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# Analysis of Complex Separation Schemes in the Presence of Chemical Reactions

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## ABSTRACT

A key feature in the analysis of extractive distillation columns is the use of difference points representing the flow rate and composition difference between the cascade section end-product and the extractive side feed(s). Also referred to as a Δ-point, it may be used to assess feasibility for complex cascades with highly non-ideal VLE behavior. We have recently generalized the concept of difference points to systems where chemical reactions take place. We have also shown that the analytical insights are independent of the actual configuration of physical equipment and apply to any partial or complete flowsheet.

This paper will demonstrate how the theory of generalized difference points may be applied to the design of complex separation cascades with reaction. Two example designs with integrated reaction and separation will be presented and analyzed for 3 and 4 components, respectively: (a) reactive distillation for the production of acetic acid from acetic

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anhydride and water and (b) reactive extractive distillation for the production of methyl acetate from acetic acid and methanol with water as a side product. The acetic acid example will illustrate how composition space can be divided into regions where feasibility with respect to distillate placement and internal reaction distribution can be performed using difference point theory. The methyl acetate design will show how a complex column can be divided into sections and analyzed using difference points to expose the role each section plays in making a feasible design.

*Key Words:* Reactive distillation design; Difference points; Feasibility; Process synthesis.



## INTRODUCTION

Process synthesis tools are invaluable when faced with the decision of choosing a technology to perform a desired task. These methods serve the purpose of finding alternative schemes that at least fundamentally have the possibility of meeting design specifications. Once a set of alternatives is postulated, each configuration can be studied more carefully to determine the most suitable design.

Synthesis techniques for ordinary distillation are fairly well-developed due to significant research efforts[1,2] over the last decade. The simplicity of geometric visualization techniques such as the well-known McCabe-Thiele method for binary distillation has led to the development of similar graphical techniques for multicomponent separation systems.[3–6] In addition to these geometric advances, iterative simulation strategies[7,8] have also received considerable attention for distillation synthesis. Many of these methods have advanced to the point where they are implemented in commercial simulation packages.[9–11]

More recently, efforts are underway to extend the ideas of ordinary distillation to reactive separation systems. Traditionally, the design of reactive columns has relied heavily on experimental work and simulation. Several techniques have emerged to visualize the combined effects of reaction and separation. One approach accounts for reaction through transformed variables[12,13] which assume simultaneous reaction and phase equilibrium on each stage of the column. Another class of algorithms[14–16] determine feasible designs for kinetically-controlled reactions under the assumption of a specified liquid holdup throughout the column. An alternative method based on difference points[17,18] not only includes the effects of reaction but also

accounts for other features of complex columns including extractive side feeds and side product draws. With further development, these tools are expected to be useful in synthesizing alternative reactive separation designs.

This paper will briefly review difference points and show how complex reactive separation systems can be analyzed and designed using this theory. Two examples will be presented—a ternary system for acetic acid production and a quaternary system for methyl acetate production. Since the focus of these examples is on conceptual feasibility, equilibrium stages will be used in all examples and heat effects will be neglected.

## GENERALIZED DIFFERENCE POINTS

### Theory Overview

The theory of generalized difference points[19–21] has been used to develop a consistent mathematical description of systems combining chemical reactions with arbitrary separation devices. One of the fundamental ideas behind this theory is that chemical reactions may be viewed as the difference between material flow of reactants and products with a "composition" given uniquely by stoichiometry. From this viewpoint, we define a difference point for a chemical reaction in Eq. 1 where $\boldsymbol{\nu}$ is the vector of stoichiometric coefficients. Since at least one element of $\boldsymbol{\nu}$ must be negative, the composition of $\boldsymbol{\delta}_R$ is non-physical.

$$\boldsymbol{\delta}_R = \frac{\boldsymbol{\nu}}{\sum_j \nu_j} \tag{1}$$

It has been shown that the reaction difference point acts as a mathematical focus in which composition changes by chemical reactions occur along a straight line (reaction vector) originating from this point. All nonlinear behavior is confined to scalar reaction rates along these vectors.

When difference points are applied to an arbitrary section of any flowsheet, the material balance can be decomposed into a sequence of straight lines representing individual balances for reaction and separation as independent mass transfer processes. The reactive lever arm rule[21] can be applied independently to each of these balances to determine relative flow rates. In addition, the distance moved along the locus of cascade difference points gives the amount of chemical reaction.

## Application

Difference points provide a means of visualizing stage-to-stage steps in complex reactive separation systems. We will illustrate how difference points can be applied to both non-reactive and reactive column sections. We will also show how difference points can be generalized to deal with the complexities of integrated reaction and separation systems.

### Non-reactive Stage-to-Stage Calculations

The system under consideration is an ideal ternary mixture with constant relative volatilities of $\boldsymbol{\alpha} = (3, 5, 1)^T$ for components A, B, and C respectively. We select the distillate product composition as $\boldsymbol{x}_D = (0.05, 0.90, 0.05)^T$ in terms of mole fractions and choose an external reflux ratio of unity. Under these conditions, the liquid composition profile for the first three stages is shown in Fig. 1(a). As expected, this rectifying profile moves away from the most volatile component (B) and toward the least volatile component (C). The liquid compositions for this profile are found using an alternating series of phase equilibrium and material balance calculations.

A closer view of the stage-to-stage calculations is presented in Fig. 1(b) using the notation shown in Fig. 2. By initially choosing a distillate product composition, we know that the liquid leaving the condenser ($\boldsymbol{x}_0$) and the vapor entering the condenser ($\boldsymbol{y}_1$) have the same composition. We proceed by taking an equilibrium step from $\boldsymbol{y}_1$ to $\boldsymbol{x}_1$. Looking at the dashed material balance drawn from the top of the column section to stage one in Fig. 2, we see that $\boldsymbol{y}_2$ depends on $\boldsymbol{x}_1$ and $\boldsymbol{x}_D$. We know that $\boldsymbol{y}_2$ is a linear combination of these two compositions where the relative placement of $\boldsymbol{y}_2$ between $\boldsymbol{x}_1$ and $\boldsymbol{x}_D$ is a function of reflux. The line segment connecting $\boldsymbol{x}_1$, $\boldsymbol{y}_2$, and $\boldsymbol{x}_D$ is the material balance for stage one. We call the composition $\boldsymbol{x}_D$ the difference point for this stage and use the notation $\boldsymbol{\delta}_1$. Once the composition $\boldsymbol{y}_2$ is located between $\boldsymbol{x}_1$ and $\boldsymbol{\delta}_1$, we take another equilibrium step to determine $\boldsymbol{x}_2$. The material balance around stage two is similar to that of stage one, and we find that $\boldsymbol{y}_3$ must fall between $\boldsymbol{x}_2$ and $\boldsymbol{\delta}_2$, the later of which is again $\boldsymbol{x}_D$. These alternating phase equilibrium and material balance steps can be continued until a pinch point is reached. A pinch point occurs in non-reactive columns when the material balance line and vapor–liquid equilibrium step are collinear to the specified end-product, or $\boldsymbol{x}_n$, $\boldsymbol{y}_n$, and $\boldsymbol{x}_D$ lie along the same straight line.[2] Since the relative placement of these three points along a line is a function of reflux, the locus of non-reactive pinch points is only parametric in reflux. In physical terms, a pinch corresponds to a zone of constant composition in the column.

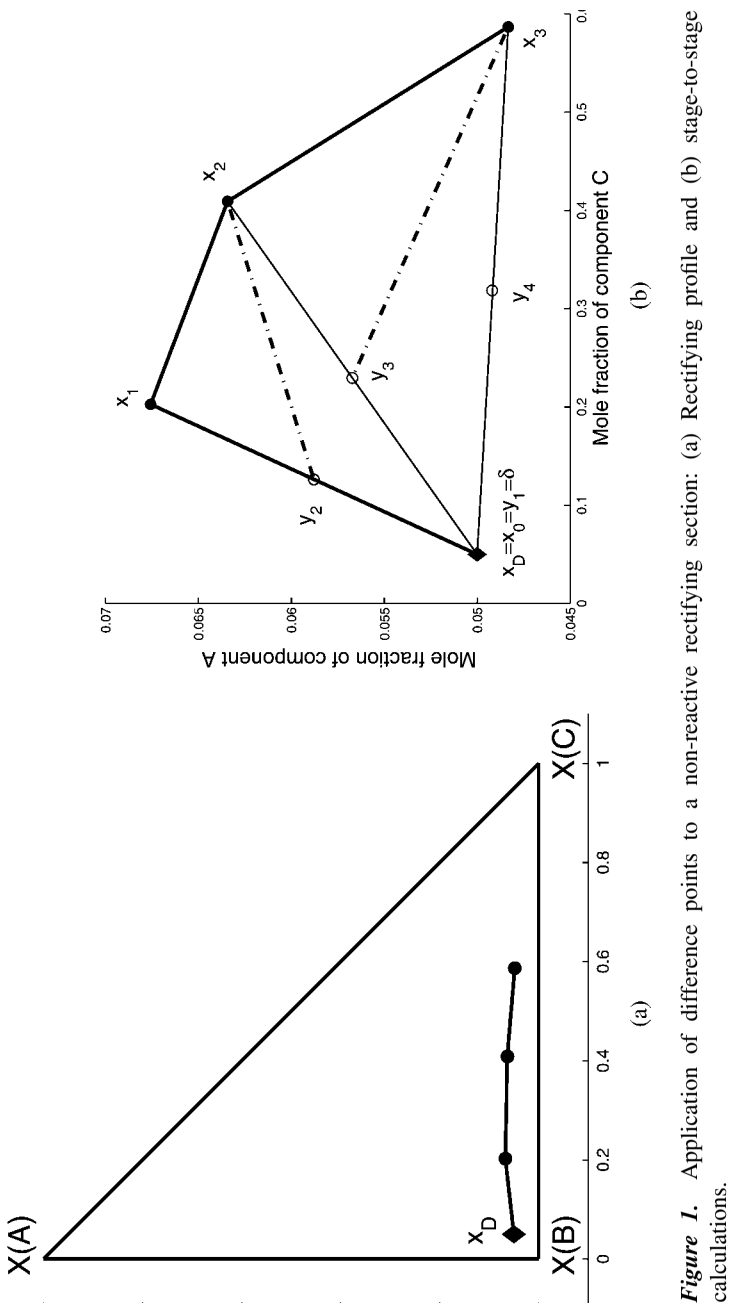



***Figure 1.*** Application of difference points to a non-reactive rectifying section: (a) Rectifying profile and (b) stage-to-stage calculations.

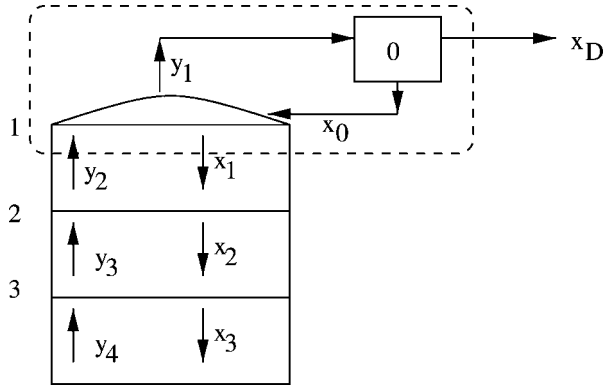



***Figure 2.*** Column section notation.



This procedure for performing stage-wise calculations can be summarized into two equations—the material balance around stage n (Eq. 2) and the phase equilibrium function (Eq. 3) where L and V represent the liquid and vapor flow rates, respectively.

$$\boldsymbol{y}_{n+1} = \alpha \cdot \boldsymbol{x}_n + (1 - \alpha) \cdot \boldsymbol{x}_D \quad \forall \quad \alpha = \frac{L_n}{V_{n+1}} \tag{2}$$

$$\boldsymbol{x}_n = \mathscr{F}(\boldsymbol{y}_n) \tag{3}$$

The stage-to-stage calculations described above illustrate an interesting point. The material balance line for a given stage in a rectifying section must join the liquid composition leaving that stage and the end-product composition which is equivalent to the difference point for the stage. The difference point remains fixed at the specified end-product composition in all ordinary distillation column sections, i.e. sections without side feeds, side draws, or reaction.

## Reactive Stage-to-Stage Calculations

Reaction adds another complexity to stage-to-stage calculations. This will be demonstrated using the same ideal system, distillate composition, and external reflux ratio. For a reaction of the form $A \rightarrow 2B$, the stoichiometric vector is $\boldsymbol{\nu} = (-1, 2, 0)^T$ and the reaction difference point is located at $\boldsymbol{\delta}_R = (-1, 2, 0)^T$. From difference point theory[19] we know that reaction moves the difference point along the line originating from the reaction difference point

and passing through the specified end-product composition ($\boldsymbol{x}_D$). The actual distance moved along this line is a function of several parameters including reaction rate, holdup, and catalyst activity. Reaction will be placed on the first three stages in our example. For illustrative purposes, we will choose equal reaction turnover steps along the locus of difference points.

The liquid composition profile for three stages of a reactive section is shown in Fig. 3(a). Since the profile is computed from the top of the column down toward the feed stage, the composition at the top of the section is rich in product (B). On the other hand, lower stages in the section have more reactant (A). A more detailed view of the material balances and phase equilibrium steps is given in Fig. 3(b). The stage-to-stage calculations begin in the same manner as for the non-reactive case. Based on the specified distillate composition, we can say $\boldsymbol{x}_0 = \boldsymbol{y}_1 = \boldsymbol{x}_D$ using the notation from Fig. 2. An equilibrium step from $\boldsymbol{y}_1$ determines the location of $\boldsymbol{x}_1$. Up to this point, the reactive profile exactly follows the non-reactive profile. To calculate the next vapor composition ($\boldsymbol{y}_2$), the difference point for stage one ($\boldsymbol{\delta}_1$) is located and a material balance line is drawn from $\boldsymbol{\delta}_1$ to $\boldsymbol{x}_1$. The location of $\boldsymbol{\delta}_1$ is determined by the cumulative amount of reaction up to and including this stage. In this example, we have selected the amount of reaction arbitrarily, but the principle and geometry are the same for any such value. Reflux determines the relative placement of $\boldsymbol{y}_2$ between $\boldsymbol{x}_1$ and $\boldsymbol{\delta}_1$. Another equilibrium step locates $\boldsymbol{x}_2$ and then $\boldsymbol{y}_3$ is found along the material balance connecting $\boldsymbol{x}_2$ and $\boldsymbol{\delta}_2$. With the difference point moving toward pure component A, material balances for each stage are also shifted closer to pure A which causes the reactive profile to be "pulled" in that direction. Additional stage-to-stage steps may reach a pinch point at which the material balance line and phase equilibrium step are collinear with the difference point, meaning that $\boldsymbol{x}_n$, $\boldsymbol{y}_n$, and $\boldsymbol{\delta}_n$ lie along a straight line. Since the relative placement of these three points along a straight line is a function of reflux and the location of the difference point depends on the cumulative reaction turnover, reactive pinch point curves are parametric in both reflux and reaction turnover. Similar techniques can also be applied to columns with extractive side feeds and side draws although only chemical reactions cause the difference point to move from stage to stage.

## Generic Cascade Sections

Difference points not only serve as a visualization tool for the individual effects of reaction and separation but also simplify the design of complex systems by allowing columns to be divided into sections and analyzed piece by piece. Complex columns can contain side feeds, side draws, and non-reactive

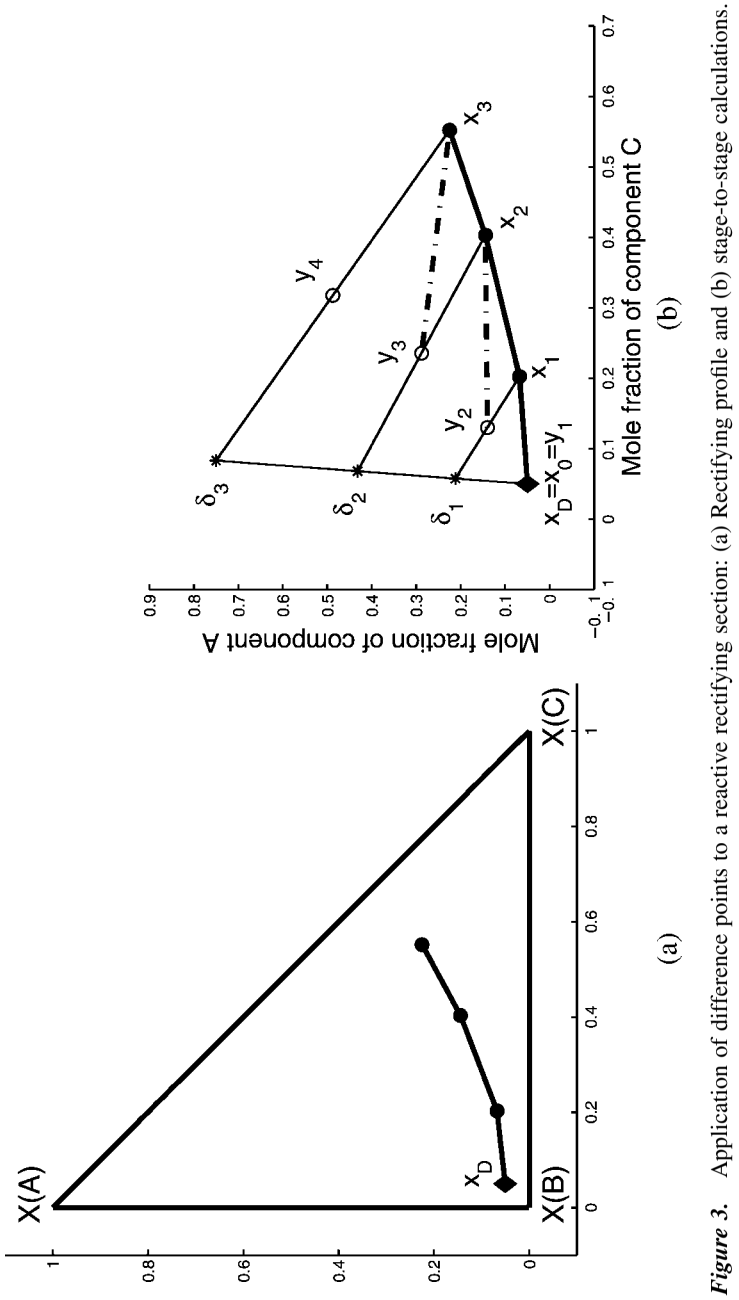



*Figure 3.* Application of difference points to a reactive rectifying section: (a) Rectifying profile and (b) stage-to-stage calculations.

and reactive stages. Column configurations with side streams cause the difference point to move at the location of the external flows. Chemical reactions, on the other hand, cause the difference point to move continuously throughout a cascade section. There are seemingly many possible ways to combine sections, but difference point theory says that the configurations shown in Fig. 4 are the only ones where the material balance lines will shift. These elementary sections can be used to capture all possible designs for combined reaction-separation systems. In addition to these basic building blocks, we need to be able to account for column sections with multiple phenomena as shown in Fig. 5. Stage-wise calculations in such a section require two steps:

(1) Calculate $\boldsymbol{\delta}_n$ based on inflows, outflows, and reaction on stages 1 to n
(2) Locate $\boldsymbol{x}_n$ and $\boldsymbol{y}_{n+1}$ from alternating material balance (Eq. 4) and phase equilibrium (Eq. 5) steps

$$\boldsymbol{y}_{n+1} = \alpha \cdot \boldsymbol{x}_n + (1 - \alpha) \cdot \boldsymbol{\delta}_n \quad \forall \quad \alpha = \frac{L_n}{V_{n+1}} \tag{4}$$

$$\boldsymbol{x}_n = \mathscr{F}(\boldsymbol{y}_n). \tag{5}$$

As seen by Eqs. 4 and 5, the behavior of reactive separation cascades is captured by a sequence of coupled difference equations. Stage-to-stage calculations in column sections with any combination of inflows, outflows, and reaction are performed in exactly the same manner except for variations in the calculation of the difference point. Similar equations can also be developed to describe stripping sections and intermediate column sections. Together, these equations will serve as the basis for computing column section profiles. Two examples will be presented to illustrate how difference points can be used to visualize and gain insight into reactive separation design.

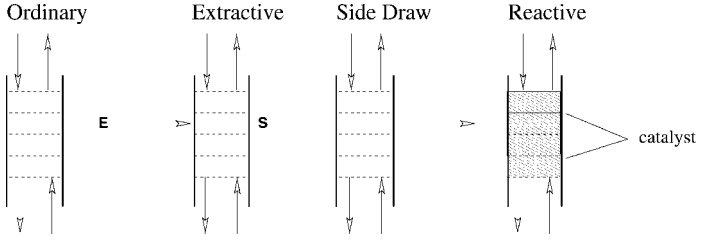



***Figure 4.*** Sectional approach to complex column design.

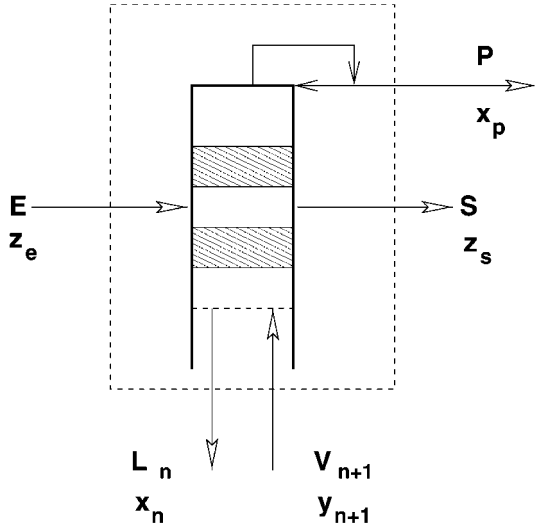



***Figure 5.*** Generic rectifying cascade section.

We will emphasize techniques for finding and evaluating feasible process configurations.

## EXAMPLE 1: ACETIC ACID PRODUCTION

The first example is a ternary system for the production of acetic acid. Acetic acid is formed from a liquid-phase reaction of acetic anhydride and water:

$$(CH_3CO)_2O + H_2O \rightleftharpoons 2CH_3COOH \tag{6}$$

At 1 atm, this system exhibits two minimum boiling binary azeotropes which are joined by a simple distillation boundary or separatrix as shown in Fig. 6. Distillation lines[22] in the upper distillation region begin at the water–acetic anhydride binary azeotrope (90°C) and terminate at pure acetic anhydride (139°C). In the lower region, the distillation lines again begin at the water–acetic anhydride azeotrope but terminate at the acetic acid corner (118°C). It is interesting to note that distillation lines in the upper portion of the lower distillation region bend sharply toward the acetic anhydride–acetic acid binary azeotrope (110°C) and approach the acetic acid corner from this binary

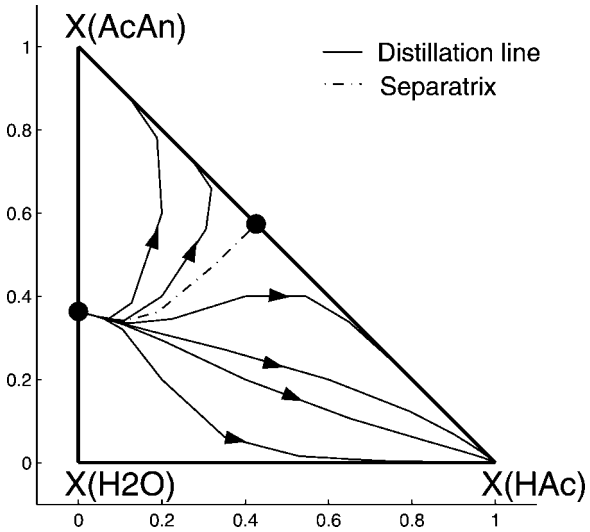



***Figure 6.*** VLE features of acetic acid system.



edge. On the other hand, distillation lines in the lower portion bend toward water (100°C) and reach pure acetic acid from the water–acetic acid edge. The VLE in this system is characterized using the NRTL activity coefficient model in conjunction with Antoine's vapor pressure correlation. All thermodynamic parameters are taken from Giessler et al.[23]

The kinetics for this system are represented by a simple mass-action rate expression given in Eq. 7. Both the forward rate constant and equilibrium constant are assumed to be independent of temperature and specified as unity.[14]

$$rate = k_f \left( x_{AcAn} x_{H_2O} - \frac{x_{HAc}^2}{K_{eq}} \right) \tag{7}$$

The chemical reaction equilibrium curve is shown in Fig. 7. The forward reaction proceeds for all compositions to the left of this curve, while the reverse reaction takes over to the right. Since this reaction is stoichiometrically balanced ($\sum_j \nu_j = 0$), the direction of composition change caused by forward chemical reaction for different feed compositions is parallel and points toward the reaction difference point. This is shown by the reaction vectors in Fig. 7. As expected, a feed of acetic anhydride and water

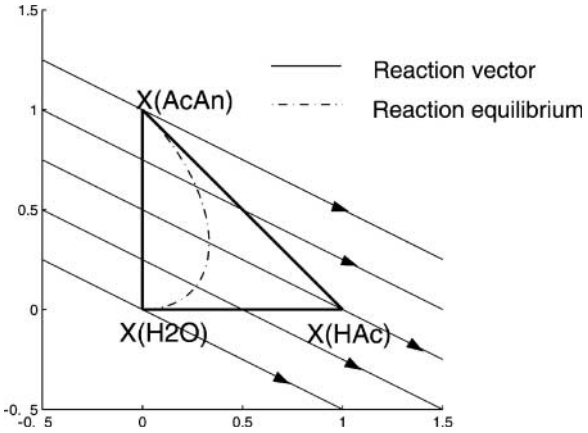



***Figure 7.*** Reaction features of acetic acid system.



in a stoichiometric ratio will react and move directly toward pure acetic acid until equilibrium prevents further conversion.

## Regional Analysis

We will divide the composition space into regions where fundamentally different designs are needed to produce acetic acid. We will confine our study to feeds along the binary water–acetic anhydride edge. To simplify the analysis, we neglect the fact that non-reactive distillation can cross the curved separatrix under special conditions.[24] This assumption limits the ways in which nearly pure acetic acid can be produced but not significantly.

As a basis for benchmarking reactive distillation designs, we will first take a look at what is possible from sequential units—a reactor followed by a distillation column—as depicted in Fig. 8. A stoichiometric feed of acetic anhydride and water is fed to the reactor. Reaction goes to equilibrium moving the profile to the equilibrium curve. This mixture is fed to a column that separates acetic acid from the unreacted acetic anhydride and water. A ternary mixture is recycled back to the reactor, and acetic acid is removed from the bottom of the column. By applying the lever arm rule to the column material balance line, we can determine relative amounts of feed, overhead recycle, and acetic acid product from the column. Since the feed

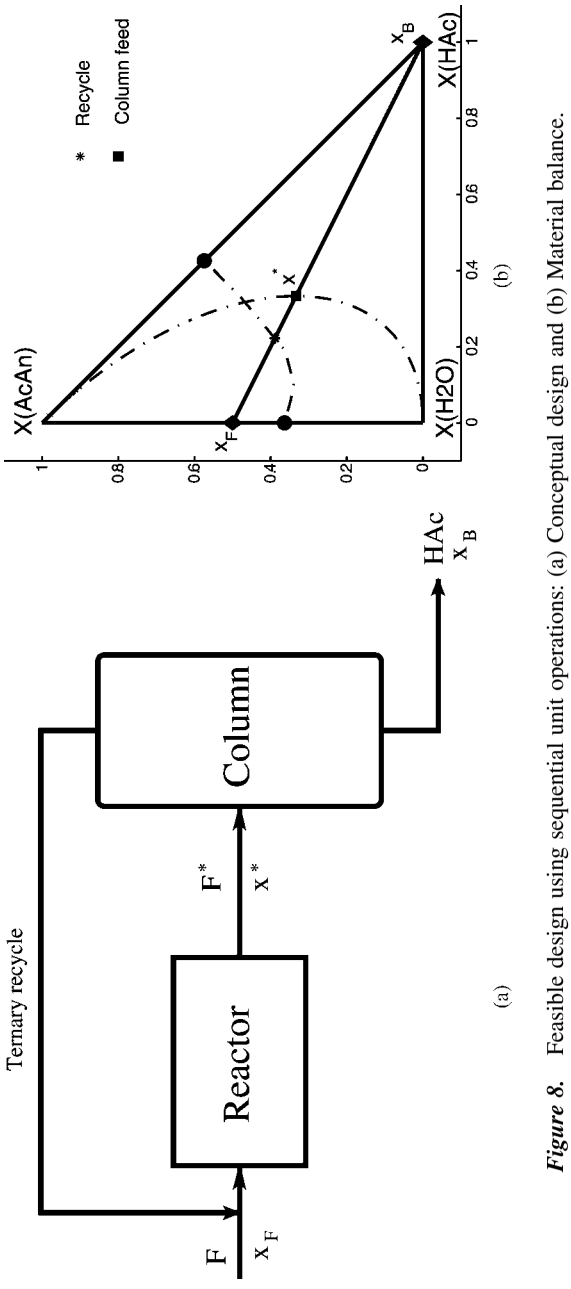



***Figure 8.*** Feasible design using sequential unit operations: (a) Conceptual design and (b) Material balance.

composition is significantly closer to the overhead composition, this column will have a large amount (6:1) of reactants recycled back to the reactor. This process is inefficient due to acetic acid product being recycled to the reactor.

To overcome the disadvantages of the sequential unit design, we will apply regional analysis to determine areas of composition space where a single reactive distillation column as shown in Fig. 9 can produce nearly pure acetic acid. Acetic acid, being the heaviest component in the lower distillation region, will always be removed from the bottom of the column. Recycle of ternary mixtures will be avoided by locating distillate products containing only unreacted feed. This implies that both the feed and distillate compositions will always lie along the water–acetic anhydride edge. If the ratio of water to acetic anhydride in the distillate is different from the ratio in the feed, a purge stream will be necessary to remove the excess and avoid buildup in the column.

To find a feasible reactive column design for a feed containing only reactants, forward reaction must take place in the column. In addition, the column profile must enter the lower distillation region where acetic acid can be recovered. We also want to avoid placing any reaction to the right of the reaction equilibrium curve because this will remove acetic acid product. Specifically, we will study feasibility for distillate products in both the lower and upper distillation regions. The key questions to be asked are how much reaction is needed and on what stages should reaction be placed to satisfy these conditions.



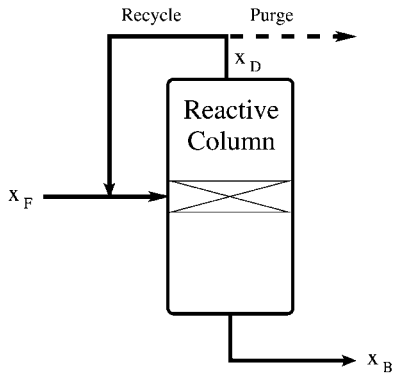



***Figure 9.*** Combined reaction-separation column configuration.

Region 1: Distillate Placed Above the Separatrix

In the upper distillation region, we need a column configuration that allows us to move across the separatrix. For a distillate composition along the binary edge as shown in Fig. 10, we see that forward reaction will move the difference point outside the composition simplex. Since material balance lines are drawn back to the difference point, any amount of forward reaction in the condenser will pull the profile outside the valid composition space leading to an infeasible design. It is therefore necessary to place non-reactive stages at the top of the rectifying section before any significant amount of reaction can occur. As indicated by the locus of difference points in Fig. 10, profiles in this region will be pulled up and to the left as a result of forward chemical reaction. Separation, on the other hand, tends to move profiles up and to the right based on the distillation lines shown in Fig. 6. Since neither reaction or separation has a vectorial component in the direction needed to cross the separatrix, rectifying profiles are confined to this distillation region. This behavior is illustrated by the rectifying profile drawn in Fig. 10 which has one reactive stage. Reaction causes the profile to move quickly away from the separatrix and toward pure acetic anhydride.



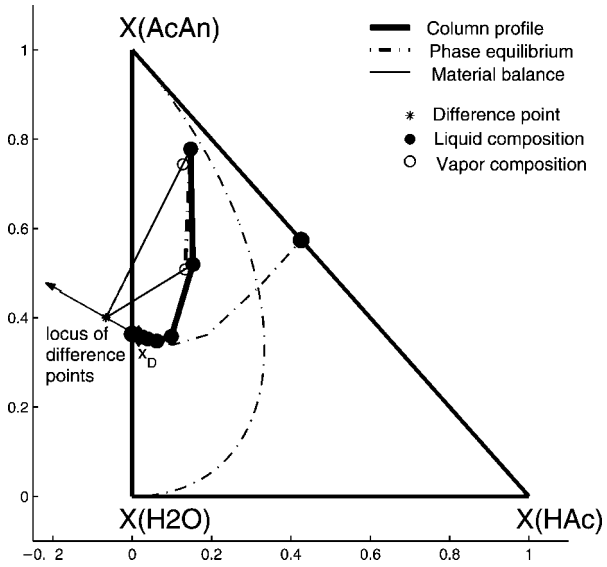



***Figure 10.*** Effect of reaction in the rectifying section.

However, the rectifying and stripping profiles must intersect to make a feasible full column.[25] Therefore, we must investigate whether or not a stripping profile can cross the separatrix. We have assumed that non-reactive profiles will not cross a distillation boundary so the only option is to place reaction in the stripping section. For a bottoms product placed close to pure acetic acid, the locus of difference points for the forward chemical reaction goes across the composition simplex as seen in Fig. 11. This is promising since material balance lines drawn to difference points inside composition space eliminates the possibility of profiles exiting the simplex. Since pure acetic acid lies in the reverse reaction region, the stripping profile must contain several non-reactive stages to move across the reaction equilibrium curve before any forward reaction can occur. An example is shown in Fig. 11 where the stripping profile crosses into the forward reaction region after twelve non-reactive stages. At this point, forward reaction is possible as long as the liquid composition remains on the proper side of reaction equilibrium. Looking at the locus of difference points originating from the specified bottoms product, we see that reaction moves the profile up and to the left. The vertical component of reaction will allow stripping profiles to cross the separatrix into the upper distillation region as long as enough reaction is carried out.



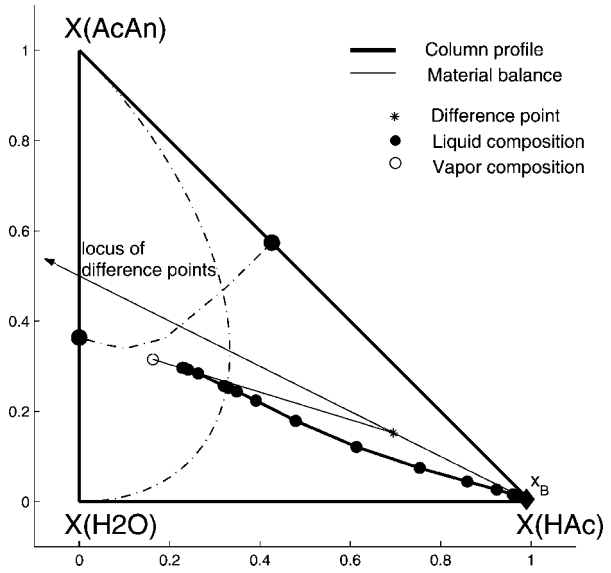



***Figure 11.*** Insufficient reaction in the stripping section.

An example of insufficient reaction in the stripping profile is illustrated in Fig. 11 where after only one reactive stage the profile still pinches before crossing the distillation boundary. It is also important that a relatively high reboil ratio is used to allow the stripping profile to get across the reaction equilibrium curve before pinching.

The regional analysis has shown that feasible designs are possible for distillates in the upper distillation region. One possible design places all reaction in the stripping section to allow the stripping profile to cross the separatrix and intersect with a non-reactive rectifying profile. A conceptual view of this design is shown in Fig. 9 with detailed stage-wise calculations given in Fig. 12. The distillate is specified just above the binary water–acetic anhydride azeotrope. The rectifying section has five non-reactive stages. The stripping profile begins with nine non-reactive stages to move the liquid composition into the forward reaction region. Reaction is placed on the next two stages of the stripping section which causes the profile to cross the separatrix and intersect the rectifying profile. This column has a total of sixteen stages and produces 99 mol% acetic acid. The design specifications are summarized in Table 1. Since the distillate in this design contains a slight excess of water compared to the feed, a fraction of the water must be removed



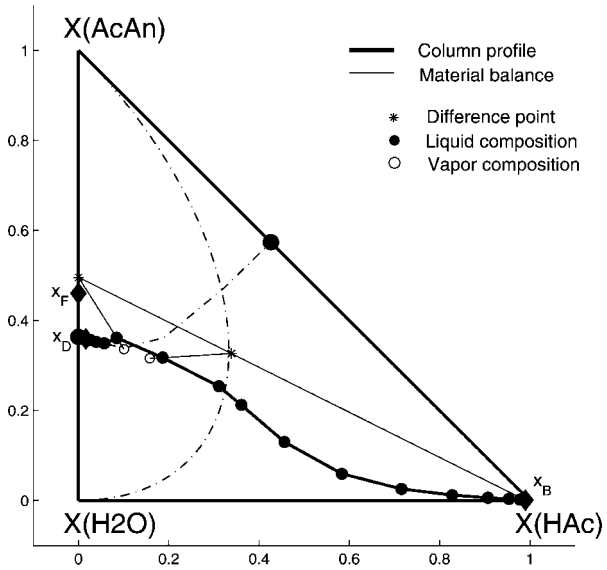



***Figure 12.*** Feasible design in upper distillation region using a single reactive distillation column.

***Table 1.*** Design specifications for column in Fig. 12.

| Design parameter | Specification |
|---|---|
| Rectifying stages | 5 |
| Stripping stages | 11 |
| Reactive stages | 2 |
| Reflux ratio | 5.0 |
| Reboil ratio | 5.3 |
| D/F | 0.25 |
| B/F | 0.75 |
| $\boldsymbol{x}_F$ | (0.46, 0.54, 0) |
| $\boldsymbol{x}_D$ | (0.359, 0.624, 0.017) |
| $\boldsymbol{x}_B$ | (0.001, 0.009, 0.990) |



from the recycle stream. The water purge would be unnecessary for a stoichiometric feed. This design has no acetic acid product recycled and operates with a high reflux so the ratio of recycle to product is only 0.33:1. These are significant advantages compared to the sequential unit design.

It is also possible to place some reaction in the rectifying section in addition to the large amount of reaction in the stripping section needed to cross the separatrix. However, by placing reaction in the rectifying section, the profile will be pulled up toward pure acetic anhydride. This will in turn require more stripping stages to make the profiles intersect. We may qualitatively argue that reaction below the feed stage and relatively few stages in the top leads to the most economical design for distillates in this region.

Although the example design has a distillate composition very close to the binary water–acetic anhydride azeotrope, similar design configurations could also be found for other distillate compositions along this binary edge. Once feasibility is established, the focus can be shifted to a detailed design.

### Region 2: Distillate Placed Below the Separatrix

We will now look at feasible designs for distillate products placed below the binary water–acetic anhydride azeotrope. Using the same explanation as done for distillates placed above the separatrix, we realize that no reaction can be placed in the condenser when the distillate is placed on the binary edge. Several non-reactive stages are needed at the top of the rectifying section to move the profile inside composition space and to a point where reaction can occur without immediately pulling the profile out. Reaction in the rectifying

section will move the profile up and to the left making it possible to cross the separatrix.

To find an intersecting stripping profile, we again need to have several non-reactive stages to move the stripping profile from the acetic acid corner across the reaction equilibrium curve. Once reaction equilibrium is crossed, forward reaction can take place in the stripping section to join the rectifying profile.

Three different reaction distribution policies are possible to find feasible full column designs. First, we could place all reaction at the top of the stripping section and find a connecting non-reactive rectifying profile. Since the non-reactive rectifying section cannot cross the separatrix, we must be careful that the two profiles intersect before reaction causes the stripping profile to cross the distillation boundary. As a second option, we could also place all reaction in the lower part of the rectifying section and join it with a non-reactive stripping section. Again, we need to ensure that the rectifying section does not cross into the upper distillation region. For the third option, we could have reaction in the middle of the column on both sides of the feed stage. This third option could result in rectifying and stripping profiles beginning in the lower distillation region but intersecting each other in the upper region. In essence, any design is conceptually feasible and the important question becomes economics.

Figure 13 shows a feasible design for a distillate in the lower distillation region with all reaction in the stripping section using the configuration shown in Fig. 9. The distillate product is placed just below the binary water–acetic anhydride azeotrope. Nine non-reactive stripping stages and one reactive stripping stage are used to purify acetic acid to 99 mol%. The reactive stripping section is joined with five non-reactive rectifying stages. Since the rectifying profile will not cross the distillation boundary, the intersection of the two column sections occurs in the lower distillation region. Like the previous design, the distillate contains a slight excess of water that must be purged in order to make the recycle work. The details of this design are presented in Table 2. This design is verified by Aspen simulation with results given in Table 3.

## Insights Gained from Difference Points

We have shown how the composition space can be divided into regions where different issues arise in finding a feasible design. To make a feasible design in the upper distillation region, enough reaction is needed below the feed stage to move the stripping profile across the separatrix. In the lower

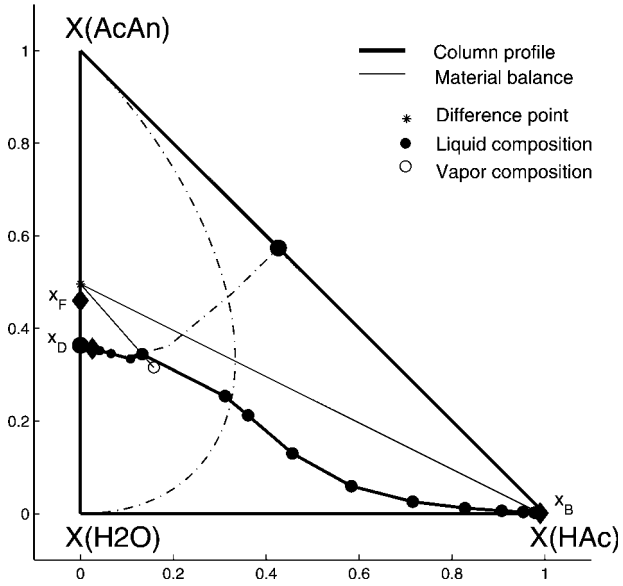



***Figure 13.*** Feasible design in lower distillation region using a single reactive distillation column.

distillation region, reaction can be placed on either side of the feed stage to find a feasible full column.

Difference points allow the process designer to quickly assess whether a particular distillate composition has the potential to give a feasible design.

***Table 2.*** Design specifications for column in Fig. 13.

| Design parameter | Specification |
|---|---|
| Rectifying stages | 5 |
| Stripping stages | 10 |
| Reactive stages | 1 |
| Reflux ratio | 10.0 |
| Reboil ratio | 5.3 |
| D/F | 0.25 |
| B/F | 0.75 |
| $\boldsymbol{x}_F$ | (0.46, 0.54, 0) |
| $\boldsymbol{x}_D$ | (0.356, 0.618, 0.026) |
| $\boldsymbol{x}_B$ | (0.001, 0.009, 0.990) |

***Table 3.*** Verification of Fig. 13 design using Aspen.

| Design parameter | Specification |
|---|---|
| Rectifying stages | 4 |
| Stripping stages | 11 |
| Reactive stages | 1 |
| Reflux ratio | 10.0 |
| Reboil ratio | 5.1 |
| D/F | 0.25 |
| B/F | 0.75 |
| $\boldsymbol{x}_F$ | (0.46, 0.54, 0) |
| $\boldsymbol{x}_D$ | (0.355, 0.615, 0.030) |
| $\boldsymbol{x}_B$ | (0.03, 0.05, 0.92) |



From regional analysis, we know how to select distillates along the binary water–acetic anhydride edge. This method also enables one to study the effects of internal reaction distribution. By visualizing the reaction and separation effects on each stage of the column, we are able to disregard infeasible designs such as Fig. 10. These insights save considerable computation time and give the designer information that is not readily available from commercial simulation packages.

## EXAMPLE 2: METHYL ACETATE PRODUCTION

The second example is a quaternary system for the production of methyl acetate from methanol and acetic acid with water as a side product. This liquid-phase reaction proceeds as follows:

$$CH_3OH + CH_3COOH \rightleftharpoons CH_3COOCH_3 + H_2O \tag{8}$$

The VLE for this system is described by the Wilson activity coefficient model with parameters taken from Song et al.[26] As shown in Fig. 14(a), there are two minimum-boiling binary azeotropes and no distillation boundaries. Separation of these components can be difficult because methyl acetate (57°C), the methyl acetate–water azeotrope (56°C), and the methyl acetate–methanol azeotrope (54°C) have close boiling points. Acetic acid (118°C) is the highest boiler followed by water (100°C) and methanol (65°C). Distillation lines in this system run from the methyl acetate–methanol binary azeotrope to pure acetic acid.

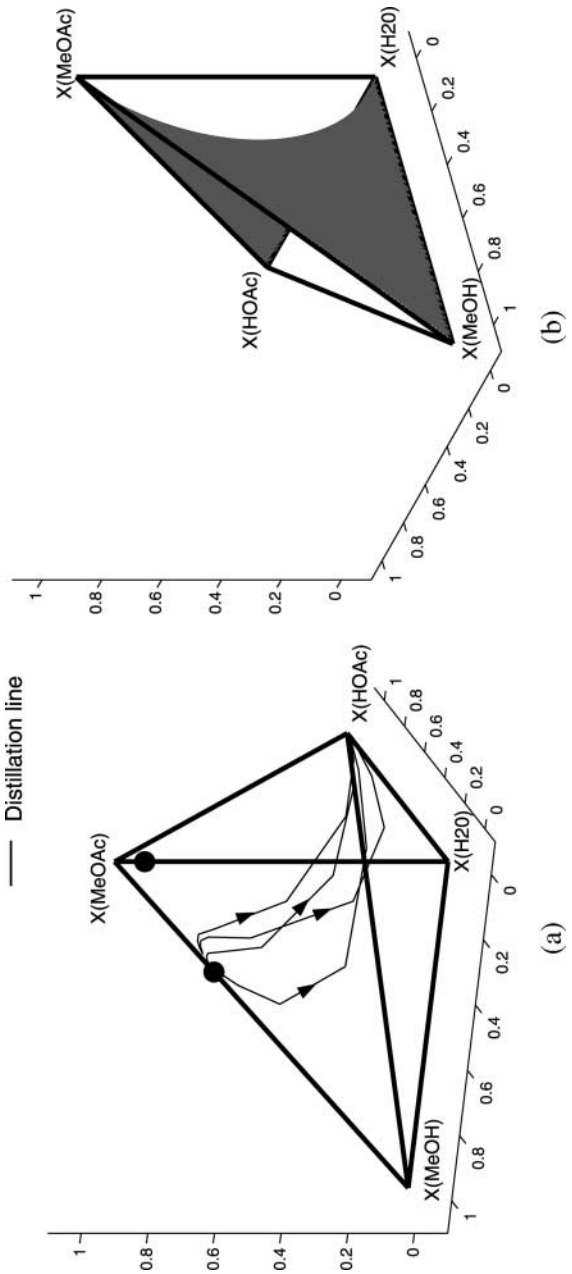



*Figure 14.* VLE and reaction features of methyl acetate system: (a) VLE features and (b) Reaction features.

A pseudo-homogeneous rate model[26] describes the kinetics for methyl acetate production. From this model, the chemical reaction equilibrium surface is computed and shown in Fig. 14(b).

## Sectional Analysis of Methyl Acetate Column

Eastman Chemical patented a reactive distillation process for methyl acetate production in 1984.[27,28] The patent illustrates how the column can be divided into four sections with each section performing a distinct task. A schematic illustration of this column is presented in Fig. 15. The column has two side feeds and produces methyl acetate off the top and water off

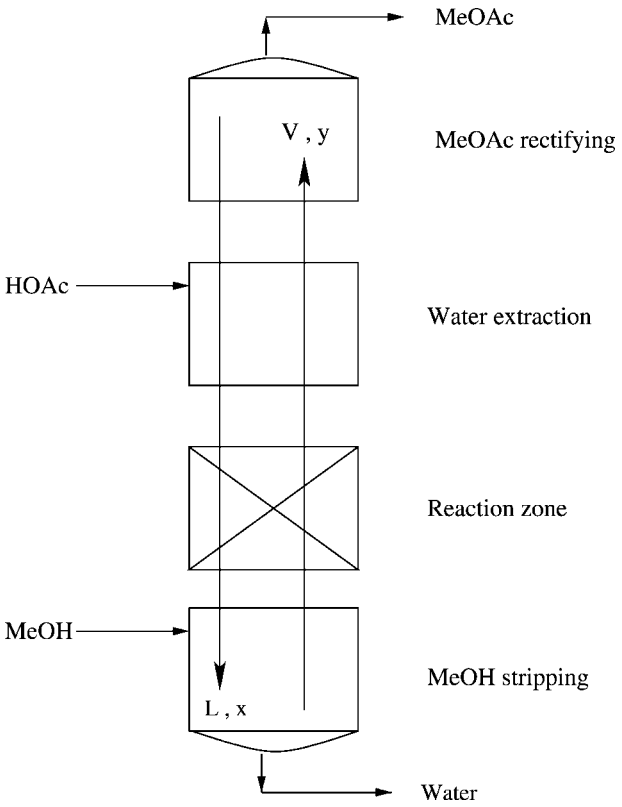



***Figure 15.*** Sectional view of methyl acetate production.

the bottom. The uppermost part of the column is a non-reactive rectifying section that separates methyl acetate product from unreacted acetic acid. This section will have a fixed difference point at the distillate product composition. The next section extracts water and methanol using acetic acid. Although catalyst is present on the stages of the extractive section, little reaction occurs and we can assume this section is non-reactive. The difference point in this case will move from the distillate composition to a different location due to the extractive side feed. However, it will remain fixed at this new location for each stage of the extractive section. The third section of the column is where the majority of the reaction takes place. Each reactive stage will move the difference point toward the reaction difference point located at $\boldsymbol{\delta}_R = (-\infty, -\infty, \infty, \infty)^T$. The final section of the column strips methanol from by-product water. Again, an insignificant amount of reaction occurs in this part of the column so the non-reactive assumption can be made. The difference point in the stripping section will initially move on the stage with the methanol side feed but will remain fixed for each stage below.



## Equilibrium Design

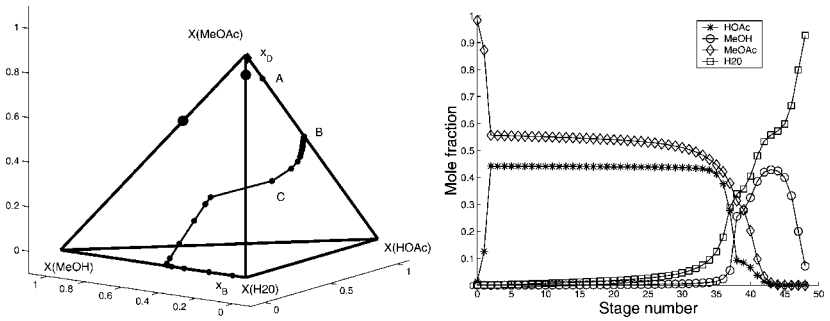
Using the sectional view, we will now apply the difference point method to validate a feasible column for methyl acetate production at 1 atm. To simplify the design, we will ignore the rate at which reaction can proceed and assume reaction moves in the forward direction until equilibrium is reached. Using the design specifications presented in Table 4, the column was simulated in Aspen Plus. Taking the VLE from the simulation, we calculated

***Table 4.*** Design specifications for equilibrium methyl acetate column.

| Design parameter | Specification |
|---|---|
| Number of stages | 50 |
| HOAc feed stage | 3 |
| MeOH feed stage | 39 |
| Distillate flow rate [kmol/hr] | 280 |
| HOAc feed flow rate [kmol/hr] | 280 |
| MeOH feed flow rate [kmol/hr] | 280 |
| Molar external reflux ratio | 1.80 |
| Reactive stages | 5 to 45 |
| VLE model | Wilson (ideal gas) |

the column profile in four sections using our difference point method. We initialize our stage-to-stage calculations by specifying a distillate composition and flow rate as well as the external reflux ratio. Difference points are computed for each stage by taking into account any side feeds or reaction that have occurred on previous stages. As described earlier, each stage-to-stage calculation proceeds by locating the difference point for stage n ($\boldsymbol{\delta}_n$), drawing a material balance line from $\boldsymbol{x}_n$ to $\boldsymbol{\delta}_n$, locating $\boldsymbol{y}_{n+1}$ along the material balance line based on internal reflux ratio, and finally taking an equilibrium step from $\boldsymbol{y}_{n+1}$ to $\boldsymbol{x}_{n+1}$. As expected, the column profiles generated using difference points matched the simulation exactly. The feasible full column profile is illustrated in Fig. 16.

The profile path in composition space can be explained using difference points. Stage one, indicated by point A in Fig. 16(a), is a non-reactive stage that separates methyl acetate from acetic acid. The difference point for this non-reactive stage is located at the distillate composition. Since the distillate mostly consists of methyl acetate and acetic acid, separation keeps the composition close to the binary edge. Stage two, located at point B, introduces a side feed of acetic acid. The additional feed moves the difference point out to $+\infty$ along the acetic acid–methyl acetate edge. Since material balance lines are drawn back to this point, the composition is moved even closer to the binary edge. There are no additional inflows or outflows from stage three so the difference point remains fixed from the previous stage. This continues to keep the composition confined to the binary edge. Reaction begins on the following stage and the slight amount of reaction pulls the difference point in




(a) (b)

***Figure 16.*** Liquid composition profiles for equilibrium methyl acetate design: (a) Column profile and (b) Composition profiles.

the direction of the reaction vectors, i.e. toward the reactant (methanol–acetic acid) edge. While it is thought that reaction should move the difference point away from the reactants and toward the products for forward reaction, the top-down approach to stage-to-stage calculations actually means product must be removed from the column as we step down stages. If the stage-to-stage calculations begin from the bottom of the column, the difference point will move in the expected direction—away from the reactants. Reaction continues on the next thirty-two stages but turnover for each stage remains under one kmol/hr. The difference point on these stages gradually moves the profile further away from the binary edge (point B) and toward point C. By moving away from this edge, more reaction is possible because more reactants are present. Increasing amounts of reaction occur on stages thirty-three to thirty-seven causing the reactant compositions (methanol and acetic acid) to increase and product compositions (methyl acetate and water) to drop. Nearly 100 kmol/hr of reaction turnover is carried out on stage thirty-eight, indicated by point C, due to the addition of the methanol side feed. While the difference point for the side feed alone pulls the profile to the methanol–water binary edge, the difference point resulting from reaction pulls the profile back into composition space keeping the design feasible. Since the flow rate of side feed (280 kmol/hr) is much larger than the reaction turnover, the movement of the difference point is more affected by the side feed. No additional inflows or outflows affect the difference point on later stages so the profile continues to move toward the fixed difference point. At the last stage, the profile terminates at nearly pure water.

There are a number of issues that arise when trying to find feasible designs using the sectional approach. For the design presented above, we began the stage-to-stage calculations by specifying a distillate composition, distillate flow rate, and external reflux ratio. The column profile is extremely sensitive to trace component specifications in the distillate product and slightly different specifications can lead to designs with significantly less conversion and more unconverted reactants in the bottoms product. Another issue pertains to meeting bottoms product specifications. By using a top-down approach for the stage-to-stage calculations, the bottoms composition is technically unknown until all calculations have been carried out. This becomes an iterative method when trying to simultaneously satisfy two end-product specifications.

This example has illustrated how difference points can be used to divide complex columns into sections. Although we have only illustrated an equilibrium design, difference points can readily be applied to systems with kinetic expressions and variable tray holdups.

## CONCLUSION

We have shown two examples to illustrate how difference points can be used to visualize stage-to-stage calculations in complex columns with extractive side feeds, side draws, and reaction. In the acetic acid example, we showed how composition space can be divided into regions where fundamentally different designs are needed. This visualization tool also allows the column to be divided into sections whereby each piece performs a different task as in methyl acetate production. Besides trying to simplify design through regional and sectional analysis, difference points provide insights into design parameters such as feed placement and internal reaction distribution that are not available from other reactive separation design methods.



## NOMENCLATURE

| | |
|---|---|
| B | bottoms flow rate [amount/time] |
| D | distillate flow rate [amount/time] |
| F | feed flow rate [amount/time] |
| $K_{eq}$ | equilibrium constant |
| L | liquid phase flow rate [amount/time] |
| V | vapor phase flow rate [amount/time] |
| $k_f$ | forward rate constant [$s^{-1}$] |
| r | molar external reflux ratio |
| $\boldsymbol{x}$ | liquid phase composition vector [mole/mole] |
| $\boldsymbol{y}$ | vapor phase composition vector [mole/mole] |
| $\boldsymbol{z}$ | arbitrary phase composition vector [mole/mole] |

### Greek Symbols

| | |
|---|---|
| $\boldsymbol{\alpha}$ | relative volatility vector |
| $\boldsymbol{\delta}$ | difference point composition vector |
| $\boldsymbol{\nu}$ | stoichiometric coefficient vector |

### Subscripts

| | |
|---|---|
| B | bottoms product |
| D | distillate product |
| F | feed |
| P | column section end-product |

| | |
|---|---|
| R | reaction difference point |
| e | side feed |
| n | composition leaving stage n |
| s | side draw |

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