REB, The Course
Class 23 Learning Activity Solution

On a molar basis, a gas phase mixture contains 20% reagent A, 45% reagent B, 25% reagent C, and 10% reagent I at 220 °C and 3 atm. The mixture is fed at a rate of 1000 L min^{-1} to a PFR with a diameter of 5 cm and a length of 1 m. A fluid at a constant temperature of 185 °C surrounds the reactor tube which has a heat transfer coefficient of 850 cal m^{-2} min^{-1} K^{-1}. The heat capacities of A, B, C, X, Y, ,Z and I are constant and equal to 12.7, 8.6, 11.3, 6.3, 14.4, 10.8, and 15.6 cal mol^{-1} K^{-1}, respectively.

Heterogeneous catalytic reactions (1) and (2) take place within the PFR with no pressure drop. The bed density is 2.3 g cm^{-3}. The rate expressions are given in equations (3) and (4). The pre-exponential factors for reactions (3) and (4) are 4.35 x 10^5 mol g^{-1} atm^{-2} min^{-1} and 2.17 x 10^6 mol g^{-1} atm^{-2} min^{-1}, respectively, and the activation energies are 19.7 and 21.3 kcal mol^{-1}, respectively. The heat of reaction 1 is 28.3 kcal mol^{-1} and the heat of reaction (2) is 29.8 kcal mol^{-1}.

What are the conversion of B, the selectivity in moles of Y per mole of Z, and the temperature at the reactor outlet?

$$A + B \rightarrow X + Y \quad (1)$$

$$B + C \rightarrow X + Z \quad (2)$$

$$r_1 = k_1 P_A P_B \quad (3)$$

$$r_2 = k_2 P_B P_C \quad (4)$$

Assignment Summary

Reactions

$$A + B \rightarrow X + Y \quad (1)$$

$$B + C \rightarrow X + Z \quad (2)$$

Rate Expressions

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

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

Reactor:

Given Constants: $y_{A,in}$ = 0.2, $y_{B,in}$ = 0.45, $y_{C,in}$ = 0.25, $y_{I,in}$ = 0.1, T_{in} = 220 °C, P = 1 atm, $\dot{V}_{in}$ = 1000 L min^{-1}, D = 5 cm, L = 1 m, T_{ex} = 185 °C, U = 850 cal m^{-2} min^{-1} K^{-1}, $\hat{C}_{p,A}$ = 12.7 cal mol^{-1} K^{-1}, $\hat{C}_{p,B}$ = 8.6 cal mol^{-1} K^{-1}, $\hat{C}_{p,C}$ = 11.3 cal mol^{-1} K^{-1}, $\hat{C}_{p,X}$ = 6.3 cal mol^{-1} K^{-1}, $\hat{C}_{p,Y}$ = 14.4 cal mol^{-1} K^{-1}, $\hat{C}_{p,Z}$ = 10.8 cal mol^{-1} K^{-1}, $\hat{C}_{p,I}$ = 15.6 cal mol^{-1} K^{-1}, $k_{0,1}$ = 4.35 x 10^5 mol g^{-1} atm^{-2} min^{-1}, $k_{0,2}$ = 2.17 x 10^6 mol g^{-1} atm^{-2} min^{-1}, E_1 = 19.7, E_2 = 21.3 kcal mol^{-1}, ΔH_1 = 28.3 kcal mol^{-1}, and ΔH_2 = 29.8 kcal mol^{-1}.

Deliverables: f_B, $S_{Y/Z}$, T_{out}

Formulation of the Equations

Reactor Model Equations:

$$\frac{d\dot{n}_A}{dz} = -\frac{\pi D^2}{4}\rho_{bed} r_1 \tag{5}$$

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

$$\frac{d\dot{n}_C}{dz} = -\frac{\pi D^2}{4}\rho_{bed} r_2 \tag{7}$$

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

$$\frac{d\dot{n}_Y}{dz} = \frac{\pi D^2}{4}\rho_{bed} r_1 \tag{9}$$

$$\frac{d\dot{n}_Z}{dz} = \frac{\pi D^2}{4}\rho_{bed} r_2 \tag{10}$$

$$\frac{d\dot{n}_I}{dz} = 0 \tag{11}$$

$$\frac{dT}{dz} = \frac{4\pi DU\left(T_{ex} - T\right) - \pi D^2 \rho_{bed} r \Delta H}{4\left(\begin{matrix}\dot{n}_A\hat{C}_{p,A} + \dot{n}_B\hat{C}_{p,B} + \dot{n}_C\hat{C}_{p,C} + \dot{n}_X\hat{C}_{p,X} \\ +\dot{n}_Y\hat{C}_{p,Y} + \dot{n}_Z\hat{C}_{p,Z} + \dot{n}_I\hat{C}_{p,I}\end{matrix}\right)} \tag{12}$$

Reactor Model Variables: z, $\dot{n}_A$, $\dot{n}_B$, $\dot{n}_C$, $\dot{n}_X$, $\dot{n}_Y$, $\dot{n}_Z$, $\dot{n}_I$, and T.

Additional Computable Unknowns: r_1, r_2, k_1, k_2, P_A, P_B, and P_C

$$k_i = k_{0,i}\exp\left(\frac{-E_i}{RT}\right) \qquad i = 1 \text{ and } 2 \tag{13}$$

$$P_I = \frac{\dot{n}_i P}{\dot{n}_A + \dot{n}_B + \dot{n}_C + \dot{n}_X + \dot{n}_Y + \dot{n}_Z + \dot{n}_I} \qquad i = A, B, \text{ and } C \tag{14}$$

IVODE Solver Inputs:

1. Initial values of the reactor model variables shown in Table 1 where

$$\dot{n}_{in} = \dot{n}_{A,in} + \dot{n}_{B,in} + \dot{n}_{C,in} + \dot{n}_{I,in} \tag{15}$$

2. Stopping criterion that z equals the final value shown in Table 1.
3. Residuals/Derivatives function that
   a. receives the PFR model variables at the start of an integration step
   b. calculates the additional unknowns, equations (13) and (14)
   c. evaluates and returns the PFR design equation derivatives, equations (5) through (12)

Table 1. Initial and final values of the PFR model variables

z	0	L
$\dot{n}_A$	$y_{A,in}\dot{n}_{in}$	
$\dot{n}_B$	$y_{B,in}\dot{n}_{in}$	
$\dot{n}_C$	$y_{C,in}\dot{n}_{in}$	
$\dot{n}_Y$	0	
$\dot{n}_X$	0	
$\dot{n}_Z$	0	
$\dot{n}_I$	$y_{I,in}\dot{n}_{in}$	
T	T_{in}	

Deliverables Equations:

$$f_B = \frac{\underline{\dot{n}}_B\Big|_{z=0} - \underline{\dot{n}}_B\Big|_{z=L}}{\underline{\dot{n}}_B\Big|_{z=0}} \tag{15}$$

$$S_{Y/Z} = \frac{\underline{\dot{n}}_Y}{\underline{\dot{n}}_Z}\Big|_{z=L} \tag{16}$$

$$T_1 = \underline{T}\Big|_{z=L} \tag{17}$$

Implementation of the Calculations

The Python script, activity_23.py, that was written to perform the calculations accompanies this solution. When the temperature profile found by assuming the equations were not stiff was plotted, it exhibited some mild oscillations. Repeating the calculations assuming the design equations to be stiff eliminated the oscillations.

Results and Discussion

The calculations were performed as described above. The conversion was 19.1%, the selectivity, 0.94 mol Y per mol Z, and the outlet temperature, 174 °C. The reactions are endothermic, and heat is being provided by the exchange fluid. The relative magnitudes of the instantaneous absorption of reaction heat and heat exchange will determine whether the temperature increases or decreases at any point in the reactor.

At the inlet the feed is hotter than the exchange fluid, so heat is transferred from it to the exchange fluid. Together with the endothermic reactions, this causes the temperature to drop. Once the temperature becomes equal to the exchange fluid temperature, it could continue to drop, or it could level off, depending on the rate of reaction (and hence the rate of heat absorption by the reaction). If the reactor is long enough, the temperature will approach the exchange fluid temperature as the rate approaches zero.

The temperature profile is plotted in Figure 1. It shows that the temperature continues to drop until it reaches a minimum at approximately 173 °C, after which it rises steadily, but slowly. The minimum represents the point where the rate of heat absorption by the reaction just equals the rate of heat addition from the exchange fluid. Prior to that point the reaction was absorbing heat faster than the exchange fluid was providing it. After that point, the heat exchanger fluid provides heat faster than the reaction absorbs it.

The initially rapid rate of temperature decrease is expected to cause the rate to decrease significantly in the first 100 cm of the reactor. Beyond that point, the temperature slowly rises, while the reactant concentration decreases. The temperature will not decrease after this point, so the reactant concentration is expected to decrease steadily with a concave upward curvature where it asymptotically approaches zero as the reactant is fully consumed. However, in this reactor the length is not sufficient for that to happen, and the conversion only reaches 19.1%.

The reactions occur in parallel and have similar dependence on the reactant concentrations, so the selectivity is not expected to vary significantly as the reaction proceeds. It will be determined primarily by the rate coefficients, which, in turn, are set by the temperature.

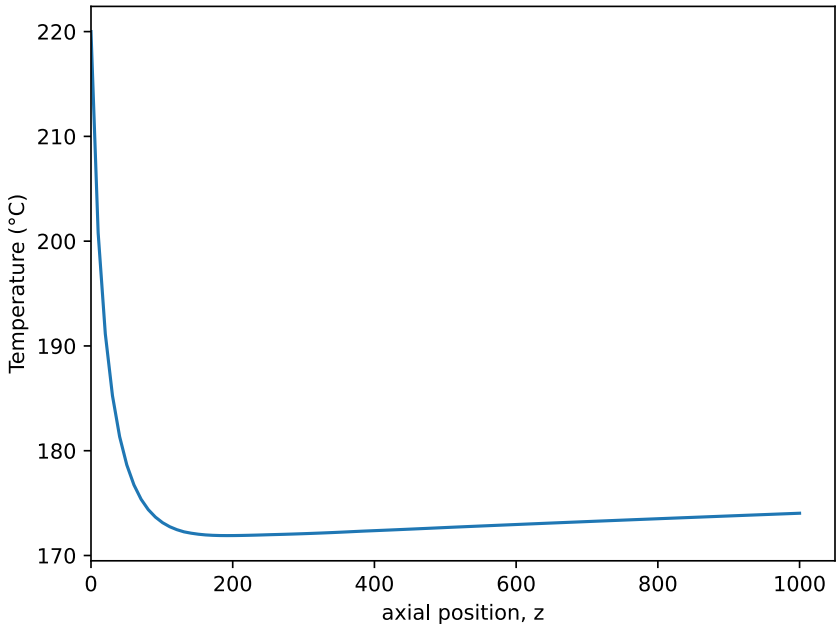

Figure 1. PFR Temperature Profile.

Deliverables

The conversion was 19.1%, the selectivity, 0.94 mol Y per mol Z, and the outlet temperature, 174 °C.