REB, The Book
Example 9.6.4 Solution

The water-gas shift, equation (1), is used to reduce the amount of CO in gas mixtures containing CO, CO_2, H_2, H_2O, and other gases. It is exothermic, ΔH = –9120 cal mol^{-1}, and reversible with the equilibrium constant given by equation (3) with $K_{0,1}$ = 0.132. The heat capacities of CO, H_2O, CO_2, H_2, and inert, I, can be take to be constant and equal to 29.3, 34.3, 41.3, 29.2, and 40.5 J mol^{-1} K^{-1}, respectively. Two reactors are often used, one operating at higher temperatures and the other at lower temperatures. The steam to CO feed ratio is often in the range from 3 to 6. Suppose the rate in the first reactor when using a certain catalyst is given by equation (2) with $k_{0,1}$ = 0.0354 mol cm^{-3} min^{-1} atm^{-2} and E_1 = 9740 cal mol^{-1}. The feed to the adiabatic reactor is at 26 atm and 320 °C, and pressure drop is negligible. Using a feed with 1 mol CO h^{-1}, 0.359 mol CO_2 h^{-1}, 4.44 mol H_2 h^{-1}, and 0.180 mol I h^{-1} as a basis, what inlet molar flow of H_2O will minimize the reactor volume if 55% of the CO must be converted? What will the outlet temperature from a reactor of that volume equal?

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

$$r_1 = k_1\left(P_{CO}P_{H_2O} - \frac{P_{CO_2}P_{H_2}}{K_1}\right) \tag{2}$$

$$K_1 = K_{0,1}\exp\left(\frac{-\Delta H}{RT}\right) \tag{3}$$

Assignment Summary

<u>Reaction</u>

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

Rate and Equilibrium Constant Expressions

$$r_1 = k_1 \left(P_{CO} P_{H_2O} - \frac{P_{CO_2} P_{H_2}}{K_1} \right) \tag{2}$$

$$K_1 = K_{0,1} \exp\left(\frac{-\Delta H}{RT} \right) \tag{3}$$

Reactor: Gas-phase, steady-state, adiabatic PFR with negligible pressure drop

Given Constants: ΔH = –9120 cal mol^{-1}, $K_{0,1}$ = 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}, $k_{0.1}$ = 0.0354 mol cm^{-3} min^{-1}atm^{-2}, E_1 = 9740 cal mol^{-1}, P = 26 atm, T_{in} = 320 °C, $\dot{n}_{CO,in}$ = 1 mol h^{-1}, $\dot{n}_{CO_2,in}$ = 0.359 mol h^{-1}, $\dot{n}_{H_2,in}$ = 4.44 mol h^{-1}, $\dot{n}_{I,in}$ = 0.180 mol h^{-1}, and f_{CO} = 0.55.

Parameter: $\dot{n}_{H_2O,in}$

Deliverables: $\dot{n}_{H_2O,in,opt} = \underset{\dot{n}_{H_2O,in}}{\arg\min}\,(V)$ and $T_{out}\Big|_{\dot{n}_{H_2O,in,opt}}$

Formulation of the Equations

Reactor Model Equations:

$$\frac{d\dot{n}_{CO}}{dV} = -r_1 \tag{4}$$

$$\frac{d\dot{n}_{H_2O}}{dV} = -r_1 \tag{5}$$

$$\frac{d\dot{n}_{CO_2}}{dV} = r_1 \tag{6}$$

$$\frac{d\dot{n}_{H_2}}{dV} = r_1 \tag{7}$$

$$\frac{d\dot{n}_I}{dV} = 0.0 \tag{8}$$

$$\frac{dT}{dV} = \frac{-r_1 \Delta H_1}{\dot{n}_{CO}\hat{C}_{p,CO} + \dot{n}_{H_2O}\hat{C}_{p,H_2O} + \dot{n}_{CO_2}\hat{C}_{p,CO_2} + \dot{n}_{H_2}\hat{C}_{p,H_2} + \dot{n}_I\hat{C}_{p,I}} \tag{9}$$

<u>Reactor Model Variables</u>: $\underline{V}$, $\underline{\dot{n}}_{CO}$, $\underline{\dot{n}}_{H_2O}$, $\underline{\dot{n}}_{CO_2}$, $\underline{\dot{n}}_{H_2}$, $\underline{\dot{n}}_I$, and $\underline{T}$

<u>Additional Computable Unknowns</u>: r_1, k_1, K_1, P_{CO}, P_{H_2O}, P_{CO_2}, and P_{H_2}

$$k_1 = k_{0,1} \exp\left(\frac{-E_1}{RT}\right) \tag{10}$$

$$P_{CO} = \frac{\dot{n}_{CO}}{\dot{n}_{CO} + \dot{n}_{H_2O} + \dot{n}_{CO_2} + \dot{n}_{H_2} + \dot{n}_I} P \tag{11}$$

$$P_{H_2O} = \frac{\dot{n}_{H_2O}}{\dot{n}_{CO} + \dot{n}_{H_2O} + \dot{n}_{CO_2} + \dot{n}_{H_2} + \dot{n}_I} P \tag{12}$$

$$P_{CO_2} = \frac{\dot{n}_{CO_2}}{\dot{n}_{CO} + \dot{n}_{H_2O} + \dot{n}_{CO_2} + \dot{n}_{H_2} + \dot{n}_I} P \tag{13}$$

$$P_{H_2} = \frac{\dot{n}_{H_2}}{\dot{n}_{CO} + \dot{n}_{H_2O} + \dot{n}_{CO_2} + \dot{n}_{H_2} + \dot{n}_I} P \tag{14}$$

Additional Uncomputable Unknown: $\dot{n}_{H_2O,in}$

IVODE Solver Inputs:

1. Initial values of the reactor model variables shown in Table 1.
2. Stopping criterion that $\dot{n}_{CO}$ equals the final value shown in Table 1.
3. Derivatives function that
   a. receives the reactor model variables at the start of in integration step
   b. calculates the additional unknowns using equations (10) - (14)
   c. evaluates and returns the design equation derivatives, equations (4) - (9)

Table 1. Initial and final values of the design equation variables.

Variable	Initial Value	Final Value
V	0	
$\dot{n}_{CO}$	$\dot{n}_{CO,in}$	$\dot{n}_{CO,out} = \dot{n}_{CO,in}\left(1 - f_{CO}\right)$
$\dot{n}_{H_2O}$	$\dot{n}_{H_2O,in}$	
$\dot{n}_{CO_2}$	$\dot{n}_{CO_2,in}$	
$\dot{n}_{H_2}$	$\dot{n}_{H_2,in}$	
$\dot{n}_{I}$	$\dot{n}_{I,in}$	
T	T_{in}	

Deliverables Equations:

$$\dot{n}_{H_2O,in,opt} = \underset{\dot{n}_{H_2O,in}}{\arg\min}\left(\underline{V}\right) \tag{16}$$

$$T_{out} = \left.\left(\left.\underline{T}\right|_{\dot{n}_{CO,out}}\right)\right|_{\dot{n}_{H_2O,in,opt}} \tag{17}$$

Implementation of the Calculations

The Python script, example_9_6_4.py, that was written to perform the calculations accompanies this solution. It defines a PFR model function and a derivatives function that solve the PFR design equations by calling an IVODE solver. The calculations begin by setting a range of values for $\dot{n}_{H_2O,in}$. The PFR design equations are then solved for each value, and the corresponding reactor volume and outlet temperature are saved. After the full range of values has been processed, the inlet H_2O feed rate that minimizes the volume is identified.

Results and Discussion

The calculations were performed as described above, and the reactor volume did not pass through a minimum. The values of the steam feed rate were changed to span the range from 3 to 6 times the CO feed rate, after which the reactor volume did pass through a minimum. Figure 1. shows the reactor volume as a function of the steam feed rate, and Figure 2 shows the outlet temperature. The minimum reactor volume, 2.2 L, occurs at an H_2O feed rate of 4.8 mol h^{-1}. The corresponding outlet temperature is 380 °C.

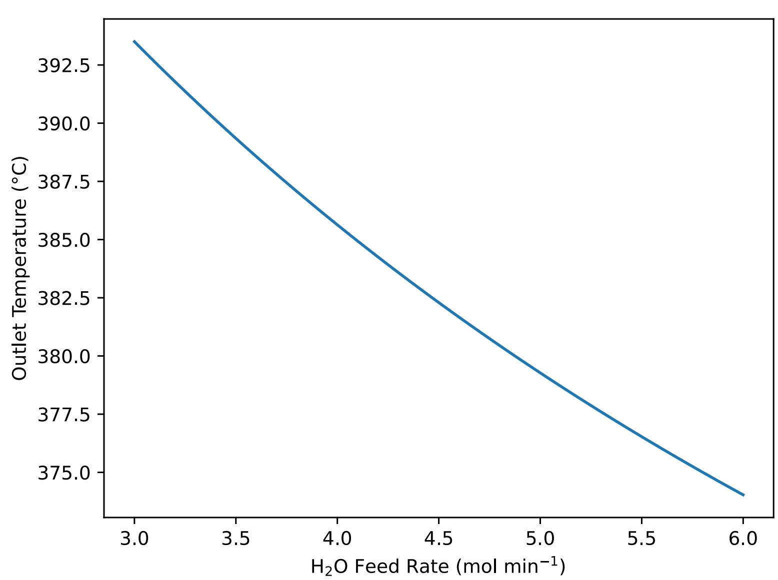

Figure 1. Reactor volume as a function of H_2O feed rate.

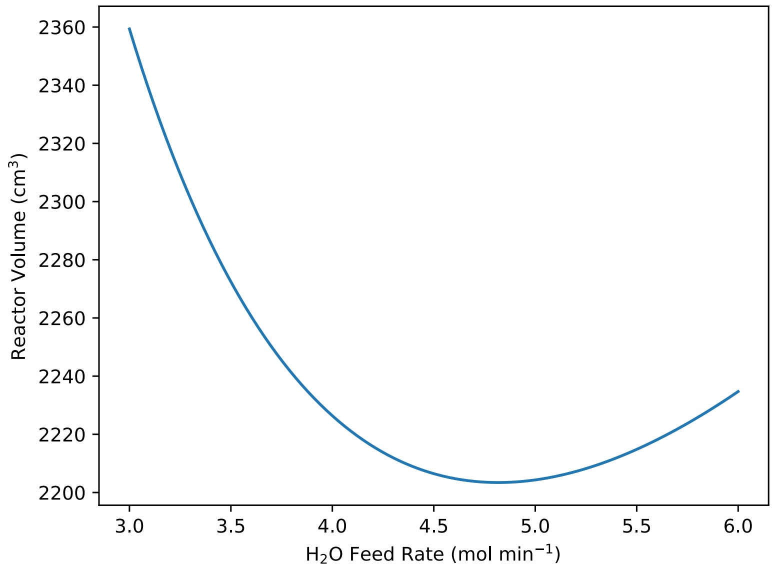

Figure 2. Outlet temperature as a function of H_2O feed rate.

The results are reasonable, based upon a quantitative analysis. First, as the amount of steam in the feed increases, it is expected that the outlet temperature will decrease if the conversion is held constant. By holding the conversion constant, the heat given off by the reaction is also constant. As the amount of steam in the feed increases, the heat of reaction gets spread across a larger number of moles, and consequently the temperature rise of the gas is smaller. Since the inlet temperature is constant, this means that the average temperature in the reactor decreases as the amount of steam in the feed increases.

With respect to the rate of reaction, increasing the steam in the feed leads to a greater average partial pressure of steam and a lower average temperature in the reactor. Examining the rate expression, it can be seen that decreasing the average temperature will cause the rate coefficient to decrease, and taken alone, this will always cause the rate to decrease. If the rate is decreasing, then the volume should increase. While that eventually does occur, Figure 1 shows that at lower steam feed rates, the volume is decreasing, so there must be other factors that are important.

The temperature also affects the equilibrium constant. It will increase as the average temperature decreases (i. e. as the steam feed rate increases). This causes the second term in parentheses in equation (2) to increase. Since that term is being subtracted, increasing it, taken alone, would also tend to decrease the rate and increase the volume. Thus, the decreasing temperature, taken alone, would lead to a steadily decreasing rate because the rate coefficient would decrease and the term containing the equilibrium constant, which is being subtracted, would increase.

However, increasing the steam feed rate will also lead to a larger average partial pressure of steam in the reactor. The rate expression shows that, taken alone, this would tend to increase the reaction rate. So, the increasing partial pressure of steam tends to increase the rate while the decreasing temperature tends to decrease it. As such, the minimum in the volume seen in Figure 1 can be explained qualitatively. At lower steam feed rates, the increased steam partial pressure predominates over the decreased temperature leading to an increase in the rate and a corresponding decrease in the volume needed to reach the fixed conversion. Eventually, the effects of increasing steam partial pressure and decreasing temperature become equal and the volume reaches a minimum. Upon further increase in the steam feed rate, the effect of decreasing temperature predominates over the effect of increasing steam partial pressure, and the rate decreases, leading to an increased reactor volume.

The water-gas shift reaction offers an excellent example of a reversible, exothermic reaction. It was noted in the assignment narrative that two reactors are often used. The reactor considered in this assignment is representative of the first of the two reactors. While the system is far from thermodynamic equilibrium, this reactor can operate at higher temperatures where the rate is larger and the corresponding volume is smaller. However, the reaction approaches equilibrium at conversions that are much smaller than desired.

Therefore in commercial practice, in order to reach higher conversions, the product stream from the first reactor is cooled and fed to a second reactor that operates at much lower temperature. The rate in the second reactor is not as large, due to the lower temperature, but the reaction can proceed to much higher conversion before it approaches equilibrium because the equilibrium constant is much smaller. This situation creates an interesting system design/oprimization situation where the total volume of the two reactors can be minimized with respect to the steam feed rate, the temperature of the feed entering the first reactor, the conversion in the first reactor, and the temperature of the feed entering the second reactor.

Deliverables

The minimum reactor volume, 2.2 L, occurs at an H~2~O feed rate of 4.8 mol h^–1^. The corresponding outlet temperature is 380 °C.