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**Collocation Methods for Distillation
Design II: Minimum Reflux**

Robert Huss

EDRC 06-197-95

COLLOCATION METHODS FOR DISTILLATION DESIGN II: MINIMUM REFLUX

Robert S. Huss and Arthur W. Westerberg

Abstract

In this second paper on collocation methods for distillation design, we address the minimum reflux problem. Existing minimum reflux techniques do not work for nonsharp splits, as they use approximate geometric criteria to simplify modeling of minimum reflux conditions to a set of pinch point calculations for sharp splits. Collocation allows exact calculation of nonsharp minimum reflux and provides the missing link that geometric criteria replace.

We examine the behavior of distillation near minimum reflux and get results consistent with prior work. We also show that sensitivity of trace species drops as less sharp splits for the key components are sought.

We have found that collocation can be applied to sharp split minimum reflux problems, but we cannot exactly reproduce Underwood's values for constant relative volatility systems due to breakdown of the model near saddle pinches. We discuss the modeling of minimum reflux conditions with collocation and discuss the difficulties we have encountered.

We can accurately calculate minimum reflux for nonsharp splits for nonideal systems, even when approaching a sharp split. We overestimate the minimum reflux for the sharp split case, using nonsharp calculations at very low impurities. We encourage discussion of the problems we have encountered.

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Introduction

Several researchers have explored and developed collocation for distillation column modeling. In the first paper in this series, we presented a collocation model which expands on prior models, addressing the problems specific to steady-state, continuous columns. In this paper we discuss use of the collocation method for minimum reflux determinations.

Minimum reflux determination is useful during the early stages of distillation design and for approximate design methods. Several methods of varying complexity and accuracy exist for determining minimum reflux. Underwood's [1945,1946,1948] method is very quick but is accurate only for ideal systems and only for sharp splits. As described in the motivation section of paper I in this series, Doherty and coworkers,[1990,1991] have done a great deal of work on distillation design and minimum reflux. Their methods rely on approximate geometrical conditions to remove the need for infinite column section calculations. The development of their techniques demonstrates how nonsharp splits should be handled, but their minimum reflux algorithms were developed only for sharp splits.

For sharp splits, Koehler et al. [1991] developed a minimum reflux determination method that uses a reversible distillation model. They have shown that for nonideal and azeotropic systems their method provides accurate results, based on comparisons to rigorous column models with a large number of trays. However, their method requires the nonkey components to be nondistributing and is based on the same geometric considerations in Doherty and coworkers.

We present an approach for minimum reflux calculations that does not require approximate geometric constraints. We discuss some interesting insights as one moves from nonsharp to sharp splits. We also discuss computational difficulties we found in realizing the theory with collocation models. By presenting both the strong and weak points of collocation for distillation

modeling we hope to initiate discussions leading to better methods.

Pinch Points

When a distillation section has a very large number of trays in it, a region of constant composition occurs. The liquid and vapor passing each other approach being in equilibrium with each other, i.e., they approach being pinched. Minimum reflux occurs when at least one column section is pinched. When modeling minimum reflux conditions, "pinch point" calculations can sometimes remove the need for tray-by-tray models of column sections. A pinch point is calculated by requiring that the liquid and vapor passing each other are in equilibrium and in mass and heat balance with the other end of the distillation section. Therefore, if one half of a column has a large number of trays and is pinched adjacent to the feed tray, the whole section can be modeled with only a pinch point calculation. This simplification can be exploited for calculation of minimum reflux.

Nonsharp Splits

A separation where all the components are distributed in some amount to both products is nonsharp. In the case of a nonsharp split, there is a feasible intersection region where the tray by tray trajectories from the top and bottom product can intersect [Wahnschafft 1992]. Figure 1 shows a ternary diagram for a nonsharp minimum reflux problem. The regions between the infinite reflux (distillation) and minimum reflux (pinch point) curves for both the top and bottom products are the only feasible regions where the trajectories can go. The darkened region that shows the intersection of the feasible space for the top and bottom trajectories shows the only feasible region for the feed tray. At minimum reflux, the bottom section will pinch in this region. Figure 2 shows a blowup of this region. Any trajectory from the bottom of the column will terminate on the pinch point curve as the number of trays increases. As the trajectory from the bottom of the column moves to the right, the reboil ratio (R) increases. However,

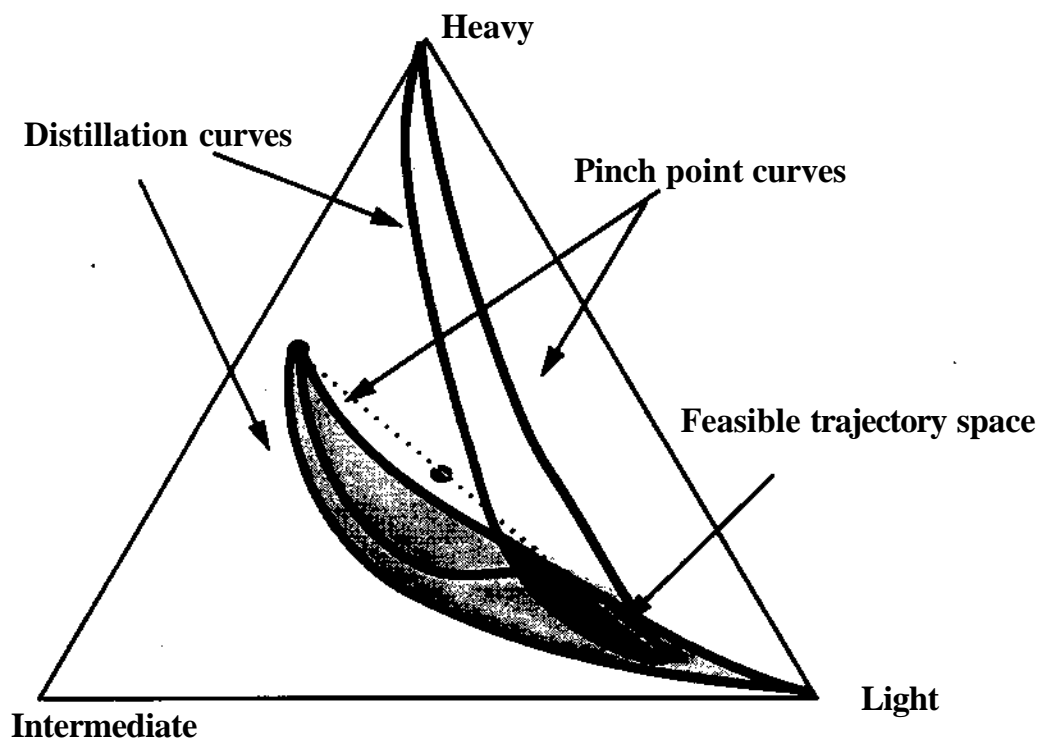


Figure 1. Pinch behavior for ternary nonsharp split

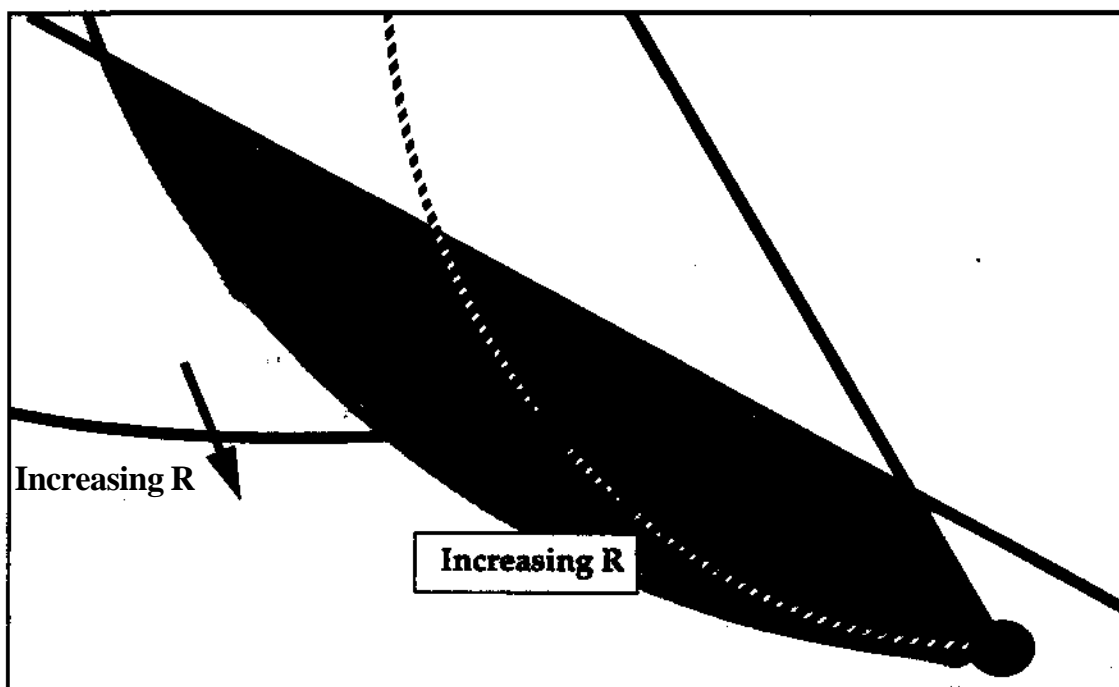


Figure 2. Blowup of Figure 1

for the top section, the pinch point curve, representing the lowest reflux ratio (R) is on the right, and the infinite reflux curve is on the left. Therefore along the pinch point curve for the top half, the left most point corresponds to minimum \bar{R} , but maximum R , and the right most point corresponds to maximum \bar{R} and minimum R . However, R and \bar{R} are linked by the mass balances and quality of the feed.

$$V = \bar{V} + (1-q)F \quad (1)$$

$$(R+1)D = \bar{R}B + (l-q)F \quad (2)$$

For any given feasible column, R and \bar{R} will decrease or increase together. Assume that the grey point is a feasible intersection point. To decrease both R and \bar{R} the column must move towards the pinch point curve. Therefore, we know that the nonsharp minimum reflux solution for this type of problem will have a pinched bottom section and a finite top section. At some point along this line, R and \bar{R} will correspond to a feasible trajectory from the top of the column. The minimum requirement to model this system is a pinch calculation from the distillate, then a feed tray model, and then a tray-by-tray or reduced order model for the bottom half of the column. We use the standard collocation model in our first paper [Huss and Westerberg, 1995a] by enforcing a pinch at the junction of the two bottom collocation sections and calculating the number of trays in the top section.

Figure 3 shows how this modeling requirement maps onto the standard collocation model. We enforce a pinch between sections 3 and 4 by adding equations forcing the liquid and vapor passing each other at the junction between the two collocation sections to be in equilibrium and removing the requirement that the liquid stream at the pinch must be on the polynomial for section 4.

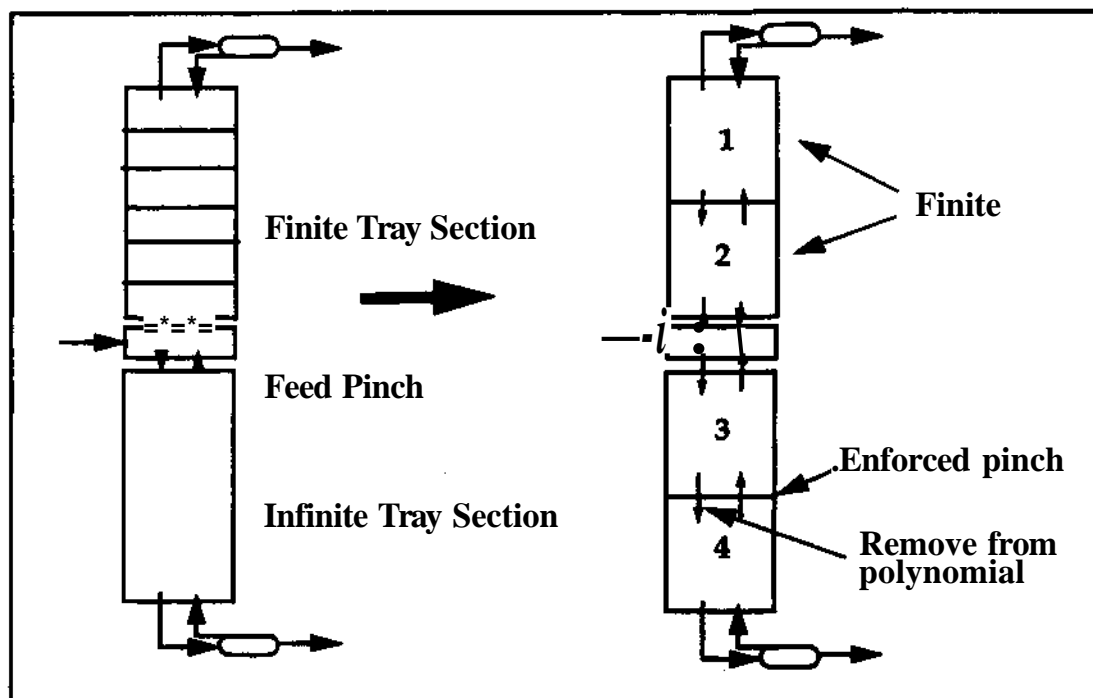


Figure 3. Mapping of nonsharp minimum reflux on to standard collocation model

Section 3 will have completely flat trajectories. We evenly split the number of trays needed in the top section between collocation sections 1 and 2. The number of trays in the top section is solved for when we completely specify the distillate. Note that this example is for a direct separation, splitting between the lightest component and the intermediate. For an indirect separation, splitting between the heaviest component and an adjacent intermediate, the column structure would be inverted, but the solution method the same.

Sharp Splits

When a sharp split is specified, one assumes that the non-key components are nondistributing. This forces a saddle pinch, since it takes an infinite number of trays to completely remove a component. Figure 4 shows the trajectory for such a case. When there is a saddle pinch, the pinch point is not adjacent to the feed because it takes an infinite number of trays to remove the nondistributed components from the feed as well as an infinite number of trays to get from the

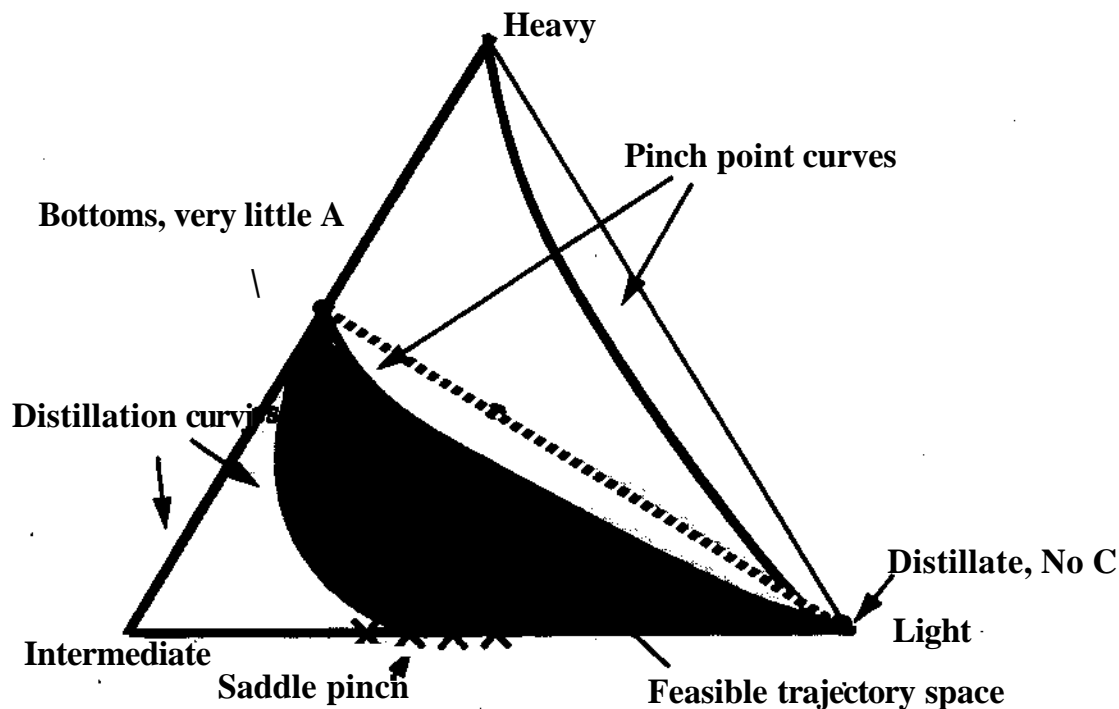


Figure 4. Pinch behavior for ternary sharp split

product to the pinch. When the pinch is not adjacent to the feed, a simple pinch point calculation is not sufficient. A pinch point calculation could determine the possible saddle pinch points, but any saddle pinch which is in mass balance with the top of the column will necessarily be in mass balance with the feed tray. The X's in Figure 4 show multiple saddle pinch points. The pinch points move to the left as the reflux ratio increases. These points represent the binary pinch point curve between the light and intermediate. There is some missing connection between the correct saddle pinch and the feed tray. Levy et al. [1985] noticed that for ideal three component systems, the saddle pinch point, the feed tray pinch point and the feed composition are colinear for sharp splits. They used this colinearity to identify the correct saddle pinch point. For more components, Julka and Doherty [1990] required that a set of pinch points, the feed composition, and the feed tray must be in a minimum volume. Kohler et al. [1991] used a minimum angle criterion for multi-component systems to achieve the same effect.

The missing connection is actually an infinite set of stage-by-stage calculations connecting the saddle pinch and the feed tray, i.e., the saddle pinch and the feed tray must lie on the same tray by tray trajectory. We proposed that a collocation model could approximate these calculations. We describe the details of our collocation methods in full detail in the first paper of this series. When defining the polynomials in terms of stage location, it is impossible to model an infinite column section because the polynomials explode as the number of stages increases. However, by performing a variable transformation on stage number, as shown in equation 3, we can write the polynomials in terms of a bounded variable. The transformation variable z will go to 1 as s goes to infinity.

$$z = 1 - e^{(-as)} \quad (3)$$

We must show that a stage-by-stage trajectory from this pinch point leads to both the top product and the feed tray. Therefore, we need an infinite column section model. This can be achieved by collocating and doing a variable transformation on the tray number so that, as the tray number goes to infinity, the reference variable goes to some finite value.

Shortcut methods that require a sharp split determine a theoretical minimum reflux for the case where the non-key components are non-distributing. However, the actual column will not achieve this theoretical split. The minimum reflux for the actual separation will be different than that for the non-distributing sharp split. Levy et al. [1985] has shown that minimum reflux decreases sharply as the impurity of the heavy nonkey decreases from 10^{-5} to 10^{-11} .

Figure 5 shows how the sharp split problem maps onto the standard collocation model. It is very similar to the nonsharp case, but we want sections 1 and 2 to bring us as close to the saddle pinch as they can. We have found that we cannot enforce a saddle pinch in the same manner as the feed pinch. When slack

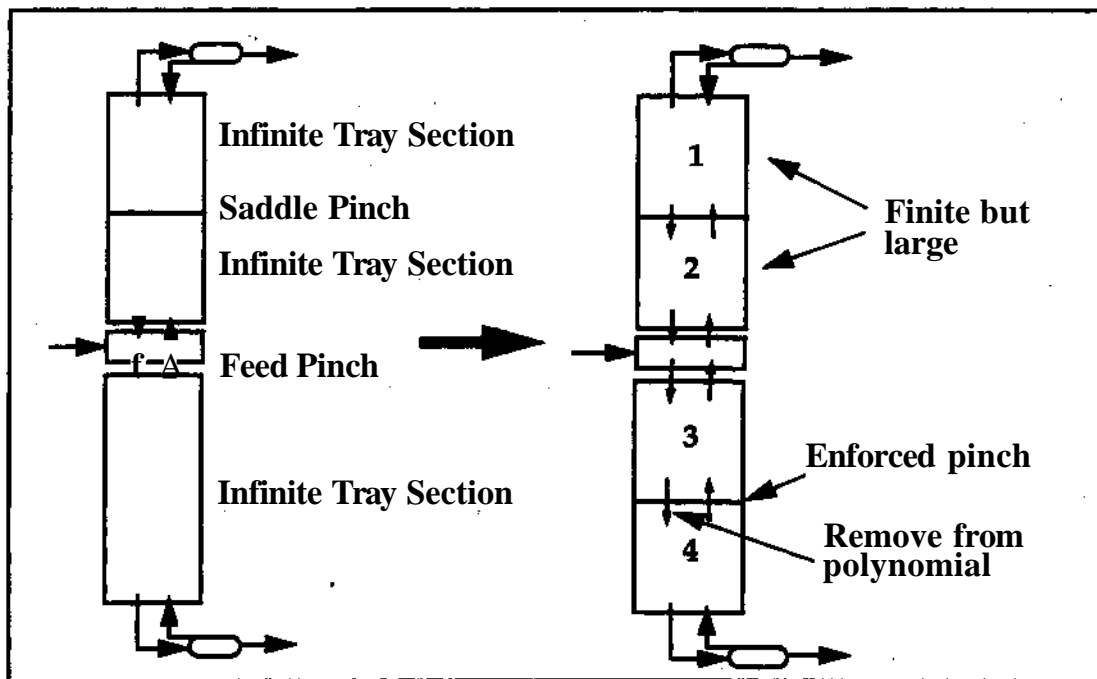


Figure 5. Mapping of sharp minimum reflux on to standard collocation model

variables are added to the equilibrium equations for the pinch point, we find that we can approach the pinch, but we cannot force the slack variables completely to zero. Inaccuracies occur that we cannot compensate for, which we will discuss later in the paper. Therefore, we approximate a sharp split minimum reflux by simulating a large column section. The number of trays needed to approximate an infinite number of trays is dependent on the relative volatilities. For components with large relative volatilities, only a few trays are necessary to approximate an infinite number of trays. Also, for multicomponent problems where a saddle pinch occurs in both column sections, we use the standard collocation model with all four collocation sections as large as possible.

Trends of Large Column Sections

We did many examples with constant relative volatility to compare with Underwood's method. We tested three ternary systems over a range of separations. We examined systems with relative volatilities of 1.5,1.2,1.0;

3.0,2.0,1.0; and 9.0,3.0,1.0.

In each test, we did a direct split, forcing a pinch adjacent to the feed in the bottom of the column, and determining the reflux vs. the number of trays in the top section. For every case, it was possible to get exactly Underwood's value of the reflux ratio with some finite but large number of trays in the top. However, it was also possible to increase the trays and get lower than Underwood's reflux ratio. When increasing the trays to larger numbers, the trajectory became unsmooth, suggesting that the model was no longer accurate.

Figure 6 shows the different reflux ratios for various recovery specifications on the light and heavy key obtained by increasing the size of the top section of the column, for the relative volatilities of 3,2,1. The large points mark the number of trays and reflux required to get various levels of impurity of the heaviest component in the distillate. These represent nonsharp minimum reflux calculations. Beyond 10^{-9} is below the error tolerance so we cannot determine nonsharp minimum reflux for these points as anything other than the answer determined for 10^{-9} . We can continue to increase the number of trays and get smaller values for the reflux ratio. The straight lines indicate the Underwood value for the various recoveries. For each recovery specification, some number of trays will give us exactly Underwood's value, but for even more trays we go below Underwood.

Figure 7 shows how the minimum reflux decreases in increasing amounts as you reduce the impurity. The grey points at zero are the Underwood values. From this plot we can see that a straight line extrapolation from two points with impurities of 10^{-7} and 10^{-8} will overestimate the minimum reflux. The degree of the overestimation depends on the degree of separation between light and heavy key.

For nonideal systems, the techniques are the same as above. However, we

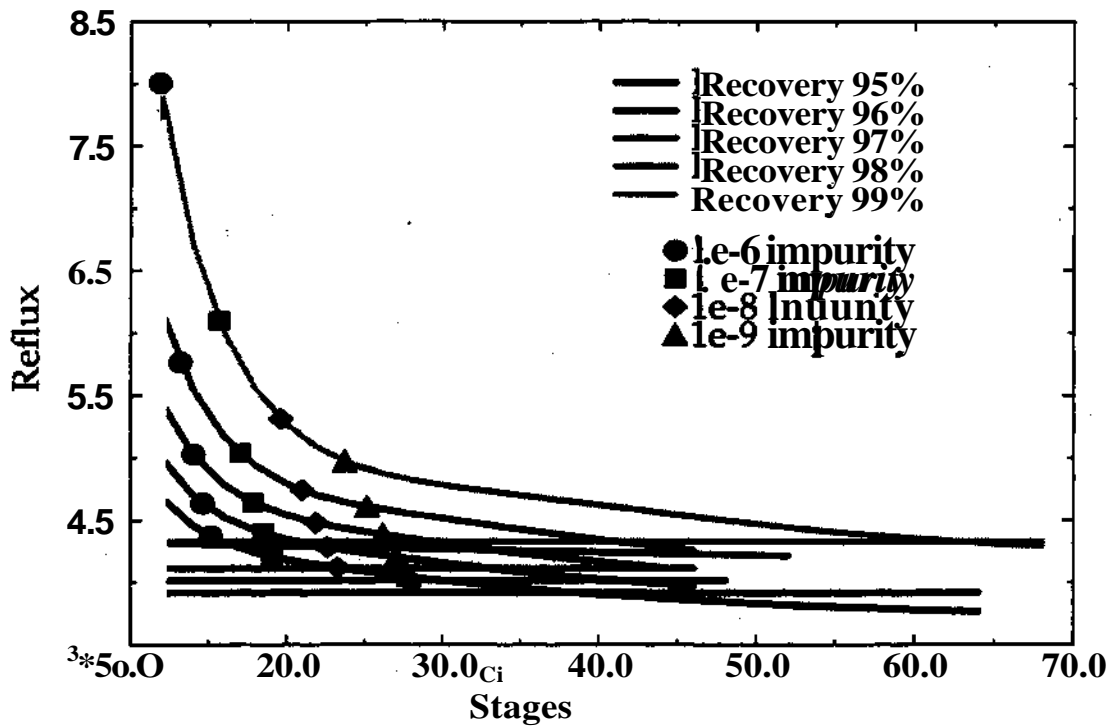


Figure 6. Increasing trays and reducing reflux Relative volatilities (3,2,1)

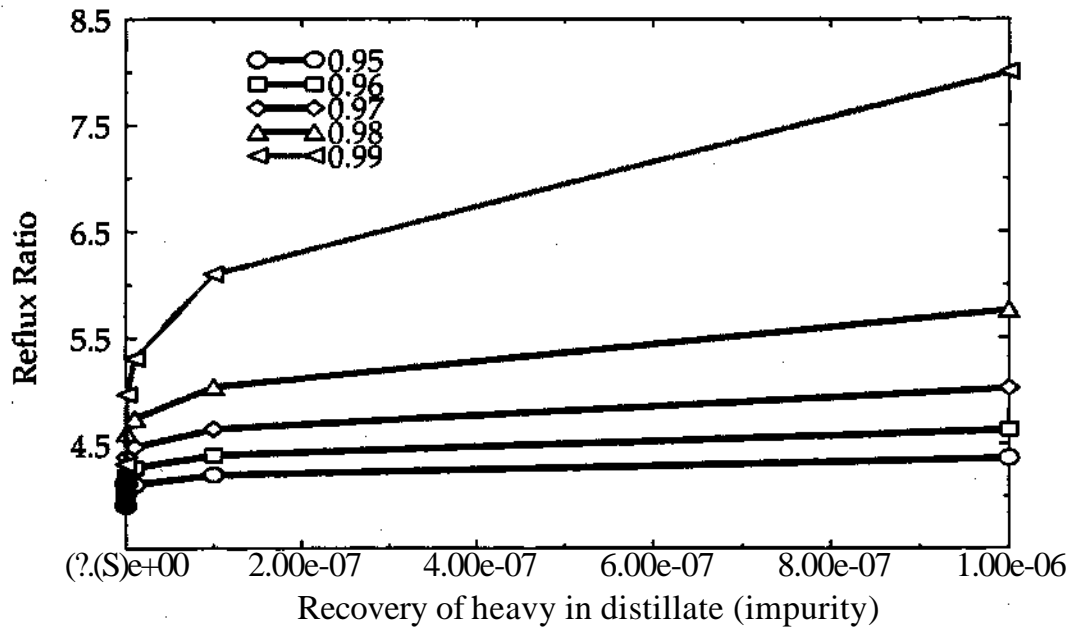


Figure 7. Reflux ratio vs. impurity of heavy component.

have no Underwood value to compare to. For nonideal systems we have successfully enforced pinches adjacent to the feed, allowing many nonsharp minimum reflux determinations. For sharp splits, the behavior was similar to the ideal examples, with inaccuracies forming at large numbers of trays. Figure 8 shows several column trajectories for nonsharp minimum reflux calculations for a propanol, isobutanol, butanol system, where propanol and isobutanol were the light and heavy key respectively. Recoveries of the light and heavy key in top and bottom respectively were 0.8,0.9,0.95, and 0.99 for the four diagrams. For each example, we varied the recovery of the heavy component, solving for the number of trays required in the top half of the column. The bottom half of the column was pinched adjacent to the feed, similar to the example shown in Figure 1. Note that the last curves of plots (a) and (b) demonstrate the poor trajectories that can occur when getting close to the saddle pinch.

Figure 9 shows the reflux ratio as a function of the impurity of the heavy component for each recovery. For lower recoveries the effect of the amount of impurity on the reflux ratio becomes smaller. For the 80% recovery example, the sharp split minimum reflux could be extrapolated to zero with very little error. However, for the 99% recovery the effect of the impurity is large, so we cannot be sure how much we are overestimating the minimum reflux for a sharp split.

Figures 7 and 9 demonstrate how nonsharp minimum reflux calculations can be useful for sharp split requirements. As Levy et al. [1985] showed, the reflux ratio can be very sensitive to the impurity of the nondistributing component. However, for lower recoveries, this sensitivity decreases significantly. Even for relatively high recoveries, we can extrapolate nonsharp minimum reflux calculations with low impurities and at worst slightly overestimate the minimum reflux ratio.

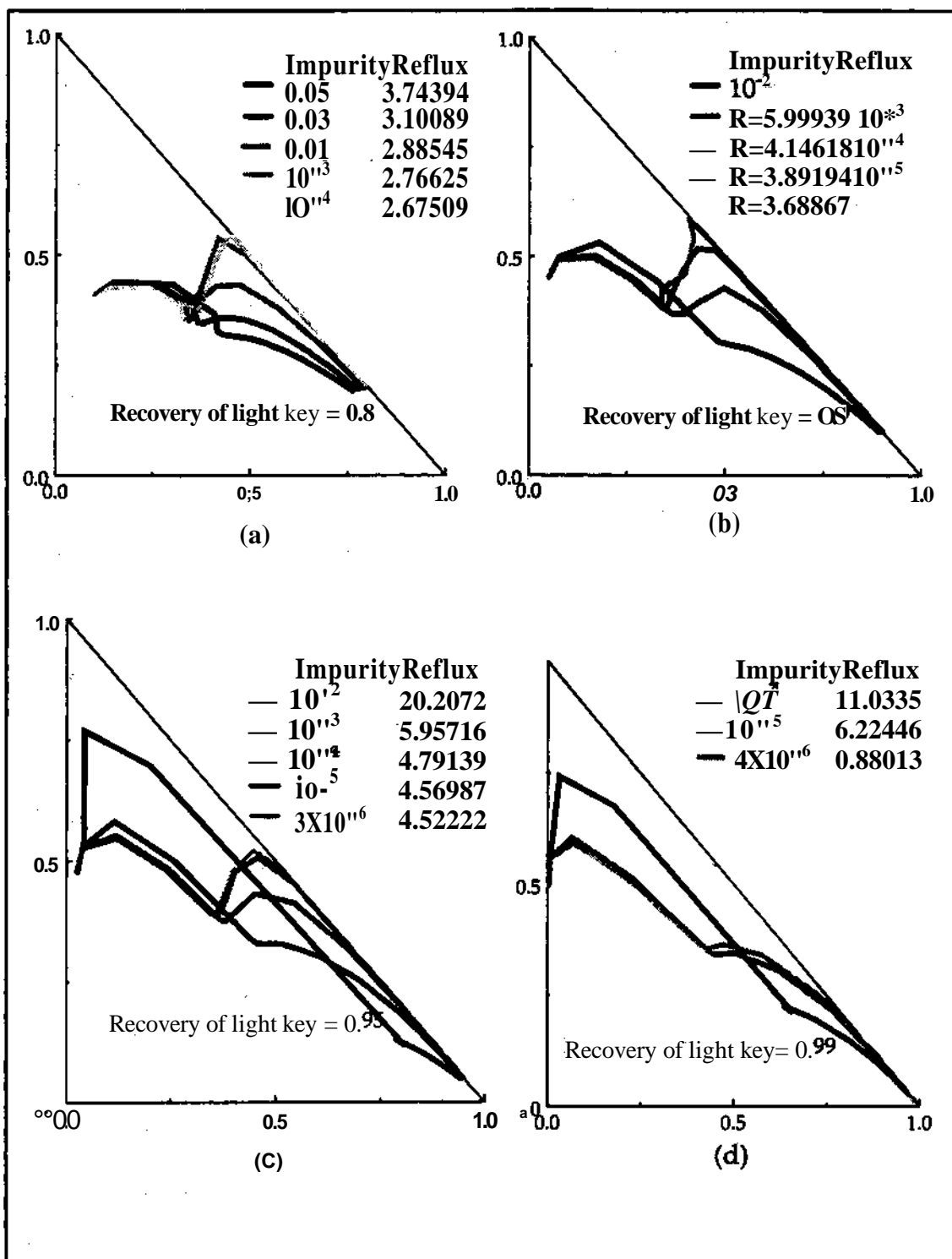


Figure 8. Several nonsharp minimum reflux calculations for propanol, isobutanol, butanol system, for varying recoveries and impurities of heavy component

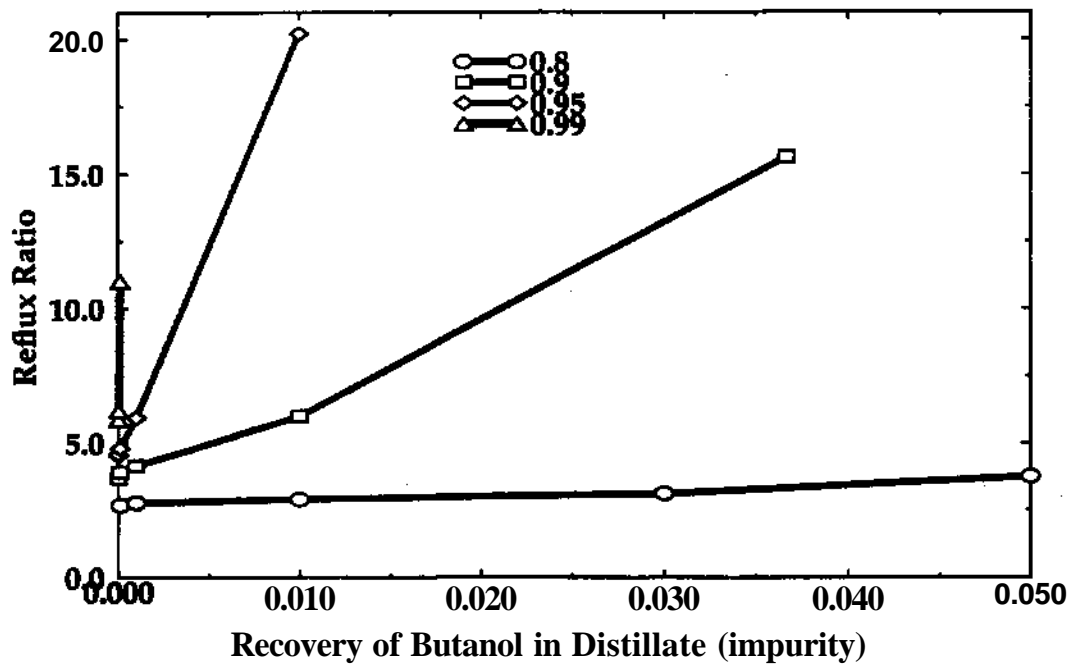


Figure 9. Reflux as a function of impurity of butanol for propanol, isobutanol, butanol system.

Error Detection

Figure 10 is an example of the inappropriate trajectories that can occur. It shows the trajectories over the transform variable z . The top of the column is on the left. The vertical lines show the boundaries of the collocation sections. The slope of the light component becomes positive at the top of the second collocation section. This should not occur. Once this ragged sort of trajectory occurs, the model can no longer be trusted. The model converges to a nonphysical solution.

Furthermore, even when the mole fraction trajectories appear smooth, the trajectories of the transformed mole fraction may not be smooth. As we describe in the first paper of this series [Huss and Westerberg, 1995a], we perform the following transformation on mole fraction.

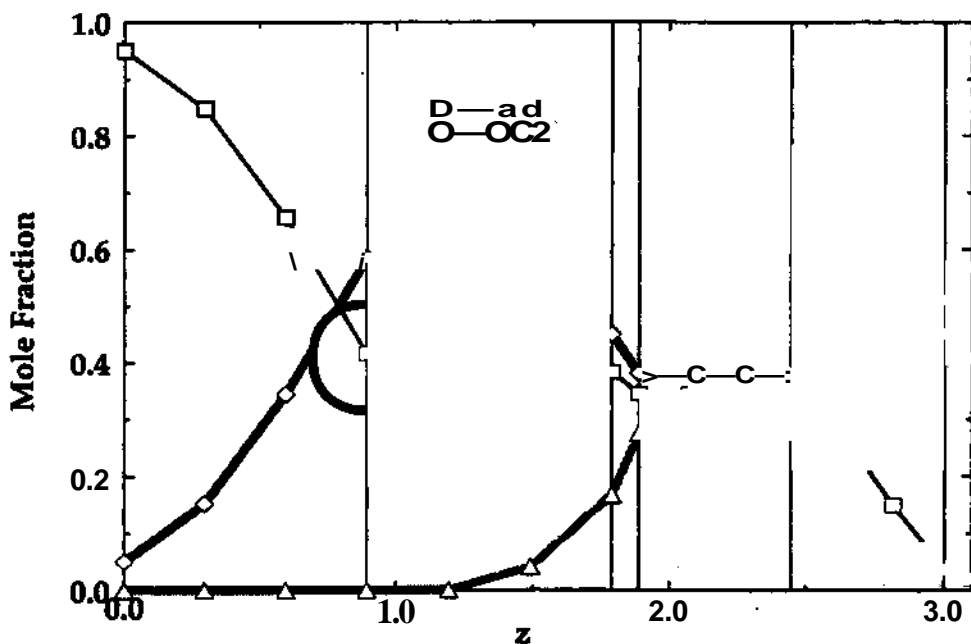


Figure 10. Example of inaccurate collocation of large column section. Relative volatilities (3,2,1)

$$2x_i - 1 = \tanh(\xi_i) \quad (4)$$

Figure 11 shows the mole fraction trajectories (x) and transformed mole fraction trajectories (\hat{x}) for the same column. The top figure looks fine, but the bottom one shows the error occurring in the trace component. One might believe that a mole fraction of less than 10^{-5} is not going to affect the model, but since we perform a variable transformation, re-emphasizing the mole fractions near zero and one, they can be very significant.

Even though we have these clear signs of inaccuracies, some of the constant relative volatility examples went below Underwood's value before the clear signs showed up. We created an extra tray in each section to test the accuracy. The test tray took its input streams from the polynomials, and we compared the output streams to the polynomial. We placed the test tray near the

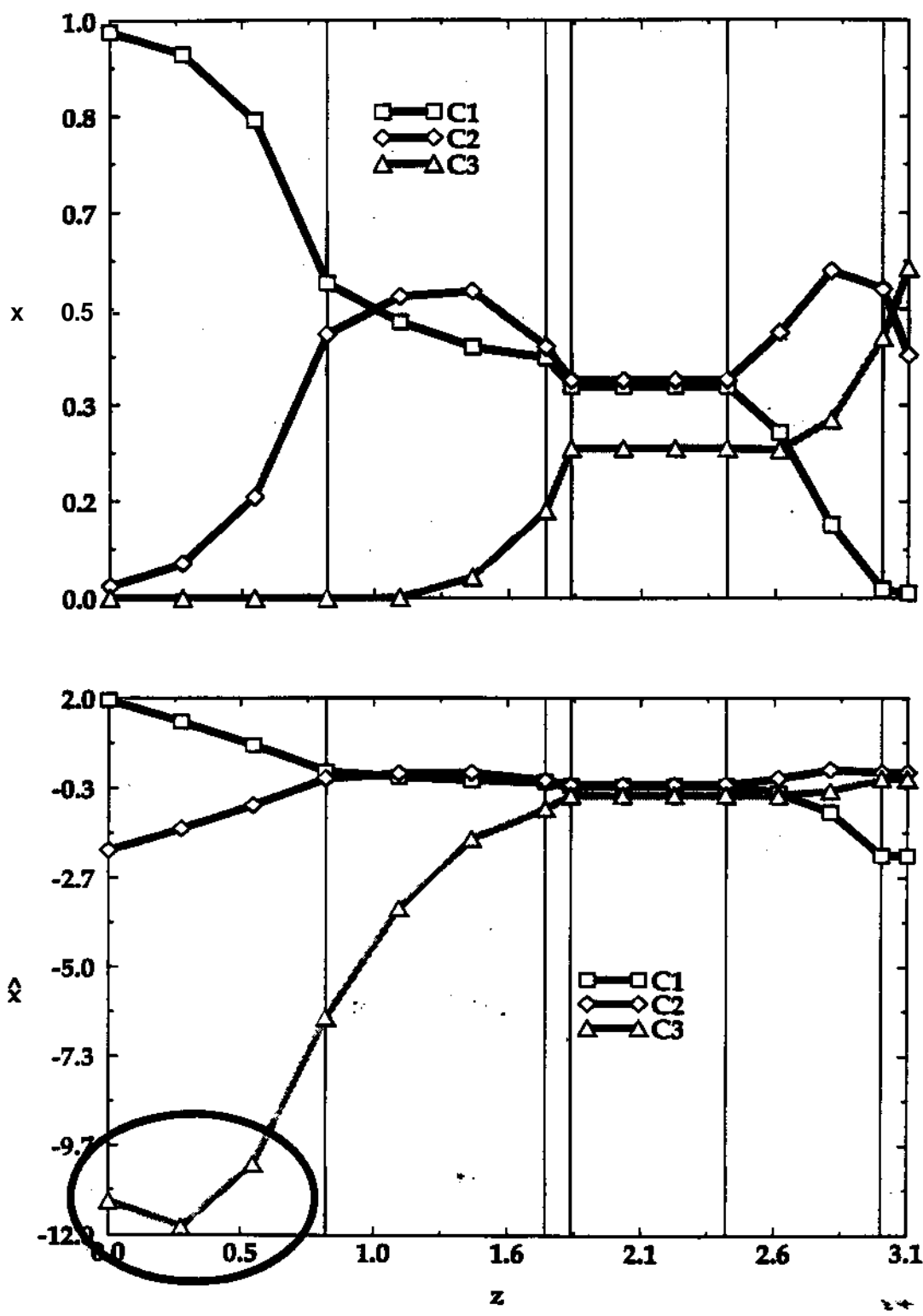


Figure 11. Example if inaccuracy in trace component Volatilities (3,2,1)

end of the collocation sections adjacent to the expected saddle pinch point. Figure 12 shows the error in four different polynomials, for a column recovering 98% of the light key and 2% of the heavy key in the distillate. C1 and C3 were the active components. The figure shows that C3 in section 1 (the top section in the column) is most sensitive. This error reflects the behavior we see in Figure 11. The other errors don't show any erratic behavior as the number of trays increases. Figure 13 shows the error in C3 in section 1 for several recoveries. They all display the same behavior. The error in the trace component in top section of the column should be a good indicator of the onset of inaccuracies. Combined with requirements that the light component monotonically decreases going down the column, and that the transformed trace component monotonically increases going down the column, we should detect any problems.

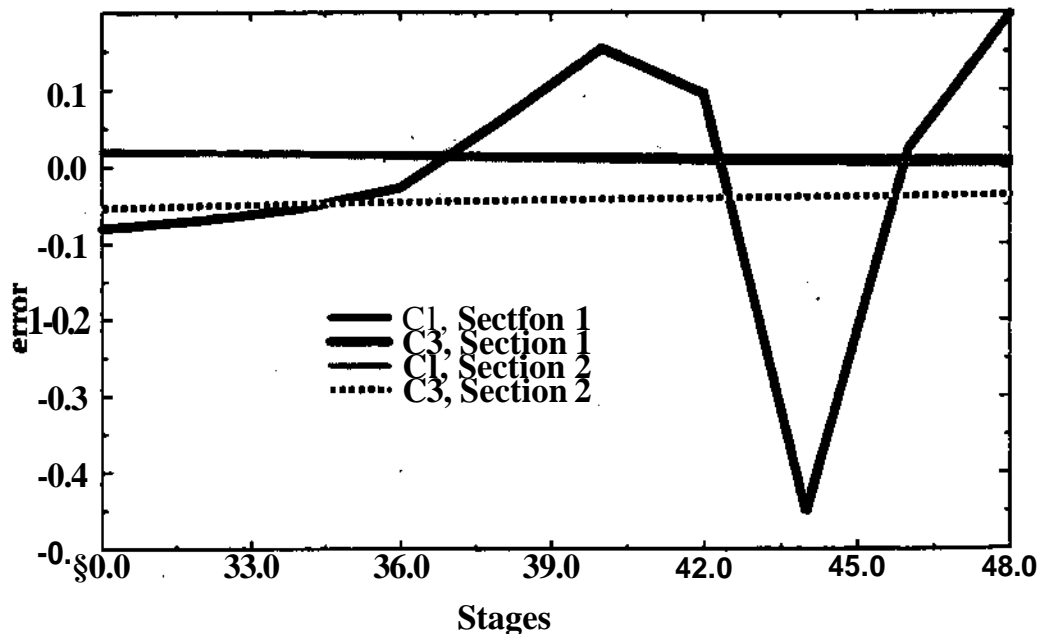


Figure 12. Error in polynomial prediction for isolated trays. Recovery of keys 98%, Relative volatilities (3,2,1)

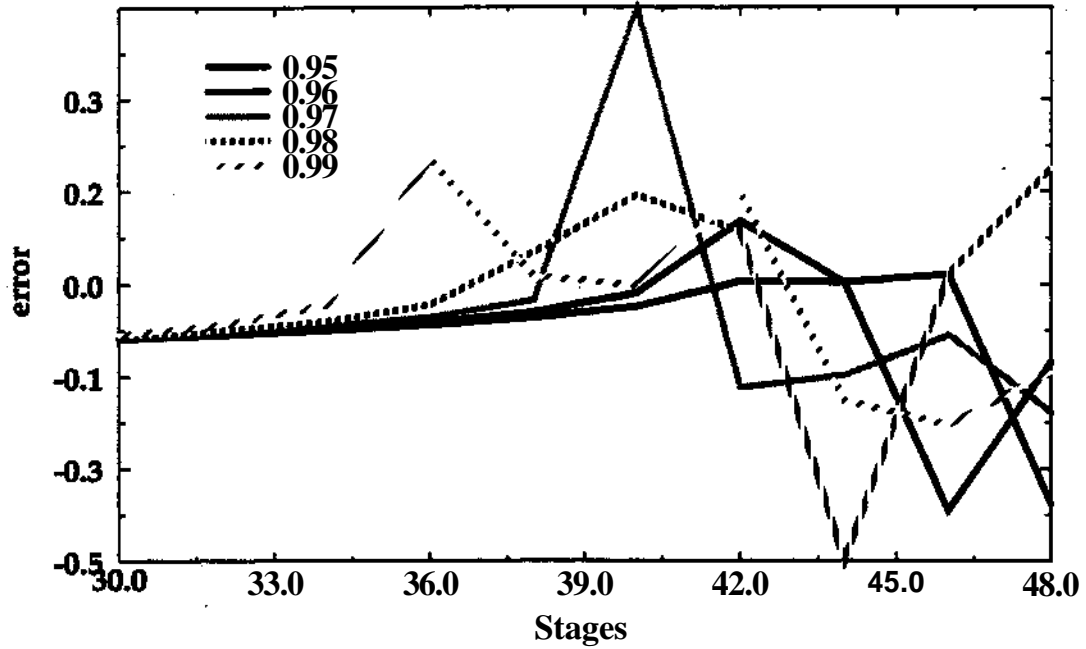


Figure 13. Error in C3, section 1 for a range of recoveries. Relative volatilities (3, 2,1)

Sharp Split Calculations

To guarantee appropriate trajectories, we added the following equations.

$$x_n^{C1} - x_{n+1}^{C1} = d \frac{J^{C1}}{n}, n = L.npoints \quad (5)$$

$$\hat{x}_n^{C3} - \hat{x}_{n+1}^{C3} = diff_n^{C3}, n = 1..npoints \quad (6)$$

We put a lower bound of zero on $diff_n^{C1}$ and an upper bound of zero on $diff_n^{C3}$. Furthermore, we place a test tray at the bottom of the top collocation section and bound the error on C3 to be between 0.1 and -0.1. Then we try to increase the number of trays as far as possible without crossing those bounds. With this technique, we tested the effect of the order of the collocation on the accuracy of

the model. Figure 14 shows the data for the 3,2,1 system, using 2,3,4, and 5 points in each collocation section in the top of the column. The plot shows reflux ratio as a function of recovery. Underwood's values are shown by the striped line. Figure 15 shows the same type of plot for the 9,3,1 system. We would expect that all the curves would at least be above minimum reflux, which is reflected in Figure 15, but the 4 point collocation in Figure 14 is below Underwood for every recovery. It is possible that error occurs in the model before the trajectories reflect this error. Figure 16 shows the same type of figure, but for 30 trays, rather than the maximum before crossing the bounds. The columns in Figure 14 each reached over 35 trays. Note that none of the models in Figure 16 are underestimating the minimum reflux, and as the number of collocation points increases we get closer to the Underwood value. This figure shows more what we would expect, getting better accuracy as the number of collocation points

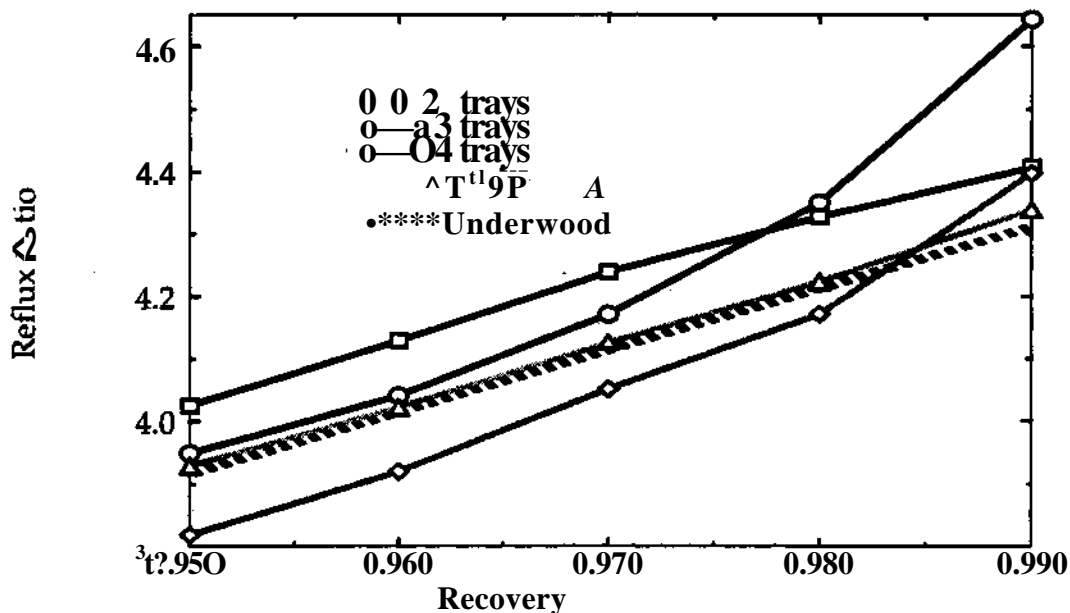


Figure 14. Reflux as a function of recovery and order. Volatilities 3,2,1

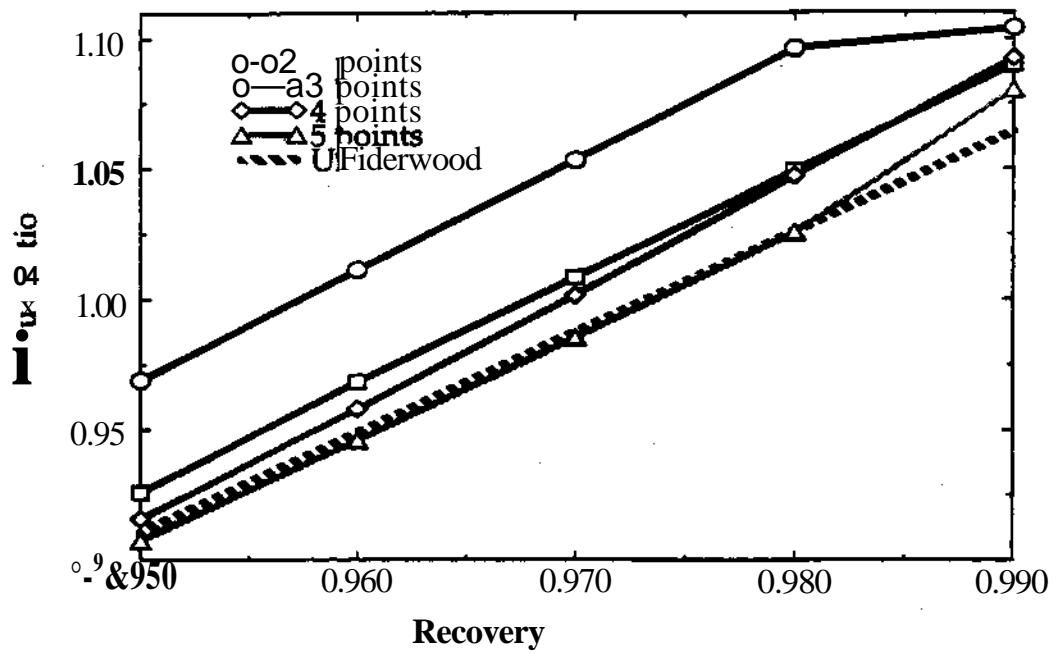


Figure 15. Reflux as a function of recovery and order. Volatilities 9,3,1

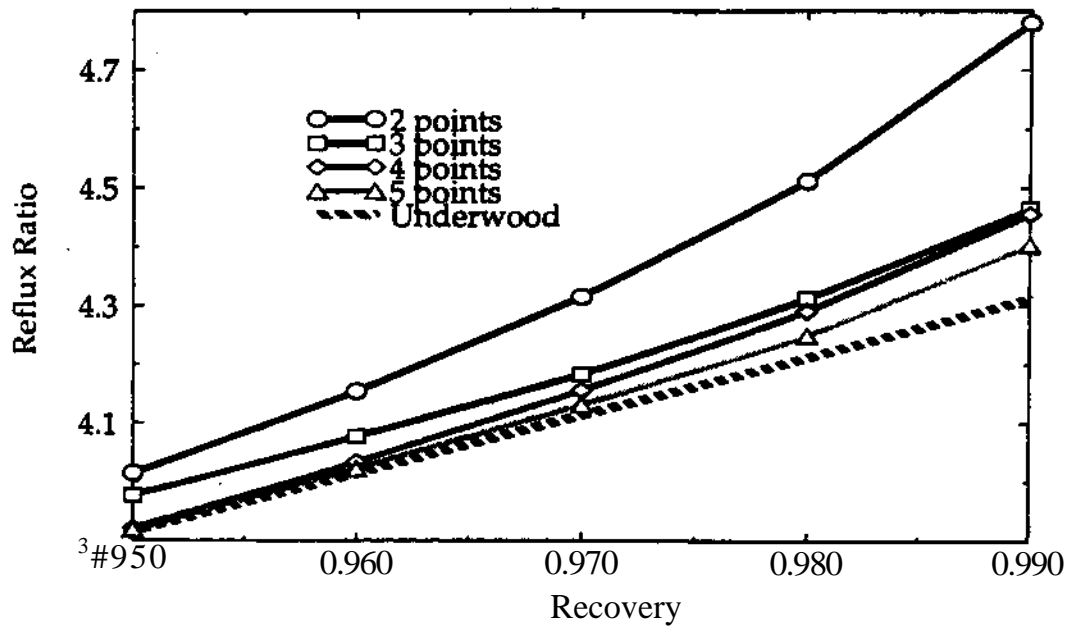


Figure 16. Reflux at 30 trays as a function of recovery and order. Relative volatilities 3,2,1

increases. It is possible that the 4 point collocation in Figure 14 is inaccurate because the fourth order polynomial produces unrealistic trajectories.

When going to large number of trays, the choice of the parameter a in equation 3 is potentially important. Experience has shown that a value of 0.1 is good for most normal problems. When we do wish to go to an infinite number of trays, ($z = 1$), it is possible to choose a such that the trajectory of one of the components is straightened out. However, our efforts to solve for the parameter a have not been successful. We have experimented with different values for a with some success. Figures 17 and 18 show the affect of a on the reflux calculations when using 2 point and 5 point collocations respectively. Each figure shows Underwood's values with a striped line and the closest approximation with a thick grey line. These figures demonstrate that 2 and 5 point collocation do not underestimate the minimum reflux when we use error detection. We believe that 2 point collocation sections are best for distillation modeling since higher order

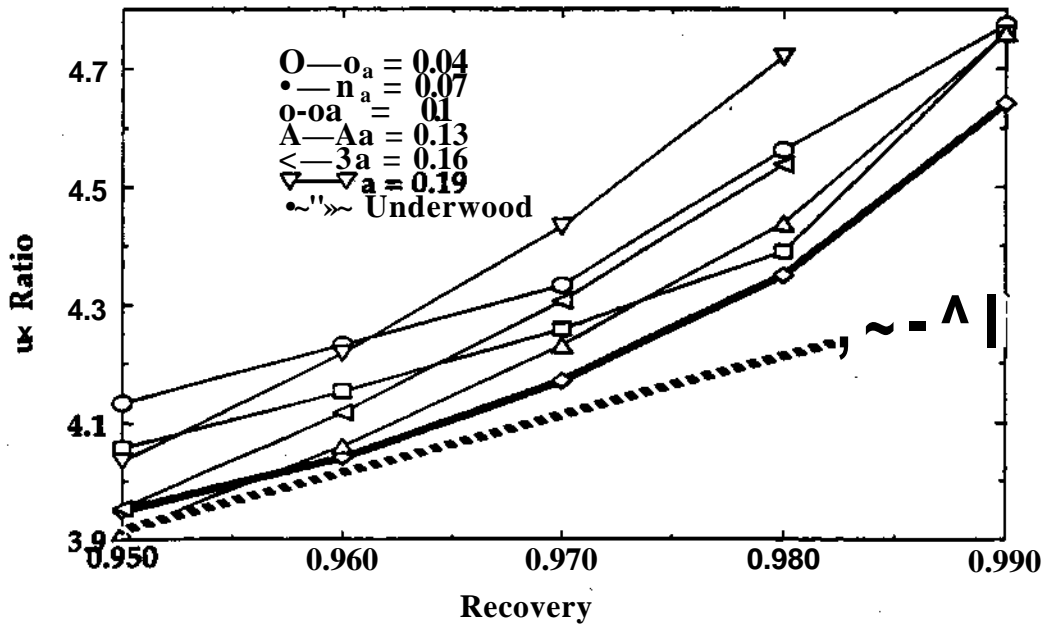


Figure 17. Effect of parameter a on reflux determination with 2 collocation points.

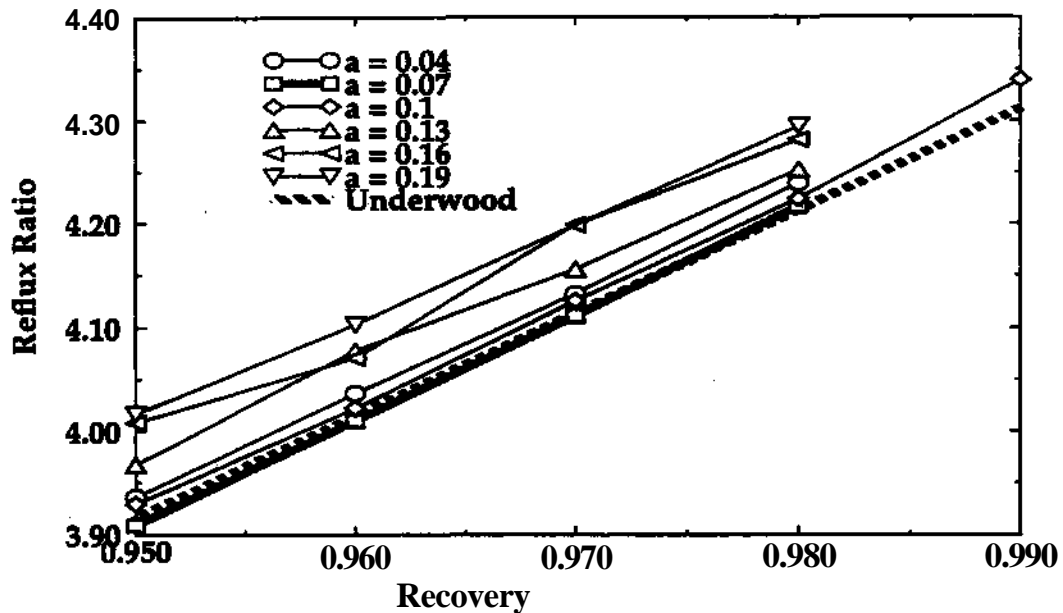


Figure 18. Effect of parameter a on reflux determination with 5 collocation points

polynomials can have trajectories that are not realistic for distillation. However, the 5 point collocation demonstrates how the accuracy can be improved with very high order, and what the trend of collocation will be if it is accurate.

Minimum Reflux Algorithm

Figure 19 shows the suggested algorithm for minimum reflux calculations using the collocation model. The first step, solving the standard collocation model to full equilibrium and heat balance is described in more detail in the third paper of this series [Huss and Westerberg, 1995b]. Through this step, we get a fully thermodynamic, heat balanced model of a very small distillation column with low reflux. If a pinch adjacent to the feed is expected, we enforce it, short circuiting the collocation section between the pinch point and the end of the column. The number of trays in this half of the column is no longer important, but to get nice looking column profiles, we fix the average slope of one of the components in that section and free up the number of trays. We discuss this

technique in detail in the third paper of this series [Huss and Westerberg, 1995b]. If no pinch adjacent to the feed is expected, we go directly to the next step, meeting the recovery specification. Again, see the third paper of this series for a detailed discussion of this technique. We free up the reflux ratio, distillate flowrate, and number of trays top and bottom while incrementing the recovery of the key components. The average slope technique mentioned above determines the number of trays in each column section.

For nonsharp splits, the only remaining step is to fix the recovery of a third component and solve for the number of trays in the finite column section. For a sharp split, we recommend two steps. First, we increase the number of trays in each section where a saddle pinch is expected, enforcing the bounds described above. This may not work for azeotropic systems. For azeotropic systems, the user would have to look at the plots of the column and decide if kinks occur, or only use the test tray to detect error. The second method is to perform two nonsharp calculations at very low impurities, but not close enough to zero to require enough trays for inaccuracies to occur. Using these two points we can extrapolate the reflux ratio at zero impurity.

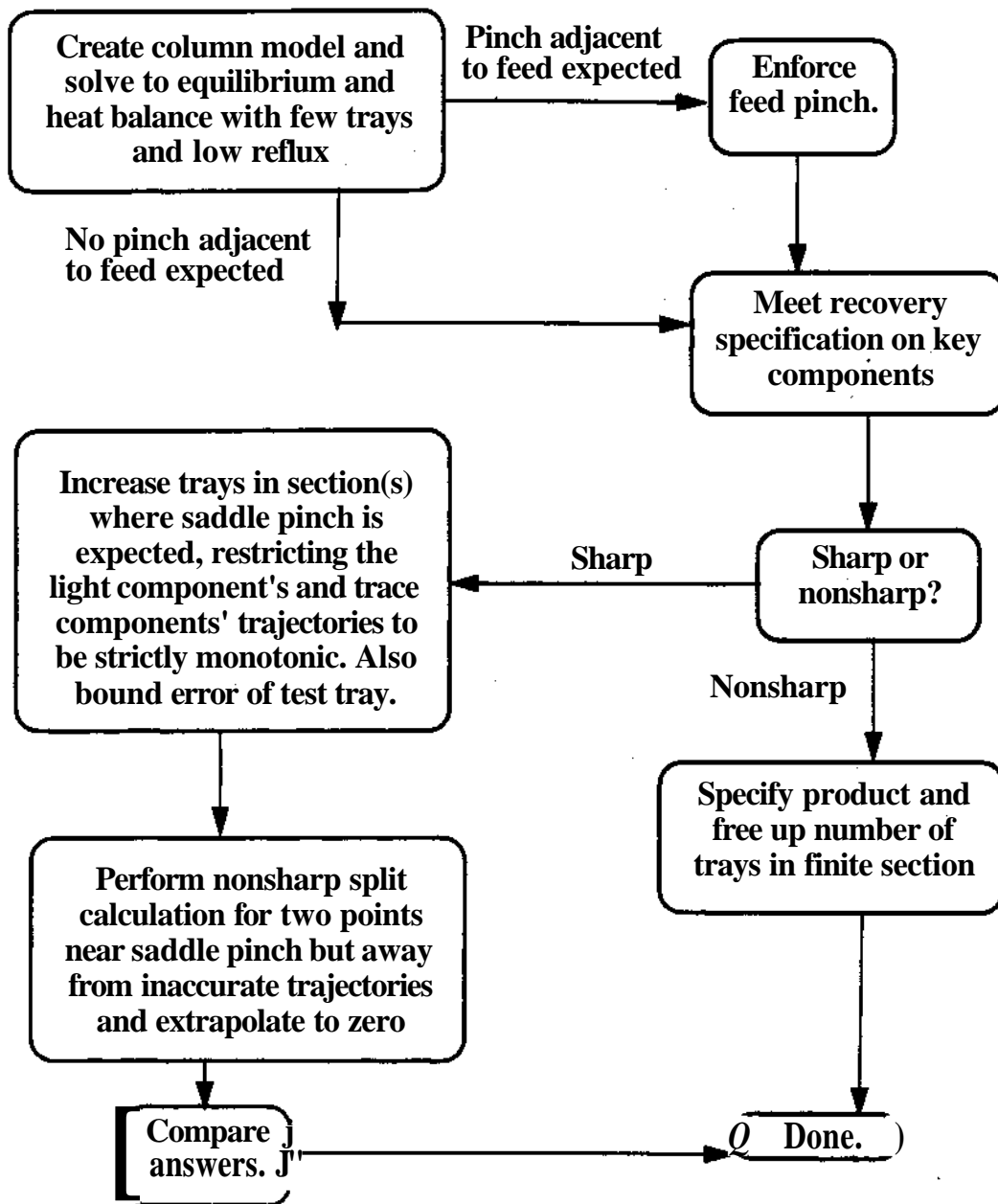


Figure 19. Minimum reflux algorithm

Difficulties

As we demonstrated in the first paper of this series [Huss and Westerberg, 1995a], the variable transformations allow us to model larger columns with

higher purities. However, as we've shown in this paper, difficulties still occur when going towards saddle pinches. In this section we explicitly list the areas where this model breaks down, providing reasons where we can. We provide this description of difficulties to encourage discussion into the problems typically encountered with any modeling technique.

When modeling a large column section in which the trajectories are flat, the collocation may develop kinks. The exponential transformation on trays reduces this effect but does not eliminate it. For an infinite column section it is theoretically possible to select a value for parameter a to straighten one of the components. However, in practice it is difficult to solve for the correct value for a . Also, when dealing with a finite number of trays, z behaves somewhat similarly to s . When this problem occurs away from a saddle pinch, it is possible to bypass the difficulty by requiring a pinch point and ignoring a collocation point. But at this point, we no longer have a collocation model for that section of the column.

Further difficulties occur when we approach a saddle pinch. The kinks in the trajectory begin to occur when going to a large number of trays, but the pinch point bypass does not work. In the case of a pinch adjacent to the feed, the collocation section adjacent to the feed will be completely flat, and the forced pinch will be at the end of that collocation section, as demonstrated in the right half of Figure 10. In that case, we essentially short-circuit the collocation section at the very bottom of the column by ignoring the polynomial definition for the liquid stream entering that section. The collocation section between the pinch point and the feed tray is capable of remaining constant throughout. But for the saddle pinch case, the collocation sections on either side of the saddle pinch have substantial change. In Figure 10, above the saddle pinch, the two remaining components change. Below the pinch, all three components are moving. When we try to enforce the saddle pinch by ignoring some polynomial definition in the top collocation section, the model fails to converge.

Conclusions

Theoretically, collocation provides the missing link for simulation of minimum reflux conditions. For nonsharp splits, we can exactly calculate the minimum reflux. For sharp splits we can approximate minimum reflux, overestimating the actual value. The minimum reflux problem exposes some weaknesses of this collocation model. Even with variable transformations enabling us to model higher purities and larger columns, the model breaks down when approaching a saddle pinch. We observe that the approach allows us to extrapolate to the saddle pinch.

Acknowledgment

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Nomenclature

- a*** **Parameter for exponential transformation of stage location**
- s*** **Stage number**
- z*** **Transformation variable on stage number**

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