

Synthesis and design of heterogeneous separation systems with recycle streams[☆]

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Abstract

Geometric methods are one of the most valuable tools for distillation process synthesis and design. The graphical representation of azeotropes, residue curves, distillation regions, and distillation boundaries provide designers with intuition, a wealth of knowledge about the entire composition space and quantitative results. In this paper we show how residue curve maps and geometric methods can be used in the synthesis and design of sequences of complex heterogeneous azeotropic distillation columns. A new algorithm for the design of heterogeneous azeotropic distillation column with top decanter is presented and applied in two design case studies of column sequences with recycle streams and top decanters. In both the cases, a feasible structure has been quickly found based on information obtained by examining the entire composition space.

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1. Introduction

Highly non-ideal mixtures of ethers, alcohols and water are commonly encountered in industrial processes. In these mixtures, numerous azeotropes, multiple distillation regions, distillation boundaries, and immiscibility gaps (regions of two or more liquid phases) are frequently encountered. Without adequate knowledge about these constraints (or opportunities) for distillation, the synthesis and design of separation systems for these mixtures can be very difficult and time consuming, especially, if the designer's only tool is a simulator.

Distillation systems are frequently "designed by simulation" or designed by "trial and error", where the configuration of the column is assumed (guessed) and all process parameters are estimated (e.g. by applying "short cut methods"). In this paper, we use residue curve maps (RCMs) and geometric methods to design separation systems with multiple-feed distillation columns, recycles and decanters. We show how analysis of the overall component space (RCMs, distillation boundaries and two-liquid phase regions) can be used for an efficient and reliable generation of feasible separation schemes. Finding the best process

configuration can be quickly achieved by analyzing the entire composition space.

2. Examining the whole separation space

One of the most useful tools to characterize azeotropic mixtures is a RCM. Each residue curve on the map is a locus of liquid compositions during a simple batch distillation process [1,2]. The singular points of the RCM are the azeotropes and pure components of the mixture. Information about the number and the nature of all azeotropes in the system is of critical importance to the design of azeotropic distillation systems [3] since existence of azeotropes can lead to multiple distillation regions and numerous distillation boundaries between them [4]. Distillation boundaries restrict products that can be obtained from a simple distillation column. As a rule, both the products (distillate and bottoms) should be in the same distillation region [5,6]. However, distillation boundaries can be crossed by mixing streams or by decanting (if a mixture forms multiple liquid phases).

Let us examine two examples of separation spaces for the following azeotropic ternary mixtures:

- benzene–ethanol–water system at 1 atm, NRTL model in liquid phase, ideal gas model in vapor phase (Fig. 1);
- di-*iso*-propyl ether–*iso*-propanol–water system at 1 atm, UNIQUAC model in liquid phase, ideal gas model in vapor phase (Fig. 2).

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Nomenclature	
B	bottoms
D	distillate
DB1, DB2, ...	distillation boundaries
f	upper to lower feed ratio
F	overall feed
F_l	lower feed
F_u	upper feed
L_1, L_2	liquids in decanter
q	feed quality (thermodynamic state of a stream)
\bar{q}	overall feed quality
r	reflux ratio
R1, R2, ...	distillation regions
s	reboil ratio
T_v	top vapor
x_i	liquid mole fraction of component i
y_i	vapor mole fraction of component i

Both systems exhibit the following topological characteristics [7]:

- one ternary heterogeneous azeotrope (unstable node);
- three binary azeotropes (saddles);
- three pure components (stable nodes);
- three distillation regions and three distillation boundaries between them;
- one immiscibility gap, which spans through all three distillation regions.

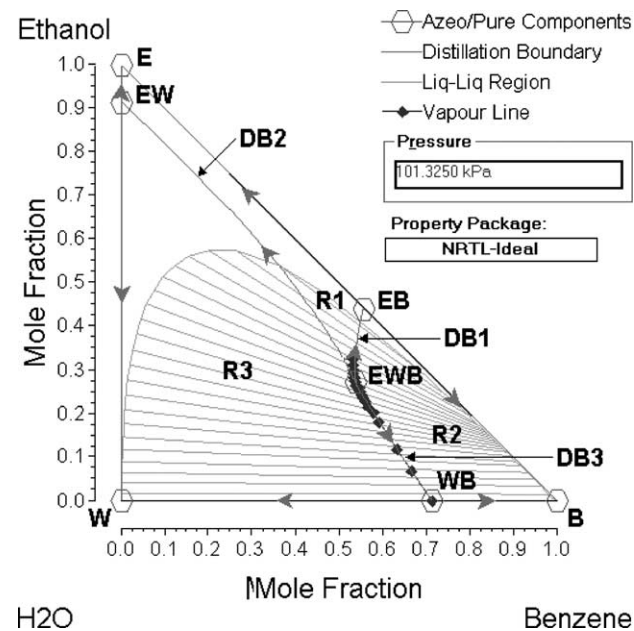


Fig. 1. Separation space for the azeotropic system benzene–ethanol–water with labeled azeotropes, distillation boundaries, liquid–liquid equilibrium region and vapor line.

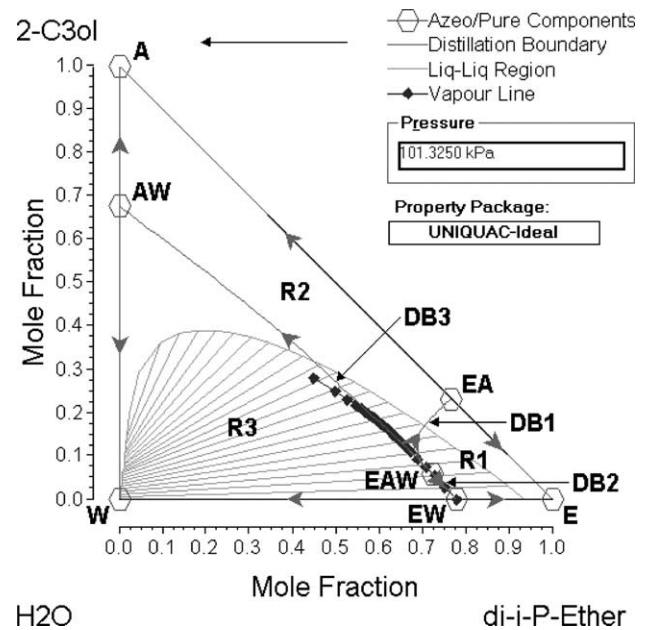


Fig. 2. Separation space for the azeotropic system di-*iso*-propyl ether–*iso*-propanol–water with labeled azeotropes, distillation boundaries, liquid–liquid equilibrium region and vapor line.

Since distillation boundaries can be crossed in decanters, a distillation column with top decanter can be a good candidate to perform separation for systems characterized by this type of RCM.

3. Heterogeneous distillation column design

For distillation column design, we use the *boundary value design method* (BVDM) [8]. The detailed algorithm for one-feed, two-product distillation column design is described in our previous paper [3]. Here, we focus on the key element of heterogeneous separation sequences—the distillation column with top decanter.

In the case of distillation column with top decanter, usually a distillate stream D (Fig. 3) is specified [9–11]. The stream composition must be placed on a tie line representing liquid–liquid equilibrium in the decanter. The decanter tie line should cross distillation boundaries. At least part of it should be in the same distillation region as the desired bottom product B . These specifications require many trial and error iterations and are useful only for ternary mixtures, where all mass balances and tie lines can be displayed on a graph. Instead, we propose to specify the composition of the vapor (T_v) leaving the column and entering the condenser such that the two liquids in the decanter can be formed from the totally condensed vapor. The tie line through the top vapor composition provides the entire range of possible distillates that can be achieved by varying the relative amounts drawn of the two liquids in the decanter. When the bottom composition (B) has been selected, the overall

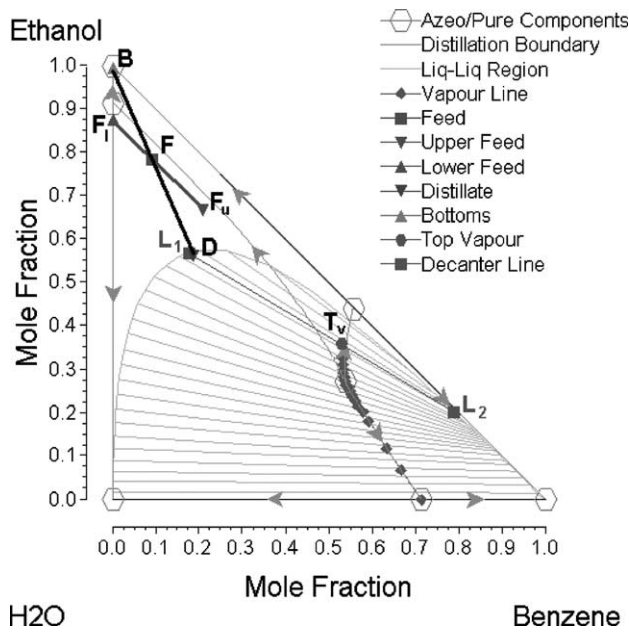


Fig. 3. Mass balances for two-feed distillation column with top decanter.

composition of the distillate can be calculated from an overall mass balance. For the column to be feasible, the top vapor composition must be in the same distillation region as the bottom composition. This procedure can be easily extended to systems with more than three components. By knowing exactly which distillation region we should place the distillation column in, we can easily select the top vapor composition since in general it should be very close to the unstable node of this region (heterogeneous azeotrope). The modified BVDM algorithm for double-feed distillation column with top decanter can be summarized as follows:

- (1) Specify column pressure.
- (2) Specify composition and thermodynamic state of the original feed (lower feed F_1 in Fig. 3).
- (3) Specify (guess) composition and thermodynamic state of the recycle stream from the second column in the sequence (upper feed F_u in Fig. 3).
- (4) Specify (guess) upper to lower feed ratio ($f = F_u/F_1$) and calculate composition of the overall feed (F):

$$x_i^F = \frac{f}{f+1} x_i^{F_u} + \frac{1}{f+1} x_i^{F_1} \quad (1)$$

- (5) Specify composition of the bottom product (B).
- (6) Select top vapor composition (T_v) in two-liquid region close to the heterogeneous azeotrope and in the same distillation region as the bottom product. Find the decanter tie line (L_1, L_2).
- (7) Calculate distillate product (D) as an intersection of the decanter tie (L_1, L_2) line and the column mass balance line through bottom product (B) and the overall feed (F , see Fig. 3).
- (8) Guess a reflux ratio (r).

- (9) Calculate overall composition of the reflux stream from the decanter mass balance:

$$x_i^R = \frac{1+r}{r} y_i^{T_v} - \frac{1}{r} x_i^D \quad (2)$$

- (10) Calculate reboil ratio (s) from the overall distillation column energy balance:

$$s = \frac{D}{B} (r + \bar{q}) + \bar{q} - 1 \quad (3)$$

where the overall feed quality (\bar{q}) is defined as

$$\bar{q} \equiv \frac{f}{f+1} q_u + \frac{1}{f+1} q_l \quad (4)$$

- (11) Compute rectifying composition profile down the column starting from the top vapor composition up to a pinch point (see for details, e.g. [8,9]).
- (12) Compute stripping composition profile up the column starting from the bottom composition up to a pinch point.
- (13) Select a point on the stripping composition profile and calculate the middle composition profile up the column starting from this point up to a pinch point or a composition boundary.
- (14) Repeat (8)–(13) until rectifying and middle composition profiles intersect in the composition space.
- (15) Count the number of stages in each section of the column.

There is an additional degree of freedom in design of two-feed distillation columns. In point (13) of the algorithm, we have to specify the upper feed location. Since this parameter can have significant effect on the total cost of the column we perform an appropriate parametric study (calculate several middle composition profiles [3,11]) and select the middle composition profile that gives the lowest total number of stages in the column.

4. Using top decanter to cross distillation boundaries

A reactor effluent contains 22 mol% of di-*iso*-propyl ether (E), 45 mol% of *iso*-propanol (A) and 33 mol% of water (W). The stream (F_1 in Fig. 4) should be separated to the desired product (pure E) and the recycle stream to the reactor (containing only A and W).

There are three distillation regions (defined by a set of singular points) in the EAW system at 1 atm (Fig. 2):

- R1: EAW, EW, EA, E;
- R2: EAW, EA, AW, A;
- R3: EAW, EW, AW, W;

and the three distillation boundaries:

- DB1 between regions 1 and 2: EAW, EA;
- DB2 between regions 1 and 3: EAW, EW;
- DB3 between regions 2 and 3: EAW, AW;

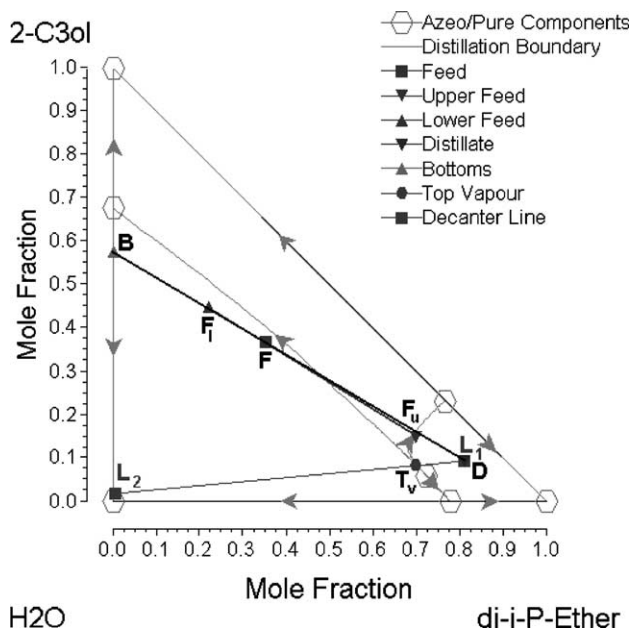


Fig. 4. Mass balance for two-feed distillation column with top decanter for the di-*iso*-propyl ether separation problem.

and one immiscibility gap that spans through all three distillation regions. EAW stands for the heterogeneous di-*iso*-propyl ether (E)–*iso*-propanol (A)–water (W) azeotrope, and EW for di-*iso*-propyl ether (E)–water (W) azeotrope, etc.

Since the feed and the main product are in different distillation regions, it is necessary to have at least two distillation columns to perform the desired separation. We need to cross the distillation boundary, and the first column (with decanter at the top) makes this possible (Fig. 4). The organic phase

(L_1) from the decanter (distillate) can be fed to the second distillation column that separates it to the desired product (pure E) and the recycle stream (F_u). The separation can be accomplished in the two-column sequence shown in Fig. 5.

Our design method has been implemented in Distil—software for conceptual design of distillation processes [12]. First, components were selected, UNIQUAC model for liquid phase and ideal gas model for vapor phase. Then interaction parameters were regressed using experimental VLE data. The thermodynamic state for all streams was set to $q = 1$ (boiling liquid) and pressures in all columns to 1 atm.

For the first distillation column double feed and saturated decanter options were selected. Then the following parameters were specified:

- original feed (lower feed): $x_E = 0.2216$, $x_A = 0.4518$;
- top vapor (in distillation region R3, close to ternary azeotrope): $x_E = 0.7$, $x_A = 0.086$;
- bottoms: $x_E = 0.001$, $x_A = 0.5798$;
- upper feed (recycle from the second column, in distillation region R1, close to distillation boundary DB1): $x_E = 0.7$, $x_A = 0.153$;
- upper to lower feed ratio: $f = 0.375$;
- reflux ratio: $r = 7.5$.

By entering a new specification for any stream entering/leaving the column, all other streams are more and more restricted by mass balances and the lower and upper limits for composition of each component in each stream can be calculated (see, e.g. Fig. 10). This allows for quick adjustment of the specifications, e.g. to manipulate x_A for bottoms to obtain distillate composition in region R1. When enough specification has been entered (all degrees of freedom has been used [3]), reboil ratio, rectifying, stripping and middle composition profiles in the column are calculated. The

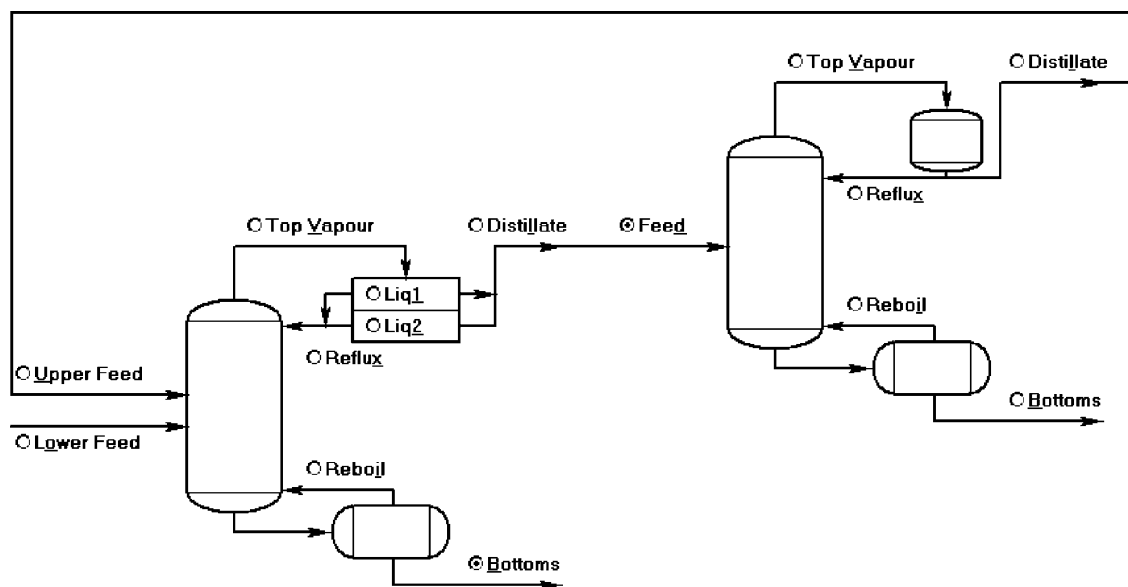


Fig. 5. PFD for the heterogeneous azeotropic distillation sequence.

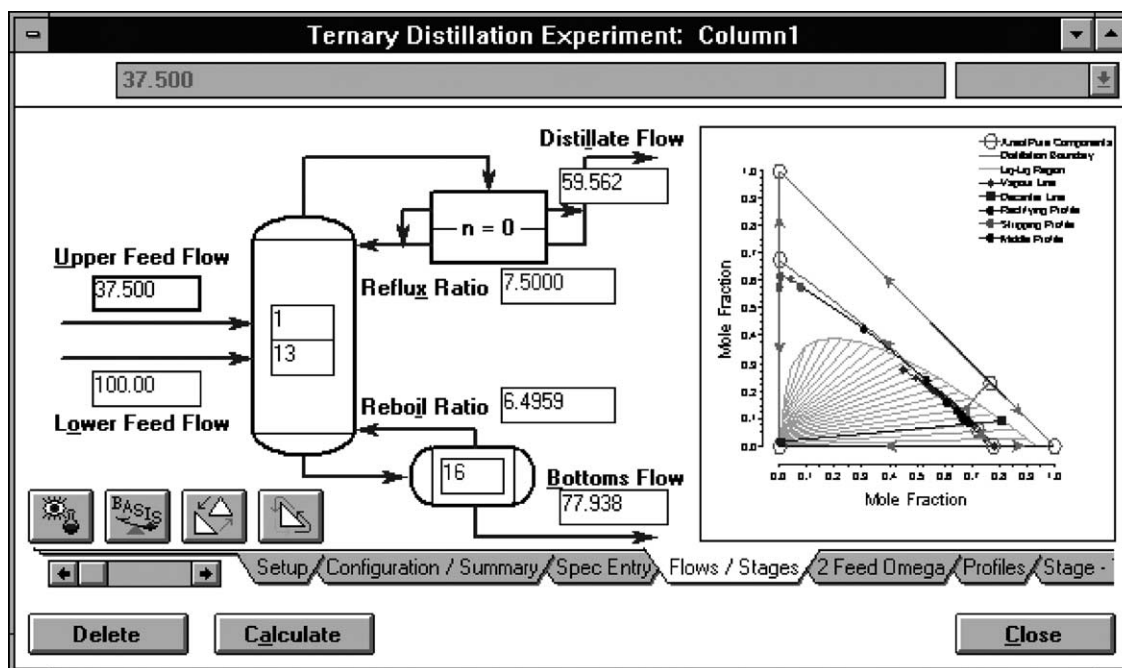


Fig. 6. Design of the first distillation column in the di-*iso*-propyl ether separation sequence.

lower feed location (13th stage) is optimized [3] and the upper feed location (first stage) is determined by intersection of middle and rectifying composition profiles. The total number of stages required for the separation is 16. Composition profiles and flow rates for the double-feed distillation column are shown in Fig. 6.

For the second distillation column the single feed option was selected. The feed composition was copied from distil-

late in column 1. Then the following parameters were specified:

- bottoms: $x_E = 0.999$, $x_W = 10^{-15}$;
- distillate (recycle to the first column): $x_E = 0.7$;
- reflux ratio: $r = 4$.

Composition profiles, flow rates and the number of stages in each section for the second distillation column are shown

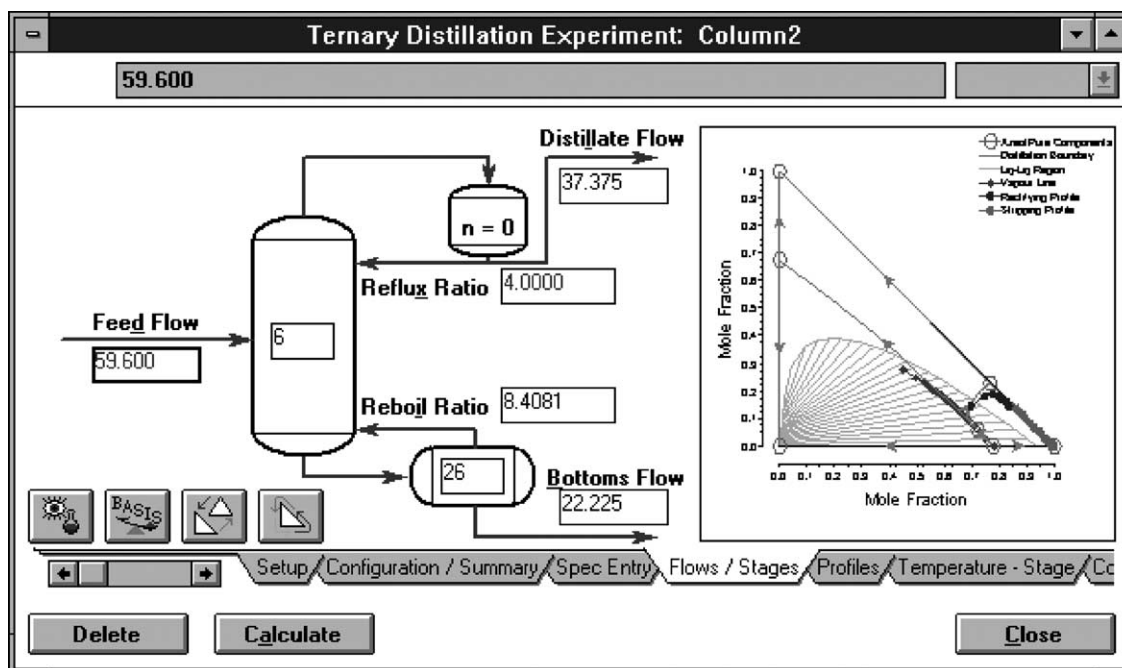


Fig. 7. Design of the second distillation column in the di-*iso*-propyl ether separation sequence.

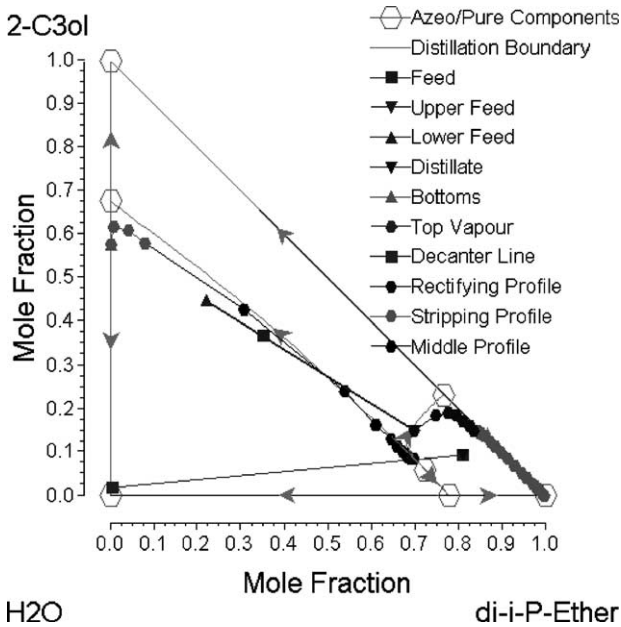


Fig. 8. Mass balance and liquid profiles for the whole di-*iso*-propyl ether separation sequence.

in Fig. 7. The whole sequence liquid composition profiles, recycle balance, decanter line and distillation boundaries are shown in Fig. 8.

There are some specifications in the algorithm, which can be optimized, e.g. reflux ratios in both columns. Furthermore, recycle calculations require multiple iterations between the first and the second column to converge recycle stream composition, which is guessed in the first column

(upper feed) and then calculated in the second column (distillate).

5. Breaking binary azeotropes by heterogeneous azeotropic distillation

The dehydration of organic alcohols is a common problem that accompanies their production. Most alcohol–water mixtures form azeotropes. This makes it impossible to separate them in a single distillation column. This is the case in a water–ethanol mixture.

Let us analyze in detail the design of a separation sequence to separate a binary mixture (88 mol% of ethanol, and 12 mol% of water) into pure components. The ethanol product can contain maximum 0.1 mol% of water. To facilitate separation, benzene can be chosen as an entrainer to break the binary azeotrope between ethanol and water. As a result we have to consider the ternary system benzene (B)–ethanol (E)–water (W) (Fig. 1), which additionally has one ternary and two binary azeotropes. At 1 atm, there are three distillation regions (defined by a set of singular points):

- R1: EWB, EB, EW, E;
- R2: EWB, EB, WB, B;
- R3: EWB, WB, EW, W;

and three distillation boundaries:

- DB1 between regions 1 and 2: EWB, EB;
- DB2 between regions 1 and 3: EWB, EW;
- DB3 between regions 2 and 3: EWB, WB;

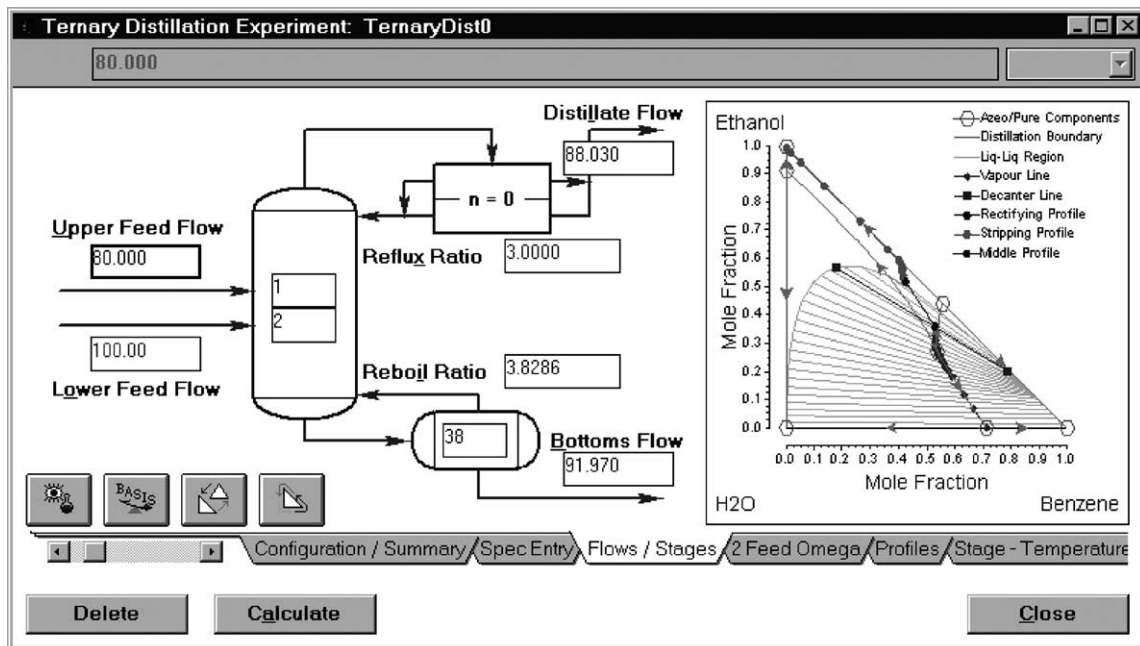


Fig. 9. Design of the first distillation column in the ethanol dehydration sequence.

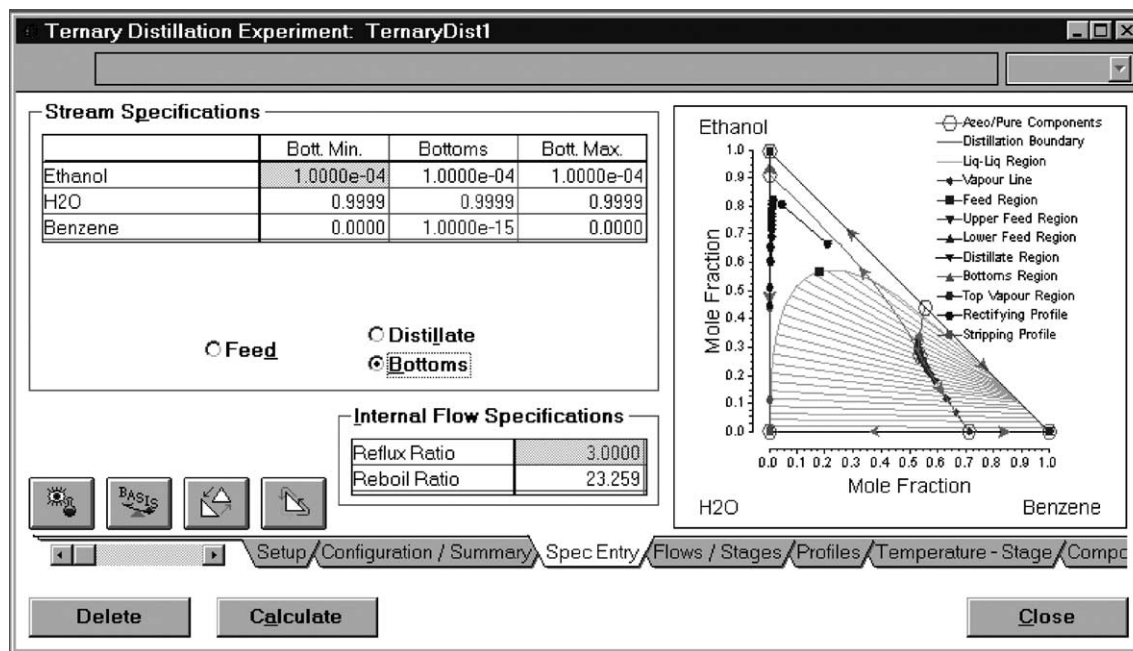


Fig. 10. Design of the second distillation column in the ethanol dehydration sequence.

and one immiscibility gap, which spans through all three distillation regions. EWB stands for the heterogeneous ethanol (E)–water (W)–benzene (B) azeotrope, and EW for ethanol (E)–water (W) azeotrope, etc. Our desired products (E and W) are in different distillation regions (R1 and R3). By applying decanters, we can cross distillation boundaries between the regions and make separation feasible.

To start synthesis of the separation sequence let us take a closer look at Fig. 3. We can take the advantage of the two-liquid phase region by selecting a top vapor composition inside the region near the ternary heterogeneous azeotrope. Then we can decant the totally condensed top vapor into an aqueous phase (most of which is taken as distillate) and an organic phase, which will be completely returned to the column. We can take 99.9% pure ethanol from the bottom of the column (it is in the same region as the top vapor). We have to add some amount of benzene to the water–ethanol mixture (lower feed to the column) to satisfy the overall column mass balance. It could be pure benzene, but instead we can use the recycle stream from the second column in the sequence. It should be added to the first column as the upper feed (Fig. 3). The distillate from the first column (aqueous phase from the decanter) must be separated to pure water and the recycle stream. This can be accomplished in one distillation column since both products belong to the same distillation region. The whole sequence resulting from the above analysis is shown in Fig. 5.

Once again we use the conceptual design software to assist us in the calculations necessary for this design. As in the previous example, the thermodynamic state for all streams was set to $q = 1$ (boiling liquid) and the pressure in both columns was set to 1 atm. First, components were selected,

NRTL model for liquid phase and ideal gas model for vapor phase. The default interaction parameters were used [12]. Two ternary distillation views have been created [12], one for the first distillation column in the ethanol dehydration sequence (double-feed, saturated top decanter, Fig. 9), second for the benzene recovery column (single-feed, no decanter, Fig. 10).

For the first distillation column the following parameters were specified:

- original feed (lower feed): $x_E = 0.88$, $x_W = 0.12$;
- top vapor (in distillation region 1, close to the ternary azeotrope): $x_E = 0.36$, $x_B = 0.53$;
- bottoms: $x_E = 0.999$, $x_B = 10^{-15}$.

At this time, the upper feed (recycle from the second column) and the upper to lower feed ratio (f) was not specified. The decanter tie line was calculated since the overall composition in decanter was already specified (equal to the top vapor composition). The aqueous phase L_1 (Fig. 3) or $L_1 +$ small amount of L_2 (to account for a not perfect phase separation in decanter) can be taken as a distillate D from the first column and put as a feed to the benzene recovery column. Additionally, the following parameters for the second column were specified:

- bottoms: $x_W = 0.9999$, $x_B = 10^{-15}$ (see Fig. 10);
- distillate (recycle to the first column, in distillation region R3, close to the distillation boundary DB2): $x_E = 0.67$;
- reflux ratio: $r = 3$.

Since sufficient specifications have been entered, the reboil ratio and rectifying and stripping profiles in the second column (Fig. 10) can be calculated. The total number of

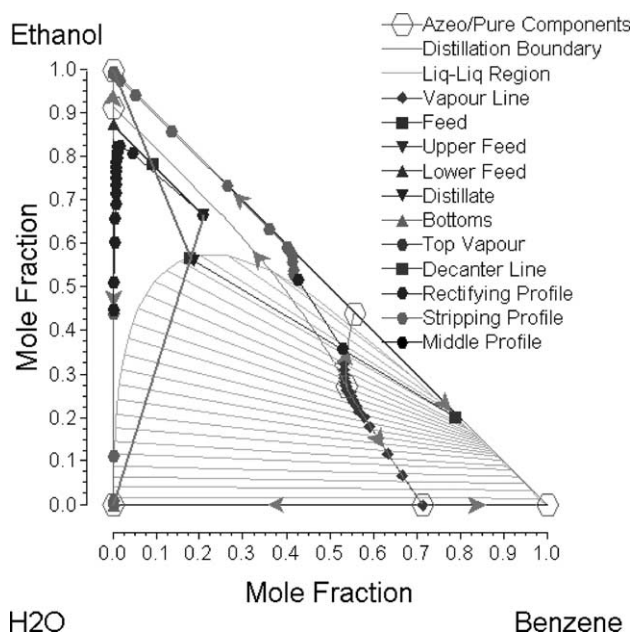


Fig. 11. Mass balance and liquid profiles for the ethanol dehydration sequence.

stages required for this separation is 22, with the feed location at the 17th stage. Next, the distillate stream from the second column was copied to the upper feed of the first column. These new specifications make it possible to close the double-feed column mass balance and calculate the upper to lower feed ratio ($f = 0.8$). After specifying the reflux ratio ($r = 3$), all remaining parameters for the first column have been calculated. Composition profiles, flow rates and the number of stages in each section of the first distillation column are shown in Fig. 9. The whole sequence mass balances, liquid composition profiles, recycle balance, decanter line and distillation boundaries are shown in Fig. 11.

6. Conclusions

RCMs and geometric methods are very useful in synthesis and design of sequences of complex azeotropic distillation

columns with recycle streams, top decanters and multiple feeds. Process configuration for difficult separation problems can be quickly found by examining the entire component space. Distillation boundaries can be effectively crossed by using distillation columns with top decanters placed in two-liquid phase regions close to heterogeneous azeotropes.

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