UNIVERSITEIT TWENTE.

# Multiphase Reactor Technology

## HC 2: Fixed Bed Reactors
## **Description & Modeling**

**Sascha Kersten**

**Fausto Gallucci**

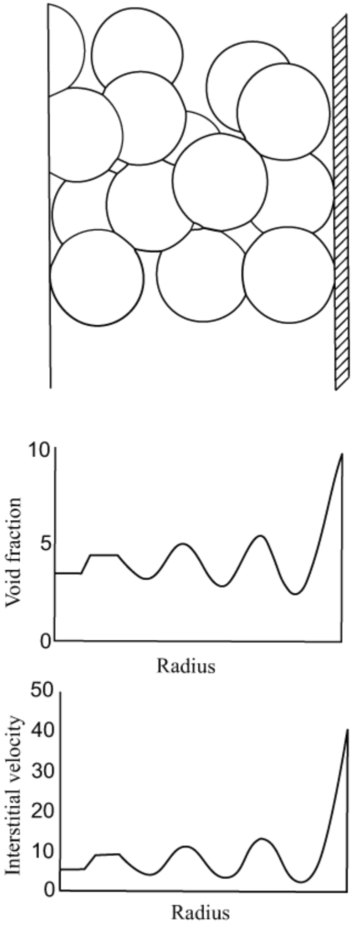
# Transport phenomena in fixed bed reactors
## description of prevailing phenomena

- Bed level:
  - ✓ Flow distribution over catalyst bed or (parallel) tubes
  - ✓ Flow inside the catalyst bed
  - ✓ Mass and heat transport in the catalyst bed

- Catalyst particle level:
  - ✓ External mass and heat transfer to the catalyst particle
  - ✓ Internal diffusion of mass and heat
  - ✓ Adsorption and chemical reaction at (internal) surface

# Velocity profile

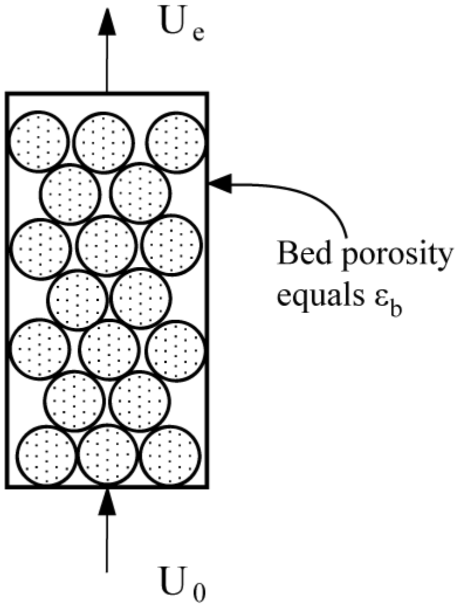
- Local / linear velocity, V
- Superficial velocity, $U_o$
  - $U_o$ = volumetric flow rate / total area
    - For a tube: $U_0 = \frac{\phi_v}{{}^{1}/{}_{4}\pi d_t^2}$
- Plug flow is a good approximation for the superficial velocity



# frictional pressure drop and flow field

- Frictional pressure drop (for example Ergun equation)

$$-\frac{dp}{dz} = 150\,\frac{(1-\varepsilon_b)^2}{\varepsilon_b{}^3}\frac{\mu U_0}{(\phi_s d_p)^2} + 1.75\,\frac{\rho_f}{(\phi_s d_p)}\frac{(1-\varepsilon_b)\,U_0^2}{\varepsilon_b{}^3}$$

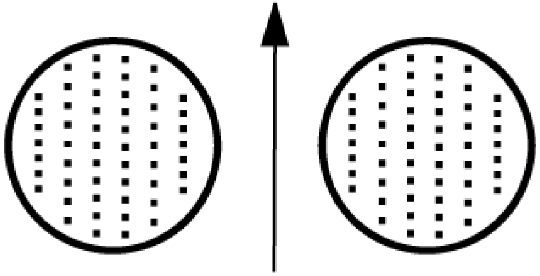



Additional equation (equation of state):

$$\rho_f = \rho_f(p)$$

$$\rho_f = \frac{M_f p}{RT_f}$$

Flow field: governed by the single phase fluid flow equations (Navier-Stokes equations)



for practical purposes we use the volume-averaged fluid equation
Averaging volume big compared to particle size but small compared to fixed bed size

## frictional pressure drop and flow field

- Continuity equation (volume averaged description): $\nabla \varepsilon_b \bar{u} = 0$

interstitial velocity in void spaces between the particles

- Brinkman equation (extension of Darcy's law for wall-bounded flow):

$$0 = -\nabla \mathrm{p} - \beta \bar{u} + \mu_e \nabla^2 \bar{u}$$

$\mu_e$ represents the effective viscosity

expression for the friction coefficient β:

viscous term only of importance near the wall region

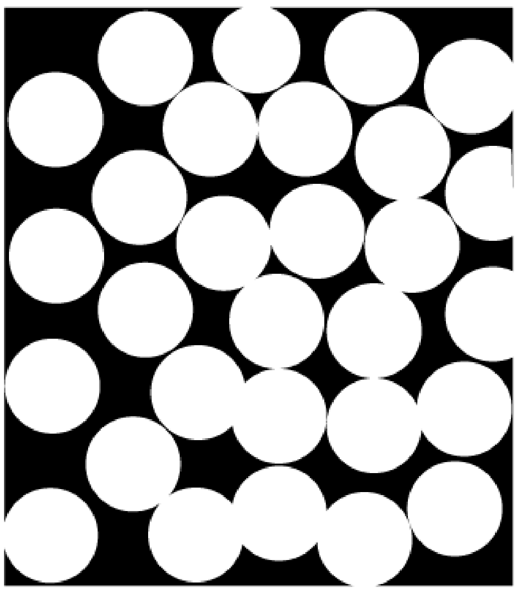
$$\beta = 150 \frac{(1-\varepsilon_b)^2}{{\varepsilon_b}^2} \frac{\mu}{\left(\phi_s d_p\right)^2} + 1.75 \frac{\rho_f}{\left(\phi_s d_p\right)} \frac{(1-\varepsilon_b)\,|\bar{u}|}{\varepsilon_b}$$

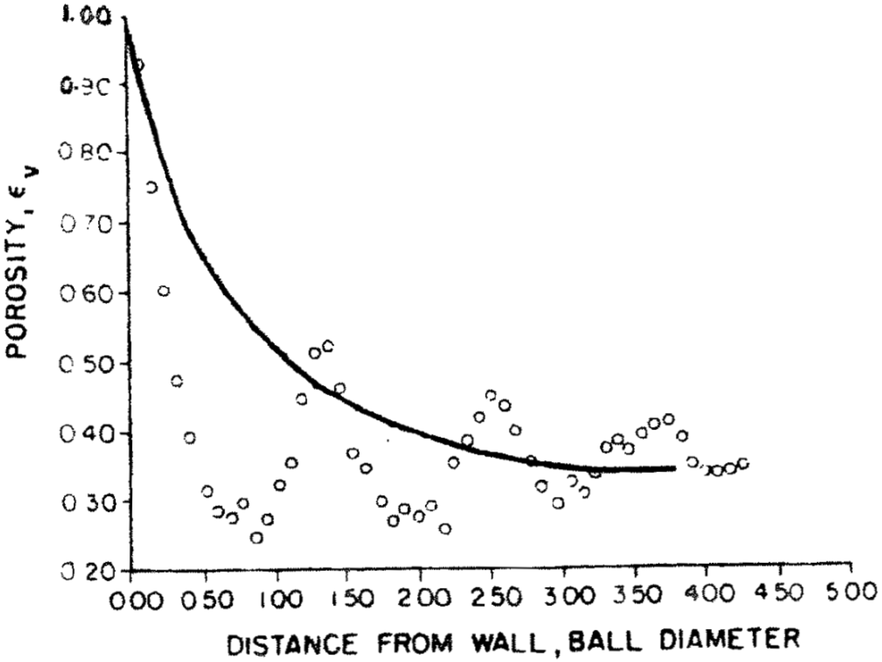
Empirical expression for porosity profile: $\varepsilon_b = \varepsilon_0 \left[1 + Cexp\left(1 - 2\frac{s}{d_p}\right)\right]$

$\varepsilon_0$ and C are fitted constants, s represents the distance from the wall

# frictional pressure drop and flow field

- Porosity profiles in fixed beds and fitted empirical equations



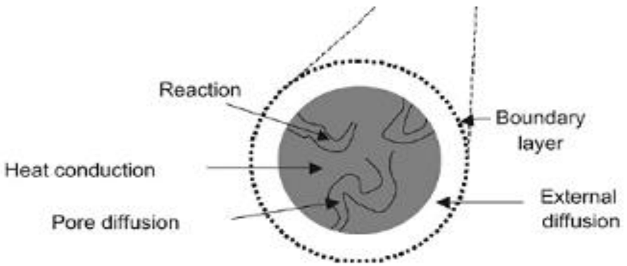



Note: preferential wall flow due to the porosity profile is only important in tubes containing relatively few (<20) particles in radial direction

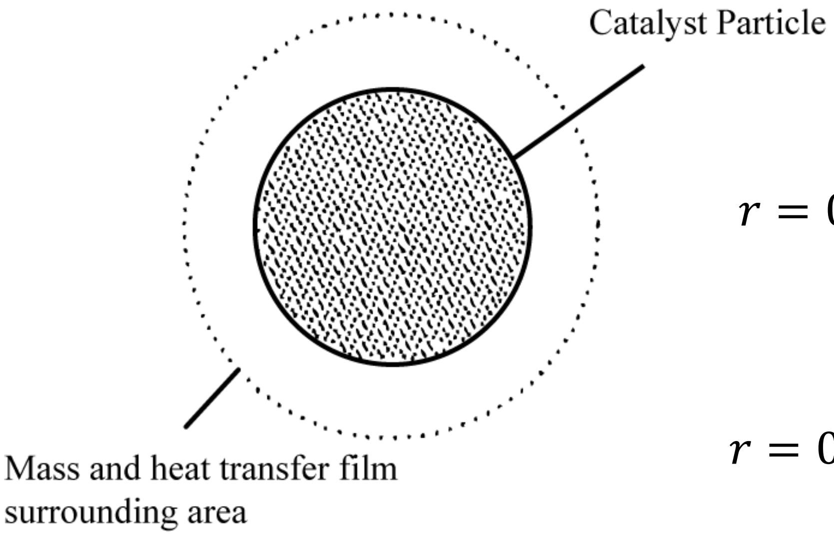
## Particle level

- Description of relevant phenomena for a catalyst particle

1) Mass transport through external boundary layer to particle
2) Diffusion of reactants through macro and micro pores
3) Chemisorption of reactants at catalyst surface
4) Surface reactions at active sites
5) Desorption of products from catalyst surface
6) Diffusion of products through micro and macro pores
7) Mass transport through external boundary from particle + corresponding superimposed heat transport



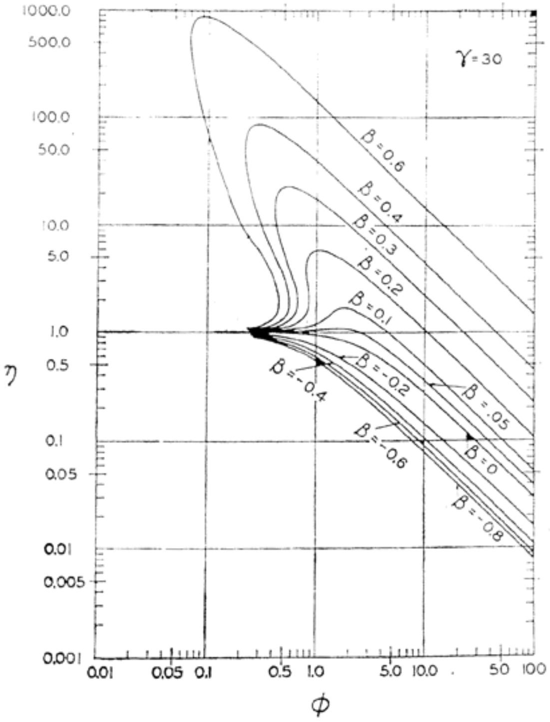
- Single spherical particle model (single reaction):
  - Species conservation equation: $$\frac{\partial C_A}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_A \frac{\partial C_A}{\partial r}\right) + r_A$$
  - Thermal energy equation: $$\rho_s C_{p,s}\frac{\partial T_s}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \lambda_S \frac{\partial T_S}{\partial r}\right) + (-r_A)(-\Delta H_{r,A})$$

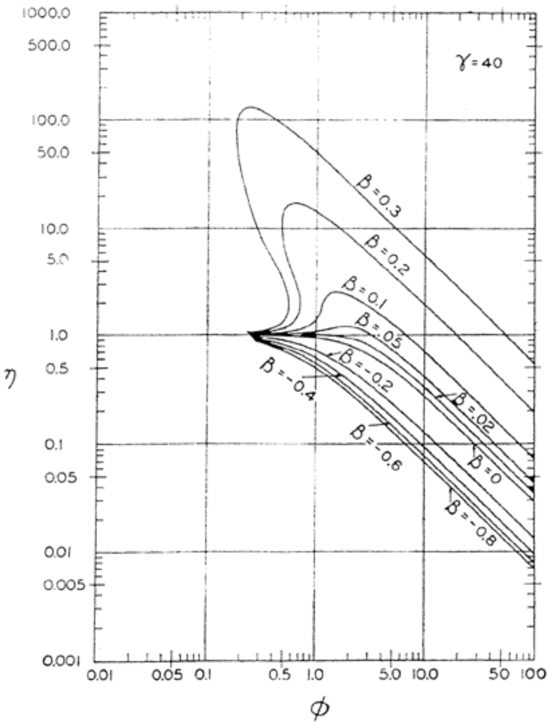



$$r = 0\text{: } \frac{\partial C_A}{\partial r} = 0 \qquad k_f(C_{A,f} - C_A) = D_A\frac{\partial C_A}{\partial r}$$

$$r = 0\text{: } \frac{\partial T_S}{\partial r} = 0 \qquad \alpha_f(T_f - T_S) = \lambda_S\frac{\partial T_S}{\partial r}$$

- Results for first order kinetics:



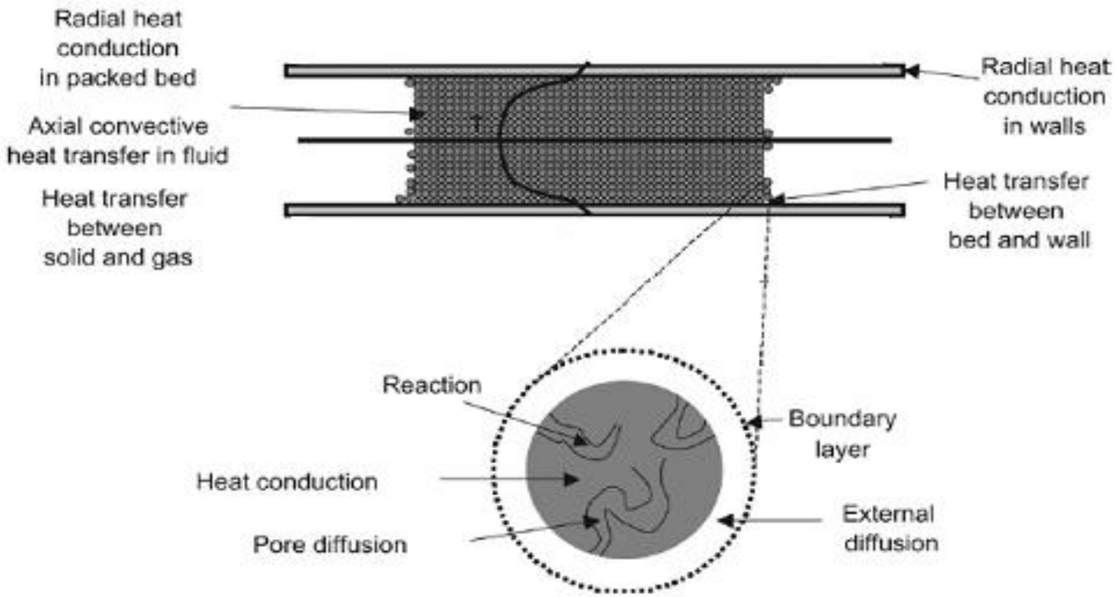

$$\phi = R\sqrt{\frac{k_0}{D_A}} \qquad \gamma = \frac{E_A}{RT_f}$$

$$\beta = \frac{C_{A,f}\left(-\Delta H_{r,A}\right)D_A}{T_f\,\lambda_S}$$

$$\beta = \frac{\Delta T}{T_f}$$

# Transport phenomena at reactor level

- Description of relevant phenomena
  - ✓ Transfer of mass and heat between particles and gas / liquid
  - ✓ Mass dispersion in radial and axial direction
  - ✓ Effective radial and axial heat conductivities



# Mass and Heat transfer between particles and fluid

- Transfer of mass and heat between particles and gas (correlation due to Gunn (1978, Int. J. Heat Mass Transfer, 21, 467)

$$Nu_p = (7 - 10\varepsilon_b + 5\varepsilon_b^2)(1 + 0.7Re_p^{0.2}Pr^{\frac{1}{3}}) + (1.33 - 2.4\varepsilon_b + 1.2\varepsilon_b^2)Re_p^{0.7}Pr^{\frac{1}{3}}$$

- With $Nu_p$, $Re_p$ and Pr respectively the particle Nusselt, Reynolds and the Prandtl number given by:

$$Nu_p = \frac{\alpha_f d_p}{\lambda_f} \qquad Re_p = \frac{\rho_f U_0 d_p}{\mu} \qquad Pr = \frac{\mu C_{p,f}}{\lambda_f}$$

- Adaption for mass transport: replace $Nu_p$ by Sherwood number $Sh_p$ and Pr by Schmidt number Sc, with $Sh_p$ and Sc given by:

$$Sh_p = \frac{k_f d_p}{D} \qquad Sc = \frac{\mu}{\rho_f D}$$

# Radial and axial dispersion coefficients

- Radial and axial dispersion coefficients
  - ✓ Radial mass dispersion coefficient: $$\frac{1}{Pe_{e,r}} = \frac{G_1}{(Re_p Sc)^{G_4}} + \frac{G_2}{1 + \frac{G_3}{(Re_p Sc)^{G_5}}}$$

fitted constants: $G_1$=0.34, $G_2$=0.08, $G_3$=10.8, $G_4$=0.8, $G_5$=1.0

  - ✓ Axial mass dispersion coefficient: $$\frac{1}{Pe_{e,z}} = \frac{E_1}{Re_p Sc} + \frac{E_2}{1 + \frac{E_3}{Re_p Sc}}$$

fitted constants: E1=0.72, E2=0.52 and E3= 9.0

Can (almost) always be neglected

dimensionless groups

$$Pe_{e,r} = \frac{U_0 d_p}{D_{e,r}} \qquad Pe_{e,z} = \frac{U_0 d_p}{D_{e,z}} \qquad Re_p = \frac{\rho_f U_0 d_p}{\mu} \qquad Sc = \frac{\mu}{\rho_f D}$$

# Heat transfer to the wall

- 1D model: $\alpha$ function of velocity, $d_p$, $d_t$ and fluid properties (see Froment and Bischoff)

$$Nu = \frac{\alpha_w d_t}{\lambda_g} = 3.5 Re_p^{0.7} e^{\left(\frac{-4.6 d_p}{d_t}\right)}$$

$$Re_p = \frac{\rho_g d_p u}{\mu_g}$$

- 2D model: effective radial conductivity
  - with our without separate $\alpha_w$ (conductivity changes near the wall)

- Pseudo 2D: 1 D model based on effective radial conductivity

# Transport phenomena in fixed bed reactors
## transport phenomena at macro scale

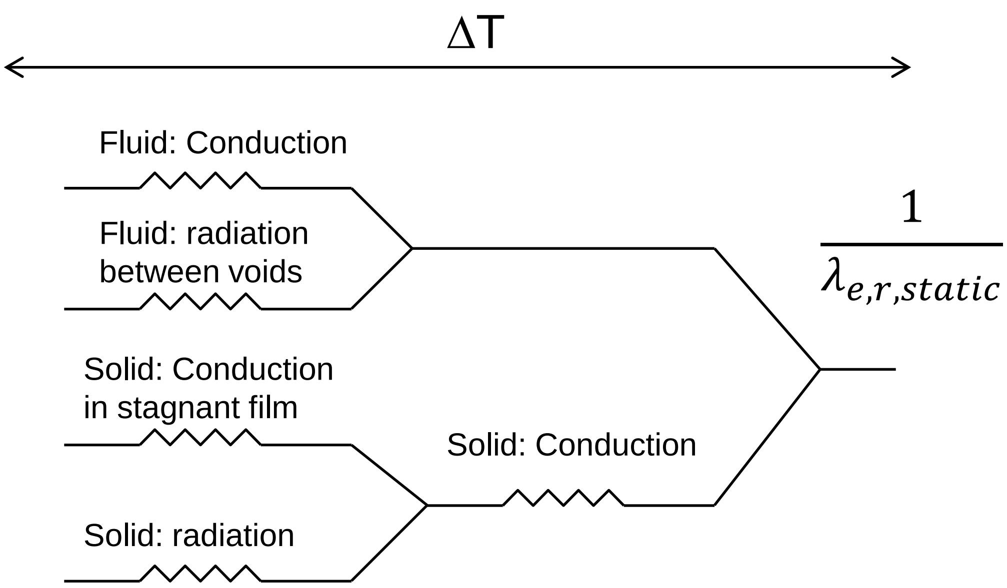
- Effective radial heat conductivity: $\lambda_{e,r} = \lambda_{e,r,static} + \lambda_{e,r,dynamic}$

Parameters influencing effective radial and axial heat conductivity:

- ✓ Conductivity of fluid and solid phases
- ✓ Bed porosity
- ✓ Pressure and temperature
- ✓ Tube and particle diameter
- ✓ Fluid flow
- ✓ Particle characteristics (PSD and shape)
- ✓ Mechanical and optical properties of the particles
- ✓ Thermodynamic and optical properties of fluid phase

# Transport phenomena in fixed bed reactors
## transport phenomena at macro scale

- The cell model of Zehner and Schuendler (1970, Chemie, Ing. Tech. **42/14**, 933) for static part of effective radial conductivity $\lambda_{e,r,static}$:




Cell model is based on combination of heat resistances in series and parallel

$$\lambda_{e,r,static} = \lambda_{b,f} + \lambda_{b,s}$$

# Transport phenomena in fixed bed reactors
## transport phenomena at macro scale

- The cell model of Zehner and Schuendler (1970, Chemie, Ing. Tech. **42/14**, 933) for static part of effective radial conductivity $\lambda_{e,r,static}$:

$$\lambda_{e,r,static} = \lambda_{b,f} + \lambda_{b,s}$$

$$\lambda_{b,f} = \left(1 - \sqrt{(1-\varepsilon_b\,)}\right)\lambda_{f,o}$$

$$\lambda_{b,s} = \sqrt{1-\varepsilon_b}\,\{\omega A + (1-\omega)\Gamma\}\lambda_{f,o}$$

$$\Gamma = \frac{2}{1-\frac{B}{A}}\left\{\frac{A-1}{\left(1-\frac{B}{A}\right)^2}\frac{B}{A}\ln\left(\frac{A}{B}\right) - \frac{B-1}{1-\frac{B}{A}} - \frac{1}{2}(B+1)\right\}$$

$$A = \frac{\lambda_{s,o}}{\lambda_{f,o}} \qquad B = 1.25\left[\frac{1-\varepsilon_b}{\varepsilon_b}\right]^{\frac{10}{9}} \qquad \omega = 0.00726 \quad \text{for spheres}$$

- $\lambda_{f,o}$ and $\lambda_{s,o}$ represent the microscopic conductivity of the fluid and solid phase

# Transport phenomena in fixed bed reactors
## transport phenomena at macro scale

- The dynamic part of effective radial conductivity $\lambda_{e,r,dynamic}$:

$$\frac{\lambda_{e,r,dynamic}}{\lambda_{f,o}} = \frac{Pe}{Pe_{r,f}} \qquad Pe_{r,f} = \frac{8}{C_{form}}\left[2 - \left(1 - 2.0\frac{d_p}{d_t}\right)^2\right]$$

- $C_{form}$ accounts for particle shape and equals 1.15 for spheres

- Effective axial conductivity: $\lambda_{e,z} = \lambda_{e,z,static} + \lambda_{e,z,dynamic}$

From Zehner and Schluender model for $\lambda_{e,r,static}$

- Dynamic contribution: $\dfrac{\lambda_{e,z}}{\lambda_{f,o}} = \dfrac{\lambda_{e,z,static}}{\lambda_{f,o}} + \dfrac{0.0145Pe}{d_p\left(1 + \frac{C}{Re_p \mathrm{Pr}}\right)}$

# Design Models for Fixed Bed Reactors

- Relevance: for design of fixed bed chemical reactors models are required to quantify the effect of important operating variables and explore the operational borders (thermal runaway etc.)
- Pressure drop can be included (see slide 4)

- Types of models

  - Homogeneous one-dimensional model
  - Homogeneous two-dimensional model

The gas and solid phase are treated as a mixture with effective properties

  - Heterogeneous one-dimensional model
  - Heterogeneous two-dimensional model

The gas and solid phase are treated as separate phases

## 1D or 2D ?

$$\frac{-r_A(T)\left(-\Delta H_{r,A}\right)d_t^2 E_a}{4\lambda_{e,r} R T_w^2}\left\{1+\left[\frac{8}{\frac{\alpha_w d_p}{\lambda_{e,r}}}\left(\frac{d_p}{d_t}\right)\right]\right\}$$

Evaluate this group in the hot spot computed from one-dimensional model: if value exceeds 0.4 then two-dimensional model is required

# Homogeneous or heterogeneous models

- Use particle model to check if there are strong interfacial and / or intra-particle temperature and concentration gradients

- Use criteria, such as the ones derived by Mears (paper is on blackboard)

# Design Models for Fixed Bed Reactors
## homogeneous one-dimensional model

$r_A$ in $mol/m^3_{reactor}/s$

- Basic assumptions: no radial gradients, no concentration and temperature differences between phases. Axial conduction and dispersion terms can be neglected

- Continuity species A: $$D_{e,z}\frac{d^2C_A}{dz^2} - U_0\frac{dC_A}{dz} + r_A = 0$$

- Energy equation:
$$\lambda_{e,z}\frac{d^2T}{dz^2} - U_0\rho_f C_{p,f}\frac{dT}{dz} - 4\frac{\alpha_w}{d_t}(T - T_w) + (-r_A)\left(-\Delta H_{r,A}\right) = 0$$

- Boundary conditions at respectively z=0 (inlet) and z=L (outlet)

$$U_0(C_{A,o} - C_A) = -D_{e,z}\frac{dC_A}{dz} \qquad \frac{dC}{dz} = 0 \qquad \text{Continuity species A}$$

$$U_0\rho_f C_{p,f}(T_o - T) = -\lambda_{e,z}\frac{dT}{dz} \qquad \frac{dT}{dz} = 0 \qquad \text{Energy}$$

Or without axial dispersion and conduction: z=0: $C_A = C_{A,o}$ and $T = T_o$

# Design Models for Fixed Bed Reactors
## homogeneous two-dimensional model

$r_A$ in $mol/m^3_{reactor}/s$

- Basic assumptions: no concentration and temperature differences between phases
- Continuity species A: $$\frac{D_{e,r}}{r}\frac{\delta}{\delta r}\left(r\frac{\delta C_A}{\delta r}\right) - U_0\frac{\delta C_A}{\delta z} + r_A = 0$$
- Energy equation: $$\frac{\lambda_{e,r}}{r}\frac{\delta}{\delta r}\left(r\frac{\delta T}{\delta r}\right) - U_0\rho_f C_{p,f}\frac{\delta T}{\delta z} + (-r_A)\left(-\Delta H_{r,A}\right) = 0$$
- Boundary conditions: $z = 0$: $C_A = C_{A,o}$ $T = T_o$

$r = 0$: $$\frac{\delta C}{\delta r} = 0 \text{ and } \frac{\delta T}{\delta r} = 0$$

$r = R_t$: $$\frac{\delta C}{\delta r} = 0 \text{ and } \lambda_{e,r}\frac{\delta T}{\delta r} = \alpha_w(T - T_w)$$

Two parameters $\lambda_{e,r}$ and $\alpha_w$ are used to describe the radial heat transport

# Design Models for Fixed Bed Reactors
## homogeneous two-dimensional model

- Effective radial heat conduction $\lambda_{e,r}$

$$\lambda_{e,r} = \lambda_{e,r,static} + \lambda_{e,r,dynamic}$$

Expressions for static and dynamic contributions have been given before

- Bed-wall heat transfer coefficient $\alpha_w$:

$$\alpha_w = \alpha_w^0 + 0.0115 \frac{d_t}{d_p} Re \qquad Re_p = \frac{\rho_f U_0 d_p}{\mu}$$

# Design Models for Fixed Bed Reactors

## heterogeneous one-dimensional model

$r_A$ in mol/$m^3_{reactor}$/s

Specific bed surface

$$a_b = \frac{6(1-\varepsilon_b)}{d_p}$$

- Fluid continuity species A:

$$U_0 \frac{dC_{A,f}}{dz} = -k_f a_b \left(C_{A,f} - C^*_{A,s}\right)$$

- Energy equation fluid:

$$U_0 \rho_f C_{p,f} \frac{dT_f}{dz} = -4\frac{\alpha_i}{d_t}\left(T_f - T_w\right) - \alpha_w a_b \left(T_f - T^*_s\right)$$

- Solid continuity species A:

$$k_f a_b \left(C_{A,f} - C^*_{A,s}\right) = \left(-r_A\left(C^*_{A,s}, T^*_s\right)\right)\eta$$

- Energy equation solid:

$$\alpha_f a_b \left(T^*_s - T_f\right) = \left(-r_A\left(C^*_{A,s}, T^*_s\right)\right)\left(-\Delta H_{r,A}\right)\eta$$

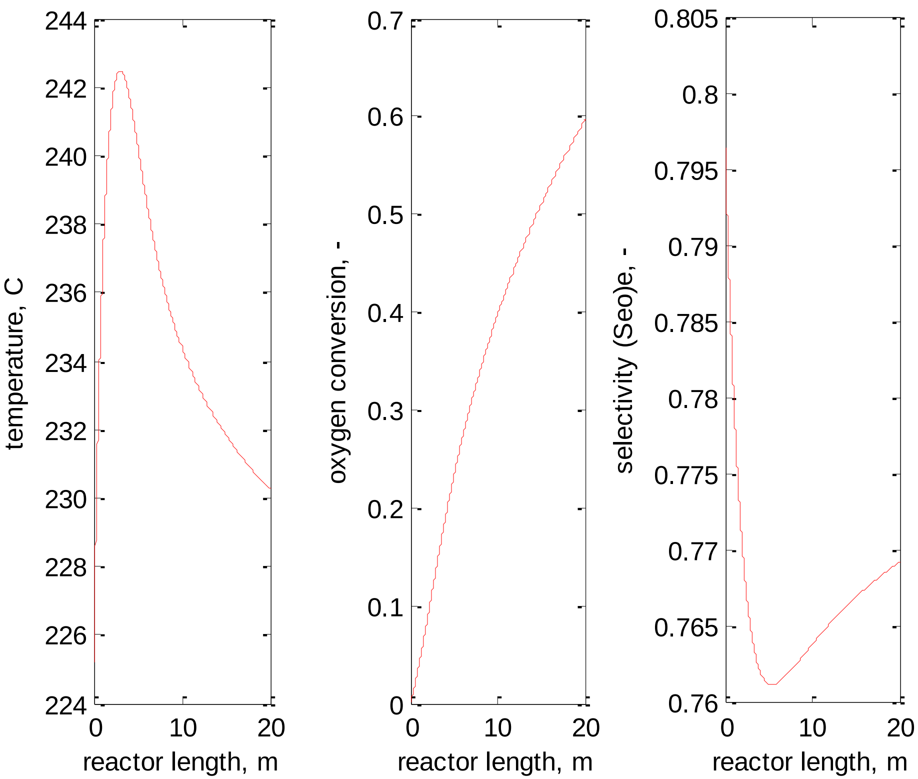
- Boundary conditions: z=0: $C_{A,f}=C_{A,o}$ and $T_f=T_{f,o}$

Superscript * denotes conditions at catalyst particles surface

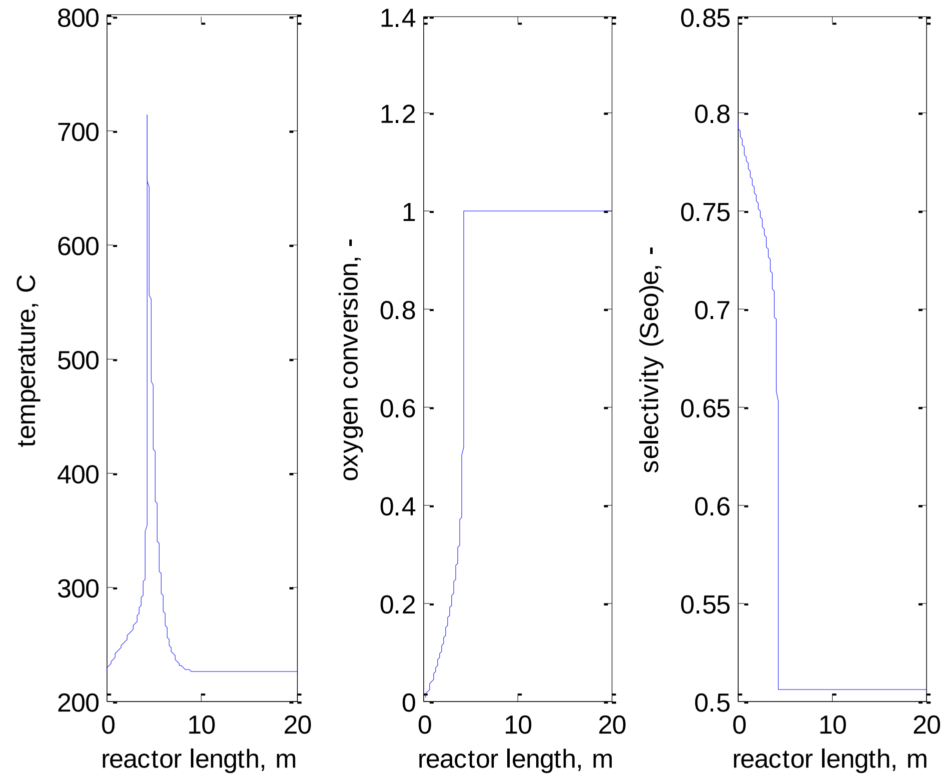
# Ethylene oxide case

## **Run away: 11% $O_2$, other conditions identical**

1-D: U = 446 W/m$^2$/K

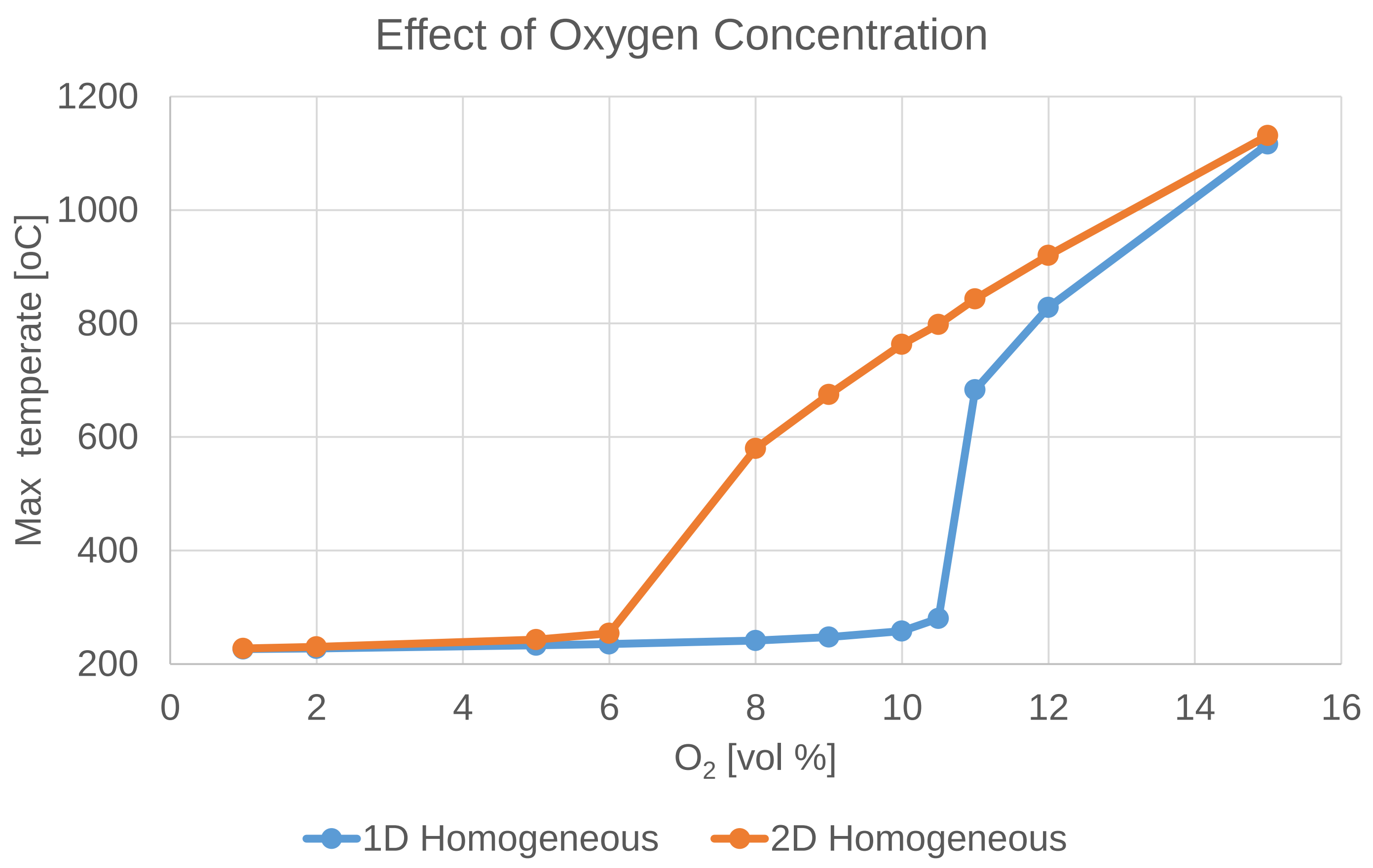



Speudo-2D: U = 316 W/m$^2$/K



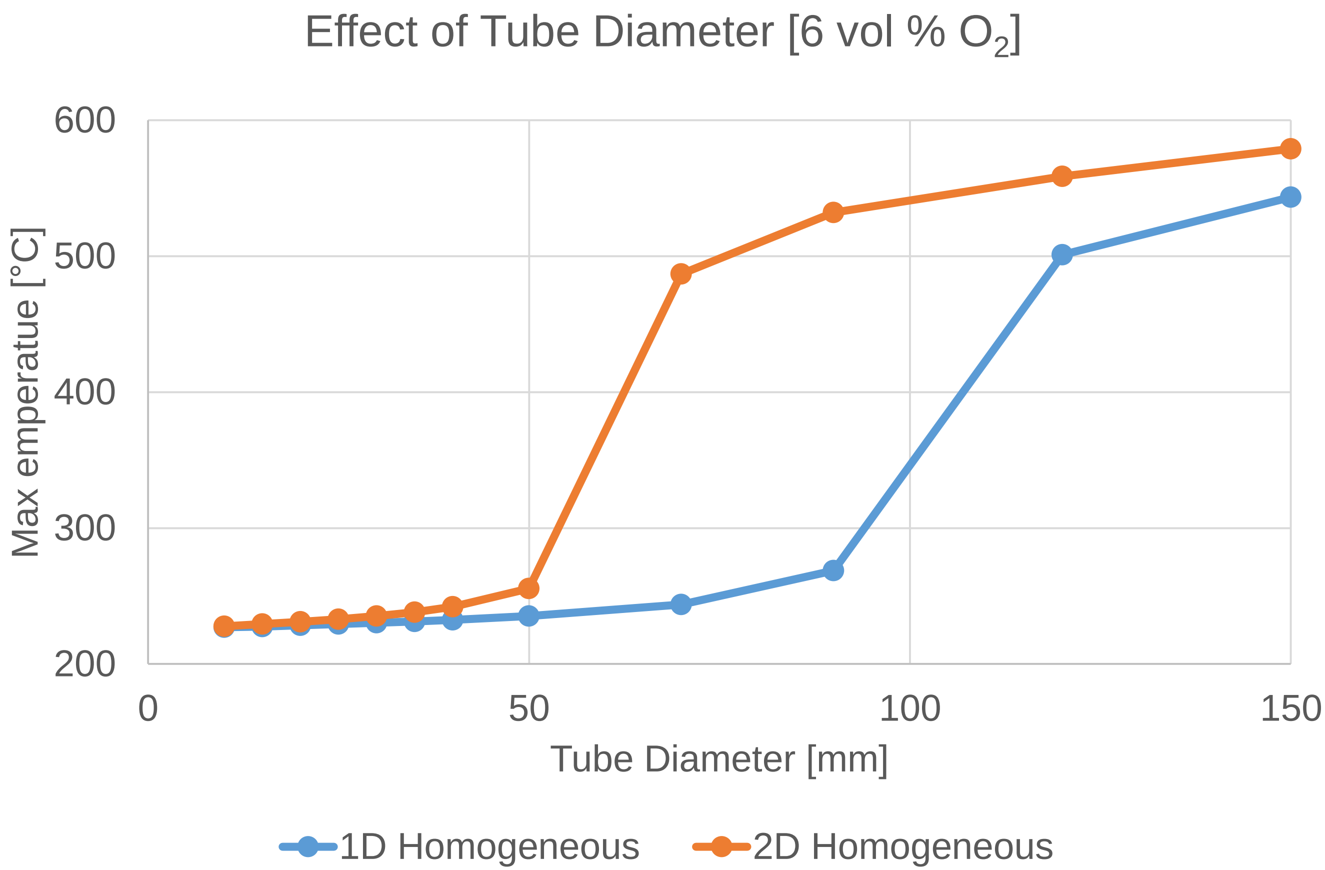
# ETHYLENE OXIDE CASE

## 1D Vs 2D MODEL (HOMOGENEOUS) – RESULT COMPARISON



# ETHYLENE OXIDE CASE

## 1D Vs 2D MODEL (HOMOGENEOUS) – RESULT COMPARISON



# To do for the workshop (Thursday)

- Derive the reactor models yourself
- Catalyst particle problems
  - Order reduction
  - BVP4C slide package on blackboard
- Fixed bed problems
  - DAE slide package on blackboard
  - Fixed bed catalyst particle slide package on blackboard