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HYDROGEN GENERATION

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2nd Summer School 2012
Crete

Learning Objectives

- Introduce: -
  - Different routes to hydrogen production...

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What is Hydrogen?

What is the Hydrogen economy?

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Hydrogen Economy

- A system to deliver hydrogen as energy
- Thought to be a cleaner method for energy…
- What is hydrogen??

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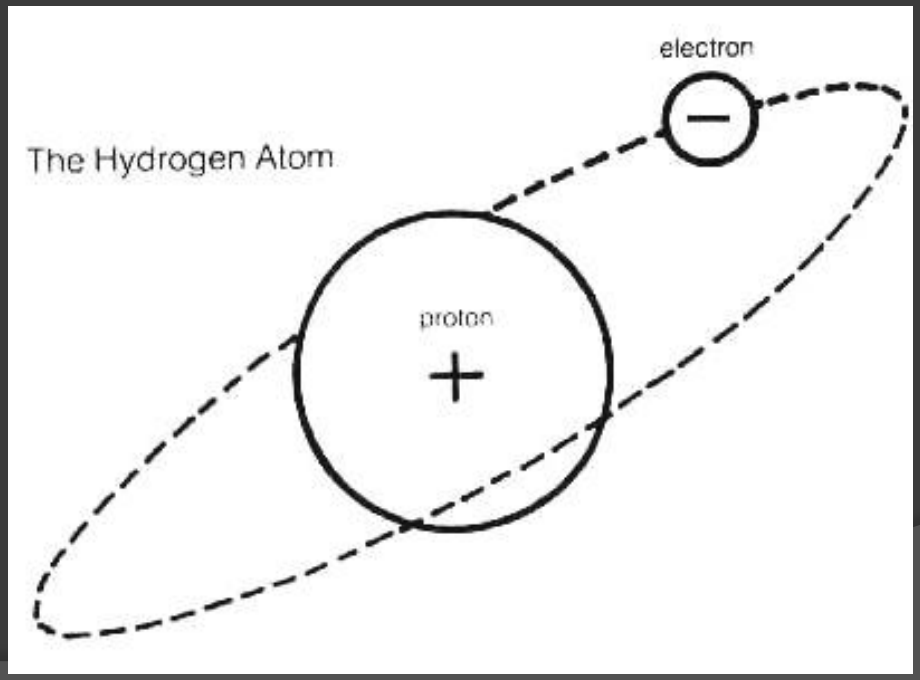
Hydrogen

- Hydrogen is the most abundant element in the universe
- However, it does not naturally exist on earth in its elemental form



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Hydrogen Stats: -

- fraction of total mass in universe
  - 75% (out of $1,6 \times 10^{60}$ kg)
- fraction of water of total mass on earth
  - 1.4 % (out of $5,97 \times 10^{24}$ kg)
- fraction of hydrogen in pure water
  - 11.2 % grav.
- fraction of water surface of total earth surface
  - 71%
- fraction of total mass on earth
  - ca. 0.15%

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Properties

- Heating value
  - upper 3,54 kWh/Nm³ (12,75 MJ/Nm³)
  - lower 3,00 kWh/Nm³ (10,8 MJ/Nm³)
- Wobbe-Index
  - upper 13,428 kWh/Nm³ (48,340 MJ/Nm³)
  - lower 11,361 kWh/Nm³ (40,898 MJ/Nm³)
- Condensing Temperature -252,77°C (20,39 K) at 0,1013 MPa
- Density 0,0899 kg/Nm³ or 70,79 kg/m³ liquid
- Thermal Capacity 14,199 J/kg*K

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How does hydrogen compare?

	Energy density	
lower heating values	volumetric	gravimetric
Hydrogen	3.00 kWh/Nm³	33.33 kWh/kg
Methane	9.97 kWh/Nm³	13.90 kWh/kg
Natural Gas	8,8 - 10,4 kWh/Nm³	10,6 - 13,1 kWh/kg
Propane	25.89 kWh/Nm³	12.88 kWh/kg
Buthane	34.39 kWh/Nm³	12.70 kWh/kg
Town Gas *	4.54 kWh/Nm³	7.57 kWh/kg
Crude Oil	10.44 kWh/l	11.60 kWh/kg
Diesel	10.00 kWh/l	11.90 kWh/kg
Gasoline	8.80 kWh/l	12.00 kWh/kg
Methanol	4.44 kWh/l	5.47 kWh/kg

* 51%vol H_2, 18%vol CO, 19%vol CH_4, 2%vol CnHm, 4%vol CO_2, 6%vol N_2

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How does hydrogen compare?

- 1 Nm^3 hydrogen corresponds to
  - 0.34 l gasoline
- 1 L liquid hydrogen corresponds to
  - 0.27 l Gasoline
- 1 kg hydrogen corresponds to
  - 2.75 kg gasoline, 2.1 kg NG etc.

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Hydrogen Cycle

Production

Storage

Applications

Economics

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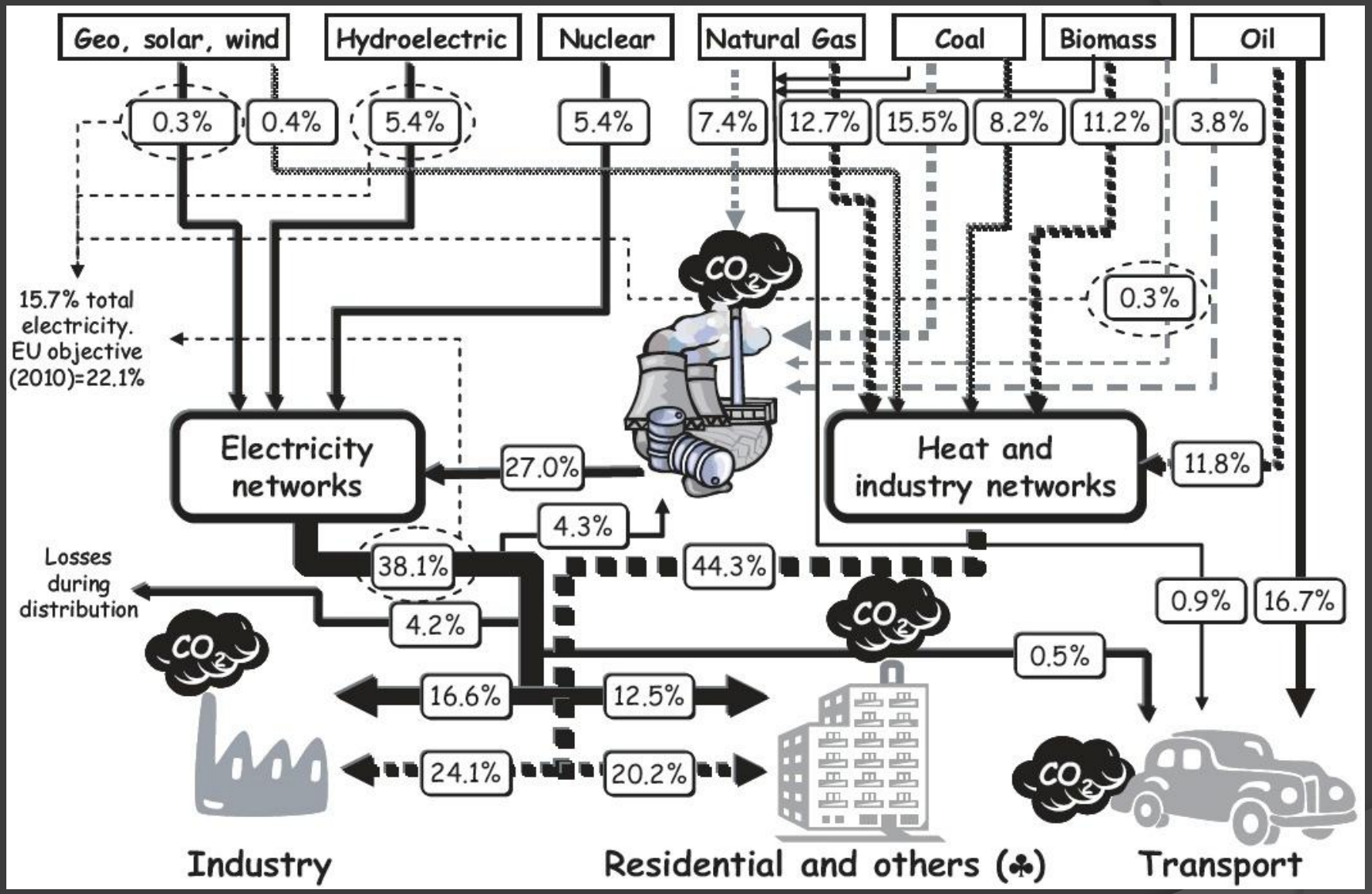

G. Marban & T. Valdes-Solis, Int. J. of Hydrogen Energy 32 (2007) 1625 – 1637

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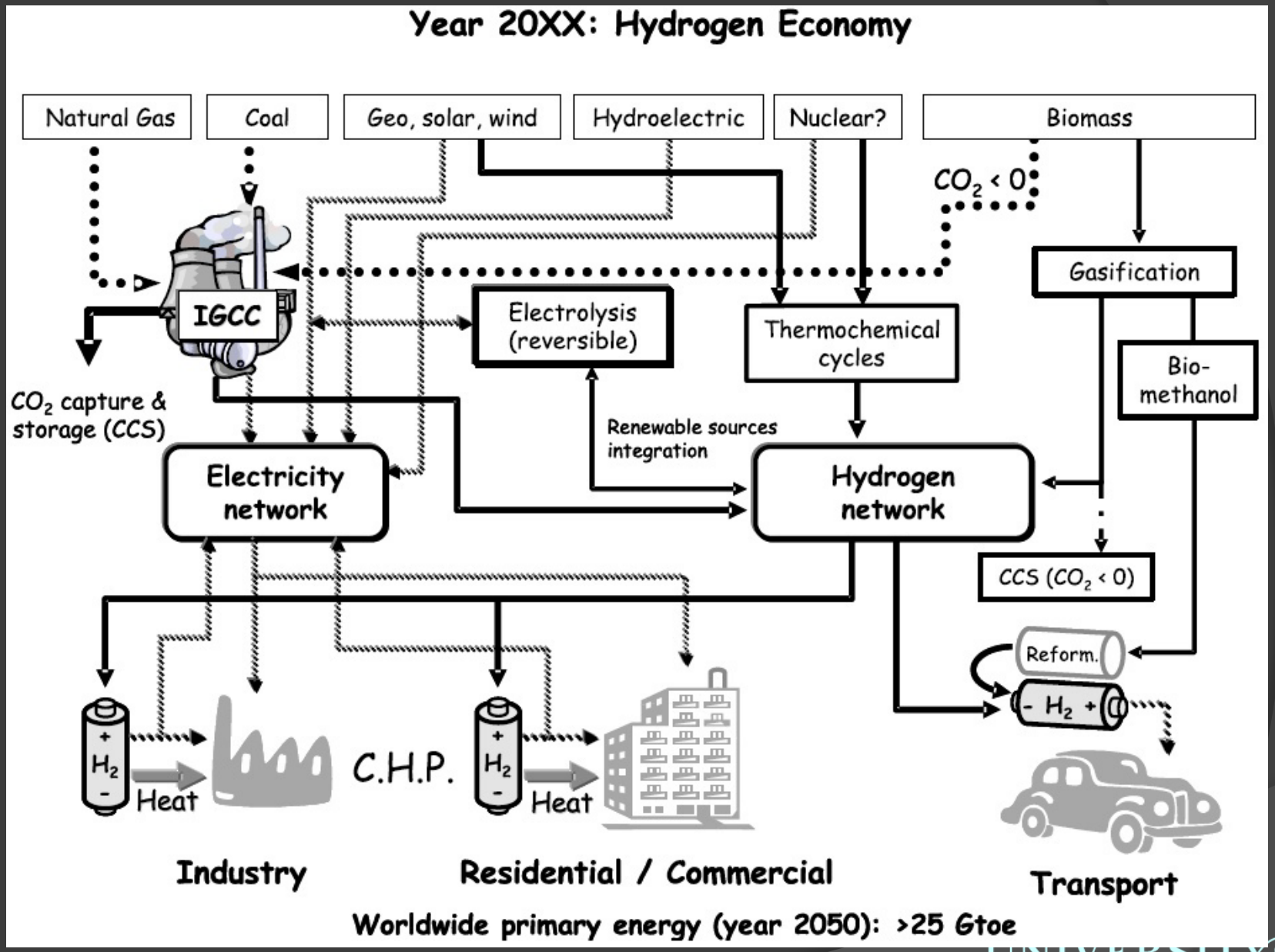

G. Marban & T. Valdes-Solis, Int. J. of Hydrogen Energy 32 (2007) 1625 – 1637

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Generation

- Almost exclusively an industrial process
- Many Methods

Origin	Billions	m^3/year	Percent
Natural Gas	240		48
Oil	150		30
Coal	90		18
Electrolysis	20		4
Total	500		100

- DOE numbers (2009)

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Generation Techniques

- Steam Methane Reforming
- Biological production
- Biocatalysed electrolysis
- Electrolysis of water
- High-pressure electrolysis
- High-temperature electrolysis
- Photo electrochemical water splitting
- Concentrating solar thermal
- Photo electrocatalytic production
- Thermo chemical production

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What we will cover…

1. Electrolysis
2. Reforming
3. Hydrocarbon Gasification
4. Thermal Water Splitting
5. Bio Production
6. Others

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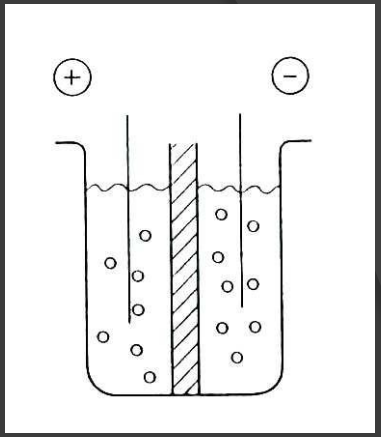
Electrolysis



- Splitting of Water

Cathode side $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Anode side $2OH^- \rightarrow 1/2\ O_2 + H_2O + 2e^-$

Balance

$$H_2O \xrightarrow{2F} H_2 + 1/2\ O_2$$

F ... Faraday constant = 96.587 C/mol

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Electrolysis

- Free enthalpy

  $\Delta G^o = 237$ kJ/mol (at 25°C, 1 bar)

  $= 2F\, U^o_o$

- It follows that

  $U^o_o = 1.23$ V

- which is the voltage necessary for water splitting (ideal case).

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Electrolysis

- Over potential exists
  - Typically 1.7 – 2.0V is needed to split water
- The ideal amount of energy needed per Nm^3 H_2 is
  - $\Delta G^o / V_N$ = 241 kJ/mol / 22,41 l/mol = 3 Wh/Nm^3
  - Standard electrolysers require about 4.2 to 4.8 kWh/Nm^3

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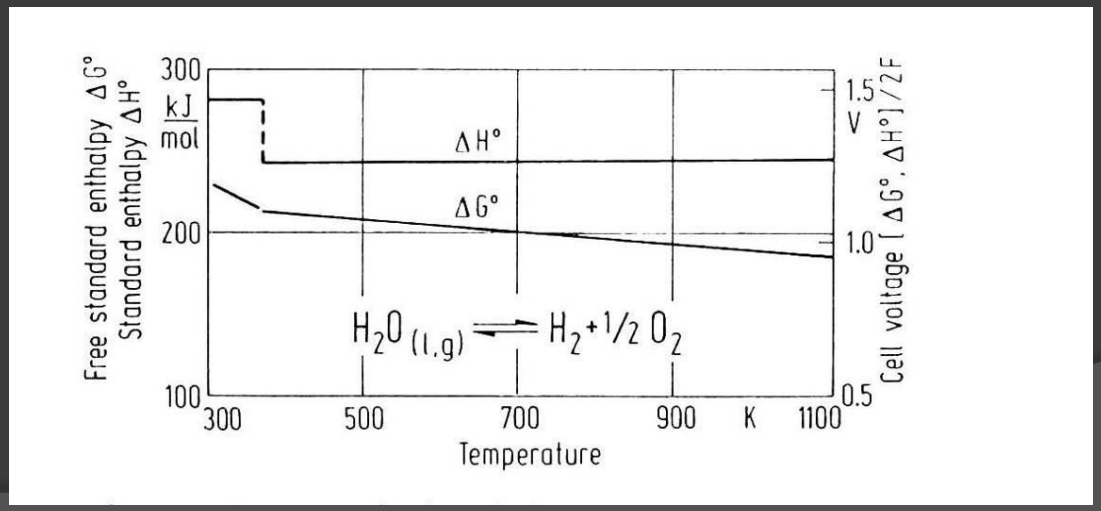
Electrolysis

- .....is temperature dependant
- Due to the relationship
  - $\Delta G^o = \Delta H^o - T \Delta S$
- The energy for splitting water can also be supplied by heat, not only electricity.



Winter/Nitsch,1988

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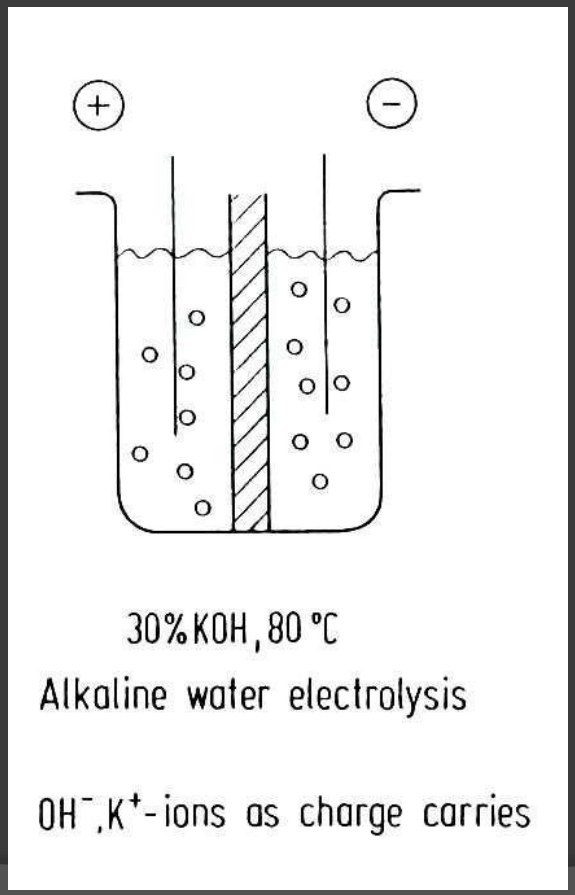
Different types

- Alkaline
- Polymer Membrane
  - PEM Fuel Cell in reverse



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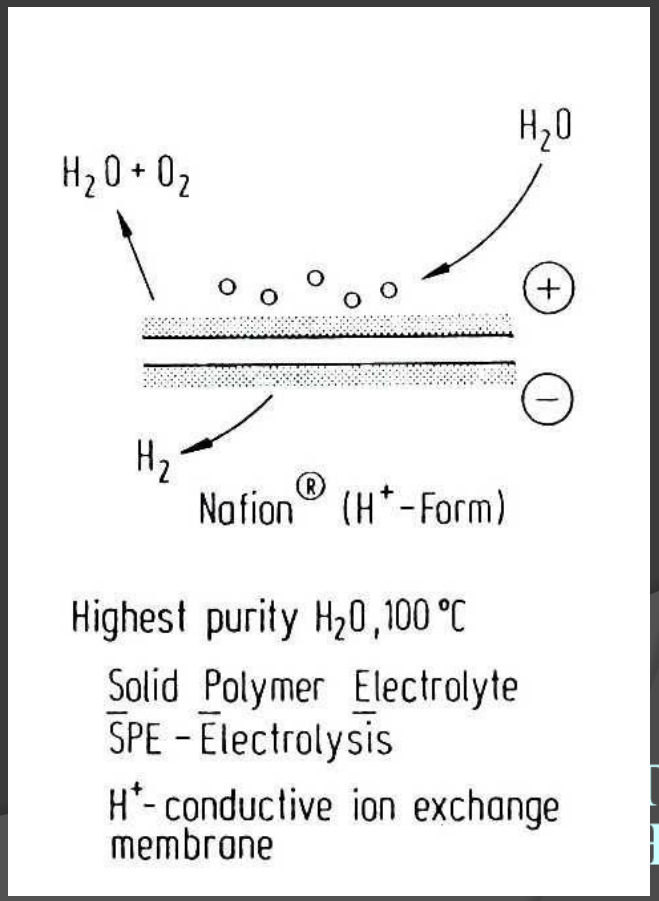
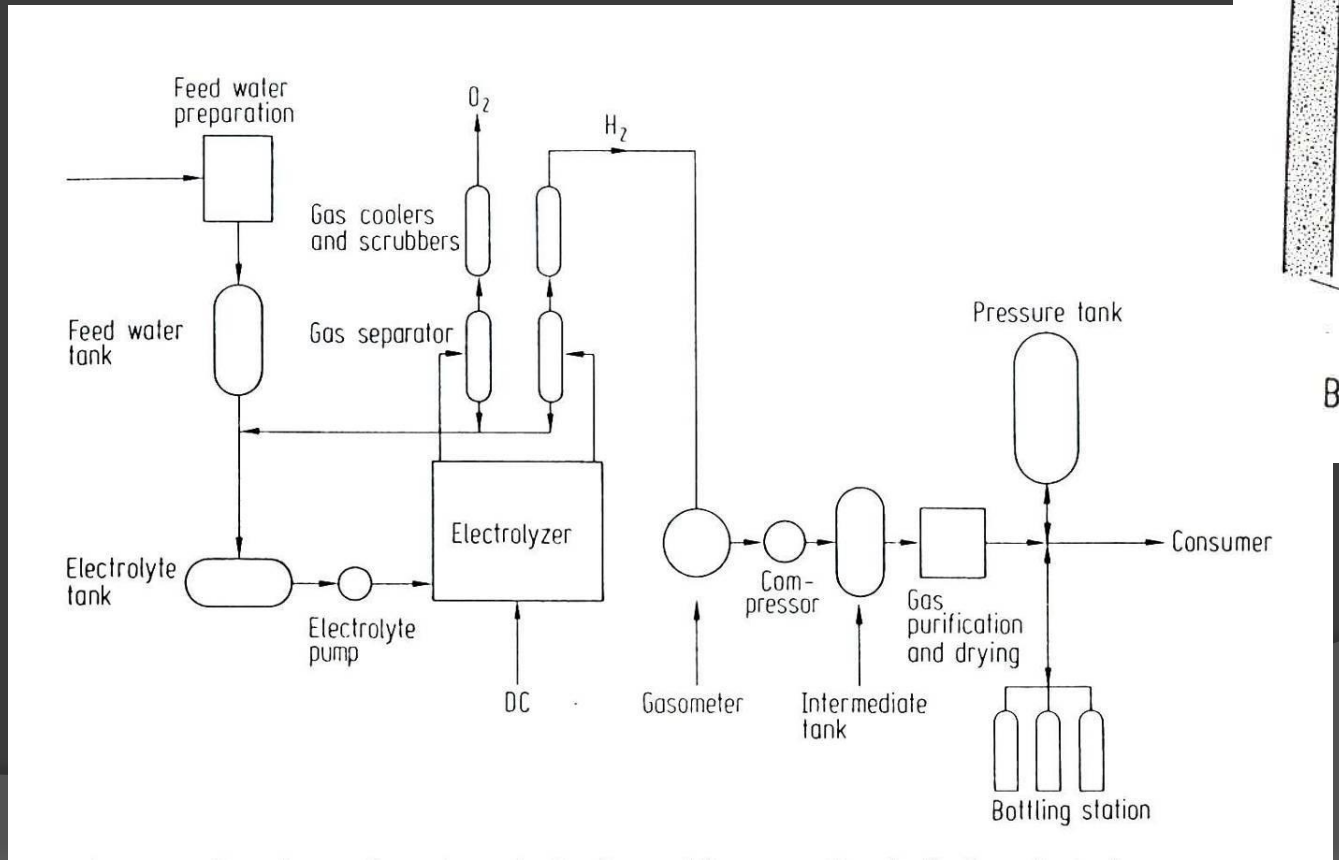
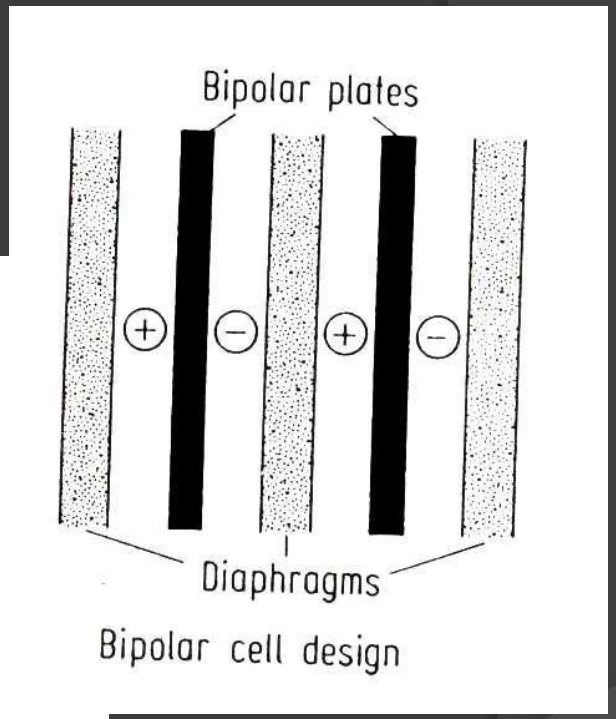


Winter/Nitsch,1988

...Design Considerations

- Materials & Stacking
- ....Balance of plant





Winter/Nitsch,1988

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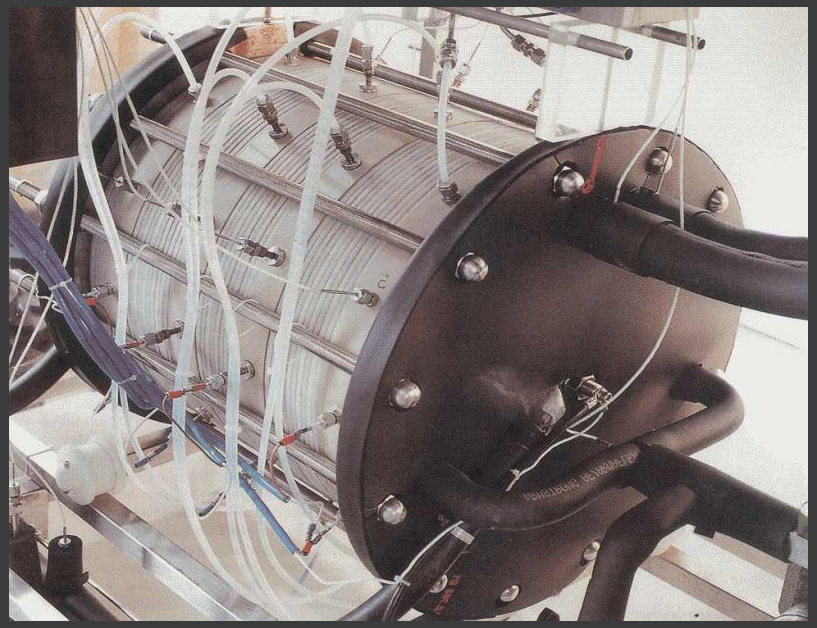
Commercial Electrolysers



Photographs courtesy DLR/FZJ/Casale & Fuel Cell Today

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Reforming

- Is the production of hydrogen from a carbon containing fuel.
  - Done by separating hydrogen and carbon
    - Oxidation of CO and/or CO_2

- Types
  - Steam Reforming
  - Partial Oxidation
  - Aoutothermic

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Steam Methane Reforming (SMR)

- Reforming of methane, the main constituent of natural gas, mainly takes place according to the two independent reactions:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H^0 = 206\,kJ/mol$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \qquad \Delta H^0 = 165\,kJ/mol$$

- These reactions are endothermic, meaning they take place under presence of catalysts with addition of heat. The reaction temperature is in the range of 500 and 900°C.

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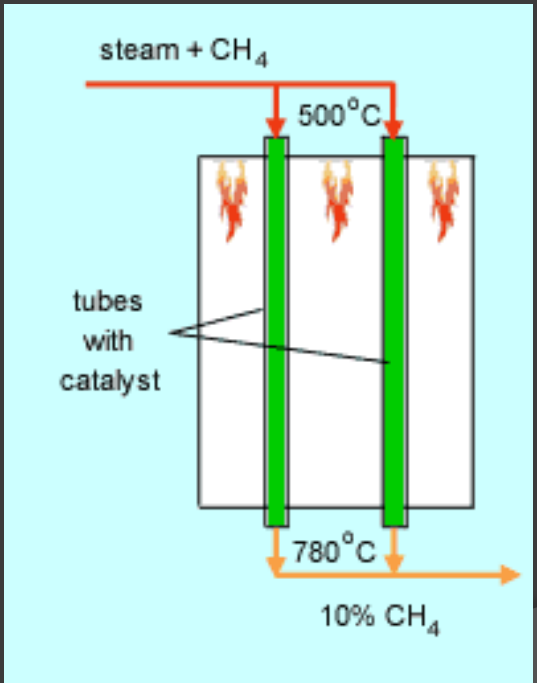
SMR

- Efficiency $\eta = H_u$ (H_2, produced) / Hu (CH_4, input)
  - ~ 75 to 85%, depending on temperature and pressure.
- Heat is supplied
  - Direct heating
  - Heat exchange



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Carbon Formation

- Steam/C ratio generally 2.5 -3

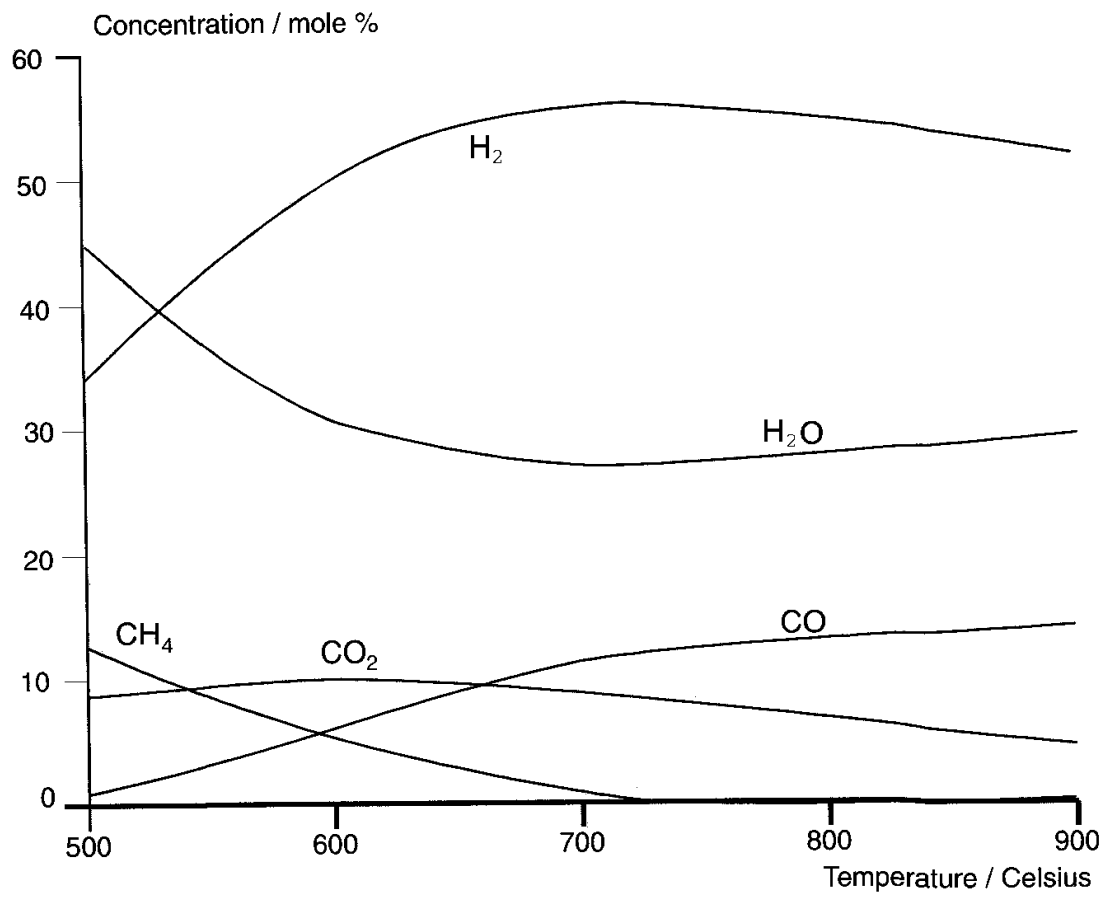

Figure 7.1 Equilibrium concentrations of steam reformation reactant gases as a function of temperature.

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Partial Oxidation (POX)

- Supplying sub-stoichiometric oxygen, methane is only partially oxidised.
- Affinity of oxygen is much higher to carbon than to hydrogen nearly exclusively carbon is oxidised.
  - Therefore pure hydrogen is produced.

$$CH_4 + \tfrac{1}{2}O_2 \leftrightarrow CO + 2H_2$$

$$\Delta H^0 = -36 kJ/mol$$

- This reaction is exothermic.
- The product gas contains less hydrogen than in SMR.
- On the other hand this process can also be applied to higher hydrocarbons (up to crude oil).

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Autothermal reforming (ATR)

- Combination of SR & POX
  - One part of the necessary oxidant is provided by the reduction of water.

$$2CH_4 + \tfrac{1}{2}O_2 + H_2O \leftrightarrow 2CO + 5H_2 \qquad \Delta H^0 = 85 kJ/mol$$

- This reaction is endothermic.
- But it consumes clearly less heat than steam reforming and produces a gas containing more hydrogen than in case of partial oxidation

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Gas Shift Reaction (Cleanup)

- Reforming processes deliver a mixture of H_2 and CO and/or CO_2.
  - Needs to be cleaned in order to produce pure hydrogen.
    - The process used is the 'Shift Reaction'

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

$$\Delta H^0 = -41 kJ / mol$$

- This reaction is exothermic and requires a catalyst.
- CO_2 then has to be removed
  - Membrane separation or by condensation.

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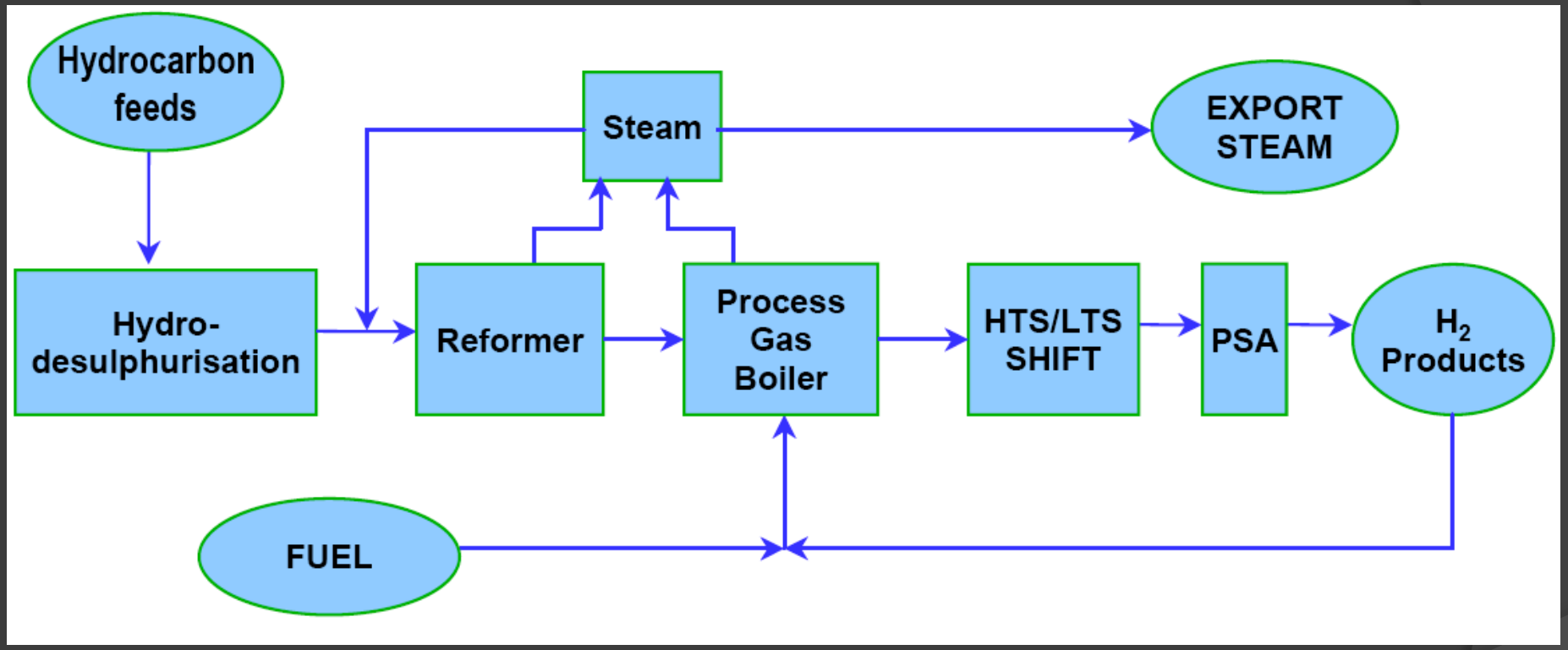
SMR System



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H_2-plant
based on Steam Reforming of Natural Gas

Gasification

- Gaseous coal is treated with steam and oxygen
  - Result is the formation of hydrogen gas, carbon monoxide, and carbon dioxide.
  - Pros - There are large supplies of coal
  - Cons – It is almost twice as expensive to produce hydrogen from coal as from natural gas due to the ratio of hydrogen to carbon, which in natural gas is 4 : 1 and in carbon is 0.8 : 1.8
- There are significant emissions of carbon dioxide associated with coal gasification.

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Coal Gasification - IGCC

- Integrated Gasification Combined Cycle (IGCC)
  - Coal is fed into a pressurised reactor, which produces ‘syngas’
- This raw syngas is cooled and ‘scrubbed’ several times.
  - This makes gasification cleaner than conventional (pulverised fuel) combustion
- IGCCs operate a ‘combined cycle’:
  - First the syngas is fired in gas turbines to produce electricity.
  - Then the hot ‘exhaust gases’ are used to generate superheated steam in a heat-recovery generator to drive a steam turbine, producing more electricity.

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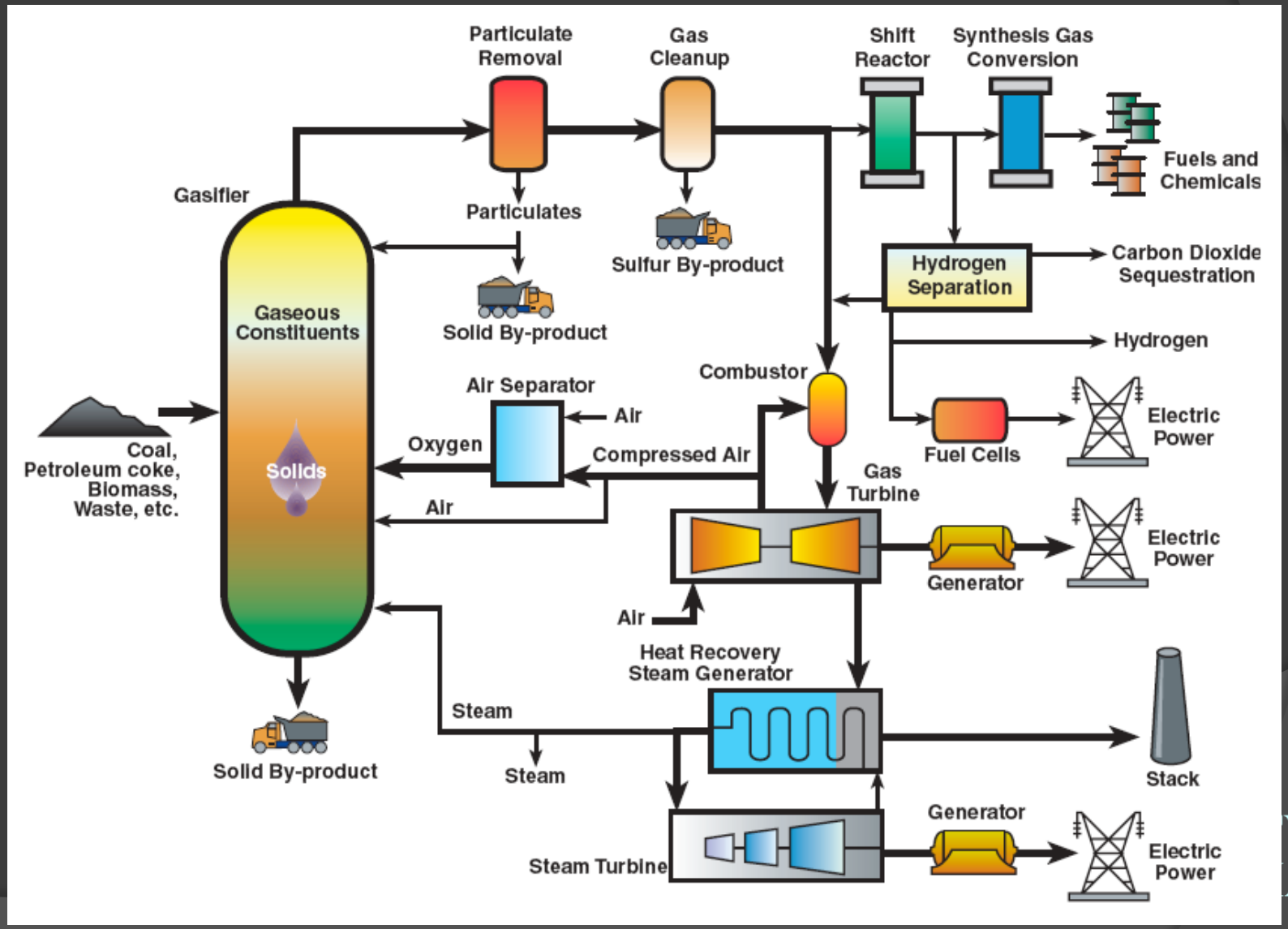
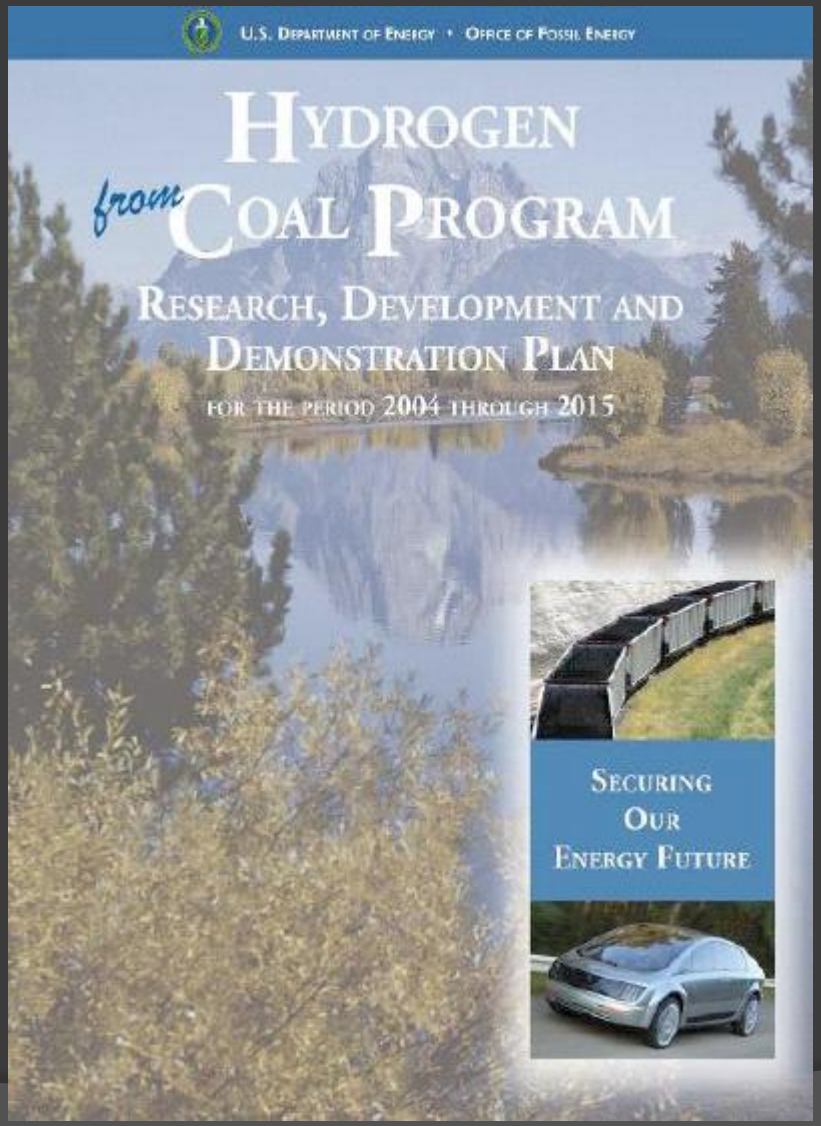
IGCC Plant


Particulate Removal
Gas Cleanup
Shift Reactor
Synthesis Gas Conversion
Fuels and Chemicals
Gasifier
Particulates
Sulfur By-product
Hydrogen Separation
Carbon Dioxide Sequestration
Gaseous Constituents
Solid By-product
Hydrogen
Combustor
Air Separator
Air
Electric Power
Coal, Petroleum coke, Biomass, Waste, etc.
Oxygen
Compressed Air
Fuel Cells
Solids
Gas Turbine
Air
Electric Power
Generator
Air
Heat Recovery Steam Generator
Steam
Solid By-product
Steam
Stack
Generator
Steam Turbine
Electric Power

Hydrogen from Coal



- R&D is estimated to reduce the cost of hydrogen from coal by 25%.
- Co-production of hydrogen and electricity can further reduce the cost of hydrogen production by 32%.

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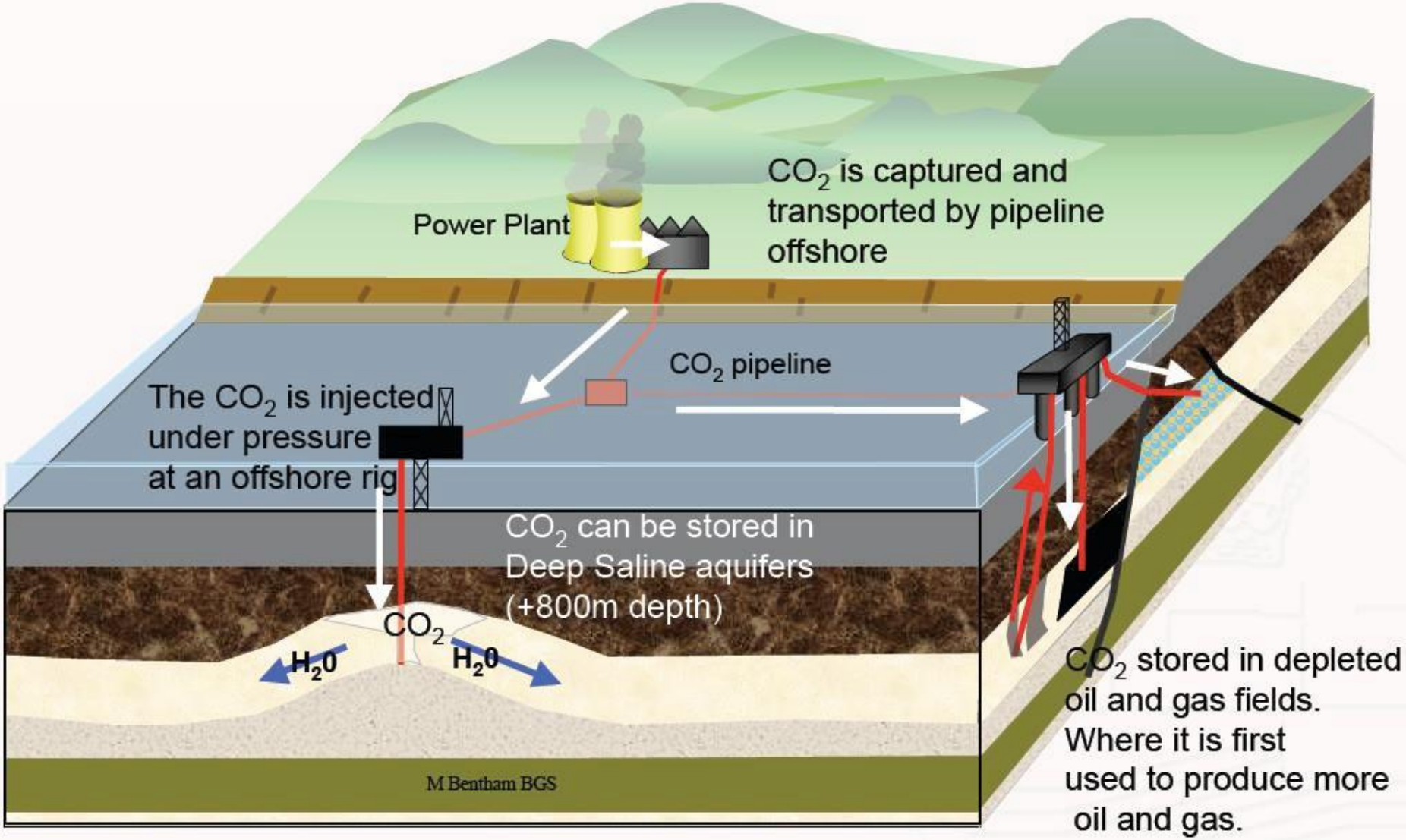

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Hydrogen from Coal

- The reservoirs in Europe would be filled after 8 to 19 years, if the total carbon dioxide emissions could be collected.
- If only the emissions from central power generation taken into account, reservoirs would be available for 23 - 55 years.
  - "Where will the Energy for Hydrogen Production come from? Status and Alternatives“ J. Schindler et al, European Hydrogen Association, 2006
- However, some geologists say more information is needed on behaviour of CO2 in different aquifer geology: world aquifer storage 40 or 400 years??
  - Stuart Haszeldine (Univ of Edinburgh) - Towards a Low Carbon Future, Royal Society, 17 Nov 2008

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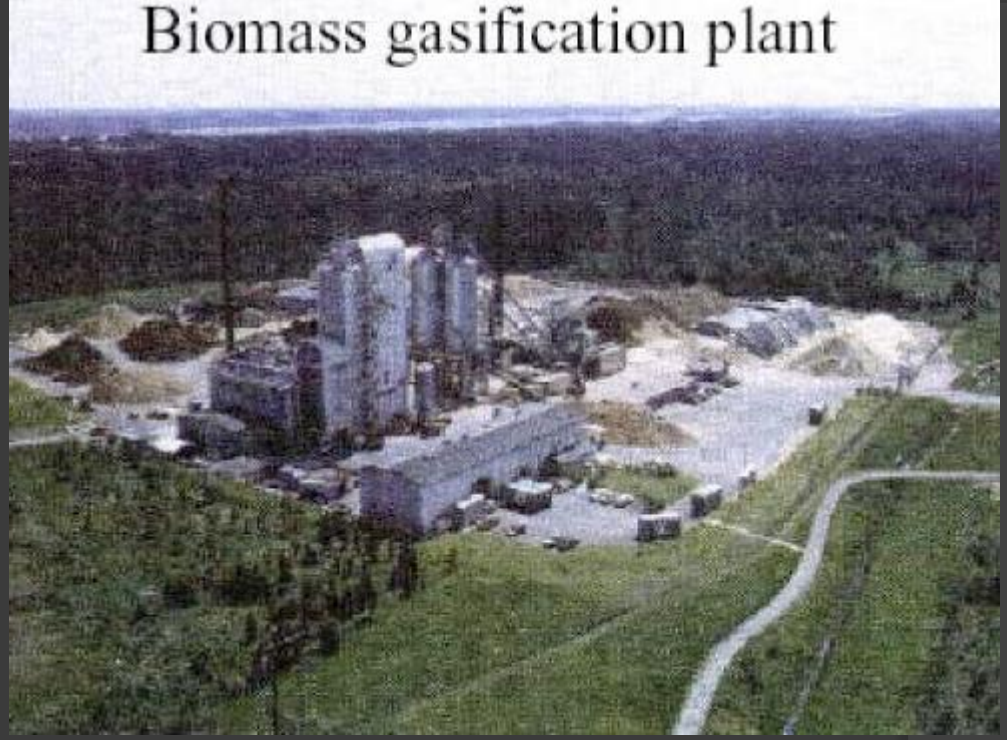
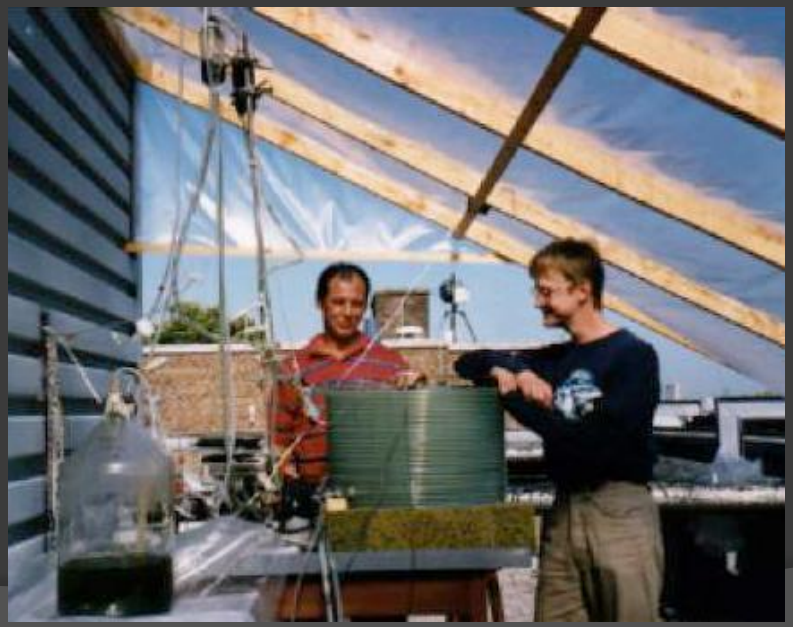
Biomass

- Wood
- Muncipal
- Biogas





… Example

- Cadburys chocolate waste
- Bacterial digestion

Prof. Lynne Macaskie,
University of Birmingham

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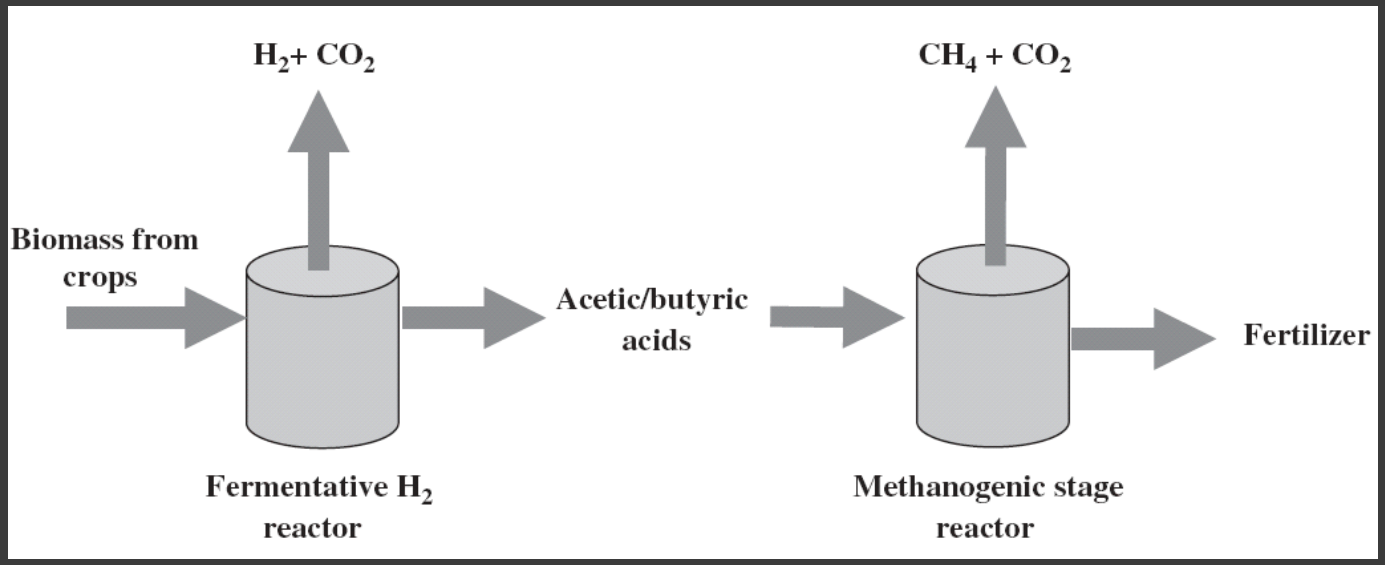
...Example



- Two-stage system for hydrogen and methane production from wet biomass.
- Use of 300,000 ha of currently unused set aside land would in the UK provide 9.6TWh of net energy, 10% as H2 and 90% as CH_4. This would correspond to savings in emissions in the order of 2.3 million tonnes of CO_2 per annum.

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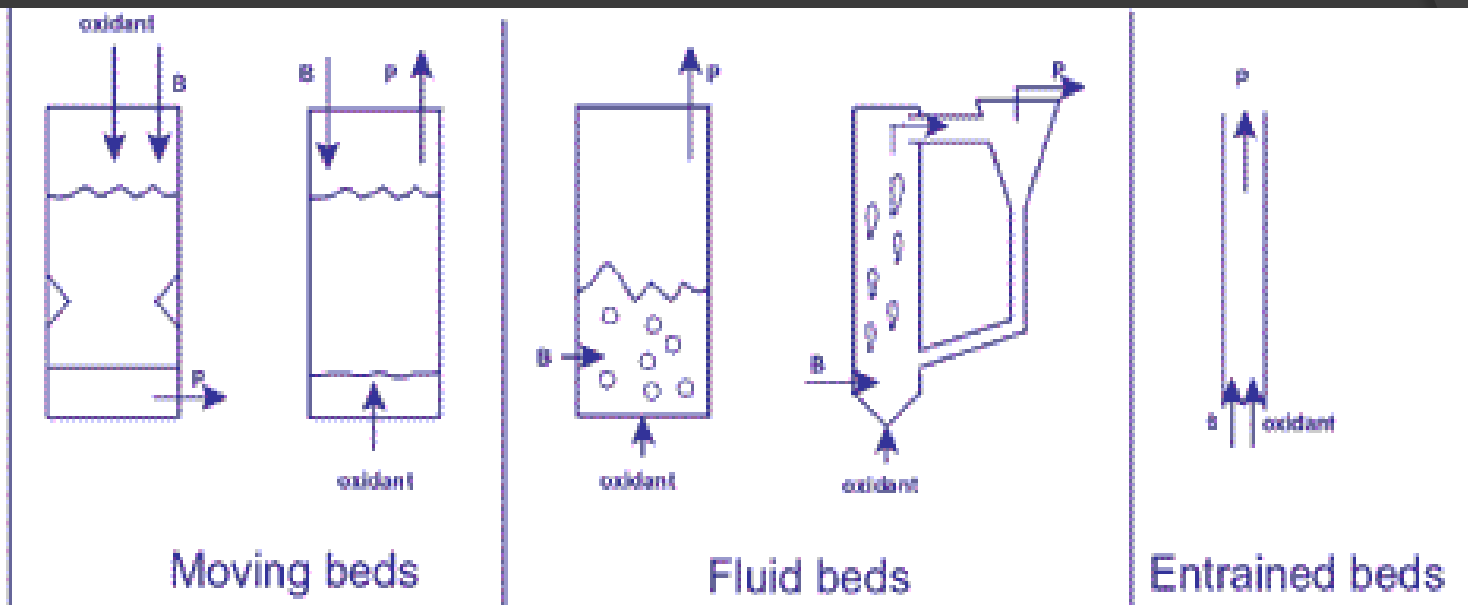
Biomass Gasification



	Moving beds		Fluid beds		Entrained beds
	Co-current	Counter current	dense	circulating	
T°C	700-1200	700-900	< 900	< 900	≈1500
tars	low	very high	intermediate	intermediate	absent
control	easy	very easy	intermediate	intermediate	very complex
scale	< 5 MW_t	< 20 M_t	10<MW_t<100	20<MW_t<?	> 100 MW_t
feedstock	very critical	critical	less critical	less critical	very fine particles

Type	H_2	CO	CO_2	CH_4	N_2	Tar	Particles
						g/m³	
Upstream/ Fxb./steam	30%	30%	10%	10%	20%	**100**	>
Downstream / Fxb./ steam	50%	25%	20%	10%	n.d.	**1**	>
Circ. Fluidised	30%	25%	25%	10%	10%	**10**	>>
Circ. Fluidised/ 2-phase	20%	20%	10%	0%	41%	**low**	>>

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Thermal splitting water

- Thermal dissociation of water occurs above 2000 K. Some activities have been focussing on cyclic processes at lower temperatures coupled especially to nuclear process heat (Ispra, General Atomic, Westinghouse). One cycle is

$$2HJ \rightarrow H_2 + J_2 \qquad \Delta H^0 = -5{,}63\, kJ/mol$$

$$J_2 + SO_2 + 2H_2O \rightarrow 2HJ + H_2SO_4 \qquad \Delta H^0 = -10\, kJ/mol$$

$$H_2SO_4 \rightarrow H_2O + SO_2 + 1/2\ O_2 \qquad \Delta H^0 = +243\, kJ/mol$$

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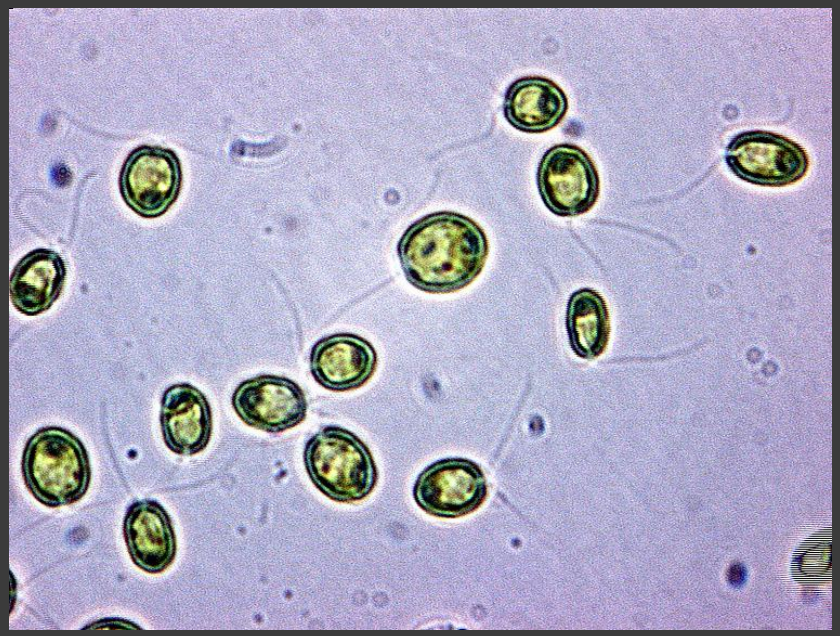
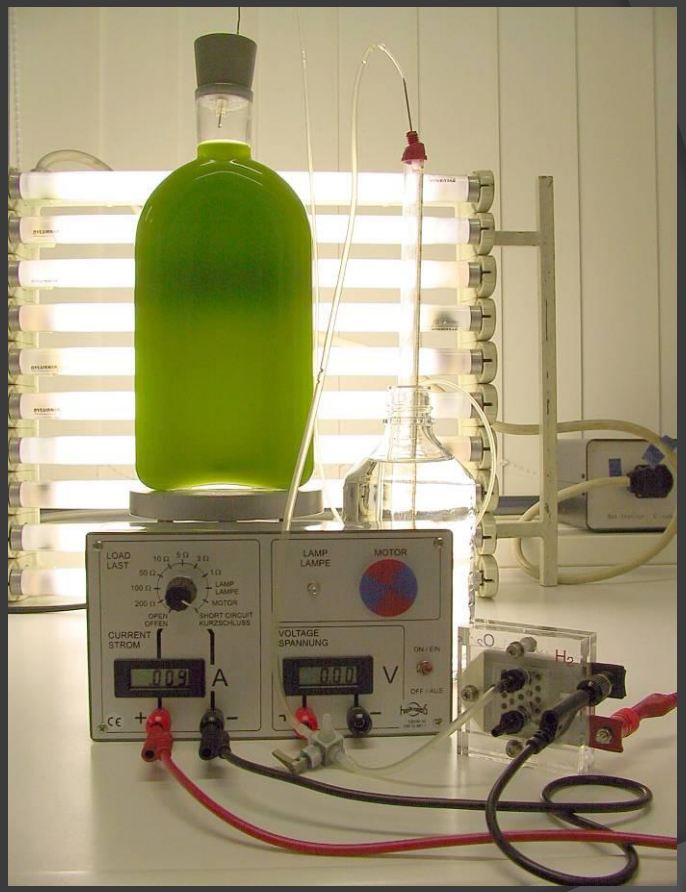
Algae





Photographs courtesy University of Bonn

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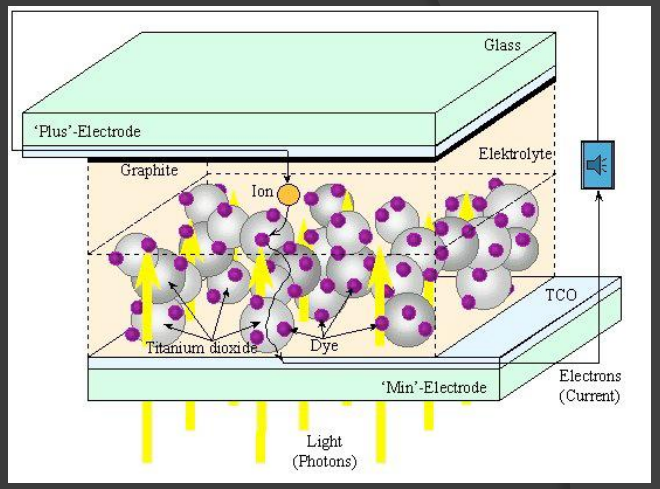
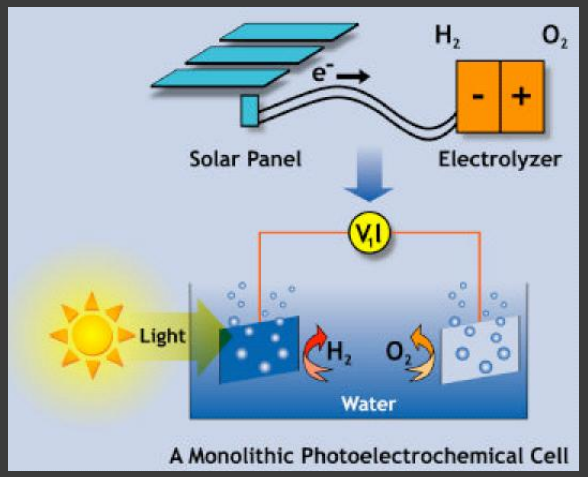
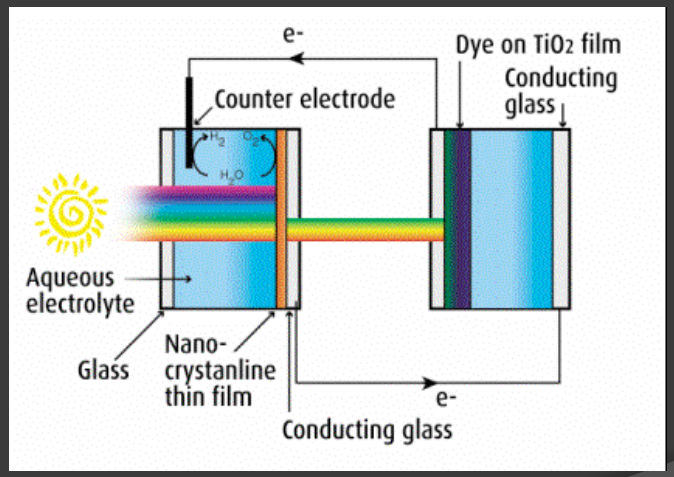
Other

- Photocatalytic water splitting
- Cracking of ammonia
- Cracking of Borates







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Issues

- Purity from electrolysers
  - Alkaline
    - 99.8% pure Hydrogen
  - PEM
    - 99.99999% Pure Hydrogen
  - High temperature
    - 99.99999% Pure Hydrogen
- Others Depend on gas clean up

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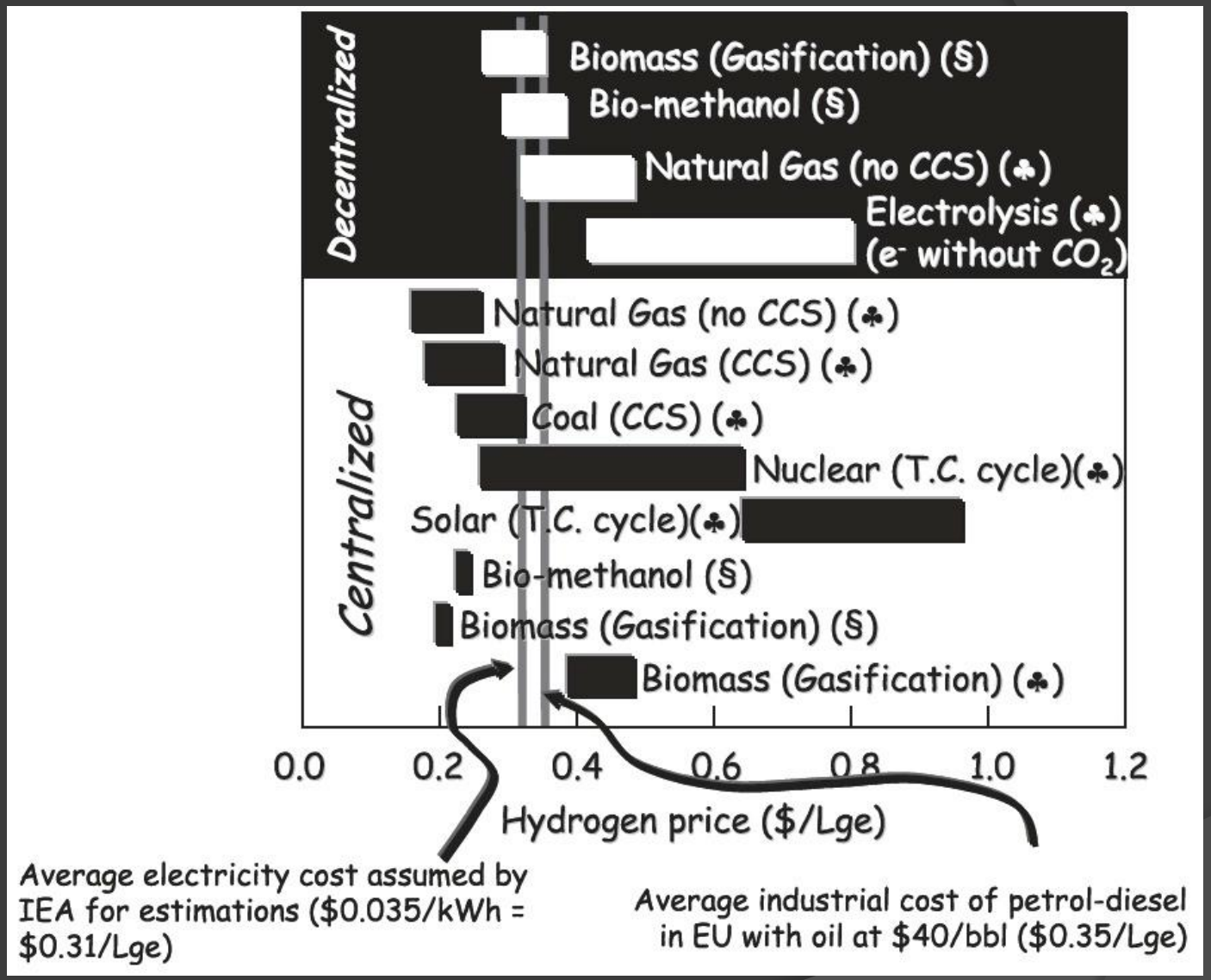
Cost



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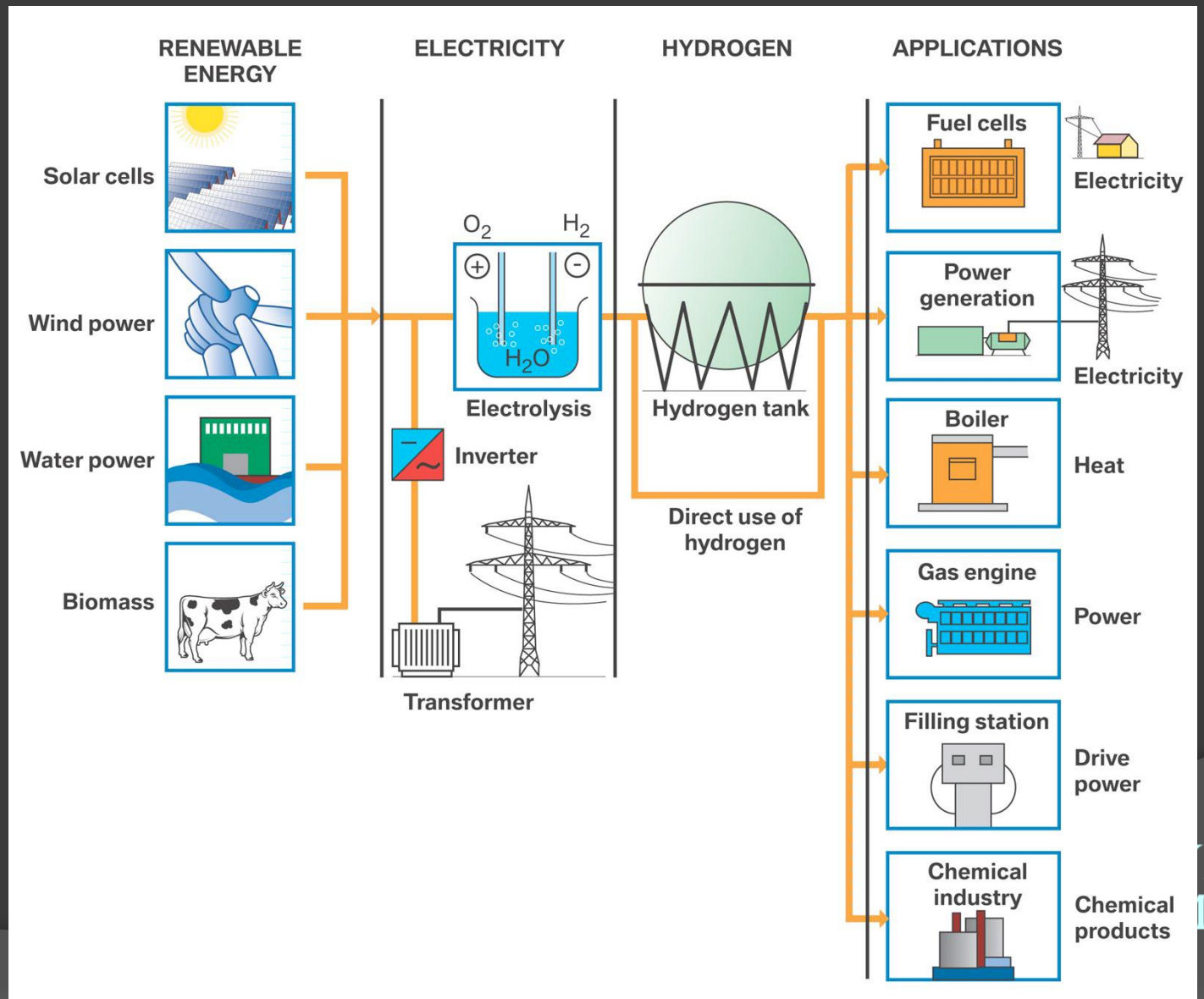
Sustainable?



Hydrogen needs to be stored

and

Hydrogen is it safe?

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Safety

- Explosive
- Hindenburg
- Codes of standards.....
- ***Hydrogen car or Petrol Car?***

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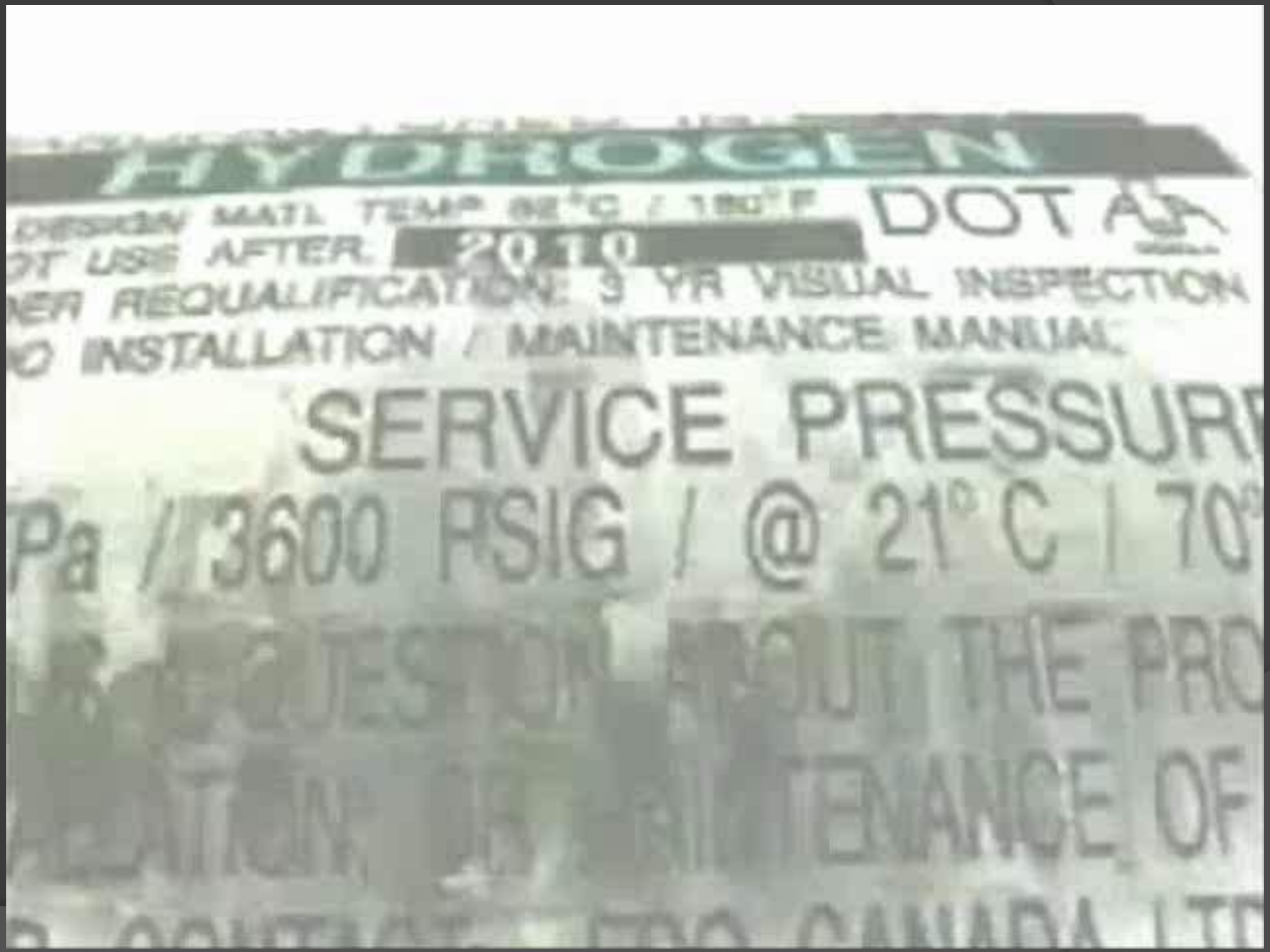
HYDROGEN
DESIGN MAT'L TEMP 82°C / 180°F
DOT USE AFTER 2010
NER REQUALIFICATION: 3 YR VISUAL INSPECTION
O INSTALLATION / MAINTENANCE MANUAL
SERVICE PRESSUR
Pa / 3600 PSIG / @ 21° C | 70
QUESTION ABOUT THE PRO
ATION OR MAINTENANCE OF

Summary

- Hydrogen Economy is a strong possibility
- Many ways of producing hydrogen
  - Is it sustainable and of correct purity?
- Many R & D barriers

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Technology	Feed Stock	Efficiency	Maturity
Steam reforming	Hydrocarbons	70 -85%	Commercial
Partial oxidation	Hydrocarbons	60 -75%	Commercial
Autothermal reforming	Hydrocarbons	60 -75%	Near term
Plasma reforming	Hydrocarbons	9 -85%	Long term
Aqueous phase reforming	Carbohydrates	35 -55%	Med. term
Ammonia reforming	Ammonia	NA	Near term
Biomass gasification	Biomass	35 -50%	Commercial
Photolysis	Sunlight + water	0.5%	Long term
Dark fermentation	Biomass	60 -80%	Long term
Photo fermentation	Biomass + sunlight	0.1%	Long term
Microbial electrolysis cells	Biomass + electricity	78%	Long term
Alkaline electrolyser	H_2O + electricity	50 -60%	Commercial
PEM electrolyser	H_2O + electricity	55 -70%	Near term
Solid oxide electrolysis	H_2O + electricity + heat	40 -60%	Med. term
Thermochemical water splitting	H_2O + heat	NA	Long term
Photoelectrochemical H_2O splitting	H_2O + sunlight	12.4%	Long term

J.D. Holladay et al , Catalysis Today 139 (2009) 244-260; http://dx.doi.org/10.1016/j.cattod.2008.08.039