CHEMICAL REACTION ENGINEERING (SKF3223)

Chapter 4:
Isothermal Reaction Design

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1 The general mole balance equation:

$$F_{A0} - F_A + \int r_A dV = \frac{dN_A}{dt}$$

2 Apply mole balance to specific reactor design equations:

$$Batch: N_{A0}\frac{dX}{dt} = -r_A V$$

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

$$PFR: F_{A0}\frac{dX}{dV} = -r_A$$

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

3 Derive:

$$-r_A = f(X)$$

4 Determine the rate law in terms of the concentration of the reacting species:

$$-r_A = k\left(C_A C_B - \frac{C_C}{K_C}\right)$$

5 Use stoichiometry to express concentration as a function of conversion

(i) Liquid-phase or constant volume batch:

$$C_A = C_{A0}(1-X)$$

$$C_B = C_{A0}\left(\Theta_B - \frac{b}{a}X\right)$$

(ii) Gas-phase $T=T_0$:

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

6 Gas with $P=P_0$ or Liquid: Combine steps **4** and **5** to obtain

$$-r_A = f(X)$$

7 Gas phase reaction with pressure drop:

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

$$y = \frac{P}{P_0}$$

Semibatch reactors:

$$V = V_0 + v_0 t$$

8 Combine mole balance, rate law and stoichiometry, transport law, and pressure drop term in an ordinary differential equation solver (ODE solver Polymath)

ALGORITHM FOR ISOTHERMAL REACTOR

1. Mole balance
2. Rate law
3. Stoichiometry (specify whether the reaction is gas or liquid phase)
4. Combine
5. Evaluate (Analytically-Appendix A1, Graphically-Chapter 2, Numerically-Appendix A4, Polymath software)

ALGORITHM TO ESTIMATE REACTION TIMES (BATCH REACTOR)

Mole balance		$\frac{dX}{dt}=\frac{-r_A}{N_{A0}}V$	
Rate law	$-r_A = kC_A$		$-r_A = kC_A^2$
Stoichiometry V=V_0		$C_A=\frac{N_A}{V_0}=C_{A0}(1-X)$	
Combine	$\frac{dX}{dt}=k(1-X)$		$\frac{dX}{dt}=kC_{A0}(1-X)^2$
Integrate $t=N_{A0}\int_0^X \frac{dX}{-r_A V}$	$t=\frac{1}{k}\ln\frac{1}{1-X}$		$t=\frac{X}{kC_{A0}(1-X)}$

ALGORITHM - CSTR

Mole balance	$V = \frac{F_{A0}.X}{-r_A}$		
Rate law	$-r_A = kC_A$		$-r_A = kC_A^2$
Space time		$\tau \equiv \frac{V}{\upsilon_0}$	
Conversion n= number of reactors	1st order: Parallel $X = \frac{\tau.k}{1+\tau.k} = \frac{Da}{1+Da}$ $Da = \tau k$	1st order: Series $X = 1 - \frac{1}{(1+\tau.k)^n}$ $C_{An} = \frac{C_{A0}}{(1+Da)^n}$	2nd order: $X = \frac{(1+2Da)-\sqrt{1+4Da}}{2Da}$ $Da = \tau k C_{A0}$

- One of important characteristic in CSTR equation is Damköhler number , Da

- Da number is a dimensionless

If Da < 0.1, then X < 0.1

If Da > 10, then X > 0.9

$$\boxed{Da = \frac{-r_{A0}.V}{F_{A0}}}$$

= Rate of reaction at entrance / Entering flow rate of A

$$\boxed{Da = \frac{kC_{A0}.V}{\upsilon_0.C_{A0}} = \tau.k}$$

First order irreversible reaction

$$\boxed{Da = \frac{kC_{A0}.V}{\upsilon_0 C_{A0}} = \tau.kC_{A0}}$$

Second order irreversible reaction

ALGORITHM – TUBULAR (GAS-PHASE)

(No pressure drop)

Mole balance		$V = F_{A0}\int_0^X \frac{dX}{-r_A}$	
Rate law	$-r_A = kC_A$		$-r_A = kC_A^2$
Stoichio-metry		$C_A = C_{A0}\frac{(1-X)}{(1+\varepsilon X)}$	
combine	$V = \frac{F_{A0}}{kC_{A0}}\int_0^X \frac{(1+\varepsilon X)}{(1-X)}dX$ $= \frac{F_{A0}}{kC_{A0}}\left[(1+\varepsilon) In \frac{1}{1-X} - \varepsilon X\right]$		$V = \frac{F_{A0}}{kC_{A0}{}^2}\int_0^X \frac{(1+\varepsilon X)^2}{(1-X)^2}dX$

PRESSURE DROPS IN REACTORS

- Liquid-phase reaction: pressure drop can totally ignored
- Gas-phase reaction: Pressure drop will be considered – is very important - key factor in the success or failure of the reactor operation
- For an ideal gas, the concentration of reacting species i:

$$C_i = C_{A0}\left(\frac{\Theta_i + v_i X}{1+\varepsilon X}\right)\frac{P}{P_0}\frac{T_0}{T}$$

$$\Theta_i = \frac{F_{i0}}{F_{A0}}, \varepsilon = y_{A0}\delta, v = stoichiometriccoefficient$$

- When $P \neq P_0$, use the differential forms of the PFR/PBR design equations

EXAMPLE

$$2A \rightarrow B + C$$

1. Mole balance - Differential form: $$F_{A0}\frac{dX}{dW} = -r_A'$$

2. Rate law: $$-r_A' = kC_A^2$$

3. From stoichiometry for gas-phase reactions: $$C_A = \frac{C_{A0}(1-X)}{1+\varepsilon X}\frac{P}{P_0}\frac{T_0}{T}$$

-r_A=f(X)

$$-r_A' = k\left[\frac{C_{A0}(1-X)}{1+\varepsilon X}\frac{P}{P_0}\frac{T_0}{T}\right]^2$$

Isothermal, T = T_0

4. Combine

$$F_{A0}\frac{dX}{dW} = k\left[\frac{C_{A0}(1-X)}{1+\varepsilon X}\right]^2\left(\frac{P}{P_0}\right)^2 \rightarrow \frac{dX}{dW} = \frac{kC_{A0}}{v_0}\left[\frac{(1-X)}{1+\varepsilon X}\right]^2\left(\frac{P}{P_0}\right)^2$$

5. Relate the pressure drop (P/P_0) to the catalyst weight → to determine X as a function of catalyst weight

PRESSURE DROPS IN PBR

- ☐ Ergun Equation:

$$\frac{dP}{dz}=\frac{-G}{\rho g_C D_P}\left(\frac{1-\phi}{\phi^3}\right)[\underbrace{\frac{150(1-\phi)\mu}{D_P}}_{\text{laminar}}+\underbrace{1.75G}_{\text{turbulent}}]$$

P = Ib_f/ft^2 (kPa)
Φ = porosity = void fraction
= volume of void / total bed volume
1-Φ = volume of solid / total bed volume
gc = 32.174 $\text{Ib}_m\text{ft/s}^2\text{Ib}_f$ (conversion factor)
Dp = diameter of particle in the bed, ft (m)
μ = viscosity of gas, Ib_m/ft.h (kg/m.s)
z = length of PBR pipe, ft (m)
u = superficial velocity = volumetric flow/cross section, ft/h (m/s)
ρ = gas density, ib/ft^3 (kg/m^3)
G = ρu = superficial mass velocity, $\text{Ibm/ft}^2\text{h}$ ($\text{kg/m}^2\text{s}$)

- ☐ Variable Gas Density: $\rho=\rho_0\frac{P}{P_0}\frac{T_0}{T}\frac{F_{T0}}{F_T}$

$$\frac{dP}{dz}=\frac{-G}{\rho_0 g_C D_P}\left(\frac{1-\phi}{\phi^3}\right)[\frac{150(1-\phi)\mu}{D_P}+1.75G]\frac{P_0}{P}\frac{T}{T_0}\frac{F_T}{F_{T0}}$$

- Simplifying yields:

$$\frac{dP}{dz} = -\beta_0 \frac{P_0}{P}\frac{T}{T_0}\frac{F_T}{F_{T0}}$$

$$\beta_0 = \frac{G(1-\Phi)}{\rho_0 g_c D_p \Phi}\left[\frac{150(1-\Phi)}{D_p} + 1.75G\right]$$

β_0 is a constant down the reactor that depends only on the properties of the PBR and the entrance conditions

- The catalyst weight up to a distance of z down the reactor is:

$$W = \underbrace{(1-\Phi)A_c}_{\text{Volume of solids}} z\rho_C$$

Density of solid catalyst

- Bulk density:

$$\rho_b = \rho_c(1-\phi)$$

- Ergun equation in terms of catalyst weight:

$$\frac{dP}{dW} = -\frac{\beta_0}{A_C(1-\phi)\rho_C}\frac{P_0}{P}\left(\frac{T}{T_0}\right)\frac{F_T}{F_{T0}}$$

- Further simplification yields:

$$\frac{dP}{dW} = -\frac{\alpha}{2}\frac{T}{T_0}\frac{P_0}{P/P_0}\left(\frac{F_T}{F_{T0}}\right)$$

$$\boxed{\alpha = \frac{2\beta_0}{A_C\rho_C(1-\phi)P_0}}$$

$$y = \frac{P}{P_0}$$

Use for multiple reactions and membrane reactors

$$\boxed{\frac{dy}{dW} = -\frac{\alpha}{2y}\frac{T}{T_0}\left(\frac{F_T}{F_{T0}}\right)}$$

$$F_T = F_{T0} + F_{A0}\delta X = F_{T0}\left[1 + \frac{F_{A0}}{F_{T0}}\delta X\right]$$

Use for single reactions in PBR

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

$$\frac{F_T}{F_{T0}} = 1+\varepsilon X$$

$$\varepsilon = y_{A0}\delta = \frac{F_{A0}}{F_{T0}}\delta$$

- ONLY for isothermal with $T/T_0=0$, $\varepsilon = 0$:

$$\boxed{y = \frac{P}{P_0} = \sqrt{(1-\alpha W)}}$$

- For isothermal with $T/T_0=0$, $\varepsilon \neq 0$:

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

$$\boxed{y = \sqrt{1-\alpha W(1+\varepsilon X)}}$$

$$\boxed{y = \frac{P}{P_0} = \left(1-\frac{2\beta_0 z}{P_0}\right)^{1/2}}$$

EXAMPLE $A \rightarrow B$

$T/T_0 = 0$, $\varepsilon = 0$, with ΔP

1 $$F_{A0}\frac{dX}{dW} = -r'_A$$

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

3 $$C_A = C_{A0}(1-X)\frac{P}{P_0} = C_{A0}(1-X)y$$

$$y = \frac{P}{P_0} = \sqrt{(1-\alpha W)}$$

$$-r'_A = kC_{A0}^2(1-X)^2\left(\sqrt{(1-\alpha W)}\right)^2$$

$$-r'_A = kC_{A0}^2(1-X)^2(1-\alpha W)$$

5 Could now solve for X given W, or for W given X.

4 $$\frac{dX}{dW} = \frac{kC_{A0}^2(1-X)^2(1-\alpha W)}{F_{A0}}$$

$$\left[\frac{1}{(1-X)^2}\right]dX = \left[\frac{kC_{A0}^2}{F_{A0}}(1-\alpha W)\right]dW$$

$$\boxed{\frac{X}{1-X} = \frac{kC_{A0}^2}{F_{A0}}\left[W - \frac{\alpha W^2}{2}\right]}$$

$$\boxed{X = \frac{\dfrac{kC_{A0}W}{v_0}\left(1-\dfrac{\alpha W}{2}\right)}{1+\dfrac{kC_{A0}W}{v_0}\left(1-\dfrac{\alpha W}{2}\right)}}$$

$$\boxed{W = \frac{1-\sqrt{1-\left[\dfrac{(2v_0\alpha)}{kC_{A0}}\right]\left[\dfrac{X}{1-X}\right]}}{\alpha}}$$

$T/T_0 = 0$, $\varepsilon = 0$, in the absence of ΔP, ($\alpha = 0$)

$$-r_A' = kC_A^2$$

$$\frac{X}{1-X} = \frac{kC_{A0}^2}{F_{A0}} W$$

$$X = \frac{\dfrac{kC_{A0}W}{v_0}}{1+\dfrac{kC_{A0}W}{v_0}}$$

with ΔP, ($\alpha \neq 0$)

$$\alpha = \frac{2\beta_0}{A_C \rho_C (1-\phi) P_0}$$

$$\alpha = \frac{2\beta_0}{A_C \rho_b P_0}$$

- X decreased with ΔP
- If we increase catalyst size, laminar terms = 0 (Ergun equation)
- By increasing the particle diameter, we decrease the pressure drop parameter (β_0) and thus increase the $-r_A$ and the X.

PRESSURE DROP IN PIPES

- Pressure drop along the length of the pipe:

$$\boxed{\frac{dP}{dL} = -G\frac{du}{dL} - \frac{2fG^2}{\rho D}}$$

D = pipe diameter, cm
u = average velocity of gas, cm/s
f = Fanning friction factor
G = ρu, g/cm^{2}s (mass velocity, constant along the length of the pipe)

EXAMPLE: Calculating X in a Reactor With ΔP (gas=phase)

$$\boxed{A+\frac{1}{2}B\rightarrow C}\qquad \Theta_B=\frac{F_{B0}}{F_{A0}}=\frac{1}{2}$$

① $$F_{A0}\frac{dX}{dW}=-r_A'$$

② $$-r_A'=kP_A^{1/3}P_B^{2/3}$$

$$P_A=C_ART$$

$$-r_A'=k(C_ART)^{1/3}(C_BRT)^{2/3}$$

$$-r_A'=kRTC_A^{1/3}C_B^{2/3}$$

③ $$C_A=\frac{C_{A0}(1-X)}{1+\varepsilon X}\left(\frac{P}{P_0}\right)=\frac{C_{A0}(1-X)y}{1+\varepsilon X}$$

$$C_B=\frac{C_{A0}(\Theta_B-X/2)y}{1+\varepsilon X}=\frac{C_{A0}(1-X)y}{2(1+\varepsilon X)}$$

④ $$-r_A'=kRTC_A^{1/3}C_B^{2/3}$$

$$-r_A'=kRT[\frac{C_{A0}(1-X)y}{1+\varepsilon X}]^{1/3}[\frac{C_{A0}(1-X)y}{2(1+\varepsilon X)}]^{2/3}$$

$$-r_A'=k\frac{P_{A0}}{C_{A0}}[\frac{C_{A0}(1-X)y}{1+\varepsilon X}]^{1/3}[\frac{C_{A0}(1-X)y}{2(1+\varepsilon X)}]^{2/}$$

Factoring $(1/2)^{2/3}$

$$-r_A'=k'\left(\frac{1-X}{1+\varepsilon X}\right)y$$

$$k'=kP_{A0}(1/2)^{2/3}=0.63kP_{A0}$$

MOLE BALANCES FOR LIQUID-PHASE REACTIONS

$$\boxed{A+\frac{b}{a}B\rightarrow\frac{c}{a}C+\frac{d}{a}D}$$

Batch	$\frac{dC_A}{dt}=r_A$	$\frac{dC_B}{dt}=\frac{b}{a}r_A$
CSTR	$V=\frac{v_0(C_{A0}-C_A)}{-r_A}$	$V=\frac{v_0(C_{B0}-C_B)}{-(b/a)r_A}$
PFR	$v_0\frac{dC_A}{dV}=r_A$	$v_0\frac{dC_B}{dV}=\frac{b}{a}r_A$
PBR	$v_0\frac{dC_A}{dW}=r_A'$	$v_0\frac{dC_B}{dW}=\frac{b}{a}r_A'$

MOLE BALANCES FOR GAS-PHASE REACTIONS

$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$$

BATCH	CSTR	PFR
$\frac{dN_A}{dt} = r_A V$	$V = \frac{F_{A0} - F_A}{-r_A}$	$\frac{dF_A}{dV} = r_A$
$\frac{dN_B}{dt} = r_B V$	$V = \frac{F_{B0} - F_B}{-r_B}$	$\frac{dF_B}{dV} = r_B$
$\frac{dN_C}{dt} = r_C V$	$V = \frac{F_{C0} - F_C}{-r_C}$	$\frac{dF_C}{dV} = r_C$
$\frac{dN_D}{dt} = r_D V$	$V = \frac{F_{D0} - F_D}{-r_D}$	$\frac{dF_D}{dV} = r_D$

GAS-PHASE REACTIONS

1

$$\frac{dF_j}{dV} = r_j$$

2

$$-r_A = k_A C_A^{\alpha} C_B^{\beta}$$

$$\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d}$$

3

$$C_j = C_{T0} \frac{F_j}{F_T} \frac{T_0}{T} y$$

$$C_A = C_{T0} \frac{F_A}{F_T} \frac{T_0}{T} y$$

$$C_B = C_{T0} \frac{F_B}{F_T} \frac{T_0}{T} y$$

$$F_T = F_A + F_B + F_C + F_D + F_I$$

$$\frac{dy}{dW} = \frac{-\alpha}{2y} \frac{F_T}{F_{T0}}$$

4

$$\frac{dF_A}{dV} = r_A$$

$$\frac{dF_A}{dV} = -k_A C_{T0}^{\alpha+\beta} \left(\frac{F_A}{F_T} \frac{T_0}{T} y \right)^{\alpha} \left(\frac{F_B}{F_T} \frac{T_0}{T} y \right)^{\beta}$$

Isothermal, $T=T_0$:

$$\frac{dF_A}{dV} = -k_A C_{T0}^{\alpha+\beta} \left(\frac{F_A}{F_T} y \right)^{\alpha} \left(\frac{F_B}{F_T} y \right)^{\beta}$$

UNSTEADY-STATE OPERATION: CSTR & SEMIBATCH

- To determine the time necessary to reach steady-state operation
- To predict the concentration, C and X as a function of time
- Analytical solutions: zero and 1st order reactions
- ODE solvers: other reaction orders

LIQUID-PHASE REACTIONS (CSTR)

$$v = v_0, \quad V = V_0, \quad \tau = V_0/v_0$$

1

$$F_{A0} - F_A + r_A V = \frac{dN_A}{dt}$$

$$C_{A0} - C_A + r_A \tau = \tau \frac{dC_A}{dt}$$

2

$$-r_A = kC_A$$

$$\frac{dC_A}{dt} + \frac{1+\tau k}{\tau} C_A = \frac{C_{A0}}{\tau}$$

3

Initial condition: $C_A = C_{A0}$ at $t = 0$:

$$C_A = \frac{C_{A0}}{1+\tau k}\{1 - \exp[-(1+\tau k)\frac{t}{\tau}]\}$$

4

t_S = the time necessary to reach 99% of the steady-state concentration, C_{AS}: ($C_A = 0.99C_{AS}$)

$$\boxed{C_{AS} = \frac{C_{A0}}{1+\tau k}}$$

Slow reactions with small k ($1 >> \tau k$):

$$\boxed{t_S = 4.6\tau}$$

Rapid reactions with large k ($\tau k >> 1$):

$$\boxed{t_S = \frac{4.6}{k}}$$

SEMIBATCH REACTOR – in terms of concentration, C

General mole balance: $r_A V(t) = \frac{dN_A}{dt}$

In terms of concentration: $r_A V = \frac{d(C_A V)}{dt} = \frac{V dC_A}{dt} + C_A \frac{dV}{dt}$

Semibatch reactor volume as a function of time: $\boxed{V = V_0 + v_0 t}$

Mole balance on A:

$$\boxed{\frac{dC_A}{dt} = r_A - \frac{\upsilon_0}{V} C_A}$$

Mole balance on B:

$$\boxed{\frac{dC_B}{dt} = r_B + \frac{\upsilon_0 (C_{B0} - C_B)}{V}}$$

SEMIBATCH REACTOR – in terms of conversion, X

$$A + B \leftrightarrow C + D$$

① $$r_A V = \frac{dN_A}{dt} = -N_{A0}\frac{dX}{dt}$$

② $$-r_A = k\left(C_A C_B - \frac{C_C C_D}{K_C}\right)$$

③ $$C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X)}{V_0 + v_0 t}$$

$$C_C = \frac{N_C}{V} = \frac{N_{A0}X}{V_0 + v_0 t}$$

③ For constant molar feed rate and no B initially in system:

$$N_B = F_{B0}t - N_{A0}X$$

$$C_B = \frac{N_B}{V} = \frac{N_{Bi} + F_{B0}t - N_{A0}X}{V_0 + v_0 t}$$

$$C_D = \frac{N_D}{V} = \frac{N_{A0}X}{V_0 + v_0 t}$$

4

$$\boxed{\frac{dX}{dt} = \frac{k[(1-X)(N_{Bi} + F_{B0}t - N_{A0}X) - (N_{A0}X^2 / K_C)]}{V_0 + v_0 t}}$$

5

At equilibrium after feedings pecies B for a time, t, the equilibrium conversion could be:

$$K_C = \frac{C_{Ce}C_{De}}{C_{Ae}C_{Be}} = \frac{N_{Ce}N_{De}}{N_{Ae}N_{Be}} = \frac{(N_{A0}X_e)(N_{A0}X_e)}{N_{A0}(1-X_e)(F_{B0}t - N_{A0}X_e)}$$

$$\boxed{t = \frac{N_{A0}}{K_C F_{B0}}\left(K_C X_e + \frac{X_e^2}{1-X_e}\right)}$$

$$\boxed{X_e = \frac{K_c\left(1+\frac{F_{B0}t}{N_{A0}}\right) - \sqrt{\left[K_C\left(1+\frac{F_{B0}t}{N_{A0}}\right)\right]^2 - 4(K_C - 1)K_C\frac{tF_{B0}}{N_{A0}}}}{2(K_C - 1)}}$$

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