REB, The Course
Class 19 Learning Activity Solution

In concentrated aqueous solutions, the irreversible condensation reaction (1) is highly exothermic, ΔH = –184 kJ mol^{-1}. The rate expression is given in equation (2) where the pre–exponential factor equals 4.866 x 10^{11} m^3 mol^{-1} min^{-1} and the activation energy equals 74.1 kJ mol^{-1}. A stirred tank reactor operating at atmospheric pressure will be charged with 4.0 L of a solution containing A at a concentration of 10 mol L^{-1} and 20°C. The reactor is cooled using water at 20 °C flowing into a perfectly mixed, 500 cm^3 shell with a heat transfer area of 550 cm^2 and a heat transfer coefficient of 8480 J m^{-2} min^{-1} K^{-1}. The cooling water flows at a steady rate of 1.0 L min^{-1}, and initially the water in the shell is at 20 °C. The reacting fluid and the cooling water may be assumed to have a heat capacity and density equal to that of water, 1 cal g^{-1} K^{-1} and 1 g cm^{-3}, respectively. A 10 M solution of B at 20 °C will be added to the reacting fluid at a constant flow rate. What is the maximum volumetric flow rate at which the base solution at 20 °C can be added to the reactor without causing the reacting fluid temperature to exceed 80 °C?

$$A + B \rightarrow 2\,Z \tag{1}$$

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

Assignment Summary

<u>Reaction</u>

$$A + B \rightarrow 2\,Z \tag{1}$$

<u>Rate Expression</u>

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

<u>Reactor</u>: Cooled, liquid-phase SBSTR

Given Constants: ΔH_1 = –184 kJ mol–1, $k_{0,1}$ = 4.866 x 10^{11} m^3 mol^{-1} min^{-1}, E_1 = 74.1 kJ mol^{-1}, P = 1.0 atm, V_0 = 4.0 L, $C_{A,0}$ = 10 mol L^{-1}, T_0 = 20°C, $T_{ex,in}$ = 20 °C, V_{ex} = 500 cm^3, A_{ex} = 550 cm^2, U = 8480 J m^{-2} min^{-1} K^{-1}, $\dot{V}_{ex,in}$ = 1.0 L min^{-1}, $T_{ex,0}$ = 20 °C, $\tilde{C}_p$ = $\tilde{C}_{p,ex}$ = 1 cal g^{-1} K^{-1}, ρ = ρ_{ex} = 1 g cm^{-3}, $C_{B,in}$ = 10 M, T_{in} = 20 °C, and T_{max} = 80 °C.

Deliverables: $\dot{V}_{in} \ : \ \max\left(\underline{T}\right) = T_{max}$

Formulation of the Equations

Reactor Model Equations:

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

$$\frac{dn_B}{dt} = \dot{n}_{B,in} - r_1 V \tag{4}$$

$$\frac{dn_Z}{dt} = 2 r_1 V \tag{5}$$

$$\frac{dT}{dt} = \frac{\dot{Q} - \dot{V}_{in}\tilde{C}_p\rho\left(T - T_{in}\right) - V r_1 \Delta H_1 + P\dot{V}_{in}}{V\tilde{C}_p\rho} \tag{6}$$

$$\frac{dT_{ex}}{dt} = -\,\frac{\dot{Q} + \dot{m}_{ex}\tilde{C}_{p,ex}\left(T_{ex} - T_{ex,in}\right)}{\rho_{ex}V_{ex}\tilde{C}_{p,ex}} \tag{7}$$

$$\frac{dV}{dt} = \dot{V}_{in} \tag{8}$$

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

Additional Computable Unknowns: r_1, k_1, C_A, C_B, $\dot{n}_{B,in}$, $\dot{Q}$, and $\dot{m}_{ex}$

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

$$C_i = \frac{n_i}{V} \qquad i = A \text{ and } B \tag{10}$$

$$\dot{n}_{B,in} = C_{B,in}\dot{V}_{in} \tag{11}$$

$$\dot{Q} = UA_{ex}\left(T_{ex} - T\right) \tag{12}$$

$$\dot{m}_{ex} = \rho_{ex}\dot{V}_{ex,in} \tag{13}$$

Additional Coupled Unknown: $\dot{V}_{in}$

$$\dot{V}_{in} \;:\; \max\left(\underline{T}\right) = T_{max} \quad \Rightarrow \quad 0 = \max\left(\underline{T}\right) - T_{max} = \epsilon \tag{14}$$

ATE Solver Inputs:

1. Initial guess for the coupled unknown

$$\dot{V}_{in,guess} = 1 \text{ L min}^{-1} \tag{15}$$

2. Residuals/Derivatives function that
   a. receives a guess for the coupled unknown
   b. uses it to solve the SBSTR design equations, (3) - (8)
   c. evaluates and returns the residual, equation (14)

IVODE Solver Inputs:

1. Initial values of the reactor model variables shown in Table 1.
2. Stopping criterion that n_A equals the final value shown in Table 1.
3. Derivatives function that
   a. receives the reactor model variables at the start of an integration step
   b. calculates the additional computable unknowns, equations (9) - (13)
   c. returns the design equation derivatives, equations (3) - (8)

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

Variable	Initial Value	Final Value
t	0	
n_A	$n_{A,0} = V_0 C_{A,0}$	$0.01 n_{A,0}$
n_B	0	
n_Z	0	
T	T_0	
T_{ex}	$T_{ex,0}$	
V	V_0	

Implementation of the Calculations

The Python script, activity_19.py, that was written to perform the calculations accompanies this solution. It defines an SBSTR model function and a derivatives function that use an IVODE solver to solve the design equations given a volumetric feed rate. It also defines a residuals function for the implicit coupled unknown equation that evaluates the coupled unknown residual given a guess for that coupled unknown. The calculations begin by defining a guess for the coupled unknown and using an ATE solver to find the actual value of the coupled unknown, which is the quantity of interest in this assignment.

Results and Discussion

The calculations were performed as described above. The ATE solver did not converge with the initial guess shown in equation (15), but decreasing it to 0.01 L min^{-1} resulted in convergence. To limit the maximum temperature to 80 °C, a feed rate of 0.016 L min^{-1} must be used. The SBSTR design equations were solved for that feed rate. The resulting temperature and conversion profiles are shown in Figures 1 and 2, respectively.

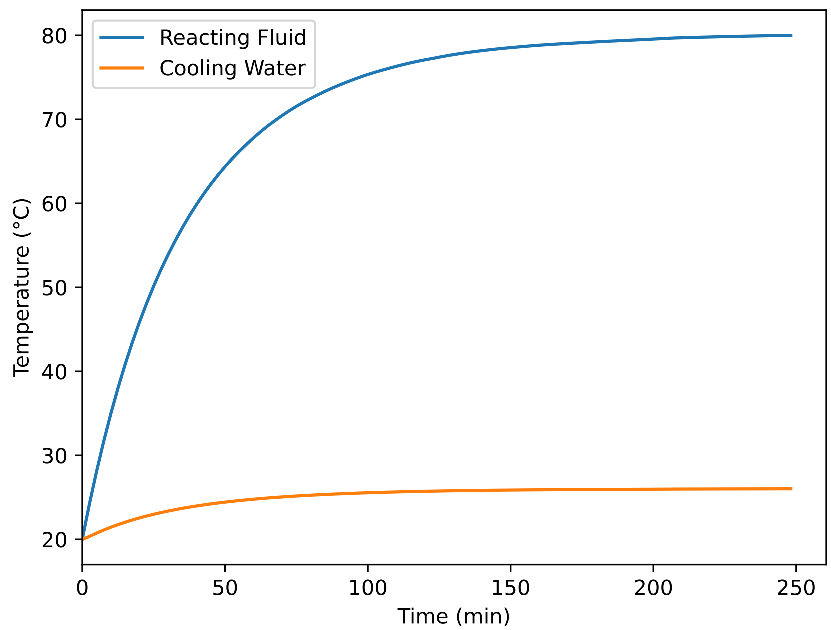

Figure 1. Temperature profile for a feed rate of 0.16 L min^{-1}.

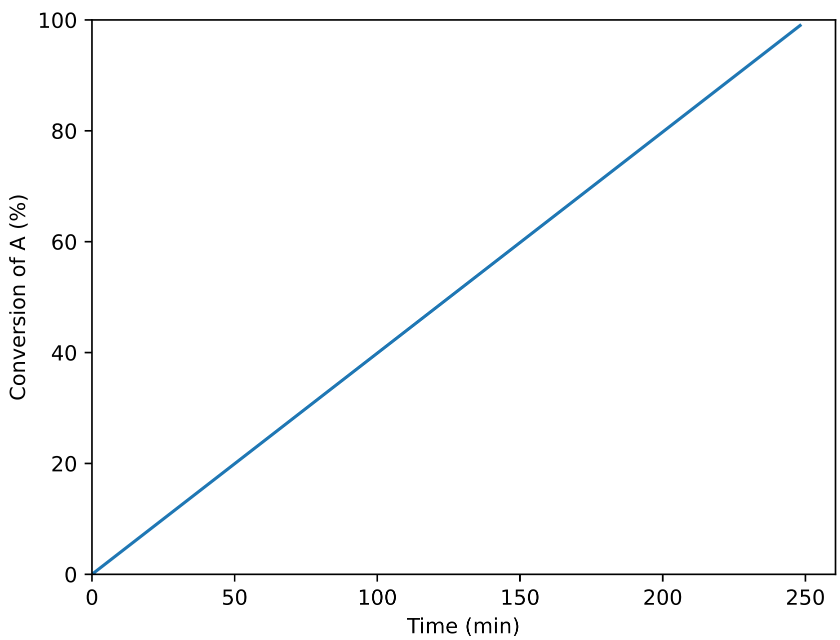

Figure 2. Conversion profile for a feed rate of 0.16 L min^{-1}.

The temperature profile in Figure 1 confirms that the reacting fluid temperature never exceeds 80 °C. Figure 2 shows that the conversion increases linearly. This indicates that the reaction is likely extremely fast so that the B is converted almost instantly as it is added. Since it is added at a constant rate, the conversion increases linearly. This is confirmed In that the maximum concentration of B over the whole process is less than 0.0001 M.

The temperature is well-controlled during the process. This suggests that if additional cooling capacity was added to the reactor, the feed rate could be increased which would shorten the processing time.

Deliverables

To limit the maximum temperature to 80 °C, a feed rate of 0.016 L min^{-1} must be used.