DIABATIC CONTINUOUS STIRRED TANK REACTORS

MODULE
9

The purpose of this module is to understand the steady-state and dynamic behavior of jacketed continuous stirred tank reactors (CSTRs), also referred to as diabatic CSTRs. After reviewing this module the student should be able to

- Understand the assumptions made in developing the classic CSTR model
- Understand the possible steady-state behavior based on an analysis of the heat generated by reaction and removed through the cooling jacket
- Understand what is meant by multiple steady-states. Develop the *hysteresis* (ignition/extinction behavior) input-output diagrams based on analysis of the heat generation and removal curves. Relate these to saddle-node and hysteresis bifurcations from Chapter 15
- Understand the dynamic behavior by linearization of nonlinear dynamic equations followed by eigenvalue analysis
- Use phase-plane analysis to understand which steady-state a given initial condition will converge to
- Realize the possibility of limit cycle behavior (Hopf bifurcations)

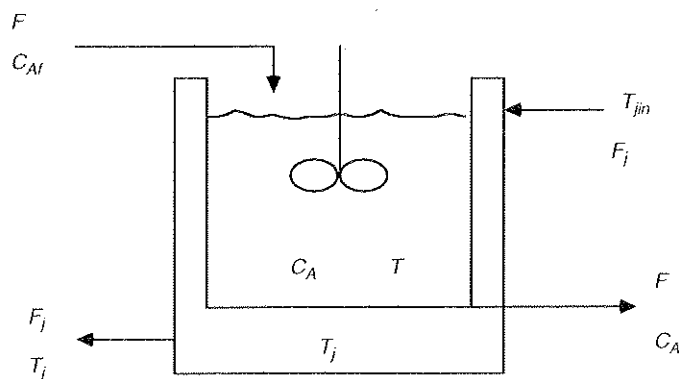The major sections in this module are:

FIGURE M9.1   Continuous stirred tank reactor with cooling jacket.

M9.7   Understanding Multiple Steady-State Behavior

M9.8   Further Complexities

M9.9   Dimensionless Model

M9.1   BACKGROUND

The most important unit operation in a chemical process is generally a chemical reactor. Chemical reactions are either exothermic (release energy) or endothermic (require energy input) and therefore require that energy either be removed or added to the reactor for a constant temperature to be maintained. Exothermic reactions are the most interesting systems to study because of potential safety problems (rapid increases in temperature, sometimes called "ignition" behavior) and the possibility of exotic behavior such as multiple steady-states (for the same value of the input variable there may be several possible values of the output variable).

In this module we consider a perfectly mixed, continuously stirred tank reactor (CSTR),[1] shown in Figure M9.1. The case of a single, first-order exothermic irreversible reaction, $A \to B$, will be studied. We will find that very interesting behavior can arise in such a simple system.

In Figure M9.1 we see that a fluid stream is continuously fed to the reactor and another fluid stream is continuously removed from the reactor. Since the reactor is perfectly mixed, the exit stream has the same concentration and temperature as the reactor fluid. Notice that a jacket surrounding the reactor also has feed and exit streams. The jacket is assumed to be perfectly mixed and at a lower temperature than the reactor. Energy then passes through the reactor walls into the jacket, removing the heat generated by reaction.

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[1]Sometimes this type of reactor is called "non-adiabatic." The term adiabatic means "no heat loss," so the term *non-adiabatic* constitutes a double negative (This point has been discussed by Barduhn, *Chem. Eng. Education*, 19, 171 (1985)). We prefer to use *diabatic* to describe this reactor.

There are many examples of reactors in industry similar to this one. Examples include various types of polymerization reactors, which produce polymers that are used in plastic products such as polystyrene coolers or plastic bottles. The industrial reactors typically have more complicated kinetics than we study in this module, but the characteristic behavior is similar.

M9.2   THE MODELING EQUATIONS

For simplicity we assume that the cooling jacket temperature can be directly manipulated, so that an energy balance around the jacket is not required. We also make the following assumptions:

- Perfect mixing (product stream values are the same as the bulk reactor fluid)
- Constant volume
- Constant parameter values

The constant volume and parameter value assumptions can easily be relaxed by the reader for further study.

M9.2.1   Parameters and Variables

The parameters and variables that will appear in the modeling equations are listed below for convenience.

A	Area for heat exchange
C_A	Concentration of A in reactor
C_{Af}	Concentration of A in feed stream
c_p	Heat capacity (energy/mass*temperature)
F	Volumetric flowrate (volume/time)
k_0	Pre-exponential factor (time^{-1})
R	Ideal gas constant (energy/mol*temperature)
r	Rate of reaction per unit volume (mol/volume*time)
t	Time
T	Reactor temperature
T_f	Feed temperature
T_j	Jacket temperature
T_{ref}	Reference temperature
U	Overall heat transfer coefficient (energy/(time*area*temperature))
V	Reactor volume
ΔE	Activation energy (energy/mol)
$(-\Delta H)$	Heat of reaction (energy/mol)
ρ	Density (mass/volume)

M9.2.2   Overall Material Balance

The rate of accumulation of material in the reactor is equal to the rate of material in by flow – the material out by flow.

$$\frac{dV\rho}{dt} = F_{in}\rho_{in} - F_{out}\,\rho$$

Assuming a constant amount of material in the reactor ($dV\rho/dt = 0$), we find that:

$$F_{out}\,\rho = F_{in}\,\rho_{in}$$

If we also assume that the density remains constant,[2] then:

$$F_{out} = F_{in} = F \quad \text{and} \quad dV/dt = 0$$

M9.2.3   Balance on Component A

The balance on component A, assuming a constant volume reactor, is:

$$V\frac{dC_A}{dt} = FC_{Af} - FC_A - rV \tag{M9.1}$$

where r is the rate of reaction per unit volume.

M9.2.4   Energy Balance

The energy balance, assuming constant volume, heat capacity and density, is:

$$V\rho c_p \frac{dT}{dt} = F\rho c_p(T_f - T) + (-\Delta H)Vr - UA(T - T_j) \tag{M9.2}$$

where $(-\Delta H)Vr$ is the rate of energy contributed by the exothermic reaction.

M9.2.5   State Variable Form of Dynamic Equations

We can write (M9.1) and (M9.2) in the following state variable form:

$$f_1(C_A,T) = \frac{dC_A}{dt} = \frac{F}{V}(C_{Af} - C_A) - r \tag{M9.1a}$$

$$f_2(C_A,T) = \frac{dT}{dt} = \frac{F}{V}(T_f - T) + \left(\frac{-\Delta H}{\rho c_p}\right)r - \frac{UA}{V\rho c_p}(T - T_j) \tag{M9.2a}$$

[2]It should be noted that the density of all streams does not need to remain constant for the modeling equations to hold. For example, Denn (1986) shows that as long as the density is a linear function of concentration, the final modeling equations are correct.

The reaction rate per unit volume (Arrhenius expression) is:

$$r = k_o \exp\left(\frac{-\Delta E}{RT}\right) C_A \qquad \text{(M9.3)}$$

where we have assumed that the reaction is first-order.

M9.3   STEADY-STATE SOLUTION

The steady-state solution is obtained when $dC_A/dt = 0$ and $dT/dt = 0$, that is:

$$f_1(C_A,T) = 0 = \frac{F}{V}(C_{Af} - C_A) - k_o \exp\left(\frac{-\Delta E}{RT}\right) C_A \qquad \text{(M9.1s)}$$

$$f_2(C_A,T) = 0 = \frac{F}{V}(T_f - T) + \left(\frac{-\Delta H}{\rho c_p}\right) k_o \exp\left(\frac{-\Delta E}{RT}\right) C_A - \frac{UA}{V\rho c_p}(T - T_j) \qquad \text{(M9.2s)}$$

To solve these two equations, all parameters and variables except for two (C_A and T) must be specified. Given numerical values for all of the parameters and variables we can use Newton's method (Chapter 3) to solve for the steady-state values of C_A and T. For convenience, we use an "s" subscript to denote a steady-state value (so we solve for C_{As} and T_s).

In this module we will study the set of parameters shown for Case 2 conditions in Table M9.1. Cases 1 and 3 are left as exercises for the reader.

M9.3.1   Solution for Case 2 Parameters Using `fsolve` and `cstr_ss.m`

The function m-file for the steady-state equations is `cstr_ss.m` and is shown in Appendix 1. The command to run this file is

```
x = fsolve('cstr_ss',x0);
```

where x0 is a vector of the initial guesses and x is the solution. Before issuing this command the reactor parameters must be entered in the global parameter vector CSTR_PAR.

TABLE M9.1   Reactor Parameters

Parameter	Case 1	Case 2	Case 3
F/V, hr^{-1}	1	1	1
k_0, hr^{-1}	14,825*3600	9,703*3600	18,194*3600
$(-\Delta H)$, kcal/kgmol	5215	5960	8195
E, kcal/kgmol	11,843	11,843	11,843
ρc_p, kcal/(m^3°C)	500	500	500
T_f, °C	25	25	25
C_{Af}, kgmol/m^3	10	10	10
UA/V, kcal/(m^3°C hr)	250	150	750
T_j, °C	25	25	25

We find that different initial guesses for the concentration and temperature lead to different solutions.

When choosing initial guesses for a numerical algorithm, it is important to use physical insight about the possible range of solutions. For example, since the feed concentration of A is 10 kgmol/m^3 and the only reaction consumes A, the possible range for the concentration of A is $0 < C_A < 10$. Also, it is easy to show that a lower bound for temperature is 298 K, which would occur if there was no reaction at all, since the feed and jacket temperatures are 298 K. Notice also that there should be a correlation between concentration and temperature. If the concentration of A is high, this means that not much reaction has occurred so little energy has been released by reaction and therefore the temperature will not be much different than the feed and jacket temperatures.

GUESS 1

High concentration (low conversion), low temperature. Here we consider an initial guess of $C_A = 9$ and $T = 300$ K.

```
x = fsolve('cstr_ss',[9;300]);

x =
    8.5636
  311.1710
```

so the steady-state solution for guess 1 is $\begin{bmatrix} C_{As} \\ T_s \end{bmatrix} = \begin{bmatrix} 8.5636 \\ 311.2 \end{bmatrix}$, that is, high concentration (low conversion) and low temperature.

GUESS 2

Intermediate concentration and temperature.

```
x = fsolve('cstr_ss',[5;350])

x =
    5.5179
  339.0971
```

so the steady-state solution for guess 2 is $\begin{bmatrix} C_{As} \\ T_s \end{bmatrix} = \begin{bmatrix} 5.518 \\ 339.1 \end{bmatrix}$.

GUESS 3

Low concentration and high temperature.

```
x = fsolve('cstr_ss',[1;450])

x =
    2.3589
  368.0629
```

TABLE M9.2   Guesses and Solutions Using `fsolve`

Guess and Solution	Guess 1	Guess 2	Guess 3
x0(1), C_A guessed	9	5	1
x0(2), T guessed	300	350	450
x(1), C_A solution	8.564	5.518	2.359
x(2), T solution	311.2	339.1	368.1

so the steady-state solution for guess 3 is $\begin{vmatrix} C_A \\ T_s \end{vmatrix} = \begin{vmatrix} 2.359 \\ 368.1 \end{vmatrix}$, that is, low concentration (high conversion) and high temperature.

The results are summarized in Table M9.2.

Other initial guesses do not lead to any other solutions, so we see that there are three possible solutions for this set of parameters. In Section M9.7 we show how to use physical insight to determine the number of steady-state solutions for this problem.

M9.4   DYNAMIC BEHAVIOR

We noted in the previous section that were three different steady-state solutions to the Case 2 parameter set. Here we wish to study the dynamic behavior under this same parameter set. Recall that numerical integration techniques were presented in Chapter 4.

The m-file to integrate the modeling equations is `cstr_dyn.m`, shown in Appendix 2. The command to integrate the equations is

```
[t,x] = ode45('cstr_dyn',t0,tf,x0);
```

where `t0` is the initial time (usually 0), `tf` is the final time, `x0` is the initial condition vector, `t` is the time vector, and `x` is the state variable solution vector. Before performing the integration it is necessary to define the global parameter vector CSTR_PAR. To plot only concentration or temperature as a function of time, use `plot(t,x(:,1))` and `plot(t,x(:,2))`, respectively.

M9.4.1   Initial Condition 1

Here we use initial conditions that are close to the low temperature steady-state. The initial condition vector is [conc, temp] = [9,300]. The curves plotted in Figure M9.2 show that the state variables converge to the low temperature steady-state.
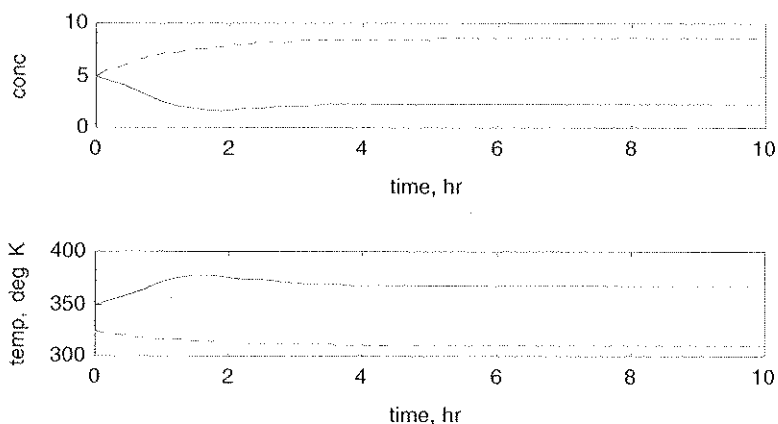
M9.4.2   Initial Condition 2

Here we use initial conditions that are close to the intermediate temperature steady-state. The initial condition vector for the solid curve in Figure M9.3 is [conc, temp] = [5,350], which converges to the high temperature steady-state. The initial condition vector for the
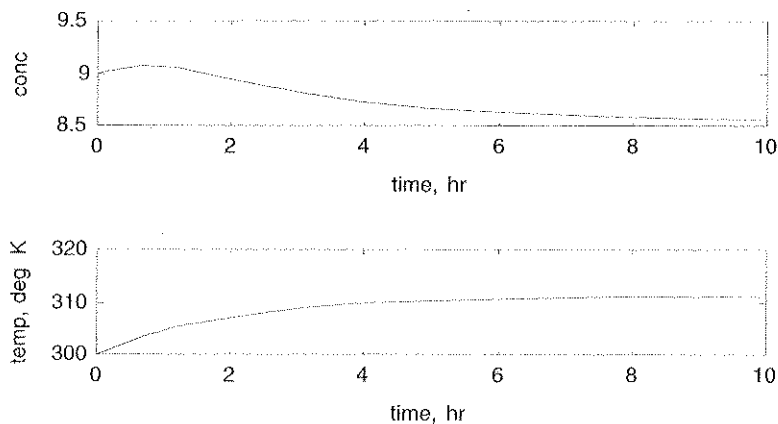
FIGURE M9.2   State variable responses with initial condition $x0 = [9;300]$.

dotted curve in Figure M9.3 is [conc, temp] = [5,325], which converges to the low temperature steady-state.

If we perform many simulations with initial conditions close to the intermediate temperature steady-state, we find that the temperature always converges to either the low temperature or high temperature steady-states, but not the intermediate temperature steady-state. This indicates to us that the intermediate temperature steady-state is *unstable*. This will be shown clearly by the stability analysis in Section M9.5.

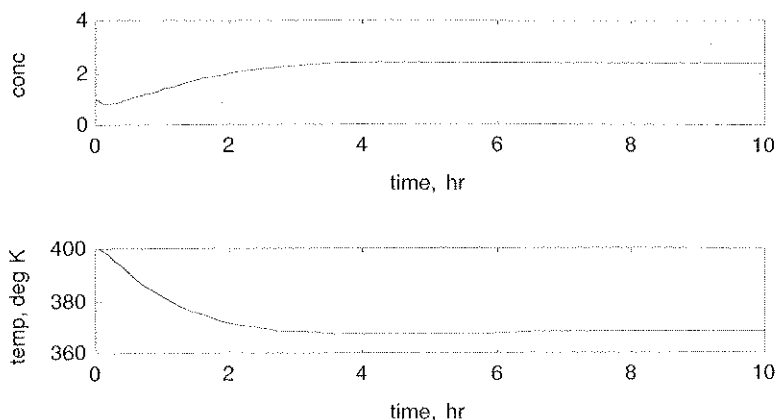**FIGURE M9.3**   State variable responses with initial condition $x0 = [5;350]$ (solid) and $x0 = [5;325]$ (dashed).

FIGURE M9.4   State variable responses with initial condition $x0 = [1;400]$.

M9.4.3   Initial Condition 3

Here we use initial conditions that are close to the high temperature steady-state. The initial condition vector is [conc, temp] = [1,400]. The curves plotted in Figure M9.4 show that the state variables converge to the high temperature steady-state.

In this section we have performed several simulations and presented several plots. In Section M9.6 we will show how these solutions can be compared on the same "phase-plane" plot.

M9.5   LINEARIZATION OF DYNAMIC EQUATIONS

The stability of the nonlinear equations can be determined by finding the following state-space form:

$$\dot{x} = A\,x + B\,u \qquad (M9.11)$$

and determining the eigenvalues of the A (state-space) matrix.

The nonlinear dynamic state equations (M9.1a) and (M9.2a) are:

$$f_1(C_A, T) = \frac{dC_A}{dt} = -\frac{F}{V}\,C_A - k\,C_A + \frac{F}{V}\,C_{Af} \qquad (M9.1a)$$

$$f_2(C_A, T) = \frac{dT}{dt} = \left(\frac{-\Delta H}{\rho c_p}\right) k\,C_A - \frac{F}{V}\,T - \frac{UA}{V\rho C_p}\,T + \frac{UA}{V\rho C_p}\,T_j + \frac{F}{V}\,T_f \qquad (M9.2a)$$

Let the state and input variables be defined in deviation variable form:

$$\mathbf{x} = \begin{bmatrix} C_A - C_{As} \\ T - T_s \end{bmatrix}$$

$$\mathbf{u} = \begin{bmatrix} T_j - T_{js} \\ C_{Af} - C_{Afs} \\ T_f - T_{fs} \end{bmatrix}$$

M9.5.1   Stability Analysis

Performing the linearization, we obtain the following elements for **A**:

$$A_{11} = \frac{\partial f_1}{\partial x_1} = \frac{\partial f_1}{\partial C_A} = -\frac{F}{V} - k_s$$

$$A_{12} = \frac{\partial f_1}{\partial x_2} = \frac{\partial f_1}{\partial T} = -C_{As}k_s'$$

$$A_{21} = \frac{\partial f_2}{\partial x_1} = \frac{\partial f_2}{\partial C_A} = \frac{(-\Delta H)}{\rho C_p}k_s$$

$$A_{22} = \frac{\partial f_2}{\partial x_2} = \frac{\partial f_2}{\partial T} = -\frac{F}{V} - \frac{UA}{V\rho C_p} + \frac{(-\Delta H)}{\rho C_p}C_{As}k_s'$$

where we define the following parameters for more compact representation:

$$k_s = k_o \exp\left(\frac{-\Delta E}{RT_s}\right)$$

$$k_s' = \frac{\partial k_s}{\partial T} = k_o \exp\left(\frac{-\Delta E}{RT_s}\right)\left(\frac{\Delta E}{RT_s^2}\right)$$

or,

$$k_s' = k_s\left(\frac{\Delta E}{RT_s^2}\right)$$

From the analysis presented above, the state-space **A** matrix is:

$$\mathbf{A} = \begin{bmatrix} -\dfrac{F}{V} - k_s & -C_{As}k_s' \\ \dfrac{(-\Delta H)}{\rho C_p}k_s & -\dfrac{F}{V} - \dfrac{UA}{V\rho C_p} + \dfrac{(-\Delta H)}{\rho C_p}C_{As}k_s' \end{bmatrix} \qquad \text{(M9.12)}$$

The stability characteristics are determined by the eigenvalues of **A**, which are obtained by solving $\det(\lambda \mathbf{I} - \mathbf{A}) = 0$.

$$\lambda \mathbf{I} - \mathbf{A} = \begin{vmatrix} \lambda - A_{11} & -A_{12} \\ -A_{21} & \lambda - A_{22} \end{vmatrix}$$

$$\det(\lambda \mathbf{I} - \mathbf{A}) = (\lambda - A_{11})(\lambda - A_{22}) - A_{12}A_{21}$$

$$= \lambda^2 - (A_{11} + A_{22})\lambda + A_{11}A_{22} - A_{12}A_{21}$$

$$= \lambda^2 - (\text{tr } \mathbf{A})\lambda + \det(\mathbf{A})$$

The eigenvalues are the solution to the second-order polynomial:

$$\lambda^2 - (\text{tr } \mathbf{A})\lambda + \det(\mathbf{A}) = 0 \qquad (M9.13)$$

The stability of a particular operating point is determined by finding the $\mathbf{A}$ matrix for that particular operating point, and finding the eigenvalues of the A matrix.

Here we show the eigenvalues for each of the three case 2 steady-state operating points. We use the function routine `cstr_amat.m` shown in appendix 3 to find the A matrices.

OPERATING POINT 1

The concentration and temperature are 8.564 kgmol/m^3 and 311.2 K, respectively.

```
»[amat,lambda] = cstr_amat(8.564,311.2)

amat =
   -1.1680    -0.0886
    2.0030    -0.2443

lambda =
   -0.8957
   -0.5166
```

Both of the eigenvalues are negative, indicating that the point is stable, which is consistent with the results of Figure M9.2.

OPERATING POINT 2

The concentration and temperature are 5.518 and 339.1, respectively.

```
»[amat,lambda] = cstr_amat(5.518,339.1)

amat =
   -1.8124    -0.2324
    9.6837     1.4697

lambda =
   -0.8369
    0.4942
```

One of the eigenvalues is positive, indicating that the point is *unstable*. This is consistent
with the responses presented in Figure M9.3.

OPERATING POINT 3

```
»[amat,lambda] = cstr_amat(2.359,368.1)

amat =
   -4.2445    -0.3367
   38.6748     2.7132

lambda =
  -0.7657 + 0.9584i
  -0.7657 - 0.9584i
```

The real portion of each eigenvalue is negative, indicating that the point is stable; again,
this is consistent with the responses in Figure M9.4.

M9.5.2   Input/Output Transfer Function Analysis

The input-output transfer functions can be found from:

$$\mathbf{G}(s) = \mathbf{C}(s\mathbf{I} - \mathbf{A})^{-1}\mathbf{B} \qquad (M9.14)$$

where the elements of the **B** matrix corresponding to the first input ($u_1 = T_j - T_{js}$) are:

$$B_{11} = \frac{\partial f_1}{\partial u_1} = \frac{\partial f_1}{\partial T_j} = 0$$

$$B_{21} = \frac{\partial f_2}{\partial u_1} = \frac{\partial f_2}{\partial T_j} = \frac{UA}{V\rho c_p}$$

The reader should find the elements of the B matrix that correspond to the second and
third input variables (see student exercise 8).

Here we show only the transfer functions for the low temperature steady-state for
Case 2. The input/output transfer function relating jacket temperature to reactor concen-
tration (state 1) is:

$$g_{11}(s) = \frac{-0.0266}{s^2 + 1.4123s + 0.4627} = \frac{-0.0575}{(1.1165s + 1)(1.9357s + 1)}$$

and the input/output transfer function relating jacket temperature to reactor temperature
(state 2) is

$$g_{21}(s) = \frac{0.3s + 0.3504}{s^2 + 1.4123s + 0.4627} = \frac{0.7573(0.856s + 1)}{(1.1165s + 1)(1.9357s + 1)}$$

Notice that the transfer function for concentration is a pure second-order system (no nu-
merator polynomial) while the transfer function for temperature has a first-order numera-