Design and test results of Catalytic Membrane Reactors for Steam Methane Reforming

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Steam Methane reforming

- Overview of C1-C3 valorisation process studies in Carena:

  \[ m = \frac{(H_2-CO_2)/(CO+CO_2)}{} = 2.1 \]

Objective: Scale-up and demonstration of steam methane reforming membrane reactor concept (\(H_2\)-production level: 2-20 Nm\(^3\)/hr)
Enhanced steam methane reforming

Hydrogen production:

- Natural gas is significant feedstock
- $\text{H}_2$-use significant for ammonia, refining and methanol

$\text{H}_2$ production plant (Praxair)
Enhanced steam methane reforming

- Steam Methane Reforming (SMR): Reliable process with economic benefit

- Problem: highly endothermic and equilibrium limited:
  1. High methane conversion at high temperature (typically 800-850°C), thus high energy consumption.

  \[
  \text{Steam reforming reaction, strongly endothermic} \\
  \Delta H^{\circ}_{25^\circ C} = +206 \text{ kJ/mol}
  \]

  \[
  \text{Water gas shift reaction, mildly exothermic} \\
  \Delta H^{\circ}_{25^\circ C} = -41 \text{ kJ/mol}
  \]

  2. SR-catalyst is placed in tubes and heat is supplied by NG-burners:
     - Tubes experience 100-150°C higher temperatures
     - Requires expensive high alloy steel (high Cr and Ni content (25-35%))

     LOWER OPERATING TEMPERATURE!!!!
Membrane Reactor concept: selective removal of a reaction product

Equilibrium conversion shift $\rightarrow$ higher CH$_4$-conversion by H$_2$-removal

$$\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2$$

Membrane-catalyst integration:

- Higher reactant conversion at the same temperature of conventional reactor
- Same reactant conversion at lower temperature (500-600°C)

About 250°C of temperature decrease for iso-conversion

Effect more pronounced at higher pressure
Enhanced steam methane reforming

natural gas (secondary)

air

combustion

heat transport

catalyst

reforming

separation

carbon

methane

water

hydrogen

H₂O

methane

CH₄

hydrogen

H₂

water

H₂O
Enhanced steam methane reforming

Single tube membrane reactor:
- Membrane: 3.8 μm Pd/αAl₂O₃, membrane area: 155 cm²
- SR-catalyst: Ni-based catalyst
- $T_{op} = 530-590 \, ^°C$
- $P_f = 25-42 \, \text{bara}$, feed: CH₄/H₂O = 1/3,
  co-current, N₂ sweep

Separation enhanced SMR shown

Scale-up: Translate single tube (TRL4) → multi tube reactor design (TRL5)
Enhanced steam methane reforming

Multi-tube reactor design aspects:

<table>
<thead>
<tr>
<th>Reactor scale-up aspects</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost aspects:</td>
<td>- Efficient usage of high pressure vessel volume</td>
</tr>
<tr>
<td>- Reactor cost</td>
<td>- 1500 euro/m² (High volume manufacturing)</td>
</tr>
<tr>
<td>- Membrane cost</td>
<td></td>
</tr>
<tr>
<td>Integration aspects</td>
<td>- Efficient distribution of heat to catalyst and membranes</td>
</tr>
<tr>
<td></td>
<td>- Efficient combination reaction/separation</td>
</tr>
<tr>
<td>Integration in process</td>
<td></td>
</tr>
<tr>
<td>Operational aspects</td>
<td>- H₂-production level (Small to large scale)</td>
</tr>
<tr>
<td></td>
<td>- Methane conversion level</td>
</tr>
<tr>
<td></td>
<td>- Operation pressure/temperature</td>
</tr>
<tr>
<td></td>
<td>- Maintenance</td>
</tr>
<tr>
<td></td>
<td>- Safety</td>
</tr>
</tbody>
</table>
Membrane reactor concept

The role of vessel cost

Vessel diameter = 3 m
Effective height = 10 m
(Total height = 12 m)
$D_{\text{mem}} = 14 \text{mm}$
Membrane cost = 1500 €/m²
50 bar, T=500 – 650°C

2035 m² membranes in a vessel
membrane cost = 3.05 M€
vessel cost = 5.73 M €
Membrane reactor concept

The role of vessel cost

<table>
<thead>
<tr>
<th>Pitch</th>
<th>Closest packing</th>
<th>Relative contribution of cost</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Membrane</td>
</tr>
<tr>
<td>D = 2</td>
<td>655 tubes per m²</td>
<td>1</td>
</tr>
<tr>
<td>D = 1</td>
<td>1473 tubes per m²</td>
<td>1</td>
</tr>
<tr>
<td>D = 1</td>
<td>368 tubes per m²</td>
<td>1</td>
</tr>
</tbody>
</table>

Physical separation membrane from catalyst/heat section

Arbitrary diameter indicating impact of membrane-catalyst-heat integration
Heat transfer coefficient = 150 W/m²K
Average $\Delta T = 200$ K

$H_2$ prod = $259$ mol/s/m³

WHSV= 5.85 kg$_{CH_4}$/hr/kg$_{cat}$

Membrane area, heated area and catalyst volume for production of 1 Nm³ $H_2$/hr

Integration of membrane/catalyst/heat: How much volume/area do you need?

Physical separation membrane and catalyst/heat section possible
Combination membrane and catalyst/heat section in steam reforming process in two configurations:

- **In-situ** within one reactor vessel (Integrated Concept)
- **In-series** coupling of membrane and heat/catalyst module (Non-integrated Concept)
Integrated membrane reactor concept

Integration of membrane/catalyst/heat:

T-profile from burner to catalyst to membrane

Compact design

Mass transport catalyst → membrane

Patent no. WO2012/112046 A1
Integrated membrane reactor concept

Efficient combination of reaction and separation:
Methane conversion and baffles

Mass transport catalyst → membrane

Feed pressure: 30 bar S/C=3
Permeate pressure: 5.5 bar

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Methane conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5-steps</td>
</tr>
<tr>
<td>650</td>
<td>64.0%</td>
</tr>
<tr>
<td>700</td>
<td>80.77%</td>
</tr>
<tr>
<td>750</td>
<td>93.05%</td>
</tr>
<tr>
<td>800</td>
<td>98.4%</td>
</tr>
</tbody>
</table>
Integrated membrane reactor concept

Construction of integrated membrane reactor:
Certification problem HP vessel: $P_{\text{operation}} < 7$ bar
SR-enhancement demonstrated

- 1.6 Nm³/hr hydrogen for 55% methane conversion at 550°C
- H₂-purity 95% → membrane selectivity improvement required
- Long term testing terminated due to burner failure
# Integrated membrane reactor concept

## Summary:

<table>
<thead>
<tr>
<th>Reactor scale-up aspects</th>
<th>Carena impact</th>
<th>Next step</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Integrated membrane reactor</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Cost aspects:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Reactor cost</td>
<td>Membrane area per vessel volume optimized</td>
<td>Reactor &lt; 5000 euro/m²</td>
</tr>
<tr>
<td>- Membrane cost</td>
<td>Scale-up: 1500 euro/m²</td>
<td></td>
</tr>
<tr>
<td><strong>Integration aspects:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Heat distribution to catalyst and membranes</td>
<td>Optimized radial T-profile</td>
<td>Homogeneous T for membranes</td>
</tr>
<tr>
<td>- reaction/separation combination</td>
<td>5 baffles</td>
<td>Multi-baffle</td>
</tr>
<tr>
<td>- Integration in process</td>
<td>Heat supply by gas turbine</td>
<td>Demonstration heat supply by GT</td>
</tr>
<tr>
<td><strong>Operational aspects:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Operation P/T</td>
<td>7 bar demonstrated</td>
<td>High P (40 bar)</td>
</tr>
<tr>
<td>- H₂-production level</td>
<td>1.6 Nm³/hr</td>
<td>&gt; 200 Nm³/hr</td>
</tr>
<tr>
<td>- H₂-purity</td>
<td>95%</td>
<td>&gt; 99%</td>
</tr>
<tr>
<td>- Methane conversion level</td>
<td>54%</td>
<td>&gt; 95%</td>
</tr>
<tr>
<td>- Lifetime</td>
<td>800 hours</td>
<td>&gt; 40,000 hours</td>
</tr>
<tr>
<td>- Feed quality</td>
<td>Pure methane</td>
<td>NG</td>
</tr>
<tr>
<td>- Maintenance</td>
<td>Not addressed</td>
<td>Maintenance plan</td>
</tr>
</tbody>
</table>
Non integrated membrane reactor concept

2 STAGE OF REFORMING REACTION AND MEMBRANE SEPARATION ORGANIZED IN AN OPEN ARCHITECTURE
Non integrated membrane reactor concept
An overall feed conversion of 57.3% was achieved at 610°C, about 26% higher than what can be achieved in a conventional reformer at the same temperature.

Coupling two reforming stage and an intermediate membrane separation module allows to overcome equilibrium conversion. The RMM architecture performed a methane conversion up to 10-12% higher than equilibrium values.
## Non integrated membrane reactor concept

### Summary:

<table>
<thead>
<tr>
<th>Reactor scale-up aspects</th>
<th>Current status</th>
<th>Next step</th>
</tr>
</thead>
<tbody>
<tr>
<td>Integrated membrane reactor</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Cost aspects:
- Reactor cost
- Membrane cost

- Membrane area per vessel volume optimized
- Scale-up: 1500 euro/m²
- Reactor and membrane < 4000 euro/m²

### Integration aspects:
- Heat distribution to catalyst and membranes
- Reaction/separation combination
- Integration in process

- Heat supply in catalyst section, lower $T_{\text{mem}}$
- R-M-R configuration
- Heat supply by gas turbine
- No further optimisation
- Multi (R-M), fluiddynamic optimization, sweep gas
- Demonstration heat supply by GT as well as other thermal medium

### Operational aspects:
- Operation P/T
- $\text{H}_2$-production level
- $\text{H}_2$-purity
- Methane conversion level
- Lifetime
- Feed quality
- Maintenance

- 10 barg
- 20 Nm³/hr
- 99,5%
- 54%
- 2,000 hours
- NG
- Modular approach
- High P (40 bar)
- > 10,000 Nm³/hr
- > 99,99%
- > 95%
- > 15,000 hours
- -
- -