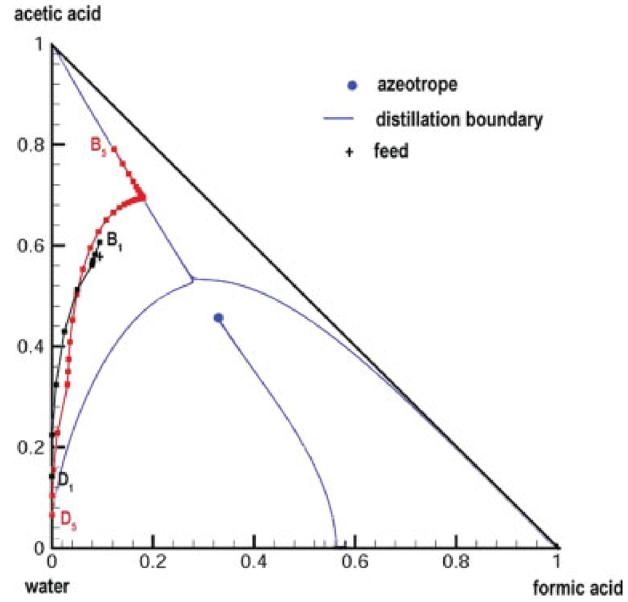

Figure 9. Minimum energy design portfolio for formic acid/acetic acid/water distillation.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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

Iter*	r_W[†]	$x_B = (x_{FA}, x_{AA})$	s_{min}	r_{min}	D[‡]
1	0.8500	(0.0944, 0.6083)	0.4660	6.8258	0.04916
2	0.7608	(0.097, 0.627)	0.8810	8.4082	0.10302
3	0.5248	(0.1065, 0.684)	1.8600	8.5162	0.23934
4	0.2673	(0.1185, 0.7640)	2.8636	7.6610	0.37283
5	0.1856	(0.1229, 0.7924)	4.4746	10.7706	0.55831
6[§]	0.1856	(0.1229, 0.7924)	4.4746	10.7706	0.54080

*Outer loop iteration number.

[†] Recovery fraction of nonkey component (water) in bottom product.

[‡] Stripping line distance measured from x_B to stripping pinch point curve.

[§] Nonpinched design.

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

We tried using Underwood's method for this distillation. In particular, we used both our own in-house computer program of Underwood's method and DSTWU from Aspen Plus with the specified key components. Both versions failed to find even a feasible solution for this distillation—no less a minimum energy design. We have also explored other physically meaningful choices of key components (e.g., FA as the light key and W as the heavy key) and still find that Underwood's method fails to find a feasible design.

Conclusions

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

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

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

*Nonpinched design.

Acknowledgments

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Appendix

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

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

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

where T denotes absolute temperature, and F_{j} is an implicit function. By the implicit function theorem, it follows that

$$\Delta y_j = (\partial y_j/\partial x_1)\Delta x_1 + \cdots + (\partial y_j/\partial x_c)\Delta x_c + (\partial y_j/\partial T)\Delta T \tag{A2}$$

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

$$\Delta x_c = -\sum_{k=1}^{c-1} \Delta x_k \tag{A3}$$

Using Eq. A3 in Eq. A2 gives

$$\Delta y_j = [(\partial y_j/\partial x_1) - (\partial y_j/\partial x_c)]\Delta x_1 + \cdots + [(\partial y_j/\partial x_{c-1}) - (\partial y_j/\partial x_c)]\Delta x_{c-1} + (\partial y_j/\partial T)\Delta T \quad j = 1, ..., c \tag{A4}$$

Summing the Δy's and noting that $\Sigma \Delta y_{\mathrm{j}} = 0$ because of the summation equation for y gives

$$\Sigma[(\partial y_j/\partial x_1) - (\partial y_j/\partial x_c)\Delta x_1 + \cdots + \Sigma[(\partial y_j/\partial x_{c-1}) - (\partial y_j/\partial x_c)]\Delta x_{c-1} + \Sigma(\partial y_j/\partial T)\Delta T \tag{A5}$$

Equation A5 can be solved for ΔT and yields

$$\Delta T = -\{\Sigma[(\partial y_j/\partial x_1) - (\partial y_j/\partial x_c)]/\Sigma(\partial y_j/\partial T)\}\Delta x_1 - \cdots - \{\Sigma[(\partial y_j/\partial x_{c-1}) - (\partial y_j/\partial x_c)]/\Sigma(\partial y_j/\partial T)\}\Delta x_{c-1} \tag{A6}$$

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

$$\Delta y_j = \{[(\partial y_j/\partial x_1) - (\partial y_j/\partial x_c)] - (\partial y_j/\partial T)[\Sigma[(\partial y_k/\partial x_1) - (\partial y_k/\partial x_c)]/\Sigma(\partial y_k/\partial T)]\}\Delta x_1 + \cdots + \{[(\partial y_j/\partial x_{c-1}) - (\partial y_j/\partial x_c)] - (\partial y_j/\partial T)[\Sigma[(\partial y_k/\partial x_{c-1}) - (\partial y_k/\partial x_c)] /\Sigma(\partial y_k/\partial T)]\}\Delta x_{c-1} \tag{A7}$$

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

$$[J_{yx}]_{jk} = \{[(\partial y_j/\partial x_k) - (\partial y_j/\partial x_c)] - (\partial y_j/\partial T)[\Sigma[(\partial y_k/\partial x_k) - (\partial y_k/\partial x_c)]/\Sigma \partial y_k/\partial T)]\} \tag{A8}$$

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