Extreme Conditions in Binary Reactive Distillation

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In certain cases, reactive distillation can be used to avoid minimum reflux pinch points and azeotropic compositions. A pinch caused when using minimum reflux is always in the nonreactive section of the column. Its location is affected by the extent of reaction occurring elsewhere in the column. This article shows how to encounter such pinch situations by McCabe-Thiele and Ponchon-Savarit diagrams. Reactive distillation columns were designed under the extreme conditions of assuming reaction equilibrium and total reflux. Putting more than one reactive stage in such a column can be harmful to column performance for an azeotropic mixture. As a function of the magnitude of the reaction equilibrium constant, when an azeotrope can be circumvented is described. A binary reactive distillation can be bypassed only under finite reflux conditions, with the reaction equilibrium constant being greater than the reaction equilibrium constant evaluated at the azeotropic composition. A rigorous simulation of actual systems is used to confirm the insights provided by these graphical methods.

Introduction

In this article, we treat the extreme conditions such as the occurrence of pinch situations and an azeotropic point, reaction equilibrium, and the total reflux to better understand the design of binary reactive distillation processes. We define the pinch point as the point where the operating line (or the material balance line) is tangent to the phase equilibrium curve regardless of whether we consider reactive or nonreactive distillation. While a pinch point can disappear by manipulating internal flow rates in a column, we cannot circumvent an azeotrope by changing the reflux or reboil ratio, as this singularity in the separation process arises from thermodynamic and not operational considerations (Hauan et al., 1999). Separation by evaporation and condensation is impossible at the azeotropic composition. We can be arbitrarily close to but not reach a pinch situation, as it requires an infinite number of stages. However, pinch analysis has been useful for designing azeotropic separation systems (Fidkowski et al., 1993; Wahnschafft et al., 1992; Westerberg and Wahnschafft, 1996) due to their limiting behaviors around the pinch points.

We will argue that a minimum reflux pinch point may occur in a reactive distillation column, with the extent of reaction affecting its location (Lee et al., 2000a,b,c). This pinch situation occurs in nonreactive stages only, and requires that we turn off the reaction. The proper distribution of reactive stages inside a column will eliminate such a potential pinch point.

The pinch point caused by using minimum reflux occurs in the McCabe-Thiele diagram for nonreactive distillation (McCabe and Thiele, 1925). For the case when the feed composition lies between the product compositions, this minimum reflux pinch point can also occur in reactive distillation for the same reason. The feed composition is outside of the product compositions in a binary reactive distillation column if the feed stream contains a pure reactant. In this case, we will show that reactive distillation cannot show a minimum reflux pinch since the final operating lines from both the rectifying and stripping sections meet below the 45-degree line, unlike a nonreactive distillation column (Lee et al., 2000c).

Reaction equilibrium is another extreme case, since infinite reaction time or infinite volume of catalyst is required to reach it. To quantify the reaction regime between kinetics and equilibria for a reactive distillation column, Barbosa and Doherty (1987), Venimadhaven et al. (1994) and Buzad and Doherty (1994, 1995) have employed the Damköhler number. Other articles describe how different magnitudes for the reaction equilibrium constant affect the behavior of a reactive azeotrope (Okasinski and Doherty, 1997a) and how to design

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a reactive distillation column with lower reaction equilibrium constants (Okasinski and Doherty, 1997b).

Sneesby et al. (1998) pointed out, when designing a reactive distillation column assuming reaction equilibrium, that increasing the total number of stages cannot always improve the column performance in terms of overall reaction conversion and product purities, and that high reflux ratios with a restricted number of stages provides better performance of a column.

In this study, we can easily sketch McCabe-Thiele diagrams by using the feasible extent of reaction under the material balance constraint or reaction equilibrium rather than specific kinetic models for reactions, and obtain design insights more quickly (Lee et al., 2000b). First we show that a minimum reflux pinch persists in a nonreactive section rather than a reactive section if there is a net reaction turnover for each reactive stage. We also discuss several cases in which we cannot encounter a minimum reflux pinch point in reactive distillation. Then, we construct McCabe-Thiele diagrams assuming reaction equilibrium and draw important design implications such as the negative effect of excessive fractionation. Finally, we show how to step past an azeotropic composition, depending on the position of the reaction equilibrium point relative to that of the azeotrope under finite and total reflux. Computer simulations confirm the graphical results for real components.

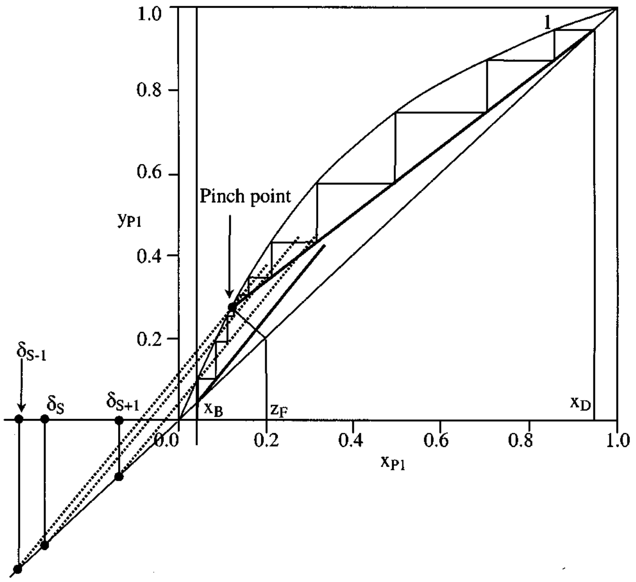

Figure 1. Pinch point at the isomerization reaction of a heavy reactant producing a light product in the stripping section.

Hereafter, dotted and dashed lines denote the reactive and the nonreactive operating lines.

Minimum Reflux Pinch in a Nonreactive Section

Liquid phase isomerization with a heavy reactant and a light product in Eq. 1 is assumed to take place inside a column and to be thermally neutral. Assume that the extent of the reaction in a column is such that the unconverted reactant, $R1$, comes out in the bottom and the product, $P1$, at the top. Then, the liquid composition of component $P1$ is the abscissa, and its vapor composition is the ordinate in a McCabe-Thiele diagram. Throughout this article, we number the stage from the top of the column.

$$R1 \Leftrightarrow P1. \tag{1}$$

Assume the reaction zone is only in the stripping section. The number of the stripping operating lines is equal to the number of reactive stages and, for constant molar overflow, the slopes of operating lines are parallel (Lee et al., 2000c). If we assume the reaction occurs in the forward direction on each reactive stage, the operating lines in the bottom section will move up as we step up the stages and the difference points move to the left as indicated in Figure 1. A pinch point can occur at a certain reaction conversion for given product specifications and heat duties in the bottom and top by turning off the reaction above stage $(s-1)$. This minimum reflux pinch point is initiated by the reaction, but the pinched zone in the column is only in the nonreactive section above the reaction zone. It cannot occur in the reactive zone, as each nonreactive stage has the same composition at the pinch point, but all reactive stages have different compositions.

If there is another reactive stage above stage $(s-1)$ in Figure 1, the pinch point disappears even if the composition profile reverses (stages 8 and 9) similar to the profiles of ternary reacting systems (Buzad and Doherty, 1994, 1995). We switch from the stripping operating line to the top operating line at stage 8 in Figure 2.

In summary, although the minimum reflux pinch can start in a reactive section, it persists in a nonreactive section. If

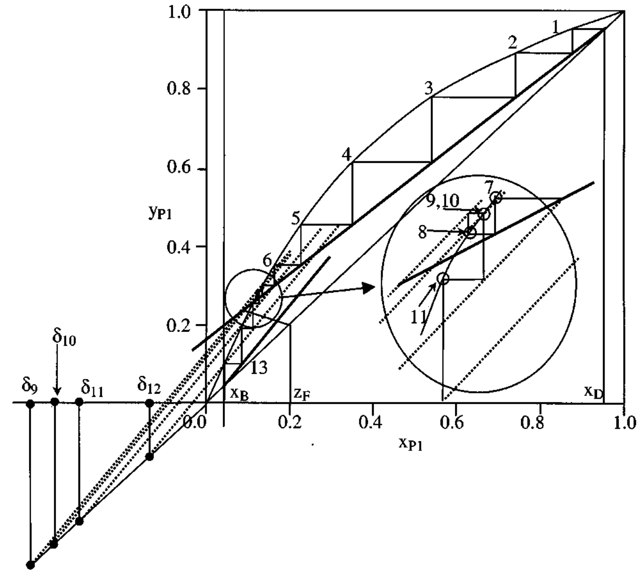

Figure 2. Pinch point disappearing at another reactive stage in Figure 1.

The number of total stages is 13.

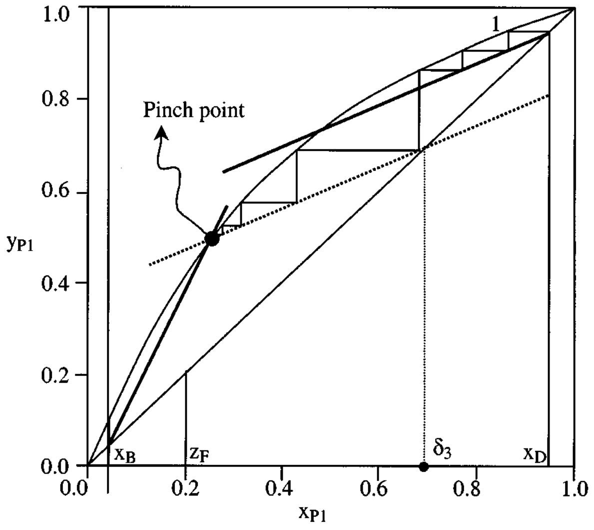

Figure 3. Minimum reflux pinch point for the reactive rectifying section.

the reaction occurs with a net reaction turnover, the minimum reflux pinch cannot occur.

Minimum Reflux Pinch Under Total Reboil

A minimum reflux pinch can occur in Figure 3 even if the reaction moves the operating lines downward and makes the size of stepping off larger in the rectifying section. This minimum reflux pinch point can disappear, as in Figure 4, if another reactive stage is introduced below the third stage while using the same reflux ratio, making the position of the difference point in the rectifying section shift to the left and the intersection point of the final rectifying operating and the stripping operating lines move to be inside the area between the phase equilibrium curve and the $y = x$ line.

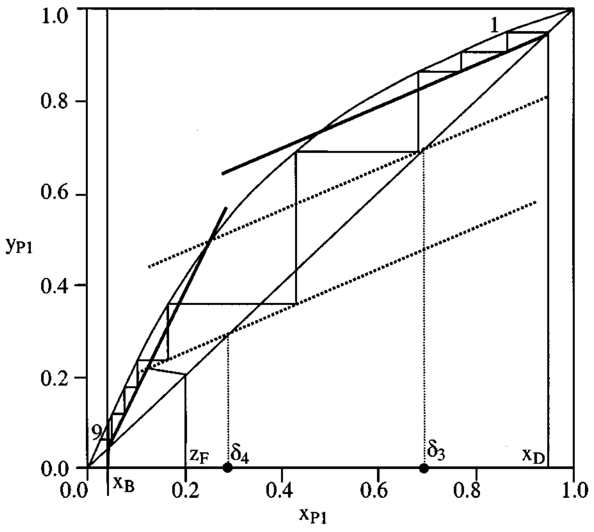

Figure 4. Eliminating the minimum reflux pinch by adding another reactive stage.

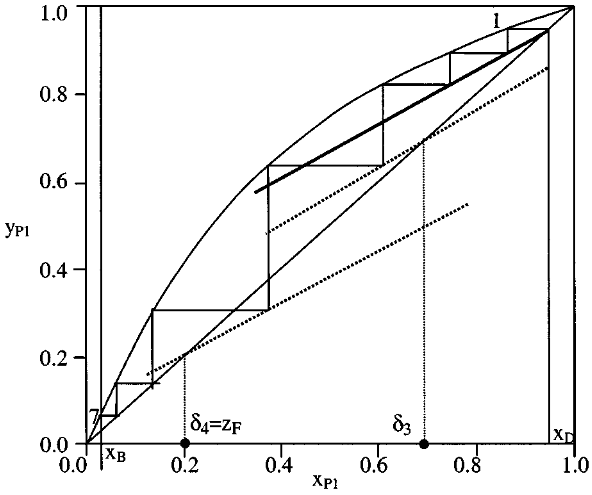

Figure 5. McCabe-Thiele diagram for no minimum reflux pinch with the reaction of *R*1 (heavy) to *P*1 (light) under total reboil.

If a column is operating under total reboil without drawing off a bottom product, but while producing a distillate, the stripping operating line is the $y = x$ line, and the final rectifying operating line intersects with the stripping operating line on the $y = x$ line. Thus, there is no minimum reflux pinch point in Figure 5. Note that we cannot discern the thermal condition of the feed stream in Figure 5 when using the McCabe-Thiele method. However, using a Ponchon-Savarit diagram, we can see the thermal condition of the feed stream as in Figure 6. The slope of the line connecting the distillate difference point, $(x_D, h_D + q_C)$ and the cascade difference points, $(\delta_3,\ h_{R,3})$ and $(\delta_4,\ h_{R,4})$ is the negative value of the heat of reaction (Lee et al., 2000a,c). This slope is positive for an exothermic reaction and negative for an endothermic re-

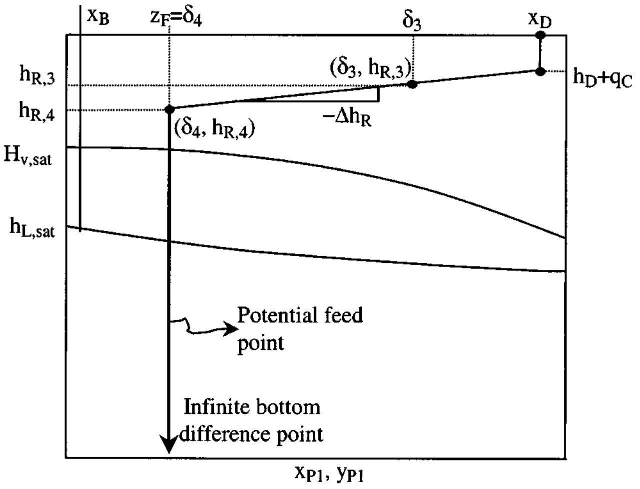

Figure 6. Ponchon-Savarit diagram for no minimum reflux pinch with the reaction of *R*1 (heavy) to *P*1 (light) under total reboil.

action. Since the isomerization is usually mildly exothermic or athermic, the feed stream can have any thermal condition, as the bottom difference point is negative infinity in Figure 6. One should note that the feed point with composition and enthalpy lies between the bottom difference point and (δ_4, $h_{R,4}$).

Even if the feed composition lies outside the product compositions or the feed composition is equal to the bottom product composition, the minimum reflux pinch does not occur under total reboil by the same argument in Figures 5 and 6.

Reaction Equilibrium on the McCabe-Thiele Diagram

The reaction equilibrium of a binary reacting mixture results in one specific equilibrium point on McCabe-Thiele and Ponchon-Savarit diagrams, assuming a fixed pressure. When we assume that the reaction in Eq. 1 takes place in the rectifying section, the reaction equilibrium constant is given by Eq. 2:

$$K_{\mathrm{eq}} = \frac{x_{P1}}{x_{R1}} = \frac{x_{P1}}{1 - x_{P1}}. \qquad (2)$$

With a feed stream of pure $R1$, the final difference point (δ_f) for the reactive rectifying section should lie to the left of the feed composition. A reaction conversion causing the final difference point to be to the right of the feed or the bottom composition is infeasible in Figure 7 due to a violation of the following total material balance:

$$F = B + D - \nu_T \xi \qquad (3)$$

$$F z_F = B x_B + (D x_D - \xi) = B x_B + D \delta_f. \qquad (4)$$

Here, ν_T is sum of the stoichiometric coefficients, which is zero for the reaction in Eq. 1, ξ is the total reaction molar turnover for the column, and δ_f is the final difference point. The feed composition should lie between this final difference point and the bottom product composition.

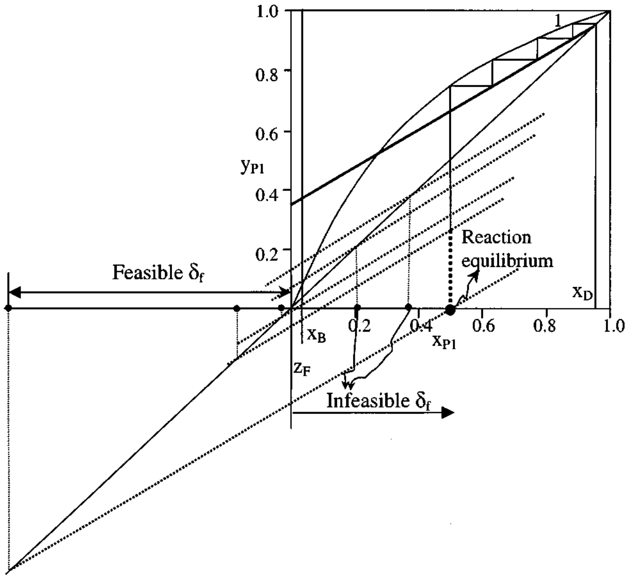

Figure 7. Feasible and infeasible locations for the difference points.

The reaction molar turnover (ξ) decreases as the difference point moves to the left for the feasible locations of the difference points.

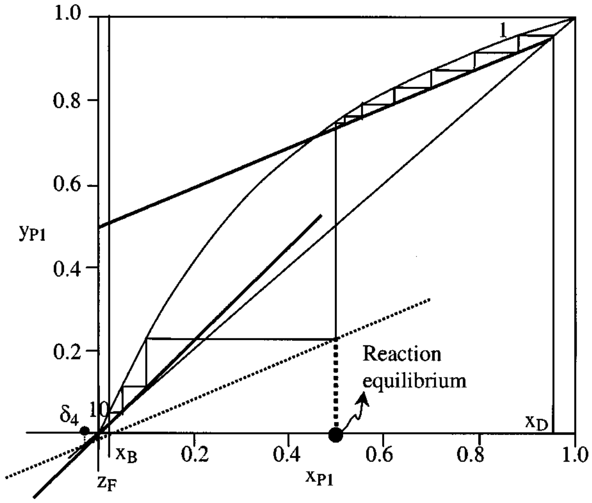

Figure 8. Ten stages for an equilibrium reaction conversion and given product specification.

The reaction is feasible in terms of material balance for the final difference point lying to the left of the feed composition in Figure 7. The overall reaction molar turnover (ξ) will increase if the final difference point approaches the feed composition. We can introduce the limit of the feasible range for the final difference point on the left side by noting that the final reactive operating line in the rectifying section should meet the x-axis at the maximum mol fraction for an x_{P1} of 0.5. If the final reactive operating line meets the x-axis at a mol fraction of greater than 0.5, switching from this reactive operating line to the stripping operating line is impossible within the valid composition space, as shown in Figure 7.

If there is one reactive stage above the feed stage, only forward reaction occurs in that stage, and stagewise calculations can start from the reaction equilibrium point. For given top and bottom product purities, the total number of stages can be calculated in Figures 8 and 9. For the same reaction conversion, ten stages are needed for the slope of the top operating line in Figure 8. If the reflux increases, which means the slope of the top operating line increases in Figure 9, seven stages satisfy the product specifications. In other words, as the reflux increases, the number of stages decreases to obtain the same reaction conversion under reaction equilibrium.

Another reactive stage in the rectifying section will cause the reaction to occur in the reverse direction, since reaction equilibrium forces the compositions of those reactive stages to be identical in Figure 10. The reactive operating line for reactive stage 4 touches the composition of the reaction equi-

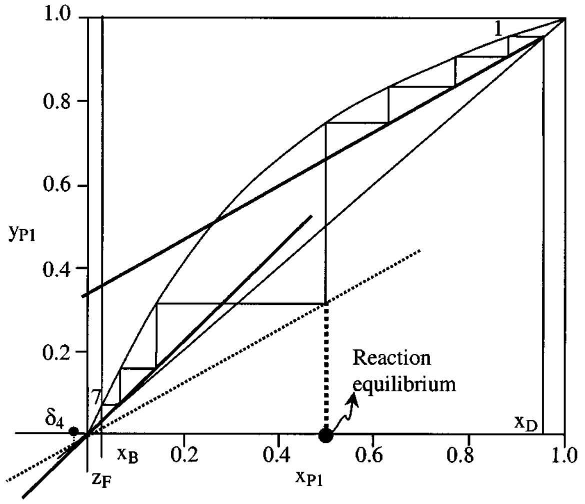

Figure 9. Higher reflux ratio with seven stages for the same equilibrium reaction conversion and product specifications as in Figure 10.

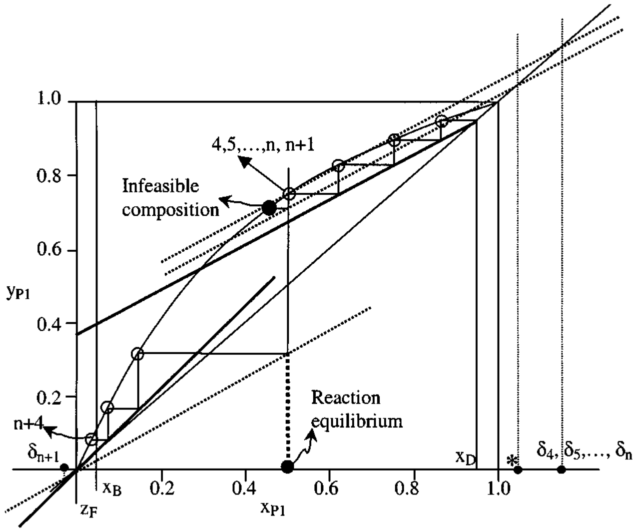

Figure 11. McCabe-Thiele diagram for (*n*-2) reactive stages in the rectifying section with the equilibrium isomerization reaction of *R*1 to *P*1.

The asterisk (*) is the difference point for the infeasible composition under reaction equilibrium.

librium on the phase equilibrium curve and confines the composition of the reactive stage to that reaction equilibrium composition. Thus, the reverse reaction occurs in stage 4 and the forward reaction takes place in stage 5.

If there are many reactive stages in the rectifying section, the reverse reaction occurs only in the uppermost reactive stage and the forward reaction only in the lowest reactive stage. The reaction does not take place between these two stages due to the constraint of reaction equilibrium. If the forward reaction occurred in those intermediate reactive stages, the composition is not the same as the reaction equilibrium point in Figure 11 and is infeasible. As the compositions of the influxes of vapor and liquid streams into the intermediate reactive stages are exactly the same as the reaction equilibrium composition, those stages do not contribute at all to reaction and separation.

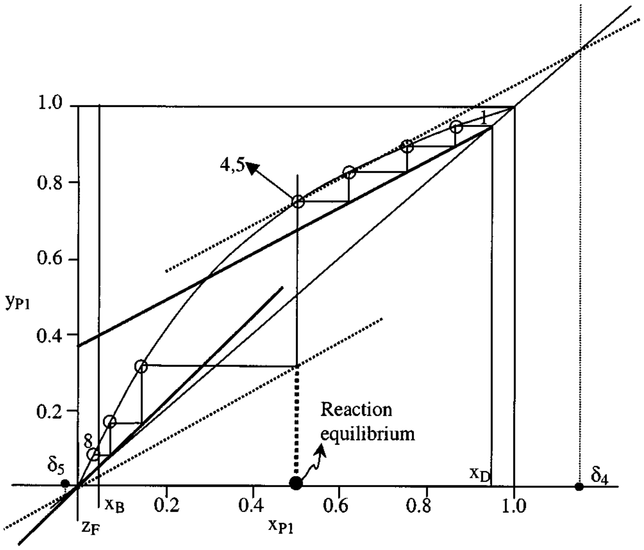

Figure 10. McCabe-Thiele diagram for two reactive stages (stages 4 and 5) in the rectifying section with the equilibrium isomerization reaction of *R*1 producing *P*1.

The open circle represents the phase-equilibrium stage.

Therefore, several reactive stages in binary reactive distillation can negatively affect overall reaction molar turnover and separation efficiency for the same total number of stages operating at constant pressure, since the reverse reaction always occurs on the uppermost reactive stage. We performed a computer simulation with the liquid phase isomerization of 1,4-dichloro-2-butene (DCL2B), producing 1,2-dichloro-3-butene (DCL3B) by using AspenPlus. Here, the mol fraction of DCL3B at the reaction equilibrium point is 0.397, and the total number of stages is fixed as eight. In the simulation, we aimed at the maximum recovery of top and bottom products (relatively pure DCL3B and DCL2B, respectively) in the column. The simulation results for three cases are available in Table 1, varying with the number of reactive stages. Overall reaction molar turnover decreases, and the reverse reaction becomes dominant as the number of reactive stages increases. The purities of top and bottom products get worse as reactive stages are added.

Figures 12, 13 and 14 contain the McCabe-Thiele diagrams for these simulations. The final difference point moves to the left of the feed composition as the number of reactive stages increases, which means that the overall reaction molar turnover decreases. The only way to obtain the same reaction molar turnover for the case of one reactive stage in Figure 12 is to increase the total number of stages if there is more than one reactive stage, as in Figures 13 and 14. If we study Figures 9, 10, and 11, we clearly understand that the number of nonreactive stages below and above the reactive section should be the same for all cases in order to have the identical

Table 1. Simulation Results for Reactive Distillation Columns with the Isomerization Reaction of 1,4-Dichloro-2-Butene (DCL2B) Producing 1,2-Dichloro-3-Butene (DCL3B) and Different Number of Reactive Stages

	Case I	Case II	Case III
Total no. of stages	8	8	8
Reactive stages	5	3,4,5	2,3,4,5
Feed stage	6	6	6
Reflux flow rate (kmol/h)	1,200	1,200	1,200
Feed stream			
Flow (kmol/h)	1,000	1,000	1,000
Mole fraction DCL2B	1.0	1.0	1.0
Reaction molar turnover (kmol/h)			
Stage 2 (ξ_2)	Not available	Not available	−247.7
Stage 3 ($\xi_3 - \xi_2$)	Not available	−205.4	0.0
Stage 4 ($\xi_4 - \xi_3$)	Not available	0.0	0.0
Stage 5 ($\xi_5 - \xi_4$)	531.8	501.1	486.4
Product flow (kmol/h)			
Distillate flow/ DCL3B purity	546.6/95.0%	295.8/90.0%	253.4/81.0%
Bottom flow/ DCL2B purity	453.4/97.2%	704.2/95.8%	746.6/95.5%

purities of products and overall reaction conversion, even if the number of reactive stages increases. Intuitively, as the compositions in all reactive stages are fixed at one point because of reaction equilibrium, the total number of stages increases in terms of the number of added reactive stages without removing the nonreactive stages, as in Figures 9, 10, and 11.

How to Destroy an Azeotrope by Equilibrium Reaction Under Finite Reflux

In this section, we deal with a maximum boiling azeotrope between *R*1 (heavy) and *P*1 (light) in the reaction in Eq. 1. We operate the column using finite reflux and assume reaction equilibrium.

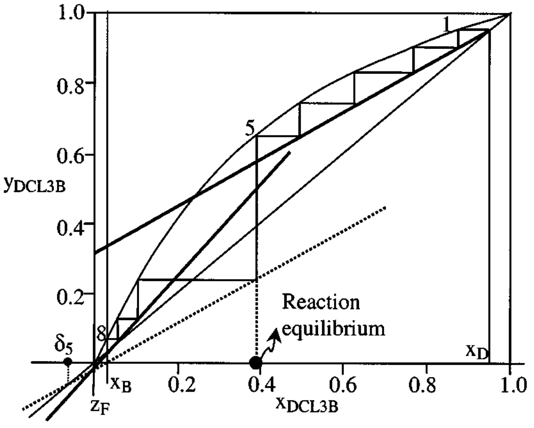

Figure 12. One reactive stage in an eight-stage column with the equilibrium reaction of 1,4-dichloro-2-butene (DCL2B) to 1,2-dichloro-3-butene (DCL3B).

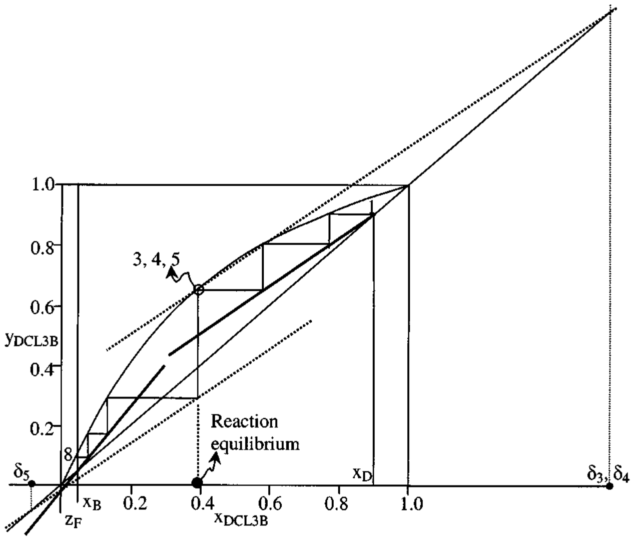

Figure 13. Two reactive stages in an eight-stage column with the equilibrium reaction of 1,4-dichloro-2-butene (DCL2B) to 1,2-dichloro-3-butene (DCL3B).

If the reactive section is only in the rectifying one and the reaction equilibrium point lies on the right side of the azeotropic composition, the azeotrope can be circumvented by one reactive stage in Figure 15. The temperature will decrease as we step down the nonreactive stages (3 to 7) below reactive stage 2.

With the reaction equilibrium on the left side of the azeotrope, the forward reaction does not occur until we pass over the azeotropic composition. With nonreactive distilla-

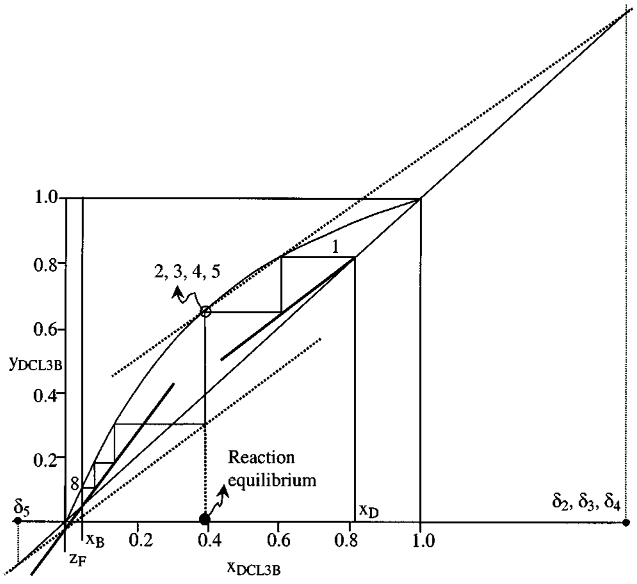

Figure 14. Four reactive stages in an eight-stage column with the equilibrium reaction of 1,4-dichloro-2-butene (DCL2B) to 1,2-dichloro-3-butene (DCL3B).

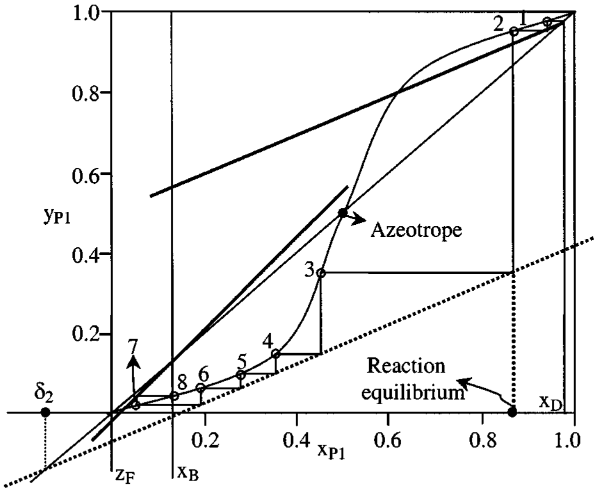

Figure 15. McCabe-Thiele diagram with a rectifying-reaction zone when the reaction equilibrium point is the right side of the azeotrope.

tion on the right side of the azeotrope, the azeotrope in Figure 16 cannot be crossed. The stream containing almost pure *R*1 will be the top product, as it is more volatile than the azeotrope that will be the bottom product.

If the azeotropic composition is identical to the reaction equilibrium, the top and bottom products will be the azeotrope and relatively pure *R*1 in Figure 17. The temperature profile in the column will reverse until we move down to the bottom of the column. From the three cases in Figures 15 to 17, we can eliminate the binary azeotrope only if the reaction equilibrium lies on the right of the azeotropic composition.

We take the isomerization of 2-phenylethanol (2-PHE) producing *para*-ethylphenol (*p*-ETP), in which a maximum boiling azeotrope exists around 55 mol % of *para*-ethylphenol (Lecat, 1949; Horsley, 1973). This azeotrope can be destroyed by the following reaction in a reactive distillation column, which was visualized in the McCabe-Thiele diagram (Lee et al., 2000d). Here, we show whether the azeotrope can be eliminated by the equilibrium reaction as a function of the magnitude of the reaction equilibrium constant. Using the UNIFAC property set in AspenPlus, the azeotrope occurs at 53.4 mol % of *para*-ethylphenol:

$$C_6H_5{-}CH_2CH_2OH(2\text{-}PHE) \Leftrightarrow CH_3CH_2{-}C_6H_4{-}OH(p\text{-}ETP). \qquad (5)$$

We can bypass the azeotrope using finite reflux as the reaction equilibrium point, 0.948 of $x_{p\text{-ETP}}$, which is estimated from Gibbs free energy in AspenPlus, is greater than the azeotropic composition, that is, the reaction equilibrium lies

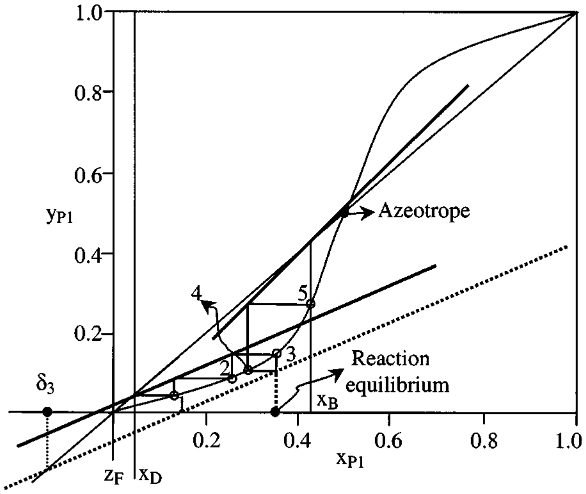

Figure 16. McCabe-Thiele diagram with a rectifying-reaction zone when the reaction equilibrium point is the left side of the azeotrope.

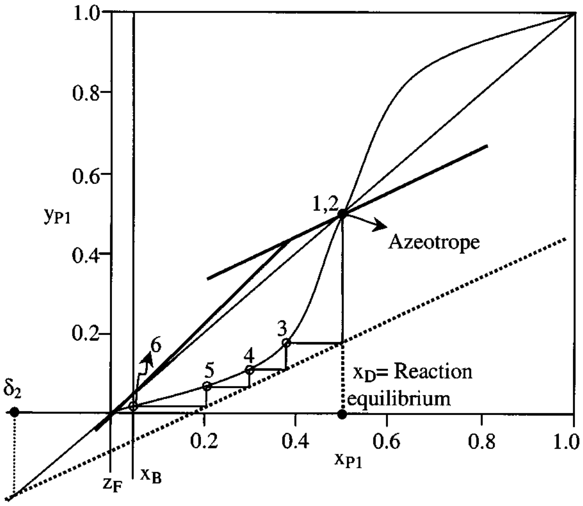

Figure 17. McCabe-Thiele diagram with a rectifying-reaction zone when the reaction equilibrium point is equal to the azeotropic composition.

Table 2. Simulation Results for a Reactive Distillation Column with the Isomerization Reaction of 2-Phenylethanol(2-PHE) to *para*-Ethylphenol (*p*-ETP)

	Case I	Case II	Case III
Reaction equil. composition in terms of *p*-ETP	0.948	0.34	0.534
Total no. of stages	8	15	9
Reactive stage	1	5	1
Feed stage	8	6	9
Reflux ratio	1	4	6
Feed stream			
Flow (kmol/h)	1,000	1,000	1,000
Mol fraction 2-PHE	1.0	1.0	1.0
Reaction molar turnover (kmol/h)	858.1	171.6	205.8
Product flow (kmol/h)			
Distillate flow/*p*-ETP purity	870/98.2%	800/8.48%	200/53.4%
Bottom flow/2-PHE purity	130/96.8%	200/48.1%	800/87.6%

on the right of the azeotrope. Case I in Table 2 shows that top and bottom products are *p*-ETP and 2-PHE. But if the reaction equilibrium point is assumed to be 0.34 in mol fraction of *p*-ETP on the left side of the azeotropic composition, the top and bottom products can be 2-PHE and the azeotrope, as in Case II of Table 2. The azeotrope and relatively pure 2-PHE become top and bottom products, with the reaction equilibrium point equal to the azeotropic composition in Case III of Table 2.

Is it Possible to Eliminate a Binary Azeotrope Using Total Reflux?

Using total reflux, can we really circumvent a binary azeotrope? Generally speaking, it is impossible to eliminate the azeotrope. Because there are no or negligible feed and product streams (relative to internal flows) under total reflux, the overall reaction molar turnover in such a column is zero. If a certain reactive stage is dominant in the forward reaction, then others definitely have reverse reaction. Thus, the final operating line below or above all reactive stages is always the $y = x$ line, since the reaction molar turnover is zero and the product streams are nonexistent. The reactive operating line within the reactive section is parallel to the $y = x$ line, and its y-intercept is offset from the origin due to reaction molar turnover.

Considering the case when reaction does not reach equilibrium, we assume the extent of the reaction on each reactive stage. Reactive distillation seems to eliminate the azeotrope if the forward reaction is dominant in the upper part of a reactive section and the reverse reaction in the lower part of the reactive section, as in Figure 18. The reactive operating line can lie below the phase-equilibrium curve for an overall positive value of the reaction molar turnover for the forward reaction in the upper reactive section. The final operating line returns to the $y = x$ line below the lower reactive section that has negative reaction molar turnover. So, stepping off by these operating lines appears to ensure that the reaction on each reactive stage circumvents the azeotrope. However, the reverse reaction cannot occur in the lower reactive section, since the reaction region is the forward reaction zone in Figure 18. What would happen if the reverse, forward, and reverse reactions take place on the reactive sections (or stages) from the top? The first, second, and third reactive operating lines can lie above, below, and equal to the $y = x$ line in Figure 19. In this case, the reverse reaction cannot also occur in the lower reactive section, as the reaction region is the forward reaction zone.

Next, let's assume the reaction on each reactive stage proceeds to reaction equilibrium. Suppose there are two consecutive reactive stages (or sections) in which the forward reaction occurs in the upper stage, and the reverse reaction takes place in the lower stage, it seems that the reaction can circumvent the azeotrope under total reflux for the reaction equilibrium point lying on the right of the azeotrope in Figure 20. However, if the upper stage has the forward reaction occur, the lower reactive stage cannot have the composition at the reaction equilibrium point in Figure 20, since the reactive operating line forces the composition of the lower stage to be away from the reaction equilibrium. With nonreactive stages between these reactive stages, the forward reaction in the upper stage can still make the composition of the lower reactive stage infeasible in Figure 21. Thus, the reverse reac-

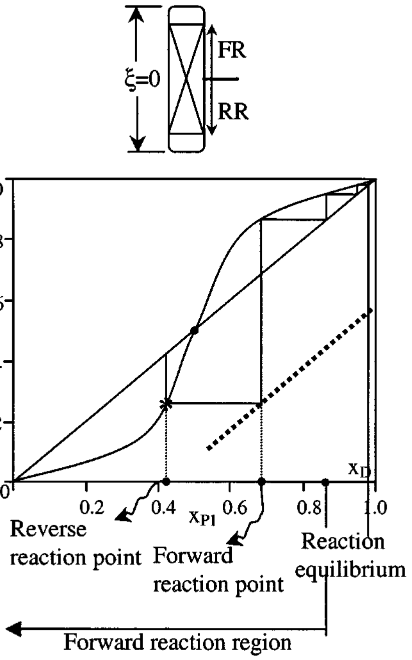

Figure 18. Infeasible reverse reaction point (*) for forward and reverse-reaction zones from the top under total reflux.

FR: forward reaction, RR: reverse reaction.

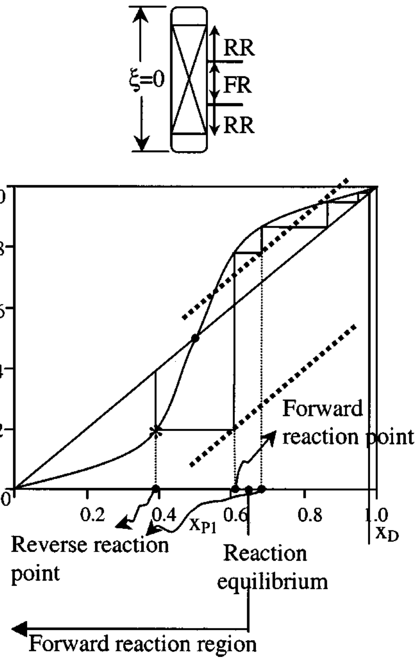

Figure 19. Infeasible reverse reaction point (*) for reverse, forward, and reverse-reaction zones from the top.

FR: forward reaction, RR: reverse reaction.

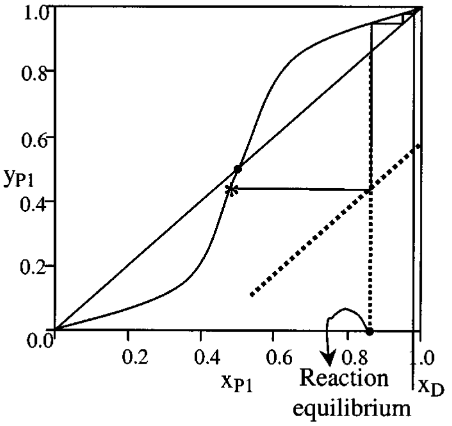

Figure 20. Infeasible reaction equilibrium composition (*) at the lower reactive stage of two reactive stages.

tion naturally occurs in the upper reactive stage and the forward reaction in the lower reactive one, since the composition around the upper section is likely to be on the right of the reaction equilibrium point, which is the reverse reaction region, and the composition around the lower section will lie within the forward reaction region. As a result, the reactive operating line lies above the $y = x$ line and touches the reaction equilibrium composition on the phase-equilibrium curve. The final operating line below the reactive section returns to the $y = x$ line. Thus, we cannot circumvent the azeotrope under total reflux. Starting from this reaction equilibrium composition in Figure 22, the top product can be pure $P1$, and the bottom one is the azeotrope.

If the reaction equilibrium point is on the left of the azeotropic composition in Figure 23, the top and bottom products will be pure $R1$ and the azeotropic, respectively, under total reflux. The reactive operating line also sits on the phase-equilibrium curve at reaction equilibrium, but the forward reaction is dominant in the upper reactive section and the reverse reaction in the lower reactive section. For the reaction equilibrium point equal to the azeotropic composition in Figure 24, all stages are trapped at the azeotrope, and the reactive operating line is the same as the $y = x$ line. Even if all stages are reactive, we cannot destroy this azeotropic

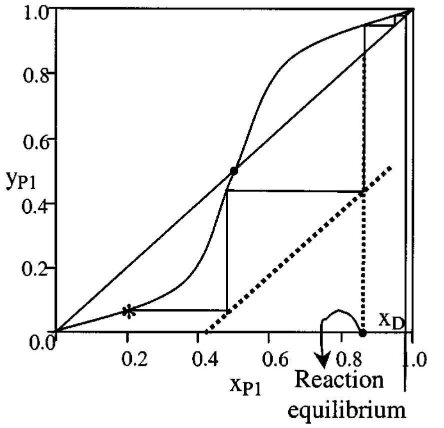

Figure 21. Infeasible reaction equilibrium composition (*) at the lower reactive stage if one nonreactive stage is between two reactive stages.

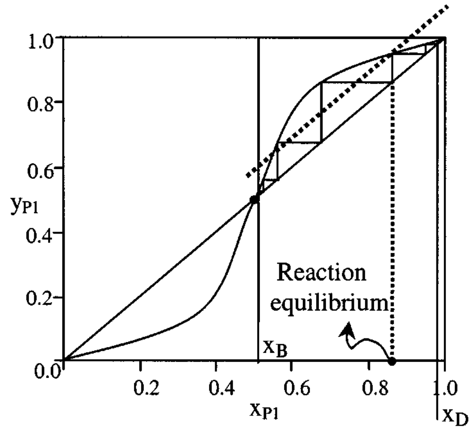

Figure 22. Feasible reactive operating line under total reflux as well as reaction equilibrium.

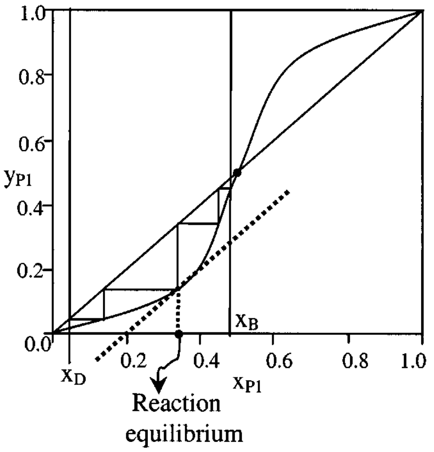

Figure 23. Feasible top and bottom products under total reflux when the reaction equilibrium point is to the left side of the azeotrope.

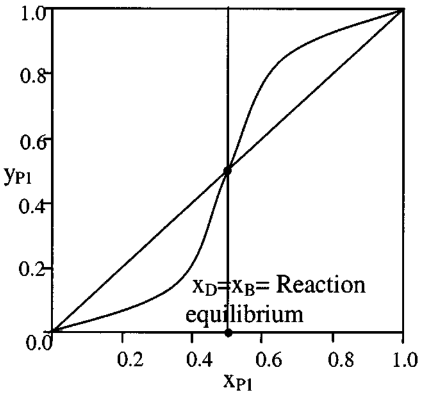

Figure 24. Feasible top and bottom products under total reflux when the reaction equilibrium point is equal to the azeotropic compositions.

Table 3. Simulation Results for a Reactive Distillation Column with the Isomerization Reaction of 2-Phenylethanol (2-PHE) to *para*-Ethylphenol (p-ETP) Under Total Reflux

	Case I	Case II	Case III
Reaction equil. composition by mol fraction of p-ETP	0.948	0.34	0.534
Total no. of stages	15	15	19
Reactive stage	1	5	3–14
Feed stage	8	6	9
Reflux ratio	10,000	40,000	60,000
Feed stream			
Flow (kmol/h)	0.1	0.1	0.1
Mol fraction 2-PHE	1.0	1.0	1.0
Reaction molar turnover (kmol/h)	0.0924	0.01267	0.0534
Product flow (kmol/h)			
Distillate flow/p-ETP purity	0.087/98.2%	0.08/2.63%	0.02/53.4%
Bottom flow/2-PHE purity	0.013/46.2%	0.02/47.2%	0.08/46.6%

composition, since all compositions converge to the reaction equilibrium point.

Table 3 gives simulation results for the reactive distillation columns, with reaction in Eq. 5 operating under total reflux. Here, we fake the situation of total reflux by having very small flow rates compared to the reflux flow rates for the feed and product streams. Top and bottom product compositions in each case of Table 3 follow the same trends as in Figures 22 to 24 if $R1$ and $P1$ correspond to 2-PHE and p-ETP, respectively.

Summarizing those two previous sections, we can obtain pure $P1$ and $R1$ as top and bottom products, respectively, when they form a maximum boiling azeotrope, by circumventing the azeotrope only if the reaction equilibrium lies to the right of the azeotropic composition and the reflux ratio is finite. This observation is applicable to a binary reacting system with a minimum boiling azeotrope for the isomerization reaction involving a light reactant forming a heavy product. For these remaining three cases, we present the results in the Appendix. The common and important thing is that there had better be at least one nonreactive stage below the rectifying reactive section or above the stripping reactive one before arriving at the feed stage to circumvent an azeotrope.

Conclusion

There are several important remarks worth mentioning for binary reactive distillation. We consider the case when the reaction has a heavy reactant to form a light product. By localizing and locating the reactive zone properly, we can eliminate a minimum reflux pinch situation. We can obviate the minimum reflux pinch by totally reboiling the heavy reactant regardless of the feed composition. If the reaction is mainly controlled by reaction equilibrium, more than one reactive stage for the azeotropic mixture will worsen the performance of a column in terms of the product purities and overall reaction conversion. We can circumvent a binary maximum boiling azeotrope between the isomer of a heavy reactant and a light product only if the reaction equilibrium point is larger than the azeotropic composition and only if the column is operated under finite reflux.

Notation

B = bottom molar flow rate
D = distillate molar flow rate
F = feed molar flow rate
h_B = molar enthalpy in the bottom product
h_D = distillate molar enthalpy
$h_{R,n}$ = enthalpy difference point at stage n in the rectifying section
K_{eq} = reaction equilibrium constant based on the mol fraction
$\underline{L}$ = liquid molar flow rate in the rectifying section
$\overline{L}$ = liquid molar flow rate in the stripping section
$P1$ = the component for isomerization reaction product
q_C = molar duty of a condenser
Δh_R = heat of reaction
$R1$ = the component for isomerization reaction reactant
$\underline{V}$ = vapor molar flow rate in the rectifying section
$\overline{V}$ = vapor molar flow rate in the stripping section
x_B = liquid composition for the bottom product
x_D = liquid composition for the distillate product
x_i = liquid composition for species i
x_n = liquid composition at stage n
y_n = vapor composition at stage n
z_F = feed composition
δ_n = difference point at stage n of the rectifying section
δ_s = difference point at stage s of the stripping section
δ_f = final difference point at the lowest stage of the rectifying section
ν_T = sum of the total stoichiometric coefficients
ξ = total molar reaction turnover flow rate
ξ_n = sum of molar turnover flow rate from the top to n stages in the reactive rectifying section
ξ_s = sum of molar turnover flow rate from bottom to s stages in the reactive stripping section

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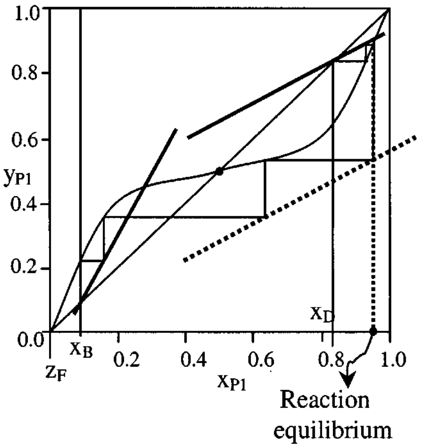

Figure A1. Breaking a minimum boiling azeotrope with a rectifying-reaction section under finite reflux as well as reaction equilibrium.

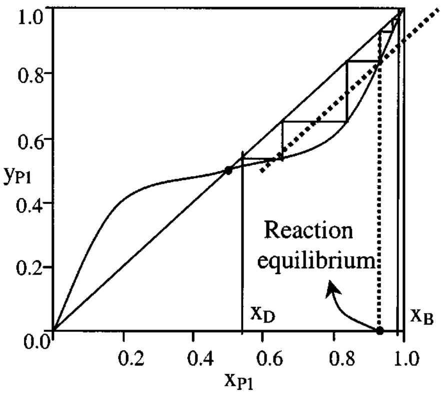

Figure A2. Feasible top and bottom products under total reflux as well as reaction equilibrium.

Appendix

Case 1: McCabe-Thiele diagrams with the isomerization of a heavy reactant to a light product and a minimum boiling azeotrope

The reaction equilibrium point should lie on the right of the azeotropic composition to circumvent the minimum boiling azeotrope using finite reflux in Figure A1. The reaction equilibrium point should become larger to produce $P1$ with higher purity at the top. Under total reflux, the top product is the azeotrope and the bottom product component, $P1$, for the reaction equilibrium point we show in Figure A2.

Case 2: McCabe-Thiele diagrams with the isomerization of a light reactant to a heavy product and a maximum boiling azeotrope

With a light reactant in the isomerization, the reaction zone should be in the stripping section to improve separation efficiency (Lee et al., 2000c). The reaction equilibrium point should be on the left of the azeotropic composition to have a case where we can circumvent an azeotrope, as we show in Figure A3. If the reaction equilibrium point is on the right of the azeotropic composition, the forward reaction cannot occur until we pass over the azeotrope. The bottom stage should be a reactive stage, as otherwise the bottom product composition shifts toward the azeotropic composition. Thus, the bottom product composition sits on the reaction equilibrium point or to the right of this point. Above the bottom reactive

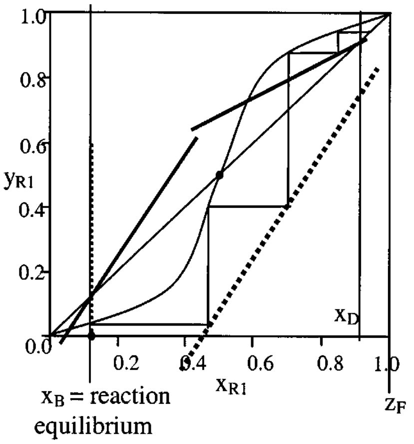

Figure A3. Circumventing a maximum boiling azeotrope under finite reflux as well as reaction equilibrium when the isomerization reaction of a light reactant (*R*1) to a heavy product (*P*1) occurs in the stripping section.

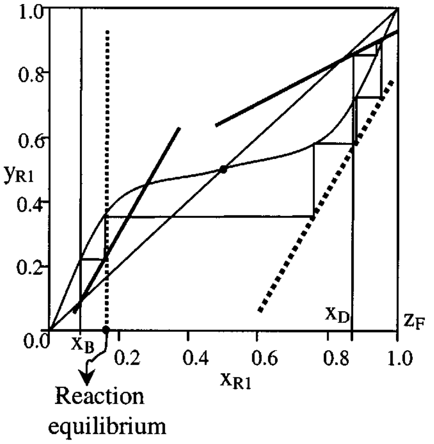

Figure A4. Circumventing a minimum boiling azeotrope under finite reflux as well as reaction equilibrium when the isomerization reaction of a light reactant (*R*1) to a heavy product (*P*1) occurs in the stripping section.

stage, there is one nonreactive stage below the feed stage in Figure A3. Under total reflux, we have the same trends of composition profiles as in Figures 22 to 24, according to the positions of reaction equilibrium points, and reaction is unable to allow us to bypass the azeotrope.

Case 3: McCabe-Thiele diagrams with the isomerization of a light reactant to a heavy product and minimum boiling azeotrope

As for the previous case, the reaction equilibrium point has to lie to the left of the azeotropic composition to allow us to circumvent a minimum boiling azeotrope. It would be best for the top stage to be the feed stage, as the composition profile is reversed in a nonreactive rectifying section. Under total reflux, reaction cannot circumvent the azeotropic composition, and tray-by-tray calculations can start from the equilibrium point, which results in the azeotrope being the top product.

Manuscript received Nov. 1, 1999, and revision received May 8, 2000.