REB, The Course
Class 18 Learning Activity Solution

Liquid-phase reaction (1) is exothermic with a heat of reaction equal to –16.6 kcal mol^{-1}. If a solution containing only A at a concentration of 2 M and a temperature of 20 °C reacts adiabatically in a BSTR, the temperature increases to 110 °C. The reaction is first order in the concentration of A as shown in equation (2). The pre-exponential factor is 2.5 x 10^8 L mol^{-1} min^{-1}, and the activation energy is 14.3 kcal mol^{-1}.

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

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

Adiabatic operation has undesirable side effects, making isothermal operation preferable. To do so, using a 0.4 L BSTR with a 0.1 L shell has been proposed. The heat transfer area is 32.5 cm^2, and the heat transfer coefficient is 0.2 cal min^{-1} cm^{-2} K^{-1}. Chilled water at 10 °C would initially fill the shell and be fed to it. The water can be taken to have a density of 1 g cm^{-3} and a heat capacity of 1 cal g^{-1} K^{-1}. The reactor temperature will not be close to isothermal if a fixed coolant flow rate is used. Consequently it has been proposed to set the cooling water flow rate to 217 g min^{-1} initially and to linearly decrease it by 212 g min^{-1} over the duration of the 60 min reaction time.

Assuming the reacting fluid density to equal 879 g L^{-1} and its heat capacity to equal 0.42 cal g^{-1} K^{-1}, plot the conversion, reacting fluid temperature, and cooling water temperature over the course of the reaction and comment on how closely the operation approaches being isothermal.

Assignment Summary

Reaction

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

Rate Expression

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

Reactor: BSTR

Given Constants: ΔH_1 = –16.6 kcal mol^{-1}, $C_{A,0}$ = 2 M, T_0 = 20 °C, $k_{0,1}$ = 2.5 x 10^8 L mol^{-1} min^{-1}, E_1 = 14.3 kcal mol^{-1}, V = 0.4, V_{ex} = 0.1 L , A_{ex} = 32.5 cm^2, U_{ex} = 0.2 cal min^{-1} cm^{-2} K^{-1}, $T_{ex,0}$ = $T_{ex,in}$ = 10 °C, ρ_{ex} = 1 g cm^{-3}, $\tilde{C}_{p,ex}$ = 1 cal g^{-1} K^{-1}, $\dot{m}_{ex,0}$ = 217 g min^{-1}, $\Delta\dot{m}_{ex}$ = 212 g min^{-1}, t_f = 60 min, ρ = 879 g L^{-1}, and $\tilde{C}_p$ = 0.42 cal g^{-1} K^{-1}.

Deliverables: f_A, T, and T_{ex} vs. t as graphs

Formulation of the Equations

Reactor Model Equations:

$$\frac{dn_A}{dt} = -r_1 V \tag{3}$$

$$\frac{dn_X}{dt} = r_1 V \tag{4}$$

$$\frac{dT}{dt} = \frac{\dot{Q} - r_1 V \Delta H_1}{\rho V \tilde{C}_p} \tag{5}$$

$$\frac{dT_{ex}}{dt} = \frac{-\dot{Q} - \dot{m}_{ex}\tilde{C}_{p,ex}\left(T_{ex} - T_{ex,in}\right)}{\rho_{ex} V_{ex} \tilde{C}_{p,ex}} \tag{6}$$

$$\frac{d\dot{m}_{ex}}{dt} = \frac{-\Delta\dot{m}_{ex}}{t_f} \tag{7}$$

Reactor Model Variables: t, n_A, n_Z, T, T_{ex}, and $\dot{m}_{ex}$

Additional Computable Unknowns:

$$k_1 = k_{0,1} \exp\left(\frac{-E_1}{RT}\right) \tag{8}$$

$$C_A = \frac{n_A}{V} \tag{9}$$

$$\dot{Q} = U_{ex} A_{ex} \left(T_{ex} - T\right) \tag{10}$$

IVODE Solver Inputs:

1. Initial values of the reactor model variables shown in Table 1
2. Stopping criterion that t equals the value shown in Table 1
3. Residuals/Derivatives function that
   a. receives the reactor model variables at the start of an integration step
   b. calculates the additional unknowns
   c. evaluates and returns the BSTR design equation derivatives

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

Variable	Initial Value	Final Value
t	0	t_f
n_A	$n_{A,0} = C_{A,0} V$	
n_Z	0	
T	T_0	
T_{ex}	$T_{ex,0}$	
$\dot{m}_{ex}$	$\dot{m}_{ex,0}$	

Deliverables Equations:

$$\underline{f}_A = \frac{n_{A,0} - \underline{n}_A}{n_{A,0}} \tag{11}$$

Implementation of the Calculations

The Python script, activity_18.py, that was written to perform the calculations accompanies this solution. It defines a BSTR model function and a derivatives function that solve the BSTR design equations using an IVODE solver. The calculations begin by using those functions to solve the design equations. The conversion is then calculated and the requested graphs are generated.

Results and Discussion

Figure 1 shows that if the reaction occurs adiabatically, the temperature increases from the initial 20 °C to 110 °C. The assignment narrative notes that undesirable side effects occur during adiabatic operation, and it suggests an operating protocol for running the reaction isothermally.

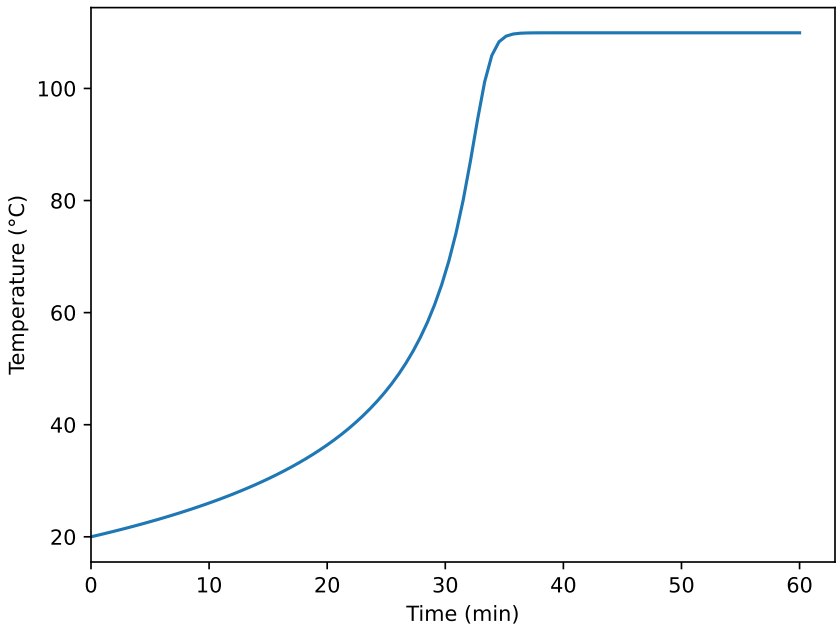

Figure 1. Temperature profile when the reaction occurs adiabatically.

The challenge in trying to operate isothermally is that the amount of heat that needs to be removed varies as the reaction progresses. It is large when the rate is high and decreases as the rate decreases. Thus, one either needs to vary the temperature of the exchange fluid or its flow rate. In a commercial operation it is easier to vary the flow rate of coolant, so the proposed protocol is to linearly decrease the coolant flow rate during processing.

Numerically there are two ways this can be implemented. One is to write a linear equation for the coolant flow rate as a function of time. Then when the coolant flow rate is needed to evaluate the derivatives, it can be calculated using the current time. The other way is to add a differential equation to the design equations which simply set the derivative of the coolant flow rate with respect to time equal to the specified rate of change. The latter approach was used in the present solution.

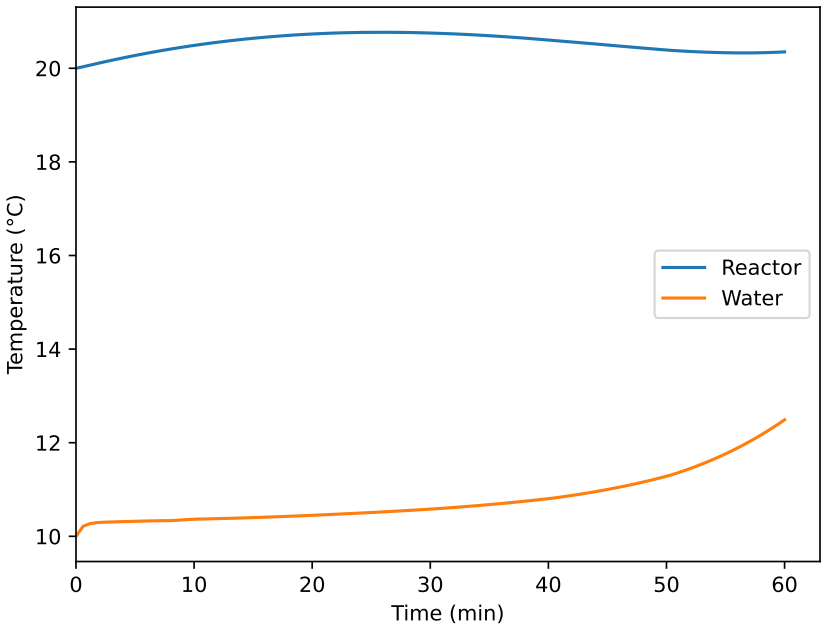

Figure 2. Temperature profiles during processing using the proposed protocol.

Figure 2 shows the reacting fluid and cooling water temperature profiles when the proposed operating protocol is used. The reactor temperature is not constant, but it deviates form 20 °C by less than one degree over the entire process. The maximum

reacting fluid temperature is 20.7 °C. This is sufficiently close to isothermal operation. To attain truly isothermal operation, the cooling water flow rate would need to be adjusted in a non-linear fashion, which would be much more challenging. Figure 2 also shows that the outlet cooling water temperature does not vary significantly either.

Figure 3 shows that the conversion increases nearly linearly during the one hour of processing, reaching a final value of 29%. It is likely that if the duration of the process was increased substantially in an attempt to reach higher conversion, the temperature would deviate by much more. This could probably be addressed by breaking the protocol into 2 or 3 stages with different rates of change of the coolant flow for each stage.

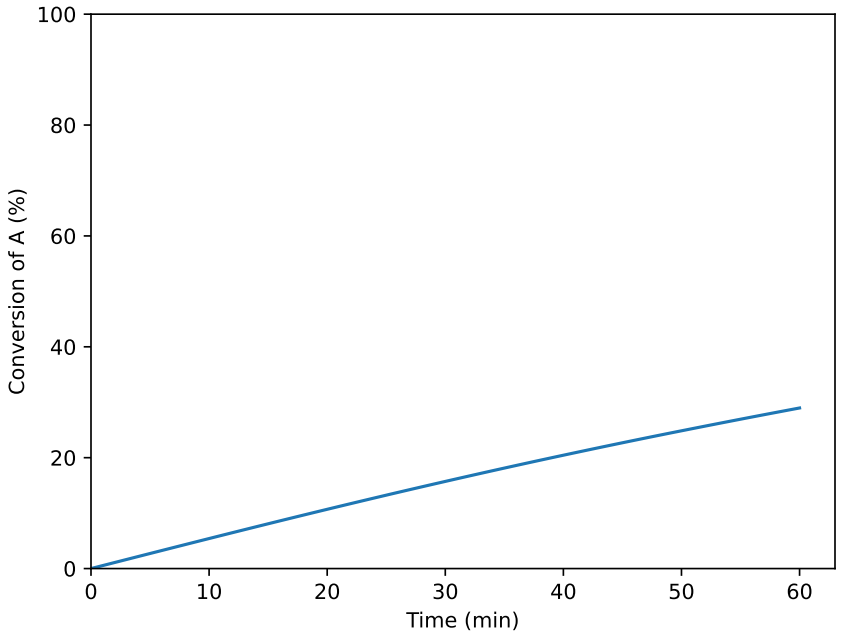

Figure 3. Conversion profile during processing using the proposed protocol.

As a check on the formulation of the model equations, the coolant flow rate was also plotted as a function of time as shown in Figure 4. The flow rate does indeed decrease linearly by 212 g min^{-1} over the course of processing.

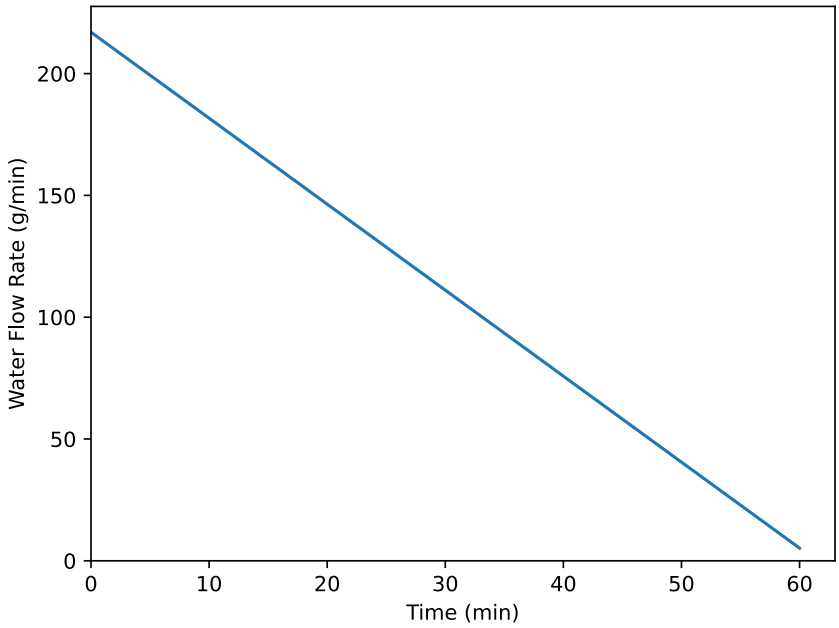

Figure 4. Calculated coolant flow rate during the proposed operational protocol.

Deliverables

The proposed operational protocol converts 29% of reagent A, and the maximum reacting fluid temperature is 20.7 °C.