Overview lecture

• **Modelling membrane permeation**
  – Porous membranes
  – Dense (supported) membranes for $\text{H}_2$
  – Dense membranes for $\text{O}_2$

• **Different reactor concepts**

• **Packed bed membrane reactors**
  – Detailed particle model for heterogeneous catalysts
  – Coupling of SDMs with particle models

• **Fluidized bed membrane reactors**
  – Phenomenological two-phase model
  – CFD-based models: discrete particle models
Modelling of membrane permeation

- Porous membranes

Membrane flux:
(Dusty-Gas-Model):

\[
N_i = \frac{1}{RT} \left( K_0 \frac{4}{3} \sqrt{\frac{8RT}{\pi \langle M \rangle}} + B_0 \frac{\langle p \rangle}{\mu_g} \right) \times \frac{\Delta p_{i,m}}{r_i + \delta_m \ln \left( \frac{r_i + \delta_m}{r_i} \right)}
\]

Parameters \( K_0 \) and \( B_0 \) depend on the pore size/structure distributions.

(a) Viscous mechanism
(b) Knudsen mechanism
(c) Surface diffusion
(d) Multi-layer diffusion
(e) Capillary condensation
(f) Molecular Sieving
Modelling of membrane permeation

• Porous membranes

Fick model: only diffusion

\[ N_i = -D_{i,eff} \frac{p}{RT} \frac{\partial x_i}{\partial r} \]

Bosanquet:

\[ D_{i,eff} = \left[ \frac{1}{D_{i,m}} + \frac{1}{D_{i,K}} \right]^{-1} \]  

(harmonic averaging of molecular and Knudsen diffusion)

Blanck’s law:

\[ D_{i,m} = \frac{1}{1 - x_i} \sum_{j=1}^{n} D_{i,j} x_j \]  

(Bosanquet + Blanck laws strictly only valid for dilute mixtures)

Effective molecular diffusion:

\[ D_{i,j}^{eff} = \frac{\varepsilon}{\tau} D_{i,j} \]  

(\(\varepsilon = \) porosity)

Effective Knudsen diffusion:

\[ D_{i,K}^{eff} = \frac{4}{3} K_0 \sqrt{\frac{8RT}{\pi M_i}} \]  

(\(\tau = \) tortuosity)
Fick’s law: What is wrong?

• Fick’s law (applied to film model):

Flux with respect to the mixture:

\[ J_i = -D_i \frac{dc_i}{dz} \]  \[ \text{[mol/m}^2\text{s]} \]

Diffusivity \[ \text{[m}^2/\text{s]} \]

Flux with respect to the interface:

\[ N_i = k \ (c_{i,0} - c_{i,\delta}) \]  \[ \text{[mol/m}^2\text{s]} \]

Mass transfer coefficient \[ \text{[m/s]} \]

Film model:

\[ k = \frac{D}{\delta} \]
Fick’s law: What is wrong?

• **Binary equimolar diffusion**

  Constant total concentration (i.e. isobaric & isothermal)
  
  \[ c_{tot} = c_1 + c_2 = \text{constant} \]

  Flux of component 1 with respect to the mixture:
  
  \[ J_1 = -D_1 \frac{dc_1}{dz} \]

  Flux of component 2 with respect to the mixture:
  
  \[ J_2 = -D_2 \frac{dc_2}{dz} \]

  Total net flux:
  
  \[ J_{tot} = \sum_{i=1}^{2} J_i = J_1 + J_2 \equiv 0 = -D \frac{d}{dz} (c_1 + c_2) \]

  provided that there is only 1 binary diffusivity \( D \), independent of composition
Fick’s law: What is wrong?

- Consider two ideal gasses separated by a porous membrane

Is the He flux equal to the Ar flux (i.e. $N_{\text{He}} = -N_{\text{Ar}}$)?

pure He high flow rate

pure Ar high flow rate

He

298 K

10^5 Pa

Ar

298 K

10^5 Pa

Multiphase Reactors Group, SPI
Fick’s law: What is wrong?

• Consider two ideal gasses separated by a porous membrane

Observation:
\[ N_{\text{He}} \approx -3 \ N_{\text{Ar}} \]
Much higher He flux despite identical concentration gradients!

Explanation:
– Movement of mixture with respect to membrane!
– Friction He-membrane < Friction Ar-membrane \( \Rightarrow \) pressure gradient
– Resulting in viscous flow from right to left: retarding He, accelerating Ar
Modelling of membrane permeation

- Porous membranes

**Extended Fick model: diffusion + d’Arcy**

Extended Fick:

\[ N_i = -D_i^{eff} \frac{p}{RT} \frac{\partial x_i}{\partial r} + x_i N_{tot} \]

accounts for net total molar flow rate

d’Arcy:

\[ N_{tot} = \left( -\frac{B_0}{\mu} \frac{\partial p}{\partial r} \right) c_{tot} = -\frac{B_0 p}{RT} \frac{\partial p}{\partial r} \]

“viscous flow”

**Extended Fick model:**

\[ N_i = -\frac{1}{RT} \left( D_i^{eff} p \frac{\partial x_i}{\partial r} + \frac{B_0 x_i p}{\mu} \frac{\partial p}{\partial r} \right) \]
Modelling of membrane permeation

• Porous membranes

Extended Fick model for tubular membrane:

\[ R_1 = r_m \]
\[ R_2 - R_1 = \delta_m \]

Steady state component continuity equation for cylindrical membrane:

\[ -\frac{1}{r} \frac{d}{dr} r N_i = 0 \quad \Rightarrow \quad -r N_i = \text{constant} = c \]

Permeation flux = flux at \( r = R_2 \):

\[ -R_2 N_{i,2} = c \quad \Rightarrow \quad N_{i,2} = \frac{-c}{R_2} = \frac{-c}{r_m + \delta_m} \]
Modelling of membrane permeation

• Porous membranes

Extended Fick model for tubular membrane:

Component continuity: \[ N_i = -\frac{c}{r} \]

Substitution of extended Fick model: \[ N_i = -\frac{1}{RT} \left( D_i^{\text{eff}} p \frac{\partial x_i}{\partial r} + \frac{B_0 x_i p}{\mu} \frac{\partial p}{\partial r} \right) \]

\[ \Rightarrow N_i = -\frac{1}{RT} \left( D_i^{\text{eff}} p \frac{\partial x_i}{\partial r} + \frac{B_0 x_i p}{\mu} \frac{\partial p}{\partial r} \right) = -\frac{c}{r} \]

Integration over the tube thickness:

\[ \Rightarrow \int_{R_i}^{R_2} D_i^{\text{eff}} p \frac{dx_i}{dr} \, dr + \int_{R_i}^{R_2} \frac{B_0 x_i p}{\mu} \frac{dp}{dr} \, dr = \int_{R_i}^{R_2} \frac{cRT}{r} \, dr \]
Modelling of membrane permeation

• Porous membranes

Extended Fick model for tubular membrane:

\[
\int_{R_1}^{R_2} D_i^{\text{eff}} p \frac{dx_i}{dr} dr + \int_{R_1}^{R_2} \frac{B_0 x_i p}{\mu} \frac{dp}{dr} dr = \int_{R_1}^{R_2} \frac{cRT}{r} dr
\]

- diffusion
- viscous flow

Important when pressure drop is negligible
Important when concentration gradient is negligible

\[
p \approx \langle p \rangle \quad \text{and} \quad x_i \approx \langle x_i \rangle
\]

\[
\Rightarrow D_i^{\text{eff}} \langle p \rangle \int_{x_{i,1}}^{x_{i,2}} dx_i + \frac{B_0 \langle x_i \rangle}{\mu} \int_{p_1}^{p_2} p dp = cRT \int_{R_1}^{R_2} \frac{dr}{r}
\]

\[
\Rightarrow D_i^{\text{eff}} \langle p \rangle \left( x_{i,2} - x_{i,1} \right) + \frac{B_0 \langle x_i \rangle}{\mu} \frac{1}{2} p_2^2 - p_1^2 = cRT \ln \left( \frac{R_2}{R_1} \right)
\]
Modelling of membrane permeation

• Porous membranes

Extended Fick model for tubular membrane:

\[ D_i^{\text{eff}} \langle p \rangle x_{i,2} - x_{i,1} + \frac{B_0 \langle x_i \rangle}{\mu} \frac{1}{2} p_2^2 - p_1^2 = cRT \ln \left( \frac{R_2}{R_1} \right) \]

Note: \( \langle x_i \rangle \frac{1}{2} p_2^2 - p_1^2 = \langle x_i \rangle \frac{1}{2} p_2 + p_1 \)
\( p_2 - p_1 = \langle p \rangle p_{i,2} - p_{i,1} \)

\[ \Rightarrow \approx \left[ D_i^{\text{eff}} + \frac{B_0 \langle p \rangle}{\mu} \right] p_{i,2} - p_{i,1} = cRT \ln \left( \frac{R_2}{R_1} \right) \]

\[ N_{i,2} = \frac{-c}{R_2} \Rightarrow N_{i,2} = \frac{1}{RT} \left[ D_i^{\text{eff}} + \frac{B_0 \langle p \rangle}{\mu} \right] \frac{\Delta p_{i,m}}{r_i + \delta_m \ln \left( \frac{r_i + \delta_m}{\delta_m} \right)} \]
Fick’s law: What is wrong?

• Consider three inert ideal gases in two-bulb system

A
N₂, CO₂

B
N₂, H₂

at \(t=0\) connected by narrow capillary

\[ x^{0}_{H_2,A} = 0 \]
\[ x^{0}_{N_2,A} = 0.50 \]
\[ x^{0}_{CO_2,A} = 0.50 \]

\[ x^{0}_{H_2,B} = 0.50 \]
\[ x^{0}_{N_2,B} = 0.50 \]
\[ x^{0}_{CO_2,B} = 0 \]

Does N₂ flow: a) from A to B?
  b) from B to A?
  c) not at all?
  d) or does it do a), b) and c)?
Fick’s law: What is wrong?

- Consider three inert ideal gases in two-bulb system

A
N₂, CO₂

at \( t=0 \) connected by narrow capillary

B
N₂, H₂

(isobaric & isothermal)

Reverse diffusion

System: hydrogen (1) - nitrogen (2) - carbon dioxide (3)

Taylor & Krishna (1993)
Fig. 5.4, p. 109
Fick’s law: What is wrong?

• Consider three inert ideal gases in two-bulb system

![Diagram showing two bulbs connected by a narrow capillary. One bulb contains N₂ and CO₂, and the other contains N₂ and H₂. At t=0, they are connected by a narrow capillary.]

Observation:
- H₂ and CO₂ change monotonically to equilibrium concentrations as expected
- N₂ initially diffuses first without concentration gradient and later even against its concentration gradient from A to B, only later bulbs go gradually back to equal compositions

Explanation:
H₂ moves from B to A, and CO₂ from A to B
N₂ molecules more friction with CO₂ than H₂ and CO₂ seems to drag N₂ along from A to B
cannot be explained with Fick’s law!
Fick’s law: What is wrong?

- Generalized Maxwell-Stefan equations:

\[
\vec{d}_i = \sum_{j=1}^{n} \frac{x_i \hat{N}_j - x_j \hat{N}_i}{c_{tot} D_{ij}}
\]

Derivation by considering binary interactions between molecules of different type:

In terms of fluxes with respect to interface \(N_i\):

Generalized driving forces:

\[
c_{tot} RT \vec{d}_i = c_i \nabla_{T,P} \mu_i + \phi_i - \omega_i \nabla p - \left( c_i \tilde{F}_i - \omega_i \sum_{j=1}^{n} c_j \tilde{F}_j \right)
\]

with:

\[
\frac{x_i}{RT} \nabla_{T,P} \mu_i = \sum_{j=1}^{n-1} \left[ \delta_{ij} + x_i \left. \frac{\partial \ln \gamma_i}{\partial x_j} \right|_{T,P,\Sigma} \right] \nabla x_j
\]

\[
\vec{d}_i = \text{driving force for component } i
\]

\[
\sum F_{\rightarrow 1} \propto x_1 x_2 \bar{u}_1 - \bar{u}_2
\]
Fick’s law: What is wrong?

- Generalized Maxwell-Stefan equations:

Rewriting in \((n-1)\) matrix notation using \(\sum_{i=1}^{n} \tilde{J}_i = 0\) \((\tilde{J}_i = \tilde{N}_i - x_i \tilde{N}_{tot})\)

In \(n-1\) matrix notation:

\[ c_{tot} \quad \tilde{d} = - B \quad \tilde{J} \]

\[ \tilde{J} = -c_{tot} \quad B^{-1} \quad \tilde{d} \]

\[ B_{ii} = \frac{X_i}{D_{in}} + \sum_{j=1}^{n} \frac{X_j}{D_{ij}} \]

\[ B_{ij} = -X_i \left( \frac{1}{D_{ij}} - \frac{1}{D_{in}} \right) \]

\(\tilde{v}\) = vector with \(n-1\) components

\([M]\) = square matrix of rank \(n-1\)

\[ \vec{d} = \begin{pmatrix} \tilde{d}_1 \\ \tilde{d}_2 \\ \vdots \\ \tilde{d}_{n-1} \end{pmatrix} \]

\[ [B] = \begin{pmatrix} B_{11} & B_{12} & \cdots & B_{1,n-1} \\ B_{21} & B_{22} & \cdots & B_{2,n-1} \\ \vdots & \vdots & \ddots & \vdots \\ B_{n-1,1} & B_{n-1,2} & \cdots & B_{n-1,n-1} \end{pmatrix} \]
Modelling of membrane permeation

• Porous membranes

Dusty Gas Model (DGM):

Based on the generalized Stefan-Maxwell equations for diffusion in multi-component mixtures

Consider membrane as one of the components in the mixture

\[
\sum_{j=1, j\neq i}^{n} \frac{x_i N_j - x_j N_i}{pD_{i,j}^{\text{eff}}} - \frac{N_i}{pD_{i,K}^{\text{eff}}} = \frac{1}{RT} \frac{\partial x_i}{\partial r} + \frac{x_i}{pRT} \left( \frac{B_0 p}{\mu D_{i,K}^{\text{eff}}} + 1 \right) \frac{\partial p}{\partial r}
\]

see e.g. Veldsink et al., Chemical Engineering Journal 57 (1995) 115-125
Modelling of membrane permeation

- **Dense Pd-membranes for H₂**
  (Pd, Pd/Ag, Pd/Au based membranes)

Mechanism involves a series of steps:

1) adsorption
2) dissociation
3) diffusion
4) re-association
5) desorption

\[
N_{H₂} = \frac{K_m}{\delta_m} \left[ p_{H₂}^{ret} n - p_{H₂}^{perm} n \right]
\]

(0.5 < n < 1)

(n = 0.5: Sieverts’ law)
Modelling of membrane permeation

- **Dense Pd-membranes for H₂**

**Bulk diffusion control:**

\[ \phi''_{\text{mole}, \text{H}_2} = -D_{\text{H,Pd}} \frac{dc_{\text{H}}}{dx} \]

Dissociation and association at equilibrium:

\[ \text{H}_2(g) \rightleftharpoons \text{H(ads)} \]

\[ C_{\text{H}} = K_H p_{\text{H}_2}^{0.5} \]

For ideal (dilute) systems: \( D_{\text{H,Pd}} \) and \( K_H \) is constant

\[ N_{\text{H}_2} = -\frac{D_{\text{H,Pd}}}{\delta_m} c_{\text{H}}^{\text{ret}} - c_{\text{H}}^{\text{perm}} = -\frac{D_{\text{H,Pd}} K_{\text{H,Pd}}}{\delta_m} \left[ p_{\text{H}_2}^{\text{ret}}^{0.5} - p_{\text{H}_2}^{\text{perm}}^{0.5} \right] \]
Modelling of membrane permeation

- **Dense Pd-membranes for H₂**

**Bulk diffusion control:**

Pure H₂ streams at permeate and retentate (i.e. no sweep gas)

\[
N_{H₂} = \frac{Q_H}{\delta_m} \left[ p_{H₂}^{ret} - p_{H₂}^{perm} \right]
\]

\[
Q_H = 1.54 \cdot 10^{-4} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-n}
\]

\[
n = 0.730
\]

(\(\Delta P(\text{support}) \leq 0.1 \text{ bar}\))

Jurriaan Boon *et al.* (ECN)
Modelling membrane permeation

- Supported Pd-membranes for $H_2$

Without sweep (i.e. only $H_2$ is present)

Bulk diffusion Pd-layer:

$$N_m = Q(T) \left( p_{H_2,r}^n - p_{H_2,p}^n \right)$$

DGM support:

$$\frac{dp}{dr} = \frac{r_m N_m}{r D_{1M}^e} \left[ -\frac{y_{H_2}}{RT} \left( 1 + \frac{B_0 p}{\mu D_{1M}^e} \right) - \frac{1 - y_{H_2}}{RT} \left( 1 + \frac{B_0 p}{\mu D_{2M}^e} \right) \right]^{-1}$$
Modelling of membrane permeation

- Supported Pd-membranes for H₂

With sweep

- Concentration polarisation
- Pd permeation
- Resistance in support
- Concentration polarisation
Modelling of membrane permeation

• Supported Pd-membranes for H₂

With sweep: *Dusty Gas Model (DGM)*:

Pressure drop H₂-support:

\[
\frac{dp}{dr} = \frac{r_m c_m}{\kappa D_{1M}^e} \left[ -\frac{y_{H_2}}{RT} \left( 1 + \frac{B_0 p}{\mu D_{1M}^e} \right) - \frac{1 - y_{H_2}}{RT} \left( 1 + \frac{B_0 p}{\mu D_{2M}^e} \right) \right]^{-1}
\]

Diffusion resistance H₂-stagnant N₂:

\[
\frac{dy_{H_2}}{dr} = -\frac{y_{H_2}}{p} \left( 1 + \frac{B_0 p}{\mu D_{1M}^e} \right) \frac{dp}{dr} - \frac{r_m c_m RT}{rp} \left( \frac{1}{D_{1M}^e} + \frac{1 - y_{H_2}}{D_{12}^e} \right)
\]

Jurriaan Boon *et al.* (ECN)
Modelling of membrane permeation

- Supported Pd-membranes for H₂

With sweep: *Comparison of different mass transfer resistances:*

![Graph showing concentration profiles with and without sweep gas flow rate.](image)

**low sweep gas flow rate**

**high sweep gas flow rate**

Jurriaan Boon *et al.* (ECN)
Modelling of membrane permeation

- Dense membranes for $O_2$
  - $O_2$ permeation flux through dense perovskites

MIEC = Mixed Ion and Electron Conducting

$O_2 \rightarrow 2O^{2-} + 4e^-$

$O_2/O^{2-} + ? \rightarrow ?$

$CH_4, CO, H_2 \rightarrow CO, CO_2, H_2, H_2O$

Wagner equation:

$$N_{O_2} = \frac{D_v}{4V_m \delta_m} \int \ln p_{O_2}^{\text{perm}} (\delta) d \ln p_{O_2}$$

$(\delta) = \text{non-stoichiometry: } \delta = \delta_0 p_{O_2}^n$

$\Rightarrow N_{O_2} = \frac{D_v \delta_0}{4V_m \delta_m n} \left[ p_{O_2}^{\text{ret}}^n - p_{O_2}^{\text{perm}}^n \right]$  

Note $n$ is typically small (and $<0$)!!

$\Rightarrow$ Compressing air not very effective!

$\Rightarrow$ Partial pressure at permeate side important!

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Modelling of membrane permeation

- **Dense membranes for O_2**

  **O_2** permeation flux through dense perovskites

  (LaCa)(CoFe)O_{3-δ}: Flux studied experimentally for reducing atmospheres

  - Greatly enhanced in presence of CO and H_2 (left)
  - Highly dependent on thickness (right), indicating bulk diffusion

  \( T = 1223 \text{ K}, \Phi_v = 200 \text{ ml/min (STP), dilution with N}_2 \)
Modelling of membrane permeation

- **Dense membranes for O₂**

  O₂ permeation flux through dense perovskite \((\text{LaCa})(\text{CoFe})\text{O}_3-\delta\)

  - CO₂ inhibits permeation rate (left)
  - Rate determined by local equilibrium of CO combustion, proportional to CO/CO₂ ratio and thus \(x_{\text{O}_2}\) (right)

  \((T = 1223 \text{ K}, \Phi_v = 200 \text{ ml/min (STP), dilution with N}_2)\)
• Dense membranes for $O_2$

$O_2$ permeation flux through dense perovskite $(LaCa)(CoFe)O_3-\delta$

- Permeation expressions derived to describe results

\[
N_{O_2} = \frac{C}{\delta_m} \exp\left(-\frac{E_{act}}{RT}\right) \left[ P_{O_2}^{ret} \, ^n - P_{O_2}^{perm} \, ^n \right]
\]

\[
\sqrt{x_{O_2}} = \frac{x_{CO_2}}{x_{CO} K_{eq}}
\]

\[n = -0.153\]
\[E_{act} = 260 \text{ kJ/mol},\]
\[C = 2.01 \cdot 10^8 \text{ (cm}^4/\text{cm}^2/\text{min, STP)}\]

Zhang et al., J. Membrane Science 291 (2007) 19-32
Modelling of membrane permeation

- Dense membranes for $O_2$
  
  $O_2$ permeation flux through dense perovskite $(\text{LaCa})(\text{CoFe})O_3-\delta$

  - Model can also accurately predict $O_2$ permeation rate for $H_2$ as reducing gas assuming local equilibrium of $H_2$ combustion

Zhang et al., J. Membrane Science 291 (2007) 19-32
Different reactor concepts

• Basic classification

  ▪ Packed bed membrane reactors: Immobilized catalyst

  ▪ Fluidized bed membrane reactors: Particles kept in suspension by fluidum
Different reactor concepts

- **Packed bed reactors:**

  - Single adiabatic bed: used for reactions with **small** heat effect
  - Multi-tubular reactor: used for reactions with a **large** heat effect
Different reactor concepts

- Packed bed membrane reactor configurations

Many different possible configurations:

- Gas addition/gas extraction
- Flat vs. tubular membranes
- Dead end membranes vs. sweep
- Co-current/countercurrent sweeping
- Catalyst as particles inside/outside membrane tubes
- Catalytically active membranes
- Supported/unsupported
- etc. etc.

Example: multi-tubular module with sweep gas
Different reactor concepts

• **Phenomenon of fluidization**

![Diagram of different reactor concepts](image)

- **Fixed Bed**
- **Minimum Fluidization**
- **Smooth Fluidization**
- **Bubbling Fluidization**
- **Slugging Fluidization**
  - Axial slugs
  - Flat slugs
- **Turbulent Fluidization**
- **Lean Phase Fluidization with pneumatic transport**

- Light object floats
- Surface is horizontal
- Levels equalize
- Solids gush from hole
- Gas or Liquid (high velocity)
**Different reactor concepts**

- **Phenomenon of fluidization**

**Particles suspended in a gas stream** ⇒ behaves as a “fluidum”

Bubbles (= voids) are formed, which create excellent mixing in the fluidized bed
Different reactor concepts

- Fluidization at large scale: Granulation and coating
Different reactor concepts

- Fluidization at large scale: FCC and olefin polymerization

FCC (Fluid Catalytic Cracking)

Ethylene/propylene polymerization
Different reactor concepts

- Fluidized bed membrane reactor configurations

Flat membranes integrated in the walls

- Immersed membrane tubes

Feed

Retentate

Permeate

Sweep in

Sweep out

Reaction zone

Regeneration zone
Different reactor concepts

- Packed bed and fluidized bed membrane reactors:
  - **Packed bed membrane reactor**
    - Simple reactor construction
    - Possibly large temperature and concentration gradients (in case of fast & strongly exothermic reactions)
    - Reactor instability
  - **Fluidized bed membrane reactor**
    - Isothermal reaction conditions
    - Catalyst attrition
    - Gas back-mixing / gas by-passing

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Packed bed membrane reactors

- **Modelling of packed bed membrane reactors**
  - **First steps:**
    - Determine what is rate limiting
    - Determine the key performance quantities
    - Determine required model accuracy in relation to available data:
      e.g. 1D/2D model? Isothermal/adiabatic? Phenomenological vs. CFD?
  - **Modelling membrane permeation:**
    - Flux constant? Permeation equation?
      Extended multi-component DGM?
  - **Modelling catalyst:**
    - Internal/external mass transfer limitations?
    - Simplify with effectiveness factors?
    - Pseudo-homogeneous models?
    - Heterogeneous models with detailed particle models?
Component mass balances \((n-1)\) using Maxwell-Stefan description for molar diffusion fluxes:

\[
\varepsilon_g \frac{\partial \rho_g}{\partial t} \omega = -\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \ n + S_r \\
S_{r,i} = M_i \ 1 - \varepsilon_g \ \rho_s \sum_{j=1}^{n_{\text{react}}} n_{j,r,j}
\]

with:

\[
 n = j + \omega \quad n_{\text{tot}} = -\rho_g \ B^{-1} \ \nabla \omega + \omega \ n_{\text{tot}}
\]

Homogeneous energy balance:

\[
1 - \varepsilon_g \ \rho_s C_{p,s} \ \frac{\partial T}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \ \lambda_{\text{eff},s} \ \frac{\partial T}{\partial r} \right) + S_h
\]

Effect of particle porosity/tortuosity via:

\[
D_{\text{eff}} = \frac{\varepsilon}{\tau} D_i \quad S_h = 1 - \varepsilon_g \ \rho_s \sum_{j=1}^{n_{\text{react}}} r_j \Delta h_{r,j}
\]
Packed bed membrane reactors

• Detailed particle model

Boundary conditions:

\[
\begin{align*}
    r &= 0 \\
    r &= r_p \\
    \frac{\partial \omega_i}{\partial r} &= 0 \\
    - \sum_{k=1}^{n_c-1} \rho_g d_{\text{eff},i,k}^0 \frac{\partial \omega_i}{\partial r} + \omega_i n_{\text{tot}} &= \sum_{k=1}^{n_c-1} k_{g\rightarrow s,ik} \rho_g \omega_{k,\text{bulk}} - \omega_k \\
    \frac{\partial T}{\partial r} &= 0 \\
    - \lambda_{\text{eff},s} \frac{\partial T}{\partial r} &= \alpha_{g\rightarrow s}^* \left( T_{\text{bulk}} - T \right)
\end{align*}
\]

+ constitutive equations for the flux correction factors etc.

⇒ Yields local production rates (source terms)
⇒ To be coupled with reactor model

Multiphase Reactors Group, SPI

TU/e Technische Universiteit Eindhoven
University of Technology
Packed bed membrane reactors

- Heterogeneous reactor model:

  **Total continuity equation gas phase:**
  \[
  \varepsilon_g \frac{\partial \rho_g}{\partial t} = - \frac{\partial \rho_g u_g}{\partial z} + \phi''_{m,\text{tot}} a_m \quad \text{with} \quad a_m = \frac{4d_i}{d_0^2 - d_i^2}
  \]

  **Component continuity equations gas phase** \((i = 1..n_c-1):\)
  \[
  \varepsilon_g \frac{\partial \rho_g \omega_i}{\partial t} = - \frac{\partial \rho_g u_g \omega_i}{\partial z} + \frac{\partial}{\partial z} \left( \rho_g D_{ax} \frac{\partial \omega_i}{\partial z} \right) + n_i a_s + \phi''_{m,i} a_m
  \]

  **Gas phase energy balance:**
  \[
  \varepsilon_g \rho_g C_{p,g} \frac{\partial T}{\partial t} = -C_{p,g} \rho_g u_g \frac{\partial T}{\partial z} + \frac{\partial}{\partial z} \left( \lambda_g \frac{\partial T}{\partial z} \right) + \sum_{i=1}^{n_c} n_i a_s H_i
  \]

  \[
  + \sum_{i=1}^{n_c} \phi''_{m,i} a_m H_i + \alpha_{b \rightarrow w} a_w (T - T_w)
  \]

  + boundary conditions (Danckwert’s type)
Packed bed membrane reactors

• **Constitutive equations:**

**Pressure drop (differential Ergun equation):**

\[- \frac{\partial p}{\partial z} = 150 \frac{\eta_g u_g}{d_p^2} \cdot \frac{1 - \varepsilon_g}{\varepsilon_g^2} + 1.75 \frac{\rho_g u_g^2}{d_p} \cdot \frac{1 - \varepsilon_g}{\varepsilon_g^3} \]

**Membrane flux equation(s), e.g. in case of O₂ addition via porous membranes:**

\[ \phi''_{m,O_2} = \frac{M_{O_2}}{RT} \left( \frac{K_0}{\eta_g} \right) \left( \frac{4}{3 \sqrt{8RT}} + \frac{B_0 \langle p \rangle}{\eta_g} \right) \frac{\Delta p_{O_2,m}}{r_i + \delta_m} \ln \left( \frac{r_i + \delta_m}{r_i} \right) \]

+ Reaction kinetics, transport parameters, physical properties
Packed bed membrane reactors

- Combining OCM + SMR in a single dual-function catalyst particle

**Catalyst particle**

**Outer shell of particle**
- Heat generation
- Ethylene production

**Inner core of particle**
- Heat consumption
  → energy integration
- Synthesis gas production
Packed bed membrane reactors

- **Novel reactor concept: PBMR for OCM/SRM with dual function catalyst**
  - Distributive O$_2$ feeding & autothermal operation!
  - Use strong internal diffusion limitations to avoid O$_2$ to the SRM
  - Ensure that C$_2$ flux out of particle is much larger than C$_2$ flux toward particle core (minimize C$_2$ losses)
  - Tune CH$_4$ conversion in OCM and SRM (autothermal operation)
Packed bed membrane reactors

- **Extension to 2D:**
  \[ \Rightarrow \text{Determination of extent & effect of concentration polarization} \]

**Continuity + Navier-Stokes eqns.**

**Continuity Equation**
\[
\frac{\partial (\varepsilon \rho_g \bar{u})}{\partial t} + \nabla \cdot (\varepsilon \rho_g \bar{u} \bar{u}) = 0
\]

**Total Momentum Balance Equation**
\[
\frac{\partial}{\partial t}(\varepsilon \rho_g \bar{u}) + \nabla \cdot (\varepsilon \rho_g \bar{u} \bar{u}) = -\varepsilon \nabla p - \beta \varepsilon \rho_g \bar{u} - \nabla \cdot (\varepsilon \bar{g}) + \varepsilon \rho_g g
\]

**Friction Coefficient**
\[
\beta = 150 \left( \frac{1 - \varepsilon}{\varepsilon} \right)^2 \frac{\mu_g}{\rho_g d_p^2} + 1.75 \frac{1 - \varepsilon}{\varepsilon} \frac{\varepsilon |\bar{u}|}{d_p}
\]

where
\[
|\bar{u}| = \sqrt{u_1^2 + u_2^2}
\]

**Component Mass Balance**
\[
\frac{\partial}{\partial t} (\varepsilon \rho_g w_i) = -\nabla \cdot (\varepsilon \rho_g \bar{u} w_i) + \nabla \cdot (\rho_g D_i \nabla w_i) + S_{r,i}
\]

with
\[
D_i = \begin{bmatrix} D_{r,i} & 0 \\ 0 & D_{z,i} \end{bmatrix}
\]

where source terms equals:
\[
S_{r,i} = (1 - \varepsilon) \rho_S M_i \sum_{j=1}^{n_i} \nu_{ij} r_j \quad \text{for } i = 1, 2, \ldots, \text{nc}
\]

Note: membrane permeation is implemented via (Danckwert’s) boundary conditions
Fluidized bed membrane reactors

- **Modelling of fluidized bed membrane reactors**
  - *First steps (same as before!):*
    - Determine what is rate limiting
    - Determine the key performance quantities
    - Determine required model accuracy in relation to available data: e.g. Phenomenological vs. CFD?
  
  - **Phenomenological model:**
    - Phenomenological = two-phase model (bubble-emulsion phase)
    - Use semi-empirical correlations for bubble and solids behaviour
    - Bubble size (and thus all other key quantities) function of axial position
    - Extent of gas phase mixing in emulsion phase via number of CSTR’s in series
  
  - **CFD model:**
    - At what scale: particle scale vs. industrial scale?
    - Computational resources? Patience?

simplify whenever possible!!!
Fluidized bed membrane reactors

- Phenomenological two-phase model:
  
  - Two phases: emulsion and bubble phase
  
  - Axial dispersion in emulsion and bubble phases via number of CSTRs in series (to be determined from experiments) (typically: emulsion phase = 1 CSTR; bubble phase large nr of CSTRs)
  
  - Emulsion phase remains at incipient fluidization conditions despite reaction or membrane permeation \( \Rightarrow \) instantaneous transfer with bubble phase
  
  - Only reaction in emulsion phase (relatively low reaction rates)
  
  - Isothermal and isobaric conditions
Fluidized bed membrane reactors

Total mass balance

\[ u_{b,n}^s A_T \rho_{b,n} - u_{b,n}^s A_T \rho_{b,n} + u_{c,n-1}^s A_T \rho_{c,n-1} - u_{c,n}^s A_T \rho_{c,n} \]
\[ + \sum_{i=1}^{n_c} \left\{ \phi_{i,mol}^{\text{membrane}} M_{w,i} A_{\text{membrane}} e_{b,n} + \phi_{i,mol}^{\text{membrane}} M_{w,i} A_{\text{membrane}} \left(1 - e_{b,n}\right) \right\} = 0 \]

Bubble phase component mass balances

\[ u_{b,n}^s A_T \rho_{b,n} - u_{b,n}^s A_T \rho_{b,n} - \sum_{i=1}^{n_c} K_{b,c,i,n} V_{b,n} \rho_{b,n} (w_{b,i,n} - w_{c,i,n}) \]
\[ + \sum_{i=1}^{n_c} \phi_{i,mol}^{\text{membrane}} M_{w,i} A_{\text{membrane}} e_{b,n} + [w_{c,i,n} SF(Q) - w_{b,i,n} SF(-Q)] = 0 \]

Emulsion phase component mass balances

\[ u_{e,n-1}^s A_T \rho_{e,n-1} - u_{e,n}^s A_T \rho_{e,n} - \sum_{i=1}^{n_c} K_{b,c,i,n} V_{b,n} \rho_{b,n} (w_{b,i,n} - w_{c,i,n}) \]
\[ - \sum_{i=1}^{n_c} \phi_{i,mol}^{\text{membrane}} M_{w,i} A_{\text{membrane}} \left(1 - e_{b,n}\right) - \left(\sum_{j=1}^{n_w} V_{j,i,n} \rho_{j,n} (1 - e_v) \right) \]
\[ - [w_{c,i,n} SF(Q) - w_{b,i,n} SF(-Q)] = 0 \]

Transfer term

\[ Q = u_{e,n-1}^s A_T \rho_{e,n-1} - u_{e,n}^s A_T \rho_{e,n} + \sum_{i=1}^{n_c} \phi_{i,mol}^{\text{membrane}} A_{\text{membrane}} \left(1 - e_{b,n}\right) \]
\[ + \sum_{i=1}^{n_c} K_{b,c,i,n} V_{b,n} \rho_{b,n} (w_{b,i,n} - w_{c,i,n}) \]
\[ u_{e,n}^s A_T = u_{e,n}^s A_T (1 - e_{b,n}) \]

where \( u_{b,0}^s A_T = u_{\text{tot}} A_T e_{b,0} \)
\[ u_{e,0}^s A_T = u_{\text{tot}} A_T \left(1 - e_{b,0}\right) \]

\( SF(x) = \) Heaviside function:
\( x < 0: SF(x) = 0, \) else \( SF(x) = x \)

- Model equations

⇒ Ratio of membrane addition/extraction to/from bubble and emulsion phases according to bubble hold-up

⇒ Transfer \( Q \) is required to maintain emulsion phase at incipient conditions
Fluidized bed membrane reactors

Energy balance (both concepts)

\[
\left\{ \sum_{i=1}^{n_c} H_i^{T_{feed}} \left( u_{b,n=0}^S A_T \rho_{b,i,n=0} + u_{e,n=0}^S A_T \rho_{e,i,n=0} \right) \right\} - \left\{ \sum_{i=1}^{n_c} H_i^{T_{out}} \left( u_{b,n=N}^S A_T \rho_{b,i,n=N} + u_{e,n=N}^S A_T \rho_{e,i,n=N} \right) \right\} \\
\pm \left\{ \sum_{i=1}^{n_c} H_i^{T_{out}} \left( \phi_{i,mole}^{''\text{membrane}} M_{w,i} A_T e_{b,n} + \phi_{i,mole}^{''\text{membrane}} M_{w,i} A_T (1 - e_{b,n}) \right) \right\} + E = 0
\]

In situ air preheating (concept 1)

Top section

\[
E = \left\{ \sum_{i=1}^{n_c} H_i^{T_{air}} \phi_{i,mole,in} M_{w,i} - \sum_{i=1}^{n_c} H_i^{T_{bottom}} \phi_{i,mole,out} M_{w,i} \right\} + \left\{ \sum_{i=1}^{n_c} H_i^{T_{bozom}} \phi_{i,mole,in} M_{w,i} - \sum_{i=1}^{n_c} H_i^{T_{wp}} \phi_{i,mole,out} M_{w,i} \right\}
\]

Bottom section

\[
E = \left\{ \sum_{i=1}^{n_c} H_i^{T_{bottom}} \phi_{i,mole,in} M_{w,i} - \sum_{i=1}^{n_c} H_i^{T_{top}} \phi_{i,mole,out} M_{w,i} \right\}
\]

H₂ combustion in the U shape membrane (concept 2)

\[
E = \left\{ \sum_{i=1}^{n_c} H_i^{T_{feedU}} \phi_{i,mole,in} M_{w,i} - \sum_{i=1}^{n_c} H_i^{T_{wp}} \phi_{i,mole,out} M_{w,i} \right\}
\]
Fluidized bed membrane reactors

• Constitutive equations

Archimedes Number

Minimum fluidization velocity

Bed voidage at minimum fluidization velocity

Projected tube area for a square bed

Rise velocity of a single bubble

Velocity of rise of swarm of bubbles

Initial bubble diameter (Porous plate distributor)

Maximum bubble diameter

Superficial bubble gas velocity

Maximum superficial bubble gas velocity

Initial superficial bubble gas velocity

\[ Ar = \frac{d^3 \rho_s (\rho_p - \rho_g) g}{\mu_g^2} \]

\[ u_{mf} = \left( \frac{\mu_g}{\rho_g d_p} \right) \left( \sqrt{(27.2)^2 + 0.0408 Ar - 27.2} \right) \]

\[ \varepsilon_{mf} = 0.586 Ar^{-0.029} \left( \frac{\rho_s}{\rho_p} \right)^{0.021} \]

\[ A_T = D_T^2 \]

\[ u_{br} = 0.711 (gd_b)^{1/3} \]

\[ u_b = u_0 - u_{mf} + 0.711 (gd_b)^{1/3} \]

\[ d_{b0} = 0.376(u_0 - u_{mf})^2 \]

\[ d_{b,max} = D_T \]

\[ \frac{u_{b,max} - u_b}{u_{b,max} - u_{b,0}} = \exp \left( \frac{0.55 A_T}{h_{mf} D_T} \right) \]

\[ u_{b,max} = u_0 - u_{mf} \]

\[ u_{b,0} = u_{br,0} \delta_{b0} \]

where \( \delta_{b0} = \left( 1 - \frac{h_{mf}}{h_f} \right) \)

⇒ Effect of internals not accounted for (correlations not available)!
Fluidized bed membrane reactors

Superficial emulsion gas velocity
\[ u_e^* = u_0 - u_b^* \]

Bubble phase fraction
\[ \delta_b = \frac{u_b^*}{u_b} \]

Emulsion phase fraction
\[ \delta_{en} = 1 - \delta_{bn} \]

Volume of emulsion phase in the \( n \)th compartment
\[ V_{e,n} = A_T \frac{h_f}{N_e} \]

Volume of bubble in the \( n \)th compartment
\[ V_{b,n} = A_T \frac{h_f}{N_b} \delta_{b,n} \]

Bubble diameter
\[ d_b = d_{b,\text{max}} - (d_{b,\text{max}} - d_{b,0}) e^{\left(\frac{\rho_3 T}{D_T}\right)} \]

Height of bed expansion
\[ h_f = h_m f \frac{C_1}{C_1 - C_2} \]

where,
\[ C_1 = 1 - \frac{u_{b,0}}{u_{b,\text{avg}}} \exp \left( -\frac{0.275}{D_T} \right) \]
\[ C_2 = \frac{u_{b}^*}{u_{b,\text{avg}}} \left[ 1 - \exp \left( -\frac{0.275}{D_T} \right) \right] \]

Average bubble rise velocity
\[ u_{b,\text{avg}} = u_0 - u_{mf} + 0.711 \left( g d_{b,\text{avg}} \right)^{\frac{1}{2}} \]

Gas exchange coefficient
\[ K_{bc} = 4.5 \left( \frac{u_{mf}}{d_p} \right) + 5.85 \left( \frac{D_{g\text{ef}}^{\frac{1}{2}}}{d_b^{\frac{5}{2}}} \right) \]
\[ K_{ce} = 6.77 \left( \frac{D_g c_{mf} u_b}{d_b^3} \right)^{\frac{1}{2}} \]
\[ \frac{1}{K_{bc}} = \frac{1}{K_{bc}} + \frac{1}{K_{ce}} \]
Fluidized bed membrane reactors

- CFD: Multi-scale modelling strategy

Larger geometry, larger scale phenomena

DNS

Discrete Particle

Particle-particle interaction

Particle-particle interaction; Bubble behavior

Continuum

Discrete Bubble

Large scale motion

Industrial size

Phenomenological

Fluid-particle interaction

“Black box”

Industrial size

Multiphase Reactors Group, SPI
Fluidized bed membrane reactors

- **Discrete Particle Model**

- Intermediate-level model
- Eulerian grid size is larger than the particle size
- Incorporation of detailed particle interaction models
- Computation limitation: $10^4 \sim 10^6$
Fluidized bed membrane reactors

- **Discrete Particle Model**

Gas phase conservation equations (3D-DPM model)

Volume-averaged Navier-Stokes equations

+ continuity equation

\[
\frac{\partial}{\partial t} \varepsilon_g \rho_g + \nabla \cdot \varepsilon_g \rho_g \vec{u}_g = 0
\]

+ momentum equation

\[
\frac{\partial}{\partial t} \varepsilon_g \rho_g \vec{u}_g + \nabla \cdot \varepsilon_g \rho_g \vec{u}_g \vec{u}_g = -\varepsilon_g \nabla p - \bar{S}_p + \nabla \cdot \varepsilon_g \bar{\tau}_g + \varepsilon_g \rho_g \bar{g}
\]

\[
\bar{\tau}_g = \mu_g \nabla \vec{u}_g + \nabla \vec{u}_g^T - \frac{2}{3} \mu_g \nabla \cdot \vec{u}_g \bar{I}
\]

**Inter-phase momentum transfer**

\[
\bar{S}_p = \frac{1}{V_{cell}} \sum_{a \in cell} \frac{\beta V^a}{1 - \varepsilon_g} \left( u_g - v_a \right) \delta (r - r_a)
\]
Fluidized bed membrane reactors

- **Discrete Particle Model**

Particle motion equations (DPM model)

1. **Translational momentum**

\[
 m_a \frac{d\bar{v}_a}{dt} = -V_a \nabla p + \frac{V_p}{1-\varepsilon_g} \bar{u}_g - \bar{v}_a + m_a \bar{g} + \bar{F}_{c,a}
\]

2. **Rotational momentum**

\[
 I_a \frac{d\omega_a}{dt} = T_a
\]

\[
\beta = 180 \frac{\mu_g \varepsilon_s^2}{d_p^2 \varepsilon_g} + 18 \frac{\mu_g \varepsilon_s^3 \varepsilon_s}{d_p^2} + 1 + 1.5 \sqrt{\varepsilon_s} + 0.31 \frac{\mu_g \varepsilon_s \text{Re}_s}{\varepsilon_g d_p^2} \left[ \varepsilon_g^{-1} + 3 \varepsilon_g \varepsilon_s + 8.4 \text{Re}_s^{-0.343} \right] \frac{1 + 10^3 \varepsilon_s}{\text{Re}_s^{-0.5} - 2 \varepsilon_s}
\]

(Cundall & Strack (1979))

\[\text{Npart: } 10^4 \text{~} 10^6\]
Flat membrane walls experiments:
Effect of gas addition/extraction on bubble phase

Gas extraction results in increase of equivalent bubble size
Gas addition results in decrease of equivalent bubble size

=> Gas extraction results in increase of equivalent bubble size
=> Gas addition results in decrease of equivalent bubble size
Fluidized bed membrane reactors

- Flat membrane walls: Effect of gas addition/extraction
  - 40 %
  - 0 %
  - +40 %

Correlation bubble behaviour and emulsion phase circulation patterns!
Fluidized bed membrane reactors

- Flat membrane walls: Effect of gas addition/extraction

-40 %

0 %

+40 %
Flat membrane walls: DPM simulations

DPM predicts same results as experiments!
Fluidized bed membrane reactors

- **Submerged membranes**
  
  Development of DPM/IBM (Immersed Boundary Model)
Concluding remarks

• Detailed reactor and particle models (and combinations thereof) may be required to adequately account for all relevant effects

• Make models as simple as possible … but not simpler!

• Use models to enhance understanding, but experimentation remains a critical component to validate the models!