REB, The Book
Example 8.4.2 Solution

The rate expressions for reactions (1) and (2) are shown in equations (3) and (4). The Arrhenius parameters for these reactions are $k_{0,1}$ = 1.83 x 10^{12} L mol^{-1} h^{-1}, E_1 = 18.0 kcal mol^{-1}, $k_{0,2}$ = 5.08 x 10^{13} L mol^{-1} h^{-1}, and E_2 = 20.5 kcal mol^{-1}. Reagent D is the desired product while reagent U is undesired. The heats of reactions (1) and (2) are –9000 and –7800 cal mol^{-1}, respectively, and solutions of A and B have a heat capacity of 863 cal L^{-1} K^{-1}.

A 2 M solution of A and a 0.5 M solution of B, both at 40 °C, are going to be used to produce D in an adiabatic semi-batch reactor operating at 1 atm. The reactor will be charged with 2000 L of the A solution, and 8000 L of the B solution will be added at a constant rate over a period of time. If the total reaction time is always 8 h, compare the overall conversion of B, the selectivity for D over U (final moles of D per final moles of U), and the yield of D from B (final moles of D per total moles of B added to the reactor) if the solution of B is added over the first 1, 3, 5, or 7 hours of operation.

$$A + B \rightarrow D \quad (1)$$

$$2B \rightarrow U \quad (2)$$

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

$$r_2 = k_2 C_B^2 \quad (4)$$

Assignment Summary

<u>Reactions</u>

$$A + B \rightarrow D \quad (1)$$

$$2B \rightarrow U \quad (2)$$

<u>Rate Expressions</u>

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

$$r_2 = k_2 C_B^2 \tag{4}$$

Reactor: Adiabatic SBSTR with a 2 stage operational protocol

Given Constants: $k_{0,1}$ = 1.83 x 10^{12} L mol^{-1} h^{-1}, E_1 = 18.0 kcal mol^{-1}, $k_{0,2}$ = 5.08 x 10^{13} L mol^{-1} h^{-1}, E_2 = 20.5 kcal mol^{-1}, ΔH_1 = –9000, ΔH_2 = –7800 cal mol^{-1}, $\breve{C}_p$ = 863 cal L^{-1} K^{-1}, $C_{A,0}$ = 2 M, $C_{B,0}$ = $C_{B,in}$ = 0.5 M, T_0 = 40 °C, P = 1 atm, V_A = 2000 L, V_B = 8000 L, and t_f = 8 h.

Parameter: t_1 = [1, 3, 5, 7] h

Deliverables: f_B, $S_{D/U}$, and $Y_{D/B}$ for each value of t_1.

Formulation of the Equations

Reactor Model Equations:

$$\frac{dn_A}{dt} = -Vr_1 \tag{5}$$

$$\frac{dn_B}{dt} = \dot{n}_{B,in} - \left(r_1 + 2r_2\right) V \tag{6}$$

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

$$\frac{dn_U}{dt} = r_2 V \tag{8}$$

$$V\breve{C}_p \frac{dT}{dt} - P\frac{dV}{dt} = -\dot{V}_{in}\breve{C}_p \left(T - T_{in}\right) - r_1 V\Delta H_1 - r_2 V\Delta H_2 \tag{9}$$

$$\frac{dV}{dt} = \dot{V}_{in} \tag{10}$$

Reactor Model Variables: $\underline{t}$, $\underline{n_A}$, $\underline{n_B}$, $\underline{n_D}$, $\underline{n_U}$, $\underline{T}$, and $\underline{V}$

Additional Computable Unknowns: k_1, C_A, C_B, k_2, $\dot{n}_{B,in}$, and $\dot{V}_{in}$

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

$$C_i = \frac{n_i}{V} \qquad i = A \text{ and } B \tag{12}$$

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

$$\begin{aligned} \dot{V}_{in} &= \frac{V_B}{t_1}; \qquad t \le t_1 \\ \dot{V}_{in} &= 0; \qquad t > t_1 \end{aligned} \tag{14}$$

Additional Uncomputable Unknown: t_1

IVODE Solver Inputs: (for each value of t_1)

1. Stage 1
    a. Initial values of the reactor model variables shown in Table 1.
    b. Stopping criterion that t 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 computable additional unknowns using equations (11) - (14)
        iii. evaluates and returns the design equation derivatives using equations (5) - (8), (10), and (15)

$$\frac{dT}{dt} = \frac{-\dot{V}_{in}\breve{C}_p\left(T - T_{in}\right) - r_1 V \Delta H_1 - r_2 V \Delta H_2 + P\dot{V}_{in}}{V\breve{C}_p} \tag{15}$$

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

Variable	Initial Value	Final Value
t	0	t_1
n_A	$n_{A,0} = C_{A,0}V_A$	
n_B	0	
n_D	0	
n_U	0	
T	T_0	
V	$V_0 = V_A$	

2. Stage 2
    a. Initial values of the reactor model variables shown in Table 2.
    b. Stopping criterion that t equals the 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 computable additional unknowns using equations (11) - (14)
        iii. evaluates and returns the design equation derivatives using equations (5) - (8), (10), and (15)

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

Variable	Initial Value	Final Value
t	t_1	t_f
n_A	$n_A\Big\vert_{t_1}$	
n_B	$n_B\Big\vert_{t_1}$	

Variable	Initial Value	Final Value
n_D	$n_D\Big\vert_{t_1}$	
n_U	$n_U\Big\vert_{t_1}$	
T	$T\Big\vert_{t_1}$	
V	$V_A + V_B$	

Deliverables Equations:

$$f_B = \frac{V_B C_{B,in} - \underline{n}_B\Big\vert_{t_f}}{V_B C_{B,in}} \tag{16}$$

$$S_{D/U} = \frac{\underline{n}_D\Big\vert_{t_f}}{\underline{n}_U\Big\vert_{t_f}} \tag{17}$$

$$Y_{D/B} = \frac{\underline{n}_D\Big\vert_{t_f}}{V_B C_{B,in}} \tag{18}$$

Implementation of the Calculations

The Python script, example_8_4_2.py, that was written to perform the calculations accompanies this solution. It defines an SBSTR function and an SBSTR derivatives function that call an IVODE solver to solve the design equations given a value for t_1. The model function solves the equations for each of the 2 stages of the operational protocol, the first being SBSTR operation and the second BSTR operation after all of the solution of B has been added. The calculations loop through the four values of t_1,

using those functions to solve the design equations and then using the results to calculate the three quantities of interest.

Results and Discussion

The calculations were performed as described above. The conversion of B, selectivity for D over U, and yield of D from B for each of the four addition times are shown in Table 3. The conversion of B decreases as its addition gets spread over longer times. This is reasonable because the later in the process that the B is added, the less time it has to react. Separate calculations show that if the reaction is run in a batch reactor the conversion is 85.7% with a selectivity for D over U of 2.88 and a yield of D from B of 50.6%.

Table 3. Effect the duration of stage 1 on conversion, selectivity and yield.

Stage 1 Duration (h)	Conversion (%)	Selectivity D/U	Yield D-B (%)
1	84.3	3.17	51.7
3	80.6	3.75	52.6
5	75.4	4.39	51.8
7	67.6	5.33	49.2

Adding the B to A over time keeps the concentration of A as large as possible at all times and keeps the concentration of B lower than if it was all added at the start. The expression for the instantaneous selectivity for D over U for these reactions, equation (19), suggests that this should result in greater selectivity, and indeed, Table 3 shows that the slower the B is added (i. e. the longer the time during which it is added), the greater the selectivity for D over U.

$$S_{D/U,inst} = \frac{k_D}{k_U}\frac{C_A}{C_B} \qquad (19)$$

However, while the selectivity is increasing, the conversion of B is decreasing. As a consequence, the yield of D from B is nearly constant at approximately 50%, passing through a weak maximum when B is added over 3 h. The processing time in all cases is

the same, 8 h. Hence, the operating costs, are basically the same. The net rate of production of D is essentially the same, too, because the yield of D is effectively constant.

In effect, the same amount of B is converted to D in all four cases, but as the addition time increases, the amount of B converted to U decreases while the amount of unreacted B increases. Comparing batch processing to semi-batch processing where the B is added during the first 7 h of the 8 h process, the same amount of D is produced at the same net rate. The difference is that in semi-batch mode there is more unreacted B while in batch mode there is more undesired U.

Semi-batch processing where the B is added during the first 7 h of the 8 h process has an advantage over batch processing in two scenarios. First, if reagent B is easily and inexpensively separable from the product mixture, not converting it to U, but instead recovering it and re-using it in a subsequent semi-batch run mitigates the low conversion.

The other scenario is when U is a valueless hazardous waste. The disposal of such a waste can add significantly to the cost of the process, thereby decreasing profits. In this scenario, even if the unconverted B cannot be separated and re-used, the cost of wasting reagent B (i. e. low conversion) may be more than offset by significantly lower expenses associated with disposal of U.

Deliverables

Table 3 summarizes the effect of varying the rate of addition of B upon conversion, selectivity and yield. As the rate of addition increases, the conversion increases and the selectivity decreases with the yield remaining approximately constant.