

Optimal design of complex azeotropic distillation columns

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Received 21 April 1999; received in revised form 16 December 1999; accepted 2 February 2000

Abstract

Geometric methods are valuable tools for process synthesis and design since they provide designers with intuition and quantitative results. The calculation and graphical representation of azeotropes, residue curves and distillation boundaries provide a wealth of knowledge about the entire composition space. This paper shows how these tools can be used for optimal design of complex azeotropic distillation columns. Two examples of the design of distillation systems of industrial importance are shown. In the first example, the second feed location of a two-feed distillation column with a top decanter is optimized. In the second example, the side stream draw-stage location of a distillation column with a top decanter and a side stream draw is optimized. In both cases, a feasible and near optimal structure has been designed based on information obtained by examining the whole composition space. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Distillation column; Azeotropic distillation; Optimization

1. Introduction

The separation of mixtures with several azeotropes and one or more two-liquid phase regions is a task commonly encountered in chemical processes. These mixtures usually have more than one distillation region that complicates the design of the distillation systems used to separate them.

Design by simulation is still the dominant method for distillation system design. For complex azeotropic distillation systems, however, this is a tedious and time-consuming *trial-and-error* method that often requires many years of experience. In this technique, all the input variables (feed flow rate, its thermodynamic state and composition) and process parameters (pressure, reflux ratio, number of stages, feed stage location) are specified, and the composition and flows of the products are calculated. This is a robust technique for establishing the performance of existing columns. For design purposes, however, it requires the estimation of the above parameters by guessing, extrapolation of existing separation systems or by applying *short-cut methods* (e.g. the Fenske–Underwood–Gilliland–Eduljee–Kirkbride method) [1]. Since these methods have been developed for ideal mixtures under several simplifying assumptions, they are not accurate for non-ideal mixtures and can give initial

estimates that are either far from the final solution or are not feasible.

Establishing feasibility as quickly as possible is very important in the design of complex azeotropic distillation systems [2] since neither all separation schemes nor all desired specifications are feasible. Using the *design by simulation* approach, these facts are often discovered only after extensive simulation studies. *Geometric methods* allow designers to find feasible separation schemes far more quickly, even for highly non-ideal azeotropic systems, by examining the overall separation space, its stationary points (azeotropes), distillation boundaries, residue curves, and rectifying and stripping profiles. Difficult separation problems that can potentially take several months of trial and error simulations to complete can be solved in a few hours instead.

There is often an extra degree of freedom in the design of some complex distillation columns. There are multiple solutions for the same design problem. All of them satisfy product specifications, but require different number of stages in the column. To obtain the best solution, we perform the appropriate parametric study and display the results of this study in a diagram, which shows the effect of the selected parameter on the total number of stages in the column. This graphical method is highly intuitive, fast and efficient. However, if there is more than one degree of freedom, the more efficient NLP or MINLP optimization method should be applied to find the best solution.

In this paper, we show how the examination of the overall separation space can help in the creation of feasible

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separation schemes. We focus on the design of complex heterogeneous azeotropic distillation columns with decanters, multiple feeds, and side stream draws, where an extra degree of freedom requires a one-parameter optimization in order to find the optimal solution among several feasible ones.

2. Getting feasible designs by examining separation space

Let us consider separation spaces for two examples of ternary azeotropic mixtures by labeling the azeotropes, distillation boundaries, two-liquid phase regions and the corresponding vapor lines. In Fig. 1, the *water–acetic acid–*n*-butyl acetate* system shows one azeotrope and one distillation region (the azeotrope is an unstable node, *n*-butyl acetate is a stable node and the other components are saddles). In the *water–butanol–*n*-butyl acrylate* system, shown in Fig. 2, there are three binary azeotropes and one ternary azeotrope. These azeotropes give rise to three distillation regions (the ternary azeotrope is an unstable node, all binary azeotropes are saddles, and all pure components are stable nodes).

In order to characterize a system, one requires knowledge of the nature of all the azeotropes and pure components in the system. This information is also necessary for distillation boundary calculation [3] since, for ternary systems, the distillation boundaries are special residue curves that connect azeotropes. The boundaries between distillation regions restrict the products that can be obtained from a simple distillation column (one feed, two products). As a rule, both products should lie in the same distillation region [4,5]. Distillation boundaries can be crossed by mixing streams or by decanting if the mixture forms multiple liquid phases (e.g. the *water–butanol–*n*-butyl acrylate* system in Fig. 2).

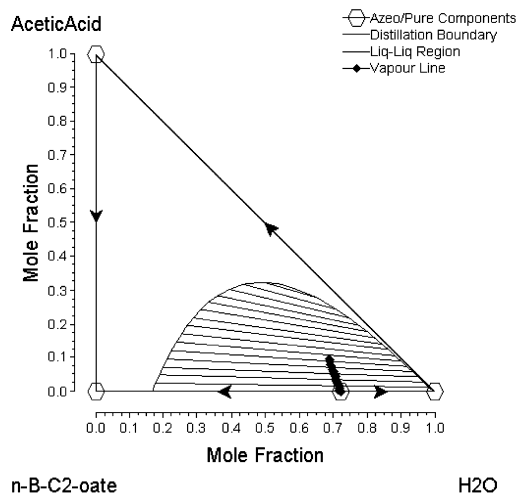


Fig. 1. Separation space for *acetic acid–water–*n*-butyl acetate* as predicted by a *UNIQUAC-Dimer* model at 101.325 kPa. The system's azeotrope, distillation boundary, liquid–liquid equilibrium region and vapor line has been labeled.

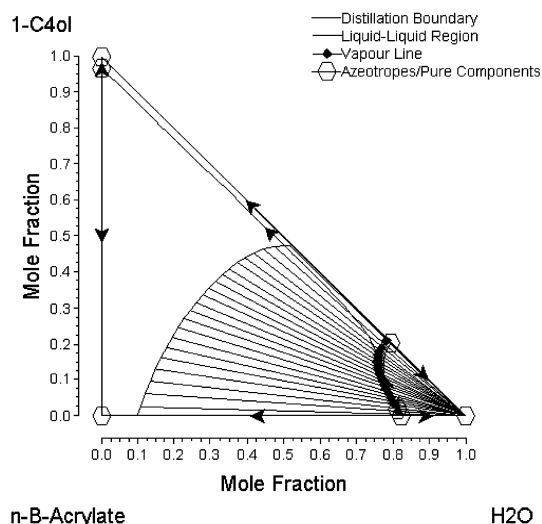


Fig. 2. Separation space for *water–butanol–*n*-butyl acrylate* as predicted by a *NRTL-Dimer* model at 26.34 kPa. The system's azeotropes, distillation boundaries, liquid–liquid equilibrium region and vapor line has been labeled.

The information about *all* azeotropes among a considered component set is of critical importance to the design of azeotropic distillation systems. We compute temperatures, compositions and stabilities (stable node, unstable node or saddle) of azeotropes predicted by thermodynamic models for multicomponent mixtures at a specific pressure by the most reliable homotopy method combined with an arc-length continuation [6]. In this method, we exploit an efficient scheme for finding all stationary points of the boiling surface, starting from pure component solutions for a hypothetical ideal mixture described by the Raoult Law at the beginning of the homotopy path (homotopy parameter $h=0$). Then, we gradually 'add non-idealities' to our model by increasing the homotopy parameter and, eventually, ending with the rigorous model for $h=1$ [7]. This calculation approach is very robust, since all solution branches are connected. The eigenvalues of the Jacobian calculated at stationary points give the stabilities of azeotropes and pure components. Thereafter, we check the topological consistency of the residue curve map via the Zharov and Serafimov topological constraint [8]. The homotopy continuation method developed for multicomponent, homogeneous mixtures has been generalized to include heterogeneous mixtures [9].

3. Distillation column design

Residue curve maps (RCMs) are very useful for the characterization of azeotropic mixtures, predicting feasible splits, selecting entrainers, and analyzing potential column operability problems [2–5,10,11]. They display the shape of the separation space, including distillation boundaries, distillation regions and azeotropes. Residue curves are

equivalent to the composition profiles of infinitely long packed column at total reflux (continuous model described by differential equations). Composition profiles of staged column at total reflux (discrete model described by finite difference equations), can be approximated by simple distillation residue curves and usually the differences between these two types of curves are small [2]. Using residue curve maps, infeasible specifications can be immediately identified, and alternative distillation sequences can be inferred without trial and error. The shapes of residue curves are very useful in the design of real finite reflux separators since they give a qualitative picture of the composition profiles in actual staged towers.

In this paper, we use the *boundary-value design method* (BVDM) [11] for the distillation column design. For a one-feed, two-product distillation column, we define the feed, specify completely distillate and bottoms (using component and overall mass balances) and select the column's internal flows (by specifying reflux or reboil ratio and using an energy balance). The composition profiles are then calculated using a combination of flashes and mass balances starting from both ends. If the composition profiles for rectifying and stripping sections of the column cross in the composition space, the column is feasible and the number of stages in each section of the column can be counted. The BVDM algorithm for a ternary one-feed two-product distillation column can be summarized as follows:

1. Specify feed composition and thermodynamic state.
2. Specify column pressure.
3. Specify three of six possible products' mole fractions.
4. Calculate the remaining products' mole fractions using mass balances.
5. Guess a value for the reflux ratio.
6. Calculate reboil ratio using energy balance.
7. Compute the composition profiles for the rectifying and stripping sections of the column starting from distillate and bottoms compositions.
8. Repeat (5)–(7) until composition profiles intersect in the composition space.
9. Repeat (2)–(7) to optimize reflux ratio and pressure.
10. Count the number of stages in each section of the column.

For distillation columns with top decanter, a side stream draw or two feeds, the algorithm requires modifications. These modifications will be explained within the following examples.

4. Degrees of freedom in design

For a c component mixture, distillation columns with one feed and two products, can be described by a total of $3c+6$ variables:

- \mathbf{x}_F , composition of the feed stream (c specifications)
- \mathbf{x}_D , composition of the distillate stream (c specifications)
- \mathbf{x}_B , composition of the bottoms streams (c specifications)

- P , column pressure
- r , reflux ratio
- s , reboil ratio
- q , feed quality
- n , number of stages in the column
- f , feed stage location

These variables are related by 3 summation equations for mole fractions in each stream, $c-2$ co-linearity conditions between \mathbf{x}_B and \mathbf{x}_D (derived from mass balances), and one condition between r and s (energy balance). The BVDM makes it possible to compute the rectifying composition profile starting from the distillate composition, and the stripping profile starting from the bottoms composition. The distillation column will be feasible only if the profiles intersect in the composition space. The point of intersection represents the composition of the liquid stream leaving the feed stage and gives extra $c-1$ constraints to the system. Consequently, the system has a total of $c+5$ degree of freedom. Once P , \mathbf{x}_F and q have been specified, the distillation column has only four remaining degrees of freedom:

- three between \mathbf{x}_B and \mathbf{x}_D ; and
- one between r and s .

For ternary systems ($c=3$), we are free to specify three product compositions (at least one in each product). The remaining compositions will be determined from co-linearity conditions. Since the column has no additional degrees of freedom for compositions, if the composition profiles intersect, the feed stage location will be fully determined.

For binary systems ($c=2$), we can independently specify only two product compositions (one in each product). Consequently, we have one extra degree of freedom in the design of a binary distillation column. The feed stage location is not fully determined and we are free to choose as a feed stage any stage between the rectifying and stripping pinches, where both profiles overlap. Often there are multiple solutions for our design problem, all of which satisfy the product specifications but require different number of stages in the column. To obtain the best solution, a one-parameter optimization is performed to minimize the total number of stages in the column. The independent variable, ω , is the normalized distance in the composition space along the profiles between both rectifying and stripping pinches.

For four or more component mixtures, the BVDM requires specification of reflux or reboil ratio and three product compositions (at least one in each product). Since $c \geq 4$, none of the products can be fully specified. Thus, for more than three components, the BVDM requires a search over the remaining $c-3$ product compositions until the column feasibility criterion is satisfied.

Ternary distillation columns with two feeds require extra specifications. The second feed composition and the feed ratio must be defined. Using a *design-by-simulation* technique, the designer is required to provide the second feed plate location. This is an extra degree of freedom in the design of double feed columns. In the BVDM, we perform an appropriate parametric study and show the results of this study

in a diagram form, which shows the effect of the second feed plate location on the number of column stages. As it is normally beneficial to select the fewest number of stages to perform a desired separation, a feed plate location corresponding to the lowest total number of stages in the column is calculated and can be selected.

In the case of a ternary distillation column with side draw, the total number of specifications changes. An extra component specification is required. A list of feasible side draws can be calculated by computing the profile from the end of the column and verifying that the candidate side stream draw will satisfy the overall mass balance. Once the final side stream specification is made, the BVDM can be resumed.

Distillation columns with top decanters need the specifications of the vapor from the column 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 range of possible distillates that can be achieved. When the bottom composition has been selected, the overall composition of the distillate can be calculated as the intersection of the decanter tie line and the column mass balance line. Specification of the top vapor is more convenient than specification of distillate, since we usually take a top vapor close to a ternary heterogeneous azeotrope and it must be in the same distillation region as the bottom composition.

It is important to note that the number of specifications (degrees of freedom) in both the BVDM and a standard simulation are the same, although the actual variables selected as specifications are different. In a simulation of a distillation column, the specifications that are typically made include the feed composition and thermodynamic state, number of stages, feed plate location, reflux ratio, and distillate flow rate. Product compositions are the results of the simulation. In the BVDM, the feed plate location and number of theoretical stages are calculated, but product compositions are specified. So, we specify what we want to achieve in distillation and calculate parameters of the column, which will accomplish our separation. If the rectifying and stripping composition profiles cross in the component space, a feasible column is guaranteed.

5. Example 1: Two-feed distillation column with top decanter

This example shows how a difficult separation caused by a tangent pinch between components can be avoided by adding an entrainer. The entrainer adds to the system a new heterogeneous azeotrope, but at the same time moves the distillation profile away from the binary pinch towards the minimum boiling azeotrope. A decanter can then be used to obtain required distillate purity in far fewer stages than in the original binary distillation.

Dehydration of acetic acid is a problem often encountered in the chemical industry. There is no azeotrope in this binary

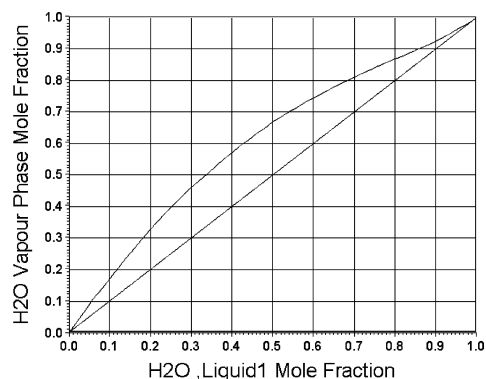
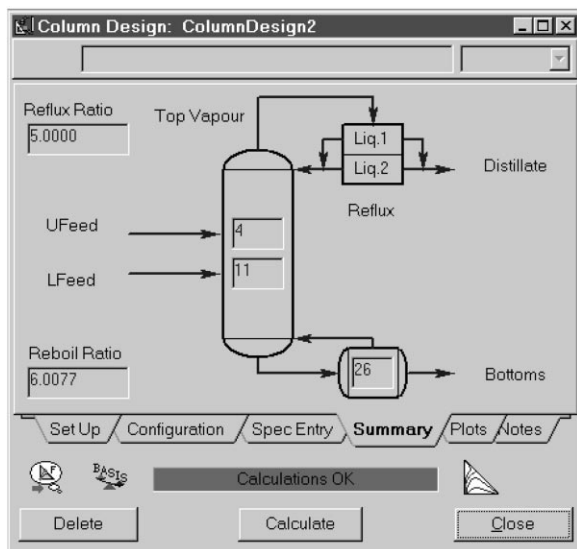


Fig. 3. x - y diagram for an acetic acid and water mixture as predicted by a UNIQUAC-Dimer model at 1 atm. Notice the strong tangent pinch at high water mole fractions.

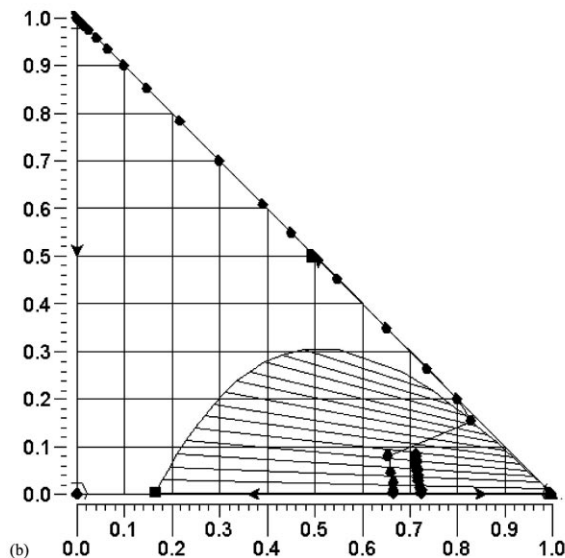
mixture at 101.325 kPa. There is, however, a tangent pinch close to pure water (Fig. 3), which makes this binary separation very expensive (high reflux and a lot of stages in the rectification part of the column) if high purity water is required (e.g. to meet environmental requirements). After selection of *n-butyl acetate* as the entrainer (quite frequently, the proper entrainer already exists in the whole process), we can examine the whole composition space for multiple liquid regions, azeotropes, and distillation boundaries as shown in Fig. 1. The entrainer adds to the system a new heterogeneous azeotrope, but at the same time creates a two-liquid region, in which a decanter can be used to obtain required distillate purity. We have two inlet streams to the column: the original *water-acetic acid* mixture and the entrainer makeup. We can mix them and introduce them to the column as a single feed stream, but it is usually a good idea to separately add streams that have different compositions to the column in different stages. A two-feed distillation column with a top decanter is what we need for this separation (Fig. 4a and b).

The BVDM algorithm for a ternary two-feed distillation column with a top decanter (with some design details specific for this case) can be summarized as follows:

1. Specify column pressure (101.325 kPa)
2. Specify upper feed composition (pure *n-butyl acetate*) and thermodynamic state (saturated liquid).
3. Specify lower feed composition (equimolar mixture of *water* and *acetic acid*) and thermodynamic state (saturated liquid).
4. Specify upper to lower feed ratio (0.001).
5. Specify bottom product (almost pure *acetic acid*: $x_{AA}=0.999\%$; trace amount of entrainer: $x_E=1.0e-6$).
6. Select top vapor composition in the two liquid region close to heterogeneous azeotrope ($x_{AA}=0.001$, $x_W=0.723$).
7. Select the aqueous liquid phase from decanter as the distillate product.
8. Guess a value for the reflux ratio ($r=5.0$).
9. Calculate reboil ratio using energy balance.
10. Calculate rectifying profile up to a pinch point.



(a)



(b)

Fig. 4. (a) Two-feed distillation column with top decanter and (b) the column liquid profiles for the acetic acid dehydration problem. Optimal $\omega=0.5786$.

11. Select one stage from the rectifying profile as the upper feed location.
12. Compute the intermediate composition profile down the column starting from the selected upper feed location.
13. Compute the stripping composition profile up the column starting from the bottom composition.
14. Repeat (8)–(13) until intermediate and stripping composition profiles intersect in the composition space.
15. Count the number of stages in each section of the column.

As mentioned before, there is an additional degree of freedom for ternary two-feed distillation column design. We have to specify the upper feed location (Point 11 of the algorithm). In the BVDM, we perform the appropriate parametric study and show the results of this study in a diagram (Fig. 5)

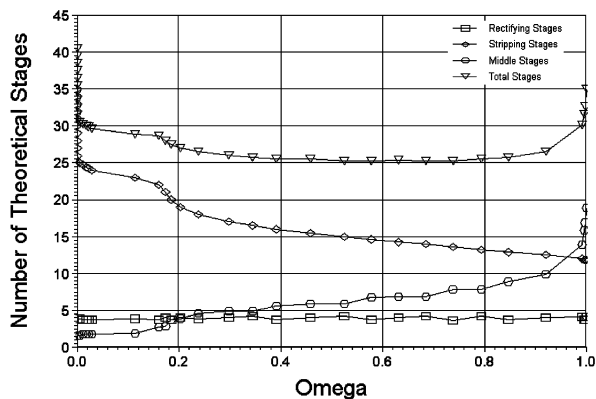
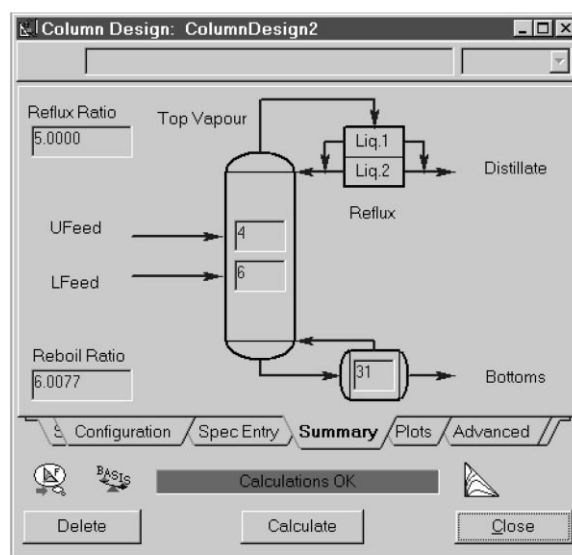
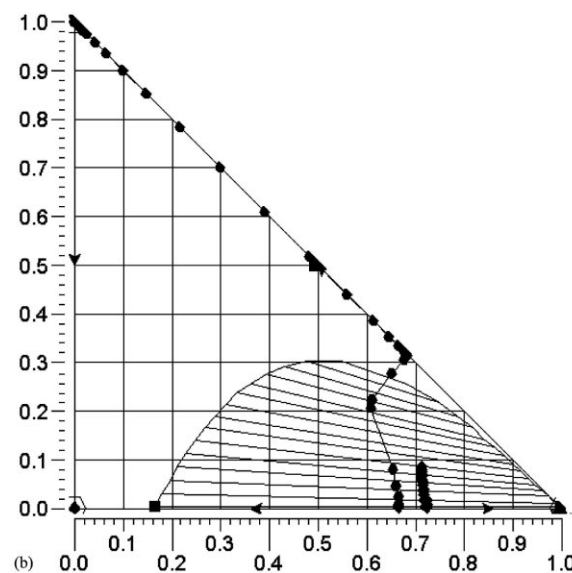


Fig. 5. ω diagram for the acetic acid dehydration problem. Selecting an ω effectively chooses the second feed location. Naturally, it is best to choose the second feed to minimize the total number of stages.

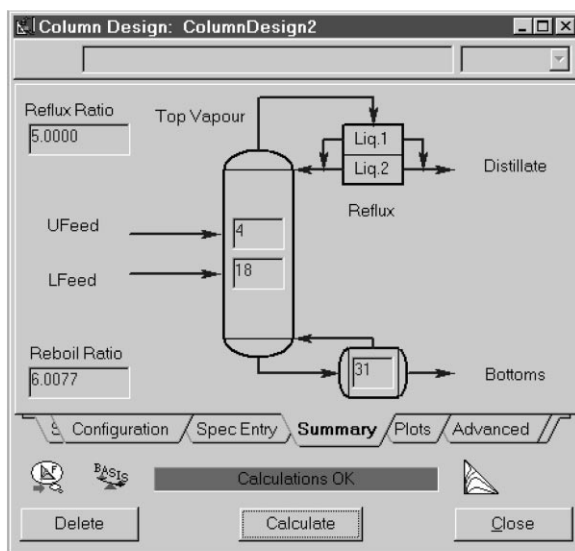


(a)



(b)

Fig. 6. (a) Two-feed distillation column and (b) the column liquid profiles for the acetic acid dehydration problem. $\omega=0.01$.



(a)

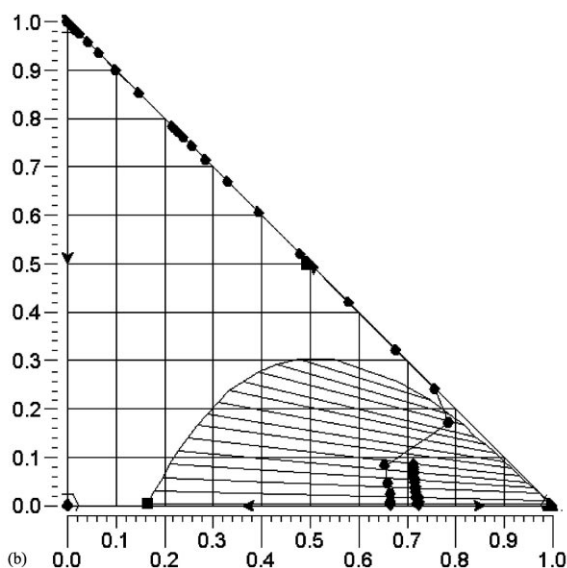
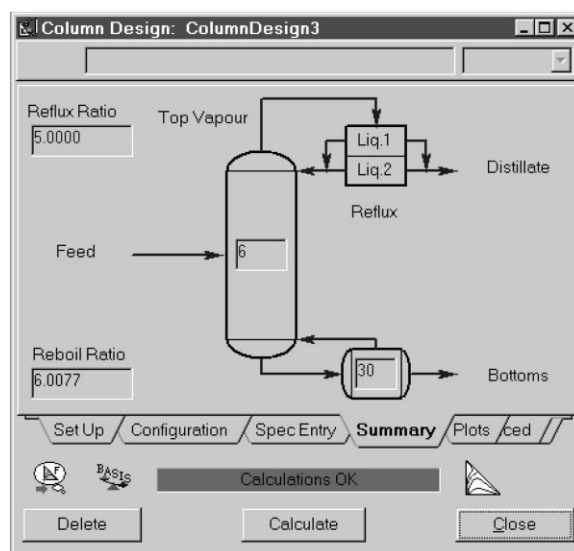


Fig. 7. (a) Two-feed distillation column and (b) the column liquid profiles for the acetic acid dehydration problem. $\omega=0.99$.

which shows the effect of the upper feed plate location on the total number of column stages as well as number of stages in each column section. As it is normally beneficial to select the fewest number of stages to perform a desired separation, a feed plate location corresponding to the lowest total number of stages in the column has been selected ($\omega=0.58$). In our case, the optimum is quite flat and selection of ω in the 0.4–0.8 range does not make a big difference in total number of stages. The results of our design (upper and lower feed locations, number of stages in the column) are shown in Fig. 4a together with column liquid profiles shown in Fig. 4b.

The independent variable, ω , is a normalized distance in composition space along the rectifying profile between the first and the last feasible upper feed plate locations. Two additional, not-optimal designs are shown in Fig. 6a and b



(a)

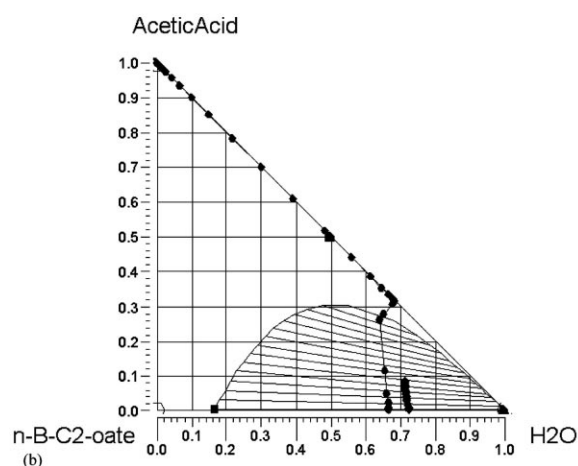
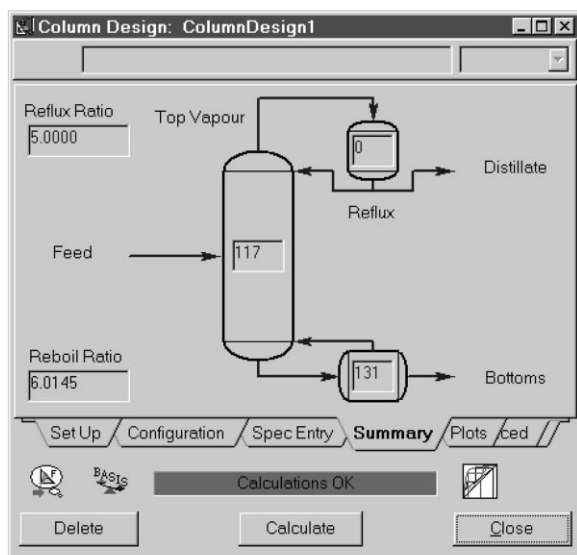


Fig. 8. (a) Single-feed distillation column and (b) the column liquid profiles for the acetic acid dehydration problem.

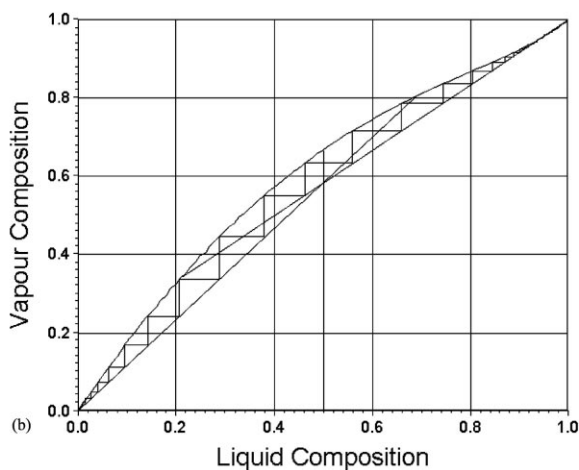
and Fig. 7a,b for $\omega=0.01$ and 0.99, respectively. Both require a total of 31 stages in the column (5 more than the optimal solution), but the stages are distributed differently between middle and stripping sections of the column.

The separation can also be achieved in a single feed column as shown in Fig. 8a,b. As expected, the design requires more stages in the column than the two feed column design. The separation is also possible without adding any entrainers. The binary distillation column shown in Fig. 9a,b requires 131 theoretical stages to produce the same *water* purity (99.78 mol%) as the columns with decanters. For a required *water* purity of 99.5 mol%, there are still 75 stages in the column, more than twice the optimal design with entrainer.

In binary distillation column design (Fig. 9a,b), we specify two product compositions (one in each product), choose reflux ratio and calculate the reboil ratio from energy balance. Then, both the rectifying and stripping profiles can



(a)



(b)

Fig. 9. (a) Binary distillation column and (b) the column composition profile for the acetic acid dehydration problem. Water purity 99.78 mol%. Notice the large number of stages near the tangent pinch.

be calculated starting at product compositions and ending at the fixed points where the operating lines intersect the equilibrium curve (see McCabe–Thiele diagram in Fig. 9b). There are at least two fixed points in each profile, one stable and one unstable node. For a reflux less than a minimum reflux, both profiles are isolated. For the minimum reflux, the profiles just touch each other (the stable nodes in both profiles are at the same point). For a reflux greater than the minimum reflux, profiles overlap and we can choose the feed stage as any stage between rectifying and stripping pinches. This is an extra degree of freedom in the design of binary distillation column. For the same reflux ratio, there are multiple designs, which satisfy product specifications but require different numbers of stages in the column. This is a good opportunity for applying a parameter optimization to obtain the best design. We have chosen the total number of stages in the column as the optimization

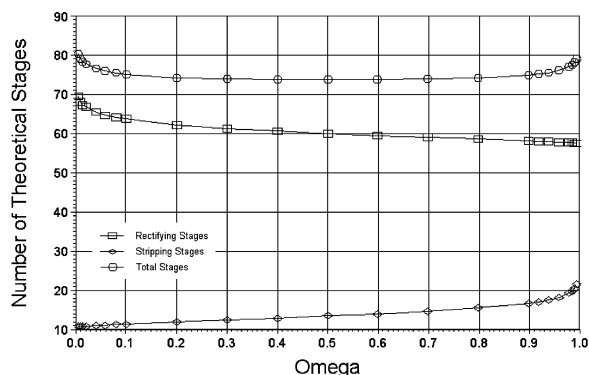


Fig. 10. Binary distillation column ω diagram.

criteria and the independent variable (ω) is a normalized distance between both rectifying and stripping pinches (Fig. 10).

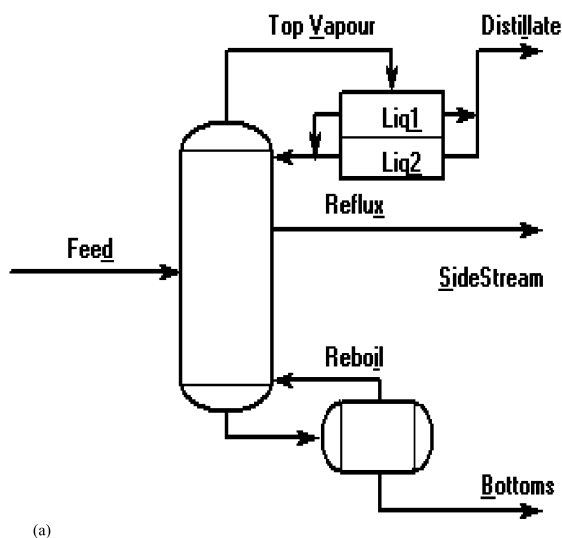
6. Example 2: Distillation column with side stream draw and top decanter

In a continuous *n-butyl acrylate* (BA) production process, the BA is made by reacting excess *butanol* (B) and *acrylic acid* in the presence of a catalyst in a heated continuous stirred tank reactor. After some preliminary separations, the product stream containing the BA, B and *water* (W) is pumped to a dehydration column to remove W and alcohol. A side draw from the column containing mostly alcohol can be recycled to the reactor without any additional purification.

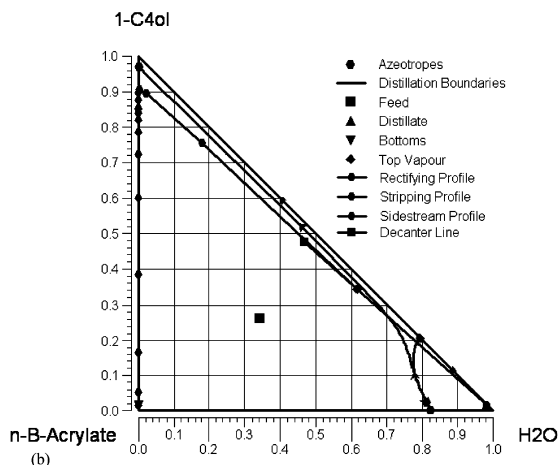
After performing a non-linear regression to estimate binary interaction parameters for the ternary system using vapor–liquid and liquid–liquid equilibrium experimental data [12–14], we can examine the whole composition space for multiple liquid regions, azeotropes, and distillation boundaries as shown in Fig. 2. The feed composition is in the distillation region defined by the BA vertex, and the BA–B, BA–B–W and BA–W azeotropes. The BA stable node (maximum boiling composition in the region) can be taken as a bottom product. The BA–B azeotrope (saddle) can be taken as a side draw stream and recycled to the reactor. The top vapor from the column can be condensed and decanted, making it possible to cross a distillation boundary and get almost pure W as a distillate. The separation can be accomplished in the distillation column shown schematically in Fig. 11a together with final liquid column profiles shown in Fig. 11b.

The BVDM for this ternary distillation column (with some design details) can be summarized as follows:

1. Specify column pressure, feed composition and thermodynamic state.
2. Specify bottom product (almost pure BA: $x_{BA}=0.99\%$; trace amount of W: $x_W=6.0e-16$).



(a)



(b)

Fig. 11. (a) Distillation column with side-stream draw and top decanter and (b) the column liquid profiles for the *n*-butyl acrylate dehydration problem.

3. Select top vapor composition in the two liquid region ($x_W=0.62$, $x_B=0.34$).
4. Select the aqueous liquid phase from decanter as the distillate product.
5. Guess a value for the reflux ratio.
6. Calculate rectifying profile.
7. Displays all stages, which can be chosen as a side stream draw stage (feasible overall mass balance).
8. Select one stage from the list.
9. Calculate reboil ratio using energy balance.
10. Compute the composition profiles for the intermediate and stripping sections of the column starting from side stream draw and bottom compositions.
11. Repeat (5)–(10) until composition profiles intersect in the composition space.
12. Count the number of stages in each section of the column.

As mentioned before, there is an additional degree of freedom in the case of a distillation column with side stream

draw. An extra specification is required. It could be a side stream draw stage number, one component mole fraction in the side stream, etc. In our algorithm, we calculate a list of feasible side stream draws by computing a profile from one end of the column and checking the overall mass balances for candidates for side draws (Point 7 of the algorithm). Then we select one stage from the list. In our example, the optimal decision is to choose the stage with maximum alcohol concentration (the closest stage to the BA–B azeotrope saddle).

Distillation towers with side stream draws can be promising alternatives to a traditional column sequences, if the side stream purity is not so important (e.g. if the side stream can be recycled to a reactor). However, if high purity is required, the reflux ratio needed to achieve such separation can be very high. Before deciding whether a traditional or side stream sequence should be chosen an economical analysis must be done.

7. Conclusions

In this paper we use residue curve maps and geometric methods to design multiple-feed distillation columns with decanters and side stream draws. Analysis of the overall component space (residue curves, distillation boundaries, and two-liquid phase regions) is essential in the generation of optimal separation schemes. It is necessary to locate the best process configuration before optimizing the selected structure since an optimal design using an average process configuration can be much more costly than an average design using a good configuration [15]. Finding the best process configuration can be quickly achieved by examining the entire component space. The visual information provided by geometric methods to a column designer result in a deeper understanding of the thermodynamic behavior and the constraints to separations encountered in the system. This creates the opportunity for a quick and creative generation of feasible solutions to difficult separation problems.

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