

OVERVIEW OF HYDROGEN AND FUEL CELL TECHNOLOGIES

Dr.-Ing. Thomas Jordan

Institut für Kern- und Energietechnik, Forschungszentrum Karlsruhe GmbH

Thomas.Jordan@iket.fzk.de

ABSTRACT

Hydrogen and fuel cell technologies are cross-cutting technologies. They interact with many research areas and require knowledge from many engineering branches. Hydrogen technologies have had an unsteady past but the new development and the worldwide growing energy demand will for sure require all facets of any energy technology including those of hydrogen and fuel cell related technologies.

Hydrogen is most versatile in its production, transportation and end use. This is indicated by the broad range of technologies shown in this report. Acceptable storage technologies for pressurised and liquefied hydrogen are available. The fuel cell development progressed considerably the last decade. The targets for prices and lifetime will be met earlier than expected. For bridging to the future conventional combustion engines might be operated already today on hydrogen. However, the pressure and temperature levels involved with some new hydrogen technologies in the hands of private users, still pose some problems to be resolved.

As hydrogen provides an efficient energy storage it will support the shift towards renewable energies and it will make the energy market more decentralised and flexible. Most of the presented technology will come closer to the end user, what will help to promote the acceptance of these new technologies.

INTRODUCTION

Little History on Hydrogen and Fuel Cells

Hydrogen was detected by the English chemist and physicist Henry Cavendish in 1766 when conducting experiments with quicksilver and sulphuric acid. As both came in contact he observed small gas bubbles. The gas could not be identified as one of the known gases. Although he assumed that this gas must have been an ingredient of the quicksilver (instead of the acid) he could describe its properties quite well.



Figure 1: Henry Cavendish (* 10. October 1731 in Nice; † 24. February 1810 in London)

Independently the French chemist Antoine Lavoisier discovered the same gas in 1787 as he wanted to demonstrate that there is mass conservation in all experiments. He evaporated water on hot iron swarft and condensed the steam and realised that there was a small loss. He managed to capture the non-condensed gas and could prove that in fact there was no mass lost. He performed experiments with the non-condensed gas and showed that it can burn. As the product was water he called it hydro-gène (“hydro” Greek for water, “genes” Greek for generating).

In 1800, only months after the English chemist William Nicholson succeeded in decomposing water into hydrogen and oxygen by electrolysis, Johann Ritter duplicated the experiment but arranged the electrodes so that he could collect the two gases separately, thus improving on the experiments of Carlisle and Nicholson



Figure 2: Sir William Grove

In the year 1839 after some communications with his colleague Schönbein Sir William Grove showed that the reverse process, namely the feeding of electrodes with hydrogen and oxygen could generate besides water an electrical voltage and current. He used sulphuric acid as electrolyte and platinum electrodes.

However with the detection of the dynamo electrical principle by Werner von Siemens 1866 the whole development of the galvanic cells including fuel cells lost their importance and alternating current power technologies dominated direct current technologies for a long time.

General Properties of Hydrogen

Hydrogen is the simplest chemical element. It has the atomic number 1 and is member of the 1st period. There are three isotopes Protium, deuterium and tritium. At normal conditions there is no atomic hydrogen and only very small amounts of the di-atomic gas H₂ (~0.5 ppm) found in the atmosphere. Instead hydrogen is bound to carbon in all organic material and to oxygen in water. Thus it is the most abundant element on earth and in the universe.

Hydrogen H₂ is the lightest gas with a density of 0.09 g/l (14 times lighter than air). It is very diffusive and a good thermal conductor. It is non-toxic, colourless, odour- and tasteless and can be approximated reasonably well by an ideal gas (up to 20 MPa).

Because of the limited natural availability of H₂, it is not an energy source.

At temperatures below 20.39 K H₂ condenses into the also colourless liquid hydrogen LH₂ with a density of 70.8 g/l (14 times lighter than water).

Around 14 K LH₂ turns into slushy hydrogen SLH₂ and finally freezes. Solid hydrogen does not have practical applications whereas SLH₂ is applied as rocket fuel due to its slightly higher energy density compared to LH₂.

The critical point of hydrogen is at 33.2 K and 1.32 MPa.

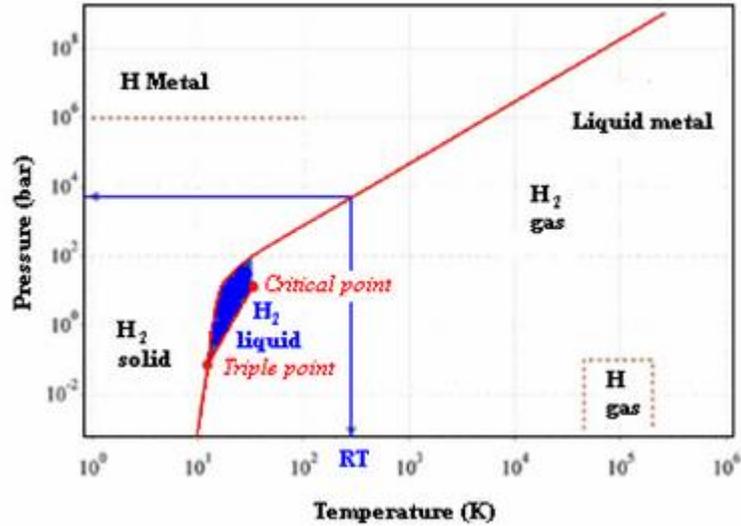


Figure 3: Phase Diagram

At normal conditions the hydrogen gas is composed of two molecular variants ortho-hydrogen (75%) and para-hydrogen (25%). They differ by their magnetic nuclear spin and therefore by their magnetic properties. The nuclear spin of both nuclei in ortho-hydrogen is aligned and in opposite direction for para-hydrogen. Thermal capacity and conductivity and other thermodynamic properties differ only very slightly. The equilibrium distribution close to 0 K consists only of para-hydrogen, see Fig. 4.

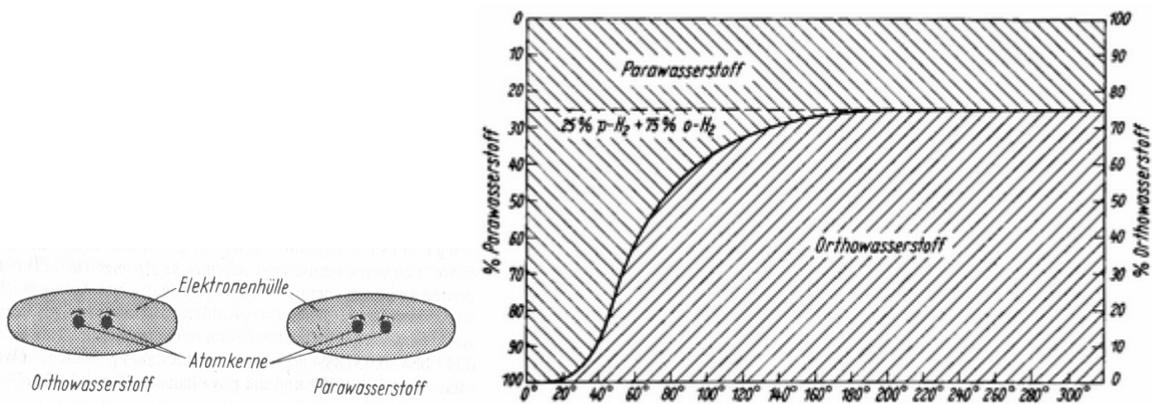


Figure 4: Ortho- and Para-hydrogen

The conversion



is slightly exothermic and happens at normal pressure only within months. Under higher pressure the conversion still needs weeks. In the liquefied hydrogen this would cause additional storage losses, the so-called boil-off. So at least in large scale production one accelerates the shift to para-hydrogen with catalysts like active carbon, iron oxide Fe(OH)₃, etc.

As the atom and the molecule have a very small size it is easy to understand that hydrogen has a very high diffusivity. The diffusivity in air, for example, is 4 times higher than the self-diffusivity of air. This may also lead to situations where vessels tested for leak tightness with other gases turn out not to be leak tight for hydrogen. This concerns also sealings and some metallic materials like iron and platinum. Together with the very high solubility, e.g. in palladium, this might even be used in purifying or cleaning techniques. On the other hand thin layers of e.g. oxides might reduce the diffusion drastically.

Different from most other gases but similar as helium hydrogen has at normal conditions a small positive Joule-Thomson coefficient, what means that it heats up in an ideal throttling process. However, this effect is relatively small, so throttling from 20 MPa to 0.1 MPa the gas would heat up by approximately 6K only. Another consequence is that for liquefaction one has to cool the gas down by other methods, for instance by heat exchange with liquid nitrogen, before the Joule-Thomson effect might be applied below the inversion temperature.

H₂ has an electro negativity of 2.2 on the Pauling scale. It reacts with all elements of the 1st group (alkali), 2nd group (alkaline earth) 16th group (chalcogen) and 17th group (halogen elements). The reaction with earth alkali elements forms salt like hydrides. It reacts with oxygen according to



If we have gaseous water on the right hand side the heat of reaction is reduced by the latent heat 44kJ/mol.

This and the reverse reaction, the water splitting, explain the function of hydrogen as an energy carrier. Instead of pure oxygen it also reacts in air. Its stoichiometric mixture with air has 29.6% vol H₂. There it needs only small energies for ignition, typically 10% of the energy required for other burning gases. However, it is inflammable (4%-76% vol in air) and in the lean or fat ends of the mixture the ignition energy is comparable to this other the other gas-air mixtures. However, without ignition or a catalyst the reaction is very slow. The flammability limits have to be regarded as having only little relevance for practical applications. They are determined in idealised laboratory conditions with the gases at rest. Usually the practical flammability range is considerably smaller.

With nitrogen it forms under high temperature and pressures ammonia, a key precursor for fertilisers. Together with carbon or carbon oxide it is used for synthesis of organic gases or liquid fuels.

Current Use of Hydrogen

Currently hydrogen is used in large scale in the petrochemical industries, in particular for the desulphurisation and saturation of hydrocarbons. Even more is used for fertiliser production. So the world wide production sums up to more than 600 billion Nm³/year, where about

- 50% are used for the ammonia synthesis
- 25% for the hydrocarbon processing and
- 25% for other applications including hardening of fat (nutrition), methanol synthesis, space craft fuels, cleaning of surfaces in the electronic, semiconductor industries, cooling and lubrication of electrical generators and corrosion protection of austenitic steels in power plants.

95% of the hydrogen is produced on-site and on demand. This means there is no need for storing or transporting the produced amounts. Most of the production is large scale, and only 5% enter the free market. In many processes like the chlorine electrolysis the hydrogen is generated as a by-product and sometimes just vented in the free atmosphere. Beside the space program there is nearly no application of hydrogen as an energy carrier, whereas the vision of the hydrogen economy requires changes in many aspects.

Future Use of Hydrogen as an Energy Carrier

The production has to be increased considerably and shifted from the still carbon based reforming technologies to CO₂ free or at least lean production technologies based on renewable biomasses or electrical current produced by sun or wind. This implies a tendency for a more distributed energy generation scheme which additionally will reduce the energy transportation needs.

The main advantage of hydrogen, the function of energy storage, requires further developments of high pressure, cryogenic or solid state storage techniques. Experience is lacking as the conventional industrial processes do not use the extreme states required for these new technologies.

Transportation in pipelines, already applied in some industrial areas, might be easily expanded to conventional natural gas pipeline networks. However, the end use in fuel cells might require new separation and cleaning processes in a residential environment.

In general the new end use of hydrogen imposes new challenges regarding safety measures. High pressure and cryogenic techniques have to be matured for the private end use. Beside demonstrated safety, only low prices, comfort and simplicity will make any new products acceptable for the private energy market.

However, the potentially high efficiencies of the energy conversion based on hydrogen energy, like in fuel cells but also in the conventional combustion techniques, offer already now CO₂ reduction when considering the whole energy chain and will help in the market penetration when the current main energy carriers become more and more expensive.

The following section will present the available production technologies, the next section will describe how hydrogen may be stored and transported and then the end use technologies, in particular fuel cells and more conventional combustion technologies, will be introduced. In the final section some references for more detailed information will be provided.

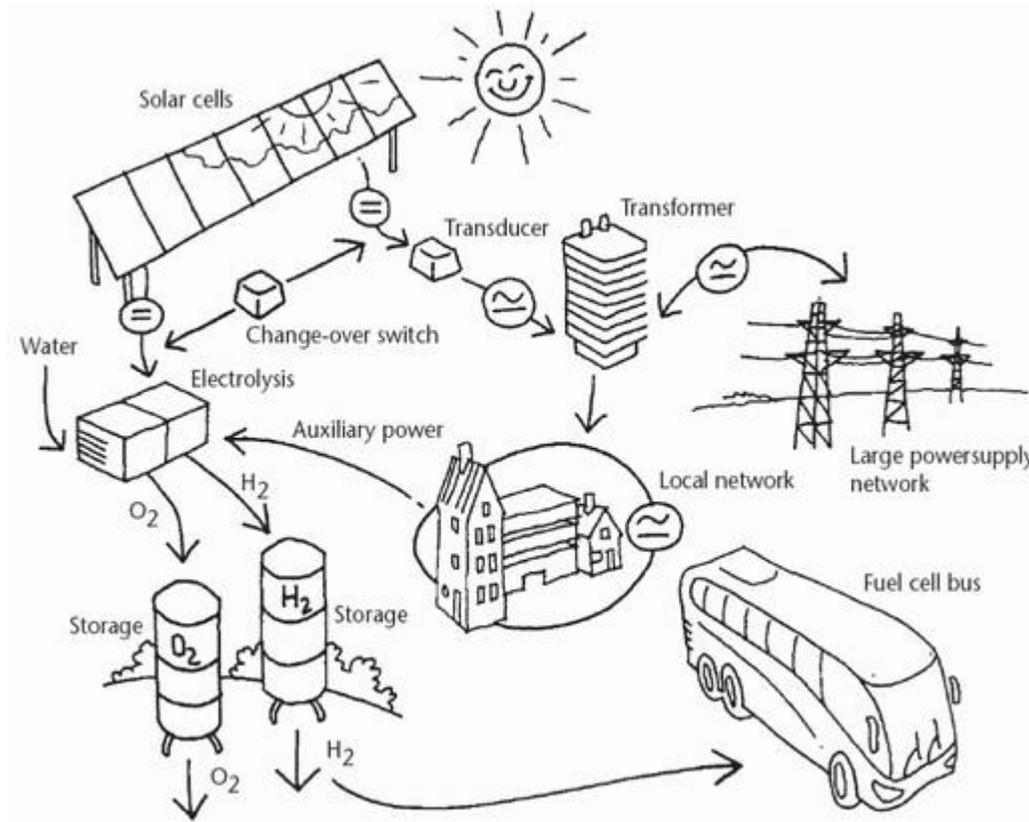


Figure 5: Hydrogen and electricity partnership in a hydrogen economy

HYDROGEN PRODUCTION

As explained in the introduction hydrogen on earth is available mainly as chemical compounds bound to oxygen in water or carbon in organic materials. Therefore hydrogen may not be considered as an energy „source“, but can be used as chemical energy storage. We have to apply any primary energy to produce hydrogen or in other words store a high as possible ratio of this primary energy in molecular hydrogen.

Hydrogen may be produced from all primary and secondary energy sources. In all cases we will either extract it from the carbon based organic materials by reforming or thermal splitting processes or split water by the use of electricity, radiation and/or heat. The latter processes will be labelled by terms ending with „...lysis“ like electrolysis, photolysis, radiolysis, pyrolysis etc.

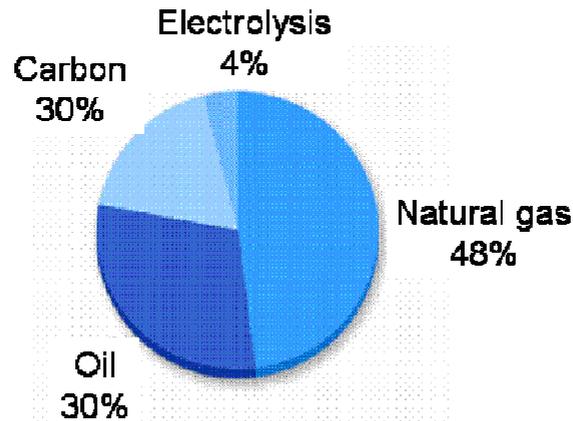
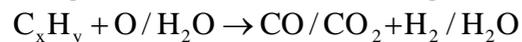


Figure 6: Sources of Hydrogen [www.airproducts.de/wasserstoff/energietraeger.htm]

Reforming Technologies

About 96% of the current hydrogen production is realised by reforming of organic material, in particular of natural gas or pure methane. Only the remainder is produced by electrolysis.

The general reaction of reforming is



Typical by-products of reforming are CO and CO₂. If air is used for oxidation techniques like the partial oxidation, nitrogen compounds might be included. In practical applications there might be intermediate reactions and other minor ingredients involved.

Depending on the energy balance of the actual reaction we differ allothermal reactions, where we have to apply further external energy or heat and autothermal reactions, where no external heat has to be provided. Additionally accounting for the oxidation agent we differ the following three main technologies:

- steam reforming for light hydrocarbons like methane,
- partial oxidation for heavy hydrocarbons like oil or coal and a
- mixed technology called autothermal reforming

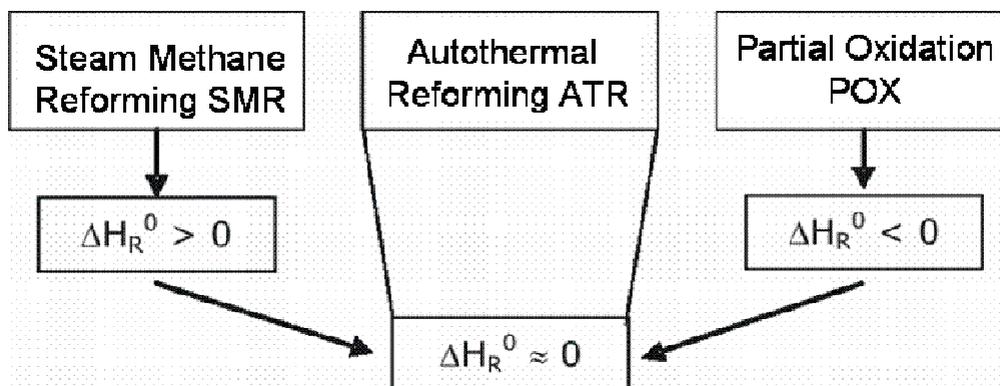


Figure 7: Types of Reforming Processes

The efficiency of the process η_{Reformer} might be calculated according to the following simplified equation:

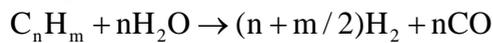
$$\eta_{\text{Reformer}} = \frac{\dot{n}_{\text{H}_2} h_{\text{H}_2}}{\dot{n}_{\text{C}_x\text{H}_y} h_{\text{C}_x\text{H}_y} + P_{\text{heat}}}$$

with $\dot{n}h$ representing the enthalpy flow of the respective components through the reactor and P_{heat} the heat power input.

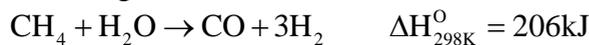
Steam Reforming

In this process light hydrocarbons, which are typically used also in other energy applications, but also middle hydrocarbons like benzene are separated in two steps in carbon oxide and hydrogen. The usual feed however is natural gas which has a large fraction of methane.

The general reaction for steam reforming is:



Applying this to a pure methane feed yields the reaction equation for the steam methane reforming SMR:



So steam reforming is an allothermal process, requiring external heating. Practically this is reached by heating the required steam and additionally heating the reactor.

SMR is the broadest established technology for hydrogen production, so that currently about 48% of the world wide hydrogen production is provided by this process. The reason is that currently this is the cheapest way to produce hydrogen with costs of approximately 2.50 €/kg H₂. (To compare a kg price with the litre price of gasoline fuel, the kg price of hydrogen may be divided by the factor 3)

There is some potential for further reduction of costs by the further development of the involved catalysts.



Figure 8: Microstructured benzene reformer (for H₂ production suitable for a 5kW fuel cell)



Figure 9: Cut through the primary large scale reformer and a view on a Linde-Natural Gas-Steam-Reformer (H₂ capacity 35.000 Nm³/h, purity after PSA 99.99 %)

SMR is currently conducted at 850°C with catalysts made of iron or nickel or oxides of these metals. As the catalysts are very sensitive against halogens, in particular chlorine or sulphur compounds natural gas has to be cleaned in a refinery before entering the reactor.

The cleaned gas is mixed with the required amount of steam and then brought in the long reformer tubes which are filled with the catalyst from the top. These tubes are heated additionally also from the top by burners, where any burning gases and the tail gas of the cleaning process are used.

The SMR is characterised by a high hydrogen conversion ratio, as with the steam we introduce another hydrogen source in the process. However, practically the conversion ratio is influenced positively by

- higher temperatures,
- lower pressures, and a
- higher S/C ratio.

Typical pressures are 2.5-3 MPa, and S/C ratios of 3. These will give a conversion ratio of 86-90%, Uhde [16]. Below an S/C of 2 carbon will be deposited on the catalyst and deteriorate its function. For similar reasons the minimum temperature in the reactor is about 450-500°C.

The incomplete reaction represented by the synthesis gas might be completed by a further slightly exothermal oxidation of the carbon monoxide in a shift reaction. In practice this is realised in a high temperature (320°C-380°C) and low temperature (200°C-240°C) shift reactor applying iron oxide catalysts. In large installations before the shift remaining in a secondary reformer remaining hydrocarbons might be reformed with oxygen to yield additional steam required for these shift reactions.

After the shift there is usually a further carbon oxide removal by an alkaline washing, partial methanising or pressure swing absorption PSA. With a PSA purities of about 99.9% and up to 99.99% can be reached, without a PSA 97%-99% are typical values.

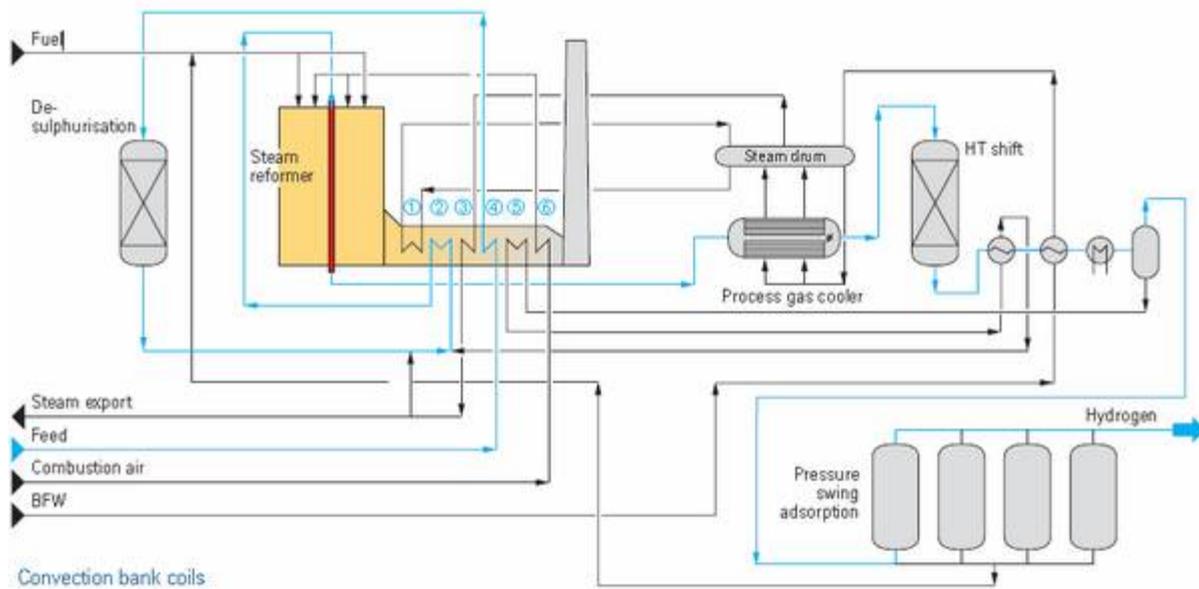


Figure 10: Flow Sheet of a Steam Reformer (Source: Uhde)



Figure 11: Large scale industrial SMR with PSA and storage

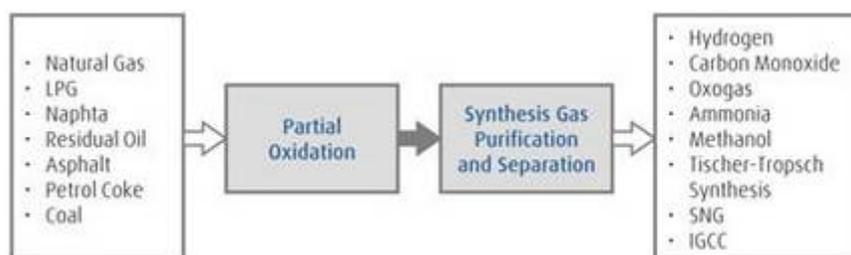
The total efficiency of a large SMR plant like shown in Fig. 11 with capacities of approximately 100000 Nm³/h (9t H₂/h). is in the order of 65%. Installations with approximately double capacity are currently planned.

Small units are economically attractive down to. 150 Nm³/h, in some special cases also 1.5 Nm³/h. Some small units are currently field tested by Tokyo Gas Co., Japan. They provide 15 Nm³/h and an efficiency of conversion rate of 76 %, Hori [20].

Micro-Steam-Reformers might be realised also using the so-called “Printed Circuit Heat Exchangers” PCHE technique. The micro channels are produced with a similar technique used to produce printed circuit boards. These micro-reactors provide huge specific surfaces and can operate at 50 MPa and up to 900°C.

Partial Oxidation

Partial oxidation (POX) of heavy oil and even coal is a usual large scale H₂ production technology. The main application is to provide synthesis gas for synthetic fuels or modern coal based power plants with an integrated CO₂ separation/sequestration process. By providing only a below stoichiometric ratio of oxygen the process is controlled.



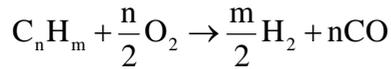
Typical POX Feeds und Products (Source Linde)

Non catalytic POX can be operated at temperatures about 1200-1450°C and typical pressures of 3-7.5 MPa (Texaco Process). The catalytic POX requires less high temperatures about 1000°C. The hydrogen yield is smaller compared to SMR and typically H₂/CO ratios of ~2 (SMR > 3) may be reached. This is an ideal mixture fort he methanol synthesis. The overall efficiencies are with approximately 50% smaller than these of a SMR.

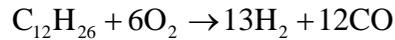
Disadvantage are a high oxygen demand, deactivation of catalysts because of carbon deposition and a high CO content in the product gas mixture requiring more efforts in the cleaning procedures.

Especially because of the expensive oxygen this technique is mainly attractive with low primary energy costs.

The general POX reaction is:



Applying fuel oil this yields



where a characteristic hydrocarbon was selected from the long list of hydrocarbons usually contained in fuel oil.

Autothermal Reforming ATR

This is in principle a combination of the SMR and POX to eliminate the need for external heating in the SMR and to have a higher conversion ratio than with POX.

Product Gas Cleaning

After the actual reforming process the gas mixture has to be processed further usually. After the described shift reactions the remaining carbon oxides may be removed by preferential oxidation, selective methanisation or cleaned by physical processes, like diffusion via membranes or absorption on large surfaces of special absorbing materials.

Pressure Swing Absorption PSA

PSA is usually a discontinuous process conducted in 5 steps:

1. Step: Absorption: Under high pressure the feed is directed in a bed of absorber material. Impurities are absorbed and the clean hydrogen leaves the absorber bed
2. Step: Saturation: When the contamination in the cleaned gas exceeds a certain value the absorber is saturated
3. Step: Depressurisation: The pressure in the absorber is reduced and the absorbed impurities are released in the gas stream now switched in the off gas, also named tail gas, branch.
4. Step: Purge: The absorber is purged with the feed until the impurities become smaller than a certain minimum value.
5. Step: Pressurisation: The exit of the absorber is switched to the clean product gas branch and the absorber bed is pressurised again.

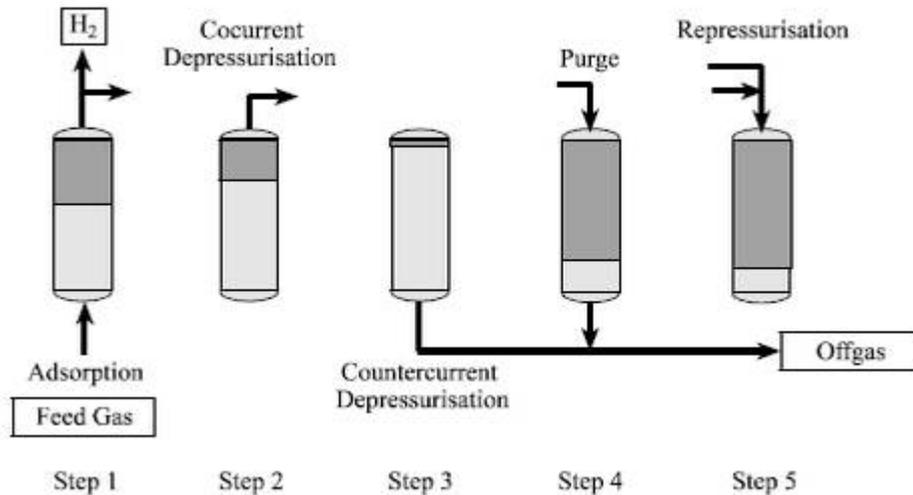
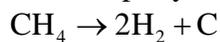


Figure 14: PSA Process

Other organic material based production techniques: Kvaerner Process

In the beginning of the 80ies at Kvaerner Engineering S.A. introduced a new technology the so-called "Kvaerner Carbon Black and Hydrogen Process", which allows to produce hydrogen based on organic materials without the by-product CO₂. To this end usually light hydrocarbons are heated in a plasma up to 1600°C and transformed into active carbon and hydrogen.

An exemplary reaction based on a methane feed is:



In 1992 there was the pilot plant HPBR KARBOMONT commissioned in Canada. It produced from 1000Nm³/h natural gas and 2100 kWel electrical energy, process steam with a power of about 1000 kW, approximately 500kg/h active carbon and 2000Nm³/h H₂. Accounting for the fact that all products have a considerable market value one could define an efficiency of 100%, where ~48% are provided by H₂, ~40% by active carbon and ~10% by the steam.



HPBR Karbomont plant

In a next step an installation delivering 100.000 Nm³ H₂/h under industry conditions is planned.

Biomass Reforming

In principle biomass is nothing but organic material which may be reformed by the above introduced processes. The gasification in a POX process or other processes is even easier as the biomass usually contains more oxygen than fossil primary energy carriers. So only little additional oxygen is required for the endothermic or autothermal processes what leads to higher efficiencies compared to the POX based gasification of coal, for instance. According to Tetzlaff [22] the large scale gasification of biomass is the most cost effective process for the production of hydrogen. He suggests 2.5 €/kWh (2006).

An advanced process adds a pyrolysis before the actual gasification. The pyrolysis generates primary gases (similar to natural gas) and coke oil. In the second step these products are mixed with steam and reformed to hydrogen and carbon oxides. The products might also include methane.

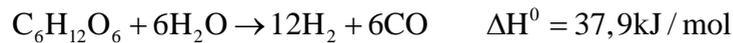
Wet biomass, like organic residential waste or manure, can be directly fermented to methane with a quite high conversion ratio. After a cleaning step which removes in particular sulphur compounds, this gas may be directly converted in electrical current in a high temperature fuel cell, in MCFCs or SOFCs for example. For use in a low temperature fuel cell like a PEM, these gases have to be reformed in hydrogen.

As the generated CO₂ in all the process chain is generated from biomasses it may be considered short-lived and therefore does not contribute to the additional human generated green house gas emissions.

Bacteria and algae may directly form hydrogen from biomasses under anaerobic conditions. The sulphur content of environment of the green algae has to be reduced that these micro

organisms change their metabolism from a methane production to hydrogen production, which actually is an intermediate step in the whole chain of reactions. The whole process requires small pressure levels and usually shows small efficiencies, maximum 33% according to Thauer [23]. In comparison methane fermentation processes can transform up to 85% of the reaction heat of the biomass in the fermentation product, i.e. methane in this case.

Alternatively wet biomass may be reformed in supercritical water. The research centre Karlsruhe has demonstrated the efficiency and attractiveness of this process in their pilot installation VERENA [32]. Celluloses transformed in the reactor at 600°C and 30 MPa in syngas according to the following prototypical reaction:



The biomass has to be grinded and mixed in the water. The mixture is pressurised and then heated in the reactor where it stays for about a minute. The hydrogen rich product gases are separated and cleaned and are directly available at a pressure of 30 MPa without further compression work. Currently there is work going on to cope with salt like deposits in the reactor.

Water Electrolysis

Water electrolysis or simply electrolysis is the splitting of water into hydrogen and oxygen with the help of electrical current. It is the reverse process of the process in a galvanic or fuel cell, where chemical energy is converted in electrical current.

The electrolysis process does not release any CO₂ directly and therefore it is the future technology for storing intermittent renewable power in the chemical storage, hydrogen. As the electrolysis uses electrical current as the energy sources the costs of the hydrogen generated by electrolysis will always be immediately coupled to the costs of this current and the same applies for the environmental footprint. Water electrolysis is also used to produce oxygen and other electrolyse processes are also used for the production of other industry gases like chlorine.

The principal features of an electrolyser are two electrodes, the anode and the cathode, separated by the electrolyte which allows electrical current flow only via ions. It isolates electrons. Usual water provides only few ions for conduction so usually acid or caustic solutions are used providing sufficient H⁺, OH⁻ or other ions.

Electrolysers are characterised by their operating temperatures and pressures and how they are build-up. The main differentiation, however, follows - similar as for fuel cells - the used electrolyte. So there are alkali-, PEM- und SOFC-electrolysers.

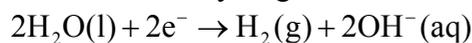
Type	Alkali	PEM	Solid Oxide
State	Marketed	Development	Research
Electrolyte	caustic solution (e.g. KOH)	Polymer membrane (e.g.. Nafion)	Doped zirconium / ceramics
Operation	Preferential steady state Up to 20 % reduction of nominal load possible	Dynamic operation possible	T=800-1000°C
+	Low cost	No corrosive fluids, high current densities, compact, high p, efficiency	High temperature application efficiency
-	Low power densities, maintenance	Expensive, small power range	Material issues

Table 1: Comparison of electrolyser types

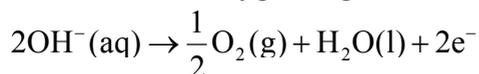
The most approved technology is the alkaline electrolyser, which is applied where access electrical power might be stored (e.g. Assuan,...). Typical costs for these types are 500 €/kW, of course depending on the absolute power of the system.

The caustic solution is usually a KOH solution for the electrolyte and the anode and the cathode are built of nickel and nickel oxide materials. The process consists of two parts.

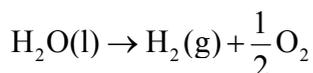
At the cathode hydrogen is formed by:



On the cathode oxygen is generated by



The sum of the reaction is the know reaction



with l=liquid, g=gaseous, aq=solved in water.

The ideal reversible cell voltage required to separate hydrogen and oxygen at normal conditions is determined by the Gibbs potential ΔG , Faraday's constant $F=96487\text{As/mol}$ (product of the electrical elementary load $e = 1.6022 \text{E-}19 \text{ C}$ and the Avogadro-constant $N_A = 6.022 \text{E}23 \text{ 1/mol}$) and the number of involved electrons in one elementary reaction (here 2):

$$E_{\text{rev}} = \frac{\Delta G}{nF} = 1,23\text{V}$$

However, this voltage requires that additional heat is provided. If all energy shall be provided by electrical power the heat of reaction has to replace the Gibbs potential. This yields an ideal theoretical voltage of

$$E_{\text{th}} = \frac{\Delta G + T\Delta s}{nF} = 1,48\text{V}$$

The dependency of this voltage on the temperature is shown in Fig .15.

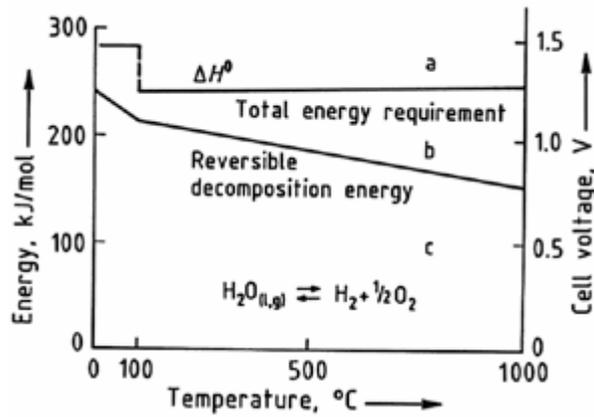


Figure 15: Theoretical ideal cell voltage dependant on the temperature

Because of irreversible losses on the electrodes (E_2, E_3) and due to resistive losses in operation additional voltage is needed. Comparing the real voltage demand with the above ideal voltages allows defining efficiency according to:

$$\eta_{\text{Elektrolyseur}} = \frac{E_{\text{th}}}{E_{\text{cell}}} = \frac{E_{\text{th}}}{E_{\text{th}} + E_2 + E_3 + E_4} = \frac{1,48\text{V}}{E_{\text{cell}}}$$

Alternatively the efficiency can be calculated relating the ideally required energy for a certain an Nm^3 of hydrogen to the actually used energy:

$$\eta_{\text{Elektrolyseur}} = \frac{\Delta h_{\text{H}_2}}{P_{\text{elektrisch}}} = \frac{3,55\text{kWh}}{P_{\text{elektrisch}} \text{Nm}^3}$$

In a PEM electrolyser with an iridium dioxide catalyst on the anode and platinum as cathode efficiencies of 93% could be reached.

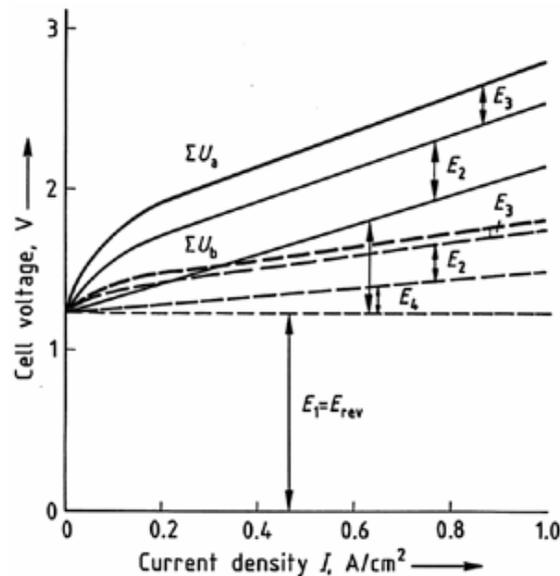


Abb. 1: Real cell voltage dependant on the current density

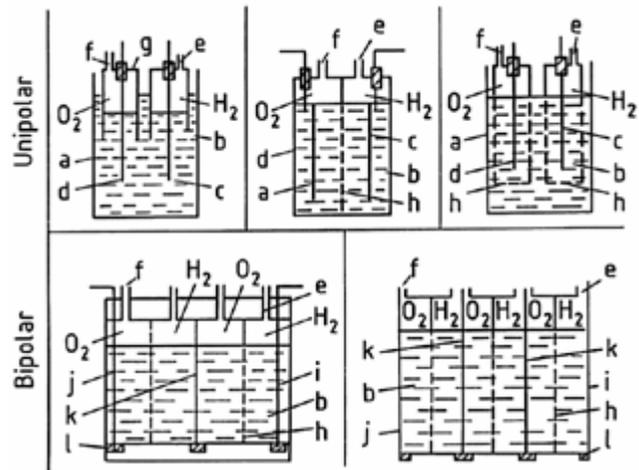


Abb. 2: Principal design

- a) cell wall; b) electrolyte; c) cathode; d) anode; e) hydrogen exit; f) oxygen exit g) gas collector
- h) diaphragm; i) external cathode; j) external anode; k) bipolar electrode; l) insulation

Single cells are connected in series by bipolar plates. This allows for an efficient and compact technology. Typically an atmospheric bipolar alkaline electrolyser needs 4 to 4.5 kWh/Nm³ H₂, what correlates to an efficiency of about 80% according to the formula above. Other typical data for this type of electrolyser are operating temperature of 70 – 90 °C, cell voltage of 1,85 – 2,05 V and current densities of about 2 to 3 kA/m². The capacities are in the range of 20-5000 Nm³/h. A capacity of ~ 500 Nm³/h requires 2 MW electrical power, Norsk Hydro [21]. The purities are without any further cleaning are 99.9% for H₂ and 99.8% for O₂.

Larger units might be composed modularly, provided sufficient space is available. One of the largest installations is located in Egypt at the Assuan dam. The maximum capacity of these Norsk Hydro installations is 33.000 Nm³/h. The hydrogen is used for fertilizer production.

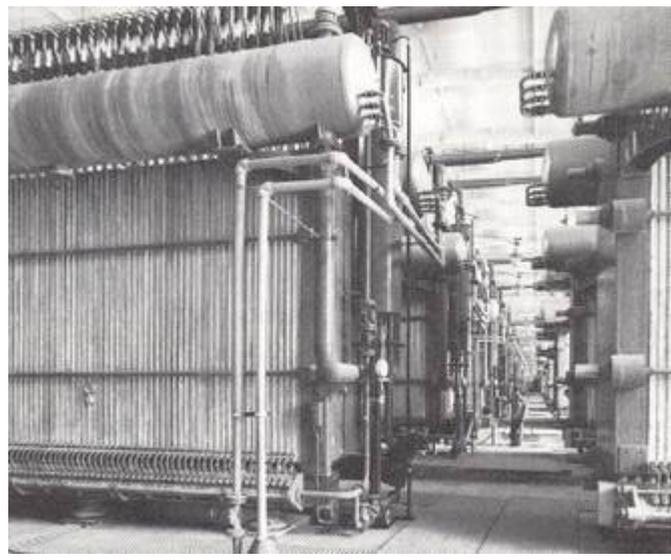


Figure 18: Norsk Hydro Elektrolyseur; ca. 485 Nm³/h ~ 2MWe; space requirements 4x13m²

The availability of electrolyzers is in general high; a typical value is 98%. However, for reliable operations the electrodes have to be protected by certain limitations regarding the dynamics of the operation. Alkali electrolyzers have to be operated at nominal power without to fast drop in the power supplied. This is a special aspect to be considered when fluctuating renewable energies like wind and sun shall be stored. Buffering peeks and applying a protective voltage when idling will prolong the lifetime of the electrodes

Thermochemical Cycle Process

Thermal dissociation is the splitting of molecules simply by applying high temperatures. Only above 2500°C steam will dissociate in hydrogen and oxygen to a considerable degree. This might be achieved directly in concentrating solar ovens. The hot gases may be separated by ceramic membranes. These membranes will allow hydrogen to diffuse but will hinder oxygen from passing. Just these temperatures generate material problems which are still not completely solved.

Therefore catalytic elements are investigated which reduce the temperature required to split water down to 900 °C. Coupled chemical reactions with additional elements which are not consumed in the process, so act as a catalyst, are investigated in particular for heat delivered from nuclear reactors or concentrating solar collectors. In the 70ies and 90ies the DoE supported large screenings and literature surveys [33]. The sulphur-iodine, the hybrid Westinghouse and the UT-3 Univ. of Tokyo Process turned out to be the most attractive cycles. The number of involved chemicals maximum temperature required, conversion ratios and efficiencies were elements in the rating.

The first two will be described in detail in the following sub-sections.

Sulphur-Iodine Cycle SI

Iodine and sulphur dioxide react in the Bunsen reaction at 120°C to hydrogen iodide and sulphuric acid. After separation the sulphuric acid is decomposed at about 900°C to oxygen and sulphur dioxide. The hydrogen iodide is decomposed at 400°C in hydrogen and iodine. Although this cycle has the highest efficiencies with up to 50 % many material issues are still to be solved. Furthermore, the amount of iodine required is quite high contributing considerably to the investment costs.

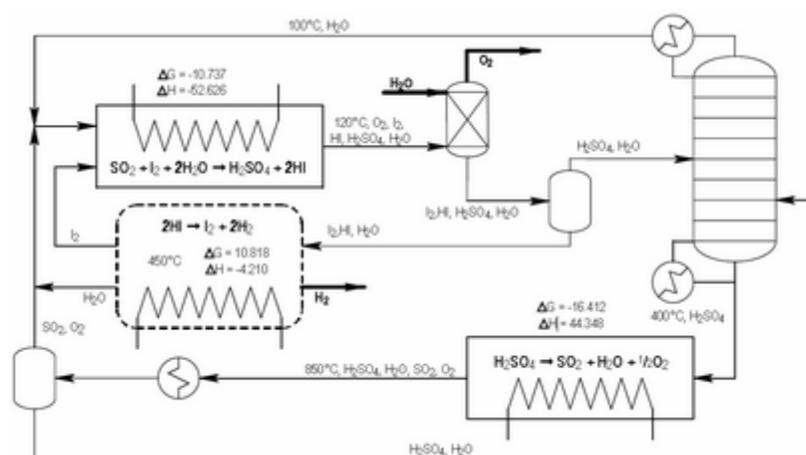
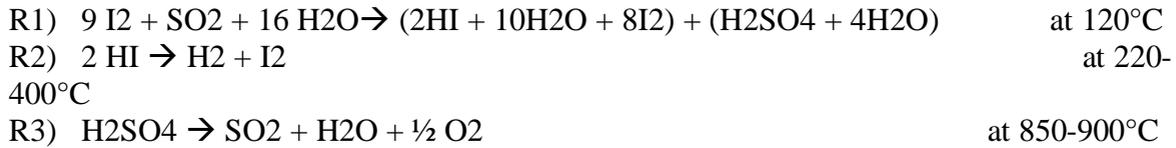


Figure 19: Sulphur-Iodine Cycle

The sulphur-iodine-cycle consists of 3 reactions:



R1 is the exothermal Bunsen reaction producing two immiscible products, sulphuric acid and an aqueous solution of hydrogen iodide and iodine. The sulphuric acid and the hydrogen iodide are dissolved by applying heat in the reaction R2 und R3. R3 with a higher heat demand occurs catalytic in the gas phase above 850°C . Hydrogen from R2 and oxygen from R3 are separated and the remainders are recycled in R1.

In summary the know reaction appears:
 $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{ O}_2$

Hybrid- Sulphur- or Westinghouse-Prozess

This cycle consists of only two reactions. Sulphur dioxide is electrolysed in an aqueous solution to hydrogen and sulphuric acid. The sulphuric acid is decomposed in the identical reaction R3) of the sulphur-iodine-cycle into oxygen and sulphur dioxide.

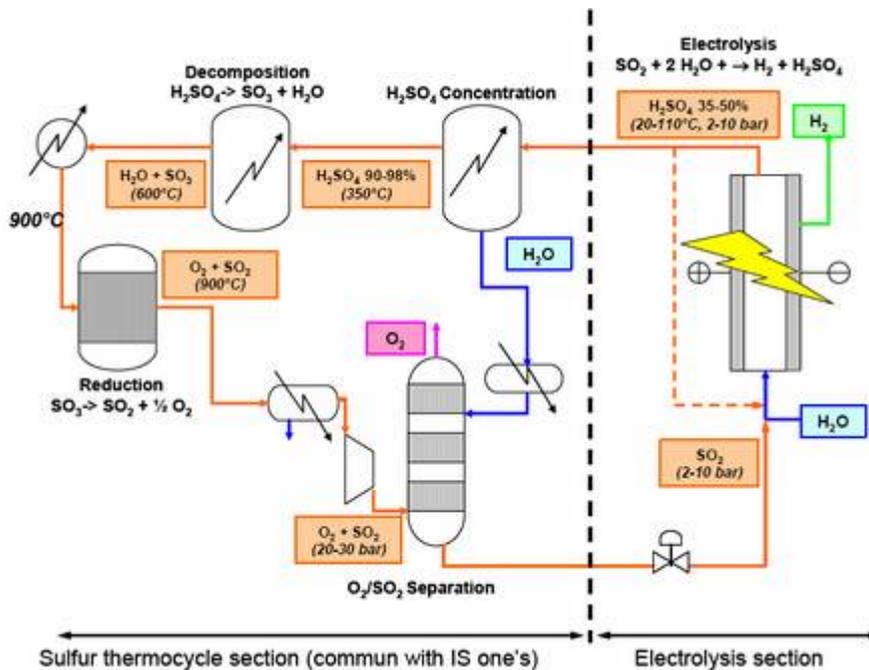
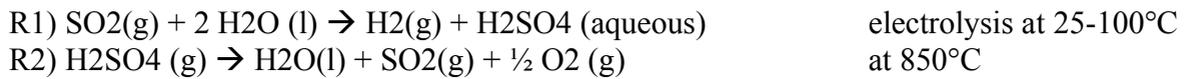


Figure 20: Westinghouse-Prozess

Thus the two reactions are:



The advantage is that this process delivers nearly similar efficiencies as the sulphur-iodine-process but need only one additional chemical component, which is moreover easily handled. The disadvantage is that the electrolysis requires expensive current and is not easily scaled to large industry applications.

Other future production processes

Photochemical Production

The basic idea behind this technology is to use the high energy photons in the solar radiation to split water. To this end special semiconductor material is used which provides band width for absorption suitable for the splitting of water. Additionally catalytic materials are required to support the conversion.

Possibly combinations of photochemical and thermochemical cycles will provide higher efficiencies and easier scaling.

Radiolysis

Radiolysis is the splitting of molecules, in particular water by radiation. The radiolysis process consists of several sub-processes with different intermediate products:



In biological systems is the radiolysis an essential step in the damaging mechanism of the radiation. Especially the formation of the OH- radical with its high reactivity is able to induce permutation or even destroy genetic material.

In nuclear reactors the energy of the fission reaction is released as α -, β - or γ -radiation or is transported with neutral fission products or neutrons. The transferred energy is measured as a linear energy transfer LET value. The conversion ratio G depends on the LET and defines the number of converted molecules per 100eV energy absorbed. For the hydrogen production additionally the thermodynamic state and the degree of turbulence in the radiated water influences G. Some typical values of G for different radiation types and water phases are

$$G(\text{H}_2) | \gamma (60\text{Co}) \text{H}_2\text{O}(\text{l}) = 0.45$$

$$G(\text{H}_2) | \gamma (60\text{Co}) \text{H}_2\text{O}(\text{g}) = 5.2$$

$$G(\text{H}_2) | (210\text{Po}) \text{H}_2\text{O}(\text{g}) = 1.8$$

In a homogeneous reactor with a G (H₂) of 1.6 around 28 kg H₂ could be produced per day and per thermal MW power. Higher attractiveness provides the radiolytic splitting of CO₂. The resulting can be used in a shift reaction with steam to produce hydrogen and CO₂ for recirculation.

In the currently installed nuclear reactors, in particular in the boiling water reactors, there is an unwanted radiolysis process producing considerable amounts of hydrogen and oxygen in stoichiometric composition, also named radiolysis gas. When these non-condensable gases accumulated in cold traps this can cause hazards. In the German reactor Brunsbüttel and in the Japanese BWR in Hamaoka this mixtures combusted with a start pressure of 7 MPa causing damage in some secondary steam loops. Although there was no direct threat to the nuclear containment a careful revision of the hydrogen management routines has to be provided for a restart of the involved reactors.

Cost Comparison

Hydrogen is always at least as expensive as the primary energy it is made. The price of the primary energy has to be divided by the overall energy conversion efficiency and capital costs have to be added. Additionally availability and maintenance cost of the involved technology contribute to the final pricing.

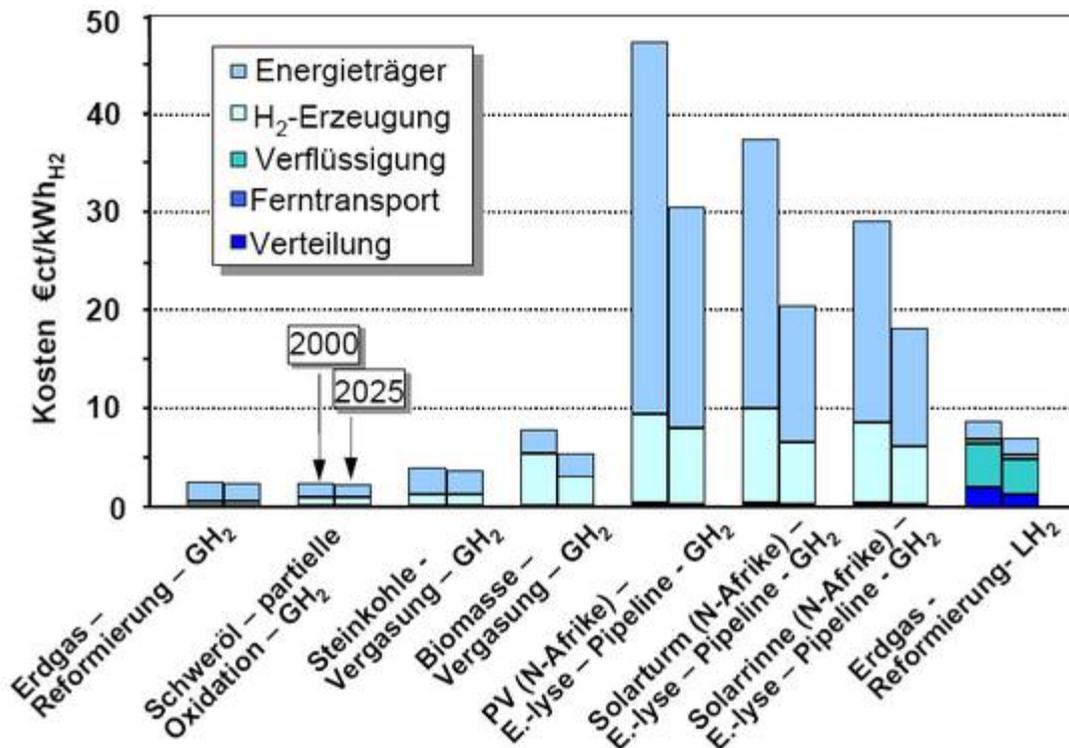


Figure 21: Hydrogen cost for different production paths
(1kWh = 3.6 MJ; cost / kWh x 33.3 → cost / kg; cost / kWh x 280 → cost / GJ)

IN the year 2007 at the demonstration site CEP in Berlin the costs for a mix of CGH₂, produced from renewable sources, and LH₂, provided from a SMR plant, were 12 €/kg. Both products are delivered by discrete transport.

STORAGE AND TRANSPORTATION [17]

Hydrogen has a very high gravimetric energy density. This makes hydrogen the preferred rocket fuel for space crafts for instance.

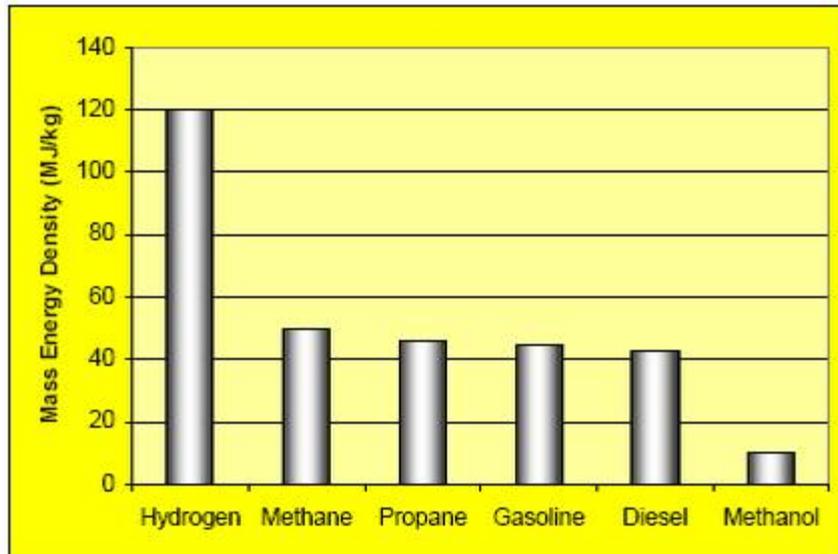


Figure 22: Comparison of Gravimetric Energy Densities

However, with its low density a reference mass of hydrogen. Say 1 kg needs a relative large space. This makes storage storing hydrogen a challenge if space is limited like for transport applications.

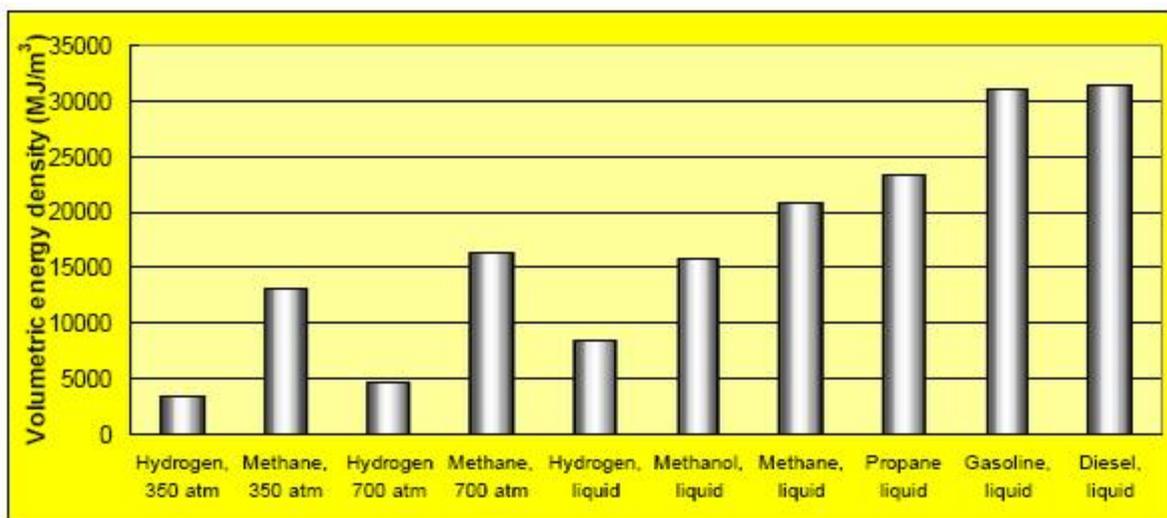


Figure 23: Comparison of Volumetric Energy Densities (Hydrogen at NTP 11 MJ/m³)

Additionally the properties of some construction materials like high strength standard steels show negative deviations when in contact with hydrogen. Hydrogen embrittlement and

hydrogen supported stress corrosion are some prominent examples here. Also the high diffusivity induces specific demands for hydrogen containers.

Practically there are three different ways of storing hydrogen in small space:

- Compression
- Liquefaction
- Physical or chemical binding to liquid or solid storage materials.

Compressed Gaseous Hydrogen CGH2

So save space hydrogen may be compressed to 20-100 MPa. This makes sense as many applications need hydrogen at higher pressure levels anyway. Limitations for storing hydrogen in a compressed form are the real gas effects which make compression to even higher pressures inefficient, and the availability and additional weight of high pressure vessels.

Especially above 15 MPa the deviations from ideal gas behaviour become evident (more than 10% in density). Instead a van-der-Waal equation of state (eos) or other advanced eos usually applying virial coefficients might be applied. However, for technical applications like compression the approximation with real gas factor Z, also named compressibility factor, is reasonably exact enough. With the definition of dimensionless Z

$$Z = \frac{pV}{RT}$$

the following values are determined

p [MPa]	0.1013	5	10	20	30	35	40	50	70	100
Z	1	1.032	1.065	1.132	1.201	1.236	1.272	1.244	1.489	1.702

Table 3: Real gas factor Z at 20°C

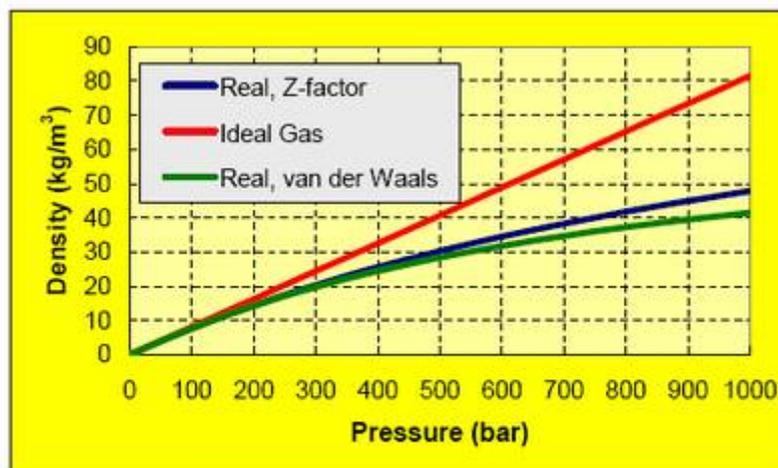


Figure 24: Comparison of the basic eos

This graph is easily transferred in a volumetric energy density graph including the liquid hydrogen LH2 as a reference:

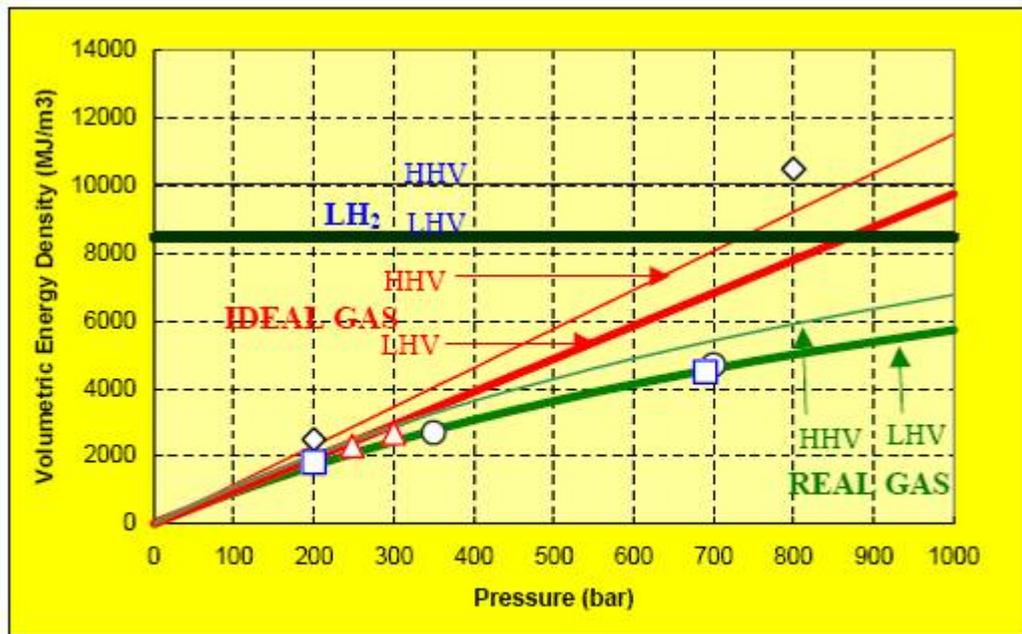


Figure 25: Volumetric Energy Density versus Pressure

Compression Work

To determine the required compression work again an eos of the gas applicable to the respective pressure range has to be used. Additionally a caloric equation is needed. To simplify the calculations an ideal isentropic adiabatic process is considered.

In general the technical compression work is the integral of specific volume (reverse density) over pressure:

$$W = \int_{p_1}^{p_2} v dp = \int_{p_1}^{p_2} \frac{dp}{\rho}$$

With the above idealisation and with the ideal gas eos this turns into:

$$W_{\Delta S=0,ideal} = \frac{\gamma}{\gamma-1} RT_1 \left[\left(\frac{p_2}{p_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right]$$

with p_1 as the starting pressure and

$$\gamma = \frac{c_p}{c_v} = 1.4$$

the ratio of specific heats. The required work for $T_1=20^\circ$ is plotted as a black line in Fig. 26.

The real compression is not isentropic. So an approximation might be via the efficiency of an adiabatic compression process according to:

$$W_{\text{compression}} = \frac{W_{\Delta S=0, \text{ideal}}}{\eta_{\text{adiabatic}}}$$

$\eta_{\text{adiabatic}}$ is around 0.75-0.85. Additionally multiplying the efficiency of the electric drive of the compressor with about 0.9 one might estimate the really required energy for compression.

Alternatively the real process might be also approximated by an interpolation of the above ideal isentropic adiabatic process and an isothermal process. To this end the work for an isothermal compression may be calculated as follows.

For an ideal gas:

$$W_{\Delta T=0, \text{ideal}} = RT \ln \frac{V_2}{V_1} \quad (\text{red line in Fig. 26})$$

For a van-der-Waals gas:

$$W_{\Delta T=0, \text{real}} = RT \ln \frac{V_2 - b}{V_1 - b} + \frac{a}{V_2} - \frac{a}{V_1} \quad (\text{green line in Fig. 26})$$

With the compressibility factor

$$W_{\Delta T=0, Z} = ZRT \ln \frac{V_2}{V_1} \quad (\text{blue line in Fig. 26})$$

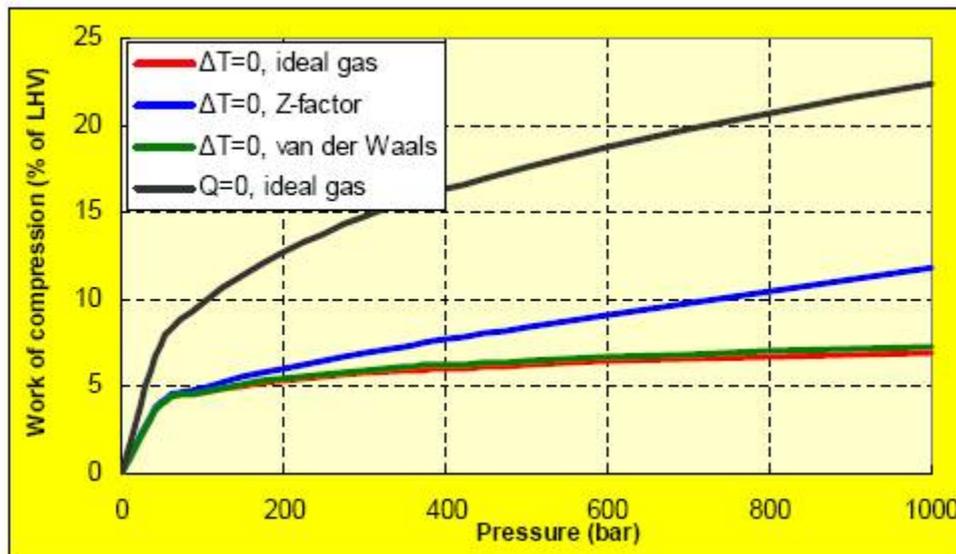


Figure 26: Work of Compression as a ratio of the LHV (120 MJ/kg) versus Pressure

The real compression follows in fact a polytropic change of state. The required work which is higher than the isentropic, adiabatic work is calculated from:

$$W_{\text{polytropic}} = \frac{n}{n-1} RT_1 \left[\left(\frac{p_2}{p_1} \right)^{\frac{n-1}{n}} - 1 \right]$$

Again the actual work of compression is larger than the calculated work and:

$$W_{\text{compression}} = \frac{W_{\text{polytropic}}}{\eta_p}$$

The polytropic efficiency η_p is often the efficiency quoted by manufacturers. From this efficiency useful relations can be derived, for instance the polytropic coefficient:

$$n = \frac{\eta_p \gamma}{1 + \eta_p \gamma - \gamma}$$

The conclusion is that the isothermal process is the most efficient one for compression. However, there is no straight forward technical realisation of this process. Instead it is approximated by a multistage polytropic compression with intermediate cooling. For this a cost benefit consideration will give an optimum for 4-5 pressure steps.

Compressor Technologies

Because of the small density and the high diffusivity special compressor technology is required. For high capacities ($>50000 \text{ Nm}^3/\text{h}$) as needed for the large process industry scales multi-stage radial compressors are applied.



Multi-stage radial compressor

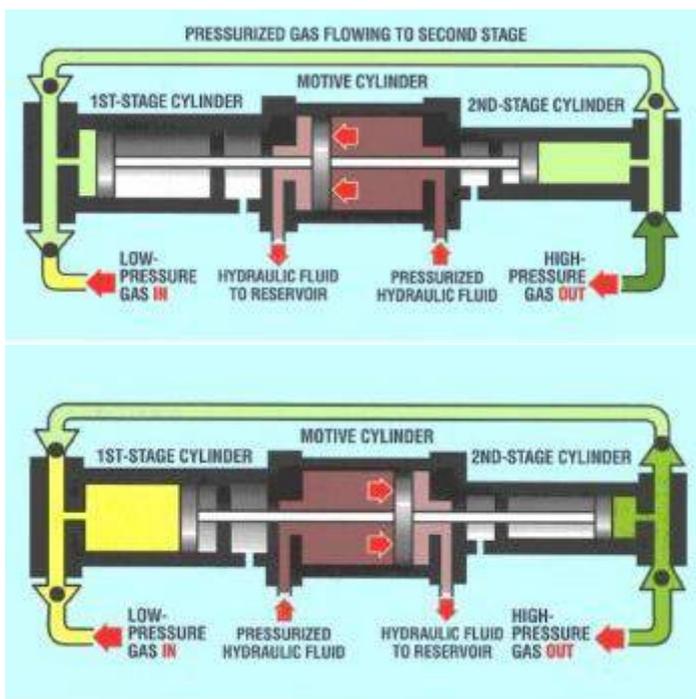
For small volume streams piston compressors are used. Depending on the hydrogen purity requirements three different sub-types are applied:

1. oil lubricated piston compressors only for applications where hydrogen is used for saturation of hydrocarbons or combustion. Not suitable for fuel cell usage or later liquefaction
2. water lubricated piston compressors, when small hydrocarbon remainders are not acceptable.
3. Non lubricated piston compressors for highest purity requirement. Piston rings made from PTFE (polytetrafluoroethylene) may be used. Leaked gases may be recycled.

A variation of the classical piston compressor are intensifiers. An intensifier consists of a hydraulic cylinder, so-called motive cylinder, coupled with two gas cylinders. The most common arrangement is a hydraulic cylinder in the centre with a gas cylinder on each side of the hydraulic cylinder.

In operation, the force of the hydraulic pressure acting on a hydraulic piston is balanced by gas pressure acting on the gas piston. As the hydraulic cylinder strokes, gas is compressed and displaced from one gas cylinder while simultaneously filling the other gas cylinder.

Intensifier designs are flexible and multiple arrangements are possible. The most common arrangements are double-ended machines that are either single stage or two stage units. Single ended units are also available [<http://www.hydropac.com/HTML/hydrogen-compressor.html>]



Stage 1, Stage 2 and realisation of a two stage intensifier (source: Hydro-Pac)

Smaller volume streams are also compressed by screw compressors. This is usually applied in small liquefaction processes.

Another alternative is the compression of the nearly non-compressible liquid hydrogen and the following evaporation. Then the efficiencies of, the required energies for the liquefaction have to be compared to these of the compression of the gas phase.

The costs for compressor technologies are compared in Fig. 27.

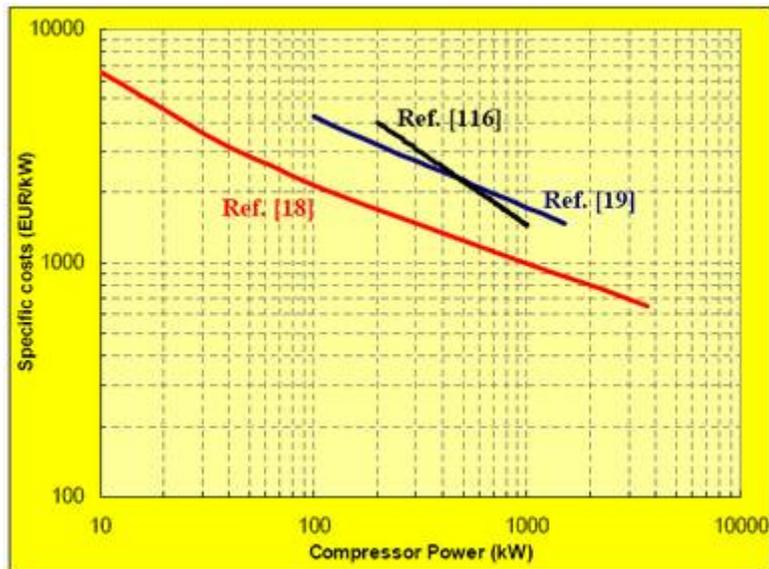


Figure 27: Costs for compressors according to [18][19] and [24]

Pressure Vessels

Storing pressurised gaseous hydrogen is currently the most developed and marketed technology. The design follows good engineering practice and is optimised regarding weight and performance. Steel vessels designed to store natural gas up to 35 MPa might be used directly or only with minor modifications. Of course a formal approval process has to indicate the applicability to hydrogen.



Figure 28: Large Storage Vessels for industry customers, 5-7 MPa, stationary (Source: Linde)

For mobile applications besides the volumetric density also the gravimetric aspect is important. So, for a hydrogen driven car the tank system has to store more than 7% weight hydrogen to be acceptable for automotive OEMs. This explains the necessity for light-weighted structural material like compound carbon fibre etc.

For automotive applications several additional demands regarding the operational conditions have to be accounted for. The refuelling of these vessels requires an excess pressure of about 15% and the actual refuelling process has to be in a comparatively short time (~3 min) to comply with the usual rest times at the refuelling stations. To allow for appropriate filling the at least for the 70 MPa target the gases have to be cooled down before the refuelling. So the vessel will undergo a cyclic mechanical and thermal loading.

There are four different types of pressure vessels currently marketed or developed:

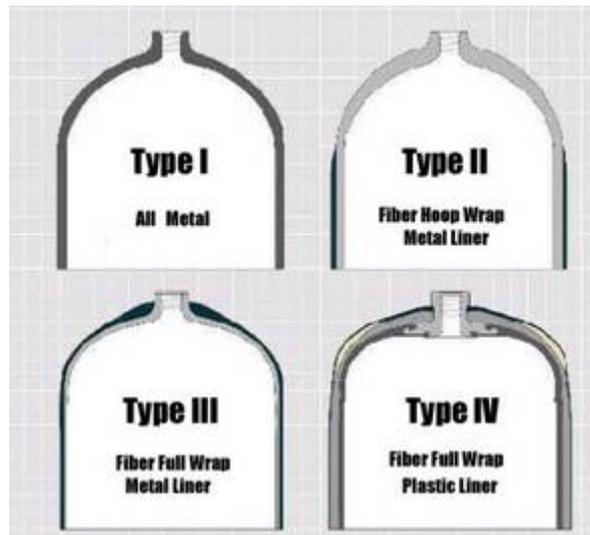


Figure 29: Types of Pressure Vessels

(Type I: full metal; Type II: load carrying liner wrapped with GFK/CFK; Type III: metallic liner only as diffusion barrier and load carrying outer fully wrapped CFK layer; Type IV: fully wrapped CFK with a plastic liner); see [www.eihp.org]

The current research is concerned with the safety testing like non-destructive inspection of Type III and Type IV vessels in particular. Cost reduction and industrial scale-up are other key issues; see [www.storhy.net].



Figure 30: Dynetek CGH2 Storage for the MAN Buses at the Munich Airport.
15 vessels, 25 MPa, total weight 960 kg, 2.58 m³

Some producers of these pressure vessels are Dynetek, COMAT (Germany), Composites Aquitaine, CEA, Ullit (France), Faber (Italy), Quantum (USA), and Raufoss Fuel Systems.

Liquid Hydrogen LH2

The boiling temperature of hydrogen is 20.39 K at 0.1013 MPa for ortho-H₂ and 20.26 K for para-H₂. Like other gases, like nitrogen, also hydrogen may be liquefied for a simplified transport or storage. Compared to CGH₂ LH₂ has a considerably higher volumetric energy density; see Fig. 25. Besides storing hydrogen LH₂ has direct applications as a fuel in space craft engineering and in basic research, bubble chambers for instance.

Liquefaction Process

The liquefaction is achieved by cooling below the boiling temperature. To this end there are several methods:

- with cold media like liquid helium in heat exchangers
- by expanding in turbines
- phase change, evaporation
- by the Joule-Thomson effect below the inversion temperature
- by the magneto-caloric effect.

As hydrogen has a negative Joule-Thomson effect (positive coefficient) at NTP it has to be pre-cooled by liquid nitrogen LN₂ for instance. With 77K the boiling temperature of LN₂ is far below the inversion temperature of hydrogen, which allows the Joule-Thomson cooling in a second step.

The magneto caloric effect is initiated by applying a magnetic field on a magnetic material. If this changes its magnetic properties this may be accompanied by a change in temperature. So

the demagnetisation of a material close to its Curie temperature can generate a temperature decrease of 1K per 1 T.

The ideal reference for the evaluation of real liquefaction processes shall be:

- 1) an isothermal compression followed by
- 2) an isentropic decompression.

The minimum needed energy may be retrieved from Fig. 31 and is about 11.8 MJ/kg. This value also includes the o-p-shift. Of course the actual value depends on starting pressure and temperature and the initial o-p-H₂ ratio. In average 15 times more energy is needed compared to the liquefaction of a kilogram of nitrogen.

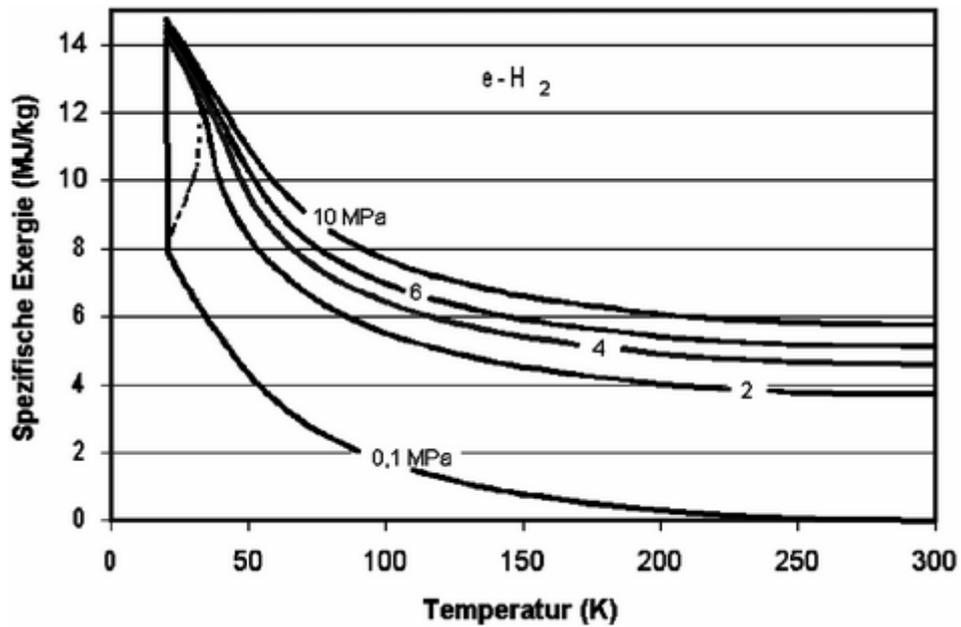


Figure 31: Minimum energies for compression / liquefaction of 1 kg starting from NTP

The real losses are indicated in the Sankey-diagram in Figure 32.

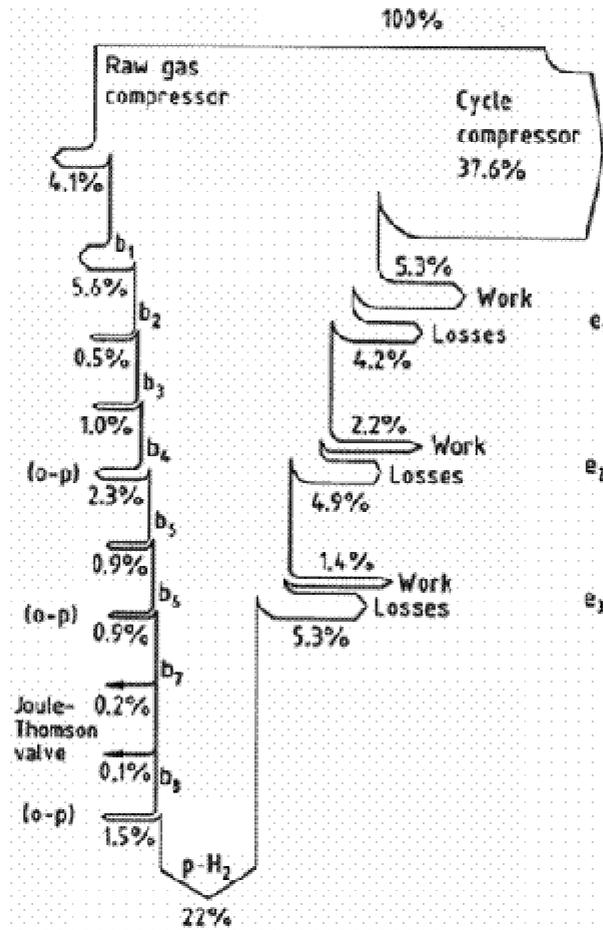


Figure 32: Sankey-Diagram

With compressors with an efficiency of about $\eta=0.8$ a total efficiency of 0.22 is reached. This corresponds to a specific energy demand of 56 MJ/kg with a 98% p-H₂ in the product.

In large facilities the thermodynamic efficiencies may be increased to 30%-35% (45-50 MJ/kg) by the following measures:

1. LN₂ for precooling,
2. more efficient compressors and turbines,
3. improved insulation,
4. more efficient heat exchangers and reactors.

By a continuous re-cycling of the boil-off in a Joule-Thomson process partial solidification in slushy hydrogen SLH₂ can be produced. This is usually used for rocket fuel.

Liquefaction Plants

Currently there are only a few hydrogen liquefaction plants worldwide, there are currently three in Europe, one in France, one in Netherlands, one in Germany the largest with 5t/d. The world largest with a capacity of 60 t/d is operated in the USA. This production serves mainly space craft applications, rocket fuel, etc. But also general supply of industry customers with

LH2 seems to be the cheaper and therefore preferred long-term path, because of the smaller transportation costs and the more diverse end use.

Large liquefaction plants use the Linde-Process, with expansion in turbines which is only possible with a certain distance to the 2-phase domain. The final expansion into the 2-phase domain is usually implemented with Joule-Thomson expansion valve.

Small units use the Linde-Sankey-Process with an initial LN2 cooling at a lower pressure level in general.

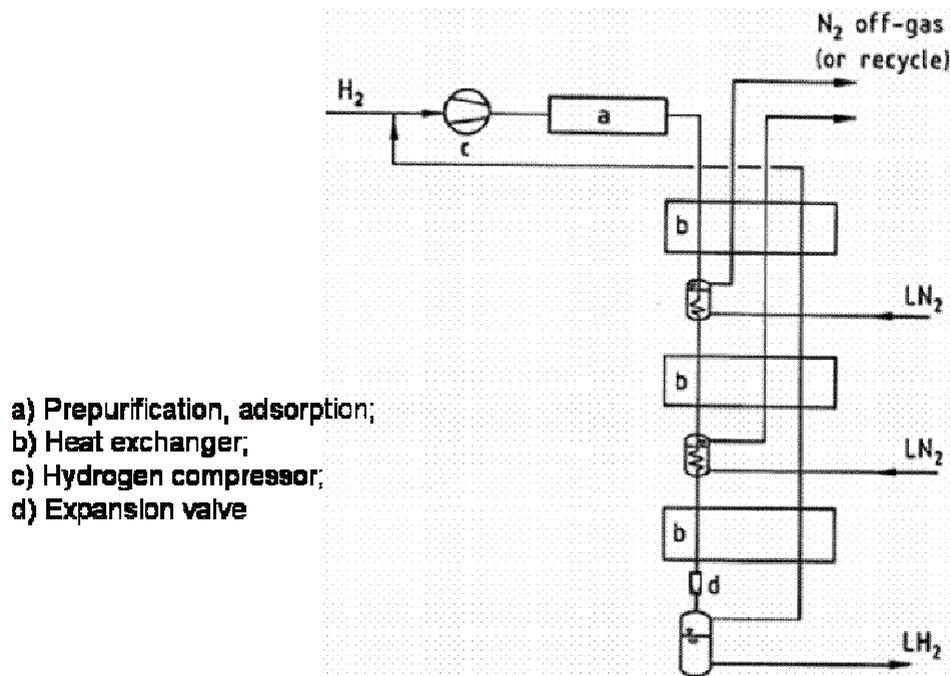


Figure 33: Linde-Sankey-Process

If the LH₂ is consumed immediately there is no need for the o-p-shift. In all liquefaction processes an initial cleaning stage is required, however. Without this careful cleaning frozen impurities could block the piping, which could lead to unavailabilities or, worse, to unsafe conditions to high level of impurities

The usual purities of 99.5% after the electrolysis or ~ 99.99% after a PSA in a reformer (SMR) may be improved by:

- adiabatic catalytic removal of oxygen at NTP with recombiners (after electrolysis);
- adsorption drying (also after electrolysis);

The heat generated in the o-p-conversion ($\Delta H=1.45$ kJ/mol) has to be removed also. The conversion is induced by catalysts made of active carbon or iron oxide in the heat exchangers.

- a) Adsorptive and catalytic precleaning;
- b1 – b8) Heat exchangers;
- c) Adsorbers at LN2 temperatures;
- d) o-p conversion reactor;
- e1 – e3) Expansion turbines;
- f1 – f2) Expansion valves;
- g1) Compressor;
- g2) Recycle compressor for H2 coolant cycle

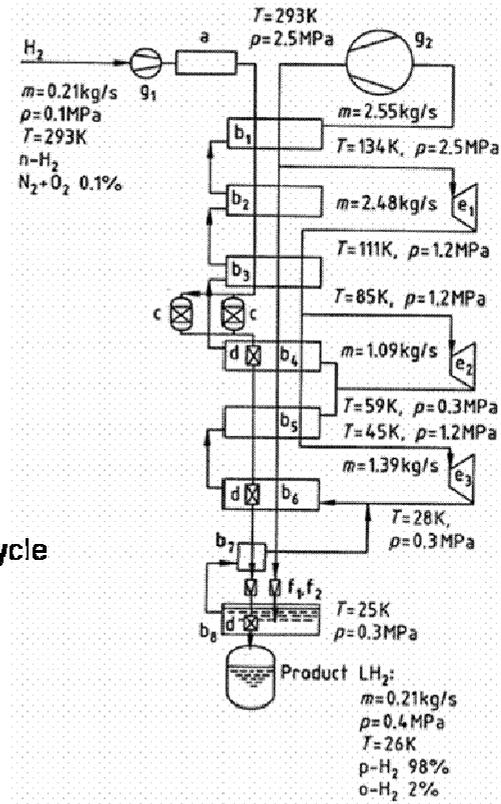


Figure 34: Linde-Process

LH2 Storage - Cryostats

There are two main classes of LH2 storage vessels: for stationary and for mobile applications: Representatives of both classes are shown in Figs. 35 and 36.



Figure 35: 3800 m3 LH2 Storage at Kennedy Space Flight Center in Florida (Source NASA)

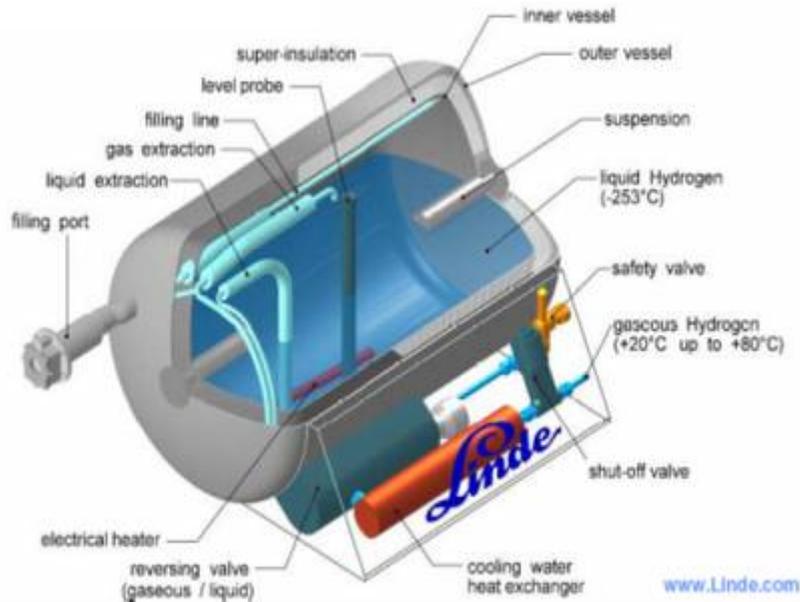


Figure 36: Schematic presentation of a 0.18m³ LH₂ Tank for automotive application (BMW 750h) produces by Magna Steyr, (Source: Linde)

The cryostat usually consists of at least 2 austenitic steel walls, in between there is „super insulation“. Additionally the volume with the super insulation may be evacuated. This reduces the losses for the small automotive cryostat to the order of 1W. This input leads to evaporation and via a pressure limiting valve to the boil-off. The boil-off corresponds to a loss of 1.5% of the stored energy per day. The typical stored mass of about 7kg will be lost in 2 months if the car was not used in this phase.

The boil-off management may reduce these losses or at least reduce the associated risk with released hydrogen by

- cold combustion with air in catalytic recombiners
- storing the boil-off gases in metal hydride storages
- re-cycling in a re-liquefaction
- direct energetic use, in a fuel cell for instance.

Of course the involved temperatures are demanding not only regarding the design of the actual storage but also regarding the compatibility of all connected technologies, like measurement techniques, armatures, valves, piping.

Solid Hydrogen Storage

(see www.storhy.net/train-in/PDF-TI/19_STORHY_Train-IN_Session_3_1_MFichtner.pdf)
 For the storage of hydrogen in solid materials two mechanisms are used: physisorption and chemisorption. In the physisorption the hydrogen molecules are absorbed by the far reaching van-der-Waals forces.

The chemisorption functions in three steps:

- 1) absorption of the molecules (similar as for physisorption)
- 2) dissociation of the molecules in atomic hydrogen

3) embedding of the atoms in the lattice

Besides the high volumetric energy density solid storage offers advantages regarding the safety. Only moderate temperatures and pressures are needed for operation, and in an accidental loss of confinement only by if heated further hydrogen is released.

Metal Hydrides

Metal hydrides are based on metallic compounds, which store hydrogen via chemisorption. The solid reaction during loading the hydrogen releases heat at relative high pressure. For releasing the hydrogen again the pressure has to be decreased and heat has to be delivered. This loading and unloading cycles may be repeated without reducing the storage capacity. For an automotive application storage systems have to optimise the thermodynamics including temperatures and pressures and the loading / unloading kinetics besides the storage densities itself. For the latter the automotive industry requires 7wt% at least.

Interstitial hydrides offer gravimetric storage densities of about 1.8wt% at 60-70°C or up to 3wt% for quasi crystal Zr-Ti-Ni alloys, which show limited reversibility however.

Magnesia compounds reach in laboratory scales up to 5-6wt% at 260-280°C and 0.1 MPa. However, their kinetic performance has to be improved.

Complex light metal hydrides, like alanates and boranates, absorb up to 8wt% at 180°C and 0,1 MPa, but the unloading is still far to slow. Catalysts like Ti or Zr are investigated.

In the Task 17 of the International Energy Agency IEA [www.ieahia.org] a database of metal hydrides has been developed, which contains more than 2400 compounds. A conclusion from this exercise is that for reversible storage systems at intermediate temperature level light metals like Na, Li and Al are the most promising candidates. Further development and research are required for cyclic stability, catalytic material, thermal management in combination with fuel cell systems etc.

Transport

Hydrogen may be transported discontinuously in storage containers or continuously in pipelines.

Discontinuous Transport

Discontinuous transport is realise in the pressure or cryogenic vessels described in the previous section. This kind of transport is, in particular for CGH₂, relatively expensive because of its low volumetric energy density. Industry gas providers prefer to distribute LH₂ at least for a medium to high demand customer.

Trucks equipped with large cryovessels may transport up to 3 tons of LH₂ what is about 10 times more mass than may be transported with a CGH₂ truck.



Figure 37: CGH2-Truck (40t total weight) with 530 kg CGH2 and LH2-Truck with 3370 kg LH2 (less than 40t total weight)

NASA operates besides such truck for land transport also small LH2 ships for sea transport. Design basis were LNG tank ships. So these ships have a double walled hull and spherical tanks. As LH2 needs for the same energy 2.5 times the volume of LNG comparatively large tanks had to be installed. Most of the losses (approximately 10%) are caused in the loading and unloading processes.

In the phase III.0-4 of the EQHHPP project a container based transportation concept with a multi layer super vacuum insulation has been developed. This concept promoted 13m containers and later 26m containers suited also for railway transportation in Europe, Northern America and Japan. The autonomy of these containers filled 90% with LH2 was 30 days. During these 30 days no boil-off had to be released. To a small degree already now such containers could be transported with the current container ships. All in all these containers would reduce the transportation costs to 50% compared to the dedicated LH2 tank ships.



Figure 38: LH2 Tanker

Continuous Transport - Pipelines

The transport of hydrogen in special high pressure pipes for moderate distances up to few hundred kilometres is a well established distribution technique. Since 1938 the chemical industries in Hüls, Ruhr area, Germany, operate a hydrogen pipeline with a length of 215 km, an inner diameter of 168-273 mm, and a maximum pressure of 2.5 MPa.

Linde operates the former East Germany Leuna pipeline networks which transport CGH₂ at a pressure up to 2 MPa to a maximum distance of 50 km. Air Liquide operates similar hydrogen pipelines in Belgium and France with a reach of 290 km with different diameters and pressures from 6.5-10 MPa. Also in Rotterdam there is a CGH₂ pipeline, 50 km in length. In USA there are several pipeline networks for CGH₂. Air Products operates in Houston, Texas, a system with a total length of 232 km since 1969. It uses diameters of 114-220 mm and pressures up to 5.8 MPa. In New Orleans, Louisiana, USA, there is a 96 km long pipeline, in the Canadian Alberta region there is a 22 km long H₂-pipeline.

All these distribution systems are operated at ambient temperatures and with a dry gas so far without any incidences or accidents. Of course this is not easily extrapolated to the larger future systems operated maybe at higher pressure levels.

There are investigations in Japan and in Europe how the existing natural gas pipeline systems might be used for the transportation of hydrogen. The first results showed that there are no obstacles to transport mixtures with a ratio up to 50% hydrogen mixed in the natural gas in the existing networks [www.naturalhy.net]. However, separation of gases for a use in low temperature fuel cells for instance is a major effort.

Some elder pipelines may be equipped with special liner so that they would carry even pure hydrogen. Of course the high diffusivity and the special effects on material have to be considered. However, it may be concluded that a broad distribution of hydrogen even with the existing pipeline networks would require only moderate investments. As there is a continuous replacement of old pipeline parts anyway, these added costs are worth while the additional features provided.

Figure 39: The European natural gas network

As the low volumetric density requires for similar power in the transport higher pumping efforts. However, the total costs and losses per MW and km are comparable to standard electricity transport



Hydrogen Pipeline

In the Kennedy Space centre are even pipelines for LH₂. However, the installed length is limited to some 100 m because of the relative high boil off losses. Currently for LH₂ pipeline transport 50 km are considered maximum.

A more advanced solution offers the coupled transport of LH₂ and superconducting electrical power and information. Thermodynamic considerations favour a system where LN₂ is transported oppositely as a heat shield, see ICEFUEL project. Still the limitations described before hold and therefore this technology is deemed to provide a distribution opportunity in residential areas with a refuelling station as a central node not further separated than a few km in maximum from the consumer.

Comparison of Storage and Transportation Techniques

Pressure vessels are state-of-the-art, available at reasonable prizes. Of course the high pressure vessels up to 70 MPa need some further evaluation also under safety aspects (local flamelet impact, non-destructive testing, etc.). The infrastructures including dispensing technologies are available and standardised.

LH₂ has a higher volumetric energy density compared to CGH₂. However, handling cryogenic liquids is not an established technology in particular for the private end use. Recent developments for appropriate new compound materials and insulations will make this option in the mid-term attractive for the distribution at least. Although the large scale production of LH₂ requires about the double energy than the production of CGH₂, most of the difference is equalised in the more effective transportation. Highly efficient cryogenic compression, less complex equipment at the refuelling station and a slightly better safety record will give further motivations for the LH₂.

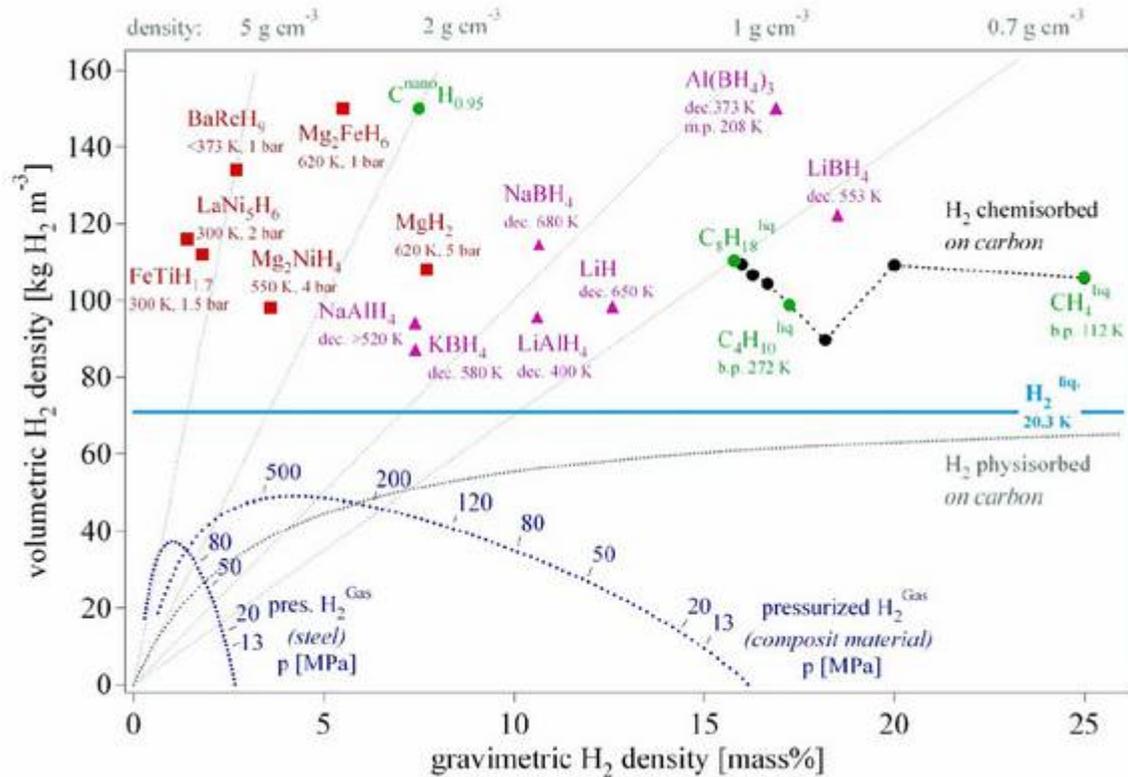


Figure 41: Volumetric versus gravimetric storage densities of storage systems

Solid storage is the long term solution, as even better storage densities and better safety performance favour this solution.

ENERGETIC USE

Fuel Cell [31]

Introduction

Systems for high efficiency energy conversion have an utmost importance, as they allow saving energy without reducing standards of living. The conventional processes for converting chemically stored energy in mechanical energy are heat power cycles. These cycles use heat as an intermediate energy currency. According to the 2nd law of thermodynamics the conversion of heat in mechanical energy limited. A perfect cycle like the Carnot cycle has still an efficiency around 50% due to limited maximum temperature and pressures at which the heat can be supplied to the machine. Without huge efforts, like coupling different cycles optimised to the different temperature levels the efficiencies of these machines will be always in the order of 50%-60% (depending on the size).

With the electrochemical processes these obstacles are removed as they convert chemical energy in the even more valuable electrical energy without the intermediate step of heat. However, the 2nd law of thermodynamics hold and even this energy conversion is not

possible without principle losses. Theoretical efficiencies of up to 83%, respectively 95%, are possible (see following section) even in small units.

This offers completely new schemes for energy supply, usage and new potential for energy saving and reduced environmental impact.

Although fuel cells have a quite long history their development was blocked by the dominance of alternate current technologies and the technical development and performance of combustion engines favoured by very cheap primary energy. Only in the 60ies the fuel cell development was pushed by the „space race“ and in the 70ies by the „energy crisis“ and the further price increase for oil. The very sensitive alkaline fuel cell was then replaced by the more stable systems using acidic electrolytes. In the 80ies high temperature fuel cells, like the molten carbonate or the solid oxide fuel cell - were further developed, suitable even for other gases like methane and also suitable for operations with a coupled steam process for instance. The current research efforts are targeted to new membranes and catalysts for the high temperature polymer electrolyte fuel cells with higher power densities, less sensitivity to impurities in the gases supply and a better low temperature performance. These systems are the most promising candidates for the currently designed fuel cell vehicles FCV.

Fuel cells differ from galvanic cells as their chemical energy is supplied from outside, whereas batteries include the chemical storage. Although fuel cells have still a relatively low power density they are easily configured in modular systems.

The (potential) applications reach from

- very small microsystems energy supply
- replacement of batteries in portable systems like laptops, digital cameras,
- stationary or mobile auxiliary power units, to
- large blocks for industry power supply.

Fuel cells are easily maintained and their availability is very high. They fuel cell stacks highly efficiently produce electrical current without local emission of pollutants. The stacks themselves even do not produce any noise.



Figure 42: Scaling of fuel cells

Two key problems are still to be resolved for a broader market entry: the price per kW has to be reduced further (factor 5-10), in particular for the automotive applications, and the lifetime of the membrane electrode assemblies has to be improved for stationary applications (factor 2-3) in particular when operated with natural gas.

Working Principle and Efficiencies of a Fuel Cell

In fuel cells hydrogen (or other organic material in special cases) and oxygen react to produce direct electrical current and water. This is the reverse reaction of the electrolyser (see section above). For this reaction both reactants are in contact with the two electrodes, the anode and the cathode, but may not come in contact directly with each other. So they are separated by a membrane which usually acts also as electrolyte. The electrolyte allows ions to transport the electrical current but does not allow electrons to pass. The combination of the membrane and electrodes is called membrane electrode assembly MEA.

The following reactions are usually supported by catalysts: hydrogen oxidation at the anode (delivery of electrons) and oxygen reduction at the cathode (electron uptake).

Depending on the actual ions transported in the electrolyte, acidic or caustic electrolyte, hydrogen is formed on the cathode or anode respectively.

The reduction and oxidation processes on the electrodes yield a voltage difference which may produce a direct electrical current in an external electrical circuit.

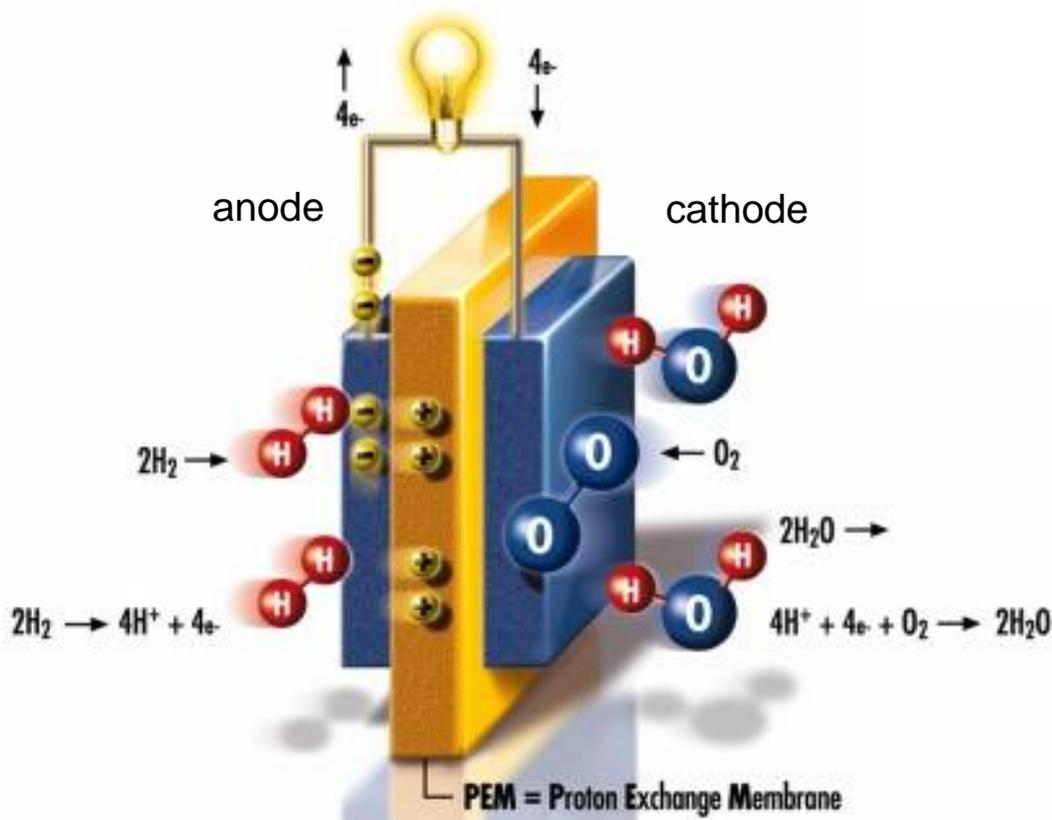
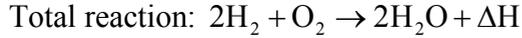
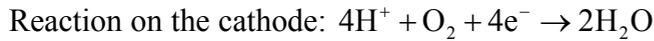


Figure 44: Working principles of a (PEM) fuel cell [www.h-tec.com]

The reactions in a hydrogen fuel cell are summarised by



The driving forces for these reactions are the different chemical potential of the partial reactions. Without the ion conduction in the electrolyte or without the current in the external circuit a thermodynamic equilibrium (voltage) is generated and the reaction stops.

Similar as for the electrolyzers the theoretically maximum voltage may be calculated based on the thermodynamics. The so-called thermoneutral or enthalpic cell voltage is:

$$U_{\text{th}}^u = \frac{\Delta H_0^u}{nF} = \frac{\Delta G_0^u + T\Delta s}{nF} = 1.25\text{V}$$

$$U_{\text{th}}^o = \frac{\Delta H_0^o}{nF} = \frac{\Delta G_0^o + T\Delta s}{nF} = 1.48\text{V}$$

In particular in the high temperature fuel cells, the product water will be in the gaseous phase the lower reaction heat yielding the above voltage of 1.25 V. As in energy technologies the lower reaction heat serves as a reference the 1.25 V value has to be chosen for consistent comparisons with conventional technologies.

Due to the described thermodynamic constraints only a fraction of the enthalpy, the Gibbs potential G , may be used for the voltage generation, an irreversible part $T\Delta S$ is transformed in heat. This defines the reversible cell voltages

$$U_{\text{rev}}^u = \frac{\Delta G_0^u}{nF} = 1.19\text{V}$$

$$U_{\text{rev}}^o = \frac{\Delta G_0^o}{nF} = 1.23\text{V}$$

This again allows defining an ideal efficiency of a fuel cell

$$\eta_{\text{max}} = \frac{\Delta G}{\Delta H} = 1 - T \frac{\Delta S}{\Delta H}$$

which is $\eta_{\text{max}} = 83.3\%$ for liquid water as product under NTP or 94.5% for steam as a product.

Besides these theoretical limits in a practical situation there will be additional losses, which reduce even the equilibrium voltage. These losses are caused by the passage and transport of reacting gases at the electrodes, recombination losses on the catalyst and resistive losses of the ion and electron currents. Typically the losses at the anode are far smaller than on the cathode.

The voltage efficiency described the ratio of the actual voltage provided in operation and the reversible cell voltage:

$$\eta_U = \frac{\Delta U}{U_{\text{rev}}} = 1 - \frac{\Delta U_D + \Delta U_R + \Delta U_{\text{Diff}}}{U_{\text{rev}}}$$

with voltage drop due to a mixed potential (catalyst and oxidation of impurities on the cathode) ΔU_D , resistive losses ΔU_R , and the diffusion limitations of the gas supply / water removal ΔU_{Diff} . The

The total efficiency may be then determined from:

$$\eta_{total} = \eta_{max} \eta_U = \frac{\Delta U n F}{\Delta H(T, p)}$$

which is dependant on the operational state defined by temperature T and pressure p. Typical values for ΔU are 0.6 to 0.9V associated with total efficiencies up to 75%.

This total efficiency may not be mixed up with the system efficiency. A fuel cell needs additional equipment for the gas processing, like an air or oxygen compressor, low temperature PEMFC need a continuous supply of moistening steam, and also for some cases the fuel has to be cleaned before used. The generated heat has to be removed by cooling cycles. These additional devices need energy and reduce the efficiency to a maximum of 60% for the whole system, currently. However, there are some promises for an increase of this system efficiency by new membranes and other catalysts.

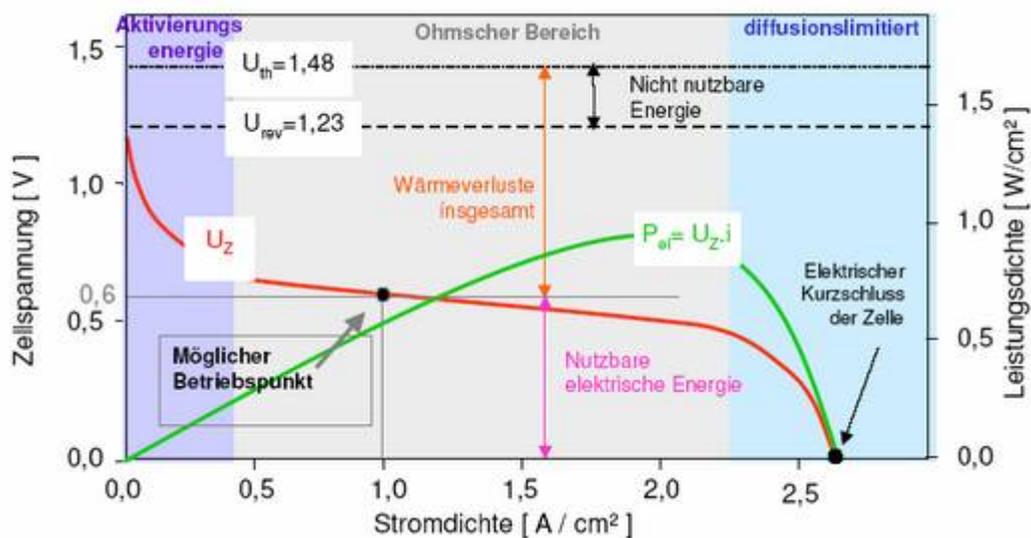


Figure 46: Schematics of a voltage versus current characteristic of a fuel cell

The characteristic in Fig. 46 implicitly depends on the operational state (temperature, pressure, oxygen ratio on cathode etc.) As the electrical power is the product of the voltage and associated current for a complete evaluation of the efficiency current efficiency or Faraday efficiency has to be accounted for.

The current efficiency described how each reactant contributes to the current I via:

$$\eta_{t,i} = \frac{I}{nFN_i}$$

So the current efficiency is specific for each reactant and dependant on the total current and thermodynamic state characterised above. The efficiency accounts for losses by recombination, parasitic reactions not contribution to the electric power, permeation losses via the electrolyte etc.

Fuel Cell Stack

The voltages derived above do not suffice for usual technical applications. So hundreds of MEA are connected in series by bipolar plates to so-called stacks providing direct voltages of up to 400V typically. Besides the electrical connection the bipolar plates serve also the purpose of gas distribution. To this end there are small channels on the bipolar plate on the anode side for the hydrogen on the cathode side for the oxygen, air respectively.

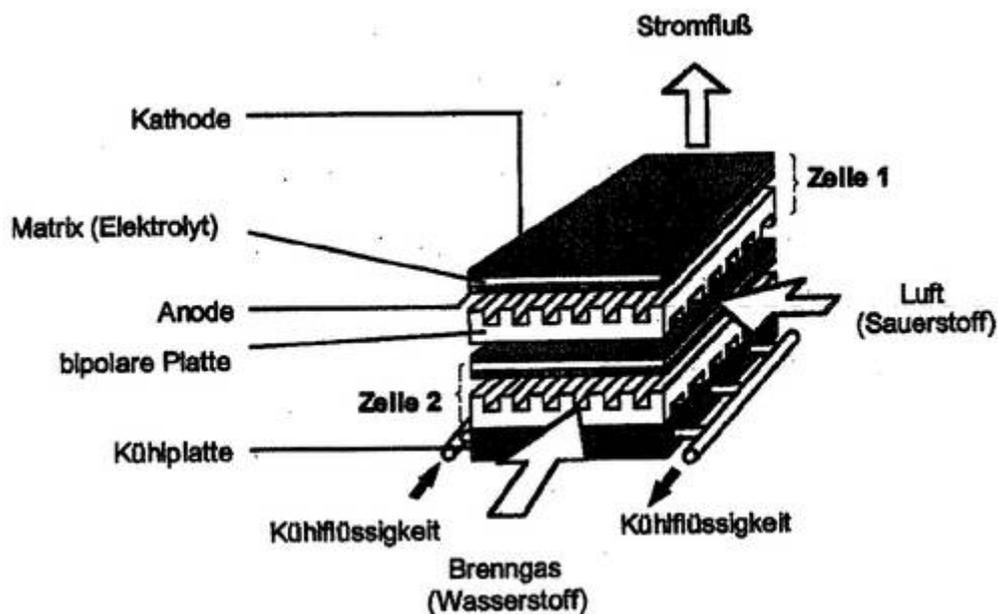


Figure 45: Principal set-up of a fuel cell stack

Fuel Cell Types

Fuel cell types are named by the electrolyte and grouped by the operating temperature. There are the following low temperature fuel cells (<100°C): alkaline fuel cell AFC, the direct methanol fuel cell DMFC and proton exchange membrane membrane fuel cell PEMFC. The middle temperature fuel cells are the high temperature PEMFC, and the phosphoric acid fuel cell PAFC. The high temperature fuel cells are the molten carbonate fuel cell MCFC and the solid oxide fuel cell.

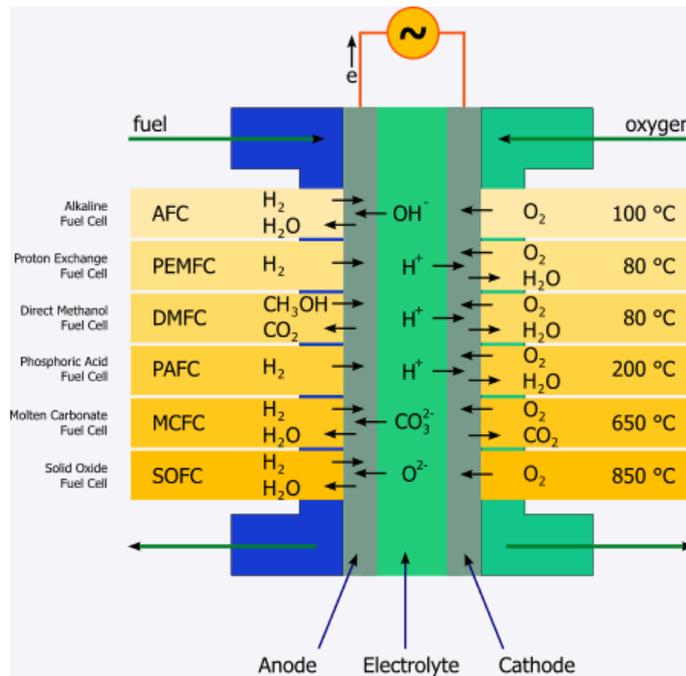


Figure 47: Fuel cell types with ions transported and operation temperatures

Low Temperature Fuel Cells

Low Temperature Fuel Cells work at temperatures below 100°C. For this operation mode catalysts are necessary to provide high enough reaction rates. The catalysts as well as the electrolyte require a high purity feed.

Alkaline Fuel Cell (AFC)

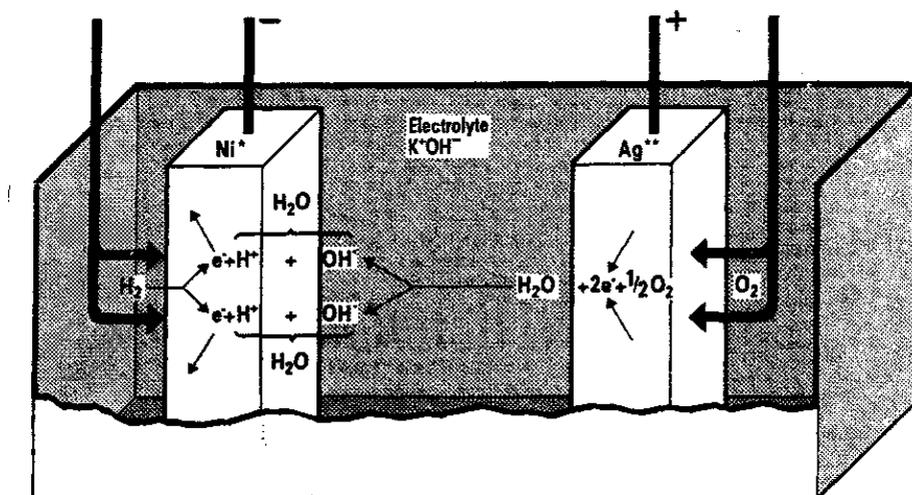
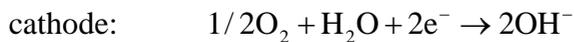
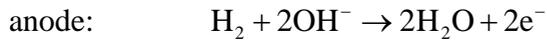


Figure 48: Schematics of an AFC

Alkaline fuel cell systems have been the earliest developments and matured already in the 50ies in particular in the USA and in Europe.

These fuel cells use a caustic potassium hydroxide solution (30 - 45 wt%). They can be operated in the wide temperature range of 20°C to 90 °C, typically at 60°C.

The reactions on the electrodes are:



The AFC works highly efficiently as the kinetics of the oxygen reduction prefers the caustic electrolyte to acidic media. On the other hand the serious disadvantage of this electrolyte is its sensitivity against carbon dioxide CO₂. Even a few ppm CO₂(> 10 ppm), like the concentration in air, will lead to the formation of carbonates, which are accumulated in the electrolyte and lead to a degradation of the fuel cell. Therefore the AFC needs high purity hydrogen and oxygen feed gases.

The low operation temperatures and the relatively small corrosivity of the potassium hydroxide solution do not cause serious material problems.

All material which favours the hydrogen dissociation like the noble metals platinum, palladium, ruthenium and their nickel or silver alloys maybe used as catalysts on the electrodes.

The anode material is usually Raney-nickel for the anode, respectively Raney-silver for the cathode, alternatively active carbon doted with noble metal particles. Raney-nickel is a pyrophore nickel based material which is produced by alloying pure nickel with silver, silicium or zink. After milling the non active metal parts are dissolved and a sponge-like metal structure remains, with a very high specific surface. The actual current conducting layer is made from pure nickel and connected to the electrode. The frames of the cells are made of plastics.

Other important components of an AFC are the electrolyte circulation and the reaction water separation.



Figure 49: AFC for the Space Shuttle (below)

The AFC is the most mature fuel cell type. It has proven its function and applicability in military and space applications, in the NASA Apollo and Space Shuttle spaceships for instance. For both applications costs are only secondary parameters. For other more conventional applications this type of fuel cell is less attractive because of the necessary cleaning efforts fro removing the CO₂ from the air or because of the additional transport

efforts for the alternatively used pure oxygen. Most companies formerly involved in the development of this fuel cell type have stopped further investments.

Proton Exchange Membrane Fuel Cell PEMFC (also Polymer Electrolyte Fuel Cell PEFC)

The electrolyte of the PEMFC is a thin gas tight, proton conduction plastic foil. It is perfluorated and sulphonated. The water content in the foil has to be kept at a certain level to maintain its ion conduction capability. This has to be guaranteed also when the cell is idling. To this end there is a continuous steam input in the electrolyte and the temperatures have to be limited by 100°C. Higher temperatures are only possible if a higher pressure suppresses the evaporation of the water in the membrane other new membranes materials are applied which do not need water. Also low temperatures below 0°C threaten the integrity of the classical membranes as the contained water freezes. To avoid this elder PEMFC needed an electrical heating keeping the temperatures above a critical limit.

- In the PEMFC the membrane has three functions:
Ion conductor as the electrolyte
- Carrying the catalyst
- Separating the gas feeds

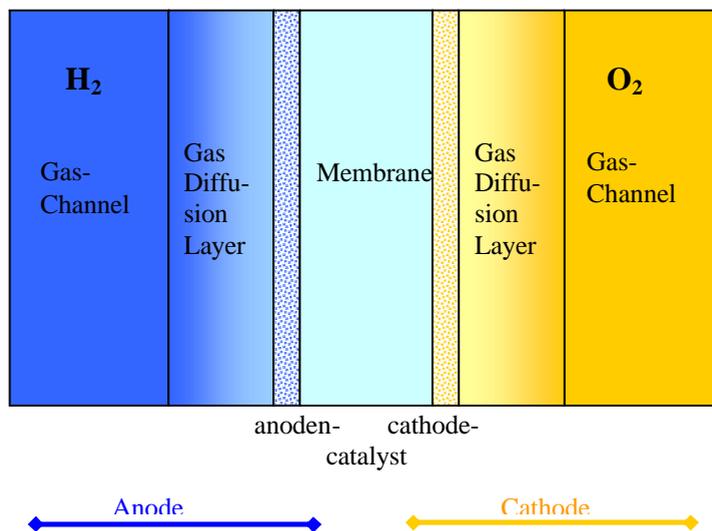
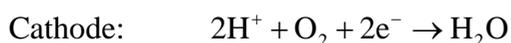


Figure 50: Schematic of the PEMFC MEA

The following reactions occur on the electrodes:



The operating temperature is because of the aforementioned reasons limited to 60°C und 80°C. The PEMFC has an excellent cold starting behaviour. On the anode hydrogen even with some CO₂ contamination from the reforming and on the cathode air may be provided. Because of the thin electrolyte (50 to 150 µm) and its high conductivity, the PEMFC has a high current, respectively power, density. The Canadian company Ballard has developed MEAs with a cell voltage of 0.5 V and current densities of about 5 A/cm². For this performance they used a Dow Chemical membrane and pure hydrogen and oxygen with 0.35 MPa. The bipolar plate connecting the MEAs electrically to the stack are made from graphite, steel alloys or from electrically conducting composites.

The gas produced by high carbon feed reforming processes contains usually up to 1% carbon monoxide (CO) even after the CO Shift without a PSA. The CO degenerates the catalyst on the anode, usually platinum. CO is adsorbed on the catalyst and deactivates it.

These feeds have to be cleaned further for the use in PEMFC to deliver a feed gas with less than 10 ppm CO.

Because of the low operating temperatures the catalysis has to be very effective. The acidic electrolyte favours noble metals as catalysts. The membrane is coated with platinum or platinum-ruthenium-alloys. The catalyst coatings have to be porous to allow the reactants to reach the membrane. On the other hand these porous layers have to be good conductors. In their vicinity a three phases boundary forms:

Hydrogen or oxygen gas /solid catalyst / wet electrolyte.

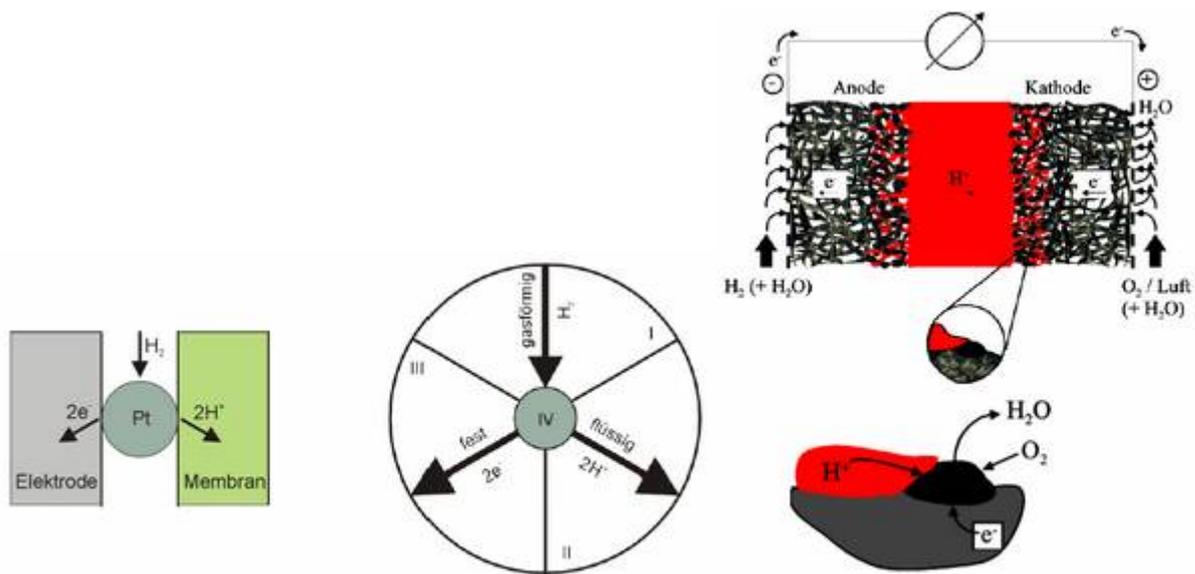
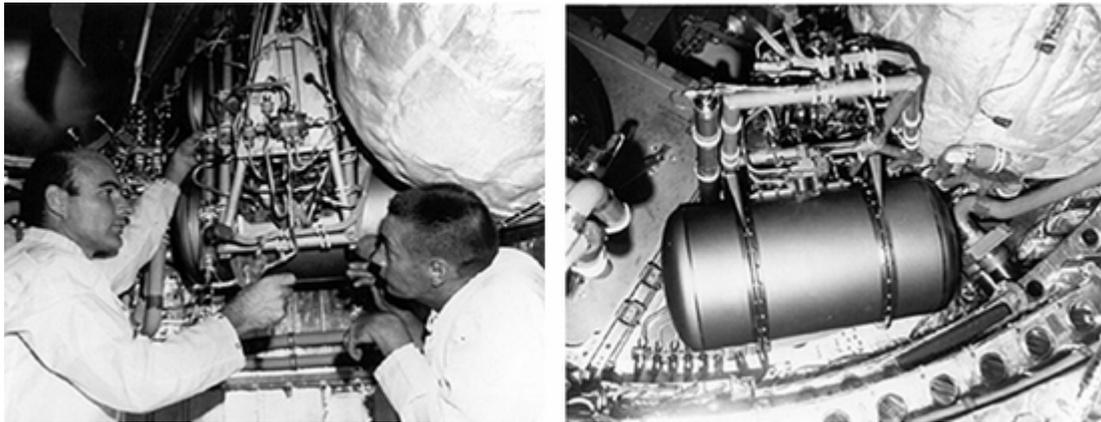


Figure 51: Micro-pore with three phases boundary

As the electrolyte foil changes density with its water content continuously it is one of the difficult tasks to fix the catalyst permanently on this foil. The diffusing electrodes connect to the bipolar plates via metallic or carbon conductors. Also these conductors have to be open for gas and water transport to allow providing or removing gases, the product water respectively.

The efficiency of a PEMFC is similar as this of an AFC, the PEMFC allows more compact integration due to its higher current density.

The first PEMFCs were built by GE in the 50ies for space applications, for instance for the NASA Gemini project (1962-1966). The development of the PEMFC has been pushed recently as it is the most promising fuel cell type for vehicle traction applications.



PEMFC for the NASA Gemini program (General Electrics)

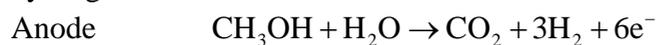
Some providers plan mass manufacturing for FCV applications by 2010. For the stationary application CHP applications with 200 - 300 kWel and small residential applications with 1- 5 kWel are distinguished. Currently there is even more development in the portable and other niche market segments. A prototypical application could be the replacement of batteries in laptops, digital cameras etc.

Some important components of a PEMFC system are the water management system, the cooling system and the electrical adaptation. However, the latter is common for all fuel cell systems.

Direct Methanol Fuel Cell DMFC

Although toxic methanol is an attractive energy carrier, as it is liquid and the handling of a liquid fuel is easier, common at least. Methanol may be directly electrochemically converted to electrical energy. This has been the motivation for the development of the direct methanol fuel cell DMFC. The design of a DMFC resembles very much this of a PEMFC. The anode is supplied with methanol instead of hydrogen and the cathode is supplied with air.

The reversible cell voltage is 1.215 V what is very close to the 1.23 V achieved with hydrogen. The reactions on the electrodes are:



The further development of the DMFC faces some technical problems. One is the diffusion and electro osmosis of the methanol, which passes the electrolyte and reaches the cathode, where it reduces the reactivity. The current catalysts on the anode do not yet provide the required efficiency, so that in general the efficiency of the DMFC is relatively small.

On the other hand neither a reformer, nor special cleaning measures have to be included. The relatively simple system design favours mobile applications, too. Up to today no large systems have been built based on DMFC.

However, there are certain chances that the DMFC technology or other direct fuel cell types like the direct ethanol fuel cell or the direct carbon fuel cell can be improved considerably by new material, catalyst, and electrolyte developments. This could redirect efforts to these technologies and increase chance for their market entry.

Middle Temperature Fuel Cells

Phosphoric Acid Fuel Cell PAFC

The PAFC is operated at 200°C with a highly concentrated phosphoric acid H₃PO₄ solution as catalyst. The application of an acidic electrolyte allows CO₂ in the hydrogen feed, as the CO₂ does not react in the acidic medium. All the functions in the cell are similar to the PEMFC. Because of the higher temperatures the requirements for the catalyst and the purity of the feeds are even lower compared to the PEMFC. It tolerates higher CO levels up to 1%mol. This makes the PAFC a good candidate for an operation coupled to the natural gas net with an intermediate reformer and a simple shift reactor. The higher temperature makes this system more flexible when it comes to a combined use of heat/steam and current in a small industry scale.

For high current densities the electrodes are designed as gas diffusion electrodes (see PEMFC). The anode base material is usually a tungsten carbide alloy; the cathode base material is a graphite-platinum compound. Both porous media provide again large specific surfaces for the reactions.

The electrolyte is not in the liquid phase as in the AFC, it is bound in a fabric-like matrix made from Teflon-covered SiC. The bipolar plates are made from graphite, similar as for the PEMFC.

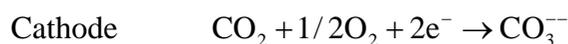
The PAFC is the fuel cell type which has the broadest commercial applications. One reference provider is the US based company ONSI, which has installed around 200 CHP systems labelled PC25, which provides 200 kW electric and 220 kW thermal power.

High Temperature Fuel Cells

Molten Carbonate Fuel Cell MCFC

The MCFC is operated at approximately 650 °C. It has carbon dioxide as a reactant and is therefore perfectly suited to cope with feeds characterised by high carbon impurities.

The reactions of the electrodes of a MCFC are:



The electrolyte is molten alkali carbonate (Li₂CO₃, K₂CO₃) fixed by a ceramic matrix made from LiAlO₂. The material for both electrodes is nickel. The nickel on the cathode is oxidised during start-up.



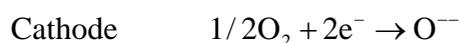
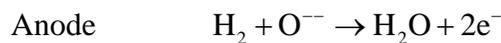
Noble metals for catalysts are not needed because of the high temperatures. A special feature of the MCFC is the gas management, which mixes the off gas from the anode with its high CO₂ content in the cathode feed, usually air. The CO₂ forms at the cathode together with the oxygen carbonate ions which are the ions transported in the electrolyte. Opposite to the other fuel cell types an increase level of CO₂ improves its performance. Special designs allow integrating the reformer stage in the fuel cell system.

One technical difficulty is the right material selection for the fuel cell frames bipolar plates etc, as the molten carbonates are very corrosive. Another problem is the solution of the NiO cathode in the electrolyte. The dissolved nickel diffuses to the anode and forms there precipitates which might even develop electrical shorts.

Internationally the MCFC technology has demonstrated its availability and performance in many demonstration projects. The installations provided typical electrical power of some hundred kW up to some MW. In Europe the HotModule system is commercialised by a MTU subsidy for the integration in middle sized CHP systems. In the USA the company Fuel Cell Energy (before Energy Research Corporation) is participating in several demonstration projects, in Japan Hitachi, IHI and Mitsubishi Electric intensively develop further the MCFC technology.

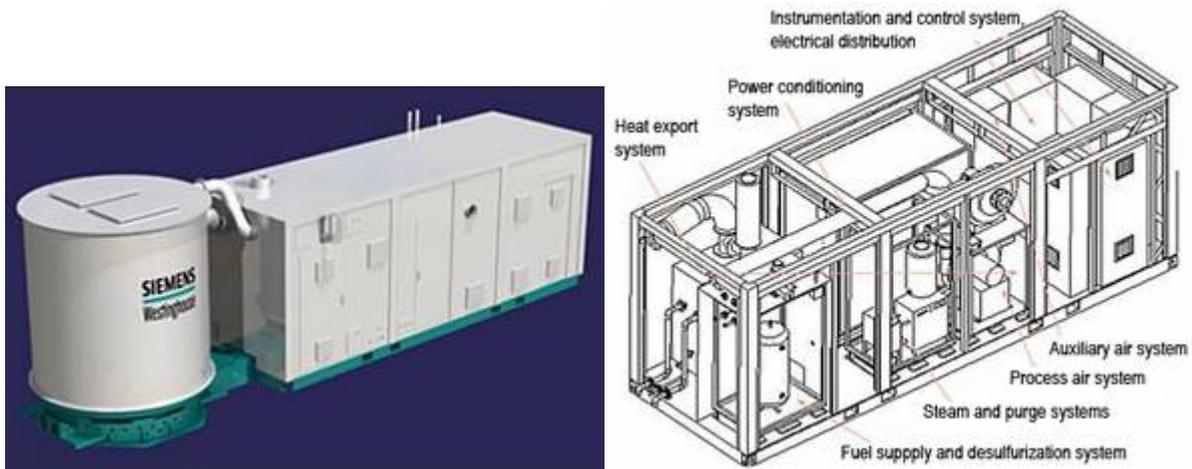
Solid Oxide Fuel Cell SOFC

The SOFC is operated at the highest temperatures - 800°C to 1.000°C - currently. The reactions on the electrodes are:



In the SOFC a ceramic made from yttrium stabilised zirconium oxide functions as electrolyte. It conducts electrical current via oxide ions O²⁻. At temperatures above 750°C this electrolyte provides a sufficiently good ion conductivity combined with gas tightness and negligible electron conductivity. The high temperature allows including the reforming stage in the fuel cell similar as for the MCFC.

The anode is made from nickel zirconium oxide and the cathode material is based on mixed oxides like lanthanum-strontium manganese. Because of the small resistivity of the electrolyte and the even higher operating temperatures the SOFC allows for higher current densities than the MCFC. Siemens Westinghouse, a leader in the SOFC technology, reports 1 A/cm² at a cell voltage of 0.7 V.



SFC-200, a 125 kW SOFC cogeneration system (Source: [Siemens Westinghouse](http://www.siemens.com))

Worldwide there are several companies researching and developing SOFC technology. There are classical planar types and a tubular design promoted by Siemens Westinghouse. The former Sulzer Hexis development is a planar type for small scale residential CHP solutions. Even high power class installations with some MW electrically are on their way.

Some problems are the thermal compatibility of the ceramic and metallic structures and the chromium caused degradation.

The high operation temperatures make a coupling to a steam cycle process highly efficient. The SOFC produces electrical current and the off gas with its 850°C produces steam which is expanded in a steam turbine. The total current efficiency of such a coupled process might reach 70%.

Fuel Cell Systems

The fuel cells need a complete infrastructure to provide electrical current. This infrastructure comprises besides the stack itself usually the gas cleaning components, gas / air compression, off gas / water management, heat management like cooling cycles and an electrical sub-system like inverter etc. Fig. 3 shows a schematic of such a system

Depending on the fuel cell type there are different requirements concerning the purity of the burning gas and the oxidiser. The purity requirements for the AFC, PEMFC and partially also for the PAFC are quite high which might increase the number of cleaning stages, what increases the system complexity and of course the costs.

There is the general tendency that with increasing operation temperature

- the purity requirements decrease,
- the efficiencies decrease slightly,
- material problems increase

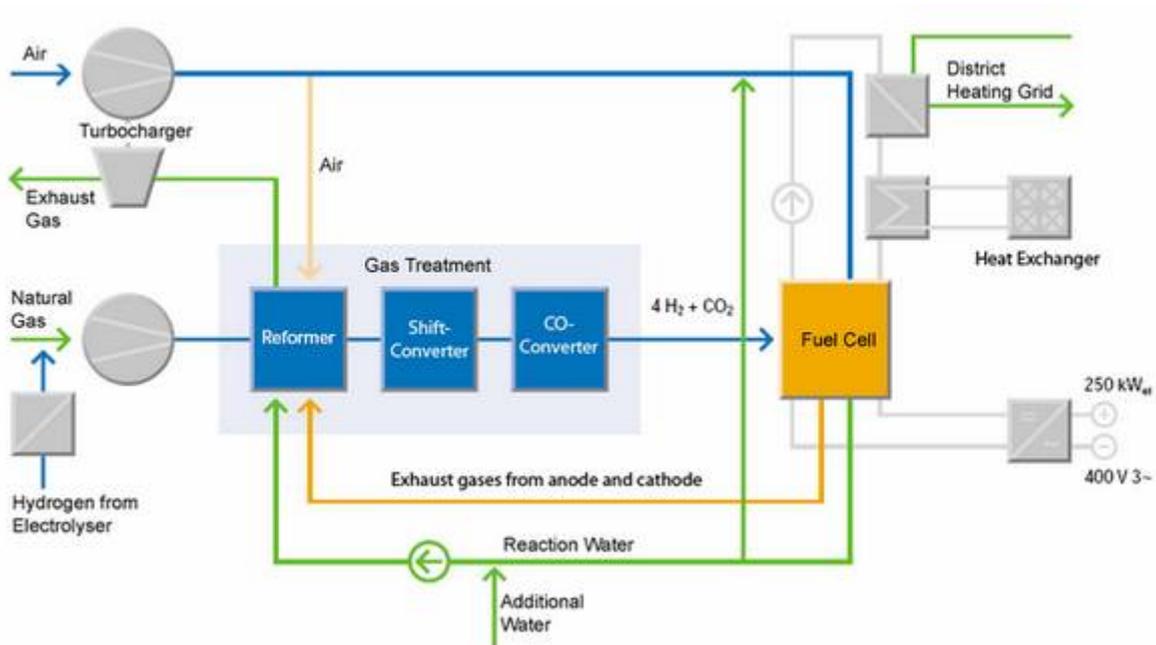


Figure 53: Fuel Cell System (Source: Department of Materials Science and Metallurgy, University of Cambridge)

Combustion

As other fuels hydrogen may be used in combination with oxygen or air in combustion processes. The released heat may be used for heating purposes, e.g. also to drive a heat power cycles as applied in vehicles or power stations for electrical power generation.

Although the actual reaction produces only water and is therefore a potentially very clean process, in the stoichiometric mixture the combustion provides relatively high temperatures which favour the formation of nitrogen oxides. However, there are some strategies to reduce this effect even below the level of NO_x production in conventional fuel combustion.

In catalytic burners, for instance, the reaction occurs at far smaller temperatures.



Figure 54: Hydrogen flame



Figure 55: Catalytic H2 Burner [25]

The essential properties of hydrogen as a burning gas are:

- wide flammability range,
- low ignition energy in the stoichiometric mixture,
- small flame arrestor gaps,
- high autoignition temperature,
- high flame velocity in the stoichiometric mixture,
- high diffusivity,
- very low density.

Internal Combustion Engines ICE

The wide flammability range allows using a wide range of mixtures for the combustion process. In particular lean mixtures are attractive, which reduce the maximum temperatures in the flames. Another positive effect of this property is that the fraction of unburnt fuel in hydrogen combustion is very low, which is further promoted by the good mixing properties of the highly diffusive gas. So hydrogen combustion can be very efficient. This has been proved during the EC HyICE project involving the automotive partner BMW as a project leader. BMW could demonstrate high efficiencies (up to 50%) in their 750h, which uses a modified standard 12 cylinder internal combustion engine in a bi-fuel mode.

The mass ratio air/fuel is with $137.3\text{g} / 4\text{g} = 34.3$ more than double compared to conventional fuels. With hydrogen this ratio can be extended in the lean region up to 180 what corresponds to an equivalence ratio of 0.2.

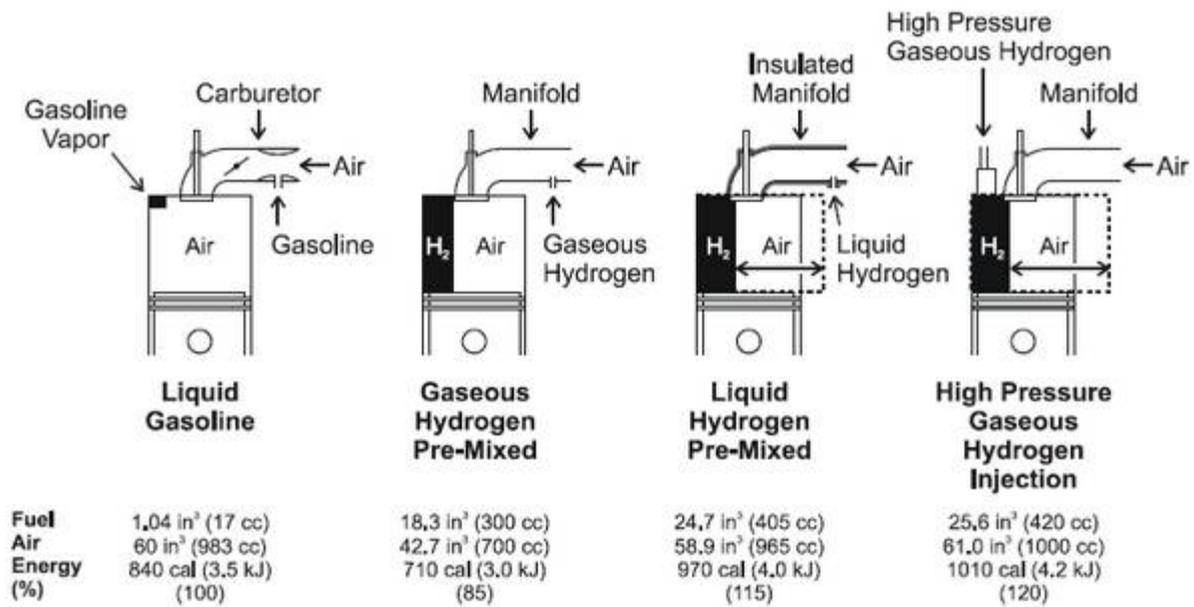


Figure 56: Comparison of relative fuel and energy fillings in an ICE

The small ignition energy and the wide flammability range guarantee reliable ignition even for lean mixtures. On the other hand this might lead to uncontrolled ignition of unburnt gases by hot spots or even by contact with other hot gases. This again might lead to the knocking phenomenon.

Because of the small flame gaps the hydrogen burns very close to structural surfaces. Again this might help to increase the efficiency. On the other side this allows the flame to escape the control volume even through very small gaps at the valves for instance and thus may lead to a flash back of the flame.



Figure 57: BMW 750h 12 cylinder Bi-Fuel Engine

The relative high autoignition temperature allows higher compression. On the other hand the low density limits the filling and the energy content. The theoretical thermodynamic efficiency of an ICE may be defined by the following formula:

$$\eta_{th} = 1 - \frac{1}{\left(\frac{V_1}{V_2}\right)^{\gamma-1}}$$

with the compression ration V_1/V_2 and the ratio of specific heats γ ($H_2 = 1.4$; Benzine = 1.1) From this equation and the other mentioned limitation, in particular the reduced energy content in the combustion volume, a slight loss in the specific power has to be expected, when a standard ICE is re-designed for H_2 use.

Other examples are the Mazda RX8 with its rotary engine, and MAN hydrogen buses with a redesign ICE. An advantage is that these engines usually may run on standard fuels still what allows a flexible market entry and in some cases a considerable range, sometimes larger than the standard vehicle.



Figure 58: ICE cars: BMW 750h (left); Mazda RX8 (right)

Some instructions for conversions are given in [www.switch2hydrogen.com/h2.htm]. There it is recommended only to use engines with a compression of less then 9.5 without turbo-loaders. In summary the tendency for early ignitions and the high diffusivity are the most critical properties which have to be accounted for in the conversion. However, from a safety point-of-view these instructions are questionable.



Figure 59: Mitsubishi Endeavour equipped with additional CGH_2 pressure vessels; small electrolyser for home refuelling in the front [www.switch2hydrogen.com/h2.htm]

The conversion of Stirling engines is even less challenging due to the different way these machines are provided with heat.

Gas Turbines

Conversion of gas turbine to run on hydrogen is in principle possible. These engines may be used for aircrafts or stationary in small power stations for peak load services. The replacement of hydrocarbons in gas turbines is furthered by the increasing demand for CO₂ separation and sequestration from the whole energy conversion process. The background is that the CO or CO₂ is more easily removed from the feed before the actual combustion than after the combustion involving further components.

The gas turbine is a well established and comparatively cheap solution with high power densities and acceptable efficiencies, in particular in large scale realisations.

There are many variations to use hydrogen as a burning gas in the complex installation of a large hydrocarbon fired power station.

The components of a gas turbine which have to be modified for a hydrogen feed are:

- the fuel pump
- the fuel injection
- the fuel control unit
- the heat exchanger
- and in case the combustion chamber geometry

In particular the whole fuel systems like piping tanks and so on have to be replaced to cope with the special properties of hydrogen.

If LH₂ shall be used additional considerations for the infrastructure and the injection have to be made.

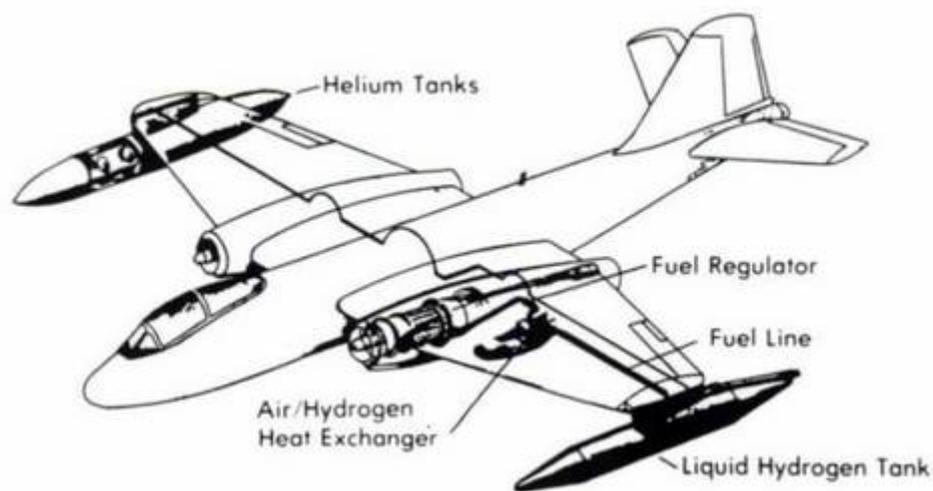


Figure 60: Modified B-57, 1956

Historically there have been some projects and positive experience already in the 50ies by US and Russian developers. In 1956/57 a B-57 Canberra was operated with hydrogen. During the flight one of the two J65 turbines were switched to the hydrogen operation. Mainly the fuel control unit was changed.

In the former UdSSR it was the group of engineers around Kusnezow, which converted a NK-8-2U Turbofan-engine to LH2. With these turbines the first time a full flight including take-off and landing was demonstrated. Similar activities were re-started in the 80ies, where Tupolev presented the first passenger aircraft TU154 running on hydrogen.

To further the developments in the 90ies Tupolev yond Daimler-Chrysler Aerospace cooperated in the Cryoplane project.



Figure 61: Cryoplane

The following figures are taken from Cryoplane reports.

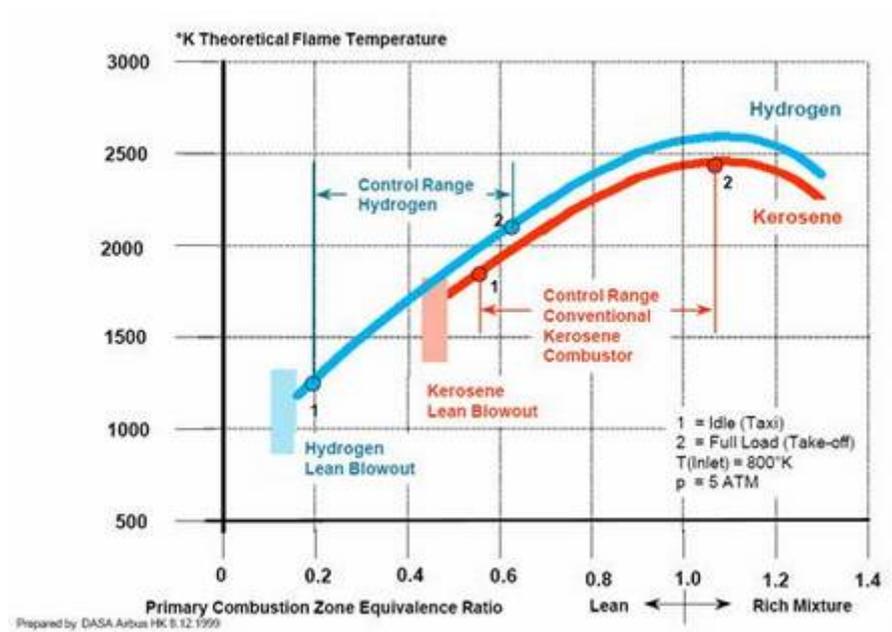


Figure 62: Flame temperature versus Equivalence Ratio (Source DASA Airbus)

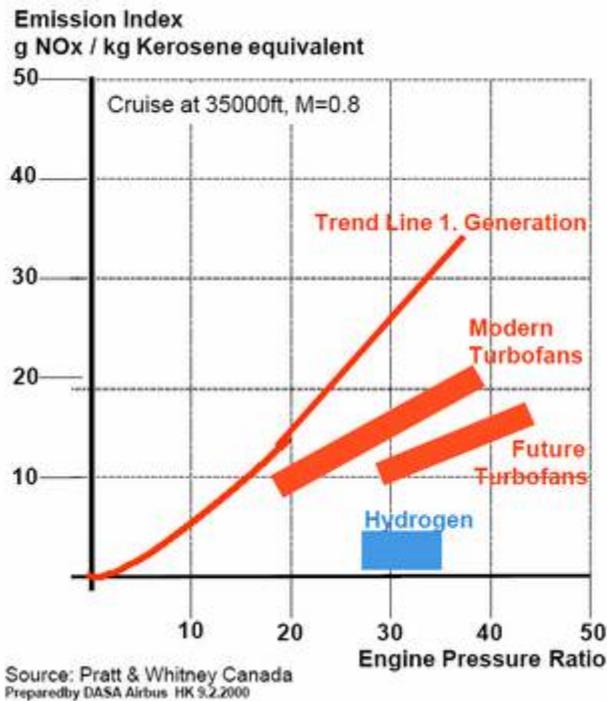


Figure 63: NOx Emission Index versus Engine Pressure Ratio (Source: Pratt & Whitney)

The above figures clearly indicate the possible advantage of using hydrogen in aircraft turbines.

Other thermal use

A mixture of hydrogen and oxygen may be used in rocket burners. The product water limits the temperatures generated and may be used immediately in a post steam cycle with a steam turbine for instance. The efficiency of such a system might be limited due to the cost for the pure oxygen and the comparatively small steam temperatures.

A special variation is the pulsed detonation engine, mainly used for flying rocket applications.

Instead of directly oxidising hydrogen with oxygen chemical cycles may be used where in a first step hydrogen reduces a metal oxide like NiO. This produces steam and the pure metal. The steam is expanded in a turbine and the metal is oxidised in the second step. The second step produces also heat which might be used to heat up a gas which might be energetically used in a gas turbine.

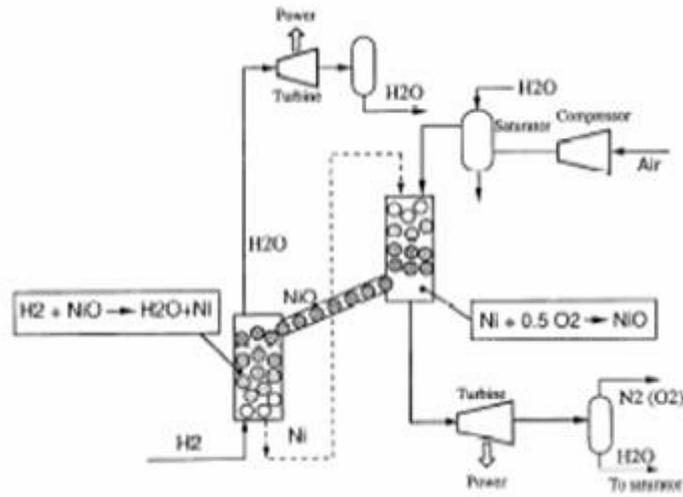


Figure 64: Schematics of a two step combustion cycle [34]

Another bridging technology is the simply mixing of hydrogen with methane or natural gas sometimes also referred to as “Hythane”. It can be shown similar as for the pipeline technologies (see EC project NATURALHY) that most of the natural gas or methane technologies tolerate considerable amounts of hydrogen without the need to change anything.

SUMMARY

Hydrogen and fuel cell technologies are cross-cutting technologies. They interact with many research areas (material, catalyst, high pressure, nanotechnologies etc...) and require knowledge from many other energy engineering branches.

Hydrogen technologies had an unsteady past but the new development and the worldwide growing energy demand will require all facets of any energy technology including those of hydrogen and fuel cell related technologies. Hydrogen may be produced at prices today which allow first market entries in niche markets. In combination with further matured and cheaper fuel cell with their potential for highest efficiencies hydrogen will enter even the automotive market within the next decade.

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