Bench-scale study of separation of hydrogen from gasification gases using a Pd-based membrane reactor

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Hydrogen production in Thermo-chemical conversion

Coal/Biomass/Waste → Gasification → CO, H₂, CO₂ → Gas Cleaning

WGS reaction: CO + H₂O ⇌ CO₂ + H₂

Catalysts → Enriched H₂ stream

H₂ Separation technologies → H₂ → CO₂

Membranes:
- PSA
- Amine Absorption (CO₂)
- Cryogenics
What is a Membrane?

Physical barrier that allows the separation of a stream into two fractions

\[ \begin{align*}
q_f & \quad \text{Feed} \\
q_p & \quad \text{Permeate} \\
q_r & \quad \text{Retentate (Residue)} \\
\end{align*} \]

Selectivity

\[ \alpha_{A/B} = \frac{y_A / y_B}{x_A / x_B} \]

Recovery

\[ S = \frac{q_p}{q_f} \]

Permeate flow-rate

\[ Q_p \]

Permeation Flux

\[ \text{Flux}_{H_2} = p_{H_2} \left( p_{H_2, \text{ret}} - p_{H_2, \text{perm}} \right) \]
# Membrane classification

<table>
<thead>
<tr>
<th>Classification Criteria</th>
<th>Categories</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>Organic</td>
<td>Made of polymers</td>
</tr>
<tr>
<td></td>
<td><strong>Inorganic</strong></td>
<td>Made of glass, <strong>metal</strong> or ceramics</td>
</tr>
<tr>
<td>Membrane structure</td>
<td>Porous</td>
<td>Transport through the pores</td>
</tr>
<tr>
<td></td>
<td><strong>Dense</strong></td>
<td>Transport through the bulk of the material</td>
</tr>
<tr>
<td>Morphology</td>
<td>Symmetrical</td>
<td>Homogeneous structure</td>
</tr>
<tr>
<td></td>
<td>Asymmetrical</td>
<td>Several layers of different characteristics. Composite membranes</td>
</tr>
</tbody>
</table>
Dense or “non-porous” membranes, the transport mechanisms rely on the principle of solution/diffusion through the bulk of the material Highly selective.
Aim & Approach

- To study hydrogen purification and separation from the main components found in syngas

  - Realistic studies conducted on **bench-scale level**
  - **Different operating conditions and gas environments**: hydrogen, binary and ternary mixtures, full synthetic syngas
  - For pure hydrogen, the **effect of pressure and temperature** on permeation was determined.
  - Studies on binary and ternary mixtures analyzed the **effect of nitrogen, carbon dioxide, steam and carbon monoxide** on hydrogen permeation.
  - **Performance under full synthetic syngas**: Gas composition expected in the future for the feed gas to the conventional Water Gas Shift Unit of Växjo Värnamo Biomass Gasification Centre (VVBGC)
Test rig

Bench-scale facility for gas separation and membrane reactor studies
2 Nm³/h, T 600°C and up to 12 bar

Feeding system:
MFC H₂ (5 l/min), N₂ (15 l/min), CO (5 l/min),
CO₂ (5 l/min), H₂O (25 cc/min)

Gas prehater + Vaporiser
MFM's Permeate & Retentate
Cooling & Venting System
PCVs Permeate & Retentate

Gas Analysis: HP5890 Series II GC, TCD detector

Membrane
Dense Pd
Tubular O.D. =2,54 cm; L= 15 cm
Membrane surface area: 0.01216 m²
Welded to a SS-316 tube
Membrane-tube assembly L=70 cm
Independent oven
Permeation studies: Pure H₂

Effect of retentate pressure on H₂ permeate flow-rate and evolution with time

Permeation increased with time, reached a maximum, decreased and reached a stationary value

An increase of operating pressure resulted in an increase of H₂ permeation

For a feed pressure above 150 kPa all H₂ was able to permeate through the membrane

Relationship between hydrogen permeation flux and driving force

Flux of pure hydrogen was plotted as a function of the difference of the square root of hydrogen partial pressure on both sides of the membrane

The membrane followed Sievert’s Law very nicely and a good correlation factor was found

Permeance is within the same range to values reported for dense Pd-membranes
Permeation studies: Pure H₂

Effect of temperature on hydrogen permeate flow-rate

Temperature favoured H₂ permeation through the membrane, especially for rises between 623 K and 673 K

Relationship between hydrogen permeability and temperature

The relationship between H₂ permeability and reciprocal temperature is presented in an Arrhenius-type equation, showing a good linear correlation.

Estimated values of apparent activation energy and pre-exponential factor for H₂ permeation are 12.96 kJmol⁻¹ and 4.33 × 10⁻⁵ mol ms⁻¹ m⁻² kPa⁻⁰.⁵; same order of magnitude to those reported in literature


**H₂ permeation in presence of nitrogen**

Influence of nitrogen content on hydrogen permeation flow-rate

Permeation decreased on increasing N₂ content in the mixture.

Polarization concentration and H₂ depletion along the length of the membrane

Permeate: Only H₂

Retentate: Only H₂ and N₂ no signs of formation of any other N-containing species

No signs of deterioration or deactivation.

When subjected to permeation with pure H₂, original permeation values restored
**H₂ permeation in presence of carbon dioxide**

**Influence of CO₂ content on H₂ permeation flow-rate**

- **Temperature:** 723 K
- **H₂ feed gas:** 4000 ml/min⁻¹
- **PpH₂ feed:** 150 kPa

**Carbon monoxide formation during separation tests using CO₂/H₂ mixtures**

**The reverse water gas shift reaction was found to be taking place**

\[ H_2 + CO_2 \rightarrow CO + H_2O \]

**CO₂ also led to a decrease of permeation**

It is believed to be due to H₂ depletion along the membrane.

**CO in the retentate gas stream as high as 7.56 % vol/vol d.b. (50% vol CO₂ and 50% vol H₂)**

**No conclusive relationship between the extent of the reaction and the ratio CO₂/H₂ in the gas**
H₂ permeation in presence of steam

Influence of H₂O content on H₂ permeation flow-rate

Permeate flow was less stable than in the case of other co-existing gases, N₂ and CO₂. The system tended to a steady state for which H₂ permeate flow-rate was very similar, regardless of steam content.
Overall comparison

Comparison of the effect of N$_2$, CO$_2$, and H$_2$O on H$_2$ permeation

- N$_2$, CO$_2$ and H$_2$O inhibit H$_2$ permeation in a reversible way.
- H$_2$ permeation flux decreases when the concentration of the co-existing gas increases.
- In the case of N$_2$, inhibition to hydrogen permeation follows a linear trend with its content in the mixture.
- CO$_2$ causes a slightly higher inhibition but it also proportional to its content in the feed gas.
- Steam shows different effects depending on its concentration in the feed gas. It inhibits H$_2$ permeation more strongly than N$_2$ or CO$_2$ when the mixture is hydrogen-rich (xH$_2$>0.5). On the other hand inhibition becomes almost independent of steam content for steam-rich mixtures (xH$_2$<0.5).
H$_2$ permeation in presence of carbon monoxide

Influence of CO on H$_2$ permeation flux

A mixture containing N$_2$ and H$_2$ was fed, N$_2$ was replaced by CO to produce the desired ternary mixture.

At 723 K, CO did not show a strong inhibition effect on H$_2$ permeation, even when feeding mixtures with as much as 18% vol CO.

Permeation flux remained very stable and secondary reactions did not occur.

Temperature, however, has a significant effect on hydrogen permeation.

Drop in H$_2$ permeation particularly noticeable when temperature was lowered from 653 K to 593 K.

Absence of secondary reactions: The analysis of the retentate stream was very stable.
Permeation in presence of full synthetic syngas

Relationship between $H_2$ permeation flux and driving force and temperature under full syngas WGS conditions

![Graph showing the relationship between hydrogen permeation flux and driving force for different temperatures and gas mixtures.](image)

Feed gas flow-rate: 10.91 l/min

- $T = 723$ K
- $T = 653$ K
- $T = 593$ K

Gas Mixture (vol%): $CO_2/CO/H_2/H_2O$ 7/19/18/56

$H_2$ feed gas = 1.88 l min$^{-1}$

Typical gas composition and operating conditions for the water gas shift stage Värnamo VVBGC in Sweden

As happened for pure hydrogen, an increase in permeation was achieved on increasing feed pressure.

Rising temperature also increased permeation.

Comparison of hydrogen recovery under pure hydrogen and full syngas WGS conditions

![Graph comparing hydrogen recovery under different conditions.](image)

Hydrogen recovery: ratio between the $H_2$ that permeates through the membrane to the $H_2$ fed into the reactor.

Production of pure hydrogen as the permeate stream is achievable under full synthetic gasification gas.

Nevertheless hydrogen recovery was smaller. (100% Recovery to less than 50%)
Conclusions

1) Separation of H₂ from main components of syngas using a Pd-based membrane has been studied at bench-scale.

2) Permeation flux followed Sievert´s Law, i.e. the hydrogen flow that permeates is proportional to the difference of the square root of the hydrogen partial pressure on both sides of the membrane.

3) A good linear relationship between hydrogen permeability and temperature was found.

4) Hydrogen separation from main components of syngas using a Pd-based membrane reactor is shown to be feasible.

5) The presence of N₂ or CO₂ resulted in a decrease of H₂ permeation.

6) CO₂ showed a slightly higher inhibition to H₂ permeation than N₂, and in addition the reverse WGS reaction was found to be taking place.

7) The presence of steam also led to a decrease of hydrogen permeation.

8) The effect of CO was also analysed. At 723 K, CO did not modify H₂ permeation, regardless CO content in the feed gas. A strong inhibition was noticed, however, on decreasing operating temperature.

9) Performance under full synthetic gasification gas showed that production of a pure hydrogen permeate stream is achievable, although hydrogen recovery was smaller.
Acknowledgements

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THANK YOU VERY MUCH FOR YOUR ATTENTION

Any Questions?