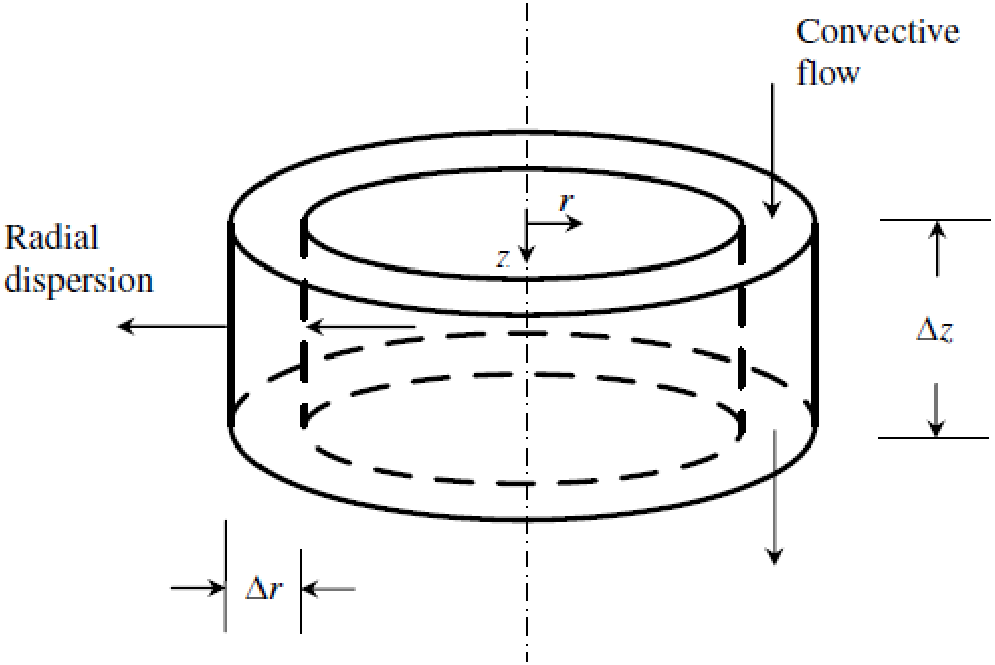
CHE 611
Advanced Chemical Reaction Engineering



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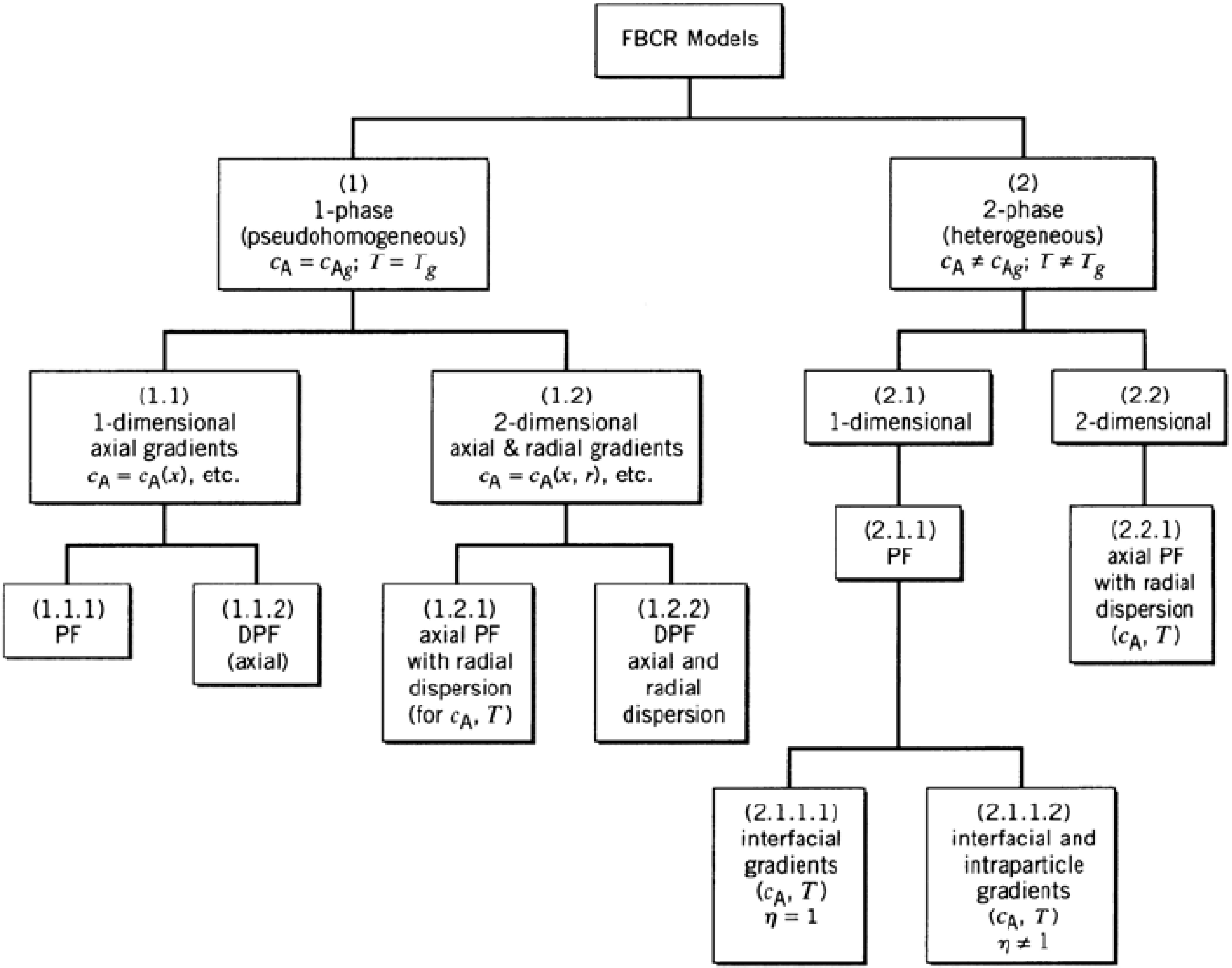
Fixed bed reactor models[10]

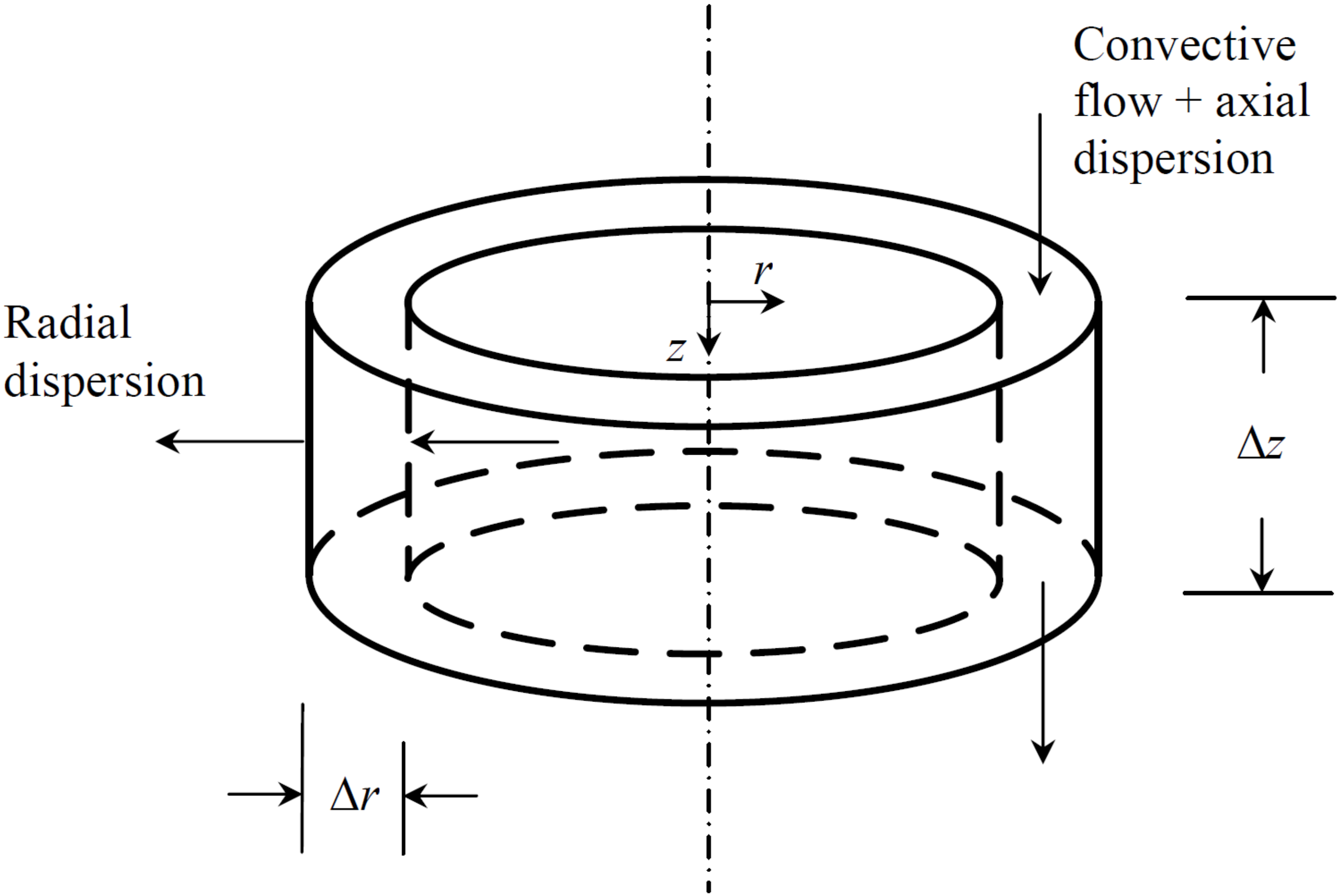


Fixed bed reactor models[10]

(1) In a "one-phase" or pseudohomogeneous model, intraparticle gradients are ignored, so that everywhere in the catalyst bed, the value of concentration (c_A) or temperature (T) is the same as the local value for bulk fluid (c_{Ag} or T_g). The actual two-phase system (fluid and catalyst) is treated as though it were just one phase. In a two-phase or heterogeneous model, intraparticle gradients are allowed, so that, locally, within the particle, $c_A \neq c_{Ag}$ and $T \neq T_g$. The effects of these gradients are reflected in the particle effectiveness factor, η (Section 8.5.4), or an overall effectiveness factor, η_o (Section 8.5.6). If the reactor operates nearly isothermally, a single value of η or η_o may be sufficient to describe thermal and concentration gradients. However, if operation is nonisothermal, η and/or η_o may vary along the length of the vessel, and it may be necessary to account explicitly for this behavior within the reactor model. A further discussion of the effects of interparticle and intraparticle gradients is presented in Section 21.6.

(2) In a one-dimensional model, gradients of c_A and T at the bed level are allowed only in the axial direction of bulk flow. In a two-dimensional model, gradients at the bed level in both the axial and radial directions are taken into account.

Steady-state two-dimensional pseudo-homogeneous model



Steady-state two-dimensional pseudo-homogeneous model

$$Mass\ balance:$$
$$\left(Rate\ of\ mass\ in\right)-\left(Rate\ of\ mass\ out\right)+\left(Rate\ of\ mass\ generation\right)$$
$$-\left(Rate\ of\ mass\ consumption\right)=\left(Rate\ of\ accumulation\ of\ mass\right)$$

$$Energy\ balance:$$
$$\left(Rate\ of\ energy\ in\right)-\left(Rate\ of\ energy\ out\right)+\left(Rate\ of\ energy\ generation\right)$$
$$-\left(Rate\ of\ energy\ consumption\right)=\left(Rate\ of\ accumulation\ of\ energy\right)$$

Steady-state two-dimensional pseudo-homogeneous model

Continuity equation (Constant D_{ea} and D_{er}):

$$D_{ea}\frac{\partial^2 c_A}{\partial z^2}+D_{er}\left(\frac{\partial^2 c_A}{\partial r^2}+\frac{1}{r}\frac{\partial c_A}{\partial r}\right)-\frac{\partial(uc_A)}{\partial z}-\rho_B\cdot(-r_A)=0$$

Energy equation (Constant $c_{p,}$ Δh_{rxn} and k_{er}):

$$k_{ea}\frac{\partial^2 T}{\partial z^2}+k_{er}\left(\frac{\partial^2 T}{\partial r^2}+\frac{1}{r}\frac{\partial T}{\partial r}\right)-Gc_p\frac{\partial T}{\partial z}+\rho_B\cdot(-r_A)(-\Delta h_{rxn})=0$$

For the derivations, see class notes and book by Missen, Ref. 10.

Steady-state two-dimensional pseudo-homogeneous model with negligible axial diffusion

Peclet number for mass transfer:

$$Peclet\ number = \frac{Mass\ trasnfer\ rate\ by\ convection}{Mass\ transfer\ rate\ by\ conduction}$$

$$Pe_{r,m} = \frac{u \cdot d_p}{D_r} = \frac{G \cdot d_p}{\rho \cdot D_r}$$

Peclet number for heat transfer:

$$Peclet\ number = \frac{Heat\ trasnfer\ rate\ by\ convection}{Heat\ transfer\ rate\ by\ conduction}$$

$$Pe_{r,h} = \frac{u \cdot d_p}{k_r} = \frac{G \cdot c_p \cdot d_p}{k_r}$$

Boundary conditions

$$X = 0 \; and \; T = T_0 \qquad z = 0$$

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

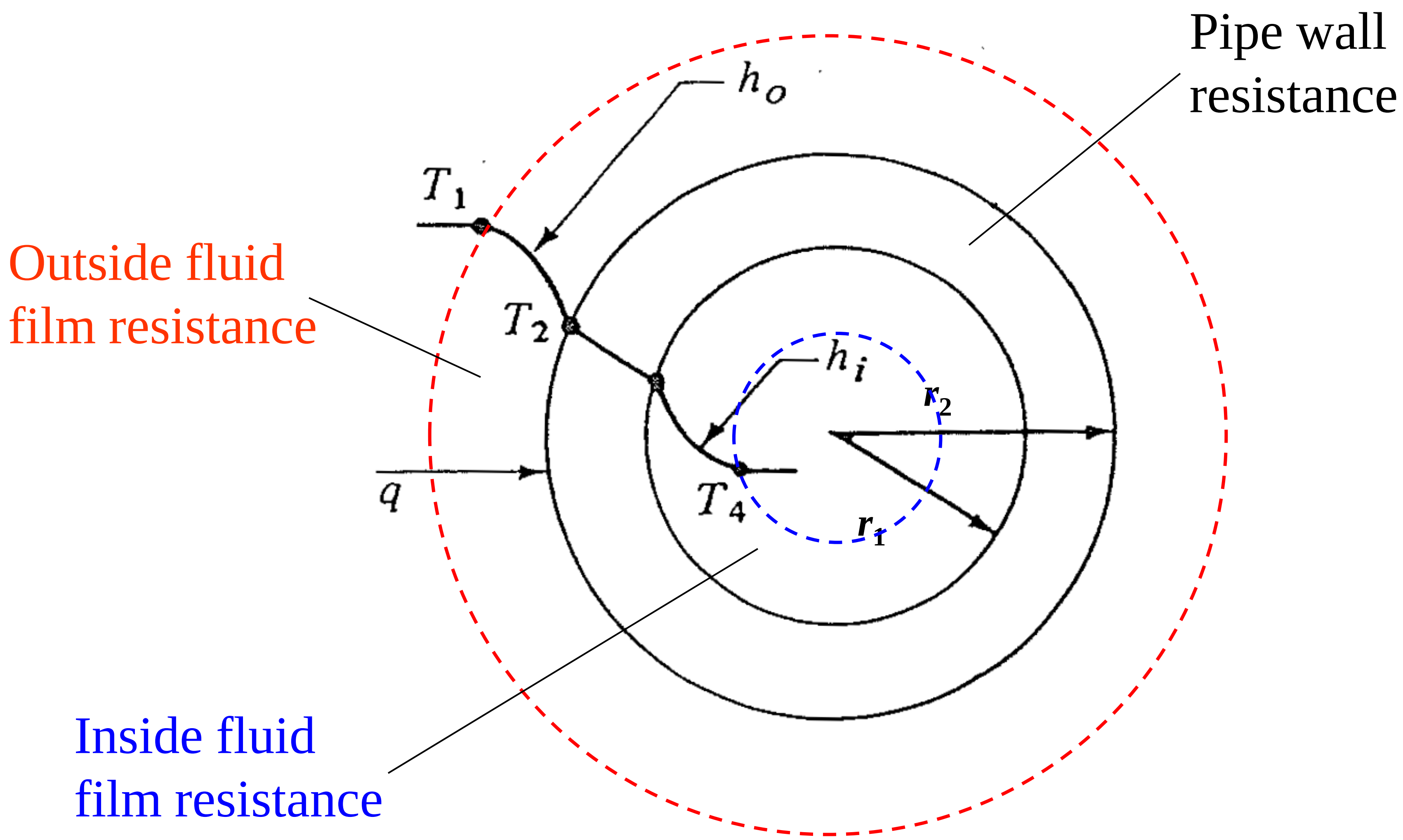
$$\frac{\partial X}{\partial r} = 0 \qquad r = R_i$$

$$-k_r \cdot \frac{\partial T}{\partial r} = U_i \cdot (T_f - T) \qquad r = R_i$$

Overall heat transfer coefficient, *U*

How can one find the overall heat transfer coefficient?

Overall heat transfer coefficients: hollow cylinder



Individual and overall heat transfer coefficients: hollow cylinder

$$\frac{1}{U_i} = \frac{1}{h_i} + \frac{A_i \cdot \ln(r_2 / r_1)}{2 \cdot \pi \cdot k \cdot L} + \frac{A_i}{h_o \cdot A_o}$$

$$\frac{1}{U_o} = \frac{A_o}{h_i \cdot A_i} + \frac{A_o \cdot \ln(r_2 / r_1)}{2 \cdot \pi \cdot k \cdot L} + \frac{1}{h_o}$$

Bed properties

$$Particle\ density = \rho_p = \frac{\rho_s}{(\rho_s \times v_P) + 1}$$

$$Bulk\ voidage = \varepsilon_B = 1 - \frac{\rho_B}{\rho_p}$$

$$Bulk\ density = \rho_B = \rho_p \cdot (1 - \varepsilon_p) \cdot (1 - \varepsilon_B)$$

$$Particle\ Reynolds\ number = Re_p = \frac{d_p \cdot G}{\mu}$$

Effective radial mass diffusivity [7]

Effective Radial Diffusivity (c)

$$N_{Jr} = -\mathcal{D}_r \left(\frac{\partial C_J}{\partial r} \right)_{z,r}$$

Typical commercial reactors with Sc=0.7

$$\frac{\varepsilon \mathcal{D}_r}{u_s D_p} = \frac{1}{m} + \frac{0.38}{Re}$$

$D_p/D > 0.1$

$m = 11$ for $Re > 400$

$m = 57.85 - 35.36 \log Re + 6.68 (\log Re)^2$
for $20 < Re < 400$

For $D_p/D < 0.1$ divide
$\mathcal{D}_r$ calculated from above by

$$\left[1 + 19.4 \left(D_p / D\right)^2\right]$$

For more general equation in terms of Re, tortuosity, and ε, see Ref. (d).

very approx.

$$\frac{u_s D_p}{E \mathcal{D}_r} = 6\text{-}20$$

Wall heat transfer coefficient [7]

Wall Heat-Transfer Coefficient (b) For two-dimensional model $h_w = \frac{q}{A_t\left(T_{R_t} - T_w\right)}$ where T_{R_t} = Temp at $r_t = R_t$	Spherical Particle* $\frac{h_w D_p}{\lambda_f} = 0.19\ Re^{0.79} Pr^{0.33}$ $20 \leq Re \leq 7600$ and $0.05 \leq D_p/D \leq 0.3$	14%	100-250 $\frac{kcal}{m^2 hr\ ^\circ C}$
	Cylindrical Particle* $\frac{h_w D_p}{\lambda_f} = 0.18\ Re^{0.93} Pr^{0.33}$ $20 \leq Re \leq 800$ and $0.03 \leq D_p/D \leq 0.2$	33%	

Effective radial thermal conductivity [7]

Effective Radial Thermal Conductivity (c)

$$-\lambda_r \left(\frac{\partial T}{\partial r_t}\right)_{r_t = R_t} = \frac{q}{A_i}$$

$$\frac{h_w D_p}{\lambda_r} \frac{\varepsilon}{1-\varepsilon} = 0.27$$

Use value of h_w to calculate λ_r

Applies: $500 < \frac{D_p G}{\mu(1-\varepsilon)} < 6000$

$0.05 < D_p/D < 0.15$

approx. $1\text{-}10 \; \frac{\text{kcal}}{\text{m}^2\,\text{hr}\,{}^\circ\text{C}}$

$$\frac{\lambda_r}{\lambda_f} = 1 - 12$$

Ergun equation for pressure drop

$$-\frac{dp}{dz} = \frac{150 \cdot G \cdot \mu}{\rho \cdot \phi_s{}^2 \cdot d_v{}^2} \cdot \frac{(1-\varepsilon_B)^2}{\varepsilon_B^3} + \frac{1.75 \cdot G^2}{\rho \cdot \phi_s \cdot d_v} \cdot \frac{1-\varepsilon_B}{\varepsilon_B^3}$$

Thermodynamic properties of a mixture

Heat capacity:

$$c_p = y_A \cdot c_{p,A}(T) + y_B \cdot c_{p,B}(T) + y_C \cdot c_{p,C}(T) + y_I \cdot c_{p,I}(T)$$

$$\frac{c_{p,i}}{R \cdot M_i} = a_{0,i} + a_{1,i} \cdot T + a_{2,i} \cdot T^2 + a_{3,i} \cdot T^3 + a_{4,i} \cdot T^4$$

Average molecular weight:

$$M_{ave} = y_A \cdot M_A + y_B \cdot M_B + y_C \cdot M_C + y_I \cdot M_I$$

Density: (applicable at low pressure)

$$\rho = \frac{p \cdot M_{ave}}{R \cdot T}$$

Thermodynamic properties of a mixture

Transport properties such as mass diffusivity, thermal conductivity, viscosity should not be taken as additive. Recommended mixing rules should be applied for such calculations. See Bird et al. Ref. 8. Chapters 1, 9, and 17.

Steady-state one-dimensional pseudo-homogeneous model with negligible axial diffusion for adiabatic operation

Continuity equation:

$$\frac{dX_A}{dz} = \frac{\pi \cdot D_i^2 \cdot \rho_B \cdot (-r_A)}{4 \cdot F_{A0}}$$

or

$$\frac{dX_A}{dz} = \frac{\rho_B \cdot (-r_A) \cdot M_0}{G \cdot y_{A0}}$$

Energy equation (Constant c_p and Δh_{rxn}):

$$\frac{dT}{dz} = \frac{\rho_B \cdot (-r_A) \cdot (-\Delta h_{rxn})}{G \cdot c_p}$$

Steady-state one-dimensional pseudo-homogeneous model with negligible axial diffusion for non-adiabatic operation

Energy equation (Constant c_p and $_{\Delta}h_{rxn}$):

$$\frac{dT}{dz} = \frac{\rho_B \cdot (-r_A) \cdot (-\Delta h_{rxn})}{G \cdot c_p} - \frac{4 \cdot U_i \cdot (T - T_f)}{G \cdot c_p \cdot D_i}$$

Steady-state one-dimensional pseudo-homogeneous model with negligible axial diffusion

What would be the boundary conditions for each case?

Packed column: A few rules of thumb

1. Usually d_p is chosen so that the ratio $D_i/d_p > 10$.
2. In one of the criteria, the effect of axial dispersion depends on the ratio of the length of the reactor to the particle size. If the ratio is 100 or more, the effect is usually negligible compared to convective mass transfer.
3. Carman-Kozeny equation is suitable for fine particles. Ergun equation works well for both laminar and turbulent regions.

Solution of partial differential equations

- Finite difference approach
- Finite element approach

Finite difference:

- Explicit methods

  (Easy to put but beware of convergence and stability)
- Implicit methods

  The Crank-Nicolson method

Finite element:

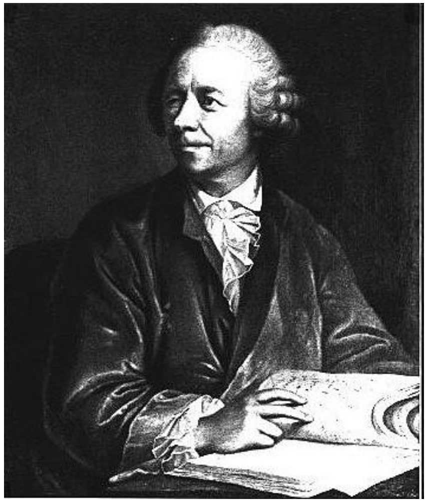
- Comsol Multiphysics (old name Femlab), Fluent etc.

Euler's method

Euler's method is employed for approximate solution of ordinary differential equations with initial value problems.

$$y_{n+1} = y_n + h \cdot f(x_n, y_n)$$

$$h = x_{n+1} - x_n$$



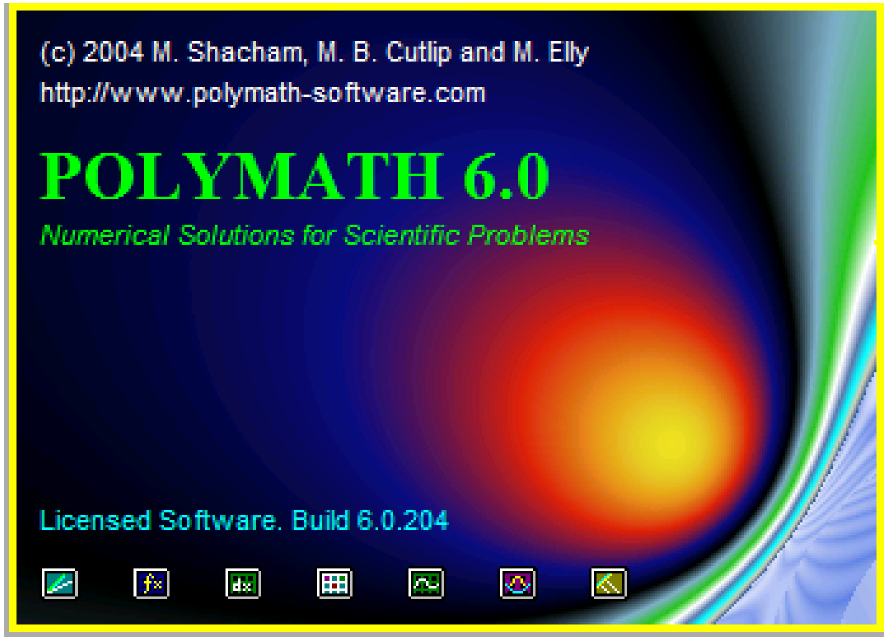
Euler 1707-1783

Take interval "*h*" as low as possible. Take at least 100 steps for the Euler's method for a better accuracy.

Runge-Kutta 4th order method has better efficiency than Euler's method.

Polymath software

Polymath software is an excellent source for solving single and simultaneous ordinary differential equations.



Problem

A gas phase adiabatic fixed bed reactor is to be designed for a dehydrogenation of methylcyclohexane (MCH) to toluene and hydrogen. The feed to the reactor is pure methylcyclohexane flowing at the rate of 100 mol/s. The temperature and pressure conditions are 360°C and 2.0 bar. Assuming the principal reaction is clean and no byproducts are formed,

a) find out the weight of the catalyst required for a total of 90% conversion of methylcyclohexane and in doing so determine the temperature and concentration profiles

b) use the Ergun equation to find out the successive pressure drop (total pressure profile) in the bed

Problem

The rate equation for the problem is given below:

$$(-r_A) = \frac{k \cdot \left(p_A - \frac{p_B \cdot p_C^3}{K} \right)}{p_A + p_B \cdot K'}$$

$$K' = \frac{K_B}{K_A} = 0.32$$

$$K = 3600 \cdot \exp\left(\frac{-217650}{8.3143} \left(\frac{1}{T} - \frac{1}{650} \right) \right), \text{ bar}^3$$

$$k = 6.60 \times 10^{-5} \exp\left(B \cdot \left(1 - \frac{594.9}{T} \right) \right), \text{ mol} \cdot \text{s}^{-1} \cdot \text{g-cat}^{-1}$$

$$B = 10.15$$

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