

Ch. 01 : Residence time distribution (RTD)

(with microfluidic assumption)

Why study RTD?

- Any dead region?
- Recirculation
- Find a suitable model to represent flow.

Experiment? pulse injection \rightarrow PFR

Step injection \rightarrow CSTR

$$\tau = \frac{V}{Q}$$

$$E\text{-function} \rightarrow E(t) = \frac{C(t)}{\int_0^\infty C(t) dt} = \frac{C(t)}{V/Q}$$

(Direct from pulse experiment)
Describe RTD curve

$$F\text{-function} \rightarrow F(t) = \int_0^t E(\tau) d\tau$$

CDF \rightarrow Step injection

$$E(q) = \frac{dF(t)}{dt}$$

$$F(0) = 0$$

$$\lim_{q \rightarrow \infty} F(t) = 1$$

$$t\text{-mean: } t_{\text{mean}} = \int_0^\infty t E(t) dt$$

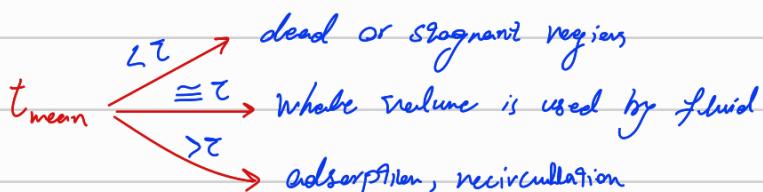
$$\text{Variance: } \sigma^2 = \int_0^\infty t^2 E(t) dt - t_{\text{mean}}^2$$

RTD for PFR: $t_{\text{mean}} = \tau$, $\sigma^2 = 0$, $F(t) = H(t)$

$$[E(t) = \delta(t-\tau)]$$

RTD for CSTR: $t_{\text{mean}} = \tau$, $\sigma^2 = \tau^2$, $F(t) = 1 - \exp(-\frac{t}{\tau})$

$$[E(t) = \frac{\exp(-\frac{t}{\tau})}{\tau}]$$



CSTR with Dead Zone

$$V = V_{dead} + V_{active} \Rightarrow V_{active} = (1-\beta)V$$

Effective space time: $\tau_{eff} = \frac{(1-\beta)V}{Q} = (1-\beta)\tau$

Thus, the E-function will be: $E(t) = \frac{\exp\left(-\frac{t}{\tau_{eff}}\right)}{\tau_{eff}} = \frac{1}{1-\beta} \frac{1}{\tau} \exp\left(-\frac{t}{\tau}\right)$

$$F(t) = 1 - \exp\left(-\frac{t}{\tau_{eff}}\right)$$

Dispersion Model \Rightarrow Deviating from PFR behavior

Assumptions \leadsto Diffusion Analogy - Monodimensional

$$\text{Mass-balance eq.} \Rightarrow \frac{\partial c_i}{\partial t} = -V \frac{\partial c_i}{\partial z} + D_{eff} \frac{\partial^2 c_i}{\partial z^2}$$

γ_{pe}

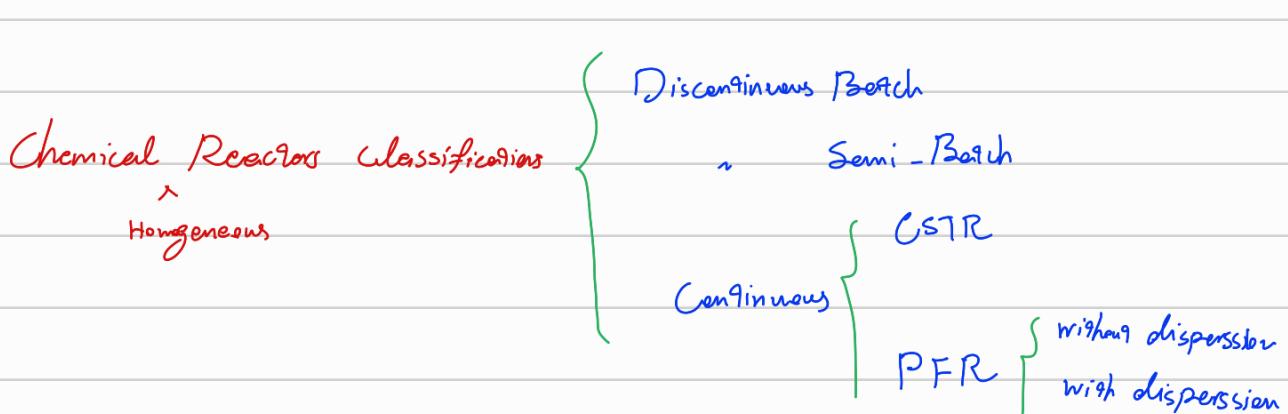
$$\Rightarrow \frac{\partial \psi_i}{\partial t} = -\frac{\partial \psi_i}{\partial z} + \boxed{\frac{D_{eff}}{L_V}} \frac{\partial^2 \psi_i}{\partial z^2}$$

$$\text{Dimensionless vars.} \Rightarrow Q = \frac{V}{L}, \quad \tau = \frac{t}{\tau}, \quad \zeta = \frac{z}{L}, \quad \Psi = \frac{c_i}{c_{i,0}}$$

Peclet Number \Rightarrow Spreading caused of molecular diffusion.

B.C  Open boundary: Undistributable \Rightarrow enter and leave more than one!
 Close boundary: Plug flow outside the vessel!

Ch. 02: Homogeneous Reactor analysis and design



Mass Balance in Batch Reactor: $\frac{dc_i}{dt} = R_i$, $R_i = \sum_{j=1}^{NR} V_{ij} r_j$ (for ideal gas)

Mass Balance in Semi-Batch Reactor: $\nabla \frac{dp_i}{dz} = \sum_{j=1}^{NR} V_{ij} r_j M M_i \nabla + (\rho_{in} - \rho) Q_{in}$

Mass Balance in CSTR Reactor: $C_{i,0} - C_i + R_i \tau = 0$
(with constant volumetric flow)

Mass Balance in PFR without dispersion: $-\rho \nabla \frac{dw_i}{dz} + \sum_{j=1}^{NR} V_{ij} r_j M M_i = 0$

velocity

B.C @ Z = 0

Mass Balance in PFR with axial dispersion:

$$-\rho \nabla \frac{dw_i}{dz} + M M_i D_{eff} \frac{d}{dz} \left(\frac{1}{RT} \frac{\partial p_i}{\partial z} \right) + \sum_{j=1}^{NR} V_{ij} r_j M M_i = 0$$

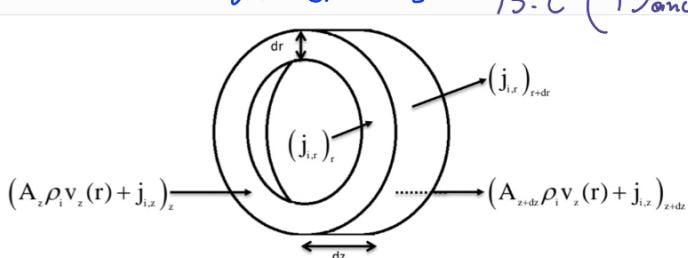
B.C (Dankwerts): $\rho v w_i|_0 = \rho v w_i|_{o+} - M M_i D_{eff} \left(\frac{1}{RT} \frac{\partial p_i}{\partial z} \right)|_{o+}$

$$@ Z = L \Rightarrow \frac{dw_i}{dz} = 0$$

If we have the isothermal condition, the mass balance will be as follows:

$$-\nabla \frac{dc_i}{dz} + D_{eff} \frac{d^2 c_i}{dz^2} + R_i = 0$$

Mass Balance in PFR with radial dispersion



B.C (Dankwerts): $\left. \alpha_z(r) \rho \right|_0 = \left. \alpha_z(r) \rho \right|_{o+} - M M_i D_{eff} \left(\frac{1}{RT} \frac{\partial p_i}{\partial z} \right)|_{o+}$

$$@ Z = L \Rightarrow \frac{\partial p_i}{\partial z} = 0$$

$$@ r = R \Rightarrow \frac{\partial p_i}{\partial r} = 0$$

$$@ r = 0 \Rightarrow \frac{\partial p_i}{\partial r} = 0$$

$$-\nabla_z (r) \frac{\partial p_i}{\partial z} + M M_i D_{eff} \frac{\partial}{\partial z} \left(\frac{1}{RT} \frac{\partial p_i}{\partial z} \right) + M M_i D_{eff} \frac{\partial}{\partial r} \left(\frac{1}{RT} \frac{\partial p_i}{\partial r} \right) + \sum_{j=1}^{NR} V_{ij} r_j M M_i = 0$$

In case of isothermal condition: $-\nabla_z (r) \frac{\partial c_i}{\partial z} + D_{eff} \frac{d^2 c_i}{dz^2} + D_{eff} \frac{1}{r} \frac{\partial c_i}{\partial r} \left(r \frac{\partial c_i}{\partial r} \right) + R_i = 0$

Energy Balance in Batch reactor:

$$\rho V \hat{C}_p \frac{dT}{dt} + \rho V \left(\hat{V} - T \left. \frac{d\hat{V}}{dT} \right|_{P_{in,i}} \right) \frac{dP}{dt} - \rho V P \frac{d(\frac{1}{P})}{dt} - V \frac{dP}{dt} = \dot{Q}_{ext} - \dot{Q}_R$$

o (for ideal gas)

$$\dot{Q}_R = \sum_1^{NC} \frac{\bar{H}_i R_i}{\rho}$$

Energy Balance in Semi-Batch reactor:

$$\rho V \left[\hat{C}_p \frac{dT}{dt} + \left(\hat{V} - T \left. \frac{d\hat{V}}{dT} \right|_{P_{in,i}} \right) \frac{dP}{dt} + \sum_1^{NC} \bar{H}_i \frac{1}{m_{in,i}} \frac{dw_i}{dt} - P \frac{d(\frac{1}{P})}{dt} - \frac{1}{P} \frac{dP}{dt} \right] = \dot{Q}_{ext} + (\hat{H}_{in} - \hat{H}) \rho_{in} \dot{Q}_{in}$$

o (for ideal gas)

proper initial condition @ $t=0$

Energy Balance in CSTR reactor: $(\dot{H}_o - \dot{H}) + \dot{Q}_{ext} = 0$

$$\dot{H}_o = \sum_{i=1}^{NC} \bar{H}_i (T_o, P_o, n_o) \dot{n}_{i,o}, \quad \dot{H} = \sum_{i=1}^{NC} \bar{H}_i (T, P, n) \dot{n}_i$$

Energy Balance in PFR:

$$-\rho V \hat{C}_p \frac{dT}{dz} - \rho V \left(\hat{V} - T \left. \frac{d\hat{V}}{dT} \right|_{P_{in,i}} \right) \frac{dP}{dz} - \rho V \sum_{j=1}^{NR} \Delta \bar{H}_{R,j} r_j + \dot{Q}_{ext} = 0$$

o (for ideal gas)

Energy Balance in PFR with axial dispersion:

$$-\rho V \left(\hat{C}_p \frac{dT}{dz} + \left(\hat{V} - T \left. \frac{d\hat{V}}{dT} \right|_{P_{in,i}} \right) \frac{dP}{dz} + \sum_{j=1}^{NC} \bar{H}_i \frac{1}{m_{in,i}} \frac{dw_i}{dz} \right) + \lambda_{eff} \frac{d^2 T}{dz^2} + \dot{Q}_{ext} = 0$$

$$B.C \text{ (Dankwerts)}: \rho V \hat{H} \Big|_0 = \rho V \hat{H} \Big|_{L+} - \lambda_{eff} \frac{dT}{dz} \Big|_{L+}$$

$$@ z=L \Rightarrow \frac{dT}{dz} = 0$$

Energy Balance in PFR with radial dispersion:

$$-\rho V_z(r) + \left[\hat{C}_p \frac{\partial T}{\partial z} + \left(\hat{V} - T \left. \frac{d\hat{V}}{dT} \right|_{P_{in,i}} \right) \frac{\partial P}{\partial z} + \sum_{i=1}^{NC} \bar{H}_i \frac{1}{m_{in,i}} \frac{\partial w_i}{\partial z} \right] + \lambda_{eff} \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) = 0$$

$$B.C \text{ (Dankwerts)}: \rho V_z(r) \hat{H} \Big|_0 = \rho V_z(r) \hat{H} \Big|_{L+} - \lambda_{eff} \frac{\partial T}{\partial r} \Big|_{L+}$$

$$@ z=L \Rightarrow \frac{\partial T}{\partial z} = 0, @ r=0 \Rightarrow \frac{\partial T}{\partial r} = 0, @ r=R \Rightarrow -\lambda_{eff} \frac{\partial T}{\partial r} = \dot{Q}_{ext}$$

Pressure profile in tubular homogeneous reactor

There's always some pressure drop inside the reactor!

Euler and fanning equation: $-\frac{dp}{dr} = \rho g \frac{dv}{dz} + 2f \rho \frac{v^2}{d_{\text{tube}}}$

$$Re = \frac{\rho v D}{\mu}$$

if $< 2100 \rightarrow f = 16/\rho e$
 if $2100 < Re < 40000 \rightarrow f = 0.0791^{-0.25}$
 else \rightarrow Fanning diagram



$$\text{Conversion of } A (\chi_A) = \frac{n_{A_0} - n_A}{n_{A_0}}$$

$$\text{Selectivity of } C (\sigma_{A \rightarrow C}) = \frac{\gamma}{\alpha} \frac{n_C - n_{C_0}}{n_A - n_{A_0}}$$

$$\text{Yield of } C (\xi_{A \rightarrow C}) = \chi_A \cdot \sigma_{A \rightarrow C}$$

examples of reaction $A \rightarrow B \rightarrow C$ = partial oxidation - production of  - Alkylation

for the large scale production \rightarrow Continuous reactors

optimum residence time $\rightarrow T_m \Rightarrow$ maximum yield of wanted product.

PFR \Rightarrow higher yield \Leftrightarrow CSTR \Rightarrow lower yield

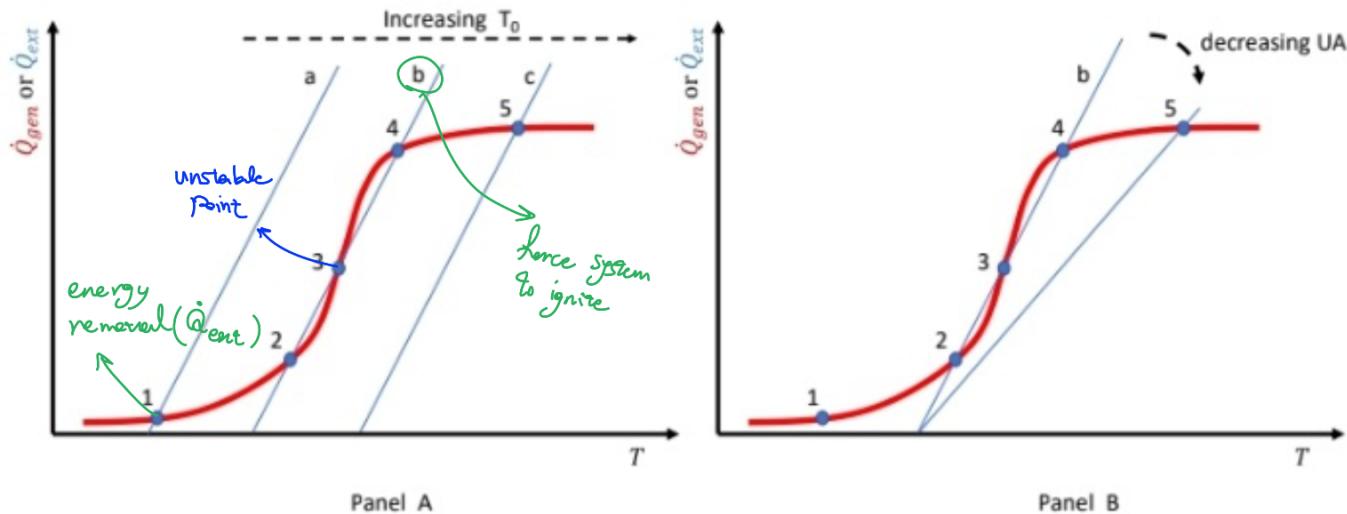


Figure 1. Heat generation and heat removal for a CSTR with an exothermic reaction.

Stability criteria: $\frac{d\dot{Q}_{\text{gen}}}{dT} < \frac{d\dot{Q}_{\text{ext}}}{dT}$

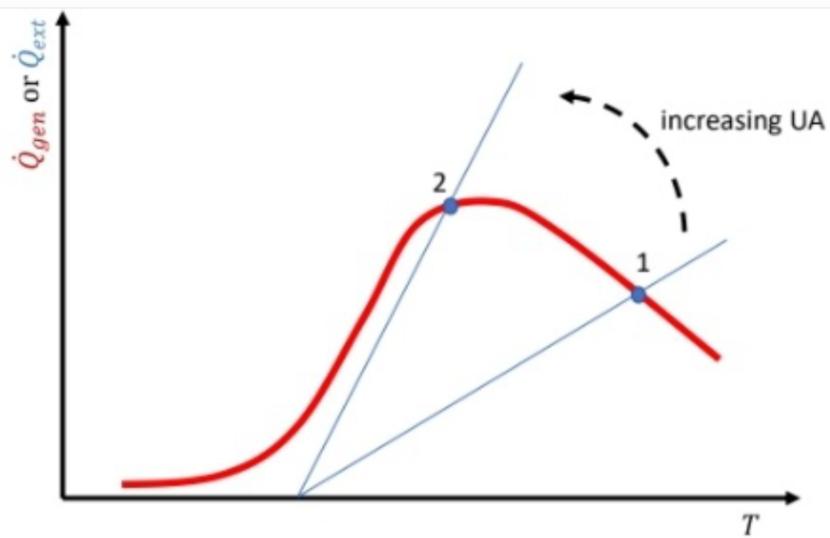


Figure 2 . Heat generation and heat removal for a CSTR with an exothermic reversible reaction.

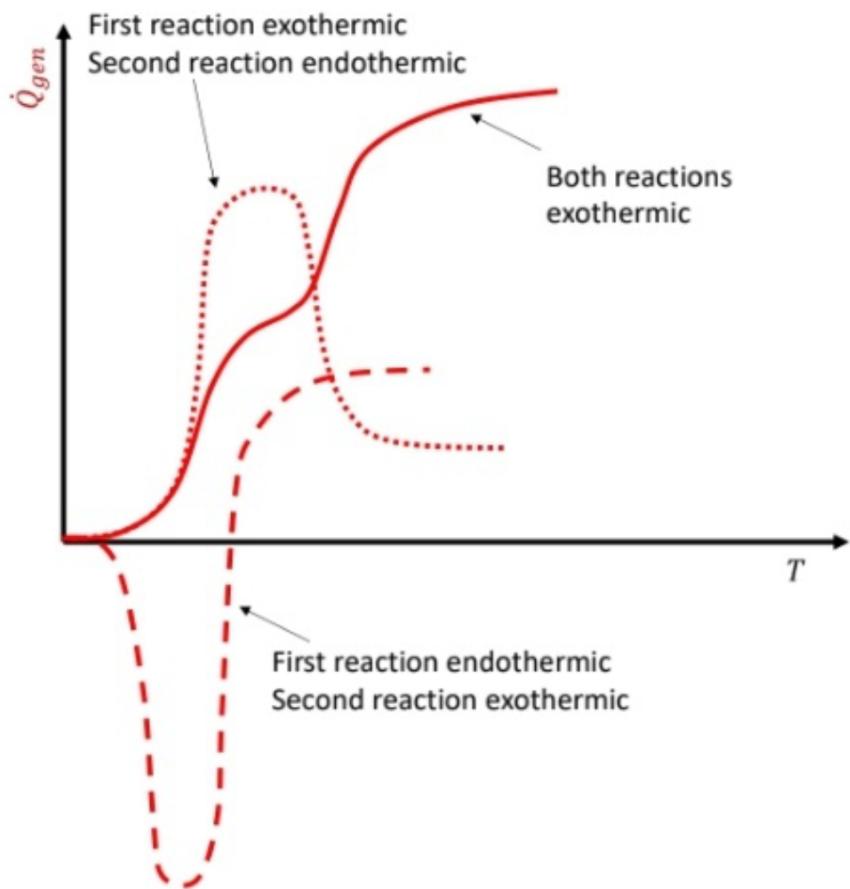
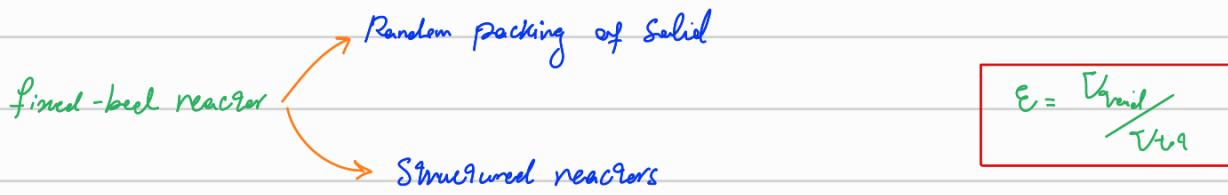


Figure 3. Heat generation curve for two consecutive reactions.

Ch. 03 : Heterogeneous Reactor Analysis and design

Gas - Solid Catalytic reactions \rightarrow Presence of active sites supported on a solid phase where reaction occurs.

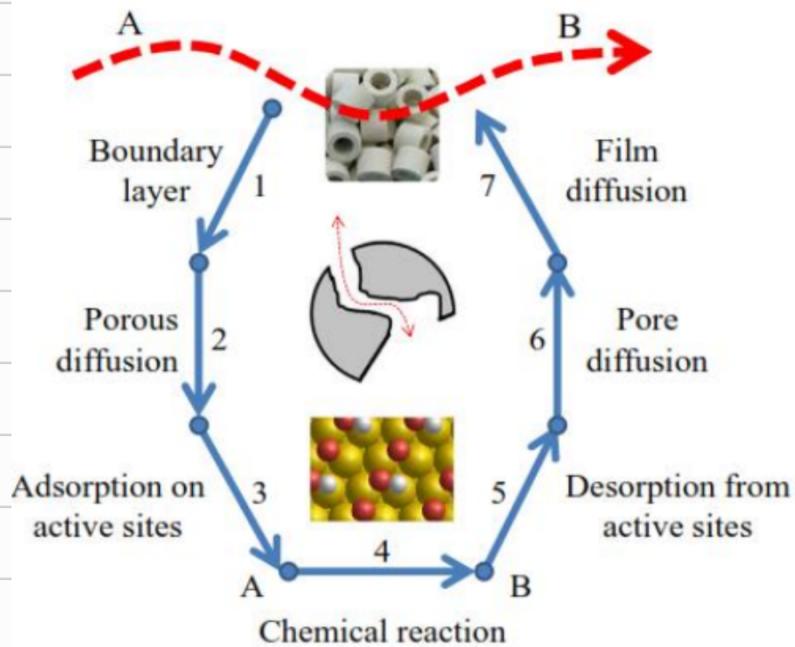


$$\epsilon = \frac{V_{solid}}{V_{tot}}$$

Arrangement type \downarrow

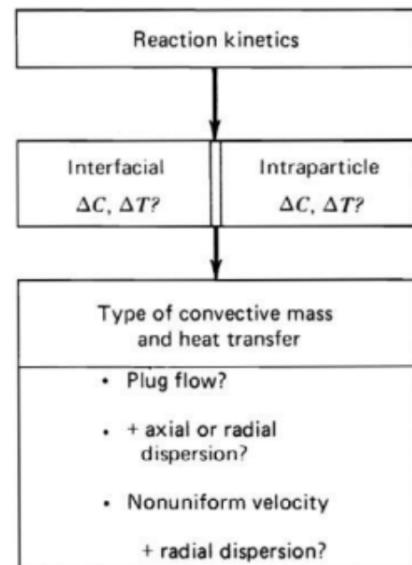
More Solid \rightarrow More interface \approx Surface per unit of vol. $\Rightarrow \alpha_v = \frac{S_{solid}}{V}$

Physical and chemical phenomena in a heterogeneous reactor:



FBR Classification

Microscale	Catalyst site
	Catalyst particle
Macroscale	Reactor



External gradient

exclude \Rightarrow Pseudo homogeneous model

include \Rightarrow heterogeneous model

Pseudo Homogeneous Model

Assumption: Concentration and Temperature gradients just in axial direction

Mass Balance for Piling flow: $\frac{d\dot{m}_i}{dV} + \sum_{j=1}^{NR} V_{ij} r_j M M_i (1-\varepsilon) \rho_{car} = 0$

I.C.: $\text{at } V=0 \Rightarrow \dot{m}_i = \dot{m}_{i,0} \quad \forall i = 1, 2, \dots, NC$

Energy Balance for Piling flow:

$$\frac{1}{U} = \frac{1}{\alpha_{ID}} + \frac{t_{tube}}{\alpha_{shell}} \frac{A_{internal}}{A_{log-mean}} + \frac{1}{\alpha_{shell}} \frac{A_{internal}}{A_{external}}$$

(Reactor can exchange energy with surrounding)

(Assume ideal gas)

$$-\dot{m} \hat{C}_p \frac{dT}{dV} - \sum_{j=1}^{NR} r_j \bar{\Delta H}_{R,j} (1-\varepsilon) \rho_{car} + U (T_{ext} - T) a_{heat,V} = 0$$

I.C.: $\text{at } V=0 \Rightarrow T=T_0$

The Heterogeneous Model

No. of trans. = $NC + 1 \Rightarrow$ No. of eqns. = $2(NC+1)$

Gas-Solid flow: $\omega_{m,i} = k_i (\rho_{i,s} - \rho_{i,g})$ heat transfer coeff for mass
 (Macroscopic) $\omega_{h,i} = h (T_s - T)$ heat transfer coeff for mass

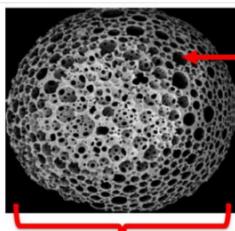
Mass Balance: $-\frac{d\dot{m}_i}{dV} + k_i (\rho_{i,s} - \rho_{i,g}) a_V = 0$

Energy Balance: $\sum_{j=1}^{NR} V_{ij} r_j M M_i (1-\varepsilon) \rho_{car} + k_i (\rho_{i,g} - \rho_{i,s}) a_V = 0$

Modeling the transport inside the Catalyst \Rightarrow Species transport properties are determined as

non-confined env. \Rightarrow Overall effect for structure and local effect for pores

local tortuous for
catalyst



Diffusion and interaction between gas and pores (local)

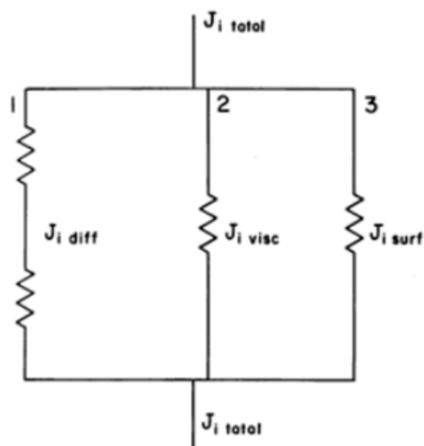
Effect of the structure (overall)

Transport of species in porous media

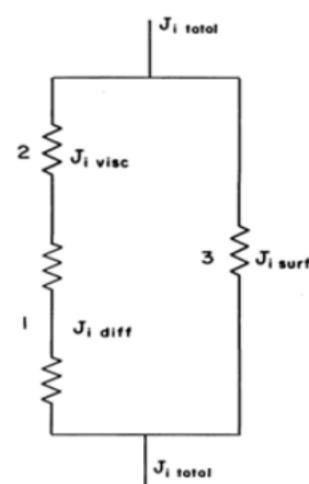
Diffusive species transport: Species flow generated by diffusive driving force

Viscous flow: Additional species of viscous flow due to the pressure gradient inside the catalyst.

Surface Diffusion: flow of molecules along the wall of the Catalyst Pore in an adsorbed layer.



Mason



Kerkhof

- I: DIFFUSIVE - FLOW BRANCH
2: VISCOUS - FLOW BRANCH
3: SURFACE - FLOW BRANCH

Diffusion Regime { Knudsen Regime (Dominant in small pores)
(Assume creeping flow) Continuum Regime (Kn << 1)

$$Kn = \frac{\lambda}{dp} \quad \begin{array}{l} \text{free path of gas molecule} \\ \text{Pore diameter} \end{array}$$

Diffusion Coeff. for intermediate pore size: $\frac{1}{D_i} = \frac{1}{D_{ic}} + \frac{1}{D_{ikn}}$



a) CONTINUUM REGIME (Kn << 1)



b) KNUDSEN REGIME (Kn >> 1)

Transport of species in adsorbed layer (for pore that $d_p < 2 \text{ nm}$)

Molecule is ready to jump into an active site

Jump into adjacent vacancy

Size that is covered by another molecule

Fail to jump \leftrightarrow all the adjoining sites are occupied

Effect of the structure on the transport properties in porous media

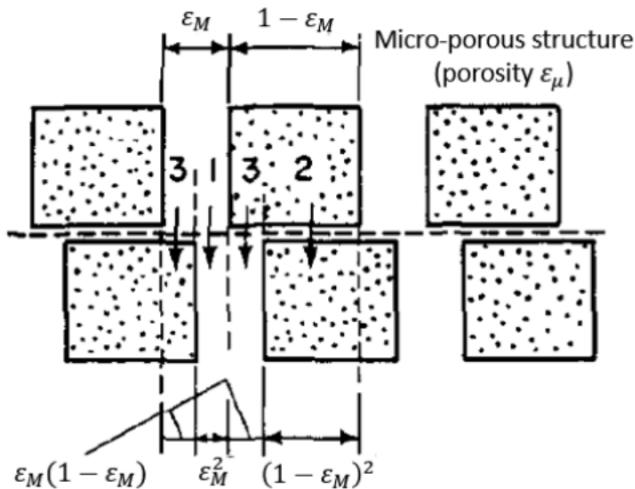
E/T model: assume avg. Pore diameter

Random Pore model: bimodal distribution of pore sizes.

Effective Diffusing

$E/T \text{ model: } D_{i,\text{eff}} = \frac{\varepsilon_i}{2} D_i$

$\text{Random Pore model: } D_{i,\text{eff}} = \varepsilon_m^2 D_i^m + \frac{\varepsilon_\mu^2 (1+3\varepsilon_m)}{1-\varepsilon_m} D_i^M$



Schematic representation of the catalyst structure according to Wakao and Smith.

Diffusion film across the Catalyst Structure

Diffusion in macro pores

~ ~ ~ micro ~

~ through ~ and macro pores in series

Modeling transport and reaction in porous media

Assume porous media as pseudo-homogeneous material

~ isothermal condition

Mass Balance

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 D_{i,\text{eff}} \frac{1}{r^2} \frac{dp_i}{dr} \right) +$$

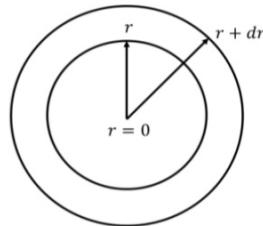


Figure 1. Spherical shell.

$$\sum_{i=1}^{NR} \alpha_{i,j} r_j p_{car} = 0$$

$$\text{B.C. } @ r=R \Rightarrow P_i = P_{i,0}, @ r=0 \Rightarrow \frac{dp_i}{dr} = 0$$

$$\text{in Case of isothermal Condition: } D_{i,\text{eff}} \frac{1}{r^2} \left(r^2 \frac{dc_i}{dr^2} \right) + \sum_{i=1}^{NR} \alpha_{i,j} r_j p_{car} = 0$$

Effectiveness factor : $\eta = \frac{\int_0^V r(V) dV}{V - V_{\text{Surface Condition}}}$ 1st order kinetics $\rightarrow \eta = \frac{3}{\varphi} \frac{\varphi \coth(\varphi) - 1}{\varphi}$

$\varphi = R \sqrt{\frac{k_r p_{car}}{D_{i,\text{eff}}}}$ Thiele modulus

$$\text{Energy Balance } \frac{1}{r^2} \frac{d}{dr} \left(r^2 \lambda_{eff} \frac{dT}{dr} \right) - P_{car} \sum_{j=1}^{NR} r_j \bar{\Delta H}_{R,j} = 0$$

$$\text{B.C.: } @ r=R \Rightarrow T = T_0, @ r=0 \Rightarrow \frac{dT}{dr} = 0$$

Estimation of the temp. gradients inside a catalyst pellet

$$\frac{(T_{r=R} - T(r))}{T_{r=R}} = \frac{(-\bar{\Delta H}_R) D_{i,\text{eff}}}{\lambda_{eff} T_{r=R}} \left(C_{i,r=R} - C_i(r) \right)$$

$$\text{Max. Temp. difference } @ C_i(r) = 0 \Rightarrow \frac{\Delta T_{max}}{T_{r=R}} = \frac{(-\bar{\Delta H}_R) D_{i,\text{eff}}}{\lambda_{eff} T_{r=R}} C_{i,r=R} = \beta \quad \text{Prater modulus}$$

Random Packed-Bed Reactors

Void fraction \Rightarrow Type of packing

Very loose : $\varepsilon_b = 0.44$
Loose : $\varepsilon_b = 0.4 - 0.41$
Packed : $\varepsilon_b = 0.375 - 0.391$
Dense : $\varepsilon_b = 0.359 - 0.375$

Height near wall need another expression, because many factors are influencing it such as pressure drop, permeability, fluid hold-up, linear velocity, RTD

$$\varepsilon = \varepsilon_b + 0.39 \exp\left(-0.35 \frac{d_t}{dp}\right)$$

internal tube diameter
particle diameter

Measure bulk height

Water displacement

Weighing a known packing trial \Rightarrow have pellets of very regular shapes.

Surface per unit of volume

$$a_V = \frac{S_{\text{solid}}}{V} = \frac{S_{\text{solid}}}{\frac{V_{\text{solid}}}{1-\varepsilon}}$$

sphere $\rightarrow a_V = \frac{n \pi d_p^2}{n \pi / 6 d_p^3} (1-\varepsilon) = \frac{6}{d_p} (1-\varepsilon)$

F_s (exerted by fluid even in stationary mode)

friction factor

F_K (associated with the motion of the fluid and that moves in the same direction as the avg. velocity in the column) $\Rightarrow F_K = A K f$

Area Kinetic energy friction factor

friction factor
in a tube

$$F_s = [(P_0 - P_L) + \rho g (h_0 - h)] \pi R^2 = (P_0 - P_L) \pi R^2$$

$$F_K = 2 \pi R L \frac{1}{2} \rho v^2 f$$

$$f = \frac{1}{4} \frac{D_h}{L} \frac{(P_0 - P_L)}{\frac{1}{2} \rho V^2}, \quad f = f(Re)$$

for non-circular tube: $f = \frac{1}{4} \frac{D_h}{L} \frac{(P_0 - P_L)}{\frac{1}{2} \rho V^2} = \frac{1}{4} \frac{R_h}{L} \frac{(P_0 - P_L)}{\frac{1}{2} \rho V^2}$

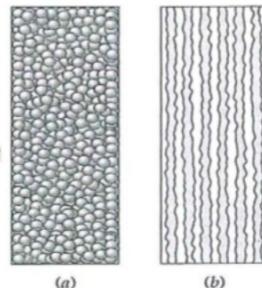


Figure 5. Conceptual model: the packed bed (a) is visualized as a bundle of tangled tubes of weird cross-section (b).

$$f_{tube} = f_{1/2}$$

friction factor for a packed bed of particles: $f_{pb} = \frac{1}{4} \frac{dp}{L} \frac{(P_0 - P_L)}{\frac{1}{2} \rho V_0^2} = \frac{1}{4 \varepsilon^2} \frac{dp}{R_h} f_{tube}$

$$\frac{\varepsilon}{\varepsilon - 1} \times \frac{dp}{6}$$

turbulent condition

laminar condition

Bailey-Kozey equation (laminar): $\frac{(P_0 - P_L)}{L} = 150 \times \frac{(1-\varepsilon)^2}{\varepsilon^3} \frac{\mu V_0}{dp^2}$

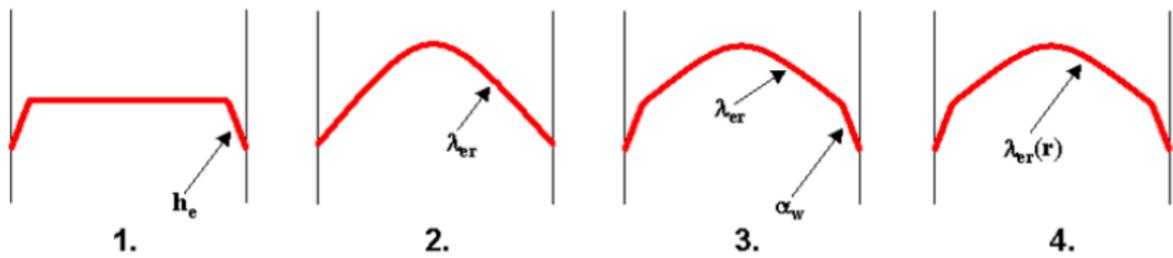
$$f_{tube} = \frac{100}{3} \frac{1}{Re_h}$$

Engen equation (transient): $\frac{(P_0 - P_L)}{L} = 150 \frac{(1-\varepsilon)^2}{\varepsilon^3} \frac{\mu u}{dp^2} + \frac{7}{4} \frac{(1-\varepsilon)}{\varepsilon^3} \frac{f V_0^2}{dp}$

Burke-Pilippen (turbulent): $\frac{(P_0 - P_L)}{L} = \frac{7}{4} \frac{(1-\varepsilon)}{\varepsilon^3} \frac{f V_0^2}{dp}$

→ Corrected form for change pressure drop: $-\frac{dp}{dz} = 150 \frac{(1-\varepsilon)^2}{\varepsilon^3} \frac{\mu u}{dp^2} + \frac{7}{4} \frac{(1-\varepsilon)}{\varepsilon^3} \frac{f V_0^2}{dp}$

- External Heat Transfer in PBR
- 1) 1D model $\Rightarrow \alpha_{1D}$
 - 2) 2D model with a constant parameter \Rightarrow radial λ_{er}
 - 3) 2D model with 2 parameters $\Rightarrow \lambda_{er}, \alpha_w$
 - 4) $\alpha_w \sim 1 \sim \text{and another one is function of radial position} \Rightarrow \lambda_{er}(r)$



2D model with 2 parameters

effective conduction \Rightarrow effective thermal conductivity ($\lambda_{e,r}$) \Rightarrow Static \rightarrow absence of flow
 \Rightarrow adiabat of the wall (α_w) \Rightarrow Dynamic \rightarrow related to the flow passing through packing

$$\lambda_{e,r} = \lambda_{s,r} + \lambda_{d,r}$$

$= \epsilon \rho C_p g D_{eff}$

Transpor through the fluid in the voids

in which the solid phase is involved

$$\frac{\lambda_{e,r}}{\lambda_g} = \frac{1}{Pr \cdot Re} \lambda_{e,r}^{Pr}$$

fixing experimental data

1D model with 1 parameter

$$\alpha_{1D} = \frac{\alpha_w}{1 + \frac{1}{A} \left(\frac{\alpha_w \alpha_{d,r}}{\lambda_{e,r}} \right)}$$

$$A = \frac{6(Bi+4)}{Bi+3}$$

Gas - Solid transport coeff.

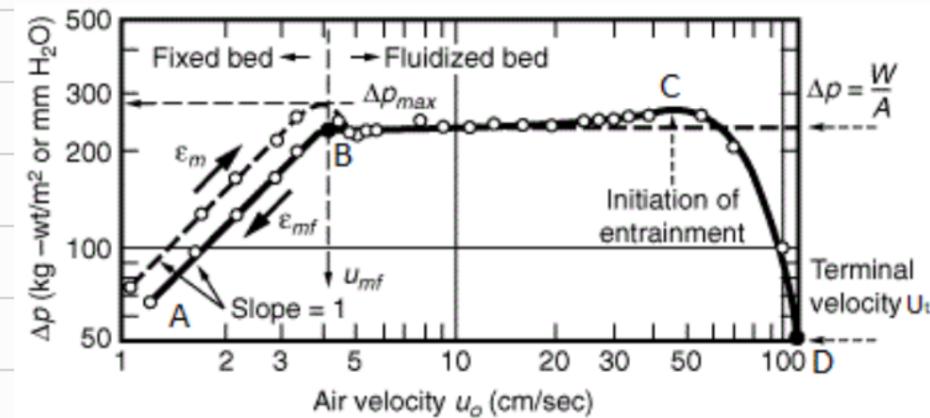
j_r Parameter : developed by Colburn for gas film $\Rightarrow j_m = \frac{Sh}{Re Sc^{1/3}}$, $j_h = \frac{Nu}{Re Pr^{1/3}}$

External Diffusion limit of the reactor : assume reaction is faster than external transport rate ($P_{i,s} \rightarrow P_{i,s,eq}$)
 $(k_i \ll k_r)$

$$-\frac{d\ln i}{dx} + k_i (P_{i,s,eq} - P_{i,g}) a_V = 0$$

Filmed bed reactors

A vertical unit where gas phase injected from the bottom by means of a distributor!



$A \rightarrow B$: fixed head configuration

$B \rightarrow C$: Fluidized bed without solid entrainment

C → D: fluidized bed with plumbate entrainment

$D \rightarrow \infty$: empty vector

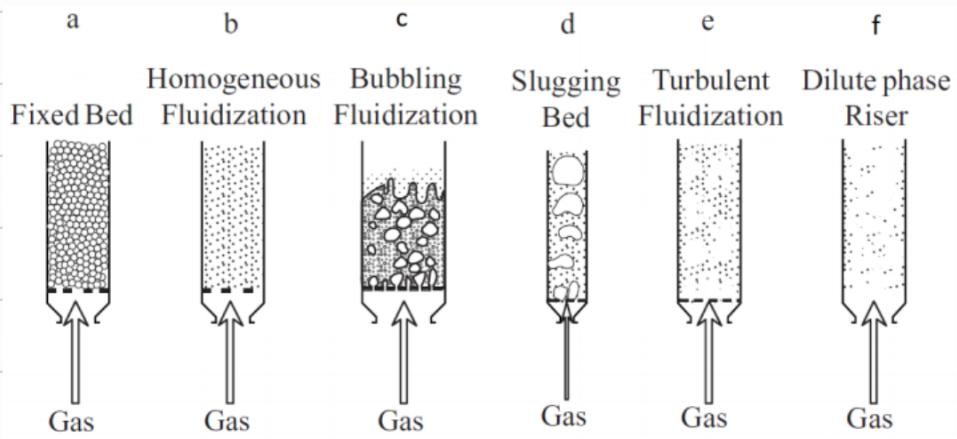
Min. fluidization velocity (V_{mf}) : equality of gas force and drag force at the inner superficial velocity.

Case : $U_0 < \text{min. fluidization velocity} \Rightarrow$ Calculating ΔP using Ergun equation.

$$\Delta P = \left[\frac{150(1-\varepsilon)^2 \rho_{gas}}{D_p^2 \rho_s \varepsilon^2} q_v + \frac{1.75 \rho_{gas}(1-\varepsilon)}{D_p \rho_s \varepsilon^3} q_v^2 \right] \text{ (H) } \xrightarrow{\text{avg. height of bed}}$$

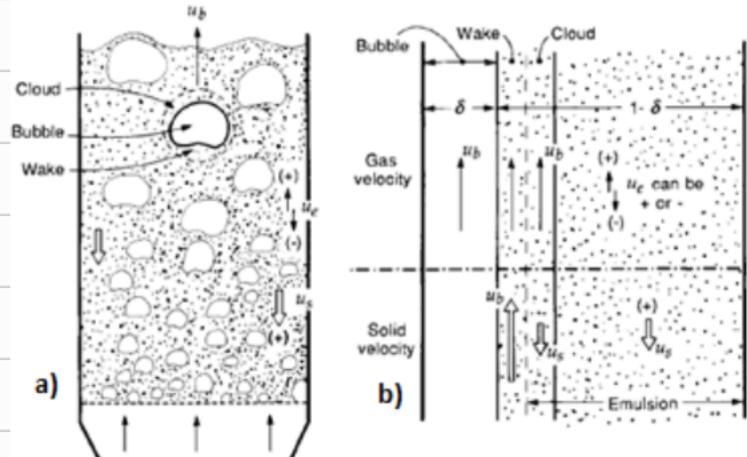
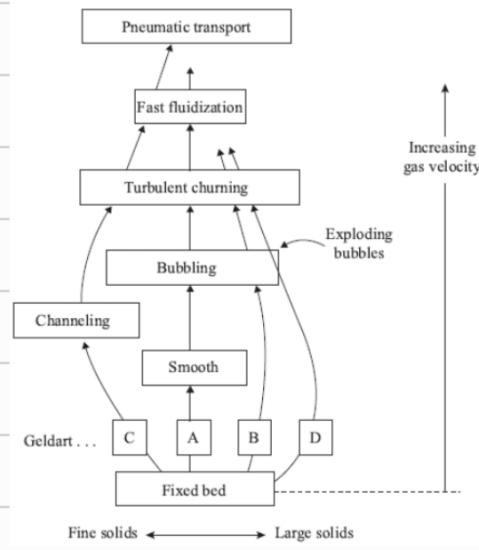
$$\rightarrow \text{if } V_0 = \text{min. fluidization velocity} \Rightarrow \Delta P_{\text{fluidizieren}} = \frac{W}{A} = \frac{\rho_{\text{solid}} (1-\varepsilon) \nu g}{A}$$

$$\text{Upper limit of fluidization} = \text{Terminal velocity} \Rightarrow V_g = \sqrt{\frac{4dp(p_s - p)g}{3\rho C_d}}$$



• Regimes of fiberization ..

Fluidized behaviors
in the function of the
Geldart group as
increasing gas velocity



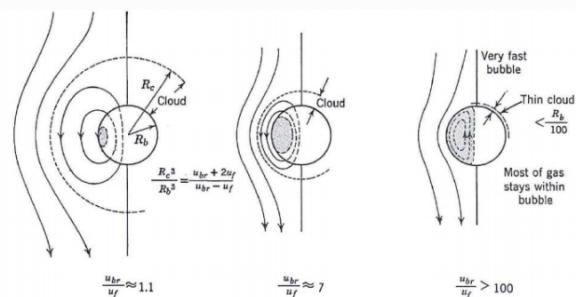
Bubbling fluidization local modeling

Emulsion: large no. of catalystic particles, $\varepsilon_e = \varepsilon_{mf}$, ΔP varies linearly

Bubbles: lower resistance for moving gas - $\eta_b > \eta_e$ - $\Delta P \approx 0$ (inside the bubble)

Cloud: surrounds the bubble - $\varepsilon_{avg} = \varepsilon_e$

wake: lower pressure (near emulsion)



Macroscopic parameters in fluidized bed

bubble volumetric fraction: $\delta = \frac{V_{\text{bubble}}}{V_{\text{tot}}} = \frac{A_{\text{bubble}}}{A_{\text{tot}}}$ bubble volumetric fraction: $f_c = \frac{V_{\text{channel}}}{V_{\text{tot}}}$

Wetted volumetric fraction: $f_w = \frac{V_{\text{wetted}}}{V_{\text{tot}}}$ Emulsion volumetric fraction: $f_e = \frac{V_{\text{emulsion}}}{V_{\text{tot}}}$

$$\eta V_{\text{solid}} = \frac{f_w \delta}{(1 - \delta(1 + f_c + f_w))} V_{\text{bubbles}}$$

rapid mass transfer \Rightarrow high surface area

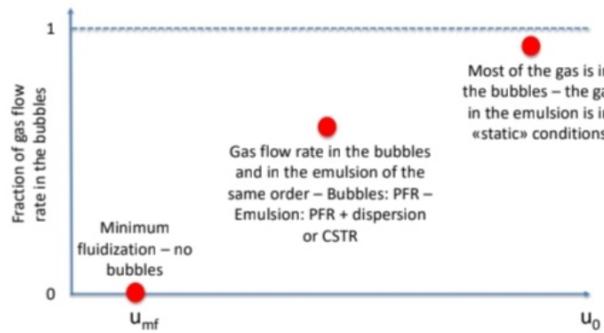
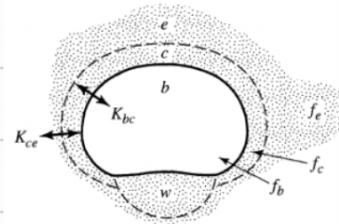


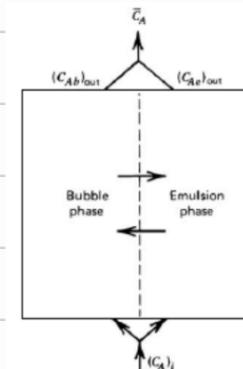
Figure 12. Fraction of gas flowrate in the bubbles.

Davidson - Harrison Model

Only for bubble and emulsion

Pass through emulsion with min. fluidization condition

under gas \rightarrow Pass through bubbles \rightarrow Conversion ≈ 0



Mass Balance

for bubbles with $(C_i^b(z=0) = C_i^\circ)$: $\frac{dF_i^b}{dz} + A_{be} K_i (C_i^e - C_i^b) \xrightarrow{\text{mass transfer coeff}}$

for emulsion: $F_{i,m}^e - F_i^e + R_i V_e + \int_0^{H_f} A_{be} K_i (C_i^b - C_i^e) dz$

Kunii - Levenspiel Method

Assumptions: 59.5% Condition - 1st order reaction

Mass Balance for Geldart A_n Particles:

The fluidization is characterized by small bubbles with a rising velocity higher than V_b .

$$\text{for bubbles with } (C_A^b(z=0) = C_A^\circ) : -v_b \frac{dc_A^b}{dz} = \gamma_b k C_A^b + k_{bc}(C_A^b - C_A^e)$$

$$\text{for cloud: } k_{bc}(C_A^b - C_A^e) = \gamma_c k C_A^c + k_{ce}(C_A^c - C_A^e)$$

$$\text{for emulsion: } k_{ce}(C_A^c - C_A^e) = \gamma_e k C_A^e$$

Note between the rel. of catalyst cloud in emulsion

Mass Balance for Geldart A_n Particles:

The fluidization is characterized by bubbles with a rising velocity similar to the rel. of gas in emulsion.

Cloud thickness of cloud \Rightarrow 2 existing phases

$$\text{for bubbles with } (C_A^b(z=0) = C_A^\circ) : -v_b^* \frac{dc_A^b}{dz} = \gamma_b k C_A^b + k_{bc}(C_A^b - C_A^e)$$

rise velocity of gas

$$= V_b + 3V_{mf}$$

$$\text{for emulsion: } -(1-\delta) U_{mf} \frac{dc_A^e}{dz} = (1-\delta)(1-\epsilon_{mf}) k C_A^e - \delta k_{bc}(C_A^b - C_A^e)$$

Mass Balance for Geldart D_n Particles:

The fluidization is characterized by bubbles with a rising velocity smaller than V_b .

Bubbles \Rightarrow slow resistance shear \Rightarrow no cloud phase

reaction just in dense parts.

$$\text{Residence time} = \frac{\text{total catalyst rel.}}{\chi}$$

$$\chi = \frac{U_{mf}}{U_0} (1-\delta)$$

$$\tau_A = (1-\delta) U_{mf} A + \delta (U_b + 3U_{mf}) A$$

Closure models

mass balance for solid bed: $H_{\text{fixed}} A P_{\text{solid}} (1-\epsilon_{\text{fixed}}) = H_{\text{bubbling}} A P_{\text{solid}} (1-\epsilon_{\text{fluidized}})$
(Assumption: constant catalyst mass)

$$\epsilon_{\text{fluidized}} = \delta + (1-\delta) \epsilon_e \approx \epsilon_{mf}$$

bubble volumetric fraction \rightarrow rising velocity of bubbles

$$\text{if } \frac{v_b}{\epsilon_{mf}} > 5 \Rightarrow \delta = \frac{v_o - v_{mf}}{v_b - v_{mf}}, \text{ if } \frac{v_b}{\epsilon_{mf}} < 5 \Rightarrow \delta = \frac{v_o - v_{mf}}{v_b + 2v_{mf}}$$

$$\text{if } \frac{v_{mf}}{\epsilon_{mf}} < U_b < 5 \frac{v_{mf}}{\epsilon_{mf}} \Rightarrow \begin{cases} v_b \approx \frac{v_{mf}}{\epsilon_{mf}} & \epsilon = \frac{v_o - v_{mf}}{v_b - v_{mf}} \\ v_b \approx 5 \frac{v_{mf}}{\epsilon_{mf}} & \epsilon = \frac{v_o - v_{mf}}{v_b} \end{cases}$$

Cloud volumetric fraction: $f_c = \frac{3}{v_{br} \epsilon_{mf} - 1}$

Emulsion volumetric fraction: $f_e = 1 - \delta - f_w \delta$ Water volumetric fraction \Rightarrow See chart

Volume ratio (γ)

$$\text{between solid and bubble} \Rightarrow \begin{cases} \approx 0 \text{ (experimental)} \\ = 0.005 \text{ (Kunii-Lefebvre)} \end{cases}$$

between cloud and bubble: $\gamma_c = (1 - \epsilon_{mf})(f_c + f_w)$

between solid and emulsion: $\delta(\gamma_b + \delta_c + \gamma_e) = (1 - \epsilon_{mf})(1 - \delta)$

$$\text{Bubble diameter} \left\{ \begin{array}{l} \text{Min: } d_{b_0} = \frac{2.78}{g} (v_o - v_{mf})^2 \\ \text{Max: } d_{bm} = 0.652 [A(v_o - v_{mf})]^{0.4} \end{array} \right.$$

Bubble size @ height of bed \Rightarrow Moni and Wen equation

Criteria: $D_t \leq 1.3 \text{ m}$, $0.5 \leq U_{mf} \leq 20 \text{ cm/s}$, $60 \leq D_p \leq 450 \mu\text{m}$, $v_o - v_{mf} \leq 48 \text{ cm/s}$

$$\frac{d_{bm} - d_b}{d_{bm} - d_{b_0}} = \exp(-0.3 \frac{D_t}{D_p})$$

$$\text{Rising bubble velocity} \Rightarrow V_b = V_{mf} - V_{mf} + V_{br} \quad \text{velocity of single bubble}$$

$$\text{if } \frac{d_b}{D_t} < 0.125 \Rightarrow V_{br} = 0.711 (g d_b)^{1/2}$$

$$\text{if } 0.125 < \frac{d_b}{D_t} < 0.6 \Rightarrow V_{br} = [0.711 (g d_b)^{1/2}] \times 1.2 \exp(-1.49 \frac{d_b}{D_t})$$

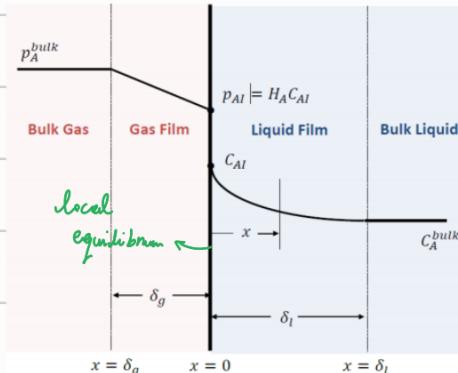
Mass transfer Coefficient

$$\text{bubble- cloud: } K_{bc} = 4.5 \left(\frac{V_{mf}}{d_b} \right) + 5.85 \left(\frac{D^{1/2} g^{1/4}}{d_b^{5/4}} \right)$$

$$\text{cloud - emulsion: } K_{ce} = 6.77 \left(\frac{D^{1/2} V_{br}}{d_b^3} \right)^{1/2}$$

$$\text{bubble - emulsion (Golden B.) : } K_{be} = 9.5 \left(\frac{V_{mf}}{d_b} \right)$$

Gas - Liquid reactions



overall rate expression =

mass transfer + reaction

Assume stagnant layer that \rightarrow small capexence ①

\rightarrow absence of concentration gradients beyond the film \leftrightarrow turbulence ②

\rightarrow Diffusion in gas film \rightarrow diffusion in liquid film \rightarrow reaction in liq. phase ③

$$\text{Film of A into gas film: } j_{A,G} = -D_{A,G} \frac{dC_{A,g}}{dx} \stackrel{\text{①}}{\Rightarrow} D_{A,G} \frac{d^2C_{A,G}}{dx^2} = 0$$

$$V_{A,G} = j_{A,G} = \frac{P_{A,A}}{\delta_G} (C_{A,g,b} - C_{A,g,i}) \quad \text{③}$$

$P_{A,A} \uparrow$

in interface \Rightarrow Concentration of A \approx Henry's law ($P_A^i = H_A C_{A,i,g}$)

Mass conservation in the liquid film: $D_{A,L} \frac{d^2 C_{A,L}}{dr^2} = r$

B.C.: @ $r=0 \Rightarrow C_{A,L} = C_{A,i,L}$ @ $r=\delta_L \Rightarrow C_{A,L} = C_{A,bulk}$

$$\lambda = \frac{C_{A,L}}{C_{A,i,L}}, \quad y = \frac{r}{\delta_L} \Rightarrow \frac{d^2 \lambda}{dy^2} = \frac{\gamma^2 \lambda}{\text{Saturation}} \quad \text{Herron modulus}$$

$$\lambda = \frac{C_{A,bulk}}{C_{A,i,L}} \frac{\sinh(\gamma y) + \sinh[\gamma(1-y)]}{\sinh(\gamma y)}$$

$$\gamma^2 = \frac{k_r \delta_L C_{A,i,L}}{D_{A,L} C_{A,i,L}} = \frac{\text{max possible conversion in the film}}{\text{max diffusional transport in the film}}$$

Absorption rate in liquid phase: $r_{A,L} = k_{A,L} C_{A,i,L} \left[\frac{\gamma \tanh(\gamma) \left[1 - \frac{\lambda_{bulk}}{\cosh(\gamma)} \right]}{k_{A,L} (C_{A,i,L} - C_{A,bulk})} \right]$

\downarrow $\gamma = \frac{C_{A,i,L}}{C_{A,bulk}}$

$$r_{A,L} = \frac{\gamma}{\tanh(\gamma)} \left(1 - \frac{\lambda_{bulk}}{\cosh(\gamma)} \right)$$

Enhancement factor: $E = \frac{r_{A,L}}{r_{A,L, \text{no rxn}}},$

$E = E(\gamma)$

- Slow reaction region, $\gamma < 0.1 \Rightarrow E \rightarrow 1$
- Intermediate region: $0.1 < \gamma < 3 \Rightarrow E \approx 1 + \frac{\gamma^2}{3}$
- Fast reaction region: $\gamma > 3 \Rightarrow E = E_{\text{instantaneous}}$

