Synthesis of Azeotropic Batch Distillation Separation Systems

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Boyd T. Safrit

Department of Chemical Engineering
Carnegie Mellon University
5000 Forbes Avenue
Pittsburgh, PA 15213

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Abstract

Batch distillation has received renewed interest as the market for small volume, high value, specialty chemicals has increased. While batch distillation is more flexible than continuous distillation because the same equipment can be used for several products and operating conditions, batch distillation can be less flexible when azeotropes are present in the mixture to be separated. Azeotropes can form batch distillation regions where the types of feasible separations can be more limited than in continuous distillation.

New types of batch column configurations, such as the middle vessel column, can help in the separation of azeotropic mixtures. We show how insights developed for continuous distillation can identify the feasible products and possible column profiles for such a column. We compare extractive distillation using the middle vessel column and a batch rectifying column. While both can often theoretically recover 100% of the pure components from a binary azeotropic mixture, the middle vessel has the benefits of a finite size still pot which is made possible by “steering” the still composition versus time. We also investigate the operation of the extractive middle vessel column by looking at the sensitivity of a profit function to some of the operational parameters.

In order to separate azeotropic mixtures in general, a sequence of batch columns must normally be used. A tool for finding the basic, continuous and batch distillation regions for any mixture is developed in order to synthesize such sequences. This tool, given an initial still composition, can determine the possible products at total reflux and reboil and infinite number of trays for a variety of batch column configurations. We then show how to use such a tool in the synthesis of all possible batch column sequences.

Acknowledgments

The majority of the work done in this thesis was carried out using the ASCEND system, which is an object-oriented equation based modeling environment. I have to first thank Kirk Abbott and Ben Allan for the years of work they put in recoding ASCEND into C and adding a much more flexible user interface. I could have never obtained the results I did without this version of ASCEND or their help in other areas of this thesis.

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A very special thanks goes to my advisor, Art Westerberg, who has guided myself and my research over the past 5 years. His famous quote that I love, “I have my Ph.D., you get yours,” says much about Art, his advising philosophy, and the way I feel about my work. He was always there for guidance and the occasional “divine intervention” but the extra confidence and pride gained in doing one’s own work is what I believe Art means in his quote.

And finally, I have to thank my family and all of the many friends I have found here in Pittsburgh for all of their support and encouragement. My life and thesis would have been considerably less tolerable without you.

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Chapter 1

Introduction and Overview

1.1 Introduction

Distillation is one of the oldest unit operations that is still in use today. The early distillation processes were batch oriented, but continuous distillation processes soon took over as the demand for products made batch distillation a less desirable choice. However, there has been a renewed interest in batch distillation as the market for small volume, high value, specialty chemicals has increased. Batch distillation is very well suited to these kinds of products. Much of the research done in distillation has been in the area of continuous processes. While there is still much to be learned about continuous distillation, there is an even larger void in the knowledge of batch distillation. This is why there has been such an increase in the number of publications investigating batch distillation synthesis, modeling, simulation, design, control, and optimization.

Batch distillation is normally thought to be more flexible than continuous distillation because batch distillation can handle multiple products and operating conditions, and the design requirement for batch distillation is less than that for continuous distillation. However, the presence of azeotropes in the mixture to be separated can make batch distillation less flexible. Azeotropes can form continuous and batch distillation regions which limit the types of feasible separations. Depending on the feed to the distillation process, the desired products may be unreachable due to the distillation boundaries and resulting distillation regions formed by the azeotropes. Batch distillation regions are normally more numerous than the continuous regions for the same mixture and the separation of the mixture into its pure components can be much more difficult than in continuous distillation.

Our goal is to separate a mixture into its pure components using batch distillation. In order to make these separations, we investigated new types of batch column configurations and determined the types of feasible products and possible column profiles for several types of batch column configurations. As mentioned above, separation by batch distillation can be complicated further by batch distillation boundaries and regions. A tool for finding the basic distillation regions was developed where a basic distillation region was defined as a set of residue curves each having a common unstable and stable node pair. We then found the continuous and batch distillation regions using the basic distillation regions from which feasible batch distillation products were determined. This tool can find the distillation regions for any mixture and requires minimal input.

The presence of azeotropes in the multicomponent mixtures also requires that sequences of columns be used in separating the mixture into its pure components. Several column configurations can be used in the proposed sequence, and it is necessary that we know what are the batch distillation regions and feasible products for each of these column configurations. Using the distillation region finding tool, we have shown that it is possible to synthesize all possible sequences of batch distillation columns using several different column configurations operating under the conditions of total reflux/reboil and infinite number of trays.

Chapters 2-5 are completed papers that have been or will be published individually. Each chapter has its own abstract, nomenclature, and a complete list of nomenclature and references is included at the end. We will first present a brief overview of each chapter.

1.2 Overview of Chapter 2

In the first paper which was published in *Industrial and Engineering Chemistry Research* (**1995**, *34*, p. 3257-3264), we present a relatively new type of batch column configuration called a middle vessel column. This column is very similar to a continuous column in that simultaneous top and bottoms products are taken. In place of a feed tray, the middle vessel column has a normal tray with a very large holdup. This tray acts like a still pot for the column.

We begin by presenting some basic concepts governing continuous and batch distillation. In particular, we look at some of the work by Van Dongen and Doherty (1985) and Bernot et al. (1990, 1991) which used residue curves in analyzing batch distillation processes and Wahnschafft et al. (1992, 1993) which developed insights into finding the feasible product regions, possible column profiles, and extractive distillation for continuous systems. We then take these insights and extend them to batch distillation for batch rectifier, stripper, and middle vessel columns. We also show how one can “steer” the middle vessel still composition versus time. We can use still path steering to increase the flexibility of the middle vessel column.

Finally, we investigate extractive batch distillation using the batch rectifier and middle vessel columns. We show that it is theoretically possible to recover 100% of a binary azeotropic mixture in its pure components using both types of column configurations with the batch rectifier requiring an infinite size still pot. Simulation studies confirm this investigation.

1.3 Overview of Chapter 3

We begin by looking at our work from the previous chapter. In particular we are interested in how one would realistically operate a middle vessel column with and without an extraction agent. We propose that the still path steering algorithm presented in the previous chapter is a good approximation to the best bottoms flow rate policy and present some evidence to this proposal. We realize that there are many adjustable parameters for the extractive middle vessel column such as reflux and reboil ratio policies, entrainer and bottoms flow rate policies, vapor boil up policies and product fraction switching times and that this type of batch operation should be solved as an optimal control problem. We look at the sensitivity of the final profit, defined as the revenue from the sale of the pure products minus the utility costs divided by the total batch processing time, to several of these optimization variables. Finally, we investigate a type of bottoms flow rate policy different than the still path steering algorithm and show that, while the new policy does increase the final profit somewhat, the normal still path steering algorithm is a good first guess.

1.4 Overview of Chapter 4

We begin this chapter by reviewing the literature on finding continuous and batch distillation boundaries and regions. We point out some deficiencies in some of this work and present our algorithm for finding the basic distillation boundaries. We first find maximum and minimum separating surfaces that separate the composition space into subregions, each having it own unstable and stable node. These separating surfaces define the basic distillation boundaries. We build all constituent 3-component systems, then all constituent 4-component systems, and so forth. In this manner, we can find the basic distillation boundaries for any mixture.

Using algorithms published by Bernot et al. (1991), we show how to find the batch distillation boundaries and the resulting batch distillation regions. We implemented our algorithms and developed a distillation region finding tool which we validated on several 4-component systems and all topologically possible 3-component systems

1.5 Overview of Chapter 5

In the last paper, we discuss how one would begin to synthesize sequences of batch distillation columns with the purpose of separating an azeotropic mixture into its pure components. Using batch column configurations that were investigated in the previous chapters, we integrated the distillation region finding tool with a batch column sequence synthesis tool that generated all possible batch column configurations under the assumption of total reflux/reboil and infinite number of trays. Using a state-task network where the states were mixtures to be separated and the tasks were different types of batch columns that could operate on the states, we were able to represent the network of all possible batch column sequences with no indication of what the best sequence would be.

1.6 Overview of Chapter 6

We present final conclusions for all of the work presented in the previous chapters. Directions for improvements and future work are highlighted.

Chapter 2

Extending Continuous Conventional and Extractive Distillation Feasibility Insights to Batch Distillation

Abstract

Researchers have begun to study a batch column with simultaneous top and bottom products, sometimes called a middle vessel column. The column is similar to a continuous column in that it has both a rectifying and a stripping section. However, instead of a feed tray, the middle vessel column has a tray with a large holdup that acts like the still pot. Using ternary diagrams, we show that one can identify the feasible products and possible column profile regions for the batch rectifier, the stripper, and the middle vessel columns using methods developed for continuous distillation. Using insights developed for continuous distillation, we also compare extractive distillation using the batch rectifier and middle vessel column and show that these columns can theoretically recover all of the pure distillate product from an azeotropic feed. However, the batch rectifier requires a still pot of infinite size. It is possible to “steer” the still pot composition in the middle vessel column by adjusting column parameters such as the product and extractive agent flow rates. Theoretically, it thus becomes possible to recover all of the distillate product without the need for an infinite still pot.

2.1 Introduction

With the renewed interest in batch distillation, some interesting work has appeared in the literature discussing novel types of batch distillation columns. One such column, usually called the middle vessel column, is very similar to a continuous distillation column in that there is a rectifying section above the feed tray and a stripping section below the feed tray. In the case of the middle vessel column shown in Figure 2.1 (disregard the extractive section for the moment), the feed tray can be thought of as a tray with a very large holdup, similar to the still pot in normal batch distillation. This type of batch column configuration was originally proposed by Devyatikh and Churbanov (1976). Meski and Morari (1993) and Devidyan et al. (1994) showed that for a 3-component constant relative volativity system (depending on, for example, reflux and reboil ratio, ratio of boilup rates in both column sections, and number of trays), the middle vessel column can accomplish quite different separations. In particular, one can remove the light component as a distillate product, the heavy component as a bottoms product, while enriching the intermediate component in the middle vessel. At the end of the distillation operation, only the intermediate component would be left in the middle vessel, thereby separating a three component mixture into its pure components with only one column. Meski et al. also showed that the middle vessel column could process the same mixture twice as fast as a typical batch column. However, their results were obtained for constant relative volativity mixtures. Hasebe et al. (1992) also studied the middle vessel column. They compared the separation of a 3-component, constant relative volativity system using a batch rectifier and stripper, shown in Figure 2.2, and the middle vessel column. They optimized the operation of these columns using as an objective function the amount of product recovered per

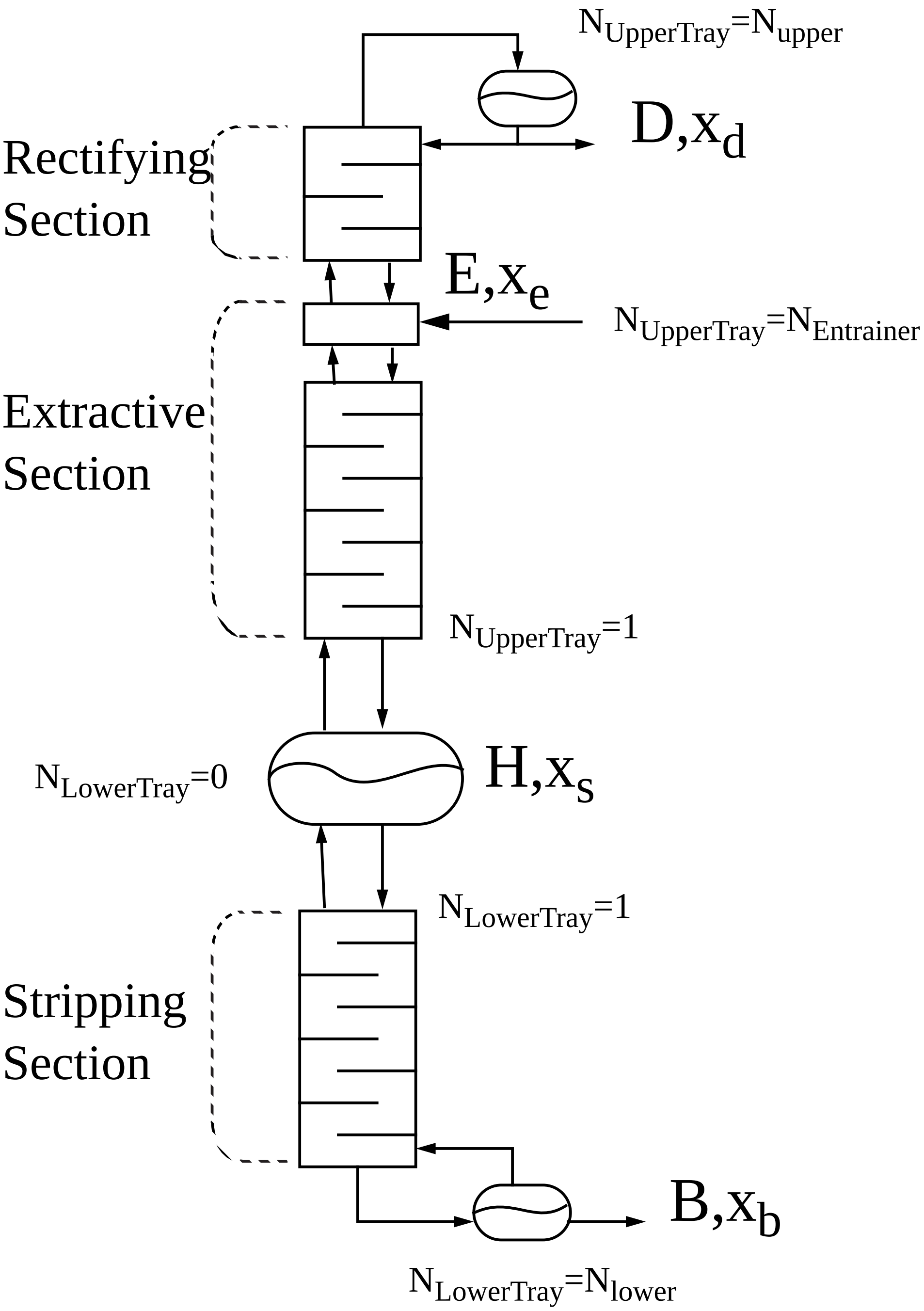

Figure 2.1: Middle Vessel Column with Extractive Section

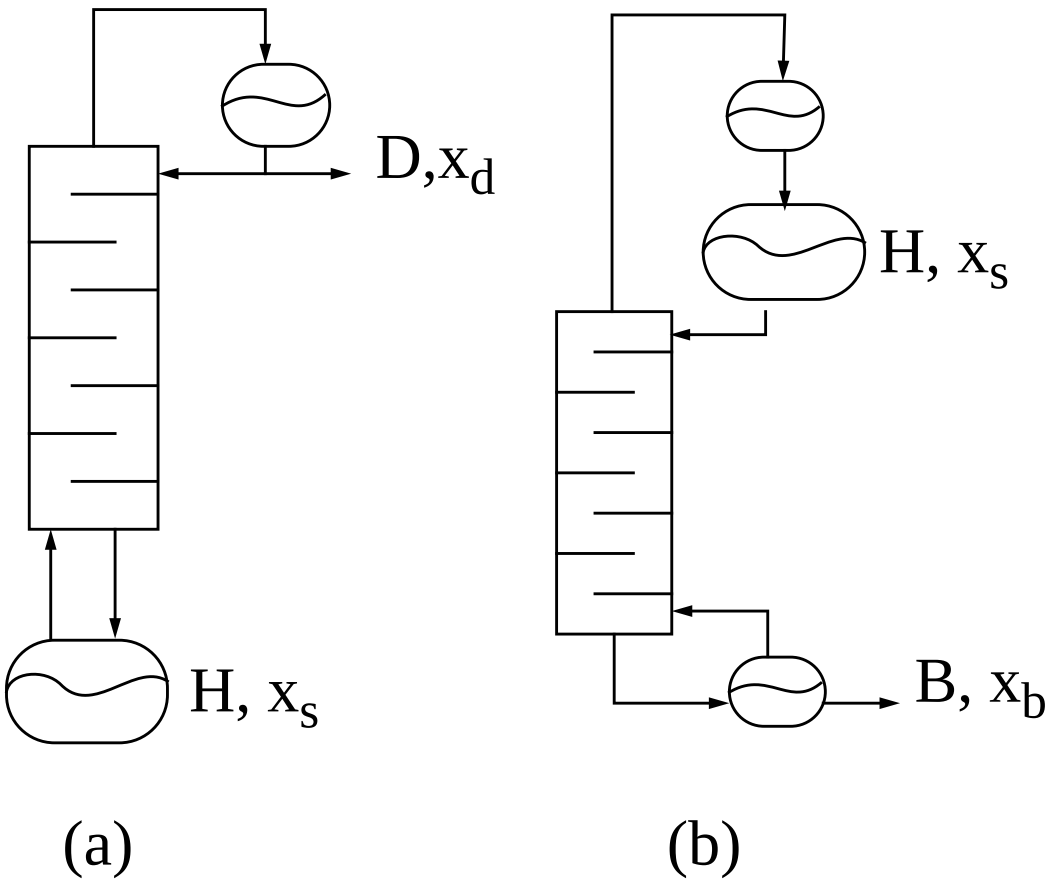

Figure 2.2: Batch Rectifier (a) and Stripper (b)

processing time and showed that the middle vessel column performed better than the rectifier in almost all cases.

For azeotropic mixtures, the work done by Van Dongen and Doherty (1985) and by Bernot et al. (1990, 1991) identified the product sequences for azeotropic mixtures in batch rectifiers (strippers) at infinite reflux (reboil) and infinite number of trays. Using only residue curve maps, they could predict the order of the distillate (bottoms) products. However, it is possible that one will remove a number of the products as azeotropes or at near azeotropic compositions. These products have to be processed in some further steps, recycled, or disposed of.

The problem of azeotropic products in continuous distillation has been studied quite extensively. One technique widely used in breaking azeotropes is that of extractive distillation, in which one feeds a heavy component, called an entrainer, close to the top of the column. This component changes the relative volativities of the azeotrope-forming species and pulls some of the components down the column that normally show up in the distillate. Wahnschafft and Westerberg (1993) carried out a graphical analysis using residue curve maps where they show why extractive distillation is possible for an appropriate entrainer. They also identified the limits of the extractive distillation.

There has been limited work in the literature regarding azeotropic batch extractive distillation. Koehler et al. (1995) discussed industrial applications of batch azeotropic and extractive distillation. Yatim et al. (1993) simulated a batch extractive distillation column using a batch rectifier. They compared their simulations to experimental data that was collected and got favorable results. They were able to recover approximately 82% of their main distillate product in relatively pure form. However, no work has been published using the middle vessel column for extractive distillation.

2.2 Basic Concepts

2.2.1 Batch Column Product Sequences and Still Paths

A distillation region is a region of still compositions that give the same product sequence when distilled using batch distillation (Ewell and Welch, 1945). Using residue curve maps, Van Dongen and Doherty (1985) and Bernot et al. (1990) identified these distillation regions and predicted the product sequences for azeotropic mixtures using a batch rectifier at infinite reflux and infinite number of trays. In identifying these products, they were also able to predict how the still composition changed versus time, sometimes called the still path. For their pseudo-steady state model of a batch rectifier, they used an overall component material balance

$$\frac{d\mathbf{x_s}}{d\xi} = \mathbf{x}_s - \mathbf{x_d} \tag{2.1}$$

where $\mathbf{x_s}$ and $\mathbf{x_d}$ are the still and distillate mole fractions and ξ is a dimensionless measure of time. $\mathbf{x_s}$ and $\mathbf{x_d}$ must lie on a line that is tangent to the instantaneous change of the still composition. The instantaneous change in still composition will be in a direction opposite that of the direction pointing to $\mathbf{x_d}$ from $\mathbf{x_s}$. Also, the column profile must follow the residue curve due to the assumption of quasi steady state operation at infinite reflux, where they have approximated the distillation curves with the residue curves in their analysis. Their quasi steady state analysis neglects holdup effects and is thus, in principle, valid only for zero holdup on all trays. However, this simplified analysis has the advantage of providing insights into the most important phenomenon, the effect of the VLE on the feasible separations.

In determining the product sequence, Bernot et al. pointed out that the first product obtained is the local minimum temperature or unstable node of the distillation region where the still composition currently resided. This product, whether one of the pure components or an azeotrope, is obtained in pure form because of the assumption of infinite number of trays. The column will continue to produce this product, with the still composition moving in a direction opposite that of the product, until the still path intersects a distillation region boundary or an edge of the composition space. At this point the product will normally switch to the next lowest temperature node. Figure 2.3 shows an

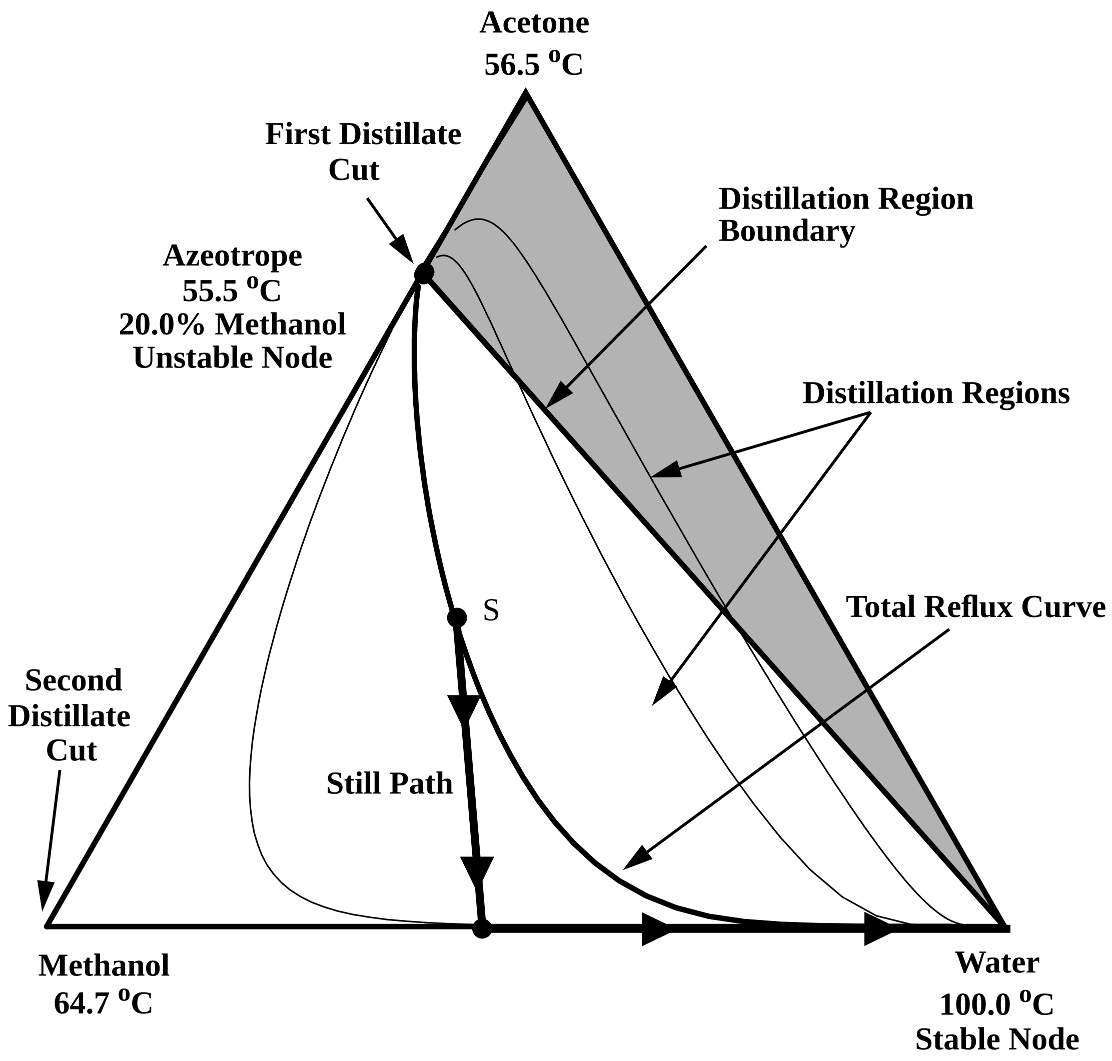

Figure 2.3: Product Sequence and Still Path for Rectifier at Infinite Reflux and Trays

example of the product sequence and a still path for a batch rectifier. The figure shows the two different distillation regions. The column profile will follow the residue curve through the still composition (total reflux curve) until it runs into the acetone/methanol azeotrope, which is the lowest temperature node in this particular distillation region, and hence the first distillate product. The still path moves directly away from the azeotropic product, required by Equation 2.1, until one has depleted all of the acetone from the system. The column profile will now lie along the methanol/water binary edge, with methanol being the next distillate product. The still path will move away from the product, toward the water vertex. The batch rectifier will continue to produce methanol as a distillate, until one has depleted all of the methanol from the system, at which point only water will remain in the column. While the example in Figure 2.3 is straightforward, the still paths and product sequences for other systems can be quite complex, as pointed out by Bernot et al. (1990, 1991).

2.2.2 Feasible Product and Possible Column Profile Regions

Several researchers have worked on identifying the feasible product regions for continuous distillation. Wahnschafft et al. (1992) were able to predict these regions for a specified feed composition using a graphical analysis of the residue curve map of the system. While residue curves closely approximate composition profiles for the total reflux situation, the curves can also be used to derive the limits for operation at any finite reflux ratio. At finite reflux ratios, the occurrence of one or more pinch points limits the feasible separations. Wahnschafft et al. showed how pinch point curves can be used to assess the feasible separations. A pinch point curve is the collection of tangent points on several residue curves, whose tangent lines point back through the product or feed. For the product pinch point curves, these points correspond to pinch points in the column where a vapor and liquid stream that pass each other are in equilibrium, requiring an infinite number of trays to carry out the specified separation at the current reflux ratio. The reflux ratio must be increased in order to bypass the pinch point. See work by Wahnschafft et al. (1992) for more details. They also were able to identify the regions of possible column profiles for both column sections, given product specifications. These regions of profiles contain all profiles that were attainable when a product was specified. Each column profile region is bounded by the total reflux curve (approximated here as the residue curve that passes through the product composition) and the product pinch point curve. So, for example, when the distillate composition is specified, it is possible to map out all of the rectifying profiles that contain the specified distillate product. For a continuous column, there is a distillate and bottoms product resulting in distillate and bottoms product pinch point curves. If the rectifying and stripping column profile regions intersect in at least one point, then a tray by tray calculation can be performed from one specified product to the other resulting in a feasible column specification. If these regions do not intersect, then there exists no tray by tray calculation between the specified products and the column is not feasible. Also, the feed composition does not necessarily need to lie in any of the possible column profile regions for the column to be feasible. But the feed composition must lie on a mass balance line between the distillate and bottoms compositions due to the overall mass balance constraint.

2.2.3 Extractive Distillation Feasibility and Operation

An extension of conventional continuous distillation, extractive distillation can be analyzed using many methods developed for conventional distillation. In a continuous or middle vessel extractive column, there are three tray sections: rectifying, extractive, and stripping, shown in Figure 2.1 for the middle vessel column. The rectifying section is responsible for separating the intended distillate product from the entrainer, while the extractive section breaks the azeotrope. Wahnschafft and Westerberg (1993) carried out a graphical analysis for continuous extractive distillation containing a 3-component mixture. As pointed out earlier, if the rectifying and stripping profile regions do not intersect, then the column is infeasible. Wahnschafft and Westerberg showed that, with the appropriate entrainer, the extractive section can “join” a rectifying profile region with a stripping region that do not intersect. Without the extractive section, the separation would be infeasible.

Wahnschafft and Westerberg showed that there are areas in the residue curve map in which the extractive section will carry out the required separation and areas in which the section will not work as required. Figure 2.4 shows an example of these regions for the acetone/methanol/water system, with the shading denoting areas where the extractive section will not work. If any of the compositions in the extractive section lie within these shaded regions, the column will not produce the intended distillate product, acetone in this case. The Δ pinch point curves mark the boundaries of these areas. The Δ point is the difference point for the geometric construction of tray by tray composition profiles in the extractive section. An overall mass balance for tray j in the extractive section produces the following equations:

$$\mathbf{V}_{\mathbf{j}-\mathbf{1}} + \mathbf{E} = \mathbf{D} + \mathbf{L}_{\mathbf{j}} \tag{2.2}$$

$$\mathbf{V}_{\mathbf{j}-\mathbf{1}} - \mathbf{L}_{\mathbf{j}} = \Delta \ldots (\mathbf{D} > \mathbf{E}) \tag{2.3}$$

$$\mathbf{L}_{\mathbf{j}} - \mathbf{V}_{\mathbf{j}-\mathbf{1}} = \Delta \ldots (\mathbf{E} > \mathbf{D}) \tag{2.4}$$

where V_j and L_j are vapor and liquid flow rates from tray j and E and D are the entrainer and distillate flow rates. Δ=D-E (or E-D) and is located on a line connecting E and D but outside of the composition triangle. The higher the ratio of E to D, the closer Δ is to E and vice versa. The composition of Δ, which again can lie outside of the composition space, can be found by:

$$\mathbf{x_{\Delta}^{i} = \frac{Dx_{d}^{i} - Ex_{e}^{i}}{D - E}, i = 1 \ldots NC - 1} \qquad \textbf{(2.5)}$$

For example, we have a Δ point and some arbitrary extractive tray composition, L_k, shown in Figure 2.4, and we take an equilibrium step to produce V_k, the vapor coming up from this tray. Then, given Equation 2.4, the liquid coming down from the tray above this, L_{k+1}, must lie on a line between the V_k and Δ. We can repeat this analysis for tray k+1 and see that, as we move up the column toward the acetone/water binary edge, the temperatures associated with each tray decrease, resulting in a feasible extractive section. The Δ pinch point curves are generated by finding the tangent points on all of the residue curves that lie on a line through Δ, as shown in Figure 2.4. Again, these curves mark the boundaries of the infeasible extractive regions.

In using extractive distillation, we can “connect” a stripping profile section with a rectifying profile that did not intersect before using the extractive section, resulting in a feasible column specification. Figure 2.5 shows an infeasible column specification because the rectifying and stripping profile regions do not intersect. These regions were calculated using the analyses shown in Section 2.2.2. The extractive section will step from the stripping profile region to the rectifying profile region, creating a path of tray by tray calculations from the specified bottoms to distillate products. There is a minimum E flow rate in which the infeasible extractive regions would occupy the entire residue curve map, resulting in no feasible space for the extractive section. In Figure 2.4 for instance, the minimum E would correspond to the case where the two infeasible extractive regions intersected at a single point or line. Increasing E would open up a space between the two regions, in which an extractive section could pass through.

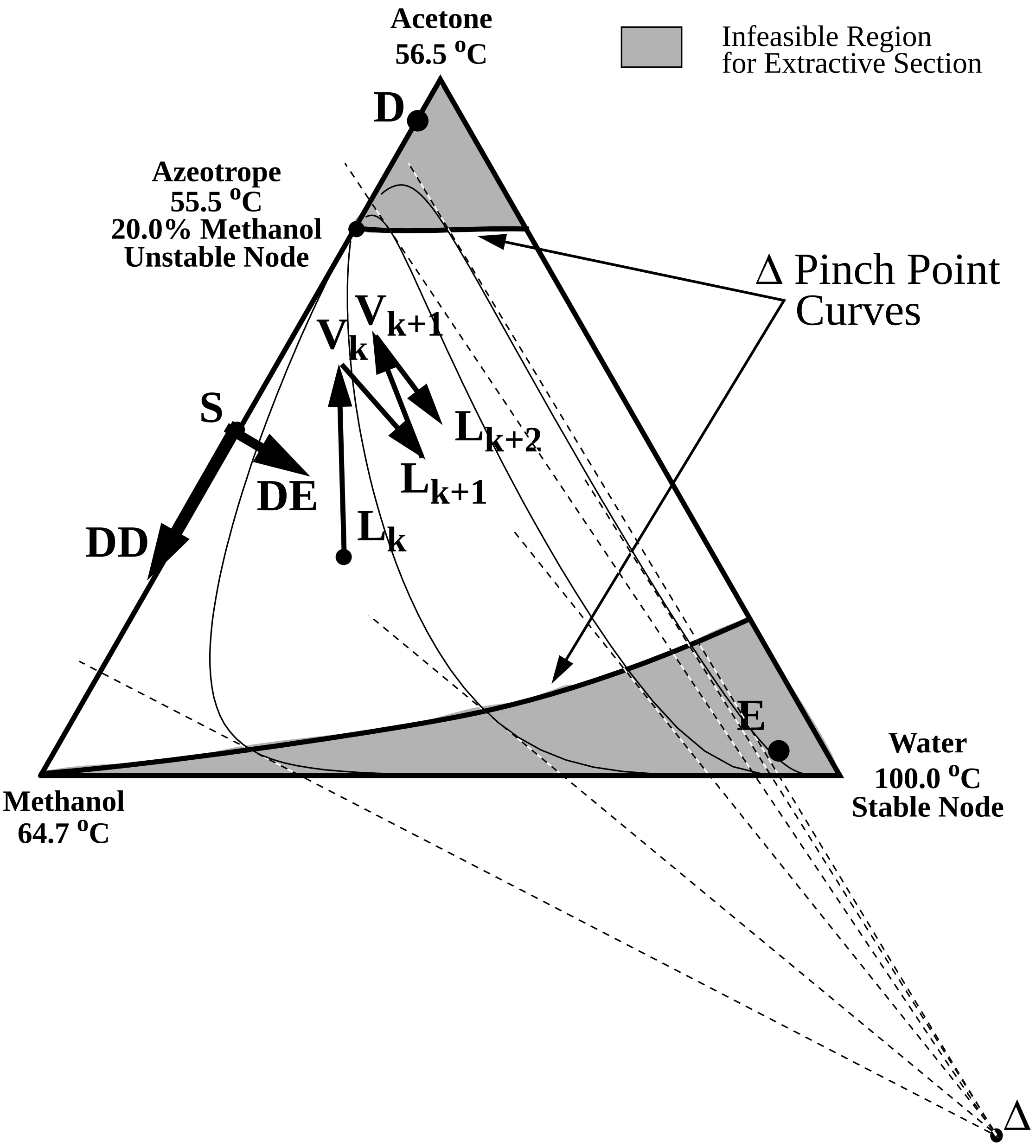

Figure 2.4: Δ Pinch Point Curves for Acetone/Methanol/Water

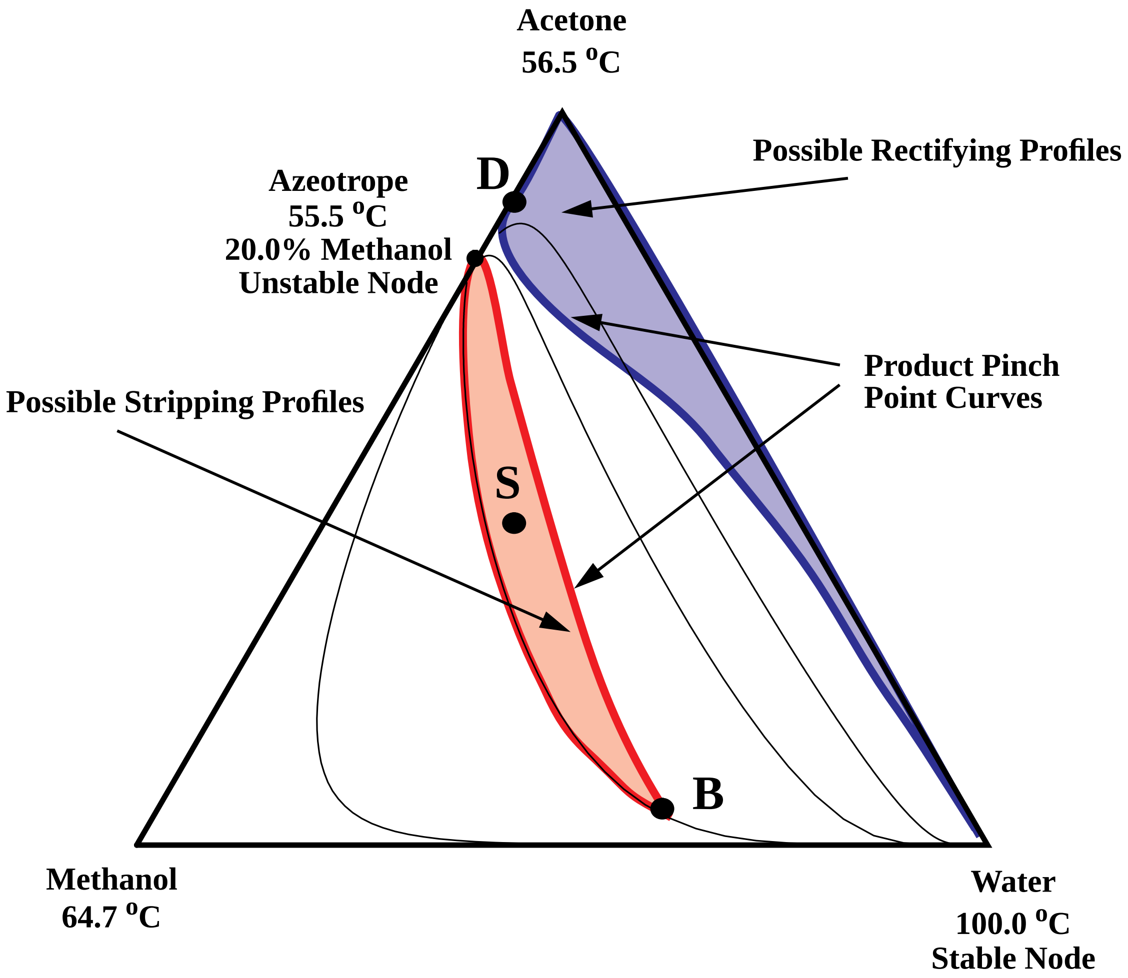

Figure 2.5: Infeasible Middle Vessel Column Specification

2.3 Insights into Batch Distillation

2.3.1 Feasible Product and Possible Column Profile Regions

The analysis presented in Section 2.2.2 for feasible product and column profile regions in continuous columns can be extended to batch distillation. One of the key differences is that the still and product compositions change with time, so the basic feasibility analysis covers only an instance in time. Also, the still composition, S, is a tray composition (when holdup effects are ignored) and must lie on the column profiles from each product just like any other tray composition. In continuous distillation, the feed composition (which in general is not the same as the feed tray composition) does not have to lie on the same column profiles as the products. For the batch rectifier, there is only one product, the distillate. Shown in Figure 2.6, the feasible product region is bounded by two curves: the total reflux curve through the specified still composition S and the tangent to the residue curve through S. The total reflux curve gives all distillate compositions that are possible at infinite reflux and varying number of trays. As the number of trays is increased, the distillate composition moves up the total reflux curve until, at infinite number of trays, the distillate composition is exactly the local minimum temperature node (pentane in Figure 2.6). The other boundary is determined at an infinite number of trays and varying reflux ratios, resulting in the existence of pinch points in the column. All of the points on this boundary give a distillate composition whose product pinch point curve will pass through S. Since S must lie on the same column profiles as each of the distillate compositions, S must also lie on the distillate pinch point curves. This defines the case of infinite number of trays and minimum reflux ratio for each distillate composition located on the tangent to the total reflux curve through S. The shaded region for the batch rectifier in Figure 2.6 shows all of the possible distillate products for the specified still composition, at various combinations of reflux and number of trays.

For the batch stripper column, the feasible product region is found in a manner similar to that for the batch rectifier column. The region is bounded by the total reboil curve through S, giving the possible bottoms compositions at infinite reboil, and the tangent to the total reboil curve through S. This latter boundary gives the bottoms compositions whose product pinch curves will pass through S. Figure 2.6 also shows the shaded region of possible bottoms products for the specified still composition.

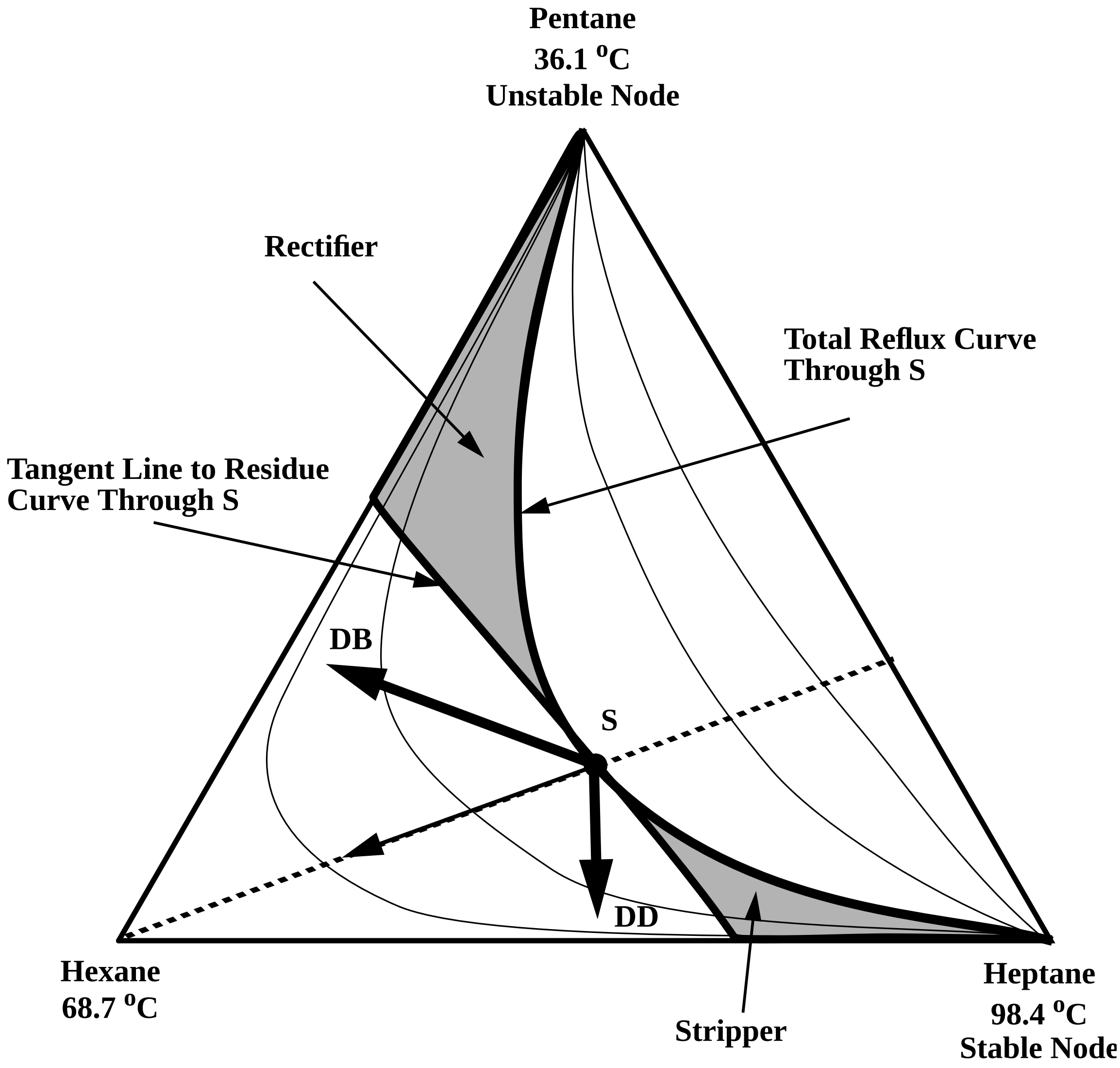

Figure 2.6: Feasible Product Regions for Batch Rectifier and Stripper

The feasible product regions for the middle vessel column can be found in the same way as for the batch rectifier and stripper. The middle vessel column is basically a batch rectifier on top of a batch stripper, with only the still pot in common. The same arguments made above concerning the feasible products for the rectifier and stripper apply for the rectifying and stripping sections of the middle vessel column. Note that while in continuous distillation the distillate, feed, and bottoms compositions must all lie on the same mass balance line, these compositions do not have to lie on a mass balance line due to the dynamic behavior of the column. So in Figure 2.6, we could have pentane as our distillate product and heptane as our bottoms product with the specified still composition S, which would be impossible in continuous distillation. If the products do lie on a straight line through S and remain there and if the distillate and bottoms flow rates are the same, the still composition will not change resulting in a constant composition column operating at minimum reflux and reboil ratio. Thus we see that the middle vessel column offers a lot of flexibility for operation, with the feasible products region being the combination of the products possible for batch rectifiers and strippers. For the current still composition S shown in Figure 2.6, the middle vessel column products could be anywhere in the respective two shaded regions.

Using the pseudo-steady state model (zero holdup on all trays except the still), the regions of possible column profiles for the batch distillation are found exactly as for continuous distillation in Section 2.2.2. For each specified product, the region of possible profiles is bounded by the total reflux curve through that product and the product's pinch point curve (see Wahnschafft et al., 1992). Figure 2.5 shows these regions for a specified distillate and bottoms product. These profiles will again only apply at the current product compositions, so if the products change, the regions of profiles will change. These profile regions contained all profiles that would contain the product in question at all combinations of the reflux or reboil ratio and number of trays.

As also seen for continuous distillation, the rectifying and stripping profile regions must intersect in at least one point for a column specification to be feasible. However, for batch distillation, there is one more necessary condition for the column specification to be feasible. S is a tray composition and thus must lie on the column profile from D and from B. If heat is added or removed from the middle vessel, the rectifying and stripping profiles will not be continuous, but they must meet at S. S must, therefore, be contained in the intersection of the two column sections so that a path of tray by tray calculations from B to S then to D can be performed. An example of an infeasible middle vessel column specification can be found in Figure 2.5. Here, the distillate and bottoms products have been specified as D and B with still composition S. Also shown are the regions of possible column profiles for each product. Each region is bounded again by the total reflux curve through its product and that product’s pinch point curve. S in Figure 2.5 is contained in the region of possible column profiles for B, so the bottom section of the column is feasible. However, S is not included within the region of possible column profiles for D, and the two regions of profiles do not even intersect in at least one point. It is not possible to perform a tray by tray calculation from S to D, hence the distillate specification is infeasible.

2.3.2 Steering the Middle Vessel Still Composition

As mentioned earlier, it is possible to separate a 3-component mixture into its pure components using a middle vessel column. By removing the lightest component overhead and the heaviest component at the bottom, the intermediate component will remain in the still. For this specific operation, column parameters (e.g. product withdrawal rates) must be chosen in such a manner that the still composition does accumulate in the intermediate component. As the still path for the batch rectifier is a function of the distillate and still compositions, the still path for the middle vessel still path is a function of the distillate, bottoms, and still compositions. From the overall component mass balance,

$$\frac{d}{d\mathbf{t}}\left(\mathbf{H}\mathbf{x}_{\mathbf{s}}\right) = -\left(\mathbf{D}\mathbf{x}_{\mathbf{d}} + \mathbf{B}\mathbf{x}_{\mathbf{b}}\right) \qquad \textbf{(2.6)}$$

we see that the direction of the still path is in a direction opposite to that of the combined directions of $\mathbf{x_s}$ to $\mathbf{x_d}$ and $\mathbf{x_s}$ to $\mathbf{x_b}$, due to the removal of the distillate and bottoms products, respectively. How these directions are combined is determined by the magnitude of D and B, based on vector addition. So, depending on the magnitude of the product flow rates, it is possible to “steer” the still composition in a variety of directions. For example, Figure 2.6 shows the residue curve map of pentane/hexane/heptane. In a middle vessel column with infinite reflux and reboil ratios and infinite number of trays, pentane will be the distillate product, while heptane will be the bottoms product. The directions DD and DB show the directions the respective product withdrawals force the still composition to move. At B = 0, the still path will move directly away from pentane until it hits the hexane/heptane binary edge, at which time hexane will become the distillate product. And at D = 0, the still path will move directly away from heptane until the still path hits the pentane/hexane binary edge with hexane becoming the new bottoms product. Between these two limiting cases, D and B can be set so that the region of possible directions is anywhere between DD and DB.

The direction of the still path can also be determined by combining the distillate and bottoms product into a “net product”, again depending on the magnitudes of the product flow rates. In Figure 2.6, if the net product is the point where the dotted line passing from hexane through S intersects the pentane/heptane binary edge, the instantaneous change of the still path would be in a direction directly opposite this, i.e., exactly toward the hexane vertex. If the still path is directed toward the hexane vertex during the entire distillation operation, only hexane will remain in the column at the end of the distillation, thereby separating a 3-component mixture using only one column.

The ability to steer the still composition in this way shows the flexibility of the middle vessel column. In the extreme, by setting B = 0, the column can act like a batch rectifier, and vice versa for a batch stripper, which may be appropriate for certain situations. This flexibility makes the middle vessel column an excellent choice for equipping a batch separation system.

2.3.3 Batch Extractive Distillation

While continuous distillation will have a constant Δ (difference) point, normal batch distillation has a constantly changing Δ point due to changing still and product compositions and flow rates. Thus it is possible for the batch extractive column to work for a period of time but then cease to produce the desired products because the still composition has intersected the Δ pinch point curves. Yatim et al. (1993) simulated a batch extractive distillation using a rectifier and also compared the results to experimental data they collected. They mention that they were able to recover approximately 82% of the distillate (acetone) from an azeotropic mixture with methanol, using water as an entrainer. The distillate that was obtained was approximately 96% acetone.

We now want to explore their results using the pinch curve analysis for the batch extractive rectifier. In Figure 2.4, their Δ point would lie along the acetone/water binary edge (the distillate product was mostly acetone and water and the entrainer was pure water) but outside the composition triangle. S marks the initial still composition they used.

As mentioned earlier, the still path for a batch rectifier is a function of the distillate and still compositions. Since now there is an entrainer feed, the still path is also a function of the entrainer composition and flow rate. The direction of the still path will be a combination of the distillate withdrawal driving the still composition directly away from the distillate composition, acetone in this case (DD in Figure 2.4), and the entrainer pulling the still composition toward the water vertex (DE in Figure 2.4) as water is continually added to the system. Since the entrainer addition is normally several times greater than the distillate withdrawal, Δ will lie close to the water vertex and the direction of the still path is more toward the water vertex. Yatim et al. were able to draw off a nearly constant composition distillate product for the main operational step. Whether or not the magnitude of the distillate flow rate was constant could not be determined from their paper. The Δ point and Δ pinch point curves will only be constant if their entrainer and distillate flow rates and compositions were constant. If we were to assume that these flow rates were constant, their still path would eventually intersect the Δ pinch point curve from the methanol vertex to the acetone/water binary edge. At this point, the extractive section would no longer be able to maintain the acetone/methanol separation, and methanol would come over in the distillate product. This could be one explanation of their limited acetone recovery of 82%. To increase the recovery of acetone during the main separation step the intersection of the still path and Δ pinch point curve could be postponed and even avoided in the rectifier by increasing the entrainer to distillate flow rate ratio, which will move the Δ point closer to the water vertex and the Δ pinch point curve toward the methanol/water binary edge. At an infinite entrainer to distillate flow rate ratio, the Δ point will become the entrainer composition, and the Δ pinch point curve will lie exactly on the methanol/water binary edge. In this case, it is theoretically possible to recover all of the distillate product because there are no infeasible extractive regions. However, increasing the entrainer flow rate will also increase the size of the still pot that is required because the entrainer, water in this case, accumulates in the still pot. Thus a 100% distillate recovery would require an infinite size still pot.

We can use the middle vessel column to overcome the problem of the still pot size limitation. Using a middle vessel column for extractive distillation, the still path is now a function of the distillate, bottoms, still, and entrainer compositions. The still path direction will be a combination of the distillate and bottoms withdrawal, driving the still away from the respective products, while entrainer addition pulls the still composition toward the entrainer vertex. The entrainer can be removed at the bottom and recycled. If the entrainer addition and bottoms withdrawal are exactly the same, the net still path will move directly away from the distillate product, eventually intersecting a Δ pinch point curve or edge of the composition space. However, if we use the still pot steering ideas described earlier, the addition and removal of entrainer could be adjusted so that the still path never intersects the Δ pinch point curves. A 100% recovery of the distillate product is theoretically possible in a 3-component mixture when the still path is steered toward the intermediate component and away from the infeasible extractive regions. In reality, however, a 100% recovery will usually not be feasible due to requirements of high number of trays, long processing times, and high reflux. However, the ability to steer around these Δ pinch point curves can be very helpful in increasing the distillate product recoveries. Also, because the entrainer is continually removed from the column, the still pot will not accumulate entrainer. The smaller still pot still may well make batch extractive distillation a more economically attractive option.

2.4 Simulation Results

We simulated both the batch rectifier and middle vessel columns using water as the entrainer for the azeotropic mixture of acetone and methanol. Both models ignored holdup effects (except in the still), i.e., we assumed a pseudo-steady state on all of the trays except for the still. We used the Wilson correlation in modeling the thermodynamics of the system with the Wilson parameters shown in Table 2.1. We integrated the columns using ASCEND (Piela et al., 1993), an equation-based modeling system, and the integrator LSODE (Hindmarsh, 1983). Table 2.2 shows the column parameters used for the simulations, while Figure 2.1 shows how we numbered the column trays.

Table 2.1: Wilson Interaction Parameters

λ(row,column)	Acetone	Methanol	Water
Acetone	1.0	0.65675	0.16924
Methanol	0.77204	1.0	0.43045
Water	0.40640	0.94934	1.0

Table 2.2: Column Parameters

Column Type	N_{Upper}	N_{Lower}	$N_{Entrainer}$	Initial Holdup	Initial Still Composition Acetone / Methanol	Still Boilup Rate
Middle Vessel	18	10	12	300 mol	50% / 50%	5.5 mol/s
Rectifier	18	-	12	300 mol	50% / 50%	5.5 mol/s

We performed the distillation operation for the middle vessel column in three steps: a period of entrainer (water) addition with no bottoms removal but with distillate (acetone) removal, a period of normal distillate and bottoms (water) removal with the bottoms recycled back as the entrainer, and a period with no entrainer addition and a distillate product consisting mainly of the intermediate component (methanol). The first step was necessary in order for the bottoms to become enriched in water so that it could be recycled back as fresh entrainer. The third step was necessary to make the final still composition meet a methanol purity specification. While all three operational steps were important in the separation of the azeotropic mixture, only the second operational step will be analyzed further.

At the beginning, the still contains 150 mol each of acetone and methanol. We carried out the first operational step mentioned previously for approximately 10 s, compared to 180 s for the second operational step. Figure 2.7 shows the product compositions versus time for the middle vessel extractive column during the main operational step, i.e., the second step. The distillate was about 96% acetone as seen in Yatim et al. (1993) and the bottoms was about 99.8% water, which we recycled back as the entrainer. The reflux and reboil ratios were calculated in order to maintain these distillate and bottoms purities. We obtained the still product, methanol, at the end of the distillation because we recovered 99.5% of the acetone as the distillate product and we removed all of the water as the bottoms product. Thus the third operation was not necessary for this particular example. This simulation demonstrates that we could separate a three component mixture using only one middle vessel column. Steering the still pot composition made this possible by avoiding the infeasible extractive section regions of the

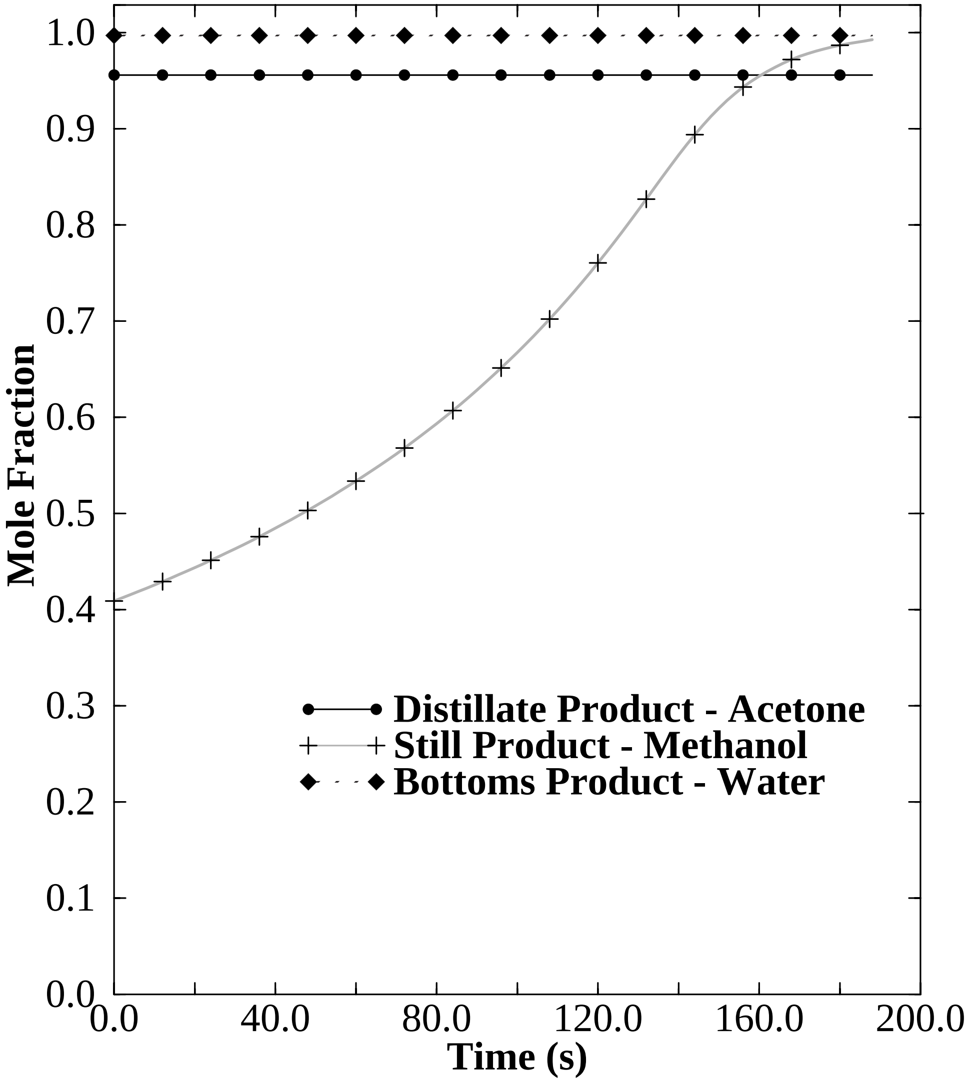

Figure 2.7: Products from Extractive Middle Vessel Column

composition space and by continually enriching the still composition in the intermediate component, methanol. In order to properly steer the still, the following constraint was added to the model:

$$\frac{Dx_d(\text{acetone})}{x_s(\text{acetone})} = \frac{(B-E)\,x_e(\text{water})}{x_s(\text{water})} \tag{2.7}$$

where **D**, **S**, **B**, and **E** denote the distillate, still, bottom, and entrainer compositions and flow rates. Equation 2.7 determines the bottoms flow rate so that the still path is directed toward the methanol vertex, away from the infeasible extractive regions. This equation assumes there is a negligible amount of water in the distillate, and a negligible amount of acetone in the bottoms and entrainer and that the entrainer and bottoms compositions are the same. It should be noted that, while we separated the three components into relatively pure components, we observed large reflux and reboil ratios and diminishing distillate flow rates resulting in long processing times. Thus, eventually we must perform an optimization to decide how far to drive the distillate recovery.

Figure 2.8 shows the still path from the simulation of the middle vessel column. The Δ pinch point curves are very similar to those calculated in Figure 2.4. We steered the still path continually at the methanol vertex which, coincidentally, kept the still path out of the infeasible extractive regions. In this particular example, steering the still path away from the infeasible extractive regions was not difficult due to the shape of these regions and the high E to D ratio. Also, the calculated bottoms flow rate was always greater than the entrainer flow rate. If these two flow rates were identical, the still composition would have moved directly away from the acetone vertex toward the methanol/water binary edge. But we had a net entrainer removal, allowing the still path to proceed toward the methanol vertex. The still path steering algorithm (Equation 2.7) we used was rather simple, and we could have used a much more complicated algorithm in the case where the infeasible extractive regions were more curved or occupied more of the composition space. Also shown is the still path for the batch extractive rectifier that was simulated. The conditions and column parameters used for the simulation of the batch rectifier were identical to those for the extractive and rectifying sections of the middle vessel column.

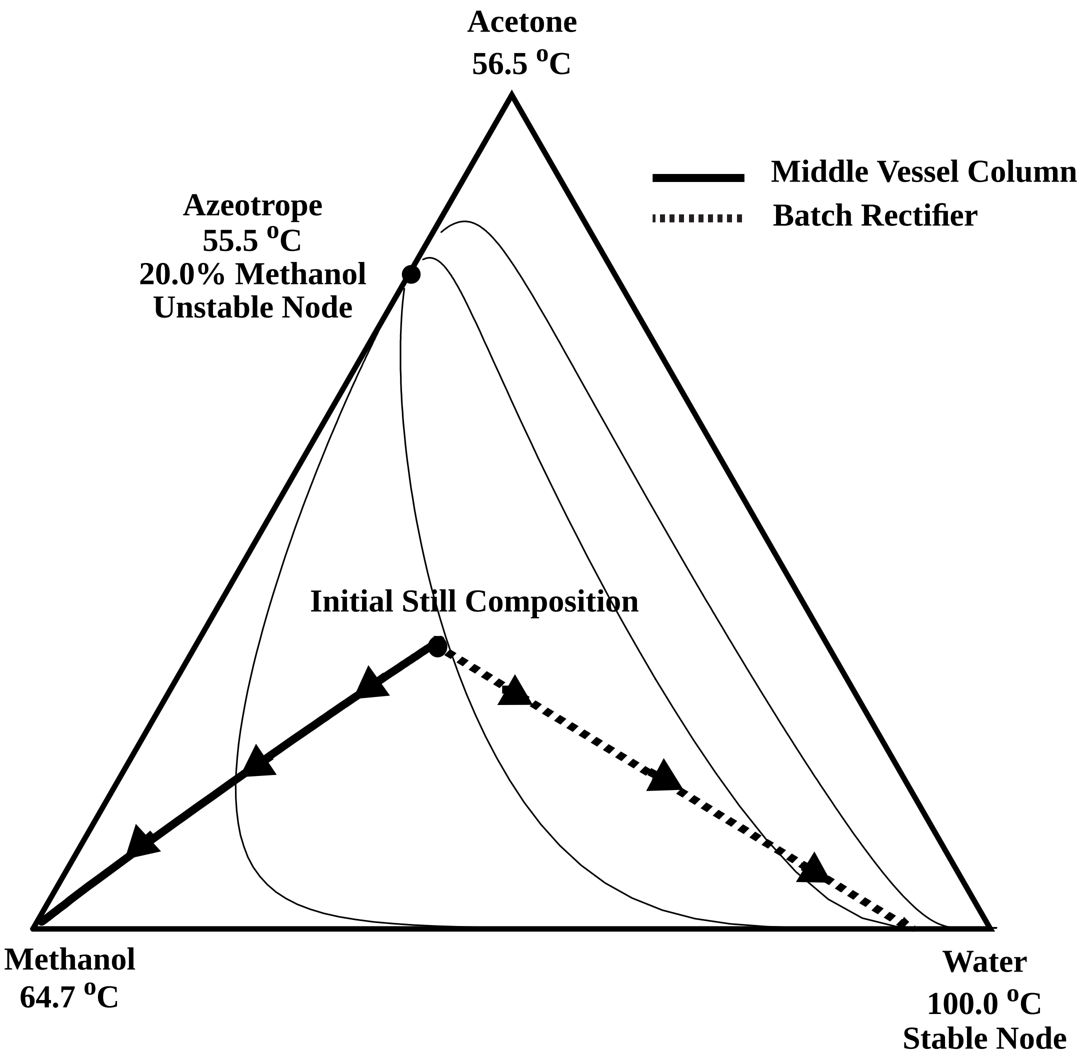

Figure 2.8: Still Paths for Extractive Batch Columns

Note that the still path for the rectifier did reach the methanol/water binary edge. The reason was that the distillate flow rate had to be continually decreased in order to meet the distillate product specification, increasing the E to D ratio. This moved the Δ point closer to the entrainer vertex which in turn shifts the lower Δ pinch point curve toward the methanol/water binary edge. The Δ pinch point curve will coincide with the methanol/ water binary edge in the limit of the Δ point being exactly the entrainer composition (an infinite E/D ratio). While the rectifier was able to remain in the feasible extractive region, it would have become infeasible if D were kept constant, keeping the Δ pinch point curves constant. Also, the final still composition for the rectifier was not pure methanol as seen in the middle vessel column. Figure 2.9 shows the still holdup versus time for the middle vessel column and the batch rectifier. The holdup for the middle vessel column decreases continually until it reaches approximately 150 mol, the initial amount of methanol in the column. However, the holdup for the rectifier increases during the entire operation, ending at an amount almost 13 times that of the middle vessel column due to the continued addition and no removal of water from the column. The contents of the rectifier's still will have to be processed in order to remove the methanol from the water.

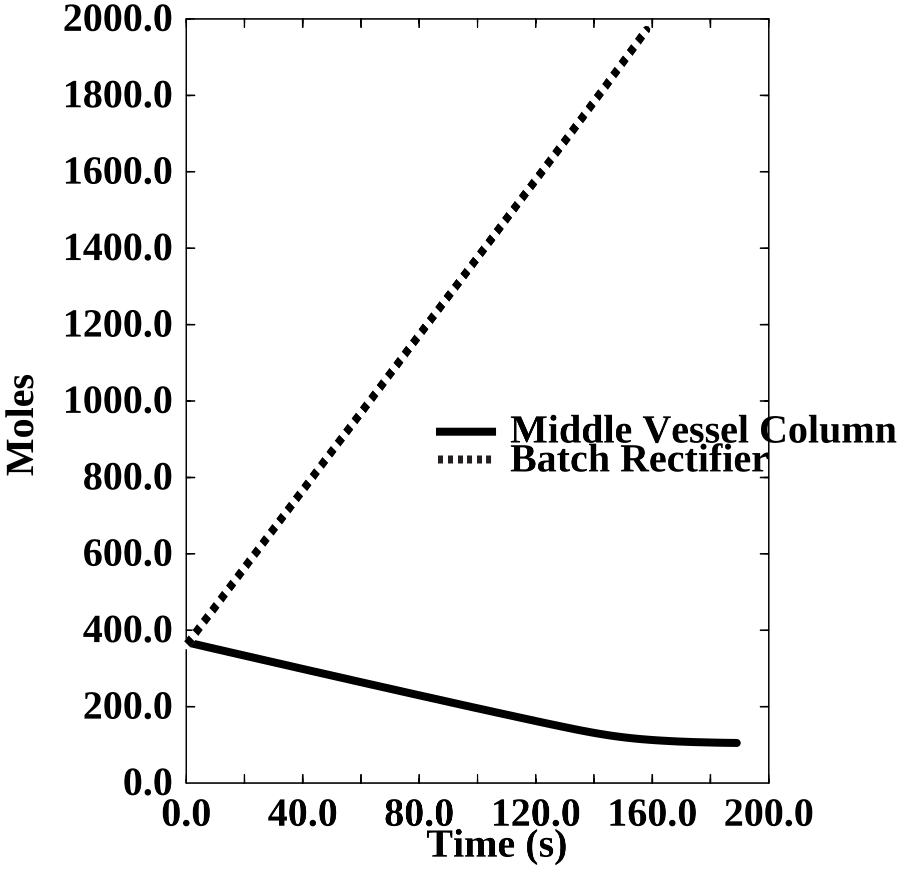

Figure 2.9: Still Pot Holdups in Extractive Batch Columns

2.5 Conclusions and Future Work

In this paper, we used graphical techniques developed for continuous distillation to examine the potential of using nonconventional batch distillation column configurations to separate azeotropic mixtures. In particular, we used the work of Wahnschafft et al. (1992) to find the regions of instantaneous feasible products for the batch rectifier and stripper and middle vessel columns. From this we showed that the still in the middle vessel column can be steered in many directions by appropriate choices of various column parameters, normally the product withdrawal rates. We were also able to show the regions of possible column profiles for the specified distillate and bottoms products and that the still composition must lie in the intersection of these regions for the middle vessel column to be feasible.

We also extended the work done for continuous extractive columns by Wahnschafft et al. (1993) to include the batch rectifier and the middle vessel column. We were able to show graphically one explanation for the limited recovery of the distillate product seen in the work of Yatim et al. (1993). We suggest it may be due to the column's extractive section becoming infeasible during the column operation. However, the capability of steering the middle vessel column's still composition enabled the theoretical 100% recovery of the distillate product without an infinite size still pot, as seen in the batch rectifier. We steered the still composition around the Δ pinch point curves which limited the distillate recovery. Simulations of the middle vessel column and batch rectifier showed that a near 100% recovery is possible in both columns, but steering the middle vessel column's still path enabled the mixture to be separated into its pure components with a much smaller required still pot size.

While the steering of the still path in the middle extractive vessel column does determine the optimal entrainer withdrawal to addition ratio, the flexibility of the middle vessel column allows for many other column parameters to be optimized. Further work is needed to investigate the sensitivity of parameters such as reflux and reboil ratios, number of trays, and product withdrawal rates, as well as the optimization of operation of this column.

2.6 Nomenclature

B = Bottoms product flow rate
D = Distillate product flow rate
DB = Still path direction due to bottoms product removal
DD = Still path direction due to distillate product removal
DE = Still path direction due to entrainer addition
Δ = Delta point
E = Entrainer flow rate
$\lambda(i,j)$ = Wilson interaction parameter, λ_{ij}
L_j = Liquid flow rate from tray j
$N_{Entrainer}$ = Entrainer feed location
N_{Lower} = Number of trays in lower section of column
N_{Upper} = Number of trays in upper section of column
S = Still or middle vessel composition
V_j = Vapor flow rate from tray j
x_b = Bottom product composition
x_d = Distillate product composition
x_Δ = Δ point composition
x_e = Entrainer composition
x_s = Still composition

2.7 Acknowledgments

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References

Bernot C., M. F. Doherty, and M. F. Malone. Patterns of Composition Change in Multicomponent Batch Distillation. *Chem. Eng. Sci.* **1990**, *45*, 1207-1221.

Bernot C., M. F. Doherty, and M. F. Malone. Feasibility and Separation Sequencing in Multicomponent Batch Distillation. *Chem. Eng. Sci.* **1991**, *46*, 1311-1326.

Devidyan A. G., V. N. Kira, G. A. Meski, and M. Morari. Batch Distillation in a Column with a Middle Vessel. *Chem. Eng. Sci.* **1994**, *49* (18), 3033-3051.

Devyatikh G. G. and M. F. Churbanov. *Methods of High Purification.* Znanie**, 1976**.

Ewell R. H. and L. M. Welch. Rectification in Ternary Systems Containing Binary Azeotropes. *Ind. Eng. Chem. Res.* **1945**, *37* (12), 1224-1231.

Hasebe S., B. B. Abdul Aziz, I. Hashimoto, and T. Watanabe. Optimal Design and Operation of Complex Batch Distillation Column. *Proc. IFAC Workshop*, London, **1992**.

Hindmarsh A. C. ODEPACK: A Systematized Collection of ODE Solvers. *Scientific Computing*. **1983**, 55-64.

Koehler J., H. Haverkamp, and N. Schadler. Zur diskontinuierlichen Rektifikation azeotroper Gemische mit Hilfsstoffeinsatz. Submitted to *Chemie-Ingenieur-Technik*. **1995.**

Meski G. A. and M. Morari. Batch Distillation in a Column with a Middle Vessel. Presented at AIChE Annual Meeting, St. Louis. **1993**, paper 152a.

Piela P., R. McKelvey, and A. W. Westerberg. An Introduction to the ASCEND Modeling System: Its Language and Interactive Environment. *J. Management Information Systems*. **1993**, *9*, 91-121.

Van Dongen D. B., and M. F. Doherty. On the Dynamics of Distillation Processes - VI. Batch Distillation. *Chemical Engineering Science*, **1985,** *40*, 2087-2093.

Wahnschafft O. M., J. W. Koehler, E. Blass, and A. W. Westerberg. The Product Composition Regions of Single Feed Azeotropic Distillation Columns. *Ind. Eng. Chem. Res.* **1992**, *31*, 2345-2362.

Wahnschafft O. M. and A. W. Westerberg. The Product Composition Regions of Azeotropic Distillation Columns. 2. Separability in Two-Feed Columns and Entrainer Selection. *Ind. Eng. Chem. Res.* **1993**, *32*, 1108-1120.

Yatim H., P. Moszkowicz, M. Otterbein, and P. Lang. Dynamic Simulation of a Batch

Extractive Distillation Process. *European Symposium on Computer Aided Process Design-2.* **1993**, S57-S63.

Chapter 3

Improved Operational Policies for Batch Extractive Distillation Columns

Abstract

We and others (Hasebe et al., 1994, Meski et al., 1993, Devidyan et al., 1994) have previously developed insights into batch distillation when using a “middle vessel” batch column. We extended earlier work on reachable product regions for continuous columns to this and other batch column configurations. Our work also examined the use of a continuously flowing extractive agent to facilitate the separation of azeotropic mixtures.

A middle vessel batch column has both an enriching and stripping section and thus both a distillate and bottoms product. In many ways it is just like a traditional continuous column, but we feed it by charging a middle tray having a very large holdup (a pot or still)

with the initial feed. Our work compared running this column with running a batch rectifier for an azeotropic mixture when using an extractive agent. We showed that both are often able in theory to recover all of the distillate component in relatively pure form, with the middle vessel accomplishing this by “steering” the still pot composition against time through the choice of reflux, reboil, entrainer and product rates. The middle vessel also requires a much smaller pot as we can continually remove and recycle the extractive agent.

In this work we show the sensitivity of the separation’s profit to the entrainer flow rate, the operation’s switching times between fractions, as well as the bottom flow rate policy for an extractive middle vessel batch column. We illustrate with an example problem.

3.1 Introduction

Recently, a novel type of batch distillation column has shown up in the literature. This column, called a complex batch column or middle vessel column, can be seen in Figure 3.1 (disregard the extractive section for the moment). It is a combination of the conventional batch column or rectifier and the inverted batch column or stripper column. The middle vessel column acts similarly to a continuous column in that distillate and bottoms products are taken simultaneously, with the middle vessel's still being a tray with a very large holdup.

Meski et al. (1993), Devidyan et al. (1994), and Hasebe et al. (1994) have studied the middle vessel column using 3-component, constant relative volativity systems. They found that the middle vessel column can accomplish quite different separations depending on reflux and reboil ratios, boilup rates in both column sections, and number of trays. Hasebe et al. (1994) also pointed out that the middle vessel column almost always performed better than the rectifier when they optimized the operation of these columns using as the objective function the total amount of product recovered divided by the total processing time.

For multifraction operation, there has been much work done for the batch rectifier but little or no work done for the middle vessel column. For example, Chiotti et al. (1989) optimized the design and operation of a batch rectifier. They used successive binary separations with an objective function being the sum of annualized investment, operating, and inventory costs. Sundaram and Evans (1993) optimized the separation of a multicomponent constant relative volativity mixture using various reflux ratio policies. Their objective function was profit per mol feed. Nonconstant reflux ratio policies

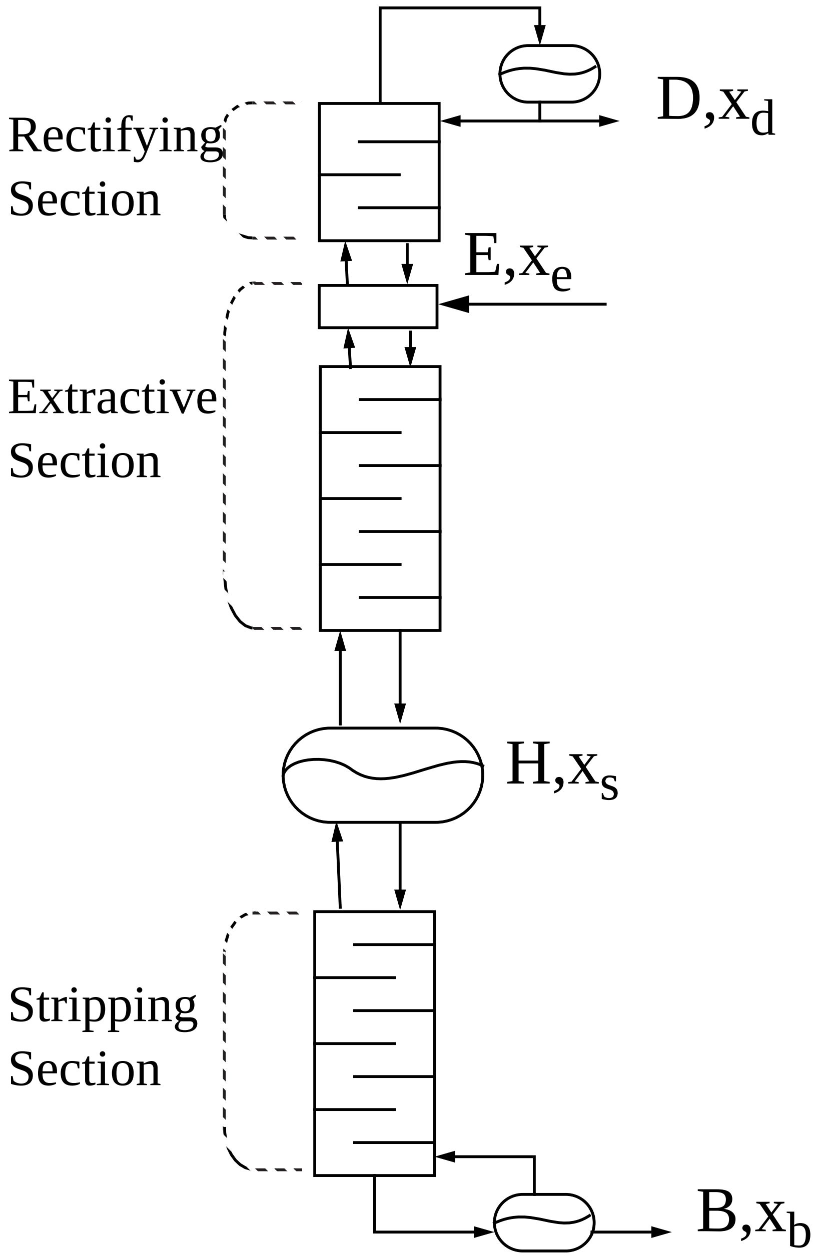

Figure 3.1: Middle Vessel Column with Extractive Section

produced an objective function that was at least 20% greater than that of using a constant reflux for each fraction. Farhat et al. (1990) maximized (or minimized) a set of product (or waste) fractions that met some set of product specifications. They assumed either a constant, linear, or exponential reflux policy for each fraction. The start and termination times for each fraction and reflux were the calculated optimization variables. They found that the linear and exponential reflux policies offered 5 to 10% more distillate product than the constant reflux policy.

For the batch separation of azeotropic mixtures, there exist distillation regions whose boundaries cannot be crossed, as also seen in conventional distillation. In batch distillation however, there may also exist additional boundaries that do not occur in continuous distillation. Using residue curve maps, Bernot et al. (1990) identified these distillation regions and boundaries. Using the methods that they developed, Bernot et al. predicted the product sequences for azeotropic mixtures using a batch rectifier at infinite reflux and infinite number of trays. In identifying these products, they also identified the change of the still composition versus time, sometimes called the still path, which was also shown on the residue curve maps. They also pointed out that the still composition will move in a direction away from the current product, until the still composition hits a distillation boundary or an edge of the composition space.

To facilitate the actual separation of azeotropes, extractive distillation is often used. In extractive distillation, normally a heavy component, called an entrainer, is fed close to the top of the column. This component changes the relative volativities of the azeotropic species and pulls some of the components down the column that normally show up in the distillate. The literature for extractive batch distillation is very scarce. Koehler (1995) discussed industrial applications of batch azeotropic and extractive distillation. Also, Yatim et al. (1993) simulated a batch extractive distillation column using a batch rectifier. They considered the azeotropic system of acetone/ methanol, while using water as the extractive agent. They recovered approximately 82% of the acetone in a relatively pure form. Safrit et al. (1995a) identified the feasible product regions for extractive distillation by extending insights developed for continuous distillation by Wahnschafft et al. (1993). Safrit et al. offered one explanation of the limited distillate recovery seen by Yatim et al. They found the regions of infeasible extractive distillation and point out that Yatim et al. may have gone into these regions (or very close to them). Safrit et al. showed that it is possible to recover 100% of the distillate product using a batch rectifier and middle vessel column. However, the rectifier required a still of infinite size, while the middle vessel did not have this limitation. One can steer the still composition of the middle vessel column towards the intermediate component, affecting a three component azeotropic separation in one column with no waste. High reflux and reboil ratios were encountered, however, demanding that an optimization of the column's parameters as well as the operation be carried out. Lang et al. (1995) extended the work of Yatim et al. (1993) by investigating different operational policies for batch extractive distillation using a batch rectifier. They implemented different policies for the reflux ratio and entrainer flow rate and compared the recoveries of these policies.

The optimization of a separation like the one above will require the solution of an optimal control problem, where the column parameters are optimized simultaneously with the optimization of the entire operation. The operation will more than likely be a multifraction operation in which the fraction switching times will become important variables in the solution of the optimal control problem. The choice of objective function will also be an important part of the optimization.

3.2 Basic Concepts

3.2.1 Feasible Products for Batch Distillation

One important issue in continuous and batch distillation is determining the feasible products for a specified feed. While much work has been done in this area in continuous distillation, batch distillation has seen little attention. Diwekar et al. (1989) and Wu et al. (1989) looked at the determination of the maximum and minimum reflux ratio, minimum number of trays, and the reachable products for these bounds when a set of product specifications is made for a batch rectifier.

Wahnschafft et al. (1992) investigated the feasible product and possible column profiles for continuous distillation. They were able to predict the regions of feasible products for a specified feed composition using a graphical analysis of the residue curve map of the system. Pinch point curves were an important part of their analysis. A pinch point curve is the collection of tangent points on several residue curves, whose tangent lines point back through the product or feed composition. For the product pinch point curves, these points correspond to pinch points in the column where a vapor and liquid stream that pass each other are in equilibrium, requiring an infinite number of trays (or increased reflux ratio) to carry out the specified separation.

For batch distillation, Safrit et al. (1995a) extended the analysis above to batch distillation. But since the products and the “feed” are continually changing in batch distillation, the feasible product and possible column profile analyses apply only at the current instance in time. Also, the still composition, S, behaves just as any other tray composition, when holdup effects are ignored. So S had to lie on the column profiles (rectifying profiles for a rectifier or rectifying and stripping profiles for the middle vessel).

This was unlike the feed composition in continuous distillation which need not lie on this tray by tray profile. Safrit et al. showed that the regions of feasible distillate products were bounded by two curves: the total reflux curve and the line that was tangent to the total reflux curve at S. At total reflux, the rectifying column profile coincided with the total reflux curve, with the distillate depending on the number of trays. The other boundary consists of the collection of distillate compositions whose product pinch point curves go through S. This boundary defined the case of an infinite number of trays and varying reflux ratio, resulting in the existence of a pinch point in the column. The possible stripping profiles for the middle vessel column were found in the same way as the rectifying profiles above, except that the reboil ratio and number of trays below the still were considered.

The regions of possible rectifying and stripping profiles were also found. With some product specifications having been made, these regions were bounded by the residue curve through the products (approximation of the total reflux curve) and the product pinch point curves. These regions applied only at the current product compositions for the middle vessel column. If the products changed, then the regions of profiles changed. For the product specifications to be feasible in continuous distillation, the regions of profiles must have intersected in at least one point. This condition applied to the middle vessel column as well. However, there was a further condition for the product specifications to be feasible in the middle vessel column. The still composition must lie in this intersection in order for the still composition to lie on both the rectifying and stripping column profiles.

3.2.2 Batch Extractive Distillation Feasibility and Operation

Safrit et al. (1995a) showed that the graphical analysis for continuous extractive distillation for 3-component mixtures also applied to batch distillation at the current instance in time. As pointed out earlier, if the rectifying and stripping profile regions did not intersect, then the column was infeasible. Extractive distillation “added” another tray section or profile region that created a path of tray by tray calculations between the previously infeasible product specifications. The extractive column, shown in Figure 3.1, has three tray sections: rectifying, extractive and stripping. The purpose of the extractive agent that is fed at the top of the extractive section is to break the azeotrope that would normally be the distillate product. Wahnschafft et al. showed that the feasibility of the extractive section could be determined from Δ pinch point curves where the Δ point was the difference point for the geometric construction of the tray by tray profiles in the extractive section and was a function of the distillate and entrainer streams. The higher the ratio of E to D, the closer Δ was to E and vice versa. In the case of E=0, the Δ point corresponded to D, and the column would have been an ordinary continuous column. These Δ pinch point curves marked the boundaries of the feasible extractive sections. Figure 3.2 shows such curves and regions for the acetone/methanol/water system. The shaded regions denote infeasible extractive section regions. If any of the extractive section tray compositions lie within these regions, the extractive section will not perform as required.

Safrit et al. used the above analysis in examining the results of Yatim et al. (1993), in which they obtained a limited recovery of the distillate, acetone in this case, when using water as an extractive agent for the acetone/methanol azeotropic mixture. Safrit et al. postulated that the still composition moved into an infeasible extractive region, thereby making the separation infeasible. They further showed that it was theoretically possible to recover 100% of the distillate product using a rectifier and a middle vessel column. The rectifier required an infinite size still pot because water was continually added to the system but never removed. Using still path steering for a middle vessel configuration, they were able to recover 99.5% of the distillate product in finite time without the need for an infinite still because water was taken out of the bottom of the column and recycled back as entrainer.

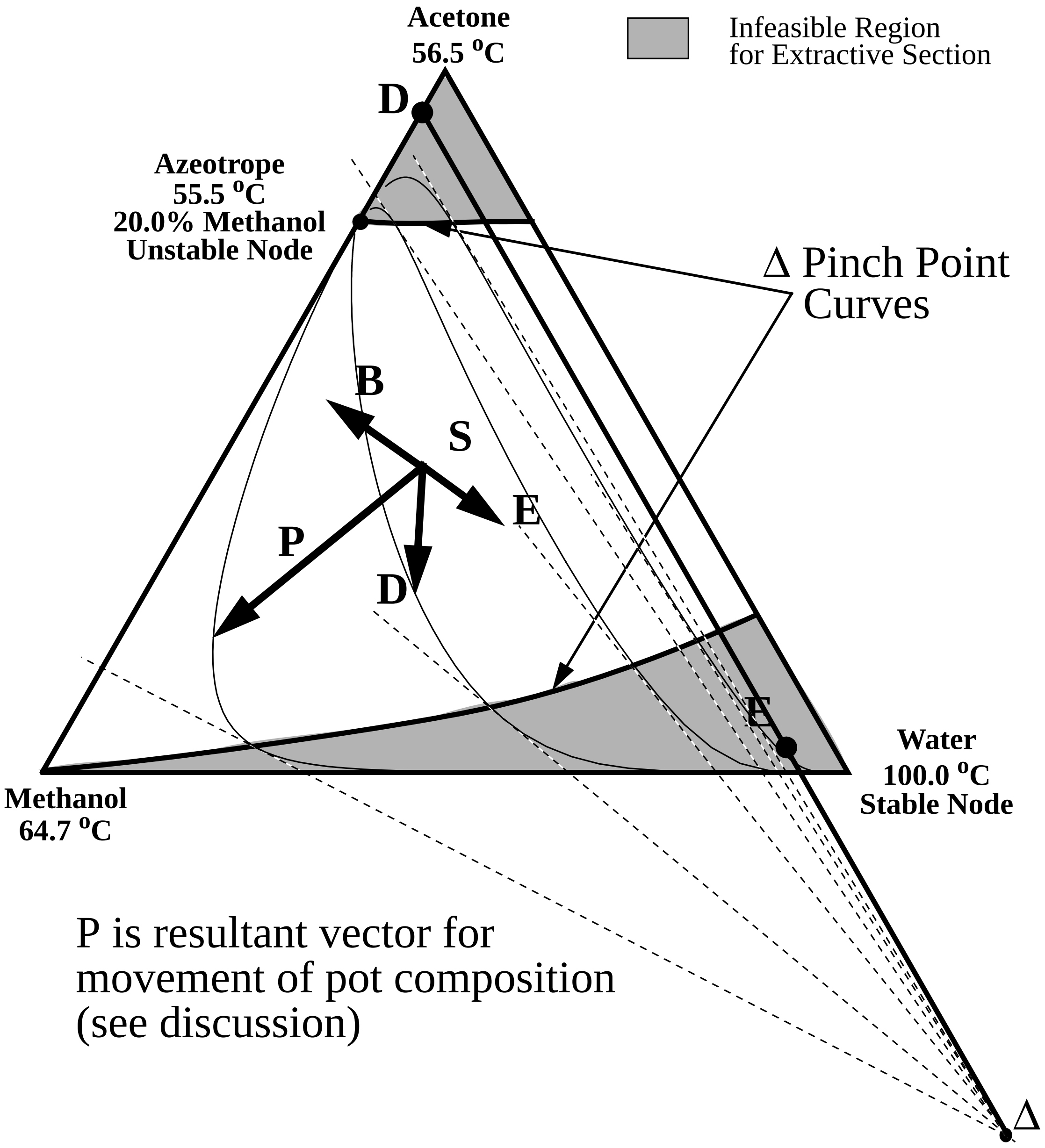

Figure 3.2: Δ Pinch Point Curves for Acetone/Methanol/Water

In reality, however, a 100% recovery would usually still not be feasible due to requirements of high number of trays, long processing times, and high utility costs. Somewhere during the middle vessel operation, the point of diminishing returns will occur. This stopping time is another variable that needs to be determined from the optimization of the middle vessel operation.

3.2.3 Flexibility of the Middle Vessel Column

Parameters such as reflux and reboil ratio, vapor boilup rates in the top and bottom sections, and distillate and bottom withdrawal rates are all variables that can be specified or calculated in different combinations such that many types of separations are possible. In particular, the product withdrawal rates greatly affect the type of separation that is carried out. Safrit et al. (1995a) found that the middle vessel column was capable of separating a three component mixture into its pure components using only one column. But the product withdrawal rates were chosen in an appropriate manner so that the still holdup became pure in the intermediate component. From the overall column component material balance, Safrit et al. showed that:

$$\frac{d}{d\mathbf{t}}\left(\mathbf{H}\mathbf{x}_{\mathbf{s}}\right) = -\left(\mathbf{D}\mathbf{x}_{\mathbf{d}} + \mathbf{B}\mathbf{x}_{\mathbf{b}}\right) + \mathbf{E}\mathbf{x}_{\mathbf{e}} \tag{3.1}$$

where **D**, **B**, and **E** represent the distillate, bottoms, and entrainer compositions and flow rates and $\mathbf{x}_\mathbf{s}$ and **H** characterize the still. The direction of the still path was in a direction opposite to that of the combined directions of $\mathbf{x}_\mathbf{s}$ to $\mathbf{x}_\mathbf{d}$ and $\mathbf{x}_\mathbf{s}$ to $\mathbf{x}_\mathbf{b}$ and $\mathbf{x}_\mathbf{e}$ to $\mathbf{x}_\mathbf{s}$. How these directions were combined was determined by the magnitude of **D**, **B** and **E**, based on vector addition. These “vectors” can be seen in Figure 3.2. If we withdraw distillate product, the pot composition P moves directly away from D; if we add entrainer, we draw the pot composition toward E; and, if we remove entrainer as the bottom product, we move the pot composition directly away from E. So, depending on the magnitude of the product flow rates and entrainer flow rate, it was possible to “steer” the still composition in a variety of directions. If we add no entrainer (vector towards E is of zero length) for instance, the direction of the still path could be determined by combining the distillate and bottoms product into a “net product”. Bernot et al. (1990) had pointed out that the instantaneous change in the still composition was in a direction directly away from the product, the net product in this case. As shown by Safrit et al., the distillate and bottom withdrawal rates could be chosen so that the direction of the still path was continuously aimed at the intermediate component. Eventually, the still composition arrived at the pure intermediate component, separating the mixture into its three pure components using only one column.

As mentioned above, the middle vessel column has many degrees of freedom from which many types of separations can be carried out. With so many combinations of these degrees of freedom from which to choose, it is necessary to optimize the column parameters. Knowing the type of separation that one wants to carry out still leaves many decisions to be made. In particular, if column parameters such as reflux and reboil ratios are allowed to vary during the column’s operation, the optimization now becomes an optimal control problem. If more than one fraction is to be taken, column parameters such as reflux and reboil ratio, and product withdrawal rates in all fractions can greatly affect the entire operation of the column during the collection of its product and waste fractions. Obviously, the choice of an objective function will also influence the final conditions of the column and its operation. With aspects of the entire operation (i.e. utility costs, product value, time constraints) being emphasized differently in different objective functions, many interesting solutions can be encountered.

3.3 Operation of Middle Vessel Column

As mentioned earlier, Safrit et al. (1995a) found that it was possible to recover nearly 100% of the distillate product when separating acetone and methanol using water as an extractive agent, also called the entrainer. They observed high reflux and reboil ratios towards the end of the operation. They had 2 operational steps: (1) initial still charged with 150 mols each of acetone and methanol, infinite reboil ratio, entrainer addition, and distillate (acetone) product removal, followed by (2) distillate and bottoms (water) product removal with entrainer (water) addition. While the mixture was separated into its pure components in finite time, there must exist a time where continuing the operation is not economically sensible. To properly optimize the operation of this column, a suitable objective function must be formulated. A general objective function could be profit per time, taking into account revenues realized from the sale of the column products and costs due to utility consumption, capital investment, inventory costs, and waste disposal. For the limiting case of only maximizing the product revenues and neglecting the related costs, the optimal operation would be very similar to the case shown by Safrit et al. The still path steering that took place may not have been an optimal way of running the column, but it must have been close as we can theoretically obtain a 100% recovery of all pure components. In addition, reflux and reboil ratio policies will come out of the solution to the optimal control problem.

However, we must include some of the costs relating to the operation of this column to obtain realistic results. In this work, we will consider product revenues along with the utility and waste costs. The objective function now has the form

max J = (product revenue - utility costs - waste costs) / total operation time (3.2)

with column parameters such as reflux and reboil ratios, vapor boilup rates, product and entrainer flow rates, operating times, etc. being the optimized variables. But what are the wastes and their associated costs? For the acetone/methanol system using water as an entrainer, the first distillate product will be acetone. Water will be taken out as a bottoms product. This water could then be purified in some later step, disposed of as waste, or, in the case of this work, produced sufficiently pure so it can be recycled back as entrainer. If the operation is cut short before the still reaches some specification on methanol (i.e. > 99%), then we have to take a waste cut in order to purify the methanol in the still. Using the results of Bernot et al. (1990), the distillate for this waste cut will be at or close to the local minimum temperature node, the acetone/methanol azeotrope because we are no longer feeding in an extractive agent. The bottoms composition will still be some water/methanol mixture. Figure 3.3 shows a schematic of this operation.

The operation has been broken into 2 periods (neglecting the initial infinite reboil period) with the first period producing our distillate product and the second period taking a waste cut in order to enrich the still in methanol. However, our waste cut will be the acetone/methanol azeotrope or very close to it. Since this mixture contains practically only the initial raw materials, we can recycle this product back to the next batch of mixture to be processed. Therefore, there is no waste cost associated with this cut, or any other cut for that matter. This also eliminates the need to include the raw material costs in the objective function because we are selling everything we process.

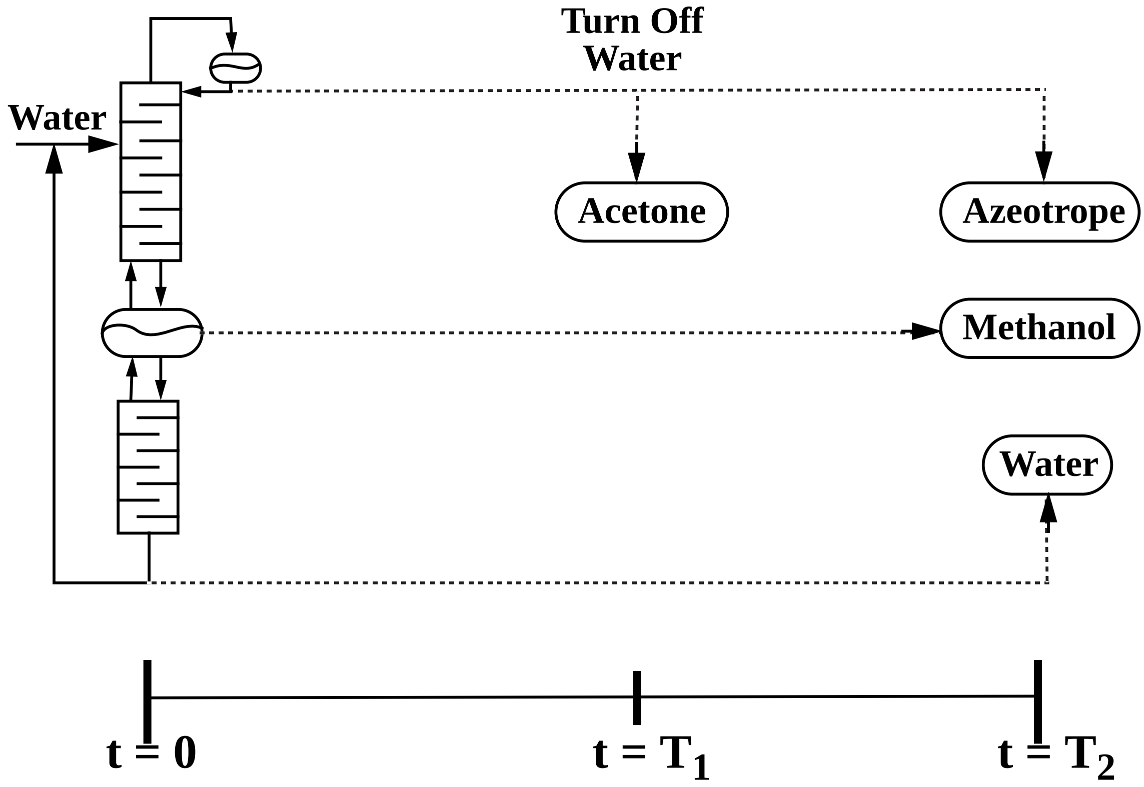

Figure 3.3: Extractive Middle Vessel Column Operation

3.4 Simulation Results

3.4.1 Nonazeotropic Mixtures

The software package Batch-Dist (Diwekar et al., 1991) was modified in order to model the middle vessel with a side feed stream. We looked at several different cases of reflux and reboil ratio policies (either constant or varying linearly or exponentially with time) and calculated the fraction switching times, as was done in Farhat et al. (1990), for each of the different policies. Initially, our optimization variables were the reflux and reboil ratio policies, bottom vapor boilup rate, and the switching time, T_1 from Figure 3.3, with T_2 being a fixed quantity. Constraints on the average product purities (distillate, still, bottoms) for every fraction could be added into the problem, as well as bounds on the optimization variables. Our objective function was similar to Farhat et al. where we were maximizing the sum of the amounts of a set of the products. The utility and waste costs were neglected initially. Each product could be assigned a weighting factor, which is a positive number for the products (product value) and negative for the waste cuts (waste disposal cost). The form of the objective function was

$$\max \sum_{i=1}^{NP} \beta_i P_i \tag{3.3}$$

where NP is the number of products, β_i is the value of product i, and P_i is the amount of product i produced. We optimized example 2 found in Farhat et al. for the middle vessel column. The convexity properties of this model were not known, so any optimized solution may only have been a local optimum.

Table 3.1 shows the comparison of our optimization with the middle vessel column and that of Farhat et al. using a rectifier. While a direct comparison is not possible due to different total number of trays for the two cases, the optimization showed again that the middle vessel column was capable of separating a three component mixture in only one fraction with no waste. Safrit et al. (1995a) accomplished this by adding an equality constraint into their model that continuously forced the still composition towards the intermediate component. However, Figure 3.4 shows the still path for our optimization (exponential reflux and reboil ratio polices), where we see that the still path is

Table 3.1: Comparison for Batch-Dist Optimization

	Trays Above Still	Trays Below Still	Number of Fractions	% Recovery of Products Const/Linear/Exp	Total Processing Time
Batch-Dist	5	5	1	100/100/100	1.5 hr
Farhat et al. (1990)	5	0	3	86.14/95.34/NR	2.3 hr

continuously aimed at the intermediate composition without the need of the extra equality constraint. The optimal way in which to run this type of separation using the middle vessel column is with the still path aimed directly at the intermediate component throughout the operation. If utility costs were included into the objective function, we would probably see that the optimum would become a two fraction operation similar to that presented in Section 3.3.

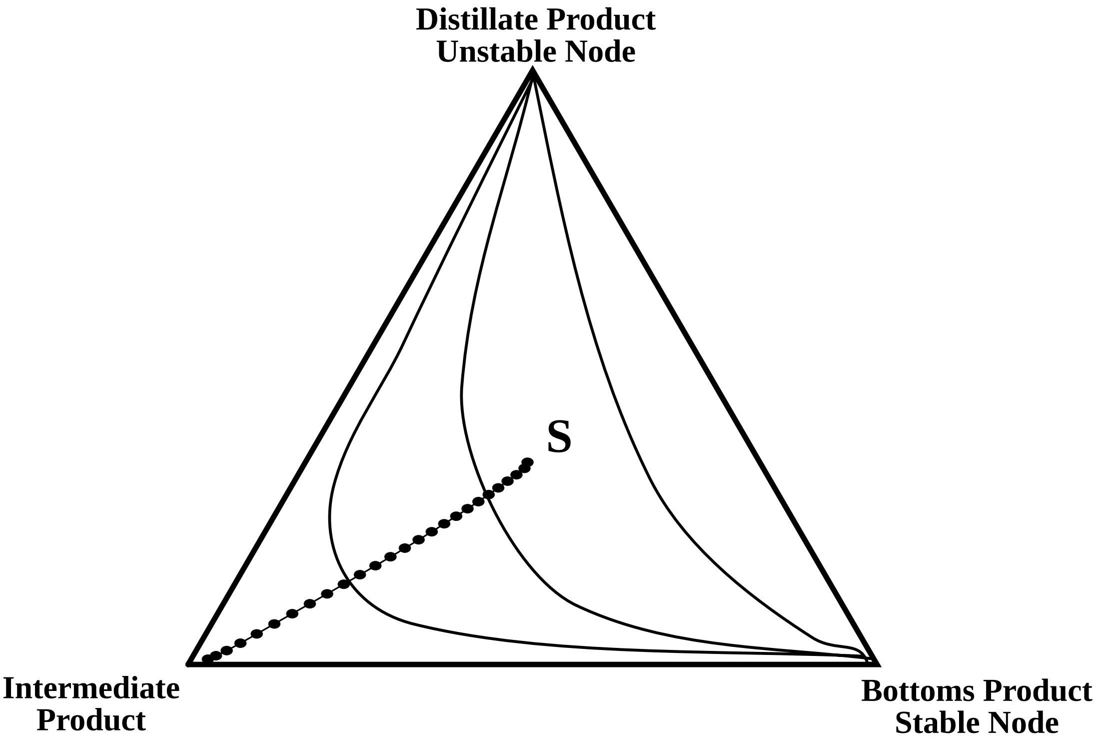

Figure 3.4: Still Path for Batch-Dist Optimization

3.4.2 Azeotropic Mixtures

The Wilson correlation was also implemented for the modeling of the thermodynamics of the system. However, the optimizer and simulation software had difficulties due to the azeotropic behavior of the system. We then used ASCEND (Piela et. al, 1993), an equation based modeling system, and LSODE (Hindmarsh, 1983) to solve the dynamic column models. But we did not have the optimization capabilities that were built into the Batch-Dist software. The reflux and reboil ratio policies were then calculated to meet the distillate ($x_{acetone}$ = 0.96) and bottoms (x_{water} = 0.997) product specifications. The ending time, T_2, was chosen as the time when the methanol composition in the still met its specification ($x_{methanol}$ = 0.99). Case studies were done, varying the switching time, T_1, and the entrainer flow rate, E. For the input data for case 1 in Table 3.2, Figure 3.5 shows how the accumulated costs and revenues change versus time in the main operational step (acetone recovery), with a maximum accumulated profit of the form in Equation 3.4 at t_{opt1}= 111s.

Table 3.2: Input Cost and Revenue Values

Case	$C_{acetone}$	$C_{methanol}$	C_{steam}	C_{CW}
1	$1 / mol	$0.3 / mol	$0.0025 / lbm	$0.006 / gal
2	$2 / mol	$0.9 / mol	$0.006 / lbm	$0.006 / gal

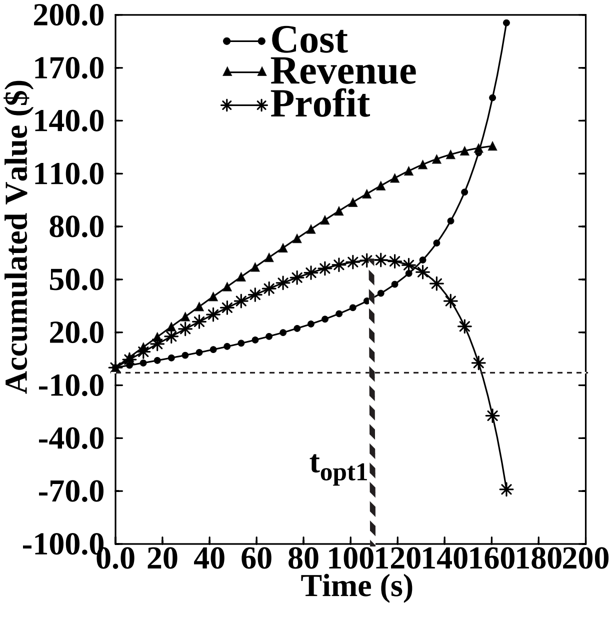

Figure 3.5: Profit vs. Time for Main Operational Step for Case 1

$$\textbf{profit} = (C_{acetone}{*}P_{acetone} + C_{methanol}{*}P_{methanol}) - (C_{steam}A_{steam} + C_{CW}{*}A_{CW}) \qquad \textbf{(3.4)}$$

We looked at the sensitivity of the objective, defined as the final profit in Equation 3.5,to changes in several of the column and operational parameters. The objective function will be sensitive to many parameters such as the reflux and reboil policies, entrainer and bottoms flow rate policies, vapor boilup ratios, fraction switching time, and the operation ending time (T_2). From Figure 3.6 we can see the sensitivity of the final profit to the

$$\textbf{max final profit} = \{(C_{acetone}{*}P_{acetone} + C_{methanol}{*}P_{methanol}) - (C_{steam}A_{steam} + C_{CW}{*}A_{CW})\} / T_2 \qquad \textbf{(3.5)}$$

entrainer flow rate, E, which is held constant in the main operational step. The final profit had a maximum around E = 6 mol/s. The values of T_1 for all of the simulations were set to

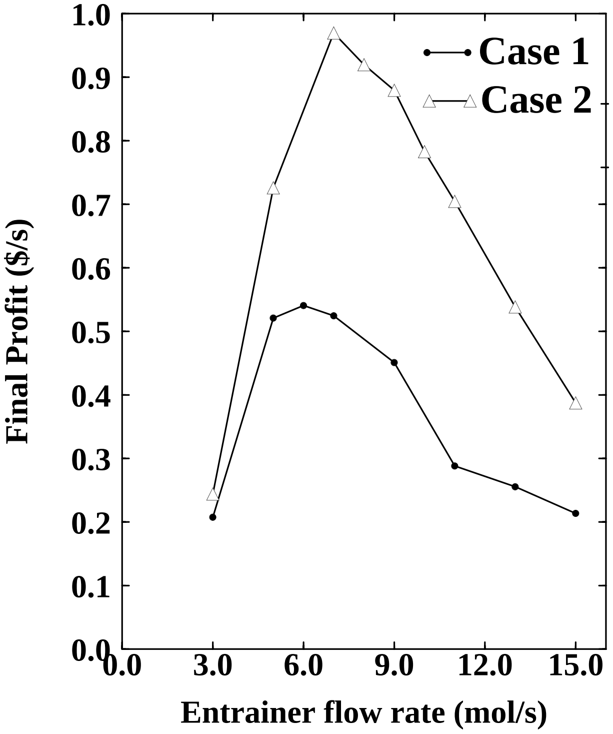

Figure 3.6: Final Profit vs. Entrainer Flow Rate

be the time where the accumulated profit was maximized in the main operational step. At low values of E, the separation between acetone and methanol became much more difficult, resulting in higher condenser duties. At high values of E where the separation was easier, the added water increased the internal column liquid flow rates, thereby increasing the duty that was required in the still and reboiler. Obviously, the entrainer flow rate will have an optimal policy, similar to what would be calculated for the reflux and reboil ratios, when the entire separation is solved as an optimal control problem.

The final profit also depended on T_1, because the second operational step had an impact on the revenue (methanol product) and cost (utilities). Figure 3.7 shows the final profit versus several different choices of T_1 with the entrainer flow rate being the one found above to maximize the final profit, E = 6 mol/s. We did not implement the stopping criterion for the second operational step exactly so there is some noise in the data in Figure

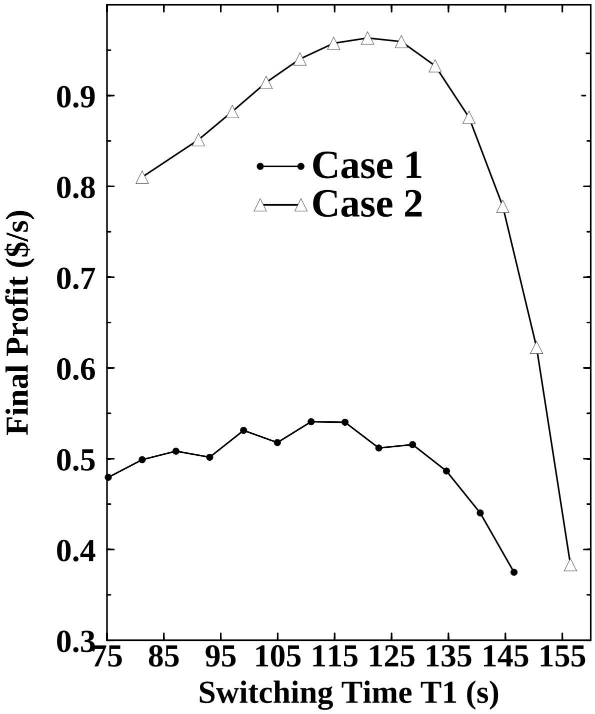

Figure 3.7: Final Profit vs. Switching Time T_1

3.7. Nonetheless, there is an obvious maximum in the final profit around T_1=112s, which comes close to t_{opt1}. Since the solution to this problem was so sensitive to product values and utility costs, we cannot make the general statement that the best value for T_1 will be the value found for t_{opt1}. Using T_1=112s and E = 6 mol/s, we recovered 82.0% of the acetone and 92.3% of the methanol that was originally charged in the column. We carried out similar simulations of the input data for case 2 in Table 3.2. Figure 3.8 shows the accumulated profit for case 2 with t_{opt1} = 121s at an entrainer flow rate = 7 mol/s. The sensitivity of the entrainer flow rate for case 2 was determined as in case 1 and is seen in Figure 3.6. The behavior was quite similar to that seen in case 1. The entrainer flow rate maximized the final profit around 7 mol/s. Because the products were worth more, the profit at the optimum entrainer flow rate was higher. We also looked at the sensitivity of the final profit to changes in T_1. Figure 3.7 shows this analysis for case 2. Again, the

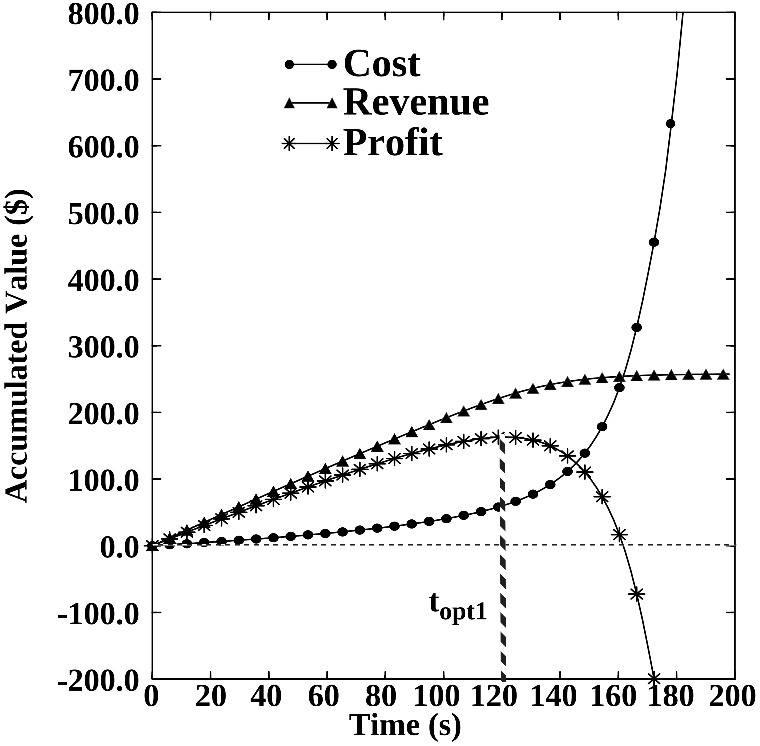

Figure 3.8: Profit vs. Time for Main Operational Step for Case 2

apparent optimum T_1 = 120s was very near the value of t_{opt1}. Using T_1=121s and E = 7 mol/s, we recovered 88.5% of the acetone and 94.9% of the methanol that was originally charged in the column. The increased product values of case 2 forced the main operational step of case 2 to recovery more of the acetone, which in turn made recovering the methanol easier and more profitable.

As mentioned, the optimal entrainer flow rate will actually be an optimal policy when the problem is solved as an optimal control problem. To illustrate this, we assumed a linear entrainer flow rate policy that was a function of time which had the form

$$\textbf{flow rate (entrainer)} = L_A\ \textbf{(mol/s)} + L_B\ \textbf{(mol/s\^{}2) * time (s)} \qquad \textbf{(3.6)}$$

Figure 3.9 shows the sensitivity of the final profit to the parameter L_B for several fixed values of L_A. There was a maximum in the final profit for each set of data. For L_A = 6.0

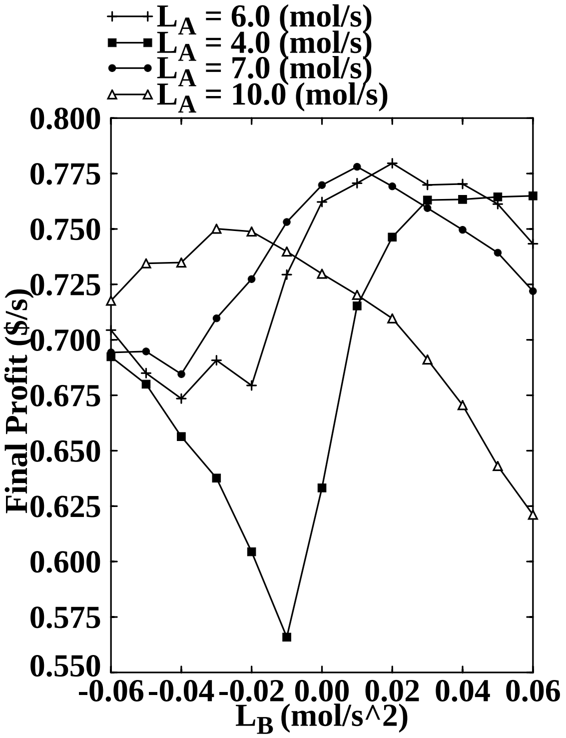

Figure 3.9: Final Profit vs. L_B for Entrainer Flow Rate

mol/s, we can see that the maximum final profit occurred when we had an almost constant entrainer flow rate throughout the main operational step while for L_A = 10 mol/s the maximum final profit occurred at a negative value for L_B. In this case, we were feeding too much entrainer in the beginning of the operational step which increased the still and reboiler duties. The negative value for L_B continuously decreased the entrainer flow rate from 10.0 mol/s until it reached a value of ~6.1 mol/s at the switching time of 130s. One interesting characteristic of Figure 3.9 is the minimum in the final profit exhibited by most of the data sets. These minima mainly occur in the region of negative L_A parameters. At first, one would think that if we continually decrease the entrainer flow rate, the reflux ratio would have to increase due to the increased difficulty of separation. This would in turn raise the condenser duty. While this situation is happening, the duty in the still is normally dominated by the large flow rate of entrainer down the column and its large heat of vaporization. There is a point in the operation when the duty is no longer dominated by the entrainer flow rate and the still duty actually decreases, resulting in the rise of the final profit vs. L_B curves on the left of Figure 3.9.

One other question that remains is how good of a first approximation of the best bottoms product removal policy is the still path steering algorithm. To illustrate this, we removed the still path steer constraint and added a constraint that equated the bottoms and entrainer flow rates for a duration of the main operational step after which we switched back to the normal still steering algorithm. By equating the bottoms and entrainer flow rates, we created another type of still path steering algorithm. Many such algorithms could have been implemented, and this one was for illustrative purposes only. A comparison of the normal still path steering algorithm and the mixed algorithm can be seen in Figure

3.10. For these examples, L_A = 6.0 mol/s and L_B = 0.2 mol/s^2. The mixed algorithm gave a final profit = 0.800644 \$/s where the normal still path steering algorithm gave a final profit = 0.779609 \$/s. In the mixed algorithm, we are not taking out as much entrainer in the bottoms which decreases the necessary reboiler duty. For the assumed utility costs for this example, the condenser duty was dominated by the still and reboiler duties. So while the condenser duty was increased because we were approaching the Δ pinch point path, the amount of bottoms product was less than in the normal still path steering algorithm resulting in a lower reboiler duty. This could be a possible explanation of the increased final profit. While the bottoms withdrawal rate will also have some optimal policy that can do better than the normal still path steering algorithm, this algorithm is a good first approximation. Also shown on Figure 3.10 is the Δ pinch point path. Each point on this

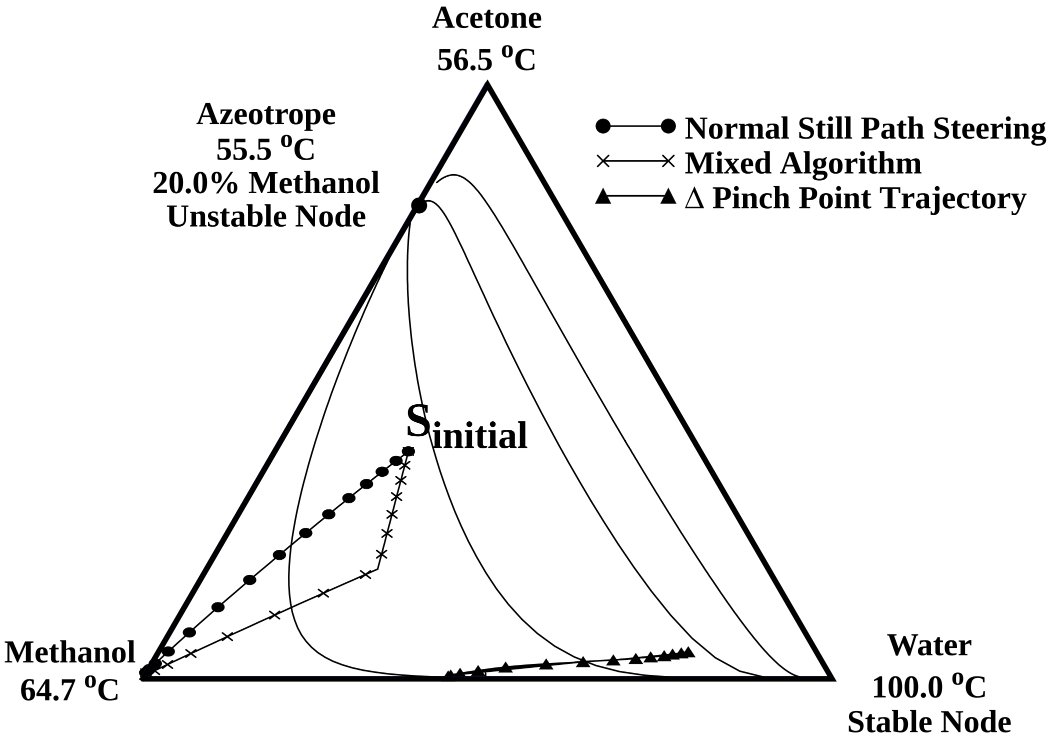

Figure 3.10: Comparison of Bottom Flow Rate Policies

trajectory is the intersection of the line connecting the current still composition and the Δ point with the current Δ pinch point curve. The Δ pinch point paths for each of the two cases shown in Figure 3.10 were, for all intensive purposes, the same. The two different bottoms flow rate policies, at least for the input parameters used, did have an affect on the final profit, but had little effect on the Δ pinch point paths. The Δ pinch point curves are a function of the distillate and entrainer streams. The steering algorithm has a small effect on these streams so the Δ pinch point paths will not change very much. We plotted these paths in Figure 3.10 to show the distance the still path and Δ pinch point paths were from each other as this distance is a measure of the difficulty of the extractive separation.

3.5 Conclusions and Future Work

Using previous work by Safrit et al. (1995a) in the analysis of extractive batch distillation using a middle vessel column, we looked at the operation and optimization of such a column in separating a three component azeotropic mixture into its pure components. While it is possible to recover nearly all of the distillate product, simulations showed that the entire operation should be done in two steps: distillate and bottoms recovery with entrainer addition, and a waste cut to purify the intermediate component in the still with no entrainer addition. For our example of separating acetone/methanol using water as an entrainer, there were no waste cuts because the distillate product in the second step was the acetone/methanol azeotrope which was recycled back to the next batch of mixture to be separated.

We also looked at the sensitivities of the final profit to various column operation parameters, in particular the entrainer flow rate policy, bottoms flow rate policy, and the switching time between operational steps. We showed that these variables do have a large effect on the final solution and should be solved for as the reflux and reboil ratio policies would be solved in an optimal control problem. While the optimal policies for the entrainer and bottoms flow rates were not obvious, the value of the switching time, T_1, that maximized the final profit for the simulations run was very near to the value of the time in which the accumulated profit was maximized in the main operational step (distillate recovery step), t_{opt1}. The problem solution was very sensitive to assumed product value and operational costs, and it was not possible to make the general statement that the best T_1 was the value of t_{opt1}. We also found that the still path steering algorithm provides a good first approximation to the bottoms flow rate policy for certain types of objective functions.

As we have shown, the operation of the extractive middle vessel column is very sensitive to variables such as reflux/reboil ratios, entrainer and bottoms flow rates, and fraction switching times. This design of this column and its operation need to be optimized simultaneously as an optimal design/control problem where the optimization will be limited by the characteristics such as the form of objective function, product values and utility costs, and the particular components that are to be separated.

3.6 Nomenclature

β_i = Weighting factor for product i
B = Bottoms product flow rate
D = Distillate product flow rate
DB = Still path direction due to bottoms product removal
DD = Still path direction due to distillate product removal
DE = Still path direction due to entrainer addition
Δ = Delta point
E = Entrainer flow rate
λ(i,j) = Wilson interaction parameter, λ_{ij}
H = Still Holdup
L_A = Constant parameter in flow rate policy equation

L_B = Linear parameter in flow rate policy equation
L_j = Liquid flow rate from tray j
$N_{Entrainer}$ = Entrainer feed location
N_{Lower} = Number of trays in lower section of column
N_{Upper} = Number of trays in upper section of column
P_i = Amount of product i
S = Still or middle vessel composition
T_1 = Fraction switching time
T_2 = Operation ending time
V_j = Vapor flow rate from tray j
x_b = Bottom product composition
x_d = Distillate product composition
x_Δ = Δ point composition
x_e = Entrainer composition
x_s = Still composition
t_{opt1} = Time of best accumulated profit

3.7 Acknowledgments

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References

Bernot C., M. F. Doherty, and M. F. Malone, **1990**. "Patterns of Composition Change in Multicomponent Batch Distillation." *Chem. Eng. Sci.*, *45*, 1207-1221.

Chiotti O. J., and O. A. Iribarren, **1989**. "An Optimization Module for Batch Distillation with Intermediate Cuts." *Comput. in Industry*, *13*, 169-180.

Devidyan A. G., V. N. Kira, G. A. Meski, and M. Morari, **1994**. Batch Distillation in a Column with a Middle Vessel. *Chem. Eng. Sci.*, *49* (18), 3033-3051.

Diwekar U. M., K. P. Madhavan, R. E. Swaney, **1989**. "Optimization of Multicomponent Batch Distillation Columns."*Industrial Engineering and Chemistry* Research, **28**, p. 1011-1017.

Diwekar U. M., and K. P. Madhavan, **1991**. "Batch-Dist: A comprehensive Package for Simulation, Design, Optimization and Optimal Control of Multicomponent, Multifraction Batch Distillation Column." *Comput. Chem. Eng.*, *12*, 833-842.

Chiotti O. J., and O. A. Iribarren, **1989**. "An Optimization Module for Batch Distillation with Intermediate Cuts." *Comput. in Industry*, *13*, 169-180.

Farhat S., M. Czernicki, L. Pibouleau, and S. Domenech, **1990**. "Optimization of Multiple-Fraction Batch Distillation by Nonlinear Programming." *AICHE Journal*, *36*, 1349-1360.

Hasebe S., B. B. Abdul Aziz, I. Hashimoto, and T. Watanabe, **1994**. "Optimal Design and Operation of Complex Batch Distillation Column." in press.

Hindmarsh A. C, **1983**. "ODEPACK: A Systematized Collection of ODE Solvers." *Scientific Computing*, 55-64.

Koehler J., H. Haverkamp, and N. Schadler, **1995**. "Zur diskontinuierlichen Rektifikation azeotroper Gemische mit Hilfsstoffeinsatz." Submitted to *Chemie-Ingenieur-Technik.*

Lang P., Lelkes Z., P. Moszkowicz, M. Otterbein, and H. Yatim, **1995**. "Different Operational Policies for the Batch Extractive Distillation." *Computers chem. Engng.*, *19*, S645-S650.

Meski G. A. and M. Morari, **1993**. "Batch Distillation in a Column with a Middle Vessel." Presented at AIChE Annual Meeting, St. Louis, paper 152a.

Piela P., R. McKelvey, and A. W. Westerberg, **1993**. "An Introduction to the ASCEND Modeling System: Its Language and Interactive Environment." *J. Management Information Systems*, *9*, 91-121.

Safrit B. T., A. W. Westerberg, U. M. Diwekar, O. M. Wahnschafft, **1995a**. “Extending Continous Conventional and Extractive Distillation Feasibility Insights to Batch Distillation.” *Ind. Eng. Chem. Res., 34*, 3257-3264.

Sundaram S., and L. B. Evans, **1993**. "Synthesis of Separations by Batch Distillation." *Industrial Engineering and Chemical Research*, **32**, p. 500-510.

Wahnschafft O. M., J. W. Koehler, E. Blass, and A. W. Westerberg, **1992**. “The Product Composition Regions of Single Feed Azeotropic Distillation Columns.” *Ind. Eng. Chem. Res.*, *31*, 2345-2362.

Wahnschafft O. M. and A. W. Westerberg, **1993**. “The Product Composition Regions of Azeotropic Distillation Columns. 2. Separability in Two-Feed Columns and Entrainer Selection.” *Ind. Eng. Chem. Res.*, *32*, 1108-1120.

Wu W., and T. Chiou, **1989**. “Determination of Feasible Reflux Ratios and Minimum Number of Plates Required in Multicomponent Batch Distillation.” *Industrial Engineering and Chemical Research*, **28**, p. 1862-1867.

Yatim H., P. Moszkowicz, M. Otterbein, and P. Lang, **1993**. “Dynamic Simulation of a Batch Extractive Distillation Process.” *European Symposium on Computer Aided Process Design-2*, S57-S63.

Chapter 4

Algorithm for Generating the Distillation Regions for Azeotropic Multicomponent Mixtures

Abstract

The azeotropic behavior of a mixture can limit the feasible separations that are possible by both continuous and batch distillation. The azeotropes can create continuous and batch distillation boundaries and regions, and knowledge of these boundaries and regions is very important during the synthesis and design of distillation based separation systems. Infeasible designs can be screened out early in the design process, saving valuable time and resources.

We propose an algorithm to find the basic distillation regions from which all of the continuous and batch distillation regions for a n-component system can be found, given all the azeotropes, their boiling point temperatures, and their node/saddle characteristics. A basic distillation region is a set of residue curves which all share the same unstable and stable node pair. Within each basic region, continuous and batch distillation regions can be determined. The continuous and batch regions give information about the types of feasible products one can obtain using either continuous or batch distillation. This algorithm can be applied to continuous columns and batch rectifiers, strippers, and middle vessel columns. The algorithm determines the boundaries and regions for all k-component systems before solving the (k+1)-component systems. In this manner, we will show how to find the distillation boundaries and regions for any n-component system.

4.1 Introduction

The separation of mixtures using distillation processes can be complicated by the presence of azeotropic behavior. Azeotropes can show up as the products of these distillations, possibly making the desired pure product impossible to produce. In this case, methods such as extractive distillation, changing the column’s operational pressure, changing the column’s feed composition, or switching to nondistillation based separation methods must be used to break the azeotrope. Azeotropes can also create distillation boundaries which form distillation regions in which the types of feasible separations are limited. It is important that one knows what these distillation boundaries and regions are for a particular mixture when one is designing a separation system for this mixture. Without the knowledge of these boundaries and regions, infeasible separation systems could be generated wasting valuable time and resources. A tool for finding the distillation boundaries and regions would be very important and helpful during the synthesis and design phase of azeotropic distillation systems.

We will define a basic distillation region as a set of distillation trajectories or residue curves that start at a particular local minimum temperature node (unstable node) and terminate at a particular local maximum temperature node (stable node). These nodes can be either azeotropes or pure components.The unstable node is the limiting distillate product meaning this node will be the distillate product for a column at total reflux and having an infinite number of trays. The stable node will be the limiting bottoms product. When sets of residue curves share an unstable or stable node but not both, a surface or boundary will separate these sets of residue curves. This surface is a basic distillation boundary. Except in the case of very curved basic distillation boundaries, the feed to the continuous distillation column determines in which basic distillation region the separation will lie. Also it is difficult to cross such boundaries without using methods like extractive distillation. Many researchers in the past have called such a distillation region a continuous region but we will show later that a continuous distillation region should represent something else.

Basic distillation regions can be broken up into continuous distillation regions and batch distillation regions where the regions tell us something about the types of feasible products one can obtain while operating in a particular distillation region. A continuous distillation region is very similar to a basic distillation region with a couple of exceptions. Figure 4.1 shows an example of a system with one basic distillation region as there is only one unstable and one stable node. For this case we have a straight line boundary A-BC that splits the basic region into two continuous regions. Using the reachable product concepts of Wahnschafft et al. (1992), we can readily show that no column profile can

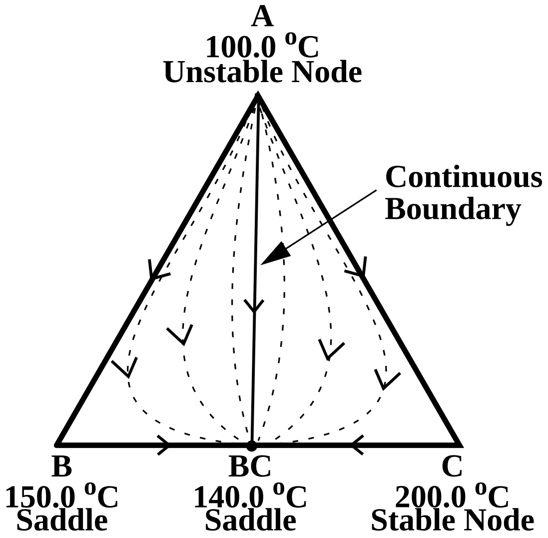

Figure 4.1: Basic vs. Continuous Distillation Regions

cross this straight A-BC boundary. Thus a continuous column could have profiles and products in either the continuous region (A, B, BC) or in the continuous region (A, C, BC) but not in both. As mentioned, many researchers have defined as continuous region what we have termed a basic region. However using our definition of a continuous region, we will see that a basic region is a building block for both continuous and batch regions. As we are about to note continuous regions are now defined similarly to batch regions as they describe the types of feasible products located within each region.

Ewell and Welch (1945) defined a batch distillation region as a region of compositions all of which produce the same product sequence upon rectification using a traditional batch column. The initial still composition determines in which batch distillation region one is operating, and the desired product cannot be obtained if it does not belong to the product sequence defined by the current batch distillation region. The batch distillation regions are subsets of the basic regions for a particular mixture and can be different for different types of batch column configurations. In Figure 4.1, there are two batch distillation regions: (A, B, BC) and (A, C, BC). The regions give information about the product sequences that can be obtained in each batch distillation region.

We shall first review the existing literature on basic and batch distillation regions where researchers have attempted to generate these regions using a variety of methods. We then present our algorithm for determining the basic, continuous, and batch distillation regions. In this algorithm, we show how to determine the distillation boundaries and regions for 3-component systems. We determine the distillation boundaries and regions for 4-component systems by calculating the distillation boundaries of all the individual 3-

component systems first. We generate surfaces in the 4-component space that separate the composition space into subregions, each containing one unstable node and one stable node. These surfaces are very similar to the 3-component systems, and we determine the distillation regions for these surfaces in the same manner as for 3-component systems. Using this approach, we show how it is possible to find the distillation regions for any n-component system when using a continuous distillation column or a batch rectifier, stripper, or middle vessel column. While we believe this algorithm to be quite general, as with all previous approaches of which we are aware, we have no proof the algorithm will work for all possible topologies. Thus for now one should validate the results. We show how we have done this validation with several examples.

4.2 Background

4.2.1 Basic Distillation

As stated earlier, a basic distillation region is defined as a set of residue curves that start at a particular unstable node and terminate at a particular stable node. Most researchers call such a region a continuous region, but we will define it as a basic region. Figure 4.2 shows a 3-component example where there are four sets of residue curves starting at either the unstable node CM or AM and ending at either the stable node M or AC. These sets of residue curves are separated by basic distillation boundaries. The boundaries that terminate at a stable node are stable separatrices, while the boundaries that start at an unstable node are unstable separatrices. These boundaries separate the composition space into basic distillation regions. Our goal is to find these boundaries by enumerating all of the distillation regions for a particular mixture.

Most of the work done in finding basic distillation regions has come out of the former Soviet Union. Serafimov, Petlyuk, and Aleksandrov (1975) presented an algorithm for finding the number of clusters of residue curves for a n-component mixture where each

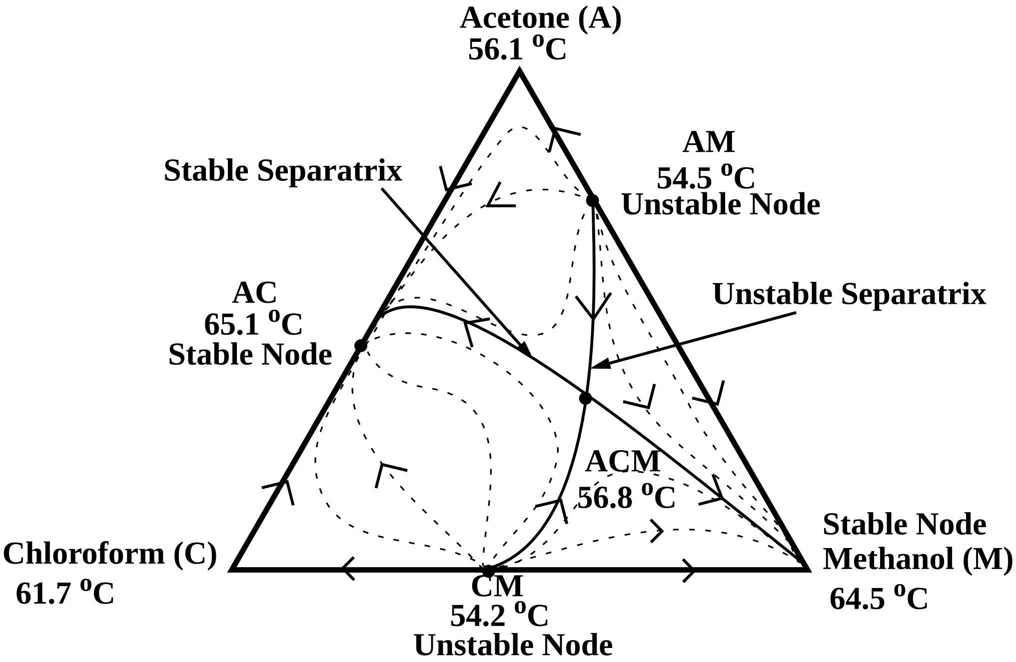

Figure 4.2: Acetone/Methanol/Chloroform Example, Bernot et al. (1990)

cluster is a different basic distillation region. They restricted themselves to solving problems containing only binary azeotropes and where the structure of the constituent 3-component mixtures is known beforehand. They also point out there was a set of nodes which created a manifold that delimit two clusters of trajectories. This manifold also contained clusters of distillation trajectories.

Petlyuk, Kievskii, Serafimov (1977) and Petlyuk (1980) found the basic distillation regions for systems with binary and ternary azeotropes only. They begin by building up all of the binary, then ternary systems. All systems after that (4, 5,..n-component) were determined by simply combining all of the previous systems as no new azeotropes were added to the systems. They generated all possible systems using different permutations of the possible connections between all of the nodes of the current system. They searched the tree of these possible systems using a depth first search and applied a feasibility test to each system. This test consisted of a list of rules and heuristics based on the assumption that the systems had no higher dimensional azeotropes than a ternary azeotrope. Similar to Serafimov, Petlyuk, and Aleksandrov (1975), these researchers recognized that manifolds separating distillation regions existed and that any binary and ternary azeotropes must lie on these manifolds.

Baburina, Platonov, and Slin'ko (1988) generated and classified the possible 3-component systems. They were able to analyze each system for feasibility using a bifurcation analysis and several conditions relating to the conjugacy of the critical points belonging to each basic distillation region. While they did not extend their analysis to more than 3-component systems, they mention in closing that their algorithm opens up the possibility of analyzing higher dimensional systems.

Serafimov (1987) presented a literature review on the thermodynamic topological analysis of azeotropic separation systems. Other than the previously mentioned work above, Doherty and Caldarola (1985) and Doherty (1985) presented a method for generating 3-component systems using a topological relationship between the nodes of the system and a set of rules and heuristics for determining the basic distillation boundaries. Matsuyama (1975) also enumerated all of the possible 3-component systems.

4.2.2 Batch Distillation

In batch distillation, the initial still composition defines in which batch distillation region one is currently operating. The rectification of this still composition will produce a sequence of products, starting with the local minimum temperature node or the unstable node. The products after the unstable node consist of a set of saddle nodes and possibly a stable node in order of increasing boiling temperatures. Each batch distillation region, therefore, is made up of a set of compositions that will produce the same product sequence when they are separated (Ewell and Welch, 1945).

The work that has been done in identifying batch distillation regions is somewhat limited. Malenko (1970a, b, c) did some interesting work in a series of papers where he first pointed out that the change in still composition versus time (still path) proceeds in a direction directly opposite that of the current distillate product during ideal fractionation (using a traditional batch rectifying column). He then stated that the still path will proceed in this direction until it hits a face of the composition space or a distillation boundary. He could then analyze a lower dimensional system since the face of the composition space where the current distillate product lies could not be reached again. He introduced the concept of a maximum temperature surface (MTS) which is a separator of distillation lines (residue curves). The MTS separated the composition space into subregions each having its own unstable node. The number of MTS's for a n-component system was one less than the number of unstable nodes that are present in that n-component space, and the dimension of the MTS is n-1 (for a 4-component system, the MTS was a planar surface of dimension 3). The nodes that make up the MTS are nodes which have more than one ridge line passing through them or, more simply put, belong to more than one set of residue curves as seen in continuous distillation. Starting with 3-component systems whose structures (batch distillation boundaries) were known, Malenko identified the MTS's for each of the 3-component systems. These MTS's then made up the MTS manifold for the 4-component system. The 4-component MTS acted like another face of the 4-component space and batch distillation boundaries were added to this manifold because Malenko pointed out that the distillation lines or the still path could not cross the MTS. Using these techniques, Malenko was able to decompose a n-component system down to n-1, n-2, etc. using the methods of MTS analysis until only 3-dimensional systems remained. The structure of these 3-dimensional systems was known a priori or calculated by hand. His work was for the batch rectifier column only.

Van Dongen and Doherty (1985) and Bernot, Doherty, and Malone (1990, 1991) did some very interesting work in finding the still and product paths and batch distillation regions for batch rectifying and stripping columns for 3 and 4-component systems. They developed the following heuristic for identifying the batch distillation regions for 3-component systems: "First the composition triangle is divided into regions each containing one unstable node. In each of these regions the other batch distillation boundaries are found by joining the unstable node to all the saddles and nodes of its region." They used the stable separatrices to divide the composition space. This algorithm applied to the batch rectifier. A similar algorithm joining each stable node to all of the saddles and nodes of its region was developed for a batch stripper. The boundaries that divided the composition triangle into subregions each containing one unstable node are the MTS's seen in Malenko's work. They also point out that the regions for a batch rectifier and stripper differ slightly when the boundaries are curved. Several 4-component examples were shown, but there was only one unstable or stable node in each example making the batch distillation regions easier to find.

Recently, Ahmad and Barton (1995a, b) have presented an algorithm for finding the batch distillation regions. They began by testing the algorithm for finding the batch distillation boundaries of Bernot, Doherty, and Malone (1991) on all possible ternary systems and pointed out that there were a few systems in which the algorithm failed to give the correct batch distillation regions. They assumed for their work that these types of systems would not occur. They defined a stable separating boundary as any edge of the composition simplex or any stable separatrix. Also defined was the concept of primary boundaries which consist of all of the 3-component batch distillation boundaries. Using these concepts, they defined their algorithm for finding the batch distillation region boundaries for a n-component mixture as:

- Find batch distillation region boundaries for all 3-component systems using the algorithm of Bernot, Doherty, and Malone (1991). These boundaries are the primary boundaries.
- Find the stable separating boundaries (stable separatrices) for all 4-component systems and add any primary boundaries not introduced earlier.
- Repeat above step for all 5-component systems, 6-component systems, etc.

They then go on to prove three main points:

- A batch distillation region consists of k vertices where k is the number of components for the current system and that the dimension of this region is k-1 (e.g. for k=3, the region will be a plane and for k=4, the region will be a 3-dimensional volume).
- The edges that make up the region are primary boundaries.
- All pairs of the k vertices that form this region must be connected by primary boundaries and there must be a path of increasing temperature between all vertices.

Some of the proofs for these statements were contained in these two papers, while the remaining proofs were referenced in a paper in preparation (Ahmad, Zhang, and Barton, 1995). They also enumerated the batch distillation regions by finding all paths between vertices that started at an unstable node and, while traversing on primary boundaries of increasing temperature, visited k-1 vertices (k was the number of components in the current system). One other interesting result from their work was the idea of using vectors that originated at some reference point and passed through the vertices of the batch distillation regions to represent the regions. In this manner, one could quickly calculate to which batch distillation region a particular composition belonged. They looked at 3, 4 and 8-component examples. But these examples contained either one unstable and/or one stable node making the batch distillation regions easier to find. If there is only one unstable node, the batch distillation boundaries are generated by simply connecting the unstable node to every other node in the composition space.

4.3 Algorithm for Finding Distillation Boundaries and Regions

As shown above, there has been a significant amount of work done in finding the distillation regions for basic and batch distillation processes. Most of these algorithms suffer from many of the same problems: they only use the temperature information about nodes in the calculation of these regions, they fail to solve difficult 4-component and higher systems, and the algorithms are difficult to understand and implement. While some of the ideas of the algorithm we will present here come from the work reviewed above, we will show that a simple, general algorithm exists for finding the basic, continuous, and batch distillation regions. Assuming straight distillation boundaries, we will show how to find the basic and continuous distillation boundaries. We next present the algorithms for finding the batch distillation boundaries after which we will generate the basic, continuous and batch distillation regions. We will find the batch boundaries and regions for a batch rectifier, stripper, and middle vessel column. However, we will first show why the stability information AND the temperature information about the system nodes are both necessary in correctly determining the distillation boundaries and regions.

4.3.1 Use of Stability and Temperature Information

As pointed out earlier, most of the algorithms created for the determination of the distillation boundaries and regions of a particular system use only the boiling points of the nodes of the system. Figure 4.3 shows an example of a system in which the temperature information about the system does not uniquely define the system. In both cases (I and II), the temperature information about the nodes is identical, but the stability information is different resulting in different distillation boundaries and regions. The stability information of a system consists of determining whether a node (pure component or azeotrope) is an unstable node, stable node, or a saddle. We show in Section 4.3.3 how to determine these stabilities for a particular system. Algorithms must use the stability and temperature information in order to correctly determine the distillation boundaries and regions for the particular system.

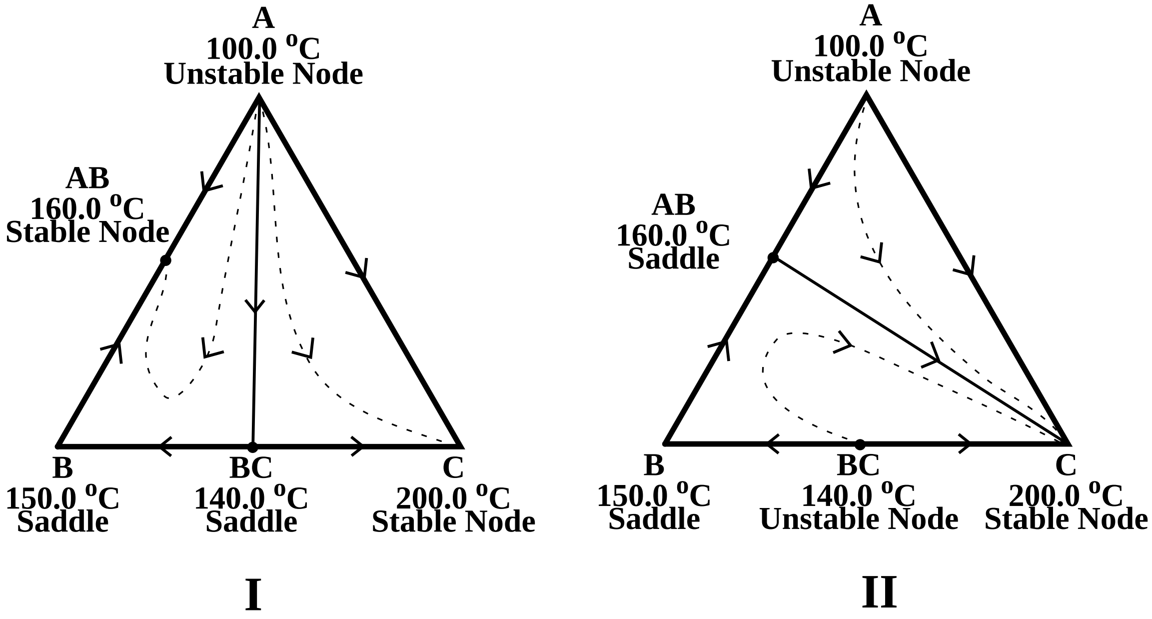

Figure 4.3: System Not Uniquely Defined by Temperature

4.3.2 Basic Distillation Boundaries for 3-Component Systems

We have seen the notion of separating planes or manifolds dividing the composition space into subregions, each containing one unstable node, in the work of several previous researchers, but not all of these researchers have grasped the true nature and importance of this separating manifold. Malenko (1970b) was the first researcher to really understand that not only does this manifold act like another face of the composition space, but that distillation boundaries exist on this manifold. He called this manifold a maximum temperature surface (MTS) as he thought this surface was a ridge in the contours of temperature profiles on a composition diagram. Van Dongen and Doherty (1984) proved that these ridges did not correspond to temperature ridges. However, some kind of separating surface does exist. Figure 4.2 shows an example of acetone/methanol/chloroform. Malenko would have identified the MTS as the surface (line) AC-ACM-M. This surface, which we will call a maximum residue surface (MaxRS), is a separating manifold that separates a composition space into subregions each containing its own unstable node (UN). Each residue curve will follow a path of increasing temperature, converging towards and terminating on the MaxRS. In this example, we create two subregions: one with AM as its unstable node (UN) and one with CM as its UN. The MaxRS separates out two sets of residue curves each having its own UN. The MaxRS also corresponds to the stable separatrix for this system, as used earlier as a separating surface in several of the other works we examined.

If we look at the behavior of the MaxRS, we again see that the MaxRS is a boundary between two UNs. Each of these UNs must be able to “see” each node on this surface meaning that a residue curve from the UN to each node on the MaxRS must exist as all residue curves terminate on the MaxRS. If the UN could not see all of the nodes on the MaxRS, then there must be some other separating surface, and we have not found the correct MaxRS. The nodes that make up the MaxRS are actually the nodes that the various UNs have in common when we traverse the various connections between nodes while increasing in temperature. For example, in Figure 4.2, all of the nodes that the UNs can reach only using the binary connections are: UNL(CM)=(C, AC, M) and UNL(AM)=(A, AC, M) where A is the acetone node, C is chloroform, and M is methanol. To complete these lists, we add the ternary azeotrope to both, getting the unstable node lists UNL(CM)=(C, AC, M, ACM) and UNL(AM)=(A, AC, M, ACM). We have to include the ternary azeotrope because every node on the composition simplex must be able to “see” the ternary azeotrope when the ternary azeotrope is a saddle. No basic distillation boundary can separate a node from the ternary saddle azeotrope. If we find the nodes that appear <u>in at least two of these lists</u>, we get the intersection list INT(CM, AM)=(AC, M, ACM). Three nodes are in common to both of the UNs and must make up the MaxRS. We add the connections ACM-AC and ACM-M to the system. Basically we connect each stable node (SN) in the intersection list to every node in the list that is not a SN unless a ternary saddle azeotrope exists, in which case we connect each SN to the ternary saddle azeotrope. This method correctly finds the stable separatrix and the MaxRS for the 3-component system.

If we look at Figure 4.2, we see that there is also a manifold that separates the composition space into subregions, each having its own SN. We will call this a minimum residue surface or MinRS. If we use the same kind of analysis as above for the UNs but now follow the directions of decreasing temperature from the SNs, we find the nodes of the MinRS to be: SNL(AC)=(A, AM, C, CM, ACM), SNL(M)=(AM, CM, ACM), and INT(AC, M)=(AM, CM, ACM). We add the connections AM-ACM and CM-ACM to the system. The MinRS forms the unstable separatrix of the system. So the MaxRS and MinRS divide the composition space into four sets of residue curves, each having its own UN and SN pair. These two manifolds determine the basic distillation regions for this example. We could also invert all of the temperatures and stability of the nodes (unstable to stable and stable to unstable) in Figure 4.2 and apply the above analysis. We would find that the “inverted” system’s MaxRS and MinRS were the original system’s MinRS and MaxRS, respectively, and would find the same basic distillation boundaries as in the original system. These two separating surfaces are composition spaces of dimension k-2, where k is the number of components (a line in this case of k=3), as seen in the literature mentioned previously.

However, we cannot rely on equating the stable separatrix to the MaxRS and equating the unstable separatrix to the MinRS as done in some of the other work. Figure 4.4 shows an example where we have two UNs and three SNs. There must be a MaxRS in this system separating out the two UNs. The stable separatrix is ABC-A. But there is a separatrix, ABC-BC, which we will call a saddle separatrix because it does not conform to the definitions of unstable or stable separatrices. This saddle separatrix connects two saddle nodes and is part of the MaxRS as it is part of the surface that separates the region into subregions, each having one unstable node. If we were looking for only the stable separatrices to make up the MaxRS, the segment ABC-BC would not be included, and the composition space would not be divided into regions, each having its own UN.

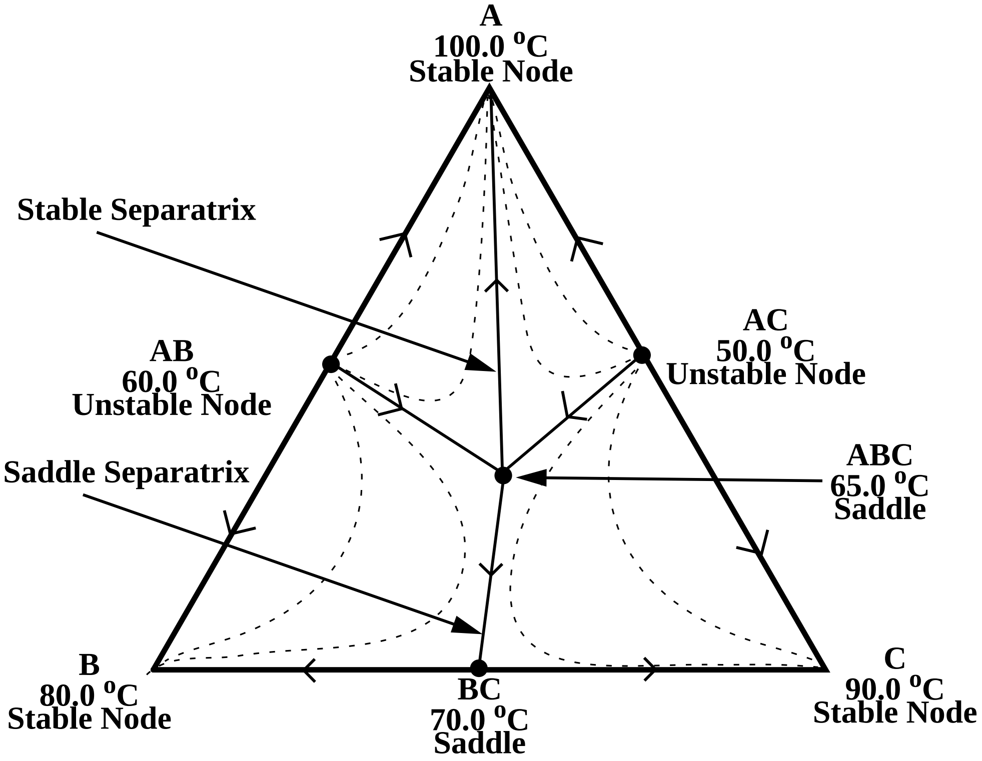

Figure 4.4: Example of Saddle Separatrix

For this example, if we find the common nodes for all of the UNs and find their intersection list we get: UNL(AB)=(A, B, ABC), UNL(AC)=(A, C, ABC), and INT(AB, AC)=(A, ABC). The only connection we can add to the system is ABC-A, or the stable separatrix. However, when we find the MinRS for this example, we get: SNL(A)=(AB, AC, ABC), SNL(B)=(AB, BC, ABC), SNL(C)=AC, BC, ABC). Noting that the intersection list contains any node in at least two of these lists we get INT(A, B, C)=(AB, AC, ABC, BC). So the connections we are able to add are AB-ABC, AC-ABC, and ABC-BC as the ternary saddle azeotrope must be connected to everything in the intersection list. By using the MaxRS and MinRS together, we are able to determine the basic distillation boundaries for 3-component systems. We can further add that any basic distillation boundaries for a 3-component system must lie on either the MaxRS or MinRS because we cannot block any node not on one of these surfaces from these surfaces. All residue curves from nodes not on one of these surfaces must either increase in temperature to the MaxRS or decrease in temperature to the MinRS.

As pointed out by Ahmad and Barton (1995a), the method of Bernot, Doherty, and Malone (1991) to find the batch distillation regions failed on two types of the 87 feasible 3-component systems that were enumerated by Doherty and Caldarola (1985). These two types consisted of a type (1) in which the ternary azeotrope is a SN connected only to a binary saddle and a type (2) where the UN is a pure component and the SN is one of this component's binary azeotropes. In type 1, the stable separatrix did not divide the composition space into regions each having its own UN. This behavior is not only a problem in finding batch regions but also in finding basic distillation boundaries. Figure 4.5 shows an example of type 1 which is the inverse of system 421-m from Doherty and

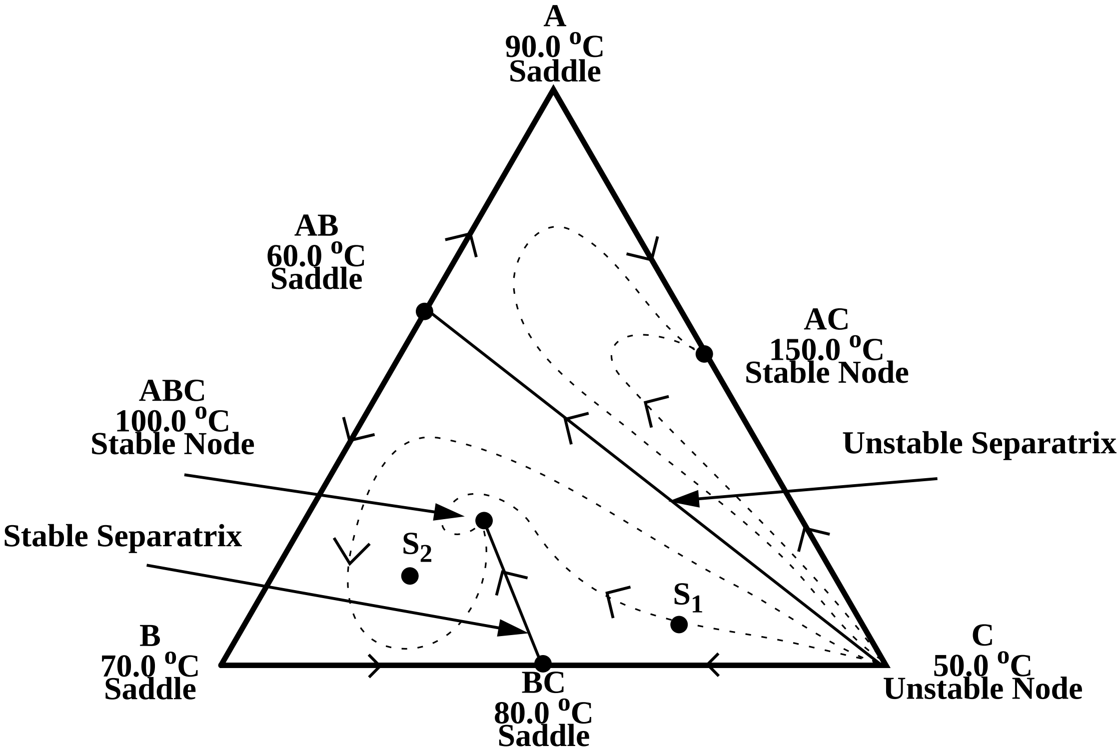

Figure 4.5: Inverse of System 421-m from Doherty and Caldarola (1985)

Caldarola (1985). In order to capture this stable separatrix connection, the following "preprocessing" step is made to our current algorithm:

- If a k dimensional azeotrope exists (where k is the total number of components in the current system) and this azeotrope is an UN (SN) and there is only one SN (UN), then any path of decreasing (increasing) temperature from a stable (unstable) node that ends in a saddle must be supplemented by the connection of the azeotrope to this saddle. This step must be done before finding the common node and intersection lists.

For the example in Figure 4.5, we would recognize that there is a k dimensional (azeotrope involving all k=3 components) azeotrope and it is an SN and there is only one UN, C. The path of increasing temperature C-BC ends in a saddle. So we must add the connection BC-ABC before we do any further analysis of the system. Applying the rest of the algorithm gives for the MinRS: SNL(AC)=(A, AB, C), SNL(ABC)=(BC, B, AB, C), and INT(AC, ABC)=(AB, C). We add the connection C-AB to the system, giving the correct structure. Every residue curve must end (start) at a SN (UN) and, if we have a residue curve that ends at a saddle while traversing in decreasing (increasing) temperature, the residue curve must terminate at the azeotrope involving all components of the particular system. This azeotrope must be a SN (UN). This additional preprocessing step correctly finds the basic distillation boundaries for all of the type 1 systems referred to above. The type 1 and 2 systems will be investigated further when we discuss finding the batch distillation boundaries.

4.3.3 Basic Distillation Boundaries for 4-Component Systems

As shown in Malenko (1970b, c) and Ahmad and Barton (1995a, b), the edges of the 4-component separating manifold or MaxRS (which is a plane) is made up of the 3-component MaxRS's (which are lines). The 4-component MaxRS acts like another face of the 4-component simplex, which are 3-component systems. The MaxRS separates the original 4-component space into separate 4-component spaces, each having its own UN. Similarly, the MinRS acts like another face of the composition space by separating the original 4-component space into subspaces each having its own SN. These two surfaces or manifolds (MaxRS and MinRS) can be found in the same manner as for 3-component systems: by finding the UNL and SNL and INT lists but only using existing connections that are basic distillation boundaries. They also have the same characteristics of their 3-component system counterparts meaning that any new connections (basic boundaries) that are to be added to the system must be between nodes on the MaxRS or MinRS (except for the case of an unstable or stable 4-component azeotrope in which case we apply the preprocessing step as before). So once we have found the MaxRS and MinRS, we can treat them as 3-component systems since they really act like faces of the 4-component mixture. But what are the stabilities of the nodes on each of these individual faces when we are treating these faces as 3-component systems? Fidkowski, Malone, and Doherty (1993) showed that by looking at the eigenvalues of **J** calculated at the pure component and azeotropic compositions (x=liquid and y=vapor) of a particular mixture such that

$$\frac{d\mathbf{x}}{d\xi} = \mathbf{x} - \mathbf{y} = \mathbf{x}(1 - \mathbf{K}),\ \xi \text{ is dimensionless time} \qquad \textbf{(4.1)}$$

$$\mathbf{J} = [\delta_{ij} - y_{ij}],\ \delta_{ij} \text{ is the Kronecker delta} \qquad \textbf{(4.2)}$$

$$\text{with } \sum_{i=1}^{n} x_i = 1 \qquad \textbf{(4.3)}$$

$$\text{where } y_{ij} = \left[\frac{\partial y_i}{\partial x_j}\right] \qquad \textbf{(4.4)}$$

one could determine the stabilities of the nodes (pure components and azeotropes) of the current system. For an n-component system, there will be n-1 eigenvalues. If all of the eigenvalues are positive, the node is an UN (all eigenvectors or residue curves move in time away from the UN); if all are negative, the node is a SN (all eigenvectors or residue curves collapse onto the SN); and if positive and negative, the node is a saddle (some eigenvectors move away and some collapse onto the saddle). For example in Figure 4.2, each node has two eigenvalues, resulting in two eigenvectors) associated with it. Node CM for instance has an eigenvector growing away from it along the chloroform/methanol binary edge. It also has an eigenvector growing away from it that points to the interior of the composition space. Since all eigenvectors grow away from the node CM, this node is an UN. Node M (methanol) also has two eigenvectors associated with it: one collapsing onto the node along the acetone/methanol binary edge and one collapsing onto the node along the chloroform/methanol binary edge. Since all eigenvectors are collapsing onto the node M, this node is a SN. And for the node ACM, there are two eigenvectors associated with it: one collapsing onto the node from the nodes AM or CM and one growing away from the node towards the nodes AC or M. The node ACM is a saddle node because it has eigenvectors that collapse and grow away from it.

If we are looking at the nodes on the MaxRS for a 4-component system, we know that these nodes must have at least one negative eigenvalue as residue curves collapse onto the MaxRS from the other nodes in the 4-component space not on the MaxRS (all residue curves terminate on the MaxRS). The remaining two eigenvalues must describe the stability of the MaxRS nodes with respect to each other. In this way we can treat the MaxRS as a 3-component system with the proper stability information. The same argument applies for the MinRS except that we can account for one positive eigenvalue from the other nodes not on the MinRS because all residue curves begin on the MinRS. The other two eigenvalues describe the stability of the MinRS nodes with respect to each other.

To find the basic distillation boundaries for the 4-component system (after having determined all of the basic distillation boundaries for the constituent 3-component systems), we apply the following algorithm:

- k=4.
- Apply the preprocessing step if necessary.
- Find UNL(unstable nodes) and the intersection list INT(unstable nodes), creating the MaxRS.
- Update the stabilities of the MaxRS nodes using the algorithm described above.
- Solve this new system as a 3-component system using the algorithm defined earlier.
- Find SNL(stable nodes) and the intersection list INT(stable nodes), creating the MinRS.
- Update the stabilities of the MinRS nodes using the algorithm described above.
- Solve this new system as a 3-component system using the algorithm defined earlier.

In this manner, we can determine all of the additional basic distillation boundaries for all of the constituent 4-component systems.

4.3.4 Basic Distillation Boundaries for n-Component Systems

As shown above, finding the basic distillation boundaries for a 4-component system breaks down to solving all of the constituent 3-component systems, finding the MaxRS and MinRS for the 4-component system, and then solving the MaxRS and MinRS as 3-component systems. This same scheme can be used to solve 5-component systems, creating a solution tree shown in Figure 4.6. One can easily see that to find the basic distillation boundaries for any n-component system, we need only recursively apply the algorithm for 3-component systems. By finding the basic distillation boundaries for all constituent ternary, then quaternary, etc. systems, we can find these boundaries for any n-component system. The final algorithm is shown below:

1) Connect all binary mixtures based on boiling point temperatures of all of the nodes.
2) Let NC = overall number of components.
3) k = 3.
4) Let MS = number of k-component systems.
5) m = 1.
    a) Apply preprocessing step if necessary.
    b) Let n = k.
    c) Find lists UNL(unstable nodes).
    d) Find the intersection list, INT(unstable nodes). These nodes define the n-2 dimensional MaxRS.
    e) Find lists SNL(stable nodes).
    f) Find the intersection list, INT(stable nodes). These nodes define the n-2 dimensional MinRS.
    g) If n = 3, goto step 5j.
    h) n = n - 1
    i) Create new systems with the MaxRS nodes and the MinRS nodes. This includes updating the stability information using the eigenvalue analysis above. With each system, goto step 5c.
    j) Save the connections (basic distillation boundaries) between each SN in the MaxRS (UN in the MinRS) to every other node in the MaxRS (MinRS) that is not a UN (SN) unless there is an azeotrope involving all of the components in this particular system in which case save connections between every SN (UN) to this azeotrope.
    k) m=m+1
    l) If m ≤ MS, goto step 5a.
6) k = k+1.
   If k ≤ NC, goto step 4.

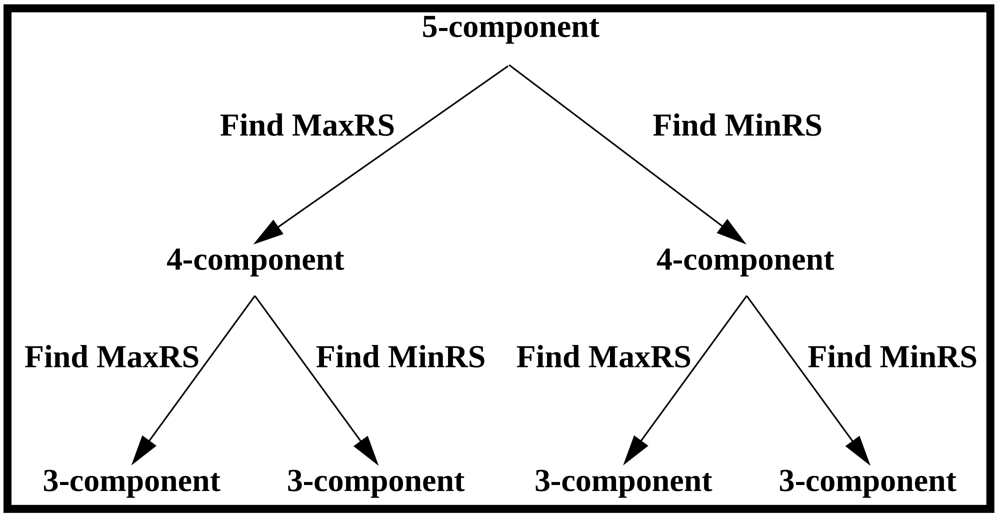

Figure 4.6: Finding Basic Distillation Boundaries for 5 Components

4.3.5 Finding the Continuous Distillation Boundaries

As mentioned earlier, basic and continuous distillation regions are very similar. Figure 4.1 shows an example system with one basic distillation region and two continuous regions. The boundary A-BC can not be crossed by a continuous column profile so this boundary is a continuous boundary. In order to find all of the additional continuous boundaries (those in addition to the basic boundaries) we simply have to connect the UN to the SN for each basic distillation region. These connections will form continuous distillation regions whose nodes more accurately describe the types of feasible products that one could obtain using continuous distillation.

4.3.6 Finding the Batch Distillation Boundaries

Now that we can find all of the basic distillation boundaries creating sets of residue curves each having their own UN and SN pair, we can place the batch distillation boundaries within each of these regions. The algorithm for placing the batch distillation boundaries of Bernot, Doherty, and Malone (1991) for a batch rectifier was shown by Ahmad and Barton (1995a) to work on almost all 3-component systems. The algorithm did not work on two types of systems. Type 1, shown in Figure 4.5, has a stable separatrix that does not completely divide the composition space into regions each having one UN because there is only one UN. If we were to rectify a initial still composition of S_1 as shown in Figure 4.5, the still path would move directly away from the UN (C vertex) until it intersects the stable separatrix. When the current still composition exactly lies on this stable separatrix, the still composition will follow the stable separatrix up to the stable ternary azeotrope as pointed out by Bernot, Doherty, and Malone (1990). The distillate will be the intersection of a line tangent to the stable separatrix at the current still composition and the B-C binary edge. If we assume that the stable separatrix is a straight line, the distillate composition will be the BC saddle azeotrope. However, if the boundary were curved, the distillate composition would vary along the B-C binary edge depending on the curvature of the separatrix. So in assuming straight distillation boundaries, the distillate product will now become the BC azeotrope with the still path following the stable separatrix until only the ternary azeotrope is left in the column (Malone, 1996). However, rectification of an initial still composition S_2 will produce the product sequence: C, AB, then B. When the algorithm of Bernot, Doherty, and Malone (1991) for finding the batch distillation boundaries for a batch rectifier is applied to this system, we will create the batch boundaries C-B and C-ABC resulting in three batch distillation regions: (C, AB, B), (C, BC, ABC), and (C, B, BC). However, how can we connect the nodes C to B when there is a binary azeotrope between B and C? There has to be a batch boundary B-C creating two batch distillation regions: (C, AB, B) where the product sequence C-AB-B can be taken (as seen for the initial still composition S_2) and (C, B, BC) which is a batch region of zero area where no products can be taken. In this case, two of the batch regions, (C, AB, B) and (C, BC, ABC), appear to occupy some of the same composition space.

Further, what about the type 2 systems? Figure 4.7 shows an example of this kind of system. This example has only one UN and one SN creating only one basic distillation region (and no basic distillation boundaries). If we were to place several initial still compositions within this composition space and separate them using a batch rectifier at total reflux and infinite number of trays, we would obtain B as our first distillate product in all cases. The change in still composition or still path will move in a direction directly opposite this distillate product until it hits an edge of the composition space or a basic boundary. In this case, the still path continues until it intersects the A-C binary edge, at which point the distillate product will switch to A. We will produce A until no more A

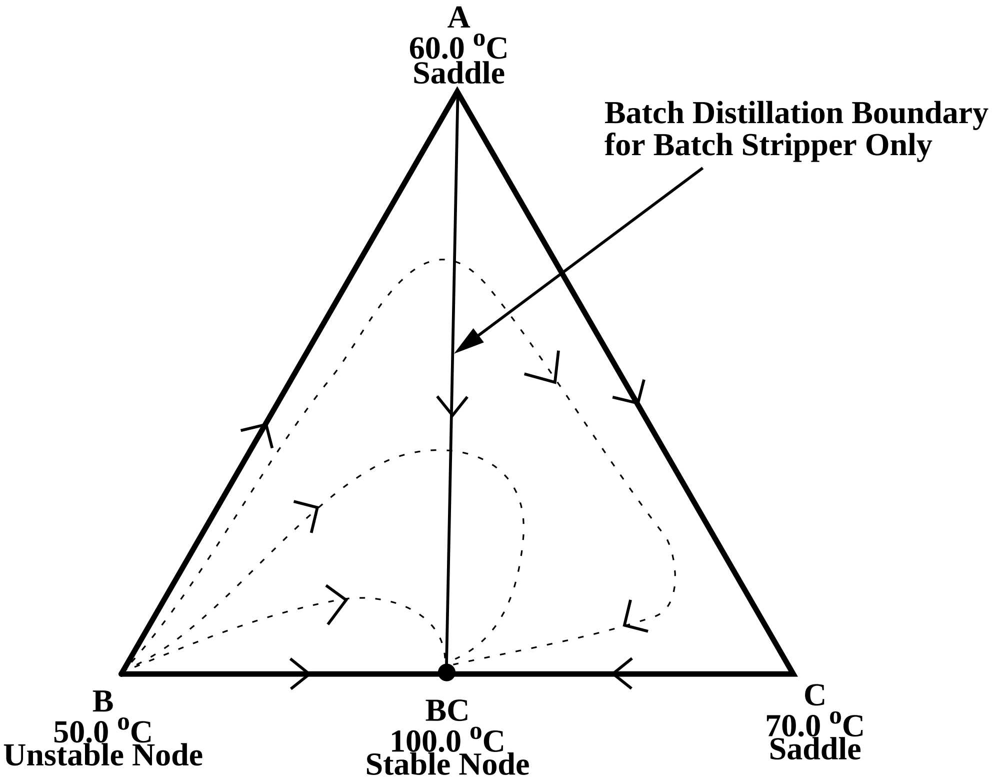

Figure 4.7: Example of Type 2 System

remains in the column leaving only C left in the column. It is impossible to produce BC as a distillate product. This example is very similar to the example shown in Figure 4.5 of the type 1 system because we have two batch distillation regions one of which has zero area, created by adding the batch boundary B-C to the system.

If we do the same experiment on the system in Figure 4.7 using an inverted batch column or batch stripper, our first bottoms product will always be BC. If the initial still composition lies to the right of the batch stripper boundary shown in Figure 4.7, the still path will intersect the A-C binary edge, producing C then A. But if the initial still composition lies to the left of the batch boundary, the still path will intersect the A-B binary edge, producing A then B. So there are two batch distillation regions, defined by the boundary A-BC, when we use the batch stripper column. With the assumption of straight distillation boundaries, the distillation boundaries for the batch rectifier and stripper are not identical, which violates behavior suggested by several researchers. Bernot, Doherty, and Malone (1991) also reported an algorithm for determining the batch distillation boundaries for the batch stripper column. This algorithm connected the SN in each continuous region to every other node in this region. Using this algorithm, we find the correct batch distillation boundaries for the batch stripper for the example in Figure 4.7. If we were to invert all of the temperatures and stabilities of the nodes in this example, we would find that the behavior of the rectifier and stripper has now been switched. The batch boundaries and regions for the original rectifier are the boundaries and regions for the “inverted system” stripper and vice versa. As long as we apply the correct algorithm for the particular batch column configuration, we can correctly identify the batch distillation boundaries.

The top and bottom section of the MVC act just like a rectifier and stripper. So the batch distillation boundaries defining the distillate product sequence are the rectifier’s boundaries and the batch distillation boundaries defining the bottoms product sequence are the stripper’s boundaries. The batch boundaries for the MVC are the batch boundaries that are in common to both the rectifier and stripper. As seen in the batch rectifier and stripper, the still path for the MVC cannot cross the batch boundaries that are also basic boundaries.

We must apply the algorithm for finding the batch boundaries to each system that we generate: all constituent 3-component systems and their corresponding MaxRS's and MinRS's, all constituent 4-component systems and their corresponding MaxRS's and MinRS's, etc. The batch distillation boundaries will, therefore, consist of all of the basic boundaries we found previously and the additional boundaries we found using the above algorithm. Again, we are assuming straight line boundaries.

4.3.7 Basic Distillation Regions

To enumerate the basic distillation regions, we must find all sets of residue curves. Starting at each UN, we find all nodes that we can reach along basic distillation boundaries and the edges of the composition space while increasing in temperature. If we collect all nodes that lie on a path to a particular SN, these nodes along with the UN and SN define the nodes that make up one basic distillation region. We do this analysis for each UN and SN pair, enumerating all of the basic distillation regions.

4.3.8 Continuous Distillation Regions

The continuous distillation regions are very similar to the basic regions. If no UN to SN connections (continuous boundaries) have been made between nodes within a basic region, the continuous and basic regions are the same. However if some continuous boundaries were added, the basic region will be split into several continuous regions. We can find the nodes that make up the continuous regions by combining the nodes on similar paths of either increasing or decreasing temperature while traversing on basic and continuous boundaries and edges of the composition space only. Two paths are similar if one of the paths contains all of the nodes of the other path. The resulting continuous region will consist of an UN, a series of saddle nodes, and a SN.

4.3.9 Batch Distillation Regions

As pointed out by Malenko (1970b, c) and Bernot, Doherty, and Malone (1990) and proved by Ahmad and Barton (1995a), the number of vertices that make up a batch distillation region for a batch rectifier is k where k is the number of components in the current system. The vertices that make up these regions includes one UN, a series of saddle nodes, and possibly a SN, and all pairs of these nodes must be connected (Ahmad and Barton, 1995a). As we saw in the examples of type 1 and type 2 systems, a batch boundary may be possible between two pure components that have a binary azeotrope between them. This boundary separated the binary azeotrope out of the batch region because the azeotrope was never a product. The boundary also connected the final pair of nodes that made up the batch distillation region, creating a set of k=3 nodes in which all pairs of nodes are connected. However, we saw earlier that for the example in Figure 4.5, it appears that two batch regions overlap. Any composition in the batch region (C, BC, ABC) will result in the product sequence C-BC-ABC and any composition not in that region but in the region (C, AB, B) will result in the product sequence C-AB-B. If a particular composition appears to lie in more than one batch region, it must actually lie in the batch region which contains the SN as the still path will intersect the stable separatrix containing this SN. So in the case of Figure 4.5, S_1 will lie in the region (C, BC, ABC).

For the batch stripping column, we use the same algorithm, except now we start at all of the SNs and follow paths of decreasing temperature. As seen for batch boundaries, the batch regions for the MVC are a combination of the rectifier and stripper columns. If the rectifier and stripper regions are the same, then the regions for the MVC are the same as the rectifier and stripper. If they are different, then the rectifying section of the MVC will be constrained to the rectifier batch region and the stripping section of the MVC will be constrained to the stripper batch region.

4.4 Example of 4-Component System

We will now apply the algorithm to the 4-component example of acetone/benzene/chloroform/methanol. After finding the basic distillation boundaries and regions, we will investigate the continuous and batch distillation boundaries and regions for the batch rectifier. Table 1 shows the input to the algorithm (not shown is the eigenvalue information about each constituent 3-component system) using UNIFAC to model the thermodynamics of the system:

Table 4.1: Acetone/Benzene/Chloroform/Methanol Example Input

Node	%A	%B	%C	%M	Tb (C)	Stability	num + eigenvalues	num - eigenvalues
A	100.0	0	0	0	56.07	S	2	1
B	0	100.0	0	0	80.14	SN	0	3
C	0	0	100.0	0	60.62	S	2	1
M	0	0	0	100.0	64.48	SN	0	3
AM	68.34	0	0	31.66	53.46	UN	3	0
AC	38.38	0	61.62	0	64.06	S	1	2
CM	0	0	65.78	34.22	53.50	UN	3	0
BM	0	39.96	0	60.04	56.53	S	1	2
ACM	25.82	0	28.72	45.46	55.93	S	1	2
ABCM	17.11	9.500	25.94	47.45	55.79	S	2	1

First, we will find the basic distillation boundaries for all of the constituent 3-component systems. Figure 4.8 shows all of these systems. After creating all of the binary systems, we

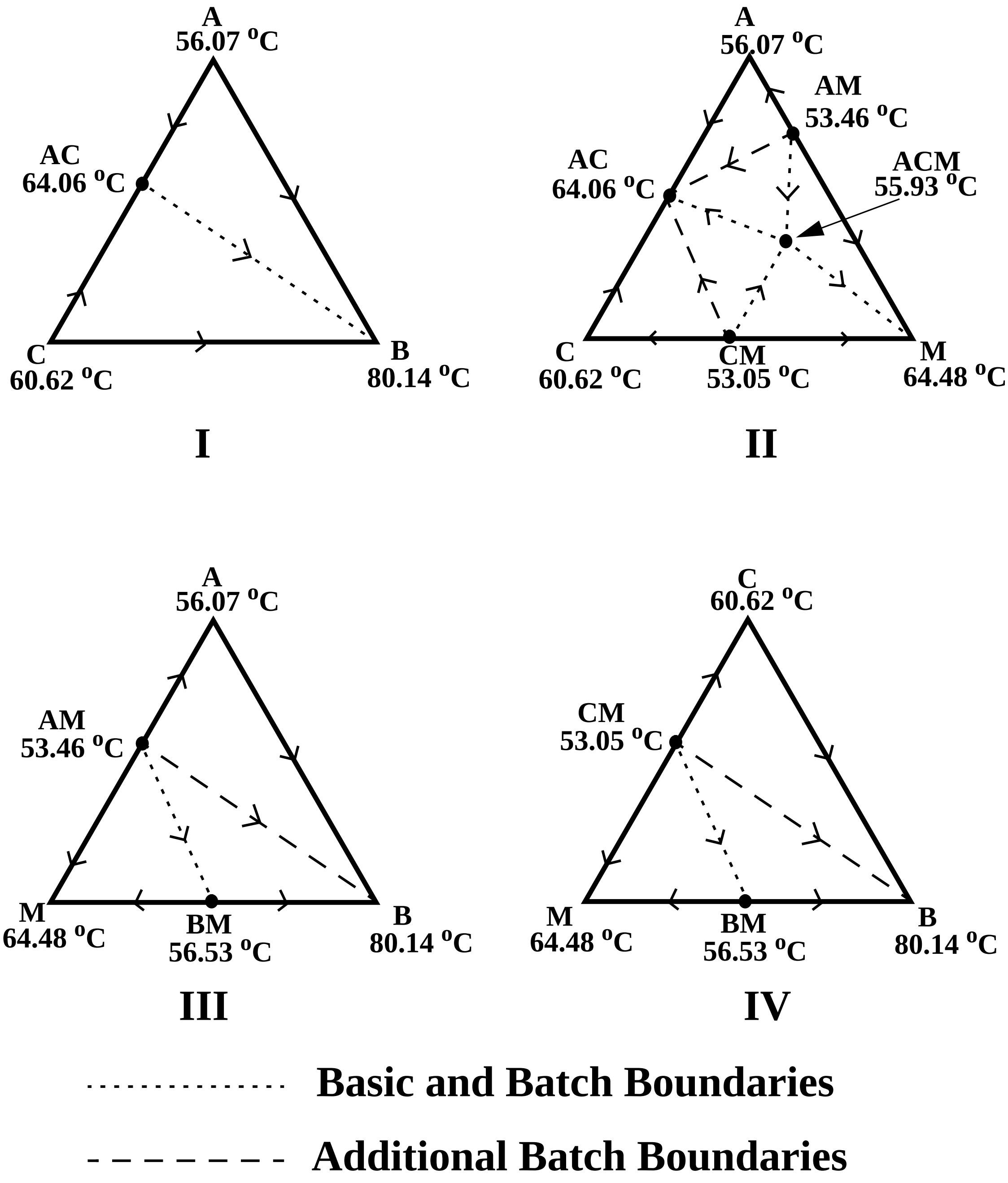

Figure 4.8: Acetone/Benzene/Chloroform/Methanol Example

must apply our algorithm to each 3-component system. For each system, we apply the preprocessing step and then find the common UN and SN node lists and their intersection lists (the MaxRS and MinRS). In finding these lists, we traverse only on connections between nodes that are preexisting basic distillation boundaries. For these 3-component systems, these links are the binary edges or connections from the preprocessing step. To these we add any ternary azeotropes which are saddles. Below we show these steps for all of the 3-component systems:

System I

No processing step because there is no ternary azeotrope

UNL(A)=(B, AC)
UNL(C)=(B, AC)
MaxRS=INT(A, C)=(B, AC)
Connect each SN to every other non-SN node in the intersection list: AC-B

SNL(B)=(A, C)
MinRS=INT(B)=empty set
No new connections

System II

There is no preprocessing step because the ternary azeotrope is a saddle

UNL(AM)=(M, A, AC, ACM)
UNL(CM)=(M, C, AC, ACM)
MaxRS=INT(AM, CM)=(M, AC, ACM)
Connect each SN to the ternary azeotrope: ACM-M, ACM-AC

SNL(M)=(AM, CM, ACM)
SNL(AC)=(A, AM, C, CM, ACM)
MinRS=INT(M, AC)=(AM, CM, ACM)
Connect each UN to the ternary azeotrope: AM-ACM, CM-ACM

System III

There is no preprocessing step because there is no ternary azeotrope

UNL(AM)=(M, A, B)
MaxRS=INT(AM)=empty set
No new connections

SNL(M)=(AM, BM)
SNL(B)=(BM, A, AM)
MinRS=INT(M, B)=(AM, BM)
Connect each UN to every other non-UN in the intersection list: AM-

BM

System IV

There is not preprocessing step because there is no ternary azeotrope

UNL(CM)=M, C,
MaxRS=INT(CM)=empty set
There are no new connections

SNL(M)=(CM, BM)
SNL(B)=(BM, C, CM)
MinRS=INT(M, B)=(CM, BM)
Connect each UN to every other non-UN: CM-BM

Figure 4.8 shows the connections (basic distillation boundaries) found in the above analysis using dotted lines (ignore the dashed lines at present). To find the basic distillation regions, we follow all paths along basic distillation boundaries from each UN to every SN that can be reached, shown below for each of the 3-component systems:

System I

A	- B	
	- AC	- B
C	- B	
	- AC	- B

System II

AM	- M	
	- ACM	- M
	- ACM	- AC
	- A	- AC
CM	- M	
	- ACM	- M
	- ACM	- AC
	- C	- AC

System III

AM	- M	
	- BM	- M
	- BM	- B
	- A	- B

System IV

CM	- M

- BM - M
- BM - B
- C - B

We collect all nodes in paths with a common starting node (UN) and ending node (SN) and find that our basic distillation regions are:

System I

(A, AC, B)
(C, AC, B)

System II

(AM, ACM, A, AC)
(AM, ACM, M)
(CM, ACM, C, AC)
(CM, ACM, M)

System III

(AM, BM, M)
(AM, BM, A, B)

System IV

(CM, BM, M)
(CM, BM, C, B)

We can now find the continuous distillation regions for the 3-component systems. First we combine nodes on similar paths of increasing temperature. For example, system III in Figure 4.8 has two basic distillation regions. There are five paths of increasing temperature: AM-M, AM-BM-M, AM-B, AM-BM-B, and AM-A-B. We combine similar paths (one path contains all nodes of the other path) and get the following lists: AM-BM-M, AM-BM-B, AM-A-B. These three lists define the three continuous distillation regions that make up this particular system. Applying this algorithm to all of the 3-component systems, we obtain the following continuous distillation regions:

System I

(A, AC, B)
(C, AC, B)

System II

(AM, A, AC)
(AM, ACM, AC)
(AM, ACM, M)
(CM, ACM, AC)
(CM, ACM, M)
(CM, C, AC)

System III

(AM, A, B)
(AM, BM, B)
(AM, BM, M)

System IV

(CM, BM, M)
(CM, BM, B)
(CM, CM B)

In order to find the remaining batch distillation boundaries for the 3-component systems, we connect each UN in the basic distillation regions found above to every other node in the basic region. These additional batch boundaries are shown in Figure 4.8 with dashed lines. The additional boundaries are for the batch rectifier. For the batch stripper, we connect each SN in each of the basic regions to every other node in that region. The batch distillation regions for the rectifier are found by finding the paths of increasing temperature containing three nodes while traversing on all batch distillation boundaries (basic and additional batch boundaries). The paths below are all of the paths obtained when looking for batch distillation boundaries containing three nodes:

System I

A	-	AC	-	B
C	-	AC	-	B

System II

AM	-	A	-	AC
	-	ACM	-	AC
	-	ACM	-	M
CM	-	ACM	-	AC
	-	ACM	-	M

- C - AC

System III

AM - A - B
- BM - B
- BM - M

System IV

CM - BM - M
- BM - B
- C - B

All pairs of nodes in the above lists are connected so the lists represent all of the 3-component batch distillation regions. In this particular example, the batch and continuous distillation regions are the same. Neither continuous or batch distillation is particularly more flexible than the other.

Now that we have determined the distillation boundaries and regions for all of the constituent 3-component regions, we must now investigate all of the 4-component systems, in this case the sole system of acetone/benzene/chloroform/methanol. First we find the 4-component MaxRS and find the distillation boundaries for the MaxRS using the 3-component algorithm just described. The same procedure is repeated for the 4-component MinRS:

4-Component System

No preprocessing step because quaternary azeotrope is a saddle.

UNL(CM)=(CM, M, ACM, AC, B, C, BM, ABCM)
UNL(AM)=(AM, A, B, ACM, AC, M, BM, ABCM)
MaxRS=INT(CM, AM)=(B, M, AC, ACM, BM, ABCM)

SNL(M)=(M, ACM, AM, CM, BM, ABCM)
SNL(B)=(A, C, AC, BM, CM, AM, ACM, ABCM)
MinRS=INT(M, B)=(AM, CM, ACM, BM, ABCM)

Figure 4.9 shows the 3-component systems that the MaxRS and MinRS create. These systems are now treated like any other 3-component system:

MaxRS

Update the stabilities of the MaxRS nodes by subtracting one negative eigenvalue from each node giving the following node stabilities:

Unstable Nodes: ABCM
Stable Nodes: B, M
Saddles: AC, ACM, BM

Preprocessing step creates connections: ABCM-ACM, ABCM-BM

UNL(ABCM)=(ABCM, BM, AC, ACM, B, M)
MaxRS=INT(ABCM)=empty set
No new connections

SNL(M)=(M, ACM, BM, ABCM)
SNL(B)=(B, BM, AC, ACM, ABCM)
MinRS=INT(M, B)=(ACM, BM, AMCB)
Connect each UN to the quaternary azeotrope: BM-ABCM, ACM-ABCM

MinRS

Update the stabilities of the MinRS nodes by subtracting one positive eigenvalue from each node giving the following node stabilities:

Unstable Nodes: AM, CM
Stable Nodes: BM, ACM
Saddles: ABCM

No preprocessing step since quaternary azeotrope is a saddle

UNL(AM)=(AM, BM, ACM, ABCM)
UNL(CM)=(ACM, BM, ABCM)
MaxRS=INT(AM, CM)=(BM, ACM, ABCM)
Connect each SN to the quaternary azeotrope: BM-ABCM, ACM-ABCM

SNL(ACM)=(AM, CM, ABCM)
SNL(BM)=(AM, CM, ABCM)
MinRS=INT(ACM, BM)=(AM, CM, ABCM)
Connect each UN to the quaternary azeotrope: AM-ABCM, CM-ABCM

With this final step, we have found all of the basic distillation boundaries for the 4-component example. The 4-component basic distillation regions are found by following the basic distillation boundaries and edges of the 4-component system of increasing temperature from each UN to the SNs. We collect the nodes which lie in paths having a common UN and SN, giving for this example the following:

<u>Basic Distillation Regions</u>

(AM, A, AC, BM, ACM, ABCM, B)
(AM, ACM, BM, ABCM, M)
(CM, ACM, BM, ABCM, M)
(CM, C, AC, BM, ACM, ABCM, B)

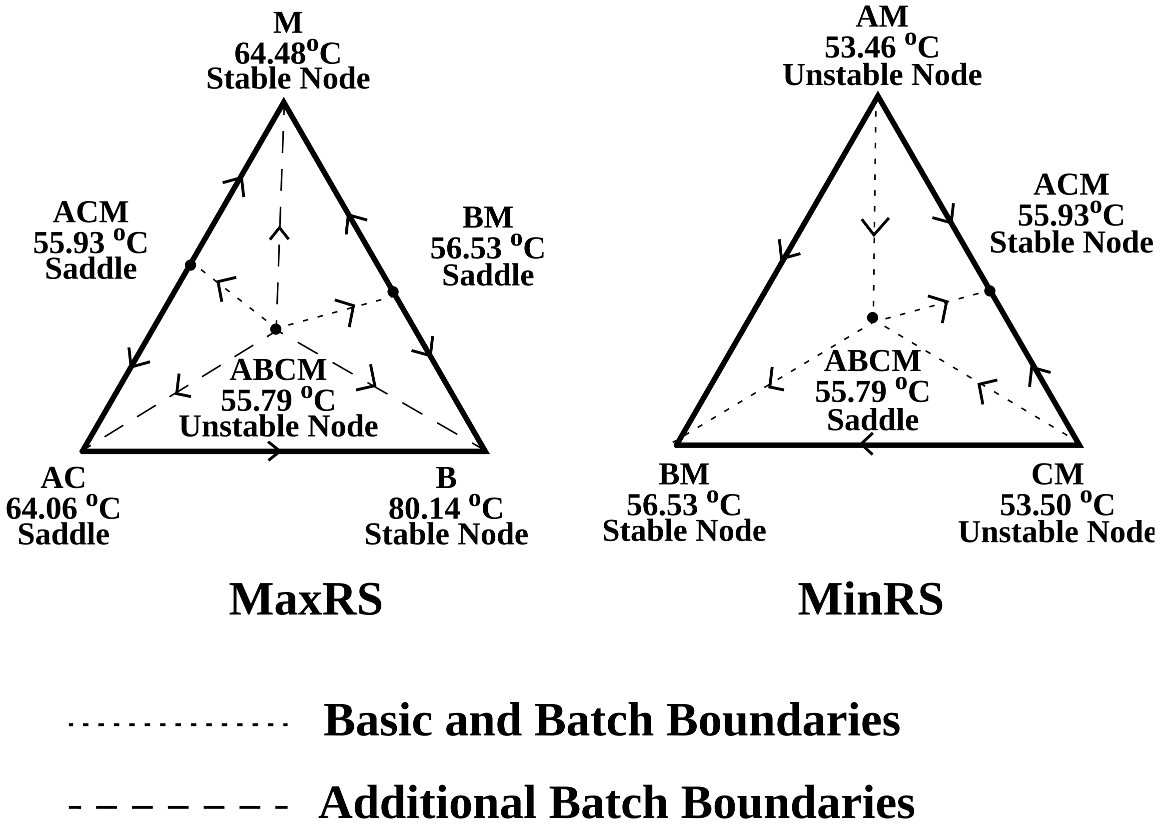

Figure 4.9: MaxRS and MinRS of 4-Component Example

The continuous distillation regions are found by combining the similar paths of increasing temperature for each basic distillation region. For the basic region (AM, A, AC, BM, ACM, ABCM, B), we can trace out the following paths of increasing temperature:

Paths of increasing temperature

AM	- A	- B		
	- A	- AC	- B	
	- ABCM	- ACM	- AC	- B
		- BM	- B	
	- ACM	- AC	- B	
	- BM	- B		

We merge the third and forth lists into a single list since the lists use the same connection (AM-ABCM). Now we must combine the similar lists. Clearly, we can combine the first and second list since the second list contains all of the first list’s nodes. In a similar manner we can combine fifth and sixth list into the “merged” third list as the third list has all of the nodes contained in the fifth and sixth list. We now have two lists, (AM, A, AC, B) and (AM, ABCM, ACM, BM, AC, B), which define the continuous distillation regions for this particular basic distillation region. If we apply this algorithm to the other three basic distillation regions, we find that all of the continuous distillation regions are:

Continuous Distillation Regions

(AM, A, AC, B)
(AM, ABCM, ACM, BM, AC, B)
(AM, ABCM, ACM, BM, M)
(CM, A, AC, B)
(CM, ABCM, ACM, BM, AC, B)
(CM, ABCM, ACM, BM, M)

To find the additional batch distillation boundaries for the batch rectifier, we connect the UN for each basic region (all of the 3-component systems, MaxRS, MinRS, and the 4-component system) to every other node in the particular system. The batch boundaries for the 3-component systems, MaxRS, and the MinRS are shown in Figures 4.8 and 4.9. All of the additional batch boundaries added to the example are:

Additional Batch Distillation Boundaries

AM - B
AM - AC

CM - AC
CM - B
ABCM-B
ABCM-M
ABCM-AC

The batch distillation regions are found by finding all paths of increasing temperature connecting n=4 nodes (n is the number of components) where all pairs of the nodes must be connected. When we apply this algorithm to the example, we obtain the following batch distillation regions:

Batch Distillation Regions

(AM, A, AC, B)
(AM, ABCM, BM, B)
(AM, ABCM, BM, M)
(AM, ABCM, ACM, AC)
(AM, ABCM, ACM, M)
(AM, ABCM, AC, B)
(CM, C, AC, B)
(CM, ABCM, BM, B)
(CM, ABCM, BM, M)
(CM, ABCM, ACM, AC)
(CM, ABCM, ACM, M)
(CM, ABCM, AC, B)

We have found all of the basic, continuous, and batch distillation boundaries and resulting regions for this 4-component example. Figure 4.10 shows the acetone/benzene/chloroform/methanol composition space with the basic and batch distillation boundaries found above. Also shown with shaded surfaces are the MaxRS and MinRS. One can easily see that the MaxRS separates out the composition space into regions each having its own UN and that the MinRS does the same thing for SNs. These two manifolds create the four basic distillation regions from which the six continuous and twelve batch distillation regions are formed. The batch distillation boundaries and regions are those that result when using a batch rectifier in the separation of this 4-component system. In order to

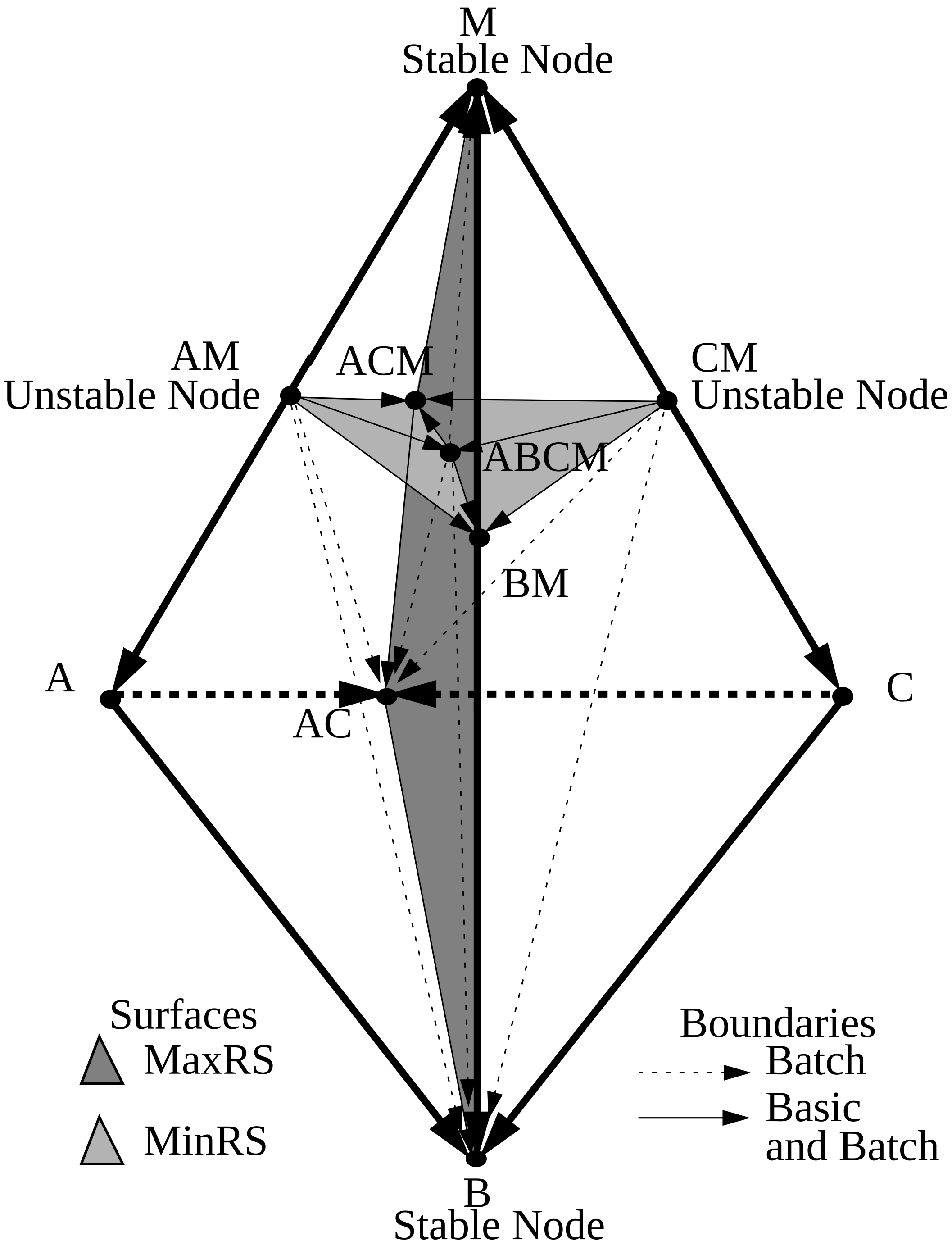

Figure 4.10: Basic and Batch Boundaries for 4-Component Example

accommodate the batch stripper or MVC, we simply have to use the algorithm explained in Section 4.3.6 for the batch stripper or MVC.

As mentioned previously, the algorithm is easily extendable to 5 or more component systems by simply breaking down each n-component system into (n-1)-component systems, then into (n-2)-component systems, and so forth. In this manner, we can determine the distillation boundaries and regions for any mixture.

4.5 Algorithm Validation

We implemented the algorithm for finding the basic, continuous and batch distillation boundaries and regions. The input to this code requires information such as that shown in Table 4.1. Examples of azeotrope finding tools presented by Fidkowski, Malone, and Doherty (1993) and Westerberg and Wahnschafft (1996) are perfect for obtaining this information. The only input that is required then are the components that make up the mixture. The azeotrope finding tool calculates the compositions, temperatures, and stability information for each of the pure component and azeotropic nodes for the system in question.

We first tested the algorithms and code by finding the basic and batch boundaries and regions for each of the 87 3-component systems enumerated by Doherty and Caldarola (1985). We correctly identified these boundaries and regions for all systems, including the type 1 and 2 systems that were identified earlier. We further tested the code against several example problems, including the 4-component example shown in Section 4.4 where we obtained the same distillation regions and boundaries as shown there. We also used the examples shown in Malenko (1970b) in testing the code. In both cases, the distillation regions and boundaries we found match those found by Malenko. Malenko’s results compared very favorably with experimental work done using the same systems.

To determine if the correct basic distillation regions were being found for a particular system, many different starting compositions were selected in order to cover the entire composition space. With each of these starting compositions, we found the UN and SN for the region containing this composition by simulating a total reflux/reboil and infinite number of trays situation. The compositions with a common UN and SN pair defined a basic distillation region. For the 4-component example shown in Section 4.4, we confirmed using these simulations that there were four basic distillation regions having the same UN/SN pairs as predicted.

We confirmed the batch distillation regions in a manner very similar to that for the basic regions. Using MultibatchDS which was a commercial version of Batch-Dist (Diwekar and Madhavan, 1991), we selected initial still compositions for the batch rectifier that would cover the composition space. We simulated the batch rectifier at high reflux and number of trays in order to find the product sequence associated with the region containing the initial still composition. We collected similar product sequences which defined the batch distillation regions. The twelve batch regions found for the 4-component example in Section 4.4 were confirmed using this technique.

4.6 Impact of Curved Boundaries

As pointed out, we used the assumption of straight line distillation boundaries in the analysis and generation of the distillation boundaries and regions of a particular mixture. There are several implications of this assumption. In Figure 4.1, we pointed out that there was a continuous boundary A-BC which created two continuous distillation regions as no column profile could cross this boundary. Figure 4.11 shows an example where such a boundary must be curved as a column profile could certainly cross the straight line boundary A-BC. The distillate product, feed, and bottoms product lie on a mass balance line and also line on the same residue curve which is an approximation of total reflux. Also as pointed out by Bernot et al. (1990, 1991) the still and product paths for batch distillation will follow the stable or unstable separatrices depending on the batch column configuration. Curved batch boundaries can cause the product composition to exhibit a varying composition in time as the still or product follows the curved separatrices. So the product sequence one obtains may be slightly different (different product sequences) than we would predict using straight line batch distillation boundaries.

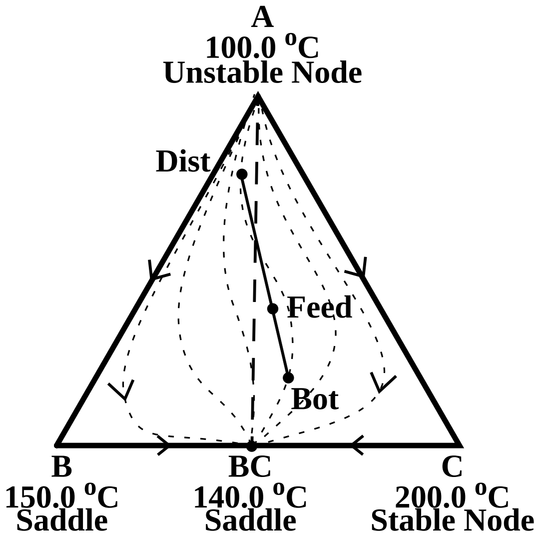

Figure 4.11: Impact of Curved Continuous Distillation Boundaries

4.7 Conclusions

The ability to find the distillation boundaries and regions of a particular mixture is very important in the synthesis and design phase of distillation-based separations systems because infeasible flowsheets can be screened out early. We first defined a basic distillation region as a region of residue curves with a common UN and SN pair. While many researchers call such a region a continuous region, we showed that a more appropriate definition of a continuous distillation region exists. We proposed an algorithm for finding the basic, continuous, and batch distillation boundaries and regions, where the basic boundaries and regions were necessary in finding the continuous and batch boundaries and regions. This algorithm found the basic boundaries first, using notions of maximum and minimum residue surfaces that separated the composition space into subregions each having its own unstable and stable node, respectively. The basic regions were found by finding clusters of residue curves sharing the same unstable and stable node pair. For each of these basic regions, we showed how to find the continuous boundaries and regions and also how to apply algorithms published by other researchers in finding the batch distillation boundaries and regions. In particular, we were able to apply these algorithms to several systems on which the algorithms were thought to fail. We showed how to extend our algorithm to 4, 5, and n-component systems. We assumed straight line distillation boundaries for these algorithms. This assumption needs to be removed so a more reasonable prediction of the distillation regions can be obtained.

We implemented these algorithms and tested and validated the resulting code on several example problems, including all possible 3-component systems. The code required only the components in question and an azeotrope finding tool to find the compositions, temperatures, and stability information of all of the pure component and azeotropic nodes. While this algorithm worked on the examples and is believed to be general and robust, strange topologies such as type 1 and 2 shown earlier may have different behaviors than that predicted by these algorithms. No formal proof of this algorithm exists at this time.

4.8 Nomenclature

UN = unstable node
SN = stable node
UNL(unstable node) = common UN list which are the nodes reached by increasing temperature from unstable node
SNL(stable node) = common SN list which are the nodes reached by decreasing temperature from stable node
INT(list_nodes) = intersection list which are the nodes appearing in a least two of the UNL or SNL of the list_nodes

4.9 Acknowledgments

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References

Ahmad B. S., and P. I. Barton, **1995a**. “Solvent Recovery Targeting for Pollution Prevention in Pharmaceutical and Specialty Chemical Manufacturing.” *AIChE Symposium Series.* **90**, p. 59 - 73.

Ahmad B. S., and P. I. Barton, **1995b**. “Synthesis of Batch Processes with Integrated Solvent Recovery and Recycling.” Presented the AIChE Annual Meeting, Miami Beach, FL.

Ahmad B. S., Y. Zhang, and P. I. Barton, **1995**. “Pollution Prevention in Pharmaceutical and Specialty Chemical Manufacturing: The Theory of Homogeneous Multicomponent Azeotropic Batch Distillation.” In Preparation.

Baburina L. V., V. M. Platonov, and M. G. Slin’ko, **1988**. “Classification of Vapor-Liquid Phase Diagrams for Homoazeotropic Systems.” *Theor. Found. Chem. Eng*. **22**, p. 390-396.

Bernot C., M. F. Doherty, and M. F. Malone, **1990**. “Patterns of Composition Change in Multicomponent Batch Distillation.”*Chemical Engineering Science*, **45,** p. 1207-1221.

Bernot C., M. F. Doherty, and M. F. Malone, **1991**. “Feasibility and Separation Sequencing in Multicomponent Batch Distillation.”*Chemical Engineering Science*, **46**, p. 1311-1326

Diwekar U. M., and K. P. Madhavan, **1991**. “Batch-Dist: A Comprehensive Package for Simulation, Design, Optimization and Optimal Control Of Multicomponent, Multifraction Batch Distillation Columns.” *Computers and Chemical Engineering*, **12**, p. 833-842.

Doherty M. F., **1985**. “The Presynthesis Problem for Homogeneous Azeotropic Distillations has a Unique Explicit Solution.” *Chem. Eng. Sci*. **40**, p. 1885-1889.

Doherty M. F. and G. A. Caldarola, **1985**. “Design and Synthesis of Homogeneous Azeotropic Distillations. 3. The Sequencing of Columns for Azeotropic and Extractive Distillations.”*Ind. Eng. Chem. Fundam*. **24**, p. 474-485.

Ewell R. H., and L. M. Welch, **1945**. “Rectification in Ternary Systems Containing Binary Azeotropes.” *Ind. Eng. Chem.*, **37**, p. 1224-1231.

Fidkowski Z. T., M. F. Doherty, and M. F. Malone, **1993**. “Computing Azeotropes in Multicomponent Mixtures.” *Computers chem. Engng*, **17**, p. 1141-1155

Malenko Y. I., **1970a**. “Physicochemical Analysis of Fractional Distillation Diagrams. I. Theoretical Basis of Method” *Russian Journal of Physical Chemistry*, **44**, p. 824-

826.

Malenko Y. I., **1970b**. "Physicochemical Analysis of Fractional Distillation Diagrams. II. Quaternary Systems" *Russian Journal of Physical Chemistry,* **44**, p. 916-919.

Malenko Y. I., **1970c**. "Physicochemical Analysis of Fractional Distillation Diagrams. III. Multicomponent (n-Component) Systems" *Russian Journal of Physical Chemistry,* **44**, p. 920-922.

Malone M. F., **1996**. Personal Correspondence.

Matsuyama H., **1975**. "Synthesis of Azeotropic Distillation Systems." Presented at the JAPAN-US Joint Seminar, Kyoto, Japan.

Petlyuk F. B., **1979**. "Structure of Concentration Space and Synthesis of Schemes for Separating Azeotropic Mixtures." *Theor. Found. Chem. Eng*. **13**, p. 683-689.

Petlyuk F. B., V. Y. Kienskii, and L. A. Serafimov, **1977**. "Method for the Isolation of the Regions of the Rectification of Polyazeotropic Mixtures using an Electronic Computer." *Theor. Found. Chem. Eng*. **11**, p. 1-7.

Serafimov L. A., **1987**. "Thermodynamic Topological Analysis and the Separation of Multicomponent Polyazeotropic Mixtures." *Theor. Found. Chem. Eng*. **21**, p.44-54.

Serafimov L. A., F. B. Petlyuk, and I. B. Aleksandrov, **1974**. "The Number of Trajectory Clusters Representing Continuous Rectification of Azeotropic Multicomponent Mixtures." *Theor. Found. Chem. Eng*. **8**, p.847-850.

Van Dongen D. B., and M. F. Doherty, **1984**. "On the Dynamics of Distillation Processes - V. The Topology of the Boiling Temperature Surface and its Relation to Azeotropic Distillation." *Chemical Engineering Science,* **39**, p. 883-892.

Van Dongen D. B., and M. F. Doherty, **198**5. "On the Dynamics of Distillation Processes - VI. Batch Distillation." *Chemical Engineering Science,* **40**, p. 2087-2093.

Wahnschafft O. M.; J. W. Koehler; E. Blass; and A. W. Westerberg, **1992**. "The Product Composition Regions of Single Feed Azeotropic Distillation Columns." *Ind. Eng. Chem. Res*., *31,* 2345-2362.

Westerberg A.W., and O. Wahnschafft, **1996**. "Synthesis of Distillation-Based Separation Processes." To appear in *Advances in Chemical Engineering*, Academic Press, **23.**

Chapter 5

Synthesis of Azeotropic Batch Distillation Separation Systems

Abstract

The sequencing of batch distillation systems, in particular batch distillation columns, can be complicated by the existence of azeotropes in the mixture. These azeotropes can form batch distillation regions where, depending on the initial feed to the batch column, the types of feasible products and separations are limited. It is very important that these distillation regions are known while attempting to synthesize sequences of batch columns so infeasible designs can be eliminated early on in the design phase. The distillation regions also give information regarding the feasible products that can be obtained when the mixture is separated using a variety of batch column configurations.

We will show how a tool for finding the batch distillation regions of a particular mixture can be used in the synthesis of batch distillation column sequences. These sequences are determined by the initial feed composition to the separation network. The network of all possible sequences will be generated using state-task networks when batch rectifying, stripping, middle vessel, and extractive middle vessel columns are allowed. We do not determine which sequence is the best as the best sequence will depend the particular application to which one is applying the algorithms. We show an example problem for illustration of this technique.

5.1 Introduction

The presence of azeotropes in a mixture can create distillation regions where the types of feasible separations are limited. The knowledge of these regions is very important when one is designing a distillation separation system because desired products may not be obtainable. The products of batch distillation in particular can be seriously limited by the distillation region in which one is operating. A sequence of several columns may be necessary in order to separate a mixture into its pure components, and several different types of columns may also have to be used. There may be many different feasible sequences where each sequence may have different benefits and drawbacks. It is important that all possible feasible sequences are generated and analyzed early in the design phase so the best possible design can be chosen.

Using a synthesis tool for finding the batch distillation regions for a particular mixture (Safrit and Westerberg, 1996), we will synthesize all possible feasible batch column sequences. The network of these sequences will be represented using a state-task network where the states are mixtures and the tasks are different types of distillations applied to the states. Using the assumption of total reflux/reboil and infinite number of trays, we will show how batch distillation regions and their associated products can be represented as a system of vectors (Ahmad and Barton, 1995). We will then use the region finding tool in conjunction with this vector representation in determining the feasible products for a particular state (mixture) when different tasks (distillation column types) are applied to these states. The network of these state-task networks will then be generated, and an example illustrating this technique will be presented. We do not offer any indication as to which sequence is the best as this will depend on the particular application. We will first review some of the existing literature on sequencing batch columns.

5.2 Background

5.2.1 Nonazeotropic Systems

The literature in the area of sequencing batch distillation columns for nonazeotropic systems is limited. While much work has been done in optimizing the product and waste cuts of a mixture for a particular kind of batch distillation column, very few researchers have investigated sequences of batch columns. There is one possible explanation of this. Because the systems are nonazeotropic, product cuts can be made to consist of a pure component as there are no azeotropes that could limit the types of feasible separations by forming batch distillation regions. One could separate a mixture into its pure components by simply taking enough product cuts using any type of batch column configuration. The need for sequencing columns is not as important and necessary as we will see it is for azeotropic systems. However, the production of waste cuts and the methods of recycling and disposing of them could make one particular kind of column more desirable than another kind of column. A particular sequence of columns may be more advantageous over another sequence when factors such as waste disposal, trace impurities, and recycle costs are factored into the problem.

Chiotti and Iribarren (1989) presented work on the optimization of a two batch column sequence used for separating a 3-component mixture. Using a simplified model for binary separations, they optimized the reflux/reboil ratio and cut locations. The global objective function was the sum of investment. They allowed the recycling of intermediate (waste) cuts to the next batch. The two column sequences generated consisted of either a rectifier followed by another rectifier, rectifier then a stripper, stripper then another stripper, and a stripper then a rectifier.

Sundaram and Evans (1993) generated the network of alternative sequences using a batch rectifier and optimized the best sequence based on waste disposal, operating, revenue, and energy costs. Using a shortcut method for a batch rectifier, they produced optimized values for the overhead product sequences, cut location, and reflux ratio policy where the reflux ratio was discretized by breaking each cut into subcuts. They mention that allowing multiple types of columns would result in a MINLP that is much more difficult to solve.

Both of these works assume a preexisting column design. In the synthesis and early design phase, this kind of information may not be available. In fact, these assumptions should not be made in the synthesis phase as these assumptions may remove feasible and desirable designs from consideration.

5.2.2 Azeotropic Systems

The need for sequencing batch columns is very important when the mixtures to be separated include azeotropes. Batch distillation can produce azeotropic products which must be recycled to other batches, disposed of in some manner, or processed in an alternative manner such as extractive distillation. Different batch column configurations can create quite different sequences because of the existence of azeotropes and the resulting batch distillation regions. A distillation region is a region of still compositions that give the same product sequence when distilled using batch distillation (Ewell and Welch, 1945). Recent work by Ahmad et al. (1995a, b) and Safrit and Westerberg (1996) have shown that finding the batch distillation regions for an n-component system is possible.

Bernot et al. (1991) used residue curve maps in creating azeotropic batch column sequences for 3 and 4-component systems. They allowed both batch rectifiers and strippers in their analysis. Using the assumption of total reflux/reboil ratio and infinite number of trays, they were able to synthesize several feasible sequences quickly using only the residue curve maps of the particular system. Any azeotropes that were produced were either broken using a specific entrainer, recycled back to the next batch, or recycled back to the reactor in the flowsheet.

Ahmad and Barton (1995a, b) have investigated finding the batch distillation regions for an n-component system and used this kind of tool in sequencing batch columns. They integrated the reaction and separation steps of a particular process and optimized a particular sequence of reactors and batch rectifiers (at total reflux ratio and infinite number of trays) that would minimize the amount of waste produced by the process. They developed a MILP formulation relating the feasible products for each batch distillation region with the equations describing the reaction kinetics and flowsheet characteristics. This optimization found the best composition and amount of solvents fed to the reactors and the best recycling options for the column products.

5.3 Determination of Batch Distillation Regions

5.3.1 Distillation Region Representation

Using the algorithms found in Safrit and Westerberg (1996), we can find all of the batch distillation regions of a particular system. These regions are made up of NC nodes (pure component and azeotrope) where NC is the number of components in the system.

But once we have found these batch regions, how do we represent them and determine which region a particular mixture lies within? Ahmad and Barton (1995a) presented a very elegant way of representing the batch regions. Using vectors from the origin to each node in a batch region, they prove that any composition in that batch region can be described as

$$\underline{\mathbf{s}} = \sum_{i=1}^{NC} \alpha_i \underline{\mathbf{n}}_i \qquad \textbf{(5.1)}$$

$$0 \geq \alpha_i \geq 1 \qquad \textbf{(5.2)}$$

where $\underline{\mathbf{s}}$ is the composition in question, $\underline{\mathbf{n}}_i$ is the composition of node i in the batch region, and α_i are the relative amounts of each batch region node that make up the composition in question. Figure 5.1 shows an example of this kind of representation. For this example, $\underline{\mathbf{n}}_\mathbf{1}$=(1, 0, 0), $\underline{\mathbf{n}}_\mathbf{2}$=(0, 1, 0), $\underline{\mathbf{n}}_\mathbf{3}$=(0, 0, 1), $\underline{\mathbf{n}}_\mathbf{4}$=(0.5, 0, 0.5), and $\underline{\mathbf{s}}$=(0.1, 0.45, 0.45). Notice that $\underline{\mathbf{s}}$ is the composition of the mixture in question. There are two batch regions in this example: AC-A-B and AC-C-B. If we were to solve for $\underline{\alpha}$ in the linear system

$$\begin{bmatrix} \underline{\mathbf{n}}_2 & \underline{\mathbf{n}}_3 & \underline{\mathbf{n}}_4 \end{bmatrix} \underline{\alpha} = \underline{\mathbf{s}} \qquad \textbf{(5.3)}$$

we would find that $\underline{\alpha}$=(0.45, 0.35, 0.2). If we assumed that S lies in the other region and were to solve for $\underline{\alpha}$ in the linear system

$$\begin{bmatrix} \underline{\mathbf{n}}_1 & \underline{\mathbf{n}}_2 & \underline{\mathbf{n}}_4 \end{bmatrix} \underline{\alpha} = \underline{\mathbf{s}} \qquad \textbf{(5.4)}$$

we would find that $\underline{\alpha}$ = (-0.35, 0.45, 0.9). From Equation 5.2, we know that the multipliers have to be positive so we have determined that S does not lie in the region AC-A-B but in the region AC-C-B. We also know that S is made up of 45% of pure B, 35% of pure C and

20% of the binary azeotrope AC. This analysis assumes straight line distillation boundaries, and the remainder of the work presented on the area of column sequencing will include this assumption.

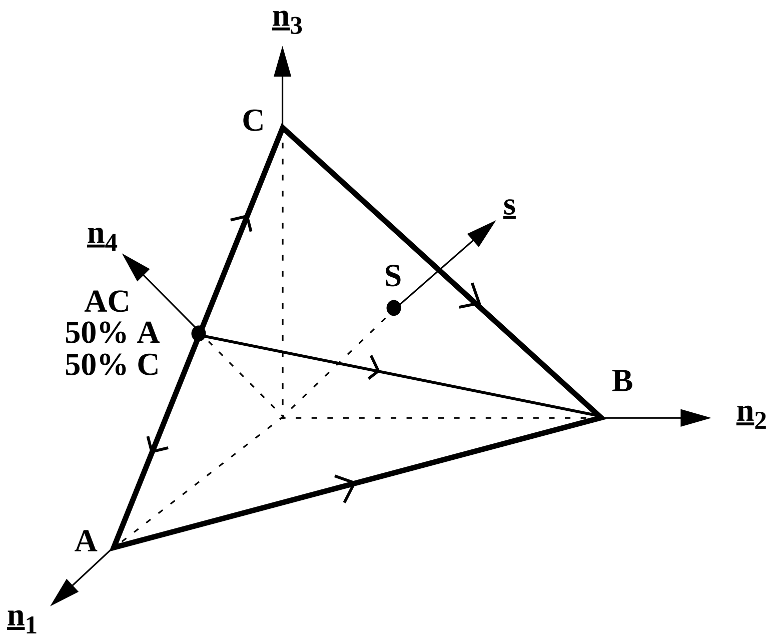

Figure 5.1: Using Vectors to Represent Batch Distillation Regions

5.3.2 Product Determination

As seen in the Section 5.3.1, we can determine the amount of each node that makes up a composition in a particular batch distillation region by looking at the vector of multipliers $\underline{\alpha}$. These multipliers can also tell us about the products one can expect to get out of a certain type of batch column configuration. We will look at four types of batch column configurations: the batch rectifier, stripper, middle vessel column (MVC), and extractive MVC. The batch regions for the rectifier and stripper can be found using the tool developed by Safrit and Westerberg (1996). These regions are not necessarily the same for these two column configurations. The multipliers tell us the actual amount of each node (product) that we would obtain by operating the batch column at total reflux/

reboil and infinite number of trays and taking NC-1 product cuts. The last product will be whatever is left in the column or the column residue. We do not have to take any waste cuts between the product cuts due to the assumption of total reflux/reboil and infinite number of trays.

Safrit et al. (1995) looked at identifying the feasible products for the MVC and showed that the top and bottoms products did not have to lie on the same material balance line as the feed as seen in continuous distillation. They also showed that, at total reflux/reboil and infinite number of trays, a MVC will produce the unstable node (UN) as a distillate product and will produce the stable node (SN) as a bottoms product. It was possible to produce a pure distillate and bottoms product simultaneously in some cases. One could also “steer” the still path in time by manipulating the product flow rates which can produce the saddle node in the 3-component system as the still product. The rectifying and stripping sections of the MVC are decoupled and act the same as a rectifier and stripper. So it is necessary to find the batch distillation regions for the rectifier and stripper when we want to analyze the MVC. These two sets of regions will be found using the same still (middle vessel) composition. Once we have found these regions, the distillate product for the MVC will be the UN for the computed batch rectifier distillation region and the bottoms product will be the SN of the computed batch stripper distillation region. The batch distillation boundaries for the MVC will consist of any batch boundaries that are common to both the rectifier and stripper. As previously mentioned, it is possible to steer the still path to a particular node. The top and bottom products can be taken in different ratios, resulting in several different possible MVC residues. There are two limiting cases for the MVC residue: a rectifier taking all of the UN as a top product followed by a stripper taking all of the remaining SN as a bottoms product and a stripper taking all of the SN as a bottoms product followed by a rectifier taking all of the remaining UN as a top product. In between these two cases, the residue of the MVC will depend on the ratio of the top and bottoms products that are being taken. For example, Figure 5.2 shows a particular basic distillation region enlarged. For the initial still composition S, a rectifier would produce a top product of the UN AB resulting in a residue of R_1 followed by a stripper would produce a bottoms product of the SN A resulting in a residue of S_1. This is one of the limiting MVC residues. The other limiting residue is found by putting S in a stripper resulting in a residue of S_2 followed by a rectifier resulting in the limiting MVC residue of R_2. From Figure 5.2, we can see that the MVC residue must lie on the plane defined by the top and bottoms products (AB and A) and the still composition (S). One way in which to find the possible MVC residues is to find all rectifier residues starting with the still composition $\overline{S}$ and letting the still composition vary from $\overline{S}$ to S_2 along the line $\overline{S}$-S_2. The possible MVC residues will consist of the all of the rectifier residues found

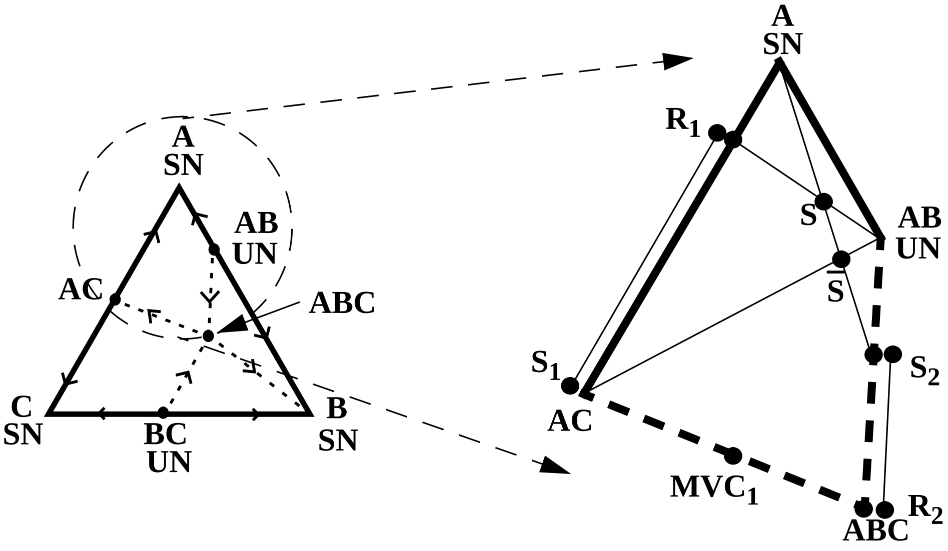

Figure 5.2: Possible MVC Residues

above. For the example in Figure 5.2, we would find that the compositions found while sweeping the still composition would be all compositions on the basic boundary ABC-AC. For the synthesis algorithm presented here (using the assumptions of total reflux/reboil and infinite number of trays), we will pick possible MVC residue compositions that are the average of each of the two nodes that make up an edge which is included in the possible MVC residues found above. The point MVC_1 on Figure 5.2 show such points for this example. There may be more than one possible MVC residue when the basic distillation region within which one is operating is made up of four or more nodes. Two of the nodes are taken up as products (UN and SN) and two more nodes are required to create multiple MVC residues.

Safrit et al. (1995a and b) investigated using a MVC as an extractive batch column by continuously feeding in an entrainer agent in the rectifying section of the MVC. They found that for certain binary azeotropic systems that the addition of an entrainer agent permitted the 100% recovery of all three pure components. In particular, they looked at a system with a minimum boiling binary azeotrope. They recovered one of the azeotrope forming components as a pure distillate product, recovered the entrainer agent as a pure bottoms product and recycled that back as entrainer agent, and steered the still composition so it would accumulate in the other azeotrope forming component. Using the extractive MVC, they were able to split certain binary azeotropes and recover practically 100% of all components in pure form. In order to pick a good entrainer agent, we could use the method of Wahnschafft and Westerberg (1993) where they looked that the infinite dilution K values ($K_i = y_i / x_i$) of the components in question. For example, Table 5.1 shows an example of the infinite dilution K values for acetone and methanol in water using the Wilson correlations to calculate the vapor-liquid equilibrium. The ratio of $K_{acetone} / K_{methanol} = 4.60$ means that in excess amounts of water, acetone is much more volatile than methanol and the methanol gets pulled down the column, thereby breaking the acetone-methanol binary azeotrope. Water is a good entrainer agent in this case. This feasibility test provides a quick and simple method of testing whether or not certain components can be used as entrainer agents for a certain mixture.

Table 5.1: Infinite Dilution K Values

in / K^{∞} of:	acetone	methanol	water
water	39.35	8.56	1.00

5.3.3 Effect of Recycling

Recycling of waste cuts or pure components has been frequently used in order to increase the level of separation that is possible for a particular mixture. In the case of curved distillation boundaries, mixing of previously separated material can even eliminate a column from the distillation column sequence (Wahnschafft et al., 1992). We have assumed straight line boundaries and total reflux/reboil and infinite number of trays, however. Looking at Equations 5.1 and 5.2, we see that mixing in a pure component or azeotrope corresponding to a node that already makes up the current batch distillation region will only alter the relative amounts of the region nodes in the mixture. The mixture will stay in the same region. Recycling in this situation does not afford any additional benefits. If the recycled mixture does not lie in the current batch region, we may be able to carry out some additional separation tasks. Figure 5.3 shows an example with three batch regions: AC-AB-A, AC-AB-B, and AC-B-C. The current mixture composition S lies in the batch region AC-AB-A. Mixing any of the nodes AC, AB, or A into S will not move

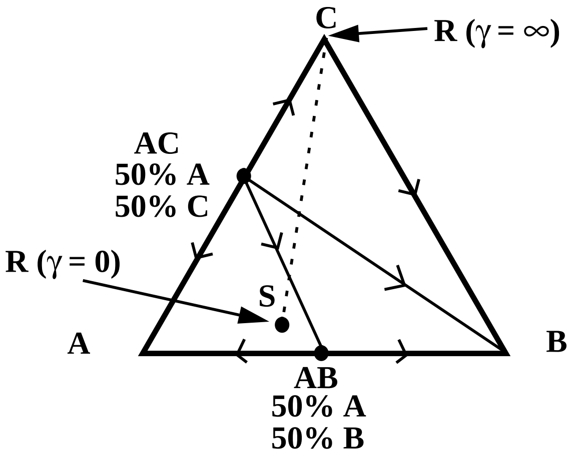

Figure 5.3: Effect of Recycle on Changing Distillation Regions

the mixture into another region. However if we mix any of the nodes B or C into S, we can possibly move into another batch region resulting in a different product sequence. For example, if we were to mix C into S, the resulting composition, R, will lie somewhere along the dotted line in Figure 5.3. Where R lies on this line depends on the relative amounts of the mixtures C and S, γ = amount C/ amount S, that are mixed together. As can be seen, we can move S into the other two batch regions by careful selection of γ. In order to explore all possible sequence alternatives, a search of all possible values of γ must be carried out so all reachable batch regions are investigated. However, we need to produce at least the amount of C that we recycle for the separation process to be feasible, as we shall now investigate.

Figure 5.4 shows another example with an associated continuous distillation configuration producing all three pure components. We have represented the distillation boundary AC-B as three different possibilities: concave (1), straight (2), and convex (3). While this configuration seems feasible for any of the three boundaries, closer

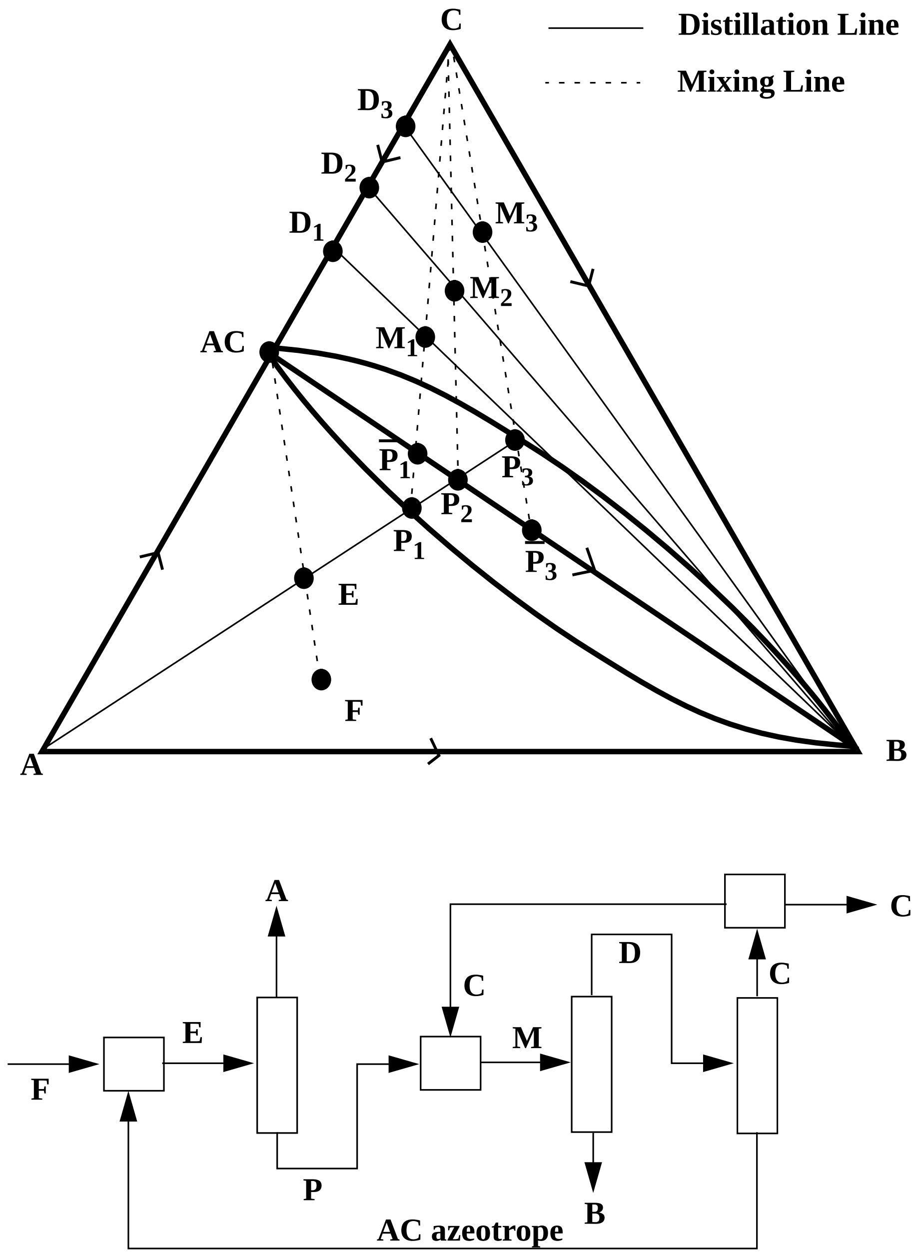

Figure 5.4: Effect of Curved Boundaries on Recycling

examination reveals that only option 3 is feasible.We know that the relative amounts of A and C remain unchanged along the line AC-B. The same can be said for the line D_2-B.

Using these facts, we can derive the following relationship

$$\frac{\overline{\mathbf{C}-\mathbf{M}_2}}{\overline{\mathbf{M}_2-\mathbf{P}_2}} = \frac{\overline{\mathbf{C}-\mathbf{D}_2}}{\overline{\mathbf{D}_2-\mathbf{AC}}} \tag{5.5}$$

where the lengths of these lines correspond to the amounts of the endpoints of the lines according to the lever rule. For example, the length of C-M_2 gives an indication of the amount of P_2 in relation to the amount of C recycled, which is determined by the length of M_2-P_2. For the case of the straight line boundary, the amount of C that is recycled is the exact same amount as the amount that can be recovered in the last column according to Equation 5.5. C is never removed from the system and will accumulate in time so this option is infeasible. For the convex boundary (3), we can derive a similar relationship to Equation 5.5 showing that

$$\frac{\overline{\mathbf{C}-\mathbf{M}_3}}{\overline{\mathbf{M}_3-\bar{\mathbf{P}}_3}} = \frac{\overline{\mathbf{C}-\mathbf{D}_3}}{\overline{\mathbf{D}_3-\mathbf{AC}}} \tag{5.6}$$

However, P_3 is the actual product composition for the bottoms product of the first column. The length of M_3-P_3 represents the amount of C that is mixed. Because the length of M_3-P_3 is less than the length of M_3-$\bar{P}_3$, the amount of C that is recovered in the last column is more than the amount that is recycled. Because of the convex boundary, the configuration with recycling is now feasible.

A similar argument can be made for the concave boundary except that length of M_1-P_1 is greater than the length of M_1-$\bar{P}_1$ meaning that the amount of C that is recycled is greater than the amount that is recovered in the last column. This option is infeasible because the distillation configuration does not produce enough C for the recycling task.

From the above examples, we can see that without curved boundaries, recycling cannot increase the level of separation in a particular separation network. One exception of this observation is shown in Figure 5.5. The distillation boundaries are straight, but, with the presence of the ternary azeotrope, the boundary AC-BC is kinked or effectively curved. If the AC-BC boundary were the straight dashed line shown in Figure 5.5, the point $\overline{P}$ could represent the top product of the first column. The nodes AC, BC, and C form

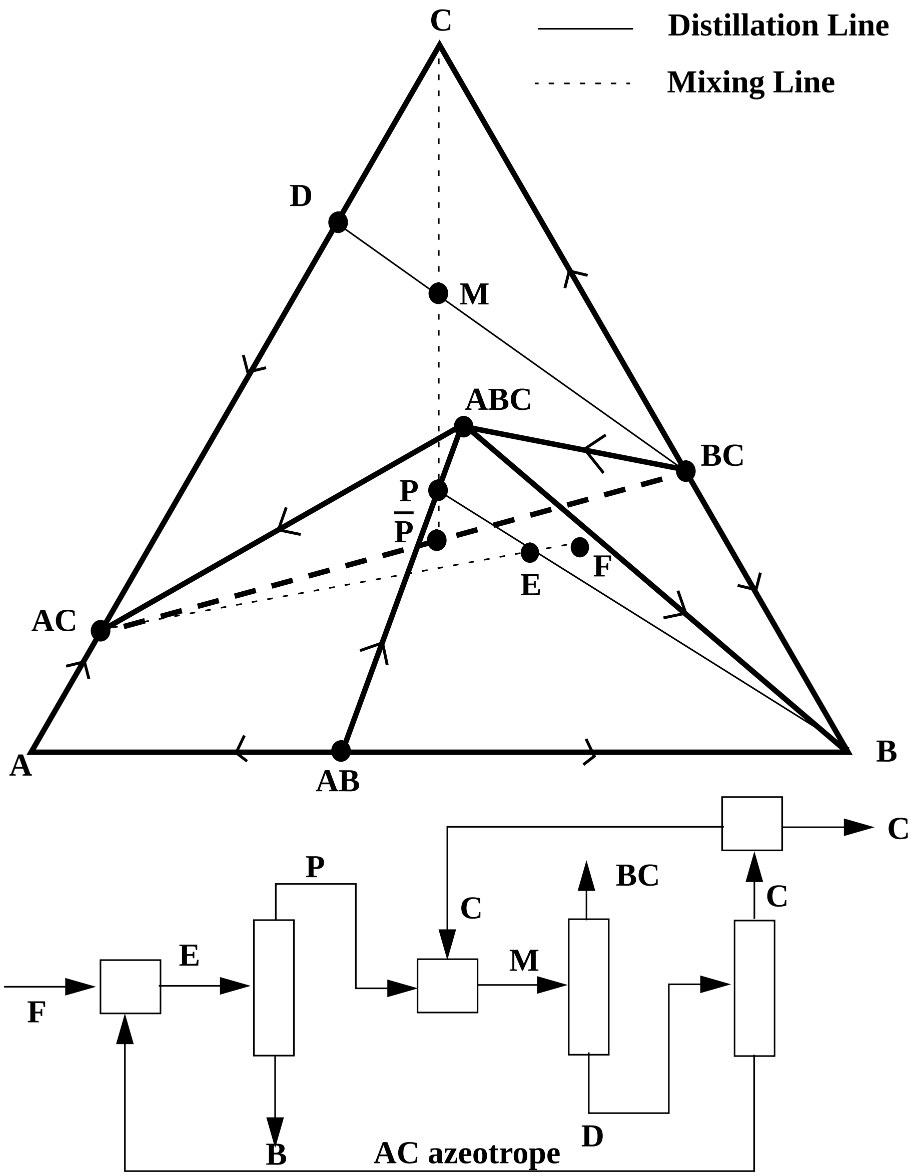

Figure 5.5: Kinked Straight Line Boundaries

a triangle on which $\overline{P}$ lies. The lengths of AC-$\overline{P}$ and BC-$\overline{P}$ represent the relative amounts of the products BC and AC and the length of M-$\overline{P}$ represents the amount of C that is recycled. Using the procedure outlined in Section 5.3.1, we know that the amount of C that can be recovered is exactly the same amount that we have recycled. Since the boundary AC-BC is kinked, the true top product composition of the first column is P. The relative amounts of the products AC and BC are the same as before but less C must be recycled to get to the same mix point M. The amount of C that is recovered in the last column, represented by the length of AC-D, is the same no matter how the boundary AC-BC is represented. As long as the top product of the first column, point P, lies above the dashed line AC-BC, the kinked boundaries allow us to derive a feasible configuration by recycling C.

As we have seen, recycling can increase the separation capabilities if the distillation column configuration can produce the required amount of recycled agent. Curved distillation boundaries are necessary in order for the configurations to be feasible so we will not include recycling in any further analysis as we have assumed straight line boundaries, and we do not account for kinks caused by the placing of multicomponent azeotropes.

5.4 Column Sequence Network

5.4.1 State-Task Representation

In order to build the network of all feasible batch column sequences, we must first find some way in which to represent the mixtures that need to be separated and the types of possible distillations that can be used. This kind of system is easily represented using a state-task network (STN) where the states are the mixtures that need to be separated and the tasks are the different types of batch column configurations that transform the states into other states. This representation was also used by Kondili et al. (1993) for the scheduling of batch processes and Sargent (1994) for the synthesis of simple and complex continuous distillation systems. A state (mixture) has a set of properties associated with it: a composition vector and the amount of the state. The tasks which can operate on the state consist of rectifier, stripper, MVC, and extractive MVC tasks. Each of these tasks transform the state into a new state and can also create others. The transformed state is the residue mixture after the product(s) is removed from the original state, and the created state(s) is the product generated by the distillation task. Only single fraction operations are considered as a multi-fraction operation can be represented as a series of single fraction operations. Table 5.2 summarizes the properties of the various tasks. The tasks will operate on the states in a manner that depends not only on the type of task but also the conditions of the state. Using the methods shown in Sections 5.3.1 and 5.3.2, we will determine within which batch region the mixture (state) lies. Every distillation configuration (task) that will be used on this mixture depends on the batch region as the particular distillation task may be infeasible for the mixture in question. For example, a

Table 5.2: Properties of the Distillation Tasks

Task	Residue State Location	Product State Location
rectifier	reboiler	top
stripper	condenser	bottom
MVC	middle vessel	top, bottom
extractive MVC	middle vessel	top, bottom

pure component or azeotrope could not be separated using a batch rectifier or stripper. The products from the distillation task will now become new states which will have all of the distillation tasks applied to them. The residue of the distillation task is also a new state which will have the distillation tasks applied also. In this manner, we can begin to build the network of column sequences and develop an algorithm for the synthesis of batch column sequences.

5.4.2 Algorithm for Generating Network

We begin to synthesize the batch column sequences by applying all of the distillation tasks to the initial mixture. With each application we create new states. To each of these which are not final products or azeotropes, we apply all the tasks, creating even more new states. We identify if a state already exists in the tree we are creating. If it does, we merge the just created state with the previously created state that is the same, converting the tree into a network. Thus we recursively apply this procedure. It continues until no tasks can be applied to any states. At this point, the entire network of batch column sequences has been built and interesting sequences can be extracted for further examination, optimization, etc. Each distillation task is outlined below as well as an overall task, Expand Task, which is the combination of all the possible distillation tasks:

Rectifier
- If state S is a pure component or azeotrope, task is infeasible and return.
- Find batch rectifier distillation region using S.
- Top product is the UN of this batch region.
- Create a new state TP with the top product.
- Calculate transformed state TS (reboiler residue) by removing TP from S.

Stripper
- If state S is a pure component or azeotrope, task is infeasible and return.
- Find batch stripper distillation region using S.
- Bottom product is the SN of this batch region.

- Create a new state BP with the bottom product.
- Calculate transformed state TS (condenser residue) by removing BP from S.

MVC

- If state S is a pure component or azeotrope, task is infeasible and return.
- Find batch rectifier distillation region using S.
- Top product is the UN of this batch region.
- Create a new state TP with the top product.
- Find batch stripper distillation region using S.
- Bottom product is the SN of this batch region.
- Create a new state BP with the bottom product.
- Calculate transformed states TS (multiple middle vessel residues) according to Section 5.3.2.
- Create a new state with TS if amount>0.

Extractive MVC

- If state S is a pure component, task is infeasible and return.
- Update S by adding in entrainer agent.
- Find batch rectifier distillation region using S.
- Top product is the UN of this batch region.
- Check infinite dilution K values of the top product forming components in the entrainer agent.
- If no components have a ratio of K values>1.5, task is infeasible and return.
- Create a new state TP with the pure components with K values>1.5 times all other K values of components not in the top product.
- Find batch stripper distillation region using S.
- Bottom product is the SN of this batch region.
- Create a new state BP with the bottom product.
- Calculate transformed state TS (middle vessel residue) by removing TP and BP from S.
- Create a new state with TS if amount>0.

Expand Task

- Apply Rectifier Task to current state.
- Apply Expand Task to rectifier task’s TS.
- Apply Expand Task to rectifier task’s TP.
- Apply Stripper Task to current state.
- Apply Expand Task to stripper task’s TS.
- Apply Expand Task to stripper task’s BP.
- Apply MVC Task to current state.
- Apply Expand Task to all of MVC task’s TSs.
- Apply Expand Task to MVC task’s TP.
- Apply Expand Task to MVC task’s BP.
- Apply Extractive MVC Task to current state.
- Apply Expand Task to Extractive MVC task’s TS.
- Apply Expand Task to Extractive MVC task’s TP.

- Apply Expand Task to Extractive MVC task's BP.

The algorithm starts by applying Expand Task to the initial state (initial batch mixture). Expand Task is recursively called on all new states until no new states can be created. The network has now been created.

5.5 Example

We will now illustrate the algorithm for building the network of batch column sequences by working through an example. The algorithm previously mentioned for building the batch column network was implemented and attached to the distillation region finding tool of Safrit and Westerberg (1996). Figure 5.6 shows the system acetone/chloroform/methanol. As can be seen, there are many azeotropes and six batch rectifier distillation regions. The regions are the same for the batch stripper. For this example, we will be using ethylene glycol (EG) as an entrainer agent. Table 5.3 shows input necessary for the region finding tool, and Table 5.4 shows the infinite dilution

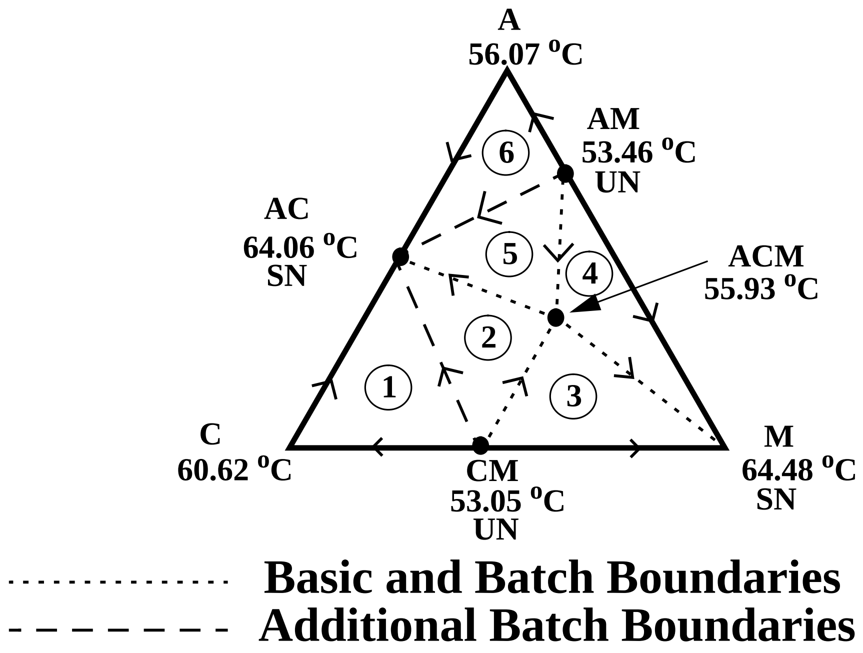

Figure 5.6: Acetone/Chloroform/Methanol Residue Curve Map

Table 5.3: Acetone/Benzene/Chloroform/Methanol Example Input

Node	%A	%C	%M	%EG	Tb (C)	Stability	num + eigenvalues	num - eigenvalues
A	100.0	0	0	0	56.07	S	2	1
C	0	100.0	0	0	60.62	S	1	2
M	0	0	100.0	0	64.48	S	1	2
EG	0	0	0	100.0	197.38	SN	0	3
AM	68.34	0	31.66	0	53.46	UN	3	0
AC	38.38	61.62	0	0	64.06	S	1	2
CM	0	65.78	34.22	0	53.50	UN	3	0
ACM	25.82	28.72	45.46	0	55.93	S	2	1

Table 5.4: Infinite Dilution K values for Example Problem

in / K^{∞} of:	acetone	chloroform	methanol	EG
acetone	1.00	0.45	1.76	0.010
chloroform	0.60	1.00	5.50	0.140
methanol	3.37	2.97	1.00	0.003
EG	41.10	46.90	25.60	1.00

K values for this system. We will assume that the ratio of the K values for extraction has to be greater than 1.5 for the extraction in question to be feasible. The factor of 1.5 is chosen here for illustrative purposes only, and the actual value chosen will depend on the economics of the extractive distillation. From Table 5.4, we can see that EG can break apart the acetone-methanol binary azeotrope (41.10/25.60=1.61 > 1.5) and the chloroform-methanol binary azeotrope (46.90/25.60=1.83 > 1.5) but not the acetone-chloroform binary azeotrope (46.90/41.10=1.14 < 1.5). EG will also separate acetone and chloroform from methanol when we are trying to break the ternary azeotrope ((41.10 and 46.90)/25.60 > 1.5). The region finding tool produced the following batch distillation regions (for the rectifier and stripper):

Batch Distillation Regions
(AM, A, AC, EG)
(AM, ACM, AC, EG)
(AM, ACM, M, EG)
(CM, C, AC, EG)
(CM, ACM, AC, EG)
(CM, ACM, M, EG)

There are no batch regions in which we can obtain more than one pure component product (other then EG) using non-extractive columns.

After we generated the batch distillation boundaries and the resulting batch regions for the four batch column configurations, we built the column network by picking a composition for the acetone/chloroform/methanol mixture to be separated. We first picked a composition S_1 in batch region 4 in Figure 5.6 such that S_1(acetone, chloroform, methanol) = (0.3, 0.1, 0.6). Using the key in Figure 5.7, the resulting batch column

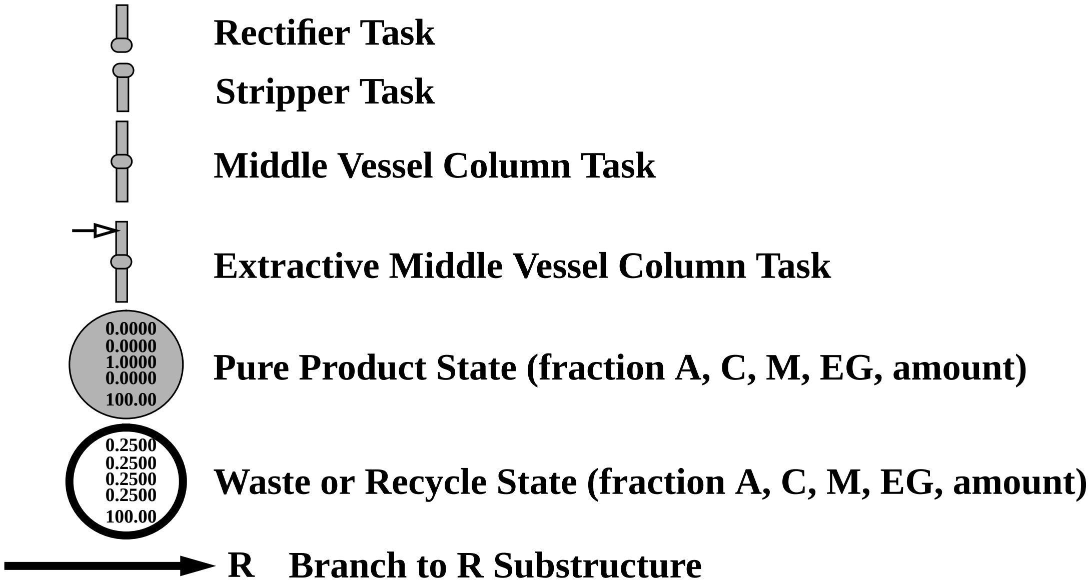

Figure 5.7: Key for Column Network Diagrams

network is shown in Figure 5.8. The rectifier, stripper, MVC, and extractive MVC branches of the network are shown in Figures 5.9, 5.10, 5.11, and 5.12. The amount of EG added to each extractive MVC was set to be the same amount of the original state sent to this task for illustrative purposes only. The actual amount of EG required would need to be determined in more detailed studies. Repeated tasks were shown with more than one arrow coming into the task.

Several interesting conclusions can be made about Example S_1. First, every sequence required at least one extractive MVC to recover at least two of the pure components. Chloroform could not be recovered in pure form as the only product containing chloroform was the acetone-chloroform binary azeotrope. This product can not be recycled back into the process unless it is used as makeup solvent. If the chloroform was the result of a reaction for instance, we could not recycle this product back as chloroform would eventually build up in the system. We could also dispose of the product as waste. Other solutions include changing entrainer agents to one that can break the acetone-chloroform azeotrope or having a set of entrainer agents from which we could pick a feasible entrainer agent.

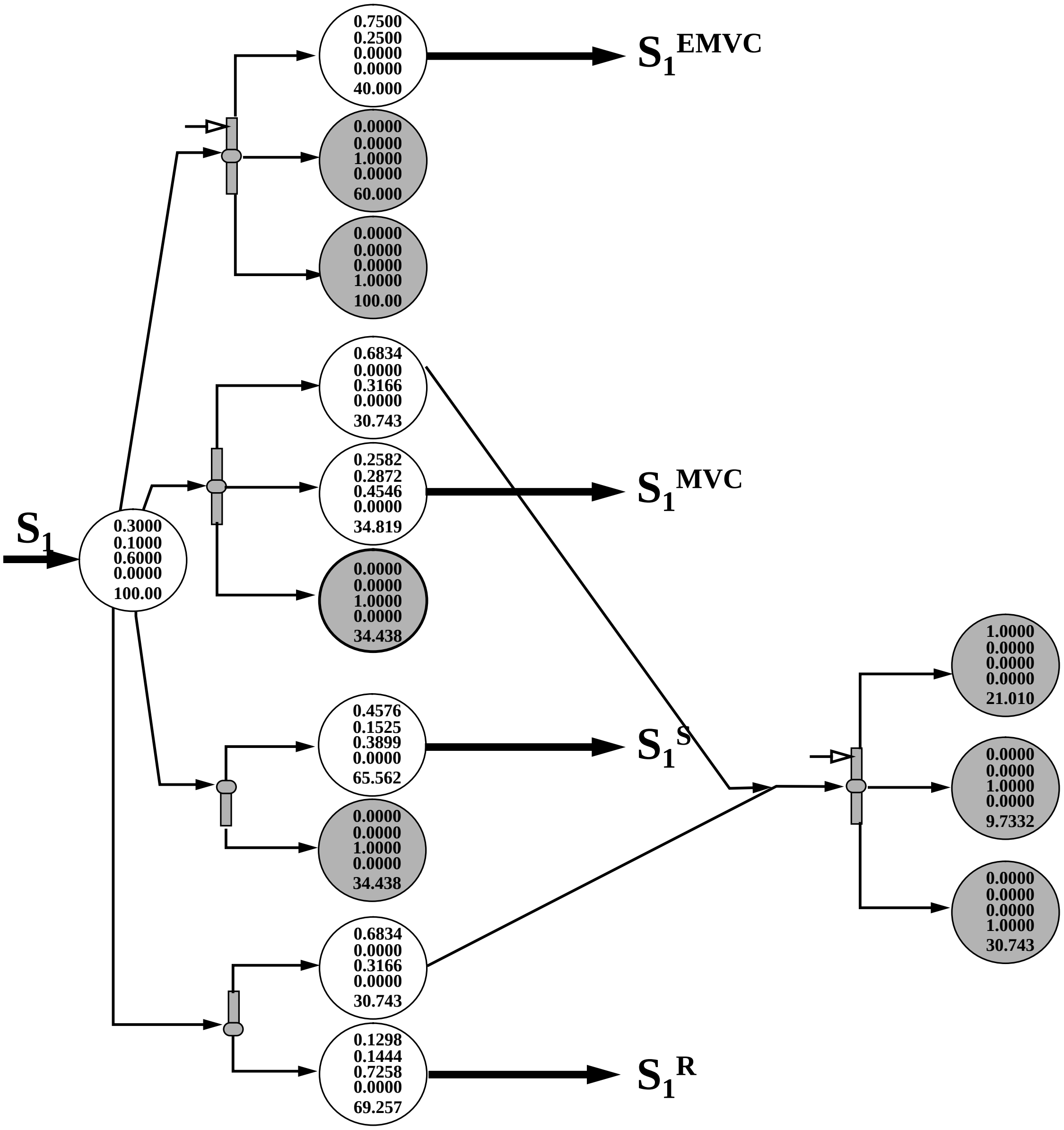

Figure 5.8: Column Network for S_1

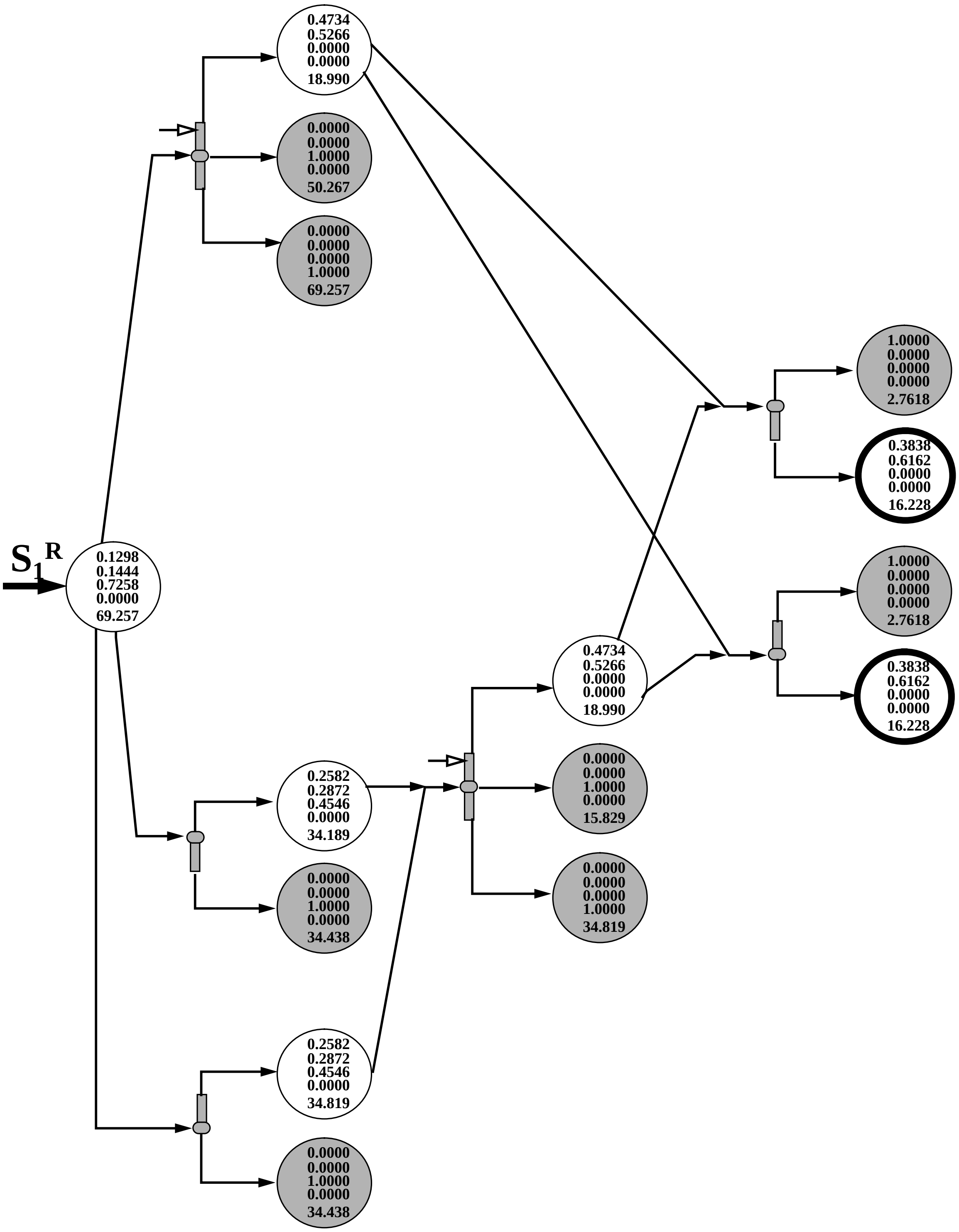

Figure 5.9: Rectifier Branch of S_1 (S_1^R) Network

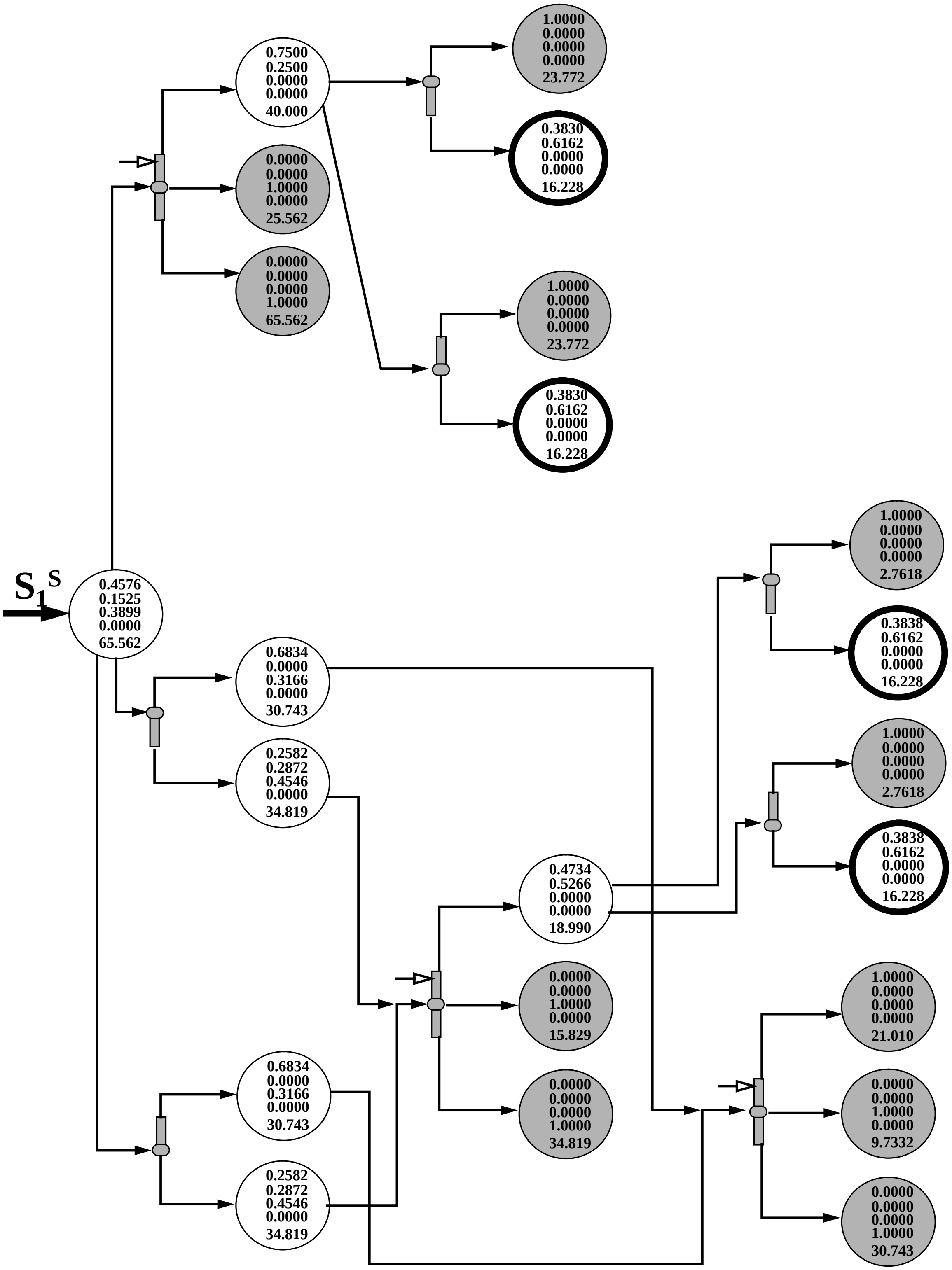

Figure 5.10: Stripper Branch of S_1 (S_1^S) Network

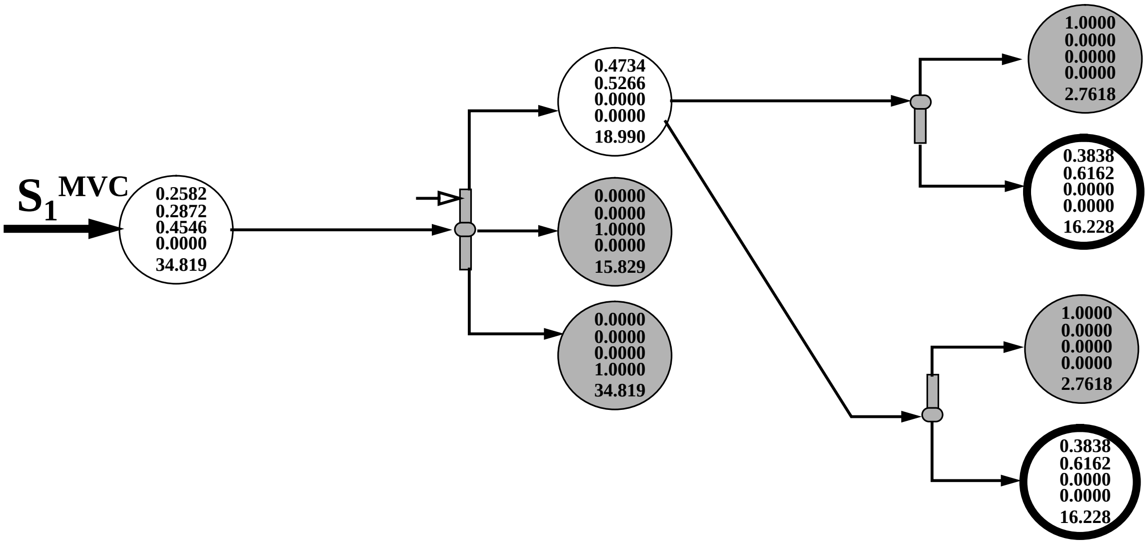

Figure 5.11: MVC Branch of S_1 (S_1^{MVC}) Network

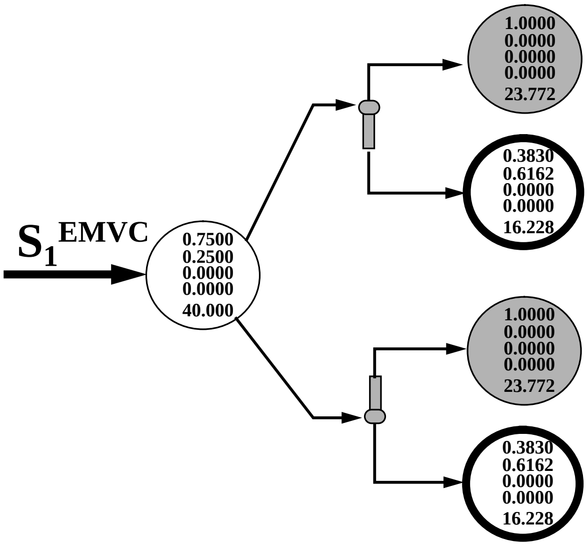

Figure 5.12: EMVC Branch of S_1 (S_1^{EMVC}) Network

Another initial composition was chosen such that S_2(acetone, chloroform, methanol) = (0.1, 0.3, 0.6). This composition was located within batch region 3 in Figure 5.6. The resulting batch column network is shown in Figure 5.13. The rectifier, stripper, MVC, and extractive MVC branches of the network for S_2 are shown in Figures 5.14, 5.15, 5.16, and 5.17. The network for S_1 and S_2 were very similar with one main difference. The chloroform-methanol binary azeotrope was the UN for the latter example meaning that we could take this as a product and separate the chloroform and methanol using an extractive MVC. So a portion of the chloroform could be removed from the mixture as a pure product with the remainder showing up again as waste product consisting of the acetone-chloroform binary azeotrope. But it may be much more feasible to recycle the waste product back into the process as the chloroform will not build up in the system as seen for Example S_1. There were actually two different recoveries of chloroform possible for Example S_2. If we took a chloroform-methanol product anywhere in the sequence, we recovered 62.92% of the chloroform and all of the other components as pure products. If we do not take a chloroform-methanol product anywhere in the sequence, the best recovery of chloroform is 46.48%. Figure 5.18 shows example sequences of each of these two kinds of chloroform recoveries.

The initial composition for the two examples drastically affected the possible pure products that were obtainable. While the two networks were very similar, only S_2 was capable of producing any pure chloroform. For the example of acetone/chloroform/ methanol, another entrainer agent could be chosen such that the acetone-chloroform binary azeotrope could be separated resulting in a 100% recovery of all pure components.

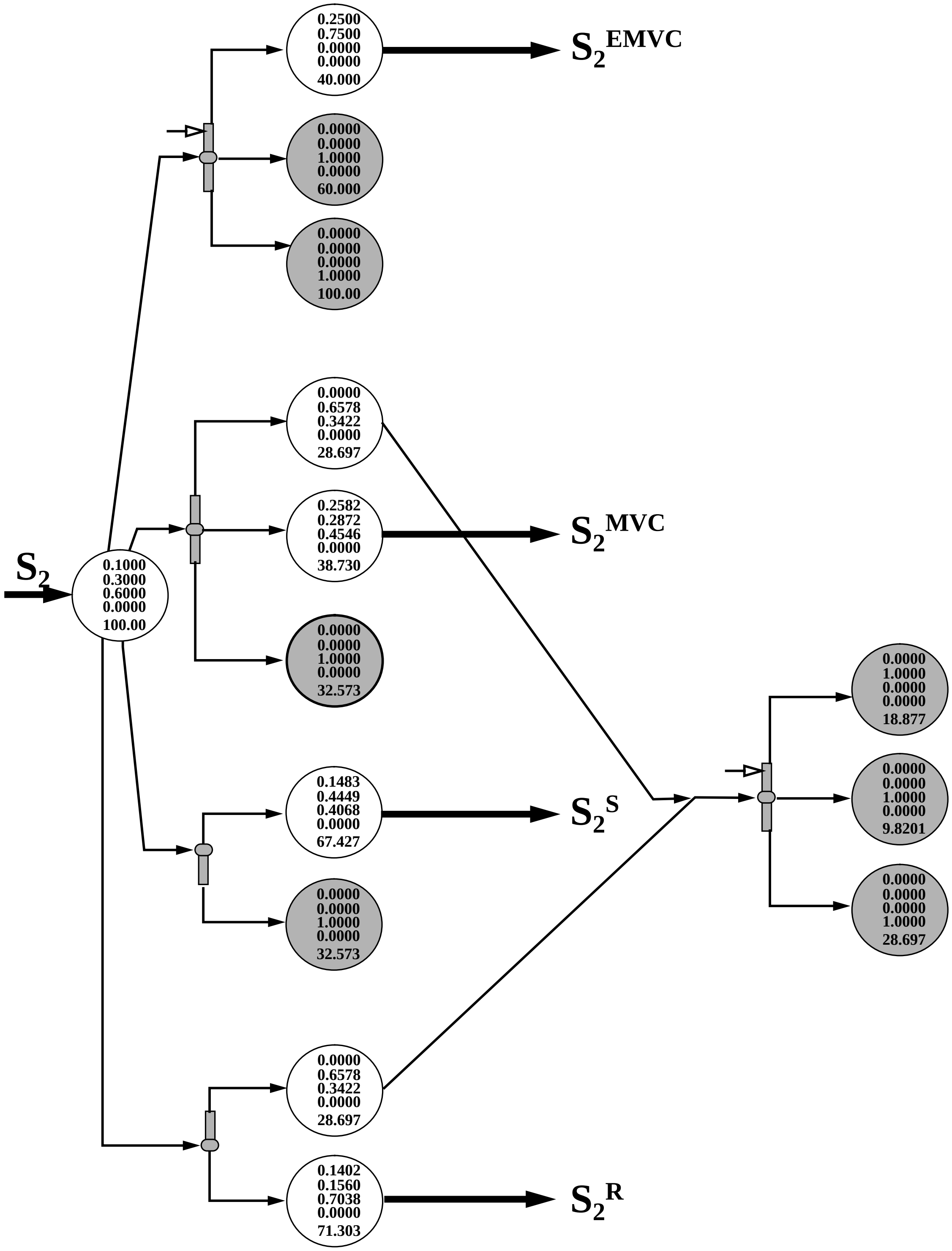

Figure 5.13: Column Network for S_2

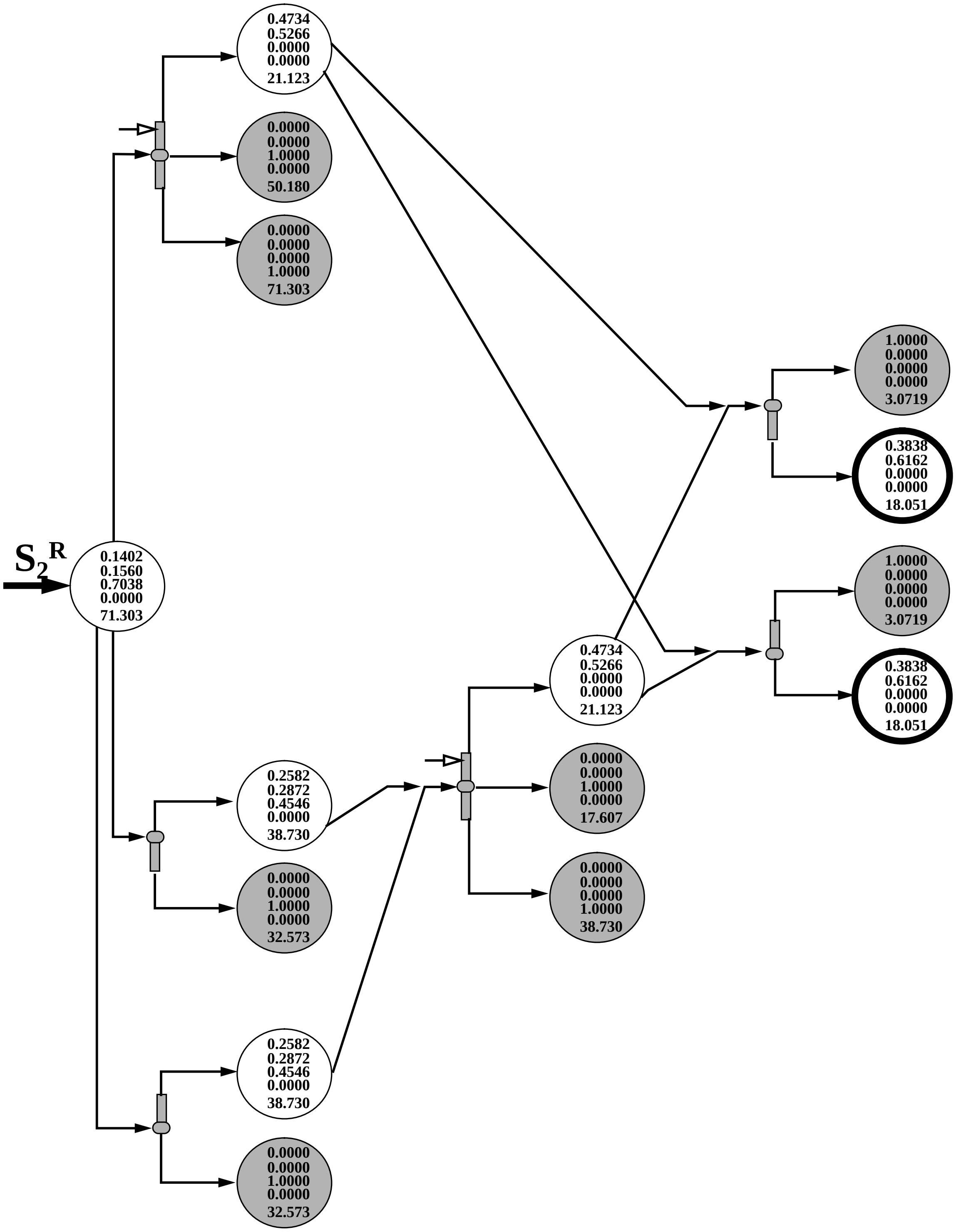

Figure 5.14: Rectifier Branch of S_2 (S_2^R) Network

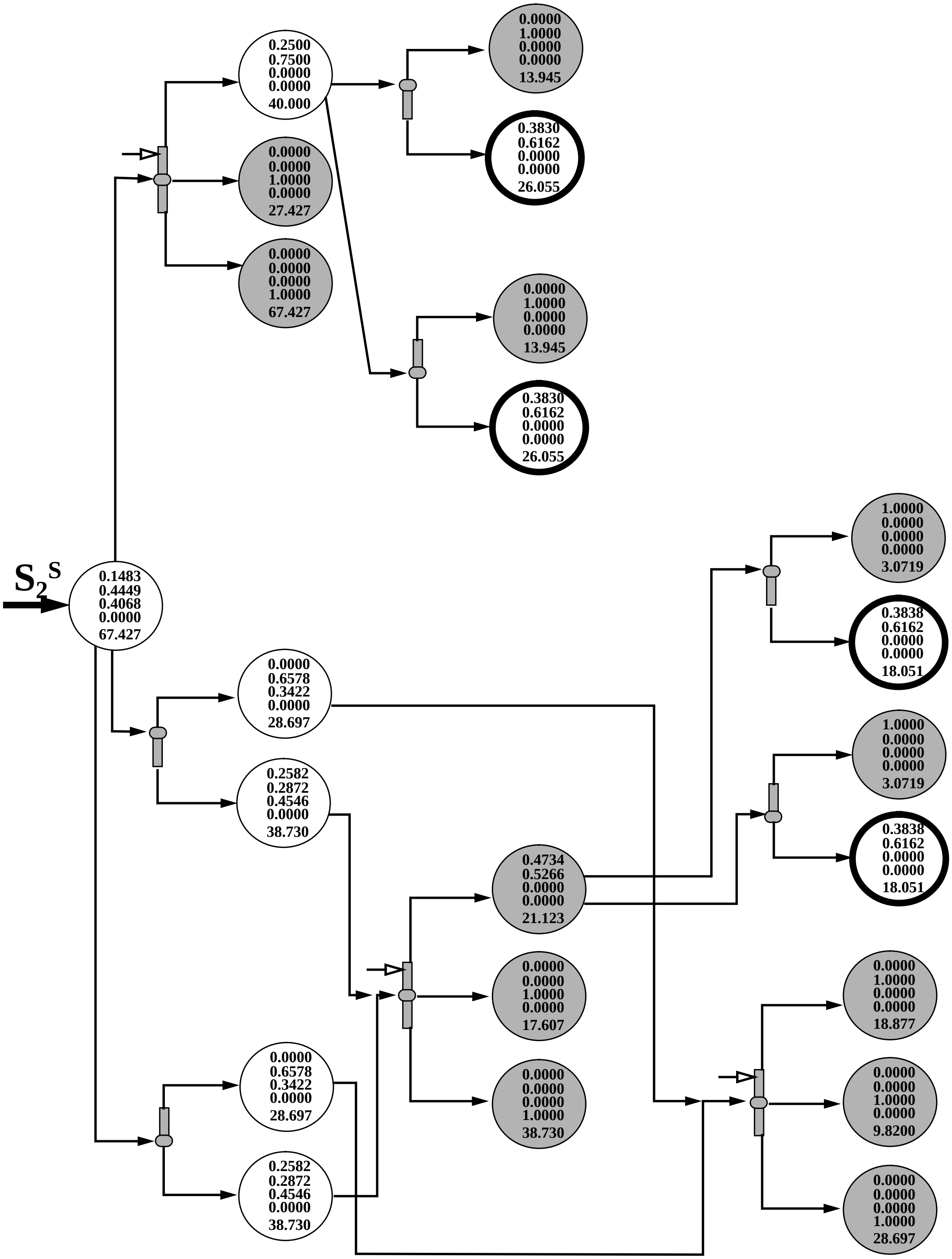

Figure 5.15: Stripper Branch of S_2 (S_2^S) Network

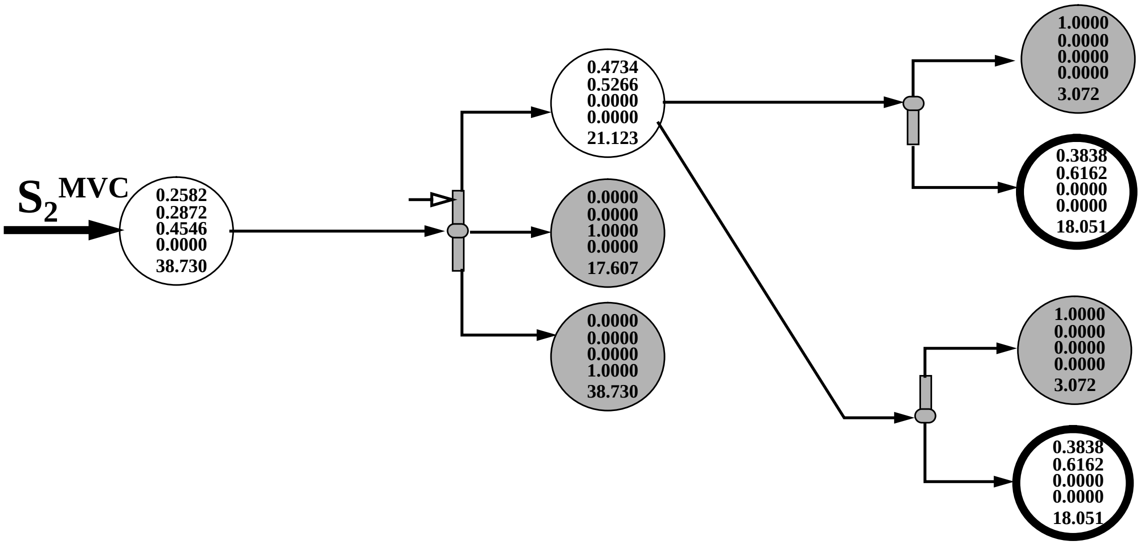

Figure 5.16: MVC Branch of S_2 (S_2^{MVC}) Network

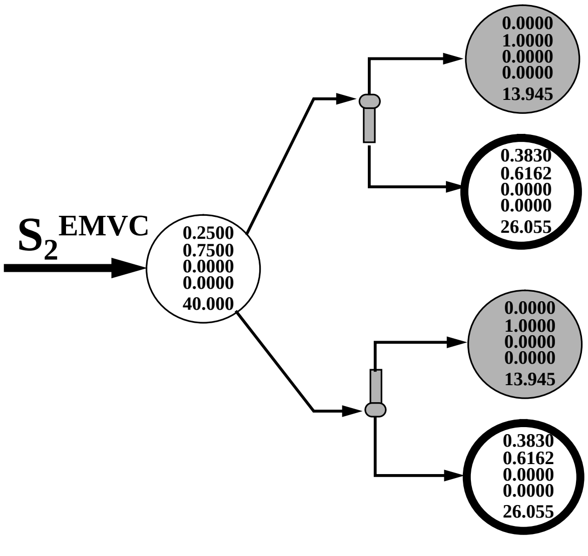

Figure 5.17: EMVC Branch of S_2 (S_2^{EMVC}) Network

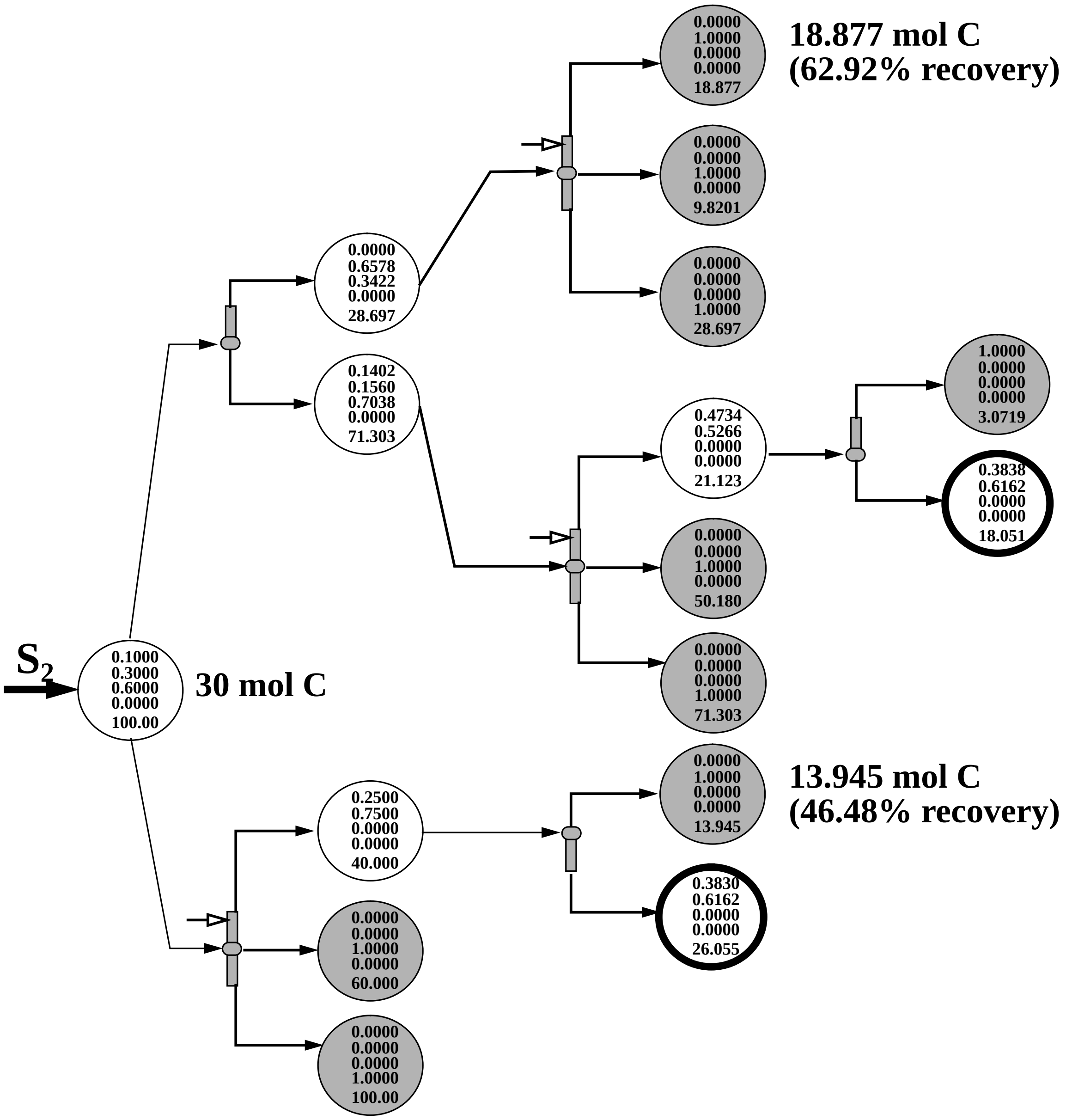

Figure 5.18: Comparison of Recoveries of Chloroform

Another interesting observation is that all instances of the MVC only have one possible residue. We showed in Section 5.3.2 that the MVC can have multiple possible residues. The basic distillation regions that Examples S_1 and S_2 occupy consist of three nodes. When all of the top product (UN) and bottoms product (SN) are removed, the only possible MVC residue is the other node in the region. Multiple MVC residues can possibly occur when the basic distillation region is made up of four or more nodes

5.6 Impact of Synthesis Assumptions

5.6.1 Straight Line Distillation Boundaries

As pointed out by Safrit and Westerberg (1996), there are several implications of assuming straight line distillation boundaries mainly dealing with the predicted batch products. The assumption does not affect the distillation region finding tool to any great degree, but it seriously affects the column sequencing algorithm presented here. The amount of a product in a particular mixture can be quite different when we allow the boundaries to be curved instead of straight. Boundary curvature may also allow a sequence to move into another batch region by using different batch column configurations in series. For example, in Figure 5.19 we could take the initial still composition S and take out a distillate product D1 using a batch rectifier. We will continue to take D1 as the distillate product with the still path moving directly away from D1 until the still path intersects the distillation boundary AC-B. If we assume straight line boundaries, this intersection would be X while the intersection would be R1 if we were using the actual curved boundary. We were able to remove more of the D1 product when we used the curved boundary. Now let us take the residue of the batch rectifier and feed it to a batch stripper. Using straight line boundaries, our bottoms product would be B2 and the residue would be the AC binary azeotrope. However, if we had used the curved boundary, our bottoms product would still have been B2, but the residue would be R2 which is in a different batch region than the initial still composition. The residue R2 would then be feed to a batch rectifier producing C as a distillate product and AC as the residue.

The amount of the AC residue product would be small as the majority of A would have already been taken out in the first column. The azeotrope can then be recycled. Recycling can also benefit from curved boundaries as we showed in Section 5.3.3. As we have shown, straight line boundaries can limit and remove the types of feasible sequences we can generate.

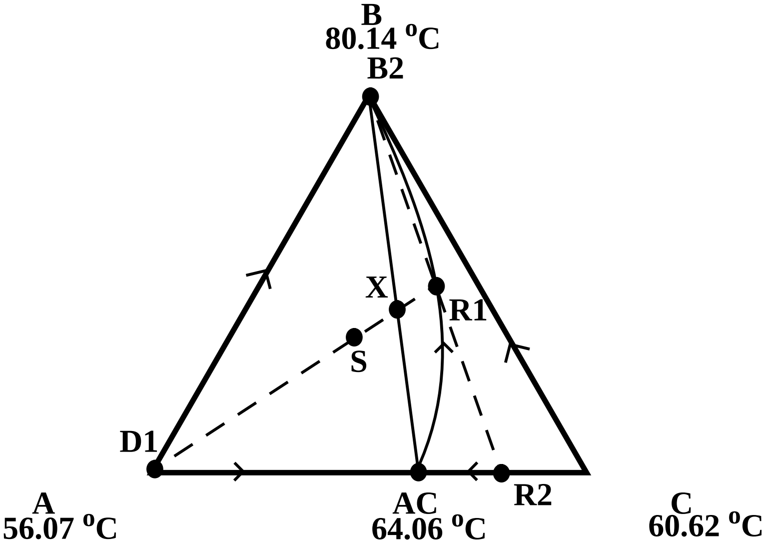

Figure 5.19: Impact of Curved Boundaries of Batch Column Sequencing

5.6.2 Total Reflux/Reboil and Infinite Number of Trays

The assumptions of total reflux/reboil and infinite number of trays affect the purity of product that can be obtained. Using these assumptions, the distillate or bottoms products using nonextractive batch columns will be the unstable or stable node respectively. If we were to relax these assumptions, the products now would be close to their original states but slightly less pure depending on how much we have relaxed the assumptions. Also, the switching between product cuts will not be instantaneous. So waste or slop cuts will have to be taken between product cuts in order to meet any purity specifications. These slop cuts must be processed further either as disposed waste or as a recycled product. And as seen in other works such as Wahnschafft et al. (1992), some very curved boundaries can be crossed at finite reflux resulting in further feasible separations.

5.7 Conclusions

Azeotropic mixtures can severely limit the feasible products one can obtain using batch distillation. These azeotropes can create batch distillation regions where the region is defined by the product sequence associated with the particular distillation region. A sequence of several batch columns consisting of different types of batch column configurations may be necessary in order to separate out the mixture into its pure components. There may also exist many of these feasible sequences, each having its own benefits and drawbacks. All of these sequences must be analyzed during the synthesis and early design phase so the best separation system is chosen for further design and analysis.

We have showed how to use a tool for finding batch distillation regions in generating the network of all possible batch column sequences. Under the assumptions of total reflux/reboil, infinite number of trays, and straight line distillation boundaries, this tool was capable of finding the distillation regions for four different batch column configurations: rectifier, stripper, middle vessel column, and extractive middle vessel column. We found that the initial mixture composition could seriously affect the types of pure component products we could obtain and that different entrainer agents were necessary in order to recover all of pure components.

The assumptions of total reflux/reboil, infinite number of trays, and straight line distillation boundaries need to be removed from the problem so the effects of recycling and remixing can be further explored. It may be possible that these assumptions remove feasible and even optimal designs from consideration as the network is sure to grow when these assumptions are removed from the problem.

5.8 Nomenclature

NC = number of components
NN = number of nodes (pure component and azeotropic)
MVC = middle vessel column
x_i = liquid mole fraction
y_i = vapor mole fraction
K = y_i / x_i
UN = unstable node
SN = stable node
$\underline{n}_i$ = i-th batch region vector (i=1..NN)
$\underline{s}$ = composition vector
α_i = i-th batch region vector multiplier (i=1..NN)

5.9 Acknowledgments

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References

Ahmad B. S., and P. I. Barton, **1995a**. “Solvent Recovery Targeting for Pollution Prevention in Pharmaceutical and Specialty Chemical Manufacturing.” *AIChE Symposium Series.* **90**, p. 59 - 73.

Ahmad B. S., and P. I. Barton, **1995b**. “Synthesis of Batch Processes with Integrated Solvent Recovery and Recycling.” Presented the AIChE Annual Meeting, Miami Beach, FL.

Ahmad B. S., Y. Zhang, and P. I. Barton, **1995**. “Pollution Prevention in Pharmaceutical and Specialty Chemical Manufacturing: The Theory of Homogeneous Multicomponent Azeotropic Batch Distillation.” In Preparation.

Bernot C., M. F. Doherty, and M. F. Malone, **1991**. “Feasibility and Separation Sequencing in Multicomponent Batch Distillation.”*Chemical Engineering Science*, **46**, p. 1311-1326

Chiotti O. J., and O. A. Iribarren, **1989**. “An Optimization Module for Batch Distillation with Intermediate Cuts.”*Computers in Industry*, **13**, p. 169-180.

Ewell R. H. and L. M. Welch, **1945**. “Rectification in Ternary Systems Containing Binary Azeotropes.” *Ind. Eng. Chem. Res.* **37** (12), p. 1224-1231.

Kondili E., C. C. Pantelides, and R. W. H. Sargent, **1993**. “A General Algorithm for Short-term Scheduling of Batch Operations-I: MILP Formulation.” *Computers and Chem. Engng.*, **17**(2)**,** p. 211-227.

Safrit B. T., A. W. Westerberg, U. M. Diwekar, O. M. Wahnschafft, **1995a**. “Extending Continuous Conventional and Extractive Distillation Feasibility Insights to Batch Distillation.” *Ind. Eng. Chem. Res.*, *34*, p. 3257-3264.

Safrit B. T., A. W. Westerberg, U. M. Diwekar, O. M. Wahnschafft, **1995b**. “Improved Operational Polices for Batch Extractive Distillation Columns.” Tech Report EDRC 06-200-95, Engineering Design and Research Center, Carnegie Mellon University.

Safrit B. T., A. W. Westerberg, **1996**. “Algorithm for Generating the Distillation Regions for Azeotropic Multicomponent Mixtures.” To be submitted to *Ind. Eng. Chem. Res*.

Sargent R. W. H., **1994**. “A Functional Approach to Process Synthesis and its Application to Distillation Systems.” Centre for Process Systems Engineering, Imperial College of Science, Technology and Medicine.

Sundaram S., and L. B. Evans, **1993**. “Synthesis of Separations by Batch Distillation.”

Industrial Engineering and Chemical Research, **32**, p. 500-510.

Wahnschafft O. M.; J. W. Koehler; E. Blass; and A. W. Westerberg, **1992**. “The Product Composition Regions of Single Feed Azeotropic Distillation Columns.” *Ind. Eng. Chem. Res.*, *31*, 2345-2362.

Wahnschafft O. M. and A. W. Westerberg, **1993**. “The Product Composition Regions of Azeotropic Distillation Columns. 2. Separability in Two-Feed Columns and Entrainer Selection.” *Ind. Eng. Chem. Res.*, *32*, 1108-112

Chapter 6

Conclusions and Future Directions

6.1 Conclusions

In order to synthesize sequences of batch distillation columns, we first explored a relatively new type of batch column configuration called a middle vessel column. Using insights developed for continuous distillation, we were able to map out the feasible product regions for the batch rectifier, stripper, and middle vessel column given the current still composition. We were also able to identify the regions of possible column profiles given product specifications and were able to determine if the product specifications were feasible. In the case of an infeasible product specification, we again used insights developed for extractive continuous distillation and found that extractive batch distillation can make some infeasible product specifications feasible. We also showed how one can "steer" the still composition versus time and separate out all pure components from a 3-component mixture. Using this still path steering, we were able theoretically to recover 100% of the pure components from a binary mixture using the extractive middle vessel column. Comparisons to the extractive batch rectifier showed that the rectifier required an infinite size still pot but the middle vessel column did not.

We then further investigated the operation of the extractive middle vessel column. There were many adjustable parameters for the extractive middle vessel column such as the reflux/reboil ratio policies, entrainer and bottoms flow rate policies, vapor boilup rate policies, and fraction switching times that affected the operation of this kind of column. Simulation studies showed that the final profit of the operation was indeed sensitive to these optimization variables. A different bottoms flow rate policy than the still path steering algorithm was simulated and found to slightly improve the final profit. However, we showed that the normal still path steering algorithm was a good first guess for the bottoms flow rate policy.

A tool for finding the continuous and batch distillation boundaries and regions for any mixture was then developed. Using maximum and minimum separating surfaces, we divided the composition space into subregions each having its own unstable and stable nodes. These subregions were the basic distillation regions from which we showed how to determine the continuous and batch boundaries and regions. The tool was validated by correctly finding the distillation regions for all topologically possible 3-component systems and several different 4-component systems. We then used this tool in synthesizing sequences of batch columns. Several different batch column configurations were used and all were operated at total reflux/reboil and infinite number of trays except for the extractive middle vessel column. Using state-task networks, we were able to represent the network of all possible batch column sequences for a particular initial composition.

6.2 Future Directions

The extractive middle vessel column, with it many adjustable parameters, needs to be investigated further. The entire three fraction operation (start-up, main distillate recovery, and waste cut step) needs to be solved as an optimal control problem with variables such as reflux/reboil ratio policies, entrainer and bottoms flow rate polices, and fraction switching times as the optimized variables. Only in solving this problem as an optimal control can the best values for these variables be found.

The assumptions of straight line boundaries and total reflux/reboil and infinite number of trays need to be removed from the batch region finding and column sequencing tools. Once these assumptions are removed, we can begin to explore recycling as a means of extending the types of feasible separation sequences. The number of feasible batch column sequences will surely increase as well. The distillation region finding tool is also sufficiently small enough that it could be placed into other software or optimization routines with the purpose of proper initialization and screening of proposed designs, finding potential products, screening of possible entrainers for a particular mixture, or optimizing process solvents and conditions for increased separation capabilities.

Nomenclature

α_i = i-th batch region vector multiplier (i=1..NN)
β_i = Weighting factor for product i
B = Bottoms product flow rate
D = Distillate product flow rate
DB = Still path direction due to bottoms product removal
DD = Still path direction due to distillate product removal
DE = Still path direction due to entrainer addition
Δ = Delta point
E = Entrainer flow rate
$\lambda(i,j)$ = Wilson interaction parameter, λ_{ij}
H = Still Holdup
INT(list_nodes) = intersection list which are the nodes appearing in a least two of the UNL or SNL of the list_nodes
K_i = relative volatitivy = y_i / x_i
L_A = Constant parameter in flow rate policy equation
L_B = Linear parameter in flow rate policy equation
L_j = Liquid flow rate from tray j
MVC = middle vessel column
$\underline{n}_i$ = i-th batch region vector (i=1..NN)
$N_{Entrainer}$ = Entrainer feed location
N_{Lower} = Number of trays in lower section of column
N_{Upper} = Number of trays in upper section of column
NC = number of components
NN = number of nodes (pure component and azeotropic)
P_i = Amount of product i
$\underline{s}$ = composition vector
S = Still or middle vessel composition
SN = stable node
SNL(stable node) = common SN list which are the nodes reached by decreasing temperature from stable node
T_1 = Fraction switching time
T_2 = Operation ending time
t_{opt1} = Time of best accumulated profit
UN = unstable node
UNL(unstable node) = common UN list which are the nodes reached by increasing temperature from unstable node
V_j = Vapor flow rate from tray j
x_b = Bottom product composition
x_d = Distillate product composition
x_Δ = Δ point composition
x_e = Entrainer composition

x_i = liquid mole fraction
x_s = Still composition
y_i = vapor mole fraction

References

Ahmad B. S., and P. I. Barton, **1995a**. “Solvent Recovery Targeting for Pollution Prevention in Pharmaceutical and Specialty Chemical Manufacturing.” *AIChE Symposium Series.* **90**, p. 59 - 73.

Ahmad B. S., and P. I. Barton, **1995b**. “Synthesis of Batch Processes with Integrated Solvent Recovery and Recycling.” Presented the AIChE Annual Meeting, Miami Beach, FL.

Ahmad B. S., Y. Zhang, and P. I. Barton, **1995**. “Pollution Prevention in Pharmaceutical and Specialty Chemical Manufacturing: The Theory of Homogeneous Multicomponent Azeotropic Batch Distillation.” In Preparation.

Baburina L. V., V. M. Platonov, and M. G. Slin’ko, **1988**. “Classification of Vapor-Liquid Phase Diagrams for Homoazeotropic Systems.” *Theor. Found. Chem. Eng*. **22**, p. 390-396.

Bernot C., M. F. Doherty, and M. F. Malone, **1990**. “Patterns of Composition Change in Multicomponent Batch Distillation.”*Chemical Engineering Science*, **45,** p. 1207-1221.

Bernot C., M. F. Doherty, and M. F. Malone, **1991**. “Feasibility and Separation Sequencing in Multicomponent Batch Distillation.”*Chemical Engineering Science,* **46**, p. 1311-1326

Chiotti O. J., and O. A. Iribarren, **1989**. “An Optimization Module for Batch Distillation with Intermediate Cuts.” *Comput. in Industry*, *13***,** 169-180.

Devidyan A. G., V. N. Kira, G. A. Meski, and M. Morari, **1994**. Batch Distillation in a Column with a Middle Vessel. *Chem. Eng. Sci.*, *49* (18), 3033-3051.

Devyatikh G. G. and M. F. Churbanov. *Methods of High Purification.* Znanie**, 1976**.

Devidyan A. G., V. N. Kira, G. A. Meski, and M. Morari, **1994**. Batch Distillation in a Column with a Middle Vessel. *Chem. Eng. Sci.*, *49* (18), 3033-3051.

Diwekar U. M., K. P. Madhavan, R. E. Swaney, **1989**. "Optimization of Multicomponent Batch Distillation Columns."*Industrial Engineering and Chemistry* Research, **28**, p. 1011-1017.

Diwekar U. M., and K. P. Madhavan, **1991**. “Batch-Dist: A comprehensive Package for Simulation, Design, Optimization and Optimal Control of Multicomponent, Multifraction Batch Distillation Column.” *Comput. Chem. Eng.*, *12*, 833-842.

Doherty M. F., **1985**. “The Presynthesis Problem for Homogeneous Azeotropic

Distillations has a Unique Explicit Solution." *Chem. Eng. Sci*. **40**, p. 1885-1889.

Doherty M. F. and G. A. Caldarola, **1985**. "Design and Synthesis of Homogeneous Azeotropic Distillations. 3. The Sequencing of Columns for Azeotropic and Extractive Distillations."*Ind. Eng. Chem. Fundam*. **24**, p. 474-485.

Ewell R. H. and L. M. Welch. Rectification in Ternary Systems Containing Binary Azeotropes. *Ind. Eng. Chem. Res.* **1945**, *37* (12), 1224-1231.

Farhat S., M. Czernicki, L. Pibouleau, and S. Domenech, **1990**. "Optimization of Multiple-Fraction Batch Distillation by Nonlinear Programming." *AICHE Journal*, *36***,** 1349-1360.

Fidkowski Z. T., M. F. Doherty, and M. F. Malone, **1993**. "Computing Azeotropes in Multicomponent Mixtures." *Computers chem. Engng*, **17**, p. 1141-1155

Hasebe S.; B. B. Abdul Aziz; I. Hashimoto; and T. Watanabe. Optimal Design and Operation of Complex Batch Distillation Column. *Proc. IFAC Workshop*, London, **1992**.

Hindmarsh A. C. ODEPACK: A Systematized Collection of ODE Solvers. *Scientific Computing*. **1983**, 55-64.

Kondili E., C. C. Pantelides, and R. W. H. Sargent, **1993**. "A General Algorithm for Short-term Scheduling of Batch Operations-I: MILP Formulation." *Computers and Chem. Engng.*, **17**(2)**,** p. 211-227.

Koehler J., H. Haverkamp, and N. Schadler, **1995**. "Zur diskontinuierlichen Rektifikation azeotroper Gemische mit Hilfsstoffeinsatz." Submitted to *Chemie-Ingenieur-Technik.*

Lang P., Lelkes Z., P. Moszkowicz, M. Otterbein, and H. Yatim, **1995**. "Different Operational Policies for the Batch Extractive Distillation." *Computers chem. Engng., 19,* S645-S650.

Malenko Y. I., **1970a**. "Physicochemical Analysis of Fractional Distillation Diagrams. I. Theoretical Basis of Method" *Russian Journal of Physical Chemistry,* **44**, p. 824-826.

Malenko Y. I., **1970b**. "Physicochemical Analysis of Fractional Distillation Diagrams. II. Quaternary Systems" *Russian Journal of Physical Chemistry,* **44**, p. 916-919.

Malenko Y. I., **1970c**. "Physicochemical Analysis of Fractional Distillation Diagrams. III. Multicomponent (n-Component) Systems" *Russian Journal of Physical Chemistry,* **44**, p. 920-922.

Malone M. F., **1996**. Personal Correspondence.

Matsuyama H., **1975**. “Synthesis of Azeotropic Distillation Systems.” Presented at the JAPAN-US Joint Seminar, Kyoto, Japan.

Meski G. A. and M. Morari, **1993**. “Batch Distillation in a Column with a Middle Vessel.” Presented at AIChE Annual Meeting, St. Louis, paper 152a.

Petlyuk F. B., **1979**. “Structure of Concentration Space and Synthesis of Schemes for Separating Azeotropic Mixtures.” *Theor. Found. Chem. Eng*. **13**, p. 683-689.

Petlyuk F. B., V. Y. Kienskii, and L. A. Serafimov, **1977**. “Method for the Isolation of the Regions of the Rectification of Polyazeotropic Mixtures using an Electronic Computer.” *Theor. Found. Chem. Eng*. **11**, p. 1-7.

Piela P., R. McKelvey, and A. W. Westerberg, **1993**. “An Introduction to the ASCEND Modeling System: Its Language and Interactive Environment.” *J. Management Information Systems, 9,* 91-121.

Safrit B. T., A. W. Westerberg, U. M. Diwekar, O. M. Wahnschafft, **1995a**. “Extending Continous Conventional and Extractive Distillation Feasibility Insights to Batch Distillation.” *Ind. Eng. Chem. Res.*, *34*, 3257-3264.

Safrit B. T., A. W. Westerberg, U. M. Diwekar, O. M. Wahnschafft, **1995b**. “Improved Operational Polices for Batch Extractive Distillation Columns.” Tech Report EDRC 06-200-95, Engineering Design and Research Center, Carnegie Mellon University.

Safrit B. T., A. W. Westerberg, **1996**. “Algorithm for Generating the Distillation Regions for Azeotropic Multicomponent Mixtures.” To be submitted to *Ind. Eng. Chem. Res*.

Sargent R. W. H., **1994**. “A Functional Approach to Process Synthesis and its Application to Distillation Systems.” Centre for Process Systems Engineering, Imperial College of Science, Technology and Medicine.

Serafimov L. A., **1987**. “Thermodynamic Topological Analysis and the Separation of Multicomponent Polyazeotropic Mixtures.” *Theor. Found. Chem. Eng*. **21**, p.44-54.

Serafimov L. A., F. B. Petlyuk, and I. B. Aleksandrov, **1974**. “The Number of Trajectory Clusters Representing Continuous Rectification of Azeotropic Multicomponent Mixtures.” *Theor. Found. Chem. Eng*. **8**, p.847-850.

Sundaram S., and L. B. Evans, **1993**. “Synthesis of Separations by Batch Distillation.” *Industrial Engineering and Chemical Research*, **32**, p. 500-510.

Van Dongen D. B., and M. F. Doherty, **1984**. “On the Dynamics of Distillation Processes - V. The Topology of the Boiling Temperature Surface and its Relation to Azeotropic Distillation.” *Chemical Engineering Science,* **39**, p. 883-892.

Van Dongen D. B., and M. F. Doherty, **198**5. “On the Dynamics of Distillation Processes - VI. Batch Distillation.” *Chemical Engineering Science,* **40**, p. 2087-2093.

Wahnschafft O. M., J. W. Koehler, E. Blass, and A. W. Westerberg, **1992**. “The Product Composition Regions of Single Feed Azeotropic Distillation Columns.*” Ind. Eng. Chem. Res.*, *31,* 2345-2362.

Wahnschafft O. M. and A. W. Westerberg, **1993**. “The Product Composition Regions of Azeotropic Distillation Columns. 2. Separability in Two-Feed Columns and Entrainer Selection.” *Ind. Eng. Chem. Res.*, *32*, 1108-1120.

Westerberg A.W., and O. Wahnschafft, **1996**. “Synthesis of Distillation-Based Separation Processes.” To appear in *Advances in Chemical Engineering*, Academic Press, **23.**

Wu W., and T. Chiou, **1989**. "Determination of Feasible Reflux Ratios and Minimum Number of Plates Required in Multicomponent Batch Distillation." *Industrial Engineering and Chemical Research*, **28**, p. 1862-1867.

Yatim H.; P. Moszkowicz; M. Otterbein; and P. Lang. Dynamic Simulation of a Batch Extractive Distillation Process. *European Symposium on Computer Aided Process Design-2.* **1993**, S57-S63.