Renewable and Alternative Energies

Topic 7. Hydrogen energy

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Topic 7. Hydrogen energy

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Topic 7. Hydrogen energy

- **7.1. General aspects**.
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- **7.4.** Applications.

7.1. General aspects

- **Hydrogen**, unlike fossil fuels, **is not a source of energy**.
- **Much of** the **existing hydrogen is in the form of water** –hydrogen ash– and considerable energy is required to extract the desired element.
- **Hydrogen is**, at best, an excellent **vector of energy**.
- It holds **great promise as:**
  1. **Fuel for land and sea vehicles**, especially when used in high efficiency fuel cells.
  2. **Fuel for large air and spacecraft** owing to its high energy-to-weight ratio when in cryogenic form.
  3. Industrial and domestic **fuel for generation of heat and electricity**.
  4. A means for **transporting large quantities of energy over long distances**.

7.1. General aspects

The advantages of hydrogen include:

- *Low pollution:*

  Hydrogen **burns cleanly**, producing only water. It is true that, depending on the flame temperature when burned in air, small amounts of nitrogen oxides may also be generated. **Pollution**, however, **may be associated with** some hydrogen **production processes**.

- *Controllability:*

  At **ambient temperatures, hydrogen reacts extremely slowly** with oxygen. **Catalysts permit adjusting the reaction speed** over a large range from very low-temperature flames to intense ones.

- *Safety:*

  Being the **lightest of all gases, it quickly rises and disperses**, while liquid fuels form pools that spread the fire.

  The **smallness** of the hydrogen molecule **causes this gas to leak easily** through tiny cracks and holes, making it difficult to accumulate in explosive concentrations.

7.1. General aspects

The advantages of hydrogen include:

- Owing to its **low density, a given volume of hydrogen contains little energy** and thus represents a much smaller hazard than natural gas or gasoline.
- At **1 atmosphere**, the **auto-ignition temperature for hydrogen is about 580°C**, whereas that for gasoline is as low as 260°C. The likelihood of accidentally starting a fire is much higher with gasoline.
- Hydrogen/air **mixtures with less than 4.1% fuel** (in volume) **will not catch fire** while the flammability limit for gasoline is 1%.
- A **pure hydrogen flame radiates little energy**, allowing firemen to get much closer to the site of a fire.
- Hydrogen **is totally nontoxic. Accumulation** of hydrogen **in high points can be prevented** by installing catalysts that cause the oxidation of the gas and its conversion to water. Odorants can be added to the hydrogen **to alert people to any escaping gas**.

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7.2. Hydrogen production

Hydrogen production can fall into one of several categories, including:

1. **Production** of hydrogen **in massive amounts at stationary plants** as, for instance, in the production of ammonia.
2. **Production** of **hydrogen in small amounts by compact on-board plants for use in fuel cell vehicles**. This last application is only now being developed and promises to become of significant economic interest.
3. **Production** of hydrogen **in modest amounts for the food industry and for other small consumers**.
4. **Production** of hydrogen **for use in compact residential or local electricity (and hot water) generation**.

7.2. Hydrogen production

The numerous processes for the production of hydrogen include:

A) Chemical.

B) Electrolytic.

C) Thermolytic.

D) Photolytic.

E) Biological.

7.2. Hydrogen production

A) Chemical

Metal-water hydrogen production:

- Small amounts of hydrogen are **produced by making aluminum chips react with caustic soda** (NaOH). This is sometimes the source of the gas used in meteorological balloons:

$$2Al + 2NaOH + 6H_2O \rightarrow 2NaAl(OH)_4 + 3H_2$$

- Another way of hydrogen production is **by the decomposition of water using aluminum's affinity for oxygen**. The basic reaction is:

$$2Al + 3H_2O \rightarrow 3H_2 + Al_2O_3$$

- This reaction is **strongly exothermic** –it causes an enthalpy change of 812 MJ per kmole of alumina produced–. **Nevertheless, aluminum appears** perfectly **stable in water** as attested by its common use in cooking utensils. **The reason is** the passivation that results from the very quick formation of **a** tough **layer of oxide that isolates the metal from contact with the oxygen in the air**. The oxide –alumina– is very hard and quite refractory. It adheres strongly to the aluminum surface.

7.2. Hydrogen production

A) Chemical

Metal-water hydrogen production:

- **Energetically**, the aluminum/water **reaction releases 812 MJ of heat** (which is wasted) **and 858 MJ in the form of 3 kmoles of hydrogen**, all per kilomole of alumina produced.
- Thus **only half of the chemical energy** of the aluminum/water reaction **is transformed into hydrogen**.
- **To regenerate the aluminum from the alumina**, we must use an **electrolytic process** that has a theoretical requirement **of 23 MJ per kg of aluminum**.
- Although the **efficiency** of the process improved, it seems improbable that it will ever much exceed the present-day value of **about 50%**.
- This means that some 50 MJ of electricity are needed to regenerate 1 kg of aluminum, which can yield 16 MJ of hydrogen. Thus, considering only the energy to recover the aluminum, the **energy efficiency of producing hydrogen by the proposed method is 32%**.

7.2. Hydrogen production

A) Chemical

Large-scale hydrogen production:

- The **bulk of the hydrogen produced** in the world **is made from fossil fuels**. Oil, naphtha, and natural gas are still the main materials used.
- Owing to their increasing scarcity, some **effort** is being made **to use** the more abundant **coal**, although the high sulfur content of many coals has **led to** serious **ecological concerns**.
- **Hydrocarbons and alcohols**, among other substances, **can yield hydrogen when submitted to partial oxidation, steam reforming, or thermal decomposition**. These **processes lead** to a **mixture of CO and H_2 called syngas**.
- When any of the above reactions is used in a fuel processor to feed fuel cells with pure hydrogen, the **efficiency, η, can be defined as:**

$$\eta \equiv \frac{\text{Lower heat value of the hydrogen delivered to the fuel cell}}{\text{Higher heat value of feed stock + higher heat value of fuel used for heat}}$$

7.2. Hydrogen production

A) Chemical

Large-scale hydrogen production:

Partial oxidation:

- Partial oxidation **is preferred when the raw material is a heavier fraction of petroleum**, while steam reforming is more convenient for lighter ones. **However**, small fuel processors for **automotive use based on partial oxidation of methanol are being seriously considered**.
- In the partial oxidation process, **air is used as oxidant**, and this results in **nitrogen being mixed with the hydrogen produced, reducing the partial pressure of the hydrogen and**, consequently, **lowering the fuel cell output**.
- Partial oxidation is accomplished **by reacting** a fuel **with a restricted** amount of oxigen:

$$C_nH_m + \frac{n}{2}O_2 \rightarrow nCO + \frac{m}{2}H_2$$

- Thus, for the **case of methane**,

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$$

- Where **oxygen** has a **greater affinity for carbon than fpr hydrogen**.

7.2. Hydrogen production

A) Chemical

Large-scale hydrogen production:

Steam reforming:

- In steam reforming, the **fuel reacts with water that adds its hydrogen** to that from the fuel **and does not introduce any nitrogen** into the reformate. This contrasts with the partial oxidation process.
- **Steam reforming** of a generalized hydrocarbon **proceeds** according to:

$$C_nH_m + nH_2O \rightarrow nCO + \left(\frac{m+2n}{2}\right)H_2$$

- This reaction is also **known as the carbon-steam reaction**.
- As an **example**, consider **carbon itself** (let m = 0 to cancel out the hydrogen in the hydrocarbon). Note that in this case, all the hydrogen comes from the water, and the fuel contributes only energy:

$$C + H_2O \rightarrow CO + H_2$$

- Consider also **methane:**

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

7.2. Hydrogen production

A) Chemical

Large-scale hydrogen production:

Thermal decomposition:

- Thermal decomposition of alcohols can be **exemplified by the methanol and ethanol reactions** indicated below:

$$CH_3OH \rightarrow CO + 2H_2$$

- And:

$$C_2H_5OH \rightarrow CO + H_2 + CH_4$$

- **All the hydrogen comes from the fuel used**.

7.2. Hydrogen production

A) Chemical

Large-scale hydrogen production:

<u>*Syngas:*</u>

- Syngas, the **mixture of CO and H_2** that results from all the reactions discussed so far, can be **used directly as fuel**.
- Syngas has been used as **domestic and industrial fuel**, but its **low energy** per unit volume makes it **unattractive if** it has to be pumped to a **distant consumer**.
- For such application, the gas **can be enriched by transforming it into methane**. This is the basis of many coal gasification processes. Observe that the preceding syngas **is dangerously poisonous** owing to the carbon monoxide it contains.
- An important **use** of syngas is as a **feedstock for** the production of an amazing number of **chemicals**. Many of these have a H/C ratio substantially larger than that of syngas. For this reason, and for its use in low temperature fuel cells, a **hydrogen enriching step** may be **needed**. This is **known as a shift reaction**.

7.2. Hydrogen production

A) Chemical

Large-scale hydrogen production:

Shift reaction:

- The shift reaction promotes **the combination of carbon monoxide with water**. The **result is carbon dioxide and more hydrogen:**

$$CO + H_2O \rightarrow CO_2 + H_2$$

- By using the shift reaction, it is **possible to adjust the H/C ratio** of syngas over a wide range of values. As an **example**, consider the production of **hydrogen from natural gas** (methane):

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

- Followed by:

$$CO + H_2O \rightarrow CO_2 + H_2$$

- With the **overall result:**

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$

7.2. Hydrogen production

A) Chemical

Large-scale hydrogen production:

Shift reaction:

- Notice that the heat of combustion of methane into liquid water is 890 MJ/kmole, while the combustion of 4 kilomoles of hydrogen, again into liquid water, yields 4 x 286 = 1144 MJ. Thus, in the above reaction, the products have more energy than the reactants - **the reaction is endothermic**.

- The **extra energy** comes from the heat necessary for the reaction to proceed. In fixed installations, this heat **usually comes from the combustion of hydrocarbons:**

$$C_nH_m + \left(n + \frac{m}{4}\right) O_2 \rightarrow nCO_2 + \frac{m}{2}H_2O$$

- In the more **compact automotive and residential uses**, the heat may convenien-tly **come from the combustion of part of the hydrogen** in the reformate.

7.2. Hydrogen production

A) Chemical

Large-scale hydrogen production:

Methanation:

- **The transformation of syngas into methane**, part of the process of transforming any fossil fuel into the (usually) more valuable “natural gas”, **is called methanation**.
- Besides being of great industrial importance, methanation is also of interest because it **provides a technique for eliminating most of the CO impurity from the stream of hydrogen** produced from carbon-bearing fuels.
- The **methanation reaction** is:

$$CO + 3H_2 \rightarrow H_2O + CH_4$$

- This is the **reverse of steam reforming of methane**. Incidentally, carbon dioxide can also be transformed into methane:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

7.2. Hydrogen production

A) Chemical

Large-scale hydrogen production:

Methanol:

- In addition to being a valuable fuel and chemical, **methanol is an important intermediate in the production of** many **other chemicals**. This is particularly true because it is **the only substance that can be produced individually and with good efficiency from syngas**.
- Methanol **may become the fuel of choice for fuel cell cars**. It can be **produced from syngas:**

$$\mathbf{CO + 2H_2 \rightarrow CH_3OH}$$

- Methanol **can also be produced** directly **from biomass such as wood**.
- There are **some problems** with the widespread use of methanol as an automotive fuel. The main problem is its **toxicity**. The other is its **low volumetric energy** concentration, which is the lead motivation for the **development of higher alcohols** and other liquids as automotive fuels.

7.2. Hydrogen production

A) Chemical

Large-scale hydrogen production:

Syncrude:

- **Syncrude** is the term that describes the **liquid products resulting from coal liquefaction**.
- Liquefaction is a **more efficient process of converting coal than gasification**. It **requires little water** and **can use all sorts of coal**, including bituminous coals that tend to cake when submitted to gasification.
- There are essentially **four syncrude processes:**
  1) The **Fischer-Tropsch process** similar to that used for production of methanol. Instead of pure methanol, the process yields a complex mixture of hydrocarbons.
  2) **Pyrolysis**, the destructive distillation of coal in the absence of air results in gases, liquids, and solids (char). Coal is flash heated because prolonged heating will cause the liquid fraction to crack forming gases.
  3) **Direct hydrogenation** of coal.
  4) **Solvent extraction** of liquids.

7.2. Hydrogen production

A) Chemical

Large-scale hydrogen production:

Hydrogen production plants:

- **Large-scale hydrogen production** starting from fossil fuels **is a mature technology**.
- The **first step** in the process is frequently the **desulfurization of the feedstock** because sulfur tends to poison the catalysts required in some of the subsequent steps.
- **Next, syngas is produced by steam reforming**. This is an endothermic reaction that requires heat input.
- The **shift reaction that eliminates most of the CO** releases substantially less heat than that needed to drive the reforming reaction. The shift reaction, being exothermic, profits from operation at low temperatures owing to equilibrium considerations. However, this **influences unfavorably the kinetics** of the reaction. **Modern** copper-based **catalysts** allow operation **at** temperatures as low as **520 K**.

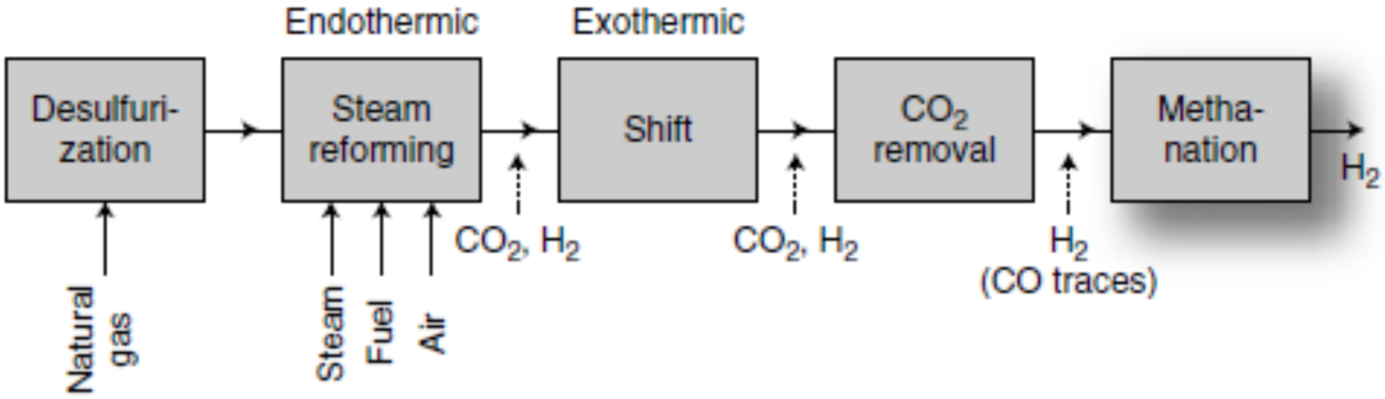
7.2. Hydrogen production

A) Chemical

Large-scale hydrogen production:

Hydrogen production plants:

- After the shift reaction, the **gas** contains large amounts of carbon dioxide **mixed with hydrogen**. This requires a CO_2 removal step. The **final step** in the hydrogen production sequence is the **elimination of residual CO**.



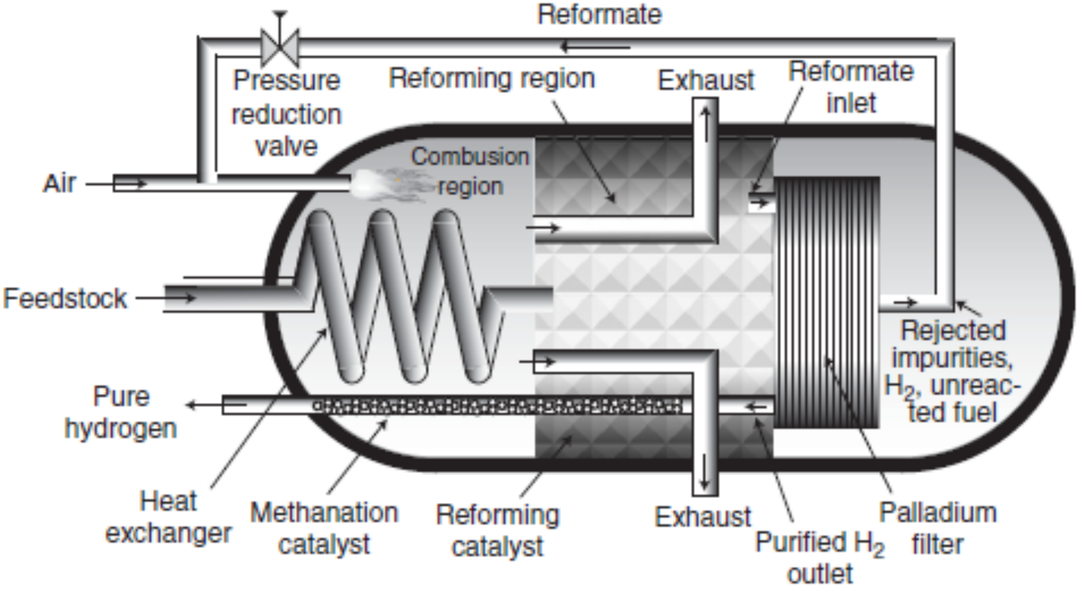
7.2. Hydrogen production

A) Chemical

Large-scale hydrogen production:

Compact fuel processors:

- **Compact fuel processors** for use in automobiles or for residential applications **are vigorously being developed at the moment**.
- Much of the **work** has been concentrated **on adapting the classical industrial hydrogen production techniques** to the much miniaturized requirements of the in situ hydrogen generators for automotive uses.



7.2. Hydrogen production

B) Elecrolytic

- Production of **hydrogen by electrolysis is a relatively old art** that has found **industrial application in the food industry** and in other activities that need only a moderate amount of the gas.
- Hydrogen produced by electrolysis has the **advantage of being easily purified**, whereas that produced from fossil fuels tends to contain several hard-to-remove contaminants.
- To a small extent, electrolytic hydrogen has been used for the **synthesis of ammonia** but ammonia plants are not the only consumers of electrolytic hydrogen. Electrolytic hydrogen is preferred **by food and pharmaceutical industries** owing to the ease with which **high purity gas can be obtained**.
- For certain applications, an **electrolyzer/fuel cell combination** constitutes an excellent way **to store energy**.
- One important future application of electrolyzers is in **hydrogen gas stations** for refueling fuel cell vehicles.

7.2. Hydrogen production

B) Elecrolytic

Electrolyzer configurations:

Liquid electrolyte electrolyzers:

- Until relatively recently, almost all water electrolyzers used liquid electrolytes. Owing to its low conductivity, **pure water cannot be used as an electrolyte: it is necessary to add a substance that increases the conductivity**.
- **Although acids satisfy this requirement** (and are used in some electrolyzers), they are frequently avoided because of corrosion problems. **Alkaline electrolytes are better**; they almost invariably use potassium hydroxide (KOH) in concentrations of 25% to 30%.
- **Electrodes must be chosen to fulfill** the following requirements:
  1) Corrosion resistance.
  2) Catalytic action.
  3) Large surface.

7.2. Hydrogen production

B) Elecrolytic

Electrolyzer configurations:

Solid-polymer electrolyte electrolyzers:

- Solid-polymer electrolyzers are dramatically **more compact** than KOH electrolyzers and do **not require electrolyte controls**.
- They can **operate** at much **higher current densities** than liquid electrolyte devices.
- They have the **disadvantage of requiring de-ionized water** and of **producing wet gases**.

7.2. Hydrogen production

B) Elecrolytic

Electrolyzer configurations:

Solid-polymer electrolyte electrolyzers:

- Their **advantages** include the following:
  1) The **electrolyte** can be made **extremely thin**, leading not only to great compactness but also to reduced series resistance.
  2) No **diaphragm is needed:** the ion-exchange membrane allows the motion of ions but not of gases.
  3) The **electrolyte cannot move**. It has constant composition, and no electrolyte concentration controls are needed.
  4) There are **no corrosives** neither in the cells nor in the gases produced.
  5) The **membrane can be strong enough to allow large pressure differentials** between the H_2 and the O_2 sides.
  6) **Large current densities** are possible.
  7) Extremely **long life** (20 years) seems possible without maintenance.

7.2. Hydrogen production

B) Elecrolytic

Electrolyzer configurations:

Ceramic electrolyte electrolyzers:

- They work at **temperatures between 450°C and 800°C, use steam** as feedstock, but **produce pure, dry hydrogen**. High temperature improves the kinetics of the reaction.

7.2. Hydrogen production

B) Elecrolytic

Electrolyzer hydrogen compression:

- **For many applications** such as ammonia production or delivery of hydrogen to fuel cell cars, **hydrogen must be available at high pressure**. Thus, a hydrogen plant must frequently include a compressor.
- The **pressure of the environment itself can be raised** by **housing the electrolyzer in a pressure vessel**. For economic reasons, one **needs compact equipment**; otherwise the cost of the pressure vessel becomes prohibitive.
- In practice, the **compression energy** is somewhat highter owing to the **decrease in the efficiency**.
- The great **advantage** of electrolytic compression is **the simplicity and economy in maintenance since there are no moving parts in the system**.
- The hydrogen production rate, $\dot{N}$, is strictly proportional to the current, ***I***, forced through the electrolyzer:

$$\dot{N} = \frac{I}{2 * q * N_0}$$

Where:

$\mathbf{q} = 1.6 \cdot 10^{-19}$; $\mathbf{N_0}$ = avogardo number (in kmol) = $6.022 \cdot 10^{26}$

7.2. Hydrogen production

C) Thermolytic

Direct dissociation of water:

- It is well known that **water vapor, at high temperatures, will dissociate into hydrogen and oxygen**.
- Hydrogen could, in principle, be separated out by using an appropriate device. Although, at a first glance, this scheme may seem attractive, **its implementation is difficult**.
- **At any realistic temperature, water will only partially dissociate**. If **F is the fraction of dissociated water**, the reaction will be:

$$(1 - F)H_2O \longleftrightarrow FH_2 + \frac{1}{2} FO_2$$

- **F will depend on the equilibrium constant K_p**, which depends on the temperature and on the exact way the chemical equation was written, however, it does not depend on pressure.

7.2. Hydrogen production

C) Thermolytic

Chemical dissociation of water:

- To circumvent the difficulties encountered with the direct dissociation of water, **several chemical reactions have been proposed**.
- In all of them, the is **no consumption of materials other than water itself**.
- The **temperatures** required for these reactions **must be sufficiently low** to permit practical implementation of the process.
- In particular, it is desirable that the **temperatures do not exceed 1100 K** to make the process compatible with nuclear fission reactors.

7.2. Hydrogen production

D) Photolytic

- The technology for **using solar light energy to produce hydrogen is well established**.
- One certainly can **produce this gas through entirely nonpolluting processes** by using photovoltaic converters whose output drives electrolyzers. The **main effort** here is to **develop processes** that can accomplish this transformation more **economically**.
- The structural formula of water, H–O–H, suggests that the **first step** in the dissociation must be **the breaking of the H–O bond** so that H and OH (or the corresponding ions) are formed.
- **Next, the OH is dissociated into O and another H**, then these atoms coalesce into diatomic molecules.
- Although there is only a 2.51 eV energy difference between a molecule of water and its elements, **to dissociate it directly, it is necessary to overcome a 5.15 eV barrier**. Thus, photons or phonons with less than 5.15 eV cannot initiate the direct water dissociation reaction.

7.2. Hydrogen production

E) Biological

- The majority of **living organisms must breathe**, that is, must **consume oxygen and release carbon dioxide** to fuel their anabolism. This is true of plants.
- However, **plants**, under the influence of light, also perform photosynthesis, the opposite of respiration: they **fix atmospheric carbon dioxide and release oxygen**. Thus, when exposed to light, plants tend to be net oxygen producers and, in the dark, net oxygen consumers.
- In principle, **some plants could generate the oxygen needed for their respiration by extracting it from water and releasing hydrogen. This occurs**, for instance, **with certain algae**.
- Since, in darkness, the plant is almost inactive, the **amount of hydrogen released is small. An enzyme—hydrogenase—promotes such release**. Hydrogenase is inhibited by the presence of oxygen and, thus, does not work when photosynthesis is active.

7.2. Hydrogen production

E) Biological

- **Melis** et al. (2000) have demonstrated a **photobiological hydrogen production** system **using the alga Chlamydomonas reinhardtii**. The system proceeds in **two stages:**
  1) **Algae are grown normally** and build up their store of carbon compounds.
  2) **Sulfur is withdrawn** from the system, **and the algae**, still exposed to light, **release hydrogen**, consuming some of the accumulated carbon.
- At present, it appears that substantially **more research is required** not only to perfect the parameters of the system but also to develop more efficient strains or algae.
- **What really counts** from a practical point of view is the cost of the gas produced and not the **efficiency of the system**. It remains to be seen if the proposed Melis system will be economically attractive.

Topic 7. Hydrogen energy

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- **7.4.** Applications.

7.3. Storage and distribution

- **Hydrogen can be stored as an element, or it can be extracted, as needed**, from some hydrogen-rich substance **using an onboard extraction process:**

  1) **Processes that alter the state or the phase of hydrogen** (hydrogen only systems):
     - **1.1.** Compression of the gas or a combination of **compression and refrigeration**.
     - **1.2.** **Liquefaction of the element**. Owing to its low critical temperature, hydrogen must **be cooled to some 20 K** to remain liquid in nonpressurized vessels.

  2) **Processes that associate hydrogen to other substances:**
     - **2.1.** **Adsorption of the gas on some appropriate substrate** such as activated carbon.
     - **2.2.** **Chemical combination** of hydrogen so as **to create a hydrogen-rich compound**. Such compounds **can be:**
       - **2.2.1.** Compounds in which H_2 is tightly bound, requiring a relatively complex chemical process for the recovery of the gas. There are, for instance, substances like **methanol, ethanol, ammonia, and water** itself that can be thought of as **"carriers" of hydrogen**.
       - **2.2.2.** **Compounds that can be reversibly transformed** into another substance with a higher (or lower) hydrogen content.
       - **2.2.3.** **Metal hydrides** that are metal-hydrogen compounds **that** can **release and absorb hydrogen reversibly by** a simple **change of temperature**.

7.3. Storage and distribution

- A number of **characteristics have to be considered** when evaluating hydrogen storage systems. They include:

1) **Gravimetric Concentration (GC).** This is the **ratio of the mass of the stored hydrogen to the overall mass of the** (loaded) **storage and recovery system**. The dimensions are kg per kg–that is, it is a **dimensionless parameter**.

2) **Volumetric Concentration (VC).** This is the **ratio of the mass of the stored hydrogen to the total volume of the storage and retrieval systems**. The dimensions are kg per m^3.

3) **Turnaround efficiency.** This can be the **ratio of the retrieved hydrogen to the amount of input hydrogen, or the ratio of the energy retrieved to the input energy**.

4) **Dormancy.** This is the **ability of the system to retain its hydrogen over a long period of time**.

7.3. Storage and distribution

Compressed gas:

- For compressed gas containers, the main **quantity of interest is the gravimetric concentration**–that is, the **ratio of the mass of the maximum amount of gas that can be stored to the mass, M_{cont}, of the container**, where the maximumm amount of gas corresponds to gas at just under the burst pressure, p_{burst}, of the vessel.
- This ratio is **proportional to the performance factor (PF)** of the container:

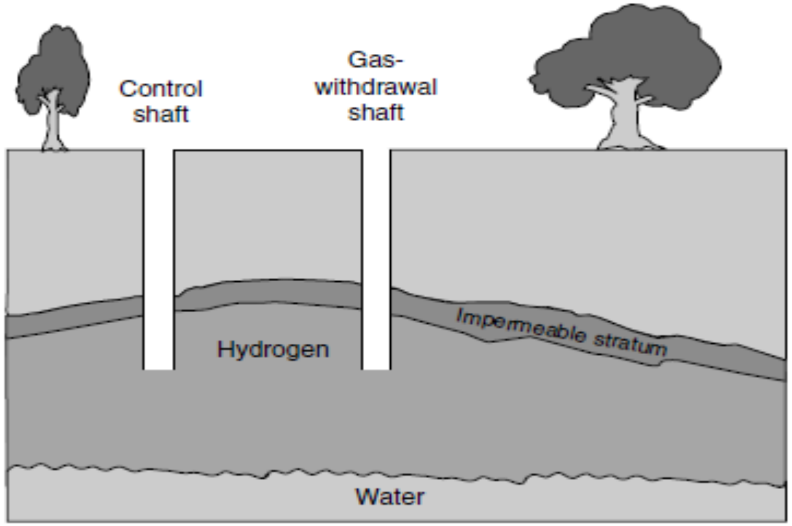
$$PF \equiv \frac{p_{burst} {}^{*} V}{M_{cont}} \qquad (J/kg)$$

- For a given material and technology for building a compressed gas container, the mass of the container is proportional to the pressure so that **the ratio** of stored gas mass to the mass of the container **is independent of the storage pressure**.
- Hence, the **only way to improve the PF is to use better materials and better technology in the construction**.

7.3. Storage and distribution

Compressed gas:

- **Small quantities of hydrogen**, as used in chemical laboratories, **can be** conveniently **stored in simple steel pressure cylinders**, usually at 150 atmospheres.
- **For fuel cell vehicles (FCVs), compressed hydrogen may be a practical way to carry the necessary fuel**. It is certainly the simplest storage system, and it requires no special equipment to retrieve the gas. What is needed are containers with a good PF.
- For very **large-scale storage**, it may be possible to **keep hydrogen in underground formations**, such as porous rocks, old mines, caves, aquifers, and exhausted natural gas deposits. At present, there is **little experience** with underground storage of hydrogen.



7.3. Storage and distribution

Compressed gas:

- Another storage arrangement for hydrogen would be the very **pipelines used for transporting the gas**. A typical trunk pipeline for natural gas can be over 1000 km long. It may have a 1.2-m diameter and operate at 6 MPa (60 atmospheres). The hydrogen stored in such a pipeline would correspond to an energy of 1000 TJ.

Cryogenic hydrogen:

- Although hydrogen was first liquefied in 1898, it was **only recently**, through the efforts of NASA, that **the technology for production and storage of large quantities of the liquid was developed**.
- The **largest storage unit** in existence is one **at Cape Canaveral, with** a capacity of **3375 m^3**. Since the density of liquid hydrogen is 71 $kg.m^{-3}$, the facility can accumulate 240,000 kg of liquid hydrogen, or 34 TJ.

7.3. Storage and distribution

Cryogenic hydrogen:

- There are **two different species of hydrogen molecules: para- and ortho-hydrogen**. In the first, the spin in the two atoms that constitute the molecule are in opposite directions, whereas in the second, the spins are in the same direction.
- In the liquid state, para-hydrogen **(p-H_2) has lower enthalpy than the ortho** form (o-H_2). At the boiling point of H_2 (20.4 K at 0.1 MPa), the difference is 1.406 MJ.kmole^{-1}.
- In hydrogen, gaseous or liquid, the **reaction p-H_2 ↔ o-H_2 goes on continuously**, and an equilibrium concentration of each species is established.
- The **equilibrium at** Standard Temperature and Pressure **(STP) corresponds to 25% p-H_2 and 75% o-H_2**, whereas at 20.4 K, the equilibrium shifts to 99.79% p-H_2.

7.3. Storage and distribution

Cryogenic hydrogen:

- **Freshly condensed hydrogen**, even if kept in a perfectly adiabatic container, **will lose** 1% of its **mass** during the first hour and 50% during the first week.
- **To minimize such losses**, o-H_2 is catalytically converted to p-H_2 during the liquefaction process. **Levels of 95% p-H_2 are desirable**.
- **Liquid hydrogen has been considered as a fuel for aircraft** but hydrogen-driven commercial airplanes will probably not be seen in the near future.
- **Present-day design efforts** for transport planes in the Mach 3 range **are based on jet fuel (kerosene) engines. However, the proposed space plane will probably need hydrogen as a fuel**.

7.3. Storage and distribution

Storage of hydrogen by adsorption:

- Both **hydrogen molecules and methane can be readily adsorbed on carbon**.
- The **gases are held in place by weak van der Waals forces so** that the **energy necessary to retrieve the fuel is small**.
- Carbon systems can be **combined with other techniques:** the **gas can be pressurized and the temperature can be lowered**. Typically, an adsorption system **using activated carbon requires 20 to 40 atmosphere pressure and liquid nitrogen temperature to hold the hydrogen.**
- These **requirements severely limit the practical application** of such systems but **carbon nanotubes promise to uptake hydrogen** much **more effectively**.

7.3. Storage and distribution

Storage of hydrogen in chemical compounds:

- The **main difficulty** encountered in the storage of hydrogen is, as pointed out, the **low density of the gas**.
- It is possible to substantially **increase the packing density by associating hydrogen with other substances**. The storage and retrieval processes consist then of the **synthesis of a hydrogen-rich compound followed**, when the gas is needed, **by its dissociation**.
- The **requirements of a practical hydrogen storing compound** include:
  - High storage capacity.
  - Low reaction energy.
  - Reversibility.
  - Fast kinetics.
  - Separability.
  - Low corrosiveness.

7.3. Storage and distribution

Storage of hydrogen in chemical compounds:

Metal hydrides:

- A majority of **the requirements** listed before **can be met by** a class of substances loosely called **metal hydrides**, or simply hydrides.
- **A number of elements form unstable hydrides** (hydrides that can easily be reversed). Magnesium, iron, titanium, zirconium, yttrium, lanthanum, and palladium are examples. **Hydrides of elements are called binary**.
- **Ternary hydrides** –hydrides formed by a combination of hydrogen with a binary compound– **are more promising**. The addition of a third element, leading to **quaternary hydrides, increases** even further **the degree of freedom** in choosing the characteristics of the system.
- As can be seen, **a large number of combinations are possible. Research in this area has only scratched the surface**.

Topic 7. Hydrogen energy

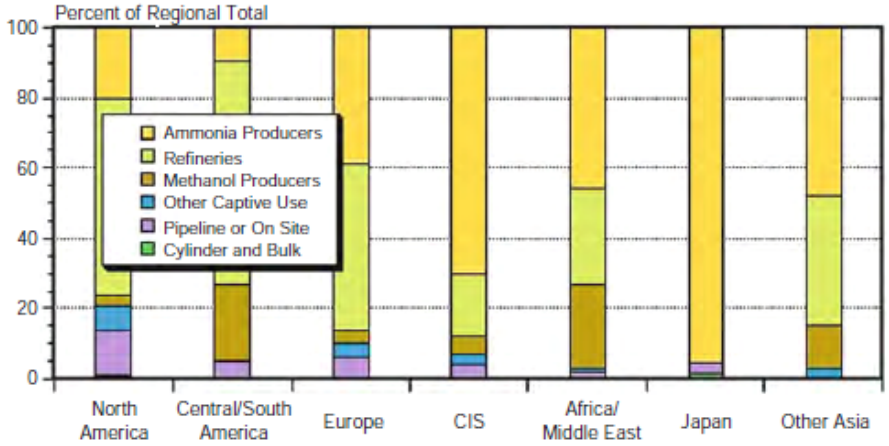
- **7.1.** General aspects.
- **7.2.** Hydrogen production.
- **7.3.** Storage and distribution.
- **7.4. Applications**.

7.4. Applications

- **Hydrogen can be used in any application in which fossil fuels are being used** today, except where carbon is specifically needed.
- Hydrogen can be used as a **fuel in furnaces, internal combustion engines, turbines and jet engines, more efficiently than fossil fuels**, i.e., coal, petroleum and natural gas.
- **Automobiles**, buses, trains, ships, submarines, airplanes and rockets **can run on hydrogen**.
- **Hydrogen can** also **be converted directly to electricity by using fuel cells**, which can be fed directly to the grid or to operate automobiles.
- Combustion of hydrogen with oxygen results in pure **steam**, which has **applications in industrial processes and space heating**.
- Moreover, hydrogen is an **important industrial gas and raw material for numerous industries**, such as the computer, metallurgical, chemical, pharmaceutical, fertilizer and food industries.

7.4. Applications

- The **major uses of hydrogen** are listed below:
  - Ammonia (NH_3) production for use in fertilizer.
  - Oil industry.
  - Semi conductor production.
  - Glass industry.
  - Hydrogenation of fats and oils.
  - Methanol production.
  - Production of HCl.
  - Plastics recycling.
  - Rocket fuel.
  - Welding and cutting.



- Total **hydrogen production worldwide is** about **550 billion Nm^3/year**. Approximately **50% of it is used for ammonia** based fertilizer production. The consumption of hydrogen in refineries per year is around 200 billion Nm^3.
- Other major uses of hydrogen include **methanol production (8%)** and its use as **fuel in space programs (1%)**.

7.4. Applications

- **95% of hydrogen production is captive**, i.e., produced at the site where it is used. The other 5% is called merchant hydrogen, which is produced and then sold for industrial and chemical uses.

- The **main objective of a hydrogen economy is to use hydrogen as** a fuel source. Its major use as fuel will be in **fuel-cell cars**. It is anticipated that by **2040, the use of hydrogen** in fuel cell powered cars and light trucks could **replace** consumption of **petroleum by about 18.3 million barrels per day**.

- The **use of hydrogen is yet to take off**, but the anticipation is that its use by most countries will **start around 2020**. An **exponential growth** following the initial period of slow growth **is expected**.

7.4. Applications

Fuel cells

Redox Reactions in a Proton Exchange Membrane (PEM) Fuel Cell

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$$

is the overall reaction

This consists of two half-reactions happening at the fuel cell's two electrodes:

anode (H_2 side): $H_2 \rightarrow 2H^+ + 2e^-$ (oxidation)

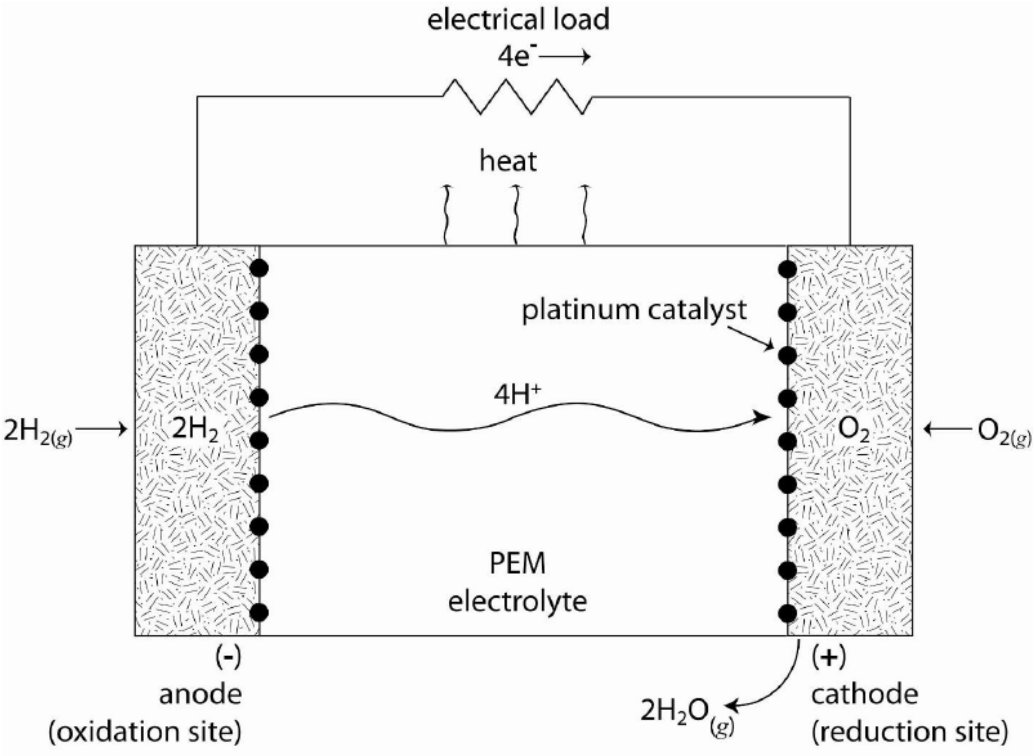
and

cathode (O_2 side): $\frac{1}{2} O_2 + 2e^- + 2H^+ \rightarrow H_2O$ (reduction)

7.4. Applications

Fuel cell operating principle

(PEM example)

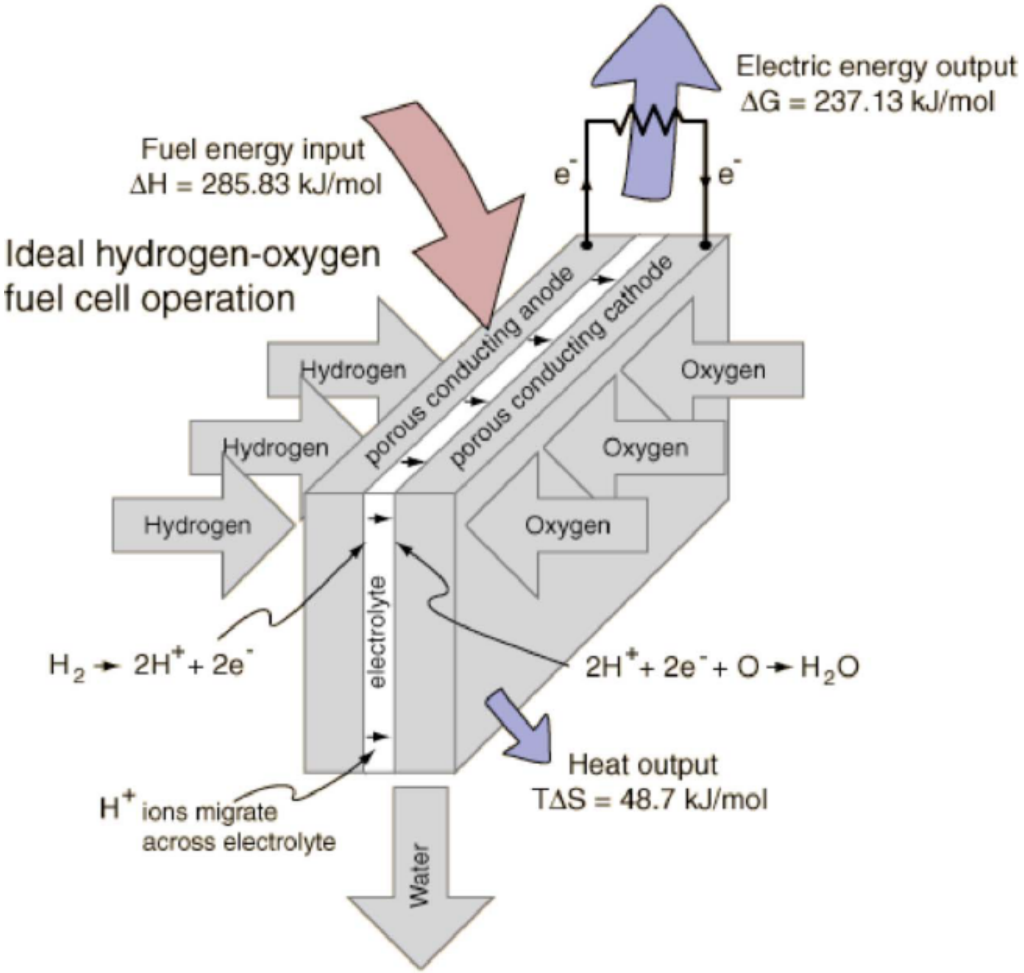


$2H_2 \rightarrow 4H^+ + 4e^-$

$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$

7.4. Applications

Fuel cells



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