REB, The Book
Example 7.4.3 Solution

The rate expression for liquid-phase reaction (1) is given in equation (2). The rate coefficient displays Arrhenius temperature dependence with a pre-exponential factor of 2.59 x 10^9 min^{-1} and an activation energy of 16.5 kcal mol^{-1}. The heat of reaction (1) may be taken to be constant and equal to –22,200 cal mol^{-1}. A solution containing only A at a concentration of 2 M and a temperature of 23 °C is going to be processed in a BSTR. The heat capacity of the solution is approximately constant and equal to 440 cal L^{-1} K^{-1}, and its density is constant.

$$A \rightarrow Z \tag{1}$$

$$r_1 = k_1 C_A \tag{2}$$

The 4.0 L BSTR has a perfectly mixed jacket with a volume of 0.5 L, a heat transfer area of 0.6 ft^2, and a heat transfer coefficient of 1.13 x 10^4 cal ft^{-2} h^$^{-1}$ K^{-1}. Cooling water at 20 °C can be fed to the jacket. The water may be taken to have a constant density of 1 g cm^{-3} and a constant heat capacity of 1 cal g^{-1} K^{-1}. A heating coil with a heat transfer coefficient of 3.8 x 10^4 cal ft^{-2} h^{-1} K^{-1} and a heat transfer area of 0.23 ft^2 can be submerged in and extracted from the reacting solution. Saturated steam at 120 °C can be admitted to the coil.

The BSTR is charged with 4 L of a 2 M solution of A at 23 °C. Initially there is no flow to the jacket, but it is filled with water, also at 23 °C. To start the batch process, the steam is admitted to the coil, and the coil is immersed in the solution. When the reacting fluid reaches 50 °C, the coil is extracted from the reacting fluid and cooling water flow to the jacket is started. When the reacting fluid reaches a temperature of 25 °C the cooling water flow is stopped, the reactor is drained and preparations for processing the next batch begin. The BSTR pressure is constant throughout all stages of processing. If the turnaround time for the reactor is 25 min, what coolant flow rate will maximize the net rate of production of Z? Plot the conversion of A and the reacting fluid temperature *vs*. reaction time corresponding to the coolant flow rate that maximizes the net rate and comment on the results.

Assignment Summary

Reaction

$$A \rightarrow Z \tag{1}$$

Rate Expression

$$r_1 = k_1 C_A \tag{2}$$

Reactor: liquid phase, non-isothermal BSTR with a 2 stage operating protocol

Given Constants: $k_{0,1}$ = 2.59 x 10^9 min^{-1}, E_1 = kcal mol^{-1}, ΔH_1 = –22,200 cal mol^{-1}, $C_{A,0}$ = 2 M, T_0 = 23 °C, $\breve{C}_p$ = 440 cal L^{-1} K^{-1}, V = 4.0 L, V_{ex} = 0.5 L, A_{ex} = 0.6 ft^2, U_{ex} = 1.13 x 10^4 cal ft^{-2} h^$^{-1}$ K^{-1}, $T_{ex,in}$ = 20 °C, ρ_{ex} = 1 g cm^{-3}, $\tilde{C}_{p,ex}$ = 1 cal g^{-1} K^{-1}, U_{coil} = 3.8 x 10^4 cal ft^{-2} h^{-1} K^{-1}, A_{coil} = 0.23 ft^2, T_{coil} = 120 °C, $T_{ex,0}$ = 23 °C, T_1 = 50 °C, T_f = 25 °C, and t_{turn} = 25 min.

Parameter: $\dot{V}_{ex}$

Deliverables: $\dot{V}_{ex,opt} = \underset{\dot{V}_{ex}}{\arg\max}\left(r_{Z,net}\right), \underline{f}_A\Big|_{\dot{V}_{ex,opt}}$ vs. $\underline{t}$, and $\underline{T}\Big|_{\dot{V}_{ex,opt}}$ vs. $\underline{t}$ as graphs.

Formulation of the Equations

Reactor Model Equations:

$$\frac{dn_A}{dt} = -Vr_1 \qquad 0 \le t \le t_f \tag{3}$$

$$\frac{dn_Z}{dt} = Vr_1 \qquad 0 \le t \le t_f \tag{4}$$

$$\frac{dT}{dt} = \frac{\dot{Q}_{ex} + \dot{Q}_{coil} - Vr_1 \Delta H_1}{V\breve{C}_p} \qquad 0 \le t \le t_1 \tag{5}$$

$$\frac{dT_{ex}}{dt} = -\left(\frac{\dot{Q}_{ex}}{\rho_{ex}V_{ex}\tilde{C}_{p,ex}}\right) \qquad 0 \le t \le t_1 \tag{6}$$

$$\frac{dT}{dt} = \frac{\dot{Q}_{ex} - Vr_1\Delta H_1}{V\breve{C}_p} \qquad t_1 \le t \le t_f \tag{7}$$

$$\frac{dT_{ex}}{dt} = -\left(\frac{\dot{Q}_{ex} + \dot{V}_{ex}\rho_{ex}\tilde{C}_{p,ex}\left(T_{ex} - T_{ex,in}\right)}{\rho_{ex}V_{ex}\tilde{C}_{p,ex}}\right) \qquad t_1 \le t \le t_f \tag{8}$$

Reactor Model Variables: $\underline{t}$, $\underline{n}_A$, $\underline{n}_Z$, $\underline{T}$, and $\underline{T}_{ex}$

Additional Computable Unknowns: r_1, k_1, C_A, $\dot{Q}_{ex}$, and $\dot{Q}_{coil}$

$$k_1 = k_{0,1}\exp\left(\frac{-E_1}{RT}\right) \tag{9}$$

$$C_A = \frac{n_A}{V} \tag{10}$$

$$\dot{Q}_{ex} = U_{ex}A_{ex}\left(T_{ex} - T\right) \tag{11}$$

$$\dot{Q}_{coil} = U_{coil}A_{coil}\left(T_{coil} - T\right) \tag{12}$$

Additional Uncomputable Unknown: $\dot{V}_{ex}$

$$\underline{\dot{V}}_{ex} = \left[100,\cdots,500\right] \text{ cm}^3 \text{ min}^{-1} \tag{13}$$

IVODE Solver Inputs:

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 BSTR model variables (t, n_A, n_Z, T, and T_{ex}) at the start of an integration step

   ii. returns the corresponding BSTR model derivatives

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	$n_{A,0} = C_{A,0}V$	
n_Z	0	
T	T_0	T_1
T_{ex}	$T_{ex,0}$	

2. Stage 2

   a. Initial values of the reactor model variables shown in Table 2

   b. Stopping criterion that T equals the final value shown in Table 2

   c. Derivatives function that

      i. receives the BSTR model variables (t, n_A, n_Z, T, and T_{ex}) at the start of an integration step

      ii. returns the corresponding BSTR model derivatives

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	$n_A\Big\vert_{t_1}$	

Variable	Initial Value	Final Value
n_Z	$n_Z\big\vert_{t_1}$	
T	T_1	T_f
T_{ex}	$T_{ex}\big\vert_{t_1}$	

<u>Deliverables Equations</u>:

$$\forall \dot{V}_{ex,n} \in \underline{\dot{V}}_{ex} \qquad r_{Z,net,n} = \left.\left(\frac{n_Z\big\vert_{t_f}}{t_f + t_{turn}}\right)\right\vert_{\dot{V}_{ex,n}} \tag{14}$$

$$\dot{V}_{ex,opt} = \underset{\dot{V}_{ex}}{\arg\max}\left(\underline{r}_{Z,net}\right) \tag{15}$$

$$\underline{f}_A\Big\vert_{\dot{V}_{ex,opt}} = \left.\left(\frac{n_{A,0} - \underline{n}_A}{n_{A,0}}\right)\right\vert_{\dot{V}_{ex,opt}} \tag{16}$$

$$\underline{T}\Big\vert_{\dot{V}_{ex,opt}} = \left(\underline{T}\right)\Big\vert_{\dot{V}_{ex,opt}} \tag{17}$$

Implementation of the Calculations

The Python script, example_7_4_4.py, that was written to perform the calculations accompanies this solution. It defines a BSTR model function and BSTR derivatives function for solving the BSTR design equations for stage 1 of the operating protocol. It also defines a second BSTR model function and derivatives function for solving the BSTR design equations for stage 2, given the initial values of the independent and dependent variables. The calculations begin by solving the design equations for stage 1. A range of values is then chosen for the coolant flow rate and the design equations for stage 2 are to get corresponding values of the net rate. The coolant flow rate that produces the maximum net rate is identified, and the BSTR design equations for stage 2 are solved using it. Those results are then used to generate the requested graphs.

Results and Discussion

The calculations were performed as described above to find the optimum coolant volumetric flow rate.. To improve precision, the range of flow rates was narrowed about that optimum value and the calculations were repeated. The net rate of production of Z is plotted as a function of the cooling water flow rate in Figure 1. The maximum net rate, 0.063 g min^{-1}, occurs at a coolant flow rate of 183 cm^3 min^{-1}. The conversion and reacting fluid temperature profiles at that coolant flow rate are shown in Figure 2 and Figure 3. Knowing the initial concentration of A and the Arrhenius parameters, the conversion and temperature profiles were used to calculate the instantaneous reaction rate profile shown in Figure 4. It shows that the rate is close to zero when the reactant is charged to the BSTR.

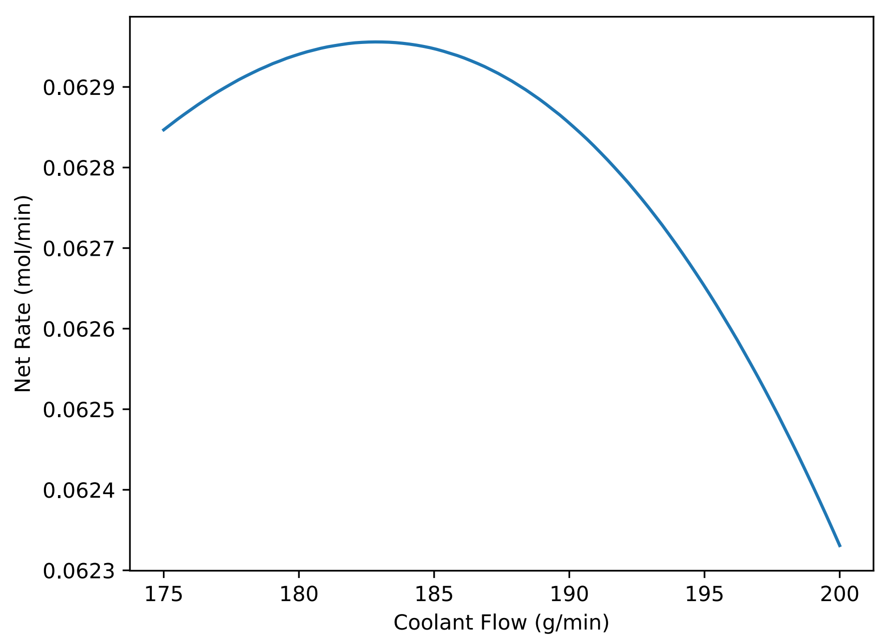

Figure 1. Net rate of production of Z as cooling water flow rate varies.

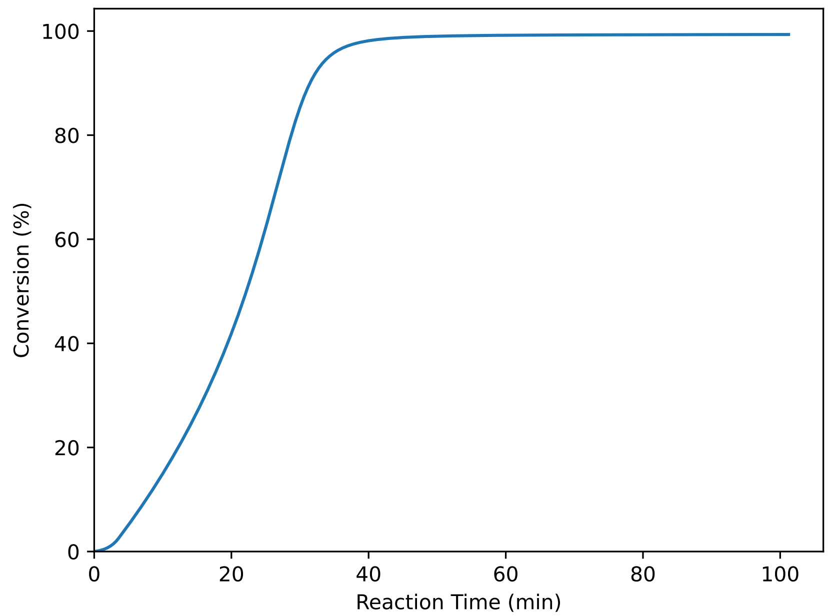

Figure 2. Conversion profile during processing with the optimum coolant flow rate.

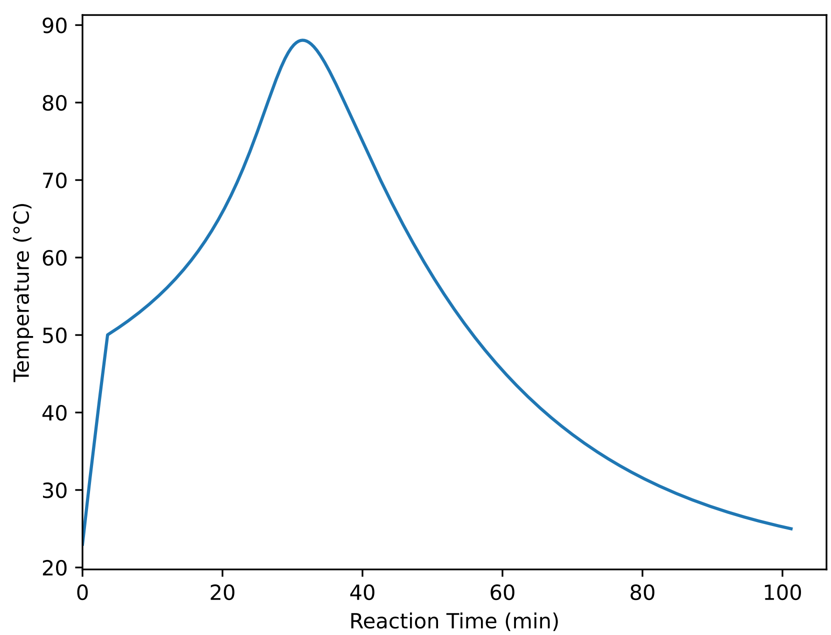

Figure 3. Temperature profile during processing with the optimum coolant flow rate.

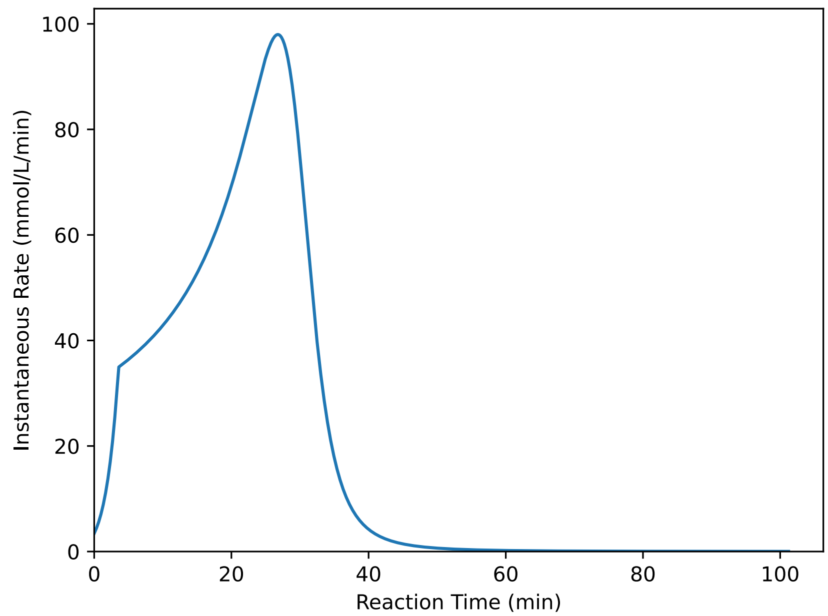

Figure 4. Instantaneous reaction rate profile during processing with the optimum coolant flow rate.

Four interesting features of Figures 1 through 4 can be rationalized qualitatively. First, Figure 3 shows a kink at approximately 2.5 min. The temperature at that point is 50 °C, and that is the point where the heating stage ends and the cooling stage begins. Just prior to the kink, the temperature was rising rapidly and nearly linearly. That indicates that the temperature rise was primarily due to the heat from the coil. After the kink, the temperature continues to rise, but not as rapidly, because the rate has become large enough that heat is being released by reaction faster than it is being removed by the coolant. The kink in Figure 4 occurs for the same reason.

The second interesting observation is that the instantaneous rate (Figure 4) reaches a maximum before the temperature (Figure 3) does. The reason for the maximum in the instantaneous rate is similar to that in Example 7.4.1 of *Reaction Engineering Basics*. Before the maximum rate is attained, two opposing factors are affecting the change in the reaction rate. The reactant concentrations are decreasing, which tends to decrease the rate, while the temperature is increasing, which tends to increase the rate. Before the maximum is reached, the temperature effect is greater than the concentration effect. When the two effects become equal, the maximum rate occurs.

In Example 7.4.1 the temperature rose continually because the reactor was adiabatic, but here Figure 3 shows that the temperature does eventually reach a maximum and then decrease. This is due to heat removal by the cooling jacket. The third interesting feature of the graphs is that the temperature continues to rise for a short period of time after the rate has reached its maximum value. Even though the rate has begun to decrease due to depletion of the reactants, the reaction is still releasing heat faster than the cooling fluid can remove it. When the temperature maximum is reached, the release of heat by reaction has become equal to the removal of heat by the coolant. After the maximum, the coolant removes heat faster than it is generated, so that after ca. 100 min the temperature reaches 25 °C and processing ends.

The conversion at this point is over 99%, but the fourth interesting feature is that the conversion is well over 90% after approximately 30 min. Put differently approximately 90% conversion occurs in the first 30 minutes, but it only increases 9% in the final 70 minutes. This suggests that it might be possible to optimize the system further.

In this assignment, the net rate was maximized with respect to the coolant flow rate. The net rate will also be affected by the duration of the heating stage, or equivalently the temperature at which the coil is removed from the reacting fluid and the coolant flow starts. If the temperatures of the cooling water or the steam could be varied, they, too, would be expected to affect the net rate. In a more realistic optimization, it would not be the net rate that would be optimized. Instead, the rate of financial profit would be maximized. The rate of financial profit would depend on the net rate of the reaction, but it would also depend on the selling price of the product, the costs of the reactant, steam, and cooling water, and a number of other factors. That type of multidimensional optimization is beyond the scope of this book, but at its core, it is similar to the simple optimization illustrated in this assignment.

Deliverables

The net rate of production of Z is maximized at a coolant flow rate of 183 $cm^3\ min^{-1}$. The conversion and reacting fluid temperature profiles at that coolant flow rate are shown in Figure 2 and Figure 3. The net rate of production of Z at these conditions is 0.063 $g\ min^{-1}$.