Sustainable Energy
Mod. I: Fuel Cells & Distributed Generation Systems

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Lesson XIII: hydrogen (production, distribution and storage)
The Hydrogen Economy (1/2)

October 2002

Very senior representatives from major European automotive and energy companies, SME, research centres, utilities, policy makers, and users associations advise on prospects for economic impact of moving towards a sustainable energy economy based on hydrogen and electricity as carriers, using fuel cells as efficient energy converters.
The Hydrogen Economy (2/2)

**A CHALLENGING EUROPEAN HYDROGEN VISION**

- **H₂ production & distribution**
- Interconnection of local H₂ distribution grids; significant H₂ production from renewables, incl. biomass gasification
- H₂ produced from fossil fuels with C sequestration

**Hydrogen-oriented economy**

- **2050**
  - H₂ use in aviation;
  - Fuel cells become dominant technology in transport, in distributed power generation, and in micro-applications
- **2040**
  - Increasing market penetration of hydrogen and fuel cell products and systems
  - FC stationary applications
  - FC mobile applications
- **2030**
  - H₂ prime fuel choice for FC vehicles
  - Significant growth in distributed power generation with substantial penetration of FCs
  - 3rd generation on-board storage (long-range)
  - Fuel cells for high temperature fuel cell systems;
  - FCs commercial in micro-applications
  - FC vehicles competitive for passenger cars
  - SOFC systems and stationary hybrid commercial (<10MW)
  - First H₂ fleets (1st generation on-board storage)
  - Series production of FC vehicles for heavy-duty H₂ and on-board reforming and other transport (boats, FC for large power units)
- **2020**
  - Stationary low temperature fuel cell systems (PEM) (<300kW)
  - Stationary high-temperature fuel cell systems (MCFC/SOFC) (<500kW)
  - H₂ ICE developed; demonstration fleets of FC-buses
  - Stationary low temperature fuel cell systems for niche commercial (<50kW)
- **2010**
  - Public incentive and private effort
  - Fuel Cells (vehicles, railway, marine, stationary, distributed and use)
  - Hydrogen production, transmission, storage and use
  - RTD: field tests, niche fleets

**Fossil fuel-based economy**

- **2000**
  - H₂ production from fossil fuels with C sequestration

**H₂ production from renewables**

- direct H₂ production from renewables, de-carbonised H₂ society
- Increasing de-carbonisation of H₂ production; renewables, fossil fuel with sequestration, new nuclear
Hydrogen LHV

Hydrogen as Alternative Fuel
comparison of fuels - heat of combustion / energy content -

heat of combustion [ MJ / kg ]

energy content [ MJ / ltr ]

www.Linde.com
Hydrogen Production (1/7)

Sources
- Fossil: Oil, Natural gas, Coal, Nuclear
- Renewable: Wind, PV, Solar, Biomass

ZERO EMISSION CONVERSION
- Refining
- Reforming
- Gasification: Therermochemical processes
- Electrolysis: Thermochemical processes
- Gasification

CO₂ sequestration

UTILIZATION
- Distributed power generation
- Residential
- Industry
- Transport
- Other

Hydrogen

H₂ pipes
H₂ storage and delivery
## Hydrogen Production (2/7)

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<tr>
<th>Process</th>
<th>Need for R&amp;D</th>
<th>Cost reduction and series production</th>
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<td>• materials, catalysts</td>
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<td>• behaviour at partial load</td>
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<td>Coal gasification and partial oxidation</td>
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<td>Biomass gasification</td>
<td>• process optimization</td>
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<td>• materials</td>
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</tr>
<tr>
<td></td>
<td>• $H_2$ quality</td>
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<td>Kvaerner process</td>
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<td>Other processes</td>
<td>• basic research</td>
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<td>thermochemical production</td>
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<tr>
<td>photochemical processes</td>
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<tr>
<td>biological processes</td>
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</tbody>
</table>
Hydrogen Production (3/7)

Hydrogen from coal

- Reactions for hydrogen generation from coal:

\[ C + H_2O \rightarrow H_2 + CO \] \textit{gasification}

\[ CO + H_2O \rightarrow H_2 + CO_2 \] \textit{shift}

- Different types of gasifiers: moving bed (450-500°C), fluidized bed (800-1000°C) and entrained bed (1200-1400°C).

- Downstream of the gasifier: cleaning units.
Hydrogen Production (4/7)

Hydrogen form hydrocarbons (1/2)

✓ Reactions for hydrogen generation through steam reforming from light hydrocarbons:

\[ C_n H_m + nH_2O \rightarrow nCO + \left( \frac{m}{2} + n \right) H_2 \]  

✓ Typical catalysts: Ni based composites or Mg oxides.

✓ Typical temperature: 800°C.

\[ nCO + nH_2O \rightarrow nCO_2 + nH_2 \]  

shift
## Hydrogen Production (5/7)

### Hydrogen form hydrocarbons (2/2)

- Reactions for hydrogen generation through partial oxidation:

  - **Methanol**
    
    \[
    CH_3OH + \frac{1}{2} O_2 \rightarrow 2H_2 + CO_2
    \]

  - **Petrol**
    
    \[
    C_8H_{18} + 4O_2 + 8H_2O \rightarrow 17H_2 + 8CO_2
    \]
Hydrogen Production (6/7)

FUEL DECARBONISATION

- **Combustion Reaction**
  \[
  \text{CH}_4 + 2\text{O}_2 \leftrightarrow \text{CO}_2 + 3\text{H}_2
  \]

- **Partial Oxidation Reaction**
  \[
  \text{CH}_4 + \frac{1}{2}\text{O}_2 \leftrightarrow \text{CO} + 2\text{H}_2
  \]

- **Steam reforming**
  \[
  \text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2
  \]

- **Shifting Reaction**
  \[
  \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2
  \]

Diagram:
- Air
- PO
- WGS
- To the separation section
- Fuel

Temperature:
- 43°C
- 230°C
Hydrogen Production (7/7)

Hydrogen form Electrolysis

- Current technology: Low temperature electrolyzers (efficiency: 65%)
- Technology under development: High temperature electrolyzers - SOEC (efficiency: 80%–85%)

Diagram:
- Hydrogen and Oxygen production from electrolysis
- Cathode reaction: \(2 \text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2 \text{OH}^-\)
- Anode reaction: \(2 \text{OH}^- \rightarrow 1/2 \text{O}_2 + \text{H}_2\text{O} + 2e^-\)
- Overall reaction: \(\text{H}_2\text{O} \rightarrow \text{H}_2 + 1/2 \text{O}_2\)
Hydrogen Storage (1/10)

- Existing technologies
  - compressed H\textsubscript{2} (p > 700 bar)
  - liquid (or gel) H\textsubscript{2}
  - glass microspheres filled with H\textsubscript{2}
  - physical adsorption (carbon nanostructures, zeolites, nanoporous materials)
  - metallic hydrides (simple and complex)
  - chemical storage (hydrides of ammonium, lithium, sodium, magnesium)

Chemical reaction for H\textsubscript{2} production:

\[
\text{MgH}_2 + 2 \text{H}_2\text{O} = \text{Mg(OH)}_2 + 2\text{H}_2
\]

- reformable fuels (methane, methanol, ethanol, oil F76)
# Hydrogen Storage (2/10)

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Storage System</th>
<th>Total Weight: Fuel + Storage System (kg)</th>
<th>Total Volume: Fuel + Storage System (liters)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressed gas hydrogen at 5000 psi$^a$</td>
<td>Advanced pressure cylinder</td>
<td>32.5 (12% $H_2$ by weight)</td>
<td>186 (700 Wh/liter)</td>
</tr>
<tr>
<td>Liquid Hydrogen$^a$</td>
<td>Dewar</td>
<td>28.5 (14% $H_2$ by weight)</td>
<td>116</td>
</tr>
<tr>
<td>Metal Hydride$^a$</td>
<td>Metal hydride (FeTiH$_{1-x}$) container with heat exchanger</td>
<td>325 (1.2% $H_2$ by weight)</td>
<td>100</td>
</tr>
</tbody>
</table>
# Hydrogen Storage (3/10)

<table>
<thead>
<tr>
<th>Technology</th>
<th>Need for R&amp;D</th>
</tr>
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<tbody>
<tr>
<td>Gaseous hydrogen</td>
<td></td>
</tr>
<tr>
<td>- on-site production</td>
<td>- on-site reformer</td>
</tr>
<tr>
<td>- long-distance pipeline transport</td>
<td></td>
</tr>
<tr>
<td>- grid distribution</td>
<td>- cost optimization for municipal grids</td>
</tr>
<tr>
<td>- pressure storage</td>
<td>- high-pressure systems (&gt; 700 bar)</td>
</tr>
<tr>
<td>- pressure storage</td>
<td>- large storage tanks (-10,000 m³)</td>
</tr>
<tr>
<td>- pressure storage</td>
<td>- materials</td>
</tr>
<tr>
<td>- filled station</td>
<td>- compressor (service life, costs)</td>
</tr>
<tr>
<td>- filled station</td>
<td>- high-pressure storage tank</td>
</tr>
<tr>
<td>- filled station</td>
<td>- optimization</td>
</tr>
<tr>
<td>- filled station</td>
<td>- filling station integration and system design</td>
</tr>
<tr>
<td>Hydride storage system</td>
<td>- storage capacity, low-temperature hydrides</td>
</tr>
<tr>
<td>Advanced storage</td>
<td>- new storage concepts</td>
</tr>
<tr>
<td>- liquefaction</td>
<td>- materials</td>
</tr>
<tr>
<td>- liquefaction</td>
<td>- efficient optimization</td>
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<tr>
<td>Liquid hydrogen</td>
<td>- concepts</td>
</tr>
<tr>
<td>- LH₂ tank</td>
<td>- reducing the filling losses</td>
</tr>
<tr>
<td>- long-distance shipping</td>
<td></td>
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<tr>
<td>- distribution by LH₂ truck</td>
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<tr>
<td>- LH₂ filling station</td>
<td>- optimization</td>
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<tr>
<td>- LH₂ filling station</td>
<td>- filling station integration and system design</td>
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<tr>
<td>- LH₂ filling station</td>
<td>- longer service life</td>
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<tr>
<td>- LH₂ filling station</td>
<td>- reliquefactation</td>
</tr>
<tr>
<td>- LH₂ filling station</td>
<td>- reducing boil-off</td>
</tr>
<tr>
<td>Safety engineering</td>
<td></td>
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<tr>
<td>- sensor technology and safety management</td>
<td></td>
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</table>
High pressure bottles: 200-250 bar

- As soon as possible 350 bar bottles will be available.
- R&D activities regards 700 bar bottles.
Liquid storage at -253°C

It is possible to store higher hydrogen quantities (at equal volume) in comparison with gas high pressure storage (pressures are low: 2-3 bar). Thermal insulation problems are completely solved.

An example comes from BMW 750h storage tank built in collaboration with LINDE.
Hydrogen Storage (6/10)

CooLH₂ tank system, source: Linde AG.

1. Inner vessel
2. Outer vessel
3. Super-insulation
4. Level probe
5. Gas extraction
6. Filling line
7. Liquid extraction
8. Filling port
9. Electric heater
10. Reversing valve (gaseous/liquid)
11. Cooling water heat exchanger
12. Main shut-off valve
13. Safety valve
14. Liquid hydrogen (−253 °C)
15. Gaseous hydrogen (+20 °C bis +80 °C)
16. Suspension
Hydrogen Storage (7/10)

Hydrogen can be chemically alloyed to different metals or metal alloys generating hydride. These composites are able to trap hydrogen at relatively low pressure.

Hydrogen enters into metal grid and goes to hold interstice spaces. A widespread hydride is LiH.

A typical R&D issue for these systems is weight.

On the other hand these systems are the best storage systems for safety.

Now several R&D activities are under development for several kind of hydrides.
Size comparison for a tank necessary for 400 km range (4 kg of hydrogen) with the state-of-the-art storage technology: magnesium hydrides ($\text{Mg}_2\text{NiH}_4$), lantanium hydrides ($\text{LaNi}_5\text{H}_6$), cryogenic liquid of $\text{H}_2$, $\text{H}_2$ at 200 bar (Source: C. Filiou, “An overview of the hydrogen solid storage solution”, European Commission, Joint Research Centre, Training Workshop Presentation, 2003).
Hydrogen Storage (9/10)

Chemical storage as NaBH₄
Catalytic reactor (packed bed)
Johnson Matthey catalyst
(3% 2 mm Ru on extruded graphite)

NaBH₄ + 2 H₂O → NaBO₂ + 4 H₂ + calore
Hydrogen Storage (10/10)

User

Storage

Fuel Tank: NaBH₄ Solution

Discharged fuel area NaBO₂

Pure Humidified H₂

Coolant Loop

Heat Exchanger

Fuel Cell

Oxygen from Air

Electric Power

Water from Fuel Cell H₂O

Hydrogen + Water Vapor

Gas/Liquid Separator

Borate (NaBO₂)

Catalyst Chamber

Fuel Pump

PM

Na⁺

NaOH

NaBO₂

NaBH₄

O₂
Hydrogen Distribution (2/3)
Hydrogen Distribution (3/3)

COAL

H₂O

H₂

Heating

Electricity

CO₂

SMR

GAS NATURAL

ACID

ELECTROLIZER

CRYOCOOLER

LH₂ a 30 bar

CGH₂ a 15 bar

LH₂ -252 °C 1.3 bar

CGH₂ -252 °C 850 bar 400 bar

LH₂ -252 °C 850 bar 400 bar

CGH₂
Hydrogen Storage and Distribution

Cost per kWh, $/kWh

- 2015 target: $2
- 2010 target: $4
- Chemical hydride: $8
- Complex hydride: $16
- Liq. H2: $6
- 10000 psi gas: $16
- 5000 psi gas: $12

Volumetric & Gravimetric Energy Density

- 2015 target: 2.7 kWh/l, 3.0 kWh/kg
- 2010 target: 1.5 kWh/l, 2.0 kWh/kg
- Chemical hydride: 1.4 kWh/l, 1.6 kWh/kg
- Complex hydride: 0.6 kWh/l, 0.8 kWh/kg
- Liq. H2: 1.6 kWh/l, 2.0 kWh/kg
- 10000 psi gas: 1.3 kWh/l, 1.9 kWh/kg
- 5000 psi gas: 0.8 kWh/l, 2.1 kWh/kg