Feasible Products in Batch Reactive Extractive Distillation

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A systematic feasibility evaluation method is presented for batch reactive distillation columns with extractive feed streams. In this batch configuration, one feasibility criterion is obtained for quaternary reactive systems by using residue curve maps and reaction equilibrium manifolds. If all reaction products are saddles and one of the binary azeotropes between the desired products and the other components is an unstable node, then a reactive rectifier with a side-feed entrainer can produce pure products regardless of the type and number of azeotropes involved in the system. © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 1484–1492, 2004

Keywords: feasibility, batch reactive extractive distillation (BRED), residue curve map (RCM), reaction equilibrium manifold, azeotrope

Introduction

Batch distillation has been used for the small-scale production of pharmaceuticals and specialty chemicals. The advantages of batch distillation, such as low capital costs, high flexibility, and ease of handling, for example, are well known. To obtain more flexibility and to circumvent phase-equilibrium limitations such as low relative volatilities and azeotropes, an extractive agent can be provided to a batch column in a side-feed stream.

Safrit et al. (1995) extended the feasibility insights of continuous extractive distillation to batch distillation. Safrit and Westerberg (1997) and Phimister and Seider (2000a, 2000b) developed the operating policies for middle-vessel extractive distillation. Lelkes et al. (1998a, 1998b) proposed a feasibility evaluation algorithm and operating policy for extractive distillation with a rectifier. Venimadhavan et al. (1999), Cuille and Reklaitis (1986), Fernholz et al. (2000), and Gadewar et al. (2000) focused attention on the derivation of operating policies for batch reactive distillation processes. However, feasibility studies on the combination of these two—batch reactive extractive distillation (BRED)—have rarely been published in the literature. In particular, no simple feasibility evaluation method based on residue curve maps (RCMs) and reaction equilibrium manifolds is available for BRED. Although BRED processes are considerably more complex than batch reactive or extractive distillation alone, they may provide the advantages of both.

In our previous article (Guo et al., 2003), we demonstrated that reactive rectifiers, strippers, and middle vessels can be used to produce pure products in ternary reaction systems of the form $bI \leftrightarrow aL + cH$. However, there are some restrictions on the application of such batch reactive distillation columns. Specifically, at least one of the products should be an unstable or a stable node in the residue curve maps and should be reachable by simple distillation. Figure 1 is a sample residue curve map that shows a system where a reactive rectifier can produce pure products from the reaction $bI \leftrightarrow aL + cH$. Figure 1 shows that the light product (L) is an unstable node (UN) and reachable by simple distillation from both distillation regions. Using this phase-equilibrium behavior, the feasibility criterion for reactive distillation has been established (Guo et al., 2003): if there is an unstable node reaction product that is reachable from all distillation regions, a rectifier can be used for producing pure products. If this UN is reachable from only one specific distillation region, a rectifier can still be used when a part of the reaction equilibrium curve lies in the same distillation region as the product. Similar results are obtained 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 are in the same distillation region as a part of

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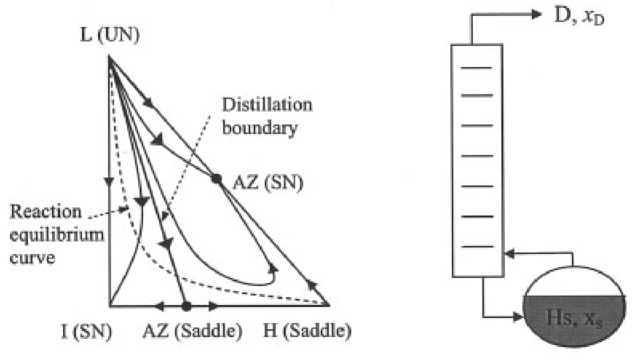


(a) RCM

(b) Rectifier

Figure 1. Typical RCM producing pure products with rectifiers.

(a) RCM with reaction equilibrium curve; (b) schematic of a batch reactive rectifier with a reactive still.

the reaction equilibrium curve. For detailed discussions, refer to our previous article (Guo et al., 2003).

For the cases where all of the products are saddles and are not reachable by simple distillation, the above applications cannot lead to pure products. For example, the RCM in Figure 2 shows that for the reaction type of $bI \leftrightarrow aL + cH$, the two products L and H are both saddles. The binary azeotrope between H and L is an unstable node and the azeotrope between H and I is a stable node. Such a residue curve map is designated RCM-031 according to the classifications of RCMs (Doherty and Caldarola, 1985; Matsuyama and Nishimura, 1977). If one uses a reactive rectifier for this system, then the top product will be the *H–L* azeotrope because it is the unstable node (the lowest boiler) in that distillation region. A reactive stripper will produce the *H–I* binary azeotrope as the bottom product because that azeotrope is the stable node (the highest boiler) in that distillation region. The reactive middle vessel cannot produce these products either because the two products are saddles.

Thus, these three batch reactive distillation columns cannot produce pure products in systems like RCM-031. However, an entrainer introduced to a batch distillation column can break the azeotrope formed between the desired products. Such a situation encourages us to study the effects of the combination of batch reactive and extractive distillation in these systems. It will be demonstrated that the combination of batch reactive and extractive distillation is an effective method to obtain desired products from many systems similar to RCM-031. The goal of this article is to present a method for assessing the feasibility of such an integrated process.

Feasibility Study of Batch Reactive Extractive Distillation (BRED)

In batch distillation, the still and product compositions change with time and thus the basic feasibility analysis should be performed in terms of time-dependent trajectories. In the case of sufficiently large reflux ratios and numbers of theoretical stages, the liquid composition profiles in the column follow simple distillation residue curves. Therefore, the RCMs, which are time-dependent, can be used to study the feasibility of BRED.

Model

Batch reactive extractive distillation is performed under an entrainer feed (Lelkes et al., 1998a) flow into a batch rectifier (see Figure 2) that consists of a total condenser, a staged column, and a still. The part of the column above the feed stage is called the rectifying section and prevents the entrainer from leaving in the distillate. The feed stage and the stages below it are called the extractive section of the column and are used for breaking azeotropes.

To simplify the feasibility study, it is assumed that the reaction $2I \leftrightarrow L + H$ occurs only in the still pot. The model is based on the assumptions of constant molar overflow and vapor–liquid equilibrium on each stage (except for the condenser). It is also assumed that the stage vapor and liquid holdups are negligible. The still, extractive, and rectifying profiles can be determined by assuming a limiting case of total reflux.

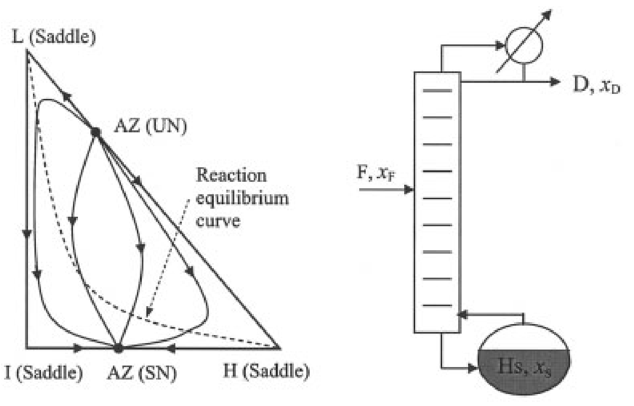
The composition trajectories

To determine the possible instantaneous composition profiles of the rectifying and extractive sections, an approximate differential model was applied because it significantly reduces the size of the problem and allows direct comparison with simple distillation residue curves.

The general formula (Eq. 1) for the composition profiles of both sections was developed by Lelkes et al. (1998a)

$$\frac{dx_i}{dh} = \frac{V}{l}\,(y_i - y_i^*) \tag{1}$$

where x_i is the liquid mole fraction of component i; y_i is vapor mole fraction of component i and is calculated as a function of x_i using a material balance (see Eqs. 3 and 5); y_i^* is in phase equilibrium with x_i; h is the plate number; and V and l are the vapor and liquid flow rates in the column, respectively. Using this differential equation for any initial composition, one can calculate the profiles for the rectifying and extractive sections. In Eq. 1, the value of V/l and the function $y(x)$ can be computed for both sections.



(a) 031

(b) Rectifier with a side feed

Figure 2. Typical RCM with saddle products.

(a) RCM with reaction equilibrium curve; (b) batch reactive extractive rectifier with a reactive still.

Rectifying Section

$$\frac{V}{l} = \frac{V}{V - D} \tag{2}$$

$$y_i = \frac{(V - D)x_i + Dx_{D,i}}{V} \tag{3}$$

Extractive Section

$$\frac{V}{l} = \frac{V}{V + F - D} \tag{4}$$

$$y_i = \frac{(V + F - D)x_i - Fx_{F,i} + Dx_{D,i}}{V} \tag{5}$$

where D and F are the flow rates of the distillate and entrainer streams and $x_{D,i}$ and $x_{F,i}$ are the liquid mole fractions of component i in the distillate and entrainer streams, respectively.

In the case of total reflux, $D = 0$ for the *rectifying section*, Eqs. 2 and 3 reduce to $V/l = 1$ and $y_i = x_i$, and Eq. 1 gives

$$\frac{dx_i}{dh} = (x_i - y_i^*) \tag{6}$$

This equation has the same form as the equation of simple distillation residue curves and the rectifying composition profiles can be approximated by the residue curves. Thus, the calculation of rectifying section profiles is not necessary and one just follows the path of the residue curve. For the *extractive section*, Eqs. 4 and 5 reduce to Eqs. 7 and 8, respectively

$$\frac{V}{l} = \frac{V}{V + F} \tag{7}$$

$$y_i = \frac{(V + F)x_i - Fx_{F,i}}{V} \tag{8}$$

and Eq. 1 gives

$$\frac{dx_i}{dh} = \frac{V}{V + F}\left[\frac{(V + F)x_i - Fx_{F,i}}{V} - y_i^*\right] \tag{9}$$

For reactant and products Eq. 9 reduces to

$$\frac{dx_i}{dh} = x_i - \frac{V}{V + F}y_i^* \tag{10}$$

Because the feed composition is pure entrainer, the liquid mole fractions of reactant and products in the entrainer are zero ($x_{F,I} = x_{F,L} = x_{F,H} = 0$). The still composition profile depends on the composition of the charge, the composition of the entrainer feed, and the reaction because there is no distillate withdrawal from the top. The still composition profile can be calculated from the material balance

$$\frac{dH_S}{dt} = F + \nu_T H_S r \tag{11}$$

and

$$\frac{d(H_S x_{S,i})}{dt} = Fx_{F,i} + \nu_i H_S r \quad i = 1, \ldots, c - 1 \tag{12}$$

where H_S is the molar liquid holdup in the still, $x_{S,i}$ is the liquid mole fraction of component i in the still, ν_T is the sum of the stoichiometric coefficients, ν_i is the stoichiometric coefficient of component i, and r is the reaction rate per mole of mixture. Given that the reaction is $2I \leftrightarrow L + H$, the sum of the stoichiometric coefficients ν_T is zero. Here, it is worth pointing out that the different stoichiometric coefficients in this decomposition reaction do not affect the general conclusion obtained from simulations. By using a dimensionless time defined by

$$d\xi = \frac{F}{H_S}dt \tag{13}$$

we can rearrange Eqs. 11 and 12 for reactant and products, and obtain

$$\frac{dx_{S,i}}{d\xi} = -x_{s,i} + \mathrm{Da}\nu_i\frac{r}{k_f} \tag{14}$$

where k_f is the forward reaction rate constant and Da is the Damköhler number, defined as

$$\mathrm{Da} = \frac{H_S/F}{1/k_f} \tag{15}$$

Equation 14 describes the rate of change of the liquid mole fractions in the still for the BRED process. The vapor phase in equilibrium with the liquid in the still and on each stage can be calculated using the phase-equilibrium relationship, $y_i P = x_i \gamma_i P_i^{Sat}$, where γ_i is estimated by the Wilson model.

For the reaction $2I \leftrightarrow L + H$, the stoichiometric coefficients (ν_i) are -2, 1, and 1, for I, L, and H, respectively. The reaction rate can be expressed as

$$r = k_f\left(x_{S,I}^2 - \frac{x_{S,L}x_{S,H}}{K_{eq}}\right) \tag{16}$$

where $x_{S,I}$, $x_{S,L}$, and $x_{S,H}$ are the liquid mole fractions of the reactant and products in the still. Thus, for products L and H and reactant I, Eq. 14 changes to

$$\frac{dx_{S,i}}{d\xi} = -x_{S,i} + \mathrm{Da}\nu_i\left(x_{S,I}^2 - \frac{x_{S,L}x_{S,H}}{K_{eq}}\right) \tag{17}$$

$x_{S,E}$ (the liquid mole fraction of entrainer in the still) can be substituted by $x_{S,E} = 1 - x_{S,L} - x_{S,H} - x_{S,I}$, because $\sum x_i = 1$. The initial composition in the still is the charge feed composition

$$x_S = x_{S0} \tag{18}$$

Equation 17 can be solved under the initial condition in Eq. 18.

For batch extractive distillation, the possible still compositions lie on the curve connecting the charge and entrainer compositions because the entrainer is the least volatile. Starting from the composition of the charge, the still composition moves toward the entrainer composition, which can be reached after infinite time. The only feasible profile for the rectifying section lies between the distillate (light pure product, L) vertex and the entrainer vertex of the composition diagram (Lelkes et al., 1998a). In the majority of extractive distillation systems, this rectifying profile runs near the edge connecting the entrainer and distillate vertices. The necessary and sufficient condition for feasibility is to have at least one extractive section profile that connects the still path with the rectifying profile (Knapp and Doherty, 1994; Lelkes et al., 1998a).

Residue Curve Map without Distillation Boundary. The system studied here is a quaternary reactive extractive distillation system, which is the ternary reaction system $2I \leftrightarrow L + H$, RCM-031 (see Figure 2), plus the entrainer component E. There are two binary azeotropes in this quaternary system: a minimum-boiling azeotrope between products L and H and a maximum-boiling azeotrope between H and I. Because of the existence of entrainer E, which is the heaviest boiler in the whole system, the stable node azeotrope between H and I (in ternary system RCM-031) becomes a saddle in the quaternary system. All of the other fixed points (I, L, H, and the L–H minimum azeotrope) retain the same dynamic properties after the introduction of the entrainer E. No distillation boundary exists in this quaternary system because there is only one UN (the L–H azeotrope) and only one SN (E). All other fixed points are saddles.

At the beginning of the BRED process, only reactant I is in the still. As the reaction proceeds, we introduce the fourth component, entrainer E, to break the L–H azeotrope during the distillation process. The principles for the selection of effective entrainers are based on the work of Foucher et al. (1991), Laroche et al. (1991), Wahnschafft and Westerberg (1993), and Dyk and Nieuwoudt (2000).

The vapor/liquid ratio used in the extractive section for our simulation is $V/l = 0.7273$. Figure 3a shows the dynamic simulation results of this quaternary reactive extractive distillation process. As the simultaneous reaction and extractive distillation proceeds, the still composition moves from the initial feed charge point (pure reactant I) to the entrainer vertex (E). Extractive profiles are calculated based on Eq. 10 and are also shown in Figure 3a. We calculate different extractive profiles that begin from arbitrarily chosen compositions on the still path. Eventually, all extractive profiles reach the edge connecting light product L and entrainer E and they arrive at the feed stage composition (see Figure 3a). Therefore, the entrainer breaks the minimum azeotrope between L and H and it is possible to obtain the pure desired product at the top of the column by rectification above the entrainer feed stage.

Because there is no distillation boundary formed in this quaternary system, a study of the effect of Damköhler number (Da) and reaction equilibrium (K_{eq}) on feasibility is not necessary. With any value of Da and K_{eq}, the still composition moves from the initial feed charge to the entrainer vertex and extractive profiles reach the edge connecting light product L and entrainer E.

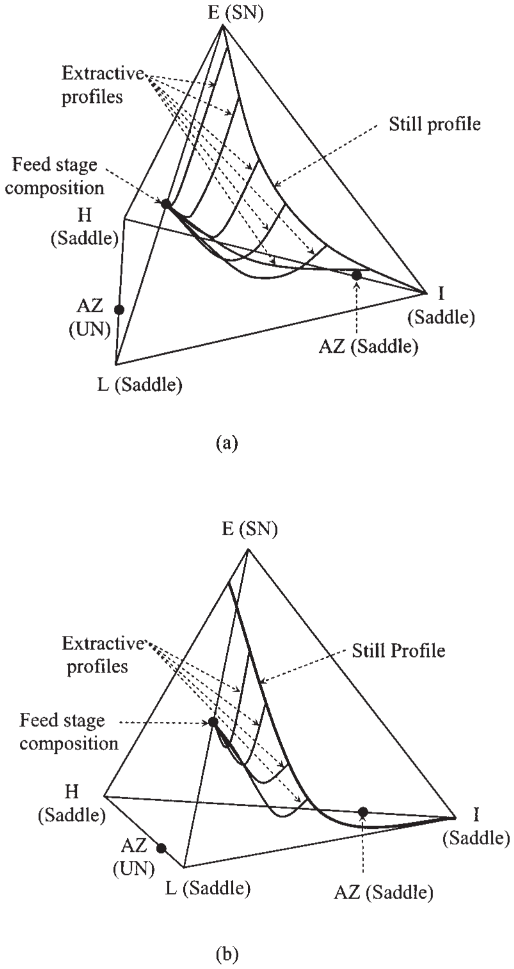


Figure 3. BRED simulation results of RCM 031 with an entrainer (no distillation boundary).

(a) Total reflux case: $V/l = 0.7273$ and Da = 1.0; (b) Finite reflux case: $R = 10.0$, $F/D = 4.0$, $V/l = 0.7273$, and Da = 1.0.

The above results are obtained using the limiting case of total reflux without product withdrawal. To describe the real process behavior with product withdrawal, a more rigorous model is developed for the dynamic simulations of BRED under finite reflux. Detailed material balance equations are summarized in the Appendix. The parameters for the simulations are as follows: a reflux ratio of $R = 10.0$, an entrainer/distillate ratio of $F/D = 4.0$, and an extractive section vapor/liquid flow ratio of $V/l = 0.7273$.

The dynamic simulation result of BRED under finite reflux is shown in Figure 3b. The still composition profile under finite reflux moves from I to the binary edge connecting entrainer E and heavy product H. Figure 3b also shows the possible extractive composition profiles between the still pot and the feed stage. It can be seen that all extractive profiles reach the same point at the L–E binary edge from different still compositions. The position of this point is a function of the entrainer flow rate, the entrainer composition, and the reflux ratio (Knapp and Doherty, 1994; Lelkes et al., 1998a). Because there is no azeotrope between L and E, we can obtain pure product L from

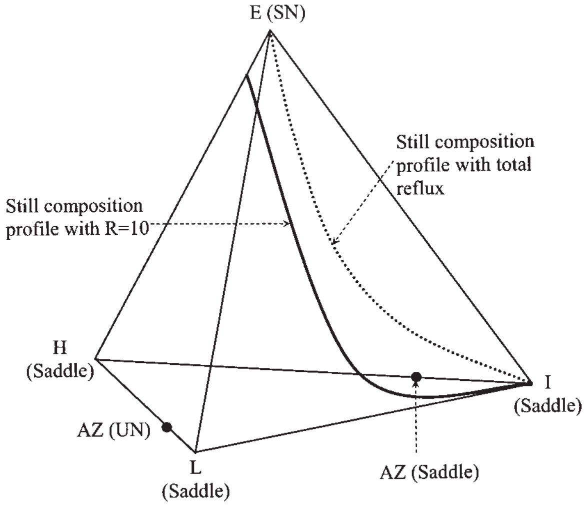


Figure 4. Comparison of the still composition profiles between total and finite reflux cases.

the top by simple rectification. Whereas *L* is removed at the top, *I* is consumed by reaction and, eventually, only *H* and *E* are left in the still pot (see Figure 3b). After the still composition profile reaches the *H–E* binary edge, we should stop feeding entrainer and start to recover *H* and *E* at the top. Because no azeotrope exists between *H* and *E*, we can get pure heavy product *H* as the second cut. Therefore, we can obtain pure saddle products by using BRED.

The still composition profiles between total reflux and finite reflux are compared in Figure 4. The two still composition profiles show one difference: the finite reflux still path reaches the *E–H* binary edge because light product *L* is withdrawn from the top, entrainer *E* is fed into the system, and heavy product *H* is generated by the reaction in the still pot. In contrast, the total reflux still path hits the entrainer vertex because no distillate is withdrawn and entrainer *E* is continuously provided until the still path reaches the entrainer vertex.

The identical behavior of the still paths can be observed for the feasibility study of nonreactive batch extractive distillation under finite and total reflux (Lelkes et al., 1998a). Despite the difference between the total and finite still paths, all possible extractive profiles under total or finite reflux reach the *L–E* binary edge in Figure 3. Once the extractive profiles hit this binary edge under total reflux, light product *L* can be recovered at the top by rectification. Thus, we can conceptually understand from the total reflux case that under finite reflux the removal of light product *L* causes reactant *I* to be consumed by reaction, and then only heavy product *H* and entrainer *E* remain in the still pot. As shown in Figure 3b, the dynamic simulation with finite reflux confirms this understanding of the simulation results with total reflux.

The system RCM 041-M (see Figure 5) is also investigated for the possibility of producing pure products (*L* and *H*), even though it has one ternary maximum azeotrope in addition to two binary azeotropes. This ternary SN azeotrope becomes a saddle when an entrainer is introduced as the highest boiler. There is no distillation boundary in this quaternary system. The dynamic simulation results of RCM 041-M with an entrainer are shown in Figure 6 for both total and finite reflux. Although there is a ternary maximum azeotrope, the results are similar to those of RCM-031 in Figure 3, indicating that BRED can produce pure products when the reaction products are saddles, regardless of the type and number of azeotropes present in the system.

The RCMs where one can produce pure products with a batch reactive extractive rectifier are summarized in Figure 7. Even though the positions of azeotropes and their properties are different, all of the RCMs show the common characteristic that the products *L* and *H* are saddles and that there exists a minimum-boiling azeotrope (UN) between *L* and *I* or *L* and *H*. To produce *L* at the top of the rectifier, such a minimum azeotrope has to be broken by an entrainer.

Residue Curve Map with Distillation Boundaries. At this point, another question can be raised about whether BRED can still feasibly produce pure products when the RCM of the reaction system $2I \leftrightarrow L + H$ has a distillation boundary that separates the reactant and products into different distillation regions. This question can be answered by the analysis of RCM-341. In Figure 8, there are two distillation regions divided by one distillation boundary. The first region is composed of one reactant and two maximum azeotropes. The two products with these two azeotropes form the second distillation region. When the fourth component, entrainer *E*, is introduced to the ternary reaction system, a distillation boundary surface is formed in this quaternary system (see Figure 9). It is found that the stable node (between *L* and *I*) in the ternary system becomes a saddle point because entrainer *E* is the heaviest boiler (SN) in the whole system. As already known, the connections of saddle–saddle and saddle–node form distillation boundaries (Rooks et al., 1998). Thus, a distillation boundary surface exists in this system. Because of this distillation boundary surface, the still composition profile is separated into two sections: one part is in the reactant distillation region and the second part is in the product region.

The extractive profiles starting from the different parts of the still profile settle down to one of the different distillation regions in both Figure 9a and b. The extractive profile starting from the reactant region reaches the stable node on the *I–E* edge, and after simple rectification the distillate at the top of the column is the reactant *I*. On the other hand, the extractive profiles originating from the second region (composed by *L*, *H*,

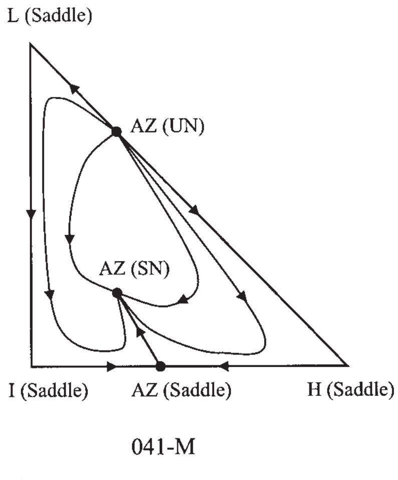


Figure 5. RCM of ternary reaction system RCM 041-M.

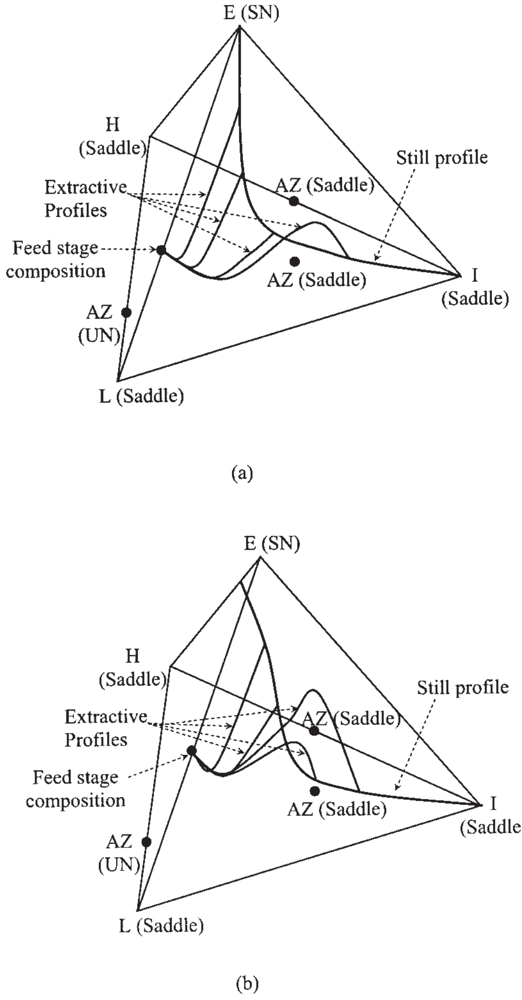


Figure 6. BRED simulation results of RCM 041-M with an entrainer (no distillation boundary).

(a) Total reflux case: $V/l = 0.63$ and Da $= 5.0$; (b) Finite reflux case: $R = 10.0$, $F/D = 4.0$, $V/l = 0.53$, and Da $= 10.0$.

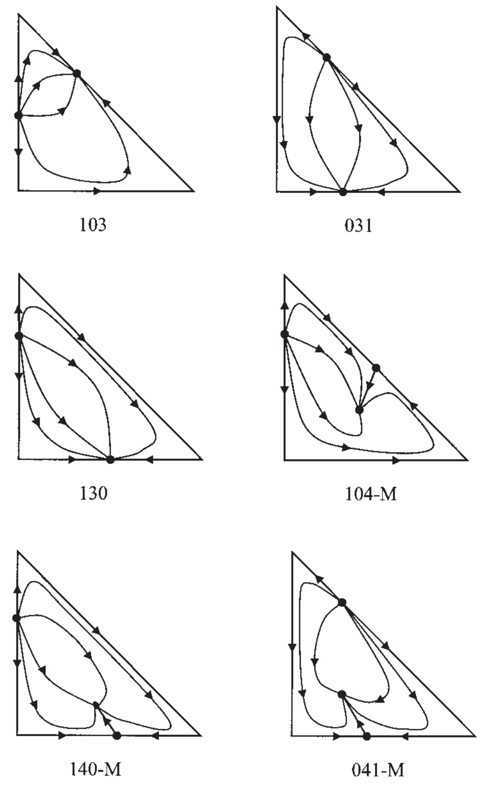


Figure 7. RCMs where we can produce pure products with an entrainer by using BRED process (no distillation boundary).

E, and two azeotropes of *L–I* and *H– I*) reach the *L–E* edge (feed stage composition). Then, the distillate is the desired pure product (*L*).

Both total and finite reflux cases show the same trends of the extractive profiles, except for the different destinations of the still paths in Figure 9. The still composition profile under total reflux eventually reaches the *E* vertex, whereas under finite reflux it reaches the *H–E* binary edge. This is the same behavior that was observed in the previous examples of Figure 3 and Figure 6. By using the simulation results with total reflux, we can conjecture the finite reflux case: *L* can be removed continuously from the top, reactant *I* is consumed by reaction, and the components left in the still are *H* and *E*. As shown in Figure 9b, the dynamic simulation with finite reflux can confirm the feasibility insight obtained from the total reflux case.

We also study the system RCM-441-M (see Figure 10), which is a more complex system and has a ternary azeotrope. There are four azeotropes in this ternary reaction system: one binary minimum azeotrope (UN) between *L* and *H*; two binary maximum azeotropes (saddles), *L–I* and *H–I*; and one ternary maximum azeotrope (one SN in the ternary system), which becomes a saddle in the presence of an entrainer *E*. *E* is the only SN in the quaternary mixture.

The simulation results of RCM-441-M with an entrainer, under total reflux and finite reflux, are shown in Figure 11a and b. Although there is a ternary maximum azeotrope, we obtain results similar to those for RCM-341 (Figure 9). This indicates that BRED can be used to produce pure products, even though the saddle products and the reactant are separated by a distillation boundary. After the still profile crosses the distillation boundary surface, the desired pure product can be produced at the top of the rectifier. The RCMs where one can produce pure products with a batch reactive extractive rectifier are summa-

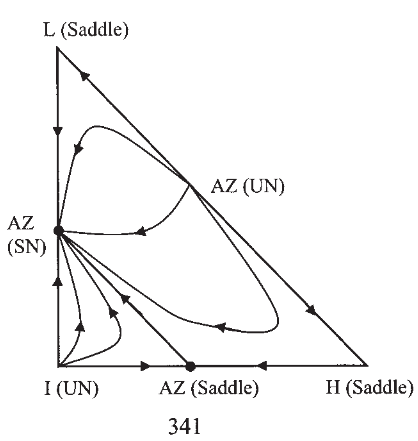


Figure 8. RCM 341 for a ternary reaction system.

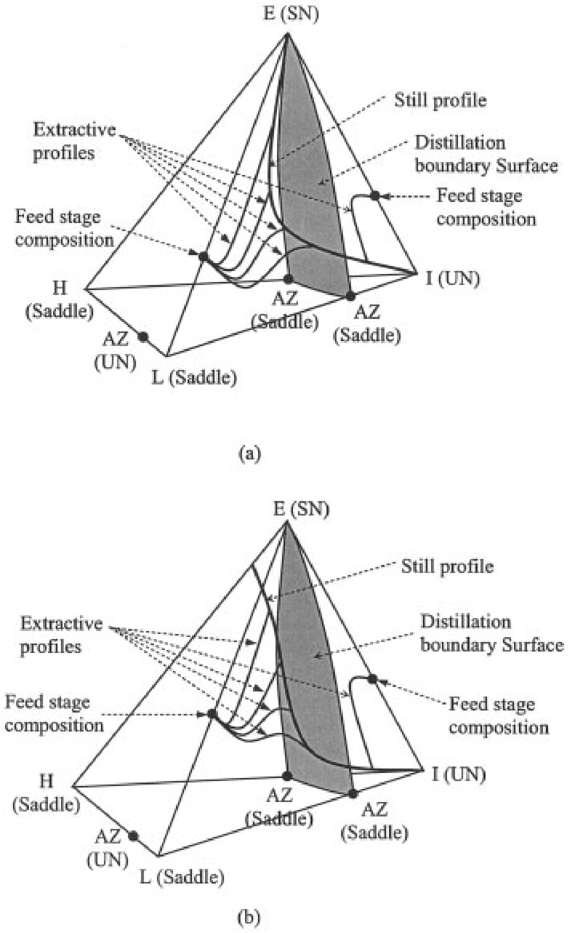


Figure 9. BRED simulation results of RCM 341 with an entrainer (with distillation boundary).

(a) Total reflux case: V/l = 0.63, and Da = 1.0; (b) Finite reflux case: R = 5.0, F/D = 3.0, V/l = 0.80, and Da = 5.0.

rized in Figure 12. All of the RCMs shown in Figure 12 have the property that the reactant and products are separated by a distillation boundary. Despite the differences between them, all of the RCMs also have the common characteristic that the products *L* and *H* are saddles, which means that they cannot be reached by simple distillation. To produce pure *L* at the top of the rectifier, an entrainer is necessary to break the azeotrope.

The common characteristic of all RCMs in Figures 7 and 12 enables us to obtain the feasibility criterion for batch reactive extractive distillation (BRED): when all reaction products are saddles and one of the azeotropes is an unstable node in the ternary system, a reactive rectifier with a side-feed entrainer stream can produce pure products regardless of the type and number of azeotropes involved in the system.

Conclusions

By using the topological information of phase and reaction equilibrium, the possible product cuts in quaternary BRED (batch reactive extractive distillation) systems were identified. One important feasibility criterion for BRED was derived: with all saddle products and the UN azeotrope, BRED can produce pure products with an entrainer. We have obtained this feasibility criterion by focusing on the RCMs where all reaction products are saddles and one of the azeotropes between two products, or between a product and a reactant, is an unstable node.

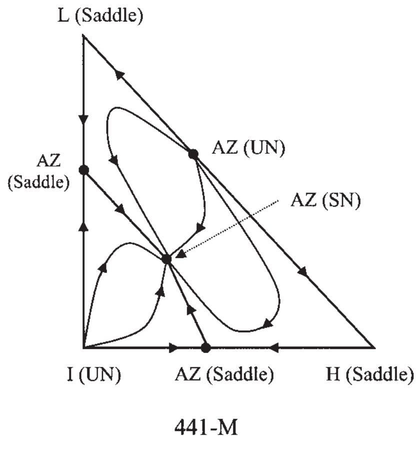


Figure 10. RCM 441-M for a ternary reaction system.

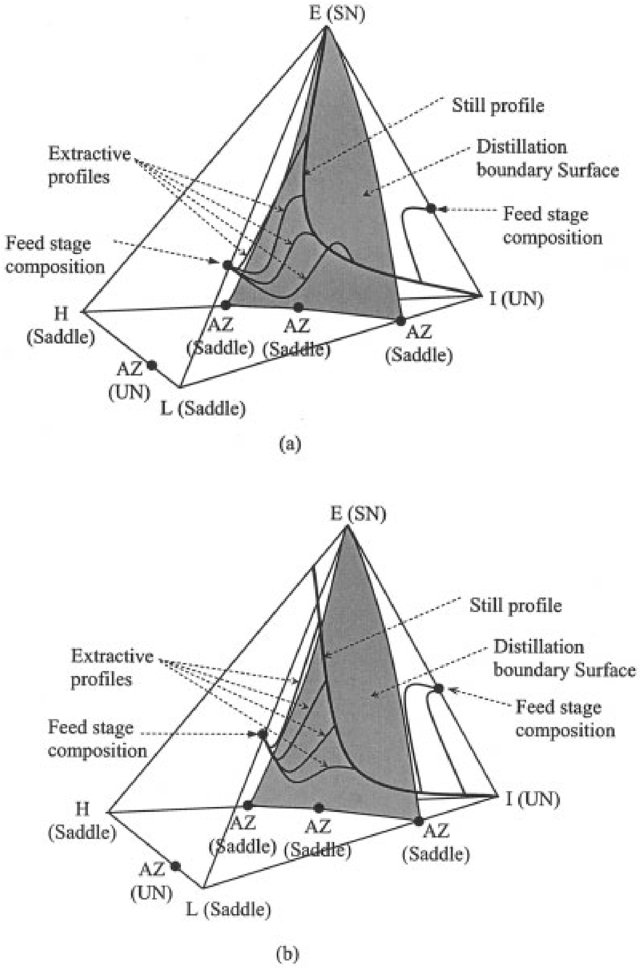


Figure 11. BRED simulation results of RCM 441-M with an entrainer (with distillation boundary).

(a) Total reflux case: V/l = 0.63, and Da = 1.0; (b) Finite reflux case: R = 5.0, F/D = 4.0, V/l = 0.53, and Da = 5.0.

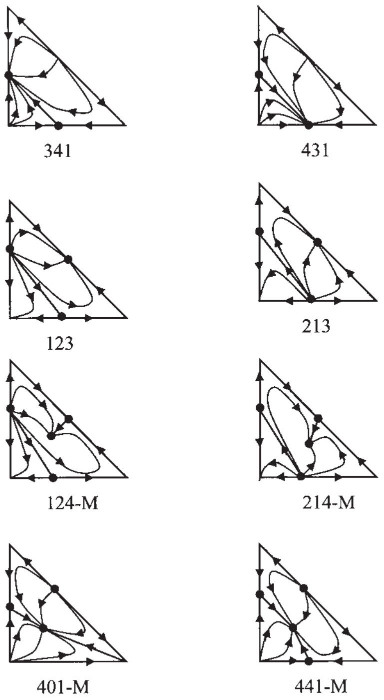


Figure 12. RCMs where we can produce pure products with an entrainer by using BRED process (with distillation boundary).

These design insights can be extended to any stoichiometry of ternary decomposition reaction ($bI \leftrightarrow aL + cH$) as long as the feasibility criterion is satisfied. This feasibility criterion is also applicable to quaternary reactions, R1 + R2 ↔ P1 + P2. If products P1 and P2 are saddles and one of the reactants (R1 or R2) works as a heavy entrainer (like acetic acid in the methyl acetate production system), then BRED can be used to produce pure products.

There are some RCMs in which the azeotrope formed with products is a stable node. Such systems are more complex and we may need a side-feed stripper to circumvent phase-equilibrium limitations. Thus, future work will extend these feasibility criteria to such systems. Even though we do not illustrate with real components, the derived feasibility criterion can be directly applied to any real systems once their reaction and phase-equilibrium data are available.

Notation

a, b, c = stoichiometric coefficients
AZ = azeotrope
B = molar bottom product flow rate
D = molar top product flow rate
Da = Damköhler number
E = entrainer
F = entrainer feed flow rate
h = plate
H = product, heavy boiler
H_s = liquid holdup in still pot
I = reactant, intermediate boiler
i = ith component
k_f = reaction rate constant
K_{eq} = reaction equilibrium constant
l = liquid flow rate
L = product, light boiler
P = pressure
r = reaction rate
SN = stable node
t = time
V = vapor flow rate
UN = unstable node
x_i = liquid mole fraction of component i in the liquid flow
x_D = liquid mole fraction in the distillate
x_B = liquid mole fraction in the bottom
x_F = liquid mole fraction in the entrainer feed
x_S = liquid mole fraction of the still pot
x_{S0} = initial liquid mole fraction of the still pot
y_i = vapor mole fraction of component i in the vapor flow
ξ = dimensionless time
γ_i = activity coefficient of component i
ν_i = stoichiometric coefficient of component i
ν_T = sum of the stoichiometric coefficients

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Appendix

Material balance of BRED under finite reflux

For the extractive section, Eq. 1 gives

$$\frac{dx_i}{dh} = \frac{V}{V + F - D}\left[\frac{(V + F - D)x_i - Fx_{F,i} + Dx_{D,i}}{V} - y_i^*\right] \tag{A1}$$

and for the reactant and products, Eq. A1 can be reduced to

$$\frac{dx_i}{dh} = x_i + \frac{D}{V + F - D}x_{D,i} - \frac{V}{V + F - D}y_i^* \tag{A2}$$

The still composition profile can be calculated from the material balance, as follows:

$$\frac{dH_S}{dt} = F - D + \nu_T H_S r \tag{A3}$$

and

$$\frac{d(H_S x_{S,i})}{dt} = Fx_{F,i} - Dx_{D,i} + \nu_i H_S r \qquad i = 1, \ldots, c - 1 \tag{A4}$$

by use of a dimensionless time, defined by

$$d\xi = \frac{F}{H_S}dt \tag{A5}$$

The sum of the stoichiometric coefficients (ν_T) is zero for $2B \leftrightarrow A + C$. We can rearrange Eqs. A3 and A4 for the reactant and products and obtain

$$\frac{dx_{S,i}}{d\xi} = -x_{s,i} - \frac{D}{F - D}x_{D,i} + \mathrm{Da}\nu_i \frac{r}{k_f} \tag{A6}$$

Equation A6 describes the rate of change of the liquid mole fractions in the still for the BRED process under finite reflux. Equation A6 can be changed to

$$\frac{dx_{S,i}}{d\xi} = -x_{S,i} - \frac{D}{F - D}x_{D,i} + \mathrm{Da}\nu_i\left(x_{S,I}^2 - \frac{x_{S,L}x_{S,H}}{K_{eq}}\right) \tag{A7}$$

Equation A7 can be solved under the initial condition $x_S = x_{S,0}$.

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