Chemical Reaction Engineering (CRE) is the field that studies the rates and mechanisms of chemical reactions and the design of the reactors in which they take place.
Lecture 8 – Tuesday 2/5/2013

• Block 1: Mole Balances
• Block 2: Rate Laws
• Block 3: Stoichiometry
• Block 4: Combine

• Pressure Drop
  • Liquid Phase Reactions
  • Gas Phase Reactions

• Engineering Analysis of Pressure Drop
Pressure Drop in PBRs

Concentration Flow System: \[ C_A = \frac{F_A}{\nu} \]

Gas Phase Flow System: \[ \nu = \nu_0(1 + \varepsilon X) \frac{T}{T_0} \frac{P_0}{P} \]

\[ C_A = \frac{F_A}{\nu} = \frac{F_{A0}(1 - X)}{\nu_0(1 + \varepsilon X)} \frac{T}{T_0} \frac{P_0}{P} = \frac{C_{A0}(1 - X)}{\Theta_B - \frac{b}{a}} \frac{T}{T_0} \frac{P_0}{P} \]

\[ C_B = \frac{F_B}{\nu} = \frac{F_{A0} \left( \Theta_B - \frac{b}{a} X \right)}{\nu_0(1 + \varepsilon X)} \frac{T}{T_0} \frac{P_0}{P} = \frac{C_{A0} \left( \Theta_B - \frac{b}{a} X \right)}{\Theta_B - \frac{b}{a}} \frac{T}{T_0} \frac{P_0}{P} \]
Pressure Drop in PBRs

Note: Pressure Drop does NOT affect liquid phase reactions

Sample Question:
Analyze the following second order gas phase reaction that occurs isothermally in a PBR:

\[ \text{A} \rightarrow \text{B} \]

Mole Balances
Must use the differential form of the mole balance to separate variables:

\[ F_{A0} \frac{dX}{dW} = -r_A' \]

Rate Laws
Second order in A and irreversible:

\[ -r_A' = kC_A^2 \]
Pressure Drop in PBRs

Stoichiometry

\[
C_A = \frac{F_A}{\nu} = C_{A0} \frac{(1 - X)}{(1 + \varepsilon X)} \frac{P}{P_0} \frac{T_0}{T}
\]

Isothermal, \( T = T_0 \)

\[
C_A = C_{A0} \frac{(1 - X)}{(1 + \varepsilon X)} \frac{P}{P_0}
\]

Combine:

\[
\frac{dX}{dW} = \frac{k C_{A0}^2}{F_{A0}} \frac{(1 - X)^2}{(1 + \varepsilon X)^2} \left( \frac{P}{P_0} \right)^2
\]

Need to find \( \frac{P}{P_0} \) as a function of \( W \) (or \( V \) if you have a PFR)
Pressure Drop in PBRs

Ergun Equation:
\[
\frac{dP}{dz} = \frac{-G}{\rho g c D_p} \left( \frac{1 - \phi}{\phi^3} \right) \left[ \frac{150(1 - \phi) \mu}{D_p} \right]_{\text{TURBULENT}} + \frac{1.75G}{D_p} \left[ \phi \right]_{\text{LAMINAR}}
\]

Constant mass flow:
\[
\dot{m} = \dot{m}_0
\]
\[
\rho \nu = \rho_0 \nu_0
\]
\[
\rho = \rho_0 \frac{\nu_0}{\nu}
\]
\[
\nu = \nu_0 \frac{F_T}{F_{T_0}} \frac{P_0}{P} \frac{T}{T_0}
\]
\[
\nu = \nu_0 (1 + \varepsilon X) \frac{P_0}{P} \frac{T}{T_0}
\]
Pressure Drop in PBRs

Variable Density

\[ \rho = \rho_0 \frac{P}{P_0} \frac{T_0}{T} \frac{F_{T_0}}{F_T} \]

\[
\frac{dP}{dz} = -G \frac{\left(1 - \phi\right)}{\rho_0 g_c D_p \phi^3} \left[ \frac{150(1-\phi)\mu}{D_p} + 1.75G \right] \frac{P_0}{P} \frac{T}{T_0} \frac{F_T}{F_{T_0}}
\]

Let

\[
\beta_0 = \frac{G}{\rho_0 g_c D_p \phi^3} \left[ \frac{150(1-\phi)\mu}{D_p} + 1.75G \right]
\]
Pressure Drop in PBRs

Catalyst Weight \[ W = zA_c \rho_b = zA_c (1 - \phi) \rho_c \]

Where \[ \rho_b = \text{bulk density} \]
\[ \rho_c = \text{solid catalyst density} \]
\[ \phi = \text{porosity (a.k.a., void fraction)} \]
\[ (1 - \phi) = \text{solid fraction} \]

\[ \frac{dP}{dW} = -\beta_0 \frac{P_0}{A_c (1 - \phi) \rho_c} \frac{T}{P} \frac{T_0}{F_T} \]

Let \[ \alpha = \frac{2\beta_0}{A_c (1 - \phi) \rho_c} \frac{1}{P_0} \]
Pressure Drop in PBRs

\[ \frac{dy}{dW} = - \frac{\alpha}{2y} \frac{T}{T_0} \frac{F_T}{F_{T_0}} \quad y = \frac{P}{P_0} \]

We will use this form for single reactions:

\[ \frac{d(P/P_0)}{dW} = - \frac{\alpha}{2} \frac{1}{(P/P_0)T_0} T (1 + \varepsilon X) \]

\[ \frac{dy}{dW} = - \frac{\alpha}{2y} \frac{T}{T_0} (1 + \varepsilon X) \]

\[ \frac{dy}{dW} = - \frac{\alpha}{2y} (1 + \varepsilon X) \quad \text{Isothermal case} \]
Pressure Drop in PBRs

\[ \frac{dX}{dW} = kC_{A0}^2 \left(1 - X\right)^2 \frac{y^2}{F_{A0} \left(1 + \varepsilon X\right)^2} \]

\[ \frac{dX}{dW} = f(X, P) \text{ and } \frac{dP}{dW} = f(X, P) \text{ or } \frac{dy}{dW} = f(y, X) \]

The two expressions are coupled ordinary differential equations. We can only solve them simultaneously using an ODE solver such as Polymath. For the special case of isothermal operation and epsilon = 0, we can obtain an analytical solution.

Polymath will combine the Mole Balances, Rate Laws and Stoichiometry.
Packed Bed Reactors

For $\varepsilon = 0$

$$\frac{dy}{dW} = \frac{-\alpha}{2y} (1 + \varepsilon X)$$

When $W = 0 \quad y = 1$

$$dy^2 = -\alpha dW$$

$$y^2 = (1 - \alpha W)$$

$$y = (1 - \alpha W)^{1/2}$$
Pressure Drop in a PBR
Concentration Profile in a PBR

\[ C_A = C_{A0}(1 - X) \frac{P}{P_0} \]
$-r_A = kC_A^2 = k(1 - X)^2 \left( \frac{P}{P_0} \right)^2$
Conversion in a PBR
**5 Flow Rate in a PBR**

For $\varepsilon = 0$:

$$f = \frac{\nu}{\nu_0}$$

$$\nu = \nu_0 \left( \frac{P_0}{P} \right)$$
\[ \nu = \nu_0 (1 + \varepsilon X) \frac{P_0}{P} \frac{T}{T_0} \]

\[ T = T_0 \quad y = \frac{P_0}{P} \]

\[ f = \frac{\nu_0}{\nu} = \frac{1}{(1 + \varepsilon X) y} \]
Example 1: Gas Phase Reaction in PBR for $\delta = 0$

Gas Phase reaction in PBR with $\delta = 0$ (Analytical Solution)

$$A + B \rightarrow 2C$$

Repeat the previous one with equimolar feed of $A$ and $B$ and:

$$k_A = 1.5 \text{dm}^6/\text{mol/kg/min}$$

$$\alpha = 0.0099 \text{ kg}^{-1}$$

Find $X$ at 100 kg
Example 1:
Gas Phase Reaction in PBR for $\delta=0$

1) Mole Balance

\[ \frac{dX}{dW} = \frac{-r'_A}{F_{A0}} \]

2) Rate Law

\[ -r'_A = kC_A C_B \]

3) Stoichiometry

\[ C_A = C_{A0} (1 - X)_y \]

\[ C_B = C_{A0} (1 - X)_y \]
Example 1: Gas Phase Reaction in PBR for δ=0

\[
\frac{dy}{dW} = -\frac{\alpha}{2y}
\]

\[2y\,dy = -\alpha\,dW\]

\[W = 0, \quad y = 1\]

\[y^2 = 1 - \alpha W\]

\[y = (1 - \alpha W)^{1/2}\]

4) Combine

\[-r_A = kC_{A0}^2 (1 - X)^2 y^2 = kC_{A0}^2 (1 - X)^2 (1 - \alpha W)\]

\[
\frac{dX}{dW} = \frac{kC_{A0}^2 (1 - X)^2 (1 - \alpha W)}{F_{A0}}
\]
Example 1:
Gas Phase Reaction in PBR for $\delta=0$

\[
\frac{dX}{(1 - X)^2} = \frac{kC_A^2}{F_A^0} (1 - \alpha W) dW
\]

\[
\frac{X}{1 - X} = \frac{kC_A^2}{F_A^0} \left( W - \frac{\alpha W^2}{2} \right)
\]

$W = 0, X = 0, W = W, X = X$

$X = 0.6 \text{ (with pressure drop)}$

$X = 0.75 \text{ (without pressure drop, i.e. } \alpha = 0\text{)}$
Example 2: Gas Phase Reaction in PBR for $\delta \neq 0$

The reaction

$$A + 2B \rightarrow C$$

is carried out in a packed bed reactor in which there is pressure drop. The feed is stoichiometric in A and B.

Plot the conversion and pressure ratio $y = \frac{P}{P_0}$ as a function of catalyst weight up to 100 kg.

Additional Information

$k_A = 6 \text{ dm}^9/\text{mol}^2/\text{kg/min}$

$\alpha = 0.02 \text{ kg}^{-1}$
Example 2: Gas Phase Reaction in PBR for $\delta \neq 0$

$A + 2B \rightarrow C$

1) Mole Balance

$$\frac{dX}{dW} = -\frac{r'_A}{F_{A0}}$$

2) Rate Law

$$-r'_A = kC_A C_B^2$$

3) Stoichiometry: Gas, Isothermal

$$\nu = \nu_0 (1 + \varepsilon X) \frac{P_0}{P}$$

$$C_A = C_{A0} \frac{(1 - X)}{(1 + \varepsilon X)} y$$
Example 2:
Gas Phase Reaction in PBR for $\delta \neq 0$

4) $C_B = C_{A_0} \frac{(\Theta_B - 2X)}{(1 + \varepsilon X)} y$

5) $\frac{dy}{dW} = -\frac{\alpha}{2y} (1 + \varepsilon X)$

6) $f = \frac{\nu}{\nu_0} = \frac{1 + \varepsilon X}{y}$

7) $\varepsilon = y_{A_0}[1 - 1 - 2] = \frac{1}{3}[-2] = -\frac{2}{3}$

$C_{A_0} = 2, F_{A_0} = 2, k = 6, \alpha = 0.02$

Initial values: $W=0, X=0, y=1$
Final values: $W=100$

Combine with Polymath.
If $\delta \neq 0$, polymath must be used to solve.
Example 2:
Gas Phase Reaction in PBR for $\delta \neq 0$

**POLYMATH Results**
POLYMATH Report 01-30-2006, Rev5.1.233

**Calculated values of the DEQ variables**

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<th>maximal value</th>
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</table>

**ODE Report (RKF45)**

Differential equations as entered by the user:
1. $d(X)/d(W) = -ra/Fao$
2. $d(y)/d(W) = -alpha*(1+eps*X)/2/y$

Explicit equations as entered by the user:
1. $eps = (1-2-1)/3$
2. $Cao = 0.2$
3. $TheataB = 2$
4. $Cb = Cao*(TheataB-2*X)/(1+eps*X)*y$
5. $Fao = 2$
6. $k = 6$
7. $Ca = Cao*(1-X)/(1+eps*X)*y$
8. $alpha = 0.02$
9. $ra = -k*Ca*Cb^2$
Example 2:
Gas Phase Reaction in PBR for $\delta \neq 0$
Gas Phase Reaction in PBR with Pressure Drop \( T = T_0 \)

**Mole Balance** \( (1) \) \[
\frac{dX}{dW} = -\frac{r_A'}{F_{A0}}
\]

**Rate Law** \( (2) \) \[-r_A' = kC_A\]

**Stoichiometry** Gas \( T = T_0 \)

\( (3) \) \[
C_A = \frac{C_{A0}(1-X)}{(1+\varepsilon X)^y}
\]

\( (4) \) \[
\frac{dy}{dw} = -\frac{\alpha(1+\varepsilon X)}{2y}
\]

\( (5)-(9) \) Parameters, \( \varepsilon, \alpha, \ldots \)

**Combine:** Polymath with combine for you
Robert the Worrier wonders: *What if* we increase the catalyst size by a factor of 2?
Pressure Drop
Engineering Analysis

\[
\alpha = \frac{2}{A_C(1-\phi)\rho_C P_0} \beta_0 = \frac{2}{A_C(1-\phi)\rho_C P_0} \left[ \frac{G(1-\phi)}{\rho_0 g C D_p \phi^3} \left[ \frac{150(1-\phi)\mu}{D_p} + 1.75G \right] \right]
\]

\[
\rho_0 = MW * C_T_0 = \frac{MW * P_0}{RT_0}
\]

\[
\alpha = \frac{2RT_0}{A_C \rho_C g C P_0^2 D_p \phi^3 MW} G \left[ \frac{150(1-\phi)\mu}{D_p} + 1.75G \right]
\]

\[
\alpha \approx \left( \frac{1}{P_0} \right)^2
\]
Pressure Drop
Engineering Analysis

A. Laminar Flow Dominant (Term 1 >> Term 2)

\[ \alpha \sim \frac{G}{A_c D_p^2 P_0^2} \]

Case 1 / Case 2

\[ \alpha_2 = \alpha_1 \left( \frac{G_2}{G_1} \right) \left( \frac{A_{c1}}{A_{c2}} \right) \left( \frac{D_{p1}}{D_{p2}} \right)^2 \left( \frac{P_{01}}{P_{02}} \right)^2 \]

Example

How will the pressure drop (e.g., \( \alpha \)) change if you decrease the particle diameter by a factor of 4 and increase entering pressure by a factor of 3

\[ D_{p2} = \frac{1}{4} D_{p1} \text{ and } P_{02} = 3P_{01} \]

\[ \alpha_2 = \alpha_1 \left( \frac{1}{4} \frac{D_{p1}}{1} \right)^2 \left( \frac{P_{01}}{3P_{01}} \right)^2 = \frac{16}{9} \alpha_1 \]
Pressure Drop

Engineering Analysis

B. Turbulent Flow Dominates (Term 2 >> Term 1)

\[ \alpha \sim \frac{G^2}{A_C D_p P_0^2} \]

\[ \alpha_2 = \alpha_1 \left( \frac{G_2}{G_1} \right)^2 \left( \frac{A_{C1}}{A_{C2}} \right) \left( \frac{P_{01}}{P_{02}} \right)^2 \left( \frac{D_{P1}}{D_{P2}} \right) \]

Again

\[ D_{P2} = \frac{1}{4} D_{P1} \text{ and } P_{02} = 3P_{01} \]

\[ \alpha_2 = \alpha_1 \left( \frac{1}{4} \frac{D_{P1}}{D_{P1}} \right) \left( \frac{P_{01}}{3P_{01}} \right)^2 = \frac{4}{9} \alpha_1 \]
End of Lecture 8
Pressure Drop - Summary

- **Pressure Drop**
  - **Liquid Phase Reactions**
    - Pressure Drop does not affect concentrations in liquid phase reactions.
  - **Gas Phase Reactions**
    - Epsilon does not equal to zero
      \[ \frac{d(P)}{d(W)} = \ldots \]
      Polymath will combine with \[ \frac{d(X)}{d(W)} = \ldots \] for you
    - Epsilon = 0 and isothermal
      \[ P = f(W) \]
      Combine then separate variables \((X,W)\) and integrate
    - Engineering Analysis of Pressure Drop
Pressure Change – Molar Flow Rate

\[
\frac{dP}{dW} = -\frac{\beta_0}{\rho A_c (1-\varphi) \rho_c} \frac{F_T P_0 T}{F_{T0} P T_0}
\]

\[
\frac{dy}{dW} = -\frac{\beta_0}{y P_0 A_c (1-\varphi) \rho_c} \frac{F_T T}{F_{T0} T_0}
\]

\[
\alpha = \frac{2\beta_0}{P_0 A_c (1-\varphi) \rho_c}
\]

Use for heat effects, multiple rxns

\[
\frac{F_T}{F_{T0}} = (1 + \varepsilon X) \quad \text{Isothermal: } T = T_0
\]

\[
\frac{dX}{dW} = -\frac{\alpha}{2y} (1 + \varepsilon X)
\]
Example 1:
Gas Phase Reaction in PBR for $\delta=0$

$$A + B \rightarrow 2C$$

$$k = 1.5 \frac{dm^6}{mol \cdot kg \cdot min} , \quad \alpha = 0.0099 kg^{-1} , \quad C_{B0} = C_{A0}$$

Case 1: \quad $W = 100 kg \quad , \quad X = ? \quad , \quad P = ?$

Case 2: \quad $D_P = 2D_{P1} \quad , \quad P_{02} = \frac{1}{2} P_{01} \quad , \quad X = ? \quad , \quad P = ?$
\[ F_{A0} \frac{dX}{dW} = -r' \]
\[ r_A = -kC_A C_B \]
\[ C_A = \frac{F_A}{F_T} y \]
\[ C_A = C_B \]
\[ \delta = 0 \text{ and } T = T_0 \therefore y = (1 - \alpha W)^{1/2} \]