Design/Optimization of Ternary Heterogeneous Azeotropic Distillation Sequences

Various strategies for sequencing heterogeneous azeotropic distillations have been explored. The design and optimization of these systems by simulation-based methods is generally acknowledged to be a very difficult problem (Kingsley and Lucia, 1988). In this article, a simple and accurate design and optimization procedure has been developed. The method does not involve any recycle convergence loops and has been applied successfully to several test problems. Unlike the simulation-based methods, our method is robust to changes in the system optimization variables (e.g., reflux ratio in the azeotropic column).

In order to demonstrate the method, we present design and optimization results for the dehydration of ethanol using a benzene entrainer. Our optimal designs consume significantly less energy than state-of-the-art designs reported in the literature.

Peter J. Ryan
Michael F. Doherty
Department of Chemical Engineering
University of Massachusetts
Amherst, MA 01003

Introduction

It is common practice to break binary azeotropes using either homogeneous or heterogeneous liquid-phase entrainers. Homogeneous entrainers make the separation possible by ensuring that there is no distillation boundary between the two components being separated. On the other hand, heterogeneous entrainers exploit liquid-phase immiscibilities to "jump" across distillation boundaries, as explained by Pham and Doherty (1989b,c).

In recent years, steady-state design and synthesis methods have been developed for each of these two classes of entrainers (Levy et al., 1985; Doherty and Caldarola, 1985; Pham and Doherty, 1989c). For ternary, homogeneous, azeotropic distillation, there is usually either one or two possible sequences for accomplishing the separation for each entrainer. There are, however, as many as five alternative sequences for each heterogeneous entrainer. There is very little published information comparing the relative merits of these various alternatives, either across or within entrainer classes. In this study we will consider the most common class of heterogeneous entrainers and present a design and optimization technique which will allow comparisons of alternative sequences based on economic and energy considerations.

Prototype Problem: Ethanol-Water-Benzene System

In previous papers we have developed generic design and synthesis methods for heterogeneous azeotropic distillation systems using arbitrary labels for the components such as A, B and C to underscore the generality of the techniques (see Pham and Doherty, 1989c). For the sake of variety and interest, we illustrate the design and optimization methods developed in this article using the dehydration of ethanol with benzene as an example. It must be emphasized, however, that the procedures apply equally to a broad range of other heterogeneous azeotropic separations (e.g., dehydration of ethanol with hexane or octane and dehydration of isopropanol with benzene).

The UNIQUAC activity coefficient model was used to represent the phase behavior of the ethanol-water-benzene system, using interaction parameters reported by Prausnitz et al. (1980). Figure 1 compares the experimental heterogeneous boiling envelope data reported by Norman (1945) to the predicted envelope calculated from the UNIQUAC and NRTL (nonrandom two-liquid) activity coefficient models. The parameters used in the NTRL calculations are the same as those used to calculate Figure 13 in Pham and Doherty (1989a). Clearly, of the two models best able to represent very complex, nonideal-phase behavior, the UNIQUAC model is the most applicable for this mixture. Figure 1 also compares the 25°C binodal data of Bancroft and Hubard (1942) to the binodal predicted by the UNIQUAC model. As can be seen, the predictions are quite good. Figure 2 shows the residue curve map for the ethanol-water-benzene system at 1 atm calculated using the UNIQUAC equation. The distillation boundaries are drawn in dashed lines between the azeotropes, and a representative set of simple distillation curves is shown (Pham and Doherty, 1989b).

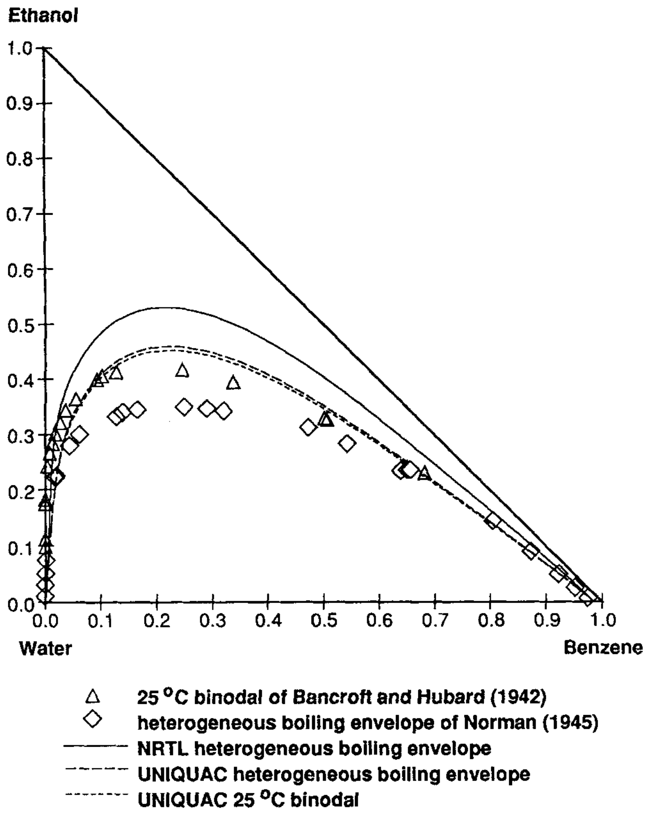

Figure 1. Phase equilibria for the mixture ethanol-water-benzene at 1 atm: calculated vs. experimental.

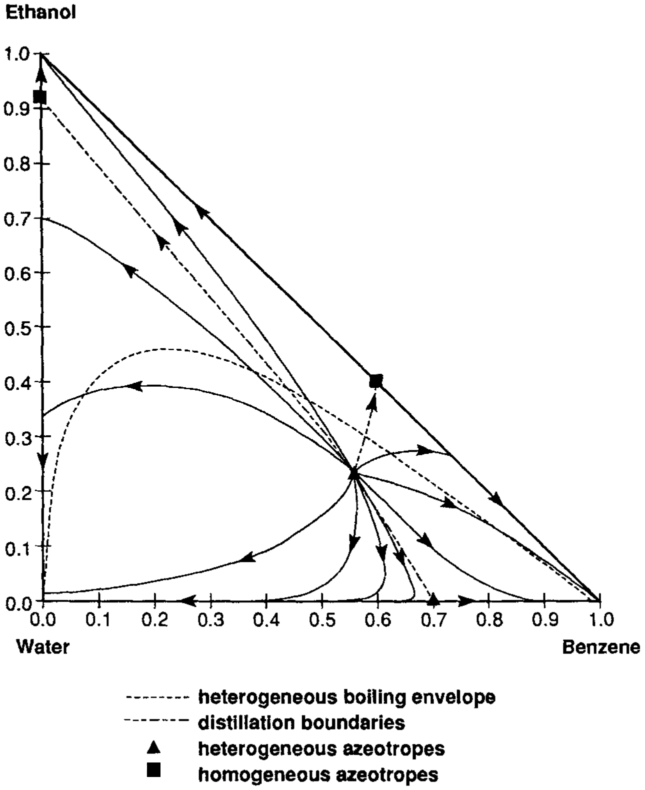

Figure 2. Residue curve map for the mixture ethanol-water-benzene at 1 atm pressure using UNIQUAC equation.

Heterogeneous systems require a means of distinguishing between absolutely stable and metastable phases, with corresponding VLE (vapor-liquid equilibrium) and VLLE (vapor-liquid-liquid equilibrium) procedures to properly model the phase equilibria. In this work, the spline stability test suggested by Ryan (1989) was used. Basically, this stability test fits a cubic spline through the endpoints of the tie lines describing the heterogeneous boiling envelope. The question of phase stability is reduced to a simple test of whether the overall liquid composition lies inside the heterogeneous boiling envelope (unstable) or outside the envelope (stable). The appropriate phase equilibrium procedure is then called depending on the results of this test.

Preliminary Screening of Alternative Sequences

The literature contains many options for sequencing heterogeneous, azeotropic distillation systems. These sequences generally consist of either three or four columns with various techniques for handling the entrainer recycle stream. In rare cases, the tie lines in the phase diagram are such that an entrainer recovery system is not needed, as in the case of dehydration of sec-butanol with di-sec-butyl ether as an entrainer (Kovach and Seider, 1987). Pham and Doherty (1989c) have given a critical review of most alternatives and explained their operation in terms of residue curve map analysis. Typical four- and three-column designs are shown in Figures 3 and 4, respectively. There are a total of four different alternatives for the three-and four-column sequences, depending on where the recycle stream returns to the process. According to Pham and Doherty (1989c), the four-column sequence has no advantage over the three-column sequence. Thus, we restrict attention to sequences containing three columns at most.

The three-column sequence has two alternative entrainer recycle designs to choose from. The entrainer recycle stream could be returned directly to the decanter (as is found in most published studies) or sent directly to the azeotropic column as either a second feed stream or mixed with the reflux stream. (These last two options are indistinguishable, since most azeo-columns have only one or two trays in the rectifying section.) Pham and Doherty (1989c) have shown that, in the former case, extremely high reflux ratios in the azeo-column (typically in excess of 25) are required. Therefore, this option was eliminated from the beginning. The remaining three-column sequence with the entrainer recycle stream returned to the reflux stream of the azeo-column was therefore taken as the most promising alternative out of all those available from the literature.

A novel two-column sequence has been suggested by Lynn (1986), which eliminates the preconcentrator and sends the dilute ethanol feed stream directly to the entrainer recovery column (Figure 5). The two alternative entrainer recycle schemes described in the three-column sequence are now reduced to a single recycle option: sending the entrainer recycle stream to the azeo-column as the primary feed for this column. The total number of alternatives for this separation is now five, compared to the two sequence alternatives available if a homogeneous azeotropic entrainer is used to dehydrate ethanol (Knight and Doherty, 1989).

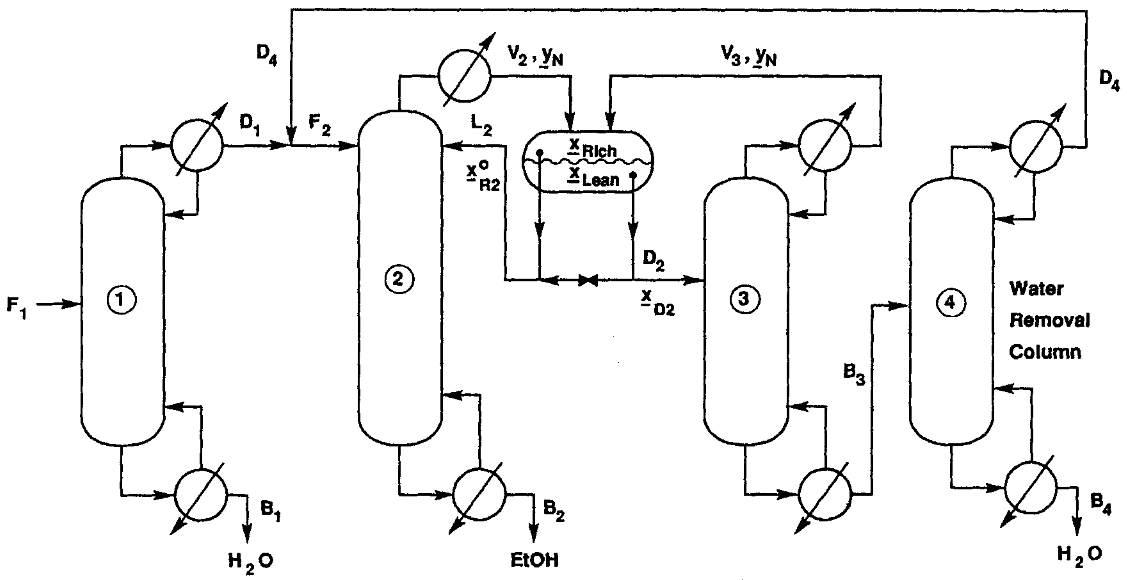

Figure 3. Four-column sequence.

Decoupling the Sequence for Design and Synthesis

The heart of every heterogeneous, azeotropic distillation sequence is the azeotropic column and its decanter. The azeotropic column can be designed either to include or exclude phase splitting on the trays of the column. Associated with the azeotropic column and decanter are an entrainer recovery column and perhaps a preconcentrator. There is always a recycle loop involved in this class of separations which returns the entrainer stream to the azeotropic column. Because of their complex configurations, these systems are difficult to design by conventional methods, which require each column to be converged separately and then the entire sequence reconverged repeatedly until the composition, temperature and flow of the recycle stream converges.

All these convergence loops can be eliminated by employing the boundary-value design procedure developed by Knight and Doherty (1989). In this procedure it is possible to specify the

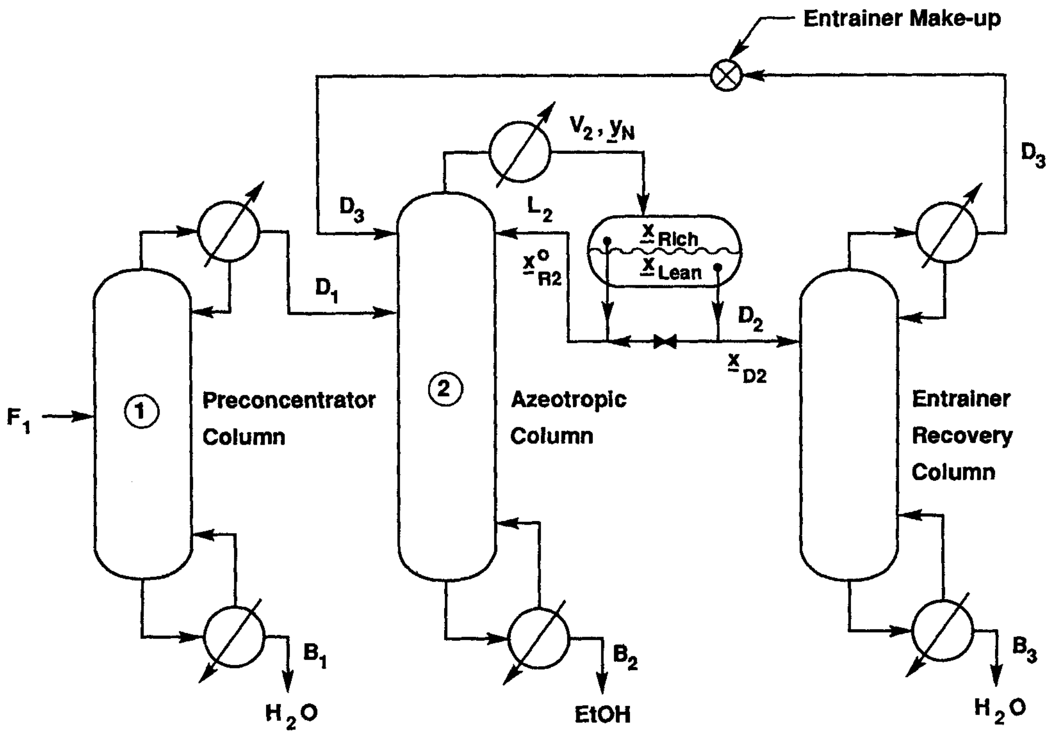

Figure 4. Three-column sequence.

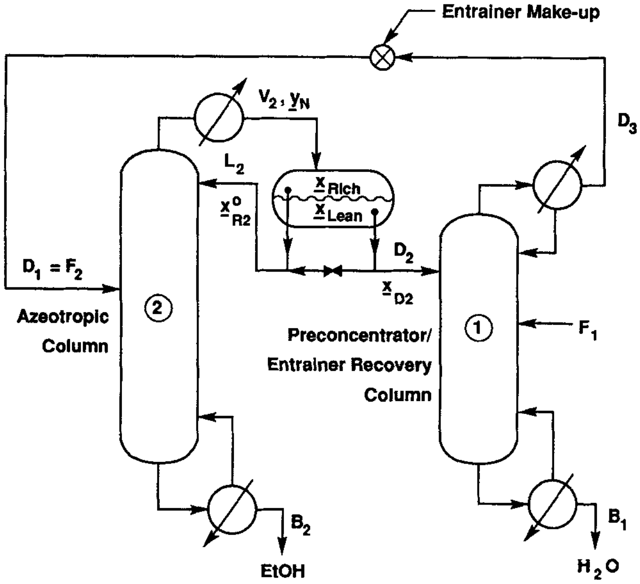

Figure 5. Two-column sequence.

state of the inputs and outputs to each column independently. Thus, they may be chosen so that all interconnections, including recycle streams, have identical composition, temperature, and flow rate at their origin and destination. The decoupling of the individual tasks enables the designer to set target specifications on all stream compositions. These target specifications in turn set the stream flow rates, provided the flow of the main process feed to the sequence is specified. This greatly simplifies the modeling of the sequence since each unit operation can be modeled separately and the total annual cost of each operation can then be combined to yield a total annual cost for the sequence.

Once suitable target composition specifications have been assigned to each independent stream in the sequence, and a flow rate of one stream (the dilute ethanol feed stream in our case, although it could just as easily be the production rate of product) has been made, material balances around the sequence will yield the flow rates of the remaining streams. Not all target specifications in a sequence can be assigned independently, since consideration must be given to intersection points of mass balance lines which share a common stream or to streams which are mixed to produce an overall stream into or out of a vessel.

To illustrate the proper assignment of target composition specifications (see Pham and Doherty, 1989c, for a detailed discussion), Figure 6 presents a set of material balance lines for the three-column sequence with independent mass balance lines drawn in solid and dependent mass balance lines drawn in dashed. The intersection point of the dependent and independent mass balance lines fixes the overall feed composition to the azeo-column. The two- and three-column sequences are designed to restrict phase splitting to the decanter entirely. This ensures the highest tray efficiencies in the azeotropic and entrainer recovery columns (Davies et al., 1987) and a better phase split in the decanter.

Column Models

Since the liquid-liquid-phase splitting which characterizes this class of separations is restricted entirely to the decanter, the column models in these sequences are similar to the models for a homogeneous distillation sequence. A boundary-value tray-by-tray method which includes heat effects was used to determine the single-phase liquid composition on each tray. The stages in the column are numbered with reference to the section in the column (stripping or rectifying). In the rectifying section, the (total) condenser is numbered zero, the first equilibrium stage from the top of the column is stage 1, and the subsequent stages are identified as the *m*th stage and incremented from this top stage toward the feed stage. In the stripping section, the reboiler is equilibrium stage zero, and the subsequent stages are identified as the *n*th stage and are incremented from the reboiler up to the feed stage. The minimum reflux ratios for the individual columns were determined using an extended version (to include heat effects) of the algorithm of Pham et al. (1989).

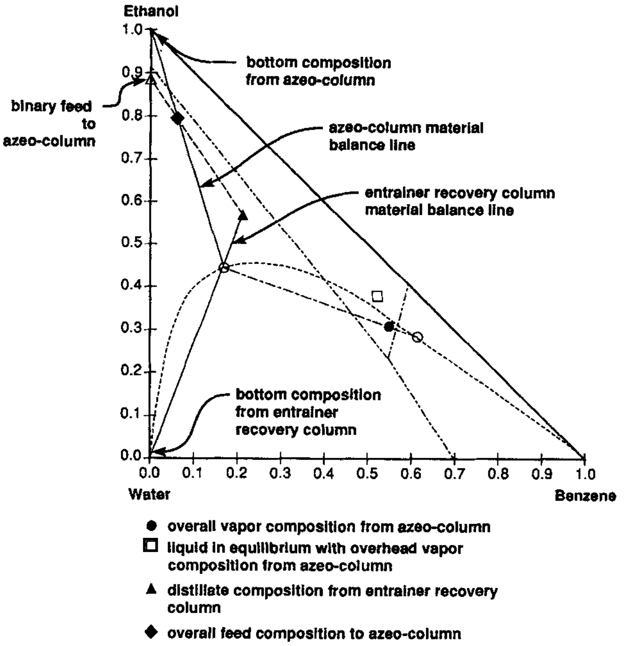

Figure 6. Material balance lines for the three-column sequence.

The stripping profile is calculated from

$$\underline{x}_{n+1} = \frac{s_n}{(s_n + 1)}\underline{y}_n + \frac{1}{(s_n + 1)}\underline{x}_B \tag{1}$$

$$s_n = \frac{h_1^L - h_{n+1}^L + s_{ext}(h_1^L - h_0^V)}{h_{n+1}^L - h_n^V} \tag{2}$$

where s_{ext} is the external reboil ratio, s_n is the reboil ratio on stage *n*, and $\underline{x}_B$ is the bottoms composition; the latter is fixed as a target and serves as an initial condition for the stripping profile. The enthalpies refer to liquid- or vapor-stream enthalpies associated with the *n*th equilibrium stage.

The rectifying profile is calculated from

$$\underline{y}_{m+1} = \frac{r_m}{(r_m + 1)}\underline{x}_m + \frac{1}{(r_m + 1)}\underline{x}_D \tag{3}$$

$$r_m = \frac{h_1 - h_{m+1}^V + r_{ext}(h_1^V - h_D)}{h_{m+1}^V - h_m^L} \tag{4}$$

where r_{ext} is the external reflux ratio, r_m is the reflux ratio on stage m, and $\underline{x}_D$ is the distillate composition; again, the latter is fixed as a target and serves as an initial condition for the rectifying profile. The boundary-value procedure for the main azeo-column and its decanter is slightly different from that for the other columns, as described by Pham et al. (1989).

In the contrast to the CMO (constant molar flow) case, the system of finite-difference equations representing the stripping profile is implicit in the independent variables $\underline{x}_{n+1}$ and s_n due to the dependence of s_n on the liquid-stream enthalpy of the $(n + 1)$th stage. Similarly, the finite-difference equations representing the rectifying profile are implicit in the independent variables $\underline{y}_{m+1}$ and r_m through the vapor-stream enthalpy of the $(m + 1)$th stage.

These systems are also very nonlinear due to the dependence of the equilibrium calculations on the UNIQUAC activity coefficient model. To solve these systems of equations, a CMO continuation method was developed and implemented with a Levenberg-Marquardt nonlinear root finding algorithm (IMSL Math Library). In the stripping section, the root finder was supplied with the CMO approximation of the liquid composition on stage $n + 1$ and the corresponding reboil ratio s_n as initial guesses. In the rectifying section, the CMO approximation of the vapor composition leaving the $(m + 1)$th stage and the corresponding reflux ratio r_m were used as initial guesses. Convergence of these systems was very fast using the CMO continuation scheme. The use of a CMO initial guess gives the continuation method an excellent predictor/corrector capability and a natural step-length adjuster between stages.

Table 1. Column Specifications

Figure	Mole Frac.	Feed $\underline{x}_F$	Bottoms $\underline{x}_B$	Distillate $\underline{x}_D$	Reflux $\underline{x}_L$	Condenser $\underline{y}_N$
7	Benzene	0.0579	0.0000	0.1657	0.6001	0.5511
	Ethanol	0.8049	0.9990	0.4439	0.2851	0.3031
	Water	0.1372	0.0010	0.3904	0.1148	0.1458
8	Benzene	0.1657	0.0000	0.2150		
	Ethanol	0.4439	0.0050	0.5743		
	Water	0.3904	0.9950	0.2107		
9	Benzene	0.1657	0.0000	0.2150		
	Ethanol	0.4439	0.0050	0.5743		
	Water	0.3904	0.9950	0.2107		
10	Benzene	0.0033	0.0000	0.0579		
	Ethanol	0.0499	0.0050	0.8049		
	Water	0.9468	0.9950	0.1372		

The intersection of the liquid composition profiles is determined at the chosen operating reflux ratio, thereby providing the total number of theoretical trays in each section of the column. The overall tray efficiency for each column was determined using O'Connell's correlation (Douglas, 1988). Each column was then priced using the operating (i.e., energy) and capital cost models described by Douglas (1988).

Figure 7 presents the liquid composition profiles for the main azeotropic column at 1.15 r_{min} for a typical target overhead vapor composition. Specifications for this column (and all other columns) are listed in Table 1. This corresponds to the optimum reflux ratio of 7.86. The numbers of theoretical trays above and below the feed are 2 and 37, respectively. Figure 8 shows the profiles for the corresponding entrainer recovery column operated at its optimal reflux ratio of 1.2, which is also about 1.15 r_{min}. For this column, the numbers of theoretical trays above and below the feed are 8 and 3, respectively.

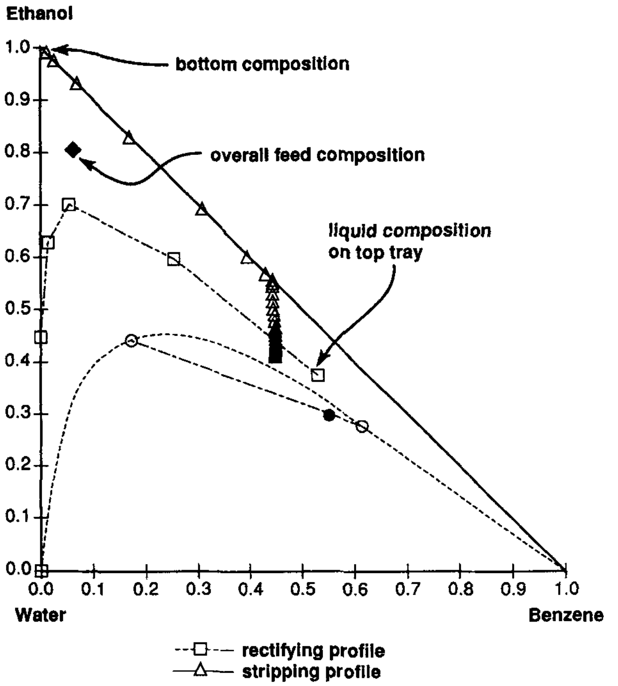

Figure 7. Composition profiles for the azeo-column at $r = 7.86$ ($r_{min} = 6.83$, $\Phi = 5.86$).

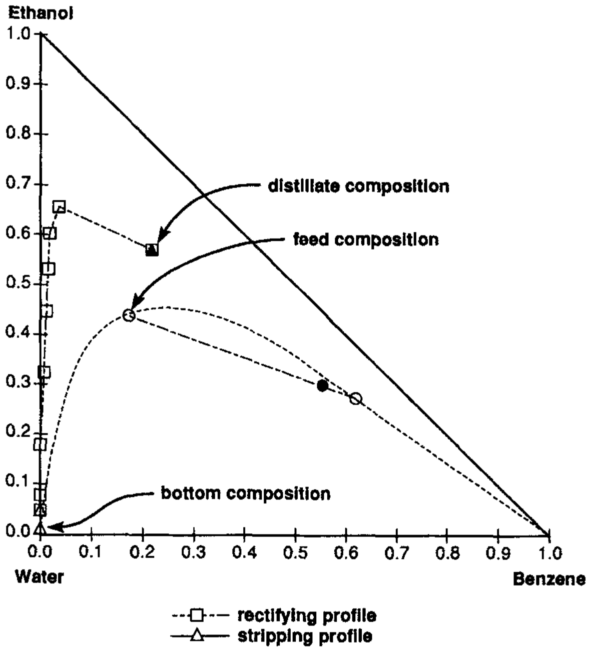

Figure 8. Composition profiles for the entrainer recovery column at $r = 1.20$ ($r_{min} = 1.05$).

Modeling the Third Column as a Stripper

Many of the commercial applications of this sequence use a stripper for entrainer recovery. Thus, we included this alternative in our study. The target distillate and bottoms compositions remain identical to those previously set for the third unit separator. Unlike the case of a distillation column, a stripper has no degrees of freedom left once these targets are set. Therefore, we solve the system of finite-difference equations (Eqs. 1 and 2) up from the bottom (i.e., starting from the initial condition $\underline{x}_1 = \underline{x}_B$) and vary the value of s_{ext} until the stripping profile passes through the liquid composition whose equilibrium vapor is the distillate specification for the stripper. This equilibrium vapor is drawn off the top tray of the stripper and fed to a total condenser which yields the specified distillate composition. Figure 9 shows the liquid composition profile of the stripper passing through the target specification, i.e., through the liquid whose equilibrium vapor is the distillate specification of the stripper. Once this is achieved, the design of the stripper is complete and it can be priced in the usual way.

Modeling the Two-Column Sequence

The main difference between the three- and two-column sequences is the modification of the entrainer recovery column to accept the dilute ethanol stream. The main azeotropic column remains absolutely unchanged with respect to the target compositions, the shapes of the rectifying and stripping profiles, the minimum reflux ratio, stream flow rates, and number of stages. The overall feed to the entrainer recovery column is now made up of two streams: the lean phase coming from the decanter and the dilute ethanol feed stream. This new overall feed composition requires that we set a new target distillate composition in order to keep the feed composition to the azeotropic column the same. Figure 10 shows the finite-difference composition profiles for the combined entrainer recovery/preconcentrator column operating at a reflux ratio of 4.05 ($\approx 1.15\ r_{min}$). The overall feed is located in the bottom lefthand corner of the composition simplex. The target distillate composition for the new entrainer recovery column is equal to the overall feed composition to the azeo-column reported in Figure 6.

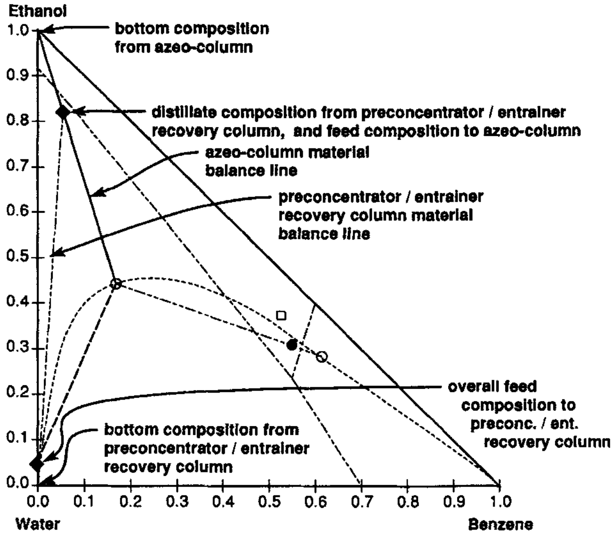

Figure 10a. Material balance lines for the two-column sequence.

Discussion and Results

Out of the five "simple" ways to sequence a ternary heterogeneous azeotropic distillation, we have performed detailed design and optimization studies on the three most promising alternatives. These are:

Alternative 1: the three-column sequence shown in Figure 4.

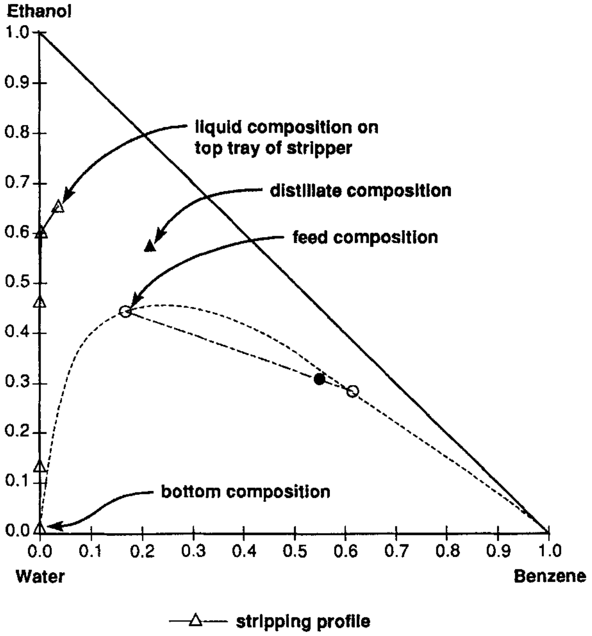

Figure 9. Composition profile for the entrainer recovery stripper at $s = 33.0$.

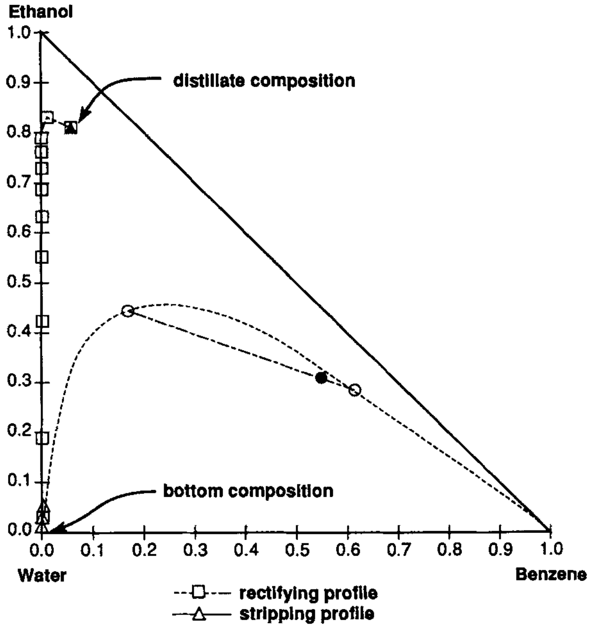

Figure 10b. Composition profiles for the preconcentrator/entrainer recovery column in the two-column sequence at $r = 4.05$ ($r_{min} = 3.55$).

Alternative 2: the same three-column sequence, but with the entrainer recovery column replaced by a stripper.

Alternative 3: the two-column sequence shown in Figure 5.

Before comparing these alternatives, we begin with an assessment of the main optimization variables for alternative 1. We will show that it is possible to develop sound heuristics for most of them. Similar heuristics apply to each of the remaining alternatives, thereby simplifying the optimizations.

For alternative 1, the principle optimization variables are expected to be the reflux ratio in the azeo-column, the position of the tie line for the mixture in the decanter, the position of the decanter composition on the decanter tie line (see Pham et al., 1989, for a discussion of the importance of these variables), and the distillate composition from the entrainer recovery column.

The reflux ratio is important because it determines the vapor rate, and therefore the capital and operating costs for this column. The position of the tie line in the decanter influences two quantities:

1) the minimum reflux ratio in the azeo-column.

2) the composition and flow rate of distillate from the main azeo-column to the entrainer recovery column. This in turn is a major factor in determining the entrainer recycle composition and flow from the entrainer recovery column back to the main azeo-column. The entrainer flow rate is normally the most important optimization variable in homogeneous azeotropic sequences (Knight and Doherty, 1989) and can be expected to play an important role in heterogeneous systems also.

The position of the decanter composition along the decanter tie line often has a strong influence on the value of $r_{\min}$ for the azeo-column (see Pham et al., 1989). Finally, the distillate composition from the entrainer recovery column is expected to be an important variable because it determines:

- The overall feed composition and flow rate to the azeo-column
- The distillate and bottoms flow rate from the azeo-column
- The distillate and bottoms flow rate from the entrainer recovery column

Figure 11 shows material balance lines for three different designs of alternative 1. Each sequence is fed with 401.6 Gg/yr of 4.2 mol % ethanol. The product purity from the azeo-column is set at 99.9 mol % ethanol, and the water purity leaving the entrainer recovery column is set at 99.5 mol % water. These specifications are essentially identical to those used by Knight and Doherty (1989) in their study of optimal, homogeneous distillation sequences. For design 1, the decanter tie line is at its bubble point (337.57 K) and positioned away from the ternary azeotrope. We refer to this tie line as the upper tie line. For design 2, the overall decanter liquid composition is taken to be the same as whatever is specified for design 1, but subcooled to 298.0 K. For design 3, the decanter tie line is at its bubble point (337.51 K) and positioned close to the ternary azeotrope. We refer to this tie line as the lower tie line. In each design, the distillate composition from the entrainer recovery column is placed close to the distillation boundary. Note what a significant influence the position of the tie line has on the distillate composition from the azeo-column and how this influences the position of the material balance line for the entrainer recovery column. Note also how the position of the distillate composition from the entrainer recovery column influences the overall feed composition to the azeo-column.

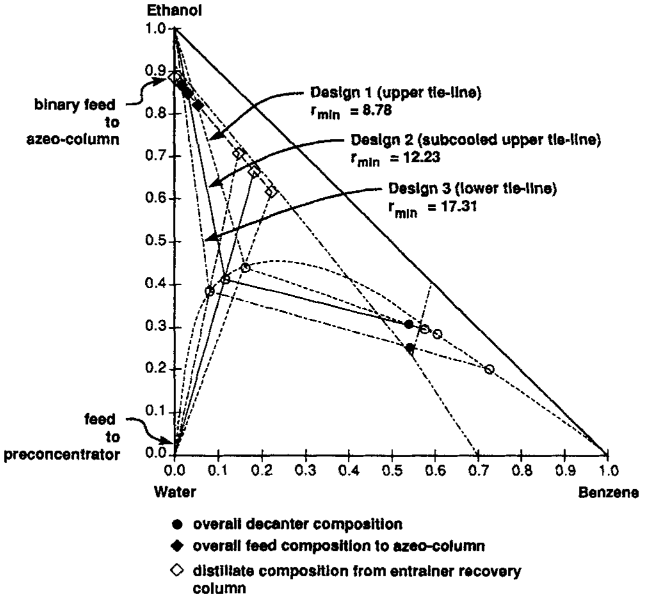

Figure 11. Three sets of material balance lines for the three-column sequence.

Extensive optimization studies indicate that the distillate composition from the entrainer recovery column is indeed an important optimization variable and that its optimum position is always close to the distillation boundary. This decreases the amount of water being recycled, or equivalently, makes the overall feed to the azeo-column richer in ethanol, which is clearly advantageous. This leads to the heuristic that the distillate composition from the entrainer recovery column should be set close to the distillation boundary, thereby removing it from the list of optimization variables.

For each tie line, the optimal position of the overhead vapor composition, i.e., overall decanter liquid composition, is found by the method proposed by Pham et al. (1989). Our calculations also indicate that the optimal reflux ratio in the azeo-column is always in the range 1.1-1.5 $r_{\min}$ and that the cost of the sequence is insensitive to this factor (see Figure 12). This leaves the position of the decanter tie line as the sole remaining optimization variable.

The minimum reflux ratio in the azeo-column can be quite sensitive to relatively small changes in the position of the decanter tie line. Thus, for design 1, $r_{\min} = 8.78$; for designs 2 and 3, the corresponding values are 12.23 and 17.31, respectively. The TAC and the specific energy consumption for each of these designs are shown in Figure 12 as a function of the reflux ratio in the azeo-column. Note that each of these measures are essentially the same for the three different designs, even though the reflux ratio in the azeo-column varies by a factor of two from design 1 to design 3. This occurs because the vapor rate leaving the reboiler in the azeo-column hardly varies from one design to another. A good approximation for the vapor rate leaving the reboiler is

$$V = (r + 1)D$$

and although r increases from one design to another, the distillate flow rate decreases, as can be seen from the material bal-

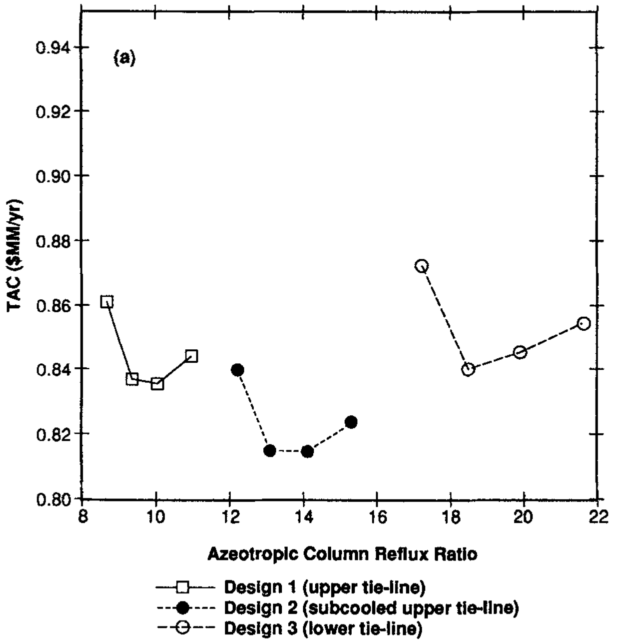

Figure 12. Total annualized cost of the three-column sequences vs. reflux ratio in the azeo-column.
Costs are based on 1986 factors reported in Douglas (1988).

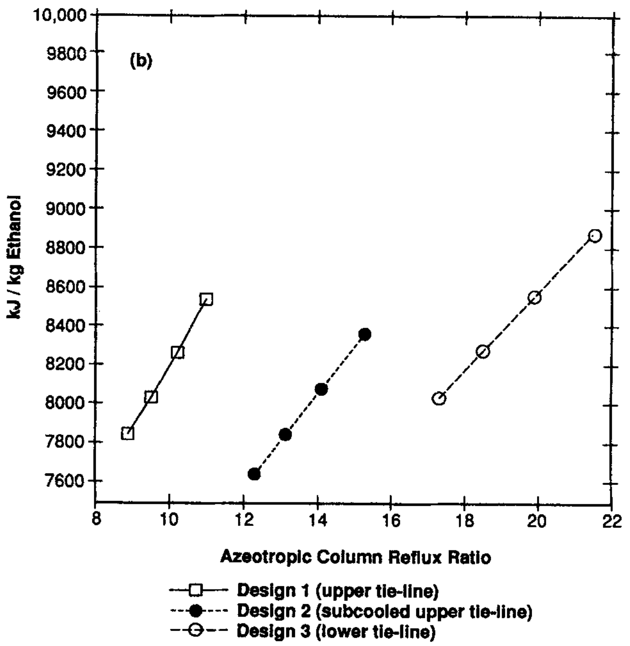

Figure 12b. Specific energy consumption for the three-column sequence (kJ/kg ethanol) vs. reflux ratio in the azeo-column.

ance lines for the azeo-column in Figure 11. The actual numerical values are given in Table 2.

In general, this fortuitous cancellation of effects cannot be expected to occur, and it is always worthwhile exploring the economic impact of variations in the decanter tie line. Thus, we propose the following procedure for design and optimization of heterogeneous azeotropic distillation sequences.

Algorithm

1. Fix the state of the process feed to the preconcentrator (column 1), $\underline{x}_{F1}, q_1$ and the pressure in each of the columns (normally atmospheric).
2. Set product compositions, $\underline{x}_{B1}$, $\underline{x}_{B2}$, $\underline{x}_{B3}$.
3. Set distillate composition from the preconcentrator near the binary azeotrope.
4. Pick a value for the overall decanter liquid composition so that it lies in the wedge between the distillation boundaries (Pham and Doherty, 1989b, c). Calculate the VLLE saturation temperature and tie line. Thus, $\underline{x}_{D2}$ is now known. This step provides a feasible decanter temperature and tie line for initializing the rest of the procedure.
5. For the current tie line, optimize the value of the decanter liquid composition so as to minimize $r_{\min}$ in the azeo-column (Pham et al., 1989).
6. Set $\underline{x}_{D3}$ near the distillation boundary and collinear with $\underline{x}_{D2}$ and $\underline{x}_{B3}$.
7. Set $r = 1.1 - 1.5\, r_{\min}$ for each column.
8. Each column in the sequence can now be designed independently by the boundary-value method. Calculate the TAC (total annualized cost) (and if desired, the specific energy consumption).
9. Optimize the TAC of the sequence with respect to the decanter temperature and $x_{D2,1}$ (with respect to the position of the decanter tie line): i.e., return to step 5 until an optimum is found.

If the cost of the sequence is insensitive to the position of the decanter tie line, as in our example, step 9 is eliminated and the preliminary design is complete at step 8. Table 3 gives the opti-

Table 2. Variables Affecting the Vapor Rate Leaving the Reboiler of the Azeo-column for Each Design

	$r_{\min}$	r^*_{opt}	D^{**}	V^{**} (at r_{opt})
Design 1 (Upper Tie Line)	8.78	10.13	0.674	7.504
Design 2 (Subcooled Upper Tie Line)	12.23	14.11	0.496	7.499
Design 3 (Lower Tie Line)	17.31	19.97	0.415	8.697

*1.154 $r_{\min}$
**kmol/min

Table 3. Optimal Designs

	Design 1	Design 2	Design 3
Azeo-Column			
Total No. of Theor. Stages	38	38	36
Feed Stage	37	37	35
Reflux Ratio (=1.154 $r_{\min}$)	10.13	14.11	19.97
Reboil Ratio	4.26	4.26	4.94
Entrainer Recovery Column			
Total No. of Theor. Stages	20	27	30
Feed Stage	3	3	3
Reflux Ratio (=1.2 $r_{\min}$)	1.44	1.68	1.80
Reboil Ratio	5.58	3.93	3.04

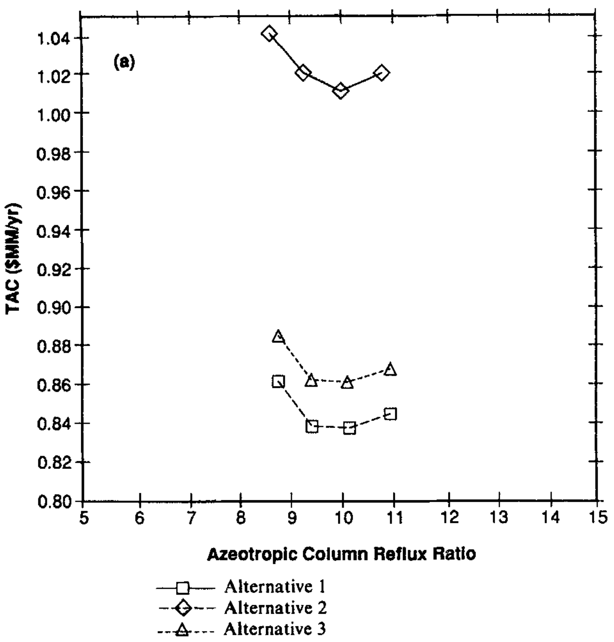

Figure 13a. Total annualized cost for alternatives 1, 2 and 3 vs. reflux ratio in the azeo-column.

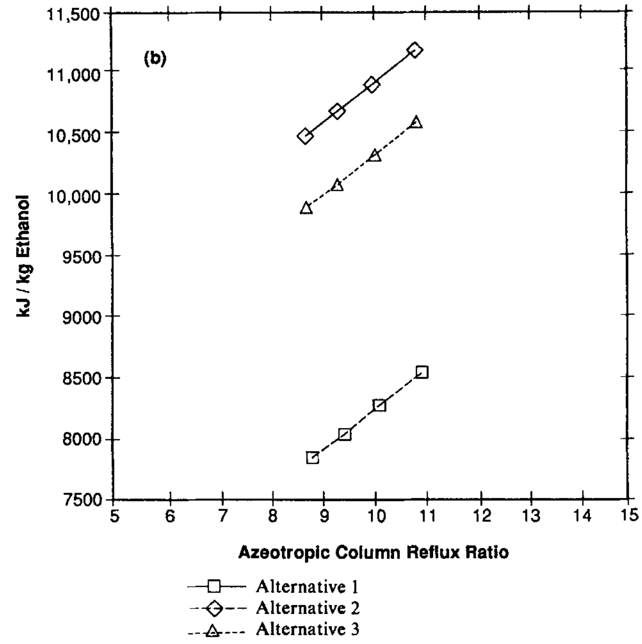

Figure 13b. Specific energy consumption for the three alternatives vs. reflux ratio in the azeo-column.

mal design variables for each of the decanter tie lines shown in Figure 11 for our example problem.

Following a similar algorithm for alternatives 2 and 3 leads us to the comparisons shown in Figure 13. The decanter tie line is taken to be the upper tie line in each case. On the basis of total annualized cost, alternatives 1 and 3 are practically indistinguishable, while alternative 2 (the three-column sequence with an entrainer recovery stripper) is about 20% more costly and consumes about 33% more energy per kg of ethanol produced than the three-column sequence. However, alternatives 1 and 3 differ significantly in terms of specific energy consumption (Figure 13b). Capital cost savings achieved by combining the preconcentrator and the entrainer recovery column in the two-column sequence is lost due to increased energy costs. (The optimal two-column sequence is 13% less expensive in capital cost than the optimal three-column sequence, but it is 21% more expensive in energy cost.) With a dilute primary feed of 4.2% ethanol, most of the alcohol dehydration takes place in the preconcentrator of the three-column sequence or the preconcentrator/entrainer recovery column of the two-column sequence. The optimal reflux ratio for the preconcentrator of the three-column sequence is 3.25 with a corresponding reboil ratio of 0.181. The optimal reflux ratio for the preconcentrator/entrainer recovery column of the two-column sequence is 4.05, and the corresponding reboil ratio is 0.295. The increase in reflux and reboil ratios is due to a different overall feed composition in the second column of the two-column sequence which is a mixture of the dilute primary feed and the distillate stream from the azeo-column.

For a fixed total flow rate, as the process feed becomes richer in ethanol, the two column sequence becomes more attractive, and by 55 mol% ethanol feed the two-column sequence and the three-column sequences have almost identical optimum performance measures (TAC ≃ $6.1 million/yr, specific energy consumption ≃ 7,200 kJ/kg). The optimum performance measures for the two-and three-column sequences are identical at 70 mol% ethanol as well (TAC ≃ $7.5 million/yr, specific energy consumption ≃ 7,300 kJ/kg).

Conclusions

Various strategies for sequencing heterogeneous azeotropic sequences have been explored. The design and optimization of these systems by simulation-based methods are generally acknowledged to be a very difficult problem. In this paper, a simple and accurate design and optimization procedure has been developed. The method does not involve any recycle convergence loops and has been applied successfully to several problems. Unlike the simulation-based methods, our method is robust to changes in system optimization variables (e.g., reflux ratio in the azeo-column).

Our experience is that for many problems, all the optimization variables, except for the position of the decanter tie line, can be set either by heuristics or calculated at their bounds (e.g., see Pham et al., 1989). The shape of the liquid-liquid envelope (and hence the spectrum of feasible decanter tie lines) varies so much from problem to problem that no general rule for positioning this tie line can be developed. Hence, this is expected to be the main optimization variable in most new problems.

For our example problem (dehydration of ethanol using a benzene entrainer), neither the total annualized cost of the sequence nor the specific energy consumption (kJ/kg ethanol produced) was sensitive to the position of the decanter tie line due to a fortuitous cancellation of large, but opposite, effects. For dilute ethanol feeds our study shows that a three-column sequence is favored on the basis of both cost and specific energy consumption over the three-column sequence with an entrainer recovery stripper. The three-column sequence is also favored over the two-column sequence on the basis of specific energy consumption (but not on cost) when the primary feed to the sequence is very dilute in ethanol. This distinction between the two- and three-column sequences is lost, however, as the primary feed stream becomes richer in ethanol. The specific energy consumption for the optimal three-column sequence is 8,200 kJ/kg ethanol (≃23,200 Btu/gal; 1 kJ/kg ethanol = 2.833 Btu/gal ethanol). This is substantially less than accepted literature values, which points out the merits of our design and optimization procedure. For example, Black (1980) reports a specific energy consumption of 34,700 Btu/gal ethanol for a 6.4 wt.% (2.6 mol %) ethanol feed using benzene as entrainer. Our optimal three-column sequence for such a feed requires only 26,500 Btu/gal, which is 24% less than the reported literature value.

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Notation

D = distillate flow rate
h = specific enthalpy
P = total pressure
r = reflux ratio
r_{min} = minimum reflux ratio
r_{ext} = external reflux ratio
s = reboil ratio
s_{ext} = external reboil ratio
T = temperature
V = vapor flow rate
$\underline{x}$ = vector of liquid mole fractions
$\underline{y}$ = vector of vapor mole fractions

Greek letters

Φ = ratio of the two liquid phases in the decanter

Subscripts

B = bottoms
D = distillate
F = feed
$B1$ = bottoms from the preconcentrator column
$B2$ = bottoms from the azeo-column
$B3$ = bottoms from the entrainer recovery column
$D1$ = distillate from the preconcentrator column
$D2$ = distillate from the azeo-column
$D3$ = distillate from the entrainer recovery column
$F1$ = feed to the preconcentrator column
$F2$ = feed to the azeo-column
$F3$ = feed to the entrainer recovery column
$, 1$ = mole fraction of benzene in a specification
$, 2$ = mole fraction of ethanol in a specification
$, 3$ = mole fraction of water in a specification
q = feed quality

hence, $x_{D2,1}$ is the product specification of benzene in the liquid distillate stream from the azeo-column.

Superscripts

L = liquid stream
V = vapor stream

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