HYDROGEN
Production and Utilization
A Future for Hydrogen ??

BioHydrogen - Bio $H_2$

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ENERGY
FOSSIL FUELS

✓ Net increase CO₂
  Global climate changes

✓ Security of Supply
  Geopolitical control
  Price increase

✓ ECO - issues

✓ Non renewable
How to Power the Economy and Still Fight Global Warming

Energy’s Future Beyond Carbon

- Cleaning up Coal
- The Nuclear Option
- Hopes for Hydrogen
- Biofuels and Renewables
- Fusion and Other Dreams
The **Kyoto Protocol to the United Nations Framework Convention on Climate Change** is an amendment to the international treaty on climate change, assigning mandatory targets for the reduction of greenhouse gas emissions to signatory nations.

Press release from the United Nations Environment Programme:

"The Kyoto Protocol is an agreement under which industrialized countries will reduce their collective emissions of greenhouse gases by 5.2% compared to the year 1990 (but note that, compared to the emissions levels that would be expected by 2010 without the Protocol, this target represents a 29% cut). The goal is to lower overall emissions of six greenhouse gases - carbon dioxide, methane, nitrous oxide, sulfur hexafluoride, HFCs, and PFCs - calculated as an average over the five-year period of 2008-12. National targets range from 8% reductions for the European Union and some others to 7% for the US, 6% for Japan, 0% for Russia, and permitted increases of 8% for Australia."
The mission of Hydrogen Now! … to accelerate the use of renewable energies!

**Renewable Hydrogen -- The Right Future?**
Ron Larson, Board Member of Hydrogen Now! ... and the American Solar Energy Society

**Renewable Hydrogen -- Can We Get There?**
Susan Hock, Carolyn Elam and Debra Sandor, NRE

**Renewable Hydrogen -- Can We Afford It?**
Margaret K. Mann and Johanna S. Ivy, NRE


New Scientist (2005)
What is Hydrogen?

✓ It’s Simple!
✓ It’s Light!
✓ It’s Everywhere!
✓ It’s non toxic!

✓ What Happens When Hydrogen Burns?

Hydrogen burns readily with oxygen, releasing considerable energy as heat and producing only water as exhaust.

When hydrogen burns in air (which is mostly nitrogen), some oxides of nitrogen (NOx, contributors to smog and acid rain) can be formed. Because no carbon is involved, using hydrogen fuel eliminates carbon monoxide, carbon dioxide, and does not contribute to global warming.
What Can We Learn from the Hindenburg Disaster?

The explosion of the luxury airship Hindenburg at Lakehurst, NJ, on May 6, 1937, serves as one of the most spectacular moments recorded by the media. Until very recently, it has aided in paralyzing the development of widespread hydrogen use as a fuel, due to concerns for safety (and viewing the fiery picture above, understandably so). But knowing the actual nature of the Hindenburg disaster, as well as knowing the behavior of hydrogen allows us to dispel this stigma associated with hydrogen.
Hydrogen – energy vector?

- production
- transportation
- storage

Technological competent, efficient and safe solutions must be found!
## COMPARATIVE PROPERTIES

energetics

<table>
<thead>
<tr>
<th>Fuel</th>
<th>KJ/g (25°C e 1 atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>141.86</td>
</tr>
<tr>
<td>Methane</td>
<td>55.53</td>
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<tr>
<td>Propane</td>
<td>50.36</td>
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<tr>
<td>Gasoline</td>
<td>47.5</td>
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<tr>
<td>Diesel</td>
<td>44.8</td>
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<tr>
<td>Methanol</td>
<td>19.96</td>
</tr>
</tbody>
</table>
Hydrogen – Physical Properties

• Colorless, no smell

• Energy
  141,9 mJ/kg – higher than other conventional fuel
  1kg of H₂ <> 2.8 kg of gasoline

• Density 0.0899 g/l
  Air is 14.4 more dense

• Phase transition (liquid to gas) -252.77 °C
  density 70.99 g/l, gasoline 750 g/l

• Diffusion coefficient 0.61 cm³/s (4 x Methane)

• H₂ flame – low emissivity

• Combustion
  In O₂ – only WATER
  In air (70% N₂) WATER (NOₓ)
  Engines – fuels … COₓ
Production of Renewable Hydrogen

• Electrolysis (based on renewable power)

• Biophotolysis (algae, cyanobacteria)

• from Biomass

 thermochemical conversion
 (gasification and water shift reaction, supercritical water gasification)

\[ \text{C}_6\text{H}_{12}\text{O}_6 + \text{O}_2 + \text{H}_2\text{O} \leftrightarrow \text{CO} + \text{CO}_2 + \text{H}_2 \]

\[ \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \]

fermentation
 direct by dark and photofermentation
 indirect by steam reforming biogas

\[ \text{CH}_4 + 2 \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 4 \text{H}_2 \]
A world fueled by hydrogen energy in this decade
- BMW – 2000...
- Opel – modelo Zafira – 2001...
- VW –1999 ... 2002
- Ford – Modelo Think ... 2002
- Peugeot –2001
- Fiat –2001
- Renault –1997
- Honda –1999
- Toyota --- Mazda
- Hyundai

- Daimler Chrysler - Man
- Renault / IVECO - Neoplan

**Projecto CUTE (Clean Urban Transport for Europe)**
Porto – Lisboa

INETI (Instituto Nacional de Engenharia e Tecnologia Industrial)
IST (Instituto Superior Técnico)
INEGI (Instituto de Engenharia Mecânica e Gestão Industrial)
Faculdade de Engenharia do Porto
FCT-UNL
Fuel Cell

Electrochemical cell that converts chemical energy of a fuel and an oxidant into electrical energy, using a system electrode / electrolyte.

**Proton Exchange Fuel Cell**

<table>
<thead>
<tr>
<th>Tecnologia</th>
<th>Potência de saída</th>
<th>Temp.de func. (ºC)</th>
<th>Electrólito</th>
<th>Aplicações</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAFC</td>
<td>&lt; 200 KW</td>
<td>150 a 200</td>
<td>Ácido fosfórico</td>
<td>Produção de energia (escala média)</td>
</tr>
<tr>
<td>PEMFC</td>
<td>50 a 250K W</td>
<td>80</td>
<td>Polímero</td>
<td>Veículos, substituto de baterias recarregáveis</td>
</tr>
<tr>
<td>MCFC</td>
<td>10KW a 2MW</td>
<td>650</td>
<td>Solução aq. carbonato</td>
<td>Aplicações elétricas</td>
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<tr>
<td>SOFC</td>
<td>&lt; 100KW W</td>
<td>Até 1000</td>
<td>Material cerâmico</td>
<td>Aplicações de grande escala, veículos</td>
</tr>
<tr>
<td>AFC</td>
<td>300W a 5KW</td>
<td>150 a 200</td>
<td>Solução aquosa</td>
<td>Produção de electricidade (pequena escala)</td>
</tr>
<tr>
<td>DMFC</td>
<td>50 a 250K W</td>
<td>50 a 100</td>
<td>Polímero</td>
<td>Aplicações médias, telemóveis, laptops</td>
</tr>
<tr>
<td>RFC</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Produção de energia em ciclo fechado</td>
</tr>
<tr>
<td>ZAFC</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Baterias</td>
</tr>
<tr>
<td>PCFC</td>
<td>-</td>
<td>700</td>
<td>Material cerâmico</td>
<td>Produção de energia (grande escala)</td>
</tr>
</tbody>
</table>

PAFC – Phosphoric Acid Fuel Cell
PEMFC – Proton Exchange Fuel Cell
MCFC – Molten Carbonate Fuel Cell
SOFC – Solid Oxid Fuel Cell
AFC – Alkaline Fuel Cell
DMFC – Direct Methanol Fuel Cell
RFC – Regenerative Fuel Cell
ZAFC – Zinc-Air Fuel Cell
PCFC – Protonic Ceramic Fuel Cell

Bacterial World covers almost all H₂ production capabilities

**H₂ Producing Microorganisms**

**Cyanobacteria, Green Algae**

\[ \text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2 \]

**Photosynthetic Bacteria**

\[ \text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightarrow 4 \text{H}_2 + 2 \text{CO}_2 \]

**Anaerobic Bacteria**

\[ \text{C}_6\text{H}_{12}\text{O}_6 + 2 \text{H}_2\text{O} \rightarrow 4 \text{H}_2 + 2 \text{CO}_2 + 2 \text{CH}_3\text{COOH} \]
SULPHATE REDUCING BACTERIA
Hydrogen Production
Lactate / sulfate (limiting factor)
HYDROGEN STORAGE

- Liquid Hidrogen
- Compressed Gas
- Gas Adsorption (Carbon / Micro-spheres)
- Metal Hydrides (High and low temperature)
  \[ M + H_2 \rightarrow MH_2 \]
- Alkaline Hidrydes
- Nanotubes (Adsorption)
- Methanol / Gasoline e other hydrocarbons
Nanotubes Carbon

Metal Hydrides

Steel or Carbon Fibers?

STORAGE

PROBLEMS and SOLUTIONS
Production / Storage / Transport / Distribution / Power plants

Wide range of utilizations

Large and small Plants

Economy of Scale

Local (83%) and decentralized (17 %)

“pipelines”

752 Km, tubing 12 in diameter (not 36 used for natural gas)

Texas, Louisiana, Califórnia e Indiana

Air Products and Chemicals Inc e Praxair Inc.

Considerations

Energy difference Hydrogen and Natural Gas

High diffusion of Hydrogen

Distribution based on gas properties (P, T and V)

Others

Cylinders and Tanks (150 a 400 bar )

Longer distances (1000 miles) – transport of liquid Hydrogen

(train, vans, ships)
BACTERIAL HYDROGENASES
CONSUMPTION AND PRODUCTION OF H2

Energy BioConversion

Hydrogen Production

\[ \text{H}_2 \leftrightarrow 2 \text{H}^+ + 2 \text{e} \]

NEW STRUCTURES

[NiFe] Hydrogenases ([NiSeFe])
[Fe]-only Hydrogenases
HYDROGEN – activation by METALS

oxidative addition \[ M^{n+} + H_2 \leftrightarrow M^{n+}H_2 \]

homolític cleavage \[ 2 M^{n+} + H_2 \leftrightarrow 2 M^{n+1}H \]

heterolític cleavage \[ M^{n+} + H_2 \leftrightarrow M^{n+}H^- + H^+ \]

HOW TO HANDLE HYDROGEN ?
WHAT WE KNOW FROM CHEMISTRY ?
BIOCATALYSIS
NEW ORGANOMETALLIC COMPOUNDS

Catalytic Center

Ni ........ S
Hydride    Proton

Heterolytic Cleavage  H:⁻    H⁺
\[ \text{H}_2\text{O} \xrightarrow{h\nu} \text{CHlorophyll P680 } + 815 \text{ mV} \xrightarrow{\text{STE} \text{ Fe/S}-600 \text{ mV}} \text{Fd - NADP} \]

\[ \frac{1}{2} \text{O}_2 \xrightarrow{2 \text{ H}^+} \text{CO}_2 \]

\[ \text{(CHOH)}_n + \text{H}_2\text{O} \]

\[ \text{Pyruvate (organic substrate)} -700 \text{ mV} \xrightarrow{} \text{Fd} \xrightarrow{} \text{Cyt c3} \]

\[ \text{Ac - CoA} \]

\[ \text{H}_2 \]

\[ \text{HASE} \approx -400 \text{ mV} \]
... the dream !!!!

H₂O → hν

H₂O → \( \frac{1}{2} \text{O}_2 \) + 2 H⁺

Complexes Mn (?)

Chlorophyll P680 + 815 mV

STE Fe/S - 600 mV

Fd/c3

Artificial carriers

HASE \( \cong -400 \text{ mV} \)

\( 2 \text{H}^+ \) → H₂
... só Química !!! ....

$H_2O \xrightarrow{h\nu} M_n, P_t, .. \xrightarrow{T E} O_2, H^+ \xrightarrow{H_2}$
Advantages of Hydrogen

- Hydrogen can be totally non-polluting (water is the exhaust).
- Hydrogen can be economically competitive with gasoline or diesel.
- Hydrogen is safer than gasoline, diesel, or natural gas.
- Hydrogen can help prevent the depletion of fossil fuel reserves.
- Hydrogen can be produced in any country.

The Stone Age did not end because they ran out of stones. The Oil Age would not end because we run out of oil.

Don Huberts, Shell Hydrogen
Conclusions

Fossil Fuels are limited

Fossil Fuels are dependent of Polytical Power

Alternatives!

HYDROGEN may be one of them!

A competitive alternative to FOSSIL FUELS requires further developments on HYDROGEN technology

(safety, production distribution, storage and utilization)