Optimal Region for Design and Control of Ternary Systems

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The trade-off between steady-state economics and dynamic controllability of recycle plants is analyzed for ternary systems. For this analysis, a boundary is first established in the composition space to identify the correct flow sheet, and then optimal trajectories for recycle plants with direct and indirect sequences are derived as the conversion varies. In the optimality regions, at any conversion, the correct separation sequence, as well as optimal reactant distribution, can also be obtained. For dynamic controllability, the reachable composition space is identified as the recycle ratios vary. The results clearly indicate that trade-off between steady-state design and dynamic control is not likely to occur, if the plant is designed along the optimal trajectories with the correct flow sheet. Rigorous nonlinear simulations also reveal that no single control structure works well over the entire composition space.

Introduction

The literature contains a large number of articles that discuss process synthesis, but the emphasis is primarily on individual process units, for example, synthesis of distillation systems, reactor networks, or heat-exchanger networks. For example, in distillation sequencing, typical heuristics include (1) remove most plentiful first, (2) remove lightest component first, (3) leave high-recovery separations to the last, and (4) leave difficult separations until last (Nishida et al., 1981; Nadgir and Liu, 1983; Douglas, 1988). However, in contrast to the rules of thumb for many other problems, sometimes the heuristics for the separation system give contradictory results. Malone et al. (1985) derive analytical criteria for the sequencing of distillation columns. The advantage of the analytical approaches is that the limitations of the results are clearly identified by the assumptions introduced in the analysis.

A typical chemical plant flow sheet has a mixture of multiple units connected both in series and in parallel (Douglas, 1988; Biegler et al., 1997). The common topology consists of a reaction section and separation sections. The textbooks of Luyben et al. (1999) and Luyben and Luyben (1997) discuss the plantwide control problems, but emphasis is on the control structure design. Much less work has treated the design of the entire plant as a single unit. Elliott and Luyben (1995, 1996) evaluate the steady-state design of a ternary system based on the total annual cost (TAC; Douglas, 1988), and controllability is assessed quantitatively using the capacity-based approach. Luyben et al. (1996) analyze the pole location of a ternary system using a simple dynamic-reactor model. Groenendijk et al. (2000) evaluate different designs using several control measures, such as, relative gain array and relative disturbance gain.

Similar to the work of Malone et al. (1985), the objective of this work is to derive analytical criteria for the design of the entire plant. This work differs from sequencing distillations work in that the feed composition to the separation units can be designed. Once the optimal design is obtained, the trade-off between design and control is evaluated based on the pole location and disturbance rejection capability. Results show that the new approach provides analytical criteria for the design and control of the entire plant for ternary systems with two recycle streams.

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The remainder of that article is organized as follows. The following section extends the simplified cost models of Malone et al. (1985), Douglas (1988), and Elliot and Luyben (1996) to recycle plants. Steady-state economics for recycle plants are evaluated for three different cases: fixed-reactor composition, fixed-reactor conversion, and variable-reactor composition. Dynamic controllability issues are addressed in the fourth section, and the concept of reachability is used to measure the inherent operability of any given plant. The fifth section discusses the problem of control structure design, and rigorous simulations are used to illustrate the operability of various designs. Extensions to one reactor, one distillation column, and one recycle stream configurations are made in the sixth section, followed by the conclusion.

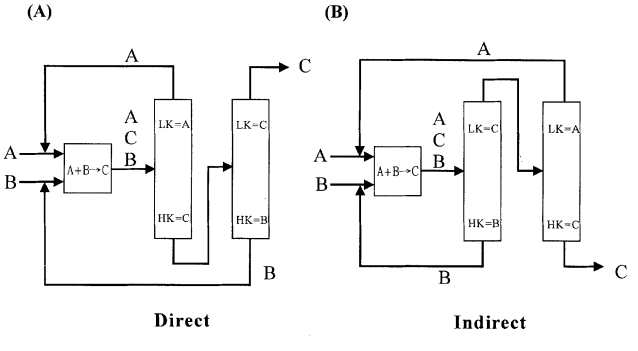
Steady-State Design

Process

In this article, we demonstrate the interaction between design and control on a complex process flow sheet. The process configuration is described in Tyreus and Luyben (1993) and Elliott and Luyben (1996). This is a ternary system with the following reaction: $A + B \rightarrow C$. Two reactants A and B are fed, separately, to a continuous stirred-tank reactor (CSTR), which is operated isothermally. The reaction rate can be expressed as

$$P = kV_R z_A z_B \tag{1}$$

where P is the total production of the product C, k is the rate constant, z_A and z_B are the mole fractions for reactants A and B, and V_R is the reactor holdup. The reactor effluent is assumed to be a saturated liquid and contains a ternary mixture of A, B, and C, because some A and B remain unreacted. In the ternary mixture, A is the light component (LK), B is the heavy component (HK), and the product C is an intermediate boiler (IK). The relative volatility is used to describe the ternary mixture, and a typical set of volatility is $\alpha_A = 4$, $\alpha_B = 1$, and $\alpha_C = 2$ (Tyreus and Luyben, 1993). To separate the intermediate boiling product (C) from the high and low boiling reactants (A and B), we need two distillation columns. For ternary systems, two distillation sequences, direct and indirect sequence (Malone et al., 1985), can be used in this flow sheet (Figure 1). For the direct sequence, reactant A (LK) is recycled from the top of the first column back to the reactor and reactant B (HK) is recycled from the bottom of the second column back to the reactor (Figure 1). The indirect sequence, on the other hand, recycles the heavy reactant (B) back to the reactor first, followed by recycling the light reactant (A) from the top of the second column, as shown in Figure 1.



Direct

Indirect

Figure 1. Alternatives for a ternary system with two recycle streams: (A) direct sequence; (B) indirect sequence.

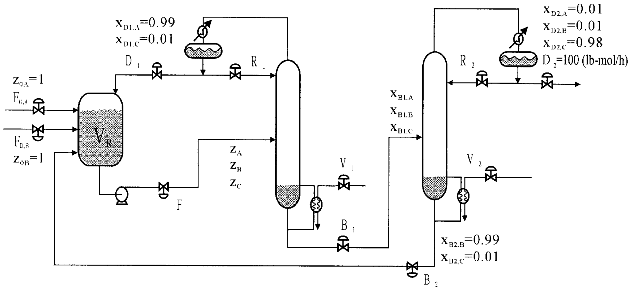


Figure 2. Ternary process with two recycles using direct sequence and corresponding notation.

For the synthesis of separation systems, we can use distillation sequence heuristics (Nadgir and Liu, 1983) or the analytical criterion of Malone et al. (1985) to choose an appropriate configuration, for example, direct or indirect. However, for the design of the entire plant, we can determine the conversion and distribution of reactants in the reactor, in addition to the distillation sequences. In other words, we can also design the "feed composition" for the distillation columns. A criterion is necessary to evaluate different flow sheets. The simplified TAC approach of Molane et al. (1985) and Douglas (1988) is taken here.

Total annual cost TAC

Steady-State Design and Equipment Sizing. In this study, the ternary process with two recycle streams contains one reactor and two distillation columns. From the mass balances for each unit, there are a number of ways to solve the nine nonlinear algebraic equations. Before getting to the steady-state design procedure, we must give some assumptions for the system. We use the direct sequence as an example (Figure 2), and the assumptions are:

(1) The process components have constant density.

(2) The flow rate of the product stream D_2 is fixed at 100 lbmol/h.

(3) The product specification is $x_{D_2,C} = 0.98$.

(4) There is no component A leaving the bottom of the second column ($x_{B_2,A} = 0$). Therefore, the composition of the heavy recycle stream, B_2, is specified to be $x_{B_2,B} = 0.99$, and $x_{B_2,C} = 0.01$.

(5) There is no component B leaving the top of the first column ($x_{D_1,B} = 0$). Therefore, the composition of the light recycle stream, D_1, is specified to be $x_{D_1,A} = 0.99$ and $x_{D_1,C} = 0.01$.

With the given specifications, we can complete the steady-state design for any given reactor conversion and reactant distribution. The steady-state conditions of all streams in the ternary recycle system are calculated from balance equations, as shown in Appendix A. Next, shortcut methods are applied to find the minimum number of trays (Fenske equation) for distillation columns, locate the feed tray location (Kirkbride equation), and size the column diameter (Appendix B). The heat-transfer areas for the reboiler and condenser are also computed from the vapor flow rates (Elliot and Luyben, 1996).

From Appendices A and B, we can determine all the process flow rates and the equipment sizes. In order to select the best steady-state design for a direct or indirect sequence, we employ economic assessment to evaluate different designs. The capital cost and operation cost of the entire plant are estimated using the correlation given in Douglas (1988), as shown in Appendix B. Therefore, the process TAC model can be expressed as

$$\mathrm{TAC} = C_1 V_R^{0.62267} + \Sigma C_2 V_i^{0.533} N_{T,i}^{0.802} + \Sigma C_3 V_i^{0.775} N_{T,i} + \Sigma C_4 V_i^{0.65} + \Sigma C_5 V_i \quad (2)$$

Equation 2 gives a rigorous expression for the TAC, and it was used by Elliot and Luyben (1996) to analyze steady-state economics for recycle plants. In Eq. 2, the TAC model consists of the following terms: the first term represents the capital cost of the reactor, the second and third terms correspond to the capital costs of distillation columns and trays, the fourth term stands for the combined capital costs for the reboiler and condenser, and the last term is the operation cost for the system. Note that the difference between Eq. 2 and the model of Malone et al. (1985) is that the reactor cost is included in terms of V_R.

Simplified TAC. Following the approach of Malone et al. (1985), the TAC model is linearized

$$TAC = K_0 + K_1 V_R + \Sigma K_2 N_{T,i} + \Sigma K_3 V_i \quad (3)$$

For the purpose of comparison, it is useful to express the simplified TAC model in terms of process variables, for example, conversion, reactant distribution, relative volatilities, and reaction-rate constant. This can be done by substituting relevant process variables for the equipment size, tray numbers, and vapor rates in Eq 3. From the mass-balance equation, we can express reactor size (V_R) as

$$V_R = \frac{P}{k z_A z_B} \quad (4)$$

where P is the production rate for the system. Next, we use Gilliland's approximation, $N_{T,i} = 2N_{\min,i}$ to find the theoretical tray, and use Fenske's equation for the minimum number of trays; (Douglas, 1988). The number of theoretical trays can be expressed as

$$N_{T,i} = 2\frac{\log\left\{\dfrac{x_{Di,LK}}{x_{Di,HK}}\dfrac{x_{Bi,HK}}{x_{Bi,LK}}\right\}}{\log\left(\dfrac{\alpha_{i,LK}}{\alpha_{i,HK}}\right)} \quad (5)$$

where LK and HK stand for key and heavy key, respectively, and the subscript i means the ith column. We also can use the mass-balance expression to estimate the vapor flow rate by the minimum reflux ratio

$$V_i = (1.2R_{m,i} + 1)D_i \quad (6)$$

It should be emphasized here that, for recycle plants, the distillate flow rate is a function of the reactor composition, because the feed flow to the separation system (F) varies as the conversion changes. Assuming 100% fractional recovery for the product C, we have

$$F = \frac{P}{z_C}$$

Therefore, the two distillate flow rates for the direct sequence are

$$D_1 = P\frac{z_A}{z_C}$$

$$D_2 = P$$

These three equations clearly demonstrate the difference between the separation system by itself and recycle plant as a whole. For the indirect sequence, similar expressions can be derived from material balances. For the first distillation column, the minimum reflux ratio equation of Glinos and Malone (1984) is adopted here

$$A/CB \quad R_m = \frac{\alpha_C(z_A + z_C)}{f z_A(\alpha_A - \alpha_C)} + \frac{z_B}{f z_A(\alpha_A - 1)} \quad (7)$$

$$AC/B \quad R_m = \frac{(z_B + z_C)/(\alpha_C - 1) + z_A/(\alpha_A - 1)}{(z_A + z_C)(1 + z_A z_B)} \quad (8)$$

where $f = 1 + 1/(100 z_C)$.

In the second distillation column, we use Underwood's equation to approximate the minimum reflux ratio

$$C/B \quad R_m = \frac{1 - z_A}{(\alpha_C - 1)z_C} \quad (9)$$

$$A/C \quad R_m = \frac{\alpha_C(1 - z_B)}{(\alpha_A - \alpha_C)z_A} \quad (10)$$

From Eqs. 4 to 10, the simplified TAC models for both the direct and indirect sequences can be expressed in terms of system conversion, reactant ratio, relative volatility, and reaction-rate constant. The following two equations give the simplified TAC models

$$TAC^D = K_0 + K_1\frac{P}{kz_Az_B} + \Sigma 2K_2\frac{\log\left\{\dfrac{x_{Di,LK}}{x_{Di,HK}}\dfrac{x_{Bi,HK}}{x_{Bi,LK}}\right\}}{\log\left(\dfrac{\alpha_{i,LK}}{\alpha_{i,HK}}\right)}$$

$$+ K_3P\left[1.2\frac{1-z_A}{(\alpha_C-1)z_C}+1\right]$$

$$+ K_3P\frac{z_A}{z_C}\left\{1.2\left[\frac{\alpha_C(z_A+z_C)}{fz_A(\alpha_A-\alpha_C)}+\frac{z_B}{fz_A(\alpha_A-1)}\right]+1\right\} \quad (11)$$

$$TAC^I = K_0 + K_1\frac{P}{kz_Az_B} + \Sigma 2K_2\frac{\log\left\{\dfrac{x_{Di,LK}}{x_{Di,HK}}\dfrac{x_{Bi,HK}}{x_{Bi,LK}}\right\}}{\log\left(\dfrac{\alpha_{i,LK}}{\alpha_{i,HK}}\right)}$$

$$+ K_3P\frac{z_A}{z_C}\left[1.2\frac{\alpha_C(1-z_B)}{(\alpha_A-\alpha_C)z_A}+1\right] + K_3P\frac{z_A+z_C}{z_C}$$

$$\times\left\{1.2\frac{(z_B+z_C)/(\alpha_C-1)+z_A/(\alpha_A-1)}{(z_A+z_C)(1+z_Az_B)}+1\right\} \quad (12)$$

Design and Analysis

With the linearized TAC model, we are able to evaluate different designs. Three cases, fixed-reactor composition, fixed conversion, and free reactor composition, are studied. The reason for this classification is that, in some reaction kinetics, a certain ratio of reactant distribution has to be maintained to prevent occurrence of side reactions, or certain concentration of a particular reactant has to be maintained to ensure process safety. From an energy-management point of view, a certain level of conversion has to be kept to ensure attainable heat removal. The first is the case of fixed-reactor effluent composition (z_A, z_B, and z_C) and, in this case, the only design alternative we have is the selection of the separation sequence. The second one is the case of fixed conversion (z_C). Here, the design variables are the distribution of reactants (z_A and z_B) and distillation sequencing. In the last case we allow the reactant effluent composition to vary (that is, variable z_A, z_B, and z_C). The design variables for this case thus become conversion, distribution of reactants, and distillation sequence. This gradual transition illustrates the similarity and difference between the syntheses of distillation systems and reactor/distillation systems.

Fixed-reactor effluent composition

When z_A, z_B, and z_C are given, a limited design space is available and the remaining design degree of freedom is distillation sequencing. On the other hand, this is the easiest one to analyze. Because, for the two design alternatives, the reactor sizes are the same (as the result of same conversion) and the feed composition to distillation columns are also the same as a result of the same fractional recoveries.

Boundary for Column Sequencing. Following Malone et al. (1985), we use the superscript D to denote the direct sequence and I to represent the indirect sequence. The difference in the costs between these two alternatives is

$$\Delta\text{TAC} = \text{TAC}^D - \text{TAC}^I \quad (13)$$

Substituting Eq. 3 into Eq. 13, we obtain

$$\Delta TAC = K_1\left\{V_R^D - V_R^I\right\} + K_2\left\{N_{T,AC}^D - N_{T,AC}^I + N_{T,CB}^D - N_{T,CB}^I\right\}$$
$$+ K_3\left\{V_{AC}^D - V_{AC}^I + V_{CB}^D - V_{CB}^I\right\} \quad (14)$$

The indirect sequence is favored when ΔTAC is positive, and the direct sequence is preferred whenever ΔTAC is negative. Equation 14 can be simplified further. First, Eq. 4 shows that the reactor volumes are the same for both configurations, that is, $V_R^D = V_R^I$. Hence, the first factor on the righthand side (RHS) of Eq. 14 becomes zero. Since the fractional recoveries are given for both sequences, Eq. 5 gives $N_{T,AC}^D = N_{T,AC}^I$ and $N_{T,BC}^D = N_{T,BC}^I$ (Malone et al., 1985). Thus, the relative costs of the recycle plant can be compared based on the total vapor requirement, and we can write

$$\Delta TAC = K_3\left(V_{AC}^D - V_{AC}^I + V_{CB}^D - V_{CB}^I\right) = K_3\Delta V \quad (15)$$

This is exactly the result of Malone et al. (1985) for sequencing distillation columns for ternary mixtures, and it agrees with the common heuristic that vapor rate is the dominate factor in fixing the separation cost. The results reveal that this heuristic can be extended to recycle plants, because the reactor costs are the same in this case.

When we substitute Eq. 5 through Eq. 10 into Eq. 15, we obtain

$$\frac{\Delta\text{TAC}}{K_3P/z_C} = 1.2\left\{\frac{z_B+z_C}{\alpha_C-1}\frac{z_Az_B}{z_Az_B+1}+\frac{1}{\alpha_A-1}\frac{z_B-fz_A+z_Az_B^2}{f(1+z_Az_B)}\right.$$
$$\left.-\frac{\alpha_C(z_A+z_C)}{\alpha_A-\alpha_C}\frac{f-1}{f}\right\}-z_A \quad (16)$$

Equation 16 can be used as a criterion for sequence selection even for recycle plants. It is useful in the initial design because the RHS is expressed in terms of relative volatilities and reactor composition. More importantly, we can construct the boundary between direct and indirect sequences by solving Eq. 16 (that is, letting the RHS of Eq. 16 be equal to zero).

Implications. Similar to the approach of Glinos and Malone (1988), we can draw the boundary when the TAC (or the total vapor rate) for the direct sequence is equal to the TAC for the indirect sequence on the composition space by solving Eq. 16. Figure 3 shows that the boundary derived from the simplified cost model is almost the same as that from a rigorous TAC calculation (Elliott and Luyben, 1996 and Appendix B). It should be noticed that the notation for reactants A and B are light and heavy keys, respectively, while the product C is the intermediate key (this is different from the typical alphabetic order for components according to the normal boiling point).

The boundary in Figure 3 suggests that the direct sequence is preferred for more than two thirds of the ternary composi-

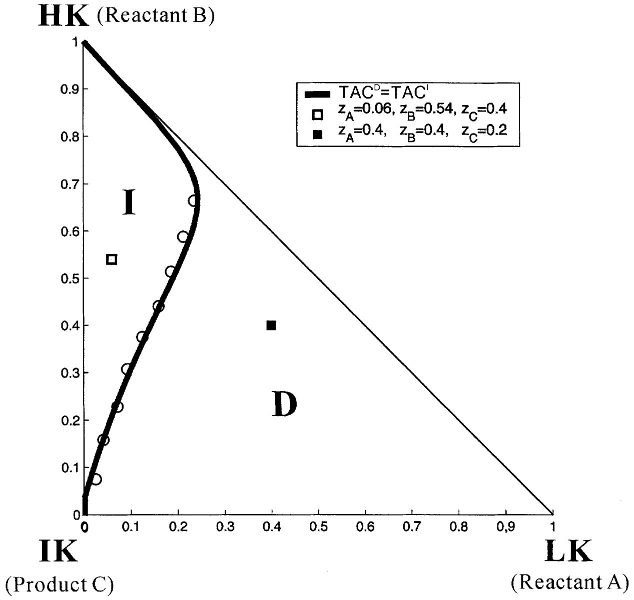


Figure 3. Boundary of equal total annual cost (TAC) for recycle plants using direct and indirect distillation sequences based on simplified TAC (solid line) and rigorous nonlinear (open circle) models.

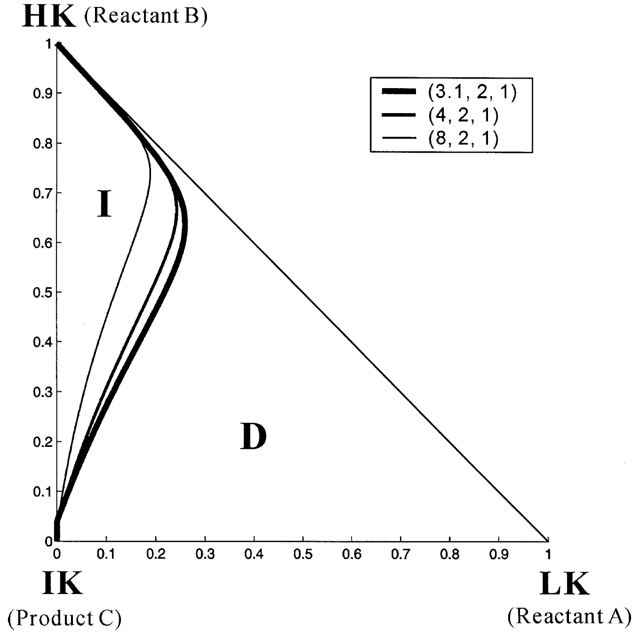


Figure 4. Effects of relative volatility on boundaries using direct and indirect sequences.

tion space and the indirect sequence is favored for very limited composition space, especially when a small amount of LK (reactant A) is presented. A simple explanation for this is that, in the direct sequence (such as Figure 1), the LK (reactant A) only boils up once, as opposed to the indirect sequence where the LK boils up two times (the LK has to be sent to the second column and taken out as the overhead product). Also note that the IK was boiled up once in both sequences and the HK are taken out as bottoms product in either sequence. The effect of relative volatility is shown in Figure 4 as we change α_A from 4 to 3.1 and to 8. The results show that as the separation of LK becomes easier (such as $\alpha_A = 8$), the composition space for the direct sequence increases and, on the other hand, the area for the direct sequence shrinks as the separation becomes more difficult (such as $\alpha_A = 3.1$). This is within one's expectation, since the relative cost for separating the LK changes.

Figures 3 and 4 are useful in completing the design of recycle plants. For example, if the reactor composition is $z_A = 0.06$, $z_B = 0.54$, and $z_C = 0.4$, then we choose the indirect distillation sequence as shown in Figure 3, and if $z_A = 0.4$, $z_B = 0.4$, and $z_C = 0.2$, the direct sequence is preferred. Therefore, with a given reactor composition, we can apply the distillation column sequencing criterion (Malone et al., 1985; Glinos and Malone, 1988) to recycle plants.

Fixed conversion

When the conversion (z_C) is given, compared to the previous case, we have one more degree of freedom, the distribution of the reactants, for example, z_A/z_B, in addition to the column sequencing. This is a more general case and, in practice, the conversion of reaction systems can be limited by available heat-transfer area, selectivity, and so on.

Optimal Paths. For a given z_C, the optimal reactant distribution can be found by taking the derivative of the simplified TAC (Eq. 3) for both sequences. First, we substitute z_B and z_C for z_A in the cost model, and then take the derivative with respect to z_B

$$\frac{\partial TAC}{\partial z_B} = \frac{\partial K_0}{\partial z_B} + \frac{\partial K_1 V_R}{\partial z_B} + \frac{\partial K_2 N_{T,i}}{\partial z_B} + \frac{\partial K_3 V_i}{\partial z_B} \tag{17}$$

Since the fractional recoveries are fixed and K_i are constant, Eq. 17 can be simplified to

$$\frac{\partial TAC}{\partial z_B} = K_1 \frac{\partial V_R}{\partial z_B} + K_3 \frac{\partial V_i}{\partial z_B} \tag{18}$$

For the direct sequence, after some algebraic manipulation, we have

$$\frac{\partial TAC^D}{\partial z_B} = K_3 \frac{P}{z_C}\left\{\left[\frac{120 z_C}{100 z_C + 1}\right]\left[\frac{\alpha_{AC} - \alpha_{AB}}{(\alpha_{AC} - 1)(\alpha_{AB} - 1)}\right] + 1.2\left(\frac{1}{\alpha_{CB} - 1}\right) - 1\right\} - \frac{K_1 P}{k}\left[\frac{1 - 2z_B - z_C}{z_B^2(1 - z_B - z_C)^2}\right] \tag{19}$$

For a given z_C, we can solve Eq. 19 (that is, $\partial TAC^D/\partial z_B = 0$) to find the optimal reactant composition distribution, that is, giving minimum TAC for the recycle plant. Similarly, for the indirect sequence, the optimal distribution of z_A and z_B can be obtained by solving

$$\frac{\partial TAC^I}{\partial z_B} = K_3 \frac{P}{z_C}\left\{1.2\left[\frac{\dfrac{\alpha_{AB}-\alpha_{CB}}{(\alpha_{AB}-1)(\alpha_{CB}-1)}}{1+z_B(1-z_B-z_C)} - \frac{\left(\dfrac{z_B+z_C}{\alpha_{CB}-1}+\dfrac{1-z_B-z_C}{\alpha_{AB}-1}\right)(1-2z_B-z_C)}{[1+z_B(1-z_B-z_C)]^2}\right] - \frac{1.2}{\alpha_{AC}-1} - 2\right\} - \frac{K_1 P}{k}\left[\frac{1-2z_B-z_C}{z_B^2(1-z_B-z_C)^2}\right] = 0 \quad (20)$$

These two analytical expressions are useful to locate the optimal reactant distribution for recycle plants with the direct and indirect sequences, respectively.

Implications. The results, Figure 5, indicate that, for both sequences, the optimal paths start from the corner of heavy reactant (B) when the conversion is low $(z_C \rightarrow 0)$ and, as the conversion (z_C) increases, they converge toward the center line (thin dashed line in Figure 5), which means equally distributed reactants (that is, $z_A = z_B$). This coincides with one's intuition, because, at low conversion, the operating cost of distillation columns dominates and excess heavy component reduces the vapor rate (such as note that we boilup the IK once in both sequences and boilup the LK once for the direct sequence and twice for the indirect sequence). At high conversion, the reactor cost dominates and 50/50 distribution of reactants (that is, $z_A/z_B = 1$) is preferred, because $z_A = z_B$ gives the smallest reactor volume when z_C is fixed. Figure 5 also shows that the optimal trajectories always lie in the composition space where the heavy reactant is greater or equal to the light reactant.

Once the optimal paths are drawn, we still need to select an appropriate distillation sequence. Again, the boundary for the distillation sequencing (Figure 3) is useful in this regard. When the boundary is drawn in Figure 5, it becomes clear that at low conversion, that is, $z_C \leq \underline{z}_C$, the indirect sequence is favored and, at higher conversion, that is, $z_C \geq \bar{z}_C$, the direct sequence is preferred. For the conversion in between, that is, $\underline{z}_C < z_C < \bar{z}_C$, we have to compute and compare TAC^D and TAC^I (Eqs. 11 and 12) to find a better sequence.

The result just shown is for an example with specific rate constant $(k = 1)$ and relative volatilities $(\alpha_A/\alpha_C/\alpha_B = 4/2/1)$, and the simplified TAC can be used to explore the effects of rate constant (k) and relative volatilities. Figure 6A reveals that, for the same relative volatilities, as the rate constants (k) decreases, the weighting of the reactor on the TAC becomes larger and, thus, the optimal paths converge toward the center line (that is, $z_A = z_B$) faster, for example, at a lower z_C. However, the boundary for the direct and indirect se-

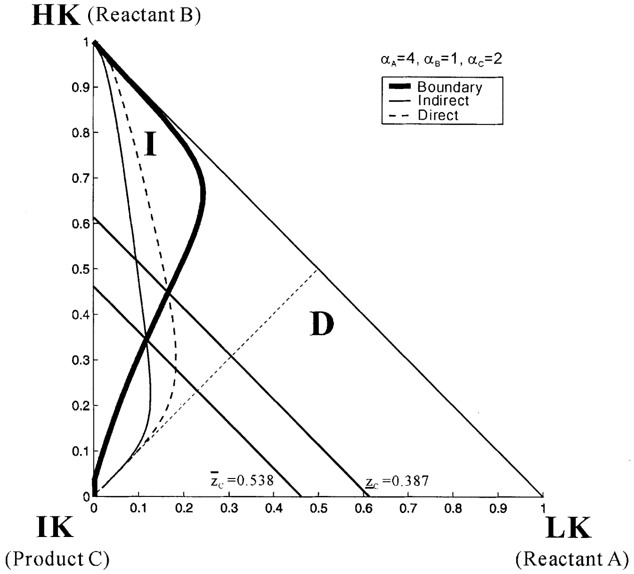


Figure 5. Optimal paths for sequences and boundaries between direct and indirect sequences.

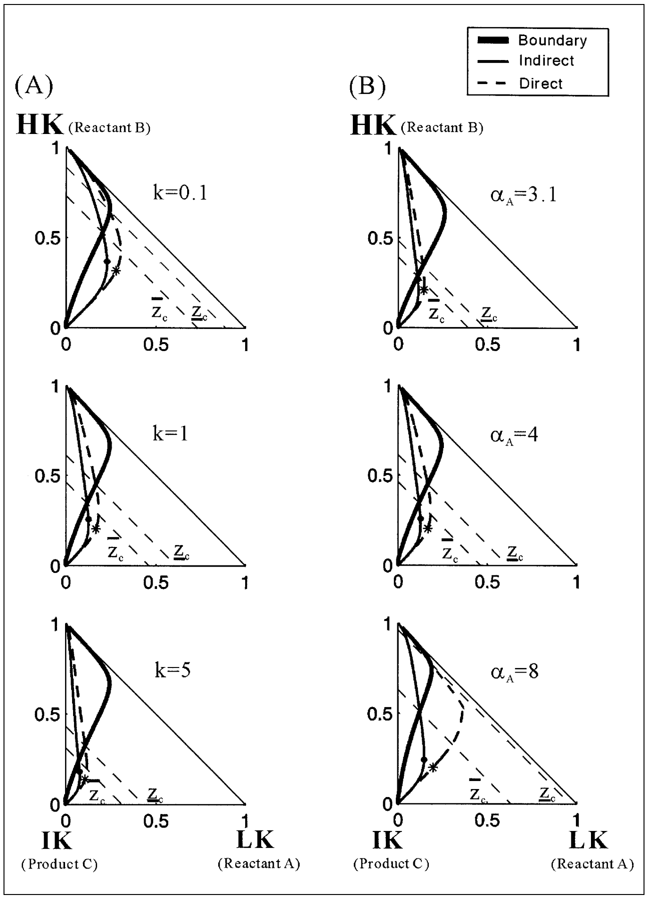


Figure 6. Effects of (A) rate constant (k), and (B) relative volatility (α_A) to boundaries and optimal paths for direct and indirect sequences.

quences remains unchanged. Therefore, the direct sequence is favored for a larger portion of the z_C toward the high conversion end (that is, $\bar{z}_C$ decreases). It will be shown later that, quantitatively, the difference between TAC^D and TAC^I is small because the reactor cost dominates the TAC at high conversion. As the separation for the light reactant becomes easier (that is, α_A increases), the optimal paths move toward the boundary faster and, as pointed out earlier, the composition space for the direct sequence also becomes larger (that is, the boundary moves toward the HK side; Figure 4). This gives a smaller $\bar{z}_C$ and, consequently, the direct sequence is favored for a larger composition range (Figure 6B). This is exactly what we expect, because, with an easy separation for the LK, the cost of the reactor becomes more important and a near balanced reactant composition leads to the direct sequence.

Variable reactor composition

When no constraint is imposed on the conversion, we have another degree of freedom, z_C. Again, the simplified TAC can be used to find the optimal composition distribution.

Optimal Reactor Composition. Following the approach in the previous section, we again substitute z_B and z_C for z_A and take the derivative with respect to z_C. For the direct sequence, we obtain

$$\frac{\partial TAC^D}{\partial z_C} = \frac{K_1 P}{k}\left[\frac{1}{z_B(1-z_B-z_C)^2}\right] - K_3 P\left\{12{,}000\left[\frac{1-z_B}{(\alpha_{AC}-1)(100z_C+1)^2} + \frac{z_B}{(\alpha_{AB}-1)(100z_C+1)^2}\right] + \frac{1.2z_B}{(\alpha_{CB}-1)z_C^2} + \frac{1-z_B}{z_C^2}\right\} \qquad (21)$$

The optimal reactor composition can be found by solving Eqs. 19 and 21 simultaneously for z_B and z_C. Similarly, for the indirect sequence, the derivative can be written as

$$\frac{\partial TAC^I}{\partial z_C} = K_3 P\left\{\frac{1.2\left[\frac{\alpha_{AB}-\alpha_{CB}}{(\alpha_{AB}-1)(\alpha_{CB}-1)}\right]}{z_C[1+z_B(1-z_B-z_C)]} - \frac{1.2(1+z_B-z_B^2-2z_Bz_C)\left(\frac{z_B+z_C}{\alpha_{CB}-1}+\frac{1-z_B-z_C}{\alpha_{AB}-1}\right)}{z_C^2[1+z_B(1-z_B-z_C)]^2} - \frac{1.2(1-z_B)}{(\alpha_{AC}-1)z_C^2} - \frac{2(1-z_B)}{z_C^2}\right\} + \frac{K_1 P}{k}\left[\frac{1}{z_B(1-z_B-z_C)^2}\right] \qquad (22)$$

and the optimal operating condition can be computed from Eqs. 20 and 22.

Implications. The results show that for the base case, $\alpha_A/\alpha_C/\alpha_B = 4/2/1$ and $k = 1$, both optimal operating conditions correspond to 63% conversion with different reactant distributions (Table 1). For the direct sequence, two reactants are almost equally distributed with $z_B/z_A = 1.22$ and, for the indirect sequence, the ratio becomes $z_B/z_A = 2.02$. Since the conversion is greater than $\bar{z}_C$, the recycle plant with the direct sequence is the true optimum, as shown in the middle graphs of Figure 7. But the two TACs only differ by 2.6%. Next, let us examine the effect of the rate constant (k) on the optimal reactor composition. At a low k value (such as $k = 0.1$), the relative cost of the reactor becomes more important and the optimal conversion is smaller $z_C \approx 0.41$ and the optimal conversion changes from $z_C = 0.41$ to $z_C = 0.76$ as k increases from 0.1 to 5, as shown in Figure 7. All the conversions are greater than $\bar{z}_C$ (Figure 6) and, thus, the process with the direct sequence results in the optimal design. Despite the variations in the optimal conversion (z_C) with k, the optimal distribution (z_B/z_A) of the reactants remains fairly constant and the value is close to 1 (Table 1) for the optimal case. The TAC for the indirect sequence is only slightly

Table 1. Optimal Design for Direct and Indirect Sequences with Different System Parameters (Rate Constant and Relative Volatility)

	Low k	Base Case	High k	Low α_A	High α_A
k	0.1	1	5	1	1
$\alpha_A/\alpha_B/\alpha_C$	4/1/2	4/1/2	4/1/2	3.1/1/2	8/1/2
$\underline{z}_C/\bar{z}_C$	0.11/0.27	0.39/0.54	0.57/0.69	0.52/0.61	0.04/0.37
$(z_C)_D/(z_C)_I$	0.41/0.41	0.63/0.62	0.76/0.74	0.65/0.63	0.61/0.61
$(z_B/z_A)_D/(z_B/z_A)_I$	1.14/1.60	1.22/2.02	1.27/2.31	1.46/2.44	1.01/1.63
$(TAC)_D/(TAC)_I$	0.961	0.974	0.982	0.987	0.918

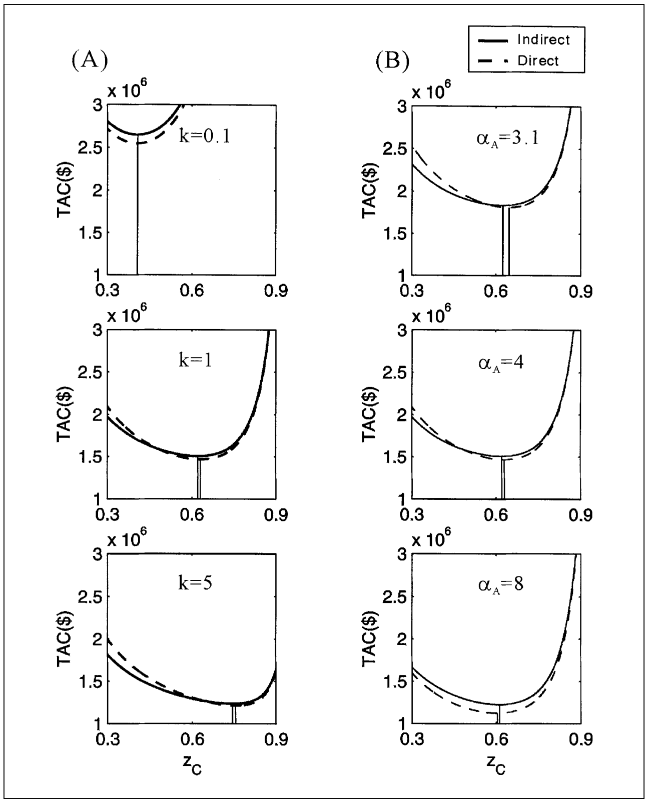


Figure 7. Optimal designs (TACs along the optimal paths) of direct and indirect sequences for different (A) rate constant (k), and (B) relative volatility (α_A).

greater than that of the direct sequence (Table 1), but the reactant distributions (z_B/z_A) are not quite equally distributed, and they range from 1.6 to 2.3 as k changes from 0.1 to 5.

Now consider the effects of relative volatility. When the separation of the light component (A) becomes easier (that is, α_A increases), the optimal conversion (z_C) decreases slightly (Figure 7) and the TAC decreases as the result of cheaper separation cost. Since the optimal z_C is greater than $\bar{z}_C$, the direct sequence is favored for all these cases (Figure 7) and the difference between TAC^D and TAC^I becomes more evident as α_A increases (but still the difference is within 10%). Again, the optimal reactor composition for the direct sequence tends to prefer equally distributed reactants ($z_B/z_A \approx 1$) as shown in Table 1 and, on the other hand, the reactant distributions (z_B/z_A) for the indirect sequence range from 2.4 to 1.6.

Several observations can be made from on-going analyses.

(1) In terms of the TAC, the optimization results tend to prefer a recycle process with the direct distillation sequence with almost equally distributed reactants. The optimal conversion can vary, but the reactant distribution (z_B/z_A) remains close to 1 (such as ranging from 1.01 to 1.46).

(2) Despite the fact that the indirect sequence gives a slightly higher TAC (TAC^I), the difference between the two in most cases is less than 10%. However, the optimal reactor composition for the indirect sequence gives a more biased reactant distribution, for example, z_B/z_A ranging from 1.6 to 2.4, as shown in Table 1.

Controllability

From steady-state economics, we can identify the region for better distillation sequencing (given z_A, z_B, and z_C), find the optimal reactant distributions for both the direct and indirect sequences (given the conversion), and locate the optimal reactor composition and distillation sequence (variable everything). Do these optima lead to dynamically operable processes? Does trade-off exist between steady-state design and dynamic control? Instead of evaluating each design separately, we would like to identify a dynamically favorable (or unfavorable) region in the composition space.

Steady-state information offers useful insight into operability (such as handling production-rate changes). Next, simple dynamic information can be employed to distinguish dynamically favorable distillation sequences in recycle plants.

From the material balances, the production-rate (P in Eq. 1) for the direct sequence can be expressed as (Wu and Yu, 1996)

$$P = \frac{kV_R}{\left(1 - x_{D_2,A} - x_{D_2,B}\right)} \frac{\left(x_{D_2,A} + RR_1 x_{D_1,A} + RR_2 x_{B_2,A}\right)}{\left(1 + RR_1 + RR_2\right)} \times \frac{\left(x_{D_2,B} + RR_1 x_{D_1,B} + RR_2 x_{B_2,B}\right)}{\left(1 + RR_1 + RR_2\right)} \tag{23}$$

where RR is the recycle ratio and, for the direct sequence, we have $RR_1 = D_1/D_2$ and $RR_2 = B_2/D_2$. Here, the second term on the righthand side of Eq. 23 corresponds to z_A and the third factor corresponds to z_B. Since $x_{D_1,A}$ and $x_{B_2,B}$ are close to 1 and $x_{D_1,B}$ and $x_{B_2,A}$ are almost 0, Eq. 23 can be simplified further

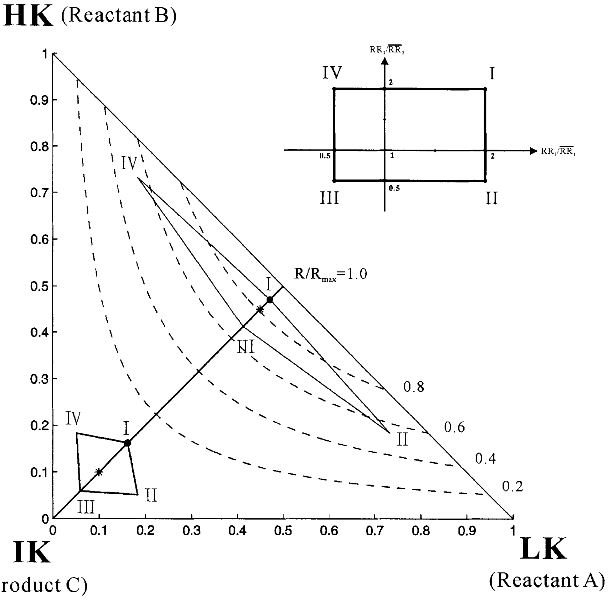


Figure 8. Reachable production rate for designs with low ($z_C = 0.1$) and high ($z_C = 0.8$) conversions and equally distributed reactants ($z_A = z_B$).

$$P = kV_R \frac{RR_1}{1 + RR_1 + RR_2} \frac{RR_2}{1 + RR_1 + RR_2} \tag{24}$$

Note that Eq. 24 can also be applied to the indirect sequence with a slightly different definition in RR, that is, $RR_1 = B_1/B_2$ and $RR_2 = D_2/B_2$.

Despite the fact that we can use the reactor temperature ($k(T)$) or the reactor holdup (V_R) to handle production-rate changes (Wu and Yu, 1996; Larsson and Skogestad, 2000), the reactor compositions (z_A and z_B) are used to accommodate the feed flow disturbance (Tyreus and Luyben, 1993, and Elliott and Luyben, 1996). Actually, this is the most severe test of the operability of the recycle plants. Therefore, in terms of control, the two recycle ratios (RR_1 and RR_2) can be considered as candidates of manipulated variables.

Similar to the work of Georgakis and coworkers (Vinson and Georgakis, 2000; Subramanian and Georgakis, 2001), we would like to explore the reachability of different designs as the manipulated variables vary. By reachability, we mean all reachable production rates as the manipulated variables change in the allowable ranges. Instead of plotting the production rate directly, we can express the production rate in the composition space as contour lines (Figure 8), because, with constant k and V_R, the production rate (P) is a function of z_A and z_B only (such as Eq. 1). In the composition space, the global optimum is when $z_A = z_B = 0.5$, and this corresponds to P^*. Note that, in practice, this is not possible, because z_C is equal to zero, but it serves as a basis for comparison. The number on the dashed line indicates the fraction of the production rate with respect to P^*.

Table 2. Reachable Production Rates as Recycle Ratios Doubled and Halved for Different Designs

(A) Varying Conversion

	Low Conversion	High Conversion
z_C	0.1	0.8
z_A/z_B	1	1
$P_{\max}/\overline{P}$	1.10	2.62
$P_{\min}/\overline{P}$	0.67	0.36
$RR_{1,\max}/\overline{RR_1}$	2.0	2.0
$RR_{2,\max}/\overline{RR_2}$	2.0	2.0
$RR_{1,\min}/\overline{RR_1}$	0.5	0.5
$RR_{2,\min}/\overline{RR_2}$	0.5	0.5

(B) Varying Reactant Distribution

	z_B Excess	z_A and z_B Equally Distributed
z_C	0.1	0.1
z_A/z_B	0.285	1
$P_{\max}/\overline{P}$	1.20	1.10
$P_{\min}/\overline{P}$	0.39	0.67
$RR_{1,\max}/\overline{RR_1}$	2.0	2.0
$RR_{2,\max}/\overline{RR_2}$	2.0	2.0
$RR_{1,\min}/\overline{RR_1}$	0.5	0.5
$RR_{2,\min}/\overline{RR_2}$	0.5	0.5

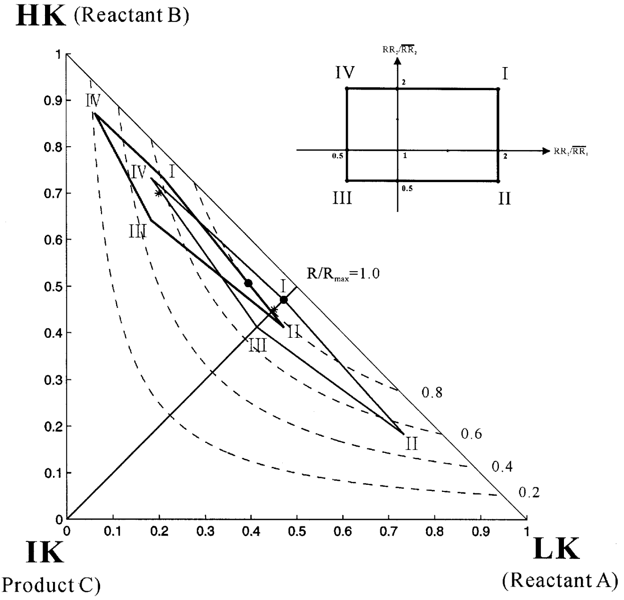


Figure 9. Reachable production rate for designs at low ($z_C = 0.1$) conversion with equally ($z_A = z_B = 0.45$) and biased ($z_A = 0.2$ and $z_B = 0.7$) distributed reactants.

Conversion

First consider the cases of high and low conversions ($z_C = 0.8$ and $z_C = 0.1$) when the reactants are equally distributed (that is, $z_A = z_B$). The input space is the case when the recycle ratios (RR_1 and RR_2) are doubled and/or halved. This gives a rectangle in the input space, as shown in the upper right corner of Figure 8. The reachable outputs are also shown in the composition space as a quadrilateral (Figure 8). For the case of high conversion ($z_C = 0.8$), the reachable production rate ranges from 36% to 262% (Table 2). In the low conversion case ($z_C = 0.1$), the reachable production rate is confined to the range of 67% and 110% of its nominal production value. Clearly, the case of high conversion has a better reachability, and thus is more controllable. Notice that this is the best achievable production rate change, and the true reachable production can be smaller because we chose a simpler control structure, and this is generally the case in practice.

The results clearly indicate that the plant with a *high conversion* is more controllable, and when the conversion is down to 10%, less than 10% of the production rate increase can be obtained. This always holds regardless of what type of controller and which control structure we choose.

Reactant distribution

Let us look at the cases where the conversion is fixed (such as $z_C = 0.1$), but the reactant distributions are different (such as $z_A/z_B = 0.45/0.45$ and $z_A/z_B = 0.2/0.7$). Again, the input space is a rectangle bounded by upper and lower limits on recycle ratios ($2\overline{RR}$ and $0.5\overline{RR}$), as shown in Figure 9. For the case of a largely reactant B excess ($z_A/z_B = 0.29$), the reachable production rate ranges from 39% to 120% (Figure 9) and, for the case of equally distributed reactants ($z_A/z_B = 1$), the reachable production rate is limited to a range of 67% to 110% (Table 2). This is a case of low conversion with $z_C = 0.1$, and the results indicate that a biased reactant distribution makes the recycle plant more controllable. Moreover, Figure 9 also reveals that a more effective path to increase the production rate is to increase the reactant with a smaller fraction, that is, z_A. In terms of an individual manipulated variable, it implies increasing the smaller recycle ratio (RR_2 for the case of indirect sequence and RR_1 for the direct sequence) is more effective in accomplishing the production-rate increase. In other words, the reachability analysis also provides insight into control structure design.

Trade-Off

The on-going analyses clearly show that any design given *small conversion* and *equally distributed reactants* is undesirable as a result of limited operability. Figure 10 shows, qualitatively, that the undesirable region for reactant composition and, quantitatively, that the size of the undesirable region can be located by specifying the acceptable ranges of production-rate variation.

Now let us compare the undesirable operating region with the optimal paths. Since the optimal paths converge to equally distributed reactants ($z_A = z_B = 1$) at a rather high conversion (Figure 6), in most cases, well-designed recycle plants will not encounter the trade-off between design and control. Possible exceptions are the case of a very slow rate constant (such as $k < 0.1$; top graph of Figure 6A) and the case of a very light reactant, A (such as $\alpha_A > 8$; bottom graph of Figure 6B). Since the optimal paths for the direct sequence tend to give equally distributed reactants (Figure 6), one way to resolve the conflict is to use the indirect sequence for these extreme conditions. Moreover, Figure 7 indicates that in that

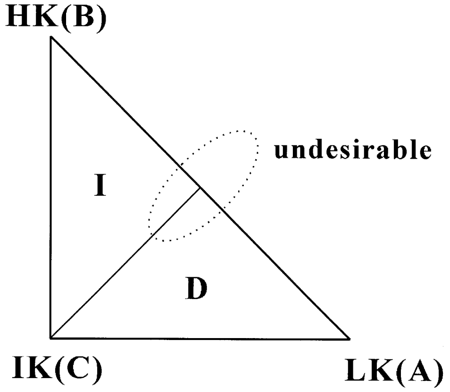


Figure 10. Undesirable regions for ternary system with two recycle streams: low conversion with equally distributed reactants.

region, the difference in TAC for both sequences is within an acceptable range. Furthermore, notice that for the cases of true optima (also allowing z_C to vary), these optimal designs are also outside the undesirable operating region, as shown in Figure 6 (optima are indicated with the symbol *). It should be emphasized here that the controllability is measured by the ability to handle production-rate changes. There are many different controllability measures: ability to handle feed quality variation, feed temperature changes, grade changes, to name three. One should always choose the most frequently encountered one to assess controllability. However, we believe, by default, the production-rate handling capability is one of the most important measures.

Table 3. Reachable Production Rates as Recycle Ratios Doubled and Halved (CS B) or as Reactant Redistributed (CS A)

Strategy	Changing RR	Changing RR	Changing z_A/z_B	Changing RR	Changing z_A/z_B
z_C	0.1	0.8	0.8	0.1	0.1
z_A/z_B	1	1	1	3.5	3.5
$P_{\max}/\overline{P}$	1.10	2.69	1	1.1	1.45
$P_{\min}/\overline{P}$	0.84	0.33	1	0.84	~ 0
$RR_{\max}/\overline{RR}$	2.0	2.0	1	2.0	1
$RR_{\min}/\overline{RR}$	0.5	0.5	1	0.5	1

Control

Tyreus and Luyben (1993) were among the first to study the control for a system with a reactor, two distillation columns, and two recycle streams. Four control structures, CS1 to CS4, were proposed, and these authors found that only two of the four control structures work. Extensions were also made by Luyben et al. (1996) and Elliott and Luyben (1996), and these extensions permit throughput to be set directly, and a reactor composition control is not required. The control structure proposed here basically follows the approach of Wu and Yu (1996), but the reactor holdup (V_R) and reactor temperature are assumed constant. The control structure for the indirect sequence has the following features (Figure 11).

(1) The production rate is set by the fresh feed of A (F_{0A}).

(2) The reactor holdup is held constant by controlling reactor effluent flow rate (F).

(3) The recycle ratio of the first column ($RR_1 = B_1/B_2 = B_1/F_{0A}$) is fixed.

(4) The bottoms composition of the first column ($x_{B_1,B}$) is controlled by changing boilup ratio (V_1/B_1).

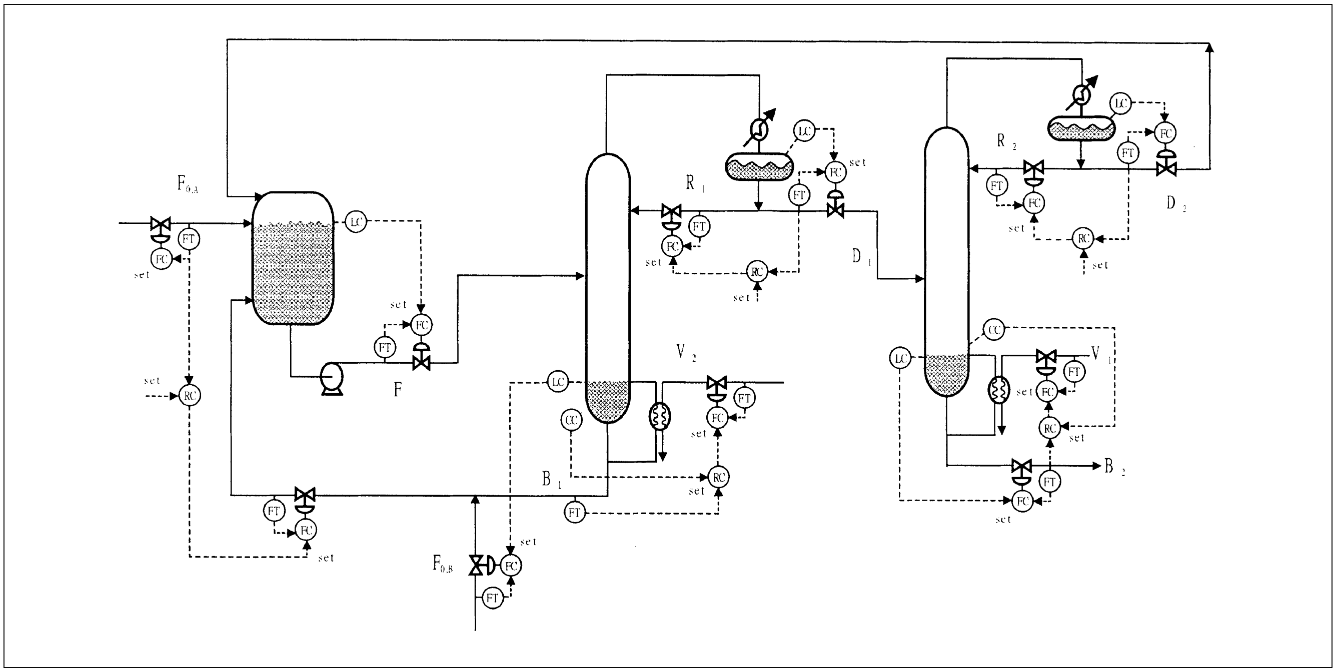


Figure 11. Control structure for the indirect sequence.

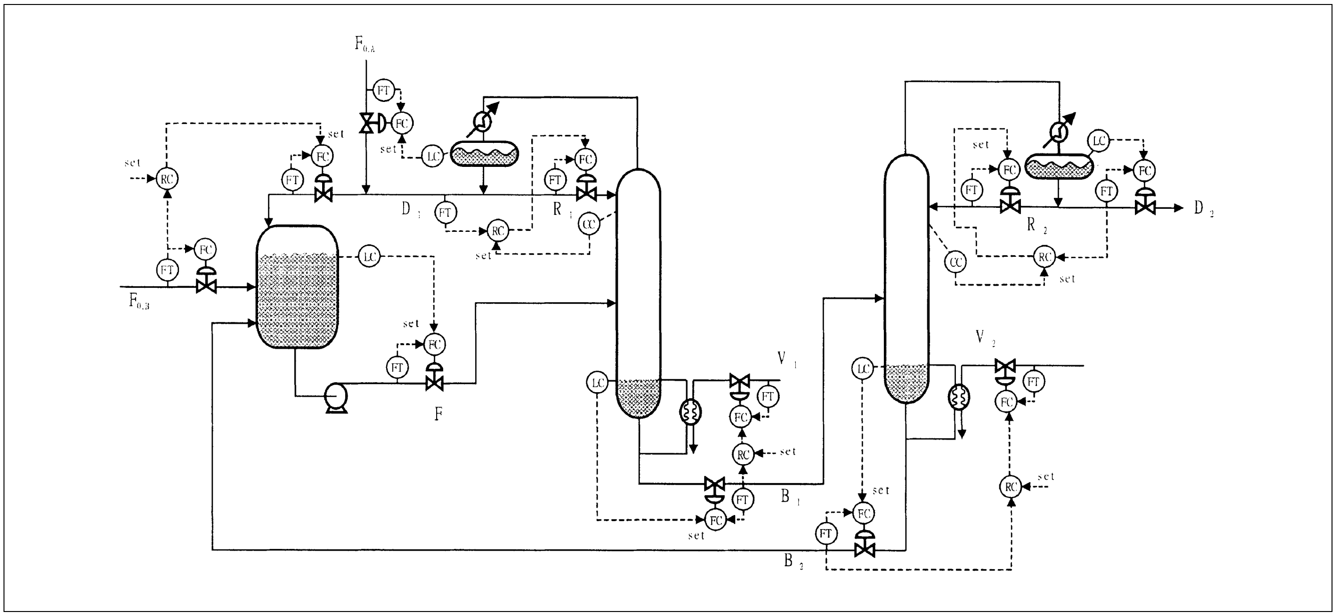


Figure 12. Mirror image of Figure 11 for the direct sequence.

(5) The bottoms level of the first column is controlled by manipulating the fresh feed of reactant B (F_{0B}).

(6) The reflux ratio of the first column (R_1/D_1) is fixed.

(7) The product composition ($x_{B_2,C}$) is held by manipulating the boilup ratio of the second column (V_2/B_2).

(8) The reflux ratio of the second column (R_2/D_2) is fixed.

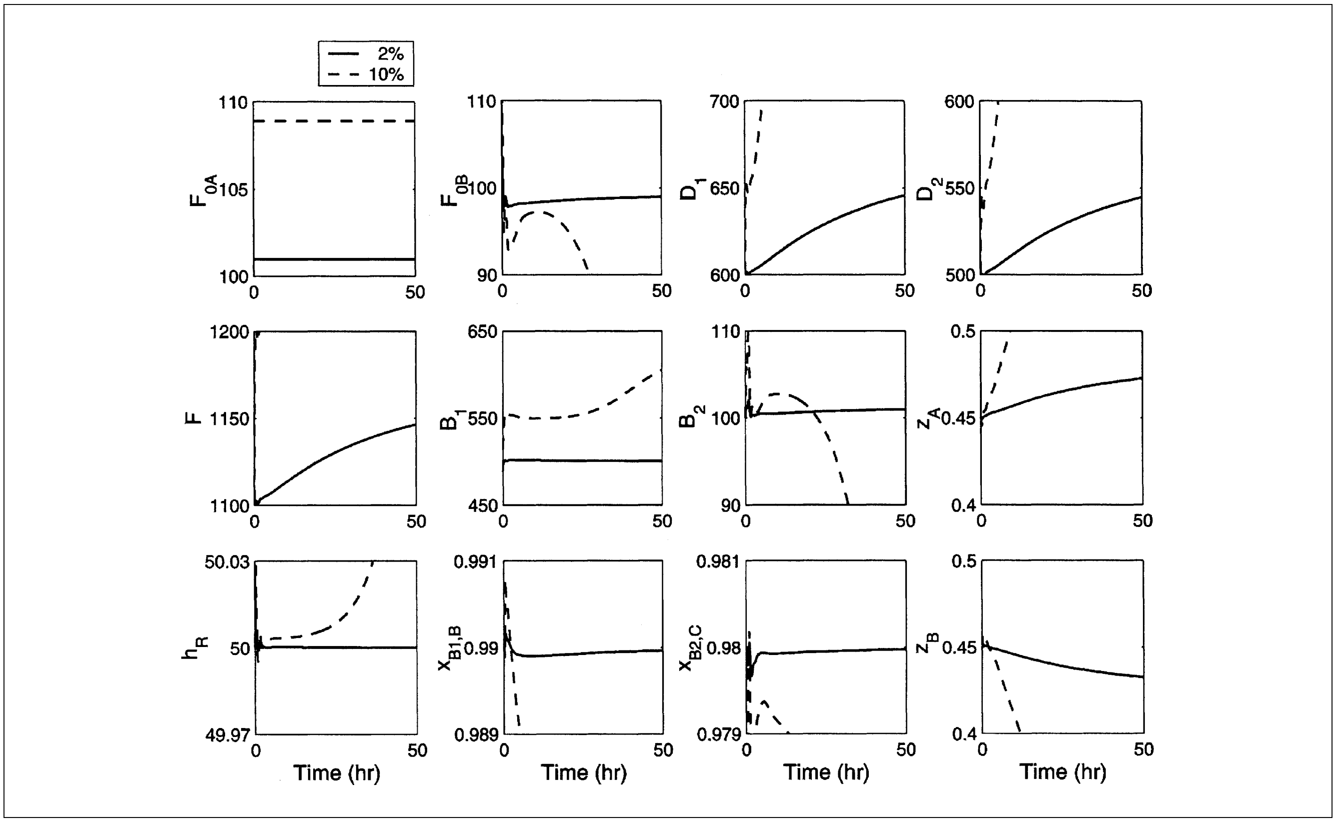


Figure 13. Closed-loop responses of production-rate increases for recycle plant using direct sequence with low conversion ($z_C = 0.1$) and equally distributed reactants ($z_A = z_B = 0.45$).

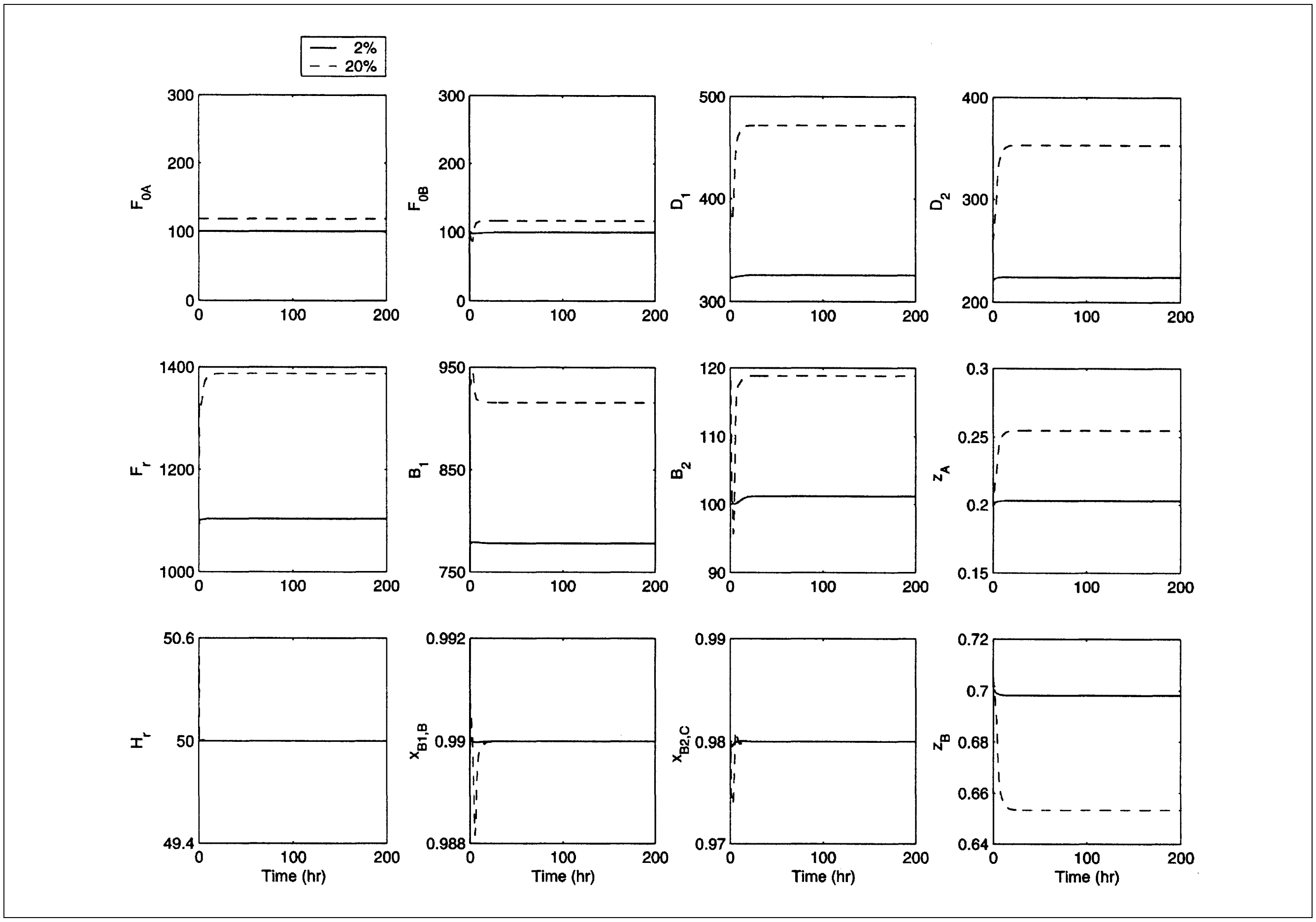


Figure 14. Closed-loop responses of production-rate changes for recycle plant using indirect sequence with low conversion ($z_C = 0.1$) and biased reactant distribution ($z_A = 0.2$, $z_B = 0.7$).

Notice that only two composition controllers are required and throughput is directly set by one of the fresh feed flows. Similarly, the mirror image of this control structure is shown in Figure 12 for the direct sequence. In order to provide a fair comparison, in the following control studies, simple PI controllers are used throughout. The ultimate gain and ultimate period are identified from relay feedback tests (Yu, 1999), and the settings are obtained using the Tyreus–Luyben method. Four minutes of analyzer dead time are added to the composition loop. Next, these two control structures are tested using rigorous models.

Low conversion and equally distributed reactants

As pointed out earlier, the case of low conversion (small z_C) with equally distributed reactants ($z_A/z_B = 1$) has limited operability. Let us take the case from Table 2 with $z_A = z_B = 0.45$ and $z_C = 0.1$ as an example. In this case, both recycle ratios are the same ($RR_1 = RR_2$) and flow rates of both recycle streams are also approximately equal ($D_1 = B_2 = 489$) for the direct sequence. For a 2% production-rate increase, reasonable closed-loop responses are observed, as shown in Figure 13. However, for a 10% production rate change, the process simply fails to maintain stability. This is within one's expectation, since the manipulation of reactor composition can increase the production up to 9% (such as Table 2 and Figure 8). Unless the reactor holdup (V_R) or reactor temperature is adjusted, it is not possible to achieve more than a 10% production-rate increase. This can also be seen from Eq. 24. Similar results are also observed with the indirect sequence.

Low conversion and biased reactant distribution

Let us take an example to illustrate the operability for systems with biased reactant distribution. Consider a case with 10% conversion ($z_C = 0.1$) and biased reactant distribution ($z_A = 0.2$ and $z_B = 0.7$). Because of the difference in the reactant distribution, for the indirect sequence (Figure 11), the recycle ratio is quite different ($RR_1 = 7.6$ and $RR_2 = 2.2$) and, similarly, B_1 is much larger than D_2 ($B_1 = 761$ and $D_2 = 217$). For the indirect sequence, we fix RR_1 and let RR_2 vary as a disturbance comes in. In terms of composition, this implies we use z_A (recall that $z_A = 0.2$ and $z_B = 0.7$) for disturbance rejection. This control scheme (Figure 11) works quite well for small (2%) and for large (20%) production-rate changes, as shown in Figure 14. This is exactly what we expect, because RR_2 (or z_A) is the most effective variable for accommodating production-rate change, as shown in the reachability plot in Figure 9.

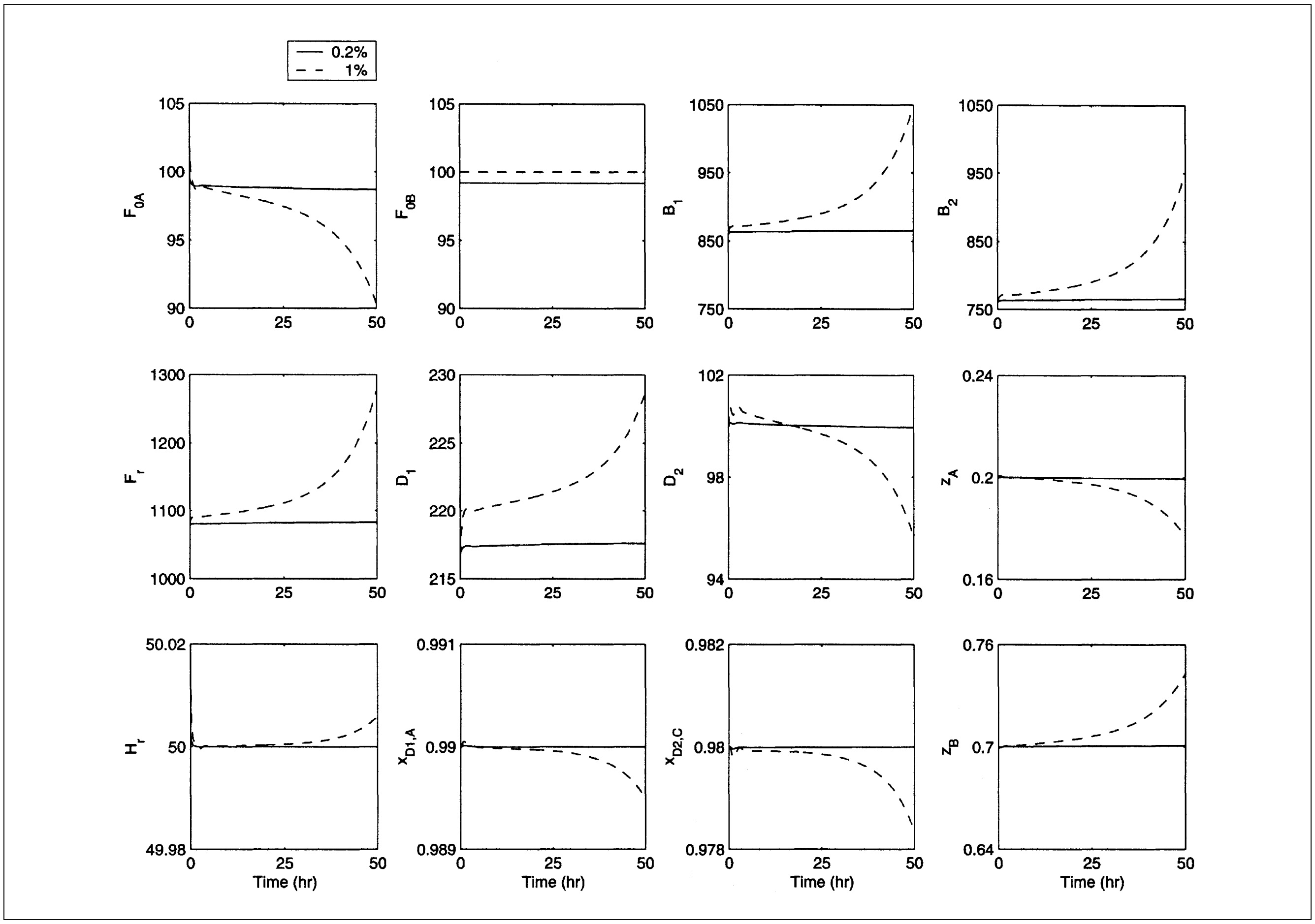


Figure 15. Closed-loop responses of production-rate changes using direct sequence (control structure of Figure 12) with low conversion ($z_C = 0.1$) and biased reactant distributed ($z_A = 0.2$, $z_B = 0.7$).

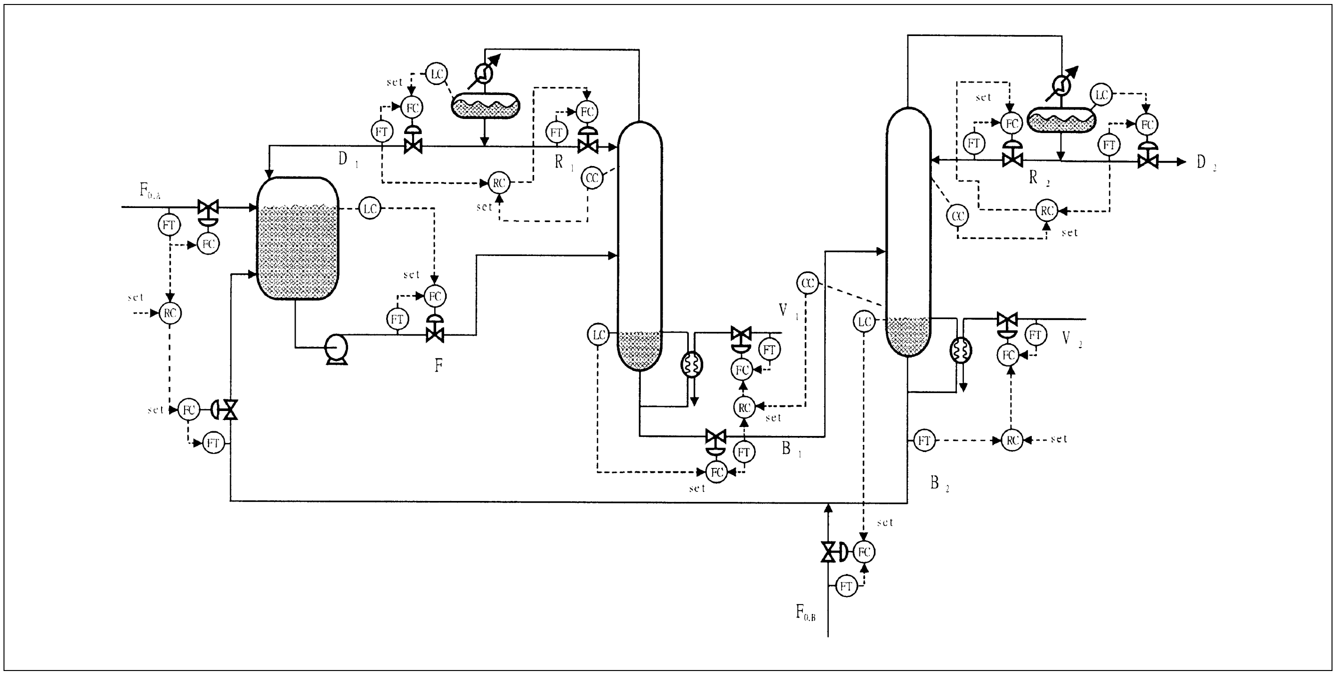


Figure 16. Modified control structure for the direct sequence with the heavy reactant in excess ($z_A < z_B$).

What will happen if the direct sequence with the given control structure in Figure 12 is employed? Simulation results show that the system simply drifts away for a "1%" production-rate increase (Figure 15). The reason is rather obvious, in that for the direct sequence, we use an inappropriate variable (RR_2 or z_B in Figure 12) to handle production-rate variations. If we modify the control structure to Figure 16, then one can have better handle production-rate changes for the given reactor composition. It then becomes clear that the control structure should be designed according to the given process and that no single control structure can perform well over the entire composition space (such as Figure 6).

High conversion and equally distributed reactants

Despite the potential problem of equally distributed reactants, the high conversion case (such as $z_C = 0.8$) gives better operability, as shown in Figure 9. Consider the case with $z_A = z_B = 0.1$ and $z_C = 0.8$ (Table 2). Here, the control structure in Figure 12 shows good control for 20% production-rate increases (Figure 17). Again, this is expected, because the design gives better reachability, as shown in Figure 9, and similar dynamic responses can be obtained for the closed-loop control with the indirect sequence. Generally, this region corresponds to global (variable reactor composition) optima, as shown in Figure 6. This again confirms the unlikely trade-off between design and control if the plant is well designed.

Optimal reactant distribution

Consider the control performance at true optima (allowing the conversion, z_C, to vary). The optima are marked with asterisks (*) and circle (●) for direct and indirect sequences, respectively, as shown in Figure 6. The direct sequence gives a lower TAC over the indirect sequence, but only by 3% for the base case (Table 1). The true optimal design for the indirect sequence is used as an example, and this corresponds to the reactor composition of $z_A = 0.125$, $z_B = 0.250$, and $z_C = 0.625$ (Table 1). Here, the proposed control structure (Figure 11) is evaluated and compared to control structure 1 (denoted as CS1) of Tyreus and Luyben (1993). Their CS1 control structure consists of the following loops (Figure 18).

(1) The production rate is set by adjusting two recycle flows (B_1 and D_2) simultaneously.

(2) The reactor holdup is controlled by the reactor effluent flow rate (F).

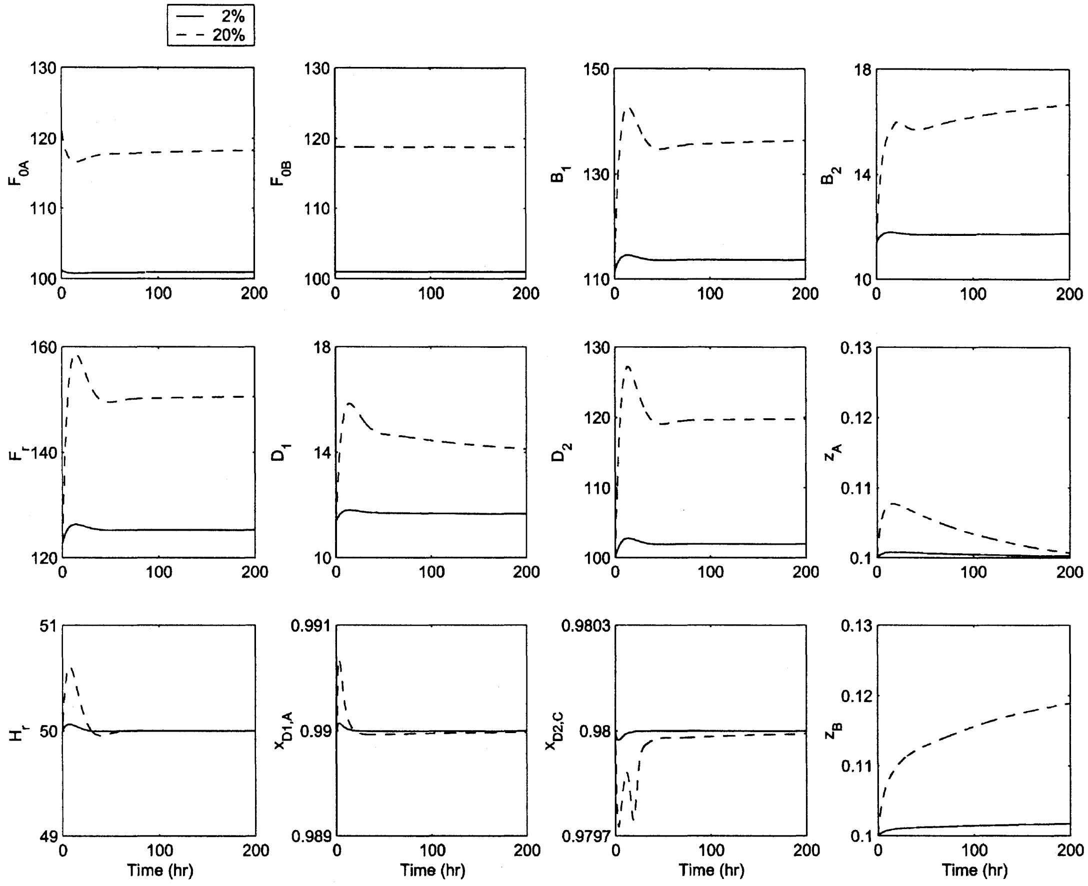


Figure 17. Closed-loop responses of production-rate increases using direct sequence with high conversion ($z_C = 0.8$) and equally distributed reactants ($z_A = z_B = 0.45$).

(3) The recycle flow of the first column (B_1) is under flow control.

(4) The bottoms level of the first column is controlled by manipulating the fresh feed of reactant B (F_{0B}).

(5) The reflux flow of the first column (R_1) is fixed.

(6) The reflux drum level of the second column is controlled by manipulating the fresh feed of reactant A (F_{0A}).

(7) The reflux flow of the second column (R_2) is fixed.

(8) The product composition ($x_{B_2,C}$) is held by manipulating the boilup rate of the second column (V_2).

(9) The impurity of reactant B in the product stream ($x_{B_2,B}$) is controlled by manipulating the boilup rate in the first column (V_1). This is cascade control structure with a secondary $x_{D_1,B}$ to V_1 loop.

Notice that only two composition controllers are required, but the throughput is set *indirectly* by changing both recycle flows. Figure 19 compares the responses for a 2.8% increase for both control structures. Better product composition ($x_{B_2,C}$) control is achieved with the proposed ratio scheme, and the reason for better performance can be seen from the reactor composition redistribution. Both reactant concentrations (z_A and z_B) only make necessary increases to accommodate this production-rate increase, while the CS1 structure results not only in an increase in z_A but also in a smaller decrease in z_B. Obviously, the paths in reactant redistribution for the CS1 structure require a much larger effort on the movement of manipulated inputs and, subsequently, a longer transition (Figure 19). This is not to say that the CS1 control structure is not a good control strategy, but, rather, it implies that the magnitude of changes in these two recycle flows should be carefully planned for production-rate change at different reactant composition distributions (Lyman and Luyben, 1996). Note that, in this work, the same magnitude of change is imposed on both streams. Nonetheless, the results indicate that the proposed ratio scheme (Figure 11) gives an acceptable performance.

Extensions

Up to now, we have investigated the ternary systems with two distillation columns and two recycle streams. The process configuration is the result of the distribution of the boiling points (that is, product C is the intermediate key). Certainly, there are cases where the product (C) can be the lightest or the heaviest component. What are the process configurations? Do the conclusions still apply? Consider, again, the second-order elementary reaction where the product is the heavy key (HK) and light key (LK), respectively. Since the relative volatilities for both reactants are adjacent to each other, we have only one distillation column in the recycle structure, as shown in Figure 20. When the product is the HK, light reactants are recycled back to the column from the top of the first (and only one) column, and a similar situation applies to the case of LK. Therefore, we do not have a column sequencing problem for these two cases.

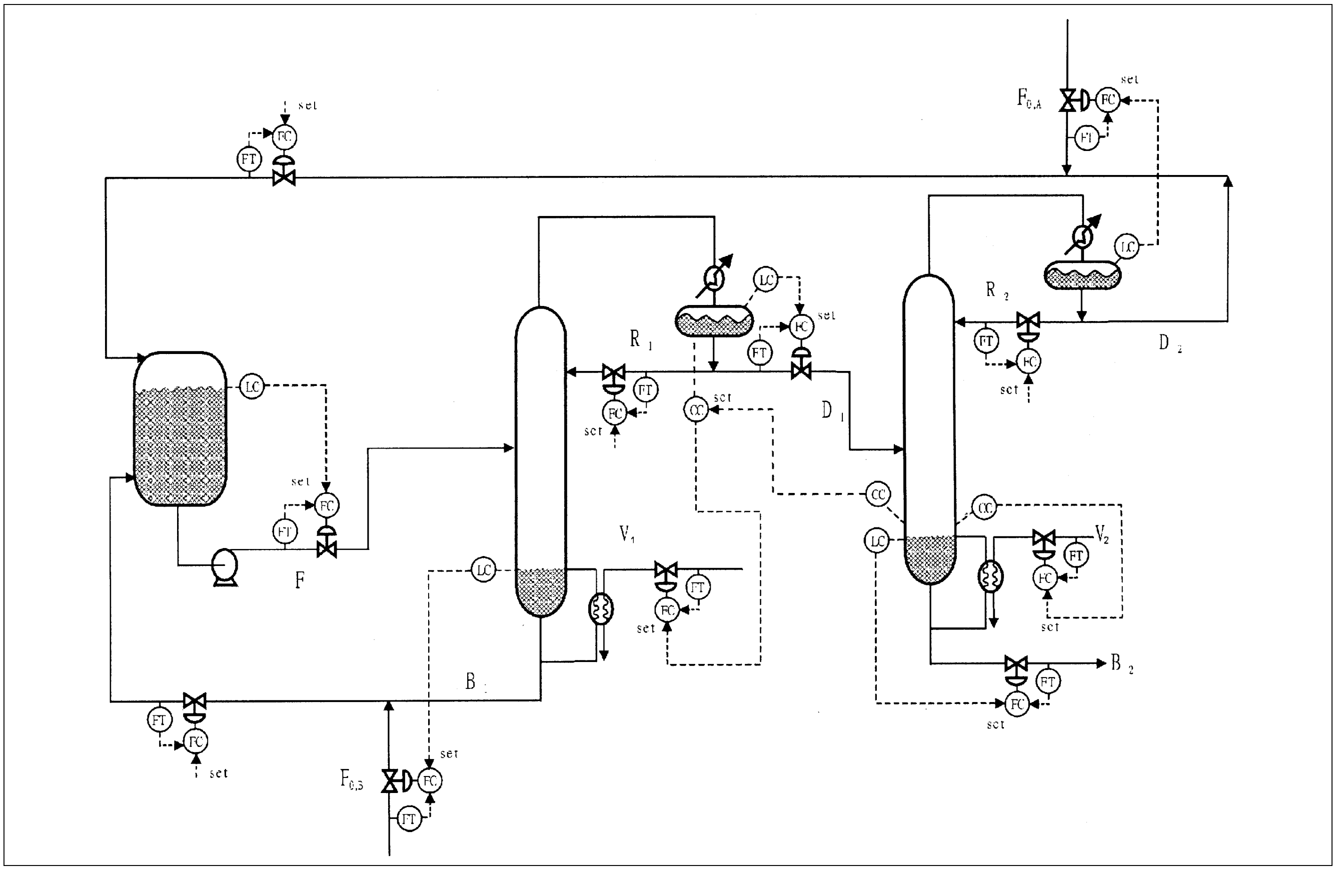


Figure 18. CS1 control structure of Tyreus and Luyben (1993).

Steady-state economics

Again, the linearized TAC models (such as Eq. 3) are derived for ternary systems with only one distillation column for both cases (heavy product and light product). Following a similar procedure in the third section, we are able to find the optimal reactant distribution (z_A and z_B) for any given conversion (z_C), such as taking the derivative of the TAC with respect to z_B. Similarly, the true optimum (the point in the composition space giving the minimum TAC) can be found following the procedure in the third section. Cheng (2002) gives a detailed description.

Let us use the flow sheet of the heavy product (Figure 20A) with the base-case parameters ($\alpha_A/\alpha_B/\alpha_C = 4/2/1$) to illustrate the steady-state economics. Here, the reactants A and B are light key and intermediate key, respectively, while the product is the heavy key (Figure 21A). The optimal path starts from the corner of light reactant A (that is, excess of light reactant, or $z_A \gg z_B$) at low conversion and converges toward equally distributed reactants (that is, $z_A = z_B$) at high conversion, as shown in Figure 21A. Specifically, at $z_C = 0.3$, the optimal reactant distribution is $z_A/z_B = 4.9$ (such as large excess in A) and, at the true optimum (corresponding to the lowest TAC), we have $z_C = 0.61$ and the reactant distribution is $z_A/z_B = 1.6$ (such as a much smaller excess of A).

The results are within one's expectation. At low convergence, the cost of the separation dominates the TAC, and a large excess of light reactant results in an easier separation and, consequently, a lower cost. On the other hand, at high conversion, the reactor cost is the dominant factor and an equally distributed reactant results in a smaller reactor (for elementary second-order reaction), and subsequently a lower TAC. Again, with the cost model and corresponding parameter, the true optimum is located around 60% conversion (c.f. two-columns case in Table 1). Similarly, for the case when the product C is LK (Figure 20B), the optimal trajectory stars from the vortex of the heavy key (reactant A) and converges to the corner of C with equally distributed reactants ($z_A = z_B$), as shown in Figure 21B. The results imply the following heuristics:

(1) At low conversion, arrange the reactant distribution for lower separator cost.

(2) At high conversion, distribute the reactant for a lower reactor cost.

Operability

Again, it is important to find out whether the trade-off between steady-state economics and dynamical controllability

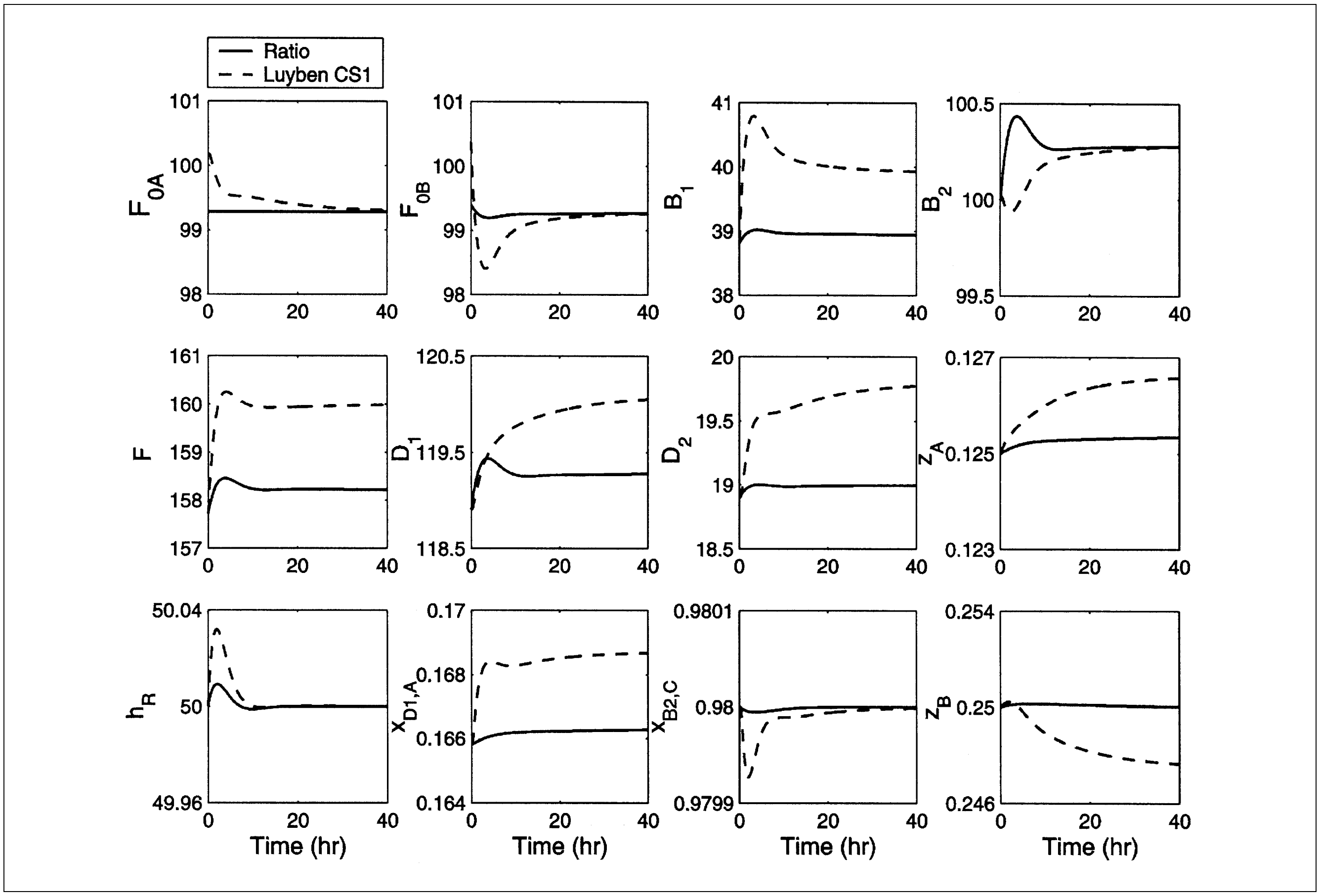


Figure 19. Closed-loop responses of a production-rate increase (+2.8%) for indirect sequence with proposed ratio control structure (solid) and CS1 control structure (dashed) at optimal reactant distribution ($z_A = 0.125$, $z_B = 0.250$, and $z_C = 0.625$).

exists. Following the procedure in the fourth section, the production rate (P) can be expressed in terms of the important operating variables. However, unlike the two-column cases, we have only one recycle stream in these flow sheets (Figure 20). From the material balance for the case of heavy product (Figure 20A), we have

$$P = \frac{kV_R}{\left(1 - x_{B_1,A} - x_{B_1,B}\right)} \frac{\left(x_{B_1,A} + RRx_{D_1,A}\right)}{(1+RR)} \times \frac{\left(x_{B_1,B} + RRx_{D_1,B}\right)}{(1+RR)} \tag{25}$$

where $RR = D_1/B_1$ is the recycle ratio. Because $x_{B_1,A}$ and $x_{B_1,B}$ are close to zero, Eq. 25 can be simplified further

$$P = kV_R \frac{x_{D_1,A} x_{D_1,B} RR^2}{(1+RR)^2} \tag{26}$$

Equation 26 reveals that there are two possible ways to handle production-rate changes. The first approach (such as CS A of Figure 22), similar to the two-column case, uses the redistribution of reactants (that is, z_A/z_B) to handle production-rate changes while fixing the recycle ratio. Regardless to the extent of the conversion, this approach is effective when one of the reactants is in excess. The second scheme (such as CS B of Figure 22) uses the recycle ratio (RR) to accommodate production-rate variation. As explained earlier, this approach is effective at high conversion, but gives poor operability at low convergence, as shown in Table 3. Table 3 clearly indicates the advantages and disadvantages of these two approaches. It also reveals that if the control structure is carefully chosen, we will not encounter a trade-off between design and control.

Similarly, if the product is the light component (Figure 20B), the expression for the production rate is

$$P = \frac{kV_R}{\left(1 - x_{D_1,A} - x_{D_1,B}\right)} \frac{\left(x_{D_1,A} + RRx_{B_1,A}\right)}{(1+RR)} \times \frac{\left(x_{D_1,B} + RRx_{B_1,B}\right)}{(1+RR)} \tag{27}$$

where $RR = B_1/D_1$. Because $x_{D_1,A}$ and $x_{D_1,B}$ are close to zero, Eq. 27 can be simplified further

$$P = kV_R \frac{x_{B_1,A} x_{B_1,B} RR^2}{(1+RR)^2} \tag{28}$$

The operability analysis can be extended to this case (C is LK) in a straightforward manner.

Control

Two control structures are devised for these two production-rate handling principles. In control structure CS A, we have the following control loops.

(1) The production rate is set by fresh feed flow of B (F_{0B}).

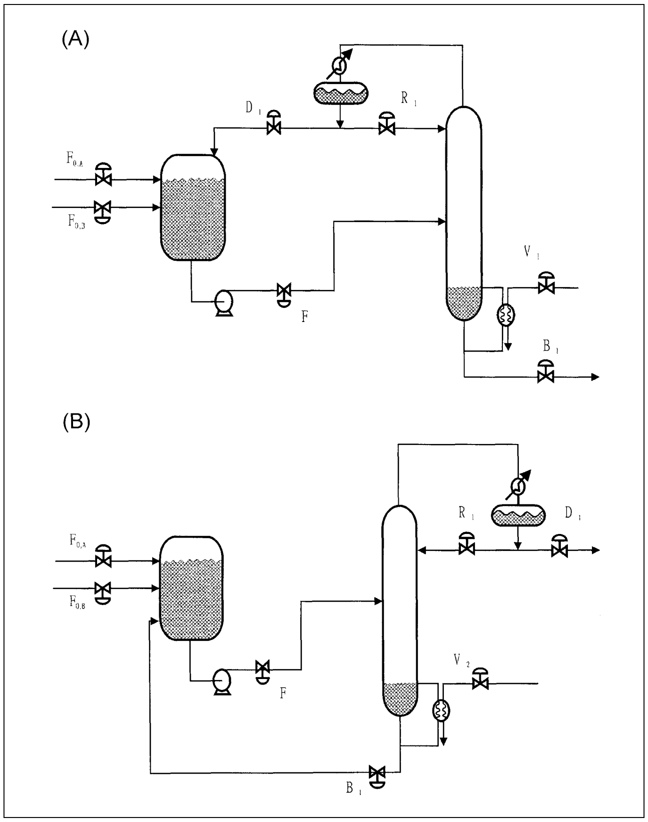


Figure 20. Ternary systems when the product is (A) heavy component (HK) and (B) light component (LK).

(2) The reactor holdup is controlled by the reactor effluent flow rate (F).

(3) The total recycle flow ($D_{TOT} = F_{0B} + D$) is ratioed to F_{0B}.

(4) The bottoms level of the column is controlled by manipulating the product flow rate (B).

(5) The reflux ratio of the column (R/D) is fixed.

(6) The reflux drum level of the column is controlled by manipulating the fresh feed of reactant A (F_{0A}).

(7) The product composition ($x_{B,C}$) is held by manipulating the boilup ratio of the column (V/B).

Because the recycle ratio (RR) is fixed, the production rate variation is handled by the redistribution of $x_{D_1,A}$ and $x_{D_1,B}$ (such as Eq. 26). This control structure will be effective for the cases of biased reactant distribution (such as the low conversion part of the optimal paths in Figure 21). Similarly, the control structure CS B consists of the following loops.

(1) The production rate is set by the fresh feed flow of B (F_{0B}).

(2) The reactor holdup is controlled by the reactor effluent flow rate (F).

(3) The top product composition ($x_{D_1,A}$) is controlled by manipulating the total recycle ratio (D_{TOT}/F_{0B}).

(4) The bottoms level of the column is controlled by manipulating the product flow rate (B).

(5) The reflux ratio of the column (R/D) is fixed.

(6) The reflux drum level of the column is controlled by manipulating the fresh feed of reactant A (F_{0A}).

(7) The product composition ($x_{B_1,C}$) is held by manipulating the boilup ratio of the column (V/B).

The difference between the two structures lies in the fact that, for CS B, the recycle ratio (RR) will be changed as a result of keeping $x_{D_1,A}$ constant. This control structure will be effective for cases of high conversion (such as the high conversion portion of the optimal paths in Figure 21).

Closed-loop responses for production-rate increases clearly indicate that control structure CS A is indeed operable for a biased reactant distribution at low conversion, as shown in

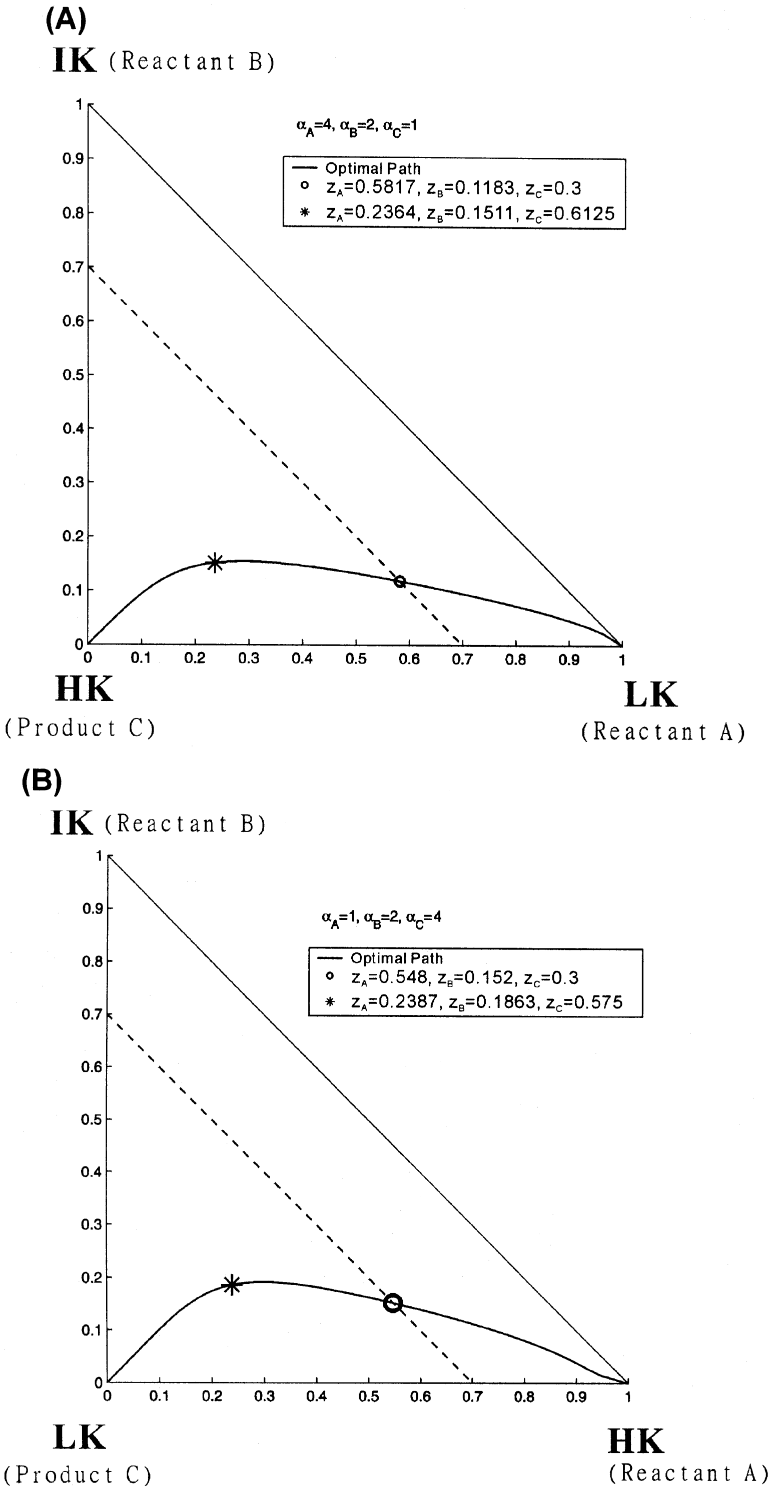
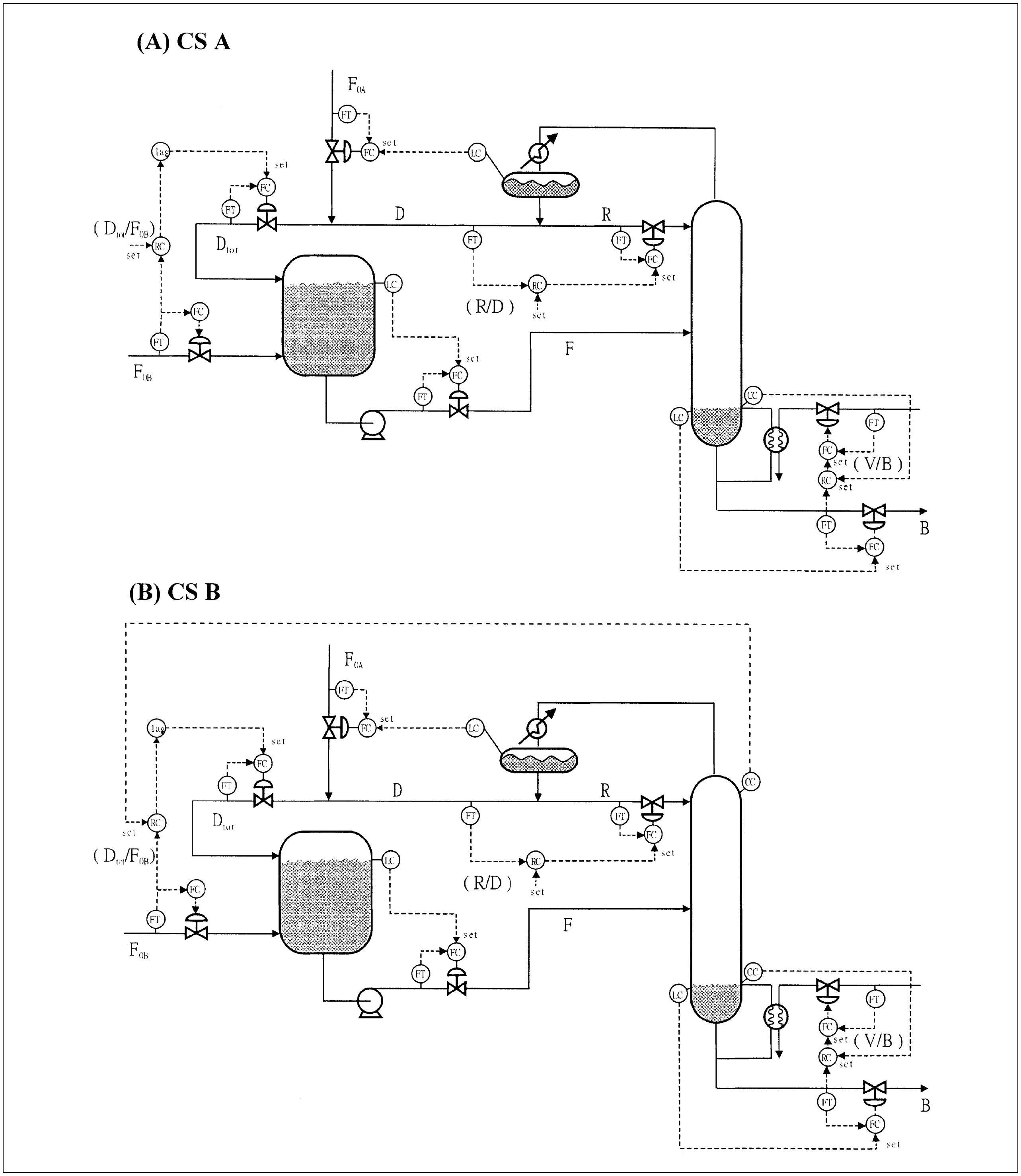


Figure 21. Optimal TAC paths when the product is (A) heavy component (HK) and (B) light component (LK), with * indicating true optima.

Figure 23A. On the other hand, CS B fails to accommodate a 30% production increase at low conversion (such as $z_C = 0.1$ and $z_A/z_B = 8$), as shown in Figure 23B. However, the opposite situation is encountered at a high conversion with equally distributed reactants (such as $z_C = 0.8$ and $z_A/z_B = 1$). For this case, the CS A structure fails to achieve a 50% production-rate increase (Figure 24A), while the CS B control structure shows acceptable operability (Figure 24B).

For the single-column configurations, the results also suggest that no single control structure (Figure 22) works well over the entire composition space (such as Figure 21). If we use control structure CS A at low conversion and CS B for


(A) CS A

(B) CS B

Figure 22. Two process control structures when product *C* is HK: (A) fixing recycle ratio (CS A); (B) controlling $x_{D1,A}$ (CS B).

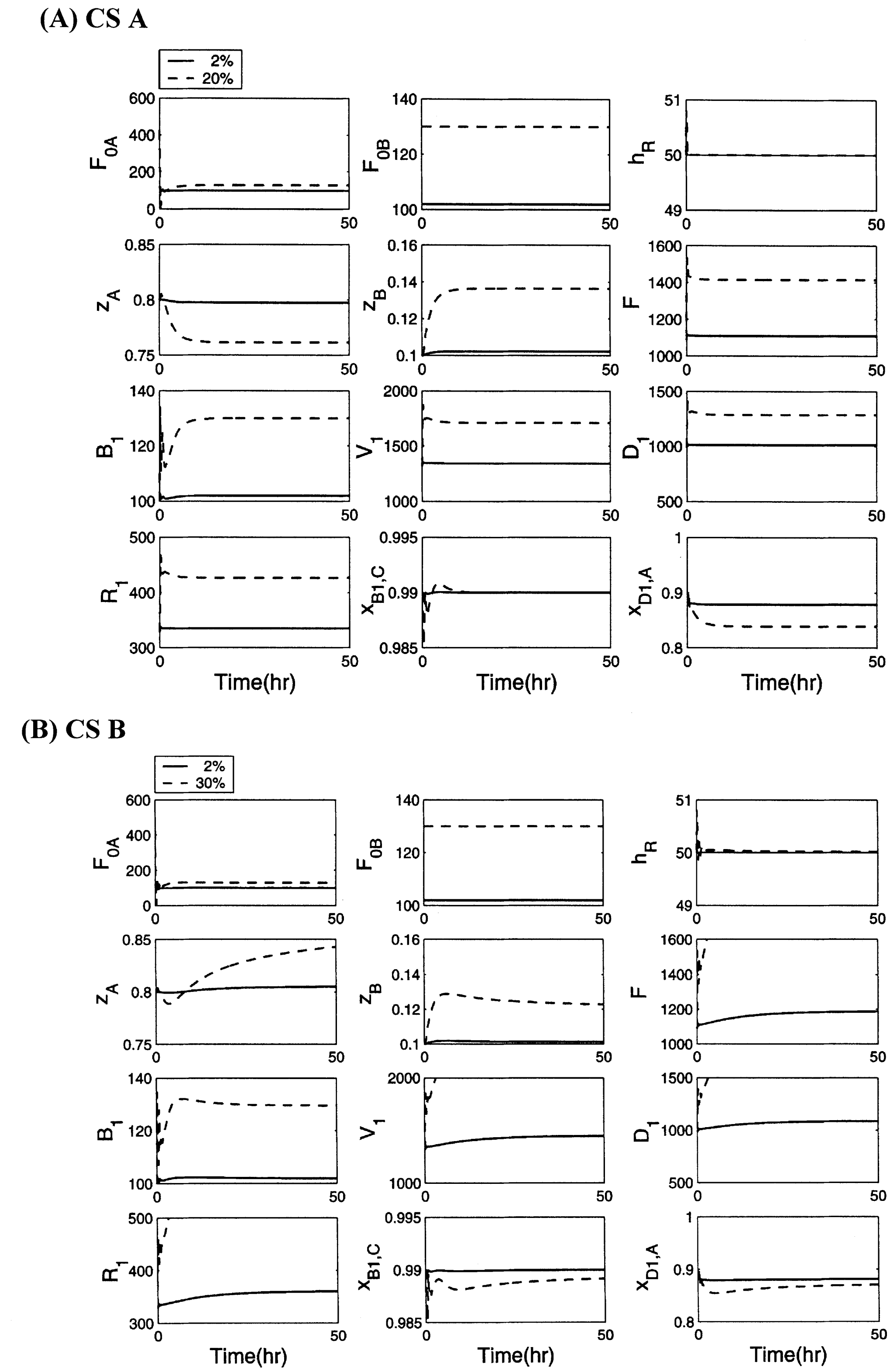
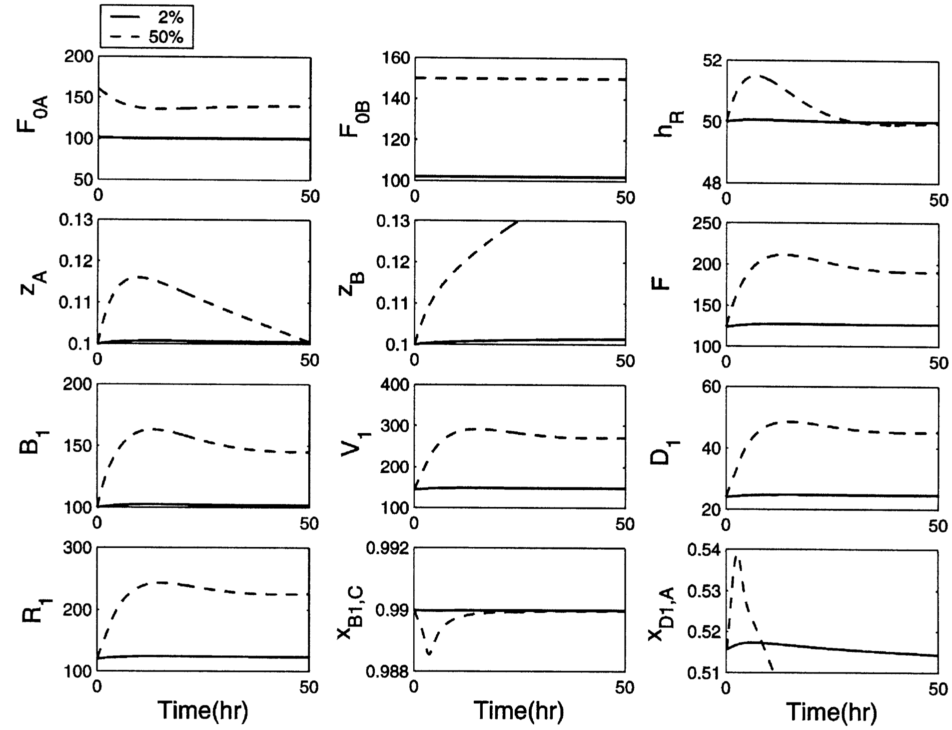
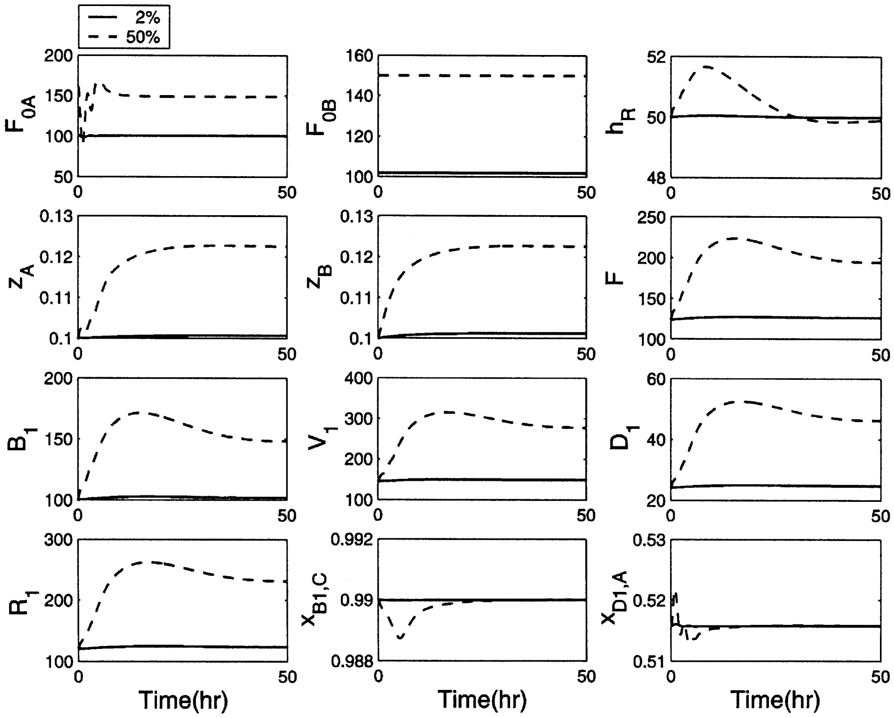


Figure 23. Closed-loop responses of production-rate increases at low conversion with excess reactant A ($z_C = 0.1$ and $z_A/z_B = 8$) for control structures: (A) CS A; (B) CS B.



(A) CS A



(B) CS B

Figure 24. Closed-loop responses of production-rate increases at high conversion with equally distributed reactants ($z_C = 0.8$ and $z_A/z_B = 1$) for control structures: (A) CS A; (B) CS B.

high conversion on the optimal paths, trade-offs between design and control are not likely to occur.

Conclusion

Based on the Underwood equation and a simple cost model, optimality regions for the direct and indirect column sequence of recycle plants are identified, and this can be used to analyze the different flow sheets for any given reactor composition. First, ternary systems with two recycle streams are studied. As the conversion varies, optimal paths for a recycle plant with direct or indirect column sequences can also be derived analytically. Given the optimality region, the correct flow sheet with the minimized TAC can be visualized on the triangular composition space for ternary systems. Next, a controllability measure, based on reachability, is also proposed, and the undesirable operating region can also be located. From the steady-state economics and dynamic controllability analyses, the results indicate that, with few exceptions, optimally designed recycle plants generally are operable. Nonlinear simulations are used to illustrate the operability for different designs. The results also show that no single control structure will work well over the entire composition space and it should be adjusted as the reactor composition varies.

If the product is the heavy component or light component, we have a recycle plant with only one distillation column. The procedure can be extended to these one-column configurations in a straightforward manner, and results also indicate that if the control structure is carefully chosen (that is, CS A at low conversion and CS B for high conversion), trade-offs between design and control are not likely to occur.

Finally, what is the possibility of extending the results to other reactions, for example, $A + B \rightarrow C + D$? In this case, if the boiling points of C and D are adjacent to each other, then the conclusion of this work applies. If not, the process configuration will be different and only the operability measure part can be applied. More importantly, we believe this work offers a systematic approach to address the trade-offs between design and control and that the procedure itself can be applied to any process.

Acknowledgment

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Notation

$A_{C,i}$ = heat-transfer area of condenser in column i
$A_{R,i}$ = heat-transfer area of reboiler in column i
B_i = bottoms flow rate from ith column
C_1, C_2, C_3, C_4, C_5 = cost coefficients for the model in Eq. 2
D_i = distillate flow rate from ith column
$D_{C,i}$ = diameter of column i
D_R = diameter of reactor
F_{0A} = fresh feed flow rate of component A
F_{0B} = fresh feed flow rate of component B
F = flow rate out of the reactor
F_i = feed flow rate in column i
HK = heavy key component
$h_{ow,i}$ = height of liquid over weir in column i
$L_{C,i}$ = height of column i
L_R = reactor height
K_0, K_1, K_2, K_3 = coefficients for the linear cost model in Eq. 3
k = specific reaction rate
LK = light key component
$M_{n,i}$ = holdup on tray n of column i
MW = average molecular weight
$N_{f,i}$ = feed tray number in column i
$N_{\min,i}$ = minimum number of trays in column i
$N_{T,i}$ = total number of trays in column i
P = production rate
$\bar{P}$ = nominal production rate
$P_{\max}$ = maximum production rate
$P_{\min}$ = minimum production rate
P^* = maximum achievable production rate in the composition space
P_s = pressure
R_{gas} = perfect gas constant
$R_{m,i}$ = minimum reflux ratio in column I
RR = recycle ratio column
$\overline{RR}$ = nominal recycle ratio
RR_j = recycle ratio in column j
$r_{(i)LK}$, $r_{(i)HK}$ = fractional recoveries of the light key and heavy key in ith column
T = reactor temperature
TAC = total annualized costs
U_C = heat-transfer coefficient for the condenser
U_R = heat-transfer coefficient for the reboiler
V_i = vapor boilup in column i
V_R = reactor holdup in moles
$V_{s,i}$ = vapor boilup in column i
$x_{Bk,j}$ = bottoms composition in kth column (mole fraction of component j)
$x_{Dk,j}$ = distillate composition in kth column (mole fraction of component j)
$x_{Fi,j}$ = feed composition in ith column (mole fraction of component j)
$\bar{z}_C$ = upper value of conversion (mole fraction), above which distinct preference is given to direct sequence
$\underline{z}_C$ = lower value of conversion (mole fraction), below which distinct preference is given to indirect sequence
z_j = reactor composition of component j (mole fraction)

Greek letters

α_j = relative volatility of component j
β_i = liquid hydraulic time constant for column i
ΔTAC = difference between the annualized costs of the direct and indirect sequences
ΔH_{vap} = heat of vaporization
ΔT_C = condenser temperature difference
ΔT_R = reboiler temperature difference
ΔV = difference of the vapor rates for the direct and indirect sequences
ρ_L = liquid density
ρ_V = vapor density in column

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Appendix A: Steady-State Design Procedure

Similar to the approach of Elliott and Luyben (1996), the steady-state design is outlined as follows.

(1) Select the reactor composition z_A and z_B.

(2) We can make the mass balance for the two distillation columns (Eq. A1–Eq. A6) to calculate the flow rate of the light recycle stream, D_1, the heavy recycle stream, B_2, and the reactor effluent flow rate, F

$$B_1 = D_2 + B_2 \tag{A1}$$

$$B_1 x_{B_1,A} = D_2 x_{D_2,A} + B_2 x_{B_2,A} \tag{A2}$$

$$B_1 x_{B_1,B} = D_2 x_{D_2,B} + B_2 x_{B_2,B} \tag{A3}$$

$$F = B_1 + D_1 \tag{A4}$$

$$F z_A = B_1 x_{B_1,A} + D_1 x_{D_1,A} \tag{A5}$$

$$F z_B = B_1 x_{B_1,B} + D_1 x_{D_1,B} \tag{A6}$$

$$B_2 = \frac{(z_A + x_{D_2,A})(x_{D_1,B} - z_B) - (z_B - x_{D_2,B})(x_{D_1,A} - z_A)}{(x_{B_2,A} - z_A)(x_{D_1,B} - z_B) - (x_{B_2,B} - z_B)(x_{D_1,A} - z_A)} D_2 \tag{A7}$$

$$D_1 = \frac{(z_B - x_{D_2,B})(x_{B_2,A} - z_A) - (z_A - x_{D_2,A})(x_{B_2,B} - z_B)}{(x_{B_2,A} - z_A)(x_{D_1,B} - z_B) - (x_{B_2,B} - z_B)(x_{D_1,A} - z_A)} D_2 \tag{A8}$$

(3) Calculate the feed composition to the second column

$$X_{B_1,i} = \frac{FZ_i - D_1 X_{D_1,i}}{B_1} \quad (i = A, B) \tag{A9}$$

(4) From the steady-state total molar balance around the process, we can get three equations

$$F_{0A} + F_{0B} = D_2 + kV_R z_A z_B \tag{A10}$$

$$F_{0A} = D_2 x_{D_2,A} + kV_R z_A z_B \tag{A11}$$

$$F_{0B} = D_2 x_{D_2,B} + kV_R z_A z_B \tag{A12}$$

(5) Calculate the reactor holdup (assuming the two fresh feed streams are purified)

$$V_R = \frac{D_2 x_{D_2,C}}{k z_A z_B} \tag{A13}$$

(6) Calculate the fresh feed flow rate of both component A (F_{0A}) and component B (F_{0B})

$$F_{0A} = (1 - x_{D_2,B}) D_2 \tag{A14}$$

$$F_{0B} = (1 - x_{D_2,A}) D_2 \tag{A15}$$

Appendix B: Equipment Sizing and TAC

In the distillation column design, we assume equimolal overflow, theoretical trays, total condensers, and partial reboilers. The reflux drums and column bases holdup are set by 5 min. The steady-state designs of all units in the ternary recycle system are calculated as follows. Note that, following the original cost models of Douglas (1988) and Elliot and Luyben (1996), American engineering units are used in cost estimation.

(1) Calculate the minimum number of trays and minimum feed tray in each column from the Fenske equation and Kirkbride equation. Set the number of trays in each column equal to two times the minimum

$$N_{T,i} = 2\frac{\log[(x_{Di,LK}/x_{Di,HK})(x_{Bi,HK}/x_{Bi,LK})]}{\log(\alpha_{LK}/\alpha_{HK})} \tag{B1}$$

$$N_{f,i} = 1 + \frac{N_{T,i}}{1 + \left[\dfrac{x_{Fi,HK}}{x_{Fi,LK}}\left(\dfrac{x_{Bi,LK}}{x_{Di,HK}}\right)^2 \dfrac{B_i}{D_i}\right]^{0.206}} \tag{B2}$$

(2) Use rating programs to determine the reflux ratio when recycle flow and product composition satisfy the specified value.

(3) Calculate the reactor diameter D_R

$$D_R = \left(\frac{2}{\pi} \frac{V_R MW}{\rho_L} \right)^{1/3} \tag{B3}$$

where MW is the average molecular weight = 66.7 and ρ_L is the liquid density = 1.20 g/cm^3.

(4) The distillation column size can be expressed as

$$D_{C,i} = \sqrt{\frac{1}{900\pi} \left(\frac{MWR_{\text{gas}}T}{P} \right)^{1/2}} V_i^{1/2} \tag{B4}$$

$$L_{C,i} = 2.4 N_{T,i} \tag{B5}$$

where R_{gas} is the perfect gas-law constant, T is the temperature, and P is the pressure, which is assumed to be 3.08 bar.

(5) We can utilize the Francis weir formula to calculate the liquid height over the weir ($h_{ow,i}$) for each column

$$h_{ow,i} = \left(\frac{F_i MW}{9600 \rho_L D_{c,i}} \right)^{2/3} \tag{B6}$$

(6) The liquid tray holdup ($M_{n,i}$) is calculated by the liquid height over the weir ($h_{ow,i}$) and a 2.54 cm weir height

$$M_{n,i} = \frac{\left(h_{ow,i} + \frac{1}{2} \right) \frac{\pi D_{c,i}^2}{4} \rho_L}{MW} \tag{B7}$$

(7) The liquid hydraulic time constant β_i (in hours) is calculated for each column

$$\beta_i = \frac{\pi D_{c,i}}{57{,}600 (h_{ow,i})^{1/2}} \tag{B8}$$

(8) The heat-transfer areas for the reboilers and the condensers in each column are calculated as

$$A_{R,i} = \frac{V_{s,i} MW \Delta H_{\text{vap}}}{U_R \Delta T_R} \tag{B9}$$

$$A_{c,i} = \frac{V_{s,i} MW \Delta H_{\text{vap}}}{U_C \Delta T_C} \tag{B10}$$

where the heat of vaporization (ΔH_{vap}) is equal to 0.581 kJ/g. The reboiler was assumed to have a heat-transfer coefficient of $U_R = 17.64$ kJ/(h°Ccm^2) and a temperature differential of $\Delta T_R = 27.8$°C. The heat-transfer coefficient, U_C, for the condenser is equal to 26.5 kJ/(h°Ccm^2) and the temperature difference is $\Delta T_C = 11.1$°C.

(9) Once all the process flow rates and the equipment size have been determined, then the capital cost and operation cost of the process are estimated using the correlation given in Douglas (1988).

(10) The capital cost of the reactor, columns, trays, and the heat exchangers (reboilers and condensers) are estimated using an M&S index of 950 (Douglas, 1988)

$$\text{Reactor cost} = \frac{\text{M\&S}}{280} 101.9 D_R^{1.066} L_R^{0.802} (2.18 + (3.67^* 1.2)) \tag{B11}$$

$$\text{Column cost}_i = \frac{\text{M\&S}}{280} 101.9 D_{C,i}^{1.066} L_{C,i}^{0.802} (2.18 + 3.67^* 1.2) \tag{B12}$$

$$\text{Tray cost} = \frac{\text{M\&S}}{280} 4.7 D_{C,i}^{1.55} L_{C,i} (1.0 + 0.0 + 1.7) \tag{B13}$$

$$\text{Heat exchanger cost}_i = \frac{\text{M\&S}}{280} 101.3 \left(A_{R,i}^{0.65} + A_{C,i}^{0.65} \right) \times (2.29 + (1.35 + 0.1) 3.75) \tag{B14}$$

(11) In the operation cost, we can directly use the vapor boilup, V_i, to evaluate the energy cost

$$\text{Operation cost} = \frac{5}{10^6} \Delta H_{\text{vap}} MW \Sigma V_i \tag{B15}$$

(12) Then the annual capital cost is assumed to be one-third of the capital cost (3-year payback). Materials of construction are stainless steel, and the design pressure is taken to be 20.7 bar. Finally, the TAC for the ternary recycle system can be expressed as

$$TAC = \frac{\text{Capital cost}}{3} + \text{Operation cost} \tag{B16}$$

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