Design and Minimum Reflux for Heterogeneous Azeotropic Distillation Columns

A simple design technique for heterogeneous distillation columns has been developed. The underlying geometric conditions which govern minimum reflux are shown to share certain common features with homogeneous distillations, but differ in some important respects. It is shown that heterogeneous columns display some unusual sensitivities to the design parameters. The most notable being the drastic swings in the composition and temperature profiles with very small changes in the level of trace impurities in the product stream.

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Introduction

There is currently no method for calculating minimum reflux ratios in heterogeneous azeotropic distillation columns. In order to carry out design and optimization of the sequences described in Pham and Doherty (1989c), it would be useful to know more about minimum reflux and its sensitivity to the design variables. In this article, we present such a study.

Problem Formulation for a Heterogeneous Distillation Column

As done previously for homogeneous distillation (Levy et al., 1985), we will develop a boundary-value procedure for the design of heterogeneous distillation columns. The model is based upon the following simplifying assumptions: 1. constant molar overflow (CMO); 2. saturated liquid feed; 3. theoretical plates; and 4. complete separation of the liquid phases in the decanter. The CMO assumption is obviously incorrect for such highly-nonideal mixtures. For the time being, however, it allows us to develop relatively simple models that can be used to explore the underlying geometry behind minimum reflux in these complex columns. Earlier work for homogeneous mixtures (Levy et al., 1985; Knight and Doherty, 1986) supports the utility of this approach.

Consider the heterogeneous distillation column shown in Figure 1. An envelope balance on component i around an arbitrary plate, n, in the rectifying section gives

$$Vy_{i,n-1} = L^{\mathrm{I}}_n x^{\mathrm{I}}_{i,n} + L^{\mathrm{II}}_n x^{\mathrm{II}}_{i,n} + Dx^o_{i,D} \quad i = 1, 2, \ldots, C-1 \tag{1}$$

If we define x^o_i to be the overall liquid-phase mole fraction of component i, then

$$Lx^o_i = L^{\mathrm{I}}_n x^{\mathrm{I}}_{i,n} + L^{\mathrm{II}}_n x^{\mathrm{II}}_{i,n} \qquad i = 1, 2, \ldots, C-1 \tag{2}$$

and

$$L = L^{\mathrm{I}} + L^{\mathrm{II}} \tag{3}$$

Equation 1 can be rewritten as

$$Vy_{i,n-1} = Lx^o_{i,n} + Dx^o_{i,D} \quad i = 1, 2, \ldots, C-1$$

or in terms of the reflux ratio [$r = L/D$], the equation for the rectifying profile becomes

$$y_{i,n-1} = \left(\frac{r}{r+1}\right) x^o_{i,n} + \left(\frac{1}{r+1}\right) x^o_{i,D} \quad i = 1, 2, \ldots, C-1 \tag{4}$$

where $\underline{x}^o_n$ is the overall liquid composition on tray n.

Similarly, the equation for the stripping profile is

$$x^o_{i,m+1} = \left(\frac{s}{s+1}\right) y_{i,m} + \left(\frac{1}{s+1}\right) x^o_{i,B} \quad i = 1, 2, \ldots, C-1 \tag{5}$$

where $s = V/B$. The reflux and reboil ratios are related by the equation (Levy et al., 1985)

$$s = (r+1)\left[\frac{x^o_{i,B} - x^o_{i,F}}{x^o_{i,F} - x^o_{i,D}}\right] \quad i = 1, 2, \ldots, C-1 \tag{6}$$

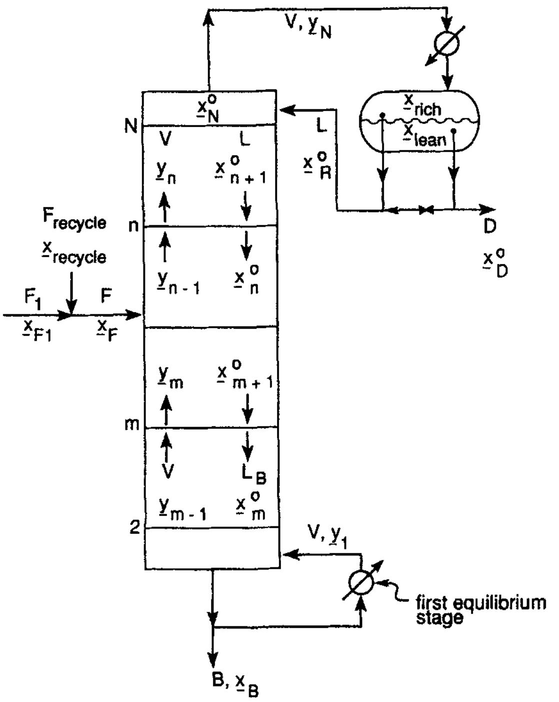

Figure 1. Schematic representation of a heterogeneous distillation column.

Even though the form of Eqs. 4 and 5 are identical to the equations describing homogeneous distillations columns, they differ in two important respects. The phase equilibrium calculations and the specification of the design variables in the two cases are completely different. In fact, specification of the design variables for heterogeneous columns must be done with great care, as is dictated by the structure of the phase diagram and the corresponding residue curve map for the mixture.

The design problem is solved as a boundary value problem in much the same spirit as the earlier work on homogeneous systems (Levy et al., 1985). In heterogeneous systems, the bottom product is typically a pure component (e.g., ethanol or isopropanol) and hence has product quality specifications on its composition. This makes the calculation for the stripping profile essentially identical to the homogeneous case. The distillate stream, however, comes from the liquid-liquid-phase separation in the decanter, and the initialization of the rectifying profile calculations is completely different from the procedure used for homogeneous systems.

Initialization of the Rectifying Calculations

Assuming that the overhead vapor is totally condensed and that the condensate is a saturated liquid, the initialization procedure is as follows:

Step 1. Pick an operating tie line for the decanter. The entrainer-lean-liquid-phase (which is normally aqueous-rich) now becomes the distillate specification $\underline{x}_D^o$ for the heterogeneous column. This is a VLLE (vapor-liquid-liquid equilibrium) calculation; at this point, the overall liquid composition used to find this tie line is arbitrary. The tie line should, however, be in the appropriate distillation region (Pham and Doherty, 1989b).

Step 2. Specify the bottoms composition, $\underline{x}_B^o$. The feed composition to this column, $\underline{x}_F^o$, lies somewhere along the material balance line for the heterogeneous column drawn from $\underline{x}_B^o$ to $\underline{x}_D^o$ (see Figure 2). When the azeo-column is placed into the entire sequence, its feed composition, $\underline{x}_F^o$, is fixed by material balance constraints for the sequence (see Ryan and Doherty, 1989).

Step 3. Pick $\underline{y}_N$ on the tie line and in the same distillation region that contains $\underline{x}_B^o$. Perform a liquid-vapor equilibrium calculation to obtain the homogeneous liquid on the top tray, $\underline{x}_N^o$. The exact position of $\underline{y}_N$ within its feasible region is a design degree of freedom. Note that the overall liquid composition in the condenser/decanter, $\underline{x}_c^o$, is equal to $\underline{y}_N$, since the incoming vapor stream from the top plate is totally condensed.

Step 4. Calculate the ratio of the two liquids, ϕ, in the condenser (Pham and Doherty, 1989c).

Step 5. Pick $r \geq \phi$ (the value of r is also a design degree of freedom).

Step 6. Calculate s from Eq. 6.

In step 1, it is sometimes useful to subcool the liquid in the condenser in order to enlarge the region of liquid-phase immiscibility (as noted in Table 1 of Pham and Doherty, 1989c). In this case, the values of $\underline{x}_{\text{rich}}$ and $\underline{x}_{\text{lean}}$ are calculated at the given pressure *and* temperature using an isothermal LLE calculation. Such situations require that the column model takes account of heat effects.

Liquid Composition Profiles and Minimum Reflux Ratio

Once the initialization is complete, the column profile is calculated as a pair of initial-value problems.

For the rectifying section:

Step i. Knowing $\underline{x}_N^o$, calculate $\underline{y}_{N-1}$ from Eq. 4.

Step ii. From $\underline{y}_{N-1}$ and P, calculate $\underline{x}_{N-1}^o$ and T_{N-1} using VLE (vapor-liquid equilibrium) or VLLE calculations depending on the material stability of composition $\underline{x}_{N-1}^o$.

Step iii. Repeat until the profile reaches its fixed point (i.e., a pinch). [See Julka and Doherty (1989) for a detailed discussion of these concepts.]

In step ii, $\underline{x}^o$ and T are predicted from the known values of $\underline{y}$ and P. When $\underline{y}$ does not lie on the vapor line, a VLE calculation must be used since we know that the vapor is in equilibrium with

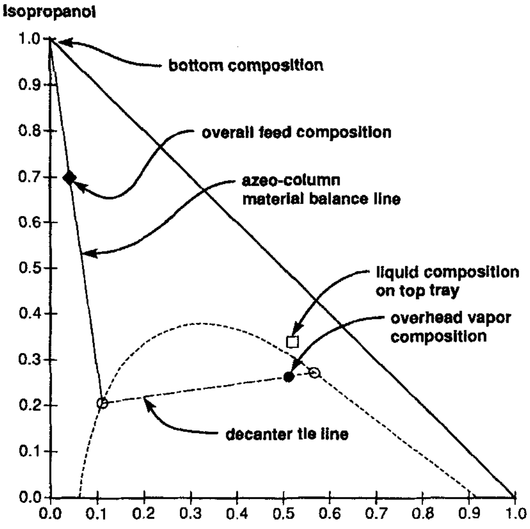

Figure 2. Azeo-column material balance line.

a homogeneous liquid. If $\underline{y}$ lies on the vapor line, a VLLE calculation must be used. The latter case can be checked since the position of the vapor line is known.

For the stripping section:

i. Knowing $\underline{x}_B^o$ and P, calculate $\underline{y}_1$ and T_1 using VLE or VLLE calculations depending on the material stability of composition $\underline{x}_B^o$.

ii. From $\underline{x}_B^o$ and $\underline{y}_1$, calculate $\underline{x}_2^o$ using Eq. 5.

iii. Repeat until the profile reaches its fixed point.

The liquid composition profile for the mixture isopropanol-water-benzene at 1-atm pressure is shown in Figure 3a. The specifications for the azeo-column corresponding to this set of liquid composition profiles (and all other azeo-column specifications) are listed in Table 1. The bottom product is 99.8 mol % isopropanol, and at the specified value of $\underline{y}_N$, the value of ϕ is 7.10. In accordance with the arguments presented in Pham and Doherty (1989c), r is chosen to be greater than ϕ, at a value of $r = 11.83$. Note that the profiles do intersect and therefore this value of r is greater than $r_{\min}$. The phase equilibrium calculations were performed using the Regular Solution model to represent the liquid-phase nonidealities (see Pham and Doherty, 1989a, for parameter values, etc). Although the phase diagram is not quantitatively accurate, it has qualitative validity and thus serves to demonstrate the column design procedures.

The reflux ratio in the heterogeneous column is reduced to $r = 8.45$ in Figure 3b, and now the profiles do not intersect. Thus, the minimum reflux ratio has been bracketed between these two values, and $r_{\min}$ is found by adjusting the value of r until the stripping profile just touches or "pinches" on the rectifying profile. Figure 3c shows such a set of liquid composition profiles, with a corresponding (minimum) reflux ratio of $r = 9.91$. Note that $r_{\min} > \phi$, which illustrates the point made by Pham and Doherty (1989c) that $\phi \leq r_{\min} < r < \infty$. The feed tray for the designs shown in Figures 3a and 3c is located at the intersection point of the stripping and rectifying profiles. There is no feed tray in Figure 3b since the design is infeasible.

Table 1. Specifications of the Azeo-Column

Figure	Mole Frac.	Feed $\underline{x}_F$	Bottoms $\underline{x}_B$	Distillate $\underline{x}_D$	Reflux $\underline{x}_R$	Condenser $\underline{y}_N$
3a	Benzene	0.0425	0.6E-06	0.1126	0.5425	0.5090
	i-Propanol	0.7000	0.9980	0.2083	0.2787	0.2732
	Water	0.2575	0.0020	0.6791	0.1788	0.2178
3b	Benzene	0.0425	0.6E-06	0.1126	0.5559	0.5090
	i-Propanol	0.7000	0.9980	0.2083	0.2808	0.2732
	Water	0.2575	0.0020	0.6791	0.1633	0.2178
3c	Benzene	0.0425	0.6E-06	0.1126	0.5490	0.5090
	i-Propanol	0.7000	0.9980	0.2083	0.2797	0.2732
	Water	0.2575	0.0020	0.6791	0.1713	0.2178
4a	Benzene	0.0425	0.1E-15	0.1126	0.5490	0.5090
	i-Propanol	0.7000	0.9999	0.2083	0.2797	0.2732
	Water	0.2575	0.0001	0.6791	0.1713	0.2178
4b	Benzene	0.0425	0.25E-05	0.1126	0.5490	0.5090
	i-Propanol	0.7000	0.9999	0.2083	0.2797	0.2732
	Water	0.2575	0.0001	0.6791	0.1713	0.2178
4c	Benzene	0.0425	0.75E-04	0.1126	0.5490	0.5090
	i-Propanol	0.7000	0.9999	0.2083	0.2797	0.2732
	Water	0.2575	0.25E-04	0.6791	0.1713	0.2178
5a	Benzene	0.0425	0.1E-15	0.1126	0.5423	0.5090
	i-Propanol	0.7000	0.9999	0.2083	0.2786	0.2732
	Water	0.2575	0.0001	0.6791	0.1791	0.2178
5b	Benzene	0.0425	0.25E-05	0.1126	0.5423	0.5090
	i-Propanol	0.7000	0.9999	0.2083	0.2786	0.2732
	Water	0.2575	0.0001	0.6791	0.1791	0.2178
5c	Benzene	0.0425	0.75E-04	0.1126	0.5423	0.5090
	i-Propanol	0.7000	0.9999	0.2083	0.2786	0.2732
	Water	0.2575	0.25E-04	0.6791	0.1791	0.2178

We should note that the minimum reflux ratio in Figure 3c conforms to the general results derived by Julka and Doherty (1989) for homogeneous distillation columns. That is, the secant line to the rectifying profile at the feed-pinch composition passes through $\underline{x}_F^o$. Note that the profile shown in Figure 3c displays only *one* pinch, namely, the pinch in the stripping profile at the feed tray. Such behavior is similar to that observed for nonsharp splits in homogeneous mixtures. All attempts to detect a second

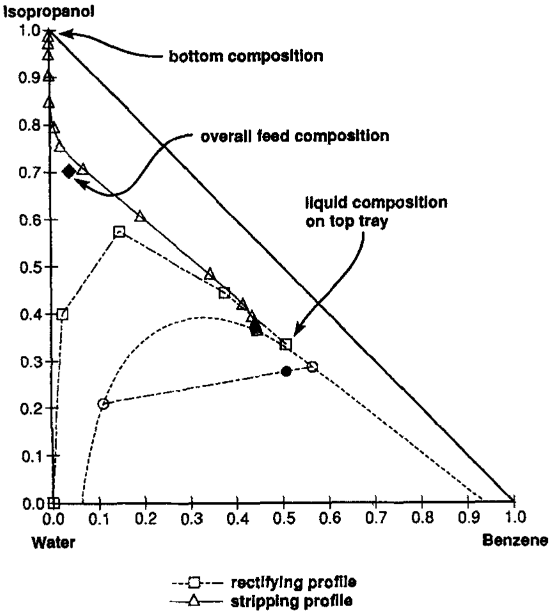

Figure 3a. Feasible column profile at a reflux ratio of 11.83 ($\Phi = 7.10$, $s = 7.78$).

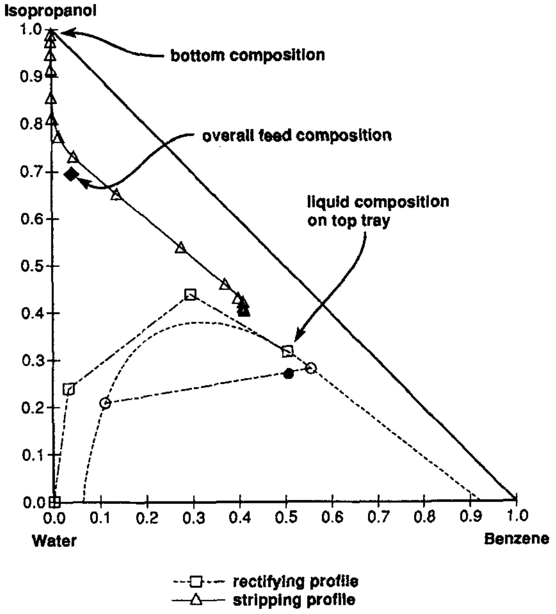

Figure 3b. Column design is infeasible at a reflux ratio of 8.45 ($\Phi = 7.10$, $s = 5.73$).

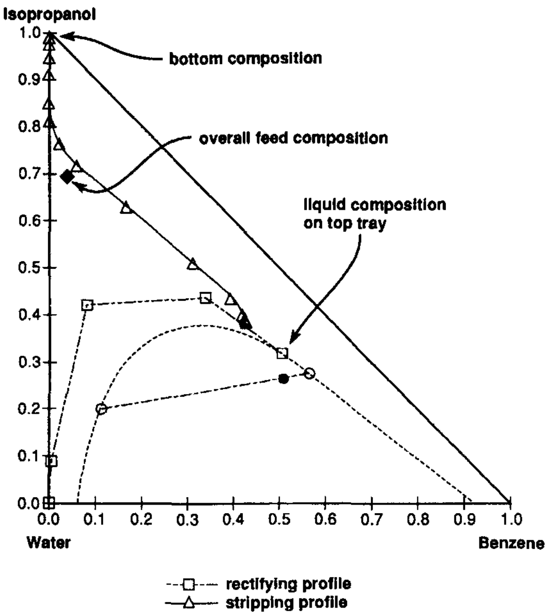

Figure 3c. Column profile at a minimum reflux ratio of 9.91 (Φ = 7.10, s = 6.61).

The liquid composition profile pinches on the rectifying section profile.

(saddle) pinch in the rectifying profile by manipulating $\underline{x}_B^o$ and $\underline{y}_N$ failed. This leads us to conclude that no second pinch exists. Therefore, the collinearity method (Levy et al., 1985; Julka and Doherty, 1989) for calculating minimum reflux in homogeneous mixtures *does not apply to heterogeneous distillation columns.*

As a final remark, we note that the stripping profile pinches on the rectifying profile in Figure 3c. This is exactly *opposite* to what happens in homogeneous distillations when the bottoms stream is a pure component (i.e., the "indirect split"). Levy (1985) has shown that homogeneous azeotropic mixtures with residue curve maps similar to the one for isopropanol-water-benzene display "normal" geometry when the bottoms product is a pure component (i.e., the rectifying profile pinches on the stripping profile at minimum reflux). Therefore, the new geometry in Figure 3c is undoubtedly induced by constraints imposed by the liquid-phase separation.

Column Sensitivity to Parameter Manipulation

For a given column pressure, feed composition, and product purity, there are *four* degrees of freedom which we are allowed to manipulate. These are: the column reflux ratio; the amount of entrainer (e.g. benzene) in the bottom product; the position of the condenser composition, $\underline{y}_N$, along its feasible range; and the position of the decanter tie line itself. The decanter tie line is positioned by choosing the amount of *one* component in the distillate specification. The other two components are then set by the intersection of the decanter tie line with the heterogeneous boiling envelope.

In our earlier calculations, completely arbitrary choices were made for the amount of entrainer in the bottom stream, and for the position of the condenser composition along the condenser/decanter tie line. As we will now see, manipulation of these variables leads to surprising results.

Manipulation of bottom composition, $\underline{x}_B^o$

Manipulation of $\underline{x}_B^o$ does not effect r_{min}. However, it does give rise to very different patterns for the liquid composition profile in the column. Consider again the mixture isopropanol-water-benzene at 1-atm pressure. We fixed the feed composition and kept the amount of alcohol in the bottoms stream at 99.9 mol %. Then, changing the trace amount of benzene in the bottom product from a mole fraction of 1×10^{-16} (i.e., close to its minimum value of zero), to 0.25×10^{-5}, and to 0.75×10^{-4} (i.e., its maximum value, close to the hypotenuse of the composition triangle) results in small changes in $\underline{x}_D^o$, $\underline{x}_L^o$, and $\underline{y}_N$ due to material balance considerations, but gives rise to no change in the value of r_{min} (=9.91). The change, however, does result in a significant shift in the liquid-phase composition profile in the column at minimum reflux, as shown in Figures 4a, b, and c.

The explanation of this effect is actually quite straightforward and can be traced to the phase diagram, or equivalently to the residue curve map, for the system. In the top distillation region, the residue curves all begin at the ternary azeotrope and end at the isopropanol vertex. Since the region is four-sided, some curves take the left-side route, some take the right-side route and the remainder take the middle route (see Figure 3, Pham and Doherty, 1989b). Therefore, if the residue curves are computed by taking an initial composition close to the isopropanol vertex and integrating the simple distillation equations backwards in time, we will find that very small changes in the initial composition will produce major changes in the routes taken by the residue curves. Since the shapes of the liquid composition profiles in continuous distillation are similar to the patterns of the residue curves, we expect to see similar sensitivities in continuous distillation systems. In fact, we anticipated this effect, which provided the motivation to perform these sensitivity studies with respect to $\underline{x}_B^o$ in the first place.

The results show that there are many possible paths which can be used for the design of a heterogeneous column, all of which generate essentially the same product compositions and

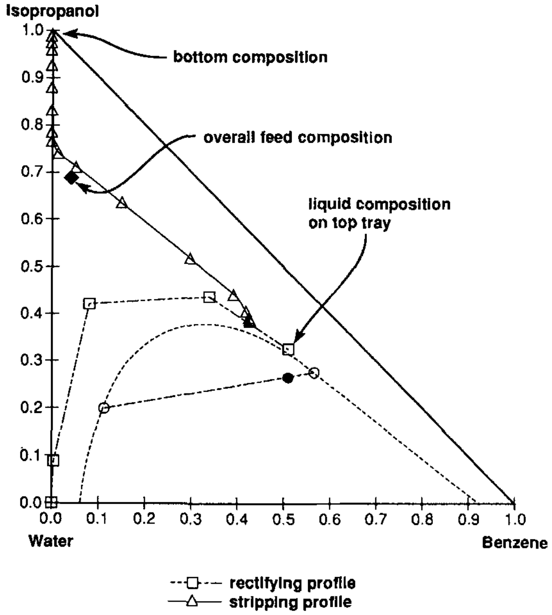

Figure 4a. Liquid composition profiles r_{min} = 9.91 (Φ = 7.10, s = 6.65) and $x_{B,benzene}$ = 1.0E-16.

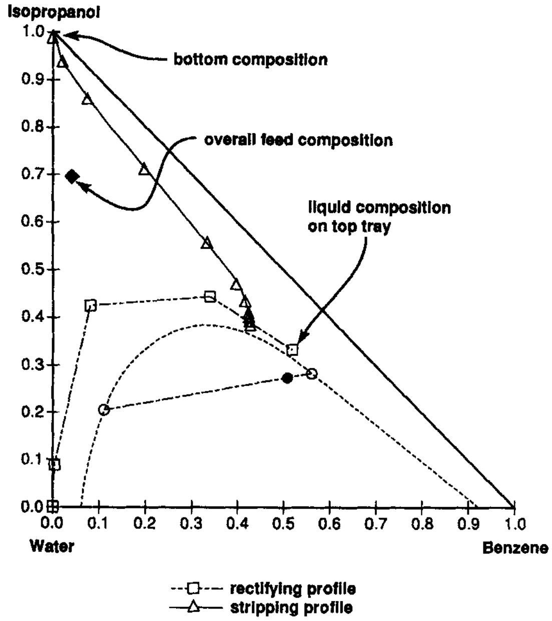

Figure 4b. Liquid composition profiles r_{min} = 9.91 (Φ = 7.10, s = 6.65) and $x_{B,benzene}$ = 0.25E-05.

minimum reflux ratios. The two limiting cases shown in Figures 4a and 4c have been observed by Bril' et al. (1977) who conducted performance calculations for this mixture and found great shifts in the column profile with changes in reflux ratio and number of plates. The latter case seems to be the conventional design pattern for the dehydration of alcohol (e.g., Robinson and Gilliland, 1950; King, 1980; Prokopakis and Seider, 1983); however, the path in Figure 4a is quite feasible also. Figures 5a, b, and c show three design paths at a reflux ratio of 11.89 (=1.2 r_{min}), where the mole fraction of benzene in the bottom product is 1 × 10^{-16}, 0.25 × 10^{-5}, and 0.75 × 10^{-4}, respectively. The number of theoretical trays required by each of these designs is 32 in the first, 15 in the second, and 17 in the third. It should be noted that the tray temperatures are very different in each design, varying by as much as 7.2°C on a given plate.

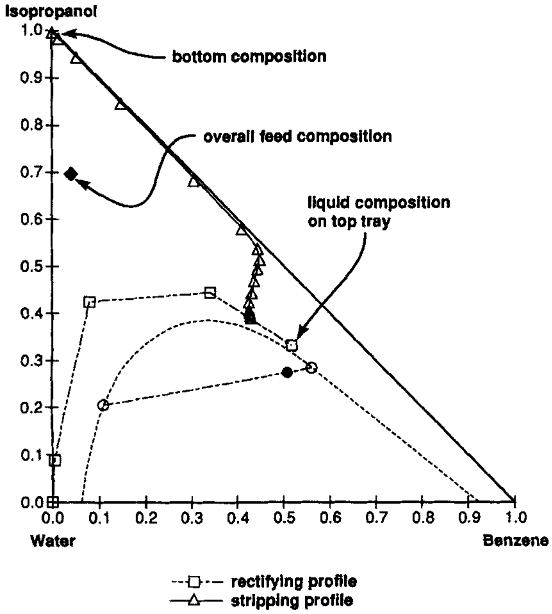

Figure 4c. Liquid composition profiles r_{min} = 9.91 (Φ = 7.10, s = 6.65) and $x_{B,benzene}$ = 0.75E-04.

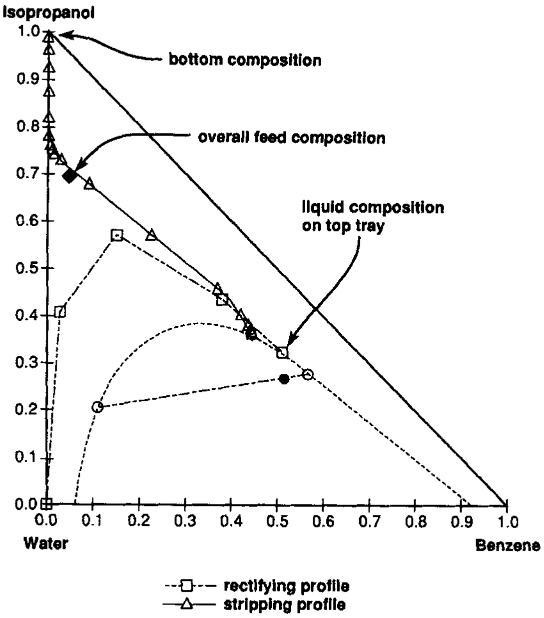

Figure 5a. Column design at r = 11.89 (=1.2 × r_{min}, Φ = 7.10, s = 7.86) and $x_{B,benzene}$ = 1.0E-16 contains 32 theoretical trays.

The great sensitivity of the shape of the column profile (and the temperatures) to the composition fluctuation of trace components in the bottom stream means that these columns may possess operability and control difficulties in the face of disturbances. This would form the basis of a good study on the operability and control of these complex processes.

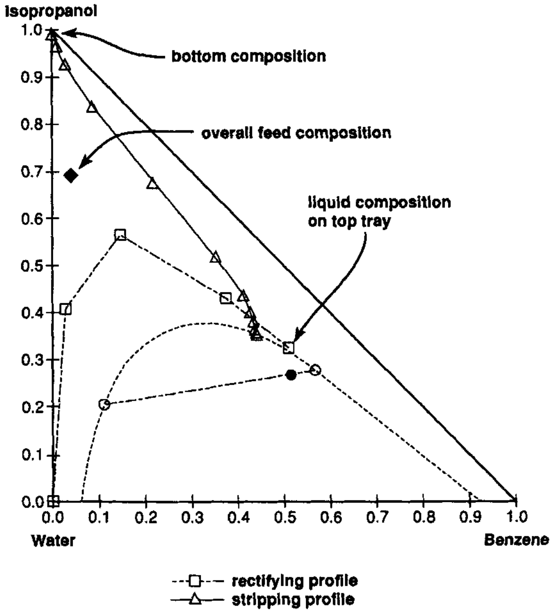

Figure 5b. Column design at r = 11.89 (=1.2 × r_{min}, Φ = 7.10, s = 7.86) and $x_{B,benzene}$ = 0.25E-05 contains 15 theoretical trays.

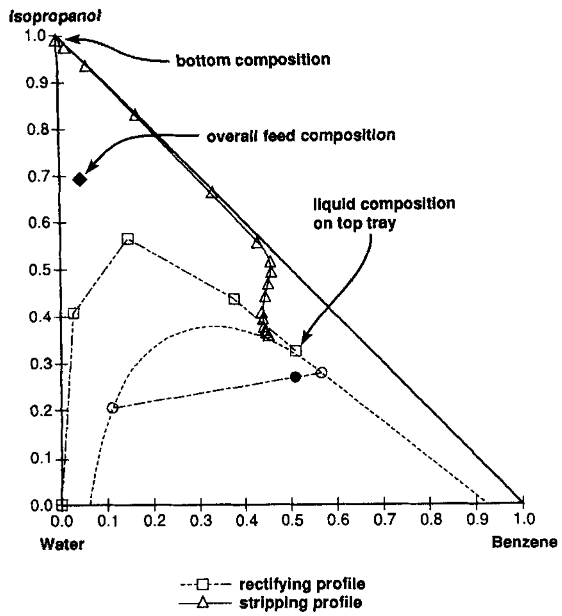

Figure 5c. Column design at r = 11.89 (=1.2 × r_{min}, Φ = 7.10, s = 7.86) and $x_{B,benzene}$ = 0.75E-04 contains 17 theoretical trays.

Manipulation of condenser composition, $\underline{y}_N$

The minimum reflux ratio decreases rapidly as $\underline{y}_N$ moves along the tie-line in its feasible range. The curve of r_{min} vs. $y_{N,benzene}$ and the straight line of ϕ vs. $y_{N,benzene}$ are shown in Figure 6. The stopping point of the two curves indicates the limiting amount of benzene in the overhead vapor stream. Any amount of benzene greater than this will cause the liquid composition on the top tray of the azeo-column, $\underline{x}_N^o$, to lie in a distillation region other than the region containing $\underline{x}_B^o$ and would make the desired separation in the azeo-column impossible.

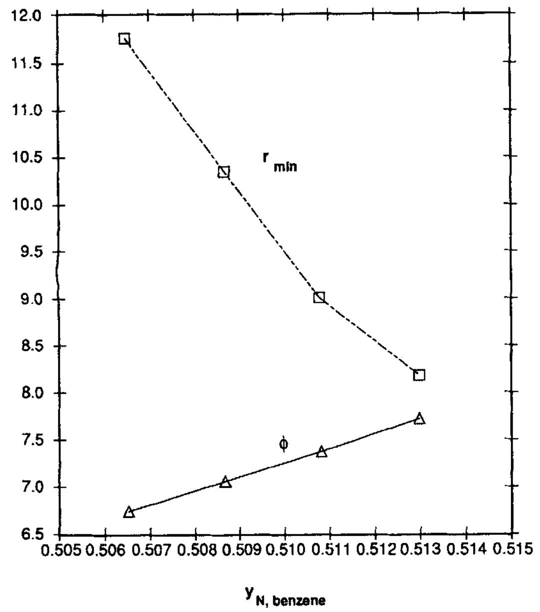

Figure 6. Feasible range of $y_{N,benzene}$.

At the lowest possible value of r_{min} (=8.17), Φ = 7.73 and $y_{N,benzene}$ = 0.513.

This extreme point also represents the lowest value of r_{min} for a given product specification. Therefore, for a given $\underline{x}_F^o$, $\underline{x}_B^o$ and $\underline{x}_D^o$, the condenser composition, $\underline{y}_N$, should be chosen in such a way that r_{min} is as small as possible. This obviously generates a design in which the least amount of entrainer-lean phase is refluxed back to the column. The smallest possible value of r_{min} corresponds to that value of $y_{N,benzene}$ which makes $r_{min} = \phi$. As this example demonstrates, this lower bound is not always attainable. In many cases, however, the value of $y_{N,entrainer}$ which makes $r_{min} = \phi$ provides a good first estimate for the lowest value of r_{min} and the corresponding condenser/decanter composition, $\underline{y}_N$ (for a given decanter tie line).

Note that, in this example, the feasible range for $y_{N,benzene}$ is about 0.503 to 0.513. If $y_{N,benzene}$ is less than 0.503, the column design is either infeasible or has high minimum reflux ratios. If $y_{N,benzene}$ is greater than 0.513, the top tray composition, $\underline{x}_N$, lies in the wrong distillation region, thereby defining an infeasible separation. This feasible range of $\underline{y}_N$ is, in fact, similar to the narrow range of the design variables found by Prokopakis and Seider (1983) for the dehydration of ethanol with benzene.

Conclusions

In this article a simple design technique has been developed for heterogeneous distillation columns. Although the method is restricted to constant molar overflow, it allows for the systematic extension to the case with nonnegligible heat effects. The method provides a simple way of calculating minimum reflux ratios, the number of trays in each section of the column, etc., for a ternary mixture capable of exhibiting heterogeneous behavior. It is shown that, for a given bottom product purity, the minimum reflux is insensitive to the relative composition of the remaining two components in the bottom stream. However, the shape of the column profile is *very* sensitive to this variable. Thus, the plate temperatures will be dependent strongly on trace impurities in the bottom stream. We have also shown that the minimum reflux ratio is very sensitive to small changes in the condenser liquid composition for our example mixture of isopropanol-water-benzene. An algorithm is provided for finding the condenser composition that generates the lowest value for r_{min}.

These results suggest that heterogeneous columns will be very sensitive to process disturbances, thus leading to unusual operability and control problems. Research on this topic may produce interesting results.

Acknowledgment

The authors are grateful for financial support provided by the Eastman Kodak Company, Eastman Chemical Division, Kingsport, Tennessee. We are indebted to Drs. J. J. Siirola and D. L. Martin for their technical advice and continued interest in our work.

Notation

B = bottom product flow rate
C = total number of species present
D = distillate product flow rate
F = feed flow rate
L = liquid flowrate inside the column or reflux flow rate
N = total number of trays
P = total pressure
r = reflux ratio
r_{min} = minimum reflux ratio
s = reboil ratio
$\underline{x}$ = vector of liquid-phase compositions
$\underline{y}$ = vector of vapor-phase compositions

y_N = overhead vapor composition
T = temperature
V = vapor flow rate

Greek letter

ϕ = ratio of the two liquid phases in the decanter

Subscripts

B = bottom
c = condenser
D = distillate
F = feed
i = species i
lean = entrainer-lean (composition)
R = reflux stream
m = plate number in stripping section
N = top tray in a heterogeneous column
n = plate number in rectifying section
rich = entrainer-rich (composition)

Superscripts

I = liquid phase one
II = liquid phase two
o = overall

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Manuscript received Dec. 20, 1988, and revision received July 24, 1989.