Nonlinear Behavior of Reactor−Separator Systems with Azeotropic Mixtures

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In this work, the behavior of a coupled nonlinear reactor−separator system is analyzed. The reactor is modeled as a continuous stirred tank reactor (CSTR) that sustains a first-order reaction of the form A→B. The separator is modeled as a flash. The effluent from the reactor is fed to the separator. Here, we assume that the liquid stream from the separator is recycled back to the reactor. The primary interest is to investigate the system when the vapor−liquid equilibrium (VLE) has an azeotrope. Under these conditions, the recycle stream can be either reactant-rich or reactant-lean depending on the feed composition to the flash. The focus is on pure mass recycle, as the two units are assumed to be decoupled energetically via heat exchangers. Two different modes of operations are considered. In the first mode of operation, the fresh feed flow rate is fixed. In the second mode of operation, the effluent flow from the reactor is fixed. In practice, these different modes of operation can be achieved using a suitable control strategy. When fresh feed to the network is flow-controlled, there is a region of dynamic instability in the solution branch corresponding to the recycle of the reactant-lean stream. In addition, coexistence of states with the recycle of reactant-rich and reactant-lean streams is possible. Our analysis indicates the presence of large regions of static and dynamic instabilities when the reactant-lean stream is recycled to the reactor and the effluent from the reactor is flow-controlled. Our results imply that the region in which the separator operates is very important in determining the behavior of the coupled system. Consequently, startup of the system is critical when the VLE of the system has an azeotrope.

1. Introduction

Coupled reactor−separator systems occur widely in the chemical process industries. The coupling between the reactor and the separator is through the recycle of the reactant-rich stream from the downstream separator to the upstream reactor (Figure 1). The analysis of earlier research in this area has focused on ideal behavior in the separator.

Luyben and Luyben,[1] for example, analyzed the case of a perfect separator, i.e., a separator with effluent streams containing only reactant A or product B. They found the recycle flow to be very sensitive to changes in fresh feed flow. Pushpavanam and Kienle[2] analyzed the separator as a flash operating under isothermal isobaric conditions. For a binary mixture, this uniquely fixes the compositions of the streams leaving the separator. This is analogous to using composition controllers on the effluent streams from a distillation column. Consequently, the compositions of the separator effluent streams can be treated as being fixed as independent parameters. When the reactor is operated nonisothermally, they found that the coupled system has a maximum of two steady states when the fresh feed is flow-controlled. Zeyer et al.[3] studied the case of isothermal reactor operation. Here, the system has a unique and stable steady-state solution, when the flash is operated at constant temperature and pressure and the reactant is the heavy component, and the reactant-rich stream is recycled. They studied the behavior of the coupled system for different modes of operation of the flash.
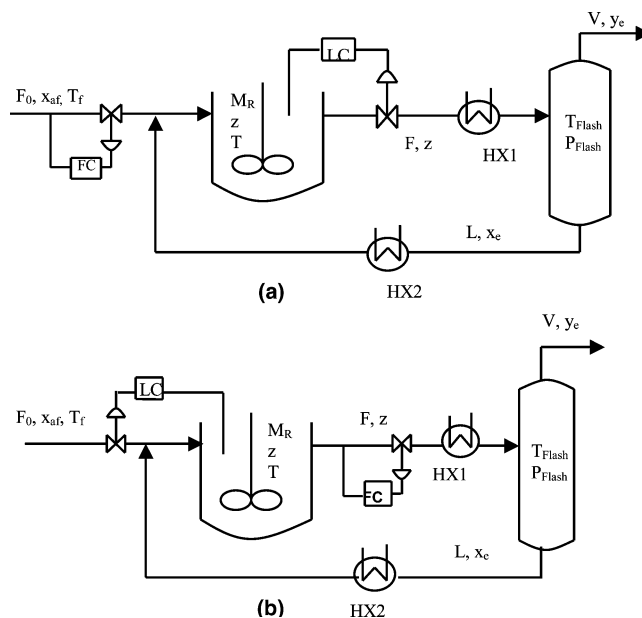

Figure 1. Two control strategies for the coupled CSTR flash system. Flow control of (a) fresh feed flow and (b) reactor effluent flow.

Bildea et al.[4] showed the existence of a critical plant Damkohler number below which no solutions exist for coupled reactor−separator networks. They restricted their analysis to reactors sustaining elementary reactions. In their analysis, they assumed the separator to be perfect. Skogestad et al.[5] analyzed a self-optimal control strategy for the operation of coupled reactor−separators. In a later paper, Bildea et al.[6] investigated polymerization reactions occurring in a coupled system. They found that their system had up to four steady states when a
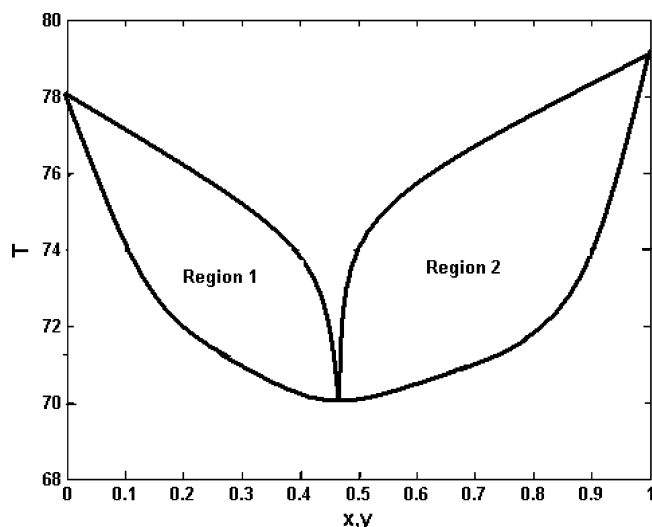
Figure 2. VLE of a binary azeotropic mixture at fixed pressure.

detailed model was used and verified these results using simulations based on Aspen Plus.

In this work, we study the behavior of a coupled reactor–separator system. The reactor is modeled as a continuous stirred tank reactor (CSTR), and the separator is modeled as a flash unit (Figure 1). A distillation column that has composition controllers on the bottoms and distillate streams is assumed to interact with the upstream reactor in a qualitatively similar manner as an isothermal, isobaric flash separating a binary mixture. The liquid stream is assumed to be recycled back (Figure 1) to the reactor. We focus our attention on the case when the binary feed mixture to the separator forms a minimum-boiling azeotrope (Figure 2). Consequently, for isothermal, isobaric operation of the flash, the effluent streams leaving can be in one of two states. This is determined by the feed composition. For the range of feed compositions when z lies in region 1, we have $x_e < z < y_e$, and for the case when z lies in region 2, we have $y_e < z < x_e$. Here, x_e (y_e) is the mole fraction of A in the liquid (vapor) stream leaving the separator. The effect of the presence of these two regions on the behavior of the coupled reactor–separator system is the main focus of the work in this paper.

The behavior of a coupled reactor–separator system has been investigated in the past for the case with $y_e < z < x_e$, i.e., when the vapor–liquid equilibrium (VLE) was considered to be ideal, and when the reactant-rich stream is recycled back.[2]

When the reactor effluent entering the flash forms an azeotrope, the recycle stream fixed in this work as the bottoms can be reactant-rich or product-rich. Our focus is on how this qualitatively influences the steady-state multiplicity, stability, and dynamic behavior of the coupled reactor–separator system. An example of an industrial system in which a reactant-lean stream is recycled is the production of acetic acid, which has been investigated in detail by Waschler et al.[7] The reaction is catalyzed with a rhodium salt, which is separated in a flash drum and recycled with unreacted liquid into the reactor. Because the reactants are light-boiling components, the recycle is lean in the reactant in this case.

The multiplicity features of homogeneous azeotropic distillation have been studied by Morari et al.[8] They described experiments for the ternary homogeneous system methanol–methyl butyrate–toluene, which demonstrated the existence of multiple steady states (output multiplicities) caused by the VLE.

For our coupled system we discuss two different modes of operation following the approach of Luyben and Luyben[1]. These

are (a) isothermal, isobaric flash and fixed fresh feed flow to the system and (b) isothermal, isobaric flash and fixed effluent flow from the reactor. The control strategies for these two modes of operation are explicitly depicted in Figure 1a and b, respectively. In Figure 1a, the fresh feed flow rate is flow-controlled, and the level in the reactor is controlled using the reactor effluent flow rate. In Figure 1b, the roles of these two flows are reversed. For each of these cases, we discuss two situations depending on whether the reactor is operated (i) isothermally or (ii) adiabatically.

2. Model Assumptions

The objective of this work is to determine the different types of qualitative behavior of the coupled system. With this in mind, we use a simplified model that retains the important features of the system, i.e., the processes occurring in each unit and the interaction between the two units. The reactor is modeled as a CSTR that is assumed to sustain an irreversible elementary first-order reaction (Figure 1). Heat exchanger HX1 brings the reactor effluent to the flash temperature. No energy is recycled from the separator to the reactor. This is accomplished by the heat exchanger on the recycle loop HX2, which changes the temperature of the bottoms from the flash to that of fresh feed. The temperature of the coolant to the reactor is assumed to be the same as the fresh feed temperature. The molar density is assumed to be independent of the composition. The molar holdup in the reactor is held constant, implying ideal level control of the reactor.

We now explain the different variables used for representing the coupled reactor–separator system being investigated. Fresh feed with mole fraction x_{af} at a flow rate of F_0 (mol/h) is fed to the system. The mole fraction leaving the reactor is z, and the reactor effluent flow rate is F (mol/h). The bottoms from the separator with mole fraction x_e is recycled to the reactor at a rate L (mol/h), and the overhead stream withdrawn from the separator leaves at a rate V (mol/h) with composition y_e. All compositions represent the mole fraction of reactant A. Heat exchangers HX1 and HX2 ensure that there is no energy coupling between the two units (Figure 1a,b).

In this work, a flash operating at constant pressure and temperature is considered. The streams exiting the flash are assumed to be in equilibrium. For a binary mixture, the liquid and vapor compositions x_e and y_e, respectively, are fixed when the pressure and temperature of the flash are fixed. For ideal mixtures, these compositions are uniquely fixed. In contrast, two sets of x_e and y_e values are possible when the mixture has an azeotrope, as illustrated in Figure 2. This is determined by the composition entering the flash. For a mixture with an azeotropic point with a temperature minimum (Figure 2) $x_e < y_e$ in region 1, and $y_e < x_e$ in region 2. In the analysis in the rest of this paper, we use two sets of compositions (x_e, y_e) for our calculations. These are (x_e^1, y_e^1) as (0.1, 0.4) and (x_e^2, y_e^2) as (0.9, 0.5) corresponding to a temperature of 74 °C. The superscript indicates the region in which the system is operating.

3. Fixed Fresh Feed Flow to the System

3.1. Isothermal Reactor. In this case, the reactor–separator network is described by the equation

$$\frac{dz}{dt} = x_{af} - y_e - Da_1 z \tag{1}$$

This equation governs the evolution of the mole fraction z of reactant A in the reactor.

Here, the Damkohler number Da_1 is $M_R k e^{-E/RT_f}/F_0$, where M_R is the molar holdup of the reactor and ke^{-E/RT_f} is the reaction rate constant. Time is rendered dimensionless using the time scale M_R/F_0.

3.1.1. Steady-State Characteristics. Setting the right-hand side to 0 in eq 1, we obtain the following equation, which describes the steady-state behavior of the reactor−separator network

$$f(z,\mathbf{p},Da_1) = x_{af} - y_e - Da_1 z = 0 \qquad (2)$$

Here, the parameter vector $\mathbf{p}$ includes the parameters x_{af} and y_e. We fix x_{af} and y_e and treat Da_1 as the bifurcation parameter. The dependence of z on Da_1 is given by $z = (x_{af} - y_e)/Da_1$.

Because the reactor effluent forms an azeotrope (see Figure 2), two values of y_e are possible: in region 1 ($x_e < y_e$) and in region 2 ($y_e < x_e$). In the first case, the reactant-lean stream is recycled, and in the latter the reactant-rich stream is recycled back from the separator to the reactor. Here, the richness or leanness is determined by comparing the mole fraction of the recycle stream to the mole fraction in the effluent from the reactor.

In Figure 3, we depict the dependence of z on Da_1 for various values of the heat of reaction parameter B. The isothermal case is depicted as a special case of this for $B = 0$.

Figure 3f shows the dependence of z on Da_1 for an isothermal reactor. The two branches of the bifurcation diagram arise because of the two regions of the VLE. This means that there are two nonoverlapping intervals of Da_1 (Figure 3f) where steady-state solution branches exist. The steady states exhibited by the system are always stable. The first branch exists for $0.56 < Da_1 < 1$, and the second branch exists for $1.5 < Da_1 < 6$. The former (latter) corresponds to the recycle of the reactant-rich (-poor) stream. These two branches arise because of a global feature of the system induced by the VLE. Bifurcation theory has to be used to analyze each of the branches separately. The extent of each of the branches is determined by the constraints imposed by $x_e < z < y_e$. Throughout this work, we have assumed (x_e^1, y_e^1) and (y_e^2, x_e^2) as (0.1, 0.4) and (0.5, 0.9), respectively. It is readily seen from eq 2 that the branches can never overlap in the feasible range. Further, as the eigenvalue of the linearized system $\lambda = -Da_1$, it is found that the solution branches are always stable. Hence, at most a single stable feasible steady-state solution is possible for this case when the reactor is operated isothermally.

3.2. Nonisothermal Reactor. The mass and energy balance equations describing the coupled reactor−separator system when the liquid stream is recycled are given by[2]

$$\frac{dz}{dt} = x_{af} - y_e - Da_1 z e^{\theta} \qquad (3a)$$

$$\frac{d\theta}{dt} = -\theta\left(\frac{y_e - x_e}{z - x_e} + \beta Da_1\right) + BDa_1 z e^{\theta} \qquad (3b)$$

where

$$Da_1 = \frac{kM_R e^{-E/RT_f}}{F_0}, \quad B = \frac{(-\Delta H)E}{C_p RT_f^2}, \quad \beta = \frac{UA}{M_R C_p k e^{-E/RT_f}},$$

$$\theta = \frac{E}{RT_f^2}(T - T_f)$$

Here, B, β, and Da_1 represent the dimensionless heat of reaction,

the dimensionless heat-transfer coefficient in the reactor, and the Damkohler number, respectively. Time is rendered dimensionless using the time scale M_R/F_0, the ratio of the reactor molar holdup to the fresh feed flow rate. In the above, we have made the exponential approximation for the Arrhenius temperature dependency, and we have assumed that there is no transportation lag between the two units. In addition, the coolant temperature, the temperature of the recycle stream before entering the reactor, and the fresh feed temperature are assumed to be equal. The heat exchanger HX2 ensures this.

The first term in the parentheses on the right-hand side of eq 3b arises from the recycle stream from the flash. This recycle stream flow is governed by the lever rule in separation systems. This specifies only the ratio of the flow of the recycle stream to the flow of the flash feed. The recycle flow is hence not a constant and varies with the reactor composition z. This is explicitly seen in eq 3b.

3.2.1. Steady-State Characteristics. Eliminating θ after setting the right-hand sides to 0 in eqs 3a,b yields the steady-state equation in the single state variable z. This is of the form

$$f(z,\mathbf{p},Da_1) = \left(\frac{y_e - x_e}{z - x_e} + \beta Da_1\right)\ln\left(\frac{x_{af} - y_e}{Da_1 z}\right) - B(x_{af} - y_e) = 0 \quad (4)$$

Here, p represents the vector of the auxiliary parameters [x_e, y_e, B, β, x_{af}], and Da_1, the Damkohler number, represents the bifurcation parameter. We now discuss the dependence of z on Da_1 as determined by the parameter $\mathbf{p}$.

Static Instability. For the adiabatic reactor, i.e., the case $\beta = 0$, it has been analytically shown[2] that eq 4 satisfies

$$f = \frac{\partial f}{\partial z} = 0, \quad \frac{\partial^2 f}{\partial z^2} \neq 0, \quad \frac{\partial f}{\partial Da_1} \neq 0 \qquad (5)$$

Following the singularity theory arguments of Golubitsky and Schaeffer,[9] Pushpavanam and Kienle[2] concluded that the system behaves such that it has either two steady-state solutions or no steady solution for different parameter combinations. This conclusion is valid as long as the analysis is restricted to the case of an ideal system where $x_e > y_e$.

When the binary mixture forms an azeotrope, the compositions of the effluent streams from the separator can be such that $x_e > y_e$ or $y_e > x_e$ as seen in Figure 2. As in the case of isothermal reactor operation, the coupled system has two steady-state branches corresponding to these situations. These branches can exist for different values of the bifurcation parameter Da_1. From eq 5, each of these branches can have a limit point for suitable values of B. Hence, the system can have no solutions, one solution, two solutions, or three solutions for different combinations of parameters. It can be shown that only one solution branch can have a limit point for a given B, so a situation where the system can admit four solutions does not arise. The dependence of z on Da_1 for the adiabatic reactor is affected only by B for a fixed (x_e^1, y_e^1) and (x_e^2, y_e^2).

The boundary limit set at $z = y_e$ is defined as the point where $f = \partial f/\partial z = 0$ at $z = y_e$. Similarly, the boundary limit set at $z = x_e$ is defined as the point where $f = \partial f/\partial z = 0$ at $z = x_e$.

Pushpavanam and Kienle[2] have shown that the boundary limit set (BLS) at $z = y_e$ is given by

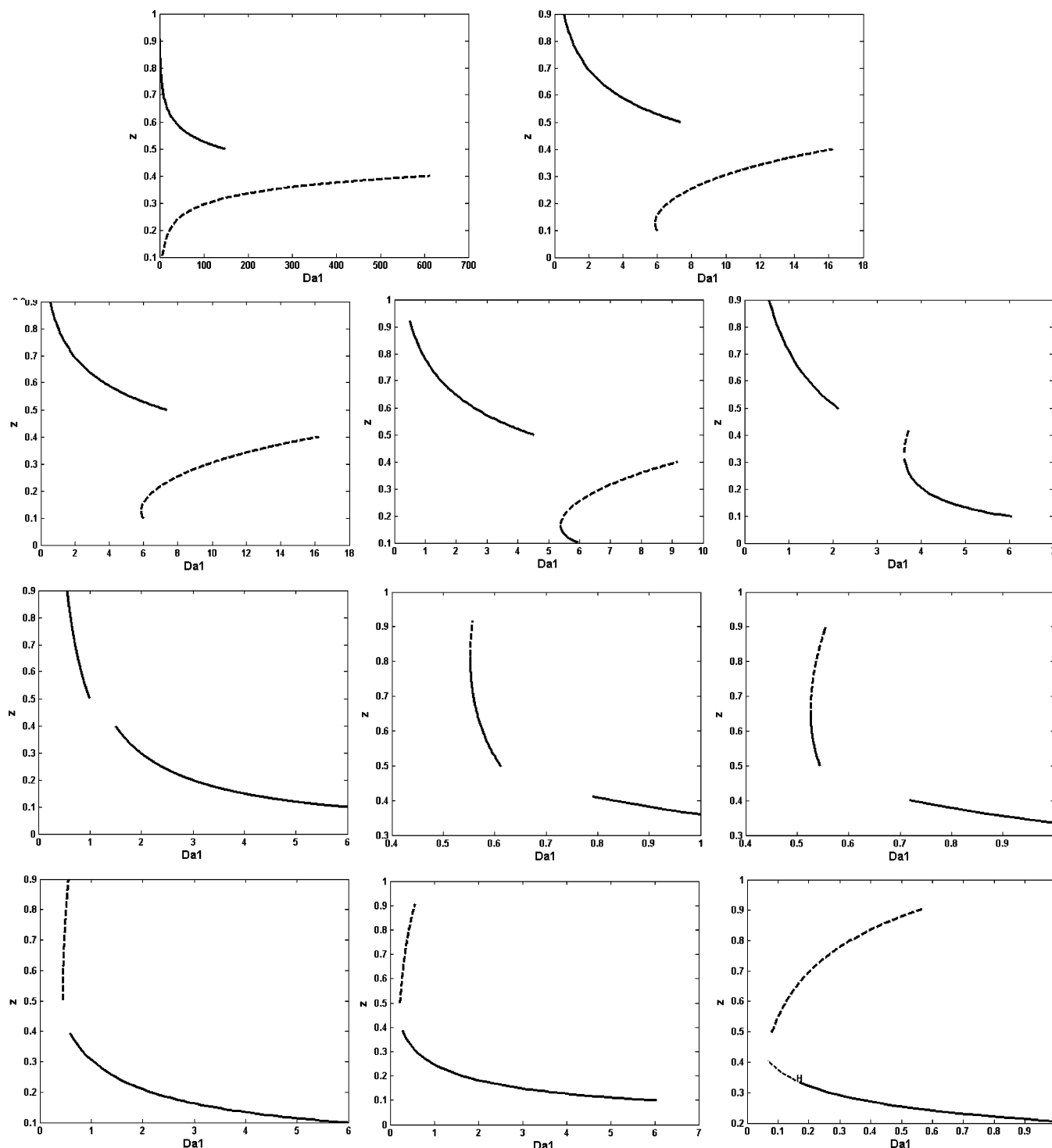$$B = \frac{x_e - y_e}{y_e(x_{af} - y_e)} = B_{cr1}$$

Figure 3. Dependency of z on Da_1, when the fresh feed to the reactor−separator network is flow-controlled and the molar holdup of the adiabatic reactor is fixed for different values of $B =$ (a) −10, (b) −4, (c) −3.5, (d) −3, (e) −1.5, (f) 0, (g) 1, (h) 1.2, (i) 1.62, (j) 3, and (k) 5 (H = Hopf bifurcation point).

and that at $z = x_e$ is given by

$$B = \frac{x_e - y_e}{x_e(x_{af} - y_e)} = B_{cr2}$$

For $x_e > y_e$, B_{cr1} and B_{cr2} are positive; for $x_e < y_e$, they are negative. The values of the BLS indicate the presence of a limit point when the reactant-lean stream is recycled provided that the reaction is sufficiently endothermic. The values of B_{cr1} and B_{cr2} when the reactant-lean stream is being recycled are given by −1.25 and −5, respectively. For $B = -1.25$, the limit point

is on $z = y_e^1$, and for $B = -5$, it moves to the $z = x_e^1$ boundary. Hence, for $B < -5$ or $B > -1.25$, there are no limit points in $0.1 < z < 0.4$.

The values of B_{cr1} and B_{cr2} when the reactant-rich stream is being recycled are 1.6 and 0.89, respectively. For $B = 0.89$, the limit point is on $z = x_e^2$, and for $B = 1.6$, the limit point is on $z = y_e^2$. Hence, for $B < 0.89$ or $B > 1.6$, there is no limit point in $0.5 < z < 0.9$.

We define $f(z,p,Da_1) = f^1(z,\mathbf{p},Da_1)$ for $\mathbf{p} = [B, \beta, x_{af}, x_e^1, y_e^1]$, and $f(z,\mathbf{p},Da_2) = f^2(z,\mathbf{p},Da_2)$ for $\mathbf{p} = [B, \beta, x_{af}, x_e^2, y_e^2]$. In addition to the four critical values corresponding to the boundary

Table 1. Critical Values of the Parameter B and Critical Conditions Satisfied for Fixed Fresh Feed (i.e., F_0 Fixed)[a]

critical value of B	criticality condition satisfied
-5	$f^1 = \dfrac{\partial f^1}{\partial z} = 0, z = x_e^1$
-3.584	$f^1 = 0, z = x_e^1$ $f^2 = 0, z = y_e^2$
-3.47	$f^1 = \dfrac{\partial f^1}{\partial z} = 0$ $f^2 = 0, z = y_e^2$
-2.31	$f^1 = 0, z = x_e^1, y_e^1$
-1.25	$f^1 = \dfrac{\partial f^1}{\partial z} = 0, z = y_e^1$
0.89	$f^2 = \dfrac{\partial f^2}{\partial z} = 0, z = x_e^2$
1.176	$f^2 = 0, z = x_e^2, y_e^2$
1.6	$f^2 = \dfrac{\partial f^2}{\partial z} = 0, z = y_e^2$
1.66	$f^1 = 0, z = y_e^1$ $f^2 = 0, z = x_e^2$
4.055	$f^1 = 0, z = y_e^1$ $f^2 = 0, z = y_e^2$

[a] $(x_e^1, y_e1) = (0.1, 0.4)$ and $(x_e^2, y_e^2) = (0.9, 0.5)$.

Table 2. Nature of the Bifurcation Diagram in Different Intervals of B for Fixed F_0[a]

B	characteristic of bifurcation diagram	representative bifurcation diagram
$(-\text{infinity}, -5)$	$0-1-2-1-0$	Figure 3a
$(-5, -3.584)$	$0-1-3-2-1-0$	Figure 3b
$(-3.584, -3.47)$	$0-1-3-2-1-0$	Figure 3c
$(-3.47, -2.31)$	$0-1-0-2-1-0$	Figure 3d
$(-2.31, -1.25)$	$0-1-0-2-1-0$	Figure 3e
$(-1.25, 0.89)$	$0-1-0-1-0$	Figure 3f
$(0.89, 1.176)$	$0-2-1-0-1-0$	Figure 3g
$(1.176, 1.6)$	$0-2-1-0-1-0$	Figure 3h
$(1.6, 1.66)$	$0-1-0-1-0$	Figure 3i
$(1.66, 4.055)$	$0-1-2-1-0$	Figure 3j
$(4.055, \text{infinity})$	$0-1-2-1-0$	Figure 3k

[a] $(x_e^1, y_e^1) = (0.1, 0.4)$ and $(x_e^2, y_e^2) = (0.9, 0.5)$

limit set, we have the additional critical values listed in Table 1. The real line represents the range of values that the parameter B can take. This is divided into several intervals by critical values of the parameter B. Table 1 indicates the different critical values as well as the criticality conditions that are satisfied. Table 2 describes the bifurcation diagram in various intervals of B. An entry of $0-1-2-1-0$ in the column corresponding to the characteristic bifurcation diagram means that the number of solutions admitted by the coupled system change from 0 to 1, from 1 to 2, from 2 to 1, and then from 1 to 0 as the bifurcation parameter Da_1 changes from 0 to infinity. We now discuss the bifurcation diagrams in the various regions in detail.

Figure 3a shows the dependence of z on Da_1 for $B = -10$. A negative value of B indicates that the reaction is endothermic. We notice that the solution branch corresponding to the recycle of the reactant-lean stream exists over the range $6 < Da_1 < 613$ and is unstable for all values of Da_1. The solution branch corresponding to the recycle of the reactant-rich stream exists over $0.56 < Da_1 < 150$ and is stable for all values of Da_1. For $6 < Da_1 < 150$, the system has two solutions, and for $0.56 < Da_1 < 6$ and $150 < Da_1 < 613$, the system has only one solution.

Figure 3b shows the dependence of z on Da_1 for $B = -4$. We notice that the solution branch corresponding to the recycle of the reactant-lean stream exists over the range $5.85 < Da_1 < 16.2$. The system has a limit point at $Da_1 = 5.85$. The solution branch corresponding to the recycle of the reactant-lean stream has two solutions for $5.85 < Da_1 < 6$, one of them being unstable and the other stable. For $6 < Da_1 < 16.2$, this solution branch has a single unstable solution, the stable solution having been rendered infeasible because it has crossed the boundary $z = 0.1$. The solution branch corresponding to the recycle of the reactant-rich stream exists over $0.56 < Da_1 < 7.4$ and is stable for all values of Da_1. For $5.85 < Da_1 < 7.4$, there is an overlap between the solution branches corresponding to the recycle of the reactant-lean stream and the recycle of the reactant-rich stream. The system has two solutions for $6 < Da_1 < 7.4$, one of which is unstable and the other stable. The system exhibits three solutions for $5.85 < Da_1 < 6$, two of which are stable and one unstable.

In Figure 3c, the value of the bifurcation parameter Da_1 for $z = x_e^1$ is greater than the value of Da_1 for $z = y_e^2$. This diagram is shown for $B = -3.5$.

Figure 3d shows the dependence of z on Da_1 for $B = -3$. Here, the limit point occurs for a Da_1 value that is greater than the Da_1 value for $z = y_e^2$. The solution branch corresponding to the recycle of the reactant-rich stream exists over the range of $Da_1 = (0.56, 4.15)$ and is stable and unique for all values of Da_1. The branch corresponding to the recycle of the reactant-lean stream exists over the range of $Da_1 = (5.4, 9.2)$. This branch has a limit point at $Da_1 = 5.4$. Thus, in the range $Da_1 = (5.4, 6)$, the system has two solutions, and in the ranges $Da_1 = (0.56, 4.15)$ and $Da_1 = (6, 9.2)$, the system has one solution. For $Da_1 < 0.56$, $Da_1 > 9.2$, and $4.15 < Da_1 < 5.4$, the system has no steady solution.

Figure 3e is plotted for $B = -1.5$. Here, Da_1 at $z = y_e^1$ is less than Da_1 at $z = x_e^1$.

Figure 3f is valid for $-1.25 < B < 0.89$. Its features have been discussed extensively in the section on isothermal reactor.

Figure 3g is drawn for $B = 1$. A limit point appears in the reactant-rich recycle branch at $z = x_e^2$ at $B = 0.89$. This limit point can be seen in Figure 3g.

Figure 3h shows the dependence of z on Da_1 for $B = 1.2$. We notice that the solution branch corresponding to the recycle of the reactant-rich stream exists over a very small region of $Da_1 = (0.525, 0.56)$. In Figure 3h, the branch corresponding to the recycle of the reactant-lean stream exists over the range of $Da_1 = (0.7, 6)$. This branch does not have any limit point and is stable for all values of Da_1. Thus, in the range $Da_1 = (0.7, 6)$, the system has one solution. In the range $Da_1 = (0.525, 0.542)$ the system has two solutions, and in the range $Da_1 = (0.542, 0.56)$, the system admits one unstable solution. For $Da_1 < 0.525$, $Da_1 > 6$, and $0.56 < Da_1 < 0.7$, the system has no steady solutions.

Figure 3i shows the dependence of z on Da_1 for $B = 1.62$. We notice that the solution branch corresponding to the recycle of the reactant-rich stream exists over the very small range of $Da_1 = (0.44, 0.56)$. This branch is unstable for all values of Da_1 as the limit point has moved below $z = 0.5$. In Figure 3i, the branch corresponding to the recycle of the reactant-lean stream exists over the range of $Da_1 = (0.59, 6)$. This branch does not have any limit point and is stable for all values of Da_1. For $Da_1 < 0.44$, $Da_1 > 6$, and $0.56 < Da_1 < 0.59$, the system has no steady solution. There is no overlap between the solution branches corresponding to the recycles of reactant-lean and reactant-rich streams.

In Figure 3j, there is partial overlap between the two branches corresponding to the recycles of the reactant-rich and -lean streams. This is drawn for $B = 3$.

Figure 3k shows the dependence of z on Da_1 for $B = 5$. There is complete overlap of the branch in the reactant-rich recycle with the other branch. We notice that the solution branch corresponding to the recycle of the reactant-lean stream exists over the range of $Da_1 = (0.07, 6)$. This branch is dynamically unstable for values in the range $0.07 < Da_1 < 0.158$ and stable for $0.158 < Da_1 < 6$. This instability is due to a Hopf bifurcation at $Da_1 = 0.158$, which is indicated by H in the figure. In Figure 3k, the branch corresponding to the recycle of the reactant-rich stream exists over the range of $Da_1 = (0.08, 0.56)$. This branch is unstable for all values of Da_1. For $Da_1 < 0.07$ and $Da_1 > 6$, the system has no steady solutions. There is an overlap between the solution branches corresponding to the recycle of the reactant-lean stream and the recycle of the reactant-rich stream for $0.08 < Da_1 < 0.56$.

For some parameters, the steady states corresponding to the recycles of the reactant-lean and reactant-rich streams coexist. The state is decided by the initial conditions. The system can also attain a steady state in one branch and evolve to a state in the other branch. This can occur when there is a disturbance in the system that results in the mole fraction in the reactor changing from region 1 to region 2 (Figure 2). In particular, there are no discrete switches or changes in the set points in controllers that cause the system to operate in the two regions. The variables that are controlled are the temperature and the pressure of the flash. Because the streams leaving the flash are in equilibrium, their compositions change depending on the reactor composition. Hence, the system analyzed is not a hybrid system but a continuous one.

We notice that the solution branches corresponding to the recycle of the reactant-lean stream in Figure 3b–e indicate that the coupled system exhibits multiple steady states even for values of B that are negative. This corresponds to endothermic reactions in the CSTR.

Endothermic reactions are not known to show multiple steady states in a stand-alone reactor (CSTR). This is explained by the fact that the autocatalytic effect with a positive feedback that causes multiple steady states in exothermic reactions is absent here. However, when the endothermic reaction takes place in a reactor–separator network (as in the present study), the system can exhibit multiple steady states when the reactant-lean stream is recycled. We now describe the physical source of an autocatalytic effect that we believe gives rise to multiple steady states when an endothermic reaction takes place in the CSTR and a reactant-lean stream is recycled back to the reactor from the separator.

Consider a perturbation in mole fraction at the exit of the reactor that results in its increase. This causes a decrease in the flow rate of the recycle stream when the reactant-lean stream is being recycled, as can be seen by applying the lever rule to the phase diagram in Figure 2. This results in an increase in the residence time of the reacting fluid. The temperature of the reactor decreases further, as the reaction is endothermic and the reactor is operated adiabatically. This causes the rate of reaction to further decrease, resulting in an accumulation of the reactant. This causes the mole fraction of reactant at the exit of the reactor to increase further. The initial perturbation of the mole fraction is thus amplified. This is an autocatalytic effect that we believe is the source of multiple steady states when the reactant-lean stream is recycled and the reaction is endothermic. This autocatalytic effect is present only in coupled reactor–

separator networks sustaining an endothermic reaction and cannot be found in stand-alone reactors.

Dynamic Instability. A stand alone adiabatic CSTR sustaining a first-order exothermic reaction does not exhibit any dynamic instability. Coupled reactor–separator systems also do not exhibit dynamic instability when the reactor is adiabatic and the molar holdup is constrained to be constant.[2] These systems can be dynamically unstable when the reactor holdup is not constrained to be constant.[10] When $y_e < z < x_e$, i.e., when the flash operates in region 2, the recycle stream is the reactant-rich stream. In this case, the system cannot exhibit any dynamic instability when the reactor is adiabatic. For $x_e < z < y_e$, the reactant-lean stream is recycled. We now show that the coupled system can exhibit dynamic instability when the reactor is adiabatic under these conditions.

The stability of the two-dimensional system is governed by the eigenvalues of the Jacobian matrix of the linearized system. The Hopf bifurcation point, i.e., the critical value of the bifurcation parameter where the dynamic instability originates, is governed by the conditions trace($\mathbf{J}$) $= 0$, det($\mathbf{J}$) > 0. The Hopf points are given by the roots of trace($\mathbf{J}$) $= 0$. This yields

$$B = \frac{1}{z} + \left(\frac{1}{x_{af} - y_e}\right)\left(\frac{y_e - x_e}{z - x_e}\right) \tag{6a}$$

The condition det(J) > 0 [assuming that trace($\mathbf{J}$) $= 0$] amounts to

$$\frac{-1}{z^2} + B\left(\frac{1}{z} + \frac{1}{z - x_e}\right) > 0 \tag{6b}$$

When $y_e > x_e$, i.e., when the reactant-lean stream is being recycled, dynamic instability can be induced in the reactor–separator system, as we can solve eq 6a [trace(J) $= 0$] subject to the condition of eq 6b [det($\mathbf{J}$) > 0].

In Figure 3k, the steady-state branch of solutions corresponding to the recycle of the reactant-lean stream is shown for $B = 5$ ($0.1 < z < 0.4$). This contains a region of dynamic instability that is caused by a supercritical Hopf bifurcation that occurs at $Da_1 = 0.158$. This introduces a region of dynamic instability, as shown in Figure 3k, for $0.07 < Da_1 < 0.158$.

Figure 4a shows the oscillatory branch of solutions originating from this Hopf bifurcation point. A stable oscillatory branch originates from the Hopf bifurcation point in this case. The oscillatory branch corresponds to stable oscillations, and the amplitude of these oscillations increases rapidly to the left of the Hopf bifurcation point. The oscillations in the vicinity of the Hopf bifurcation point are shown in Figure 4b. It is important to note that, during the course of the oscillations, the composition in the reactor, z, does not exceed the bounds set by y_e and x_e. Consequently, the model equations are valid throughout the course of the dynamic evolution. There is hence no switching between the two regions in which separation can occur. Should the amplitude of the oscillations be large and violate the constraints imposed by the constant compositions of the streams leaving the separator, then it would be necessary to use a multiple model approach for the simulation of the system behavior. We would then have to change the governing equations using a discrete switch. Similarly, if there were a large disturbance in the operating conditions, the system could deviate from one region to another in Figure 2. Once again, we would have to check conditions on the state variables and switch the governing equations of the system in a dynamic simulation.
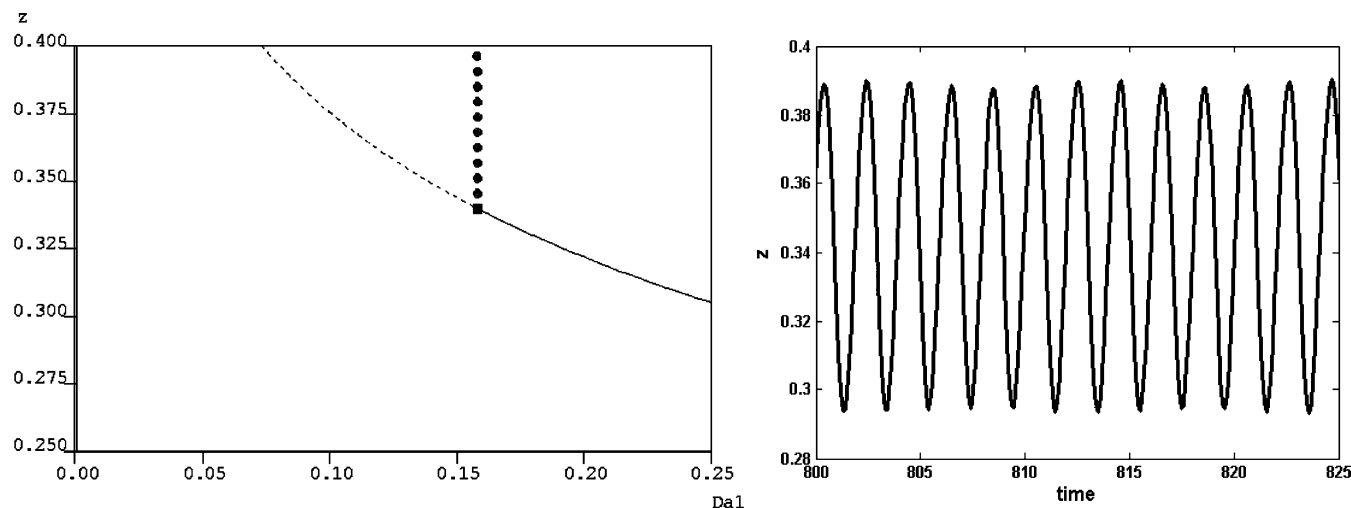
Figure 4. (a) Dependency of z on Da_1, when the fresh feed to the reactor−separator network is flow-controlled and the molar holdup of the reactor is fixed, showing the oscillatory branch of solutions (adiabatic reactor, $B = 5$). (b) Oscillations in the vicinity of the Hopf bifurcation point shown in part a. These self-sustained oscillations arise when the fresh feed to the reactor is flow-controlled and the molar holdup of the reactor is fixed (adiabatic reactor, $B = 5$).

The assumption of equilibrium in the flash implies that it is at a quasisteady state. This essentially implies that the flash responds very quickly to disturbances and is hence very fast compared to the reactor. The controls on the temperature and pressure are assumed to be perfect. Because the adiabatic reactor coupled to a separator cannot exhibit dynamic instability,[2] the dynamic instability discussed above is hence only due to the coupling of the two units and the recycle of the reactant-lean stream. In particular, it is not induced solely by nonlinear interactions present in the individual units.

We now explain the physical basis for these oscillations. Because the reaction is exothermic, the rate of the reaction increases as the reaction proceeds because of the rise in temperature. However, this increased rate of reaction causes the mole fraction at the exit of the reactor to decrease, which, in turn, causes an increase in the flow rate of the recycle stream as the reactant-lean stream is being recycled. This causes a decrease in the residence time in the reactor, which, in turn, leads to a decrease in the rate of the reaction. This causes an increase in the mole fraction at the exit of the reactor. This again causes the reaction rate to increase, and the cyclic behavior is sustained. The two phenomena discussed, i.e., the exothermic nature of the reaction and the recycle of the reactant-lean stream, can cause periodic cycles of decrease and increase in the mole fraction at the exit of the reactor. Thus, for a suitable combination of parameters, the system outputs can be in a periodic state even though the inputs to the system are maintained constant. No Hopf bifurcation points have been found for the case $x_e > y_e$,[2] i.e., when the reactant-rich stream is recycled and the reactor is adiabatic.

4. Fixed Effluent Flow F from the Reactor

4.1. Isothermal Reactor. In this case, the material balance that describes the evolution of the coupled reactor−separator system is given by

$$\frac{dz}{dt} = \frac{(x_e - z)(x_{af} - y_e)}{(x_e - y_e)} - Da_2 z \qquad (7)$$

Here, Da_2 is given by $ke^{-E/RT_f} M_R/F$. Time is rendered dimensionless using M_R/F, i.e., the ratio of the molar holdup to the effluent flow rate.

4.1.1. Steady-State Behavior. Setting the right-hand side to 0 in eq 7, we obtain the steady states of the reactor−separator network. These are the solutions to

$$f(z, Da_2, \mathbf{p}) = \frac{(x_e - z)(x_{af} - y_e)}{(x_e - y_e)} - Da_2 z = 0 \qquad (8)$$

Here, the parameter vector p includes x_{af}, x_e, and y_e. We treat Da_2 as the bifurcation parameter.

As in case of the fresh feed F_0 being flow-controlled, the bifurcation diagram of z vs Da_2 shows two branches. This is due to a global feature induced by the VLE as explained earlier. In this case, this global feature causes multiple steady states even when an isothermal reactor is coupled with an isothermal, isobaric flash. For the range of $0 < Da_2 < 1$ (Figure 5a), we observe two possible steady-state branches for the system under consideration. One of them is stable, and the other is unstable. The unstable (stable) one corresponds to the recycle of the reactant-lean (reactant-rich) stream. For $1 < Da_2 < 1.5$, there is one unstable solution, and for $Da_2 > 1.5$, there are no steady solutions.

We now propose a physical explanation for the instability seen when the reactant-lean stream is recycled. Consider the reactor composition and the flash temperature when the system is operating with a recycle stream lean in the reactant. We consider the system to be initially at a steady state in region 1 of the VLE (Figure 2). A positive disturbance is given only in z, i.e., the value of z increases. All other variables are assumed to be at the steady state. The recycle flow rate now decreases. Because the level of the reactor has to be maintained, the fresh feed flow increases. This effectively results in an increase in the concentration of the stream entering the reactor because the fresh feed has a higher concentration than the recycle stream. The residence time in the reactor is fixed because the reactor effluent flow rate is fixed and the holdup is constant, and hence, the concentration of the reactor increases further, amplifying the initial disturbance and resulting in instability. A similar effect is present for the case when the mole fraction in the reactor decreases because of a negative disturbance. From this analysis, we can conclude that the recycle of a reactant-lean stream is inherently unstable.

4.2. Nonisothermal Reactor. The equations that describe the coupled reactor−separator system when the effluent F from the
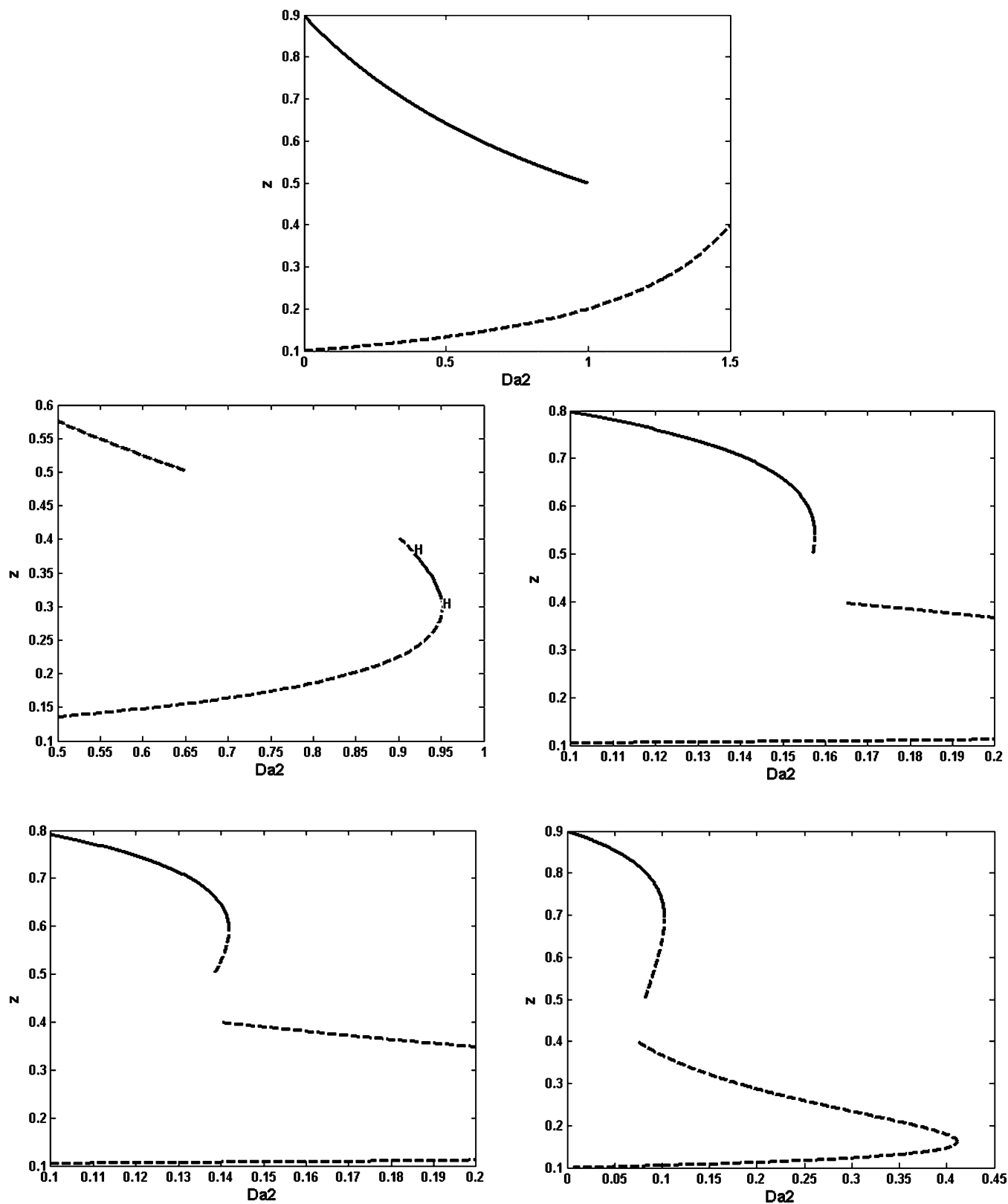
Figure 5. Dependency of z on Da_2, when the effluent from the reactor in a reactor−separator network is flow-controlled and the molar holdup of the reactor is fixed. $B =$ (a) 0, (b) 0.85 (H = Hopf bifurcation point), (c) 3.7, (d) 3.95, and (e) 5.

reactor is flow-controlled and the reactor is operated nonisothermally are given by

$$\frac{\mathrm{d}z}{\mathrm{d}t} = \frac{(x_e - z)(x_{af} - y_e)}{(x_e - y_e)} - Da_2 z e^{\theta} \tag{9a}$$

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = -\theta(1 + \beta Da_2) + BDa_2 z e^{\theta} \tag{9b}$$

where Da_2 is as defined for eq 7 and B, β, and θ are as defined in the case of fresh feed under flow control. Time is rendered dimensionless as for eq 7.

4.2.1. Steady-State Characteristics. The steady states are obtained by setting the right-hand sides of eqs 9a and b to 0. Eliminating θ between these equations, we obtain a scalar equation in z that describes the steady-state behavior of the coupled reactor−separator system as

$$g(z,\mathbf{p},Da_2) = \\ \log\left[\frac{(x_e - z)(x_{af} - y_e)}{(x_e - y_e)Da_2 z}\right] - \frac{B(x_e - z)(x_{af} - y_e)}{(x_e - y_e)(1 + \beta Da_2)} = 0 \quad (10)$$

Equation 10 describes the composition inside the reactor at steady state, with p representing the vector of parameters [x_e, y_e, B, β, x_{af}] and the Damkohler number Da_2 representing the bifurcation parameter.

We now discuss the dependence of z on Da_2 as determined by parameter p.

Static Instability. The solution of eq 10 consists of two branches, one corresponding to a reactant-rich recycle stream and the other to a reactant-lean recycle stream. For the adiabatic reactor, i.e., the case $\beta = 0$, and recycle of the reactant-rich stream, we can analytically show that the highest-order singularity that eq 10 satisfies is

$$g = \frac{\partial g}{\partial z} = \frac{\partial^2 g}{\partial z^2} = 0, \quad \frac{\partial g}{\partial Da_2} \neq 0, \quad \frac{\partial^3 g}{\partial z^3} \neq 0 \quad (11)$$

Hence, a maximum number of three solutions is feasible. However, for the particular values of x_e^2 and y_e^2 chosen in the current study (0.9 and 0.5, respectively), the highest-order singularity is always outside the feasible range. The highest-order singularity that lies within the feasible range for the particular values of x_e^2 and y_e^2 chosen satisfies

$$g = \frac{\partial g}{\partial z} = 0, \quad \frac{\partial^2 g}{\partial z^2} \neq 0, \quad \frac{\partial g}{\partial Da_2} \neq 0 \quad (12)$$

Therefore, a maximum number of two solutions is possible for the reactant-rich recycle and the choice of x_e^2 and y_e^2 in this paper.

The boundary limit set in this case at $z = y_e$ is given by $B = x_e/[y_e(x_{af} - y_e)] = B_{cr}$. The other critical value of B corresponding to the limit point on x_e tends to infinity, so the limit point can never be on x_e. In the present case, $B_{cr} = 3.6$, so for $B_{cr} > 3.6$, we have a limit point on the branch corresponding to the recycle of the reactant-rich stream.

When the reactant-lean stream is recycled, it can be shown that the highest-order singularity for the chosen set of parameters that eq 10 satisfies is

$$g = \frac{\partial g}{\partial z} = 0, \quad \frac{\partial^2 g}{\partial z^2} \neq 0, \quad \frac{\partial g}{\partial Da_2} \neq 0 \quad (13)$$

Using singularity theory arguments from Golubitsky and Schaeffer,[9] we conclude that, when the reactant-lean stream is recycled, the system behaves as if it has two solutions or no solution for different vectors p.

The boundary limit set in this case at $z = y_e$ is given by $B = x_e/[y_e(x_{af} - y_e)] = B_{cr}$. For the choice of (x_e^1, y_e^1), we obtain $B_{cr} = 0.416$, so when $B > 0.416$, there is a limit point on the branch corresponding to the recycle of the reactant-lean stream. As discussed for the reactant-rich recycle, the boundary limit set does not exist for $z = x_e^1$.

We define $g(z,p,Da_2) = g^1(z,\mathbf{p},Da_2)$ when $\mathbf{p} = [B, \beta, x_{af}, x_e^1, y_e^1]$ and $g(z,\mathbf{p},Da_2) = g^2(z,\mathbf{p},Da_2)$ when $\mathbf{p} = [B, \beta, x_{af}, x_e^2, y_e^2]$.

Table 3. Critical Values of the Parameter B and Critical Conditions Satisfied for Fixed Effluent from the Reactor[a]

critical value of B	criticality condition satisfied
0.4167	$g^1 = \frac{\partial g^1}{\partial z} = 0, z = y_e^1$
3.6	$g^2 = \frac{\partial g^2}{\partial z} = 0, z = y_e^2$
3.885	$g^1 = 0, z = y_e^1$ $g^2 = \frac{\partial g^2}{\partial z} = 0$
4.0545	$g^1 = 0, z = y_e^1$ $g^2 = 0, z = y_e^2$

[a] $(x_e^1, y_e^1) = (0.1, 0.4)$ and $(x_e^2, y_e^2) = (0.9, 0.5)$.

Table 4. Nature of the Bifurcation Diagram in Different Intervals of B When F Is Fixed[a]

B	characteristic of bifurcation diagram	representative bifurcation diagram
$(-\infty, 0.4167)$	2−1−0	Figure 5a
$(0.4167, 3.6)$	2−1−2−0	Figure 5b
$(3.6, 3.885)$	2−3−1−2−0	Figure 5c
$(3.885, 4.055)$	2−3−4−2−0	Figure 5d
$(4.055, \infty)$	2−3−4−2−0	Figure 5e

[a] $(x_e^1, y_e^1) = (0.1, 0.4)$ and $(x_e^2, y_e^2) = (0.9, 0.5)$.

Table 3 summarizes the critical values of B and the criticality conditions satisfied by the system. The behavior of the system between these critical values is summarized in Table 4. These tables are applicable for the case when F is flow-controlled and for the chosen values of (x_e^1, y_e^1) and (x_e^2, y_e^2).

Figure 5b shows the dependence of z on Da_2 for $B = 0.85$. We notice that the solution branch corresponding to the recycle of the reactant-rich stream exists over the region $0 < Da_2 < 0.65$. This branch is stable for all values of Da_2. The solution branch corresponding to the recycle of the reactant-lean stream exhibits a limit point at $Da_2 = 0.951$, and it exists for $0 < Da_2 < 0.951$. The solution branch exhibits two solutions for $0.9 < Da_2 < 0.951$. The system has two Hopf bifurcation points at $Da_2 = 0.95$ and $Da_2 = 0.917$ that are indicated by H in the figure. This introduces a region of dynamic instability on the stable branch. The system has two solutions in the region $0.9 < Da_2 < 0.951$. They are both unstable in $0.9 < Da_2 < 0.917$ and $0.95 < Da_2 < 0.951$. One of them is stable in $0.917 < Da_2 < 0.95$, and the other is unstable. The system as a whole admits two solutions in $0 < Da_2 < 0.65$. This arises because there is an overlap between the solution branches corresponding to the recycles of the reactant-lean and -rich streams. In the region $0.65 < Da_2 < 0.9$, the system admits one solution.

Figure 5c is for $B = 3.7$. Here, a limit point appears on the reactant-rich recycle stream branch. This occurs for a value of Da_2 that is lower than $Da_2(y_e^1)$. The two segments of the reactant-lean recycle branch are connected as in Figure 5e. This is not seen because we have restricted the scale on the x axis to 0.2, to depict the limit point clearly.

Figure 5d is for $B = 3.95$. Here, Da_2 at $z = y_e^1$ is lower than the Da_2 value where the limit point occurs when the reactant-rich stream is recycled.

In Figure 5e, Da_2 at $z = y_e^1$ occurs at a lower value than that for $z = y_e^2$. Figure 5e shows the dependence of z on Da_2 for $B = 5$. We notice that the solution branch corresponding to the recycle of the reactant-rich stream exists over the range $Da_2 = (0, 0.1)$. This branch has a limit point at $Da_2 = 0.1$. The range of Da_2 (0.08, 0.1) has two steady states on this branch, one of which is stable and the other unstable. The solution branch
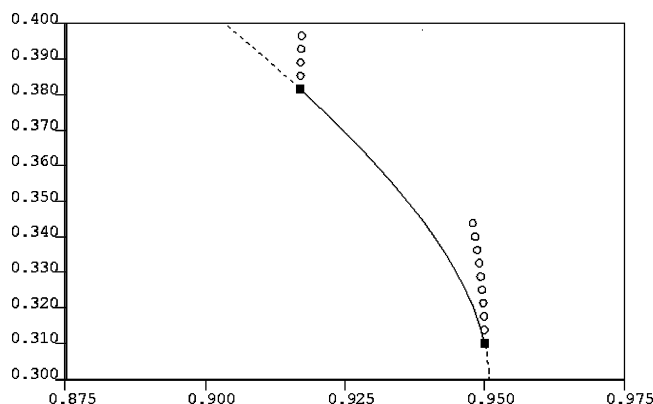
Figure 6. Dependency of z on Da_2, when the effluent from the reactor in a reactor–separator network is flow-controlled and the molar holdup of the reactor is fixed, showing the oscillatory branch of solutions (adiabatic reactor, $B = 0.85$) from the Hopf bifurcation points.

corresponding to the recycle of the reactant-lean stream exists over $0 < Da_2 < 0.41$. This branch is unstable for all Da_2 and exhibitss a limit point at $Da_2 = 0.41$. The system as a whole has three solutions for $0.072 < Da_2 < 0.08$, two of which are unstable and one stable, and four solutions for $0.08 < Da_2 < 0.1$, three of which are unstable and one stable.

Dynamic Instability. As discussed already, coupled reactor–separator systems are not known to show dynamic instability when the reactor is adiabatic. However, for $x_e < z < y_e$, when the reactant-lean stream is recycled, the system can exhibit dynamic instability. The stability of the two-dimensional system is governed by the eigenvalues of the Jacobian matrix.

The Hopf bifurcation point is governed by the conditions $\text{trace}(\mathbf{J}) = 0$, $\det(\mathbf{J}) > 0$ (where $\mathbf{J}$ is the Jacobian matrix). The Hopf points are given as the roots of $\text{trace}(\mathbf{J}) = 0$.

This yields

$$B = \left(\frac{1}{x_e - z}\right)\left(\frac{x_e - y_e}{x_{af} - y_e} + \frac{x_e}{z}\right) \tag{14a}$$

and $\det(\mathbf{J}) > 0$ [when $\text{trace}(\mathbf{J}) = 0$] results in

$$\frac{-x_e^2}{z^2} + \left(\frac{B}{z}\right)(x_e - z)^2 > 0 \tag{14b}$$

It can be established analytically that, when $x_e > y_e$, no solution exists that satisfies eqs 14a,b. On the contrary, when $y_e > x_e$, i.e., when the reactant-lean stream is being recycled, dynamic instability can be induced in the reactor–separator system, as we can solve the equation $\text{trace}(\mathbf{J}) = 0$ that satisfies the condition $\det(\mathbf{J}) > 0$. In Figure 6, we show the limit cycle branch emerging from the Hopf bifurcation points of Figure 5b, when the reactant-lean stream is recycled. The system admits two subcritical Hopf bifurcations at $Da_2 = 0.95$ and 0.91. Unstable oscillatory branches of solutions originate at these Hopf bifurcation points. Here again, the oscillations are induced solely by the coupling between the two units, as explained before.

In the Appendix, we demonstrate analytically that an isothermal reactor coupled to a flash under constant heating when the fresh feed rate is flow-controlled is dynamically and statically stable. In this model, we have assumed that the reactor has a finite holdup and that the energy balance is at a quasisteady state. This proof can also be extended to other flow configurations. The coupled system, however, shows dynamic instability when the reactor is nonisothermal. This is caused by the

nonlinearity induced by the Arrhenius temperature dependency and not by the coupling between the reactor and the separator.

Conclusions

In this work, we have studied the influence of an azeotrope on the nonlinear behavior of a reactor–separator network for two different modes of operation. In one of the modes, F_0, the fresh feed to the system, is flow-controlled, and in the other, F, which is the effluent from the reactor, is flow-controlled. The presence of an azeotrope gives rise to two different values of (x_e, y_e) that can be in equilibrium for isothermal and isobaric operation of a flash. As a consequence, the coupled system can admit two branches of steady-state solutions. These two branches are such that one corresponds to the recycle of the reactant-rich stream and the other corresponds to the recycle of the reactant-lean stream. For the chosen parameter sets of (x_e^1, y_e^1) and (x_e^2, y_e^2), the maximum number of steady states when F_0 (fresh feed to the system) is flow-controlled is three, and the maximum when F (effluent from the reactor) is flow-controlled is four.

Another significant result is that the coupled reactor–separator system admits multiple steady states even for endothermic reactions in an adiabatic reactor when the reactant-lean stream is recycled and F_0 is flow-controlled. The physical source of a positive feedback effect that gives rise to these multiple steady states has been identified. Exothermic reactions show multiple steady states when the reactant-rich stream is recycled. This corroborates the results of earlier research.[2]

Adiabatic reactors both in the stand-alone case and in reactor–separator networks are not known to exhibit dynamic instability. However, when the reactant-lean stream is recycled, the adiabatic reactor sustaining an exothermic reaction can exhibit sustained oscillations for both control strategies.

Acknowledgment

Appendix

The equations that govern the coupled system behavior for an isothermal reactor coupled to a flash heated at a constant rate Q_{fl} are described below. The assumptions are that the holdup in the flash is finite and the energy balance is at a quasisteady state.

Reactor. The material balance of reactant A is given by

$$\frac{d(M_R z)}{dt} = F_0 x_f + L x_e - F z - M_R k z$$

where

$$k = k_0 \exp(-E/RT_R) \tag{A1}$$

The total material balance is given by

$$M_{fl}\frac{dx_e}{dt} = F z - V y_e - L x_e \tag{A2}$$

For variable reactor holdup, the component material balance can be simplified by substituting eq A2 into eq A1

$$M_R\frac{dz}{dt} = F_o(x_f - z) + L(x_e - z) - M_R k z \tag{A3}$$

For constant reactor holdup, the component and total material balances simplify to

$$M_R \frac{dz}{dt} = F_0 x_f + L x_e - F z - M_R k z$$

where

$$k = k_0 \exp(-E/RT_R) \qquad (A4)$$

$$0 = F_o + L - F \qquad (A5)$$

Flash. The material balance for component A is given by

$$M_{fl} \frac{dx_e}{dt} = F z - V y_e - L x_e \qquad (A6)$$

Assuming constant holdup in the flash, the total material balance is

$$0 = F - V - L \qquad (A7)$$

The quasistatic energy balance of the flash yields

$$0 = F C_p (T_R - T_{fl}) - V \Delta h_v + Q_{fl} \qquad (A8)$$

The vapor flow rate V has to be equal to F_o in view of the overall material balance of the plant. F, the effluent from the CSTR, can be obtained from the energy balance (eq A8) as

$$F = \frac{F_o \Delta h - Q_{fl}}{C_p (T_R - T_{fl})} \qquad (A9)$$

and the liquid flow rate from the flash L is

$$L = F - F_o \qquad (A10)$$

The component and material balances can be written as

$$M_R \frac{dz}{dt} = F_o x_f + (F - F_o) x_e - F z - M_R k z \qquad (A11)$$

$$M_{fl} \frac{dx_e}{dt} = F z - F_o y_e - (F - F_o) x_e \qquad (A12)$$

The Jacobian is given by

$$J = \begin{pmatrix} -\dfrac{F}{M_R} - k & \dfrac{1}{M_R}\left[L + (x_e - z)\dfrac{dF}{dx_e} \right] \\[3mm] \dfrac{F}{M_{fl}} & \dfrac{1}{M_{fl}}\left[-L - F_o \dfrac{dy_e}{dx_e} - (x_e - z)\dfrac{dF}{dx_e} \right] \end{pmatrix} \qquad (A13)$$

From eq A8, we obtain

$$\frac{dF}{dx_e} = \frac{F}{(T_R - T_{fl})} \frac{dT_{fl}}{dx_e} \quad (T_R > T_{fl}) \qquad (A14)$$

Necessary and sufficient conditions for the stability of a second-order system are

$$\det(J) > 0 \qquad (A15)$$

$$\text{trace}(J) < 0 \qquad (A16)$$

We know that dy_e/dx_e is always positive for thermodynamically stable systems and dT_{fl}/dx_e is positive for compositions $z \in II_R$ and negative for compositions $z \in II_L$.

From eq A14, the sign of dF/dx_e is same as the sign of dT_{fl}/dx_e. Moreover, the product $(x_e - z)dF/dx_e$ is always positive throughout the range of compositions. It is readily shown that the trace of the Jacobian is always less than 0 and the determinant of the Jacobian is always greater than 0. This ensures that the steady states are stable.

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