REB, The Book
Example 7.4.4 Solution

A BSTR will be charged with 1 atm of A and 2 atm of B at 25 °C. The reactor volume is 2 L, and it has a jacket with an area of 600 cm^2 and an overall heat transfer coefficient of 0.6 cal cm^2 min^{-1} K^{-1}. The temperature of the coolant in the perfectly-mixed jacket is maintained at 30°C by a temperature controller. Gas phase reactions (1) and (2) take place within the reactor; the corresponding rate expressions are given in equations (3) and (4). The rate coefficients display Arrhenius temperature dependence with pre-exponential factors of 3.34 x 10^9 and 1.47 x 10^{10} mol cm^{-3} min^{-1} atm^{-2} for reactions (1) and (2), respectively, and activation energies of 20.5 and 21.8 kcal mol^{-1}. The heat of reaction (1) is constant and equal to –6,300 cal mol^{-1}; that of reaction (2) is constant and equal to –6,900 cal mol^{-1}. The heat capacities of A, B, D, Z and U are constant and equal to 7.4, 8.6, 10.7, 5.2 and 10.3 cal mol^{-1} K^{-1}, respectively.

What reaction time will maximize the yield (moles of D per initial mole of A), and what will the yield and the conversion of A equal at that reaction time?

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

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

$$r_1 = k_{0,1} \exp\left(\frac{-E_1}{RT}\right) P_A P_B \tag{3}$$

$$r_2 = k_{0,2} \exp\left(\frac{-E_2}{RT}\right) P_D P_B \tag{4}$$

Assignment Summary

Reactions

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

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

Rate Expressions

$$r_1 = k_{0,1} \exp\left(\frac{-E_1}{RT}\right) P_A P_B \tag{3}$$

$$r_2 = k_{0,2} \exp\left(\frac{-E_2}{RT}\right) P_D P_B \tag{4}$$

Reactor: gas-phase, non-isothermal BSTR

Given Constants: $P_{A,0}$ = 1 atm, $P_{B,0}$ = 2 atm, T_0 25 °C, V = 2 L, A = 600 cm^2, U = 0.6 cal cm^2 min^{-1} K^{-1}, T_{ex} = 30°C, $k_{0,1}$ = 3.34 x 10^9 mol cm^{-3} min^{-1} atm^{-2}, $k_{0,2}$ = 4.99 x 10^9 mol cm^{-3} min^{-1} atm^{-2}, E_1 = 20.5 kcal mol^{-1}, E_2 = 21.8 kcal mol^{-1}, ΔH_1 = –6,300 cal mol^{-1}, ΔH_2 = –6,900 cal mol^{-1}, $\hat{C}_{p,A}$ = 7.4 cal mol^{-1} K^{-1}, $\hat{C}_{p,B}$ = 8.6 cal mol^{-1} K^{-1}, $\hat{C}_{p,D}$ = 10.7 cal mol^{-1} K^{-1}, $\hat{C}_{p,Z}$ = 5.2 cal mol^{-1} K^{-1}, and $\hat{C}_{p,U}$ = 10.3 cal mol^{-1} K^{-1}.

Parameter: t_f

Deliverables: $t_{opt} = \arg\max_t \left(Y_{D/A}\right), Y_{D/A}\Big|_{t_{opt}}, f_A\Big|_{t_{opt}}$

Formulation of the Equations

Reactor Model Equations:

$$\frac{dn_A}{dt} = -r_1 V \tag{5}$$

$$\frac{dn_B}{dt} = \left(-r_1 - r_2\right) V \tag{6}$$

$$\frac{dn_D}{dt} = \left(r_1 - r_2\right) V \tag{7}$$

$$\frac{dn_Z}{dt} = \left(r_1 + r_2\right) V \tag{8}$$

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

$$\begin{aligned} -V\frac{dP}{dt} + \left(n_A\hat{C}_{p,A} + n_B\hat{C}_{p,B} + n_D\hat{C}_{p,D} + n_Z\hat{C}_{p,Z} + n_U\hat{C}_{p,U}\right)\frac{dT}{dt} \\ = \dot{Q} - \left(r_1\Delta H_1 + r_2\Delta H_2\right) V \end{aligned} \tag{10}$$

$$\begin{aligned} -RT\left(\frac{dn_A}{dt} + \frac{n_B}{dt} + \frac{n_D}{dt} + \frac{n_Z}{dt} + \frac{n_U}{dt}\right) + V\frac{dP}{dt} \\ -R\left(n_A + n_B + n_D + n_Z + n_U\right)\frac{dT}{dt} = 0 \end{aligned} \tag{11}$$

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

Additional Computable Unknowns: r_1, P_A, P_B, r_2, P_D, and $\dot{Q}$

$$P_A = \frac{n_A RT}{V} \tag{12}$$

$$P_B = \frac{n_B RT}{V} \tag{13}$$

$$P_D = \frac{n_D RT}{V} \tag{14}$$

$$\dot{Q} = UA\left(T_{ex} - T\right) \tag{15}$$

IVODE Solver Inputs:

1. Initial values of the reactor model variables shown in Table 1
2. Stopping criterion that t equals the final value shown in Table 1
3. Derivatives function that

a. receives the reactor model variables (t, n_A, n_B, n_D, n_Z, n_U, T, and P) at the start of an integration step
b. returns the corresponding values of the reactor model derivatives

$$\boldsymbol{M} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \sum_i \left(n_i \hat{C}_{p,i} \right) & -V \\ RT & RT & RT & RT & RT & R \sum_i n_i & -V \end{bmatrix} \tag{16}$$

$$\underline{g} = \begin{bmatrix} -r_1 V \\ \left(-r_1 - r_2 \right) V \\ \left(r_1 - r_2 \right) V \\ \left(r_1 + r_2 \right) V \\ r_2 V \\ \dot{Q} - \left(r_1 \Delta H_1 + r_2 \Delta H_2 \right) V \\ 0 \end{bmatrix} \tag{17}$$

$$\begin{bmatrix} \frac{dn_A}{dt} \\ \frac{n_B}{dt} \\ \frac{n_D}{dt} \\ \frac{n_Z}{dt} \\ \frac{dn_U}{dt} \\ \frac{dT}{dt} \\ \frac{dP}{dt} \end{bmatrix} = \boldsymbol{M}^{-1}\underline{g} \tag{18}$$

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

Variable	Initial Value	Final Value
t	0	t_f
n_A	$n_{A,0} = \frac{P_{A,0}V}{RT_0}$	
n_B	$n_{B,0} = \frac{P_{B,0}V}{RT_0}$	
n_D	0	
n_Z	0	
n_U	0	
T	T_0	
P	$P_0 = P_{A,0} + P_{B,0}$	

Deliverables Equations:

$$\underline{Y}_{D/A} = \frac{\underline{n}_D}{n_{A,0}} \tag{19}$$

$$t_{opt} = \arg\max_{t} \left(\underline{Y}_{D/A} \right) \tag{20}$$

$$\underline{f}_A = \frac{n_{A,0} - \underline{n}_A}{n_{A,0}} \tag{21}$$

$$Y_{D/A,max} = \underline{Y}_{D/A} \Big|_{t_{opt}} \tag{22}$$

$$f_A = \underline{f}_A \Big|_{t_{opt}} \tag{23}$$

Implementation of the Calculations

The Python script, example_7_4_3.py, that was written to perform the calculations accompanies this solution. It defines a BSTR model function and a BSTR derivatives function that solve the design equations, (5) through (11) given a final reaction time. (The derivatives function uses the matrix form of the equations, (16) through (18). The calculations begin by choosing a final reaction time (this might need to adjusted; it needs to be large enough that the yield passes through a maximum before reaching it).

Results and Discussion

Figure 1 shows the variation of the yield as a function of the reaction time. The maximum yield, 0.69 mol D per mol A, occurs at a reaction time of 12.1 min. The conversion of A at that reaction time is 88.2%. Then it simply solves the design equations to get the molar amounts, temperature and pressure at times between time zero and that chosen value. The results are used to calculate the yield at each reaction time, and then the time where the yield reaches a maximum is found.

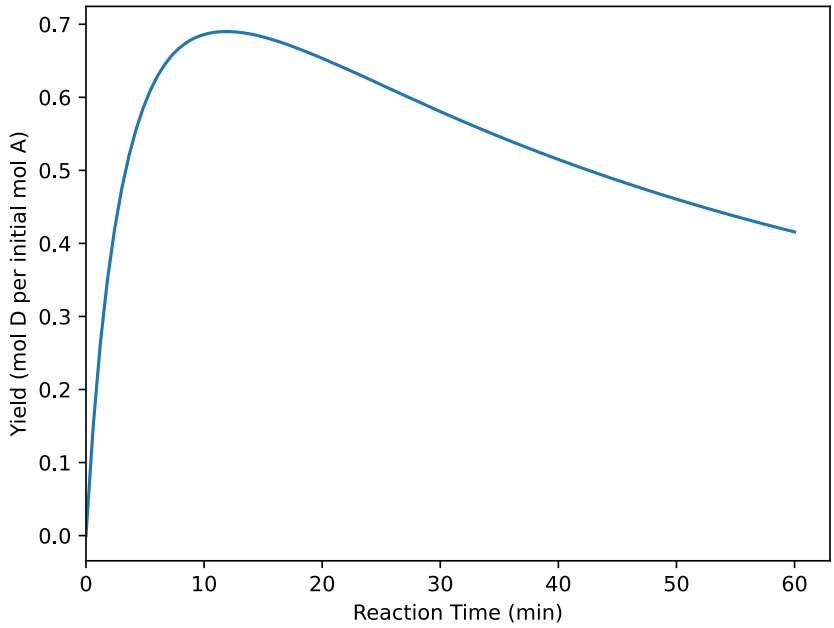

Figure 1. Yield of D as a function of reaction time.

Reactions (1) and (2) constitute a series-parallel reaction network. The desired product, D, is an intermediate product. It is produced in reaction (1) and consumed in reaction (2). The yield of an intermediate product is expected to pass through a maximum as the reaction time increases as seen in Figure 1. This can be predicted qualitatively as long as the effect of temperature is comparable for the two reactions.

At the start of the reaction, the concentrations of A and B will be large and those of D, U, and Z will be zero. The rate of reaction (1) will be positive while that for reaction (2) will be zero. Consequently, during a very brief interval at the start of the reactive process, the concentrations of A and B will decrease and the concentrations of D and Z will increase.

During the next brief interval in time, the rate of reaction (1) will be smaller because the concentrations of A and B will be smaller, and the rate of reaction (2) no longer will equal zero because a small amount D will be present leading to a positive rate. The concentrations of A and B will again decrease and the concentration of Z will again increase. It can be expected that the rate of reaction (1) will be greater than the rate of

reaction (2) because only a small concentration of D will be present, so the concentration of D, and its yield, will again increase, as can be seen in Figure 1.

For as long as the rate of reaction (2) remains smaller than the rate of reaction (1), the amount of D will be increasing, but its rate of increase will get smaller and smaller. The reason for this is that the concentrations of A and B will be decreasing, and hence the rate of generation of D by reaction (1) will be decreasing. At the same time, the rate of consumption of D by reaction (2) will be increasing as the concentration of D builds. This can be seen in Figure 1 where the curvature of the yield plot is initially concave downward.

Eventually, the rate of reaction (2) will become equal to the rate of reaction (1). For that instant in time, the yield of D will not be changing. This corresponds to the maximum in Figure 1. At times beyond the maximum the rate of reaction (1) is less than the rate of reaction (2), so the concentration of D decreases. As the concentrations of both reactants, A and D, continue to decrease, both reactions (1) and (2) become slower and slower. This can be seen at larger reaction times in Figure 1 where the curve is concave upward. Eventually, at very large reaction time, the rates will equal zero and all of the D will have been consumed.

In this example series-parallel reactions are occurring where the desired product is produced in one reaction and consumed by another. This assignment shows that the reaction time has a significant effect upon the amount of the desired product. Other process parameters such as the initial composition or temperature will also affect the results, but for series and series-parallel reactions their effect on the selectivity is often weaker. Temperature can be an effective parameter for adjusting the selectivity of multiple reactions if the activation energies of the reactions differ significantly. That was the case in Example 7.4.2 of *Reaction Engineering Basics*, and indeed, the discussion following that example showed that changing the temperature did have a significant effect.

Deliverables

A reaction time of 12.1 min maximizes the yield of D from A at 0.69 mol D per mol A, with an 88.2% conversion of A.