Feasible Products in Batch Reactive Distillation

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A systematic feasibility evaluation for batch reactive distillation systems is addressed. In each batch configuration, feasibility criteria are obtained for ternary reactive systems by using residual curve maps (RCMs) and reaction equilibrium manifolds. If one of the reaction products is an unstable node (UN) and is reachable from all distillation regions, a rectifier can be used for producing pure products. Even if this unstable node is only reachable from one specific distillation region, a rectifier can still be used when a part of the reaction equilibrium curve lies within the same distillation region as the product. Symmetric results are conserved for a batch stripper with one stable node (SN) product. Finally, pure products are produced in middle-vessel columns when the UN and SN products share the same distillation region with a part of the reaction equilibrium curve. Although these criteria are obtained for ternary systems, they can be extended to multicomponent reactive systems.

Introduction

Batch distillation is a traditional unit operation in the chemical industry. Recently, there has been increased interest in batch distillation processes because of its applicability to small-scale production of specialty chemicals. A single batch-distillation column can separate multiple components and can easily handle a wide range of feed compositions and varied degrees of difficulty of separation. Batch distillation is also attractive because of its lower capital cost.

There are three types of batch configurations (see Figure 1): rectifier, stripper (Robinson et al., 1950), and middle-vessel column (Hasabe et al., 1992; Davidyan et al., 1994). The conventional batch-distillation column (Figure 1a) is called a rectifier because the products are collected from the top of the column. In contrast, if products are obtained from the bottom of the column, then it is called a stripper (Figure 1b). For a middle-vessel column (Figure 1c), the mixture to be separated is loaded into the middle vessel between two separation sections and the products are simultaneously withdrawn from the top and the bottom of the column.

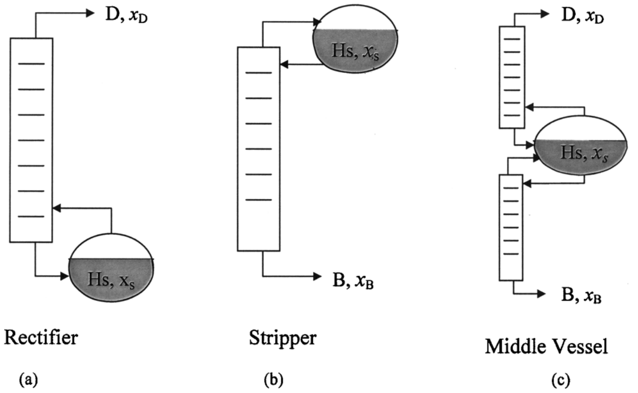

Figure 1. Batch-distillation columns with reaction occurring in the charge drums.

Recently, there have been a lot of publications focusing on batch-distillation processes. Some of them have studied optimal operation policies for batch distillation (Hasabe et al., 1997; Safrit and Westerberg, 1997; Bonny, 1999; Sørensen, 1999; Kim and Diwekar, 2000, for example). Many feasibility studies on nonreactive batch distillation also can be found in the literature (Bernot et al., 1991; Safrit et al., 1995; Ahmad and Barton, 1996; Lotter and Diwekar, 1997; Lelkes et al., 1998; Lang et al., 2000; Phimister and Seider, 2000, for example) where simple information of distillation or residue curve maps (RCMs) are used to identify feasible product cuts. However, no geometric feasibility analyses for desired product cuts in batch *reactive* distillation systems have been found in the literature. The main reason for this is the lack of knowledge about the interaction between distillation and reaction. Thus, a feasibility evaluation method to identify possible product cuts needs to be developed by combining simple information of RCMs and reaction equilibrium manifolds.

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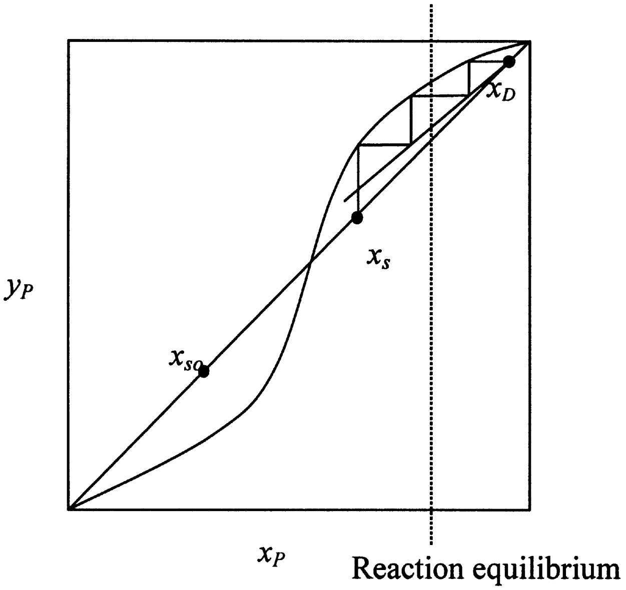

Figure 2. Batch-rectifier analysis for a max. boiling azeotropic system using McCabe-Thiele diagrams.

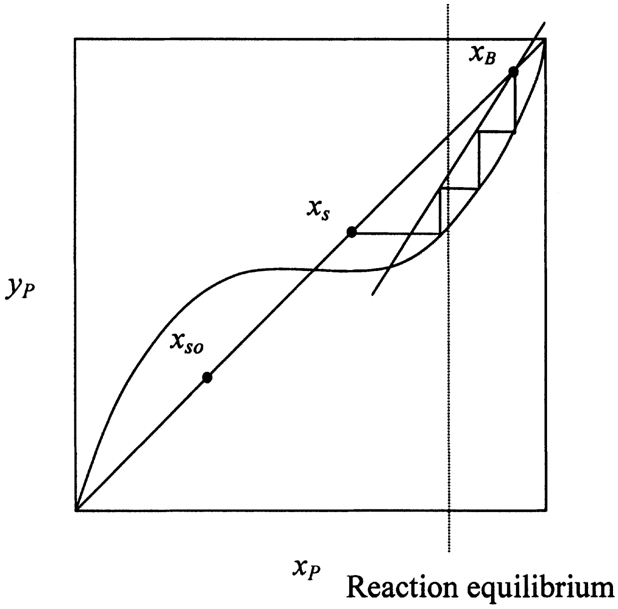

Figure 3. Batch-stripper analysis for a min. boiling azeotropic system using McCabe-Thiele diagrams.

To simplify the feasibility study, it is assumed that the reaction only occurs in the initial feed-charge drums for each batch column, as shown in Figure 1. The composition profiles of the reactive feed drum are time dependent and can be estimated by using the reaction equilibrium curve, while RCMs are used for the composition profiles of nonreactive stages. In this study, the analysis will be focused on azeotropic systems. The following part of this article will analyze binary reactive systems in the batch rectifier, the stripper, and the middle-vessel column. Following that, the feasibility analysis for ternary systems will be studied for the three types of columns. The feasibility analysis will be confirmed by using dynamic simulations.

Feasibility of Binary Reactive Systems

In order to understand the feasibility of batch-reactive distillation processes, the binary isomerization reaction of $R \leftrightarrow P$ will be reviewed here (Lee et al., 2001). A maximum boiling azeotrope exists in the binary system shown in Figure 2. In this system, product P is more volatile than reactant R. Figure 2 illustrates how a batch rectifier avoids the maximum boiling azeotrope. As the reaction occurs in the still pot, the still composition moves toward the reaction equilibrium and crosses the azeotropic composition. Thus, the rectifier produces pure product P at the top. Figure 3 shows that a batch stripper can break a binary minimum boiling azeotrope. In this system, product P is the heavy component, and reactant R is the light component. It can be seen that the overhead drum composition can cross the azeotropic composition and move to the reaction equilibrium. The minimum boiling azeotrope is avoided because of the reaction. Thus, the pure product P can be produced at the bottom of the column.

Is it possible to evade a maximum boiling azeotrope using a batch stripper? With the same initial charge in the overhead drum as in the still pot of Figure 2, the bottom product is the azeotrope in Figure 4. Although the reaction forces the still composition to cross the azeotropic composition, the bottom product is still the maximum boiling azeotrope since it is the heaviest boiler in the system. Thus, the batch stripper cannot produce pure product, P. Similarly, a batch rectifier is not suitable for producing pure products when a minimum boiling azeotrope exists in the binary system. Even if the re-

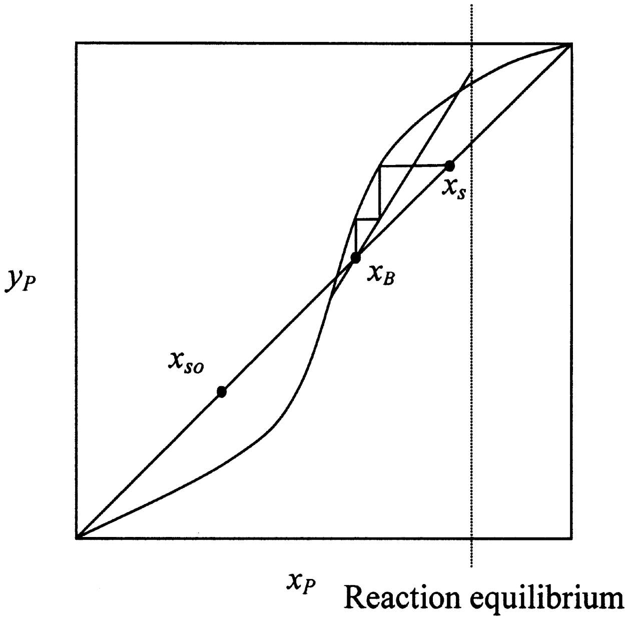

Figure 4. Batch-stripper cannot break a binary max. boiling azeotrope.

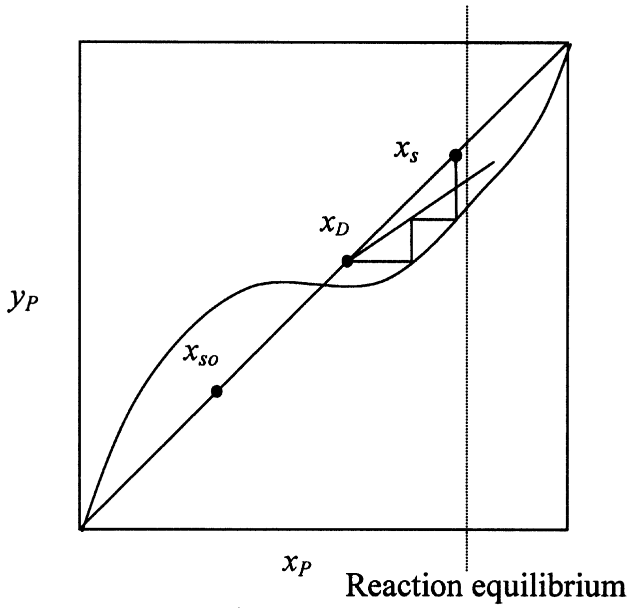

Figure 5. Batch-rectifier cannot eliminate a binary minimum boiling azeotrope.

action allows the still composition to cross the azeotropic composition, the top product is the minimum boiling azeotrope because it is the lightest boiler in such systems (see Figure 5).

These results indicate that a batch rectifier can be used to evade a maximum boiling azeotrope and that a batch stripper can circumvent a minimum boiling azeotrope. To break the azeotropes and produce the desired products, the system must satisfy the following condition: any azeotropic compositions must lie within the forward reaction zone, as shown in Figures 2 and 3. When using a middle-vessel column, pure products can be obtained at the top if the system has a maximum boiling azeotrope under total reboil at the bottom, which is similar to the operation of a batch rectifier. It can also produce pure products at the bottom when the system has a minimum boiling azeotrope under total reflux at the top, which behaves like a batch stripper.

Feasibility of Ternary Reactive Systems

Can these binary design insights be extended to multicomponent reactive systems? To answer this question, ternary batch-reactive distillation systems are studied in this section.

Batch Rectifier

The results of binary batch-reactive distillation design suggest that a batch rectifier and a batch stripper can be used to circumvent maximum and minimum boiling azeotropes, respectively. However, even if these insights are valid for some cases, they could fail for other multicomponent mixtures due to different types of phase equilibrium and reaction stoichiometries.

In order to simplify the feasibility study for the ternary reactive systems, the study starts with the simple decomposition reaction of $2B \leftrightarrow A + C$. In this ternary system, product A is the light boiler, C is the heavy boiler, and reactant B is the intermediate boiler throughout this discussion. The conceptual design model used to describe all three types of batch-reactive distillation is similar to those proposed by Venimadhavan et al. (1999) for a batch rectifier. It is assumed that the reaction only occurs in the feed-charge drum. The model is based on constant molar overflow and vapor–liquid equilibrium on each stage. The other assumptions are that V/L holdups on each stage are negligible compared to those of the feed-charge drums. The method used in this work to determine the still and distillate paths is based on the limiting case of a large number of stages N, and infinite reflux ratio r.

Mass Balances

The material balances for the column shown in Figure 1a are given as

$$\frac{dH_S}{dt} = -D + \nu_T H_S r \tag{1}$$

and

$$\frac{dH_S x_{S,i}}{dt} = -Dx_{D,i} + \nu_i H_s r \tag{2}$$

where H_S is the liquid holdup in the still, D is the distillate flow rate, $x_{S,i}$ is the liquid-phase mole fraction of component i in the still, $x_{D,i}$ is the mole fraction of component i in the distillate, ν_i is the stoichiometric coefficient of component i, ν_T is the sum of the stoichiometric coefficients ($\nu_T = \Sigma_{i=1}^{c} \nu_i$), and r is the reaction rate per mole of mixture. A dimensionless time, ξ, is defined as

$$d\xi = \frac{D}{H_S} dt \tag{3}$$

Equations 1 and 2 can be rearranged to get

$$\frac{dx_{S,i}}{d\xi} = (x_{S,i} - x_{D,i}) + Da(\nu_i - \nu_T x_{S,i})\left(x_{S,B}^2 - \frac{x_{S,A}x_{S,C}}{Keq}\right) \tag{4}$$

See Appendix A1 for the detailed derivation.

Example. The sample RCM is shown in Figure 6. There are two binary azeotropes: one is a maximum boiling azeotrope (stable node) between A and B, while the other is a minimum boiling azeotrope (saddle) between B and C. According to the RCM classification (Matsuyama and Nishimura, 1977; Doherty, and Caldarola, 1985), it is called 320 (see Appendix B). Equation 4 can be used to describe the composition profiles of products A and C. In Eq. 4, $x_{S,B}$ can be substituted by $x_{S,B} = 1 - x_{S,A} - x_{S,C}$, based on $\Sigma x_i = 1$. The initial composition in the still is the feed composition

$$x_S = x_{S,0} \tag{5}$$

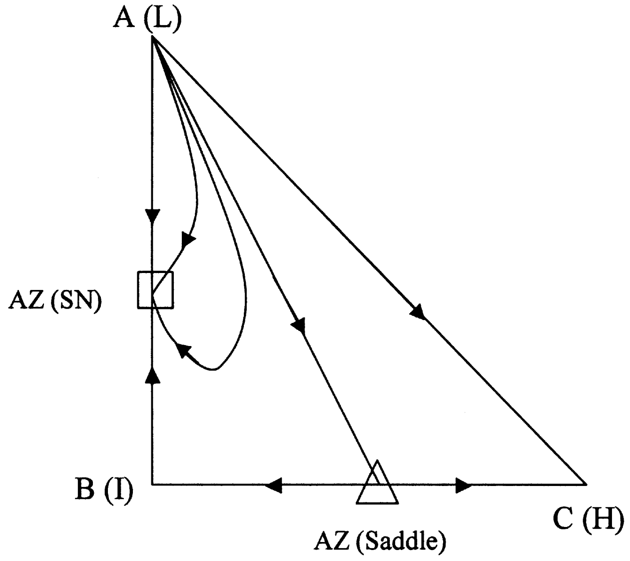

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Figure 6. Residue curve map 320 for batch-rectifier simulation.

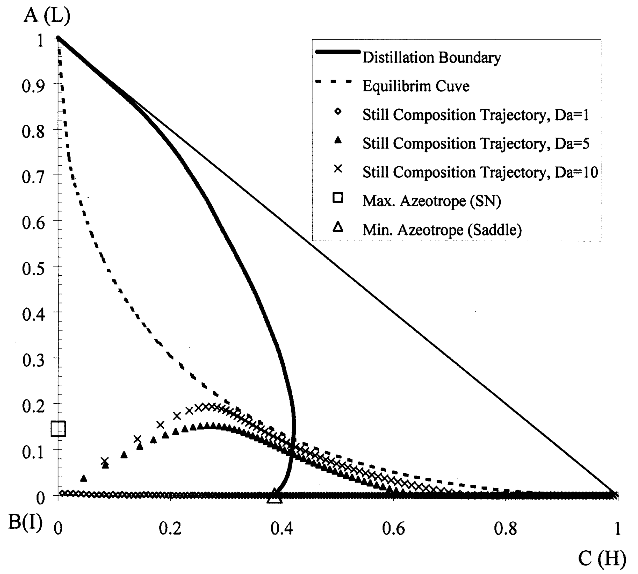

Figure 7. Simulation result of RCM 320 with a batch-reactive rectifier.

The distillate composition (x_D) can be related to still composition by distillation under total reflux. The procedure for tray calculations is described in Appendix A1.

Column Configuration

In RCM 320, there are two distillation regions, as shown in Figure 6. The initial feed charge in the still pot of the batch rectifier is pure reactant B. The dynamic simulation result of 320 (see Figure 7) shows that the still pot composition (x_S) moves toward the reaction equilibrium curve as the reaction proceeds. Then it approaches the C vertex, while product A is retrieved at the top and reactant B is consumed. Regardless of the still composition, the top product is always pure A because A is the lightest boiling component in both distillation regions. Since B and C remain in the still and A is removed continuously from the top of the column, the still composition moves toward the $B-C$ binary edge. As reactant B is consumed by the reaction, the still composition crosses the distillation boundary and approaches vertex C. Thus, the batch-reactive rectifier can produce pure products A and C.

The effect of Damköhler number (Da) on still composition is also shown in Figure 7. As the value of Da increases, the still composition profiles get closer to the reaction equilibrium curve. However, with any value of Da used for simulation, the still composition can cross the distillation boundary and pure products can be produced.

Although there are two distillation regions in 320, the light product A is an unstable node and can be reached from both regions by nonreactive rectification. Because of this, the light boiler can be removed at the top of the rectifying section regardless of the location of the still composition trajectories in the RCM. Since A is drawn off from the top and reactant B is consumed by the reaction, only the heavy boiler C will remain in the still pot. Thus a batch-reactive rectifier can be used to produce pure products. The RCMs where we can produce pure products with a batch-reactive rectifier are summarized in Figure 8, which shows the differences between them. For example, the number of azeotropes changes from 1 (020) to 4 (324-M) and azeotrope types change from binary (023) to ternary (024-M). However, all the RCMs show the common characteristic that the light boiler is an unstable node and is reachable from all nonreactive distillation regions. This common characteristic enables us to obtain the first feasibility criterion with a batch-reactive rectifier: when the light product is an unstable node and can be reached from all distillation regions, a batch rectifier with reaction can produce pure products regardless of the number of azeotropes involved in the system.

At this point, another question can be raised about whether a rectifier can still feasibly produce pure products when the light product is an unstable node but is not reachable from all distillation regions. This question can be answered by the analysis of RCM 430. In 430, there are two maximum boiling azeotropes: one is a stable node and the other is a saddle. These two azeotropes form one distillation boundary and divide the RCM into two distillation regions. The light product A is the unstable node and not reachable from distillation region I (see Figure 9). In Figure 9, the simulation result shows that the still pot composition (x_S) moves toward the reaction equilibrium curve as the reaction proceeds. It also indicates the importance of Da in this situation. If the value of Da is large enough (for example, $Da = 5$), the still composition crosses the distillation boundary, enters distillation region II, and moves toward vertex C. Since A is removed continuously from the top of the column (in distillation region II) and reactant B is consumed by the reaction, the still composition eventually approaches vertex C. Therefore, the batch-reactive rectifier can produce the pure products of A and C. With $Da = 1$, the still composition does not cross the distillation boundary and it stays in distillation region I. The top

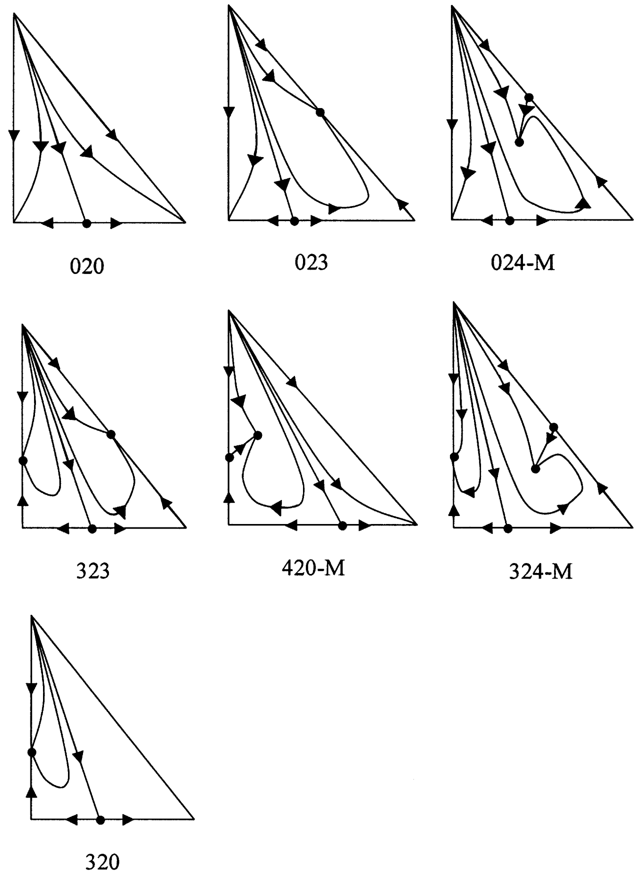

Figure 8. RCMs that satisfy the first feasibility criterion when using a batch-reactive rectifier.

product will be reactant *B*, since it is the lightest boiler in distillation region I. Thus, the desired pure products cannot be produced with $Da = 1$. Only with a higher reaction holdup (that is, $Da = 5$) can the reaction force the still composition to cross the distillation boundary and enter the region where product is reachable by nonreactive distillation.

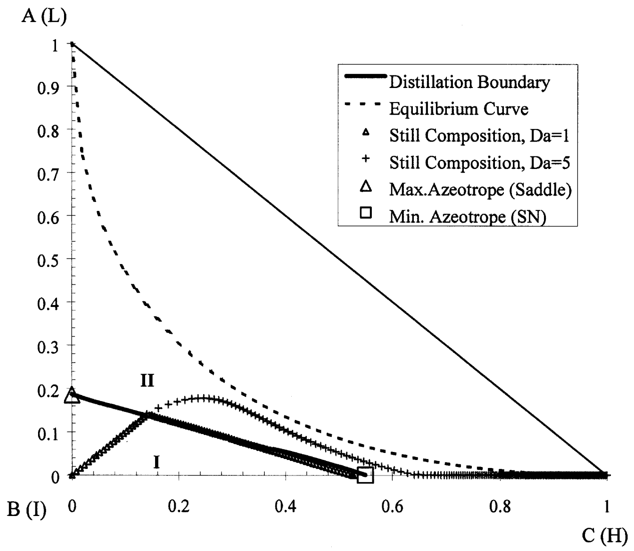

Figure 9. Simulation result of RCM 430 with a batch-reactive rectifier.

Another important aspect of determining the feasibility is *the location of the reaction equilibrium curve* in Figure 9. If one wants to produce the desired products with a rectifier, the still composition must enter the region where the light boiler (unstable node) is reachable by nonreactive distillation. The necessary condition for this is that the reaction equilibrium curve should lie within the same distillation region that the light boiler does. Then, the still composition can cross the distillation boundary and enter the same distillation region where the product (UN) and the reaction equilibrium curve lie. When the still composition enters distillation region II, light product *A* (the lightest boiler in this region) can be removed from the top and the still pot composition will move to the binary edge of *B* and *C*. Then, the still composition trajectory approaches the heavy boiler (*C*) while reactant *B* is consumed. Thus, a batch-reactive rectifier can be used to produce pure products.

If the unstable node and the reaction equilibrium curve are not in the same region, the still composition trajectory cannot enter the region where the UN product is reachable by distillation because the still composition stays in distillation region I. Since reactant *B* is the lightest boiler in distillation region I, no pure products (*A* and *C*) can be produced at the top no matter what *Da* is used.

The RCMs where pure products can be produced with a batch-reactive rectifier under such conditions are summarized in Figure 10. The RCMs show the common characteristic that the product is an unstable node and reachable from one distillation region by nonreactive distillation. The unstable node product can be produced if and only if the reaction equilibrium curve lies in the same region as the unstable node. Therefore, the second criterion for using batch-reactive rectifiers is as follows: if one of the reaction products is an unstable node and parts of the reaction equilibrium curve lie within the same distillation region that the product lies, then the rectifier with a reactive feed drum can produce pure products. These design insights can also be extended to any stoichiometry of ternary decomposition reaction $bB \leftrightarrow aA + cC$, as long as either feasibility criterion is satisfied.

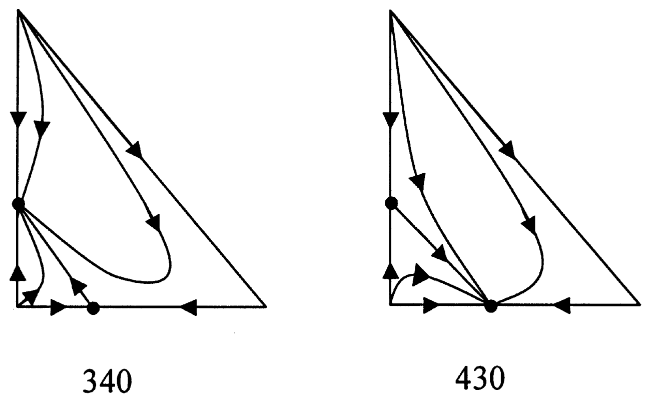

Figure 10. RCMs that satisfy the second feasibility criterion when using a batch-reactive rectifier.

Batch Stripper

As discussed in binary reactive distillation systems, the batch stripper in Figure 1b can destroy a minimum boiling azeotrope by reaction and produce pure products at the bottom of the column. For the feasibility study of ternary systems, the same type of reaction, $2B \leftrightarrow A + C$, is used. Also in this section, A is the light boiler, C is the heavy boiler, and reactant B is the intermediate boiler. The assumptions used for batch-reactive strippers are the same as those for batch-reactive rectifiers.

Mass Balances

The material balances for the column shown in Figure 1b are as follows

$$\frac{dH_S}{dt} = -B + \nu_T H_S r \tag{6}$$

and

$$\frac{dH_S x_{S,i}}{dt} = -Bx_{B,i} + \nu_i H_S r \tag{7}$$

where B is the bottom flow rate, and $x_{B,i}$ is the mole fraction of component i in the bottom.

Dimensionless time, ξ, is defined as

$$d\xi = \frac{B}{H_S} dt \tag{8}$$

Equations 6 and 7 can be rearranged to give

$$\frac{dx_{S,i}}{d\xi} = (x_{S,i} - x_{B,i}) + Da(\nu_i - \nu_T x_{S,i})\left(x_{S,B}^2 - \frac{x_{S,A}x_{S,C}}{Keq}\right) \tag{9}$$

See Appendix A2 for the detailed derivation.

Example. The considered example is as follows: there are two binary azeotropes, as shown in Figure 11. One is the minimum boiling azeotrope (UN) between B and C, and the other is the maximum boiling azeotrope (saddle) between A and B. This sample RCM is 410 (see Appendix B). Equation 9, which describes the overhead drum composition of components A and C, respectively, can be solved under the initial condition $x_S = x_{S,0}$. For detailed calculations, see Appendix A2.

Column Configuration

The dynamic simulation result of 410 in a batch-reactive stripper is shown in Figure 12. The overhead drum composition (x_S) moves toward the reaction equilibrium curve as the reaction proceeds, crosses the distillation boundary, and approaches the vertex of light boiler A. It indicates that the batch-reactive stripper can produce pure products C and A since the heavy boiler C is drawn off at the bottom and the overhead drum composition reaches vertex A after crossing the distillation boundary.

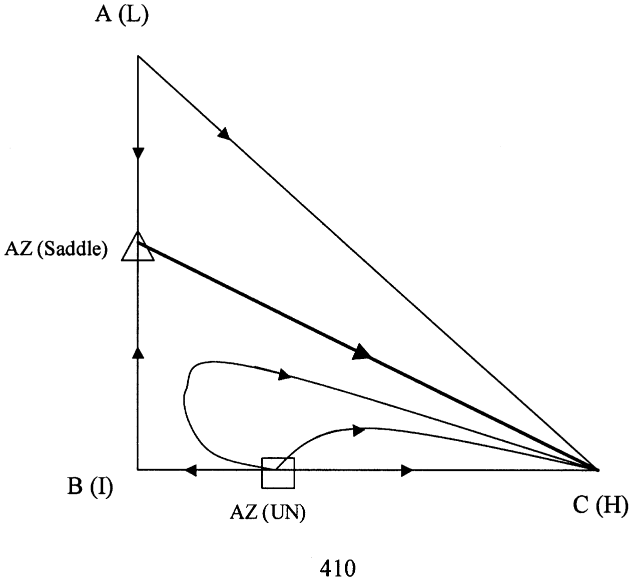

Figure 11. Residue curve map 410 for batch-reactive stripper simulation.

In RCM 410, the heavy product C is a stable node in the two distillation regions and can be reached from both regions by nonreactive distillation on each stage. Thus, the heavy boiler C can be removed at the bottom of the stripper regardless of the location of the drum composition trajectories in the RCMs. Since C is retrieved at the bottom, the overhead drum composition moves to the binary edge of A and B. At the same time, reactant B is consumed by reaction. Finally, only product A remains in the drum and the drum composition trajectory approaches the vertex of pure A. Thus, the batch-reactive stripper can be used to produce pure

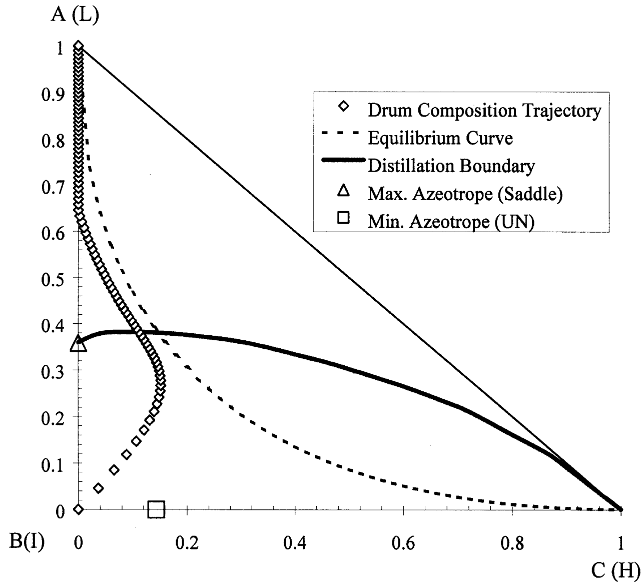

Figure 12. Simulation result of RCM 410 with a batch-reactive stripper.

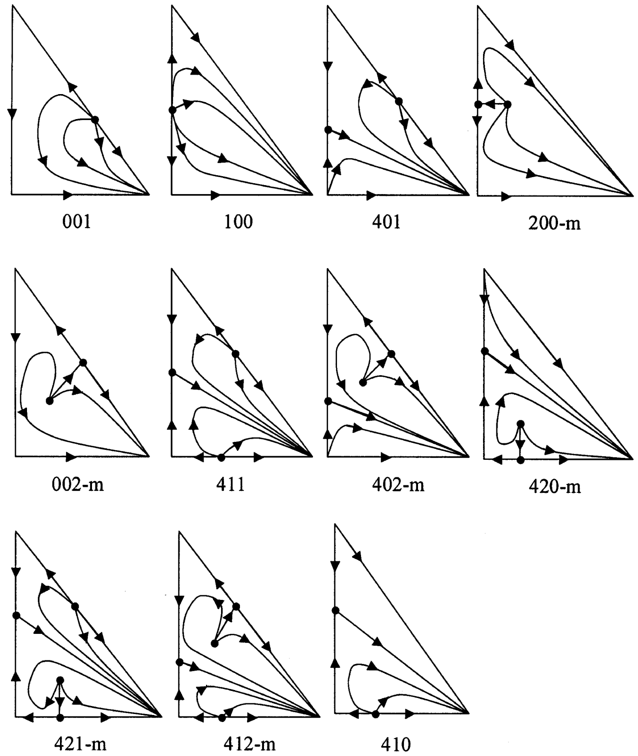

Figure 13. RCMs that satisfy the first feasibility criterion when using a batch-reactive stripper.

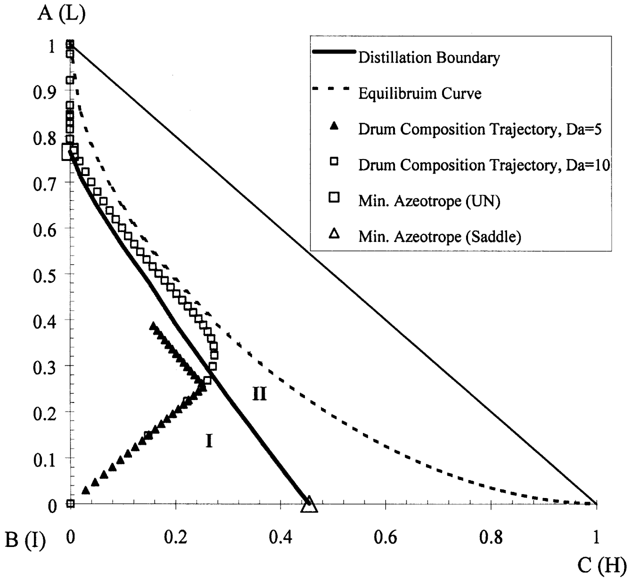

Figure 14. Simulation result of RCM 120 with a batch-reactive stripper.

products. The RCMs where pure products are reachable with batch-reactive strippers are summarized in Figure 13. Although it shows the differences between the RCMs, such as the numbers, types, and locations of azeotropes, all the RCMs have the same characteristic that the heavy boiler is a stable node and reachable from all distillation regions. Therefore, the first feasibility criterion for batch-reactive strippers is: regardless of the types, numbers, and locations of azeotropes involved in the RCM, when one of the products is the stable node and can be reached from all distillation regions, batch-reactive strippers can produce pure products.

In the same way as for the batch-reactive rectifier, does a batch stripper function to produce pure products when the heavy product is a stable node but not reachable from all distillation regions? To answer this question, RCM 120 in Figure 14 is studied. The dynamic simulation result for this system explains how a stripper works under such situations. In 120, two minimum boiling azeotropes exist: one is an unstable node and the other is a saddle. The distillation boundary formed by these two azeotropes divides the RCM into two distillation regions. The heavy product C is the stable node and is located in distillation region II. It is not reachable by nonreactive distillation from distillation region I (the initial feed composition region). The simulation result (Figure 14) shows that the overhead drum-composition (x_S) moves toward the reaction equilibrium curve as the reaction takes place. The effect of different Da's on drum-composition profiles is also illustrated. With $Da = 10$, the drum-composition can cross the distillation boundary. After crossing the boundary and entering distillation region II, the drum-composition profile moves toward the binary edge of A and B, and eventually approaches vertex A. Therefore, a batch-reactive stripper can produce pure products C and A. On the contrary, when $Da = 5$, the drum composition fails to cross the boundary and stays in distillation region I. In this case, the bottom product will be reactant B, since B is the heaviest boiler in distillation region I. Thus, the desired pure products cannot be produced.

The importance of the location of the reaction equilibrium curve should also be noted. The reaction equilibrium curve has to lie in the same region as the stable node product so that the reactive drum composition can cross the distillation boundary. Once the distillation boundary is crossed, the heaviest product (C: SN) is reachable by nonreactive distillation on the stages of the stripper. If the reaction equilibrium curve lies within distillation region I in Figure 14, the reactive drum composition cannot cross the distillation boundary starting from reactant B. Then, no pure products can be produced regardless of the values of Da applied.

The RCMs where pure products can be produced with batch-reactive strippers under such conditions are summarized in Figure 15. The RCMs show the common feature that the heavy boiler is a stable node and reachable from one distillation region. Based on the preceding results, the second

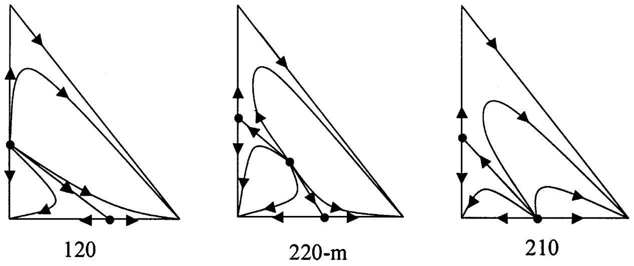

Figure 15. RCMs that satisfy the second feasibility criterion when using a batch-reactive stripper.

feasibility criterion for using batch-reactive strippers is: if one of the reaction products is a stable node and part of the reaction equilibrium curve lies within the same distillation region that the product does, then a stripper with a reactive feed drum can produce pure products. Whenever either of these two feasibility criteria for batch strippers is satisfied, these insights can be extended to any ternary decomposition reaction of $bB \leftrightarrow aA + cC$, or composition reaction of the form $bB + aA \leftrightarrow cC$.

Batch middle vessel

Another system studied here has the heavy (SN) and the light (UN) products lying in the same distillation region and not reachable from the feed-charge composition by nonreactive distillation. Under such conditions, the middle-vessel column shown in Figure 1c is a possible choice for producing pure products. The same type of reaction, $2B \leftrightarrow A + C$, will be discussed in this part of the study. The assumptions used for the batch-reactive middle-vessel are the same as those for the batch-reactive rectifier and stripper.

Mass Balances

Material balances for the column shown in Figure 1c are as follows

$$\frac{dH_S}{dt} = -D - B + \nu_T H_S r \tag{10}$$

and

$$\frac{dH_S x_{S,i}}{dt} = -Dx_{D,i} - Bx_{B,i} + \nu_i H_S r \tag{11}$$

Dimensionless time, ξ, is defined as

$$d\xi = \frac{D+B}{H_S} dt \tag{12}$$

Equations 10 and 11 can be rearranged to give

$$\frac{dx_{S,i}}{d\xi} = \left(x_{S,i} - \frac{x_{D,i} + x_{B,i}}{2} \right) + Da(\nu_i - \nu_T x_{S,i})\left(x_{S,B}^2 - \frac{x_{S,A} x_{S,C}}{Keq} \right) \tag{13}$$

See Appendix A3 for the detailed derivation.

Example. The RCM considered here has one binary minimum azeotrope (UN) between B and C, and one ternary azeotrope (saddle). The RCM is shown in Figure 16 and is called 010-S (see Appendix B). In this system, Eq. 13 will depict the middle-vessel composition profiles of components A and C. The distillate and bottom product compositions (x_D and x_B) can be related to the middle-vessel composition by using distillation curves under total reflux (see Appendix A1) and total reboil ratios (see Appendix A2), respectively. So, Eqs. 13 can be solved under the initial condition $x_S = x_{S,0}$.

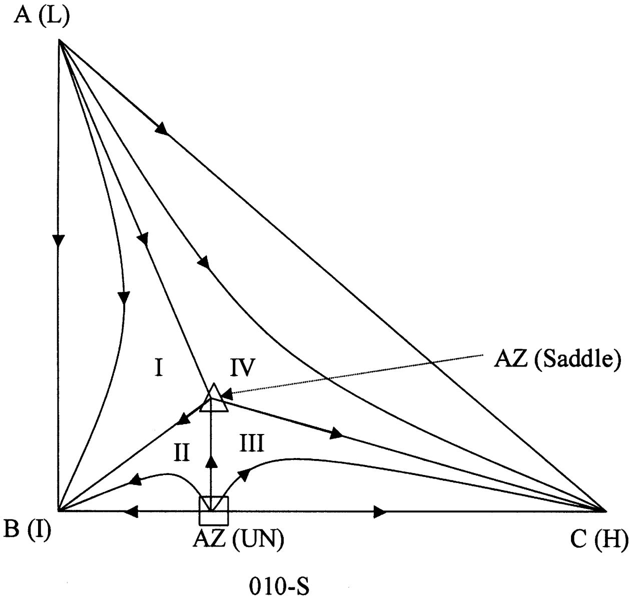

Figure 16. Example residue curve map 010-S for batch middle-vessel simulation.

Column Configuration

The RCM is divided into four regions by distillation boundaries. In distillation region IV, the light and heavy products are the unstable and stable nodes, respectively, and reachable by nonreactive distillation from this region. The initial feed charge in the middle vessel is pure reactant B, as shown in Figure 17. Its location is different from the distillation region where the two products lie. The dynamic simulation result shows that as the reaction proceeds, the middle-vessel composition (x_S) moves toward the reaction equilibrium curve. At the same time, the heavy boiler, product C,

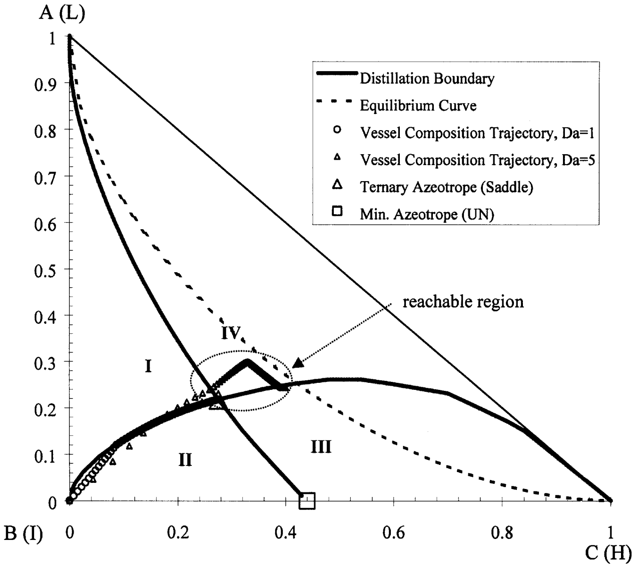

Figure 17. Simulation result of RCM 010-S with a batch-reactive middle vessel.

and the light boiler, product A, are retrieved at the bottom and top, respectively. Since products A and C are continuously removed and reactant B is consumed by the reaction, the still composition will remain relatively stable in distillation region IV. So the batch-reactive middle vessel can be used to produce pure products A and C simultaneously. The derivation of optimal operating policies is not the concern of this article. However, careful control of the batch operation is needed to maintain the middle-vessel composition within distillation region IV.

The effect of Da's on the middle-vessel composition is also shown in Figure 17. With $Da = 1$, the vessel composition profile moves toward the reaction equilibrium curve. However, it cannot cross the distillation boundary and cannot enter distillation region IV. Therefore, the pure products cannot be produced. As the value of Da increases, for example, $Da = 5$, the vessel composition gets closer to the reaction equilibrium curve, crosses the distillation boundary, and enters distillation region IV. In distillation region IV, pure products A (UN) and C (SN) are reachable by nonreactive distillation in each section and can be produced at the top and bottom, respectively. So, the larger reaction holdup can force the vessel composition to cross the distillation boundary and to enter the desired distillation region. As mentioned in the design of the batch-reactive rectifier and stripper, the position of the reaction equilibrium curve will restrict the vessel composition trajectory. When the reaction equilibrium curve lies in the same region that two products lie in, then it is possible for the vessel composition to cross the boundary with the reaction in the middle vessel, thus producing pure products. If the products and the reaction equilibrium curve are not in the same region (products are not reachable by nonreactive distillation), then the vessel composition cannot cross the boundary and no pure products can be produced in spite of a high value of Da.

In Figure 18, we summarized the RCMs where pure products can be produced with a batch-reactive middle-vessel column. The RCMs shared the common characteristic that the heavy boiler (SN) and the light boiler (UN) lie within the same distillation region. Therefore, the feasibility criterion for the batch middle vessel is obtained: when reaction products are stable and unstable nodes, respectively, and part of the reaction equilibrium curve lies within the same distillation region that the products do, then a batch-reactive middle vessel can be used to produce pure products. This feasibility criterion can be extended to different stoichiometries of the decomposition reaction $bB \leftrightarrow aA + cC$ when these conditions are satisfied.

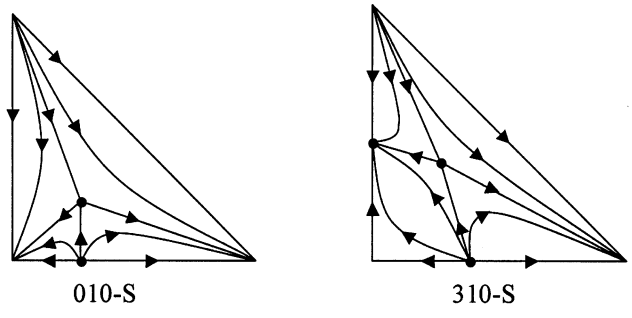

Figure 18. Summarized RCMs where a batch-reactive middle vessel is applicable.

Substitution for middle vessel

Also for RCM 010-S, a stripper or a rectifier can replace the middle vessel if the distillation boundaries and the reaction equilibrium curve are located in the correct way. Figure 19 shows that the distillation boundary between the ternary azeotrope and the vertex A moves closer to the binary edge of light and intermediate components (starting from Figure 17). This behavior allows the possibility of using a batch stripper to produce pure products. Obviously, the RCM still satisfies the criterion that the light product should be an unstable node and part of the reaction equilibrium curve must be located in the same region that the light product lies in. It can be observed in Figure 19 that as the reaction proceeds, the still composition profile ($Da = 5$) moves toward the equilibrium curve, crosses the distillation boundary, and enters the reachable region for heavy product C. Thus the production of pure products is possible by substituting a stripper for a middle vessel. Please note that Da has to be high enough to cross the boundary. Likewise, if the distillation boundary approaches the edge of B and C in the same manner as shown in Figure 19, then a rectifier can be substituted for the middle-vessel column. Whenever possible, the replacement of a middle-vessel column by a stripper or a rectifier yields more economic savings, since one nonreactive section can be eliminated.

Conclusions

The results of a geometric feasibility method (using McCabe-Thiele diagrams) for binary batch-reactive distillation systems indicate that a batch rectifier can be used to evade a maximum boiling azeotrope and that a batch stripper can similarly circumvent a minimum boiling azeotrope.

By using the simple information of phase and reaction equilibrium, the possible product cuts in ternary reactive systems have been identified and the feasibility criteria for three basic batch-reactive columns have been derived. When a reaction product is an unstable node and reachable by nonreactive distillation from all distillation regions, pure products can be produced with a batch-reactive rectifier. If one of the reaction products is an unstable node and is not reachable by nonreactive distillation from all regions, then a batch-reactive rectifier still can be used to produce pure products. However, to do that, the following conditions must be satisfied: (1) part of the reaction equilibrium curve lies in the same distillation region that the product does, and (2) Da is high enough to cross the distillation boundary. Symmetric results are applicable to a batch-reactive stripper with one stable node product.

For more complex RCMs, reaction products are unstable and stable nodes lying within the same distillation region but are not reachable from the initial feed charge region. In this case, a middle vessel can be applied to produce pure products when parts of the reaction equilibrium curve lie in the same region that the UN and SN do. Based on the derived feasibility criteria, a middle vessel can be substituted by a stripper or a rectifier in accordance with the locations of reaction equilibrium curve and distillation boundaries.

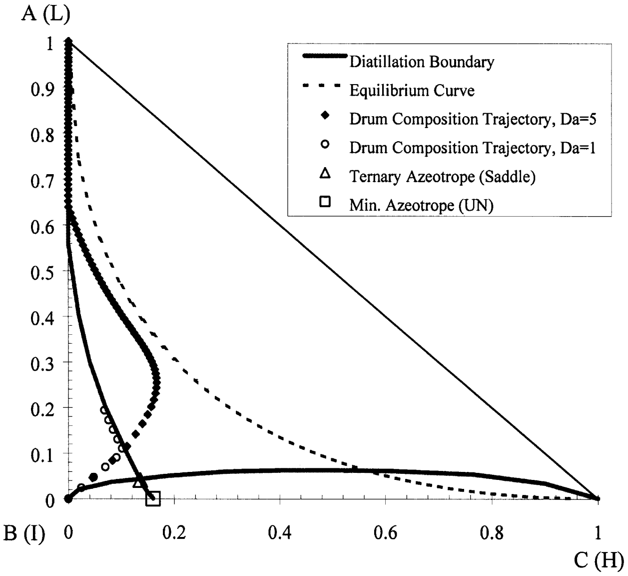

Figure 19. Stripper as a substitution for a middle-vessel column.

We have obtained the feasibility criteria of batch-reactive systems by focusing on the RCMs that have at least one of the products as an unstable node or stable node. There are some RCMs in which all products are saddles. Such systems are more complex and we may need side feed/product streams or to include reactive stages to circumvent phase-equilibrium limitations. Thus, in future work, the feasibility criteria will be extended to the systems where all products are saddles. The derived feasibility criteria can be directly applied to any real systems once their reaction and phase-equilibrium data are available. These feasibility insights for three batch-reactive columns could facilitate the derivation of optimal operating policies for integrating reaction and distillation.

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Notation

AZ = azeotrope
B = molar bottom-product flow rate
B_0 = initial molar bottom-product flow rate
D = molar top-product flow rate
D_0 = initial molar top-product flow rate
Da = Damköhler number
H_s = liquid holdup in still pot
H_{s0} = initial liquid holdup in still pot
i = ith component
k = reaction rate constant
K_{eq} = reaction equilibrium constant
r = reaction rate
SN = stable node
t = time
UN = unstable node
x_B = liquid mole fraction in the bottom product
x_D = liquid mole fraction in the distillate
x_S = liquid mole fraction of the still pot
x_{S0} = initial liquid mole fraction of the still pot
x_p = liquid mole fraction of product P
y_p = vapor mole fraction of product P

Greek letters

ξ_p = dimensionless time
ν_i = stoichiometric coefficients of component i
ν_T = sum of the stoichiometric coefficients

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Appendix A

A1: Derivation of material-balance equation for a batch-reactive rectifier

Equation A1 can be derived from Eqs. 1, 2, and 3

$$\frac{dx_{S,i}}{d\xi} = (x_{S,i} - x_{D,i}) + \frac{H_S}{D}(\nu_i - \nu_T x_{S,i})r \tag{A1}$$

The Damköhler number, Da, is the ratio of characteristic residence time to a characteristic reaction time, and is defined as

$$Da = \frac{H_{S,0}/D_0}{1/k_{f,ref}} \tag{A2}$$

where $H_{S,0}$ is the initial molar holdup in the still, D_0 is the initial distillate flow rate, and $k_{f,ref}$ is the forward reaction rate constant evaluated at a reference temperature, T_{ref}. Equation A1 can be rewritten as

$$\frac{dx_{S,i}}{d\xi} = (x_{S,i} - x_{D,i}) + Da\frac{H_S}{H_{S,0}}\frac{D_0}{D}(\nu_i - \nu_T x_{S,i})\frac{r}{k_{f,ref}} \tag{A3}$$

Choosing $D_0/D = H_{S,0}/H_S$ (Venimadhaven et al., 1999), Eq. A3 is reduced to

$$\frac{dx_{S,i}}{d\xi} = (x_{S,i} - x_{D,i}) + Da(\nu_i - \nu_T x_{S,i})\frac{r}{k_{f,ref}} \tag{A4}$$

Forward reaction rate expression r is

$$r = k_f\left(x_B^2 - \frac{x_A x_c}{K_{eq}}\right) \tag{A5}$$

Let $k_f = k_{f,ref}$ (ignore the temperature effect), then rewrite Eq. A4 and get Eq. 4

$$\frac{dx_{S,i}}{d\xi} = (x_{S,i} - x_{D,i}) + Da(\nu_i - \nu_T x_{S,i})\left(x_B^2 - \frac{x_A x_C}{Keq}\right) \tag{4}$$

The pseudo-steady-state material balances for the column are

$$y_{n-1,i} = \frac{R}{R+1}x_{n,i} + \frac{1}{R+1}x_{D,i}\ (n = 1,\ldots,N; i = 1,\ldots,c) \tag{A6}$$

where y_0 is the composition of vapor in phase equilibrium with x_S.

The total condenser leads to the relationship

$$x_{D,i} = y_{N,i} \tag{A7}$$

A2: Derivation of material-balance equation for a batch-reactive stripper

Equation A8 is derived from Eqs. 6, 7, and 8:

$$\frac{dx_{S,i}}{d\xi} = (x_{S,i} - x_{B,i}) + \frac{H_S}{B}(\nu_i - \nu_T x_{S,i})r \tag{A8}$$

The Damköhler number, Da, is defined as

$$Da = \frac{H_{s,0}/B_0}{1/k_{f,\mathrm{ref}}}$$

Equation A8 can be rewritten as

$$\frac{dx_{S,i}}{d\xi} = (x_{S,i} - x_{B,i}) + Da(\nu_i - \nu_T x_{S,i})\frac{r}{k_{f,ref}} \tag{A9}$$

Forward reaction rate expression r is the same as Eq. A5.

Ignore the temperature effect, $k_f = k_{f,ref}$, then rewrite Eq. A9 and get Eq. 9

$$\frac{dx_{S,i}}{d\xi} = (x_{S,i} - x_{B,i}) + Da(\nu_i - \nu_T x_{S,i})\left(x_B^2 - \frac{x_A x_C}{Keq}\right) \tag{9}$$

The pseudo-steady-state material balances for the column are

$$y_{n,i} = \frac{s+1}{s}x_{n+1,i} + \frac{1}{S}x_{B,i} \quad (n = 1,\ldots,N; i = 1,\ldots c) \tag{A10}$$

where x_0 is the composition of liquid in phase equilibrium with y_S.

The total reboiler leads to the relationship

$$x_{B,i} = y_{N,i} \tag{A11}$$

A3: Derivation of material-balance equation for a batch-reactive middle vessel

Equation A12 is derived from Eqs. 10, 11, and 12

$$\frac{dx_{S,i}}{d\xi} = \left(x_{S,i} - \frac{Dx_{D,i} + Bx_{B,i}}{D+B}\right) + \frac{H_s}{D+B}(\nu_i - \nu_T x_{S,i})r \tag{A12}$$

The Damköhler number, Da, is defined as

$$Da = \frac{H_{S,0}/(D_0 + B_0)}{1/k_{f,ref}} \tag{A13}$$

Equation A12 can be rewritten as

$$\frac{dx_{S,i}}{d\xi} = \left(x_{S,i} - \frac{Dx_{D,i} + Bx_{B,i}}{D+B}\right) + Da\frac{H_S}{H_{S,0}}\frac{D_0 + B_0}{D+B} \times (\nu_i - \nu_T x_{S,i})\frac{r}{k_{f,ref}} \tag{A14}$$

Choosing $(D_0 + B_0)/(D + B) = H_{S,0}/H_S$, Eq. A14 is reduced as

$$\frac{dx_{S,i}}{d\xi} = \left(x_{S,i} - \frac{Dx_{D,i} + Bx_{B,i}}{D + B}\right) + Da(\nu_i - \nu_T x_{S,i})\frac{r}{k_{f,ref}} \tag{A15}$$

Forward reaction rate expression r is same as Eq. A5.

Let $k_f = k_{f,ref}$, then rewrite Eq. A15 and get Eq. A16

$$\frac{dx_{S,i}}{d\xi} = \left(x_{S,i} - \frac{Dx_{D,i} + Bx_{B,i}}{D + B}\right) + Da(\nu_i - \nu_T x_{S,i})\left(x_B^2 - \frac{x_A x_C}{Keq}\right) \tag{A16}$$

From the total material balances, it will be easy to get $D = B$. Assuming that the flow rates in the two separate columns are constant and exactly the same, then Eq. A16 reduces to Eq. 13

$$\frac{dx_{S,i}}{d\xi} = \left(x_{S,i} - \frac{x_{D,i} + x_{B,i}}{2}\right) + Da(\nu_i - \nu_T x_{S,i})\left(x_B^2 - \frac{x_A x_C}{Keq}\right) \tag{13}$$

and x_D and x_B are obtained from Appendixes A1 and A2.

Appendix B

The RCMs (Figure 6, 8, 10, 11, 13, 15, 16, and 18) are drawn in standard orientation with the light component, A, at the top vertex, the intermediate component, B, at the bottom left vertex, and the heavy component, C, at the bottom right vertex. The first three digits signify the type of binary azeotrope on the $A-B$, $B-C$, and $C-$A edges of the triangle, respectively. The numbers are assigned by the following rules (Matsuyama and Nishimura, 1977; Doherty, and Caldarola, 1985):

0 = no azeotrope;
1 = binary minimum-boiling azeotrope, unstable node;
2 = binary minimum boiling azeotrope, saddle;
3 = binary maximum boiling azeotrope, stable node;
4 = binary maximum boiling azeotrope, saddle.

The single letter after the first three digits signifies the type of ternary azeotrope.

m = minimum boiling ternary azeotrope, unstable node;
M = maximum-boiling ternary azeotrope, stable node;
S = intermediate boiling ternary azeotrope, saddle.

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