Case Study 3
Non-Adiabatic (Diabatic) CSTR

Objectives:

• Develop the dynamic model of a diabatic CSTR

• Understand the steady-state behavior (multiple steady-state)

• Understand the dynamic behavior by simulations and by linearization of nonlinear dynamic equations followed by eigenvalue analysis

• Understand the possible steady-state behavior based on an analysis of the heat generated by reaction and removed through the cooling jacket
Process Description

• 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 problems and the possibility of special behavior such as multiple steady-states

• Consider a CSTR with a single, first-order exothermic irreversible reaction

\[ A \rightarrow B \]

\[ r = k_0 \exp\left(\frac{-E}{RT}\right)C_A \]

Assumptions:
• Perfect mixing
• Constant volume
• Constant parameter values
Developing the Dynamic Model

- For simplicity we assume that the cooling jacket temperature can be directly manipulated, so that an energy balance around the jacket is not required.

- Overall material balance

\[
\frac{d(V\rho)}{dt} = F_i\rho - F\rho \quad \Rightarrow \quad F = F_i
\]

- Material balance on component A

\[
V \frac{dC_A}{dt} = FC_{Af} - FC_A - rV
\]

- Energy balance around the reactor

\[
V \rho c_p \frac{dT}{dt} = F \rho c_p (T_f - T) + (-\Delta H) Vr - UA(T - T_j)
\]

- Modeling equations

\[
f_1(C_A, T) = \frac{dC_A}{dt} = \frac{F}{V} (C_{Af} - C_A) - r
\]

\[
f_2(C_A, T) = \frac{dT}{dt} = \frac{F}{V} (T_f - T) + \left(\frac{-\Delta H}{\rho c_p}\right) r - \frac{UA_v}{V \rho c_p} (T - T_j)
\]
Steady-State Solution

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

$$
\begin{align*}
\frac{f_1 (C_A, T)}{V} &= \frac{F}{V} (C_{Af} - C_A) - k_0 \exp\left(\frac{-E}{RT}\right) C_A \\
\frac{f_2 (C_A, T)}{V} &= \frac{F}{V} (T_f - T) + \left(\frac{-\Delta H}{\rho c_p}\right) k_0 \exp\left(\frac{-E}{RT}\right) C_A - \frac{UA}{V \rho c_p} (T - T_j)
\end{align*}
$$

- Parameter values

$$
\begin{align*}
\frac{F}{V} &= 1 \text{hr}^{-1} & \rho c_p &= 500 \frac{\text{kcal}}{\text{C m}^3} & k_0 &= 9703 \times 3600 \text{hr}^{-1} \\
T_f &= 25^\circ \text{C} & -(\Delta H) &= 5960 \frac{\text{kcal}}{\text{kgmol}} & E &= 11843 \frac{\text{kcal}}{\text{kgmol}} \\
T_j &= 25^\circ \text{C} & \frac{UA}{V} &= 150 \frac{\text{\text{kcal}}}{{}^\circ \text{C m}^3 \text{hr}} & C_{Af} &= 10 \frac{\text{kgmol}}{\text{m}^3}
\end{align*}
$$
Steady-State Solution

- Different initial guesses for the concentration and temperature lead to different solutions
  - **Guess 1:** high concentration (low conversion), low temperature
    \(C_A = 9\) and \(T = 300K\)
    \[
    \begin{bmatrix} \frac{C_{As}}{T_s} \end{bmatrix} = \begin{bmatrix} 8.564 \\ 311.2 \end{bmatrix} \quad \text{(low temperature steady-state)}
    \]
  - **Guess 2:** intermediate concentration and temperature
    \(C_A = 5\) and \(T = 350K\)
    \[
    \begin{bmatrix} \frac{C_{As}}{T_s} \end{bmatrix} = \begin{bmatrix} 5.518 \\ 339.1 \end{bmatrix} \quad \text{(intermediate temperature steady-state)}
    \]
  - **Guess 3:** low concentration and high temperature \((C_A = 1\) and \(T = 450K\))
    \[
    \begin{bmatrix} \frac{C_{As}}{T_s} \end{bmatrix} = \begin{bmatrix} 2.359 \\ 368.1 \end{bmatrix} \quad \text{(high temperature steady-state)}
    \]
- Other initial guesses do not lead to any other solutions, so there are three possible solutions for this set of parameters
Dynamic Behavior

- Simulate the *unforced response* for initial conditions that are close to different steady-state points

  - **Initial condition 1**: close to the low temperature steady-state  
    \((C_A = 9 \text{ and } T = 300\text{K}) \Rightarrow \text{converge to the low temperature steady-state}\)

  - **Initial condition 2**: close to the intermediate temperature steady-state  
    \((C_A = 5 \text{ and } T = 350\text{K}) \Rightarrow \text{converge to the high temperature steady-state}\)  
    \((C_A = 5 \text{ and } T = 325\text{K}) \Rightarrow \text{converge to the low temperature steady-state}\)

  - **Initial condition 3**: close to the high temperature steady-state  
    \((C_A = 1 \text{ and } T = 400\text{K}) \Rightarrow \text{converge to the high temperature steady-state}\)

*The temperature always converges to either the low temp. or high temp. steady-states, but not the intermediate temp. steady-state → unstable steady-state*
- Initial condition 1 ($C_A = 9, T = 300K$)

- Initial condition 2
  (blue: $C_A = 5, T = 350K$)
  (red: $C_A = 5, T = 325K$)

- Initial condition 3 ($C_A = 1, T = 400K$)

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low temp. steady-state

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high temp. steady-state
The stability of the nonlinear equations can be determined by finding the state-space form and determining the eigenvalues of $A$

$$\dot{x} = Ax + Bu$$

where the state, input, and output vectors are in deviation form

$$x = \begin{bmatrix} C_A - C_{As} \\ T - T_s \end{bmatrix} = \text{state variables} \quad u = \begin{bmatrix} T_j - T_{js} \\ C_{Af} - C_{Af_s} \\ T_f - T_{fs} \end{bmatrix} = \text{input variables}$$

Two nonlinear dynamic state equations

$$f_1(C_A, T) = \frac{dC_A}{dt} = \frac{F}{V} (C_{Af} - C_A) - kC_A$$

$$f_2(C_A, T) = \frac{dT}{dt} = \frac{F}{V} (T_f - T) + \left( \frac{-\Delta H}{\rho c_p} \right) kC_A - \frac{UA}{V \rho c_p} (T - T_j)$$
• The elements of the state-space $A$ matrix are found by $A_{ij} = \left. \frac{\partial f_i}{\partial x_j} \right|_{x_s,u_s}$

$$
A_{11} = \left. \frac{\partial f_1}{\partial x_1} \right|_{x_s,u_s} = \left. \frac{\partial f_1}{\partial C_A} \right|_{x_s,u_s} = -\frac{F}{V} - k_s
$$

$$
A_{12} = \left. \frac{\partial f_1}{\partial x_2} \right|_{x_s,u_s} = \left. \frac{\partial f_1}{\partial T} \right|_{x_s,u_s} = -C_A k_s
$$

$$
A_{21} = \left. \frac{\partial f_2}{\partial x_1} \right|_{x_s,u_s} = \left. \frac{\partial f_2}{\partial C_A} \right|_{x_s,u_s} = \frac{(-\Delta H)}{\rho c_p} k_s
$$

$$
A_{22} = \left. \frac{\partial f_2}{\partial x_2} \right|_{x_s,u_s} = \left. \frac{\partial f_2}{\partial T} \right|_{x_s,u_s} = -\frac{F}{V} + \frac{(-\Delta H)}{\rho c_p} C_A k_s - \frac{UA}{V \rho c_p}
$$

where $k_s = k_0 \exp\left(\frac{-E}{RT_s}\right)$, $k_s' = k_0 \exp\left(\frac{-E}{RT_s}\right)\left(\frac{E}{RT_s^2}\right) = k_s \left(\frac{E}{RT_s^2}\right)$

$$
\Rightarrow A = \begin{bmatrix}
-\frac{F}{V} - k_s & -C_A k_s'

\frac{(-\Delta H)}{\rho c_p} k_s & -\frac{F}{V} + \frac{(-\Delta H)}{\rho c_p} C_A k_s' - \frac{UA}{V \rho c_p}
\end{bmatrix}
$$
Stability Analysis

• The eigenvalues of the $\mathbf{A}$ matrix determine the stability of the steady-state operating points
  
  – **Operating point 1**: $C_A = 8.564$ and $T = 311.2$K
    
    $\lambda_1 = -0.8957$, $\lambda_2 = -0.5166$
    
    ➔ **Stable (node)**
  
  – **Operating point 2**: $C_A = 5.518$ and $T = 339.1$K
    
    $\lambda_1 = -0.8369$, $\lambda_2 = 0.4942$
    
    ➔ **Unstable (saddle)**
  
  – **Operating point 3**: $C_A = 2.359$ and $T = 368.1$K
    
    $\lambda_1 = -0.7657 + 0.9584i$, $\lambda_2 = -0.7657 - 0.9584i$
    
    ➔ **Stable (focus)**
Phase-Plane Plot

cstr with multiple steady-states

temperature, deg K

concentration, kgmol/m^3
Multiple Steady-State Behavior

• Solving for \( C_A \) as a function of reactor temperature ( \( dC_A/dt = 0 \) )

\[
\frac{F}{V} (C_{Afs} - C_{As}) - k_0 \exp\left(\frac{-E}{RT_s}\right) C_{As} = 0 \implies C_{As} = \frac{\frac{F}{V} C_{Afs}}{\frac{F}{V} + k_0 \exp\left(\frac{-E}{RT_s}\right)}
\]

• Solving for reactor temperature ( \( dT/dt = 0 \) )

\[
\frac{F}{V} (T_{fs} - T_s) + \left(\frac{-\Delta H}{\rho c_p}\right) k_0 \exp\left(\frac{-E}{RT_s}\right) C_{As} - \frac{UA}{V \rho c_p} (T_s - T_{js}) = 0
\]

\[
\implies F \rho c_p (T_s - T_{js}) + UA(T_s - T_{js}) = (-\Delta H)V k_0 \exp\left(\frac{-E}{RT_s}\right) C_{As}
\]

\[Q_{\text{rem}} = \left( -UA T_{js} - F \rho c_p T_{fs} \right) + \left( UA + F \rho c_p \right) T_s \quad Q_{\text{gen}} = (-\Delta H)V k_0 \exp\left(\frac{-E}{RT_s}\right) C_{As}\]

Energy removed by flow and heat exchange

Heat generated by reaction
Effect of Design Parameters

- $Q_{\text{rem}}$ is a line as a function of $T_s$
  \[
  Q_{\text{rem}} = (-UAT_{js} - F \rho c_p T_{fs}) + (UA + F \rho c_p) T_s
  \]
  \[\text{intercept} \quad \text{slope}\]
  - Changes in jacket or feed temperature shift the intercept, but not the slope. Changes in $UA$ or $F$ affect both the slope and intercept.

- $Q_{\text{gen}}$ is a ‘S-shape’ curve as a function of $T_s$
  \[
  Q_{\text{gen}} = (-\Delta H) V k_0 \exp\left(\frac{-E}{RT_s}\right) C_{As} = (-\Delta H) V \frac{k_0 \exp\left(\frac{-E}{RT_s}\right) \left(\frac{F}{V} C_{Afs}\right)}{F/V + k_0 \exp\left(\frac{-E}{RT_s}\right)}
  \]

- A steady-state solution exists when there is an intersection of the $Q_{\text{rem}}$ and $Q_{\text{gen}}$ curves
• Possible intersections of heat generation and heat removal curves

  – The slope of the heat removal curve is *greater* than the maximum slope of the heat generation curve
    ➔ only one possible intersection

  – The slope of the heat removal curve is *less* than the maximum slope of the heat generation curve
    ➔ three possible intersections
Hysteresis Behavior

- **Hysteresis Behavior**: the behavior is different depending on the "direction" that the input are moved.

- Increase jacket temperature ($A \rightarrow E$)

- Steady-state input-output diagram

\[ F \rho c_p \left( T_s - T_{fs} \right) - (-\Delta H) V k_0 \exp\left( \frac{-E}{RT_s} \right) C_{As} = T_{js} + \frac{T_s}{UA} \]

Reactor temperature

Jacket Temperature

Unstable (4-6)

1 $\rightarrow$ 2 $\rightarrow$ 3 $\rightarrow$ 4 $\rightarrow$ 8 $\rightarrow$ 9

9 $\rightarrow$ 8 $\rightarrow$ 7 $\rightarrow$ 6 $\rightarrow$ 2 $\rightarrow$ 1