Lecture 7 packed beds

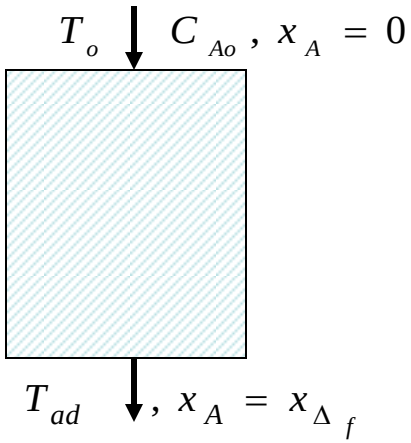
Reactor Scale Considerations: Gas-Solid Systems

Solid catalyzed gas reactions are mainly conducted in

- Adiabatic massive packed bed reactors
- Wall cooled tubular reactors
- Fluidized beds
- Risers (part of circulating fluidized beds)

Reactor models vary from pseudo-homogeneous to heterogeneous, from one dimensional to three dimensional, from assumed flow pattern to computed flow and transport fields. The needed sophistication depends on the reaction system.

Adiabatic Packed Beds



Key Issues:

- Adiabatic temperature rise
- Pressure drop
- Optimal rate
- Explosion and runaway potential

$$T_{ad} = T_o + \frac{(-\Delta H_{rA})\, C_{Ao}}{\rho\, C_p}\, x_{A_f}$$

$$\frac{\Delta P}{L} = \frac{E_1\, \mu\, U_g\, (1-\varepsilon_B)^2}{d_p^{\,2}\, \varepsilon_B^{\,3}} + \frac{E_2\, \rho_g\, U_g^{\,2}\, (1-\varepsilon_B)}{d_p\, \varepsilon_B^{\,3}}$$

$$(-\overline{R}_A) = \eta_o\, (-R_A)_b$$

T_o = Feed temperatu re

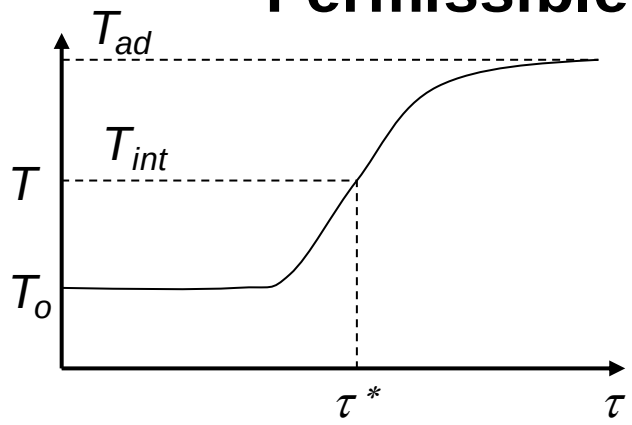
ΔH_{r_A} = Heat of reaction

C_{Ao} = Feed concentrat ion of limiting reactant

$\rho\, C_p$ = Mean specific heat per unit volum e of reaction mixture

x_{A_f} = Conversion of limiting reactant achieved in the bed

Permissible Adiabatic Temperature Rise



$$\Delta T_{ad\ \max} = T_{ad} - T_o$$

$$= \frac{\left(-\Delta H_{r_A}\right) C_{Ao}}{\rho C_p}$$

If T_{ad} is not permissible limit operation to $T \le T_{\inf}$ which requires limiting conversion by having $\tau < \tau^*$

For n-th order reaction then yields

$$\theta_{\inf} = \gamma \frac{T_{\inf} - T_o}{T_o} = \frac{\gamma}{2n}\left[\sqrt{\gamma^2 + 4n\left(\gamma^2 + \delta\right)} - 2n - \gamma\right] \qquad (1)$$

$$\left(Da\ \delta\right)^* = \int_o^{\theta_{\inf}} \frac{e^{-\gamma\theta/(\theta+\gamma)}}{\left(1 - \frac{\theta}{\delta}\right)^n} d\theta \qquad (2)$$

$$\gamma = \frac{E}{RT_o};\quad \delta = \beta\gamma = \frac{\left(-\Delta H_{r_A}\right) C_{Ao}}{\rho C_p T_o} \times \frac{E}{RT_o}$$

$$Da = \frac{\tau}{\tau_R} = \frac{\left(-R_A\right)_o \tau}{C_{Ao}} = k_o e^{-\gamma} C_{Ao}^{\,n-1} \tau$$

$$x_{\max} = \frac{\theta_{\inf}}{\delta}$$

For n-th order reaction the for which temperature must be kept below inflection point temperature

$$\theta < \theta_{\inf} \Rightarrow T < T_{\inf}$$

The requirement is to keep $\tau < \tau^*$ where τ^* can be obtained from Eq (3) below

$$\frac{k_o \; e^{-E/RT_o} \; C_{Ao}{}^{n} \left(-\Delta H_{r_A}\right) E \; \tau^*}{R \rho \; C_p \; T_o{}^{2}} = \left(Da \;\; \delta\right)^* \qquad (3)$$

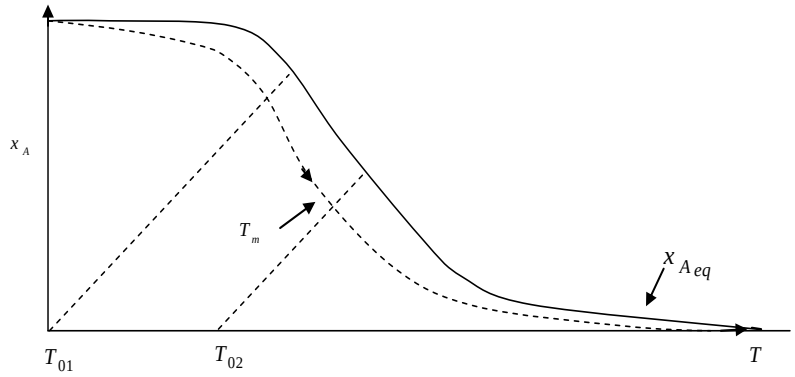
Where the numerical value of $\left(Da \;\; \delta\right)^*$ is calculated from Eq (2).

For a conservative estimate based on zeroth order reaction

$$\left(Da \;\; \delta\right)^*_{app} = 1$$

In addition composition of fuel (HC) and oxygen is kept outside explosion limits.

Exothermicity of Oxidation Reactions Limits Equilibrium Conversion



On x_A vs T plot $x_{A_{eq}}$ is the locus of zero rates

Also plotted is the locus of maximum rates (T_m *Line*) obtained from $\partial r / \partial T = 0$

Adiabatic lines with two different feed temperatures are also plotted.

The lower the T_o the higher exit conversion can be reached.

So high exit conversion requires staging of multiple adiabatic beds – increasing the cost.

Observed reaction rate at any point of the reactor is the product of the local overall effectiveness factor η_o and the rate attainable at that location in absence of transport limitations

$$\left(-R_A\right)_{obs\ \ local} = \left(-\eta_o \left(-R_A\right)_{bulk}\right)_{local}$$

e.g. for first order process

$$\eta_o = \frac{1}{\frac{1}{\eta} + \frac{k\ d_p}{6\ k_g}}$$

$$\eta = \frac{\tanh \wedge_p}{\wedge_p} \qquad \wedge_p = \frac{d_p}{6}\sqrt{\frac{k}{D_e}}$$

$$\eta_o \propto d_p^{-\alpha} \qquad \alpha > 0$$

$$\eta_o \propto k_g \propto U_g^{\beta}; \qquad \beta > 0$$

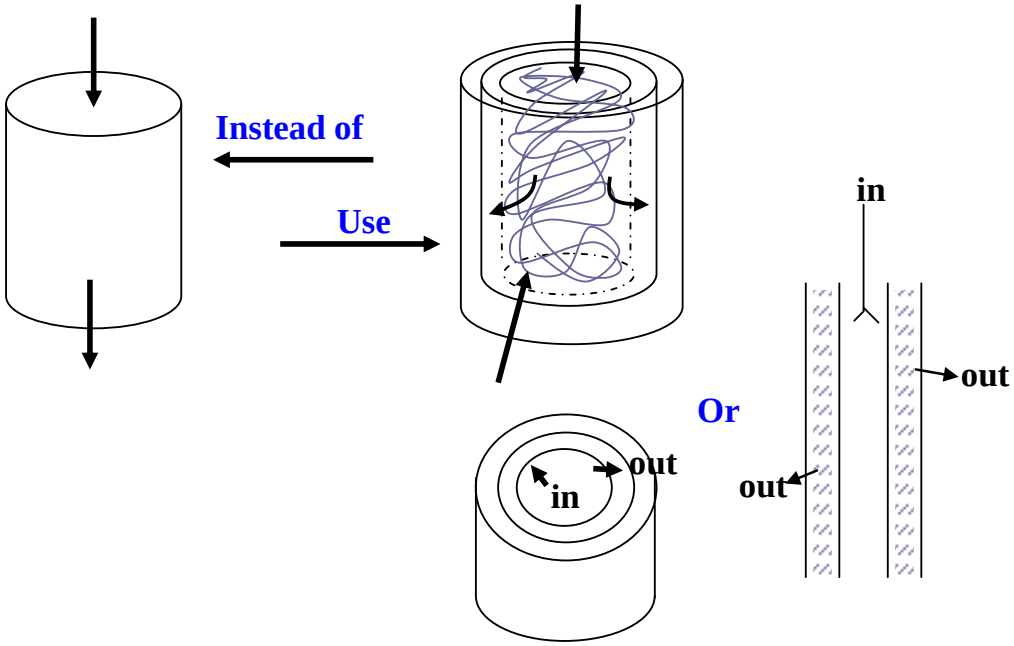
But

$$\frac{\Delta P}{L} = \frac{E_1\ \mu\ U_g\ \left(1-\varepsilon_B\right)^2}{d_p^{\,2}\ \varepsilon_\beta^{\,3}} + \frac{E_2\ \ell\ U_g\ \left(1-t_B\right)}{d_p\ \varepsilon_\beta^{\,3}}$$

$$d_p \downarrow, \quad U_g \uparrow \qquad \eta_o \uparrow \qquad \frac{\Delta P}{L} \uparrow$$

$\therefore$ **Compromise between pressure drop and overall effectiveness factor (i.e. volumetric productivity) is sought.**

To allow higher volumetric productivity $\overline{m}_v$ at reduced power dissipation $(\dot{V}\ \Delta P)$ one tries for a given size of small catalyst particles to use radial flow reactor or flat pane type reactors that minimize bed depth and superficial gas velocity

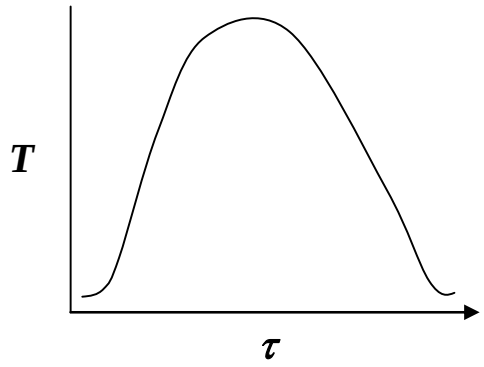


Mass of catalyst divided by volumetric federate

$\tau_w = W/Q_g$ = const. for scale up

∴ **Elaborate designs that combine radial or panel flow and interstage (between beds) cooling for staged adiabatic reactions is available in the patent literature.**

∴ **To improve on conversion per pass use cyclic reverse flow operation switch flow direction periodically.(see theses and papers by M. Kulkarni and R.C. Ramaswamy in CREL)**



This yields an inverse ∪ ∩ temperature profile conducive to achieve higher exit conversion

Practiced commercially on sulfuric acid plants and in VOC combustion.

Scale-up of Adiabatic Reactors

From bench scale data is not straight forward because lab reactors are rarely adiabatic. The procedure is to use:

- Same d_p, same catalyst, same bed packing procedure
- Same feed composition and same temperature
- Ensure good flow distribution in lab scale (e.g. $d_t/d_p > 30$)
- Ensure proximity to plug flow in large scale
- Same space time

Design of massive adiabatic packed bed reactors

- Developed by licensors of technologies that use them and involves incorporation of staged adiabatic reactors with inter-stage reactant or inert cold shot cooling as well as cooling of the recycle streams.

- Designs are available for pancake, panel and radial flow reactors to reduce pressure drop. Flow distribution and pressure drop evaluated by some CFD models.

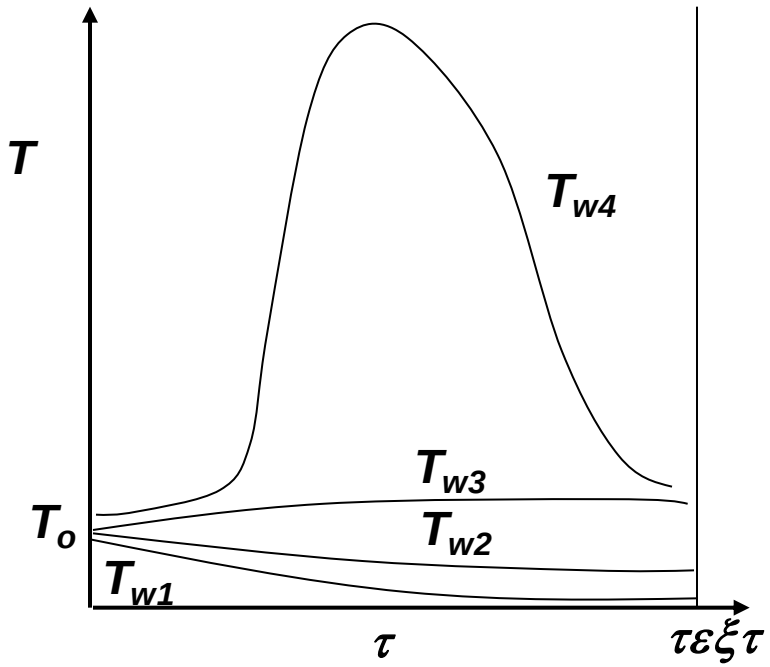
- Reactor performance calculated based on plug flow assumptions; sometimes axial dispersion model is used. However, large extent of back mixing can arise due to natural convection effects when temperature rise is large.

- Better models for characterization of packed structures and for computation of the flow field are needed.

Wall Cooled Tubular Reactors

- Plug flow is needed to favor the intermediate
- Cooling is needed to prevent runaway combustion and other undesired reactions

These systems are prone to hot spots and extreme parametric sensitivity.



A small increase in wall (T_w) i.e. coolant temperature could lead to enormous increase in peak temperature

For an n-th order irreversible reaction the temperature variation with conversion is given by

$$\frac{d\theta}{dx_A} = \delta e^{-\theta/(1+\theta/.\gamma)}(1-x_A)^{-n}\left[\underbrace{e^{\theta/(1+\theta/\gamma)}(1-x_A)^{n}}_{y_1(\theta)} - \underbrace{\frac{\kappa}{\delta}\theta}_{y_2(\theta)}\right]$$

$$\delta = \beta\gamma = \frac{(-\Delta H_{R_A})C_{Ao}}{\rho C_p T_o} \times \frac{E}{R T_o}$$

$$\kappa = \frac{\tau_R}{\tau_h} = \frac{4 U C_{Ao}}{(-R_A)_o d_t \rho C_p}$$

$$\theta = \gamma \frac{T - T_o}{T_o}$$

U = overall heat trans fer coeficient

$(-R_A)_o = k_o e^{-E/RT_o} C_{Ao}^{\,n}$ = rate evaluated at feed conditions

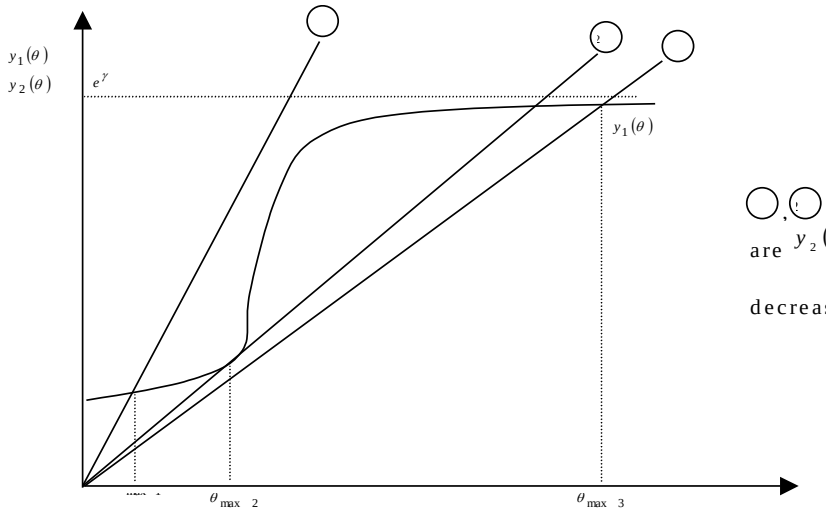
d_t = tube diameter

C_{Ao} = feed concentrat ion

For avoidance of hot spots one needs

$$y_i(\theta) = y_2(\theta) \Rightarrow \theta_{\max}$$

$$\left.\frac{dy_1}{d\theta}\right|_{\theta_{\max}} < \left.\frac{dy_2}{d\theta}\right|_{\theta_{\max}}$$



, , are $y_2(0)$ for decreasing $\frac{\kappa}{\delta}$

This implies that to avoid hot spots one must have

$$e^{\theta/(1+\theta/\gamma)} = \frac{\kappa}{\delta}\theta \qquad \textbf{(x)}$$

$$\frac{1}{\left(1+\frac{\theta}{\gamma}\right)^2} e^{\theta/(1+\theta/\gamma)} \le \frac{\kappa}{\delta} \qquad \textbf{(xx)}$$

Substitute (x) into (xx)

$$\frac{1}{\left(1+\frac{\theta_{\max}}{\gamma}\right)^2}\theta_{\max} = 1$$

Find $\theta_{\max}$, substitute into (x) and get $\left(\frac{\kappa}{\delta}\right)$ critical. Using approximations one gets

$$T_{\max} = \left(\frac{1}{\gamma}+1\right)T_o \qquad \text{and} \qquad \frac{\kappa}{\delta} \ge e$$

Resulting in

$$d_t \le \frac{4\,U\,RT_o^{\,2}\,e^{-1}}{E\left(-\Delta H_{rA}\right)k_o\,e^{-E/RT_o}\,C_{Ao}^{\,n}}$$

Determines maximum permissible tube diameter.

Multi-tubular wall cooled (tube in shell) reactors are used extensively (e.g. ethylene oxide production etc.).

Lurgi is a key licensor of multitubular reactor technology, up to 40,000 tubes 1 to 2 inches in diameter in a single shell.

Key issues:

- Select safe tube diameter (as discussed)
- Pack each tube with identical amount of catalyst (W_T)
- Have perfect flow distribution so that for each tube $W_T / \dot{V}_o = const$

Scale up – Trivial (Usually)

- Run one tube in the lab until you get desired result for conversion, selectivity, determine production rate F_{p_L}
- Find number of tubes needed for commercial production rate

$$N = \frac{F_{p_c}}{F_{p_L}}$$

- Use identical tubes and coolant, identical W , $\dot{V}_o$ in each tube as in the lab

Potential Problems (Troubleshooting)

- Catalyst for plant and lab different
- Tubes not packed carefully with same size of pellets and same amount as in the lab
- Flow distribution imperfect so $(W/\dot{V}_o)_{tube}$ varies from tube to tube
- Feed temperature different in plant and lab
- Feed of different composition in plant and lab
- Different coolant and coolant circulation rate used (could affect U)

To learn whether tube operates optimally one must:

- Determine whether plug flow is approached
- Assess magnitude of radial temperature differences
- Assess transport effects and determine difference in gas and solid temperature locally
- Assess internal diffusional effect / and heat effects if needed

Approximate criteria for all of the above are readily available in reaction engineering text books.

For more detailed analysis need

- Kinetic forms and rate parameters
  Use models of increased degree of sophistication
- Pseudo homogeneous – 1D
- Pseudo homogeneous – 2D
- Heterogeneous – 1D
- Heterogeneous – 2D

Obtain parameters (e.g. h_p, h_w etc) from a) correlations ; b) detailed CFD

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Wall Cooled Packed Tubular Reactors

- The key to improved performance is in improving the heat transfer coefficient on the tube side. Dixon and his team at Worcester Polytechnic Institute have shown how to do that by systematic application of CFD to packing of spheres in tubes. Extensions to extrudates are under way.

- The selection of the right level model for packed beds is discussed in a series of papers by Balakotiah (U of Houston) and his coworkers.

Novel uses of packed beds

- Dynamic operation such as in the reverse flow process for exothermic reactions to achieve better conversion
- Coupling of exothermic and endothermic reactions in directly coupled adiabatic reactors
- Coupling of exothermic and endothermic reactions in indirectly coupled adiabatic reactor in dynamic operation (reactor –regenerator concept)

See doctoral theses at Washington University in St. Louis of

-Milind Kulkarni, and

-R.C. Ramaswamy

and their associated published papers with M.P.Dudukovic and P.A. Ramachandran from the late 1990s until the present.