SHRINKING SOLIDS
COCURRENT and
COUNTERCURRENT

PLUG FLOW

Shrinking solids

$aA(s) + bB(s) \rightarrow gG(s)$

Plug Flow

$W(g)$ = mass of solids in the bed

$\rho_B(g/cm^3)$ = density of solids

$C_{B0}(mol/cm^3)$ = molar density of solids

$$X_B = \frac{R_0^3 - R^3}{R_0^3} = \text{fractional conversion}$$

$F_{B0}\left(\frac{mol\ B}{s}\right)$ = molar feed rate of solids

$R_{B-}\left(\frac{mol\ B}{cm^3\ solids\ s}\right)$ = reaction rate of B

$$F_{B0}\frac{dX_B}{dW} = \frac{R_{B-}}{\rho_B}$$

$$R_{B-} = \frac{4\pi R^2 C_{B0}\left(\frac{dR}{dt}\right)}{\frac{4}{3}\pi R^3} = \frac{3C_{B0}\mathcal{R}}{R\rho_B}$$

$$-\mathcal{R} = +\frac{dR}{dt} = -kC_A^m R^\alpha$$

$\left(\frac{cm}{s}\right)$

$\alpha = 0$ kinetic control

$\alpha = -\frac{1}{2}, 1, -1$ diffusion
- turbul
- conv

$\alpha = 1$

other

[illegible] 1991

$$a\,A(g) + b\,B(s) = p\,P(g)$$

Plug Flow Solids — Shrinking solids

Plug Flow gas (fluid) — $\boxed{\text{cocurrent}}$ spherical

Rate Law $\quad \frac{dR}{dt} = -k\,C_A^{n}\,R^{\alpha} = -\mathcal{R}$ $\qquad \mathcal{R} = -\frac{dR}{dt}$

$\mathcal{R} > 0$

$$F_{B0}\frac{dX_B}{dW} = \frac{3C_{B0}}{R\rho_0}\mathcal{R}$$

$$\boxed{X_B = 1-\left(\frac{R}{R_0}\right)^3} \qquad dX_B = -\frac{3R^2}{R_0^3}\,dR$$

$$\frac{3F_0R^2}{R_0^3}\frac{dR}{dW} = -\frac{3C_{B0}}{R\rho_0}\mathcal{R}$$

$$\boxed{\frac{dR}{dW} = -\frac{R_0^3C_{B0}}{F_{B0}R^3\rho_0}\mathcal{R} \quad ; W=0 \quad R=R_0}$$

$$-\frac{d}{dW}(Q_g C_A) - \frac{3aC_{B0}}{bR\rho_0}\mathcal{R} = 0$$

$$\boxed{\frac{d}{dW}(Q_g C_A) = -\frac{3}{R}\left(\frac{aC_{B0}}{b\rho_0}\right)\mathcal{R} \quad ; W=0 \quad Q_gC_A = Q_{g0}C_{A0}}$$

$$\frac{d}{dW}\Big[F_{B0}X_B\frac{a}{b} + \overbrace{Q_gC_A}^{F_A}\Big] = 0$$

$$Q_gC_A + \frac{a}{b}F_{B0}X_B = Q_{g0}C_{A0}$$

$$C_A = \frac{Q_{g0}}{Q_g}C_{A0} - \frac{a}{b}\frac{F_{B0}}{Q_g}X_B$$

$$C_A = \frac{Q_{g0}}{Q_g}C_{A0} - \frac{aF_{B0}}{b\,Q_g}X_B$$

$$C_A = C_{A0}\frac{Q_{g0}}{Q_g}\left[1 - \frac{aF_{B0}}{bF_{A0}}X_B\right]$$

$$\boxed{C_A = C_{A0}\left(\frac{Q_{g0}}{Q_g}\right)\left[1 - \beta X_B\right]}$$

$$\boxed{\beta = \frac{a F_{B0}}{b F_{A0}}}$$

Ideal gas law

$$\frac{Q_g}{Q_{g0}} = \frac{T}{T_0}\frac{P_0}{P}(1 + \epsilon_A X_A) = \frac{T P_0}{T_0 P}(1 + \epsilon_A \beta X_B)$$

$$X_A = \frac{F_{A0} - F_A}{F_{A0}}$$

$$\boxed{\epsilon_A = \frac{(\Sigma \nu_i)}{(-\nu_A)} y_{A0}}$$

$$\frac{d}{dW}\left[F_{B0} X_B \frac{a}{b} + F_A\right] = 0$$

$$F_A + F_{B0} X_B \frac{a}{b} = F_{A0}$$

$$F_{A0} - F_A = F_{A0} X_A = F_{B0} X_B \frac{a}{b}$$

$$\boxed{X_A = \frac{a F_{B0}}{b F_{A0}} X_B = \beta X_B}$$

$$\boxed{C_A = C_{A0} \frac{T_0 P}{T P_0} \frac{1 - \beta X_B}{1 + \epsilon_A \beta X_B}}$$

$$\boxed{X_B = 1 - \left(\frac{R}{R_0}\right)^3}$$

Assume $\epsilon_A = 0$

$T = \text{const}$

$P = \text{const}$

$$C_A = C_{A0}(1 - \beta X_B)$$

$\varepsilon_A = 0$ assumed to gas phase

$$\frac{dR}{dW} = -\frac{R_0^3 C_{B0}}{F_{B0}\rho_B}\frac{\mathcal{R}}{R^3}$$

$$\frac{dR}{dW} = -\left(\frac{R_0^3 C_{B0}}{F_{B0}\rho_B}\right)\frac{k C_A^m R^\alpha}{R^3}$$

$$\frac{dR}{dW} = -\left(\frac{R_0^3 C_{B0} k}{F_{B0}\rho_B}\right) C_{A0}^m (1-\beta X_B)^m R^{\alpha-3}$$

$$\frac{dR}{dW} = -\left(\frac{R_0^3 C_{B0} k C_{A0}^m}{F_{B0}\rho_B}\right)\left[1-\beta+\beta\left(\frac{R}{R_0}\right)^3\right] R^{\alpha-3}$$

$$W = \frac{F_{B0}\rho_B}{C_{B0} k C_{A0}^m}\frac{1}{R_0^3}\int_R^{R_0}\frac{dR}{\left[1-\beta+\beta\left(\frac{R}{R_0}\right)^3\right]R^{\alpha-3}}$$

$$\frac{F_{B0}\rho_B}{C_{B0}} = \dot{m}_{B0}\ (g/s)$$

$$\tau_{space} = \boxed{\frac{W}{\dot{m}_{B0}} = \frac{1}{k C_{A0}^m R_0^3}\int_R^{R_0}\frac{dR}{\left[1-\beta+\beta\left(\frac{R}{R_0}\right)^3\right]R^{\alpha-3}}}$$

$\frac{1}{GHSV}$

— Large excess gas $C_{A0} = \text{const}$ $\beta \Rightarrow 0$

— Stoichiometric ratio $\beta = 1$

Large excess of gas: $\beta \to 0$

$$\frac{W}{\dot{m}_{B0}} = \frac{1}{k C_{A0}^{\,n} R_0^3} \int_R^{R_0} R^{3-\alpha}\, dR$$

$$= \frac{R_0^{\,3-\alpha+1} - R^{\,3-\alpha+1}}{k C_{A0}^{\,n} R_0^3 (3-\alpha+1)} = \frac{R_0^{\,4-\alpha} - R^{\,4-\alpha}}{k C_{A0}^{\,n} R_0^3 (4-\alpha)}$$

$$\boxed{\frac{W}{\dot{m}_{B0}} = \frac{R_0^{\,1-\alpha}}{k C_{A0}^{\,n} (4-\alpha)} \left[ 1 - \left(\frac{R}{R_0}\right)^{4-\alpha} \right]}$$

Stoichiometric ratio $\beta = 1$

$$\frac{W}{\dot{m}_{B0}} = \frac{1}{k C_{A0}^{\,n}} \int_R^{R_0} R^{-\alpha}\, dR = \frac{R_0^{\,1-\alpha} - R^{\,1-\alpha}}{k C_{A0}^{\,n} (1-\alpha)}$$

$$\boxed{\frac{W}{\dot{m}_{B0}} = \frac{R_0^{\,1-\alpha}}{k C_{A0}^{\,n} (1-\alpha)} \left[ 1 - \left(\frac{R}{R_0}\right)^{1-\alpha} \right]}$$

$$\frac{W_{\beta=0}}{W_{\beta=1}} = \frac{1-\alpha}{4-\alpha} \frac{\left[ 1 - \left(\frac{R}{R_0}\right)^{4-\alpha} \right]}{\left[ 1 - \left(\frac{R}{R_0}\right)^{1-\alpha} \right]}$$

For complete reaction $R = 0$

$$\boxed{\frac{W_{\beta=0}}{W_{\beta=1}} = \frac{1-\alpha}{4-\alpha} = \begin{cases} \frac{1}{4} & \alpha = 0 \\ \frac{2}{5} & \alpha = -1 \\ \frac{1}{2} & \alpha = -2 \end{cases}}$$

$$\frac{dR}{dt} = -kC_A^n R^\alpha$$

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$\alpha = 0$

$$\tau_{B=0} = \frac{R_0}{4kC_{A0}^n} \qquad \tau_{B=1} = \frac{R_0}{kC_{A0}^n}$$

$$\frac{\tau_{B=1}}{\tau_{B=0}} = 4$$

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$\alpha = -\frac{1}{2}$

$$\tau_{B=0} = \frac{R_0^{3/2}}{\frac{9}{2}kC_{A0}} = \frac{2R_0^{3/2}}{9kC_{A0}} \qquad \tau_{B=1} = \frac{R_0^{3/2}}{\frac{3}{2}kC_{A0}^n} = \frac{2R_0^{3/2}}{3kC_{A0}^n}$$

$$\frac{\tau_{B=1}}{\tau_{B=0}} = 3$$

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$\alpha = -1$

$$\tau_{B=0} = \frac{R_0^2}{5kC_{A0}^n} \qquad \tau_{B=1} = \frac{R_0^2}{2kC_{A0}^n}$$

$$\frac{\tau_{B=1}}{\tau_{B=0}} = \frac{5}{2} = 2.5$$

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$\alpha = 1$

$$\tau_{B=0} = \frac{1}{3kC_{A0}^n} \qquad \tau_{B=1} = \infty \qquad \frac{\tau_{B=1}}{\tau_{B=0}} = \infty$$

$\alpha = 1/2$

$$\tau_{B=0} = \frac{R_0^{1/2}}{kC_{A0}^n \, 7/2} = \frac{2}{7}() \qquad \tau_{B=1} = \frac{R_0^{1/2}}{\frac{1}{2}kC_{A0}^n} = 2() \qquad \frac{\tau_{B=1}}{\tau_{B=0}} = 7$$

$\alpha = 0$ kinetic control

To set $R = 0$

$\beta \Rightarrow 0$

$$\tau_{w_{\beta=0}} = \frac{W}{\dot{m}_{B0}} = \frac{R_0}{4 k C_{A0}^{n}}$$

In excess gas

$\beta \Rightarrow 1$

$$\tau_{w_{\beta=1}} \quad \frac{W}{\dot{m}_{B0}} = \frac{R_0}{k C_{A0}}$$

$$\boxed{\frac{\tau_{w_{\beta=0}}}{\tau_{w_{\beta=1}}} = \frac{1}{4} = 0.25}$$

1/4 size of bed required

$\alpha = -\frac{1}{2}$

$$\tau_{w_{\beta=0}} = \frac{R_0^{3/2}}{\frac{9}{2} k C_{A0}^{n}} = \frac{2R_0^{3/2}}{9kC_{A0}^{n}} \qquad \frac{\tau_{\beta=0}}{\tau_{\beta=1}} = \frac{2}{9} \cdot \frac{3}{2}... = \frac{1}{3} = 0.333$$

$$\tau_{w_{\beta=1}} = \frac{R_0^{3/2}}{3/2\, k C_{A0}^{n}} = \frac{2R_0^{3/2}}{3kC_{A0}}$$

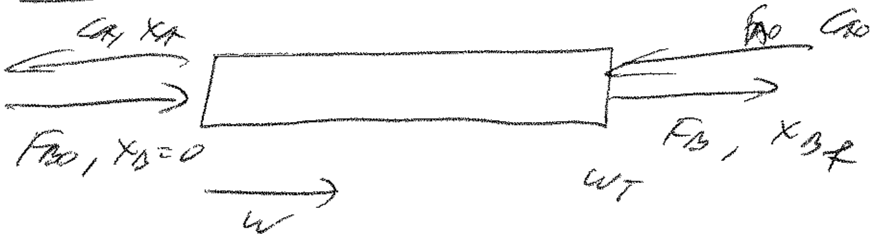
$\alpha = -1$ diffusion control, $R = 0$

$$\tau_{w_{\beta=0}} = \frac{R_0^{2}}{5 k C_{A0}^{n}}$$

$$\boxed{\frac{\tau_{\beta=0}}{\tau_{\beta=1}} = \frac{2}{5} = 0.4}$$

$$\tau_{w_{\beta=1}} = \frac{R_0^{2}}{2 k C_{A0}^{n}}$$

## COUNTERCURRENT FLOW




$$F_{B0} \frac{dX_B}{dW} = \frac{3 C_{B0}}{R \rho_B} \mathcal{R}$$

$$W = 0 \qquad X_B = 0$$

$$+\frac{d}{dW}(Q_g C_A) = +\frac{dF_A}{dW} = \frac{3}{R} \frac{a C_{B0}}{b \rho_B} \mathcal{R}$$

$$W = W_T \qquad C_A = C_{A0}, \quad F_A = F_{A0}$$

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$$\frac{d}{dW}\left[F_A - \frac{a}{b} F_{B0} X_B\right] = 0$$

$$F_A - \frac{a}{b} F_{B0} X_B = F_{A0} - \frac{a}{b} F_{B0} X_{Bf}$$

$$F_A = F_{A0} - \frac{a}{b} F_{B0} (X_{Bf} - X_B)$$

$$\boxed{F_A = F_{A0}\left[1 - \beta (X_{Bf} - X_B)\right]} \qquad \beta = \frac{a F_{B0}}{b F_{A0}}$$

$$C_A = C_{A0} \frac{Q_{g0}}{Q_g}\left[1 - \beta (X_{Bf} - X_B)\right]$$

$$\frac{Q_g}{Q_{g0}} = \frac{T P_0}{T_0 P}(1 + \varepsilon_A X_A)$$

$$\boxed{X_A = \beta (X_{Bf} - X_B)}$$

$$C_A = C_{A0}\frac{T_0 P}{T P_0}\;\frac{1-\beta(X_{Bf}-X_B)}{1+\epsilon_A\beta(X_{Bf}-X_B)}$$

$$X_B = 1-\left(\frac{R}{R_0}\right)^3$$

$$dX_B = -\frac{3R^2}{R_0^3}\,dR$$

$$\boxed{\text{Let}\quad T=\text{const}\quad P=\text{const}\quad \epsilon_A = 0}$$

$$C_A = C_{A0}\left[1-\beta(X_{Bf}-X_B)\right]$$

$$\frac{dR}{dW} = -\left(\frac{R_0^3 C_{B0}}{F_{B0}\rho_B}\right)\frac{k C_A^n R^\alpha}{R^3}$$

$$\frac{dR}{dW} = -\frac{R_0^3 C_{B0}\, k C_{A0}^n}{F_{B0}\rho_B}\left[1-\beta(X_{Bf}-X_B)\right]R^{\alpha-3}$$

$$X_{Bf} = 1-\left(\frac{R_f}{R_0}\right)^3 \qquad X_B = 1-\left(\frac{R}{R_0}\right)^3$$

$$X_{Bf}-X_B = \left(\frac{R}{R_0}\right)^3-\left(\frac{R_f}{R_0}\right)^3$$

$$\frac{dR}{dW} = -\left(\frac{R_0^3 C_{B0}\, k C_{A0}^n}{F_{B0}\rho_B}\right)\left[1+\beta\left(\frac{R_f}{R_0}\right)^3-\beta\left(\frac{R}{R_0}\right)^3\right]R^{\alpha-3}$$

$$\frac{F_{B0}\rho_B}{C_{B0}} = \dot{m}_{B0}$$

$W=0 \quad R=R_0 \qquad\qquad W=W_T \quad R=R_f$

$$\frac{W}{\dot{m}_{B0}} = \frac{1}{kC_{A0}^{n} R_0^3} \int_R^{R_0} \frac{dR}{\left[1+\beta\left(\frac{R_f}{R_0}\right)^3 - \beta\left(\frac{R}{R_0}\right)^3\right] R^{\alpha-3}}$$

$$\boxed{\frac{W_T}{\dot{m}_{B0}} = \frac{1}{kC_{A0}^{n} R_0^3} \int_{R_f}^{R_0} \frac{dR}{\left[1+\beta\left(\frac{R_f}{R_0}\right)^3 - \beta\left(\frac{R}{R_0}\right)^3\right] R^{\alpha-3}}}$$

large excess gas $\beta \to 0$

$$\frac{W_T}{\dot{m}_{B0}} = \frac{1}{kC_{A0}^{n} R_0^3} \int_{R_f}^{R_0} R^{3-\alpha}\, dR$$

$$= \frac{R_0^{1-\alpha}}{kC_{A0}^{n}(4-\alpha)}\left[1 - \left(\frac{R}{R_0}\right)^{4-\alpha}\right] \quad \text{QED}$$

Same as cocurrent

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Stoichiometric rate $\beta = 1$

$$\frac{W_T}{\dot{m}_{B0}} = \frac{1}{kC_{A0}^{n} R_0^3} \int_{R_f}^{R_0} \frac{dR}{\left[1+\left(\frac{R_f}{R_0}\right)^3 - \left(\frac{R}{R_0}\right)^3\right] R^{\alpha-3}}$$

For complete reaction of particle $\underline{R_f = 0}$

$$\frac{W_{T\,comp}}{\dot{m}_{B0}} = \frac{1}{kC_{A0}^{n}} \int_0^{R_0} \frac{dR}{\left(R_0^3 - R^3\right) R^{\alpha-3}}$$

$$= \frac{1}{kC_{A0}^{n}} \int_0^{R_0} \frac{dR}{\left(R_0^3/R^3 - 1\right) R^{\alpha}}$$

CCF-4

Compare cocurrent and countercurrent

let $r = \frac{R}{R_0} \leq 1$

$$\frac{dR}{R^\alpha} = \frac{R_0\, dr}{R_0^\alpha\, r^\alpha} = R_0^{1-\alpha} \frac{dr}{r^\alpha}$$

<u>COCURRENT FLOW</u> (REACTOR SIZE FOR COMPLETE CONVERSION)

$\underline{\beta = 1}$ slack

$$\frac{W_{CF\,comp}}{\dot{m}_{B0}} = \frac{R_0^{1-\alpha}}{k C_{A0}^n} \int_0^1 r^{-\alpha}\, dr = \frac{R_0^{1-\alpha}}{k C_{A0}^n (1-\alpha)}$$

<u>COUNTERCURRENT FLOW</u>

$$\frac{W_{CCF\,comp}}{\dot{m}_{B0}} = \frac{R_0^{1-\alpha}}{k C_{A0}^n} \int_0^1 \frac{r^{-\alpha}\, dr}{\left(\frac{1}{r^3} - 1\right)} = \frac{R_0^{1-\alpha}}{k C_{A0}^n} \int_0^1 \frac{r^{3-\alpha}\, dr}{1 - r^3}$$

but $\frac{1}{r} \geq 1$ $\quad \frac{1}{r} - 1 > 0$

$0 \leq r \leq 1$

$$\frac{W_{CCF\,comp}}{\dot{m}_{B0}} = \frac{R_0^{1-\alpha}}{k C_{A0}^n} \int_0^1 r^{3-\alpha} \sum_{n=0}^{\infty} (r^3)^n\, dr$$

$$= \frac{R_0^{1-\alpha}}{k C_{A0}^n} \int_0^1 \sum_{n=0}^{\infty} r^{3n+3-\alpha}\, dr$$

$$= \frac{R_0^{1-\alpha}}{k C_{A0}^n} \sum_{n=0}^{\infty} \left(\frac{1}{3n+4-\alpha}\right)$$ not convergent?

$$\frac{W_{CCF\ cum}}{\dot{m}_{B0}} = \frac{R_0^{1-\alpha}}{kC_{A0}^{\ n}}\left[\frac{1}{4-\alpha} + \frac{1}{7-\alpha} + \frac{1}{10-\alpha} + \frac{1}{13-\alpha} + \frac{1}{16-\alpha} + \cdots\right]$$

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Look again

$$\frac{W_{T\ cum}}{\dot{m}_{B0}} = \frac{R_0^{1-\alpha}}{kC_{A0}^{\ n}}\int_0^1 \frac{R^{3-\alpha}}{1-R^3}\,dR$$

~~Let $(1-R^3) = x$~~ $\quad x = R^3 \qquad dx = 3R^2\,dR$

$R = x^{1/3} \qquad dR = \frac{1}{3}\frac{1}{x^{2/3}}\,dx$

$$\int_0^1 \frac{R^{3-\alpha}}{1-R^3}\,dR = \int_0^1 \frac{(x^{1/3})^{(3-\alpha)}\,dx}{3\,x^{2/3}(1-x)} = \frac{1}{3}\int_0^1 \frac{x^{1-\frac{\alpha}{3}}}{x^{2/3}(1-x)}\,dx$$

$$= \frac{1}{3}\int_0^1 \frac{x^{1/3-\alpha/3}}{1-x}\,dx$$

$$= \frac{1}{3}\int_0^1 \frac{x^{(1/3-\alpha/3)}}{1-x}\,dx = \frac{1}{3}\int_0^1 \frac{x^{\frac{1-\alpha}{3}}}{1-x}\,dx = \frac{1}{3}\int_0^1 x^{\frac{1-\alpha}{3}}\sum x^{3}\,dx$$

$$= \frac{1}{3}\int_0^1 \sum x^{\frac{3n+1-\alpha}{3}}\,dx = \cancel{\frac{1}{3}}\sum \frac{\cancel{3}\ 1}{3n+4-\alpha}$$

The problem is that at $W=0$ fresh solids at $R=R_0$, $X_B=0$ meet totally reacted gas at $\beta=1$, i.e. $C_A=0$. This occurs at the reactor end entrance for solids

$$\left.\frac{dR}{dt}\right|_{W=0} = -0 \quad \text{or} \quad \frac{dt}{dR} = \infty \, !$$

If we do not quite react the solids completely then the problem is doable, say $\frac{R_f}{R_0} = \epsilon$ $(\epsilon \ll 1, \epsilon > 0)$ then $X_{Bf} = 1 - \epsilon^3$

$$\frac{W_T}{\dot{m}_{B0}} = \frac{R_0^{1-\alpha}}{k C_{A0}^{n}} \int_{\epsilon}^{1} \frac{r^{3-\alpha}\, dr}{(1+\epsilon^3 - r^3)}$$

and there is no singularity at $r=1$

Alternatively we can take $bF_{A0} > aF_{B0}$ say slight excess $\beta = 1-\epsilon$

$$\frac{WT}{\dot{m}_{B0}} = \frac{R_0^{1-\alpha}}{k C_{A0}^{n}} \int_{r_f}^{1} \frac{r^{3-\alpha}\, dr}{(1+\beta r_f^3 - \beta r^3)}$$

Now we can take $r_f = 0$ if $\beta = 1-\epsilon$

$$\frac{WT}{\dot{m}_{B0}} = \frac{R_0^{1-\alpha}}{k C_{A0}^{n}} \int_{0}^{1} \frac{r^{3-\alpha}\, dr}{1-(1-\epsilon) r^3}$$

and there is no singularity at $r=1$