REB, The Course
Class 22 Learning Activity Solution

Hill and Root[1] describe the adiabatic oxidation of sulfur dioxide, reaction (1), in a steady-state, packed-bed PFR. A feed containing 8% SO_2, 13% O_2, and 79% N_2 at 1 atm and 370 °C was fed to the first of two reactors at 0.149 lbmol s^{-1}. It was assumed to have an effective viscosity of 0.09 lb h^{-1} ft^{-1}. Spherical catalyst particles with a diameter of 0.25 in formed a packed bed with a porosity of 0.4 and a density of 0.6 g cm^{-3}. The reactor diameter was 6 ft, and it operated at a conversion of 0.81. The rate expression shown in equation (2) was used with $k_{0,f}$ = 1.745 x 10^5 mol s^{-1} g_{cat}^{-1} $atm^{-1.5}$, E_f = 31 kcal mol^{-1}, $k_{0,r}$ = 7.59 x 10^9 mol s^{-1} g_{cat}^{-1} atm, and E_r = 53.6 kcal mol^{-1}. Their analysis assumed no pressure drop, but after completing the analysis they estimated the pressure drop and found it to be significant. They suggested that the pressure drop could be decreased by using a larger reactor diameter.

Repeat their analysis, accounting for pressure drop, for reactors with diameters of 3, 6, and 9 ft and comment on the results. Specifically calculate the required catalyst volume and the pressure drop, and plot the temperature as a function of axial position in the reactor. Selected thermodynamic data are given in Table 1 where the heats of formation are in cal mol^{-1}, and the heat capacities of the reagents in cal mol^{-1} K^{-1} can be calculated using the coefficients, α_i, β_i, γ_i, and δ_i, with temperatures in K.

$$SO_2 + \frac{1}{2}O_2 \rightleftarrows SO_3 \tag{1}$$

$$r = \frac{k_f P_{SO_2} P_{O_2} - k_r P_{SO_3}\sqrt{P_{O_2}}}{\sqrt{P_{SO_2}}} \tag{2}$$

$$\hat{C}_{p,i} = \alpha_i + \beta_i T + \gamma_i T^2 + \delta_i T^3 \tag{3}$$

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[1] C. G. Hill, Jr, and T. W. Root. “Introduction to Chemical Engineering Kinetics and Reactor Design,” 2nd Ed. Wiley, Hoboken, NJ, 2014.

Table 1. Thermodynamic Data

i	$\Delta H_{f,i}\Big\vert_{298\,K}$	α_i	β_i	γ_i	δ_i
SO_2	–70950	5.697	0.016	–1.185 x 10^{-5}	3.172 x 10^{-9}
O_2	0	6.713	–8.79 x 10^{-7}	4.175 x 10^{-6}	–2.544x 10^{-9}
SO_3	–94470	12.13	0.00812		
N_2	0	7.44	–0.00324	6.4 x 10^{-6}	2.79 X 10^{-9}

Assignment Summary

To simplify the notation, let D represent sulfur dioxide; O, oxygen; T, sulfur trioxide; and I, nitrogen

Reaction

$$D + \frac{1}{2}O \rightleftarrows T \tag{1}$$

Rate Expression

$$r_1 = \frac{k_f P_D P_O - k_r P_T \sqrt{P_O}}{\sqrt{P_D}} \tag{2}$$

Reactor: Gas-phase, steady-state, adiabatic, packed-bed PFR

Given Constants: $y_{D,in}$ = 0.08, $y_{O,in}$ = 0.13, $Y_{I,in}$ = 0.79, P_{in} = 1 atm, T_{in} = 370 °C, $\dot{n}_{in}$ = 0.149 lbmol s^{-1}, μ = 0.09 lb h^{-1} ft^{-1}, D_p = 0.25 in, ε = 0.4, ρ_{bed} = 0.6 g cm^{-3}, f_D = 0.81, $k_{0,f}$ = 1.745 x 10^5 mol s^{-1} g_{cat}^{-1} $atm^{-1.5}$, E_f = 31 kcal mol^{-1}, $k_{0,r}$ = 7.59 x 10^9 mol s^{-1} g_{cat}^{-1} atm, E_r = 53.6 kcal mol^{-1}, and $\Delta H_i\Big\vert_{298K}$, α_i, β_i, γ_i, and δ_i in Table 1.

Parameters: $\underline{D} = [6,8,10]$ ft

Deliverables: V_{cat}, $-\Delta P$, and T vs. t as a graph, all for each value of D

Formulation of the Equations

Reactor Model Equations:

$$\frac{d\dot{n}_D}{dz} = \rho_{bed}\frac{\pi D^2}{4}\left(-r_1\right) \tag{4}$$

$$\frac{d\dot{n}_O}{dz} = \rho_{bed}\frac{\pi D^2}{4}\left(-\frac{1}{2}r_1\right) \tag{5}$$

$$\frac{d\dot{n}_T}{dz} = \rho_{bed}\frac{\pi D^2}{4}\left(r_1\right) \tag{6}$$

$$\frac{d\dot{n}_I}{dz} = 0 \tag{7}$$

$$\frac{dT}{dz} = -\frac{\pi D^2}{4}\frac{r_1\Delta H_1}{\dot{n}_D\hat{C}_{p,D} + \dot{n}_O\hat{C}_{p,O} + \dot{n}_T\hat{C}_{p,T} + \dot{n}_I\hat{C}_{p,I}} \tag{8}$$

$$\frac{dP}{dz} = -\frac{1-\varepsilon}{\varepsilon^3}\frac{G^2}{\rho D_p}\left[\frac{150\left(1-\varepsilon\right)\mu}{D_pG} + 1.75\right] \tag{9}$$

Reactor Model Variables: z, $\dot{n}_D$, $\dot{n}_O$, $\dot{n}_T$, $\dot{n}_I$, T, and P

Additional Computable Unknowns: r_1, k_f, k_r, P_D, P_O, P_T, ΔH_1, $\hat{C}_{p,D}$, $\hat{C}_{p,O}$, $\hat{C}_{p,T}$, $\hat{C}_{p,I}$, and G

$$k_i = k_{0,i}\exp\left(\frac{-E_f}{RT}\right) \qquad i = f \text{ and } r \tag{10}$$

$$P_i = \frac{\dot{n}_i}{\dot{n}_D + \dot{n}_O + \dot{n}_T + \dot{n}_I}P \qquad i = D, O, \text{ and } T \tag{11}$$

$$\Delta H_1\Big|_{298K} = \Delta H_{f,T}\Big|_{298K} - \Delta H_{f,D}\Big|_{298K} - \frac{1}{2}\Delta H_{f,O}\Big|_{298K} \tag{12}$$

$$\Delta\alpha = \alpha_T - \alpha_D - \frac{1}{2}\alpha_O \tag{13}$$

$$\Delta\beta = \beta_T - \beta_D - \frac{1}{2}\beta_O \tag{14}$$

$$\Delta\gamma = \gamma_T - \gamma_D - \frac{1}{2}\gamma_O \tag{15}$$

$$\Delta\delta = \delta_T - \delta_D - \frac{1}{2}\delta_O \tag{16}$$

$$\begin{aligned}\Delta H_1 = \Delta H_1\Big|_{298K} &+ \Delta\alpha\,(T - 298K) + \frac{\Delta\beta}{2}\left(T^2 - (298K)^2\right) \\ &+ \frac{\Delta\gamma}{3}\left(T^3 - (298K)^3\right) + \frac{\Delta\delta}{4}\left(T^4 - (298K)^4\right)\end{aligned} \tag{17}$$

$$G = \frac{4\left(\dot{n}_D M_D + \dot{n}_O M_O + \dot{n}_T M_T + \dot{n}_I M_I\right)}{\pi D^2} \tag{18}$$

IVODE Solver Inputs:

1. Initial values of the reactor model variables shown in Table 2
2. Stopping criterion that $\dot{n}_D$ equals the final value shown in Table 2.
3. Derivatives function that
   a. receives the reactor model variables at the start of an integration step
   b. calculates the additional unknowns using equations (2), (3), and (10) through (18)
   c. evaluates and returns the design equation derivatives, equations (4) - (9)

Table 2. Initial and final values of the design equation variables.

Variable	Initial Value	Final Value
z	0	
$\dot{n}_D$	$\dot{n}_{D,in}$	$\dot{n}_{D,out} = \dot{n}_{D,in}\left(1 - f_D\right)$
$\dot{n}_O$	$\dot{n}_{O,in}$	
$\dot{n}_T$	0	
$\dot{n}_I$	$\dot{n}_{I,in}$	
T	T_{in}	
P	P_{in}	

Deliverables Equations: (for each value of D

$$V_{cat} = \frac{\pi D^2}{4} z \Big|_{\dot{n}_D = \dot{n}_{D,out}} \tag{19}$$

$$-\Delta P = P_{in} - P \Big|_{\dot{n}_D = \dot{n}_{D,out}} \tag{20}$$

Implementation of the Calculations

The Python script, activity_22.py, that was written to perform the calculations accompanies this solution. It defines a PFR model function and a deliverables function that solve the design equations for a given value of the reactor diameter using an IVODE solver. The calculation loop through the three values of the diameter, solving the design equations and calculating the quantities of interest.

Results and Discussion

The calculations were performed as described above. The catalyst volumes and the pressure drops for the three reactor diameters are shown in Table 3. The temperature profiles are shown in Figure 1.

Table 3. Required Catalyst Volume and Pressure Drop for the three Specified Reactor Diameters

Diameter (ft)	Catalyst Volume (ft^3)	Pressure Drop (atm)
6	266	0.124
8	249	0.035
10	246	0.014

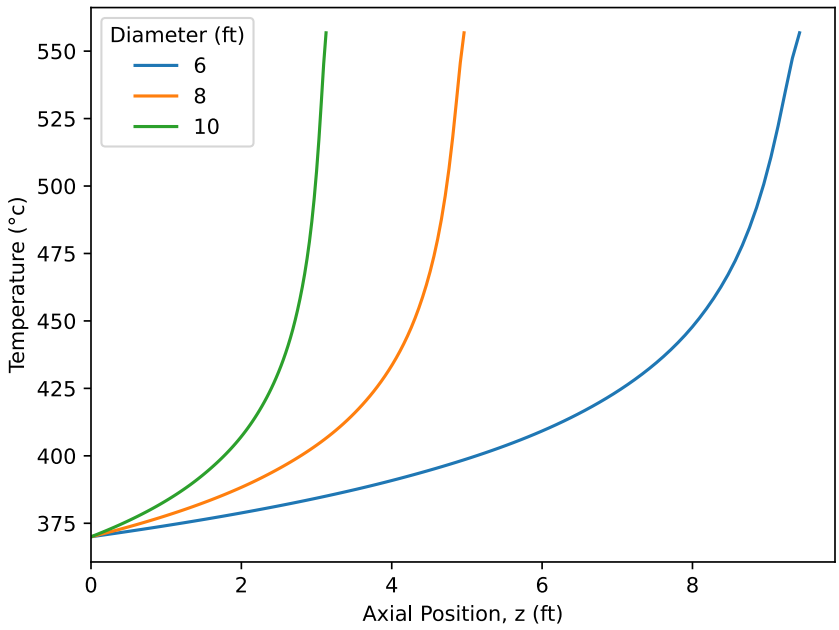

Figure 1. Temperature Profiles for Three Reactor Diameters.

Figure 1 shows that the outlet temperature from all three reactors is the same. This is expected because each reactor is adiabatic, and the feed and conversion are the same. As the figure shows, the only difference is the reactor length required to reach the final conversion. As expected, the length decreases as the reactor diameter increases. The PFR model assumes perfect mixing in the radial direction. The larger the diameter, the more catalyst is present in a thin reactor cross-section, and so the greater the conversion.

Table 3 shows that the catalyst volume is almost the same for all three cases. In fact, if there were no pressure drop, the volume would be exactly the same and equal to 243 ft^3. This is true, only because the reactor is adiabatic. Since no heat is being transferred through the reactor wall, the conversion at any point in the reactor only depends upon the cumulative catalyst volume up to that point. If heat were being transferred, the conversion would depend on both the cumulative catalyst volume and the cumulative heat transfer area. For a cylindrical reactor, the ratio of the volume to the wall area changes as the diameter changes.

In this analysis, the reactors are adiabatic, but still the reactor volume changes as the diameter changes. The reason for this is that the pressure drop varies with reactor diameter. Specifically, the pressure drop decreases as the reactor diameter increases. As the pressure decreases, the partial pressures of the reagents decrease, and hence the rate decreases. Thus, a reactor with a larger pressure drop has a lower rate, requiring additional volume to reach the same conversion.

In the reactor with a 6 ft diameter, the pressure drops by over 12%, while in the reactor with an 8 ft diameter it drops by only 3.5%. Pressure drop is caused by friction between the flowing fluid and the solid surfaces (walls and catalyst particles) in the reactor. In a larger diameter reactor, the distance from the inlet to the outlet is shorter than in a smaller diameter reactor. Hence, since the fluid flows a shorter distance, it experiences less friction, and the pressure drop is not as large.

When packed bed reactors operate adiabatically, the diameter is often large for this reason. If heat also must be transferred to or from the reacting fluid, it often is not possible to use a large reactor diameter, because that results in a heat transfer area that is too small.

Deliverables

The catalyst volumes and the pressure drops for the three reactor diameters are shown in Table 3. The temperature profiles are shown in Figure 1.