Production of Hydrogen

RJ Allam
Air Products
Why Hydrogen?

\[ \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \quad \Delta H \text{ -57.8 kcal/mole} \]

- \text{H}_2 \text{ is an energy vector, is converted to water which has minimal environmental impact.}
- \text{H}_2 \text{ is a non-polluting fuel for transportation vehicles and power production}
- \text{Currently road vehicles emit about the same quantity of CO}_2 \text{ as power production.}
- \text{H}_2 \text{ can be produced from fossil fuels with CO}_2 \text{ capture and storage or from renewables}
# Production of Hydrogen Options

<table>
<thead>
<tr>
<th>Method</th>
<th>Characteristics</th>
</tr>
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<tbody>
<tr>
<td>Photolysis</td>
<td>catalytic-water splitting</td>
</tr>
<tr>
<td>Electrolysis</td>
<td>water</td>
</tr>
<tr>
<td>Power for electrolyser</td>
<td>ambient $\rightarrow$ high temperature</td>
</tr>
<tr>
<td></td>
<td>ambient $\rightarrow$ high pressure</td>
</tr>
<tr>
<td>Thermal splitting</td>
<td>water</td>
</tr>
<tr>
<td>$\Xi^m$ conc as function of temp</td>
<td>high temperature</td>
</tr>
<tr>
<td></td>
<td>freeze equilibrium</td>
</tr>
<tr>
<td>Fossil fuel Conversion</td>
<td>Heat, water, oxygen, catalytic</td>
</tr>
<tr>
<td>Far Future</td>
<td>Non fossil fuel alternatives based on sunlight, renewables and nuclear</td>
</tr>
<tr>
<td>Present</td>
<td>Fossil fuels</td>
</tr>
</tbody>
</table>
Carbon Containing Fuels

Coal
Natural gas
Refined Hydrocarbons
Heavy refinery waste
Biomass

Lignite → Anthracite
Ethane → Fuel Oil
Tar → Petcoke
## Reactions

<table>
<thead>
<tr>
<th>Category</th>
<th>Reaction</th>
<th>Change in ΔH</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reforming With Steam - Catalytic</strong></td>
<td>CH(_4) + H(_2)O ↔ CO + 3H(_2)</td>
<td>+ ΔH</td>
</tr>
<tr>
<td>Natural gas and light hydrocarbons</td>
<td>CO + H(_2)O ↔ H(_2) + CO(_2)</td>
<td>- ΔH</td>
</tr>
<tr>
<td><strong>Partial Oxidation - Non Catalytic</strong></td>
<td>C + (\frac{1}{2})O(_2) → CO</td>
<td>- ΔH</td>
</tr>
<tr>
<td>Any hydrocarbon or carbonaceous feedstock</td>
<td>CO + H(_2)O ↔ CO(_2) + H(_2)</td>
<td>- ΔH</td>
</tr>
<tr>
<td><strong>Thermal Decomposition</strong></td>
<td>CH(_4) → 2H(_2) + C</td>
<td>+ΔH</td>
</tr>
<tr>
<td>Only limited application as co-product in carbon black manufacture</td>
<td>CO + H(_2)O ↔ H(_2) + CO(_2)</td>
<td>- ΔH</td>
</tr>
</tbody>
</table>
General Arrangement For CO$_2$-free Hydrogen Production

- **Fuel** flows through
- **Oxygen** flows through
- **Syngas Generation**
- **Heat Recovery**
- **Shift reactors**
- **H$_2$ purification / CO$_2$ separation**
- **Export Steam**
- **CO$_2$**
- **Waste Fuel Gas**
- **H$_2$**
## CO₂ Separation Technologies Capabilities

<table>
<thead>
<tr>
<th></th>
<th>Adsorption</th>
<th>Membrane</th>
<th>Absorption</th>
<th>Cryogenic</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Feed Pressure</strong></td>
<td>Low to High</td>
<td>Medium to High</td>
<td>Low to High</td>
<td>Medium to High</td>
</tr>
<tr>
<td><strong>CO₂ Pressure</strong></td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td>Low to Medium</td>
</tr>
<tr>
<td><strong>CO₂ Purity</strong></td>
<td>Medium to High</td>
<td>Low to Medium</td>
<td>Medium to High</td>
<td>High</td>
</tr>
<tr>
<td><strong>CO₂ Recovery</strong></td>
<td>Medium to High</td>
<td>Low</td>
<td>High</td>
<td>High</td>
</tr>
</tbody>
</table>
H₂ Production
Separation Methods

Separation of pure H₂ and pure CO₂ from syngas

Absorption

Scrubbing with a solvent

Physical solvents:
- Rectisol – low temperature methanol
- Selexol – Polyether

Selective for H₂S and CO₂ following COS hydrolysis
Favour high partial pressure of impurity
Used primarily when POX coal/tar

Chemical solvents – usually based on amines
  Single component absorption H₂S and CO₂
  High heat requirement
  Suitable for low partial pressure of impurity
H₂ Production
Separation Methods

Separation of pure H₂ and pure CO₂ from syngas

**Adsorption**

- Pressure swing used for most H₂ separations from syngases
- Can achieve 90% H₂ recovery from 22 bar SMR gas. Typical 3-10 min cycle time
- Low capital cost, high reliability
- Can be used for simultaneous pure H₂ and pure CO₂ recovery at high purity
Process Characteristics
Open Systems

- External heating of a catalytic reactor
- Combustion products vented to atmosphere
- CO$_2$-free flue gas requires H$_2$ fuel for the furnace, or
- Oxyfuel furnace operation could be used.

50,000 Nm$^3$/hr Steam Natural Gas Reformer
Current Technology
Steam Methane Reforming (SMR)

- **Limitations**
  - Carbon formation at low steam; carbon ratio
  - Higher hydrogen pressure limits CH₄ conversion
  - High CH₄ conversion requires high temperature
  - Excess steam production
  - Cooling by waste heat boiler to limit Boudouard carbon formation
  - Low NOₓ levels required in stack gas

- **Challenges**
  - Reduce steam to carbon ratio
  - Low NOₓ long flame burners
  - Materials limitations in alloys used for tubes
  - Reduce excess steam production by air preheat and pre-reforming
Process Characteristics
Closed Systems

- Pressurised reactors with heat supplied by direct oxidation with oxygen
- No venting of combustion products

Natural Gas → Oxygen → Partial Oxidation
Natural Gas → Oxygen → Steam → Autothermal Reformer

POX
Catalyst
Current Technology
Autothermal Reformer (ATR)

- **Limitations**
  - Must use a clean, light hydrocarbon feed
  - Cost of oxygen
  - Limitation in $\text{H}_2$ pressure
  - Limitation in exit temperature
  - Excess steam production
  - Needs waste heat boiler to limit Boudouard carbon formation

- **Challenges**
  - Reduce steam to carbon ratio
  - Increase $\text{CH}_4$ conversion by increasing temp
  - Carbon free burner operation
  - Increase in vessel size/throughout
Current Technology
Partial Oxidation (POX)

Suitable for any carbonaceous feed – favoured for coal

Many configurations…

- Fixed/moving bed – Lurgi
- Fluidised bed – Winkler
- Entrained bed (1325°C → 1450°C)
  - Texaco
    - water slurry coal feed
    - high pressure: 70 bar
    - usually water quench
    - favoured for H₂ production because of excess H₂O present
    - combined sour gas CO shift and COS hydrolysis
  - Shell
    - dry coal feed, nitrogen entrainment
    - pressure limitation: 40bar (coal)
    - waste heat boiler, higher efficiency
    - needs added steam for shift and H₂ production
    - often configured with a COS hydrolysis reactor upstream of H₂S removal and CO shift reactor downstream of H₂S removal
CO₂-Free Power and Hydrogen From Coal Fuelled System

Coal → Gasification → Quench/Heat Recovery → Shift reactors → CO₂/H₂S Physical Absorption System → H₂ Product

100 bar CO₂ → H₂ for Power Generation

H₂ Purification

Coal, Water/N₂, Oxygen → Gasification

Ash/Slag → Quench/Heat Recovery

H₂ for Power Generation

H₂ Purification

Texaco

Grinding, slurrying → Gasifier 1300°C 75 bar → Quench gas, water → Quenched gas, water → Scrubber water → Syngas → Water → Oxygen production → Air → Vent → Coal → Quench make-up water

Shell
Production of Hydrogen
ATR/GHR Integration

- Possibility of using high temperature H₂/CO/CO₂ syngas to heat a Gas Heated Reformer (GHR)
- No excess steam production
- Extra 30% H₂ production
- Boudouard carbon formation in GHR shell side
H₂ Production
Emerging Technologies

• Micro reactor/Multichannel Heat Exchanger

Either
– Low temperature POX
  • Air purified
  • 45% H₂ – fuel cell feed (PEM)
  • Followed by direct air/CO
  • Oxidation to reduce CO<10ppm

• SMR
  – Separate air/fuel gas catalytic combustion passages and adjacent SMR passages
Production of Hydrogen
Plate-Fin Reformer

Catalyst can be a surface coating or a porous insert.

Need to match the heat release rate with the steam hydrocarbon reforming rate.

Very compact and potentially low cost system

Fuel Gas + Air

Natural Gas + Steam

Metal

Combustion Catalyst

Metal

Reforming Catalyst

Metal

Metal

Micro Reactor
A + B → C

Heat Exchange Plate

Reaction Plate

Mixing Plate

Heat Exchange Fluid
H₂ Production
Emerging Technologies

- Micro reactor/Multichannel Heat Exchanger

In General

- Catalyst can be deposited on metal surfaces or used in a porous insert
- Removable catalyst elements are possible
- Very high volumetric productivity for SMR reactor
- Whole H₂ plant can be integrated with a plate-fin reformer configuration

Challenges

- Novel arrangements to allow catalyst change out
- Capable of either small scale or very large scale use
- Requires balanced performance between SMR/fuel combustion
ITM Hydrogen/Syngas: A Revolutionary Technology Using Ceramic Membranes

- Ion Transport Membranes (ITM)
  - Non-porous multi-component ceramic membranes
  - High oxygen flux and high selectivity for oxygen
  - Operate at high temperatures, typically over 700 °C
- ITM Hydrogen/Syngas combines air separation and methane partial oxidation into a single unit operation, resulting in significant cost savings

\[
\text{CH}_4 + O^{2-} \rightarrow \text{CO} + 2\text{H}_2 + 2e^- \\
\frac{1}{2}\text{O}_2 + 2e^- \rightarrow O^{2-}
\]
Integrated Development Program Addresses Key Technical Challenges with Broad Development Team

- Develop fabrication methods
- Produce ceramic membranes for testing
- Develop stable material compositions
- Characterize material properties and performance

- Process design and economic evaluation
- Membrane and reactor design
- Lab-scale testing: ambient pressure and elevated pressure
- Process Development Unit (PDU)
- SEP and PCTDU
Advantages of Planar Membrane Systems

- Compactness
- Good mass and heat transfer
- Amenable to standard ceramic processing methods

Ceramic Wafer Stack

- Syngas Products (H₂ and CO)
- Natural Gas Feed (external)
- Air Feed (internal)
- Porous Support/Catalyst
- Active Membrane
- Flow Channels
PDU Ceramic Membranes Contain Essential Features of Full-Size Commercial Membranes

- ITM Hydrogen/Syngas ceramic membranes have internal features for manifolding and air flow, while supporting > 400 psi pressure differential
- Membrane fabrication processes are robust and scaleable
ITM Hydrogen/Syngas: Combines Oxygen Production and Syngas Production Into a Single Reactor to Achieve Over 30% Capital Cost Savings

Conventional Process (ATR and Air Sep Unit) with Separate Oxygen and Syngas Production

Over 30% Capital Cost Savings

ITM Hydrogen/Syngas Reactor Combines Oxygen Separation and Syngas Production

Syngas to Product Conversion: (hydrogen, clean liquid fuels, chemicals)

Natural Gas Feed

Steam

Fuel Feed Preheat and Treatment

Oxygen

Autothermal Reformer

Main Air Compressor

Front End Cleanup

Low Pressure Column

Main Heat Exchanger

Main Reboiler

High Pressure Column

N2

Waste

ITM H₂/Syngas Reactor

in-line burner

blower

Fuel

Air

ITM Hydrogen/Syngas Reactor

Combines Oxygen Separation and Syngas Production

Over 30% Capital Cost Savings
Production of Hydrogen
Simultaneous Separation/Reaction

- Enhanced conversion of feedstock to hydrogen by removing one of the product continuously
- \( \text{H}_2 \) removal from steam reformer using a palladium diffusion surface
  - low pressure \( \text{H}_2 \), high pressure \( \text{CO}_2 \)
    \[
    \text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2
    \]
- Adsorption of \( \text{CO}_2 \) at high temperature in a shift converter/adsorber
  - Typical high temperature adsorbents are substituted hydrotalcites or lithium silicate for \( \text{CO}_2 \)
  - high pressure \( \text{H}_2 \), low pressure \( \text{CO}_2 \)
    \[
    \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2
    \]
- In both cases, hot \( \text{H}_2 \) is produced (400 - 600°C)
Production of Hydrogen
Steam Electrolysers

![Graph showing voltage vs. current density for different steam electrolysis systems: HOT ELLY (1000°C), LLNL, 1999 (900°C), and LLNL, 2000 (900°C) with an improved anode.]
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