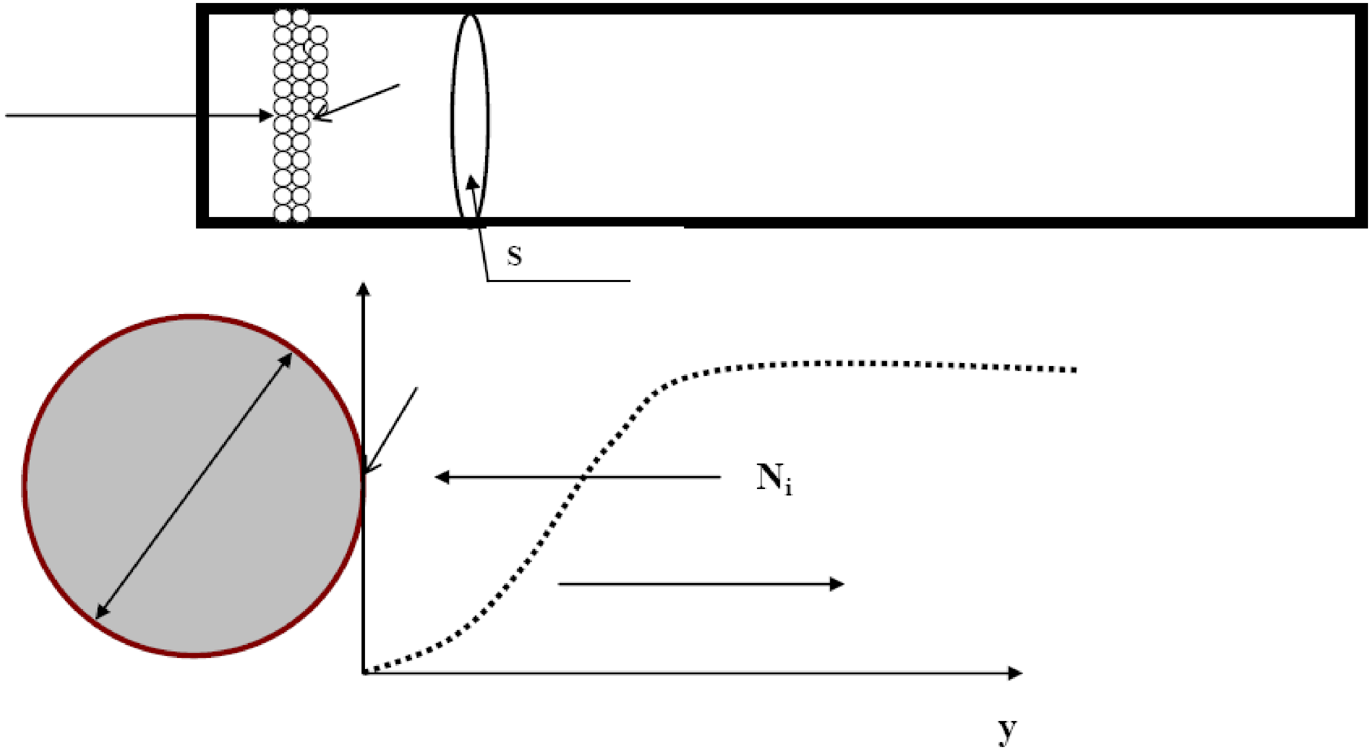
13. Models of catalytic reactors

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education
MINISTRY OF EDUCATION, YOUTH AND SPORTS

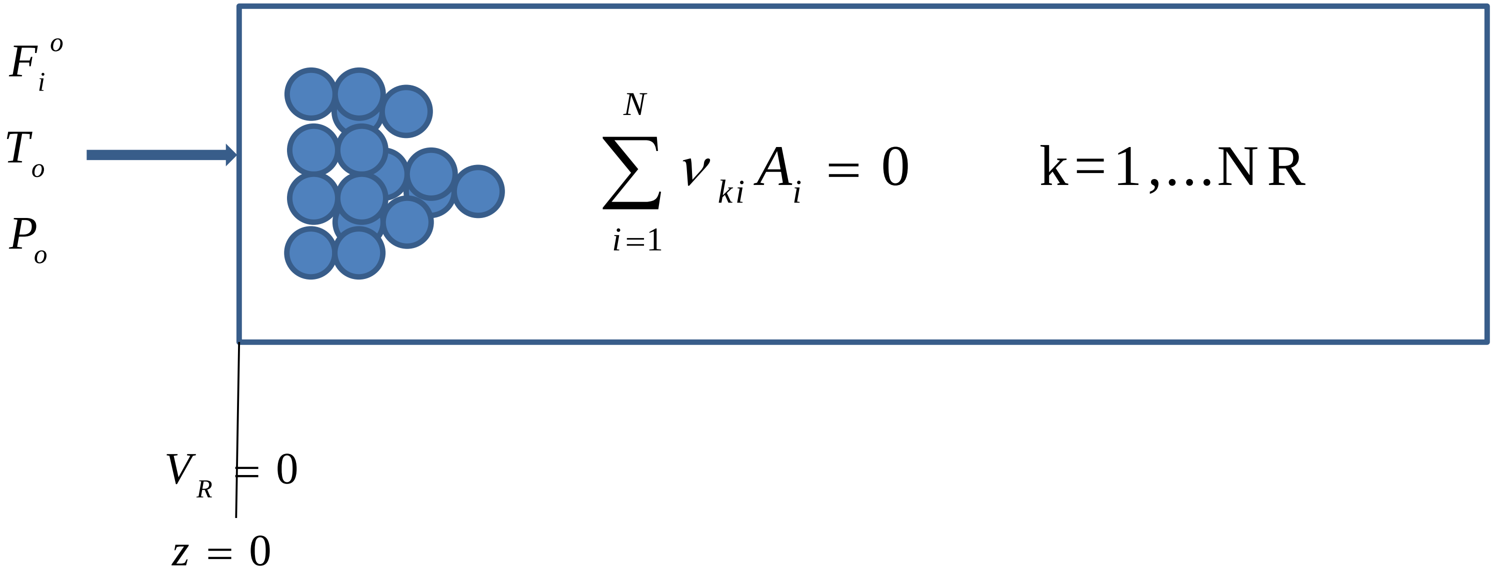
Model equations involve:

- Balance equations for components of reaction mixture in both gas phase and porous catalytical particle
- Balance of energy (enthalpy)
- Balance of momentum
- Flux constitutive equations for component and energy fluxes



	Pseudo homogeneous	Heterogeneous
1-D	• withou axial dispersion (pure plug flow) • with axial dispersion	Gradients of concentration and temperature between phases
2-D	Radial dispersion	

1-D pseudo homogeneous model without axial dispersion



We make the following assumptions:

1. Particles of catalyst are small compared to the length of reactor
2. Plug flow in the bed, no radial profiles
3. Neglect axial dispersion in the bed
4. Neglect concentration and temperature gradients in solid catalyst
5. Neglect concentration and temperature gradients in external fluid film
6. Steady state

In the fluid phase, we track the molar flows of all species, the temperature and the pressure. Generally, we can no longer neglect the pressure drop in the tube because of the catalyst bed – Ergun equation.

$$\frac{\mathrm{d}F_i}{\mathrm{d}z} = S_R \rho_b \sum_{k=1}^{NR} \nu_{ki} r_{M,k}$$

$$F c_p \frac{\mathrm{d}T}{\mathrm{d}z} = S_R \left[\rho_b \sum_{k=1}^{NR} \left(-\Delta_r H_k\right) r_{M,k} + \frac{4}{d_R} \omega \left(T_m - T\right) \right]$$

$$\frac{\mathrm{d}P}{\mathrm{d}z} = -\left[150 \frac{\mu_f}{d_p^2} \frac{\left(1-\varepsilon_b\right)^2}{\varepsilon_b^3} \mathrm{v}_f^o + 1.75 \frac{\rho_f}{d_p} \frac{\left(1-\varepsilon_b\right)}{\varepsilon_b^3} \left(\mathrm{v}_f^o\right)^2 \right]$$

$$z = 0, F_i = F_i^o, T = T_o, P = P_o$$

μ_f - fluid dynamic viscosity (Pa.s)
ρ_f - fluid density (kg/m^3)
v_f^o - superficial fluid mean velocity (m/s)
ε_b - bed porosity (-)
d_p - catalyst particle diameter (m)
ρ_b – bed apparent density (kg/m^3)
S_R – (empty) reactor cross section area (m^2)

Numerical solution gives $F_i(z), T(z), P(z)$

Example

Consider the oxidation of CO and C_3H_6 in a catalytic converter containing spherical catalyst pellets with particle radius 0.175 cm (0.05 mass % Pt on Al_2O_3). The initial composition of gas mixture is 2 % mol CO, 3 % O_2, 0.05 % C_3H_6 + N_2, total initial molar flow rate is between 0.1 – 2.0 mol/s. Converter has the diameter 10 cm and volume 4.3 litres. Bed porosity is 0.4 and catalyst bed density is 1100 kg/m³. The reactions of interest are

$$CO_{(g)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{2(g)}$$

$$C_3H_{6(g)} + \frac{9}{2} O_{2(g)} \rightarrow 3CO_{2(g)} + 3H_2O_{(g)}$$

$$r_{M,1} = \frac{k_1(T)\, c_{O_2} c_{CO}}{\left(1 + K_{CO} c_{CO} + K_{C_3H_6} c_{C_3H_6}\right)^2} \qquad \text{mol/g/s}$$

$$r_{M,2} = \frac{k_2(T)\, c_{O_2} c_{C_3H_6}}{\left(1 + K_{CO} c_{CO} + K_{C_3H_6} c_{C_3H_6}\right)^2} \qquad \text{mol/g/s}$$

$$k_1(T) = 7.07 \times 10^{19} \exp\left[-\frac{13106}{T}\right] \qquad \text{cm}^6/(\text{molgs})$$

$$k_2(T) = 1.47 \times 10^{21} \exp\left[-\frac{15109}{T}\right] \qquad \text{cm}^6/(\text{molgs})$$

$$K_{CO} = 8.099 \times 10^{6} \exp\left[\frac{409}{T}\right] \qquad \text{cm}^3/\text{mol}$$

$$K_{C_3H_6} = 2.579 \times 10^{8} \exp\left[-\frac{191}{T}\right] \qquad \text{cm}^3/\text{mol}$$

Oh, S.H., Cavenish J.C., Hegedus L.L., AICHE J. 26 (1980) 935.

Data from http://webbook.nist.gov/chemistry/:

$c_{p,i}(750\ \text{K}):$

$c_{p,CO} = 31.5\ \ \text{J/mol/K} \quad \Delta H_{f,298.15} = -110.53\ \text{kJ/mol}$

$c_{p,O_2} = 33.4\ \ \text{J/mol/K}$

$c_{p,CO_2} = 50.0\ \ \text{J/mol/K} \quad \Delta H_{f,298.15} = -393.52\ \text{kJ/mol}$

$c_{p,N_2} = 31.1\ \ \text{J/mol/K}$

$c_{p,C_3H_6} = 123.9\ \ \text{J/mol/K} \quad \Delta H_{f,298.15} = 20.41\ \text{kJ/mol}$

$c_{p,H_2O} = 38.12\ \ \text{J/mol/K} \quad \Delta H_{f,298.15} = -241.83\ \text{kJ/mol}$

Viscosity of $N_{2(g)}$ at 750 K:

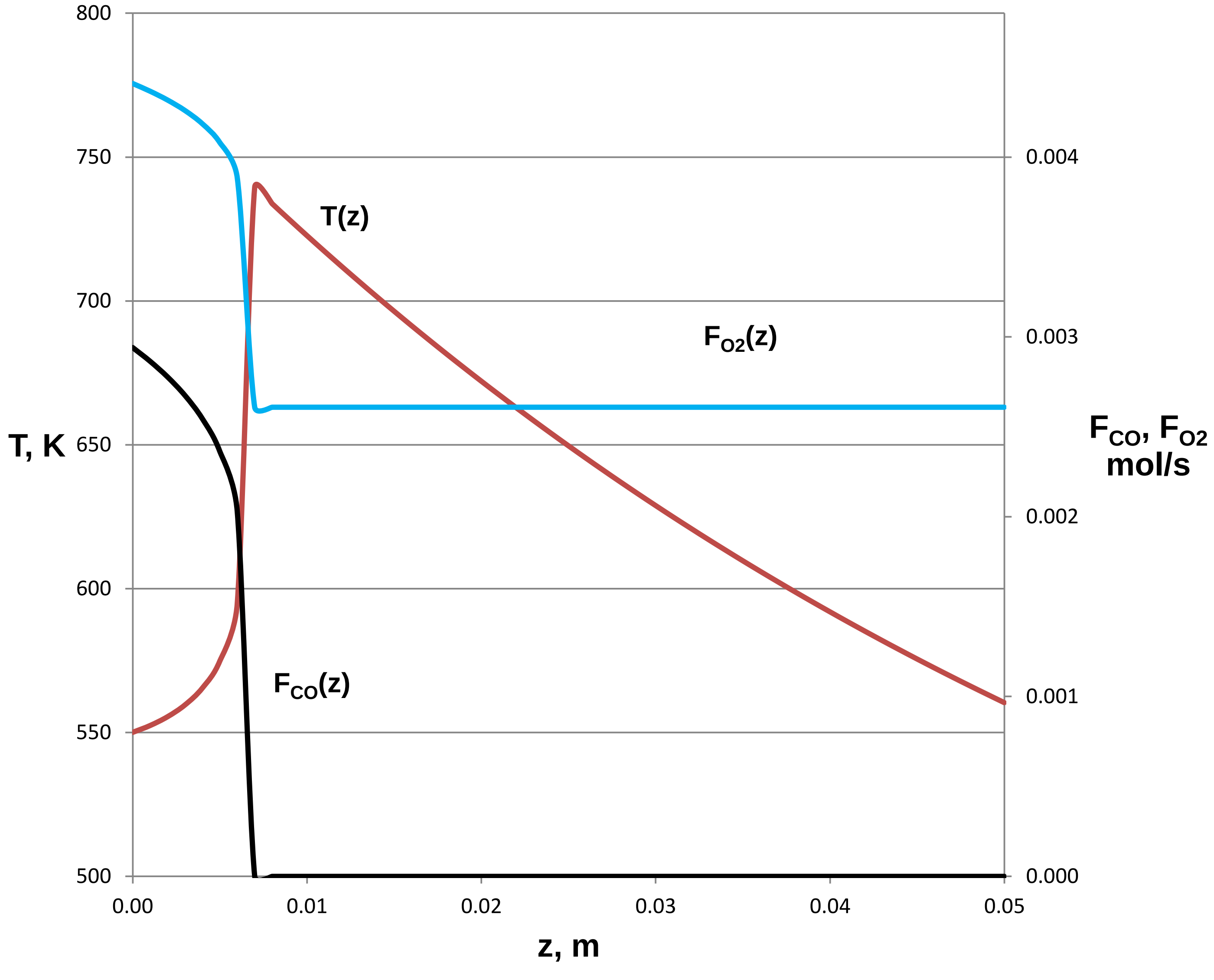
$\mu_f = 3.44 \times 10^{-5}\ \ \text{Pa.s}$

Data supplement:

$\omega = 230\ \text{W/(m}^2\text{K)} \quad T_m = 325\ \text{K}$

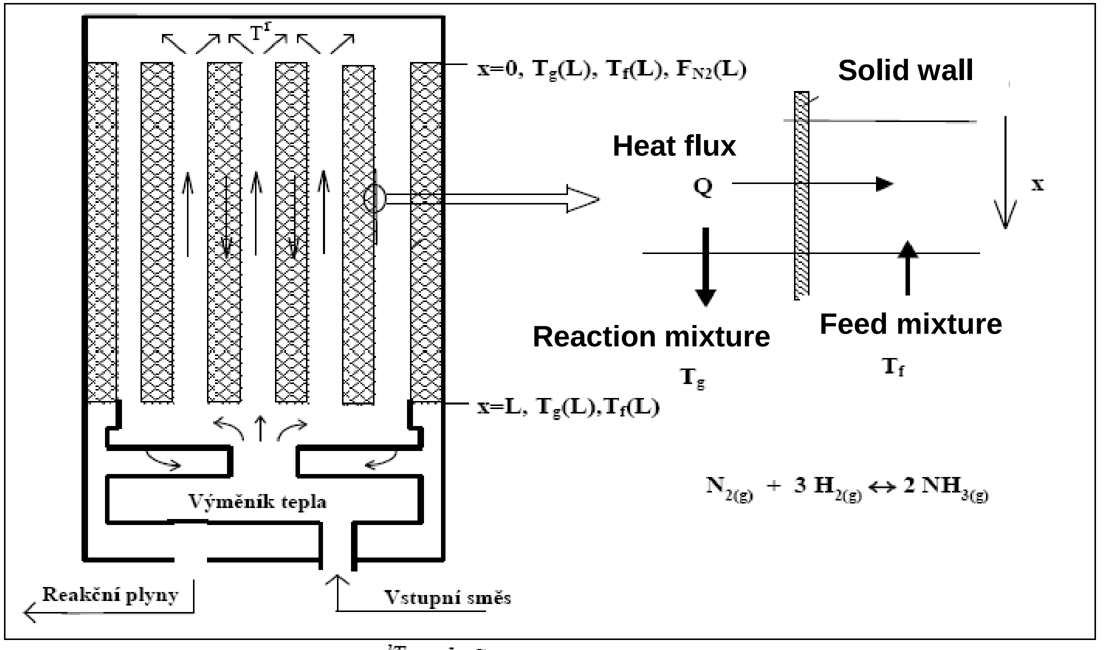
$T_o = 500\ \text{K} \quad P_o = 202\ \text{kPa}$

Numerical integration done by SIRK42E



Discussion: internal x external mass and heat transfer

Ammonia synthesis catalytic reactor



$$\frac{dT_f}{dx} = \frac{k_c\, S_1}{G\, c_{pf}}\left(T_f - T_g\right)$$

$$\frac{dT_g}{dx} = \frac{k_c\, S_1}{G\, c_{pg}}\left(T_f - T_g\right) + \frac{\left(-\Delta H_r\right)}{G\, c_{pg}} R_{N_2}$$

$$\frac{d\, F_{N_2}}{dx} = -R_{N_2}$$

$$R_{N_2} = K_1(T)\frac{p_{N_2} p_{H_2}^{1.5}}{p_{NH_3}} - K_2(T)\frac{p_{NH_3}}{p_{H_2}^{1.5}}$$

$$K_1(T) = 1{,}79.10^4 \exp[-\frac{87090}{RT}] \qquad K_2(T) = 2{,}57.10^{16} \exp[-\frac{198464}{RT}] \qquad R = 8{,}314\ \mathrm{J.mol^{-1}}.K^{-1}$$

Boundary conditions

$x = 0,\ T_g = T_f,\ F_{N2} = F^o_{N2}$

$x = L,\ T_f = T^o_f$

Feed temperature	15°C
Feed flow rate	26400 kg/hr
Pressure	190 bar
Length of reactor tubes	L=8.5 m
Tube internal diameter	d_t=0.078 m
Number of tubes	N_t=41
Global heat transfer coefficient	ω=2093 kJ/m^2/hr/K=$2096\times10^3/3600$ W/m^2/K
Temperature of reaction mixture in catalyst inside of tube	$T_R[K]$
Temperature of reaction mixture in the shell	$T_F[K]$
Component partial pressure	p_i [bar]

1-D pseudo homogeneous model with axial dispersion

$$\varepsilon D_{ai} \frac{d^2 c_i}{dz^2} - v_s \frac{dc_i}{dz} + \nu_i r_V = 0$$

$$\lambda_{am} \frac{d^2 T}{dz^2} - v_s \rho_g c_{pm} \frac{dT}{dz} + (-\Delta H_r) r_V + \frac{4K}{d_t}(T_m - T) = 0$$

Boundary conditions

$$z = 0 \qquad -\varepsilon D_{ai} \frac{dc_i}{dz} + c_i . v_s = c_i^o . v_s \qquad -\lambda_{am} \frac{dT}{dz} + v_s \rho_g c_{pm} T = v_s \rho_g c_{pm} T_o$$

$$z = L \qquad \frac{dc_i}{dz} = 0 \qquad \frac{dT}{dz} = 0$$

Dimensionless form

$$x = \frac{z}{L} \qquad Y_i = \frac{c_i}{c_i^o} \qquad \vartheta = \frac{T}{T_o}$$

Bilanční rovnice přejdou na tvar

$$\frac{1}{Pe_{Mi}} \frac{d^2 Y_i}{dx^2} - \frac{dY_i}{dx} + Da_i R(Y_k, \vartheta) = 0$$

$$\frac{1}{Pe_H} \frac{d^2 \vartheta}{dx^2} - \frac{d\vartheta}{dx} + \beta R(Y_k, \vartheta) = 0$$

$$x = 0 \qquad \frac{1}{Pe_{Mi}} \frac{dY_i}{dx} = Y_i - 1 \qquad \frac{1}{Pe_{Mi}} \frac{d\vartheta}{dx} = \vartheta - 1$$

$$x = 1 \qquad \frac{dY_i}{dx} = 0 \qquad \frac{d\vartheta}{dx} = 0$$

kde

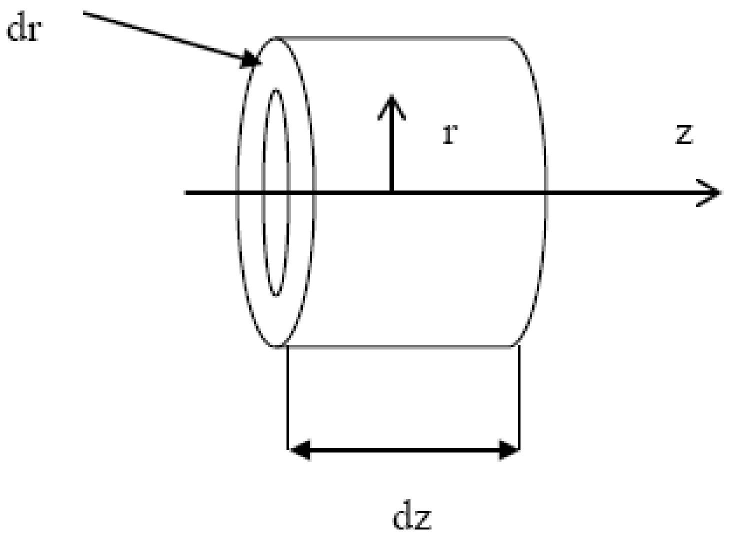
$$Pe_{Mi} = \frac{v_s L}{\varepsilon D_{ai}} \qquad Pe_H = \frac{v_s L}{\lambda_{am}} \qquad \mathrm{Da}_i = \frac{L r_V (c_k^o, T_o)}{c_i^o v_s} \qquad \beta = \frac{L r_V (c_k^o, T_o)(-\Delta H_r)}{v_s c_{pm} \rho_g v_s T_o}$$

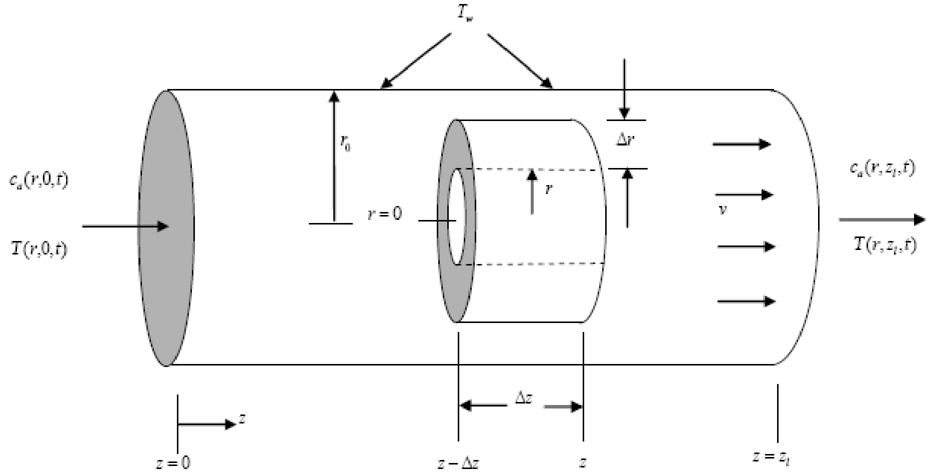
2-D pseudo homogeneous model with axial and radial dispersion

$$N_i = -D_{ai}\frac{\partial c_i}{\partial z} - D_{ri}\frac{\partial c_i}{\partial r} + y_i\sum_{j=1}^{NS} N_j = -D_{ai}\frac{\partial c_i}{\partial z} - D_{ri}\frac{\partial c_i}{\partial z} + c_i.\mathrm{v}$$

$$N_H = -\lambda_{am}\frac{\partial T}{\partial z} - \lambda_{rm}\frac{\partial T}{\partial r} + \mathrm{v}\rho_g c_{pm} T$$

Balance element of volume





Balance equations

$$D_{ri}\left(\frac{\partial^2 c_i}{\partial r^2} + \frac{1}{r}\frac{\partial c_i}{\partial r}\right) + D_{ai}\frac{\partial^2 c_i}{\partial z^2} - \mathrm{v}_s\frac{\partial c_i}{\partial z} + \nu_i r_V = 0$$

$$\lambda_{rm}\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right) + \lambda_{am}\frac{\partial^2 T}{\partial z^2} - \mathrm{v}_s \rho_g c_{pm}\frac{\partial T}{\partial z} + (-\Delta H_r) r_V = 0$$

Boundary and initial conditions

$$z = 0, \qquad 0 < r < r_o$$

$$-D_{ai}\frac{\partial c_i}{\partial z} + v c_i = v c_i^o$$

$$-\lambda_{am}\frac{\partial T}{\partial z} + v\rho_g c_{pm} T = v\rho_g c_{pm} T_o$$

$$r = r_o$$

$$\frac{\partial c_i}{\partial r} = 0 \qquad -\lambda_{rm}\frac{\partial T}{\partial r} = h_w(T - T_m)$$

$$r = 0$$

$$\frac{\partial c_i}{\partial r} = 0 \qquad \frac{\partial T}{\partial r} = 0$$

Fluidized bed catalytic reactor

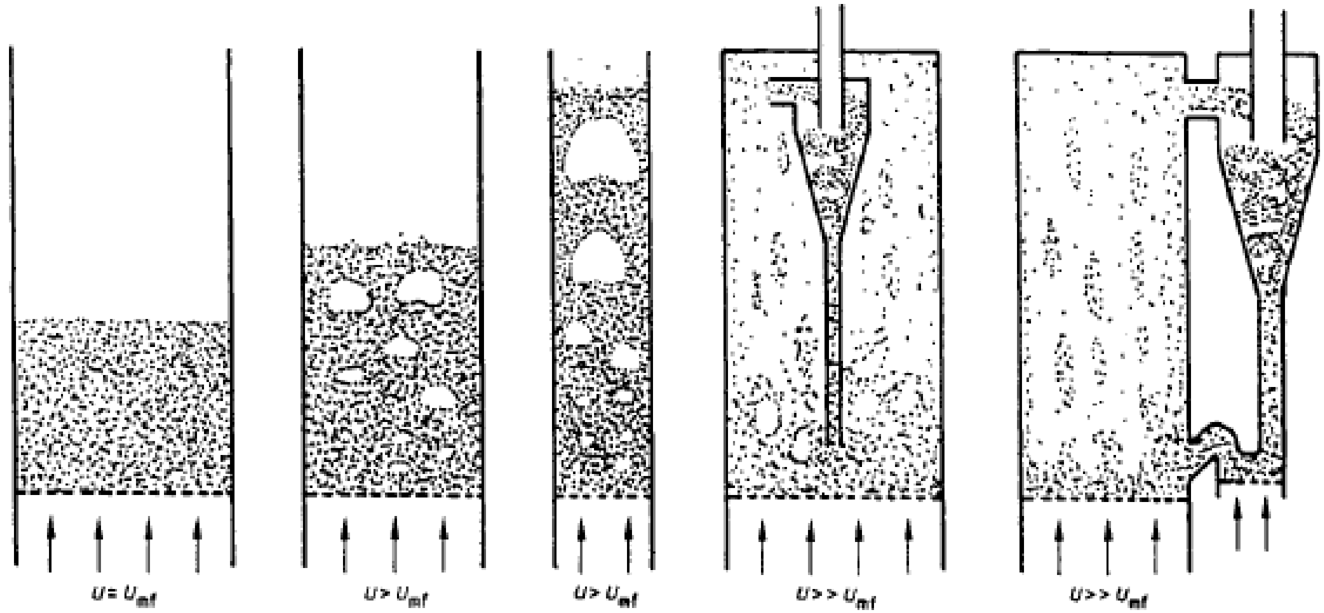


Figure 2. Forms of gas–solids fluidized beds.

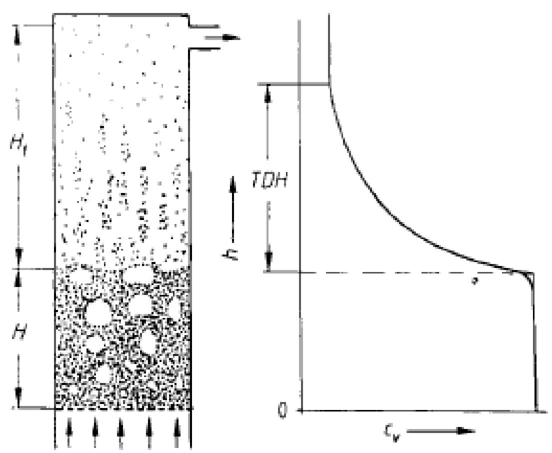


Figure 7. Schematic drawing of fluidized bed and freeboard.

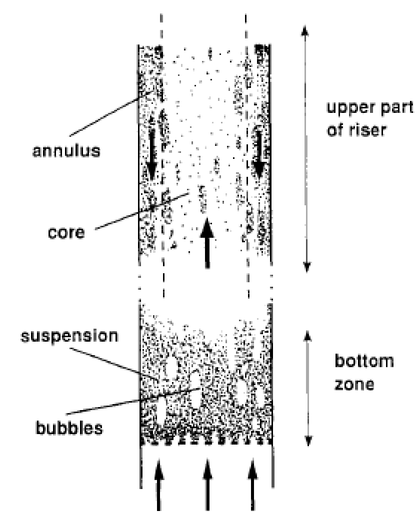


Figure 9. Schematic diagram of flow structure in a circulating fluidized bed.

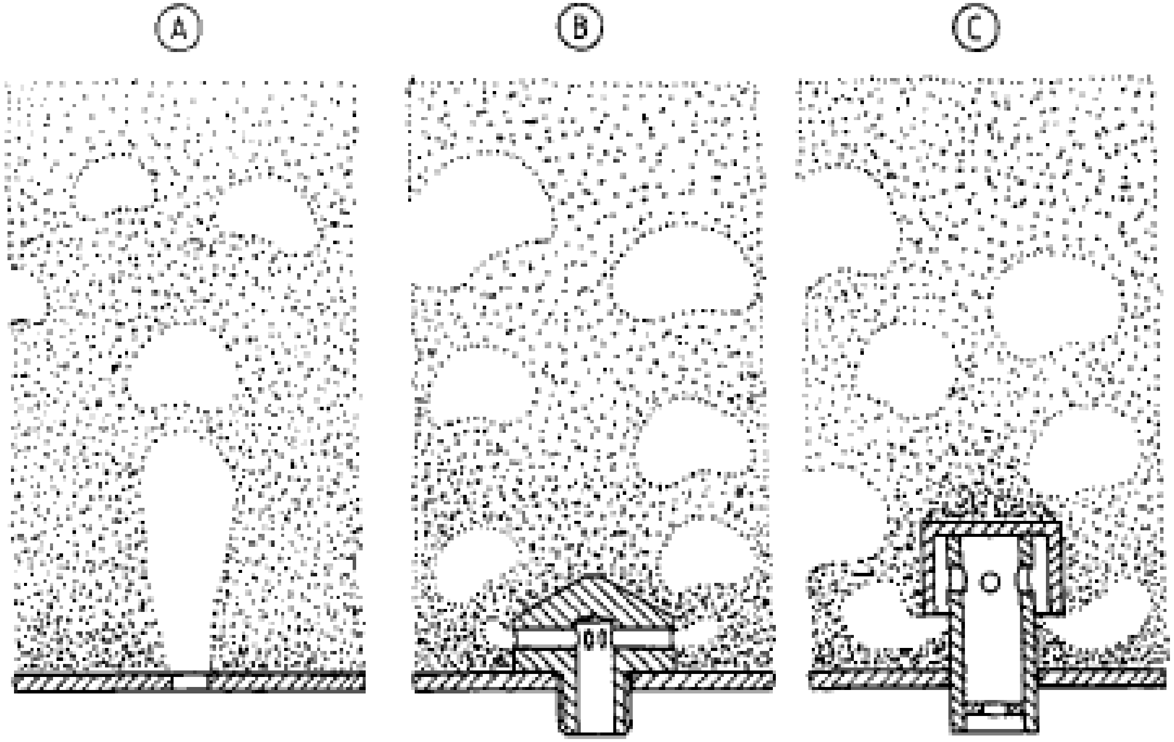


Figure 4. Industrial gas distributors: (A) perforated plate; (B) nozzle plate; (C) bubble-cap plate.

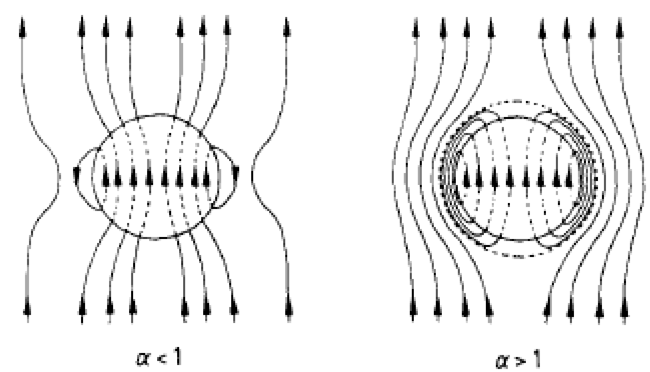


Figure 5. Gas flow for isolated rising bubbles in the Davidson model [30].

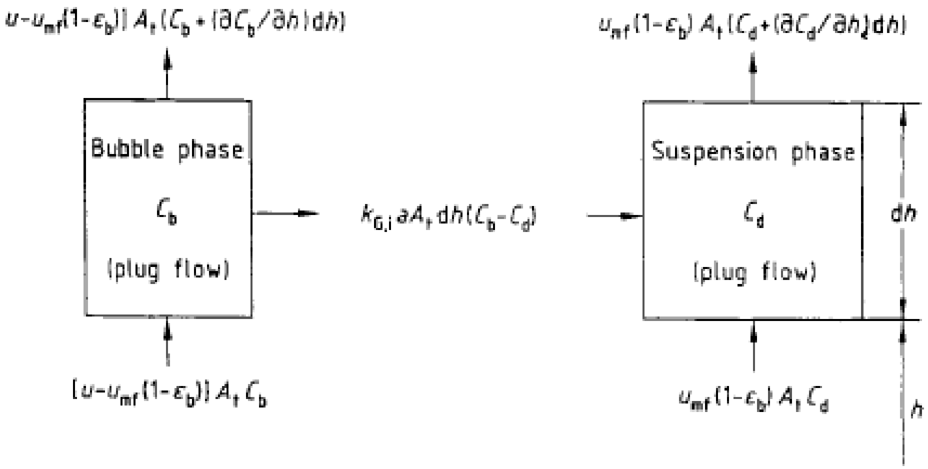


Figure 20. Two-phase model of the fluidized-bed reactor.

$$\varepsilon_b \frac{\partial C_{bi}}{\partial t} = -[u - u_{mf}(1-\varepsilon_b)] \times \frac{\partial C_{bi}}{\partial h} - k_{G,i} \times a \times (C_{bi} - C_{di}) \quad (26)$$

and, for the suspension phase

$$(1-\varepsilon_b)[\varepsilon_{mf} + (1-\varepsilon_{mf})\varepsilon_i] \frac{\partial C_{di}}{\partial t} = -u_{mf}(1-\varepsilon_b) \times \frac{\partial C_{di}}{\partial h} + k_{G,i} \times a \times (C_{bi} - C_{di}) + (1-\varepsilon_b) \times (1-\varepsilon_{mf})\rho_s \sum_{j=1}^{M} \nu_{ij} r_j \quad (27)$$

In eqs 26 and 27 the following simplifying assumptions have been made:

(i) Plug flow through the suspension phase at an interstitial velocity (u_{mf}/ε_{mf}).
(ii) Bubble phase in plug flow, bubbles are solids free.
(iii) Reaction in suspension phase only.
(iv) Constant-volume reaction (Ref. 99 shows how to handle a change in the number of moles).
(v) Sorption effects are neglected (see Ref. 102 for handling sorption).

Here ε_i is the porosity of the catalyst particles, a is the local mass-transfer area per unit of fluidized-bed volume, which can be calculated as

$$a = \frac{6\varepsilon_b}{d_v} \quad (28)$$