Steady-State Multiplicity in an Adiabatic Continuous Stirred Tank Reactor with Vapor Recycle

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The multiplicity features of a continuous stirred tank reactor with vapor recycle have been studied for a dimerization reaction with second-order kinetics. Such reaction systems are common in the polymer industry. The aim of the analysis is to provide a simple design methodology that will ensure safe operation of the reactor. It is shown that solutions with and without vapor recycle exist. The bifurcation set for the system is calculated, and 11 different bifurcation diagrams arise. A linear relationship exists between the system parameter values, when these are normalized by their values at the ignition point. This leads to a simple method for defining a safe operating point for the system under a defined disturbance.
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Introduction

Reaction systems that utilize continuous stirred tank reactors (CSTRs) with recycle of unreacted components are widely used in the polymerization industry.[1] The reaction frequently takes place in an inert solvent. A simulation study of such a system using Aspen Plus™ indicated the possibility of multiple steady-state behavior; this behavior was confirmed by performing repeated simulations with differing parameter values. As has been shown by Vadapalli and Seader,[2] calculation using simulators of systems that show bifurcation can be difficult. These authors developed code to add to the Aspen Plus™ simulator that implements an arc length continuation. Then, they were able to plot bifurcation diagrams of an adiabatic CSTR and a homogeneous azeotropic distillation.

A number of authors have studied systems with reaction and evaporative cooling. Rodrguez et al.[3] analyzed a reactive flash with constant split fraction and no recycle and showed that the ratio of the activation energy to the heat of vaporization must be greater than one for multiplicity to occur. Waschler et al.[4] studied an isobaric reactive flash with vapor recycle. They considered a binary system with equimolar reaction A → B. These authors present elegant results for the bifurcation behavior of this system for zero-, first-, and second-order kinetics, under the assumption that the Clausius–Clapeyron equation can be used to describe the vapor–liquid equilibrium, and that the heats of vaporization of the two species are equal. The authors do not consider the case where vapor does not form. Solorzano and Ray[5] considered the dynamic behavior of the same system including jacket cooling and included the cases of volatile reactant, volatile or nonvolatile product (liquid or solid), and volatile solvent. They considered the case of first-order reaction. In an exhaustive analysis, they showed that up to seven steady states are possible.

In this article, an analytic model is developed for a ternary system with a nonvolatile solvent, where the vapor pressures of the reactant and product are different. The reaction considered is the dimerization of ethylene to 1-butene, with second-order kinetics. This leads to a change in moles over the reactor. It is shown that cases where vapor does or does not form are possible. The bifurcation behavior of this system is presented, and a methodology for designing for safe control of the system is given.

Reaction System

The reactor studied is shown in Figure 1.

The make-up M consists of pure ethylene vapor that joins the recycled vapor V. The mixture is cooled to below its bubble point, and mixed with a solvent stream S consisting of pure 1-octene. The feed enters the adiabatic reactor where the irreversible second-order reaction

$2C_2H_4 \rightarrow C_4H_8$

occurs in the liquid phase. 1-Butene is assumed to be the only product. A liquid product is removed from the reactor, and the vapor recycled. The holdup and pressure in the reactor are assumed to be held constant by a control system, and the condenser duty is controlled in such a way that the temperature into the reactor is constant.

System Models

Mole balances are written for the three components

$$Px_1 = M - k(T_R)e^{\frac{E}{RT_R}(1-T_R/T)}V_1x_1^2 \quad (1)$$

$$Px_2 = \frac{k(T_R)e^{\frac{E}{RT_R}(1-T_R/T)}V_1x_1^2}{2} \quad (2)$$

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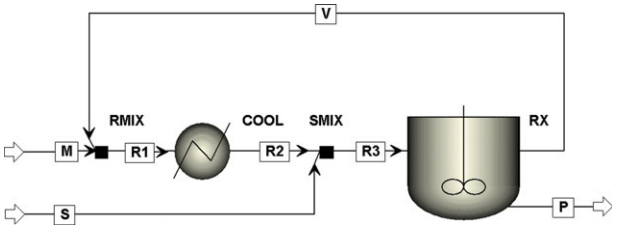

Figure 1. Reactor system.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$Px_3 = S \tag{3}$$

Elimination of P, x_2, and x_3 together with nondimensionalization yields

$$\mathrm{Da}f\left(x_1^3 - 2x_1^2\right) - 2\left(1 + \frac{\mathrm{Da}}{\mathrm{Ds}}\right)x_1 + 2 = 0 \tag{4}$$

where

$$\theta = \frac{T}{T_\mathrm{R}}, \quad \mathrm{Da} = \frac{kV_\mathrm{l}}{M}, \quad \gamma = \frac{E}{RT_\mathrm{R}}, \quad \mathrm{Ds} = \frac{kV_\mathrm{l}}{S}, \quad f(\theta) = \exp\left(\gamma\left(1 - \frac{1}{\theta}\right)\right) \tag{5}$$

The reference temperature T_R is taken to be the inlet temperature to the reactor.

One further equation is required to solve the system. Two cases arise depending on whether or not vapor is formed in the reactor.

Vapor Recycle Absent

In this case, the necessary equation is the energy balance over the reactor

$$(Mm + Ss)c_\mathrm{p}(T - T_\mathrm{R}) - kV_\mathrm{l}fx_1^2(-\Delta H_\mathrm{R}) = 0 \tag{6}$$

Equation 6 may be written in terms of nondimensional quantities as

$$\left(1 + 4\frac{\mathrm{Da}}{\mathrm{Ds}}\right)(\theta - 1) - \beta f\mathrm{Da}x_1^2 = 0 \tag{7}$$

where

$$\beta = \frac{-\Delta H_\mathrm{R}}{mc_\mathrm{p}T_\mathrm{R}} \tag{8}$$

The coefficient 4 in the first term of Eq. 7 is the ratio of molecular weights of the 1-octene solvent and ethylene.

Equations 4 and 7 may be combined to yield the following equation for θ

$$\mathrm{Ds}(1 - \theta + 2\beta)\sqrt{\frac{(\theta - 1)}{f}}\lambda^3 + 2\mathrm{Ds}(\theta - 1 + \beta)\lambda^2 - 6\sqrt{\frac{(\theta - 1)}{f}}\lambda + 8 = 0 \tag{9}$$

where

$$\lambda^2 = \left(1 + 4\frac{\mathrm{Da}}{\mathrm{Ds}}\right)\frac{1}{\beta\mathrm{Da}} \tag{10}$$

The model has four parameters. The solution of Eq. 9 will be referred to as the no-vapor solution.

Vapor Recycle Present

For this case, the vapor–liquid equilibrium in the reactor determines the concentrations of ethylene and 1-butene. Due to its much lower volatility, the solvent is assumed to be absent in the vapor, and the vapor–liquid equilibrium relationships are

$$y_1 = k_1x_1, \quad y_2 = k_2x_2 \tag{11}$$

with

$$y_1 + y_2 = k_1x_1 + k_2x_2 = 1 \tag{12}$$

Equation 12 may be used together with the mole balances to yield a second relationship for the Damkohler number

$$\mathrm{Da} = \frac{2\mathrm{Ds}(k_1x_1 - 1)}{\mathrm{Ds}fk_1x_1^3 - \mathrm{Ds}f(k_2 + 1)x_1^2 - 2k_1x_1 + 2} \tag{13}$$

Equations 4 and 13 may be combined to give the following cubic equation in x_1, parameterized by θ

$$\mathrm{Ds}f(k_2 - k_1)x_1^3 + \mathrm{Ds}f(1 - k_2)x_1^2 - 2k_1x_1 + 2 = 0 \tag{14}$$

The solution for Eq. 14 is referred to as the vapor solution.

The equilibrium constants k_i are given by an Antoine type equation

$$k_i = e^{a_i - b_i/\theta} \tag{15}$$

Due to the vapor–liquid equilibrium expressions (15), this model has seven parameters.

The energy balance is not needed to calculate the temperature and ethylene mole fraction, but it is required to calculate the vapor flow rate. For the existence of vapor in the reactor, it is necessary that the energy removed by the liquid product is less than that generated by reaction, or

$$\left(1 + 4\frac{\mathrm{Da}}{\mathrm{Ds}}\right)(\theta - 1) - \beta f\mathrm{Da}\ x_1^2 \le 0 \tag{16}$$

If the equality holds in Eq. 16, the vapor and no-vapor solutions are identical. If the inequality does not hold vapor will not be produced, and the calculated solution is not physically realistic. If the inequality does hold, then vapor is formed and provides an additional mechanism for energy removal, satisfying the energy balance for the system.

Results

Due to the large number of parameters in the equations, the results presented here do not consider variations in the nondimensional enthalpy of reaction and the vapor–liquid equilibrium expression coefficients. This reduces the number of parameters in each model to three: the two Damkohler numbers and the dimensionless activation energy.

The base case values for the results in this section are given in Table 1. The activation energy is typical for the reaction catalyzed by transition metal complexes, as listed by Pillai et al.[6] The effects of variation in this quantity are discussed later.

Table 1. Base Case Values

Parameter	Value
T_R (K)	300
E (J/mol)	50,000
γ	20.097
β	2.76
a_1	2.63
b_1	2.06
a_2	3.99
b_2	5.60

The coefficients for the equilibrium constants in Eq. 15 have been fitted from Aspen Plus™ simulation results, as has the nondimensional enthalpy of reaction. The coefficients b_i are related to the heats of vaporization by the equation

$$b_i = \frac{\Delta H_v}{RT_R} \tag{17}$$

As shown in Table 1, the calculated heats of vaporization are quite different for the two components, implying the assumption of equal heats of vaporization made by Waschler et al.[4] would not be valid in this case.

Figure 2 shows the solution of Eqs. 9 and 14 for Ds = 0.2 and $\gamma = 20.097$. The solution with vapor flow (indicated by the solid line) yields the classic S-shaped diagram, whereas the no-vapor solution (indicated by the dashed line) is a mushroom. Figure 2 has been drawn on a logarithmic scale to show the entire behavior. However, the area of practical interest is in a more limited range of Damkohler numbers. This range is shown in Figure 3.

The vapor and no-vapor branches do not intersect at low temperatures, but there is an intersection at θ near 1.7. At higher temperatures, the inequality (16) holds and no vapor is formed. The vapor solution is stable in a small range of Damkohler numbers from 0.144 to 0.165. If the Damkohler number is increased further ignition to the no-vapor solution occurs. The no-vapor solution is stable from large Da down to a Da of 0.242. At this point, reducing the Damkohler number further results in ignition.

By varying the parameter Ds, different bifurcation diagrams may be obtained. Figure 4 shows the six bifurcation diagrams that occur for the base case value of the activation energy. For clarity, different scales are used on each figure,

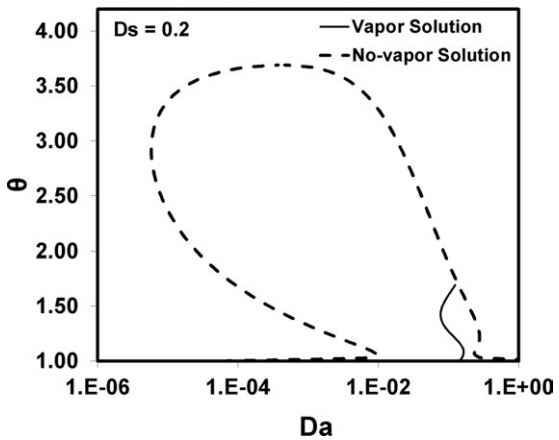

Figure 2. Bifurcation diagram for Ds 0.2: solid lines—vapor solution and dashed lines—no vapor solution.

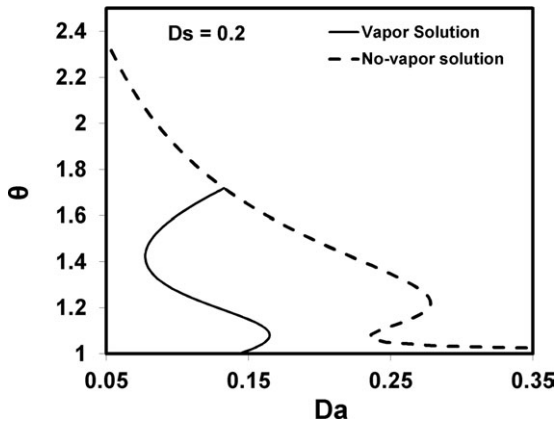

Figure 3. Bifurcation diagram for Ds 0.2—reduced Da range: solid lines—vapor solution and dashed lines—no vapor solution.

and the no-vapor solution at very low Damkohler numbers has been omitted.

The vapor solution has an S shape for values of Ds from 0.146 to 0.97 (Figure 4d). At higher values of Ds, the ignition point temperature is below the inlet temperature, which is not physically realistic. Then, the vapor solution has only an extinction point (Figure 4f).

The no-vapor and vapor ignition solutions are tangent to each other near a Ds value of 0.146. For values of Ds less than this value, the vapor solution is discontinuous (Figures 4b,c). The vapor solution ceases to exist where it intersects the no-vapor solution as a result of inequality (16) holding. There can be one, two, or three Damkohler numbers at which the vapor solution ceases to exist.

The solution without vapor flow is an isola for values of Ds less than 0.092 (Figures 4a,b); for values greater than this up to 0.35, the solution is a mushroom (Figures 4c,d). At a Ds value of 0.35 hysteresis occurs for the ignition and extinction points on the right-hand side of the curve (Figure 4e).

One, two, three, four, or five solutions are possible. The unusual presence of an even number of solutions is caused by the loss or gain of one solution when the vapor and no-vapor solutions intersect, as well as when a limit point occurs at a temperature lower than the feed temperature.

Classification of the Possible Bifurcation Diagrams and Maximum Number of Solutions

To obtain a better understanding of the system, the parameter regions corresponding to different bifurcation diagrams have been determined, following the method proposed by Balakotaiah and Luss.[7] The analysis above shows that the model exhibits hysteresis and isola varieties, together with boundary limit sets and boundary tangent sets. These varieties and sets divide the parameter space into regions with qualitatively different bifurcation diagrams are described later.

When the hysteresis variety is crossed for a certain set of parameters typically two limit points appear or disappear as a hysteresis loop forms or collapses. For a system defined by

$$h(y, \mu, \boldsymbol{p}) = 0 \tag{18}$$

where y is an operating variable, μ a slowly changing operating variable or bifurcation variable, and $\boldsymbol{p}$ is a vector

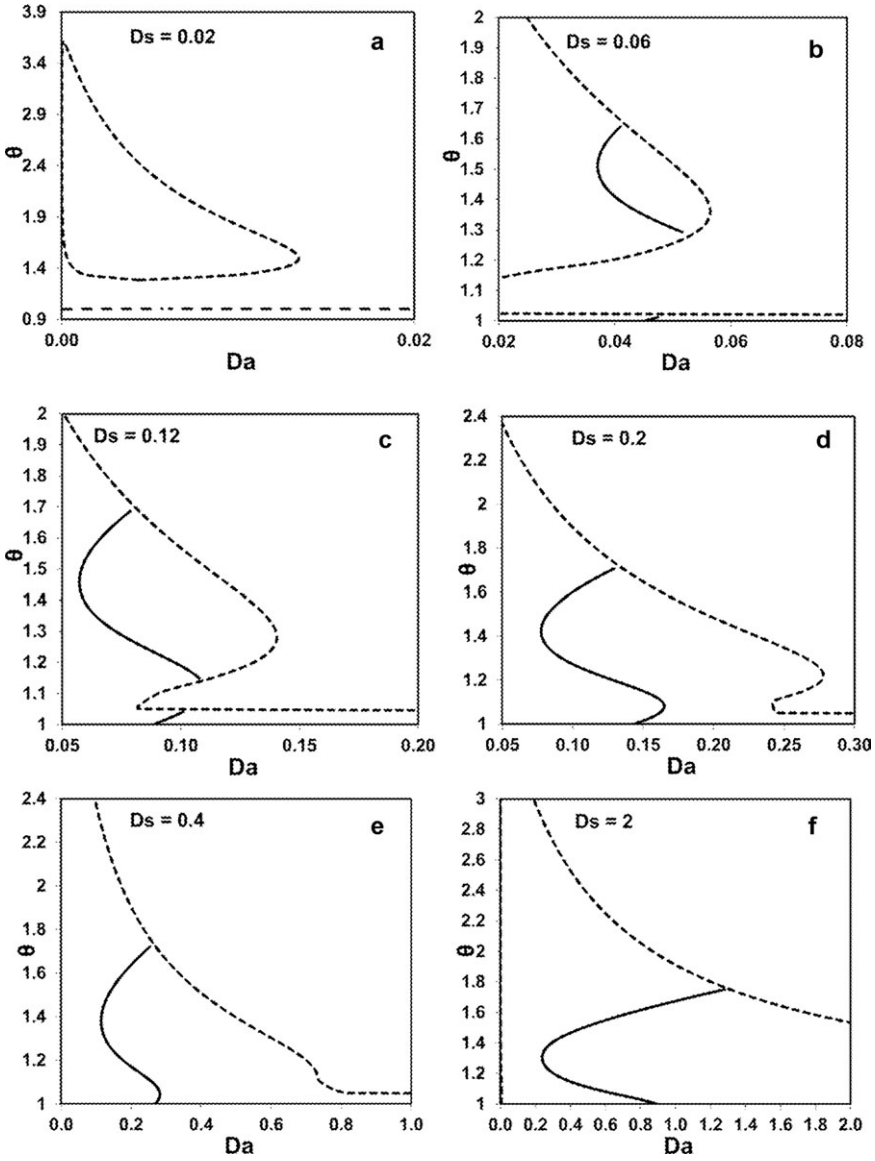

Figure 4. Bifurcation diagrams for base case activation energy: solid lines—vapor solution and dashed lines—no vapor solution.

of parameters, the hysteresis variety is found by solving the set of equations

$$h(y,\mu,\boldsymbol{p}) = \frac{\partial h}{\partial y}(y,\mu,\boldsymbol{p}) = \frac{\partial^2 h}{\partial y^2}(y,\mu,\boldsymbol{p}) = 0 \tag{19}$$

When the isola variety is crossed typically two limit points appear or disappear and the bifurcation diagram either separates locally into two isolated curves or an isolated branch of solutions appear or disappear. The isola variety is found by solving the set of equations

$$h(y,\mu,\boldsymbol{p}) = \frac{\partial h}{\partial y}(y,\mu,\boldsymbol{p}) = \frac{\partial h}{\partial \mu}(y,\mu,\boldsymbol{p}) = 0 \tag{20}$$

The boundary limit set consists of all possible parameter values at which a limit point exists at a feasible boundary or

$$h(y,\mu,\boldsymbol{p}) = \frac{\partial h}{\partial y}(y,\mu,\boldsymbol{p}) = 0 \tag{21}$$

at $y = y_b$ or $\mu = \mu_b$ where b refers to a lower or upper feasible boundary.

For this problem, the boundary limit sets are associated with the vapor solution crossing either $\theta = 1$or the condition (16).

Balakotaiah and Luss[7] define the boundary tangent set at the set of parameters at which the bifurcation becomes tangential to the y boundary. Here, this definition is extended to cover the current case of a system defined by two separate sets of equations that may intersect. Thus, for two functions h_1 and h_2, the boundary tangent set is found from

$$h(y,\mu,\boldsymbol{p}) = \frac{\partial h_1}{\partial y}(y,\mu,\boldsymbol{p}) = h_2(y,\mu,\boldsymbol{p}) = \frac{\partial h_2}{\partial y}(y,\mu,\boldsymbol{p}) = 0 \tag{22}$$

The boundary tangent sets are associated with the vapor and no-vapor solutions becoming tangent to each other; the crossing of this set leads to an appearance or disappearance of the vapor solution.

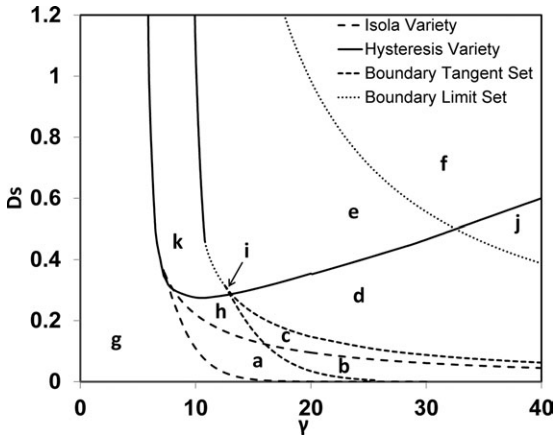

Figure 5. Global classification of the possible bifurcation diagrams.

The analysis is performed with the Damkohler number as the bifurcation parameter and the dimensionless activation energy and solvent Damkohler numbers as parameters. Solutions for equations (19)–(22) are found using a numerical search procedure, with the required derivatives calculated analytically by differentiation of Eqs. 9 and 14. The resulting classification of the bifurcation diagrams is shown in Figure 5.

The no-vapor solution exhibits a hysteresis variety, which is continuous; the near vertical left-hand side of this variety is associated with hysteresis at low Da, whereas the right-hand side indicates hysteresis at high Da. There are two branches of the isola variety; the upper isola branch is associated with the appearance of the isola, whereas the lower branch delineates the disappearance of the isola.

The vapor solution exhibits a discontinuous hysteresis variety. There exist two boundary limit sets. The leftmost of these arises when a limit point is at the feed temperature, whereas the rightmost is associated with a limit point occurring at the intersection with the no-vapor solution.

The boundary tangent set has two branches; the branches arise when the vapor and no-vapor solutions are tangent at low and high temperatures, respectively.

Eleven qualitatively different bifurcation diagrams are found, indicated by the letters a–k in Figure 5. The letters a–f correspond to bifurcation diagrams shown in Figure 4, whereas bifurcation diagrams corresponding to letters g–k are shown in Figure 6. The latter do not occur for the base case activation energy.

The maximum number of solutions to the equations is determined by calculating the highest codimension singularity of the model, defined as that n for which the function and its first n derivatives vanish. The hysteresis varieties shown in Figure 5 define the loci for which the second

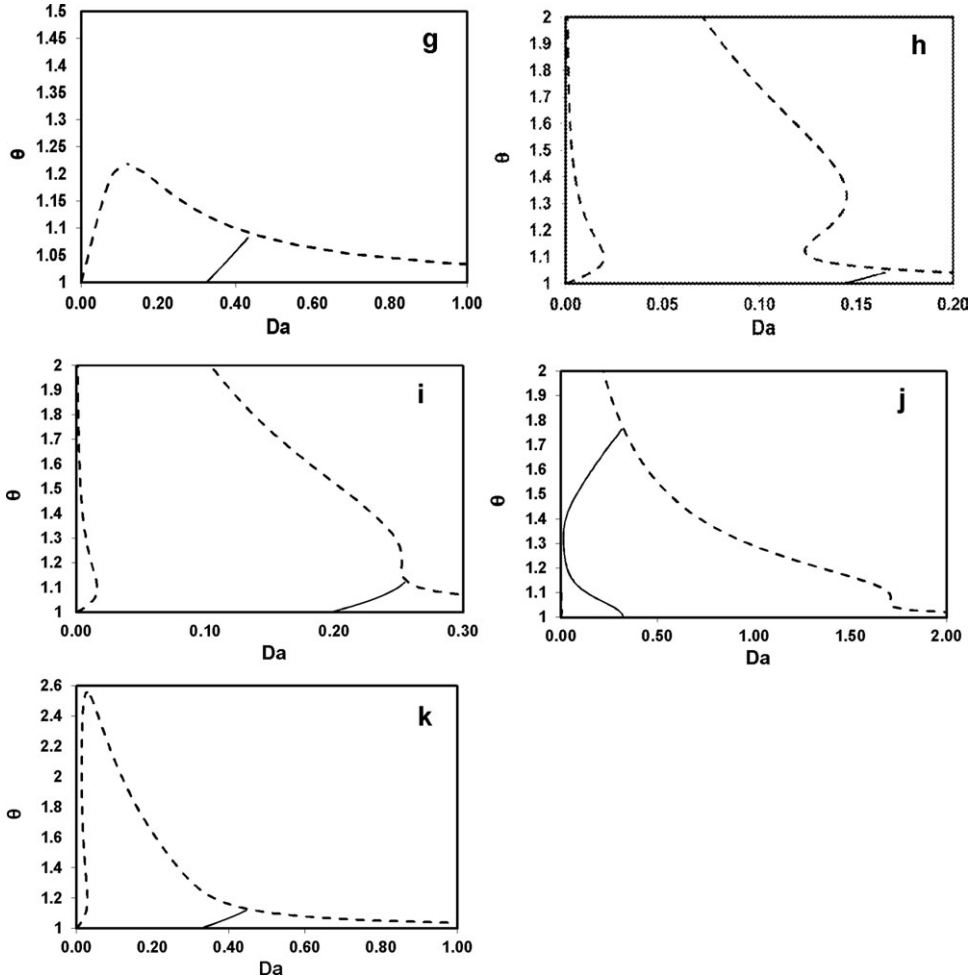

Figure 6. Bifurcation diagrams not found for base case: solid lines—vapor solution and dashed lines—no vapor solution.

Letters refer to regions shown in Figure 5.

derivatives are zero. The third derivatives with respect to θ were computed along the hysteresis varieties. In no case did this derivative vanish, indicating that the highest codimension singularity for both vapor and no-vapor solutions is two, that is, each model can have at most three solutions. It is the combination of the two models that give rise to five solutions for some parameters. It is, however, possible that a higher codimension singularity exists for other values of the dimensionless enthalpy of reaction and equilibrium constant coefficients.

Discussion

The analysis above agrees with the results of Solorzano and Ray[5] in showing up to five steady states with two separated regions of three steady states. The results for the vapor solution agree qualitatively with those given by Waschler et al.,[4] although the latter authors do not give values for the case of second-order reaction. These authors do not consider the no-vapor case.

Practical Implications

The design of the system is to operate on the vapor solution; in this section, safe operation of the reactor in this region is analyzed further.

Operation of the system at low temperatures with vapor flow is limited by both the presence of the ignition point in this curve and the loss of vapor flow, when the boundary limit and tangent sets are crossed. For the base case activation energy, these limits are Ds = 0.146 and $\theta = 1.1$ (corresponding to the boundary limit set) and Ds = 0.97 and $\theta = 1$ (corresponding to the boundary tangent set).

A design methodology has been developed for this region in which a vapor solution ignition point exists. The method is based on the result (shown in the Appendix) that near the ignition point, the following relationship holds

$$\frac{\sigma}{\sigma_{ig}} - 1 = -\frac{2 - x_1}{g(2 - x_1) + 3x_1 - 4}\left(\frac{Da}{Da_{ig}} - 1\right) \qquad (23)$$

where $\sigma = 1 + \frac{Da}{Ds}$, $\sigma_{ig} = \sigma$ at ignition point, Da_{ig} = Damkohler number at ignition point, Ds_{ig} = Ds at ignition point; and $g = \gamma/b_1$

The first term on the right-hand side of Eq. 23 is bounded between $\frac{1}{g-2}$ and $\frac{1}{g-1}$. For the base case values, g is 9.74, and this term is between 0.114 and 0.129. For the purposes of the design procedure shown here, this value will be considered constant at 0.12, and Eq. 23 is written as

$$\frac{\sigma}{\sigma_{ig}} = 1.12 - 0.12\frac{Da}{Da_{ig}} \qquad (24)$$

Figure 7 shows the values of Da_{ig} and σ_{ig} plotted against the dimensionless temperature. The figure is drawn for the base case activation energy. For other activation energies Eqs. A6 and A7 may be used.

The design procedure is shown below with an example:

1. Select a reactor inlet temperature (for example 300 K)
2. Select a reactor operating temperature (e.g., 315 K)
3. Calculate the dimensionless temperature (1.05)
4. Read off the ignition point values from Figure 7 (σ_{ig} 1.72, Da_{ig} 0.26)
5. Specify the maximum expected fractional reduction η in the make-up flow to the reactor (e.g., 0.5)

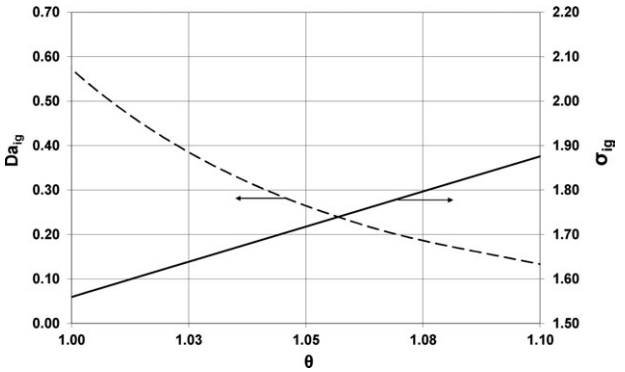

Figure 7. Da, σ at ignition vs. dimensionless temperature.

6. For safety $Da/Da_{ig} > 1/\eta$ (2)
7. The design Da is then Da_{ig}/η (0.52)
8. Using Eq. 24 calculate σ/σ_{ig} (0.88)
9. The design σ is then $\sigma/\sigma_{ig} * \sigma_{ig}$ (1.51)
10. The design Ds is then $Da/(\sigma - 1)$ (0.52/0.51 = 1.02).
11. Using the relationship that Da/Ds = S/M, the design operation is with a solvent to make-up ratio of 1.02. Ignition will occur at a flow rate of half the nominal, when the solvent to make-up ratio is 0.36.

Without knowledge of the location of the ignition point, the designer may specify an operating point too close to the ignition point, even if an accurate simulation model of the system is used. For example, suppose the Damkohler number is specified as 0.38 and the solvent Damkohler number as 0.61 (S/M = 0.62). Ignition would then occur with a reduction in make-up flow of only 25%.

Conclusions

The multiplicity behavior of a CSTR with vapor recycle has been studied using singularity theory with a distinguished parameter. The bifurcation parameter used is the Damkohler number, and the parameter space was divided into areas with unique bifurcation diagrams, using the dimensionless activation energy and solvent Damkohler number as parameters. The system can operate with or without vapor flow, and interesting bifurcations occur when these two solutions intersect. The system exhibits one to five steady states.

A mapping of the system parameters at the ignition point, together with a relationship for the same parameters as a function of the ignition point values, leads to a straight-forward method for developing a design for safe operation. Although the figure presented here is only valid for the particular system considered, the calculations are not too complex to repeat for other systems.

As a topic for future research, the dynamics of the system would be of great interest. In particular, the stability of the branches where the vapor and no-vapor solutions intersect has not yet been established.

Acknowledgments

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Notation

a_i = coefficient for calculation of equilibrium constant
b_i = coefficient for calculation of equilibrium constant

c_p = specific heat capacity, J/g/K
Da = Damkohler number based on make-up flow
Ds = Damkohler number based on solvent flow
E = activation energy of the reaction, J/mol
f = activation energy function
$g = \frac{\gamma}{b_1}$
h = steady-state function (Eq. 18)
h_1, h_2 = steady-state functions (Eq. 22)
k_1 = equilibrium constant for ethylene
k_{10} = equilibrium constant for ethylene at feed temperature
k_2 = equilibrium constant for 1-butene
$k(T_R)$ = reaction rate constant at temperature T_R, mol/m^3/s
m = molecular mass of ethylene, g/mol
M = molar flow rate of make-up, mol/s
P = molar flow rate of reactor effluent, mol/s
R = the universal gas constant, J/mol/K
T_R = inlet temperature to the reactor, K
s = molecular mass of octene, g/mol
S = molar flow rate of solvent, mol/s
V = molar flow rate of vapor, mol/s
V_1 = volume of liquid in the reactor, m^3
x_1 = liquid phase mole fraction of reactant
x_2 = liquid phase mole fraction of product
x_3 = liquid phase mole fraction of solvent
y = operating variable
y_b = operating variable at boundary of feasible region
y_1 = vapor phase mole fraction of reactant
y_2 = vapor phase mole fraction of product

Greek

β = dimensionless enthalpy of reaction
ΔH_R = enthalpy of reaction, J/mol
ΔH_v = enthalpy of vaporization, J/mol
γ = dimensionless activation energy
η = expected fractional reduction in make-up flow
λ = Dimensionless quantity (Eq. 10)
μ = bifurcation variable
μ_b = bifurcation variable at boundary of feasible region
θ = dimensionless temperature
σ = total feed to reactor divided by make-up flow

Literature Cited

1. Forestière A, Olivier-Bourbigou H, Saussine L. Oligomerization of monoolefins by homogeneous catalysts. *Oil Gas Sci Technol Rev IFP*. 2009;64:649–667.
2. Vadapalli A, Seader JD. A generalized framework for computing bifurcation diagrams using process simulation programs. *Comput Chem Eng*. 2001;25; 445–464.
3. Rodrguez I, Zheng A, Malone M. Parametric dependence of solution multiplicity in reactive flashes. *Chem Eng Sci*. 2004;59:1589–1600.
4. Waschler R, Pushpavanamb S, Kienlea A. Multiple steady states in two-phase reactors under boiling conditions. *Chem Eng Sci*. 2003;58: 2203–2214.
5. Solorzano M, Ray WH. Multiplicity and stability of chemical reactors with evaporative cooling. *Ind Eng Chem Res*. 2008;47:9025–9039.
6. Pillai SM, Ravindranathan M, Sivaram S. Dimerization of ethylene and propylene catalyzed by transition-metal complexes. *Chem Rev*. 1986; 86:353–399.
7. Balakotaiah V, Luss D. Global analysis of the multiplicity features of multi-reaction lumped parameter systems. *Chem Eng Sci*. 1984;39: 865–881.

Appendix

To derive Eq. 23, the system is simplified by assuming that there is no 1-butene in the vapor. This is a reasonable assumption for the relatively low temperatures at and below the ignition point, given the lower volatility of the 1-butene compared to ethylene.

Under this assumption, the mole fraction of ethylene in the liquid is given by

$$x_1 = \frac{1}{k_1} \tag{A1}$$

The equilibrium constant k_1 may be written as

$$k_1 = k_{10}\exp\left(b_1\left(1-\frac{1}{\theta}\right)\right) = k_{10}f^{\frac{b_1}{\gamma}} = k_{10}f^{1/g} \tag{A2}$$

where

$$k_{10} = \exp(a_1 - b_1) \tag{A3}$$

Equations A1 and A2 give

$$f = (k_{10}x_1)^{-g} \tag{A4}$$

Substituting this relationship into Eq. 4 gives a single equation for the ethylene mole fraction

$$F = \frac{\mathrm{Da}(x_1^3 - 2x_1^3)}{(k_{10}x_1)^g}2\sigma x_1 + 2 = 0 \tag{A5}$$

Differentiation of Eq. A5 with respect to x_1 and solution of the resulting two equations gives the following relationships at the ignition point

$$\mathrm{Da}_{ig} = \frac{-2(k_{10}x_1)^g}{(g-2)x_1^3 + 2(1-g)x_1^2} \tag{A6}$$

$$\sigma_{ig} = \frac{(g-3)x_1 - 2g + 4}{(g-2)x_1^2 + 2(1-g)x_1} \tag{A7}$$

The derivative $d\sigma/d\mathrm{Da}$ may be found from the expression

$$\frac{d\sigma}{d\mathrm{Da}} = -\frac{\frac{\partial F}{\partial \mathrm{Da}}}{\frac{\partial F}{\partial \sigma}} = \frac{x_1^2 - 2x_1}{-2(k_{10}x_1)^g} \tag{A8}$$

Multiplication of this expression by Eq. A2 and division by Eq. A3 yields the following expression for the derivative $d\sigma/d\mathrm{Da}$ at the ignition point

$$\frac{d\sigma}{d\mathrm{Da}} = -\frac{2-x_1}{g(2-x_1) + 3x_1 - 4}\frac{\sigma_{ig}}{\mathrm{Da}_{ig}} \tag{A9}$$

The aim of the calculation is to compare operation at a particular temperature with operation at the same temperature at the ignition point. Equation A4 implies that a constant mole fraction trajectory is equivalent to a constant temperature trajectory. The right-hand side of Eq. A9 is, therefore, constant for a particular temperature, and the left-hand side can be replaced by $(\sigma - \sigma_{ig})/(\mathrm{Da} - \mathrm{Da}_{ig})$. This yields Eq. 23.

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