7. Mass and Energy Balances on Plug Flow Packed Bed Reactor (PFPBR)

- In a fixed-bed reactor the catalyst pellets are held in place and do not move with respect to a fixed reference frame.

- Material and energy balances are required for both the fluid, which occupies the interstitial region between catalyst particles, and the catalyst particles, in which the reactions occur.

- The following figure presents several views of the fixed-bed reactor. The species production rates in the bulk fluid are *essentially zero*. That is the reason we are using a catalyst.

- Essentially all reaction occurs within the catalyst particles. The fluid in contact with the external surface of the catalyst pellet is denoted with subscript s.
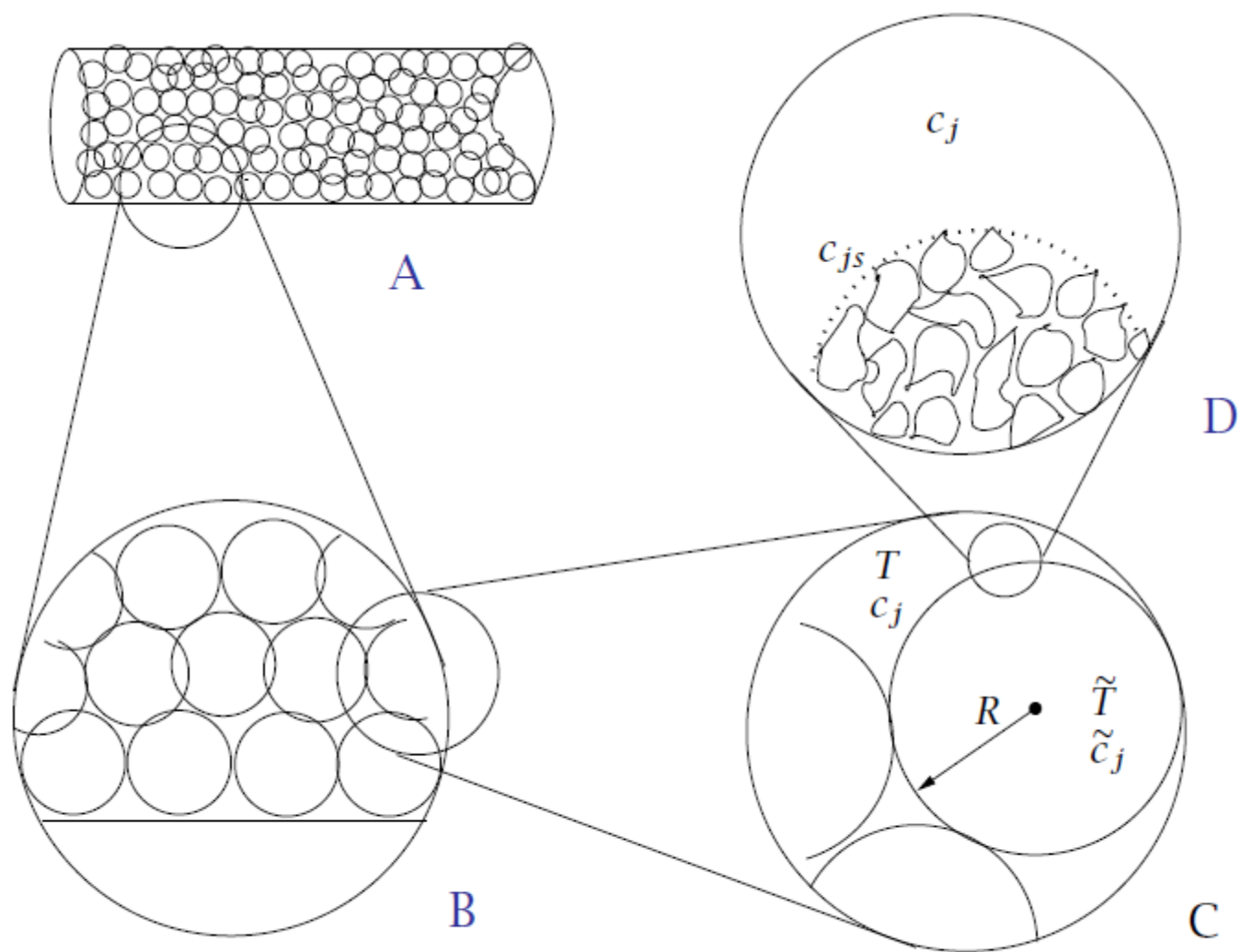
Figure 1: Expanded views of a fixed-bed reactor.

During any catalytic reaction the following steps occur:

1. transport of reactants and energy from the bulk fluid up to the catalyst pellet exterior surface,

2. transport of reactants and energy from the external surface into the porous pellet,

3. adsorption, chemical reaction, and desorption of products at the catalytic sites,

4. transport of products from the catalyst interior to the external surface of the pellet, and

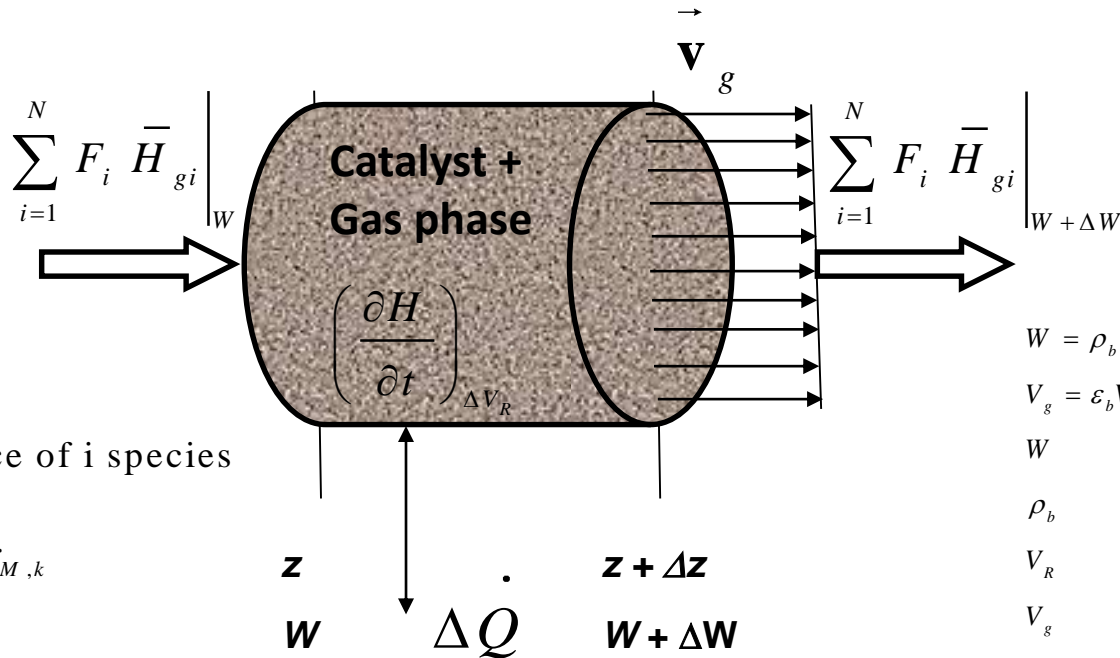5. transport of products into the bulk fluid.

The coupling of transport processes with chemical reaction can lead to concentration and temperature gradients within the pellet, between the surface and the bulk, or both.

- In the fixed-bed reactor, we keep track of two phases. The fluid-phase streams through the bed and transports the reactants and products through the reactor.

- The reaction-diffusion processes take place in the solid-phase catalyst particles.

- The two phases communicate to each other by exchanging mass and energy at the catalyst particle exterior surfaces.

We make the following assumptions:

1. Uniform catalyst pellet exterior. Particles are small compared to the length of the reactor.

2. Plug flow in the bed, no radial profiles.

3. Neglect axial diffusion in the bed.

4. Steady state.

Balances on Plug Flow Packed Bed Reactor (PFPBR)

$$\left.\sum_{i=1}^{N} F_i \, \overline{H}_{gi} \right|_W$$

Catalyst + Gas phase

$$\left.\sum_{i=1}^{N} F_i \, \overline{H}_{gi} \right|_{W+\Delta W}$$

$$\vec{\mathbf{v}}_g$$

$$\left(\frac{\partial H}{\partial t} \right)_{\Delta V_R}$$

Molar balance of i species

$$\frac{dF_i}{dW} = \sum_{k=1}^{NR} \nu_{ki} r_{M,k}$$

z $\dot{\Delta Q}$ **z + Δz**

W   **W + ΔW**

$$W = \rho_b S_R z = \rho_b V_R \qquad V_R = V_g + V_s$$

$$V_g = \varepsilon_b V_R \qquad V_s = (1 - \varepsilon_b) V_R$$

W	mass of catalyst [kg]
ρ_b	bulk density of the catalyst [kg/m^3]
V_R	total volume of reactor [m^3]
V_g	volume of the gas phase in reactor [m^3]
V_s	volume of the catalyst in reactor [m^3]
ε_b	bed porozity, $\varepsilon_b = \dfrac{V_g}{V_R}$ [−]

Overall enthalpy balance involved both gas and solid phase

$$\left(\frac{\partial H}{\partial t} \right)_{\Delta V_R} = \Delta V_R \frac{dP}{dt} + \left.\sum_{i=1}^{N} F_i \, \overline{H}_{gi} \right|_W - \left.\sum_{i=1}^{N} F_i \, \overline{H}_{gi} \right|_{W+\Delta W} + \Delta \dot{Q}$$

in the steady state

$$0 = \left.\sum_{i=1}^{N} F_i \, \overline{H}_{gi} \right|_W - \left.\sum_{i=1}^{N} F_i \, \overline{H}_{gi} \right|_{W+\Delta W} + \Delta \dot{Q} \Rightarrow \frac{d}{dW} \sum_{i=1}^{N} F_i \, \overline{H}_{gi} = \frac{d\dot{Q}}{dW}$$

ideal mixture $\Rightarrow \overline{H}_{gi}(T, P, composition) = h_i(T)$

$$\sum_{i=1}^{N} \left(\frac{dF_i}{dW} h_i(T) + F_i \frac{dh_i(T)}{dW} \right) = \sum_{i=1}^{N} \left(\sum_{k=1}^{NR} \nu_{ki} r_{M,k} \, h_i(T) + F_i \frac{dh_i(T)}{dT} \frac{dT}{dW} \right) =$$

$$= \sum_{k=1}^{NR} \Delta_r H_k r_{V,k} + \frac{dT}{dW} \sum_{i=1}^{N} F_i c_{pi} = \frac{d\dot{Q}}{dW}$$

$$\frac{dF_i}{dW} = \sum_{k=1}^{NR} \nu_{ki} r_{M,k} \qquad \sum_{i=1}^{N} \nu_{ki} h_i = \Delta_r H_k \qquad \frac{d\dot{Q}}{dW} = \omega(T_e - T) \frac{dS_t}{dW}$$

Circular cross section

$$\frac{dT}{dW} = \frac{1}{\sum\limits_{i=1}^{N} F_i c_{pi}} \left[\sum_{k=1}^{NR} (-\Delta_r H_k) r_{M,k} + \frac{4\omega}{\rho_b d_R}(T_e - T) \right] \qquad \frac{dS_t}{dW} = \frac{\pi d_R dz}{\rho_b \pi \dfrac{d_R^2}{4} dz} = \frac{4}{\rho_b d_R}$$

Enthalpy balance

$$\frac{dT}{dW} = \frac{1}{\sum\limits_{i=1}^{N} F_i c_{pi}} \left[\sum_{k=1}^{NR} (-\Delta_r H_k) r_{M,k} + \frac{4\omega}{\rho_b d_R}(T_e - T) \right]$$

Initial conditions

$$W = 0, \ F_i = F_i^o, T = T^o$$

Molar balance of i species

$$\frac{dF_i}{dW} = \sum_{k=1}^{NR} \nu_{ki} r_{M,k}$$

One reaction, constant heat capacity of species.
Profiles of conversion and temperature are given by following equations:

$$\frac{dT}{dW} = \frac{1}{F^o\left[\sum\limits_{i=1}^{N} y_i^o c_{p,i} + \dfrac{y_j^o}{|\nu_j|}\Delta c_p X_j\right]}\left[(-\Delta H_r)r_M + \frac{4\omega}{\rho_b d_R}(T_e - T)\right]$$

$$\frac{dX_j}{dW} = -\frac{\nu_j}{F_j^o} r_M(X_j, T) = \frac{|\nu_j|}{F_j^o} r_M(X_j, T)$$

$$W = 0,\ T = T_o,\ X_j = 0$$

$$\frac{dF_i}{dW} = \nu_i r_M = \frac{\nu_i}{\nu_j}\frac{dF_j}{dW}$$

$$X_j = \frac{F_j^o - F_j}{F_j^o}$$

$$F_i - F_i^o = \frac{\nu_i}{\nu_j}\left(F_j - F_j^o\right) = -\frac{\nu_i}{\nu_j}F_j^o X_j$$

$$\sum_{i=1}^{N} F_i c_{p,i} = \sum_{i=1}^{N} c_{p,i}\left(F_i^o - \frac{\nu_i}{\nu_j}F_j^o X_j\right) =$$

$$= F^o\left[\sum_{i=1}^{N} y_i^o c_{p,i} + \frac{y_j^o}{|\nu_j|}\Delta c_p X_j\right]$$

Limiting cases
1.Isothermal reactor

$$\frac{dT}{dW} = 0 = \left[(-\Delta H_r)r_M + \frac{4\omega}{\rho_b d_R}(T_e - T)\right] \Rightarrow (-\Delta H_r)r_M = -\frac{4\omega}{\rho_b d_R}(T_e - T)$$

$$T = T_o$$

2.Adiabatic reactor

$$\frac{dT}{dW} = \frac{1}{F^o\left[\sum_{i=1}^{N} y_i^o c_{p,i} + \frac{y_j^o}{|\nu_j|}\Delta c_p X_j\right]}\left[(-\Delta H_r)r_M\right] = \frac{F_j^o(-\Delta H_r)}{|\nu_j|F^o\left[\sum_{i=1}^{N} y_i^o c_{p,i} + \frac{y_j^o}{|\nu_j|}\Delta c_p X_j\right]}\frac{dX_j}{dz} =$$

$$= \frac{y_j^o\left(-\Delta_r H^o - \Delta c_p(T-T^o)\right)}{\left[|\nu_j|\sum_{i=1}^{N} y_i^o c_{p,i} + y_j^o\Delta c_p X_j\right]}\frac{dX_j}{dz}$$

$$\int_{T^o}^{T}\frac{dT}{y_j^o\left(-\Delta_r H^o - \Delta c_p(T-T^o)\right)} = \int_{0}^{X_j}\frac{dX_j}{\left[|\nu_j|\sum_{i=1}^{N} y_i^o c_{p,i} + y_j^o\Delta c_p X_j\right]}$$

$$T = T^o + \frac{y_j^o(-\Delta_r H^o)X_j}{|\nu_j|\sum_{i=1}^{N} y_i^o c_{p,i} + y_j^o\Delta c_p X_j}$$ **Cf. adiabatic BATCH, CSTR and PFR**

Catalytic PFR
Profile of pressure is calculated using Ergun equation:

$$-\frac{dP}{dz} = 150 \frac{\mu_f}{d_p^2} \frac{(1-\varepsilon_b)^2}{\varepsilon_b^3} v_f^o + 1.75 \frac{\rho_f}{d_p} \frac{1-\varepsilon_b}{\varepsilon_b^3} \left(v_f^o\right)^2 = A_1 \mu_f v_f^o + A_2 \rho_f \left(v_f^o\right)^2$$

μ_f fluid dynamic viscosity [Pa.s]

ρ_f fluid density [kg/m^3]

v_f^o superficial fluid mean velocity [m/s]
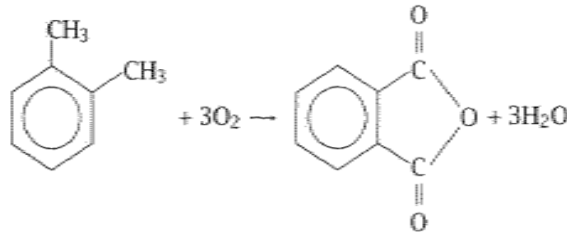
$$v_f^o = 4\dot{m} / (\rho_f \pi d_R^2)$$

$\dot{m}$ mass flowrate [kg/s]

ε_b bed porosity [-]

d_p catalyst particle (equivalent) diameter [m]

Example

Oxidation of o-xylene to phthalic anhydride[1]

The gas phase oxidation is highly exothermic. The reaction is carried out in PFR tube bundles with molten salt circulating as the heat transfer fluid. The o-xylene is mixed with air before entering the PFR. The large excess of oxygen leads to a pseudo-first order rate expression

$$r_V = k\left(T_o\right)\exp\left[-\frac{E}{R}\left(\frac{1}{T}-\frac{1}{T_o}\right)\right]c_1 \qquad A_1 = \text{o-xylene}$$

Calculate the temperature and composition profiles.

1. Rawlings, G.B., Ekerdt, J.G., Chemical Reactor Analysis and Design Fundamentals, Nob Hill Publ., Madison, Wisc. 2002.

Data

k(To), s^{-1}	To, K	Tm, K	P, bar	L, m	d$_R$, m
1922.6	625	625	1.01	1.5	0.025
C$_p$, kJ/kg/K	y$_1^o$	E/R, K	Δ_rH, kJ/mol	G, kg/s	ω, kJ/m^2/s/K
0.992	0.019	1.3636x 10^4	-1.361x 10^3	2.6371x 10^{-3}	0.373

F$_1$(z) kmol/s

T(z) K