Distillation is the most widely used separation process in the chemical process industries. In a typical chemical plant, distillation columns and their support facilities can account for about one-third of the total capital cost and more than half of the total energy consumption. Consequently, the design and optimization of the distillation train have a critical impact on the economics of the entire process.

In general, at phase equilibrium, the compositions of the coexisting vapor and liquid phases are different. Distillation exploits this difference in the relative volatilities of the individual components in the mixture to achieve the desired separation. For many mixtures, the order of the components’ relative volatilities does not change over the entire range of mixture compositions. However, some mixtures exhibit one or more azeotropes, or points at which the compositions of the coexisting liquid and vapor phases are the same. As a result, it is not possible to separate these mixtures into their pure constituents via distillation alone.

An azeotrope can be either homogeneous, containing one liquid phase, or heterogeneous, consisting of two liquid phases. Heterogeneous azeotropes can be easily separated using a decanter coupled with one or more distillation columns, which exploits both vapor-liquid and liquid-liquid equilibrium driving forces. Homogeneous azeotropic compositions that are pressure-sensitive can be separated using pressure-swing distillation, which utilizes two or more distillation columns operating at different pressures together with appropriate recycle strategies to achieve the desired separation. However, if the change in azeotrope composition is small, the pressure-swing distillation sequence will have very large recycle flowrates, resulting in an uneconomical process.

In all other cases, the only way to separate homogeneous azeotropic mixtures via distillation is by adding an extraneous component, referred to as an entrainer or mass-separating agent, to facilitate the separation. Entrainers are also used to enable the separation of non-azeotropic mixtures where the direct separation is either not feasible due to process constraints (e.g., maximum operating temperature) or highly uneconomical (e.g., due to the presence of a severe tangent pinch, as in the case of acetic acid and water).

An entrainer facilitates the separation of an azeotropic mixture by selectively altering the relative volatilities of the components in question, thereby effectively “breaking” the azeotrope. The entrainer is specific to the mixture in question — e.g., benzene is a feasible entrainer for separating ethanol and water, but not for separating ethanol and methyl ethyl ketone — so there are no universal entrainers.

Because the choice of an entrainer determines the separation sequence (the number and order of distillation columns and decanters, and how they are interconnected), and hence the overall economics of the process, entrainer selection is a critical step in the synthesis and conceptual design of azeotropic distillation processes. Entrainers are commonly selected based on prior experience with the same or a similar process. This approach rarely identifies novel entrainers that could have a dramatic impact on the economics of the entire process.

**Residue curve map technology**

One methodology for determining entrainer feasibility utilizes residue curve map (RCM) technology. A residue curve map is a geometric representation of the vapor-liquid equilibrium (VLE) phase behavior of multicompo-
Component mixtures, highlighting, in particular, those properties that directly impact distillation (1). It represents a collection of residue curves, or trajectories of liquid-phase compositions (mole or mass fractions) as they change with time. Pure-component vertices, connected by lines that form the binary edges, bind this composition space. The boiling points of the pure components and any existing binary, ternary, or multicomponent azeotropes (mole/mass fractions and boiling points) are indicated on the diagram. The composition trajectories move from the lightest component in the mixture to the heaviest — *i.e.*, the temperature continually increases as the liquid gets richer in the heavier component. The directions of the curves are consistent with the curves on the binary edges.

The general properties of residue curves and how to sketch the maps are explained in detail in Ref. 1.

The RCM for the ternary system containing acetone, methanol, and methyl ethyl ketone (MEK) is illustrated in Figure 1. The composition space is drawn first, the pure component compositions and temperatures are indicated at the vertices, and the azeotropes (binary or ternary) and their temperatures are marked. As shown in Figure 1a, this system forms two homogenous binary azeotropes (acetone/methanol and methanol/MEK) and no ternary azeotropes. Once the temperatures are indicated, an arrow is added on each of the binary edges in the direction of increasing temperature, *i.e.*, from lightest boiler to heaviest boiler (including both pure components and azeotropes). The residue curves originate at the lightest boiler, the acetone-MEK azeotrope, and go in the direction of either MEK or methanol, creating an imaginary boundary connecting the two binary azeotropes. The dividing curve is called a distillation boundary.

The presence of azeotropes divides the composition space into distillation regions separated by the distillation boundary such that the residue curves in each region go in different directions (*i.e.*, toward different components). As shown in Figure 1b, the distillation boundary divides the composition space into Region 1, acetone/methanol-MEK/MEK, where the residue curves go toward MEK, and Region 2, acetone/methanol-MEK/methanol, where the residue curves go toward methanol. In the case of a multicomponent mixture where more than one azeotrope may exist, multiple distillation boundaries may also exist. A distillation boundary exists if the residue curves begin at the same point but end at different points (*i.e.*, in different regions), or if they begin at different points but end at the same point (*i.e.*, from different regions).

A distillation boundary represents an impassible boundary for distillation (although it may be crossed using other separation techniques, such as liquid-liquid phase separation, solid-liquid separation, etc.), and the distillate and bottoms product for each column must lie in the same distillation region. Consequently, the presence, location and structure of these boundaries are critical in determining the multicomponent distillation feasibility. The general properties and more examples of distillation boundaries are explained in detail in Ref. 1.

RCM technology has been extensively tested and verified in industry. Residue curve maps have been used to systematically synthesize distillation sequences to achieve a desired separation, to determine novel separation sequences, and to identify and evaluate entrainers (1–3). RCM technology can also be extended to reactive distillation — depicting the appearance of new azeotropes created by the reaction (reactive azeotropes), and allowing material
balances and sequences of operations to be determined.
The nature of the RCM changes with the extent of reaction, i.e., depending on reaction kinetics (4).

To evaluate entrainer feasibility using RCM methodology, first compute the RCM for the system consisting of the azeotropic components to be separated and the candidate entrainer. Next, check the phase behavior of the system to determine whether a liquid-liquid phase envelope exists. If one does exist, a liquid-liquid phase region for the system components can be generated at a certain temperature (e.g., at the temperature of the heterogeneous azeotrope, at the temperature where the liquid-liquid region is the largest, or at a desired operating temperature). The tie-lines indicate the two-phase compositions. Then draw an envelope over the RCM composition space, superimposing the composition scale (rather than the temperature scale). The candidate entrainer is feasible if either (a) the entrainer does not divide the components to be separated into different distillation regions, or (b) the entrainer induces a liquid-liquid phase separation and there exists a liquid-liquid equilibrium tie-line crossing the distillation boundary. Once a feasible entrainer is identified, the corresponding separation sequences can be systematically synthesized from the structure of the RCM (1, 5).

The workflow for screening entrainers

Various commercial computer tools are available for generating residue curve maps from a thermodynamic physical-property model for the system. However, in the early stages of process development, when decisions regarding the process structures are generally made, such detailed thermodynamic models for the system are generally not available and can be very expensive to develop.

Therefore, a step-by-step approach in which the likely separation boundaries and feasible separation sequences are first “sketched” is recommended. This synthesis activity is coordinated with suitable experiments and modeling to verify the feasibility of the candidate processes. This allows a more comprehensive search with minimum effort, while greatly facilitating process development (6).

For entrainer selection, the approach begins by sketching the structure of the RCM (and liquid-liquid phase equilibrium, if necessary) from only the azeotropic temperature, and approximating composition and solubility data using the methodology previously described (and discussed in detail in Ref. 1).

To screen entrainers and determine the sequence for separating a mixture of components A and B:

1. Compile a list of candidate entrainers. Some criteria for compiling this list include:

   a. components that are already present in the process, especially reactants
   b. components that are present on the plant site (so no new chemical is introduced in the plant’s waste-treatment unit)
   c. water (since it forms heterogeneous azeotropes with many components, the separation is easier, although the use of water may increase the load on the waste treatment facility)
   d. entrainers used for the same or similar components
   e. commonly available chemicals.

2. Prepare an RCM for each candidate entrainer:

   a. If a detailed thermodynamic physical-property model is available, compute the RCM for the system of A, B and the entrainer. If only a partial model is available, the remaining mixture properties can be modeled using UNIFAC, provided the predictions are in agreement with available azeotrope data.
   b. If no physical-property model is available, sketch the structure of the RCM from available azeotropic temperature, composition (approximate) and solubility (approximate) data.
   c. If neither a physical-property model nor azeotrope data are available, the required information can either be estimated using group contribution methods or an educated guess. These can then be verified experimentally.

3. From the structure of the RCM, determine if the candidate entrainer is feasible for separating components A and B, i.e., both A and B lie in the same distillation region, or the entrainer introduces a liquid-liquid tie-line that crosses the distillation boundary dividing components to be separated into different distillation regions.

4. Synthesize all the corresponding separation sequences — the number of distillation columns and decanters, and their interconnections — from the structure of the RCM by mass balance. Do this for each feasible entrainer.

5. Identify the entrainer feasibility conditions for the most promising candidate entrainers if their feasibility was determined from either azeotropic data or estimated using group contribution techniques (2b or 2c above). Subsequently, experimentally verify any of the conditions whose validity may be in doubt. Once these conditions have been verified, a detailed thermodynamic physical-property model for the mixture can be developed from experimental data.

6. Design, simulate and optimize the separation sequences.

Types of experiments

After identifying the key properties or missing data that need to be verified, determine which experiments are appropriate to confirm the characteristics desired in an
entrainer. Various types of vapor-liquid experiments (i.e., vapor-liquid and liquid-liquid equilibrium measurements) can be used in different steps of the entrainer selection process.

To determine the structure of the RCM for an entrainer, the boiling point and azeotrope data for the various binary pairs and/or ternary combinations need to be known. An experimental device known as a spinning-band distillation apparatus is used to determine the nature, composition and temperature of the azeotrope. This device consists of a spinning band that simulates the stages of distillation, such that the lightest boiler in the mixture (minimum-boiling azeotrope or pure component) is distilled first. In the case of heterogeneous azeotropes, this vapor contains multiple liquid phases and the composition for each needs to be determined. Maximum-boiling azeotropes are less prevalent and more difficult to measure. They are measured in a vapor-liquid equilibrium apparatus as outlined in the next paragraph. Experiments at different pressures can indicate how the azeotrope changes with pressure.

To build a thermodynamic physical-property model for use in detailed system design (Step 5), vapor-liquid and liquid-liquid equilibrium data are needed. These data can be collected in an apparatus wherein the mixture is first equilibrated; vapor and liquid samples are then taken and the compositions measured. For a heterogeneous system, additional experiments are needed to measure the phase splitting of an equilibrated mixture at a certain temperature. These can indicate the behavior of the liquid-liquid tie-lines, which is important in determining the feasibility of the distillation sequence. Experiments at different temperatures can indicate how the size of the liquid-liquid region changes so that the optimal decanter temperature can be selected. Some experimental devices allow experiments to be conducted at pressures other than atmospheric. The composition and temperature data are then used to determine thermodynamic model parameters by regression.

**Example 1. Is acetone a feasible entrainer for separating isopropanol and water?**

The first step in determining if acetone is a feasible entrainer for separating isopropanol and water, which form a minimum-boiling homogeneous azeotrope, is to compute the residue curve map for the isopropanol/water/acetone system (Figure 2). An analysis of this RCM shows that the system exhibits a distillation boundary that divides the composition space into two distillation regions. Since water and isopropanol lie in different distillation regions, and acetone does not induce a liquid-liquid phase separation, acetone is not a feasible entrainer for separating water and isopropanol.

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**Figure 2.** An RCM for isopropanol/water/acetone at 1.0 atm shows a distillation boundary that divides isopropanol and water into two separate distillation regions. Therefore, acetone is not a feasible entrainer for separating isopropanol and water.

**Figure 3.** In the RCM corresponding to classic extractive distillation for a given A-B-E system such that the isovolatility curve intersects the B-E edge of the composition space, B will be the distillate from the extractive column. An industrial separation corresponding to this RCM is water (A), ethanol (B), and ethylene glycol (E).

**Figure 4.** An extractive-distillation sequence for separating A and B using entrainer E requires a double-feed extractive column.
Figure 5. A pseudo-binary VLE diagram for ethanol/water at fixed ethylene glycol compositions shows that as the ethylene glycol composition is increased, the ethanol/water pseudo-azeotrope moves toward ethanol and eventually disappears. At this point, ethanol is more volatile, so it will be the distillate from the extractive column in Figure 4.

Example 2. Extractive distillation

In extractive distillation, a heavy (high-boiling, low-volatility) entrainer is used to separate a mixture exhibiting a minimum boiling azeotrope. The typical extractive-distillation entrainer has a higher boiling point than the pure components, and it does not form any azeotropes with either of the pure components.

A common industrial example of extractive distillation is the use of ethylene glycol to separate ethanol and water. The residue curve map corresponding to a similar extractive distillation is shown in Figure 3. Since this RCM does not exhibit any distillation boundary, the components to be separated (A and B) lie in the same distillation region, and hence the candidate entrainer (E) is feasible. Analysis of the extractive distillation RCM reveals that A and B (at all feed compositions) can be separated using the sequence shown in Figure 4. Note that the first column, the extractive column, must be a double-feed column, with two separate feed locations and stages, both above and below each feed. The entrainer is introduced at the upper feed location and the feed to be separated is introduced at the lower location. One of the components is recovered as the distillate from the extractive column and the other as the distillate from the second column, the entrainer recovery column.

The isovolatility curve (the locus of points at which the relative volatility of A and B is equal to 1) can be used to determine which of the two components, A or B, is the distillate from the extractive column. This curve (Figure 3) starts at the binary azeotrope and ends at one of the other edges of the composition triangle. If it intersects the B-E edge, then B will be the distillate from the extractive column; alternatively, if it intersects the A-E edge, then A will be the extractive-column distillate. In addition, the closer the intersection is to the pure component A or B, the better the entrainer for this separation (i.e., the smaller the entrainer-to-feed ratio). Therefore, the isovolatility curve can be used to quickly and efficiently rank candidate entrainers for extractive distillation.

The component recovered as the extractive-column distillate can also be determined using a pseudo-binary phase diagram, in which VLE data are plotted on an entrainer-free basis (Figure 5). As the amount of entrainer is increased, the composition of the pseudo-azeotrope (i.e., the point at which the pseudo-binary VLE curve crosses the 45-deg. line) changes until it completely disappears. The more volatile of the two components at this point will be the distillate from the extractive column. The smaller the composition of the entrainer at which the pseudo-binary azeotrope disappears, the better the entrainer is (smaller entrainer-to-feed ratio). Consequently, pseudo-binary phase diagrams can also be used to rank candidate extractive-distillation entrainers. In addition, these diagrams are very useful for understanding the effect of mixed extractive-distillation entrainers.

Example 3. Using water to separate n-butanol and n-butyl acetate

Since butanol and water form a minimum-boiling homogeneous azeotrope, they cannot be separated without the use of an entrainer. One possible candidate entrainer is water. The residue curve map for butanol/butyl-acetate/water (Figure 6) shows that this system exhibits three binary azeotropes (butanol/butyl-acetate [homogeneous], butanol/water [heterogeneous], butyl-acetate/water [heterogeneous]) and a heterogeneous ternary azeotrope, and three distillation boundaries divide the composition space into three distinct distillation regions. Note that butanol and butyl acetate lie in different distillation regions. However, since this mixture also exhibits a multiple-liquid-phase region, with tie-lines that cross the boundary separating butanol and butyl acetate into different distillation regions, water is a feasible entrainer for separating butanol and butyl acetate.

The RCM in Figure 6a is similar but not identical to the classical ethanol/water/benzene example. The flowsheet sequence in Figure 6b also resembles one of the feasible sequences for separating ethanol/water using a heterogeneous entrainer. The difference in the RCMs is in the nature of the multiple-liquid-phase region. The ethanol/water/benzene system has a Type I phase enve-
Reactions and Separations

lope, i.e., only a single binary pair (namely benzene/water) exhibits a liquid-liquid behavior, whereas the butanol/butyl-acetate/water system has a Type II envelope, where two binary pairs (butanol/water and butyl-acetate/water, show heterogeneous behavior.

Table 1 lists all the thermodynamic conditions that water must satisfy in order for it to be a feasible entrainer for separating butanol and butyl acetate.

### Table 1. Water must satisfy all the following thermodynamic conditions in order for it to be a feasible entrainer for separating butanol and butyl acetate.

- Water and butanol form a minimum-boiling heterogeneous azeotrope
- Water and butyl acetate form a minimum-boiling heterogeneous azeotrope
- Water, butanol and butyl acetate form a ternary heterogeneous azeotrope
- The boiling point of the ternary azeotrope is lower than the boiling point of butanol and butyl acetate azeotrope
- The boiling point of the ternary azeotrope is lower than the boiling point of butanol and water azeotrope
- The boiling point of the ternary azeotrope is lower than the boiling point of butyl acetate and water azeotrope
- One end of the liquid-liquid equilibrium tie-line passing close to the ternary azeotrope must lie in the butyl acetate distillation region

A key advantage of using a residue curve map for entrainer selection is that it can be used to find novel entrainers and/or separation sequences. Consider water as a potential entrainer for separating a binary mixture containing 50 mol% diethoxymethane (DEM) and 50 mol% ethanol. This binary mixture forms a minimum-boiling homogeneous azeotrope (2). The residue liquid-liquid phase separation and there exists a liquid-liquid equilibrium tie-line crossing the distillation boundary).

An RCM sequencing analysis finds that butanol and butyl acetate can be separated using the arrangement shown in Figure 6b. The binary feed and the distillate from the second column are fed to the first distillation column, either at the same feed location or at different points. High-purity butanol is recovered as the bottoms product, while the overhead vapor is condensed and sent to a decanter. The water-rich (i.e., entrainer-rich) phase is refluxed back to the first column, while the entrainer-lean phase is sent to the second distillation column, where high-purity butyl acetate is recovered as the bottoms product. The distillate from the second column is a mixture of all three components and is recycled back to the first distillation column. This sequence is feasible for all butanol/butyl-acetate feed compositions. The material balance for this sequence is depicted in Figure 6a.

The butanol/butyl-acetate/water separation can also be carried out using another sequence where the order of the separations is reversed — butyl acetate is recovered from the first column, butanol from the second. This sequence is also valid for all butanol/butyl-acetate feed compositions. Which scheme is more economical is a function of the feed composition and how the sequences can be integrated with the rest of the process. This can be determined only after the conceptual design and simulation of both separation sequences.

Example 4. Diethoxymethane/ethanol separation using water

A key advantage of using a residue curve map for entrainer selection is that it can be used to find novel entrainers and/or separation sequences.

![Figure 6a. An RCM for the mixture n-butanol, n-butyl acetate and water at 1 atm exhibits liquid-liquid equilibrium tie-lines crossing the distillation boundary that separates butanol and butyl acetate.](image)

![Figure 6b. This sequence for separating n-butanol and n-butyl acetate using water as an entrainer is feasible for all butanol and butyl acetate feed compositions.](image)
The water/ethanol/DEM system at 1.0 atm exhibits: two homogeneous binary azeotropes (ethanol/water, ethanol/DEM), one heterogeneous binary azeotrope (water/DEM), and a ternary homogeneous azeotrope; three distillation boundaries (connecting the ternary azeotrope to each of the binary azeotropes); and a multiple-liquid-phase region (with tie-lines that cross the distillation boundary connecting the ternary azeotrope to the DEM/water azeotrope), as seen in the RCM.

The system exhibits three binary azeotropes and a ternary azeotrope, and it has three distillation boundaries. It also exhibits a multiple-liquid-phase region.

Water is not a typical heterogeneous entrainer (for example, as benzene is for ethanol dehydration or water is for separating butanol and butyl acetate), because the ternary azeotrope does not lie in the multiple-liquid-phase region. However, a detailed analysis of this RCM shows that it should be possible to use water to separate the binary mixture using the sequence of three distillation columns and a decanter shown in Figure 8. This separation sequence exploits the multiple-liquid-phase regions with tie-lines that cross the distillation boundary connecting the DEM/water azeotrope to the ternary azeotrope as well as the curved nature of the distillation boundary that connects the ternary azeotrope to pure ethanol. Since some of the properties used to compute the RCM were estimated using group contribution methods, the latter condition needs to be verified experimentally. (In addition to this sequence, others can be synthesized as well.)

**Final thoughts**

Although the RCM-based methodology is very powerful and can be used to find innovative new separation sequences and identify novel entrainers, several limitations have hindered its widespread use in industry. While there are now good commercially available tools for computing and sketching residue curve maps, they still require either a good physical-property model or an extensive azeotrope database. A bigger limitation is that interpreting the structure of the RCM and synthesizing feasible separating sequences requires significant knowledge and expertise in RCM technology. However, new software programs have recently become available that significantly reduce this hurdle and make the technology accessible to process engineers and chemists.

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**Literature Cited**