Hydrogen Purification Technologies Overview
2021 ARPA-E Methane Pyrolysis Annual Program Review Virtual Meeting

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Overview of H₂ Purification Technologies

PSA (Pressure swing adsorption)
- Most common method used in H₂ plants
- Suitable for small to very large capacities
- Requires feed at pressure
- Produces H₂ at pressure and impurities are removed at near-ambient pressure in tail gas
- H₂ purity of up to 99.9999 vol.% achievable

Membranes
- Used in niche H₂ separation applications (e.g. syngas ratio adjustment, recovery from H₂-rich off gases)
- Economical at lower capacities
- Requires feed at pressure
- Produces H₂ at low pressure and impurities are removed at about feed pressure in the retentate
- Product H₂ compressor may be required
- H₂ purity is 95 – 98% vol. from a single stage
PSA technology: Layered Bed for $H_2$ Purification

Layer 1: non adsorbed product
Layer 2: adsorbed impurities (design basis for PSA)
Layer 3: aromatics, $H_2S$, $H_2O$, $HCl$
Layer 4: strong adsorption forces

He, H2, N2, CO, CH4, CH4, C2Hn, C3Hn, CO2, C3Hn, C4Hn, C5+, aromatics

weak adsorption forces
PSA Equipment – Supplied as Package Unit

- Adsorber Vessel and Tail Gas Drum
- Prefabricated Valve Skid
- Process Control System
- Adsorbent Material
Applications for PSA Hydrogen Recovery

**Feed Gas**

**Feed Gas Sources**

- **Synthesis Gases:**
  - Steam Reformer
  - Partial Oxidation
  - Gasification
  - CH4 pyrolysis

- **Refinery Off-Gases:**
  - Catalytic Reformer
  - CCR
  - Aromatic Plants
  - other H2-rich streams

- **Petrochemical Off-Gases:**
  - Ethylene Plants
  - Methanol Plants
  - Ammonia Plants

- **Coke Oven Gas**

**Pure Hydrogen Product**

**Hydrogen Consumers**

- Refinery:
  - Hydrocracker
  - Hydrodesulfurization

- Ammonia Synthesis

- MeOH Synthesis

- Petrochemical Processes:
  - Olefin & Polyolefin
  - Aromatics
  - Hydrogen Peroxide

- Others:
  - Iron & Steel Industry
  - Float Glass Production
  - Food Industry
  - Electronic Industry
  - H2 Fuel / Fuel Cells

**Typical Ranges**

<table>
<thead>
<tr>
<th></th>
<th>Feed Gas Sources</th>
<th>Pure Hydrogen Product</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pressure</strong></td>
<td>5 – 70 bar(a)</td>
<td>1.1 – 7 bar(a)</td>
</tr>
<tr>
<td><strong>H2 content</strong></td>
<td>30 – 99 vol. %</td>
<td>99 – 99.999 vol.%</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>10 – 40 °C</td>
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<tr>
<td><strong>Flow</strong></td>
<td>Up to 500,000 Nm3/h</td>
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**Tailgas (Impurities + H2)**

Utilized as Fuel Gas:
- to fuel gas network
- to reformer furnace

**Typical Range**

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<tr>
<td><strong>Pressure</strong></td>
<td>99 – 99.999 vol.%</td>
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Polymeric Membranes in Gas Separation

Glassy Polymers

- Gases dissolve into surface
- Diffusion controlled transport
- More soluble components permeate quicker (small molecule → high flux)
- \( \text{H}_2, \text{He}, \text{CO}_2 \) removal/recovery processes

Typical Permeation Properties

<table>
<thead>
<tr>
<th>Slow</th>
<th>Glassy-Polymer</th>
<th>Fast</th>
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<tbody>
<tr>
<td>( \text{C}<em>6\text{H}</em>{14} )</td>
<td>( \text{C}_3\text{H}_8 )</td>
<td>( \text{C}_2\text{H}_6 )</td>
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01/12/2021  Hydrogen Purification Technologies Overview – presented at the 2021 ARPA-E Methane Pyrolysis Annual Program Review Virtual Meeting
Membrane Applications for Hydrogen Separation

- Syngas H₂:CO ratio adjustment by removing some hydrogen
- Hydrogen extraction from NG-H₂ mixture
- Hydrogen recovery from refinery off-gas streams
- Hydrogen recovery from purge streams in different processes
- H₂ rejection from olefin streams
Considerations for H₂ Purification in Methane Pyrolysis Plants

- Pre-cleanup including separation of solids and liquids from raw H₂ stream
- Feed compression to desired pressure for separation
- Full characterization to define all the components including trace impurities
- Integration of purification technology with CH₄ pyrolysis
- H₂ purification technology selection and optimization will depend on
  - Production capacity
  - Feed pressure and composition
  - Product purity and recovery targets
  - Product and tail gas or retentate pressures
  - Integration with rest of the process (use of tail gas or retentate)

Final Solution Could be PSA, Membranes (Single or Multi-Stage) or Membrane-PSA Hybrid
Thank you for your attention.

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