REB, The Course
Class 21 Learning Activity Solution

A gas mixture at 140 ºC and 1.0 atm and containing 30% A and 70% B is fed to a steady-state PFR at a flow rate of 0.45 L min^{-1}. The PFR diameter is 4 cm and there is no pressure drop along its length. An external fluid, also at a temperature of 140 ºC, is fed at a rate of 20 g min^{-1} to a perfectly mixed shell surrounding the reactor tube. The heat capacity of that fluid is 1.4 J g^{-1} K^{-1}, and the heat transfer coefficient is 1.3 x 10^{-6} kJ min^{-1} cm^{-2} K^{-1}.

Reactions (1) and (2) occur within the reactor at a space time of 20 min. The rate expressions for the reactions are given in equations (3) and (4). The pre-exponential factors for reactions (1) and (2) are equal to 1.65 × 10^{4} mol min^{-1} cm^{-3} atm^{-2} and 3.24 × 10^{4} mol min^{-1} cm^{-3} atm^{-2}, respectively. The activation energies for reactions (1) and (2) are equal to 78 kJ mol^{-1} and 86 kJ mol^{-1}, respectively. The standard heats of reactions (1) and (2) are −35.1 kJ mol^{-1} and −32.6 kJ mol^{-1}, respectively. The heat capacities of the reagents, in J mol^{-1} K^{-1}, are A: 78.3, B: 81.1, D: 75.4, Z: 68.3 and U: 76.3.

$$A + B \rightarrow D + Z \tag{1}$$

$$D + B \rightarrow U + Z \tag{2}$$

$$r_1 = k_1 P_A P_B \tag{3}$$

$$r_2 = k_2 P_D P_B \tag{4}$$

What are the conversion of A, the selectivity for D over U, the outlet temperature and the exchange fluid temperature?

Assignment Summary

<u>Reactions</u>

$$A + B \rightarrow D + Z \tag{1}$$

$$D + B \rightarrow U + Z \tag{2}$$

Rate Expressions

$$r_1 = k_1 P_A P_B \tag{3}$$

$$r_2 = k_2 P_D P_B \tag{4}$$

Reactor: Steady-state, cooled, gas-phase PFR

Given Constants: T_{in} = 140 ºC, P = 1.0 atm, $y_{A,in}$ = 0.30, $y_{B,in}$ = 07, $\dot{V}_{in}$ = 0.45 L min^{-1}, D = 4 cm, $T_{ex,in}$ =140 ºC, $\dot{m}_{ex}$ = 20 g min^{-1}, $\tilde{C}_{p,ex}$ = 1.4 J g^{-1} K^{-1}, U_{ex} = 1.3 x 10^{-6} kJ min^{-1} cm^{-2} K^{-1}, τ = 20 min, $k_{0,1}$ = 1.65 × 10^4 mol min^{-1} cm^{-3} atm^{-2}, $k_{0,2}$ = 3.24 × 10^4 mol min^{-1} cm^{-3} atm^{-2}, E_1 = 78 kJ mol^{-1}, E_2 = 86 kJ mol^{-1}, ΔH_1 = −35.1 kJ mol^{-1}, ΔH_2 = −32.6 kJ mol^{-1}, $\hat{C}_{p,A}$ = 78.3 J mol^{-1} K^{-1}, $\hat{C}_{p,B}$ = 81.1 J mol^{-1} K^{-1}, $\hat{C}_{p,D}$ = 75.4J mol^{-1} K^{-1}, $\hat{C}_{p,Z}$ = 68.3 J mol^{-1} K^{-1}, and $\hat{C}_{p,U}$ = 76.3 J mol^{-1} K^{-1}.

Deliverables: f_A, $S_{D/U}$, T_{out}, and $T_{ex,out}$.

Formulation of the Equations

Reactor Model Equations:

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

$$\frac{d\dot{n}_B}{dz} = \frac{\pi D^2}{4}\left(-r_1 - r_2\right) \tag{6}$$

$$\frac{d\dot{n}_D}{dz} = \frac{\pi D^2}{4}\left(r_1 - r_2\right) \tag{7}$$

$$\frac{d\dot{n}_Z}{dz} = \frac{\pi D^2}{4}\left(r_1 + r_2\right) \tag{8}$$

$$\frac{d\dot{n}_U}{dz} = \frac{\pi D^2}{4}\left(r_2\right) \tag{9}$$

$$\frac{dT}{dz} = \frac{\pi D U_{ex}\left(T_{ex} - T\right) - \frac{\pi D^2}{4}\left(r_1 \Delta H_1 + r_2 \Delta H_2\right)}{\dot{n}_A \hat{C}_{p,A} + \dot{n}_B \hat{C}_{p,B} + \dot{n}_D \hat{C}_{p,D} + \dot{n}_Z \hat{C}_{p,Z} + \dot{n}_U \hat{C}_{p,U}} \tag{10}$$

<u>Reactor Model Variables</u>: $\underline{z}$, $\underline{\dot{n}}_A$, $\underline{\dot{n}}_B$, $\underline{\dot{n}}_D$, $\underline{\dot{n}}_Z$, $\underline{\dot{n}}_U$, and $\underline{T}$

<u>Additional Computable Unknowns</u>: r_1, r_2, k_1, k_2, P_A, P_B, and P_D

$$k_i = k_{i,0} \exp\left(\frac{-E_i}{RT}\right) \qquad i = 1 \text{ and } 2 \tag{11}$$

$$P_i = \frac{\dot{n}_i}{\dot{n}_A + \dot{n}_B + \dot{n}_D + \dot{n}_Z + \dot{n}_U} \qquad i = A, B, \text{ and } D \tag{12}$$

<u>Additional Coupled Unknown</u>: T_{ex}

$$\dot{Q} = \pi D U_{ex} \int_0^L \left(T_{ex} - T\right) dz \tag{13}$$

$$0 = \dot{Q} + \dot{m}_{ex} \tilde{C}_{p,ex}\left(T_{ex} - T_{ex,in}\right) = \epsilon \tag{14}$$

<u>IVODE Solver Inputs</u>:

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
    b. calculates the additional unknowns, equations (11) and (12)
    c. evaluates and returns the design equation derivatives, equations (5) through (10)

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

Variable	Initial Value	Final Value
z	0	$L = \dfrac{4\tau\dot{V}_{in}}{\pi D^2}$
$\dot{n}_A$	$\dot{n}_{A,in} = y_{A,in}\dfrac{\dot{V}_{in}P}{RT_{in}}$	
$\dot{n}_B$	$\dot{n}_{B,in} = y_{B,in}\dfrac{\dot{V}_{in}P}{RT_{in}}$	
$\dot{n}_D$	0	
$\dot{n}_Z$	0	
$\dot{n}_U$	0	
T	T_{in}	

ATE Solver Inputs:

1. Initial guess for the coupled unknown, T_{ex}
2. Residual function that
   a. receives a guess for the coupled unknown
   b. solves the PFR design equations to get $\underline{z}$ and $\underline{T}$
   c. evaluates and returns the coupled unknown residual using equations (13) and (14)

Deliverables Equations:

$$f_A = \frac{\dot{n}_{A,in} - \underline{\dot{n}}_A\Big|_{z=L}}{\dot{n}_{A,in}} \tag{15}$$

$$S_{D/U} = \frac{\underline{\dot{n}}_D}{\underline{\dot{n}}_U}\Bigg|_{z=L} \tag{16}$$

$$T_{out} = \underline{T}\Big|_{z=L} \tag{17}$$

Implementation of the Calculations

The Python script, activity_21.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 given a value for T_{ex} by calling an IVODE solver. It also defines an uncoupled unknown residual function that evaluates ϵ given a guess for T_{ex}. The calculations begin by calculating T_{ex} using an ATE solver and the coupled unknown residual function. It then solves the PFR design equations and calculates the quantities of interest.

Results and Discussion

The calculations were performed as described, and the results are shown in Table 2. The conversion and the selectivity for D are both high. The outlet temperatures of both the reacting gas and the exchange fluid are within 10 °C of their inlet value (140 °C). The reactions are both exothermic, but heat is being removed by the exchange fluid.

Table 2. Quantities of Interest

Quantity	Value	Units
f_A	86.6	%
$S_{D/U}$	3.13	mol D per mol U
T_{out}	148	°C
$T_{ex,out}$	145	

There are two possibilities for the temperature in the center section of the reactor. One is that the heat removal is so effective that the temperature is always close to that of the exchange fluid. The other possibility is that the temperature rises considerable within the reactor, but it decreases near the outlet where the rate is low, and consequently the amount of heat being released is low. It is always a good idea to calculate the temperature profile in a situation like this to make sure the temperature remains reasonable at all locations within the reactor.

Figure 1. shows the temperature profile for this reactor. The exchange fluid temperature is also plotted in that figure. At the inlet, the exchange fluid is warmer than the reacting fluid, and so it heats the reacting fluid. However, most of the temperature rise is due to the heat being released by the reaction. (The exchange fluid cannot heat the reacting fluid higher than the temperature of the exchange fluid, 145 °C.) The temperature rises to a maximum level of 173 °C before passing through a maximum and then decreasing.

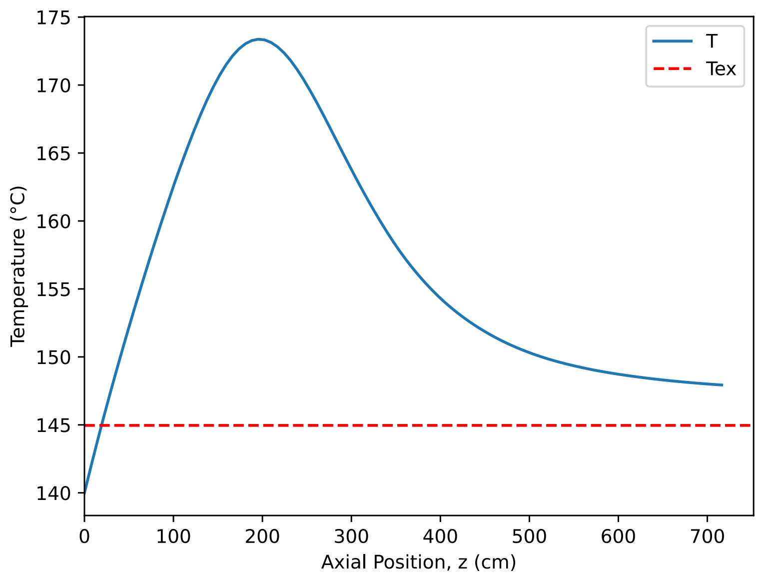

Figure 1. Temperature profile in the PFR.

Prior to reaching the maximum temperature, the reaction is releasing heat faster than the exchange fluid can remove it. Farther into the reactor, where the reactant partial pressure has decreased, the rate of reaction, and hence the rate of heat release, decreases. The maximum temperature is the point where the heat release and heat removal are just equal. Beyond the maximum, the rate of heat removal exceeds the rate of heat generation.

In this reactor, assuming that no degradation or undesired side reactions occur at the higher temperatures, the temperature rise is modest and under control. Just because the outlet temperature is close to the inlet, it is always possible that the temperature rose to an unacceptably high level within the reactor, but cooled back down before reaching the outlet. Plotting the temperature profile shows whether the rate of temperature rise or the maximum temperature is unacceptably large within the reactor.

Deliverables

The conversion is 86.6%, the selectivity for D over U is 3.13, the outlet temperature is 148 °C and the exchange fluid temperature is 145 °C.