Integrated membrane reactor testing and modeling

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OUTLINE

• Integrated Membrane Reactor
• Mathematical Modeling
• Experimental Results
• Model Validation
• Simulation Results
Experimental Set-Up in CPERI

- Electric Furnace simulating Molten Salts as heat Fluid (<550°C)
- Pd-Ru Membrane on ceramic support ($d_m=5 \mu m$, 0.0176 m$^2$)
- Ni-Pt / CeZnLa Catalyst on SiC*

Pilot Plant installed at CPERI/CERTH

Experimental Conditions

- Inlet Temperature: 450 °C
- Reactor’s Wall Temperature: 500 °C
- Reaction Zone Pressure: 10 bara
- Permeation Zone Pressure: 1-1.3 bara
- Steam to Carbon Ratio (S/C): 2.5 – 3.5

Simplified Process Flow Diagram

* Palma, Castaldo, Ciambelli, Iaquaniello, Applied Catalysis B: Environmental, 2014
Experimental Set-Up in CPERI

- Ceramic foam supported catalyst (SiC) provides better radial thermal conductivity *
- Use of sweep gas (N$_2$, H$_2$O) provides higher driving force for hydrogen removal.

*Turchetti, Monteleone, Annesini, Chemical Engineering Transactions, 2011*
Mathematical Modeling

Methane steam reforming Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction Enthalpy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane steam reforming</td>
<td>( \Delta H^0_{298} = 206 \text{ kJ/mol} )</td>
</tr>
<tr>
<td>Water-Gas swift</td>
<td>( \Delta H^0_{298} = -41 \text{ kJ/mol} )</td>
</tr>
<tr>
<td>Methane steam reforming</td>
<td>( \Delta H^0_{298} = 165 \text{ kJ/mol} )</td>
</tr>
</tbody>
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- Reaction Kinetic rate expressions based on Langmuir-Hinshelwood mechanism (Xu & Froment, 1989)

\[
R_1 = \frac{k_1}{P_{H_2}^{2.5}} \left[ \frac{P_{CH_4} P_{H_2O} - P_{H_2}^3 P_{CO}}{K_1} \right]
\]

\[
R_2 = \frac{k_2}{P_{H_2}^{2.5}} \left[ \frac{P_{CO} P_{H_2O} - P_{H_2}^3 P_{CO_2}}{K_2} \right]
\]

\[
R_3 = \frac{k_3}{P_{H_2}^{3.5}} \left[ \frac{P_{CH_4}^2 P_{H_2O}^2 - P_{H_2}^4 P_{CO_2}}{K_3} \right]
\]

\[
DEN = 1 + K_{CH_4} P_{CH_4} + K_{CO} P_{CO} + K_{H_2} P_{H_2} + \frac{K_{H_2O} P_{H_2O}}{P_{H_2}}
\]

\[
k_i = A_i \exp \left( - \frac{E_{i,j}}{R_i T} \right), i = 1,2,3
\]

\[
K_i = B_i \exp \left( - \frac{E_{i,j}}{R_i T} \right), i = CH_4, H_2O, CO, CO_2, 1,2,3
\]
Mathematical Modeling

Assumptions:

i. Steady-state operation

ii. Plug-flow conditions

iii. Ideal-gas behavior

iv. Constant density of reactive mixture

v. 100% selectivity of the membrane towards $H_2$

vi. 2D pseudo-homogeneous model in reaction zone

vii. 1D model in permeation zone

viii. Backmixing in axial direction is negligible

ix. Constant temperature and pressure in permeation zone

x. Heat exchange between permeation and reaction zones is negligible

xi. The heating jacket is not modeled and the wall temperature is considered to be constant
The 2D pseudo-homogeneous model consists of:

i. **Mass balance for every component in reaction and permeation zone**

\[
\frac{\partial (uC_i)}{\partial z} = \frac{\varepsilon D_{er}}{u} \left( \frac{1}{r} \frac{\partial (uC_i)}{\partial r} + \frac{\partial^2 (uC_i)}{\partial r^2} \right) + \rho_b \sum_{j=1}^{3} R_j v_{i,j} \quad i = CH_4, H_2O, H_2, CO, CO_2
\]

\[
\frac{\partial (u_p C_{i,p})}{\partial z} = \frac{2}{r_i} N_m, i = H_2, \frac{\partial (u_p C_{i,p})}{\partial z} = 0, i \neq H_2
\]

ii. **Energy balance in reaction zone**

\[
u \rho C_p \frac{\partial T}{\partial z} = k_r \left( \frac{1}{r} \frac{\partial T}{\partial r} - \frac{\partial^2 T}{\partial r^2} \right) + \rho_b \sum_{j=1}^{3} \Delta H r_j R_j
\]

iii. **Momentum balance in reaction zone**

\[
\frac{\partial P}{\partial z} = \frac{f G \mu (1 - \varepsilon)^2}{\rho d_p^2 \varepsilon^3}, f = 150 + 1.75 \frac{\text{Re}_p}{1 - \varepsilon}, \text{Re}_p = \frac{G d_p}{\mu}
\]
Mathematical Modeling

Hydrogen flux through the membrane (Sievert's law)

\[
Q_{\text{mem}} \exp \left( -\frac{E_{\text{mem}}}{R_g T_m} \right) \frac{N_m}{d_m} \left( p_{H_2,r}^{0.5} - p_{H_2,p}^{0.5} \right)
\]

Boundary Conditions

\[ z = 0, \forall r : \quad (uC_i) = (uC_i)_{\text{in}}, T = T_{\text{in}}, P = P_{\text{in}}, (u_p C_{H_2,p}) = 0, (u_p C_{H_2O,p}) = (u_p C_{H_2O,p})_{\text{in}} \]

\[ r = r_o, \forall z : \quad \frac{\partial (uC_i)}{\partial r} = 0, k_r \frac{\partial T}{\partial r} = h_w (T_w - T) \quad i = CH_4, H_2O, H_2, CO, CO_2 \]

\[ r = r_i, \forall z : \quad \frac{\partial (uC_i)}{\partial r} = 0, i \neq H_2, \frac{d_m}{Pe_m} \frac{\partial (uC_i)}{\partial r} = N_m, i = H_2, \frac{\partial T}{\partial r} = 0 \]

Modeling equations have been discretized using a backward finite differencing scheme in the axial direction and an orthogonal collocation finite element scheme (OCFE) in the radial direction.
Experimental Results

Permeability tests with $\text{H}_2/\text{N}_2$ binary mixtures

- Membrane permeability is proportional to hydrogen molar fraction in the reaction zone.
- Ideal Permeability: $40 \ \text{Nm}^3/\text{m}^2 \ \text{h \ bar}^{0.5}$
- Effective Permeability: $15 \ \text{Nm}^3/\text{m}^2 \ \text{h \ bar}^{0.5}$

$T=470 \ \degree \text{C} \quad P_{\text{reac}}=4, 6, 9 \ \text{bara} \quad P_{\text{mem}}=1.5 \ \text{bara}$

$\text{H}_2$ molar fraction

Permeability, $\text{Nm}^3/\text{m}^2 \ \text{h \ bar}^{0.5}$
Experimental Results

Sweep gas Effect

Methane Conversion

Pure Hydrogen Production

$T=480 \degree C \quad S/C=3 \quad P_{\text{reac}}=10 \text{ bara} \quad P_{\text{mem}}=1.3 \text{ bara}$

- Sweep gas ($N_2: 0.5 \text{ L/min}$) results to higher methane conversion.
- Methane conversion is higher for lower inlet methane flowrates.
- Maximum methane conversion: 95 %.
Experimental Results

S/C Effect

Methane Conversion

$T=480 \, ^{\circ}C \quad S/C=2.5, \, 3, \, 3.5 \quad P_{\text{react}}=10 \, \text{bara} \quad P_{\text{mem}}=1.3 \, \text{bara}$

- Only minor changes occur to methane conversion by changing the steam to carbon ratio.
Experimental Results

Methane inlet flowrate and sweep gas Effect

- Sweep gas ($N_2$: 0.5 L/min) results to higher methane conversion.
- Methane conversion is higher for lower inlet methane flowrates.
- Maximum methane conversion: 99%.
- Pure hydrogen production has a maximum (for the specific membrane reactor).
Experimental Results

Outlet steam composition

Without Sweep Gas  
With Sweep Gas (0.5 L/min)

\[ T = 480 \, ^\circ C \quad S/C = 2.5 \quad P_{\text{react}} = 10 \, \text{bara} \quad P_{\text{mem}} = 1 \, \text{bara} \]

- The lower the methane inlet flowrate the bigger the contribution of the membrane.
Simulation results referring to the cases where sweep gas was used are in good agreement with the experimental results, while simulation results referring to the case where no sweep gas was used a slight deviation is observed.

The mathematical model was tested and validated at different condition (P, S/C). The mathematical model shows good predictive power of the methane conversion in the membrane reactor.
Conclusions

- No signs of catalyst deactivation were observed during the six-week experimental campaign of continuous 24h experiments.
- By analyzing the used catalyst only a slight quantity of carbon was detected (0.28% w/w) that is oxidated at higher temperature.
- Membrane performance was stable, but a loss of selectivity was observed (<3%vol. of the permeate)
- A membrane reactor enhances the methane conversion compared to a traditional reactor.
- Sweep gas results to further enhancement of methane conversion
- Pure Hydrogen production exhibits a maximum at moderate methane inlet flowrates (1 L/min CH$_4$ and 2 L/min CH$_4$)
The European Commission is acknowledged for its support

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Thank You for Your Attention!