Simulation, integration and assembly of pilot scale membrane reactors

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Pd membrane workshop
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Why Hydrogen?

- **HGS:**
  - Hydrogen Generation Systems
  - HGSV: 5 Nm³/h
  - HGSL: 50 Nm³/h
  - HGSC: 100 Nm³/h

- **GPS:**
  - Gas Purification Systems
Outlook

- Autothermal Reforming Membrane Reactor (ReforCELL)
- Water Gas Shift Membrane Reactor (DEMCAMER)
  - System layout
  - Reactor specs and description
  - Simulation & Design
  - Integration
- Economics
Autothermal Reforming Membrane Reactor
(ReforCELL)
ATR-MR System layout

ATR-MR (600°C) Retentate

H₂

HX-2 air+H₂O reaction

CMP NG

Vacuum

Anode

PEM Fuel Cell

Cathode

P-3

HX-8 (Recov)

Cooling circuit

HX-1 Burner

HX-7

HX-0 Sep

HX-4 HX-6 Vac.P.

P-1

Airbrn

Air ÅTR

CMP air

H₂O reaction

(H2O reaction)

ATR-MR

Retentate

Cooling circuit

Air cath

Anode

PEM Fuel Cell

Cathode

P-3

HX-8 (Recov)

Cooling circuit

HX-1 Burner

HX-7

HX-0 Sep

HX-4 HX-6 Vac.P.

P-1

Airbrn

Air ÅTR

CMP air

H₂O reaction

(H2O reaction)
Specifications:

- Maximum $H_2$ output 5 Nm$^3$/h
- Nominal CHP operation $\approx$ 3.7 Nm$^3$/h
- Partial loads 30%
- Maximum temperature 600 $^\circ$C
- Fluidized bed
- 7 bar$_g$ reaction
- 300 mbar$_a$ hydrogen
**Challenges:**

- Fluidization regime !!
  - > minimum fluidization ($u_{mf}$)
  - < terminal velocity ($u_t$)
- Hotspots (oxidation at inlet section)
- Adequate back-mixing
- Slugging
- Kinetic limitations
- Membrane area
- Manifolding
- Sealing
Challenges:

- Adequate back-mixing

**Aspect ratio membrane section (@u_0/u_{mf}=8)**

- Pitch = L/d_t
Challenges:

- Load modulation
### Fluidization performance

<table>
<thead>
<tr>
<th>Result</th>
<th>Max.</th>
<th>CHP</th>
<th>CHP @40%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen production</td>
<td>Nm³/h</td>
<td>5.0</td>
<td>3.7</td>
</tr>
<tr>
<td>Fluidization regime at ATR inlet (z=0)</td>
<td>u₀/uₘₙ</td>
<td>7.0</td>
<td>5.2</td>
</tr>
<tr>
<td>Fluidization regime at inlet to membrane section (z=1)</td>
<td>u₁/uₘₙ</td>
<td>9.8</td>
<td>7.3</td>
</tr>
<tr>
<td>Actual to terminal velocity at ATR inlet (z=0)</td>
<td>u₀/uₜ</td>
<td>0.88</td>
<td>0.75</td>
</tr>
<tr>
<td>Actual to terminal velocity at inlet to membrane section (z=1)</td>
<td>u₁/uₜ</td>
<td>0.73</td>
<td>0.62</td>
</tr>
<tr>
<td>Axial slugging at inlet to membrane section (z=1)</td>
<td>yes</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Axial slugging within membrane section (z=1-2)</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Bed level rise</td>
<td>mm</td>
<td>173</td>
<td>132</td>
</tr>
</tbody>
</table>
Considerations:

- **Geometry**
  - Simple assembly
  - Maintenance
  - Possibility to change single membranes vs. whole assembly

- **Membrane sealing:**
  - Welding, brazing, unions?

- **Particle size**
  - Particle separation

- **Attrition problems?**
  - Membranes shielded or not

- **1 membrane fails?**
  - Single outlet => Shutdown
  - Multiple independent outlets => close only failing section
Considerations:

• Controls
  o Fast response
  o Good accuracy in BOP & instrumentation

• Transportation

• Weather protection
  o Indoors ? Outdoors ?

• Startup/shutdowns
  o Frequent shutdown vs. standby mode
Water Gas Shift Membrane Reactor
(DEMCAMER)
### Specifications

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen output</td>
<td>Nm³/h</td>
<td>5</td>
</tr>
<tr>
<td>Hydrogen recovery factor*</td>
<td>%</td>
<td>90</td>
</tr>
<tr>
<td>CO conversion</td>
<td>%</td>
<td>95</td>
</tr>
<tr>
<td>Hydrogen purity</td>
<td>%</td>
<td>99.9 %</td>
</tr>
<tr>
<td>Feed pressure</td>
<td>bar</td>
<td>6</td>
</tr>
<tr>
<td>Inlet temp</td>
<td>°C</td>
<td>&gt;300</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Feed comp.</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>3.8</td>
</tr>
<tr>
<td>H2</td>
<td>44.8</td>
</tr>
<tr>
<td>CO</td>
<td>9.2</td>
</tr>
<tr>
<td>CO₂</td>
<td>4.7</td>
</tr>
<tr>
<td>H₂O</td>
<td>34.7</td>
</tr>
<tr>
<td>N₂</td>
<td>2.8</td>
</tr>
</tbody>
</table>

* \[ HRF = \frac{F_{H_2,perm}}{F_{H_2,feed} + F_{CO,feed}} \]
• Packed bed 1D model:
  
  – Effectiveness factor. Weisz and Hicks, (1962)
  – Concentration polarization coefficient. Cavarella, Barbieri, Drioli (2009)
  – Convective heat transfer terms: Li & Finayson (1977) ; Kern (1997)
• Packed bed 1D model:

CO conversion and $\text{H}_2$ Recovery as a function of feed temperature. Sweep factor 0.06, membrane area 0.152 m$^2$.

$\text{H}_2$ Recovery as a function of sweep factor for different membrane area. Feed temperature 330°C.
- Packed bed 1D model: Temperature and species profiles

Molar flow rate profiles on reaction side along the reactor length. Membrane area 0.179 m² (13 membrane tubes), sweep factor 0.12, Feed temperature 360 °C.

Temperatures profiles, on reaction side and permeation side, along the reactor length. Membrane area 0.179 m² (13 membrane tubes), sweep factor 0.12, feed temperature 360 °C.
Response to feed flow

Outlet temperature of retentate and permeate stream as a function of sweep factor. Feed molar flow rate 7.6 mol/min, feed temperatures 360 °C.

H₂ Recovery and H₂ permeate molar flow rate as a function of feed molar flow rate. Sweep molar flow rate 0.93 mol/min, feed temperatures 360 °C.
Design:

- Packed bed reactor
- Design $H_2$ output 5 Nm$^3$/h
- Design pressure 8.5 bar$_g$
- Sweep flow (steam), 1.0 kg/h counter current
- $< 0.2$ m$^2$ membrane area
WGS-MR
Reactor simulation & design
Temperature monitoring:

- 6 TC’s:
  - 3 level TC reading
  - 2 radius
- Removable sheath. Open-end type.
- Replaceable
Membrane technology:
• TECNALIA, membrane deposition
• RAUSCHERT, supports
• TECNALIA / TUE, sealing

Catalyst technology:
• HYBRID CATALYSIS
- Assembly
- Suitable for outdoors
Economics
Economics

The road towards exploitation

Alternative market vs. Mainstream

- Opportunities?
  - Dehydrogenation
  - High value chemicals
  - H₂ upgrading

- H₂ production from NG reforming
  - Compete with well established and economical solutions with H₂ delivered pressurized (PSA).
  - PSA low installation costs. Durability »15 years
  - Membranes < 500 €/(Nm³/h) for ~15yr ??
The road towards exploitation

VS.