REB, The Book
Example 8.4.3 Solution[1]

The hydrolysis of acetic anhydride, reaction (1), can run away thermally in a batch reactor, but this can be prevented using semi-batch operation. Suppose the rate can be described using the rate expression shown in equation (2) where the reaction is first order in acetic anhydride with a pre-exponential factor of 1.192 x 10^{15} min^{-1} and an activation energy of 97,600 J mol^{-1}. The heat of reaction may be taken to be constant and equal to -58,615 J mol^{-1}.

$$\left(CH_3CO\right)_2 O + H_2O \rightarrow 2CH_3CO_2H \tag{1}$$

$$r_1 = k_1 C_{\left(CH_3CO\right)_2 O} \tag{2}$$

The reacting fluid is cooled by water that is fed to the perfectly mixed, 300 cm^3 reactor jacket at 60 °C and 250 cm^3 min^{-1}. The product of the heat transfer area and the heat transfer coefficient, UA, equals 260 cal min^{-1} K^{-1}.

The reactor operates at atmospheric pressure and initially contains an ideal liquid mixture of 67 cm^3 of water, 283 cm^3 of acetic acid (the solvent and product) and 0.30 cm^3 of sulfuric acid at 60 °C. Initially the temperature of the water in the jacket is 60 °C, too. The heat capacity of the fluid in the reactor may be taken to be constant and equal to 2.68 J cm^{-3} K^{-1}. A total of 350 cm^3 of acetic anhydride at 21 °C needs to be processed. To do so, it will be fed to the reactor at a constant volumetric flow rate until all of it has been added, after which the reactor will operate in batch mode until the reacting fluid cools to 65 °C. At no time during processing can the reacting fluid temperature exceed 95 °C. What volumetric feed rate will minimize the processing time, and at that feed rate what will the final conversion of A equal? Plot (a) the temperature of the fluid in the reactor and (b) the concentration of acetic anhydride in the reactor as a function of processing time when that feed rate is used.

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[1] This problem is loosely based upon the work of Haldar and Rao (Chem. Eng. Tech. **15**, 34 (1992) and Chem. Eng. Tech. **15**, 39 (1992)), but the rate expression was modified and additional assumptions regarding fluid and reactor properties were introduced. This was done to avoid intricate details from obscuring the basic approach to the analysis of a semi-batch reactor. Therefore, the results presented here should not be used for engineering purposes, but rather the original work should be consulted.

You may assume the liquid mixture to be ideal, and that the densities of acetic anhydride, acetic acid, and water are constant and equal to 1.082, 1.0, and 1.049 g cm^{-3}, respectively. Their molecular weights are 102, 18, and 60 g mol^{-1}, respectively, and the heat capacity of acetic anhydride being added to the reactor can be taken to be 168.2 J mol^{-1} K^{-1}.

Assignment Summary

To simplify the notation, A represents acetic anhydride, W represents water and Z represents acetic acid.

Reaction

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

Rate Expression

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

Reactor: Non-isothermal SBSTR with a 2 stage operational protocol

Given Constants: $k_{0,1}$ = 1.192 x 10^{15} min^{-1}, E_1 = 97,600 J mol^{-1}, ΔH_1 = –58,615 J mol^{-1}, V_{ex} = 300 cm^3, $T_{ex,in}$ = 60 °C, $\dot{V}_{ex}$ = 250 cm^3 min^{-1}, UA = 260 cal min^{-1} K^{-1}, P = 1 atm, $V_{W,0}$ = 67 cm^3, $V_{Z,0}$ = 283 cm^3, $V_{cat,0}$ = 0.30 cm^3, T_0 = 60 °C, $T_{ex,0}$ = 60 °C, $\check{c}_p$ = 2.68 J cm^{-3} K^{-1}, V_A = 350 cm^3, T_A = 21 °C, T_f = 65 °C, T_{max} = 95 °C, ρ_A = 1.082 g cm^{-3}, ρ_W = 1.0 g cm^{-3}, ρ_Z = 1.049 g cm^{-3}, M_A = 102, M_W = 18, M_Z = 60 g mol^{-1}, and $\hat{C}_{p,A}$ = 168.2 J mol^{-1} K^{-1}.

Parameter: $\dot{V}_{A,in}$

Constraint: $T < T_{max}$

Deliverables: $\dot{V}_{A,opt} = \underset{\dot{V}_{A,in}}{\arg\min}\left(\underline{t}_f\right), f_{A,f}$, and $\underline{T}\Big|_{\dot{V}_{opt}}$ and $\underline{C}_A\Big|_{\dot{V}_{opt}}$ vs. $\underline{t}\Big|_{\dot{V}_{opt}}$ as graphs

Formulation of the Equations

Reactor Model Equations:

$$\frac{dn_A}{dt} = \dot{n}_{A,in} - Vr_1 \tag{3}$$

$$\frac{dn_W}{dt} = -Vr_1 \tag{4}$$

$$\frac{dn_Z}{dt} = 2Vr_1 \tag{5}$$

$$V\check{C}_p\frac{dT}{dt} - P\frac{dV}{dt} = \dot{Q} - \dot{n}_{A,in}\hat{C}_{p,A}\left(T - T_{in}\right) - Vr_1\Delta H_1 \tag{6}$$

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

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

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

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

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

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

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

$$\dot{m}_{ex} = \dot{V}_{ex}\rho_{ex} \tag{12}$$

$$\dot{n}_{A,in} = \frac{\dot{V}_{in}\rho_A}{M_A} \tag{13}$$

$$\begin{aligned} \dot{V}_{in} &= \dot{V}_{A,in} && 0 \le t \le t_1 \\ \dot{V}_{in} &= 0 && t > t_1 \end{aligned} \tag{14}$$

Additional Uncomputable Unknown: $\dot{V}_{A,in}$

$$\underline{\dot{V}}_{A,in} = \left[38,\cdots,40\right] \text{ cm}^3 \text{ min}^{-1} \tag{15}$$

IVODE Solver Inputs: (for each value of $\dot{V}_{A,in}$)

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 (9) - (14)
        iii. evaluates and returns the design equation derivatives using equations (3) - (5), (7), (8), and (16)

$$\frac{dT}{dt} = \frac{\dot{Q} - \dot{n}_{A,in}\hat{C}_{p,A}\left(T - T_{in}\right) - Vr_1\Delta H_1 + P\dot{V}_{in}}{V\breve{C}_p} \tag{16}$$

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	$t_1 = \frac{V_A}{\dot{V}_{in}}$
n_A	0	
n_W	$n_{W,0} = \frac{V_{W,0}\rho_W}{M_W}$	
n_Z	$n_{Z,0} = \frac{V_{Z,0}\rho_Z}{M_Z}$	
T	T_0	
T_{ex}	$T_{ex,0}$	
V	$V_0 = V_{W,0} + V_{Z,0} + V_{acid,0}$	

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 reactor model variables at the start of an integration step
        ii. calculates the computable additional unknowns using equations (9) - (14)
        iii. evaluates and returns the design equation derivatives using equations (3) - (5), (7), (8), and (16)

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	
n_A	$n_A\big\vert_{t_1}$	
n_W	$n_W\big\vert_{t_1}$	
n_Z	$n_Z\big\vert_{t_1}$	
T	$T\big\vert_{t_1}$	
T_{ex}	$T_{ex}\big\vert_{t_1}$	T_f
V	$V\big\vert_{t_1}$	

Deliverables Equations:

$$\forall \dot{V}_{A,in,n} \in \underline{\dot{V}}_{A,in} \quad \begin{pmatrix} t_{f,n} = \underline{t}\big\vert_{T=T_f} & \max \underline{T} \leq T_{max} \\ t_{f,n} = \infty & \max \underline{T} > T_{max} \end{pmatrix} \tag{17}$$

$$\dot{V}_{A,opt} = \underset{\dot{V}_{A,in}}{\arg\min} \left(\underline{t}_f \right) \tag{18}$$

$$t_{opt} = \underset{\dot{V}_{A,in}}{\min} \left(\underline{t}_f \right) \tag{19}$$

$$f_{A,f} = \frac{\frac{\rho_A V_A}{M_A} - \left(\underline{n}_A \Big|_{\dot{V}_{opt}} \right) \Big|_{t_{opt}}}{\frac{\rho_A V_A}{M_A}} \tag{20}$$

$$\underline{C}_A \Big|_{\dot{V}_{opt}} = \frac{\underline{n}_A \Big|_{\dot{V}_{opt}}}{\underline{V} \Big|_{\dot{V}_{opt}}} \tag{21}$$

Implementation of the Calculations

The Python script, example_8_4_3.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 for both stages of the protocol given a value for the inlet volumetric flow rate. The calculations begin by defining a range of volumetric feed rates and calculating the processing time for each of them. If, for any feed rate, the temperature exceeds the specified maximum temperature, the processing time is set to infinity. The feed rate that minimizes the processing time is then identified, and the design equations are solved for that optimum feed rate. Finally, the quantities of interest are calculated and the requested graphs generated.

Results and Discussion

The optimization results are shown in Table 3. The acetic anhydride concentration profile is shown in Figure 1 and the temperature profile is shown in Figure 2. A feed rate of 39 cm^3 min^{-1} results in the minimum processing time, 16.9 min, that meets the temperature constraint. At the end of processing, the conversion of acetic anhydride is 100%.

Table 3. Optimization Results

item	value	units
Minimum Total Processing Time	16.9	min
Semi-Batch Processing Time	9.0	min
Optimum Feed Rate	39.0	$cm^3\ min^{-1}$
Maximum Temperature	94.7	°C
Maximum Cooling Water Temperature	77.6	°C
Acetic Anhydride Conversion	100.0	%

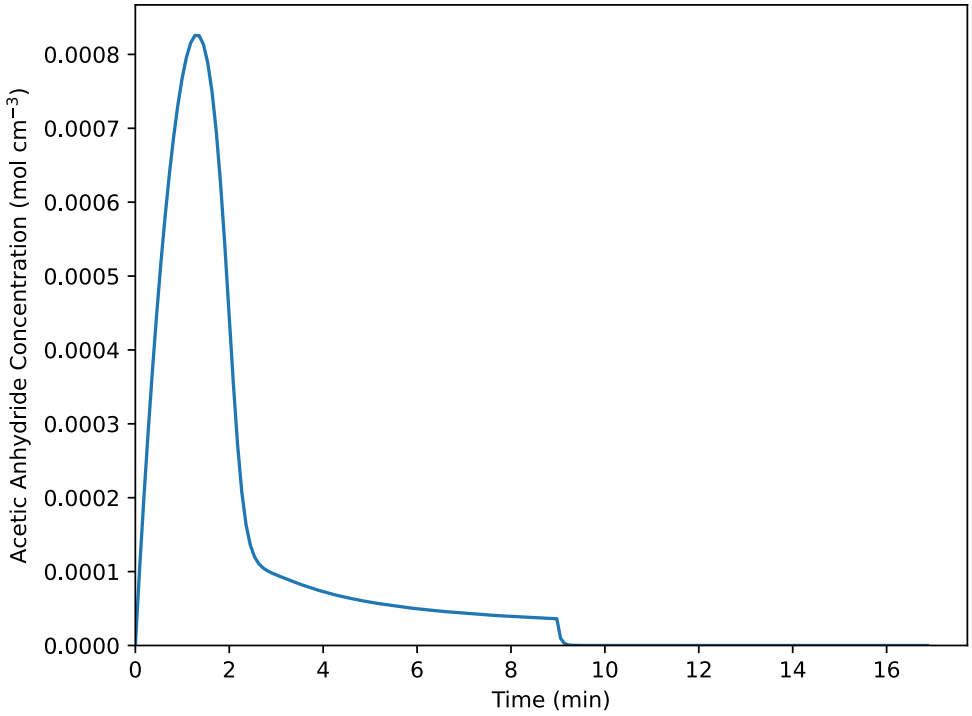

Figure 1. Acetic acid concentration profile for the optimized SBSTR.

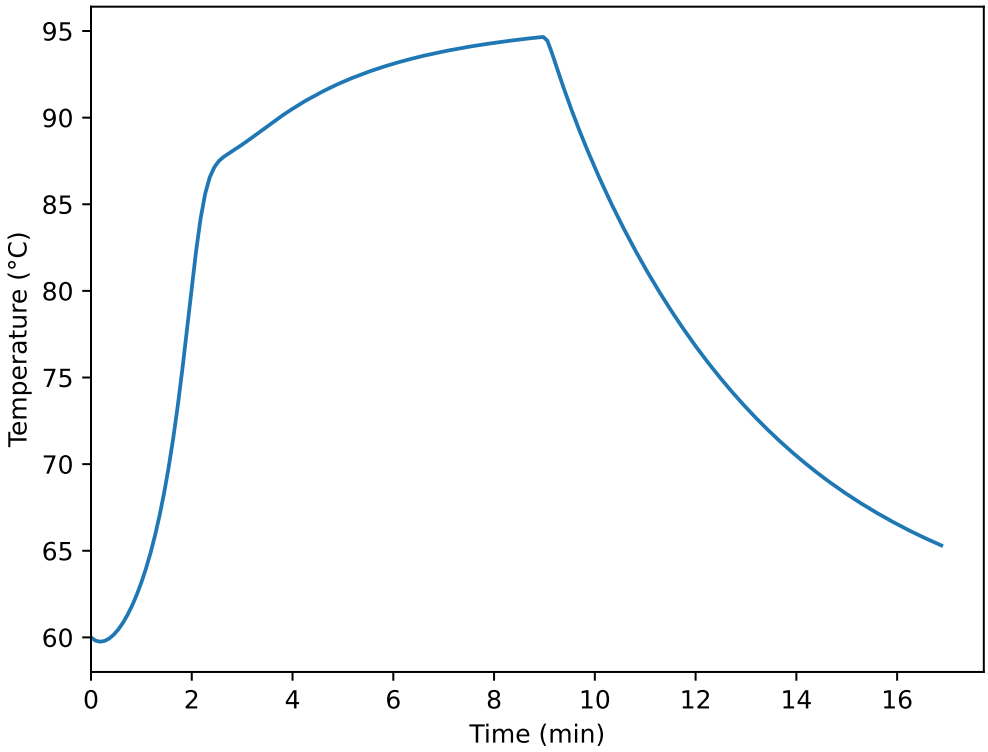

Figure 2. Temperature profile for the optimized SBSTR.

Figure 1 shows that the reacting fluid temperature just reaches 95 °C at the end of semi-batch processing. If the acetic anhydride was fed any faster, the temperature would exceed the specified maximum. Lowering the feed rate would increase the processing time. Table 3 shows that the cooling water reaches a maximum temperature of 77.6 °C.

The shapes of the profiles are consistent with a qualitative analysis of the process. During semi-batch processing two factors are at work with respect to the reactant concentration and three factors are at work with respect to the temperature. The flow into the reactor tends to increase the reactant concentration while the reaction tends to decrease it. Figure 1 shows that the concentration rises steadily until it passes through

a maximum. Prior to the maximum, the feed is adding A faster than the reaction is consuming it. After the maximum, the opposite is true. Of course increasing the concentration tends to increase the rate and decreasing it tends to decrease the rate. Once the feed stops, at 9 min, the concentration quickly drops to zero.

As for temperature, the cold feed and the cooling water remove heat and tend to lower the temperature while the reaction releases the heat of reaction. Figure 2 shows that initially the temperature drops very slightly. This is a result of the cold feed; heat generation is negligible because the reactant concentration is near zero making the rate very small. As the concentration of A increases the rate increases, which, in turn, increases the amount of heat being released in the system. At about the point where the concentration reaches its maximum, the temperature rise slows. This occurs because the decreasing concentration reduces the rate thereby lowering the heat being released by the reaction. Finally, at 9 min, after all of the A has been added, the rate goes to zero and heat is no longer being released into the system. From that point forward, the temperature drops as heat is removed by the cooling water.

Deliverables

A volumetric feed rate of 39 cm^3 min^{-1} yields the smallest processing time (9 min) that satisfies the maximum temperature constraint. With that feed rate, 100% of the acetic anhydride is converted. The acetic acid concentration and temperature profiles for that volumetric feed rate are shown in Figures 1 and 2.