Ultra-compact micro structured palladium membrane reactors for hydrogen production

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Director, Institute for Micro Process Engineering (IMVT), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany
1. Introduction – Micro structured membrane reactors for hydrogen production

2. On-site steam methane reforming – The µ-Enhancer

3. Dehydrogenation of liquid organic hydrogen carriers – The system MCH / TOL

4. Simplified modeling of a micro channel membrane reactor will wall-coated catalyst
   1. Derivation of the governing equations
   2. Flexible solution using Matlab®

5. Some points to remember
Hydrogen supply < 80,000 m³/h
High pressure and purity (~10-20 bar, >99.999%)
WHY MEMBRANE REACTORS IN HYDROGEN PRODUCTION?

- Equilibrium shift
- Integrated purification

Steam methane reforming

\[ CH_4 + H_2O \rightleftharpoons CO + 3H_2 \]
\[ CO + H_2O \rightleftharpoons CO_2 + H_2 \]

\[ CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2 \]

more energy-efficient, lower OPEX

simpler process, reduced CAPEX
**BENCHMARK IN MEMBRANE-ASSISTED SMR**

**Tokyo Gas**

Modular reformer system:
40 m\(N^3\)/h \(H_2\)

**Modules:**

Yasuda et al., 2005, ICCMR-7, Cetraro

Kurokawa et al., 2010, Demonstration of Highly-Efficient Distributed Hydrogen Production from Natural Gas with CO\(_2\) Capture, WHEC2010, Essen

Senju hydrogen station, Tokyo
Benefits:

• Very large membrane surface area per catalyst volume (ca. \(10^3 \text{ – } 10^6 \text{ m}^{-1}\))
• Negligible mass transport resistance towards membrane even for high-flux membranes
• Efficient heating by hot gas or catalytic combustion of retentate with air
• High compactness / low weight / modular plant design
KIT’s µ-EnH$_2$ancer project

- Preparation of defect-free membranes
- Concepts for thermal and mechanical stability

- Membrane integration by laser welding
- H$_2$ permeation experiments
- Mass transport performance

- Preparation of Rh/Al$_2$O$_3$ catalysts
- Activity and stability tests
- Reaction kinetics without membrane

1) Boeltken et al., CE&P: Process Intensif. 67 (2013) 136-147
4) Boeltken et al., Int. J. Hydr. Energy 41 (2014) 18058-18068
MODULAR MEMBRANE REACTOR DESIGN

Pre-reforming stage
- Cracking of higher hydrocarbons (natural gas)
- Build-up of $\text{H}_2$ partial pressure (by reforming)

Reforming stage
- Reforming
- $\text{H}_2$ separation

Retentate combustion zone
- Heat transfer to the reforming zone
• Modules built from high-temperature corrosion-resistant material (Nicrofer)
• Microchannels by chemical etching (500 x 200 µm)
• Thin palladium foil, i.e., typically 12 µm, sandwiched between two etched microsieves to provide mechanical stability
• Microsieves coated with inorganic diffusion barrier layer to prevent membrane degradation at high temperature
• Catalyst layers by inkjet printing (10-15 µm, 50 mm pre-reforming, 70 mm reforming/membrane)
Variation of retentate pressure; W/F = 0.33 g_{Cat} h / mol CH\textsubscript{4}; S/C = 3

Conversion is close to equilibrium considering the fraction of hydrogen removed

Activity of catalyst high enough to respond to H\textsubscript{2} removal

### COMPARISON TO PREVIOUS / OTHER SYSTEMS

<table>
<thead>
<tr>
<th>Reference</th>
<th>sPd [μm]</th>
<th>APd [cm²]</th>
<th>Catalyst</th>
<th>T [K]</th>
<th>Δp [bar]</th>
<th>XCH₄ [%]</th>
<th>φH₂ [%]</th>
<th>W/F [gCat h/molCH₄]</th>
<th>APd/Vₐ [m²/m³]</th>
<th>VH₂/Vₐ [Nm²/(m³*h)]</th>
<th>VH₂/APd [Nm²/(m²*h)]</th>
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<tbody>
<tr>
<td>Uemiya et al. [4]</td>
<td>20</td>
<td>25.1</td>
<td>Ni-based</td>
<td>773</td>
<td>8</td>
<td>90</td>
<td>91</td>
<td>64.75</td>
<td>39.3</td>
<td>230</td>
<td>5.9</td>
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<tr>
<td>Tong et al. [6]</td>
<td>8</td>
<td>20</td>
<td>Ni/Al₂O₃</td>
<td>823</td>
<td>10</td>
<td>72</td>
<td>51</td>
<td>74.71</td>
<td>110.1</td>
<td>1289</td>
<td>11.7</td>
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<td>Hwang et al. [14]</td>
<td>6.2</td>
<td>33.2</td>
<td>Ni-based</td>
<td>813</td>
<td>20</td>
<td>79</td>
<td>96</td>
<td>n.a.</td>
<td>6.3</td>
<td>58</td>
<td>9.2</td>
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<tr>
<td>Tokyo Gas [15,35]</td>
<td>20</td>
<td>98918.4</td>
<td>Ni-based</td>
<td>823</td>
<td>8.7</td>
<td>79</td>
<td>n.a.</td>
<td>n.a.</td>
<td>8.1</td>
<td>33</td>
<td>4.1</td>
</tr>
<tr>
<td>μ-Enh₂ Cancer [this work]</td>
<td>12.5</td>
<td>26.3</td>
<td>Rh/Al₂O₃</td>
<td>823</td>
<td>11</td>
<td>87</td>
<td>92</td>
<td>0.33</td>
<td>41/66</td>
<td>472/739</td>
<td>12.1</td>
</tr>
</tbody>
</table>

- Sweep gas 500 ml/min Ar (pH₂,Perm = 0.38 bar).
- Sweep gas 470 ml/min N₂.
- Vacuum (pH₂,Perm = 0.4 bar).
- Effective membrane module with thinner microstructured foils.

| Fernandez | 3-5 | 160 | Ni-based | 823 | 1.27 | 76 | 20 | n.a. | 8.0 | 21 | 3.0 |
| Mahecha-Botero | 25 | 1800 | Ni-based | 823 | 8.97 | 80 | 62.5 | n.a. | 22.5 | 125 | 5.5 |

- Highest hydrogen production rate per membrane area
- High volumetric hydrogen production rate
- Very compact 41/66 m⁻¹


2) Tong et al., Catal. Today 2006, 111, 147 - 152.
NEW SYSTEM WITH FLUIDIC HEATING ESTABLISHED

Combustion fuel in (e.g. retentate)

Combustion off-gas out

Air for combustion in

Retentate out

Hydrocarbons and water in

Reformer modules

Combustion modules

Hydrogen out

Sweep gas in (optional)
NEW MODULES

**Combustion module**
5 plates, 7.2 mm height

- Gas distribution
- Combustion fuel feeding
- Combustion fuel distribution into plate 4
- Oxidant gas feeding and combustion
- Gas distribution

**Reforming module**
8 plates; 9.4 mm height

- Gas distribution
- Hydrogen removal
- Etched micro sieve support
- Palladium foil
- Etched micro sieve support
- Reforming zone
- Pre-reforming zone
- Gas distribution

**Module with integrated reforming and combustion zones**
11 plates; 14.4 mm height

- Gas distribution
- Combustion fuel feeding and distribution into plate 3
- Oxidant gas feeding and combustion
- Gas distribution
- Gas distribution
- Permeate gas
- Etched micro sieve support
- Palladium foil
- Etched micro sieve support
- Reforming zone
- Pre-reforming zone
- Gas distribution

- all plates fabricated
- microchannel plates awaiting coating with new catalyst
- new porous metal-supported membranes in preparation

Dittmeyer et al., ICCMR-13 2017
EXHIBITION

Are you a technology or solution provider and would like to actively contribute to this conference?

The exhibition is an integral part of the IMRET and offers a unique opportunity to promote your technologies, products and services. Equipment suppliers, engineering companies as well as research institutes are invited to participate in the exhibition.

VENUE

Gartenhalle Karlsruhe
Festplatz 3
76137 Karlsruhe / Germany

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IMRET 2018, OCT. 21-24, KARLSRUHE

FIRST ANNOUNCEMENT

21 – 24 October 2018
Karlsruhe · Germany

IMRET 2018
15th International Conference on Micro Reaction Technology
www.dechema.de/IMRET2018

INVITATION TO IMRET 15

For its 15th edition, the International Conference on Micro Reaction Technology (IMRET) is coming back to where it all began. Since the start of this “place to be” for chemists, chemical engineers and micro systems engineers, the event has demonstrated a variety of new applications in chemical engineering, chemistry, related disciplines like energy supply, and even more different fields such as analytics, life science and medicine. Yet, as each of the involved disciplines has seen amazing progress, the mission of providing an effective platform for exchange is more topical than ever.

IMRET 15 therefore sets out to become once more the place where new developments regarding all facets of micro process engineering and flow chemistry will be jointly discussed for mutual benefit.

IMRET 15 will take place in the city of Karlsruhe from 21 October to 24 October 2018, organised by DEHEMA e.V. with the support of the German ProcessNet Working Group Microreaction Engineering, the IMRET Steering Committee and the International Flow Chemistry Society.

TOPICS / DATES / COMMITTEE

CONFERENCE TOPICS

› Mixing and heat transfer in micro systems
› Reactions and catalysis in flow systems
› Downstream processing
› Modelling/simulation
› Fabrication of micro-structured devices
› Process automation, sensors, digitalisation
› Modular plant concepts
› New applications in chemistry, biology, energy etc.
› Industrial implementation

IMPORTANT DATES

October 2017 Submission of abstract is open
February 2018 End of abstract submission
April 2018 Notification of acceptance
May 2018 Final programme
21-24 October 2018 IMRET 15 takes place

LOCAL ORGANISING COMMITTEE

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Fraunhofer Institute for Chemical Technology ICT

SUPPORTED BY:

ProcessNet Working Group Microreaction Engineering and International Flow Chemistry Society

www.dechema.de/IMRET2018
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Rh loading (%)</th>
<th>H₂ chemisorption results</th>
<th>TEM results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Rh active sites (A&lt;sub&gt;chem&lt;/sub&gt;)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Rh dispersion&lt;sup&gt;c&lt;/sup&gt; (%)</td>
</tr>
<tr>
<td>5Rh/FAl</td>
<td>3.85</td>
<td>174</td>
<td>47</td>
</tr>
<tr>
<td>5Rh/SAl</td>
<td>2.75</td>
<td>117</td>
<td>44</td>
</tr>
<tr>
<td>1Rh/FAl</td>
<td>0.94</td>
<td>69</td>
<td>75</td>
</tr>
<tr>
<td>1Rh/SAl</td>
<td>0.84</td>
<td>59</td>
<td>73</td>
</tr>
<tr>
<td>0.2Rh/FAl</td>
<td>0.20</td>
<td>13</td>
<td>69</td>
</tr>
<tr>
<td>0.2Rh/SAl</td>
<td>0.20</td>
<td>12</td>
<td>61</td>
</tr>
</tbody>
</table>

- a. Rh loading derived from ICP-OES.
- b. From H₂ uptake in chemisorption assuming a stoichiometry of H/Rh = 1.
- c. Ratio of active Rh from H₂ chemisorption and Rh content from ICP-OES.
- d. From metal dispersion by H₂ chemisorption.
- e. From TEM measurements.
- f. Derived from TEM results.
In cooperation with Forschungszentrum Jülich (Martin Bram, IEK-1)

**Concept**

- **Pd:** ca. 4 - 12 µm (foil or SPS coating)
- **8-YSZ:** ca. 20 - 40 µm
- **Sinter metal:** ca. 1 mm

Dittmeyer et al., ICCMR-13 2017

**Test specimen**

- Crofer 22 APU Dense plate
- Crofer 22 APU Porous sinter metal
- Crofer 22 APU Dense plate

**Testing unit**

- Crofer 22 APU Dense plate
- Crofer 22 APU Porous sinter metal
- Crofer 22 APU Dense plate

Boeltken et al., CE&P 2013, 67,136-147

**Transfer to membrane reformer modules**

ca. 75 x 35 mm
Porosity: 27 ± 4% (29.5 ± 0.9%)
Thickness: 1.08 ± 0.05 mm

N₂ permeability: 0.162 ± 0.003 µmol/m/s/Pa
N₂ permeance: 1.5 × 10⁻⁴ mol/m²/s/Pa
COATING WITH POROUS 8YSZ

Forschungszentrum Jülich (Martin Bram, IEK-1, Paul Kant, IMVT)
SINGLE VERSUS DOUBLE LAYER COATING

Forschungszentrum Jülich (Martin Bram, IEK-1, Paul Kant, IMVT)

Layer thickness derived from SEM (Matlab® routine)
DOUBLE LAYER COATING

Forschungszentrum Jülich (Martin Bram, IEK-1, Paul Kant, IMVT)

Double coating avoids thinning of layer close to weld seam

Metal
Weld seam
Sinter metal

500 μm
Forschungszentrum Jülich (Martin Bram, IEK-1, Paul Kant, IMVT)

Nice smooth surface for coating with thin Pd or Pd alloy layer
SUSPENSION PLASMA SPRAYING OF PD NANOPARTICLES

In cooperation with the German Aerospace Center (Sayed-Asif Ansar, Dirk Ullmer, TT, Stuttgart)

- Stable suspension of Pd nanoparticles obtained
- Injection system and plasma parameters being optimised
- First coating experiments performed on test specimen (Pd layers are not yet gastight)
- Transfer to membrane reformer modules

Application background

Liquid organic reaction cycle (LORC) for long-term storage of intermediate temperature heat

MCH dehydrogenation to toluene:

\[ C_7H_{16} \rightleftharpoons C_7H_8 + 3H_2 \]

Catalyst: 1 wt.-% Pt/γ-Al₂O₃

Influence of pressure on the deactivation rate.

T = 325° C. modified contact time W/F 4000 kg s m⁻³ (1 bar) and 750 kg s m⁻³ (9 bar). MCH/N₂ 50/50.

• Kinetic studies in BERTY-type recycle reactor showed much slower deactivation by carbon formation.
Micro Packed-Bed Membrane Reactor – First Design

<table>
<thead>
<tr>
<th>Module</th>
<th>$Q_0$ mol·m$^{-1}$·s$^{-1}$·Pa$^{-0.5}$</th>
<th>$E_a$ kJ·mol$^{-1}$</th>
<th>$Q$ (350 °C) mol·m$^{-1}$·s$^{-1}$·Pa$^{-0.5}$</th>
<th>$S$-</th>
</tr>
</thead>
<tbody>
<tr>
<td>membrane B</td>
<td>$2.8 \times 10^{-7}$</td>
<td>14.6</td>
<td>$1.7 \times 10^{-8}$</td>
<td>&gt;3000</td>
</tr>
<tr>
<td>membrane C</td>
<td>$2.0 \times 10^{-6}$</td>
<td>26.7</td>
<td>$1.1 \times 10^{-8}$</td>
<td>&gt;25,000</td>
</tr>
<tr>
<td>membrane D</td>
<td>$3.7 \times 10^{-7}$</td>
<td>16.8</td>
<td>$1.5 \times 10^{-8}$</td>
<td>&gt;85,000</td>
</tr>
<tr>
<td>Boeltken et al. [18]</td>
<td>$2.6 \times 10^{-7}$</td>
<td>14.6</td>
<td>$1.6 \times 10^{-8}$</td>
<td>&gt;30,000</td>
</tr>
</tbody>
</table>

Effect of hydrogen on deactivation. W/F = 250 kg s m\(^{-3}\).

350° C, 9 bar
back permeation of H\(_2\) in entrance region

348° C, 1 bar
perfect back mixing, i.e., H\(_2\) concentration at reactor effluent level

400° C, 9 bar
no back mixing, i.e., low H\(_2\) partial pressure in entrance region

Carbon content stable around 0.8 wt.-% (TGA, 400° C, BERTY reactor, up to 25 h)
REGNERATION IN PLACE

Procedure

- 1 h treatment in a flow of 5 ml/min air plus 50 ml/min N₂ for during off the deposits
- 1 h treatment in a flow of 50 ml/min H₂ for reduction of the catalyst surface

T = 400° C.
P_{Ret} = 9 bar.
W/F = 250 kg·s·m⁻³.
X_{Eq.} = 99%.

Reduced bed height of 0.5 mm / enlarged area

On-going work:

- Further optimisation of reactor geometry based on simulations (optimised bed height, longer packed bed section).
- Catalyst improvement regarding coking.
- Scale-up and test in integrated process.

\[ T = 350^\circ \text{C}, \ P_{\text{Rel}} = 28-31 \text{ bar}, \ W/F = 125 \text{ kg} \cdot \text{s} \cdot \text{m}^{-3}. \]
CSTR material balance for component $i$:

$$0 = q(x) \cdot c_i(x) - q(x + dx) \cdot c_i(x + dx) + j_i(x + dx) \cdot A$$

$$0 = \left[ u(x) \cdot c_i(x) - u(x + dx) \cdot c_i(x + dx) \right] \cdot w \cdot h + k_{ig} \cdot \left( c_i^* (x + dx) - c_i(x + dx) \right) \cdot w \cdot dx$$
new flow velocity \( u(x+dx) \) for ideal gas and constant pressure:

\[
\begin{align*}
\begin{aligned}
\begin{array}{c}
u(x + dx) \cdot w \cdot h = u(x) \cdot w \cdot h + \\
\sum_i k_{ig} \cdot \left( c_i^* (x + dx) - c_i (x + dx) \right) \cdot w \cdot dx \cdot \frac{RT}{p}
\end{array}
\end{aligned}
\end{align*}
\]

\[
\text{total volume flow to/from layer}
\]

\[
\text{total molar flux to/from layer}
\]

\[
\begin{align*}
\begin{aligned}
u(x + dx) = u(x) + \frac{dx}{h} \cdot \frac{RT}{p} \sum_i k_{ig} \cdot \left( c_i^* (x + dx) - c_i (x + dx) \right)
\end{aligned}
\end{align*}
\]

in material balance:

\[
0 = u(x) \cdot \left[ c_i (x) - c_i (x + dx) \right] - \frac{dx}{h} \cdot \frac{RT}{p} \cdot \left[ \sum_i k_{ig} \cdot \left( c_i^* (x + dx) - c_i (x + dx) \right) \right] \cdot c_i (x + dx) + ...
\]

\[
\begin{align*}
\begin{aligned}
k_{ig} \cdot \left( c_i^* (x + dx) - c_i (x + dx) \right) \cdot \frac{dx}{h}
\end{aligned}
\end{align*}
\]

concentration on the surface is given by reaction/diffusion inside layer
now, the situation with Pd membrane:
CSTR material balance component i (reaction side):

\[
0 = q(x) \cdot c_i(x) - q(x + dx) \cdot c_i(x + dx) + j_i(x + dx) \cdot A + j_{i,M}(x + dx) \cdot A_M
\]

\[
0 = \left[ u(x) \cdot c_i(x) - u(x + dx) \cdot c_i(x + dx) \right] \cdot w \cdot h + k_{ig} \left( c_i^*(x + dx) - c_i(x + dx) \right) \cdot w \cdot dx + ... \]

\[... j_{i,M}(x + dx) \cdot w \cdot f_{i,M} \cdot dx \]
the membrane flux connects both compartments:

\[ j_{i,M}(x + dx) = -\frac{Q_{H_2}}{S_M} \cdot (RT)^{0.5} \cdot \left( c_{H_2}^{0.5}(x + dx) - c_{H_2,p}^{0.5}(x + dx) \right) \quad \text{for } i = H_2 \]

\[ j_{i,M}(x + dx) = 0 \quad \text{for } i \neq H_2 \]

here \( j_{i,M} \) is positiv if hydrogen enters the reaction compartment via the membrane.
again, new flow velocity \( u(x+dx) \) for ideal gas and constant pressure:

\[
\begin{align*}
u(x + dx) \cdot w \cdot h &= u(x) \cdot w \cdot h + \\
&\quad \left[ \sum_i k_{ig} \cdot \left( c_i(x + dx) - c_i(x + dx) \right) \right] \cdot w \cdot dx \cdot \frac{RT}{p} + ...
\end{align*}
\]

**total volume flow to/from layer**

**total molar flux to/from layer**

\[
\begin{align*}
&\quad \frac{Q_{H_2}}{S_M} \cdot \left( RT \right)^{0.5} \cdot \left( c_{H_2}^{0.5}(x + dx) - c_{H_2,p}^{0.5}(x + dx) \right) \cdot w \cdot f_M \cdot dx \cdot \frac{RT}{p}
\end{align*}
\]

**total molar flux to/from permeate**

**total volume flow to/from permeate**

\[
\begin{align*}
u(x + dx) &= u(x) + \frac{dx}{h} \cdot \frac{RT}{p} \left[ \sum_i k_{ig} \cdot \left( c_i(x + dx) - c_i(x + dx) \right) - ...
\end{align*}
\]

\[
\begin{align*}
&\quad f_M \cdot \frac{Q_{H_2}}{S_M} \cdot \left( RT \right)^{0.5} \cdot \left( c_{H_2}^{0.5}(x + dx) - c_{H_2,p}^{0.5}(x + dx) \right)
\end{align*}
\]
in material balance:

concentration on the surface is given by reaction/diffusion inside layer

concentration in the permeate (has to be determined by permeate side material balance)
CSTR material balance component \( i \) (permeate side):

\[
0 = q_p(x) \cdot c_{i,p}(x) - q_{p}(x + dx) \cdot c_{i,p}(x + dx) - j_{i,M}(x + dx) \cdot A_M
\]

\[
0 = \left[ u_p(x) \cdot c_{i,p}(x) - u_p(x + dx) \cdot c_{i,p}(x + dx) \right] \cdot w_p \cdot h_p - j_{i,M}(x + dx) \cdot w \cdot f_M \cdot dx
\]
here as well, new flow velocity $u_p(x + dx)$ for ideal gas and constant pressure:

$$u_p(x + dx) \cdot w_p \cdot h_p = u_p(x) \cdot w_p \cdot h_p + ...$$

$$... \frac{Q_{H_2}}{S_M} \cdot \left( \frac{RT}{S_M} \right)^{0.5} \cdot \left( c_{H_2}^{0.5}(x + dx) - c_{H_2,p}^{0.5}(x + dx) \right) \cdot w \cdot f_M \cdot dx \cdot \frac{RT}{p}$$

**total molar flux to/from permeate**

**total volume flow to/from permeate**

$$u_p(x + dx) = u_p(x) + \frac{dx}{h_p} \cdot f_M \cdot \frac{w}{w_p} \cdot \frac{(RT)^{1.5}}{p} \cdot \frac{Q_{H_2}}{S_M} \left( c_{H_2}^{0.5}(x + dx) - c_{H_2,p}^{0.5}(x + dx) \right)$$

note that pressure $p$ here is the permeate pressure, which is in general different from the reaction side pressure
in material balance:

\[ 0 = u_p(x) \cdot \left[ c_{i,p}(x) - c_{i,p}(x + dx) \right] + \ldots \]

\[ \cdots \cdot \frac{dx}{h_p} \cdot f_M \cdot \frac{w}{w_p} \cdot \frac{(RT)^{1.5}}{p} \cdot \frac{Q_{H_2}}{S_M} \cdot \left( c_{H_2}^{0.5}(x + dx) - c_{H_2,p}^{0.5}(x + dx) \right) \cdot c_{i,p}(x + dx) - \ldots \]

\[ \cdots \cdot \hat{J}_{i,M} \cdot f_M \cdot \frac{dx}{h_p} \]

again, note that pressure \( p \) here is the permeate pressure, which is in general different from the reaction side pressure
now, we need to solve the ODE for the layer:

**Standard ODE (constant diffusivity):**

\[ 0 = D_i \cdot \frac{d^2 c_i}{dy^2} + R_i(c_i, T) \]

- different diffusivities \( D_i \) in the two layers can be handled via position-dependent effective diffusivity \( D_i(y) \)
- the presence of different catalysts in the two layers can also be handled via position-dependent catalyst mass concentrations \( \rho_{\text{Cat},j}(y) \)
Effective diffusivity as step function:

\[ D_i = D_{i,\text{Core}} + f(y) \cdot (D_{i,\text{Shell}} - D_{i,\text{Core}}) \]

Catalyst mass concentrations as step functions:

\[ \rho_{\text{Cat,Core}}(y) = [1 - f(y)] \cdot \rho_{\text{Core}} \]
\[ \rho_{\text{Cat,Shell}}(y) = f(y) \cdot \rho_{\text{Shell}} \]
ODE SYSTEM FOR POSITION-DEPENDENT DIFFUSIVITY

\[ D_i(y) \cdot \frac{dc}{dy}(y) \cdot dx \cdot w + D_i(y+\Delta y) \cdot \frac{dc}{dy}(y+\Delta y) \cdot dx \cdot w + \frac{R_i(y) + R_i(y+\Delta y)}{2} \cdot \Delta y \cdot dx \cdot w \]

\[ 0 = -D_i \cdot \frac{dc}{dy} + \left[ D_i + \frac{dD_i}{dy} \cdot \Delta y \right] \left[ \frac{dc}{dy} + \frac{d^2 c_i}{dy^2} \cdot \Delta y \right] + \frac{R_i + \frac{dR_i}{dy} \cdot \Delta y}{2} \cdot \Delta y \]

\[ 0 = \frac{dD_i}{dy} \cdot \frac{dc}{dy} + D_i \cdot \frac{d^2 c_i}{dy^2} \cdot \Delta y + \frac{dD_i}{dy} \cdot \frac{d^2 c_i}{dy^2} \cdot (\Delta y)^2 + R_i \cdot \Delta y + \frac{1}{2} \cdot \frac{dR_i}{dy} \cdot (\Delta y)^2 \]

\[ \frac{d^2 c_i}{dy^2} = -\frac{R_i(y)}{D_i(y)} - \frac{1}{D_i(y)} \cdot \frac{dD_i(y)}{dy} \cdot \frac{dc}{dy} \quad \text{extra term} \]
\[
\frac{d^2 c_i}{dy^2} = -\frac{R(y)}{D_i(y)} - \frac{1}{D_i(y)} \cdot \frac{dD_i(y)}{dy} \cdot \frac{dc_i}{dy}
\]

where:

\[
\frac{dD_i(y)}{dy} = \left( D_{i,\text{core}} - D_{i,\text{shell}} \right) \cdot \frac{df}{dy}
\]

and:

\[
\frac{df}{dy} = \frac{df}{dy'} \cdot s = \frac{1}{s} \cdot \left( 1 - \tanh^2 \left( \frac{y' - y'_0}{2\pi \cdot f_s} \right) \right) \cdot \pi \cdot f_s
\]

due to:

\[
s = h_{\text{core}} + h_{\text{shell}} \quad y' = \frac{y}{s} \quad y'_0 = \frac{h_{\text{core}}}{s}
\]
\[
\frac{d^2 c_i}{dy^2} = -\frac{R(y)}{D_i(y)} - \frac{1}{D_i(y)} \frac{dD_i(y)}{dy} \frac{dc_i}{dy}
\]

Boundary conditions:

\[\begin{align*}
    & y=0 & \quad y=h_{\text{Core}}+h_{\text{Shell}} \\
    & \frac{dc_i}{dy} \bigg|_{y=0} = 0 & \quad \text{infinite mass transfer rate} \\
    & D_i,\text{Shell} \cdot \frac{dc_i}{dy} \bigg|_{y=h_{\text{Core}}+h_{\text{Shell}}} = k_{lg} \left( c_i(x+dx) - c_i^*(x+dx) \right) & \quad \text{concentration on top of double layer}
\end{align*}\]

concentration in bulk phase

\[c_i \bigg|_{y=h_{\text{Core}}+h_{\text{Shell}}} = c_i(x+dx)\]
Case 1: infinite mass transfer rate

\[ c_i \big|_{y-h_{\text{Crew}}+h_{\text{Shell}}} = c_i (x + dx) \]

flux from/to layer is expressed with the concentration gradient at top of the double layer

\[ 0 = u(x) \cdot \left[ c_i (x) - c_i (x + dx) \right] - \frac{dx}{h} \cdot \frac{RT}{p} \cdot \left[ \sum_i k_{ig} \cdot \left( c_{i}^* (x + dx) - c_i (x + dx) \right) \right] - \ldots \]

\[ \ldots \cdot f_{M} \cdot \frac{Q_{H_2}}{S_M} \cdot \left( \frac{RT}{0.5} \right) \cdot \left( c_{H_2}^{0.5} (x + dx) - c_{H_2,p}^{0.5} (x + dx) \right) \cdot c_i (x + dx) + \ldots \]

\[ \ldots \cdot k_{ig} \cdot \left( c_{i}^* (x + dx) - c_i (x + dx) \right) \cdot \frac{dx}{h} + j_{i,M} \cdot f_{M} \cdot \frac{dx}{h} \]

where:

\[ k_{ig} \cdot \left( c_{i}^* (x + dx) - c_i (x + dx) \right) = -D_{i,\text{Shell}} \cdot \frac{dc_i}{dy} \bigg|_{y-h_{\text{Crew}}+h_{\text{Shell}}} \]
\[ 0 = u(x) \cdot \left[ c_i(x) - c_i(x + dx) \right] - \frac{dx}{h} \cdot \frac{RT}{p} \cdot \sum_i D_{i,\text{Shell}} \cdot \left. \frac{dc_i}{dy} \right|_{y^{h_{\text{Core}}+h_{\text{Shell}}}} - \ldots \]

\[ \ldots \cdot f_M \cdot \frac{Q_{H_2}}{S_M} \cdot \left( RT \right)^{0.5} \cdot \left( c_{H_2}^{0.5}(x + dx) - c_{H_2, p}^{0.5}(x + dx) \right) \cdot c_i(x + dx) - \ldots \]

\[ \ldots \cdot D_{i,\text{Shell}} \cdot \left. \frac{dc_i}{dy} \right|_{y^{h_{\text{Core}}+h_{\text{Shell}}}} \cdot \frac{dx}{h} + j_{i,M} \cdot f_M \cdot \frac{dx}{h} \]

rearranging:

\[ c_i\bigg|_{y^{h_{\text{Core}}+h_{\text{Shell}}}} = c_i(x + dx) = \frac{u(x) \cdot c_i(x) - \frac{dx}{h} \cdot \left[ D_{i,\text{Shell}} \cdot \left. \frac{dc_i}{dy} \right|_{y^{h_{\text{Core}}+h_{\text{Shell}}}} - j_{i,M} \cdot f_M \right]}{u(x) - \frac{dx}{h} \cdot \frac{RT}{p} \cdot \sum_i D_{i,\text{Shell}} \cdot \left. \frac{dc_i}{dy} \right|_{y^{h_{\text{Core}}+h_{\text{Shell}}}} + f_M \cdot \frac{Q_{H_2}}{S_M} \cdot \left( RT \right)^{0.5} \cdot \left( c_{H_2}^{0.5}(x + dx) - c_{H_2, p}^{0.5}(x + dx) \right)} \]

- \( c_{H_2,p}(x+dx) \) is found from the hydrogen material balance for permeate side for given sweep gas flow rate, permeate pressure and reaction side hydrogen concentration.
- owing to Sievert’s law this requires the solution of a nonlinear equation.
Flexible approach - 1D cascade of cells with the option to limit the concentration change per cell via step size control

• solved profiles for one cell are used as initial guess for subsequent cell
• mole flows in both compartments are updated based on solved profiles
• graphics for monitoring progress of the calculation
• material balance checks
• heat balance not yet implemented
• pressure drop along channel neglected

*bvp4c* - *reliable boundary value problem solver with adaptive grid*

• CSTR material balance and membrane transport integrated in the definition of the boundary conditions
• nonuniform catalyst distribution and effective diffusivity - two distinct layers approximated by S-shaped distribution function

*Exchangeable kinetics and permeation*
Matlab Program – Graphical Output

Concentration in layer

Concentration along reactor

Conversion and selectivity

Atom balances

H2 permeate flow

Flow velocities
First commercial applications of membrane reactors may appear in:

- small-capacity hydrogen production for industrial uses via on site reforming (low pressure, moderate purity),
- hydrogen generation from LOHC in the context of hydrogen logistics,
- rather than in large-scale reforming or WGS.

Transport effects may have a big influence on reactor performance (yield, selectivity, space time yield, etc.); this holds especially for membrane reactors where the reactions kinetics should not only match the usual heat and mass transport rates but also the permeation kinetics.

Matlab is a flexible platform for building your own customised models for „multiscale“ reactor simulation.
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Thank you for your attention

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