Problem Set 4

Problem 1. \((RC(O)OCH_2)_3 \rightarrow (RCH_2)_3 + 3\ CO_2\)

\[ r = k[(RC(O)OCH_2)_3] \]

\[ r = k[A] \]

Given:

\[ T_0 = 150 \text{ C} \quad k(T_0) = k_0 = 5 \times 10^{-3} \text{ (min}^{-1}) \]

\[ \text{Ea} = 85 \text{ kJ/mol} \]

\[ F_{A,0} = 2.5 \text{ mol/min} \quad y_{A,0} = 1 \quad T = 227 \text{ C} \]

\[ X = 0.9 \quad P = 10 \text{ atm} \]

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

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

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.

<table>
<thead>
<tr>
<th>Species</th>
<th>Feed Rate to Reactor (mol/min)</th>
<th>Change within Reactor (mol/min)</th>
<th>Effluent Rate from Reactor (mol/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>( F_{A0} )</td>
<td>(-F_{A0}X)</td>
<td>( F_A = F_{A0}(1 - X) )</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
<td>( F_{A0}X )</td>
<td>( F_B = F_{A0}X )</td>
</tr>
<tr>
<td>C</td>
<td>0</td>
<td>( 3F_{A0}X )</td>
<td>( F_C = 3F_{A0}X )</td>
</tr>
<tr>
<td>Total</td>
<td>( F_{A0} )</td>
<td></td>
<td>( F_T = F_{A0}(1 + 3X) )</td>
</tr>
</tbody>
</table>

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

\[
\nu = \nu_0 \left( \frac{F_T}{F_{T0}} \right) = \nu_0 \left( \frac{F_{A0}(1 + 3X)}{F_{A0}} \right) = \nu_0(1 + 3X) = \frac{F_{A0}RT}{P} \left(1 + 3X\right)
\]

a) CSTR

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

\[
V_{\text{CSTR},A} = \frac{F_{A0}X}{\left(-r_A\right)_{\text{exit}}} = \frac{F_{A0}X}{k[A]} = \frac{F_{A0}X}{kF_{A0}(1 - X)} = \nu_0 \left(1 + 3X\right) \frac{F_{A0}X}{PK(1 - X)} = \frac{F_{A0}RT(1 + 3X)X}{PK(1 - X)}
\]

Plugging in numbers:

\[
V_{\text{CSTR},A} = \left( \frac{2.5 \text{ mol}}{\text{min}} \right) \left( \frac{0.82 \text{ L \cdot atm}}{\text{mol \cdot K}} \right) \left( \frac{500.15 \text{ K}}{1 + 3(0.9) \times 0.9} \right) = 1655.36L \approx 1.7 \times 10^3 L
\]

Cite as: William Green, Jr., and K. Dane Wittrup, course materials for 10.37 Chemical and Biological Reaction Engineering, Spring 2007. MIT OpenCourseWare (http://ocw.mit.edu), Massachusetts Institute of Technology. Downloaded on [DD Month YYYY].
b) PFR
Neglect pressure drop, so $\nu$ equation is the same as above. The design equation for a PFR in terms of conversion is (Eq 2-16 in Fogler):

$$V_{pfr, b} = F_{A_0} \int_0^X \frac{dX}{r_A} = F_{A_0} \int_0^X \frac{dX}{k[A]} = F_{A_0} \int_0^X \frac{dX}{F_A} = F_{A_0} \int_0^X \frac{F_{A_0}RT(1+3X)}{PK} \frac{dX}{F_{A_0}(1-X)}$$

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:

$$ \int_0^{x_2} \frac{(1+mx)}{(1-x)} dx = (1+m) ln \left[ \frac{1}{1-x_2} \right] - mx_2$$

Integrating and plugging in numbers gives:

$$V_{pfr, b} = \frac{F_{A_0}RT}{PK} \left[ (1+3) ln \left( \frac{1}{1-X} \right) - 3X \right] = \frac{2.5 \text{ mol/min}}{(10 \text{ atm})} \left( 0.082 \text{ L-atm/mol} \cdot K \right) (500.15K) \left[ 4 \ln \left( \frac{1}{1-0.9} \right) - 3(0.9) \right]$$

$$= 323.63 L \approx 3.2 \cdot 10^2 L$$
c) Now find X in a CSTR/PFR combination for a given V.

First: PFR then CSTR, where the volume of each is ½ 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 \( X = X_1 \):

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

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:

```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:

\[
x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)}
\]

where \( f'(x_n) \) is the derivative of \( f \), 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:
\[
0 = F_{A1} - F_{A2} + r_A \left( \frac{V_{\text{CSTR,a}}}{2} \right) = F_{A0}(1 - X_1) - F_{A0}(1 - X_2) = \frac{kV_{\text{CSTR,a}}}{2} [A] = F_{A0}(X_2 - X_1) = \frac{kV_{\text{CSTR,a}}}{2} \left( \frac{F_{A2}}{V} \right)
\]
\[
0 = F_{A0}(X_2 - X_1) - \frac{kV_{\text{CSTR,a}}}{2} \left( \frac{PF_{A0}(1 - X_2)}{F_{A0}RT(1 + 3X_2)} \right) = F_{A0}(X_2 - X_1) - \frac{kV_{\text{CSTR,a}}P}{2RT} (1 - X_2)
\]
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 \(V = \frac{1}{2} V_{\text{CSTR,a}}\) and \(X = X_1:\)
\[
\frac{1}{2} V_{\text{CSTR,a}} = \frac{F_{A0}RT(1 + 3X_1)X_1}{Pk(1 - X_1)} \quad \Rightarrow \quad \frac{1}{2} V_{\text{CSTR,a}} - \frac{F_{A0}RT(1 + 3X_1)X_1}{Pk(1 - X_1)} = 0
\]
Plugging in numbers and solving gives \(X_1 \approx 0.83\)

A mole balance on the PFR gives (see pg 15-16 in Fogler):
\[
0 = F_{A}\left[1 - F_{A} + \frac{r_A}{dV} \Delta V\right]
\]
Rearrange, divide by \(\Delta V\) and take the limit as \(\Delta V\) approaches zero to get:
\[
\frac{dF_A}{dV} = r_A \quad \Rightarrow \quad dV = \frac{dF_A}{r_A} = d\left[F_{A0}(1 - X)\right] = -F_{A0}dX = F_{A0} \frac{dX}{r_A}
\]
Integrate with the limits \(V = 0\) when \(X = X_{A1}\) and \(V = \frac{1}{2} V_{\text{PFR,b}}\) when \(X = X_2\) to get:
\[
\frac{1}{2} V_{\text{PFR,b}} = F_{A0} \int_{x_1}^{x_2} \frac{dX}{r_A} = F_{A0} \int_{x_1}^{x_2} \frac{dX}{k[A]} = F_{A0} \int_{x_1}^{x_2} \frac{dX}{F_{A0} \frac{F}{k}} = F_{A0} \int_{x_1}^{x_2} \frac{F_{A0}RT(1 + 3X)}{PkF_{A0}(1 - X)} dX = \frac{F_{A0}RT}{pk} \int_{x_1}^{x_2} \frac{(1 + 3X)}{(1 - X)} dX
\]
From integration by parts (or an integral table):
\[
\int_{x_1}^{x_2} \frac{(1 + mX)}{(1 - X)} dX = (1 + m)\ln\left(\frac{1 - X_1}{1 - X_2}\right) + m(X_1 - X_2) \quad \Rightarrow \quad \frac{1}{2} V_{\text{PFR,b}} = \frac{F_{A0}RT}{pk} \left[(1 + 3)\ln\left(\frac{1 - X_1}{1 - X_2}\right) + 3(X_1 - X_2)\right]
\]
\[
\frac{F_{A0}RT}{pk} \left[(1 + 3)\ln\left(\frac{1 - X_1}{1 - X_2}\right) + 3(X_1 - X_2)\right] - \frac{V_{\text{PFR,b}}}{2} = 0
\]
Plugging in numbers and solving gives \(X_2 \approx 0.93\)
Now, consider an isothermal batch reactor system with $P_0 = 2.7$ atm. Make a stoichiometric table for the batch system (see table 3-3 in Fogler)

<table>
<thead>
<tr>
<th>Species</th>
<th>Initially (mol)</th>
<th>Change (mol)</th>
<th>Remaining (mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$N_{A0}$</td>
<td>$-N_{A0}X$</td>
<td>$N_A = N_{A0}(1 - X)$</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
<td>$N_{A0}X$</td>
<td>$N_B = N_{A0}X$</td>
</tr>
<tr>
<td>C</td>
<td>0</td>
<td>$3N_{A0}X$</td>
<td>$N_C = 3N_{A0}X$</td>
</tr>
<tr>
<td>Total</td>
<td>$N_{A0}$</td>
<td></td>
<td>$N_T = N_{A0}(1 + 3X)$</td>
</tr>
</tbody>
</table>

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):

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

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

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

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

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

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

Rearrange and integrate:

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

Plug in numbers to get:

$$V_{batch} = \frac{\left(2.5\ \frac{mol}{min}\right) \ln\left(\frac{1}{1 - X}\right) RT}{kP_0} = \frac{\left(2.5\ \frac{mol}{min}\right) \ln\left(\frac{1}{1 - (0.9)}\right) \left(0.082\ \frac{L\cdot atm}{mol\cdot K}\right)\{500.15K\}}{\left(0.206255\ min^{-1}\right)\{2.7\ atm\}} = 423.94L \approx 4.2\cdot 10^2L$$

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.