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Extending Continuous Conventional and Extractive Distillation Feasibility Insights to Batch Distillation

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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.

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 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 three-component constant relative volatility 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, 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 volatility mixtures. Hasebe et al. (1992) also studied the middle vessel column. They compared the separation of a three-component constant relative vola-

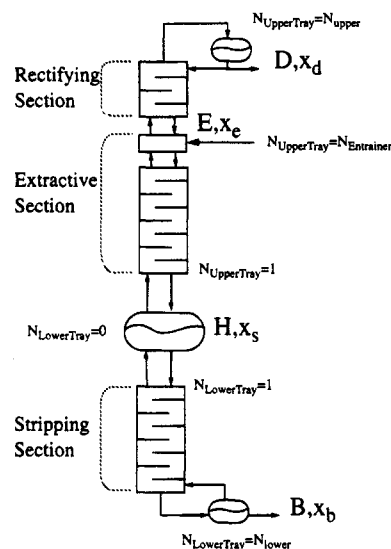


Figure 1. Middle vessel column with extractive section.

tivity system using a batch rectifier and stripper, shown in Figure 2 (parts a and b), and the middle vessel column. They optimized the operation of these columns using as an objective function the amount of product recovered per 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

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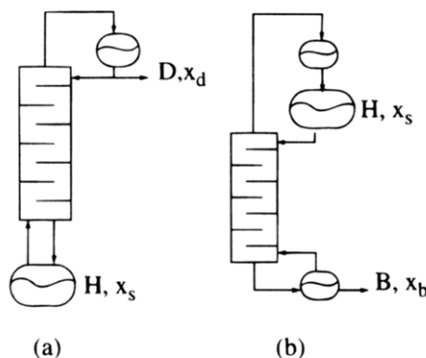


Figure 2. Batch rectifier (a) and stripper (b).

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 volatilities 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. Basic Concepts

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

$$\frac{dx_s}{d\xi} = x_s - x_d \quad (1)$$

where x_s and x_d are the still and distillate mole fractions and ξ is a dimensionless measure of time. x_s and 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 x_d and x_s . Also, the

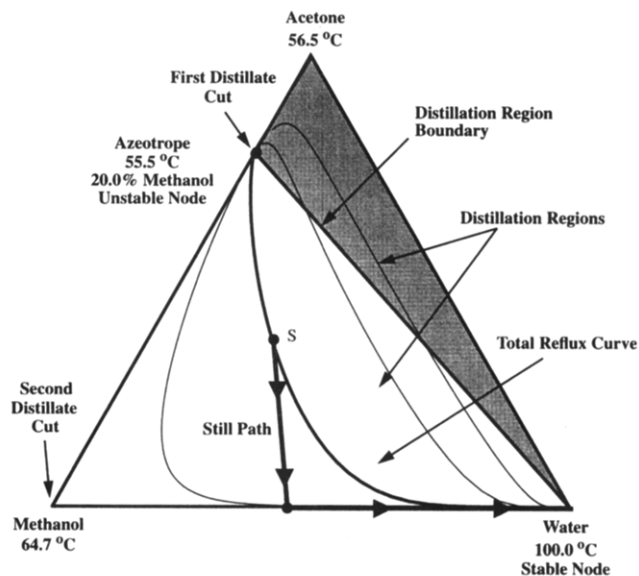


Figure 3. Product sequence and still path for batch rectifier at infinite reflux and trays.

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 3 shows an 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 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 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. 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.

2.3. 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 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 three-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

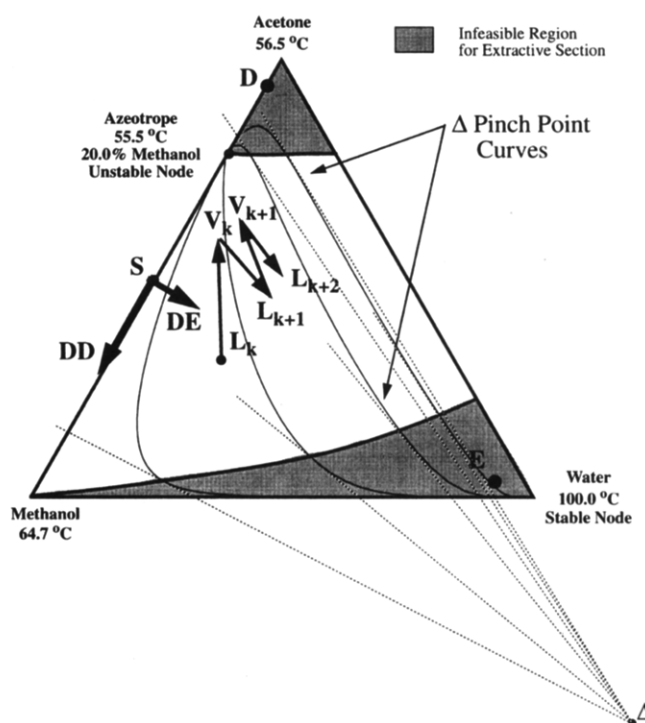


Figure 4. Δ pinch point curves for acetone/methanol/water.

section will carry out the required separation and areas in which the section will not work as required. Figure 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:

$$V_{j-1} + E = D + L_j \quad (2)$$

$$V_{j-1} - L_j = \Delta \dots (D > E) \quad (3)$$

$$L_j - V_{j-1} = \Delta \dots (E > D) \quad (4)$$

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. $\Delta = D - E$ (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:

$$x_{\Delta}^i = \frac{Dx_d^i - Ex_e^i}{D - E}, \quad i = 1 \dots \text{NC} - 1 \quad (5)$$

For example, we have a Δ point and some arbitrary extractive tray composition, L_k , shown in Figure 4, and we take an equilibrium step to produce V_k , the vapor coming up from this tray. Then, given eq 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

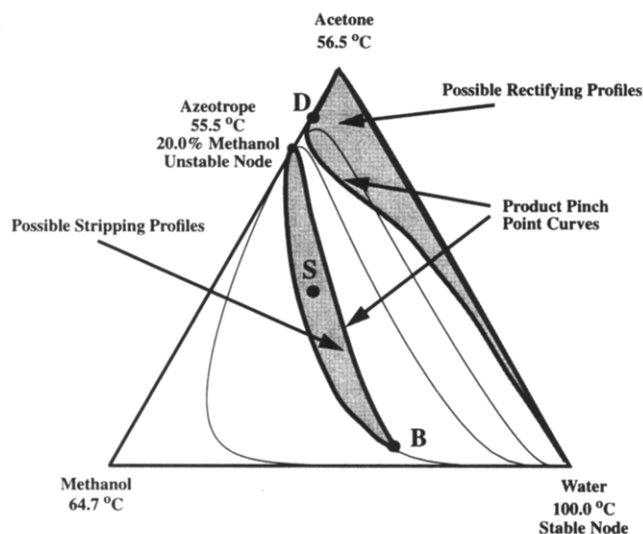


Figure 5. Infeasible middle vessel column specification.

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 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 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. 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 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.

3. Insights into Batch Distillation

3.1. Feasible Product and Possible Column Profile Regions. The analysis presented in section 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 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

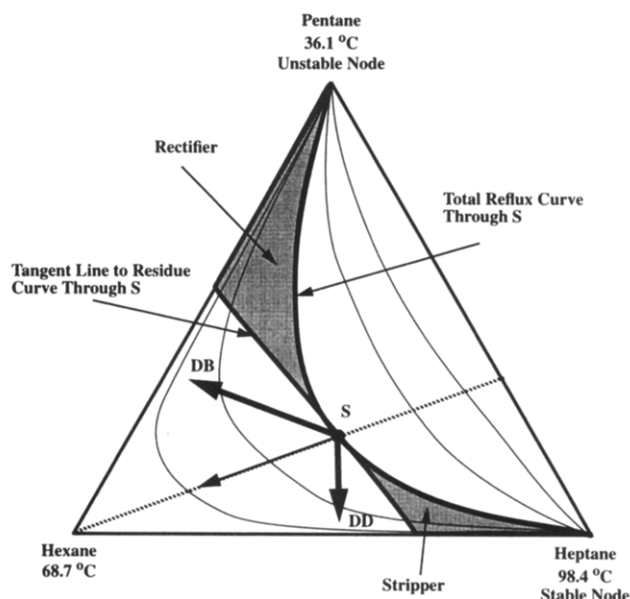


Figure 6. Feasible product regions for batch rectifier and stripper.

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 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 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 6 also shows the shaded region of possible bottoms products for the specified still composition.

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 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 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. 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 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 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 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.

3.2. Steering the Middle Vessel Still Composition. As mentioned earlier, it is possible to separate a three-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 is a function of the distillate, bottoms, and still compositions. From the overall component mass balance,

$$\frac{d}{dt}(Hx_s) = -(Dx_d + Bx_b) \quad (6)$$

we see that the direction of the still path is in a direction opposite to that of the combined directions of x_s to x_d and x_s to 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 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 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 three-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.

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 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 4), and the entrainer pulling the still composition toward the water vertex (DE in Figure 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 three-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

Table 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. Column Parameters

column type	N_{Upper}	N_{Lower}	$N_{\text{Entrainer}}$	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

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.

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 1. We integrated the columns using ASCEND (Piela et al., 1993), an equation-based modeling system, and the integrator LSODE (Hindmarsh, 1983). Table 2 shows the column parameters used for the simulations, while Figure 1 shows how we numbered the column trays.

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 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

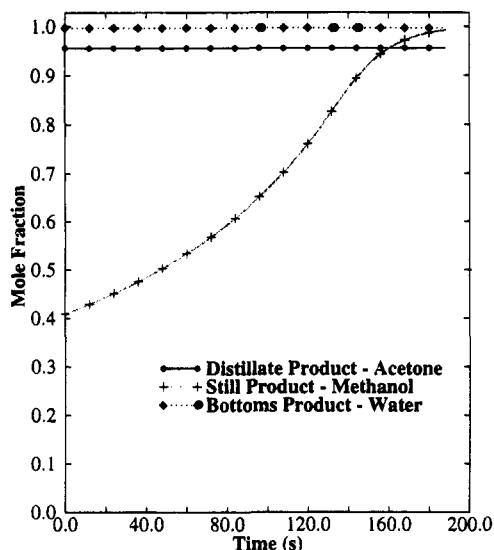


Figure 7. Products from extractive middle vessel column.

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

$$\frac{Dx_d(\text{acetone})}{x_s(\text{acetone})} = \frac{(B - E)x_e(\text{water})}{x_s(\text{water})} \quad (7)$$

where D , S , B , and E denote the distillate, still, bottom, and entrainer compositions and flow rates. Equation 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 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 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 (eq 7) we used was rather simple, and we could have used a much more complicated algorithm in the case where the infeasible extractive

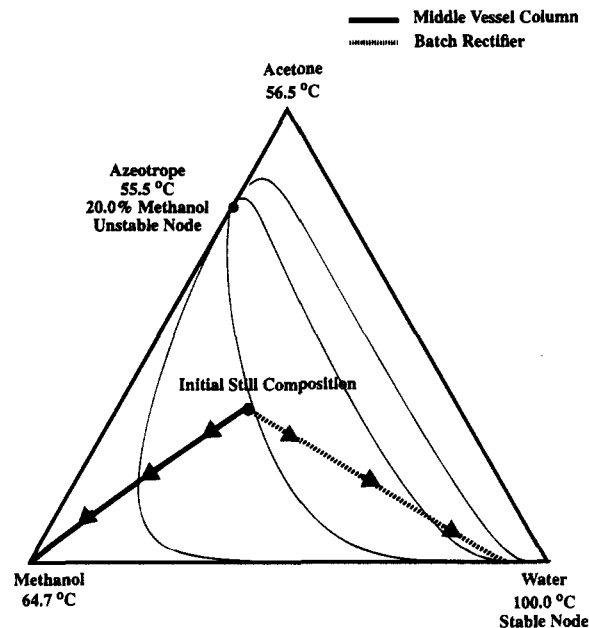


Figure 8. Still paths for extractive batch columns.

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. 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 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.

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

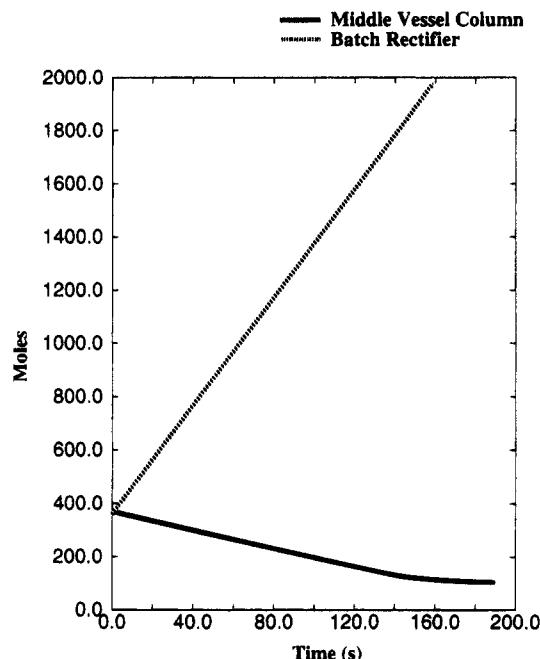


Figure 9. Still pot holdups in extractive batch columns.

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.

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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
 $N_{\text{Entrainer}}$ = 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

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