REB, The Book
Example 12.4.2 Solution

The water-gas shift reaction, equation (1), is exothermic, ΔH = –9120 cal mol^{-1}, and reversible. The equilibrium constant can be approximated using equation (2) with $K_{0,1}$ = 0.132. The heat capacities of CO, H_2O, CO_2, H_2, and inert, I, can be taken to be constant and equal to 29.3, 34.3, 41.3, 29.2, and 40.5 J mol^{-1} K^{-1}, respectively. Two packed bed reactors in series are used to process a feed consisting of 1 mol CO h^{-1}, 0.359 mol CO_2 h^{-1}, 4.44 mol H_2 h^{-1}, 0.180 mol I h^{-1}, and 9.32 mol H_2O h^{-1} at 26 atm and 445 °C. The volume of the first packed bed is 685 cm^3, and it is packed with a high-temperature catalyst for which the rate is given by equation (3) with $k_{0,1}$ = 0.0354 mol cm^{-3} min^{-1} atm^{-2} and E_1 = 9740 cal mol^{-1}. The product stream leaving the first packed bed passes through a heat exchanger. Chilled water at 20 °C flowing at a rate of 1100 g h^{-1} enters the other side of the heat exchanger and exits the heat exchanger at 50 °C. The volume of the second packed bed is 3950 cm^3, and the packing is a low-temperature catalyst for which the rate also is given by equation (3), but with $k_{0,1}$ = 1.77 x 10^{-3} mol cm^{-3} min^{-1} atm^{-2} and E_1 = 3690 cal mol^{-1}. Pressure drop in the reactors is negligible. What are the overall conversion of CO and the temperature of the product gas leaving the second packed bed reactor?

$$CO + H_2O \rightleftarrows CO_2 + H_2 \tag{1}$$

$$K_1 = K_0 \exp\left(\frac{-\Delta H}{RT}\right) \tag{2}$$

$$r = k\left(P_{CO}P_{H_2O} - \frac{P_{CO_2}P_{H_2}}{K}\right) \tag{3}$$

Assignment Summary

The information from the assignment narrative is summarized below. Figure 1 shows a schematic representation of the system. The stream numbers from that figure are used as subscripts to differentiate between the flow streams.

Reaction

$$CO + H_2O \rightleftarrows CO_2 + H_2 \tag{1}$$

Rate Expression

$$r = k\left(P_{CO}P_{H_2O} - \frac{P_{CO_2}P_{H_2}}{K}\right) \tag{3}$$

Reactors: Two adiabatic, steady-state PFRs with negligible pressure drop, connected in series with cooling between as shown in Figure 1.

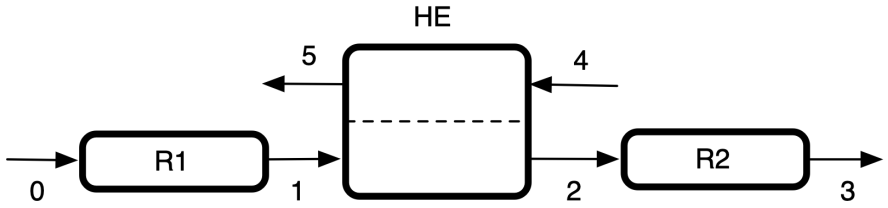

Figure 1. Schematic representation of the reactor network with reactors, R1 and R2, and a heat exchanger, HE.

Given Constants: ΔH = –9120 cal mol^{-1}, K_0 = 0.132, $\hat{C}_{p,CO}$ = 29.3 J mol^{-1} K^{-1}, $\hat{C}_{p,H_2O}$ = 34.3 J mol^{-1} K^{-1}, $\hat{C}_{p,CO_2}$ = 41.3 J mol^{-1} K^{-1}, $\hat{C}_{p,H_2}$ = 29.2 J mol^{-1} K^{-1}, $\hat{C}_{p,I}$ = 40.5 J mol^{-1} K^{-1}, $\dot{n}_{CO,0}$ = 1 mol h^{-1}, $\dot{n}_{CO_2,0}$ = 0.359 mol h^{-1}, $\dot{n}_{H_2,0}$ = 4.44 mol h^{-1}, $\dot{n}_{I,0}$ = 0.180 mol h^{-1}, $\dot{n}_{H_2O,0}$ = 9.32 mol h^{-1}, P = 26 atm, T_0 = 445 °C, V_{R1} = 685 cm^3, $k_{0,R1}$ = 0.0354 mol cm^{-3} min^{-1} atm^{-2}, E_{R1} = 9740 cal mol^{-1}, T_4 = 20 °C, $\dot{m}_4$ = 1100 g min^{-1}, T_5 = 50 °C, V_{R2} = 3950 cm^3, $k_{0,R2}$ = 1.77 x 10^{-3} mol cm^{-3} min^{-1} atm^{-2}, and E_{R2} = 3690 cal mol^{-1}.

Deliverables: f_{CO} and T_3

PFR Model Function

The purpose of the PFR model function is to solve the PFR design equations for either reactor. This is done numerically by calling an IVODE solver. Any necessary quantities that are not given, and cannot be calculated, will be passed to it as arguments. If the PFR derivatives function requires any quantities that cannot be passed to it as arguments, the PFR model function will make them available to it as global variables. The PFR derivatives function described here also must be written.

PFR Model Equations:

$$\frac{d\dot{n}_{CO}}{dV} = -r \tag{4}$$

$$\frac{d\dot{n}_{H_2O}}{dV} = -r \tag{5}$$

$$\frac{d\dot{n}_{CO_2}}{dV} = r \tag{6}$$

$$\frac{d\dot{n}_{H_2}}{dV} = r \tag{7}$$

$$\frac{d\dot{n}_{I}}{dV} = 0 \tag{8}$$

$$\frac{dT}{dV} = \frac{-r\Delta H}{\dot{n}_{CO}\hat{C}_{p,CO} + \dot{n}_{H_2O}\hat{C}_{p,H_2O} + \dot{n}_{CO_2}\hat{C}_{p,CO_2} + \dot{n}_{H_2}\hat{C}_{p,H_2} + \dot{n}_{I}\hat{C}_{p,I}} \tag{9}$$

PFR Model Variables: V, $\dot{n}_{CO}$, $\dot{n}_{H_2O}$. $\dot{n}_{CO_2}$, $\dot{n}_{H_2}$, $\dot{n}_{I}$, and T

Additional Computable Unknowns: r, k, K, P_{CO}, P_{H_2O}, P_{CO_2}, and P_{H_2}.

$$k_1 = k_0 \exp\left(\frac{-E}{RT}\right) \tag{10}$$

$$P_i = \frac{\dot{n}_i}{\dot{n}_{CO} + \dot{n}_{H_2O} + \dot{n}_{CO_2} + \dot{n}_{H_2} + \dot{n}_I} P \qquad i = CO, H_2O, CO_2, \text{ and } H_2 \tag{11}$$

Additional Uncomputable Unknowns: k_0, E, $\dot{n}_{CO,in}$, $\dot{n}_{H_2O,in}$, $\dot{n}_{CO_2,in}$, $\dot{n}_{H_2,in}$, $\dot{n}_{I,in}$, T_{in}, and V_{PFR}

IVODE Solver Inputs:

1. Initial values of the reactor model variables

$$V_{initial} = 0 \tag{12}$$

$$\dot{n}_{i,initial} = \dot{n}_{i,in} \quad \begin{matrix} i = CO, H_2O, CO_2, H_2, \text{ and } I \\ in = 0 \text{ or } 2 \end{matrix} \tag{13}$$

$$T_{initial} = T_{in} \quad in = 0 \text{ or } 2 \tag{14}$$

2. Stopping criterion

$$V_{final} = V_i \quad i = R1 \text{ or } R2 \tag{15}$$

3. Derivatives function that
   a. receives values of the PFR model variables at the start of an integration step
   b. can access the current values of k_0 and E
   c. calculates the additional unknowns using equations (2), (3), (10), and (11)
   d. evaluates and returns the PFR design equation derivatives using equations (4) - (9)

Heat Exchanger Model

The heat exchanger model can easily be solved analytically, so a heat exchanger function is not required. After solving the PFR design equations for the first PFR to get the molar flow rates and temperature for stream 1, the heat exchanger mole balances, equation (16), can be used to get the molar flow rates for stream 2. Noting that the

mass flow rate of the coolant is constant, $\dot{m}_5 = \dot{m}_4$, the heat exchanger energy balance shown in equation (17) can then be used to calculate the temperature of stream 2.

Heat Exchanger Model Equations:

$$\dot{n}_{i,2} = \dot{n}_{i,1} \quad i = CO, H_2O, CO_2, H_2, \text{ and } I \tag{16}$$

$$T_2 = T_1 - \frac{\dot{m}_4 \tilde{C}_{p,H_2O_{(l)}} \left(T_5 - T_4\right)}{\sum_i \left(\dot{n}_{i,1} \hat{C}_{p,i}\right)} \tag{17}$$

Deliverables Function

The purpose of the deliverables function is to use the PFR model function and the heat exchanger model equations to calculate the conversion and temperature of stream 3.

Deliverables Function

1. Use the PFR model function to solve the design equations for reactor R1 and get the molar flow rates and temperature of stream 1.
2. Solve the heat exchanger model equations to get the molar flow rates and temperature of stream 2.
3. Use the PFR model function to solve the design equations for reactor R2 and get the molar flow rates and temperature of stream 3.
4. Calculate the conversion

$$f_{CO} = \frac{\dot{n}_{CO,0} - \dot{n}_{CO,3}}{\dot{n}_{CO,0}} \tag{18}$$

Implementation of the Calculations

The Python script, example_12_4_2.py, that was written to perform the calculations accompanies this solution. It is structured as follows.

1. Import necessary libraries.

2. Make the given constants, adjusted experimental inputs, and measured responses available wherever they are needed.
3. Declare a global variable to make quantities that cannot be passed to the derivatives function as arguments available to it.
4. Define the PFR model, PFR derivatives, and deliverables functions as described above.
5. Call the deliverables function.

Results and Discussion

The calculations were performed as described above. The outlet temperature in stream 3 is 282 °C, and the conversion is 99.4%. A configuration like that shown in Figure 1 is used in commercial water-gas shift systems. There are several catalysts available for the reaction. Some are active and stable at higher temperatures (325 to 500 °C), some at lower temperatures (180 to 250 °C), and some at lower steam to CO ratios. However, none of the catalysts alone are capable of reaching high CO conversion in a single reactor.

The high temperature catalysts offer a greater reaction rate, which reduces the reactor volume. However, the equilibrium constant decreases with increasing temperature. As a consequence, equilibrium prevents the system from reaching high CO conversion in a single reactor. The low temperature catalysts operate at temperatures where equilibrium does not prevent high CO conversion. However, the adiabatic temperature rise that accompanies the reaction limits the conversion. At high conversion in a single reactor, the temperature increases to the maximum that the catalyst can withstand, thereby limiting conversion. In addition, the rates at the lower temperatures are smaller resulting in larger reactor volumes. Catalysts that con operate at lower steam to CO ratios also become limited by the adiabatic temperature rise. Operating at lower steam to CO decreases the equilibrium conversion and it causes the reactor temperature to rise faster.

A system like that depicted in Figure 1 circumvents the problems associated with a single reactor system. Reactor R1 uses a high-temperature catalyst and converts the majority of the CO. Because the temperature is high, the rate is large and that keeps the

volume of reactor R1 smaller. However, the high temperature also limits the conversion that is possible. Therefore the product from reactor R1 is cooled and fed to reactor R2 which uses a low-temperature catalyst. While the rate is smaller in reactor R2, equilibrium does not limit the conversion, and because much of the conversion is accomplished in reactor R1, the temperature rise in reactor R2 does not exceed the maximum temperature the catalyst can withstand.

The system examined in this assignment is not optimized. Typically dry feed composition and the final conversion of CO are fixed based upon the intended use of the hydrogen. A multi-dimensional optimization can be performed to find the process parameters that minimize the total volume of the reactors. The optimization variables include the steam to CO ratio in stream 0, the temperature of stream 0, the conversion in reactor R1, and the temperature of stream 2.

Deliverables

The temperature and overall conversion for the four process streams are listed in Table 1.

Table 1. Temperature and Overall Conversion in the Four Process Streams.

Stream Number	Conversion (%)	Temperature (°C)
0	0.00	445
1	57.0	488
2	57.0	214
3	99.4	282