REB, The Book
Example 9.6.3 Solution

The gas-phase decomposition of A according to reaction (1) takes place at steady-state in a PFR. The feed to the reactor is 75% A and 25% inert gas flowing at 100 cm^3 s^{-1} (0.44 g s^{-1}), 3 atm and 400 °C. The reactor diameter is 2.5 cm and its length is 8 m. It is surrounded by a shell containing a molten salt at a constant temperature of 375 °C. The heat transfer coefficient between the reactor and shell is 187 kJ h^{-1} m^{-2} K^{-1}. The reaction is catalytic, and the reactor is packed with catalyst particles with a 0.25 cm diameter, a sphericity of 0.7, and a bed porosity of 0.60.

The rate expression for reaction (1) is given in equation (2) where $k_{0,f}$ = 9.0 x 10^{17} mol cm^3 s^{-1} atm^{-1}, E_f = 285 kJ mol^{-1}, $k_{0,r}$ = 4.09 x 10^{-4} mol cm^{-3} s^{-1} atm^{-4}, and E_r = 85 kJ mol^{-1}. The heat of reaction is constant and equal to 200 kJ mol^{-1}. The heat capacities of the reagents are also constant: $\hat{C}_{p,A}$ = 11.7 cal mol^{-1} K^{-1}, $\hat{C}_{p,Y}$ = 8.3 cal mo^{-1} K^{-1}, $\hat{C}_{p,Z}$ = 4.3 cal mol^{-1} K^{-1}, and $\hat{C}_{p,I}$ = 5.8 cal mol^{-1} K^{-1}. The viscosity may be assumed to be constant and equal to 0.027 cP. What are the outlet temperature, pressure and conversion?

$$A \leftrightarrows Y + 3Z \tag{1}$$

$$r_1 = k_f P_A - k_r P_Y P_Z^3 \tag{2}$$

Assignment Summary

Reaction

$$A \leftrightarrows Y + 3Z \tag{1}$$

Rate Expression

$$r_1 = k_f P_A - k_r P_Y P_Z^3 \tag{2}$$

Reactor: Gas-phase, steady-state PFR heated by a constant temperature exchange fluid

Given Constants: $y_{A,in}$ = 0.75, $y_{I,in}$ = 0.25, $\dot{V}_{in}$ = 100 cm^3 s^{-1}, $\dot{m}_{in}$ = 0.44 g s^{-1}, P_{in} = 3 atm, T_{in} = 400 °C, D = 2.5 cm, L = 8 m, T_{ex} = 375 °C, U = 187 kJ h^{-1} m^{-1} K^{-1}, D_p = 0.25 cm, Φ_s = 0.7, ε = 0.60, $k_{0,f}$ = 9.0 x 10^{17} mol cm^3 s^{-1} atm^{-1}, E_f = 285 kJ mol^{-1}, $k_{0,r}$ = 4.09 x 10^{-4} mol cm^{-3} s^{-1} atm^{-4}, and E_r = 85 kJ mol^{-1}, ΔH_1 = 200 kJ mol^{-1}, $\hat{C}_{p,A}$ = 11.7 cal mol^{-1} K^{-1}, $\hat{C}_{p,Y}$ = 8.3 cal mol^{-1} K^{-1}, $\hat{C}_{p,Z}$ = 4.3 cal mol^{-1}K^{-1}, $\hat{C}_{p,I}$ = 5.8 cal mol^{-1} K^{-1}, and μ = 0.027 cP.

Deliverables: T_{out}, P_{out}, and f_A.

Formulation of the Equations

Reactor Model Equations:

$$\frac{d\dot{n}_A}{dz} = -\frac{\pi D^2}{4} r_1 \tag{3}$$

$$\frac{d\dot{n}_Y}{dz} = \frac{\pi D^2}{4} r_1 \tag{4}$$

$$\frac{d\dot{n}_Z}{dz} = 3\frac{\pi D^2}{4} r_1 \tag{5}$$

$$\frac{d\dot{n}_I}{dz} = 0.0 \tag{6}$$

$$\frac{dT}{dz} = \frac{\pi D U \left(T_{ex} - T\right) - \frac{\pi D^2}{4} r_1 \Delta H_1}{\dot{n}_A \hat{C}_{p,A} + \dot{n}_B \hat{C}_{p,I} + \dot{n}_Y \hat{C}_{p,Y} + \dot{n}_Z \hat{C}_{p,Z}} \tag{7}$$

$$\frac{dP}{dz} = -\frac{1-\varepsilon}{\varepsilon^3} \frac{G^2}{\rho \Phi_s D_p} \left[\frac{150\,(1-\varepsilon)\,\mu}{\Phi_s D_p G} + 1.75 \right] \tag{8}$$

Reactor Model Variables: $\underline{z}$, $\underline{\dot{n}}_A$, $\underline{\dot{n}}_Y$, $\underline{\dot{n}}_Z$, $\underline{\dot{n}}_I$, $\underline{T}$, and $\underline{P}$.

Additional Computable Unknowns: r_1, $k_{1,f}$, $k_{1,r}$, P_A, P_Y, P_Z, G, $\dot{m}$, and ρ

$$k_{1,j} = k_{0,f} \exp\left(\frac{-E_j}{RT}\right) \qquad j = f \text{ and } r \tag{9}$$

$$P_i = \frac{\dot{n}_i}{\dot{n}_A + \dot{n}_Y + \dot{n}_Z + \dot{n}_I} P \qquad i = A, Y, \text{ and } Z \tag{10}$$

$$\dot{m} = \dot{m}_{in} \tag{11}$$

$$G = \frac{4\dot{m}}{\pi D^2} \tag{12}$$

$$\rho = \frac{\dot{m} P}{\left(\dot{n}_A + \dot{n}_Y + \dot{n}_Z + \dot{n}_I\right) RT} \tag{13}$$

IVODE Solver Inputs:

1. Initial values of the reactor model variables shown in Table 1.
2. Stopping criterion that z equals the final value shown in Table 1.
3. Derivatives function that
   a. receives the reactor model variables at the start of an integration step
   b. calculates the additional unknowns using equations (9) through (13)
   c. evaluates and returns the design equation derivatives, equations (3) through (8)

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

Variable	Initial Value	Final Value
z	0	L
$\dot{n}_A$	$\dot{n}_{A,in} = y_{A,in}\dfrac{P_{in}\dot{V}_{in}}{RT_{in}}$	
$\dot{n}_Y$	0	
$\dot{n}_Z$	0	
$\dot{n}_I$	$\dot{n}_{I,in} = y_{I,in}\dfrac{P_{in}\dot{V}_{in}}{RT_{in}}$	
T	T_{in}	
P	P_{in}	

<u>Deliverables Equations</u>:

$$T_{out} = \underline{T}\Big|_{z=L} \tag{14}$$

$$P_{out} = \underline{P}\Big|_{z=L} \tag{15}$$

$$f_A = \frac{\dot{n}_{A,in} - \underline{\dot{n}}_A\Big|_{z=L}}{\dot{n}_{A,in}} \tag{16}$$

Implementation of the Calculations

The Python script, example_9_6_3.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 using an IVODE solver. The calculations involve solving the design equations and calculating the quantities of interest.

Results and Discussion

The calculations were performed as described above. The outlet temperature is 364 °C, the outlet pressure is 2.92 atm, and the conversion is 77.7%. This system is similar to that of Example 9.6.1 in that while the feed is at 400 °C and the heat exchange fluid is at 375 °C, the gas leaving the reactor is at 364 °C. Apparently the heat absorbed due to reaction greater than that provided by the heat exchange fluid.

The pressure drop here is only 0.08 atm, but there was no way of knowing that without performing the calculations. Performing the analysis assuming constant pressure yields an outlet temperature of 362 °C and a conversion of 78.6%, indicating that ignoring the pressure drop did not affect the calculated outlet temperature and conversion significantly. However, it is difficult to predict the magnitude of the pressure drop in a packed bed. Consequently, it is wise to account for it in case it proves to be more significant.

Deliverables

The specified PFR has an outlet temperature of 364 °C, an outlet pressure of 2.92 atm, and the conversion is 77.7%.