REB, The Course
Class 20 Practice Assignment Solution

Example 7.4.2 in REB, the Book, described a cooled, 10 L BSTR wherein reagents A and B reacted to produce X, Y, and Z as in equations (1) and (2). Starting with a 65°C solution containing A at 5 mol L^{-1} and B at 7 mol L^{-1}, 45% of the A reacted in 30 min with a selectivity of 4.2 mol X per mol Z. The discussion noted that maintaining a high concentration of B or decreasing the temperature might increase the selectivity. It showed that lowering the temperature did increase the selectivity, but decreased the rate, and hence, the conversion.

$$A + B \rightarrow X + Y \tag{1}$$

$$A \rightarrow Z \tag{2}$$

It has been suggested that one might start with separate 65 °C 5 L solutions, one containing 10 mol A per liter and the other 14 mol B per liter. Mixing 5 L of each of these would give the same 10 L solution used in the BSTR above. The same reactor could be used as an SBSTR that operates at 1 atm and initially contained only the 14 M solution of B. Then the 10 M solution of A could be added at a constant feed rate. The rationale for this suggestion is that this would keep the concentration of B as high as possible and improve the selectivity. Assess this suggestion by simulating the SBSTR process for feed rates of 0.25 L min^{-1} and 0.5 L min^{-1}, keeping the conversion the same at 45%. That is, after all of the solution of A has been added, allow the reaction to continue in batch mode until the overall conversion reaches 45%. Compare the differences between the BSTR and SBSTR processes and explain them qualitatively.

Here are relevant data from Example 7.4.2: V = 10 L, V_{ex}= 1.4 L, U = 138 cal ft^{-2} min^{-1} K^{-1}, A_{ex} = 1200 cm^2, $T_{ex,in}$ = 40 °C, $\dot{m}_{ex}$ = 100 g min^{-1}, ρ = 1.0 g cm^{-3}, ρ_{ex} = 1.0 g cm^{-3}, $\tilde{C}_p$ = 1.0 cal g^{-1} K^{-1}, $\tilde{C}_{p,ex}$ = 1.0 cal g^{-1} K^{-1}, $C_{A,0}$ = 5.0 M, $C_{B,0}$ = 7.0 M, $T_{ex,0}$ = 40 °C, ΔH_1 = –16.7 kcal mol^{-1}, ΔH_2 = –14.3 kcal mol^{-1}, $k_{0,1}$ = 9.74 x 10^9 L mol^{-1} min^{-1}, E_1 = 20.1 kcal mol^{-1}, $k_{0,2}$ = 2.38 x 10^{13} min^{-1}, E_2 = 25.3 kcal mol^{-1}, $f_{A,f}$ = 0.45, t_f = 30 min, and T_0 = T_{in} = 65 °C.

$$r_1 = k_1 C_A C_B \quad (3)$$

$$r_2 = k_2 C_A \quad (4)$$

Assignment Summary

Reactions

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

$$A \rightarrow Z \quad (2)$$

Rate Expressions

$$r_1 = k_1 C_A C_B \quad (3)$$

$$r_2 = k_2 C_A \quad (4)$$

Reactor: Liquid-phase, 2-stage, cooled SBSTR

Given Constants: V_A = V_B = 5 L, V_{ex}= 1.4 L, U = 138 cal ft^{-2} min^{-1} K^{-1}, A_{ex} = 1200 cm^2, $T_{ex,in}$ = 40 °C, $\dot{m}_{ex}$ = 100 g min^{-1}, ρ = 1.0 g cm^{-3}, ρ_{ex} = 1.0 g cm^{-3}, $\tilde{C}_p$ = 1.0 cal g^{-1} K^{-1}, $\tilde{C}_{p,ex}$ = 1.0 cal g^{-1} K^{-1}, $C_{A,0}$ = 10.0 M, $C_{B,0}$ = 14.0 M, $T_{ex,0}$ = 40 °C, ΔH_1 = –16.7 kcal mol^{-1}, ΔH_2 = –14.3 kcal mol^{-1}, $k_{0,1}$ = 9.74 x 10^9 L mol^{-1} min^{-1}, E_1 = 20.1 kcal mol^{-1}, $k_{0,2}$ = 2.38 x 10^{13} min^{-1}, E_2 = 25.3 kcal mol^{-1}, f_A = 0.45, and T_0 = T_{in} = 65 °C.

Parameter: $\underline{\dot{V}}_{in} = [0.25, 0.5]$ L min^{-1}

Deliverables: t_f, T_f, $T_{ex,f}$, and $S_{X/Z}$ for each value of $\dot{V}_{in}$

Formulation of the Equations

Reactor Model Equations:

$$\frac{dn_A}{dt} = \dot{n}_{A,in} + \left(-r_1 - r_2\right) V \tag{5}$$

$$\frac{dn_B}{dt} = -\, r_1 V \tag{6}$$

$$\frac{dn_X}{dt} = r_1 V \tag{7}$$

$$\frac{dn_Y}{dt} = r_1 V \tag{8}$$

$$\frac{dn_Z}{dt} = r_2 V \tag{9}$$

$$\frac{dT}{dt} = \frac{\dot{Q} - \rho_{ex}\dot{V}_{in}\tilde{C}_{p,ex}\left(T - T_{in}\right) - V\left(r_1 \Delta H_1 + r_2 \Delta H_2\right) + P\dot{V}_{in}}{\tilde{C}_p \rho V} \tag{10}$$

$$\frac{dT_{ex}}{dt} = \frac{-\dot{Q} - \dot{m}_{ex}\tilde{C}_{p,ex}\left(T_{ex} - T_{ex,in}\right)}{\rho_{ex} V_{ex} \tilde{C}_{p,ex}} \tag{11}$$

$$\frac{dV}{dt} = \dot{V}_{in} \tag{12}$$

Reactor Model Variables: $\underline{t}$, $\underline{n}_A$, $\underline{n}_B$, $\underline{n}_X$, $\underline{n}_Y$, $\underline{n}_Z$, $\underline{T}$, $\underline{T}_{ex}$, $\underline{V}$

Additional Computable Unknowns: $\dot{n}_{A,in}$, r_1, k_1, C_A, C_B, r_2, k_2, $\dot{Q}$

$$\dot{n}_{A,in} = \dot{V}_{in} C_{A,0} \tag{13}$$

$$k_i = k_{0,i} \exp\left(\frac{-E_i}{RT}\right) \quad i = 1 \text{ and } 2 \tag{14}$$

$$C_i = \frac{n_i}{V} \quad i = A \text{ and } B \tag{15}$$

$$\dot{Q} = UA\left(T_{ex} - T\right) \tag{16}$$

Additional Uncomputable Unknowns: $\dot{V}_{in}$

IVODE Solver Inputs: (for each value of $\dot{V}_{in}$)

1. Stage 1
   a. Initial values of the reactor model variables shown in Table 1
   b. Stopping criterion that V equals the final value shown in Table 1
   c. Derivatives function that
      i. receives the reactor model variables at the start of an integration step
      ii. calculates the additional unknowns, equations (13) - (16)
      iii. evaluates and returns the design equation derivatives, equations (5) - (12)

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

Variable	Initial Value	Final Value
t	0	
n_A	0	
n_B	$C_{B,0}V_B$	
n_X	0	
n_Y	0	
n_Z	0	
T	T_0	
T_{ex}	$T_{ex,0}$	
V	V_B	$V_A + V_B$

2. Stage 2
   a. Initial values of the reactor model variables shown in Table 2
   b. Stopping criterion that n_A equals the final value shown in Table 2
   c. Derivatives function that
      i. receives the reactor model variables at the start of an integration step
      ii. calculates the additional unknowns, equations (13) - (16)
      iii. evaluates and returns the design equation derivatives, equations (5) - (12)

Table 2. Initial and final values of the design equation variables for stage 1.

Variable	Initial Value[1]	Final Value
t	$t\big\|_{t_1}$	
n_A	$n_A\big\|_{t_1}$	$C_{A,0}V_A\left(1-f_A\right)$
n_B	$n_B\big\|_{t_1}$	
n_X	$n_X\big\|_{t_1}$	
n_Y	$n_Y\big\|_{t_1}$	
n_Z	$n_Z\big\|_{t_1}$	
T	$T\big\|_{t_1}$	
T_{ex}	$T_{ex}\big\|_{t_1}$	
V	$V\big\|_{t_1}$	

[1] t_1 is the time when stage 1 ended.

<u>Deliverables Equations</u>:

$$S_{X/Z} = \frac{n_{X,f}}{n_{Z,f}} \tag{17}$$

Implementation of the Calculations

The Python script, practice_20.py, that was written to perform the calculations accompanies this solution. It defines an SBSTR function and a derivatives function that use solve the design equations for a given volumetric feed rate using an IVODE solver. The calculations loop through the two specified values of the volumetric flow rate solving the design equations and calculating the quantities of interest.

Results and Discussion

The calculations were performed as described above, and the results are shown in Table 3. In Example 7.4.2, conversion of 45% of the A took 30 min and resulted in a selectivity of 4.2 mol X per mol Z.

Table 3. Effect of Feed Rate on SBSTR Selectivity

Feed Rate (L/min)	Processing Time (min)	Final T (°C)	Final Coolant T (°C)	Selectivity (X/Z)
0.25	42.7	90.6	67.7	4.46
0.50	36.4	91.5	67.9	4.34

If the SBSTR feed rate was infinite, the SBSTR would become a BSTR with a processing time of 30 min and a selectivity of 4.2 mol X per mol Z. Table 3 shows that as the feed rate decreases, both the processing time and the selectivity increase. As was the case when the temperature was decreased in Example 7.4.2, the temperature decrease had the desired effect of increasing selectivity, together with the undesired effect of increasing processing time.

It isn't clear that the changes here are a result of maintaining a high concentration of B. All of the B was added at the start of the batch process, just as it was here. In other words, both the BSTR and SBSTR kept the concentration of B as high as possible for as long as possible. The effect seen here may actually be related to the decrease in the final temperature. The lower the feed rate, the coolant can remove more heat, and Example 7.4.2 showed that lowering the temperature had a much larger effect on both processing time and selectivity compared to the changes seen here.