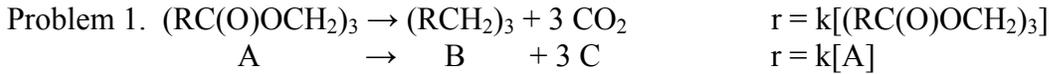


Problem Set 4



Given:

$T_0 = 150 \text{ C}$   $k(T_0) = k_0 = 5 \cdot 10^{-3} \text{ (min}^{-1}\text{)}$   $E_a = 85 \text{ kJ/mol}$   
 $F_{A,0} = 2.5 \text{ mol/min}$   $y_{A,0} = 1$   $T = 227 \text{ C}$   
 $X = 0.9$   $P = 10 \text{ atm}$

First, find k at the reaction temperature using Eq 3-21 from Fogler:

$$k(T) = k(T_0) \cdot e^{\frac{E}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right)} = \left( 5 \cdot 10^{-3} \frac{1}{\text{min}} \right) \cdot e^{\frac{85 \text{ kJ/mol}}{8.314 \cdot 10^{-3} \text{ kJ/(mol}\cdot\text{K)}} \left( \frac{1}{423.15 \text{ K}} - \frac{1}{500.15 \text{ K}} \right)} = 0.206255 \text{ min}^{-1}$$

Next, make a stoichiometric table for the flow system (see Table 3-4 in Fogler). This table applies to both a PFR and CSTR reactor.

Species	Feed Rate to Reactor (mol/min)	Change within Reactor (mol/min)	Effluent Rate from Reactor (mol/min)
A	$F_{A0}$	$-F_{A0}X$	$F_A = F_{A0}(1 - X)$
B	0	$F_{A0}X$	$F_B = F_{A0}X$
C	0	$3F_{A0}X$	$F_C = 3F_{A0}X$
Total	$F_{A0}$		$F_T = F_{A0}(1 + 3X)$

Since this is a gas-phase reaction, with a change in the total number of moles, the volumetric flow rate ( $v$ ) will not be constant. Simplify Eq 3-41 in Fogler for the steady state (constant P and T) ideal gas case to:

$$v = v_0 \left( \frac{F_T}{F_{T0}} \right) = v_0 \left( \frac{F_{A0}(1 + 3X)}{F_{A0}} \right) = v_0(1 + 3X) = \frac{F_{A0}RT}{P}(1 + 3X)$$

a) CSTR

The design equation for CSTR volume in terms of conversion is (Eq 2-13 in Fogler):

$$V_{CSTR,a} = \frac{F_{A0}X}{(-r_A)_{exit}} = \frac{F_{A0}X}{k[A]} = \frac{F_{A0}X}{k \left( \frac{F_A}{v} \right)} = \frac{v_0(1 + 3X)F_{A0}X}{kF_{A0}(1 - X)} = \frac{F_{A0}RT(1 + 3X)X}{Pk(1 - X)}$$

Plugging in numbers:

$$V_{CSTR,a} = \frac{\left( 2.5 \frac{\text{mol}}{\text{min}} \right) \left( 0.082 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \right) (500.15 \text{ K})(1 + 3(0.9))0.9}{(10 \text{ atm}) \left( 0.206255 \frac{1}{\text{min}} \right) (1 - 0.9)} = 1655.36 \text{ L} \approx 1.7 \cdot 10^3 \text{ L}$$

b) PFR

Neglect pressure drop, so  $v$  equation is the same as above. The design equation for a PFR in terms of conversion is (Eq 2-16 in Fogler):

$$V_{PFR,b} = F_{A0} \int_0^X \frac{dX}{-r_A} = F_{A0} \int_0^X \frac{dX}{k[A]} = F_{A0} \int_0^X \frac{dX}{k \frac{F_A}{v}} = F_{A0} \int_0^X \frac{F_{A0} RT(1+3X)}{PkF_{A0}(1-X)} dX = \frac{F_{A0} RT}{Pk} \int_0^X \frac{(1+3X)}{(1-X)} dX$$

From integration by parts (or an integral table):

$$\int_{x_1}^{x_2} \frac{(1+mx)}{(1-x)} dx = (1+m) \ln \left[ \frac{1-x_1}{1-x_2} \right] + m(x_1 - x_2)$$

When  $x_1 = 0$ , this simplifies to:  $\int_0^x \frac{(1+mx)}{(1-x)} dx = (1+m) \ln \left[ \frac{1}{1-x_2} \right] - mx_2$

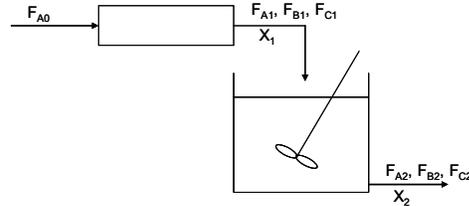
Integrating and plugging in numbers gives:

$$V_{PFR,b} = \frac{F_{A0} RT}{Pk} \left[ (1+3) \ln \left( \frac{1}{1-X} \right) - 3X \right] = \frac{\left( 2.5 \frac{\text{mol}}{\text{min}} \right) \left( 0.082 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (500.15 \text{K})}{(10 \text{atm}) \left( 0.206255 \frac{1}{\text{min}} \right)} \left[ 4 \ln \left( \frac{1}{1-0.9} \right) - 3(0.9) \right]$$

$$= 323.63 \text{L} \approx 3.2 \cdot 10^2 \text{L}$$

c) Now find X in a CSTR/PFR combination for a given V.

First: PFR then CSTR, where the volume of each is  $\frac{1}{2}$  the volume calculated in parts a and b.



PFR equation will be the same as derived in part b, but with  $V = \frac{1}{2} V_{PFR,b}$  and  $X = X_1$ :

$$\frac{1}{2} V_{PFR,b} = \frac{F_{A0} RT}{Pk} \left[ (1+3) \ln \left( \frac{1}{1-X_1} \right) - 3X_1 \right] \Rightarrow \frac{V_{PFR,b} Pk}{2F_{A0} RT} - (1+3) \ln \left( \frac{1}{1-X_1} \right) + 3X_1 = 0$$

There are many methods that can be used to find the roots of the above equation (solver function in Excel, fsolve in Matlab, etc). For example, using fsolve in Matlab:

```
function [Xpfr]=partc;

X0=0.1; %initial guess for X_pfr

[Xpfr] = fsolve(@pfr_eqn,X0);

return

function F = pfr_eqn(X)

k = 0.206255; %1/min
T = 227+273.15; %K
FA0 = 2.5; %mol/min
P = 10; %atm
R = 0.082; %L*atm/mol/K
V_pfr_b = 323.63; %L, from part b calculation

F = V_pfr_b*P*k/(2*FA0*R*T) - (1+3)*log(1/(1-X)) + 3*X;

return
```

Can also solve for  $X_1$  by hand using an iterative method. For example, using the Newton-Raphson Method:

$$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)} \quad \text{where } f'(x_n) \text{ is the derivative of } f, \text{ evaluated at } x = x_n.$$

Keep iterating until  $x_{n+1} \approx x_n$ .

Regardless of the method used, should find that  $X_1 \approx 0.75$

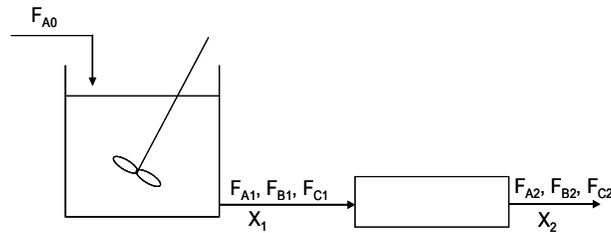
A mole balance on the CSTR gives:

$$0 = F_{A1} - F_{A2} + r_A \left( \frac{V_{CSTR,a}}{2} \right) = F_{A0}(1 - X_1) - F_{A0}(1 - X_2) - \frac{kV_{CSTR,a}}{2} [A] = F_{A0}(X_2 - X_1) - \frac{kV_{CSTR,a}}{2} \left( \frac{F_{A2}}{\nu} \right)$$

$$0 = F_{A0}(X_2 - X_1) - \frac{kV_{CSTR,a}}{2} \left( \frac{PF_{A0}(1 - X_2)}{F_{A0}RT(1 + 3X_2)} \right) = F_{A0}(X_2 - X_1) - \frac{kV_{CSTR,a}P}{2RT} \frac{(1 - X_2)}{(1 + 3X_2)}$$

Again, solve the above equation either by hand or with a program to find that  $X_2 \approx 0.95$

Now: CSTR followed by PFR, where the volume of each is  $\frac{1}{2}$  the volume calculated in parts a and b.



CSTR equation will be the same as derived in part a, but with  $V = \frac{1}{2} V_{CSTR,a}$  and  $X = X_1$ :

$$\frac{1}{2} V_{CSTR,a} = \frac{F_{A0}RT(1 + 3X_1)X_1}{Pk(1 - X_1)} \Rightarrow \frac{1}{2} V_{CSTR,a} - \frac{F_{A0}RT(1 + 3X_1)X_1}{Pk(1 - X_1)} = 0$$

Plugging in numbers and solving gives  $X_1 \approx 0.83$

A mole balance on the PFR gives (see pg 15-16 in Fogler):

$$0 = F_A|_V - F_A|_{V+\Delta V} + r_A \Delta V$$

Rearrange, divide by  $\Delta V$  and take the limit as  $\Delta V$  approaches zero to get:

$$\frac{dF_A}{dV} = r_A \Rightarrow dV = \frac{dF_A}{r_A} = \frac{d[F_{A0}(1 - X)]}{r_A} = \frac{-F_{A0}dX}{r_A} = F_{A0} \frac{dX}{-r_A}$$

Integrate with the limits  $V = 0$  when  $X = X_{A1}$  and  $V = \frac{1}{2} V_{PFR,b}$  when  $X = X_2$  to get:

$$\frac{1}{2} V_{PFR,b} = F_{A0} \int_{X_1}^{X_2} \frac{dX}{-r_A} = F_{A0} \int_{X_1}^{X_2} \frac{dX}{k[A]} = F_{A0} \int_{X_1}^{X_2} \frac{dX}{k \frac{F_A}{\nu}} = F_{A0} \int_{X_1}^{X_2} \frac{F_{A0}RT(1 + 3X)}{PkF_{A0}(1 - X)} dX = \frac{F_{A0}RT}{Pk} \int_{X_1}^{X_2} \frac{(1 + 3X)}{(1 - X)} dX$$

From integration by parts (or an integral table):

$$\int_{x_1}^{x_2} \frac{(1 + mx)}{(1 - x)} dx = (1 + m) \ln \left[ \frac{1 - x_1}{1 - x_2} \right] + m(x_1 - x_2) \Rightarrow \frac{1}{2} V_{PFR,b} = \frac{F_{A0}RT}{Pk} \left[ (1 + 3) \ln \left[ \frac{1 - X_1}{1 - X_2} \right] + 3(X_1 - X_2) \right]$$

$$\frac{F_{A0}RT}{Pk} \left[ (1 + 3) \ln \left[ \frac{1 - X_1}{1 - X_2} \right] + 3(X_1 - X_2) \right] - \frac{V_{PFR,b}}{2} = 0$$

Plugging in numbers and solving gives  $X_2 \approx 0.93$

Now, consider an isothermal batch reactor system with  $P_0 = 2.7 \text{ atm}$ . Make a stoichiometric table for the batch system (see table 3-3 in Fogler)

Species	Initially (mol)	Change (mol)	Remaining (mol)
A	$N_{A0}$	$-N_{A0}X$	$N_A = N_{A0}(1 - X)$
B	0	$N_{A0}X$	$N_B = N_{A0}X$
C	0	$3N_{A0}X$	$N_C = 3N_{A0}X$
Total	$N_{A0}$		$N_T = N_{A0}(1 + 3X)$

d) The volume of the batch reactor is fixed, so the change in moles as the reaction proceeds will cause an increase in P. For an isothermal, constant volume batch reactor (Eq 3-38 in Fogler, rearranged):

$$P = P_0(1 + 3X) = 2.7 \text{ atm}(1 + 3(0.9)) = 9.99 \text{ atm}$$

e) Want to process 2.5 mol/min of cooking oil in the batch reactor (assume that the down time between batches is negligible).

$$\frac{N_{A0}}{t_{\text{react}}} = 2.5 \frac{\text{mol}}{\text{min}} \Rightarrow N_{A0} = \left(2.5 \frac{\text{mol}}{\text{min}}\right) t_{\text{react}}$$

$$\text{Assuming ideal gas, } V_{\text{batch}} = \frac{N_{A0}RT}{P_0} = \frac{\left(2.5 \frac{\text{mol}}{\text{min}}\right) t_{\text{react}} RT}{P_0}$$

Find  $t_{\text{react}}$  from design equation for a constant volume batch reactor (Eq 2-6 in Fogler):

$$\frac{dX}{dt} = \frac{-r_A V}{N_{A0}} = \frac{k[A]V}{N_{A0}} = \frac{k \frac{N_A V}{V}}{N_{A0}} = \frac{k N_{A0}(1-X)}{N_{A0}} = k(1-X)$$

Rearrange and integrate:

$$\int_0^X \frac{dX}{(1-X)} = k \int_0^t dt \Rightarrow \ln\left(\frac{1}{1-X}\right) = kt \Rightarrow t_{\text{react}} = \frac{1}{k} \ln\left(\frac{1}{1-X}\right)$$

Plug in numbers to get:

$$V_{\text{batch}} = \frac{\left(2.5 \frac{\text{mol}}{\text{min}}\right) \ln\left(\frac{1}{1-X}\right) RT}{k P_0} = \frac{\left(2.5 \frac{\text{mol}}{\text{min}}\right) \ln\left(\frac{1}{1-(0.9)}\right) \left(0.082 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) (500.15 \text{K})}{(0.206255 \text{ min}^{-1})(2.7 \text{ atm})} = 423.94 \text{ L} \approx \boxed{4.2 \cdot 10^2 \text{ L}}$$

e) Since the characteristic reaction time is on the order of minutes, a flow reactor is recommended for this process. If minimizing volume is the most important design criteria, a single PFR is the best choice. If maximizing conversion is the most important design criteria, the half-size PFR followed by a half-size CSTR is the best choice.