



Living Example Problem

The economic incentive
\$ = 89¢/gal
vs. 72¢/gal

The algorithm



Following the Algorithm

Example 8-3 Liquid-Phase Isomerization of Normal Butane

Normal butane, C_4H_{10} , is to be isomerized to isobutane in a plug-flow reactor. Isobutane is a valuable product that is used in the manufacture of gasoline additives. For example, isobutane can be further reacted to form iso-octane. The 2004 selling price of *n*-butane was 72 cents per gallon, while the price of isobutane was 89 cents per gallon.

The reaction is to be carried out adiabatically in the liquid phase under high pressure using essentially trace amounts of a liquid catalyst which gives a specific reaction rate of 31.1 h^{-1} at 360 K. Calculate the PFR and CSTR volumes necessary to process 100,000 gal/day (163 kmol/h) at 70% conversion of a mixture 90 mol % *n*-butane and 10 mol % *i*-pentane, which is considered an inert. The feed enters at 330 K.

Additional information:

$$\Delta H_{\text{Rx}} = -6900 \text{ J/mol} \cdot \text{butane}, \quad \text{Activation energy} = 65.7 \text{ kJ/mol}$$

$$K_C = 3.03 \text{ at } 60^\circ\text{C}, \quad C_{A0} = 9.3 \text{ kmol/dm}^3 = 9.3 \text{ kmol/m}^3$$

Butane

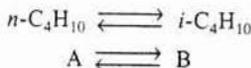
i-Pentane

$$C_{P_{n-B}} = 141 \text{ J/mol} \cdot \text{K}$$

$$C_{P_{i-P}} = 161 \text{ J/mol} \cdot \text{K}$$

$$C_{P_{i-B}} = 141 \text{ J/mol} \cdot \text{K} = 141 \text{ kJ/kmol} \cdot \text{K}$$

Solution



$$\text{Mole Balance: } F_{A0} \frac{dX}{dV} = -r_A \quad (\text{E8-3.1})$$

$$\text{Rate Law: } -r_A = k \left(C_A - \frac{C_B}{K_C} \right) \quad (\text{E8-3.2})$$

$$\text{with } k = k(T_1) e^{\left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right]} \quad (\text{E8-3.3})$$

$$K_C = K_C(T_2) e^{\left[\frac{\Delta H_{\text{Rx}}}{R} \left(\frac{1}{T_2} - \frac{1}{T} \right) \right]} \quad (\text{E8-3.4})$$

Stoichiometry (liquid phase, $v = v_0$):

$$C_A = C_{A0}(1 - X) \quad (\text{E8-3.5})$$

$$C_B = C_{A0}X \quad (\text{E8-3.6})$$

Combine:

$$-r_A = kC_{A0} \left[1 - \left(1 + \frac{1}{K_C} \right) X \right] \quad (\text{E8-3.7})$$

Integrating Equation (E8-3.1) yields

$$V = \int_0^X \frac{F_{A0}}{-r_A} dX \quad (\text{E8-3.8})$$

Energy Balance: Recalling Equation (8-27), we have

$$\dot{Q} - \dot{W}_s - F_{A0} \sum (\Theta_i C_{p_i} (T - T_0)) - F_{A0} X [\Delta H_{Rx}^\circ(T_R) + \Delta C_p (T - T_R)] = 0 \quad (8-27)$$

From the problem statement

$$\text{Adiabatic: } \dot{Q} = 0$$

$$\text{No work: } \dot{W}_s = 0$$

$$\Delta C_p = C_{p_B} - C_{p_A} = 141 - 141 = 0$$

Applying the preceding conditions to Equation (8-29) and rearranging gives

$$T = T_0 + \frac{(-\Delta H_{Rx}^\circ)X}{\sum \Theta_i C_{p_i}} \quad (E8-3.9)$$

Parameter Evaluation

$$\begin{aligned} \sum \Theta_i C_{p_i} &= C_{p_A} + \Theta_1 C_{p_1} = \left(141 + \frac{0.1}{0.9} 161 \right) \text{ J/mol} \cdot \text{K} \\ &= 159 \text{ J/mol} \cdot \text{K} \end{aligned}$$

$$T = 330 + \frac{-(-6900)X}{159}$$

$$\boxed{T = 330 + 43.4X} \quad (E8-3.10)$$

where T is in degrees Kelvin.

Substituting for the activation energy, T_1 , and k_1 in Equation (E8-3.3), we obtain

$$k = 31.1 \exp \left[\frac{65,700}{8.31} \left(\frac{1}{360} - \frac{1}{T} \right) \right] (h^{-1})$$

$$\boxed{k = 31.1 \exp \left[7906 \left(\frac{T-360}{360T} \right) \right] (h^{-1})} \quad (E8-3.11)$$

Substituting for ΔH_{Rx} , T_2 , and $K_C(T_2)$ in Equation (E8-3.4) yields

$$K_C = 3.03 \exp \left[\frac{-6900}{8.31} \left(\frac{1}{333} - \frac{1}{T} \right) \right]$$

$$\boxed{K_C = 3.03 \exp \left[-830.3 \left(\frac{T-333}{333T} \right) \right]} \quad (E8-3.12)$$

Recalling the rate law gives us

$$-r_A = k C_{A0} \left[1 - \left(1 + \frac{1}{K_C} \right) X \right] \quad (E8-3.7)$$

Equilibrium Conversion

At equilibrium

$$-r_A \equiv 0$$

and therefore we can solve Equation (E8-3.7) for the equilibrium conversion

$$X_e = \frac{K_C}{1 + K_C} \quad (\text{E8-3.8})$$

Because we know $K_C(T)$, we can find X_e as a function of temperature.**PFR Solution**

It's risky business to ask for 70% conversion in a reversible reaction.

Find the PFR volume necessary to achieve 70% conversion and plot X , X_e , $-r_A$, and T down the length (volume) of the reactor. This problem statement is risky. Why? Because the adiabatic equilibrium conversion may be less than 70%! Fortunately, not for the conditions here $0.7 < X_e$. In general, we should ask for the reactor volume to obtain 95% of the equilibrium conversion, $X_f = 0.95 X_e$.

We will solve the preceding set of equations to find the PFR reactor volume using both hand calculations and an ODE computer solution. We carry out the hand calculation to help give an intuitive understanding of how the parameters X_e and T vary with conversion and temperature. The computer solution allows us to readily plot the reaction variables along the length of the reactor and also to study the effect of reaction and reactor by varying the system parameters such as C_{A0} and T_0 .

Solution by Hand Calculation to perhaps give greater insight and to build on techniques in Chapter 2.

We will now integrate Equation (E8-3.8) using Simpson's rule after forming a table (E8-3.1) to calculate $(F_{A0}/-r_A)$ as a function of X . This procedure is similar to that described in Chapter 2. We now carry out a sample calculation to show how Table E8-3.1 was constructed. For example, at $X = 0.2$.

$$(a) \quad T = 330 + 43.4(0.2) = 338.6 \text{ K}$$

$$(b) \quad k = 31.1 \exp \left[7906 \left(\frac{338.6 - 360}{(360)(338.6)} \right) \right] = 31.1 \exp(-1.388) = 7.76 \text{ h}^{-1}$$

$$(c) \quad K_C = 3.03 \exp \left[-830.3 \left(\frac{338.6 - 333}{(333)(338.6)} \right) \right] = 3.03 e^{-0.0412} = 2.9$$

$$(d) \quad X_e = \frac{2.9}{1 + 2.9} = 0.74$$

$$(e) \quad -r_A = \left(\frac{7.76}{\text{h}} \right) (9.3) \frac{\text{mol}}{\text{dm}^3} \left[1 - \left(1 + \frac{1}{2.9} \right) (0.2) \right] = 52.8 \frac{\text{mol}}{\text{dm}^3 \cdot \text{h}} = 52.8 \frac{\text{kmol}}{\text{m}^3 \cdot \text{h}}$$

$$(f) \quad \frac{F_{A0}}{-r_A} = \frac{(0.9 \text{ mol butane/mol total})(163. \text{ kmol total/h})}{52.8 \frac{\text{kmol}}{\text{m}^3 \cdot \text{h}}} = 2.78 \text{ m}^3$$

Sample calculation for Table E8-3.1

Continuing in this manner for other conversions we can complete Table E8-3.1.

Make a Levenspiel plot as in Chapter 2.

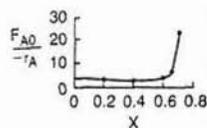


TABLE E8-3.1 HAND CALCULATION

X	T (K)	k (h^{-1})	K_C	X_e	$-r_A$ ($\text{kmol}/\text{m}^3 \cdot \text{h}$)	$\frac{F_{A0}}{-r_A}$ (m^3)
0	330	4.22	3.1	0.76	39.2	3.74
0.2	338.7	7.76	2.9	0.74	52.8	2.78
0.4	347.3	14.02	2.73	0.73	58.6	2.50
0.6	356.0	24.27	2.57	0.72	37.7	3.88
0.65	358.1	27.74	2.54	0.718	24.5	5.99
0.7	360.3	31.67	2.5	0.715	6.2	23.29

In order to construct a Levenspiel plot, the data from Table E8-3.1 ($F_{A0}/-r_A$ vs. X) was used in Example 2-7 to size reactors in series. The reactor volume for 70% will be evaluated using the quadrature formulas. Because ($F_{A0}/-r_A$) increases rapidly as we approach the adiabatic equilibrium conversion, 0.71, we will break the integral into two parts.

$$V = \int_0^{0.7} \frac{F_{A0}}{-r_A} dX = \int_0^{0.6} \frac{F_{A0}}{-r_A} dX + \int_{0.6}^{0.7} \frac{F_{A0}}{-r_A} dX \quad (\text{E8-3.14})$$

Using Equations (A-24) and (A-22) in Appendix A, we obtain

$$V = \frac{3}{8} \times \frac{0.6}{3} [3.74 + 3 \times 2.78 + 3 \times 2.50 + 3.88] \text{m}^3 + \frac{1}{3} \times \frac{0.1}{2} [3.88 + 4 \times 5.99 + 23.29] \text{m}^3$$

$$V = 1.75 \text{ m}^3 + 0.85 \text{ m}^3$$

$$V = 2.60 \text{ m}^3$$

You probably will never ever carry out a hand calculation similar to above. So why did we do it? Hopefully, we have given the reader a more intuitive feel of magnitude of each of the terms and how they change as one moves down the reactor (i.e., what the computer solution is doing), as well as to show how the Levenspiel Plots of ($F_{A0}/-r_A$) vs. X in Chapter 2 were constructed. At exit, $V = 2.6 \text{ m}^3$, $X = 0.7$, $X_e = 0.715$, and $T = 360 \text{ K}$.

Computer Solution

PFR

We could have also solved this problem using Polymath or some other ODE solver. The Polymath program using Equations (E8-3.1), (E8-3.10), (E8-3.7), (E8-3.11), (E8-3.12), and (E8-3.13) is shown in Table E8-3.2.

TABLE E8-3.2. POLYMATH PROGRAM ADIABATIC ISOMERIZATION

Differential equations as entered by the user

(1) $d(X)/d(v) = -ra/Fa0$

Explicit equations as entered by the user

- (1) $Ca0 = 9.3$
 (2) $Fa0 = .9 * 163$
 (3) $T = 330 + 43.3 * X$
 (4) $Kc = 3.03 * \exp(-830.3 * ((T - 333)/(T * 333)))$
 (5) $k = 31.1 * \exp(7906 * ((T - 360)/(T * 360)))$
 (6) $Xe = Kc / (1 + Kc)$
 (7) $ra = -k * Ca0 * (1 - (1 + Kc) * X)$
 (8) $rate = -ra$

Why are we doing this hand calculation? If it isn't helpful, send me an email and you won't see this again.



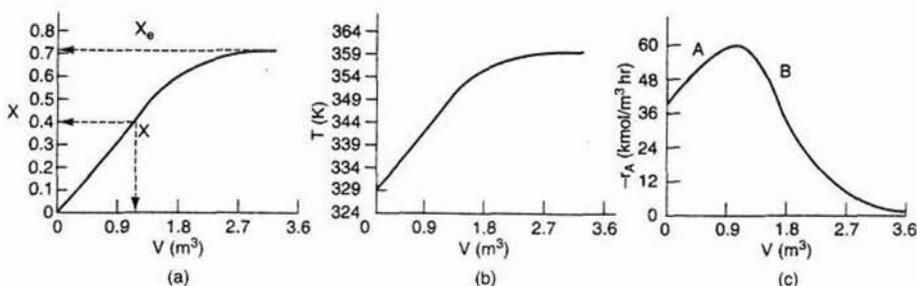


Figure E8-3.1 Conversion, temperature, and reaction rate profiles.

Look at the shape of the curves in Figure E8-3.1. Why do they look the way they do?

The graphical output is shown in Figure E8-3.1. We see from Figure E8-3.1(a) that 1.15 m³ is required for 40% conversion. The temperature and reaction rate profiles are also shown. One observes that the rate of reaction

$$-r_A = \underbrace{kC_{A0}}_A \underbrace{\left[1 - \left(1 + \frac{1}{K_C} \right) X \right]}_B \quad (\text{E8-3.15})$$

goes through a maximum. Near the entrance to the reactor, T increases as does k , causing term A to increase more rapidly than term B decreases, and thus the rate increases. Near the end of the reactor, term B is decreasing more rapidly than term A is increasing. Consequently, because of these two competing effects, we have a maximum in the rate of reaction.

CSTR Solution

Let's calculate the adiabatic CSTR volume necessary to achieve 40% conversion. Do you think the CSTR will be larger or smaller than the PFR? The mole balance is

$$V = \frac{F_{A0}X}{-r_A}$$

Using Equation (E8-3.7) in the mole balance, we obtain

$$V = \frac{F_{A0}X}{kC_{A0} \left[1 - \left(1 + \frac{1}{K_C} \right) X \right]} \quad (\text{E8-3.16})$$

From the energy balance, we have Equation (E8-3.10):

$$\begin{aligned} \text{For 40\% conversion} \quad T &= 330 + 43.4X \\ T &= 330 + 43.4(0.4) = 347.3 \end{aligned}$$

Using Equations (E8-3.11) and (E8-3.12) or from Table E8-3.1,

$$\begin{aligned} k &= 14.02 \text{ h}^{-1} \\ K_C &= 2.73 \end{aligned}$$

Is
 $V_{\text{PFR}} > V_{\text{CSTR}}$
 or
 $V_{\text{PFR}} < V_{\text{CSTR}}?$

Then

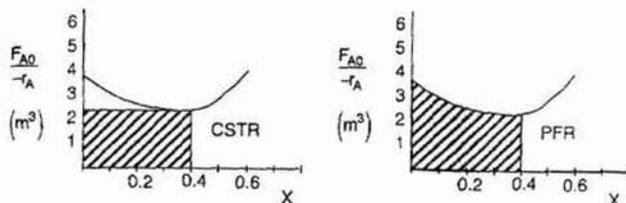
$$-r_A = 58.6 \text{ kmol/m}^3 \cdot \text{h}$$

$$V = \frac{(146.7 \text{ kmol butane/h})(0.4)}{58.6 \text{ kmol/m}^3 \cdot \text{h}}$$

$$V = 1.0 \text{ m}^3$$

We see that the CSTR volume (1 m^3) to achieve 40% conversion in this adiabatic reaction is less than the PFR volume (1.15 m^3).

One can readily see why the reactor volume for 40% conversion is smaller for a CSTR than a PFR by recalling the Levenspiel plots from Chapter 2. Plotting $(F_{A0}/-r_A)$ as a function of X from the data in Table E8-3.1 is shown here.



The PFR area (volume) is greater than the CSTR area (volume).

8.4 Steady-State Tubular Reactor with Heat Exchange

In this section, we consider a tubular reactor in which heat is either added or removed through the cylindrical walls of the reactor (Figure 8-3). In modeling the reactor, we shall assume that there are no radial gradients in the reactor and that the heat flux through the wall per unit volume of reactor is as shown in Figure 8-3.

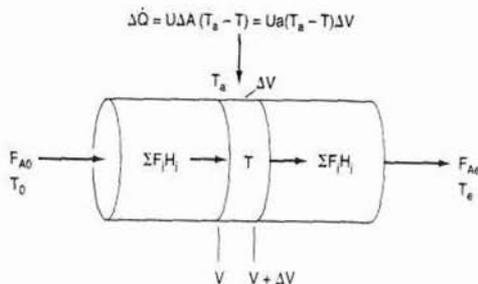


Figure 8-3 Tubular reactor with heat gain or loss.

8.4.1 Deriving the Energy Balance for a PFR

We will carry out an energy balance on the volume ΔV with $\dot{W}_s = 0$. Equation (8-10) becomes

$$\Delta \dot{Q} + \sum F_i H_i|_V - \sum F_i H_i|_{V+\Delta V} = 0 \quad (8-31)$$

The heat flow to the reactor, $\Delta\dot{Q}$, is given in terms of the overall heat transfer coefficient, U , the heat exchange area, ΔA , and the difference between ambient temperature T_a and the reactor temperature T .

$$\Delta\dot{Q} = U\Delta A(T_a - T) = Ua\Delta V(T_a - T)$$

where a is the heat exchange area per unit volume of reactor. For the tubular reactor

$$a = \frac{A}{V} = \frac{\pi DL}{\frac{\pi D^2 L}{4}} = \frac{4}{D}$$

where D is the reactor diameter. Substituting for $\Delta\dot{Q}$ in Equation (8-31) and dividing Equation (8-31) by ΔV , and taking the limit as $\Delta V \rightarrow 0$, we get

$$Ua(T_a - T) - \frac{d\Sigma(F_i H_i)}{dV} = 0$$

Expanding

$$Ua(T_a - T) - \Sigma \frac{dF_i}{dV} H_i - \Sigma F_i \frac{dH_i}{dV} = 0 \quad (8-32)$$

From a mole balance on species i , we have

$$\frac{dF_i}{dV} = r_i = v_i(-r_A) \quad (8-33)$$

Differentiating the enthalpy Equation (8-19) with respect to V

$$\frac{dH_i}{dV} = C_{P_i} \frac{dT}{dV} \quad (8-34)$$

Substituting Equations (8-33) and (8-34) into Equation (8-32), we obtain

$$Ua(T_a - T) - \underbrace{\Sigma v_i H_i}_{\Delta H_{R_x}} (-r_A) - \Sigma F_i C_{P_i} \frac{dT}{dV} = 0$$

Rearranging, we arrive at

This form of the energy balance will also be applied to multiple reactions.

Heat "Generated"	Heat Removed
$\frac{dT}{dV} = \frac{r_A \Delta H_{R_x} - Ua(T - T_a)}{\Sigma F_i C_{P_i}}$	

(8-35)

which is Equation (T8-1G) in Table 8-1. This equation is coupled with mole balances on each species [Equation (8-33)]. Next we express r_A a function of either the concentrations for liquid systems or molar flow rates for gas systems as described in Section 4.7.

We will use this form of the energy balance for membrane reactors and also extend this form to multiple reactions.

We could also write Equation (8-35) in terms of conversion by recalling $F_i = F_{A0}(\Theta_i + \nu_i X)$ and substituting this expression into the denominator of Equation (8-35).

$$\text{PFR energy balance} \quad \boxed{\frac{dT}{dV} = \frac{Ua(T_a - T) + (r_A)(\Delta H_{Rx})}{F_{A0}(\sum \Theta_i C_{P_i} + \Delta C_p X)}} \quad (8-36)$$

For a packed-bed reactor $dW = \rho_b dV$ where ρ_b is the bulk density,

$$\text{PBR energy balance} \quad \boxed{\frac{dT}{dW} = \frac{Ua(T_a - T) + (r'_A)(\Delta H_{Rx})}{\sum F_i C_{P_i}}} \quad (8-37)$$

Equations (8-36) and (8-37) are also given in Table 8-1 as Equations (T8-1E) and (T8-1F). As noted earlier, having gone through the derivation to these equations it will be easier to apply them accurately to CRE problems with heat effects. The differential equation describing the change of temperature with volume (i.e., distance) down the reactor,

$$\text{Energy balance} \quad \boxed{\frac{dT}{dV} = g(X, T)} \quad (A)$$

Numerical integration of two coupled differential equations is required.

must be coupled with the mole balance,

$$\text{Mole balance} \quad \boxed{\frac{dX}{dV} = \frac{-r_A}{F_{A0}} = f(X, T)} \quad (B)$$

and solved simultaneously. If the coolant temperature varies down the reactor we must add the coolant balance, which is

$$\boxed{\frac{dT_a}{dV} = \frac{U_a(T - T_a)}{\dot{m}_c C_{P_c}}} \quad (C)$$

A variety of numerical schemes can be used to solve the coupled differential equations, (A), (B), and (C).

Example 8-4 Butane Isomerization Continued—OOPS!

When we checked the vapor pressure at the exit to the adiabatic reactor in Example 8-3 where the temperature is 360 K, we found the vapor pressure to be about 1.5 MPa for isobutene, which is greater than the rupture pressure of

the glass vessel being used. Fortunately, there is a bank of ten partially insulated ($Ua = 5000 \text{ kJ/h} \cdot \text{m}^3 \cdot \text{K}$) tubular reactors each 6 m^3 over in the storage shed available for use. We are also going to lower the entering temperature to 310 K . The reactors are cooled by natural convection where average ambient temperature in this tropical location is assumed to be 37°C . The temperature in any of the reactors cannot rise above 325 K . Plot X , X_e , T , and the reaction rate along the length of the reactor. Does the temperature rise above 325 K ?

Solution

For ten reactors in parallel

$$F_{A0} = (0.9)(163 \text{ kmol/h}) \times \frac{1}{10} = 14.7 \frac{\text{kmol A}}{\text{h}}$$

The mole balance, rate law, and stoichiometry are the same as in the adiabatic case previously discussed in Example 8-3; that is,

Same as
Example 8-3

Mole Balance:

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} \quad (\text{E8-3.1})$$

Rate Law and Stoichiometry:

$$r_A = -kC_{A0} \left[1 - \left(1 + \frac{1}{K_C} \right) X \right] \quad (\text{E8-3.7})$$

with

$$k = 31.1 \exp \left[7906 \left(\frac{T-360}{360T} \right) \right] \text{ h}^{-1} \quad (\text{E8-3.11})$$

$$K_C = 3.03 \exp \left[-830.3 \left(\frac{T-333}{333T} \right) \right] \quad (\text{E8-3.12})$$

At equilibrium

$$X_e = \frac{K_C}{1 + K_C} \quad (\text{E8-3.13})$$

Recalling $\Delta C_p = 0$, Equation (8-36) for the partially insulated reactor can be written as

$$\frac{dT}{dV} = \frac{\text{Heat "Generated" } - \text{Heat Removed}}{F_{A0} C_{pA}} = \frac{r_A \Delta H_{R_x} - Ua(T - T_a)}{F_{A0} C_{pA}} \quad (\text{E8-4.1})$$

where and $C_{p0} = \sum \Theta_i C_{p_i} = 159 \cdot \text{kJ/kmol} \cdot \text{K}$, $Ua = 5000 \text{ kJ/m}^3 \cdot \text{h} \cdot \text{K}$, $T_a = 310 \text{ K}$, and $\Delta H_{R_x} = -6900 \text{ kJ/mol}$. These equations are now solved using Polymath. The Polymath program and profiles of X , X_e , T , and $-r_A$ are shown here.

ODE Report (RKF45)

Differential equations entered by the user

[1] $d(X)/d(V) = -raFa0$

[2] $d(T)/d(V) = ((ra*\Delta H) - Ua*(T - Ta))/CpoFa0$

Explicit equations as entered by the user

[1] $Ca0 = 9.3$

[2] $Fa0 = .9*163*.1$

[3] $Kc = 3.03*\exp(-830.3*(T-333)/(T*333))$

[4] $k = 31.1*\exp(7906*(T-360)/(T*360))$

[5] $Xe = Kc/(1+Kc)$

[6] $ra = -k*Ca0*(1 - (1+1/Kc)*X)$

[7] $\Delta H = -6900$

[8] $Ua = 5000$

[9] $Ta = 310$

[10] $Cpo = 159$

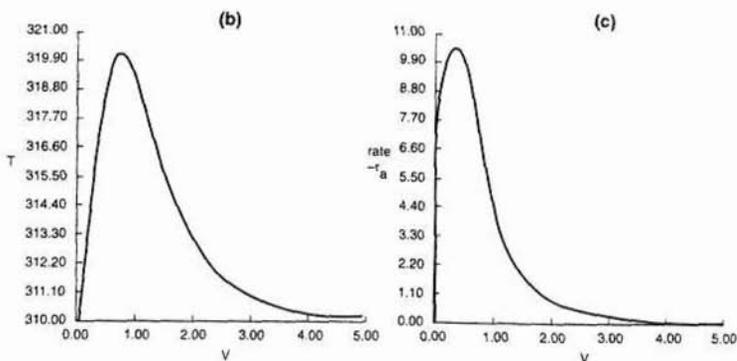
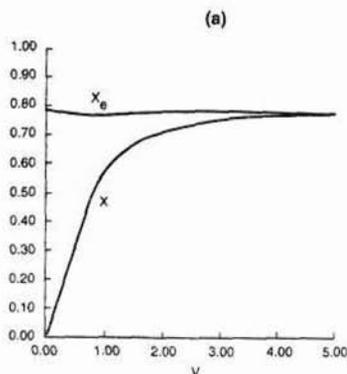
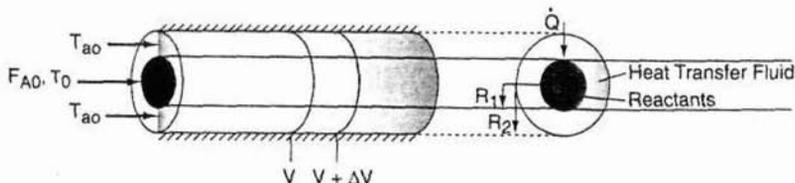


Figure E8-4.1 (a) Conversion profiles, (b) temperature profile, and (c) reaction rate profile.

We see that the temperature did not rise above 325 K.

8.4.2 Balance on the Coolant Heat Transfer Fluid

The heat transfer fluid will be a coolant for exothermic reactions and a heating medium for endothermic reactions. If the flow rate of the heat transfer fluid is sufficiently high with respect to the heat released (or adsorbed) by the reacting mixture, then the heat transfer fluid temperature will be constant along the reactor.

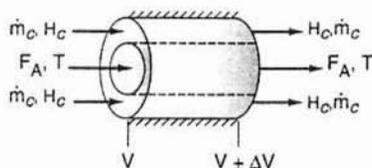


In the material that follows we develop the basic equations for a coolant to remove heat from exothermic reactions, however these same equations apply to endothermic reactions where a heating medium is used to supply heat.

By convention \dot{Q} is the heat **added** to the system. We now carry out an energy balance on the coolant in the annulus between R_1 and R_2 and between V and $V + \Delta V$. The mass flow rate of coolant is \dot{m}_c . We will consider the case where the outer radius of the coolant channel R_2 is insulated.

Case A Co-Current Flow

The reactant and the coolant flow in the same direction



The energy balance on the coolant in the volume between V and $(V + \Delta V)$

$$\left[\begin{array}{c} \text{Rate of energy} \\ \text{in at } V \end{array} \right] - \left[\begin{array}{c} \text{Rate of energy} \\ \text{out at } V + \Delta V \end{array} \right] + \left[\begin{array}{c} \text{Rate of heat added} \\ \text{by conduction through} \\ \text{the inner wall} \end{array} \right] = 0$$

$$\dot{m}_c H_c|_V - \dot{m}_c H_c|_{V+\Delta V} + Ua(T - T_a)\Delta V = 0$$

where T_a is the coolant temperature, and T is the temperature of the reactant mixture in the inner tube.

Dividing by ΔV and taking limit as $\Delta V \rightarrow 0$

$$-\dot{m}_c \frac{dH_c}{dV} + Ua(T - T_a) = 0 \quad (8-1)$$

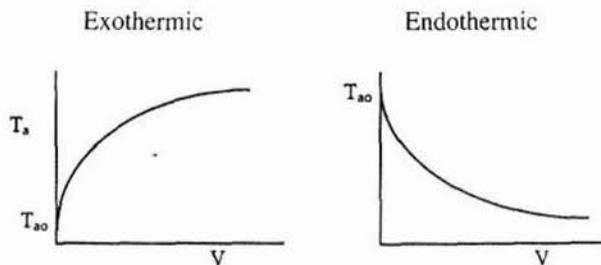
The change in enthalpy of the coolant can be written as

$$\frac{dH_c}{dV} = C_{p_c} \frac{dT_a}{dV} \quad (8-2)$$

the variation of coolant temperature T_a down the length of reactor is

$$\boxed{\frac{dT_a}{dV} = \frac{Ua(T - T_a)}{\dot{m}_c C_p}} \quad (8-3)$$

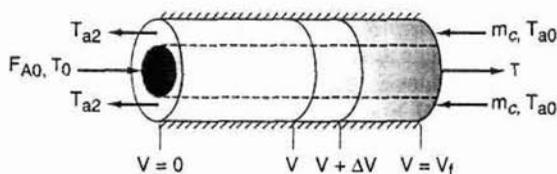
Typical heat transfer fluid temperature profiles are shown here for both exothermic and endothermic reactions



Heat Transfer Fluid Temperature Profiles

Case B Counter Current Flow

Here the reacting mixture and coolant flow in opposite directions for counter current flow of coolant and reactants. At the reactor entrance, $V = 0$, the reactants enter at temperature T_0 , and the coolant exits at temperature T_{a2} . At the end of the reactor, the reactants and products exit at temperature T while the coolant enters at T_{a0} .



Again we balance over a differential reactor volume to arrive at reactor volume.

$$\frac{dT_a}{dV} = \frac{Ua(T_a - T)}{\dot{m}_c C_{p_c}} \quad (8-41)$$

At the entrance $V = 0 \therefore X = 0$ and $T_a = T_{a2}$.

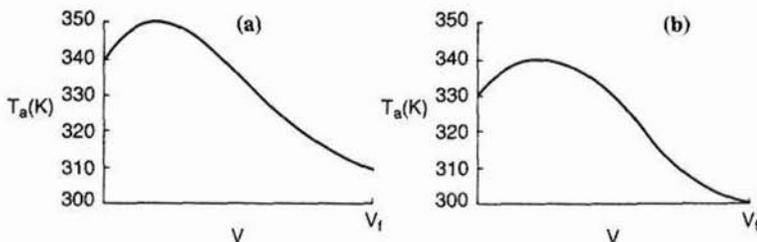
At exit $V = V_f \therefore T_a = T_{a0}$.

We note that the only difference between Equations (8-40) and (8-41) is a minus sign $[(T_a - T) = -[T_a - T]]$.

Solution to this counter current flow problem to find the exit conversion and temperature requires a trial-and-error procedure.

1. Consider an exothermic reaction where the coolant stream enters at the end of the reactor ($V = V_f$) at a temperature T_{a0} , say 300 K. We have to carry out a trial-and-error procedure to find the temperature of coolant exiting the reactor.
2. Assume a coolant temperature at the feed entrance ($X = 0, V = 0$) to the reactor to be $T_{a2} = 340$ K as shown in (a).

3. Use an ODE solver to calculate X , T , and T_a as a function of V .



We see from Figure (a) that our guess of 340 K for T_{a2} at the feed entrance ($V = 0$ and $X = 0$) gives an entering temperature of the coolant of 310 K ($V = V_f$), which does not match the actual entering coolant temperature of 300 K.

4. Now guess a coolant temperature at $V = 0$ and $X = 0$ of 330 K. We see from Figure (b) that an exit coolant temperature of $T_{a2} = 330$ K will give a coolant temperature at V_f of 300 K, which matches the actual T_{a0} .

We now have all the tools to solve reaction engineering problems involving heat effects in PFR for the cases of both constant and variable coolant temperatures.

Table 8-3 gives the algorithm for the design of PFRs and PBRs with heat exchange for case A: conversion as the reaction variable and case B: molar flow rates as the reaction variable. The procedure in case B must be used when multiple reactions are present.

TABLE 8-3. PFR/PBR ALGORITHM FOR HEAT EFFECTS

A. Conversion as the reaction variable



1. Mole Balance:

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} \quad (\text{T8-3.1})$$

2. Rate Law:

$$-r_A = k_1 \left(C_A C_B - \frac{C_C^2}{K_C} \right) \quad (\text{T8-3.2})$$

$$k = k_1(T_1) \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] \quad (\text{T8-3.3})$$

for $\Delta C_p \cong 0$.

$$K_C = K_{C2}(T_2) \exp \left[\frac{\Delta H_{R2}^0}{R} \left(\frac{1}{T_2} - \frac{1}{T} \right) \right] \quad (\text{T8-3.4})$$

3. Stoichiometry (gas phase, no ΔP):

$$C_A = C_{A0}(1-X) \frac{T_0}{T} \quad (\text{T8-3.5})$$

$$C_B = C_{A0}(\Theta_B - X) \frac{T_0}{T} \quad (\text{T8-3.6})$$

$$C_C = 2C_{A0}X \frac{T_0}{T} \quad (\text{T8-3.7})$$



Living Example Problem

TABLE 8-3. PFR/PBR ALGORITHM FOR HEAT EFFECTS (CONTINUED)

4. Energy Balances:

$$\text{Reactants: } \frac{dT}{dV} = \frac{Ua(T_a - T) + (-r_A)(-\Delta H_{RX})}{F_{A0}[C_{pA} + \Theta_B C_{pB} + X \Delta C_p]} \quad (\text{T8-3.8})$$

$$\text{Coolant: } \frac{dT_a}{dV} = \frac{Ua(T - T_a)}{\dot{m}_c C_{pc}} \quad (\text{T8-3.9})$$

B. Molar flow rates as the reaction variable

1. Mole Balances:

$$\frac{dF_A}{dV} = r_A \quad (\text{T8-3.10})$$

$$\frac{dF_B}{dV} = r_B \quad (\text{T8-3.11})$$

$$\frac{dF_C}{dV} = r_C \quad (\text{T8-3.12})$$

2. Rate Law:

$$-r_A = k_1 \left(C_A C_B - \frac{C_C^2}{K_C} \right) \quad (\text{T8-3.2})$$

$$k = k_1(T_1) \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] \quad (\text{T8-3.3})$$

$$K_C = K_{C2}(T_2) \exp \left[\frac{\Delta H_{RX}^{\circ}}{R} \left(\frac{1}{T_2} - \frac{1}{T} \right) \right] \quad (\text{T8-3.4})$$

3. Stoichiometry (gas phase, no ΔP):

$$r_B = r_A \quad (\text{T8-3.13})$$

$$r_C = 2r_A \quad (\text{T8-3.14})$$

$$C_A = C_{T0} \frac{F_A}{F_T} \frac{T_0}{T} \quad (\text{T8-3.15})$$

$$C_B = C_{T0} \frac{F_B}{F_T} \frac{T_0}{T} \quad (\text{T8-3.16})$$

$$C_C = C_{T0} \frac{F_C}{F_T} \frac{T_0}{T} \quad (\text{T8-3.17})$$

4. Energy Balance:

$$\text{Reactor: } \frac{dT}{dV} = \frac{Ua(T_a - T) + (-r_A)(-\Delta H_{RX})}{F_A C_{pA} + F_B C_{pB} + F_C C_{pC}} \quad (\text{T8-3.18})$$

If the coolant temperature, T_a , is not constant, then the energy balance on the coolant fluid gives

$$\text{Coolant: } \frac{dT_a}{dV} = \frac{Ua(T - T_a)}{\dot{m}_c C_{pc}} \quad (\text{T8-3.19})$$

where \dot{m}_c is the mass flow rate of the coolant (e.g., kg/s, and C_{pc} is the heat capacity of the coolant (e.g., kJ/kg·K). (See the CD-ROM for the examples in the Chapter 8 Summary Notes and the Polymath Library for the case when the ambient temperature is not constant.)



Following the Algorithm

Living Example Problem
Pb T-8.3Variable coolant
temperature

Summary Notes

TABLE 8-3. PFR/PBR ALGORITHM FOR HEAT EFFECTS (CONTINUED)

Case A: Conversion as the Independent Variable

$$k_1, E, R, C_{T0}, T_a, T_0, T_1, T_2, K_{C2}, \Theta_B, \Delta H_{Rx}, C_{pA}, C_{pB}, C_{pC}, Ua$$

with initial values T_0 and $X = 0$ at $V = 0$ and final values: $V_f = \text{---}$

Case B: Molar Flow Rates as the Independent Variables

Same as Case A except the initial values are F_{A0} and F_{B0} are specified instead of X at $V = 0$

Note: The equations in this table have been applied directly to a PBR (recall that we simply $W = \rho_b V$) using the values for E and ΔH_{Rx} given in Problem P8-2 (m) for the *Living Example Problem 8-T8-3* on the CD-ROM. Load this *Living Example Problem* from the CD-ROM as you vary the cooling rate, flow rate, entering temperature, and other parameters to get an intuitive of what happens in flow reactors with heat effects. After carrying out this exercise, go to the **WORKBOOK** in the Chapter 8 Summary Notes on the web/CD-ROM and answer the questions.

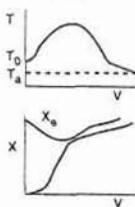
The following figures show representative profiles that would result from solving the above equations. The reader is encouraged to load the *Living Example Problem 8-T8-3* and vary a number of parameters as discussed in P8-2 (m). Be sure you can explain why these curves look the way they do.



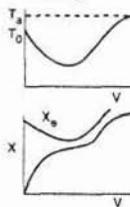
Summary Notes

Be sure you can explain why these curves look the way they do.

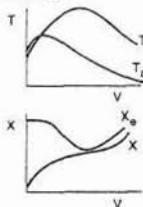
Constant T_a
reversible exothermic
reaction in a PFR with
heat exchange



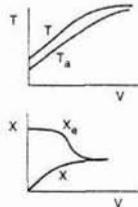
Constant T_a
endothermic reaction
in a PFR with
heat exchange



Variable T_a
exothermic
counter-current
exchange



Variable T_a
exothermic
co-current exchange

**Example 8-5 Production of Acetic Anhydride**

Jeffreys,⁴ in a treatment of the design of an acetic anhydride manufacturing facility states that one of the key steps is the vapor-phase cracking of acetone to ketene and methane:



He states further that this reaction is first-order with respect to acetone and that specific reaction rate can be expressed by

$$\ln k = 34.34 - \frac{34,222}{T} \quad (\text{E8-1})$$

where k is in reciprocal seconds and T is in kelvin. In this design it is desired to feed 7850 kg of acetone per hour to a tubular reactor. The reactor consists of a bank of 1000 1-inch schedule 40 tubes. We will consider three cases:

⁴ G. V. Jeffreys, *A Problem in Chemical Engineering Design: The Manufacture of Acetic Anhydride*, 2nd ed. (London: Institution of Chemical Engineers, 1964).

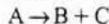
- Gas-phase endothermic reaction example
1. Adiabatic
 2. Heat exchange T_a is constant
 3. Heat exchange T_a is variable

- CASE 1** The reactor is operated *adiabatically*.
- CASE 2** The reactor is surrounded by a *heat exchanger* where the heat-transfer coefficient is $110 \text{ J/m}^2 \cdot \text{s} \cdot \text{K}$, and the temperature of the heating medium, T_w , is *constant* at 1150 K .
- CASE 3** The heat exchanger in Case 2 now has a variable heating medium temperature.

The inlet temperature and pressure are the same for both cases at 1035 K and 162 kPa (1.6 atm), respectively. Plot the conversion and temperature along the length of the reactor.

Solution

Let $A = \text{CH}_3\text{COCH}_3$, $B = \text{CH}_2\text{CO}$, and $C = \text{CH}_4$. Rewriting the reaction symbolically gives us



- 1. Mole Balance:**
$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} \quad (\text{E8-5.2})$$

- 2. Rate Law:**
$$-r_A = kC_A \quad (\text{E8-5.3})$$

- 3. Stoichiometry** (gas-phase reaction with no pressure drop):

$$C_A = \frac{C_{A0}(1-X)T_0}{(1+\varepsilon X)T} \quad (\text{E8-5.4})$$

$$\varepsilon = y_{A0}\delta = 1(1+1-1) = 1$$

- 4. Combining yields**

$$-r_A = \frac{kC_{A0}(1-X)T_0}{1+X} \quad (\text{E8-5.5})$$

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} = \frac{k}{v_0} \left(\frac{1-X}{1+X} \right) \frac{T_0}{T} \quad (\text{E8-5.6})$$

To solve this differential equation, it is first necessary to use the energy balance to determine T as a function of X .

- 5. Energy Balance:**

CASE 1. ADIABATIC OPERATION

For no work done on the system, $\dot{W}_s = 0$, and adiabatic operation, $\dot{Q} = 0$ (i.e., $U = 0$), Equation (8-36) becomes

$$\frac{dT}{dV} = \frac{(-r_A) \{ -[\Delta H_{R_x}^\circ(T_R) + \Delta C_p(T - T_R)] \}}{F_{A0}(\sum \Theta_i C_{P_i} + X \Delta C_p)} \quad (\text{E8-5.7})$$

Because only A enters,

$$\sum \Theta_i C_{P_i} = C_{P_A}$$

and Equation (E8-5.7) becomes

$$\frac{dT}{dV} = \frac{(-r_A) \{ -[\Delta H_{R_x}^\circ(T_R) + \Delta C_p(T - T_R)] \}}{F_{A0}(C_{P_A} + X \Delta C_p)} \quad (\text{E8-5.8})$$

$$\dot{Q} = 0$$

6. Calculation of Mole Balance Parameters on a Per Tube Basis:

$$F_{A0} = \frac{7,850 \text{ kg/h}}{58 \text{ g/mol}} \times \frac{1}{1,000 \text{ Tubes}} = 0.135 \text{ kmol/h} = 0.0376 \text{ mol/s}$$

$$C_{A0} = \frac{P_{A0}}{RT} = \frac{162 \text{ kPa}}{8.31 \frac{\text{kPa} \cdot \text{m}^3}{\text{kmol} \cdot \text{K}} (1035 \text{ K})} = 0.0188 \frac{\text{kmol}}{\text{m}^3} = 18.8 \text{ mol/m}^3$$

$$v_0 = \frac{F_{A0}}{C_{A0}} = 2.037 \text{ dm}^3/\text{s} \quad V = \frac{5 \text{ m}^3}{1000 \text{ tubes}} = 5 \text{ dm}^3$$

7. Calculation of Energy Balance Parameters:

a. $\Delta H_{R_x}^\circ(T_R)$: At 298 K, the standard heats of formation are

$$H_{R_x}^\circ(T_R)_{\text{acetone}} = -216.67 \text{ kJ/mol}$$

$$H_{R_x}^\circ(T_R)_{\text{ketene}} = -61.09 \text{ kJ/mol}$$

$$H_{R_x}^\circ(T_R)_{\text{methane}} = -74.81 \text{ kJ/mol}$$

$$\begin{aligned} \Delta H_{R_x}^\circ(T_R) &= H_B^\circ(T_R) + H_C^\circ(T_R) - H_A^\circ(T_R) \\ &= (-61.09) + (-74.81) - (-216.67) \text{ kJ/mol} \\ &= 80.77 \text{ kJ/mol} \end{aligned}$$

b. ΔC_p : The mean heat capacities are:

$$\text{CH}_3\text{COCH}_3: C_{p_A} = 163 \text{ J/mol} \cdot \text{K}$$

$$\text{CH}_2\text{CO}: C_{p_B} = 83 \text{ J/mol} \cdot \text{K}$$

$$\text{CH}_4: C_{p_C} = 71 \text{ J/mol} \cdot \text{K}$$

$$\begin{aligned} \Delta C_p &= C_{p_B} + C_{p_C} - C_{p_A} = (83 + 71 - 163) \text{ J/mol} \cdot \text{K} \\ \Delta C_p &= -9 \text{ J/mol} \cdot \text{K} \end{aligned}$$

See Table E8-5.1 for a summary of the calculations and Table E8-5.2 and Figure E8-5.1 for the Polymath program and its graphical output. For adiabatic operation, it doesn't matter whether or not we feed everything to one tube with $V = 5 \text{ m}^3$ or distribute the flow to the 1000 tubes each with $V = 5 \text{ dm}^3$. The temperature and conversion profiles are identical because there is no heat exchange.

TABLE E8-5.1. SUMMARY ADIABATIC OPERATION

Adiabatic PFR

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} \quad (E8-5.2)$$

$$r_A = \frac{kC_{A0}(1-X)}{(1+X)} \frac{T_0}{T} \quad (E8-5.5)$$

$$\frac{dT}{dV} = \frac{(-r_A)(\Delta H_{R_x})}{F_{A0}(C_{p_A} + X \Delta C_p)} \quad (E8-5.8)$$

$$k = 8.2 \times 10^{14} \exp\left(\frac{-34,222}{T}\right) \text{ s}^{-1} = 3.58 \exp\left[34,222\left(\frac{1}{T_0} - \frac{1}{T}\right)\right] \text{ s}^{-1} \quad (E8-5.9)$$

$$\Delta H_{R_x} = \Delta H_{R_x}(T_R) + \Delta C_p(T - T_R) \quad (E8-5.10)$$

TABLE E8-5.1. SUMMARY ADIABATIC OPERATION (CONTINUED)

Parameter Values		
$\Delta C_p = -9 \text{ J/mol} \cdot \text{K}$	$\Delta H_{\text{Rx}}^{\circ}(T_R) = 80.77 \text{ J/mol}$	$T_0 = 1035 \text{ K}$
$C_{pA} = 163 \text{ J/mol/A/K}$	$C_{A0} = 18.8 \text{ mol/m}^3$	$T_R = 298 \text{ K}$
$V_f = 5 \text{ dm}^3$	$F_{A0} = 0.376 \text{ mol/s}$	

TABLE E8-5.2. POLYMATH PROGRAM ADIABATIC OPERATION

ODE Report (RKF45)

Differential equations as entered by the user

- [1] $d(X)/d(V) = -r_A/F_{A0}$
 [2] $d(T)/d(V) = -r_A \cdot (-\Delta H) / (F_{A0} \cdot (C_{pa} + X \cdot \Delta C_p))$

Explicit equations as entered by the user

- [1] $F_{A0} = .0376$
 [2] $C_{pa} = 163$
 [3] $\Delta C_p = -9$
 [4] $C_{A0} = 18.8$
 [5] $T_0 = 1035$
 [6] $\Delta H = 80770 + \Delta C_p \cdot (T - 298)$
 [7] $r_A = -C_{A0} \cdot 3.58 \cdot \exp(34222 \cdot (1/T_0 - 1/T)) \cdot (1 - X) \cdot (T_0/T) / (1 + X)$

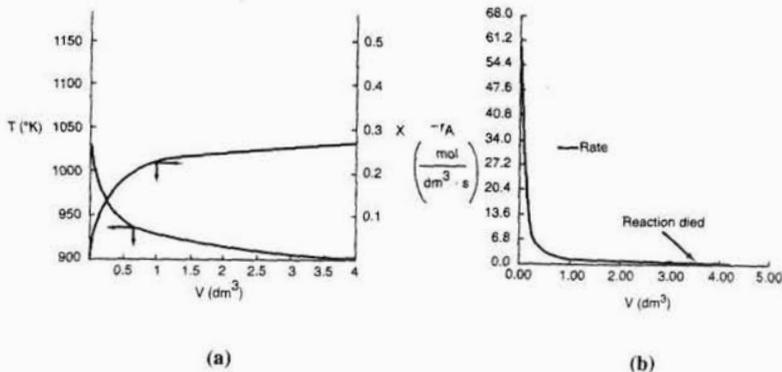


Figure E8-5.1 Conversion and temperature (a) and reaction rate (b) profiles.

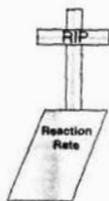
As temperature drops, so does k and hence the rate, $-r_A$, drops to an insignificant value.

Note that for this adiabatic endothermic reaction, the reaction virtually *dies out* after 3.5 m^3 , owing to the large drop in temperature, and very little conversion is achieved beyond this point. One way to increase the conversion would be to add a



Living Example Problem

Adiabatic endothermic reaction in a PFR



path of a reaction

diluent such as nitrogen, which could supply the sensible heat for this endothermic reaction. However, if too much diluent is added, the concentration and rate will be quite low. On the other hand, if too little diluent is added, the temperature will rise and virtually extinguish the reaction. How much diluent to add is left as an exercise [see Problem P8-2(e)].

A bank of 1000 1-in. schedule 40 tubes 1.79 m in length correspond to a volume of 1.0 m^3 and gives 20% conversion. Ketene is unstable and tends to explode, which is a good reason to keep the conversion low. However, the pipe material and schedule size should be checked to learn if they are suitable for these temperatures and pressures.

CASE 2. HEAT EXCHANGE WITH CONSTANT HEATING MEDIUM TEMPERATURE

Let's now see what happens as we add heat to the reacting mixture. See Figure E8-5.2.

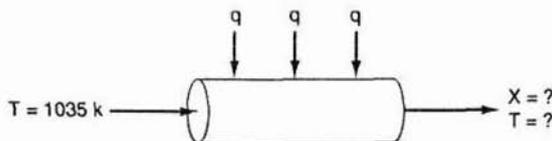


Figure E8-5.2 PFR with heat exchange.

1. Mole Balance:

$$\text{(Step 1)} \quad \frac{dX}{dV} = \frac{-r_A}{F_{A0}} \quad (\text{E8-5.1})$$

Using the algorithm: (Step 2) the **rate law** (E8-5.3) and (Step 3) **stoichiometry** (E8-5.4) for the adiabatic case discussed previously in Case 1, we (Step 4) combine to obtain the reaction rate as

$$\text{(Step 4)} \quad -r_A = kC_{A0} \left(\frac{1-X}{1+X} \right) \frac{T_0}{T} \quad (\text{E8-5.2})$$

5. Energy Balance:

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (-r_A)(-\Delta H_{R_x}(T))}{F_{A0}(\sum \Theta_i C_{p_i} + X \Delta C_p)} \quad (\text{E8-5.3})$$

For the acetone reaction system,

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (r_A)(\Delta H_{R_x}(T))}{F_{A0}(C_{p_A} + X \Delta C_p)} \quad (\text{E8-5.4})$$

PFR with heat exchange

6. Parameter Evaluation:

a. *Mole balance.* On a per tube basis, $v_0 = 0.002 \text{ m}^3/\text{s}$. The concentration of acetone is 18.8 mol/m^3 , so the entering molar flow rate is

$$F_{A0} = C_{A0}v_0 = \left(18.8 \frac{\text{mol}}{\text{m}^3} \right) \left(2 \times 10^{-3} \frac{\text{m}^3}{\text{s}} \right) = 0.0376 \frac{\text{mol}}{\text{s}}$$

The value of k at 1035 K is 3.58 s^{-1} ; consequently, we have

$$k(T) = 3.58 \exp \left[34,222 \left(\frac{1}{1035} - \frac{1}{T} \right) \right] \text{ s}^{-1} \quad (\text{E8-5.11})$$

- b. *Energy balance.* From the adiabatic case in Case I, we already have $\Delta C_p \cdot C_{p_A}$. The heat-transfer area per unit volume of pipe is

$$a = \frac{\pi DL}{(\pi D^2/4)L} = \frac{4}{D} = \frac{4}{0.0266 \text{ m}} = 150 \text{ m}^{-1}$$

$$U = 110 \text{ J/m}^2 \cdot \text{s} \cdot \text{K}$$

Combining the overall heat-transfer coefficient with the area yields

$$Ua = 16,500 \text{ J/m}^3 \cdot \text{s} \cdot \text{K}$$

We now use Equations (E8-5.1) through (E8-5.6), and Equations (E8-5.10) and (E8-5.11) along with Equation E8-5.12 in Table E8-5.3 in the Polymath program (Table E8-5.4), to determine the conversion and temperature profiles shown in Figure E8-5.3.

$$V_f = 0.001 \text{ m}^3 = 1 \text{ dm}^3$$

TABLE E8-5.3. SUMMARY WITH CONSTANT T_a HEAT EXCHANGE

We now apply Equation (8-36) to this example to arrive at Equation (E8-5.12), which we then use to replace Equation (E8-5.8) in Summary Table E8-5.1.

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (r_A)[\Delta H_{Rx}]}{F_{A0}(C_{p_A} + X \Delta C_p)} \quad (\text{E8-5.12})$$

with

$$Ua = 16,500 \text{ J/m}^3/\text{s/K}$$

$$T_a = 1150 \text{ K} \quad (\text{E8-5.13})$$

Per tube basis

$$v_0 = 0.002 \text{ m}^3/\text{s}$$

$$F_{A0} = 0.0376 \text{ mol/s}$$

$$V_f = 0.001 \text{ m}^3 = 1 \text{ dm}^3$$

Everything else is the same as shown in Table E8-5.1.

One notes that the reactor temperature goes through a minimum along the length of the reactor. At the front of the reactor, the reaction takes place very rapidly, drawing energy from the sensible heat of the gas causing the gas temperature to drop because the heat exchanger cannot supply energy at an equal or greater rate. This drop in temperature, coupled with the consumption of reactants, slows the reaction rate as we move down the reactor. Because of this slower reaction rate, the heat exchanger

supplies energy at a rate greater than reaction draws energy from the gases and as a result the temperature increases.

TABLE E8-5.4. POLYMATH PROGRAM FOR PFR WITH HEAT EXCHANGE

POLYMATH Results

Example 8-5 Production of Acetic Anhydride with Heat Exchange (Constant T_a) 08-16-2004. Rev5.1.232

ODE Report (RK45)

Differential equations as entered by the user

- [1] $d(X)/d(V) = -r_a/F_{A0}$
 [2] $d(T)/d(V) = (U_a(T_a - T) + r_a \Delta H) / (F_{A0}(C_{pa} + X \Delta C_p))$

Explicit equations as entered by the user

- [1] $F_{A0} = .0376$
 [2] $C_{pa} = 163$
 [3] $\Delta C_p = -9$
 [4] $C_{A0} = 18.8$
 [5] $T_0 = 1035$
 [6] $\Delta H = 80770 + \Delta C_p(T - 298)$
 [7] $r_a = -C_{A0} \cdot 3.58 \cdot \exp(34222 \cdot (1/T_0 - 1/T)) \cdot (1 - X) \cdot (T_0/T) / (1 + X)$
 [8] $U_a = 16500$
 [9] $T_a = 1150$



Living Example Problem

PFR with
heat exchange
constant coolant
temperature T_a

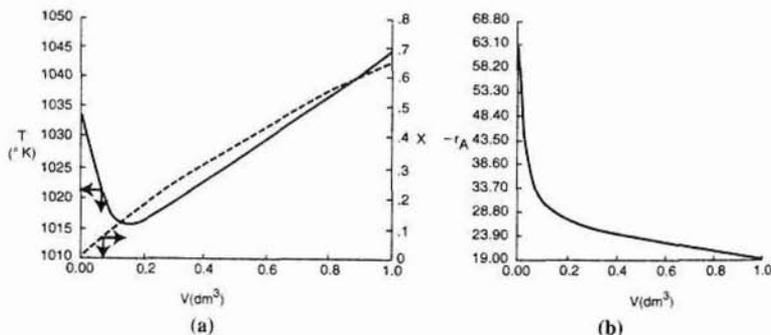


Figure E8-5.3 Temperature and conversion profiles in PFR. Temperature and conversion (a) and reaction rate (b) profiles in a PFR with constant heating medium temperature, T_a .

CASE 3. HEAT EXCHANGE WITH VARIABLE HEATING MEDIUM TEMPERATURE

Air will also be used as a heating stream in a co-current direction entering at a temperature of 1250 K and at molar rate of (0.11 mol/s). The heat capacity of the air is 34.5 J/mol · K.

Solution

For co-current flow

$$\frac{dT_a}{dV} = \frac{U_a(T - T_a)}{\dot{m}_c C_{p_c}} \quad (\text{E8-5.7})$$

$$\dot{m}_c C_{p_c} = \left(0.11 \frac{\text{mol}}{\text{s}}\right) \left(34.5 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right) = 3.83 \text{ J/s} \cdot \text{K}$$