UNESCO Headquarters
Paris, 5 - 9 July 1993

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World Solar Summit
Sommet solaire mondial

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High-level Expert Meeting
Réunion d'experts de haut niveau

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Energy and Hydrogen

L'Énergie et l'hydrogène

High-level Expert Meeting
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ISES UNESCO CEE Ademe

Energy and Hydrogen
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Co-ordinator :

Barra
L.
Head of Hydrogen Project, ENEA
Italy

Co-Authors :

Gretz
Head of the Unit "Energy Environment Interaction"
CEC Joint Research Center, Ispra Establishment
Italy

Giacomazzi
G.
CEC Joint Research Center, Ispra Establishment
Italy

Stuart
A.K.
The Electrolyser Corporation Ltd.
Canada

Eichert
H.
Head of Research Programme "Hydrogen Energy Technology",
DLR, Institute for Technical Thermodynamics
Germany

Beck
N.R.
Manager Hydrogen and Electrochemistry, Alternative Energy
Division, Energy Mines and Resources Canada
Canada

Frankl
P.
Scientist, Engineering Faculty, University of Rome
Canada

Pede
G.
ENEA
Italy

The authors are responsible for the choice and the presentation of the facts of this discussion paper submitted to the High-level Expert Meeting of the World Solar Summit, as well as for the opinions which are expressed therein. These do not bind the Organisers of the World Solar Summit. Les auteurs de ce document de discussion soumis à la réunion d'experts de haut niveau du Sommet solaire mondial sont responsables du choix et de la présentation des faits figurant dans leurs contributions, ainsi que des opinions qui y sont exprimées, lesquelles n'engagent pas les organisateurs du *Sommet solaire mondial.*

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EXCERPT

"- On trouvera autre chose, dit Harbert.

- Il faut l'espérer, répondit Gédéon Spilett, car enfin sans charbon, plus de machines, et sans machines, plus de chemins de fer, plus de bateaux à vapeur, plus d'usines, plus rien de ce qu'exige le progrès de la vie moderne!

- Mais que trouvera-t-on? demanda Pencroff. L'imaginez-vous, monsieur Cyrus?

- A peu près, mon ami.

- Et qu'est-ce qu'on brûlera à la place du charbon?

- L'eau, répondit Cyrus Smith.

- L'eau, s'écria Pencroff, l'eau pour chauffer les bateaux à vapeur et les locomotives, l'eau pour chauffer l'eau!

- Oui, mais l'eau décomposée en ses éléments constitutifs, répondit Cyrus Smith, et décomposée, sans doute, par l'électricité, qui sera devenue alors une force puissante et maniable, car toutes les grandes découvertes, par une loi inexplicable, semblent concorder et se compléter au même moment. Oui, mes amis, je crois que l'eau sera un jour employée comme combustible, que l'hydrogène et l'oxygène, qui la constituent, utilisés isolément ou simultanément, fourniront une source de chaleur et de lumière inépuisables et d'une intensité que la houille ne saurait avoir. Un jour, les soutes des steamers et les tenders des locomotives, au lieu de charbon seront chargés de ces deux gaz comprimés, qui brûleront dans les foyers avec une énorme puissance calorifique. Ainsi donc, rien à craindre. Tant que cette terre sera habitée, elle fournira aux besoins de ses habitants, et ils ne manqueront jamais ni de lumière ni de chaleur, pas plus qu'ils ne manqueront des productions des règnes végétal, minéral ou animal. Je crois donc que lorsque les gisements de houille seront épuisés, on chauffera et on se chauffera avec de l'eau. L'eau est le charbon de l'avenir."

Jules Verne (1828-1905)
"L'Ile Mystérieuse" (1874)

FOREWORD

Hydrogen is the lightest element in nature: its molecular weight is only 2.016. The density of gas at 1 atm and 20 °C is 83. 764 g/m^3; besides, it liquefies at a very low temperature, around -253 °C. As a consequence, hydrogen is quite difficult to store in suitable form, without paying a high price in terms of energy density - both by weight and by volume - and sometimes also in terms of energy expenditure.

On the contrary, hydrogen offers attractive characteristics as a fuel: the lower heating value is about 33.3 kWh/kg and 3 kWh/normal cubic meter. When combustion happens with pure oxigen there is release of water alone. When combustion takes place with air some nitrogen oxides are produced, but they can be strongly reduced by a proper control of combustion. If hydrogen is used to produce electric energy in a fuel cell no pollutants are brought into the athmosphere. So hydrogen is almost an ideal fuel from an evironmental point of view.

Unfortunately, hydrogen is not available at the free state. However, it is largely aboundant in many compounds, among which the most familiar and diffused is water. Thus, the utilization of the environmentally sound characteristics of hydrogen can be exploited if hydrogen is produced by an energy source environmental benign itself. This is the case of solar energy in all its renewable forms: sun radiation, wind, biomass, hydropower and so on.

The chains to produce, store, transport and use hydrogen can be very different. For instance, one can produce hydrogen through electrolysis by using solar electricity, produced, in turn, by photovoltaic or wind or hydropower plants or through a thermodynamic process; production can be made also from biomass by different methods. Other technological options are also under investigation. Storage and/or transport can be performed in different ways, according to the operating conditions and to the final uses.

This report discusses the state of the art and the perspectives of the main technologies related both to production, storage, safety, transport and utilization of hydrogen. On the contrary, there is not a systematic evaluation of costs. In fact, it is quite impossible to consider all the possible chains from hydrogen production till end user. Besides, there are a lot of technologies involved in order to realize a hydrogen based economy. While some of them - like electricity production from hydropower - are well established and known and cheap, many others (photovoltaic conversion, biomass exploitation, fuel cells, storage techniques, etc.) still need large efforts to become more efficient and effective. Evaluation of economic goals achievable on each of these technologies is of course a matter of discussion. However, many forecasts made in the past failed. That means that also these forecasts are affected by large errors. Thus uncertainties related to the complication of chains from hydrogen production till end user add to uncertainties about the development of each technology. For this reason we preferred not to attempt an extensive evaluation of hydrogen attainable cost. Some indications on costs achievable in a particular chain and with present day technologies are given in Chapt. 8.1.

However, many of hydrogen related technologies are still in the research and development stage and large improvements are expected. Besides, technical feasibility of an energy system based on renewables, electricity and hydrogen is out of question. Finally, strong research and industrial sinergies are possible, and significant environmental benefits can be achieved in the near-mid term by using hydrogen in some particular applications, like transports. Thus, also when the precautionary remarks about costs are accounted for, it appears of capital importance to push towards an energy system based on renewable energy, electricity and hydrogen: only this system, in fact, is able to give us clean, suitable and inexhaustible energy.

1. A SHORT HISTORY OF RESEARCH ON HYDROGEN

The universe is thought to consist of up to 75% hydrogen and 23% helium from which all other elements are believed to have originated. The source of energy for our world is of course the sun, an active fusion reactor burning in every second 400 million tons of hydrogen, to form helium. This reaction provides the solar energy reaching the planet, in the order of 10^{15} kWh/year. The well known solar energy recovery methods (photovoltaics, solar thermal, wind turbines and hydraulic) are able to act as useful energy sources for us because of the "hydrogen reactor" in the sun.

Hydrogen is the simplest of all chemical elements. It consists of a single proton and one electron but, on earth, is rarely found in its molecular form. Seventy-five percent of the earth's surface is covered with water which consists of hydrogen and oxygen.

On May 2, 1800, the British scientists Nicolson and Carlisle, motivated by Professor Alessandro Volta's 1793 paper "Account of Some Discoveries by Mr. Galvani with Experiments and Observations on Them" and a further announcement of March 20, 1800, decided to duplicate Volta's "battery pile" experiment; they accidentally discovered that hydrogen and oxygen gases were released from a drop of water which separated the two wires from the terminals of the Volta Pile. Thus was born the study of terrestrial hydrogen production via electrochemical water decomposition. During the 1800's, Davy, Faraday and many other eminent and pioneering investigators defined the phenomena and laws of electrochemistry.

Commercialization of water electrolysis technology as a method to produce hydrogen began in the very early 1900's, primarily for the production of cutting and welding gases. The industrial uses of hydrogen have expanded continuously since that time, as well as the sources and methods of production.

In electrolysis of water, all industrially significant designs use strong alkali solution as the electrolyte, to carry the current between the anode, at which the oxygen is evolved, and the cathode at which the hydrogen is evolved. Potassium hydroxide is the preferred solution but it is recycled within the apparatus and only pure water must be continuously added. Since earliest days, there have been two generic cell design approaches, and both remain in common use today. Installations of "unipolar" electrolysers consist of separate cell units connected electrically in series, with each cell containing an appropriate number of anode-cathode pairs connected internally in parallel. These cells can obtain quite high capacities, up to 120000 amperes per cell unit. The alternative "bipolar" electrolyser design consists of a horizontal stack of electrodes which are each anodic on one side and cathodic on the other; the cells are separated electrically by insulating gaskets at the edges and the current passes from one end of the cell stack through to the other. With both design approaches, the hydrogen and oxygen gases are kept separate by means of porous diaphragms. Both cells evolve hydrogen and oxygen at high purity.

There are, of course, advantages and disadvantages inherent in each design approach. A pioneering industrial bipolar cell was that of Schmidt which evolved into the Oerlikon/Brown Boveri electrolyser of Switzerland. The bipolar approach has been favoured by European designers and several types are available today.

Similarly, among the many unipolar designs, the most common today is that of the Stuart cell from Canada, which is used throughout the world but which evolved originally with the purpose of producing storable clean hydrogen fuel from the abundant hydroelectric energy of Niagara Falls.

The ratio between lower heating value of produced hydrogen and electric energy spent to produce it can reach 70% in today's electrolysers. Well designed systems are capable of absorbing the intermittent energy of sun and wind, with complete flexibility.

Beyond water electrolysis, other methods of hydrogen production were developed including electrolysis of salts such as sodium chloride to produce three products: chlorine gas, hydrogen gas and sodium hydroxide; another way is the non-electrochemical route of reacting steam with hydrocarbon to produce hydrogen and carbon dioxide. To date, water electrolysis supplies less than 1% of the world's hydrogen requirements, the great bulk of which is produced by the reaction of steam with natural gas. Hydrogen is also produced by oxygen/steam gasification of solid carbonaceous materials, such as coal, peat or biomass, again producing hydrogen and carbon monoxide, followed by conversion of the carbon monoxide to hydrogen by reaction with steam and the evolution of carbon dioxide. During the second world war, the Fischer-Topsch synthesis was developed in Germany; the process allowed to obtain large quantitities of hydrogen based fuel, deriving from coal gasification with high temperature water vapour.

In essence, to produce hydrogen the basic challenge is to split water; and this can be done using either electricity from renewable sources or carbon from fossil or biomass sources, the latter accompanied by release of carbon dioxide.

Other non-fossil technologies at experimental stage include photoelectrolysis (directly using sunlight) and biological hydrogen supply using algae.

Between 1970 and 1990, research work on water electrolysis was directed mainly to improve the technology for non-energy hydrogen applications, such as metallurgical furnace atmosphere (annealing of silicon steel, flat glass production, lamp filaments etc.), chemical processing (hydrogenation of edible oils and fatty acids, hydrogen peroxide, chemical intermediates), cutting and welding gases and the cooling of generators in thermal power stations. With the exception of a few large (greater than 100 MW) plants for nitrogen fertilizer in India, Norway, Egypt and the former Soviet Union, water electrolysis plants tended to be small for reliable on-site hydrogen generation for industrial purposes.

In the early 1970s, concern over the instability of supply and the price of hydrocarbon energy ignited the world into taking action to develop alternative energy supply systems, including hydrogen as a form of energy carrier.

Conferences around the world, including the 1972 THEME Conference in Miami and later the first World Hydrogen Energy Conference in 1974, also in Miami, began to focus the attention of scientists and engineers from countries throughout Europe, Canada, the U.S.A., Latin America, Russia and Asia on the role which hydrogen could play in a world more independent of oil.

In 1978, some ten member countries of the International Energy Agency commenced a program on hydrogen development under the Hydrogen Implementing Agreement, with several technical annexes, as a means to achieve global cooperation in hydrogen research including production, transportation, storage, utilization, safety and economics. Activities, coordinated between government bodies, have been taking place since 1978, in countries such as Germany, U.S.A., Canada, Sweden, Switzerland, Italy, Belgium and Japan and within the research program of the European Community. In this manner, countries participate in areas of mutual scientific interest and a mechanism for broad cooperation has been created.

In parallel to international cooperation in research, many state entities and commercial organizations have focused resources on advancing electrolysis to improve energy efficiency and to lower capital cost. European and North American companies have taken the lead in this area. In addition to alkaline electrolysis as described above, there is advanced work in the more experimental areas of Proton Exchange Membrane (PEM) electrolysis and in high temperature electrolysis of water vapour, using solid oxides electrolyte.

In mid 1980's the Euro-Quebec-Hydro-Hydrogen-Pilot-Project (EQHHPP) was launched by the Commission of European Communities. The project allowed a wide cooperation among many countries and operators and gave a significant impulse toward the studies for hydrogen production from hydroelectricity, handling, transport and use in many sectors.

Lead by Germany, the two main projects Solar-Wasserstoff-Bayern (SWB) and Hydrogen from Solar Energy (HYSOLAR) were initiated by Germany industries, utilities and research centers, to demonstrate renewable hydrogen production, storage and utilization (for heat and electricity production and to fuel vehicles).

Italy, Switzerland and some other European countries have also undertaken research on clean hydrogen production, storage and applications.

In North America, the Electrolyser Ltd. in Canada has undertaken over the past four years a development program for directly-coupled photovoltaic hydrogen generators and energy storage systems; it has produced a unique combination of PV and electrolyser to form a

UNICELL-CLUSTERS^{TM}, which can produce hydrogen from the solar energy without the need for significant operator attention, controls or intermediate power conditioning.

At Humboldt State University in California, a system which directly couples photovoltaic panels to an electrolyser to produce hydrogen and oxygen has been in successful operation for approximately two years.

Japan announced in December, 1992, its intention to fund approximately $U.S. 2.5 billion over 27 years to develop World Energy Networks (WE-NET) as part of its efforts to diversify its imported energy sources. The energy will be collected from areas of the world which are rich in renewables and transported as hydrogen to Japan (and to other industrialized countries which seek imported clean energy).

In summary, research on hydrogen, particularly on its production by water electrolysis from renewable energy sources and on hydrogen applications, is continuing to be developed to meet the clean energy needs of the future.

2. WHY SOLAR HYDROGEN?

It is general opinion that the present day energy system, mainly based on fossil fuels, is not suitable for a long period in order to satisfy increasing energy demand. There are many reasons for which this opinion is growing day by day:

-Fossil fuels are destined for exhaustion: we are depleting our resources of coal, oil, methane and other fuels million times faster than nature can replace them; as consequence, with today's rate of energy demand, resources will exhaust indipendently from the ascertained reserves.

-The combustion of fossil fuels is giving a dramatic contribution to environmental pollution: it is calculated that the increase in carbone dioxide in the atmosphere in mainly due to the combustion of fossil fuels. Apart from the discussion on the eventual effects of such a phenomenon (the so-called greenhouse effect), that are still to be certified, it is evident that this trend is going to modify the athmosphere composition: if we are not yet able to tell about the consequences, it could be too late to recover the situation once unfavourable consequences will be certified. Other pollutants, like sulphur and nitrogen oxides, are generated because of energy production. These compounds have been individuated as the responsible of acid rains, that are causing serious damages to forests and human buildings. Finally, in urban areas extensive use of cars with internal combustion engines fed by conventional fuels, coupled with heating systems, is causing important damages to artistic heritage and building patrimony. Not to tell about the undoubtable negative effects on human health due to most of pollutants.

-The present world population uses on average 1.6 tonnes of fossil fuel per capita per year, but there is a wide distribution in energy consommation from industrialized countries to developing countries. While, for example, in United States energy use is about 5.5 tonnes per capita per year, in poorer countries this figure is even 10 times and more lower. Besides, in such countries the standard of living is very poor and the growing of population impressive. It is of capital importance to reduce international tensions by helping developing countries to improve their socio-economical situation. In the current situation that would mean more energy use and, as a consequence, faster depletion of resources and increase of environmental pollution. We have the duty to find a new energy system and to make it available for developing countries.

- Solar energy in its various direct on indirect forms is abundant as shown in Tab. 2.1 and widely spread in all countries of the world.

Type of energy	Theoretical potential	Exploitable potential	Current utilization
Solar radiation	19000 (1)	14 (2)	≈ 0
Wind energy	270	2.2	≈ 0
Biomass	70	4.6	0.6
Hydropower	3.8	1.7	0.1
Ocean thermal, wave and tidal	17	0.8	≈ 0
Total	≈ 20000	≈ 23	≈ 0.7

Table 2.1- Annual solar energy in its renewable forms available on earth (values in Gtoe/year)-Annual world energy consumption (1990) ≈ 8 Gtoe

(1) Insolation hitting continent surface

(2) Value calculated on the basis of exploitation of 1% of continent area, for production of 40% heat, 40% hydrogen and 20% electricity

Solar radiation is mainly available in the "sun belt"; coastal zones very often dispose also of wind and of energy from the sea; in continental and high latitude zones it is possible a large utilization of biomass and hydroenergy too.

While it is convenient to strenght the efforts in order to better utilize the existing resources, to reduce energy intensity and to reduce pollution, nevertheless, in a long term perspective it seems inevitable the development of a new energy system, based on new, renewable and ineuxhaustible sources, among which solar energy in all its forms has very significant chances.

In conclusion, solar energy will play an increasing role in the future.

Now, why hydrogen in connection with solar energy?

We can start from the point of view of end users. In principle, end users do not need energy. They want services: lighting, heating and cooling, transport, and so on. Energy is one of the means to produce these services. Energy should be delivered in form suitable to satisfy the services. As a consequence, the primary energy shall be exploited and carried to the user according to the demand. Of course, demands can change, because end users change in time. One can shortly follow this evolution in most industrialized societies.

The mankind started by using wood and the force of animals, that were the main fuels for many millenia.

After them, the coal pushed very impressively the progress, playing a fundamental role in the industrial revolution. In the present century, the most important fuel in industrialized countries has been oil. In the last decades natural gas acquired a significant share in the energy market. All these fuels are characterized by the fact that they can play also the role of energy carrier. Besides, they are characterized by an increasing content of hydrogen.

Turn by turn proper technologies for transport from the minings to end users were developed. In some cases, other forms of energy other than fossil and derived fuels are needed, and they are produced by properly converting primary energy carriers. So, we are observing an increasing demand of electric energy, a very efficient, clean, flexible, controllable secondary energy carrier, suitable for many appliances and able to provide for advanced services.

Fossil fuels gave us an impressive help toward progress in many countries of the world.

But now the emerging issues discussed above are compelling us to find other sources - renewables and non polluting - and new energy carriers, consistent both with end user demand and with the technologies utilized for exploitation of renewable energy sources.

What are the energy carriers for the future? We can say that electric energy has demonstrated to be suitable for this role. But electricity alone cannot satisfy all energy demands, because it is hard to imagine it can furnish all services we need. Within the present structure of the industrialized countries energy system the electricity accounts for less than 1/3 of total consumption, the other parts being devoted to other services, like transports and industry.

Hydrogen emerges as an ideal candidate for the role of solar energy carrier together electricity.

Hydrogen is consistent with the end user demands. It is flexible and, in principle, can substitute conventional fossil carriers in all applications. Gaseous hydrogen is transportable similarly to conventional gaseous fuels. Suitable technologies for transport of liquid hydrogen have been and are being developed. As a fuel, hydrogen can be burnt very efficiently either conventionally or catalytically. Due to its characteristics, it can progressively penetrate in the energy system without requiring sudden changes in its structure. Hydrogen is well known because it is the most used element in chemical industry: each year about 500 billion of Normal Cubic Meter are produced and employed for non energetic uses, without significant problems, also from the point of view of safety. Last, but not least, hydrogen is clean: the combustion of hydrogen produces mainly water vapour and, in minor part, nitrogen oxides. The latter can be strongly reduced by properly controlling the combustion and when fuel cells are used.

Hydrogen can be produced efficiently exploiting solar energy in all its forms (Fig. 2.1) by means of many technologies. In association with photovoltaic, wind and hydroelectricity, electrolysis offers the chance to produce hydrogen with efficiencies up to 70% today and much higher in perspective. Some efficient technologies are being investigated for hydrogen production from biomass. Some other technologies, still at laboratory stage, are presently studied in order to produce hydrogen from solar energy.

Hydrogen can be also used as storage medium for intermittent renewable sources. Electric grids can hardly accept intermittent power - like wind and photovoltaic plants directly connected to the grid - in quantities exceeding 10-20% of total network power, in order not to affect reliability of supplying. This fact introduce an upper limit in the contribution of such sources to energy demand satisfaction. Taking into account the low capacity factor of wind and photovoltaic systems (lower than 20%, against 55-60% of conventional plants) one can conclude that the contribution of intermittent sources to electric energy balance would be at maximum of the order of 7-8%. Remembering that in industrialized countries electric energy accounts only for about one 1/3 of total energy consumption, the contribution of intermittent sources to overall energy needs would be in the order of some percent in spite of their enormous potential. The implementation with a hydrogen based storage system allows to overcome this limitation. Further, one can imagine that hydrogen produced by these sources could be employed in non-electric uses. As a consequences, also intermittent sources could be fully exploited as forms of solar energy, in order to satisfy both electric and non electric energy needs.

The exploitaion of solar resources based on the production of electric energy and hydrogen allows to prefigure a new, environmentally sound, inexhaustible and cyclic energy system, schematically shown in Fig. 2.2. Primary sources - sun radiation, wind, hydroenergy, etc. - are converted into hydrogen and electricity. This latter is directly conveyed to electric appliances, while hydrogen, after transport and storage if needed, is used where it is requested. On the other hand, electricity can be converted to hydrogen through electrolysis; hydrogen, in turn, can be converted to electricity by fuel cells or advanced generators. Water employed for hydrogen production is restored during hydrogen combustion. If proper technologies are utilized no emissions or low emissions are produced, and there is only one external input to the system: the inexhaustible primary sources.

Many suggestions have been made regarding the better "political" path to attain this long term goal. In Germany, the country which performs the strongest effort on hydrogen, the following path has been suggested:

-first stage: saving energy and using it efficiently, while the new system is under investigation;

-second stage: still energy saving and wide use of dispersed solar energy; progressive introduction of solar hydrogen;

-third stage: massive exploitation of all renewable energy sources and use of hydrogen and electricity as energy carriers.

It seems very important to point out that a long way has to be covered to reach the final goal. The new energy system based on solar energy and hydrogen is not for the near term and a full diffusion of it will happen after decades of research, development and demonstration. Regarding to achievable costs, it is hard to make reliable forecasts. The goal attainable with today's available technologies can be evaluated using the Euro-Quebec-Hydro-Hydrogen-Pilot-Project as a reference. For the future, particularly if technologies still in development are considered (like photovoltaic conversion of solar energy), the parameters are too numerous and many uncertainties can affect the forecasts.

In conclusion, there are many, different technologies involved in the new energy system, at different state of development: some of theme are quite mature, like hydroelectricity; wind is near to maturity; some others - like photovoltaics, fuel cells, advanced technologies for hydrogen production and storage - need a strong effort to cut down the costs and to improve performances. Though, we can affirm that, while it is out of question that performances and costs are to be dramatically improved in order to get the system largely diffused, technical feasibility of important parts of the system under discussion has been demonstrated, unlike some other energy technologies that receive strong financial support for development.

Uncertainties about costs cannot be a reason to delay the engagement on hydrogen related technologies. In fact, the synergy between pollution and growing energy needs of emerging countries could lead to an explosion of environmental problems. Considering the present global situation this occurence can be foreseen as very probable even in a near future. In such a case, energy cost will become of a minor importance, while other parameters, like sustainability, inexhaustibility and diffused availability will be the major requirements to be fulfilled. In order to afford these issues, we shall dispose at any moment of a sustainable energy system. The effort must be performed mainly by developed countries, because they have been and are major responsible for environmental pollution; besides, developed countries very often have represented the "model" for less developed countries. From that, a responsibility to make available a new energy system arises, in order to allow developing countries to use sustainable technologies supporting their socio-economic growth.

Besides, there are some other advantages from an immediate involvement in hydrogen technologies: a progressive adaptation of people to hydrogen would be possible; secondly, there are many applications, like transports, in which hydrogen can give significant contribution in terms of local environmental benefits in near-mid term.

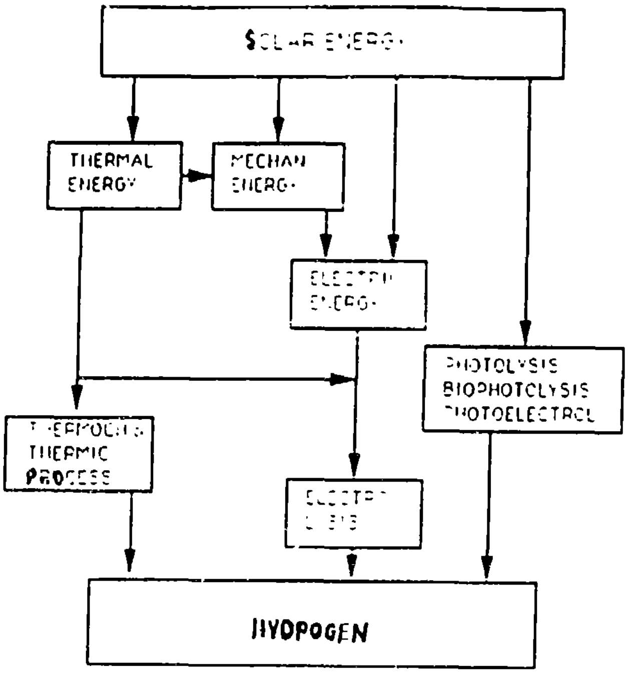


Fig 2 1 - Diagram of possible path for hydrogen production from solar energy

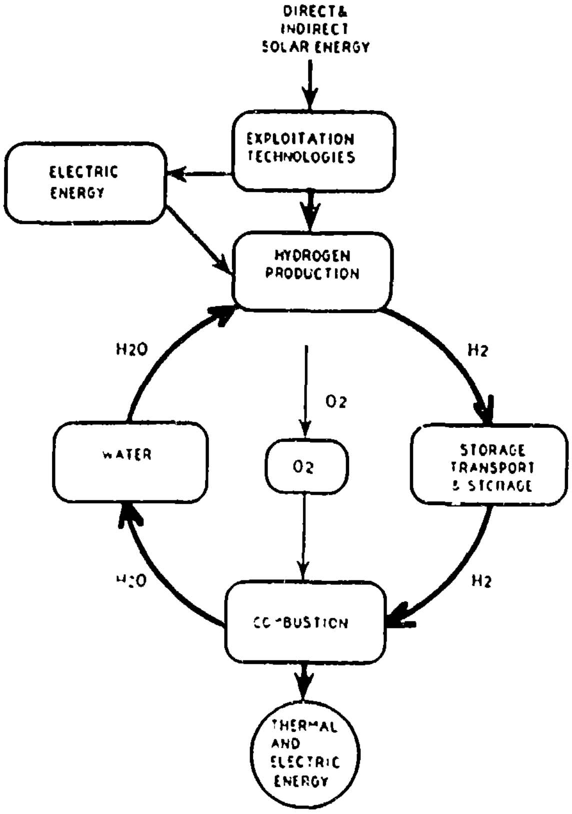


Fig 2 2 - Scheme of the cyclic energy system based on solar energy, electricity and hydrogen

3. SAFETY CHARACTERISTICS OF HYDROGEN

Safety is a major issue facing the development and widespread use of hydrogen technology. Both for technical reasons and to achieve public acceptance of hydrogen, potential hazards and safety measures must be addressed in current and future R&D programs. Comprehensive knowledge of relevant safety considerations as well as of standard accident situations is of great importance if gaseous and liquid hydrogen is to replace well-known fuels such as methane, LPG, or gasoline on a large scale. All aspects of hydrogen energy technology, including production, storage, transportation and utilization, must utilize safety strategies to prevent operational incidents and serious accidents and limit accident consequences to an acceptable minimum. Accidental release of hydrogen is the most significant hazard and can have serious consequences. To prevent or minimize the consequences, the following must be investigated:

- Hydrogen-air mixture formation and dispersion under specific initial and boundary conditions (release to free atmosphere or inside confinements, continuous or instantaneous release), and the resulting flammable mixture volume;
- Uncontrolled combustion following ignition and the resulting pressure rise;
- Resulting damage to surroundings by thermal radiation and pressure.

During the past few decades, studies on hydrogen safety, records on hydrogen incidents and accidents, as well as a great deal of basic research activities on combustion processes have been published. Safety aspects of hydrogen as an energy carrier are receiving increasing interest in connection with national and international hydrogen energy technology programs. The International Association for Hydrogen Energy's (IAHE), Committee on Hydrogen Safety, compiled the knowledge gaps affecting the widespread utilization of hydrogen in energy technology (Table 3.1).

The basis of all safety considerations in the production, transport, storage and use of large amounts of combustible energy carriers is the determination of their ignition, combustion and potential detonation behaviour and the associated pressure build-up in accident situations. Accidents which can lead to the formation of ignitable combustible-air mixtures are usually initiated by fuel leakages caused by inadequate design, material defects, embrittlement, corrosion, mechanical overload, manufacturing faults, collision (vehicles) or insufficient maintenance. A careful distinction must be made between combustion processes in totally or partially confined areas and in the free atmosphere.

The decisive factor in the damage potential of uncontrolled released combustible gases and evaporating propellants and fuels in case of ignition is the possibility of the acceleration of the flame front to fast turbulent deflagration and its sudden transition to detonation. Experiments in which gaseous and liquid hydrogen has been released in the free atmosphere and in totally or partially confined areas show that the transition from deflagration to detonation is virtually impossible in the free atmosphere. To realize a hydrogen-air mixture detonation in the free atmosphere, an initial detonator of sufficient strength would be needed. This type of initiation is irrelevant under realistic accident conditions.

It cannot be ruled out, however, that in case of accidental release of combustibles into totally or partially confined areas a deflagration of combustible-air mixtures in a proper composition could turn into a detonation through interaction with shock waves and turbulence-promoting structures.

One of the most important safety protection goals in the use of hydrogen in energy supply systems is therefore to prevent deflagration-detonation transition in buildings, pipeline systems and containments. Safe designs are of crucial importance in hydrogen energy safety technology, and there are promising possibilities.

3.1 - Safety parameters and characteristics

To assess the potential risks and hazards of hydrogen as an energy carrier, it is helpful to compare its important physical and chemical safety characteristics and parameters with those

- FLAMMABILITY/DETONABILITY LIMITS
  - Effects of Nonflammable Mixture Components
  - Effects of Flammable Mixture Components
  - Effects of Temperature, Pressure, Flow Turbulence, Confinement, Catalytic Surfaces, etc.

- EXPLOSIVE YIELDS
- Cloud Dispersion (Slush, Liquid, or Gas Release)
- Effects of Confinement on Overpressure
- Effects of Vents on Relief of Explosion Overpressure
- Effects of Ignition Energy Level on Deflagration and Detonation
- Solid Air/Oxygen Contaminants (in Slush or Liquid)
- Explosion Energy from Vapour Cloud Ignition

- COMBUSTION
  - Transition to detonation (e.g. Turbulence, Confinement, Transition Distance, etc.)
  - Safety Criteria for Burners (e.g. Flash Suppression, Flame Stability, Emissions, etc.) Materials Compability
  - Consequences of Combustion (e.g. Thermal Radiation and Emissions)

- PRODUCTION/STORAGE/HANDLING
  - Production Methods (Biochemical, Photoconversion, Thermochemical, etc.)
  - Slush Technology
  - Venting and Flaring
  - Static Charge Built-up in Pipeflow and Vessels
  - Contamination Sampling (Air/Oxygen in Liquid/Slush)
  - Materials Compatibility with Hydrogen
  - High Pressure Technology
  - Storage Safety Issues (e.g. Quantity-Distance-Relationships, Permeation Through Soils, Consequences of Leakage and Rupture, Metal Hydrides, etc.)

Tab. 3.1 - List of hydrogen safety knowledge gaps (preliminary). Listed at the 1st Meeting of IAHE Committe on hydrogen safety, July 24th 1990

of other combustible gases, e.g. methane (natural gas) and propane, which are currently used on a large scale. The most important data are summarized in Table 3.1.1.

Ignition Limits and Ignition Energy

The necessary pre-condition for the ignition of released combustible gases and vapours is a certain mixture ratio, with air for example, and an ignition source with sufficient ignition energy. There is a lower and a upper ignition limit. Self-sustained flame propagation in the mixture is impossible beyond these limits. Aside from the mixture composition, the ignition limits also depend principally on the ignition energy itself, the initial pressure and the initial temperature of the mixture as well as the relative humidity in the fuel-air mixture.

The ignitable concentration range is widened by a strong increase in ignition energy. Altogether, however, this effect is small, especially in terms of self-sustained flame propagation. Initial pressure in the mixture prior to ignition also affects the range of flammability. The upper ignition limit, in particular, is displaced to higher hydrogen concentrations by increased initial pressure. A decrease in the initial pressure to below normal causes a narrowing of the ignitable concentration range, ultimately to the point where self-sustained flame propagation cannot take place.

Relative humidity has only little effect. The ignition range is extended in dry fuel-air mixtures. On the other hand, the strong reaction-inhibiting effect of water vapour must be taken into account if there is a ternary mixture of hydrogen, air and steam.

Hydrogen's wide ignition range is a disadvantage in comparison with other fuels when considering the potential risks. On the other hand, the lower ignition limits of hydrogen and methane differ very little. The lower ignition limit of propane has even lower values. In practice, it is the lower ignition limit that is of crucial importance in most accident situations.

The minimum ignition energy for hydrogen in air (0.02 mJ, Table 3.1.1) is about one order of magnitude smaller than that of other combustible gases. The ignition energy must be large enough to produce a flame kernel of critical size so that it will be not extinguished again immediately by the surrounding colder, unburnt gas or cold walls and components, respectively. However, even weak ignition sources that are present in almost every case, such as sparks from electrical switches, relays, motors and metal struck against each other as well as electrostatic discharge, release more energy than necessary to ignite even methane, propane or other fuels.

In addition, catalytically-active surfaces can ignite hydrogen-air mixtures far below the spontaneous self-ignition temperature of 858 K. On both sides of the stoichiometric mixture with air, the necessary minimum ignition energies of hydrogen-air and methane-air mixtures rise steeply and practically coincide at the lower ignition limit and are still in the order of magnitude of about 10 mJ (weak ignition sources).

Quenching distance

A flame front extinguishes itself when entering a gap of a certain and, similar to the minimum ignition energy, depends heavily on the mixture composition.

Burning velocity

Burning velocity is a fundamental safety parameter of a combustible gas mixture and must not be confused with flame front velocity. Flame front velocity is the total of the burning velocity and the displacement velocity of the unburnt gas mixture. The higher the normal burning velocity of a combustible gas, the greater the tendency towards transitions from deflagration to detonation if there are sufficiently long travel distances for the flame front in pipelines or closed rooms. The normal burning velocity is the progression of a laminar flame front relative to the unburnt gas mixture and is theoretically computable as a function of the mixture composition, temperature and pressure.

One of hydrogen's important safety characteristics is its high normal burning velocity. Table 3.1.2 shows the maximum and the stoichiometric burning velocity of hydrogen-, methane-, and propane-air mixtures. In addition, Fig. 3.1.1 shows the effect of the mixture composition on the laminar burning velocity. Hydrogen's high normal burning velocity is, combined with a strong temperature dependence, one of the most important reasons for the acceleration from laminar to turbulent hydrogen flame fronts and for the transition of a deflagration into a detonation.

Flame Temperature, Radiation and Burning Time

The flame temperatures of the most important combustible gases and fuel vapours differ very little from each other in stoichiometric mixture with air, Table 3.1.1.

Hydrogen flames exhibit only a fraction of the flame radiation of natural gas flames.

Traffic accidents with released liquid hydrogen fuel involve lower risk potentials for drivers, passengers and pedestrians due to liquid hydrogen's very short evaporation and burning times in comparison with conventional fuels such as gasoline, when released in equivalent energy amounts, and because of the very fast dispersion of evaporating hydrogen in the free atmosphere.

Detonation Velocity and Detonation Overpressure

One of the most substantial potential dangers of combustible gases and fuels is the overpressure caused by deflagration and especially by detonation. The existing boundary conditions determine the resulting overpressure. In confined cubical or spherical containers or rooms, deflagrations of stoichiometric mixtures of hydrogen, methane and propane and most of the combustible vapours with air cause a uniform maximum pressure rise of about 8:1. On the other hand, the time-dependent pressure rise during combustion can take on very different values under otherwise similar initial and boundary conditions. A considerably higher maximum pressure increase rate must be reckoned with in the case of long containers and pipelines. Thus, the shape of the container must be included in safety considerations.

Deflagration overpressures in the magnitude of 0.1 bar occur in confined areas as well as in the open. In confined areas and containers filled with stoichiometric combustible gas-air mixture, detonations cause a maximum pressure increase of about 20:1 and, thus, more than double the value of the adiabatic deflagration. However, considerably higher pressure rises can be achieved during the deflagration to detonation transition process. Theoretically, this transition is much more easily possible with hydrogen than with other combustible gases, with the exception of acetylene.

Explosion Energy

The explosion energy released with the ignition of a combustible gas-air mixture causes pressure wave loads on containers and structures. The theoretical released explosion energy of gas is often referred to in terms of equivalent amounts of trinitrotoluene (TNT). The explosive strength of TNT can be reproduced and is the standard for judging the explosion potential of various substances.

Nevertheless, the representation of the explosion potential in equivalent amounts of TNT can only be used for the explosion's effects over long distances from the explosion itself. The differences between TNT and combustible gas-air mixtures are considerable in terms of impact at a short distance from the explosion site. However, even though the TNT-comparison concept has basic flaws it will continue to be used until non-ideal explosions, such as those with combustible gases, can be clearly characterized by corresponding parameters.

The theoretical TNT equivalent can be calculated for various combustible gases. These theoretical maximum values for the explosion potential of hydrogen, methane, and propane are given in TNT equivalents in Table 3.1.1. It should be noted that for the storage of the same amount of energy, the values of the total TNT equivalent for the combustible stored differ only very little between hydrogen and the other gases.

In a quantitative evaluation of danger potential, the decisive factor is that only a fraction of the theoretical explosion energy is set free in an accidential release of large amounts of combustible gases or outflow of liquid fuels including hydrogen. Experiments and analysis show that less of 10 % of the amount released in an explosion is located within the ignition limits at any time.

3.2 - Deflagration and detonation behaviour

In order to control accident situations in which large amounts of combustible gases and quickly evaporating liquid fuels are released and ignited, it is crucially important to have the most accurate information about the pressure-time function of the deflagration taking place and about the criteria and mechanisms of a possible acceleration of the deflagration to a detonation. Complex interrelationships are involved here. Depending on the existing start-up and boundary conditions, the same combustible gas-air mixture can adopt burning velocities which differ by orders of magnitude.

Laminar burning velocities of stoichiometric mixtures of conventional combustible gases such as methane or propane with air are about 0.5 m/s, and those of corresponding laminar flame velocities amount to several m/s for these gases, and more than 10 m/s for hydrogen-air mixtures. Via flame acceleration and the transition from laminar to turbulent burning, turbulent flame speeds of several hundred m/s can be achieved, which holds in principle for all combustible gas-air mixtures.

The higher the turbulent burning velocity and the corresponding flame velocity, the easier is the transition to detonation. A detonation spreads relative to the unburnt gas mixture at supersonic speed with a typical velocity of several km/s. A detonation front consists of a strong shock and a reaction zone. The rise in temperature in the shock leads to self-ignition of the combustible gas-mixture under shock so that the reaction front is coupled to the compression shock and moves at detonation speed. A deflagration expands at subsonic speed and can, therefore, change the thermodynamic state and the flow of the unburnt gas mixture downstream of the flame front due to the expansion of the combustion products and of the pressure waves emanating from the flame front.

Turbulences create additional increases in burning velocity and, thus, further acceleration of the flame front. Aside from the rise in the degree of turbulence in an unburnt mixture downstream of the flame front due to obstacles, each acceleration of the flame front itself causes forward and backward facing compression shocks. These shocks are reflected from solid walls, meet the flame front again and once more increase the burning velocity through positive feed-back.

Depending on initial and boundary conditions, flame front accelerations leading to the transition to detonation can take place with all combustible gases. However, such transitions are unlikely when the deflagration takes place in the free atmosphere or if the necessary running lengths in pipelines and rooms are not available.

During the deflagration-to-detonation transition process high and sharp pressure peaks occur, Fig. 3.2.1. A stable detonation can only exist if:

- the mixture composition is within the (classical) detonability limits, and
- the geometrical boundary conditions, e.g. the tube diameter, allow the existence of a detonation.

The "plane" detonation front actually has a complex, instationary three-dimensional structure, where the significant length scale is the detonation cell size λ. Detonation cell size can be associated with kinetic data and therefore seems to be a fundamental property of these gas mixtures. The dependence of detonation cell size on the mixture composition for different fuels is shown in Fig. 3.2.2.

The failure or re-initiation of detonations when leaving a channel or tube depends on the detonation cell size to diameter ratio and defines the critical tube diameter $d_c = 13\ \lambda$ for circular cross sections and $d_c \approx 10\ \lambda$ for rectangular channels.

In tubes, the diameter poses a geometrical boundary condition for the existence of a stable detonation, $\lambda \geq \pi d$ for direct detonation initiation and $\lambda \leq d$ for deflagration-to-detonation transition processes in cylindrical tubes. For rectangular channels of width w and a ratio of width/height << 1, the relation $\lambda \leq w$ holds.

Combustible	Hydrogen H_2	Methane CH_4	Propane C_3H_8	Gasoline
Density $NTP^{1)}$-Gas (kg/m^3)	0.0838	0.6512	1.8700	4.4
Autoignition Temperature (K)	858	813	760	501-744
Flame Temperature in Air $(K)^{2)}$	2318	2148	2385	2470
Minimum Energy for Ignition in Air (mJ)	0.02	0.29	0.26	0.24
Flammability Limits in Air (Vol.-%)	4-75	5.3-15.0	2.1-9.5	1.0-7.6
Detonability Limits in Air (Vol.-%)	$13-65^{3)}$	6.3-14.0	$2.5-8.2^{4)}$	1.1-3.3
Detonation Velocity in Air $(km/s)^{2)}$	2.0	1.8	1.85	1.4-1.7
Detonation Overpressure $(kPa)^{2)}$	1470	1680	1825	
Laminar Burning Velocity $(cm/s)^{2)}$	263	42	46	45

1) NTP: Normal Temperature and Pressure. 293.15 K, 101.3 kPa
2) Stoichiometric Mixture
3) Limits of Quasi-Detonation Regime
4) Extrapolated from Detonation Cell Size

Table 3.1.1 SAFETY-RELEVANT PROPERTIES OF COMBUSTIBLES

Combustible Gas	v_{max} cm/s	C_{max} Vol.-%	v_{stoi} cm/s	C_{stoi} Vol.-%
H_2	346.0	42.5	237.0	29.58
CH_4	43.0	10.17	42.9	9.50
C_3H_8	47.2	4.27	46.0	4.07

Table 3.1.2 - COMPARISON OF MAXIMUM AND STOICHIOMETRIC BURNING VELOCITIES
(NTP-Conditions)

The flame front velocity - either deflagration or detonation - is shown in Fig. 3.2.3 . Obstacles in the flame path give rise to the so-called quasi-detonation regime, where a state similar to a regular Chapman-Jouguet detonation can be achieved inside the obstacle section. Leaving this section, the quasi-detonation sometimes will decay to a "normal" deflagration.
In the entire detonation range, hydrogen proves to be much more sensitive to the transition to detonation than methane and other hydrocarbons. But it would be premature to conclude that hydrogen in principle has a greater risk potential in accident situations. In order to achieve a detonation or, first of all, the transition from deflagration to detonation, the mixture composition must be within the detonation limits of hydrogen in air. From a realistic safety point of view, however, the lower detonation limit is more important, which in case of hydrogen is rather high, 18 vol.-%, in contrast to methane, 6.3 vol.-%, and which seldom should be exceeded in realistic accident situations. Nevertheless, the important research task remains to prevent detonation or at least make it less likely even in those rare cases where mixtures with a near-stoichiometric composition occur. Deflagrations and detonations in totally or partially confined areas are the main problems for safe use of combustible gases, including hydrogen as an energy carrier.
The combustion process and, in particular, the deflagration-to-detonation transition behaviour, can be influenced to some extent by adding inhibitors, which can be non-reacting components like nitrogen or water vapour, or even lowly-burning hydrocarbons. Fig. 3.2.4 shows the influence of water vapour and methane on the flame velocities of stoichiometric hydrogen-air mixtures. It is important to note that, with the addition of about 8 % of methane, a deflagration-to-detonation transition is completely suppressed under the given experimental conditions.

3.3 - Impact of liquid hydrogen accidents

In accident situations, the mass of liquid hydrogen which may potentially be released ranges from about 100 l (typically a car tank) up to some 1000 m^3 (storage tanks).
The prediction of the evaporation of liquid hydrogen, depending on soil and ambient conditions, cloud formation and the resulting volume of the flammable cloud, is an essential topic for further modelling and scaling of experimental data.
The spread and evaporation of liquid fuels such as LH_2, LNG or gasoline are often based on relatively simple models. Application of these models to hydrogen spills have shown that the agrement is poor. Nevertheless, these models can be used for comparing fuels like liquid hydrogen and LNG in terms of evaporation rate and time, Fig. 3.3.1. Liquid hydrogen, compared to other fuels, has very short evaporation and dispersion times. As a consequence, hydrogen fires last for only a relatively short time, e.g. few seconds for a car tank. This is an important safety feature and a real advantage of hydrogen.

3.4 - Impact of blast waves of burning clouds

The impact of burning hydrogen-air clouds on the surroundings can be only roughly estimated by application of the TNT-equivalent described above because of the basic flaws of this method. The pressure wave developed during combustion strongly depends upon the flame velocity, which also can be only roughly estimated, depending on the geometrical and atmosperical boundary conditions. In spite of the differing burning velocities, the explosive yield of hydrocarbon-air and hydrogen-air vapour cloud explosions differ very little, and are <4 %.

3.5 - Summary and conclusions

Every energy technology has its specific risks. The aim of safety technology, therefore, is to minimize these risks by:
- preventive safety measures and
- mitigation measures.

Priority should be given to the preventive measures. The risk of technical systems is defined by the product of the probability of a certain accident and the amount of damage. Today risks are evaluated by means of probabilistic safety analysis, which is an excellent tool to identify weak points in complex technical systems.

In industry, there is a great deal of experience in safe handling of hydrogen. However, the systematics of industrial safety measures cannot simply be transferred to a hydrogen energy system, where untrained personnel have to safely handle hydrogen.

Therefore, a basic safety strategy with the following approaches is needed for the widespread use of hydrogen energy technologies:

- Measures to prevent incidents and accidents:
  - appropriate design
  - appropriate material selection
  - quality assurance
  - repeated non-destructive testing.
- Measures to mitigate accident consequences:
  - specification of safety distances
  - use of inhibitors
  - odorization (where possible)
  - reliable and simple hydrogen sensors and warning devices.

The ignition of accidentially-released combustibles cannot realistically be excluded, neither for hydrogen nor for any other combustible. Therefore, possible accident scenarios involving liquid or gaseous hydrogen have to be compared to other combustibles, taking into account the specific aspects of hydrogen evaporation, cloud formation, combustion, and blast and thermal impact on the surroundings. Numerical modelling of turbulent combustion, flame acceleration, and detonations as well as of evaporation, cloud formation, and dispersion need to be further developed and improved for the prediction of the impact of hydrogen release in accidential situations. The main safety problem in the use of combustible gases, including hydrogen as an energy carrier, is the self-acceleration of combustion processes in totally or partially confined areas. Therefore, one of the most important goals is to prevent the transition of deflagrative combustion processes to detonation. Preventive and mitigating measures offer possibilities to realize a basic safety strategy for the widespread use of hydrogen energy technologies with high safety standard. Based on the current level of technology and based on decades of industrial experience dealing with hydrogen, this goal can be reached.

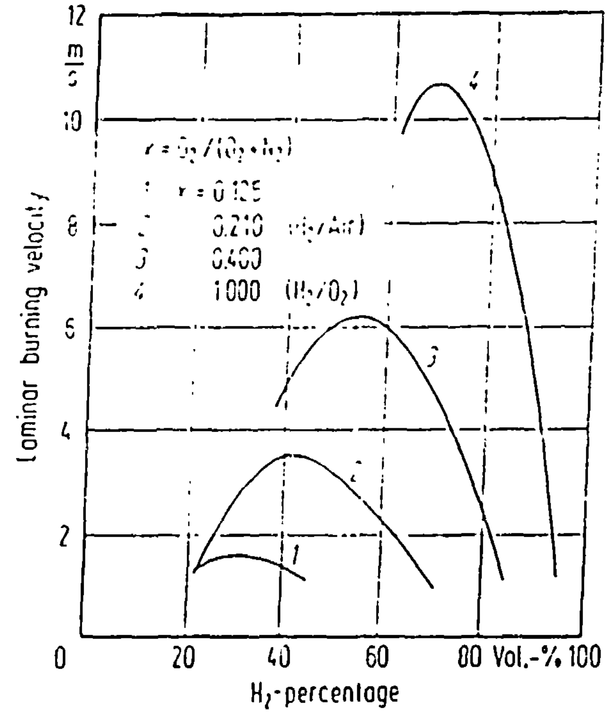


Fig. 3.1.1 - Laminar Burning Velocity of Hydrogen-Air Mixtures at 300 K

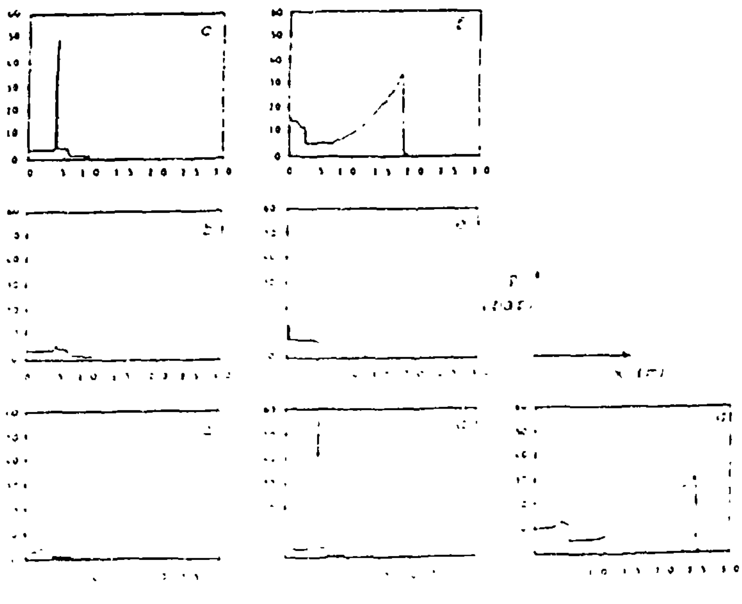


Fig. 3.2.1 - DDT-Process in a Tube, Numerical Simulation

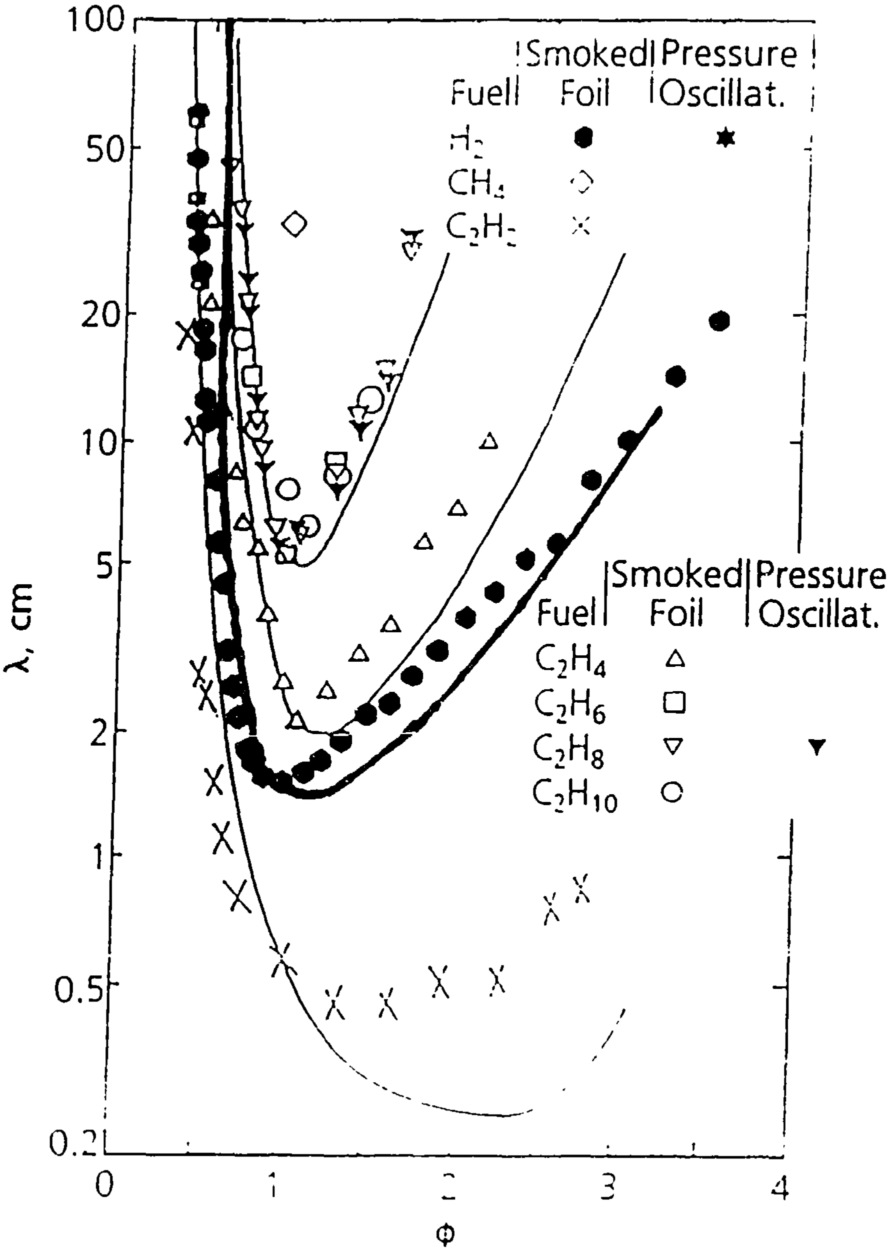


Fig. 3.2.2 - Detonation Cell Size for Different Fuel-Air Mixtures

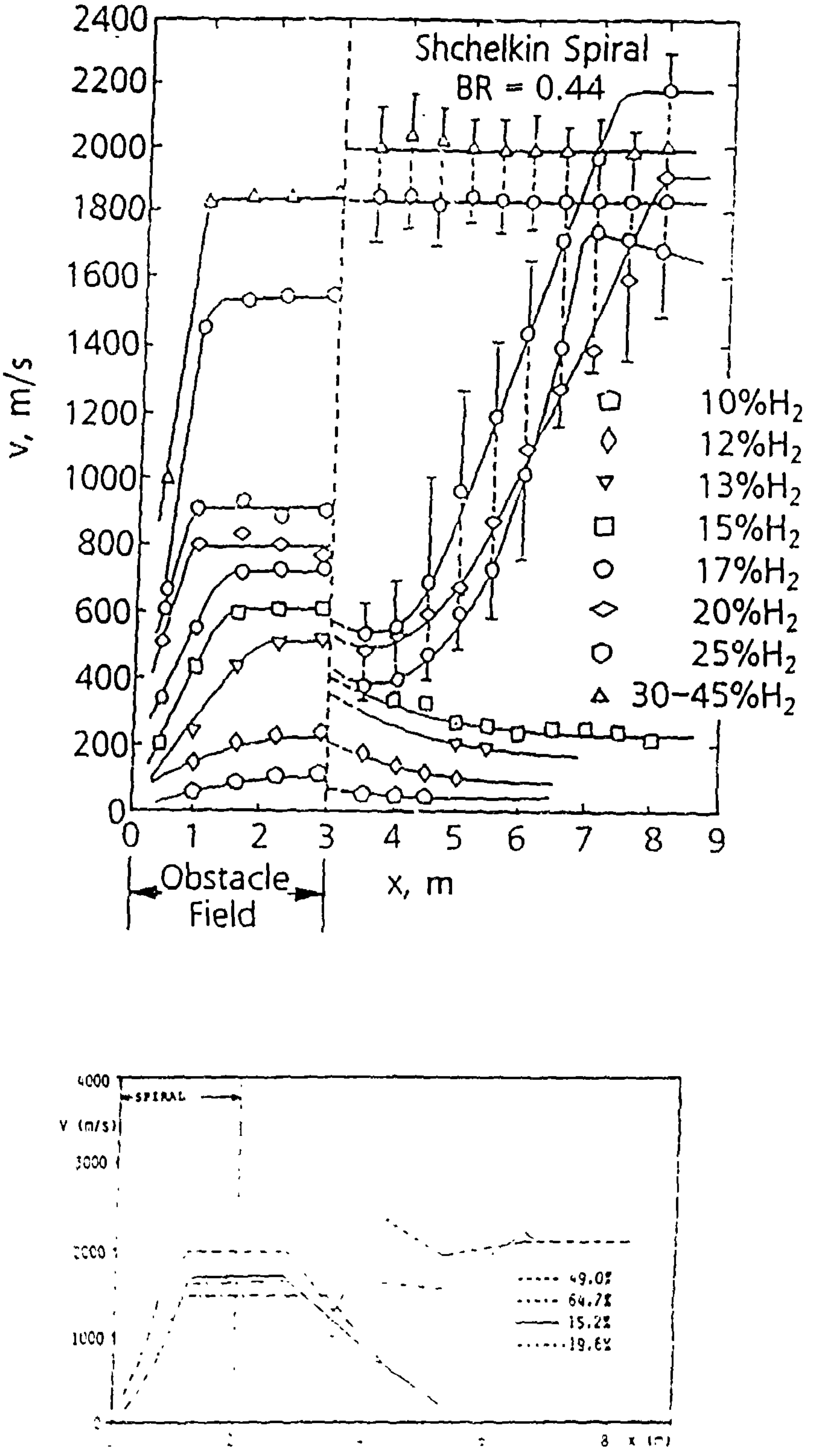


Fig. 3.2.3 - Flame and Detonation Velocities for Hydrogen-Air Mixtures in Tubes: Measurements

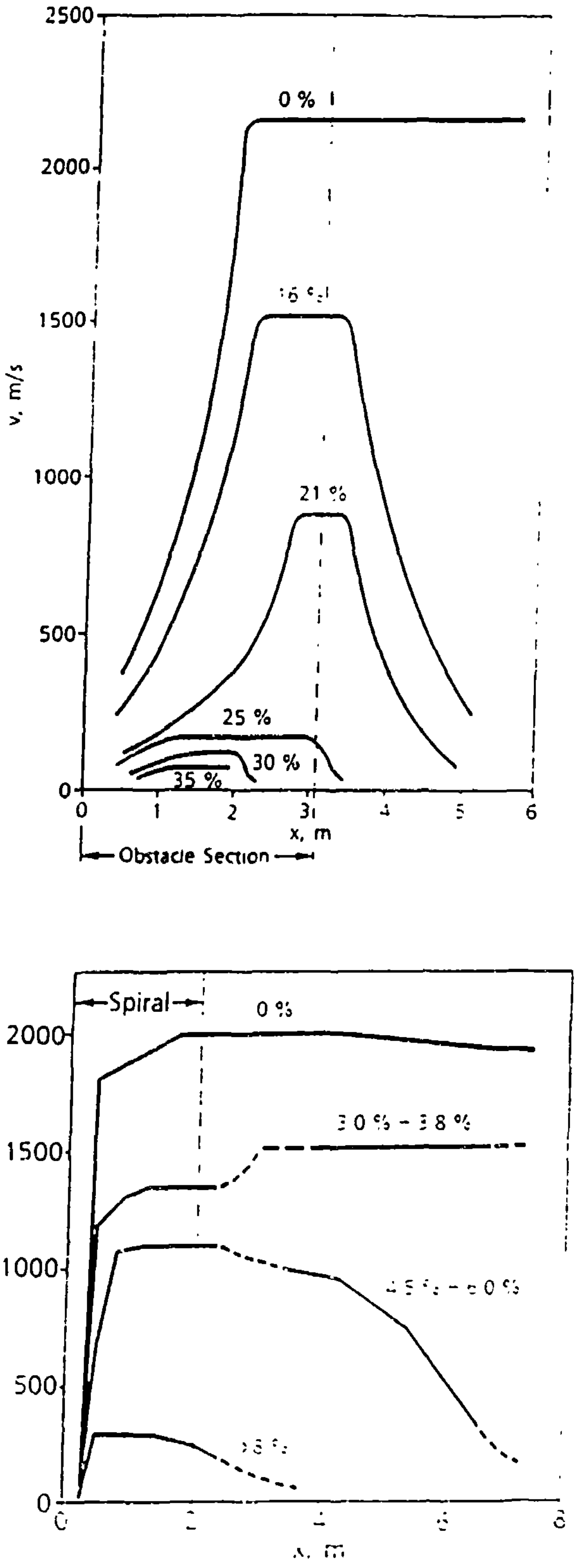
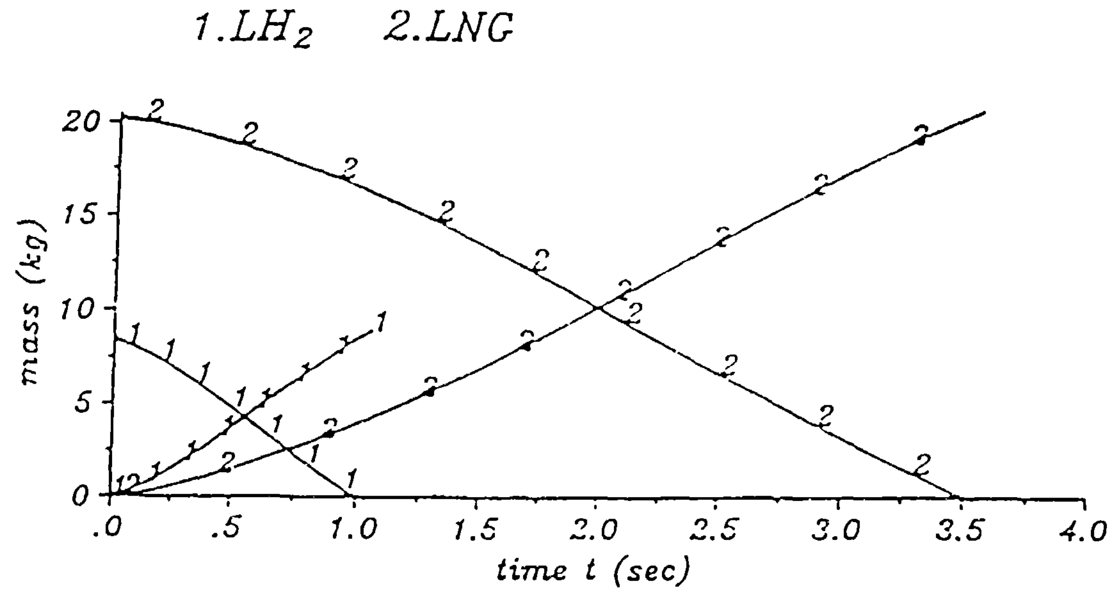


Fig. 3.2.4 - Influence of Water Vapour (top) and Methane (bottom) on Flame and Detonation Velocities



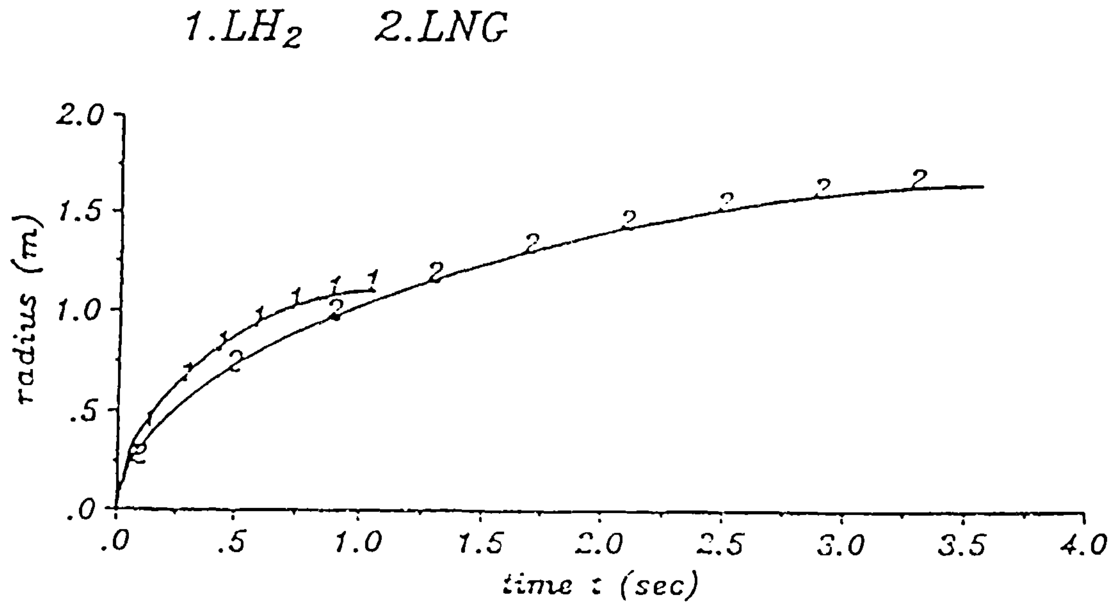


Fig. 3.3.1 - Spread and Evaporation of LNG and Liquid Hydrogen.
Same Energy Content: Mass Evaporation Rate and Total Mass Evaporated (top) and Spill Radius (bottom)

4. SOME APPLICATIONS OF HYDROGEN

Traditional applications of hydrogen in large non-direct energy use include synthesis of ammonia for fertilizers (2000 Nm^3 per tonne of NH_3), production of methanol (210 Nm^3 per tonne of CH_3OH), hydrotreating of naphta and coking distillates, coal conversion to liquid and gaseous fuels and many other chemical and metallurgical processes.

The demand for hydrogen in these types of commodity and energy application grew between 1970 and 1987 at a compounded rate of approximately 5.5%. The 1987 world demand for hydrogen was 123000 tonnes per day. If this were to be produced by electrolysis, approximately 265000 MW of installed primary generating capacity would be required, approximately 10% of the world's 1987 installed capacity for electricity production.

It is expected that the growth for hydrogen in the traditional industrial applications will continue to equal or exceed the average economic growth of countries which produce and use hydrogen (as opposed to the import of finished products such as ammonia and gasoline).

Beyond conventional industrial markets, there is expected to be large growth in the demand for hydrogen in developed nations due to environmental regulatory changes. On the surface, these changes are not intended to cause the world to move towards hydrogen but, due to the chemistry inherent in producing products which are more environmentally friendly, the result will be large increases in the demand for the products of electrolysis: hydrogen and oxygen.

Some of these regulated changes which are occurring or anticipated in developed nations include:

- The reduction in the aromatic content of "reformulated gasoline" will reduce the amount of hydrogen produced at oil refineries - this will in turn create requirements for new investment in hydrogen production equipment to counteract the shortfall. Future requirements to reduce sulphur in diesel fuel and, in Canada and some other countries, the fact that indigenous crudes are becoming heavier will add to the hydrogen demand.
- The switch from chlorine bleaching of wood pulp toward treatment with oxygen and hydrogen peroxide has two significant results: a reduction in the supply of low cost "fuel value" hydrogen from by-product chloralkali plants; and the requirement for new hydrogen supplies to make hydrogen peroxide - again creating new investment in hydrogen production equipment.
- The September 1990 California Air Resources Board Vehicle Emission regulations have mandated clean fuels and zero emission vehicles starting in 1998 (less than five years from the present). This will provide a market for clean fuels which will grow to other jurisdictions, and a particular opportunity for the fuel cell/electric vehicle powered by hydrogen.
- North American acid rain legislation will add to the cost of primary electricity generation by conventional sources. This will assist in the competitiveness of sustainable primary sources. These sustainable sources offer special opportunities for effective integration of hydrogen production.
- The Rio Conference and other world accords on the relief of global (upper atmosphere) environmental problems, such as global warming and ozone depletion, will create new niche (including some very large niche) opportunities for hydrogen and oxygen. The accords will favour processes which involve hydrogen addition to crude oil, as opposed to the alternative of carbon rejection (coking) processes; in turn this may lead to faster acceptance of the integration of fossil fuels with non-fossil (sustainably produced) hydrogen sources, thus extending and "cleaning" existing hydrocarbon resources. Further a carbon tax (which exists in certain European countries and is likely to spread) will assist the competitiveness of sustainably produced energy.
- Finally, it can be speculated that new environmentally-based government initiatives in many countries will create opportunities for clean hydrogen and oxygen related industrial process technologies.

All of the above trends toward hydrogen and oxygen have a number of "common characteristics". First, they are environmentally driven; second, none were overtly caused by governments specifically stipulating that hydrogen and oxygen must be provided; third, they profoundly affect the world's hydrogen (and oxygen) mass balance. Demand for hydrogen will expand at a rate higher than the average industrial growth rate of the economies of the world. As an example, the 1990 Clean Air Act in the USA is expected to cause compounded growth in hydrogen consumption at a 10% annual rate for cleaner gasoline over the next five years. If this new demand for hydrogen were to come from renewable electrical sources, approximately 18 GW of continuous capacity would be required by 1998.

Because the growth in hydrogen (and oxygen) for the energy economy is based on both expected industrial growth and (for the first time) environmental requirements, the case for hydrogen is doubly credible.

Hydrogen uses can be grouped in two categories: stationary applications and mobile applications.

4.1 Stationary applications

Stationary applications of hydrogen vary as to both capacity and end use. Hydrogen for cleaner fossil fuels, as a transition to complete renewables-based fossil-independent systems, will be by far the largest requirement in total energy terms and value in the coming decades. Already, in countries like Canada this is a $ 6 billion per year business and growth will continue. The source of the hydrogen for such applications as the upgrading of heavy oil and bitumen will probably be the steam reforming of natural gas; although it should be pointed out that if Canada were to stop all exports of natural gas and apply it solely to hydrogen for "upgrading", natural gas reserves would be consumed before approximately 50% of the heavy oil reserve was recovered. Thus a non-fossil source of primary energy is eventually needed for hydrogen production, to recover useful fuels from the abundant heavy hydrocarbon resources of an essentially hydrocarbon-rich country.

Beyond the upgrading of hydrocarbons in an environmentally sustainable manner, the direct substitution of hydrocarbon fuel by non-fossil fuel is the next largest stationary energy application for hydrogen. To date, two global international efforts are addressing this subject. The Euro-Québec-Hydro-Hydrogen Pilot Project envisions collection of off-peak or environmentally sound hydraulic energy and its transfer to Europe, in a hydrogen energy carrier mode via water electrolysis and liquefaction, for applications including power generation. The recently announced Japanese WE-NET project foresees the import into Japan (on the GW scale) of renewably-produced hydrogen energy, collected from areas of the world which have abundant renewable resources (solar and hydroelectyric). In Japan the hydrogen would be used for, among other purposes, electricity generation. The latter can be made, for instance, by gas turbine and combined cycle gas and steam plants. These plants are today operated on natural gas, but there are no fundamental problems associated with the use of hydrogen. Very high efficiency are expected to be reached: more than 50% in term of electric energy and 80-85% in the case of heat and electricity generation. Lifetime of these plant should be increased by use of hydrogen and the pollution will be limited to nitrogen oxides.

A further and, may be, more convenient way to generate electricity is offered by steam generators based on hydrogen-oxigen combustion. Conventional power stations are usually operated by mantaining the so-called spinning reserve for power regulating purposes. Hydrogen-oxigen steam generators could replace spinning reserve, making the conventional stations able to operate at their full power. As a consequence, electricity generation based on hydrogen and oxigen is valuable not only because of their energy production but also in term of more efficient use of electric generation system. Many operators, mainly in Germany and in Japan, are working on this theme, trying to individuate the better way to control the combustion and to apply it for load peak electricity generation. The research is at very advanced stage: 70 MW_{th} prototype has been realized and patented by the company Fichtner in Germany. The steam generators under investigation make use of compressed hydrogen and oxigen, that are mixtured and ignited by a dedicated plug, and a flame and vapour are produced;

the heat is used to vaporise some more water and then the steam is sent to the turbine. It is believed that hydrogen-oxigen steam generators can be compact and have sufficiently low investment cost. The main contribution to electric energy cost is given by hydrogen and oxigen cost. However, in the near term the hydrogen could be produced by water electrolys during off peak operation of conventional plants: this application of fossil derived hydrogen can sustain the transition towards non fossil hydrogen.

A technology to produce electricity which is well on its way to commercialization, using hydrogen and oxygen as its fuel, is the fuel cell. Fuel cells are electrochemical devices which consume hydrogen and oxygen to produce direct current electricity and water without the limitations of the Carnot cycle on combustion efficiency. When the hydrogen is produced from a renewable primary energy source, there are no other emissions. There are five types of fuel cell: alkaline, polymer exchange membrane, phosphoric acid, molten carbonate and solid oxide. Each type has unique characteristics as to operating temperature, required hydrogen (and oxygen) purity, optimal size range and necessary peripheral equipment (which is also dependent on the purity of the hydrogen and oxygen used). Today's fuel cells can convert hydrogen to electricity at very high efficiencies. Many plants based on phophoric acid technology have being realized in several countries, with power in the order of MW. These plants can be up to 50% efficient (in terms of electric energy) when operated on pure hydrogen, and even more than 70% if heat is recovered. Alkaline fuel cells operated on oxigen can be more than 60% efficient, but this technology still needs large development; anyway, in perspective they can offer an electrical efficiency up to 70%. Solide oxide fuel cells are expected to have about 60% of electric efficiency and more than 90% when heat is recovered. Fuel cells operate essentially silently and can be scaled down to small capacities (<50 kW) with reasonable economy (unlike combustion generators which, in their most efficient design, tend to have larger system sizes). Thus fuel cells should provide flexible and efficient hydrogen-to-electricity conversion technology for both centralised and distributed stationary applications.

Hydrogen can be used in flame burners, that are today well established for other fuel gases. Hydrogen fuelled burners are already employed in chemical industry and there are some prototypes for household applications. This kind of appliances can operate near 100% efficiency. The main advantage of using hydrogen is of course low pollution. If hydrogen is produced from non polluting sources very low pollution takes place along the entire process, due to some nitrogen oxides.

Hydrogen can act as a cooking fuel and heating fuel, through the use of catalytic burners which can be nearly 100% efficient as well as provide humidification: this device offers the further advantage of eliminating nitrogen oxides too. Such technologies may find application in developing countries which have suffered from deforestation, soil erosion and related agricultural problems because of an ever-more-desperate search for wood fuel; and may serve well the needs of remote communities in developed countries.

Finally, as already told, hydrogen can be used as storage medium for intermittent renewable sources, allowing to overcome the limitation of their intermittency. Further, one can imagine that hydrogen produced by these sources could be employed in non-electric uses. As a consequence, also intermittent sources could be fully exploited as forms of solar energy, in order to satisfy both electric and non electric energy needs. The use of hydrogen as a storage means will significantly increase the cost of renewable electric energy but, on the other hand, it will strongly increase the value of electricity too. At present, some economic evaluation on attainable cost have been performed in the case of photovoltaic plants. It has been calculated that, if all technical and economical goals will be achieved, a medium size photovoltaic station operating with a (gaseous on ground) storage system based on electrolytic hydrogen and with a fuel cell to regenerate electricity can give electric energy at about 0.22 $/kWh: this value does not seem so high if societal costs of conventional generation are taken into account.

4.2 Mobile applications

Mobile applications of hydrogen include ground, aerospace, aviation and other transportation sectors. Mobile applications present important environmentally leveraged markets for renewably produced hydrogen.

Ground mobile applications can be classified according to the size of vehicle (buses and trucks or cars) and to the kind of traction (electric motors fed by fuel cell or internal combustion engines). Electric vehicles with fuel cell and hydrogen are zero emission; conventional vehicles modified for hydrogen present a near-zero emission level referring to all pollutants, except nitrogen oxides. The latter can be significantly reduced by a proper control of combustion, for example by lowering the temperature in combustion chamber. However, hydrogen can represent a feasible and economically sustainable way to reach zero or quasi-zero emission level in transportation sector.

The emissions of the conventional urban vehicles include those substances which cause local ground level pollution (nitric oxides, unburnt hydrocarbons, carbon monoxide, etc.), the regional pollution problem of acid rain and the world problem of global warming due to emissions of carbon dioxide and other chemicals including uncombusted methane. Hydrogen vehicles can contribute to the relief of all three types of pollution. For example, it is quite possible that a fuel cell bus, when returning to a fuelling station which produces hydrogen by electrolysis of water using photovoltaics or wind turbines, could return the water which was used originally to produce the hydrogen. Thus, if the hydrogen is produced from renewable sources, no other emissions occur in the production process and the utilization process thus gains further benefit. The energy flow is from the sun to the wheels of the vehicle; hydrogen and oxygen are carriers for the sun, and water is recycled.

Further, hydrogen presents an opportunity to close the zero emission cycle being established in California, where vehicles which do not emit any hydrocarbon, carbon monoxide or nitrogen compounds will be required beginning in 1998. Battery-electric and hydrogen fuel cell-electric vehicles are the only known technologies which can achieve this objective. Howewer, significant strides are being made by companies such as Mazda, Daimler-Benz and BMW to achieve zero emissions of nitric oxide from internal combustion engines.

A hydrogen vehicle provides advantage over a battery-electric vehicle because energy can be stored on-board more effectively as hydrogen than as electricity in a storage battery. Both energy density and power density are significantly higher for hydrogen. Further, refilling time is lower than battery recharging time. Last, hydrogen storage tanks have a physical life which is measured in decades as opposed to the years projected for most batteries under consideration.

Nevertheless, major technical challenges for large introduction of hydrogen vehicles into transportation sector are just storage and infrastructures. In fact, due to low density of hydrogen, it is quite difficult to store it in quantity sufficient for long ranges. Besides, the refilling is not as easy as for conventional fuels, because it requires proper appliances, and time in the order of some ten minutes. On the contrary, the running of hydrogen operated vehicles is quite well established, mainly as far as internal combustion engines are concerned. Companies such as BMW, Daimler-Benz and Mazda are leaders in the field of developing, testing and demonstrating that hydrogen can be used safely and effectively. During the 1980's a small fleet of vehicles produced by Daimler-Benz demonstrated over 750000 total km in urban driving cycles in Berlin and Stuttgart without any hazardous problems. Mazda is pushing toward internal combustion engine cars fed by hydrogen; this company claims that hydrogen cars, with metal hydrides storage, can represent an effective alternative to electric vehicle (with batteries) because of the larger range and of reduced costs. According to Mazda, a hydrogen car should cost only 20% more than a conventional car, against the 100% of electric cars.

Anyway, storage and infrastructures are less compelling problems when municipal city buses are considered. In such vehicles, hydrogen on board storage can be made with today's available technologies easier than in small cars, due to availability of larger areas and volumes to arrange containers. A range of 200-300 km can be reached by using conventional storage, like pressurized vessels. Central filling stations allow to overcome the problem of the time and appliances required for hydrogen supplying in the case of municipal transport utilities. Thus, public transportation sector could represent an important market niche for hydrogen also in the near-mid term.

Many experiences are being performed regarding hydrogen fuelled buses, based both on electric motor and fuel cell and on conventional engine.

Regarding the first kind, Ballard Power Systems in Canada has developed a 120 kW fuel cell driven bus of modest size; this bus received its operating license and appropriate insurance in February of 1993 and is now travelling the roads of Vancouver with success. Other hydrogen bus projects in North America and Europe are underway; these examine a variety of technology combinations including fuel-cell electric hybrid systems, hydrogen and natural gas mixtures, and liquid and compressed hydrogen for internal combustion engines. A lot of operators are involved in activities, among which Daimler-Benz, BMW, Ansaldo, Man Linde, De Nora. The urban electric transit bus driven on hydrogen has been targeted as a highly advantageous environmental technology. The urban public transit driving cycle includes numerous starts and stops, circumstances under which internal combustion engines perform relatively poorly, while fuel cells show high performances also at partial load operations.

On the other hand, the use of hydrogen to supply buses with internal combustion engine is quite attractive for some other reasons. In this case, in fact, only some modifications on the bus are needed and they can be made on the base of the large experience gained on conventional cars fed by hydrogen. Besides, conventional fuels accounts only for about 10% or less of total transportation cost of municipal transport utility. Thus, the conversion of conventional buses to hydrogen could represent an economically sustainable step toward the ultimate hydrogen fuel cell bus.

After the urban bus, the passenger vehicle, particularly fleet passenger vehicles which can take advantage of small fuelling infrastructures, represent the next environmentally desirable opportunity for hydrogen.

Renewably-based fuelling for hydrogen vehicles is being demonstrated in California where The Electrolyser Corporation has supplied a system which, commencing in late June 1993, produced photovoltaic hydrogen and compressed it to 5000 psi to fuel a Ford Ranger pick-up with combustion engine.

A further field that is being explored is the utilization of hydrogen-methane mixtures. Some experiences are currently running in Colorado: first activities concerned the use of a mixture 15% hydrogen and 85% methane (by volume). Results showed an impressive reduction od pollutants: hydrocarbons and nitrogen oxides were 50% and 33% respectively of those measured on pure methane vehicle. When considering that methane is well known, largely used and accepted (also in transportation sector: only in Italy there are about 250000 vehicles running on methane) and believed suitable for public transportation to reduce pollution, the use of hydrogen-methane mixtures could be a realistic way to attain further reduction of pollution and could represent a "bridge" toward pure hydrogen.

Beyond ground mobile transportation, other applications of recent interest include aerospace. The best known use of hydrogen and oxygen for energy purposes is in NASA's space shuttle program. Liquid hydrogen an oxygen have been assisting the propulsion of spacecraft for decades. Further, these fuels are more environmentally benign than the solid oxide fuels which are also used.

Work in Europe, the USA and Russia has occurred on the development of liquid hydrogen aircraft. In April 1988 in Russia a commercial Tupolev 155 jet fuelled with liquid hydrogen was demonstrated from take-off to landing. In the 1950's a hydrogen-fuelled aeroplane (B57 Canberra) was tested successfully in the USA in level flight only. Within the framework of Euro-Quebec-Hydro-Hydrogen Pilot Project, Deutsche Airbus is developing a version of the Airbus to operate on liquid hydrogen, named the Cryoplane. The most significant motovation of the initiative is the short pollution offered by hydrogen. A first complete re-design of a A300 has been already performed: main problems are given by the bigger volumes of cryogenic reservoir, about 4 times greater than that of kerosene for the same range range. On the other hand, the advantages include a 30% reduction in take-off weight for the same payload and range, leading to less fuel and less noise. The product of combustion is almost entirely water vapour with some nitric oxide emission. Ground level pollution at airports is substantially reduced as compared to that with current fossil fuels.

The next generation of space flight rockets will including the Ariane 5 (a carrier for large payloads as well as astronauts) and the SÄNGER horizontal take-off and landing space plane. Liquid hydrogen and oxygen will be the fuel of choice.

Niche applications, but still large in cumulative energy terms, for hydrogen (and oxygen) include submarines, mining vehicles and other specialty vehicles where zero pollution is important.

With fully matured hydrogen system technologies, countries which are without indigenous hydrocarbon but which possess renewable energy sources can not only avoid serious atmospheric pollution but also can improve their economic position by substituting indigenous renewable fuels for fossil fuel imports. A further benefit is that since renewable energies such as wind and photovoltaics are already well dispersed, the need for costly energy transmission infrastructure can be avoided. Energy supply can be added incrementally to meet energy demand where and as needed.

5. SELECTED TECHNOLOGIES OF HYDROGEN PRODUCTION FROM RENEWABLES: STATUS AND PERSPECTIVES

Hydrogen can be produced in several ways and by a variety of technologies. In general, there are two categories:
- hydrocarbon-based
- non-hydrocarbon-based processes.

In industry, the production method is chosen generally (but not always) in accordance with quantity requirement: small, medium or large. The large requirements are characteristically based on a hydrocarbon source. The small requirements for on-site production are usually met by non-hydrocarbon methods such as electrolysis; for medium requirements the choice depends upon local factors such as relative costs and availability of hydrocarbon and non-hydrocarbon feed stock.

Hydrocarbon-based technologies currently dominate the industrial market place, to an estimated 97% or more. These production methods are: steam reforming and partial oxidation. Hydrogen (or a hydrogen-rich gas) is produced by reaction with steam alone or with steam and oxygen; waste products are trace hydrocarbons and large quantities of carbon dioxide. Only if biomass is used as the carbon source can the associated hydrogen production be called sustainable.

There are numerous non-hydrocarbon-based methods of hydrogen production which will gain in importance as the world continues to evolve sustainable energy policies, particularly those that limit hydrocarbon emissions.

5.1 Water Electrolysis

Water electrolysis is the process whereby electrical energy (direct current) is passed through a conductive acqueous electrolyte, resulting in the separation of water into its two constituents, hydrogen and oxygen.

In general, an electrolyser is composed by a set of elementary cells, usually series connected, properly arranged in a frame; in turn, the elementary cell consists of a solution in which two electrodes are immersed: they are separated by a membrane, in order to avoid the diffusion of oxigen into hydrogen and viceversa. An electrolyser is characterized by the cell voltage in function of current density, for the various values of working temperature. The efficiency with respect to the absorbed electric energy is the ratio: energy content of the produced hydrogen (upper or lower value)/ electric energy consumption. Here we refer to the lower heating value. The voltage-current curve gives good information on performances because the efficiency is inversely proportional to the voltage, while the current density determines the electrode area: under the same conditions of hydrogen production, the higher the current density, the lower the electrode area and, as a consequence, the lower the investment cost.

A "good" electrolyser should tend to have a cell voltage as low as possible with a current density as high as possible. These two conditions conflict with each other and research activities should find the best arrangement between them. In turn, for a given temperature the difference between the minimum voltage for water dissociation and the effective voltage is mainly due to ohmic resistance and anodic and cathodic overvoltages. Anyway, the principal parameter affecting cell voltage is working temperature.

In fact, there are several types of electrolysers and these can be classified by temperature. Solid oxide electrolysis (solid electrolyte) occurs at approximately 1,000 °C and has the potential to be greater than 100% efficient in electrical energy terms, since additional heat is provided to sustain production. Work in the USA, Russia, Japan and Germany is proceeding at the research level and the technology is still some years far from commercialization.

Main problems to overcome are related to the need for high temperature heat sources on one hand and to the difficulty of having available materials for such temperatures on the other.

Electrolysis in alkaline fused hydroxide melts can take place at medium temperatures of 300°C-450 °C but corrosion problems occur and this process is not yet commercial.

That leaves moderate temperature electrolysis between 70 °C and 150 °C operating temperature. Within the mentioned range of temperature there are several commercially available electrolysers but few recommend operating temperatures above 90 °C for practical long term industrial service. Technically successful cells have been developed using a polymer membrane as the electrolyte, such as the MEMBREL Cell by Asea Brown Boveri and the SPE cell developed by General Electric and sold by Hamilton Standard. At the moment these are limited in commercial industrial use but do find applications in niche markets such as submarines and aerospace.

This kind of electrolyser is characterized by simplicity in operation and maintenance because of the absence of corrosive liquids, but it requires very costly materials. As a consequence, polymer electrolysers will become an effective option only if less expensive materials are found for substitution of present day employed ones.

Alkaline electrolysers are the commonly used type, covering more than 99% of the today's market, amounting to about 10 MW per year. For the alkaline electrolysis processes, the reactions are:

(ate the cathode) $4H_2O + 4e^- \Longrightarrow 2H_2 + 4OH^-$

(at the anode) $4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$

(for the cell) $2H_2O \longrightarrow 2H_2 + O_2$

The alkaline electrolyte is not consumed in the process.

In the commercially available alkaline electrolysers the cathode is made of steel or nickel, while the anode is of nickel. The electrolyte is a solution of KOH not larger than 30% by weight, this limit being imposed by corrosion problems. Operating temperature is less than 90°C because of the diaphragm, made of asbestos, that dissolves at higher temperatures. Today commercial electrolysers have efficiencies up to 70%, that means an electric energy consumption of about 4.3 kWh per normal cubic meter of hydrogen.

Beyond temperature limit considerations, two other factors are of primary importance: geometric configuration and operating pressure.

Geometric configuration involves making a choice between a bipolar design and a unipolar design. In a bipolar cell, each electrode has a dual polarity - i.e. it is anodic on one side producing oxygen, and cathodic on the other producing hydrogen.

Electrolysis in a unipolar cell (Fig. 5.1.1) involves single electrode polarities producing the same gas on both sides of the electrode. Due to its geometry, a bipolar design (Fig. 5.1.2) has shorter resistive paths than a unipolar cell. Unipolar cells find advantages in their simplicity, low cost, long stable life, and high Faraday efficiency (very important in renewable sources based applications where a wide range of current densities are experienced). Overall energy efficiencies are comparable.

A particular effective kind of cell arrangement is the "Zero gap": it allows to press electrodes against diaphagms, thus achieving a significant reduction of cell electric resistance. Further achievement could be gained by pressurized operating electrolysis; this has been an option to which developers of electrolysis cells are giving great attention. It would seem simpler and more efficient to pressurise water externally to feed a pressure electrolyser than to compress gas after electrolysis at atmospheric pressure. The difficulty lies in the fact that the electrolyser must then become a pressure vessel (or be contained within one) which produces two gases at different rates, separated by a thin porous separator; and detailed external pressure balancing is required. The greatest danger in electrolysis is for the gases to mix due to pressure imbalance either internally or externally. Beyond the inherent hazard of having compressed oxygen and compressed hydrogen within the same pressure containment vessel, the electrolyser becomes more expensive due to the need to overcome stresses and leakage problems which are induced by pressurisation. To date, 30 to 35 Bar appears to be the highest

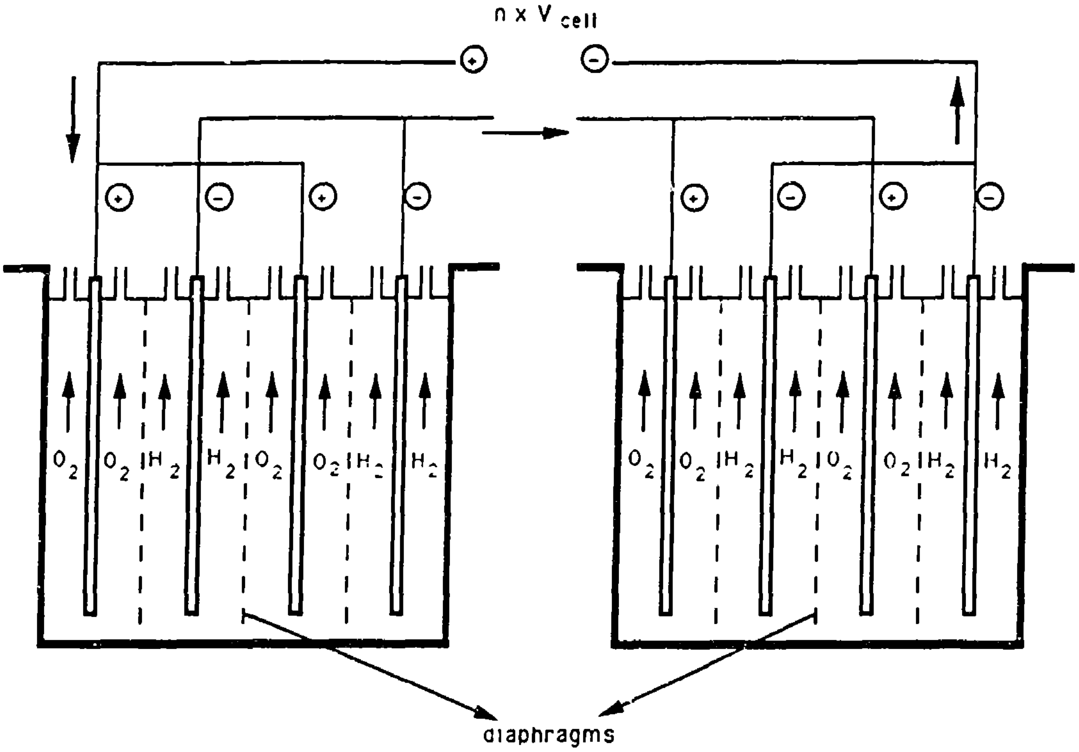


Fig. 5.1.1 - Unipolar electrolyser cell design

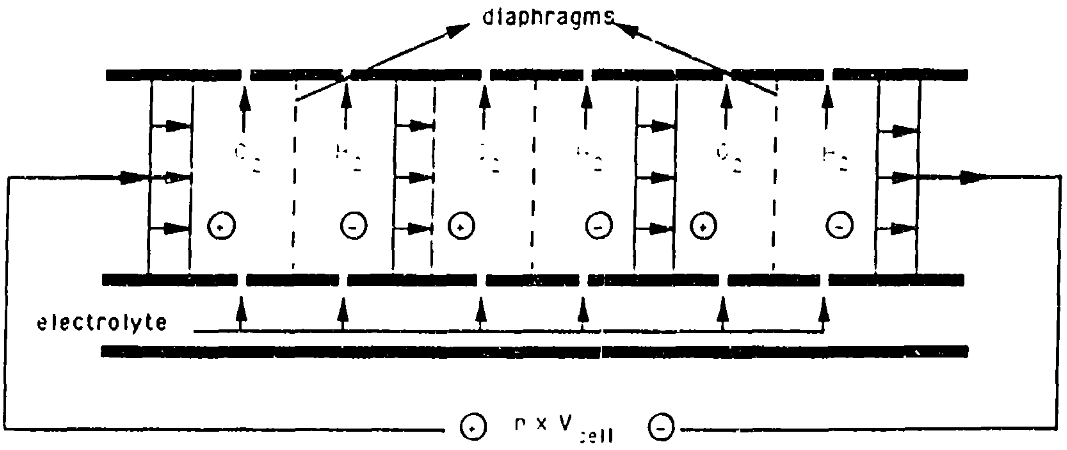


Fig. 5.1.2 - Bipolar electrolyser cell design

pressure which manufacturers try to achieve. In situations where the gas is needed at higher pressure (for example 200 to 300 Bar), additional external compression is required.
Efficiency can be increased by using more resistant materials, in order to achieve higher values of temperature: this problem involves mainly the research on diaphragms better than asbestos. Finally, the use of proper electrocatalyst coatings for electrodes can facilitate the evolution of hydrogen and oxigen: that allows a reduction of the overvoltages at the cathode and the anode, resulting in a further reduction of cell operating voltage.
In the perspective of water electrolysis from intermittent renewable sources (wind and solar), particular attention must be payed to the direct connection of the electrolyser to the generator. In such a case, intermittent power is supplied to the electrolyser and some problems of efficiency and safety can arise. Though this field still requires in depth investigation, some preliminary experiences conducted by Electrolyser Corp. Ltd, within the HYSOLAR project and by other operators have shown the possibility of directly connecting the electrolyser to intermittent generators without significant losses.
Fig. 5.1.3 describes the voltage-current curves of today electrolysers and the expected evolution arising from research efforts.
Tab. 5.1.1 gives a rough situation of industrial available electrolysers. Today's electrolysers have a cost of about 600 $/kW; in perspective, a reduction up to to a half can be anticipated.
At present, many large plants for water electrolysis are working in the world, mainly where electric energy is available at low cost: electric energy cost, in fact, accounts for more than 70% of the total cost of the produced hydrogen. The larger plants are located at Assuan (Egypt, 33000 normal cubic meters/h, Nm^3/h), Nangal (India, 30000 Nm^3/h), Ryukan and Ghomfjord (Norway, each about 28000 Nm^3/h), Trail (Canada, 15000 Nm^3/h). Large plants are based on alkaline technology.

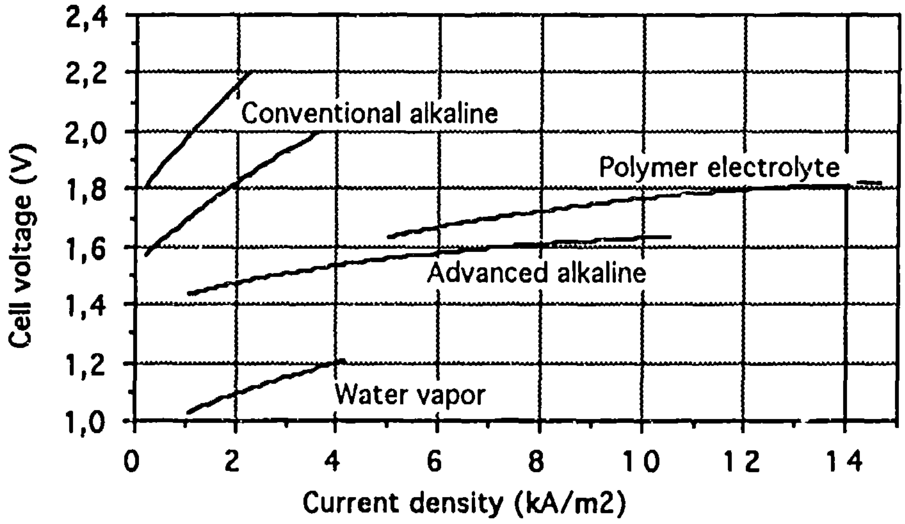


Fig. 5.1.3 - State of the art and expected performances of cell electrolysers in term of voltage-current curve

Manifacturer //////// Parameter	Electrolyser	Brown Boveri	Norsk Hydro	De Nora	Lurgi
Geometry	Monopolar	Bipolar	Bipolar	Bipolar	Bipolar
Pressure (bar)	1	1	1	1	30
Temperature (°C)	70	80	80	80	90
Concentr. KOH (% by weight)	28	25	25	29	25
Current density (A/cm^2)	0.25	0.20	0.17	0.15	0.20
Cell voltage (V)	1.85	2.04	1.75	1.85	1.86
Spec. electr. cons. ($kWh\text{-}DC/Nm^3\text{-}H_2$)	4.8	4.9	4.3	4.6	4.5

Tab. 5.1.1 -Characteristics of main commercially available electrolysers

5.2 Hydrogen from Biomass

Renewable hydrogen can also be produced in a non-electrochemical manner by the gasification of biomass materials such as forest and agricultural residues, urban wastes or wood chips from biomass plantation. The basic reaction is:

$$2C_xH_y + nO_2 \rightarrow yH_2 + 2xCO \text{ (plus other higher hydrocarbons)}$$

The feedstock is introduced into a gasifier at high temperature where it is broken to form a gas. The output gas mainly consists of hydrogen, methane and carbon monoxide. Methane, in turn, can by converted into hydrogen and carbon monoxide, thus obtaining the cited total reaction. This gas can be useful for a variety of purposes including local fuel. It is possible to remove carbon monoxide having pure hydrogen.

Many biomass gasifiers have been experimented at laboratory and pilot plant scale. Besides, several gasifiers developed for methanol production appear suitable for hydrogen production. All appliances required in order to convert the hydrogen, carbon monoxide and methane mixture are quite well established. So, one can conclude that hydrogen production from biomass seems to be very promising in a not so far future.

Besides, when the above process is integrated with water electrolysis, a further improvement can be made. First, the oxygen for the partial gasification can be supplied by the electrolyser. Next, the hydrogen from the electrolyser can be added to to the gasifier output to produce synthesis gas (CO plus $2H_2$), from which "renewable fossil fuels" can be produced. When synthesis gas is passed over the correct catalyst, methanol can be made.

This "electrolytic methanol" is a relatively easily made and transportable fuel which can be used for cooking and as transportation fuel in developing nations, or transported to developed nations for cleaner fuel and energy generation applications. A renewable fuel (produced from reasonably available global resources) would then be displacing to advantage non-renewable fossil fuel.

5.3 Other non-hydrocarbon routes

Beyond gasification and water electrolysis, there are additional hydrogen production methods which, in time, may play important roles. These include:

- thermal water splitting (very high temperature)
- thermochemical cycles which use high temperature heat to split water
- photoelectrolysis in which sunlight directly splits water into hydrogen and oxygen
- photobiology where microorganisms produce hydrogen
- radiolysis

Among the options discussed in this chapter it is likely that, in the foreseeable future, only water electrolysis and gasification of biomass will be economically available and will be the methods choosen at a significant commercial scale for sustainable hydrogen production; however development of all methods mentioned here is worth pursuing as the needs and resources of the regions of the world often require quite different approaches.

6 - HYDROGEN STORAGE: STATUS AND PERSPECTIVES

In chemical industry hydrogen is among the most used elements; as a consequence, many techniques of hydrogen storage are satisfactorily known and used. Nevertheless, that does not mean that the corresponding technologies can be considered so mature that they can be massively employed in a future new energy system based on renewable energy sources, electricity and hydrogen. On the contrary, hydrogen storage methods employed today appear quite adequate only in the present day structure of hydrogen production and utilization; in fact, chemical industry makes use of hydrogen in the neighbourhood of production sites and in time not so much delayed. When that does not occur - as may be in space industry - hydrogen storage costs are marginal with respect to total costs of enterprise.

Large use of hydrogen needs the availability of many technologies of storage, cheaper than today available, and suitable for the various applications. From this point of view, hydrogen storage represents one of the most important, not yet satisfactorily solved problems.

Hydrogen storage can be referred to two main sorts of applications: stationary and mobile applications. Among the former, in a long term perspective, seasonal storage of hydrogen appears very important in order to overcome the problems related with the intermittence of solar and wind sources. Transportations by air and road require proper storage technologies in order to meet low volume and/or weight reservoir requirements.

Generally speaking, technical parameters for the evaluation of the suitability of a storage technique can vary from an application to an other one. Apart from costs, in the case of air transportation, for example, energy density per unit of weight is of paramount importance, while in private road transportation this parameter is not sufficient, being the energy density per unit of volume important too. For seasonal stationary storage other performances can be more significant than energy density, like, for example, hydrogen losses by evaporation.

Parameter ///// Technology	Energy density (kWh/kg)	Energy density (kWh/l)	Process temp.(°C)	Energy need (% LHV H_2)	H_2 losses (%/day)
Compressed in small cylinders (≥ 200 bar)	0.5-2	0.5-1	room	5-7	≈ 0
Liquid dewars	6	1.7-2	-253	25-40	0.1-3
Metal hydrides	0.4-1.5	1-1.2	-10/300	10-26	≈ 0
Methylcyclohexane	1	0.7	500	20	≈ 0
Activated carbons	up to 1	up to 0.6	-200/-100	5-7	?
Caverns	not appl.	0.3	room	0.05	0.01-0.03
Glass$^{(*)}$ encapsulation	2.3	1.4	400	4-5	?

Tab. 6.1 - Main characteristics of conventional and advanced hydrogen storage technologies (energy densities include tank weight and volume)

$^{(*)}$ Theoretical values

Good parameters for overall evaluation are: for ground level mobile applications - when hydrogen is proposed as a fuel for internal combustion engines or fuel cells powered vehicles - the range of the hydrogen powered vehicle, for a given load; for stationary applications the duty cycle in hours, expressed by the ratio E_c(kWh)/Ip(kW), where E_c is the energy capacity of the storage and Ip is the user's installed power.

Storing hydrogen is difficult mainly because of the chemical and physical characteristics of this element. At Normal Temperature and Pressure (293.15 K and 1.013 bar) hydrogen is gaseous, with a very low density, close to only 0.084 kg/m^3, thus storage of gas, even compressed, requires big volume and weight of vessel. Liquefaction happens at about 20 K: that means large expenditure of energy for liquefaction and proper reservoirs for storage. In addition, safety problems very often compel to use dedicated devices that complicate handling and storage of hydrogen.

At present, the most employed technics for hydrogen storage are pressurization of gas and liquefaction. Other techniques under investigation are metal or liquid hydrides, low pressure adsorption on activated carbon and glass microencapsulation. Hydrogen in cavernes is being investigated starting from some experience in hydrogen short pipelines and from the konw-how gained on other kind of fuels.

Tab. 6.1 summarizes the main characteristics - state of the art and expected - of conventional and advanced hydrogen storage technologies.

6.1 Gaseous Hydrogen

The storage of hydrogen as a compressed gas is by far the most common way of storage for current applications and, as a consequence, it has become an old and well established technology.

High pressure storage in steel or aluminium bottles or medium and low pressure storage in spherical or cylindrical vessels is safe and reasonably cheap for the most part of industrial uses, as proved by many and many years of successful experience.

Nevertheless, if we consider hydrogen as an energy carrier and not as an industrial gas, these favourable characteristics of traditional compressed hydrogen storage are not satisfactory, expecially if we refer to weights and volumes for mobile systems and to storage costs for seasonal storage tasks.

On the other hand, compressed hydrogen storage is well known, easy to handle and energetically favourable, 4-8 times more than liquid hydrogen storage, in comparison with which there are no boil-off losses.

Gaseous hydrogen storage for vehicles

The range of a vehicle, for a given pay-load, depends on its energy consumption and on its energy storage capacity, that in turn is a function of the energy weight density of the fuel storage system. As a consequence, low energy density storage systems like compressed hydrogen cylinders, heavier and bulkier than some other storage systems, are feasible and cheaper for short range vehicles, whilst for longer ranges duty high cost of liquid hydrogen is counterbalanced by low storage weight and consequent low fuel consumptions.

The large volume occupied on board by the gas bottles limits compressed hydrogen storage in cylinders to vehicles like lorries or buses, where the bottles compartment can be arranged on the roof of the vehicle or under the bodywork.

The gas low energy density is therefore a serious handicap for on board storage, where it reduces range and payload ratio, when coupled with heavy weight of conventional steel containers.

So, in consideration of a future widespread presence in the automotive or aeronautical markets, performance requirements of large high pressure gas containers for on-board storage or portable gas containers must be focused on low weight and cost, high energy content, coupled with high safety standards and low maintenance needs.

Moreover, enhanced environmental performances, which in this case mean recyclability or reconditioning, are probably going to become more and more important, especially for automotive applications, in accordance with the more and more increasing attention paid to the problem of reuse of non-metallic parts of vehicles.

Mechanical performances of a high pressure container are related to a parameter K = PV/W, where P is the design pressure, V is the volume and W is the weight.

For constant technology, K is a constant, that is, for steel vessels, between 140/240 bar l/kg, the upper value corresponding to compressed natural gas (CNG) steel cylinders for automotive use. State of the art performance for fiber glass reinforced (FGR) aluminium gas cylinders is 333 bar l/kg and for carbon fiber reinforced (CFR) cylinders with thermoplastic liner (design pressure 300 bar) it is 525 bar l/kg.

A parametric study on the specific transport cost ($ /km kg, on payload) for several kind of fuels has proved that for a low energy density fuel like hydrogen, an achievable value for this constant is 700 bar l/kg, corresponding to 2 kWh/kg when filled with hydrogen. Fire and crash resistance will be additionally required mechanical performances.

Functional and operational design criteria of such storage systems must satisfy those well established for conventional cylinders, like reliability, safe handling and refuelling, plus those peculiar for composite structures, like gas permeability, maintenability and durability.

Legislation & Safety requirements regarding such a kind of products are stated for steel vessels, but only few European countries, like Germany, have a regulation for composite high pressure containers.

Continuous fiber reinforced containers have not yet proved duration characteristic like metallic ones have; in addition, recyclability or reconditioning should be demonstrated in order these containers become enviromentally and economically effective.

Commercially available cylinders show an energy density of about 0.5 kWh/kg and 0.5 kWh/l. Great improvements can be achieved by innovative high pressure composite containers, which weigh only one third of usual high pressure metallic containers. In comparison, energy densities achievable in liquid dewars, discussed below, are much higher.

Fig. 6.1.1 shows total transport costs of hydrogen powered vehicles as a function of range, fuel production costs and vehicles gross weight, for a given payload. As a consequence of low production and investment costs of compressed hydrogen (CH_2), total cost is lower for CH_2 powered vehicles for short range duties, up to 250-300 km, where we have a break-point with liquid hydrogen powered vehicles, lighter and thus less consuming. This is a typical range for public urban transport, where near-zero emission vehicles like hydrogen fuelled busses could justify higher costs.

It is important to note that already today in Italy, where the consumer price of CNG is much lower than the gasoline price for fiscal reasons, there is a network of gas-filling station capable of ensuring the operation of more than 250000 automobiles; many public transport companies are introducing CNG powered busses, for their lower enviromental impact and good operational capability.

Gaseous hydrogen storage for stationary applications

For compressed hydrogen storage, cylindrical vessels up to 30 bar or spherical vessels are of common use.

Cylindrical vessels are generally used for geometrical volumes up to 1000 m^3, because easier to make and to install; spherical vessels can be of medium size (diameter 5-10 m, pressure 10-20 bar) or large size (diameter 20-40 m, pressure 5-10 bar).

Specific weight of a pressure vessel is a function only of its shape, cylindrical or spherical, and of material charactheristics, namely maximum strength and specific weight, and it is not a function of gas pressure or vessels dimensions.

As a matter of fact, for a spherical vessel having a volume V and a weight W

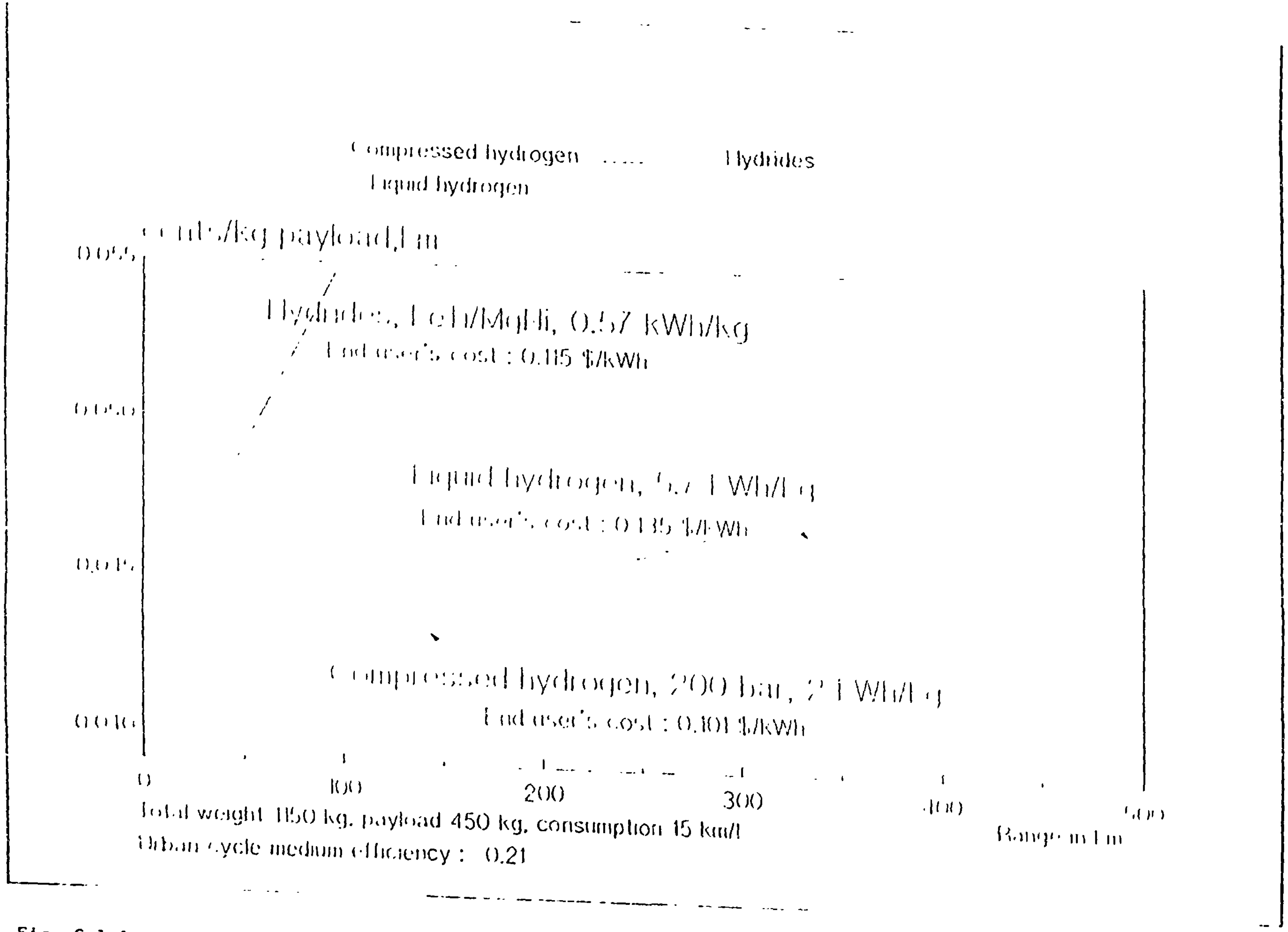


Fig. 6.1.1 - Expected costs for hydrogen vehicles (hydrogen production cost 0.075 $/kWh)

$V = f(r^3)$ and $W = f(r^2)*s*\rho$

where r is the radius, s the wall thickness and ρ the material specific weight, the gas content G is a function of geometrical volume and pressure p only, $G = f(r^3)*p$.

The maximum pressure p is a function of the maximum material strength σ_m, wall thickness s and radius r, given by $p = s*2\sigma_m/r$. So vessels specific weight $S = W/G$ is a function only of the ratio ρ/m.

For example, for carbon steel ASTM 285 grB, specific weight is 17 kg/Nm^3 for cylindrical vessel and 12.5 kg/Nm^3 for spherical vessel, whatever their dimensions and pressure may be. As the vessel cost depends on its total weight and, for a given capacity need, this does not depend on its dimensions and pressure, there is no reason to exceed with them, so being forced to use thick plates that require hot-working.

Specific convenience of such a kind of storage systems is strongly affected by their usage frequency. From analytical analysis it results that gaseous storage for stationary applications can be effective when daily charging and discharging cycles occur, while, on the contrary, the utilization for seasonal storage (5-10 charging and discharging cycles per year) leads to an additional cost up to 1/3 \$/kWh, which seems prohibitively high. As a consequence, this kind of storage is suitable only for certain kind of applications.

6.2 Liquid Hydrogen

Hydrogen produced by electrolysis and other known technologies is in gaseous form. Storage in liquid form requires proper technologies of liquefaction. Before discussing dewars for storage of liquid, we shall discuss liquefaction processes.

Liquid hydrogen is odourless and colourless and has a normal boiling point of 20.3 K. At this temperature, the density is only 70.8 kg/m^3, so hydrogen is one of the most light liquids. A particular property of hydrogen is that it can exist in two different molecular forms: ortho-hydrogen and para-hydrogen. The two molecules differ in orientation of angular momentum, or spin, of the two protons that constitute the nuclei of each molecule. When the two protons have the spins oriented in the same direction, the molecule is ortho. When nuclear spins are oriented in opposite direction, the molecule is para.

At room temperature, para-hydrogen is about 25%, while at boiling point temperature it tends to nearly 99.8% at thermodynamical equilibrium. The change does not happen instantaneously, but on the contrary it is quite slow, so that fresh, quicly liquefied hydrogen could have practically the room temperature ortho-para composition. Then ortho to para conversion starts with exothermic reaction: a quantity of heat close to 310 cal/mol is released, to be compared to a heat of vaporisation of para-hydrogen of 216 cal/mole: as a consequence, a serious - peculiar of hydrogen - problem of boil off must be accounted for: for instance, if fresh liquid hydrogen contains the same para concentration than at room temperature, after 8 days about 50% of hydrogen is vaporised.

This problem is overcome by a catalytic conversion of ortho-hydrogen into para-hydrogen during the liquefaction process. An arbitrary level of 95% of para content has been established for hydrogen liquefied commercially.

In any case, the degree of conversion is dependent upon the foreseen application. Of course the catalytic conversion from ortho to para is energy-expensive due to the heat removal.

Conventional liquefaction processes

In spite of these technological challenges, liquefaction and storage of hydrogen is a quite well established technique, developed at industrial level for many uses, among which space applications. This is not surprising if one bears in mind that hydrogen was liquefied by Prof. J. Dewar in May 1898 at the Royal Institute of London. Prof. Dewar in 1892 also developed a vacuum insulated vessel for cryogenic-fluid storage. The industry for the so called "permanent" gases liquefaction started between the end of the 19th Century and the beginning of the 20th Century; Linde AG was established in 1879, while l'Air liquide was established by G. Claude in 1902. In the 1950-60's large plants for liquefaction of hydrogen and storage were available in many countries. The largest containers for liquid hydrogen are at Kennedy Space Center in USA, that disposes of two spherical containers, with a capacity of more then 3.2 Ml each.

At present, many industries are able to produce and store liquid hydrogen, like Linde, Air Products and Chemicals, l'Air Liquide, etc.

The process of hydrogen liquefaction, as well as all refrigeration processes, can be seen as a process of entropy reduction. It is usual to represent the thermodynamic cycle in a temperature-entropy diagram, with a further quantity, like pressure, as parameter. In this case, the refrigeration process can be, in principle, reduced to an isothermal compression, followed by an adiabatic expansion. In fact, the most used thermodynamic systems are based on these two transformations.

Starting from the compressed gas, it is possible to obtain a refrigeration through an adiabatic expansion, by spending external work (isoentropic expansion): this is true for any temperature. Besides, for real gases, it is possible to obtain refrigeration by expanding the gas in valves based on Joule-Thomson effect, starting from a temperature lower than the so called "inversion maximum temperature" (isoenthalpic expansion). Most refrigerators are based on these two kind of expansions. In almost all cases they use cyclically an isothermal compression and then an adiabatic expansion. The final design of the refrigerator strongly depends mainly on its use and size.

Many cycles and corresponding technological processes are utilized, very often using liquid nitrogen as precoolant. Without being complete, we can mention the following ones: Linde-Hampson, Claude, helium-hydrogen condensing cycles, whose flow diagrams are shown in Figg. 6.2.1, 6.2.2 and 6.2.3 respectively.

Good indicators of cycle performances are: the liquid yield, i.e. the fraction of gas total flow that is liquefied; the work required per unit mass of gas compressed; the work required for unit mass of gas liquefied and, finally the figure of merit, defined as the ratio between the work required per mass unit of gas liquefied in the ideal reversible cycle and the work calculated for the actual cycle. The value of these parameters can vary according to the values of pressure, temperature, etc. among the various stages. However, Claude cycle is estimated as one of the most valuable cycles. In any case, apart from costs, the evaluation of cycle performances has to be joined to a careful appraisal of component efficiencies. Heat exchangers, compressors, valves strongly affect overall process efficiency.

Good plants require an amount of energy for hydrogen liquefaction of about 10 kWh/kg. Bearing in mind that 1 kg of hydrogen has a lower heat content of 30 kWh, one can conclude that about one third of hydrogen energy content must be spent for liquefaction. This value is about three times the value arising from simple thermodynamic consideration. As a consequence, some improvements are possible. In particular, efforts can be performed to reduce losses in the components, but also a careful analysis of physical parameters and plant architecture, including hydrogen pressure outside the compressors, the number of expansion turbines, gradients of temperature among the various stages and better ways to operate ortho-para conversion can give good results.

Magnetic refrigeration

An alternative system to liquefy hydrogen is Magnetic refrigeration (MR) that could create new opportunities through its promise of higher efficiencies and lower capital investment costs.

As already told, compressors and expansion engines are major sources of inefficiencies and can pose a barrier to substantial improvements of conventional liquefier efficiencies. Magnetic refrigeration has the potential to break this efficiency barrier.

In MR, solid magnetic substances are used instead of the working gas and the magnetic field is used instead of the compressor and the expander in order to produce refrigeration. From a thermodynamic point of view, the basic MR cycle is similar to the mechanical cycle. When a gas is compressed at constant temperature, the order of the system is increased (the entropy decreased) since the molecules are moved closer together without increasing their random velocities. When the gas then expands reversibly and adiabatically (constant entropy) the velocity and thus the temperature of the gas decreases in order to maintain the same degree of order or entropy. In solid magnetic material the way of ordering is, however, different. The isothermal application of an external magnetic field (analogous to compressing gas isothermally) tends to align the randomly oriented magnetic moments, thereby introducing order in the system. If the magnetic field is removed reversibly and adiabatically (corresponding to reversible adiabatic expansion of the gas) the entropy remains constant and the temperature of the material decreases in order to preserve the same degree of order.

In addition to higher efficiency, the advantages foreseen for MR over mechanical refrigeration are lower capital and operating costs, compactness and higher reliability. The last two advantages are due to solid working material instead of gas, few moving parts and slow speeds.

A comparison between the cost of producing liquid hydrogen by conventional methods and the projected costs for the MR technology shows that MR could lead to substantial cost reductions, especially for liquefaction capacities below 10 t/d. For example, the foreseen reduction (in the cost of liquefying 1 kg of hydrogen) from a 1 t/d plant is about 40% and could be as much as 60%.

The efficiency advantage of MR over the mechanical systems could also lead in the long term to more effective large scale liquefiers and thus make liquid hydrogen more price competitive with respect to other liquid fuels.

The application of MR concepts in the 20-300 K temperature range started in the mid-seventies and several proof-of-concept devices have been built in the last decade. Most of these devices were designed to provide cooling using room temperature heat sinks and one of them used liquid nitrogen. None of these devices achieved the projected efficiency, cooling power or temperature lift. The key problem areas were identified as being: heat transfer inefficiencies between the magnetic material and the regenerative fluid; flow control; efficient applications of large magnetic forces; system design; materials.

In the last few years, some of the problems have been solved and progress has been made towards others, especially in the 20-77 K range. This range is considered by many as a first step toward the realization of a hydrogen liquefier starting from room temperature. However, many challenges still remain to be addressed before a magnetic liquefier which fulfils all the promises of this technology can be finally achieved.

The realization of an advanced all-magnetic hydrogen liquefier using room temperature heat sinks would require the development of complex ferromagnetic materials suited for reversible magnetic cycle operating over wide temperature ranges between 300 K and 20 K. The limited entropy range of ordinary ferromagnets becomes a major source of inefficiency when the temperature span of the refrigerator is increased. The Japanese are leading the research efforts in this area.

Another interesting approach to the material problem is based on the use of nanocomposites consisting of magnetic species diluted in non magnetic matrices. Although such a material is yet to be processed, numerical modelling of their magnetic refrigeration cycles shows that nanocomposites could have higher magnetocaloric effects than ordinary ferromagnets and would thus require lower magnetic fields to achieve the same results, which is clearly a big advantage. However, the analysis also shows that, like ordinary ferromagnets, the non-ideality of simple nanocomposites would be a source of major inefficiency if the refrigerator is to be operated over a greater temperature range.

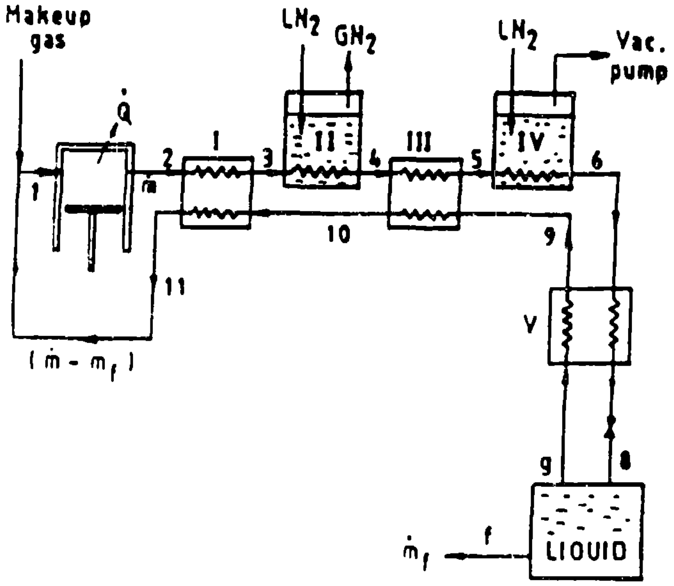


Fig. 6.2.1 - Flow diagram of precooled Linde-Hampson cycle

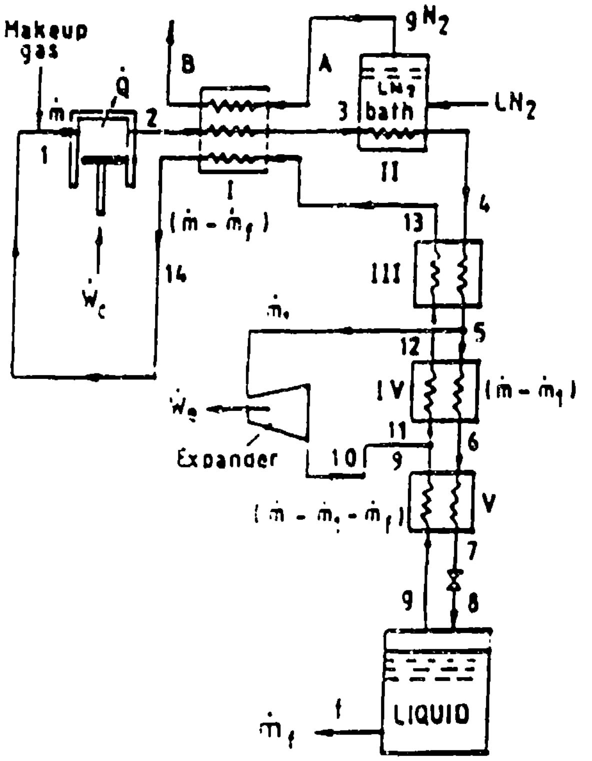


Fig. 6.2.2 - Flow diagram of a Claude cycle hydrogen liquefier

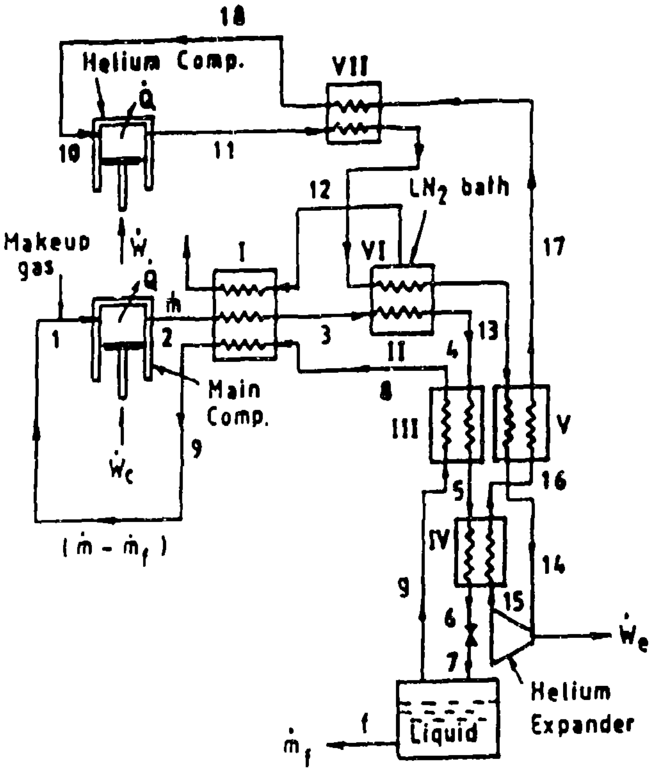


Fig. 6.2.3 - Flow diagram of helium-hydrogen condensing cycle

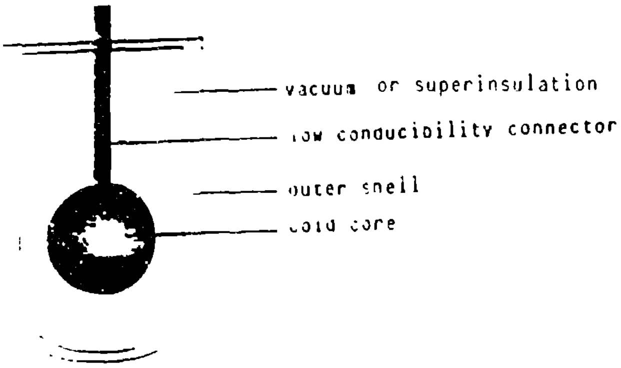


Fig. 6.2.4 - General scheme of a dewar

If optimized nanocomposites can be conceived, and most importantly processed, their potential for reducing the magnetic field requirements could lower the cost of MR which presently relies on low temperature superconductors to provide the needed high magnetic fields.

The realization of an advanced magnetic hydrogen liquefier with room temperature heat sinks would eliminate the compressors and expanders of the mechanical systems. Only then could the efficiency barrier of these systems be completely broken. Initial estimates indicate that the capital cost of magnetic liquefiers is lower than that of conventional liquefiers.

Before the promises of magnetic liquefaction are realized significant work needs to be done. For example, better magnetic materials are absolutely needed to improve the temperature span of magnetic cycles. Serious efforts are required to find better magnetic materials in order to achieve efficient magnetic refrigeration between room temperature and 20 K. The heat exchange problems must also be solved. Finally, proof-of-concept designs should be demonstrated.

Progress has been made in the United States in the development of a 1 ton/day hybrid cryogen/magnetic hydrogen liquefier. Work in Canada addresses materials and systems. The Japanese and the German research, which is presently geared toward the development of materials and computer modelling of magnetic refrigeration cycles, will have profound influence on the realization of efficient magnetic hydrogen liquefiers.

In order to move closer to applying magnetic refrigeration technology, research is required in the following areas:

-Development of magnetic materials for external and active magnetic regeneration;
-Examination of nanocomposites;
-Numerical modelling of magnetic refrigeration cycles.

Liquid hydrogen storage

Liquefied hydrogen is usually stored in horizontal or vertical vessels at industrial sites. These vessels are called dewars in honour of their inventor.

The design of a vessel for liquid hydrogen is mainly affected by the problem of reducing the heat inflow to the minimum extent. In fact, also in a well designed vessel, heat can reach the liquid both by radiation, conduction and convection. Besides, in the case of hydrogen, one must carefully take into account the mentioned problem related to the boil-off. If para concentration in liquid hydrogen is only 90%, after 10 days about 10% of hydrogen is vaporized. That confirms the importance of making a near complete ortho-para conversion.

In general, the design of the vessel requires the knowledge of thermal properties of materials and mechanisms of heat transfer, in relation to gas latent heat of vaporization and normal boiling point, quite severe in the case of hydrogen.

Liquid hydrogen vessels can be classified according to their foreseen use, for stationary storage or for transports. A further important parameter is the time the hydrogen has to be stored, because it is evident that a vessel which is to store liquid for a long time must be more effective than one destined for short time storage. Other considerations regard the fact that vessels for transports have some other limitations like geometry and weight.

Many constraints are related to tightness, mainly of welds and seals, and to the severe problems arising from thermal contraction. Further constraints can arise when lightness is an important parameter.

Finally, safety considerations require an outer shell able to withstand fire without losing insulation (liquid fill, drain, vent and instrumentation lines etc). In addition, the piping has to be considered, but the present technology assures a great solution for this problem.

The scheme of containers, shown in fig. 6.2.4, is derived from the above design considerations: it is generally double walled with a vacuum space between. The vacuum space can be filled with some kind of insulating materials, like perlite for large vessels, or a certain number of aluminium foil layers separated by plastic aluminized foils, both for large highly insulated and small size containers.

In any case, a great number of liquid hydrogen vessels have been built and, as a consequence, design and fabrication techniques techniques are well known.

Though, some hydrogen losses happen from the containers.

Large containers show a loss rate of about 0.1% per day, losses in transport containers account for less than 1% per day, while small size containers, like those used in liquid hydrogen fuelled vehicles, show losses that can reach 2-3% per day. These quite different figures are due to the fact that losses are proportional to the ratio surface/volume of the container. The smaller the container, the higher the losses.

We can conclude with some considerations on safety aspects, that have been a major concern during the development of hydrogen liquefaction technology. The basic problems are to maintain the physical separation of hydrogen and air and, in addition, to eliminate all ignition sources such as sparks and flames.

Besides, some other precautions have to he taken, like providing for remote control of system in order to stop the hydrogen flow in the event of a pipe failure. The monitoring of oxygen impurity is also important in order to avoid considerable concentration of this element into hydrogen. Physical location of some components outdoors could be necessary to provide maximum dispersion of leakages.

Nevertheless, the large experience gained permits to consider hydrogen liquefaction and storage as a safe state-of-the art technology.

6.3 Innovative Concepts

Underground gaseous storage

Underground storage of very large quantities of natural gas was first tried in U.S.A., where oil industry development led to the availability of exausted oil fields or gas fields in convenient locations to store natural gas coming from geografically less favourable areas.

Afterwards, storage of this type has been used in many countries like URSS, France, Belgium, Germany, for natural or manifactured gas, in underground existing cavities, whether natural like acquifers or artificial like abandoned coal mines, or in storage cavities formed by nuclear explosions or by water escavation in massive salt formations. The volume of such reservoirs can arrive up to several hundred millions cubic meters, the compressing station power up to 20 MW and the storage pressure up to 200 bar.

The reservoir is then linked to the surface installations by means of one or more wells properly equipped and the gas is injected in the cavity until the design pressure has been reached, calculated to ensure that the cement of the lining of the drill hole will not be damaged.

When the stored gas is manifactured (town gas), as near Beynes, France, or Kiel, Germany, the hydrogen content varies from 50% to 65%. In both cases, no technical problems had arisen due to the transfer of hydrogen through the covering rocks.

Especially noticeable is the Beynes example, where above the rock covering the acquifer in which the gas is stored, a rock of exceptional thinnes, there is another acquifer. Well, no trace of hydrogen has ever be found in the gases extracted under vacuum from its water.

With hydrogen, when it has to be used in processes requiring high purity, it would be better to use cavities or formations that have never contained hydrocarbons. Anyway, the feasibility of underground cavern storage of relevant quantities of hydrogen has been demonstrated in the United Kingdom - a rather unique field validation case - where three salt-mine caverns are connected to a 16 km long hydrogen distribution grid (see Tab. 7.1.1) for industrial purposes.

The economics of the underground hydrogen storage would suffer the consequences of the lower energy volume density of this gas, compared to natural gas, thus for any given quantity of energy the storage capacity should be about four times greater.

For a seasonal storage, when the filling frequency is about 5-10 cycles per year, operational costs, 0.006-0.04 \$/kWh, of underground storage is the lowest, compared to seasonal storage of liquid hydrogen, estimated to be around 0.06-0.12 \$/kWh, and of methylcyclohexane, 0.04 \$/kWh.

Underground caverns thus appear as the most promising means for seasonal storage of large amounts of hydrogen. This is particularly valuable when hydrogen is to be produced by renewable intermittent primary sources.

Liquid organic hydrides

Methylcyclohexane is a liquid organic hydride used as hydrogen carrier for automotive purposes and derived from the hydrogenation of toluene.

Toluene is hydrogenated in chemical plants with a well known technology and is dehydrogenated on-board with additional input of thermal energy, part of which is extracted from the exaust gases from the combustion engine. The free gaseous hydrogen goes to the engine and the toluene returns to a tank for a new cycle.

This cycle was also proposed in order to provide seasonal storage of electricity derived from renewable energy resources like hydroelectric and photovoltaic and can also pursue the additional target of storing electrical energy during off-peak periods, when the electrical energy is cheaper.

Storage of hydrogen with methylcyclohexane in tanks under atmospheric pressure appears attractive because its further distribution to trucks or busses could be implemented through the utilization of the existing infrastructure of the liquid-fuel distribution system.

The following Methylcyclohexane-Toluene-Hydrogen (MTH) was proposed by Taube and Shucan for Switzerland, in order to use surplus of electric production in summer, deriving from the massive hydropower and nuclear electricity production:

-Production of hydrogen via electrolysis
-Hydrogenation of toluene : 16 kg of toluene + 1 kg H_2 = 17 kg methylcyclohexane
-Seasonal storage, and distribution of methylcyclohexane
-On board dehydrogenation of 17 kg methylcyclohexane;
  the latter process is performed by means of catalytic system heated up to 400 °C by the exaust gasses and an additional burning of 0.2 kg of additionally produced H_2 gas
-Residue: 16 kg toluene to the tank that is recycled

In the proposed scheme, an installed capacity of electrolysis of 20 MW could provide enough fuel for 140 trucks with a average mileage of 100000 km/year. The cost of an amount of energy equivalent to one liter of diesel fuel has been estimated in 0.9 $.

A 16 tons demonstration trucks has been designed, constructed and experimentally tested, with hydrogen on-board production of 3 gH_2/s, corresponding to a thermal power of 360 kW. Weight and volume of the apparatus for the catalytic dehydrogenation are 750 kg and $1 m^3$, so this system is not suitable for a car, but only for lorries and busses.

Metal hydrides

Hydrogen can be bound with certain metals and alloys at operating pressures lower than 50 bar, and then released as a gas only when heat is added. This kind of storage attains a decisive safety advantage in vehicular storage in comparison to compressed gas vessels or cryogenic tanks.

Depending on the alloy, hydrogen content in hydrides theoretically ranges from 1% to 12% (LiH), corresponding to gravimetric energy densities (excluding reservoir and heat exchanger) from 0.3 kWh/kg to 4 kWh/kg, and volumetric energy densities higher than the NBP density of liquid hydrogen. Unfortunately in front of these promising features, many hydrides have several drawbacks, namely high desorption temperature and high reaction enthalpy - the energy needed for dehydrogenation and release of hydrogen - high sensitivity to effects of impurities in the hydrogen gas, and high costs. For instance, LiH, that appears so promising in terms of theoretical energy densities, requires more than 63% of hydrogen's lower heating value for desorption, thus losing most practical effectiveness.

A distinction has to be made between high and low desorption temperature hydrides. For vehicular storage, it has been frequently suggested that the internal combustion engine can supply waste heat to dissociate the hydrides, but one has to recognize that most heat is available at low temperature, as cooling system waste heat.

So, high temperature hydrides like pure Magnesium and Vanadium hydrides, which attain hydrogen contents up to 7.7%, are not suitable for vehicular storage, because practically no hydrogen can be removed from the high temperature storage unit during city driving, unless by burning part of fuel, with an energy loss of about 25%. Besides, one must consider that when the hydrogen-powered prime mover for transportation will be the mobile fuel cell, the amount of available waste energy as well as its temperature will probably be significantly lower than that from internal combustion engines.

On the other hand, the principal shortcomings of low temperature hydrides, principally Iron-Titanium alloys, are their low gravimetric density (max. 2%), so the additional weight of the storage system strongly limits the range and performances of hydrogen powered vehicles.

In order to roughly quantify this effect, refer to Tab. 6.1, where data include weights and volumes of reservoirs and auxiliary systems.

An extensive investigation has been carried out to develop a low cost, high energy, long lasting, low temperature hydride, but it is worth nothing that 15 years of research on hydrides have failed to produce the ideal candidate, and Daimler-Benz and BMW have adapted their hydrogen-powered vehicles to liquid hydrogen or high pressure compressed hydrogen, with additional advantages for the developments of high pressure injection system, so ensuring higher specific power and lower emissions. On the other hand, primarly because of the safety advantages offered by this storage system, research on hydrides should be further incentivated and implemented.

Additional work in this sense is carried on i.e. at Florida Solar Energy Center, mainly focusing on improving the kinetics of the dehydriding and rehydriding processes of special MgH_2-Mg systems.

Glass microencapsulation for hydrogen storage

A new concept of high pressure hydrogen storage is to store compressed hydrogen gas by glass microencapsulation, utilizing the strong temperature dependence of hydrogen permeability through the selected glass and its very high tensile strength .

While massive samples of glass are usually brittle and do not possess sufficient strength (10-15 kg/mm^2), thin hollow glass fiber or microspheres have very high strength, up to 3-400 kg/mm^2, thanks to the good quality of the surface and absence of structure defects, as results from Fig. 6.3.1.

The strengths in a structure like a tube or a sphere are a direct function of the ratio radius/thickness, called "aspect ratio", according to the well known relations, valid for spheres and cylinders respectively:

$$\sigma_S = pr/2s \qquad \sigma_C = pr/s$$

where σ_S and σ_C are the tensile strength of material in a sphere and in a cylinder, which are to be lower than the ultimate strength, p is the pressure and s is the wall thickness.

The weight of hydrogen that can be stored in a sphere depends on the pressure and on the void fraction, that is a direct function of the ratio r/s too.

So, the storage capacity becomes very large when the aspect ratio and the internal pressure increase, which are contradictory requirements for a given material maximum strength.

An optimum hydrogen volume density is obtained for r/s = 4 (for upper and lower value the function is constantly decreasing), while the hydrogen weight density is a constantly increasing function of r/s.

The optimum hydrogen volume density corresponds to a microspheres density close to 1.4 g/cm^3.

If we assume a packing fraction of 0.7 and an achievable burst strength of 100 kg/mm^2, we can attain a maximum volume density of 100 g/l, corresponding to an energy density of 3.4 kWh/l and an energy density of 3.35 kWh/kg. These values are referred to the microspheres and not to the whole storage system, so the system related values are lower, expecially for

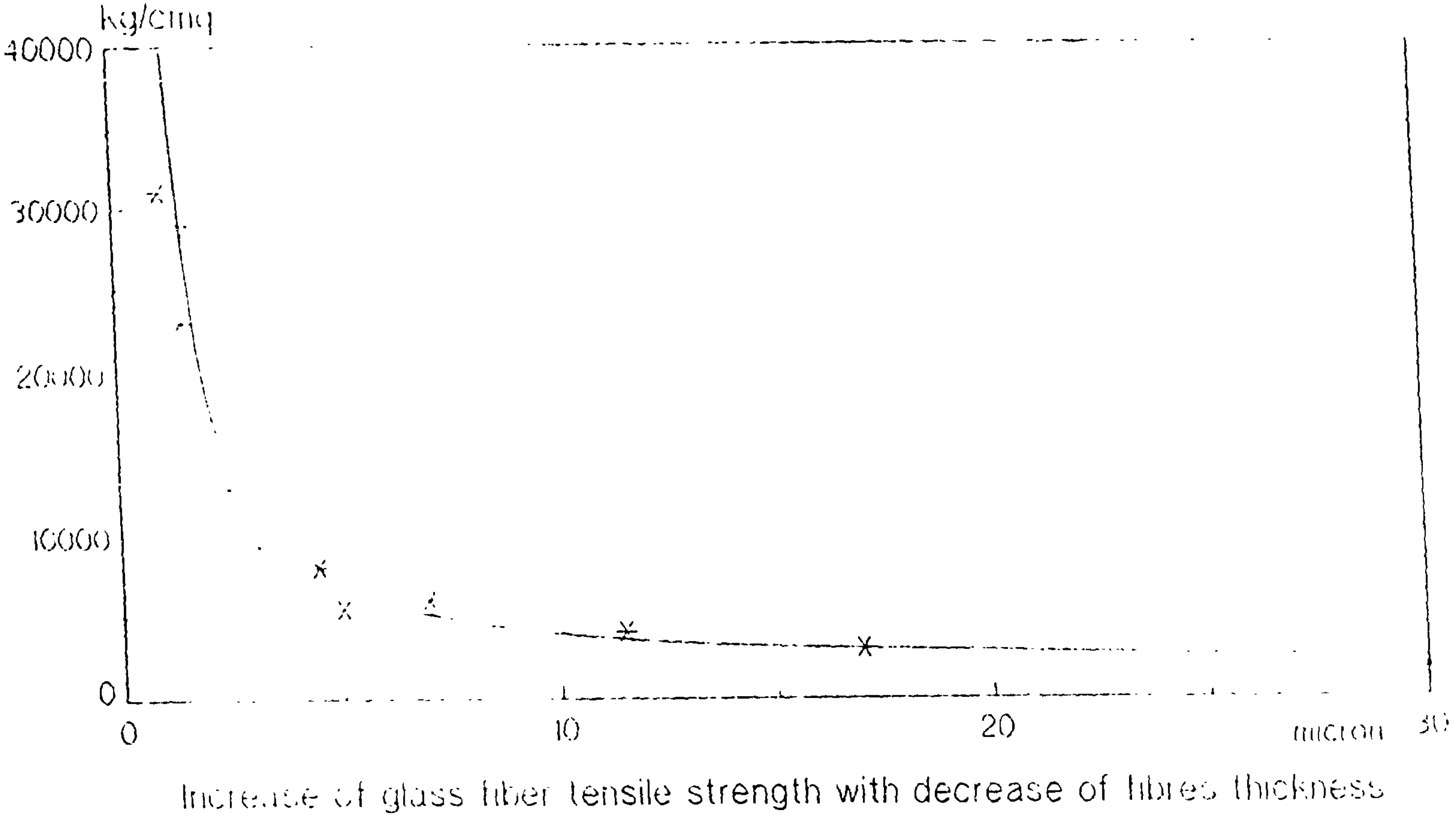


Fig. 6.3.1 - **Ultimate tensile strength of glass fibres**

volume density. First experiences suggest a reduction of energy densities due to the whole system of about 60% by volume and 30% by weight.

However, today's state of the art is quite far from these theoretical performances. Some experiences performed in France by St. Gobain, which prepared and tested a lot of glass microspheres, showed a hydrogen energy densities of 0.5 kWh/l and 0.5 kWh/kg (without including reservoir).

Anyway, hydrogen storage by microspheres is estimated to have low capital cost, to be attractive from a safety point of view and reasonably cheap in terms of energy expenditure.

As a consequence, further experimental work is recommended in order to ameliorate the knowledge of this technological option. Experiments should regard mainly mechanical properties and permeability of glass in spherical form, improvement of their mechanical strength by metallic coating, acid etching with hydrofluoric acid, chemical hardening etc.

Low pressure adsorption storage of hydrogen

Low pressure gas storage tanks are very actractive on a vehicle for two reasons:

-a low pressure tank does not require a cilindrical or spherical shape, so it can be placed anywhere, like a petrol tank;

-it presents better safety features with respect to other storage techniques.

The increasing success of natural gas vehicles, due to their lower exhaust emissions, has promoted the adsorption technology for natural gas storage, where the cylinders are filled with a hygh porous material able to offer high surface-area.

When the cylinders are filled with compressed gas, a part of the gas adsorbs on the surface of the solid - for example activated carbon, whose cost is fairly low - thanks to the Van der Waals interaction between the solid atoms and the gas molecules, and the pressure is lowered. So, for a given charge pressure, the total capacity increases and it is the sum of excess adsorption, mainly confined to micropores, and the bulk phase in macropores and voids among the carbon particles.

The amount of gas stored is a function of the amount and nature of the surface area of the chosen porous solid, and of course it depends on the operating conditions of the system, storage pressure and temperature.

For compressed natural gas storage, operating conditions are room temperature and a pressure as low as 35 bar, but for hydrogen one should operate at a much lower temperature, close to 80-150 K, and at a pressure of 40-60 bar to attain favourable energy density.

Up to now, the best result was reached with AX-21 activated carbon with a surface area of 3000 m^2/g: at liquid nitrogen temperature, 77 K, and at 35 bar, hydrogen weight storage density was about 50 g/kg of adsorbent and 25 g/l of adsorbent. While it is hard to imagine lower temperatures, a further enhancement of pressure at 77 K does not give significant improvements.

Further, the system requires a cryogenic tank, with a liquid N_2 cooled heat shield. If we assume that these components reduce the energy densities as in the case of metal hydrides, in the cited conditions of pressure and temperature maximum energy densities of 1 kWh/kg and 0.5 kWh/l can be anticipated.

Anyway, some progress can be made by minimizing the volume of the storage system; that can be achieved be realizing an adsorbent with high bulk density. A solidification method has been developed to increase the bulk density of activated carbon, obtaining a capacity improvement factor of more than two, and so improving the volumetric storage capacity of methane by more than 50% and of hydrogen by 34% at 35 bar.

The investigation of economics of H_2 adsorption storage has shown that this option compares very favorably with the other options, thanks to the lower cost of storage unit compared to compressed vessels and metal hydrides and to the lower energy consumption compared to liquid hydrogen.

Moreover, it should be noted that none of the activated carbon available commercially have been optimized for hydrogen. The availability of activated carbons optimized for hydrogen could greatly increase the competivity of this storage option.

7. HYDROGEN TRANSPORT: STATUS AND PERSPECTIVES

Hydrogen transport assumes relevant importance when large production plants are expected in sites far from utilization places. At present, two main options are foreseenable: gaseous hydrogen transport via pipelines is conceivable when long terrestrial distances are to be covered or local distribution networks are to be implemented. Liquid hydrogen transport in cryogenic dewars appears as the best solution in the case of transoceanic transport.

7.1 - Gaseous hydrogen via pipelines

Gaseous hydrogen transport is a well established technique in industry: several hydrogen pipe networks successfully operating in Europe and in the United States for many decades have fully demonstrated the feasibility, also in safety terms, of hydrogen transport, handling and distribution.

Nevertheless, in view of a future use of hydrogen as an energy vector, much larger quantities of gas should be shipped than those currently distributed in industry. In order to figure out how pipelines networks transporting such an amount of hydrogen should be alike, it is useful to refer to the existing natural gas distribution system. Indeed, natural gas and hydrogen transportation and storage are similar from a technological point of view. Of course, some peculiar characteristic of hydrogen, namely its low density, which increases leakage problems, its high chemical activity, which, under certain conditions, can lead to hydrogen embrittlement of metals, and its low energy density, have to be taken into account for careful analysis.

The longest and oldest hydrogen pipeline network is located in the Ruhr area of Germany, where it is being operated by Huels AG without interruptions since 1939. The totally 210 km. long network (extensions have been added up to 1982) interconnects 18 industrial plants (4 producers and 14 consumers), helping to meet the hydrogen demand and to optimize the distribution in the Rhein-Ruhr industrial area. The pipeline network has no in-line compressor stations and is constructed in seamless carbon steel.

No relevant damage from deposits or corrosion by hydrogen has been shown. The observed leakage rate is negligible.

Other large networks are being operated by Air Liquide in Western Europe (France, Belgium and Netherlands) and by Air Products in Texas, U.S.A. The technical characteristics of these and other main hydrogen pipelines networks are summarized in the following table:

Network location	Overall length	Operating pressure	Tube diameter
Germany	210 km	up to 22 bar	100-300 mm
Western Europe	330 km (several sections)	up to 100 bar	100 mm
Texas, U.S.A.	158 km (two sections)	35 - 55 bar	80 - 300 mm
Sweden	9 km (6 sections)	0.1 - 28 bar	50 - 250 mm
United Kingdom	16 km	50 bar	

Tab. 7.1.1 - Main hydrogen pipelines operating in the world

The typical maximum amount of yearly shipped hydrogen by a single major grid (i.e. Germany or U.S.A.) ranges up to 300 mio Nm^3/y, its maximum capacity being relevantly higher.
All pipelines are made of normal carbon or low alloy steels, and have not shown relevant damages due to the transportation of high purity hydrogen for several decades. In Japan, low alloy steel pipes have been employed for pure hydrogen with pressures up to 400 bar.
The existence of all these networks ought to definitely prove itself as a field validation of the technical feasibility of safe transportation of very high grade purity hydrogen over long distances.

The energy perspective
Being hydrogen transport in pipelines a well established technique in industry, one major issue has still to be addressed, namely that using hydrogen as energy vector would imply the need for the transport of much larger quantities of gas than those currently shipped in industry. In order to make a rough comparison, data of (former Western) Germany can be used: while hydrogen yearly transported in industry amounts nearly to 300 mio Nm^3, the natural gas shipment in 1985 has been of approx. 50 billions Nm^3, equivalent to roughly 150 billions Nm^3 of hydrogen to be transported.
In principle, the issue of transporting such large amounts of hydrogen does not present unsormountable challenges in itself, and can be tackled by starting from the experience in transporting natural gas. However, at least three characteristics of hydrogen originating major tecnological challenges have to be carefully considered when designing a hydrogen pipeline network:
1) the high chemical activity of hydrogen: molecular hydrogen dissociates at the surfaces and atomic hydrogen can penetrate in the lattice structure of steels. This phenomenon is called hydrogen embrittlement and leads to a loss of ductility and to stress cracking, with an overall effect of a drastic reduction of the durability and strength of the material. Embrittlement is a function of the nature of the metal, the operating pressure and hydrogen purity: as the pressure increases, the degree of embrittlement increases, depending on the steel alloy. Moreover, it tends to be a more severe problem with increasing hydrogen purity.
Anyway, the expected operation conditions of a future hydrogen pipeline network system appear to be compatible with the currently employed steels in hydrogen pipes. Indeed, the low-strength, mild or low alloy steels employed in the existing hydrogen pipelines have not been adversely affected by the transportation of high purity hydrogen (much more pure than required for energy transmission purposes) for many years. From a technological point of view, there is no question that suitable materials are currently available for safe and reliable use of hydrogen as energy vector in most conceivable scenarios.
2) the low density of hydrogen, which requires particular care in designing seals, meters and compressors, in order the pipes to be leakproof.
3) the low volumetric energy density of hydrogen, which influences the transmission capacity of the pipeline network. Hydrogen has only about one third of the energy contained in an equal volume of natural gas. Thus, if the final energy quantity available to the user has to be maintained, more hydrogen has to be transmitted per unit time. This is partially achieved by the fact that, being less viscous, hydrogen will flow about 2.5 times faster than methane through a section of pipeline in which pressure is almost constant. Under these conditions, hydrogen transmits about 80 percent as much energy carried by methane. However, over long distances pressure drops considerably and, as a consequence, hydrogen requires more pumping energy, thus a larger compression capacity, in order be transported. If the total transmission flow rate is to be maintained, the compressor capacity must be increased by a factor 3.8, the relative power compression requirement being even higher.
Turbocompressors for hydrogen transport at typical operating pressures of natural gas pipelines do not exist yet, but they may be developed from the existing natural gas technology without significant design changes. The volume capacity of a turbocompressor is the same for hydrogen and natural gas; thus, a hydrogen reciprocating compressor would be 3.8 times

larger. Due to size limitations and pressure ratio achievable in one stage, multi-stage compressors stations might be rather employed.

Similar to natural gas, long distance pipe transportation of hydrogen requires gas storage facilities; moreover, hydrogen pipes will have the same safety and control systems of natural gas lines, in order to check gas flow, pressure, density, to detect leakages, and to split up the grid in case of system failures.

Finally, cost minimizing calculations show that hydrogen pipelines ought to have larger diameters (up to 2 meters, at 120 bar operating pressure, to be compared with the 1.2 m and 80 bar typical of present long-distance natural gas pipelines).

Several works in literature have tried to assess costs of hydrogen transport through pipelines. Usually, comparative results with the natural gas transport are given. These assessments estimate hydrogen transport to be more expensive by a factor 1.3 to 2 per unit energy than natural gas transmission. The cost analyses typically include the use of turbocompressors powered by gas from the pipeline. Because of the larger compression power requirements for hydrogen, its transmission costs are more sensitive to its production costs than methane.

On the other hand, when hydrogen production cost is high (for example solar photovoltaic hydrogen), the transmission cost of hydrogen weights in limited way on the total cost to the end user. In fact, some studies assessing the cost of importing solar hydrogen via pipelines from North Africa to Germany show that, even in a long term perspective (photovoltaic electricity cost around 0.07 $/kWh), the cost of long distance transmission does not exceed 20% of the total cost of solar hydrogen to the German end user, which is estimated around 0.14 $/kWh. In any case, the long distance transport of gaseous hydrogen shows higher transmission efficiencies and lower cost than the long distance electricity transmission and subsequent hydrogen production by electrolysis in Germany.

Suitability of existing natural gas grid for hydrogen transport

It has been frequently suggested by many sources that the existing natural gas network could be used for hydrogen transportation. This would clearly imply enormous economic advantages and could even play a strategic role in a long-term transition to a hydrogen economy. However, the suitability of the existing grid for hydrogen transport must be very carefully examined, and several considerations have to be done before assuming final conclusions on this matter.

On one hand, several studies in the past have shown that steels employed for natural gas transportation are little sensitive to hydrogen embrittlement at tipycal operating conditions, thus being at behalf of hydrogen transportation in the existing pipelines. Moreover, hydrogen rich gases, as "town gas", has been safely distributed in Europe and U.S.A. for many years in the past.

On the other hand, the existing natural-gas pipeline systems employ a large variety of steels of different fabrication procedures, and show a big range of different diameters and thicknesses. Thus, the suitability of natural gas lines for hydrogen transport must be very carefully assessed case-by-case (eventually basing on recorded heat treatments of the steels, welding practices, etc.), not only as far employed steels are concerned, but also considering all the compression, seals and metering equipment requirements. The possible use of impurities inhibiting hydrogen embrittlement needs further research as well, in order their successful effect to be undoubtly assumed.

Suitability assessments have to be done at any of the three levels in which the natural gas network is usually structured: long distance pipes, national grid, local distribution networks. At international level, it has to be reminded that significant improvements in compression capacity are needed in order the same amount of energy to be transmitted by 100% hydrogen. Apart from the technological challenge, this causes at least a logistical problem, because a stop of the natural gas flow for all the time needed for modifications of the line is not conceivable.

At national level, which is usually divided in high pressure and mid pressure lines, the situation would be slightly better. Indeed, mid pressure distribution requires less pumping energy, and lower operating pressures reduce the probability of hydrogen embrittlement of steels. Thus, part of the national grid could in principle result suitable for hydrogen transportation. Nevertheless, final conclusions about suitability can only be driven after a careful analysis of the single local situation. As far this is concerned, a very recent report to the German Parliament assesses that 100% hydrogen transportation in the existing German natural gas grid would not satisfy the current safety standards typical for hydrogen transmission lines in industry.

Finally, local gas-distribution networks do not show problems, as far the energy-delivery capacity is concerned. Indeed, they do not usually include in-line compressor stations, and at typical distribution pressures the lower energy density of hydrogen is practically totally compensated by its higher viscosity. In this case, only the pipe materials compatibility problem still has to be considered. Cast-iron, mild and low alloy steels are suitable for hydrogen use, whilst where plastic lines are employed, particular care has to be given to their analysis, because the permeability of some plastic compounds is relevantly higher to hydrogen than to natural gas.

In conclusion, it can be said that in principle at least some sections of the existing natural gas network could result compatible for hydrogen transportation. More particularly, national and local distribution lines should be given higher priority for their suitability assessment, because of their lower pressure operating conditions. The latter give rise to less compelling requirements on materials and compression equipments, thus making hydrogen transport more plausible.

Moreover, this suggests the possibility of building national hydrogen production plants, which could introduce at least a fraction of hydrogen in selected sections of the existing national natural gas grids.

Again, the assessment of the percentage of hydrogen that could be directly added into the existing natural gas lines is subject of bright controversy and rather speculative discussion. Once more again, no definitive conclusions can be drawn on this matter without further research aiming at locally assessing the suitability of the existing lines for the transport of a certain percentage of hydrogen.

Implementing such a research would be highly desirable, because it would incentivate the development both of the many hydrogen end-use technologies able to work with hydrogen-natural gas mixtures (these mixtures appear to bring significant environmental benefits compared with 100% natural gas feed) and hydrogen production technologies, thus allowing a gradual transition towards a hydrogen energy system.

7.2 Liquid Hydrogen

Hydrogen, being a secondary energy (an energy vector), has to be generated with a primary energy source. Hydrogen can be produced by electrolysis in a clean way using an indirect solar energy source such as hydro-electricity.

The total technically exploitable hydro-energy in the world is about $7 \cdot 10^7$ TJ/y (considering an average load factor in the order of 65%).

If hydrogen is produced in areas far from Europe and separated by the sea it has to be stored and transported by ships. New types of ships are needed.

Hydrogen can be stored in solid hydrides, liquid hydrides, methanol, ammonia or as liquefied hydrogen. All these hydrogen vectors have been studied.

Methanol, ammonia and liquid hydrides require hydrogenation and dehydrogenation plants and are dangerous to health and environment; solid hydrides present problems for loading and discharging. With these systems of storage, hydrogen is supplied to the sites of utilisation in gaseous form (GH_2). If liquid hydrogen is required, liquefaction is needed.

Liquid hydrogen (LH_2) was found to be the most suitable for maritime transportation in a less polluting and economically acceptable energy system.

Aspects of LH_2 maritime transportation

The development of the LH_2 ship concepts is based on the already existing liquefied natural gas (LNG) ships. Hydrogen transportation by ship presents some main problems.

The first problem is the low density of the payload (LNG density = 0.47 kg/m^3, LH_2 density = 0.071 kg/m^3). This means that LH_2 ships need ballast to attain a seafaring draught. As the centre of gravity of the ship then lies very low, the lines of the ships must be so designed that a good sea-going behaviour is obtained.

Other solutions have been studied, such as catamarans and SWATHs (Small Waterplane Area twin Hull) to obtain sufficient cargo volumes with small buoyancy.

The large specific volume of LH_2 requires big ships for relative small amount of LH_2 cargo, which in turn implies need of ballast. If ballast is water, a large weight of unpaying load must be transported. This fact indicates that a good solution could be a double cargo ship (normal cargo and LH_2). This was made for small quantities of LH_2; for large amounts dedicated ships seem to be necessary.

The second problem is the low LH_2 temperature (20 K) in conjunction with the low volumetric heat of vaporisation. As the ambient temperature is considerably higher than the LH_2 temperature, heat flows into the LH_2 tanks and some of the load is vaporised. Insulation is, therefore, essential. This vaporisation is expressed as a percentage of the cargo weight per day. Using special vacuum-perlite insulation or other types of vacuum insulation, this rate can be reduced to 0.1% day or less.

The third problem is that of safety. International rules and regulations are lacking; LH_2 is not considered in the IGC Code (IMO - International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk - 1983).

In any case, on 18.12.1990 the BAM (German Federal Institute for Material Research) declared liquid hydrogen not to be more dangerous than LNG and LPG and that there is no objection to the transport of liquid hydrogen in 2G type ships (n rules) (A type 2G ship is a gas carrier intended to transport products which require significant preventative measurements to preclude the escape of such cargo).

Transport of liquid ydrogen has been investigated within the framework of Euro-Quebec-Hydro-Hydrogen Pilot Project (EQHHPP), described in chap. 8.

The EQHHPP reference case for liquid hydrogen transport is the following:

- Hydropower	100 MWe
- Electrolyzer efficiency	74%
- Annuity (8% interest, 15 yr pay back)	11.7%
- Load factor	95%
- Port of loading	Seven Islands (Québec)
- Port of discharging	Hamburg
- Hydrogen delivered in Hamburg	610 GWh/y
- Plant investment costs	414.6 MECU
- Specific hydrogen energy costs	13-15 cents$_{ECU}$/kWh
- Hydrogen transmission efficiency	74%

Barge carrier for Liquid Hydrogen Maritime transportation

The most salient new component in the EQHHPP is the LH_2 ship. the new concept of a barge ship was studied in Phase II and adopted. The ship is ballasted with water (Fig. 7.2.1).

The cylindrical tanks have a total LH_2 capacity of 15000 m^3. This capacity is divided into 5 tanks (213 t, 3000 m^3 of LH_2 each tank) which can be filled up to 85%. The geometrical volume is correspondingly larger.

The tanks are built with two concentric skins. The space between the two skins is evacuated to minimise convective heat transfer. To limit the heat supply caused by thermal radiation the space between the skins is filled with Perlite. This elaborate insulation (super insulation) is necessary to limit the evaporation to a value of 0.1%/day. The tanks are so designed that the rise in pressure because of the heat leakage is controlled.

These large tanks will be mounted on buoyant barges (Fig. 7.2.2).

The ship is designed with ice class E4 for a speed of 18 knots, driven by two propellers each fitted with a medium speed diesel engine of 5290 kW.

Five barges are loaded on the ship. When the ship has to be loaded or discharged, additional ballast water is pumped into the ship so as to lower it. The barges may then be floated in or out with the aid of a winch through the rear gate into the loading area. A hoist system, similar to the derricks of a ship, lifts the barges onto land on a rail system, by which they can be transported to a previously decided position.

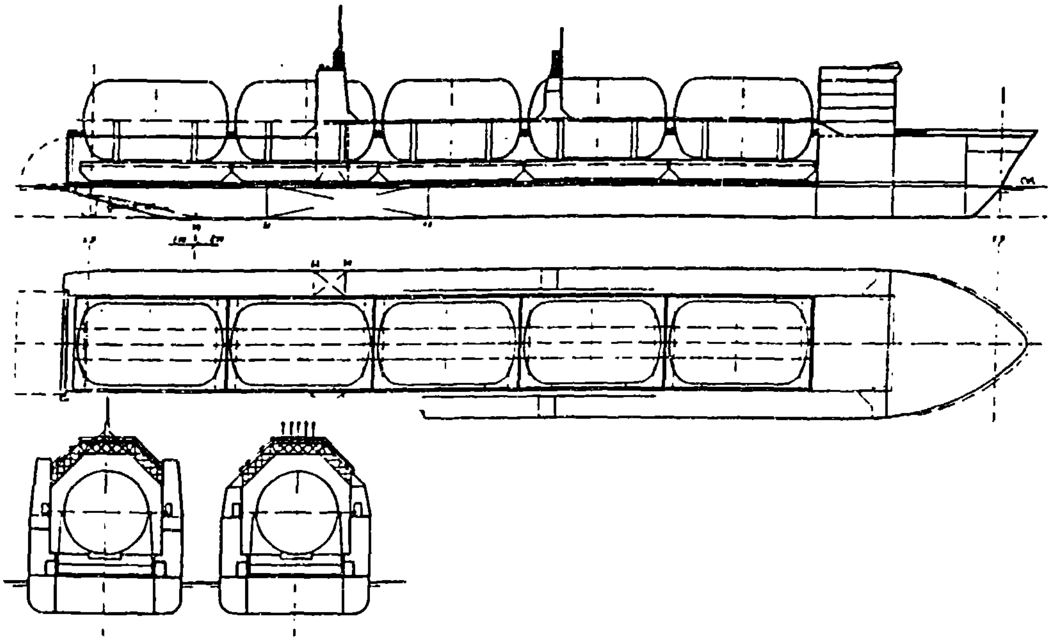


Fig. 7.2.1 - LH_2 Barge Carrier

Source: Thyssen Nordseewerke

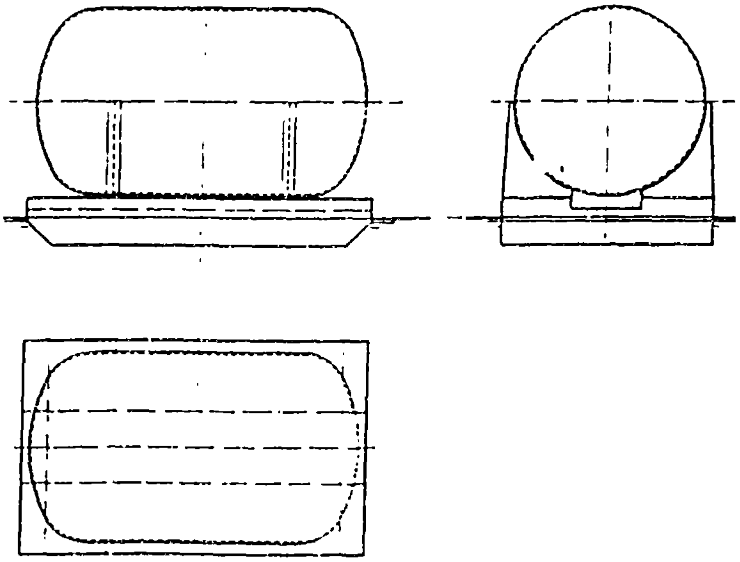


Fig. 7.2.2 - LH_2 tank barge

Source: Thyssen Nordseewerke

The concept of removable tanks avoid transfer losses and makes the use of loading arms unnecessary, which is the case for tanks integral to the ship. The hydrogen gas evaporated from the LH_2 can be contained in the tanks for 50 days; the tanks also act as storage containers on land. For safety reasons during transport, the tanks are provided with separated pipings to a blow off stack arranged amidships. All other safety systems are arranged in decentralised fashion on the barges.

The double hull construction and the separation between the barges make the barge carrier safe in case of collision or grounding.

The calculated LH_2 maritime transportation cost is about 2.2 ¢ECU/kWh. The calculation was based on the following data:

- LH_2 annual production : 15900 tons
- Round voyage : 22 days
- Total round voyages per year : ~ 16

During the EQHHPP Phase III-0 both the design of the LH_2 ship and of the superinsutated LH_2 containers were recalculated (Fig. 7.2.3).

For the ship the following modifications were adopted:

- the basic geometry of the hullform was changed;
- the main propulsion drive will be diesel electric with the diesel motor outside the cargo area;
- exhaust gas funnels and vent masts were also arranged outside the cargo area;
- the double bottom height was reduced from 7 to 5 m, resulting in a lower depth and a smaller docking draught (from 10 to 8 m);
- ballast water for docking was reduced (from 18000 to 9000 t) and consequently the double hull was reduced by 1.5 m (3 m of breadth reduction).

The LH_2 barge carrier and the barger tank system will be in accordance with the International Regulations for the Design and Equipment of Liquefied Gas Carrier developed by the International Maritime Organisation (IMO). It is the view of the Canadian Coast Guard, the German Ministry for Transport and Germanischer Lloyd that the IMO-IGC Code must be complied with. Since hydrogen is not part of the Code, equivalence must be ensured.

The LH_2 tanks design is at present studied in depth ("Scale Studies for Advanced Technologies for Hydrogen Storage - Germanischer Lloyd, Thyssen Nordseewerke, L'Air Liquide, BMW, BAM, MPA).

Aluminium/fiberglass foils are now considered as radiation shields for the vacuum insulation tanks. The expected evaporation rate is 0.05% day. the materials for the inner vessel should be SA 240 Grade 340 L/1.4306 and SA 516 grade 60 for the outer vessel. The water capacity is 3600 m^3.

Other concepts for maritime liquid hydrogen transportation

Some solutions for the problem were studied during the years but not elaborated in depth as the LH_2 Barge Carrier concept.

Among these, two preliminary projects can be mentioned: the LH_2 ships ballasted with fuel oil and the LH_2 "Jumbo" container ship.

a) LH_2 ships ballasted with fuel oil

These ships are based on the following concept. The forward zone of the ships is provided with special tanks capable of containing all the fuel necessary for a round trip (2x3000 nautical miles) plus an additional quantity to obtain the necessary weight with an acceptable draught. At departure of the ship from an European port, without cargo, the fuel in the tanks is sufficient for draught and stability. At arrival at the site of LH_2 production, the draught is decreased due to fuel consumption. At departure, the LH_2 cargo is loaded and the residual fuel is sufficient for draught and stability. This concept favours high speed (the fuel weight increases with propulsion power). The size of the ships is nevertheless limited, because for

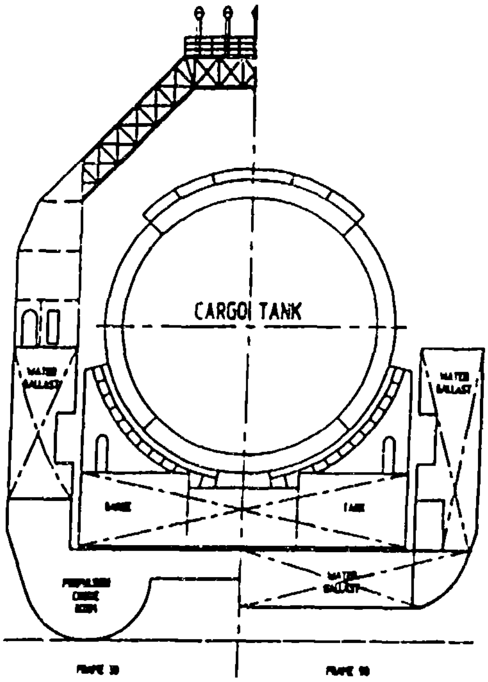


Fig. 7.2.3 - Sections of the new design

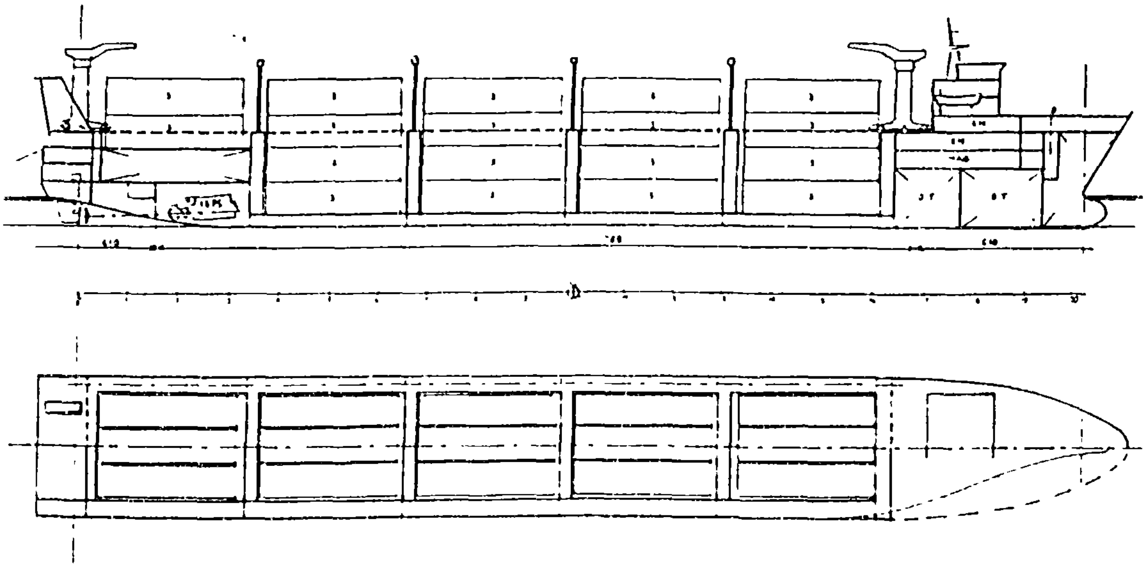


Fig. 7.2.4 - 16500 m^3 "Jumbo" container ship

the same speed the propulsion power does not sufficiently increase with size, to require a quantity of fuel corresponding to the draught and stability.
Single-hull ships (with cylindrical containers), one catamaran and one SWATH have been studied. All the ships have a speed of 17.5 knots.
The work was done by L.G.A. Gastechnik-Remangen, Germany in 1988, under contract with the Commission of the European Communities.
The catamaran will have the lowest fuel consumption (basis 17.5 knots) of all three hull variants and this unique advantage will considerably increase with higher travelling speeds.
The SWATH ship offers some advantages regarding acceleration and, subsequently, the construction of the cargo containment would be facilitated. The relatively uneasy hydrodynamic resistance of the buoyancy system may be a disadvantage of the SWATH ship.

b) "Jumbo" container ship
A preliminary feasibility study was made in 1989 for a container ship, ballasted with water, capable of carrying 54 Jumbo containers (3600 m^3 each, filling rate 85%) (Fig. 7.2.4). The total capacity is 16500 m^3 LH$_2$ on1170 t LH$_2$.
The service speed is 18 knots and the main engine output is 11200 kW;
The vessel is of a completely open hold type (hatchless) and it is equipped with gantry cranes (self loading and discharging of the Jumbo containers).
The containers are equipped with a frame allowing stacking inside the ship. Vent stack of each container is connected to the main vent stack of the ship.
The Jumbo container ship can berth alongside any conventional container quay without requesting extra diving depth.
There are 54 LH$_2$ tanks (Fig. 7.2.5) with multilayer super insulation.
The gas evaporated can be contained in the tanks for more than 60 days. the containers can act as storage containers and can be transported by road.

Prospective studies
Following the opinion of some German Organisations on the large hydrogen supply required worldwide in the future, studies have been done for the maritime transport of large quantities of LH$_{\surd}$ by Germanischer Lloyd (GL)., Howaldtswerke Deutsche Werft (HDW) and Noell-LGA, which examined different design of ships. The studies were supported by the German Ministry for Research and Development (BMFT).
Two transport concept were studied:
- Dock ship (capacity: 8150 t LH$_2$)
- SWATH ship (capacity 8150 t LH$_2$).

a) LH$_2$ dock ship
The "dock" ship should transport five spherical tanks (double shell) vacuum insulated with an outer diameter of ~40m, mounted on floating barges which can be floated in or out of the semi-submerged barge carrier by means of tugs (Fig. 7.2.6). The concepts is the same as used for the EQHHPP LH$_2$ barge carrier.

The main propulsion motor should be a slow-speed engine with a power of 36000 kW, for a speed of 16 knots.

b) SWATH ship
The LH$_2$ tanks are spherical, positioned on platforms (Fig. 7.2.7). the boiled-off gas should be used in the auxiliary boiler for the production of auxiliary electrical energy.
The propulsion system should be diesel electric with the diesel motor fore on the deck and the electric motor aft, with a power of 36000 kW for a speed of 17.5 knots.
The platforms should be discharged at the arrival of the ship and positioned on special foundations by immersion of the ships. After the unloading of the LH$_2$, the platforms should be loaded with the same system.

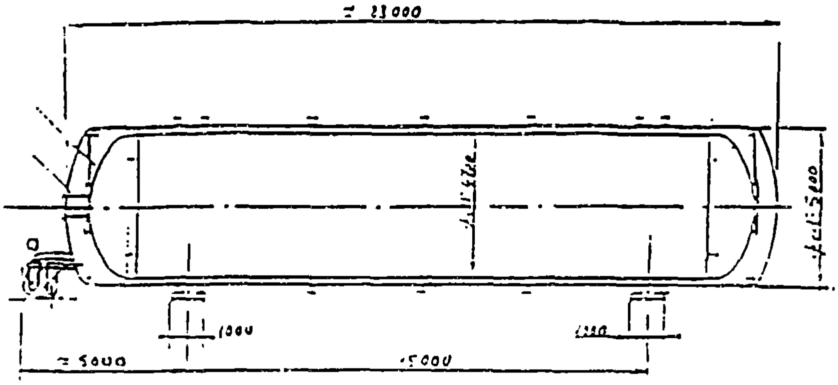


Fig. 7.2.5 - 305 m^3 LH_2 tank Source: L'Air Liquide

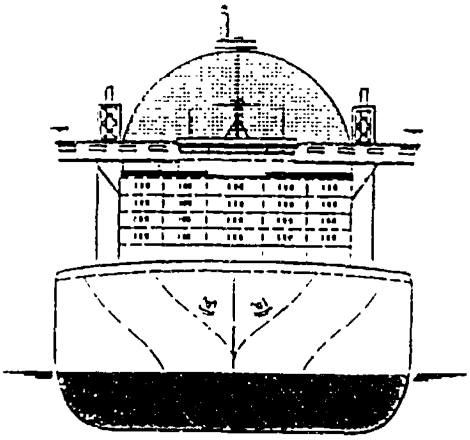


Fig. 7.2.6 - LH_2 Dock ship Source: GL,HDW,LGA

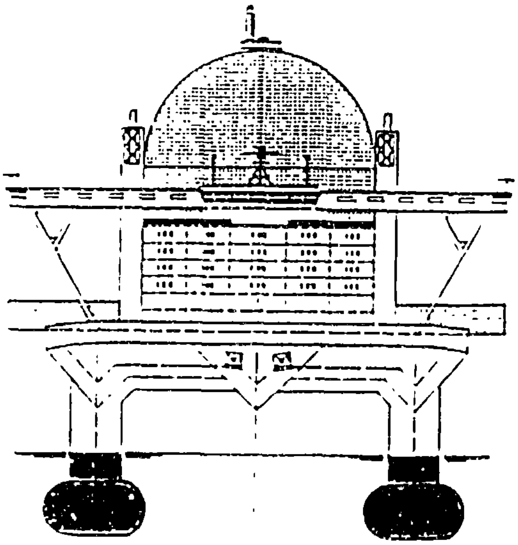


Fig. 7.2.7 - SWATH ship Source: GL,HDW,LGA

Safety
The safety characteristics of hydrogen are discussed in detail in Chapter 3 of the Report. Nevertheless attention must be paid to the importance of avoiding explosions in case of hydrogen losses, letting them escape into the open air. For the maritime LH_2 transportation it is a good solution to have the LH_2 tanks on the ship's deck (or for the EQHHPP barge carrier).
The IMO IGC-Code regulates the maritime transport of liquefied gases. Liquid hydrogen is not included, nevertheless the main safety principles of this Code for LNG ships may be extrapolated for the sea transport of LH_2. Equivalence must be used.
The important declaration made by MAM is mentioned in the Introduction.
Further studies have to be performed to homogenise the existing national and international rules and regulations.

8 - THE OPERATORS: ACTIVITIES AND PROGRAMS

A significant number of countries are involved in activities on hydrogen, both through government bodies and industrial companies. In many cases the activities and programs belong to international agreement: this is the case, for example, of Euro Quebec Hydro-Hydrogen Pilot Project (EQHHPP), launched by the Joint Research center of Ispra of European Community.

8.1 - The Euro Quebec Hydro-Hydrogen Pilot Project (EQHHPP)

The concept of a hydrogen-based, clean, renewable energy system, conceived by the Joint Research Centre Ispra of the Commission of the European Communities, is currently investigated by European and Canadian Industries, coordinated by the JRC-Ispra of the Commission of the European Communities and the Government of Québec.

The 100 MW pilot project is to demonstrate the provision of clean and renewable primary energy in the form of already available hydroelectricity from Québec converted via electrolysis into hydrogen and shipped to Europe, where it is stored and used in different ways: electricity/heat cogeneration, vehicle and aviation propulsion, steel fabrication and hydrogen enrichment of natural gas for use in industry and households (Fig. 8.1.1).

For reasons of thermodynamic properties, availability of technology and end use, two different modes of vectorisation have been investigated namely liquid hydrogen (LH_2) and methycyclohexane (MCH) in order to have hydrogen in both forms, liquid and gaseous.

The project is to be carried out in 4 phases:

- Phase I : assessment; completed by March 1987
- Phase II : detailed system definition, January 1989 - March 1991
- Phase III, 0 . hydrogen application demonstration programme; 1991 - 1997
- Phase III : detailed engineering & specifications; planned to last 1-2 years
- Phase IV : construction; planned to last 4-5 years.

In Phase II, the detailed system definition, the Phase I results have been updated, cost calculations refined, environmental analyses undertaken and questions of safety and regulations investigated. Phase II has indicated costs of the electrolytic hydrogen, produced with hydropower which would be available at 2 $cents_{ECU}$/kWh (cents of European Unit of Account, reference price for cost calculation) shipped to and stored in a European port, of 14.8 $cents_{ECU}$/kWh in the form of liquid hydrogen.

The present Phase III,0 is a hydrogen demonstration programme on the utilization of hydrogen in the fields of vehicle and aviation propulsion, steel fabrication and advanced techniques of liquid hydrogen storage. This phase also involves detailed studies of safety measures and codes, along with socio-economic studies on the comparison of hydrogen with conventional fuels.

In the following, the results of Phase II investigations, based on the EQHHPP's concept described in Ref. 82, and a short review of present Phase III, 0 are given.

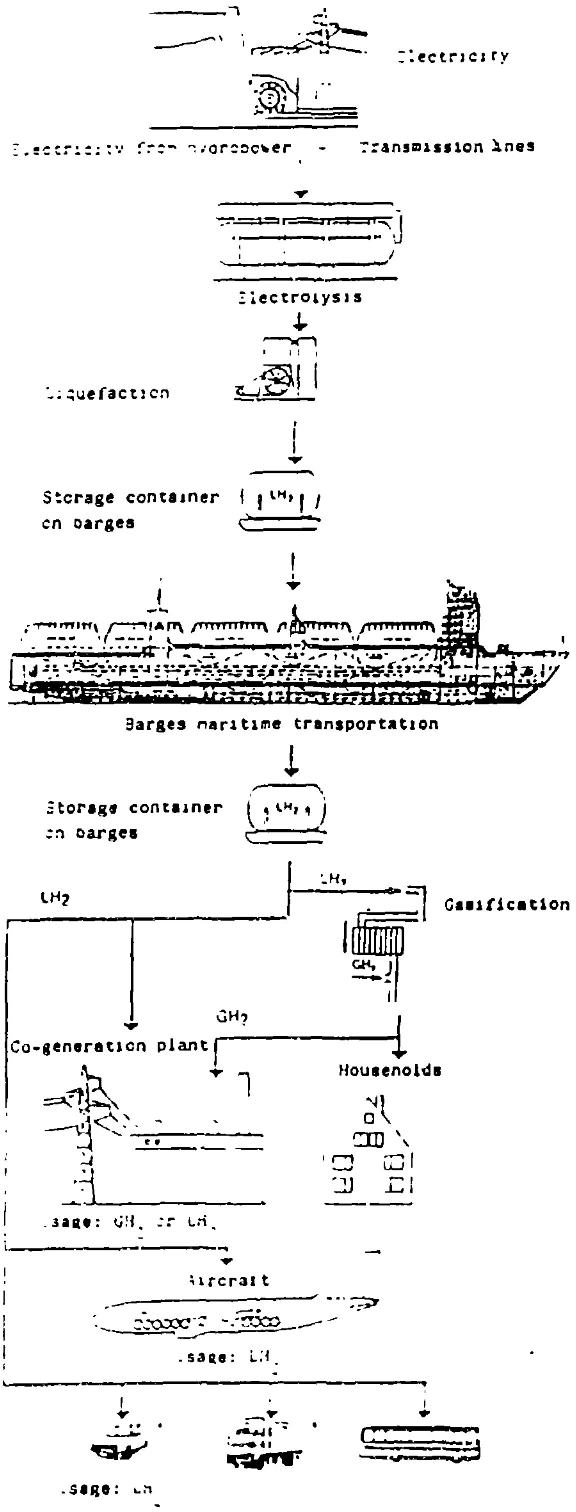


Fig. 8.1.1. ·The Concept of the EQHHPP Project.

The Partners

The industrial partners involved in the projects are (alphabetically):
Air Liquide Canada (CND), AEG AG (D), Ansaldo Ricerche (I), Autobus MCI (CND), Blohm & Voss AG (D), BMW AG (D), CONOC Continental COntractors (D), Daimler-Benz AG (D), DECHEMA (D), Ecole Polytechnique (CND), Electrolyser Inc. (CND), FEDNAV Ltd. (CND) Fenco Lavalin Inc. (CND), Fraunhofer Institut für Systemtechnik und Innovationsforschung (D), Gaz Métropolitain (CND), GERAD (CND), Germanischer Lloyd AG (D), Hamburger Hochbahn AG (D), Hamburgische Elektrizitäts - Werke AG (D) Hamburger Gaswerke GmbH (D), Holinger GMbH (D), Hamburgische Gesellschaft für Wirtschaftsförderung GmbH (D), Hydrogen Industry Council (CND), Hydrogen System NV (B), Institut Français du Pétrole (F), Joint Research Centre Ispra of the Commission of the European Communities (I), L'Air Liquide SA (F), Linde AG (D), Messerschimtt-Bölkow-Blohm GmbH (D), Messer-Griesheim GmbH (D), Paul Scherrer Institut (CH), Pratt & Withney (CND), Reederei August Bolten (D), SNC/FW Ltd (CND), Staatliche Materialprüfungs-anstalt der Universität Stuttgart (D), STCUM (CND), Technische Hochschule Darmstadt (D), Technische Universität Hamburg - Harburg (D), The LGL Group Ltd (CND), Thyssen-Nordseewerke GmbH (D), Uhde GmbH (D), Union Eléctra Fenosa SA (E), Universidad da Las Palmas de Gran Canaria (E), VTG-Paktank GmbH (D), Université Concordia (CND), Université Laval (CND).

Project management

Phase II of the project was managed by a Joint Management Group (JMG) consisting of the Ludwig-Bölkow-Stiftung (LBS), Ottobrunn, Germany, and Hydro Québec (HQ), Montreal, Québec. For the subsequent Phases III,0 III and IV, the Demonstration Projects and Realization, a new Arbeitsgemeinschaft for the European side has been established, an ARGE consisting of the Ludwig-Bölkow Systemtechnik (LBST), Ottobrunn, Germany, and CONOC Continental Contractors GmbH, Hamburg, Germany.

Reference Case (LH_2 vector)

For the reference case, i.e. the LH_2 vector

- hydropower	100	MW
- electrolysis (net)	74	%
- annuity (8% interest, 15 yr pay back)	11,7	%
- load factor	95	%

the main characteristics are:

- hydrogen delivered in Hamburg	74	MW = 614 GWh/y
- hydrogen transmission efficiency	74	%
- plant investment costs	415	Mio ECU
- specific hydrogen energy costs	14,8	cents$_{ECU}$/kWh

The cumulative costs and their percentage distribution are pictured in Figures 8.1.2 and 8.1.3.
The most salient new component in Phase II is the LH_2 ship. The LH_2 is transported in 5 vessels, containing 3000 m^3 LH_2 each, fixed on barges which are loaded on a barge carrier, therewith transporting altogether 15.000 m^3 LH_2, described in chapt. 7.2. The containers are super-insulated with no boil-off for 50 days. The floating barges permit individual towing on the water ways from the arrival sites to the users.
On October18, 1990 the BAM (German Federal Institut for Material Research) declared that liquid hydrogen would be not more dangerous than LNG and LPG and that it has no objection to the transport of liquid hydrogen in 2 G type ships (IMO rules).

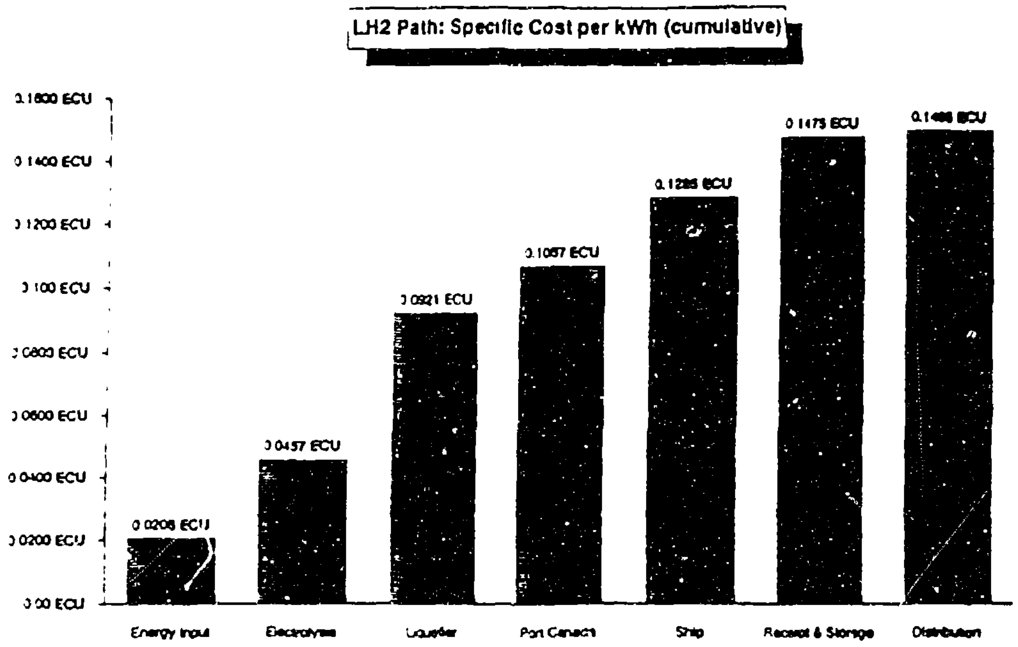


Fig. 8.1.2 - Specific costs in ECU/kWh (LH_2 reference case).

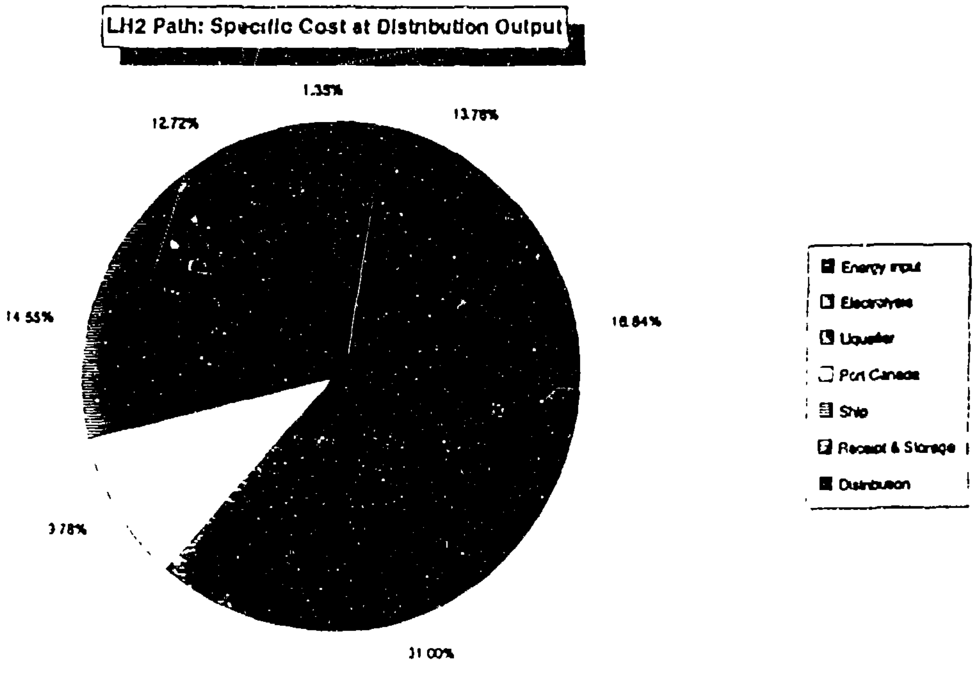


Fig. 8.1.3 - Specific costs distribution (LH_2 reference case).

Costs

The cost of liquid hydrogen, produced with hydropower at 2 cents_{ECU}/kWh, shipped to Europe and stored in the port of Hamburg are 14.8 cents_{ECU}/kWh (sensitivity analysis indicates a 19% impact on the production cost by doubling electricity cost).

The specific product costs and their breakdown for the LH_2 vector (reference case) are given in cited Fig. 8.1.2 and 8.1.3.

The specific product costs of gasous hydrogen (GH_2) from the MCH vector are 12 cents_{ECU}/kWh if dehydrogenated with hydrogen, the specific product costs are 15.3 cents_{ECU}/kWh. Therewith, the product costs of the MCH vector are higher than those of the LH_2 vector if it is dehydrogenated with clean hydrogen which has to be the case if the product is to be clean in all its steps from production to utilisation. Furthermore, the user's profile requires 62 MW LH_2 and 12 MW GH_2 . To satisfy this, 62 MW of the GH_2 in case of the MCH vector have to be liquefied by part of the GH_2 arrived at Hamburg, a procedure which brings to product costs of the LH_2 from the MCH vector up to 22 cents_{ECU}/kWh.

The investment costs contain the battery limit costs as specified by the industrial partners and the costs for off-sites and auxiliaries. In addition, indirect costs and interest incurred during construction are included. The complete cost figures are therefore higher than the costs of the naked plants at the battery limits.

A standardized calculation for depreciation was used with an interest rate of 8% and a capital payback period of 15 years resulting in a constant annuity of 11.7% (1990 money). The operating costs include energy consumption and consumables.

Vector selection

Weighting the pros and cons of the LH_2 vector vs. the MCH vector, i.e. considering the advantages of MCH:

- unlimited storage periods,
- transport and storage in existing normal oil product ships and containers

against disadvantages:

- the energy intensive dehydrogenisation and the liquefaction done at the user's site whereas the energy intensive liquefaction of LH_2 is done with abundant hydropower in Québec,
- MCH as well as toluene are petrochemical products and therewith environemntally less advantageous than LH_2,
- its product (GH_2) is not adapted to the user's profile, about 80% of hydrogen use being in the form of LH_2,

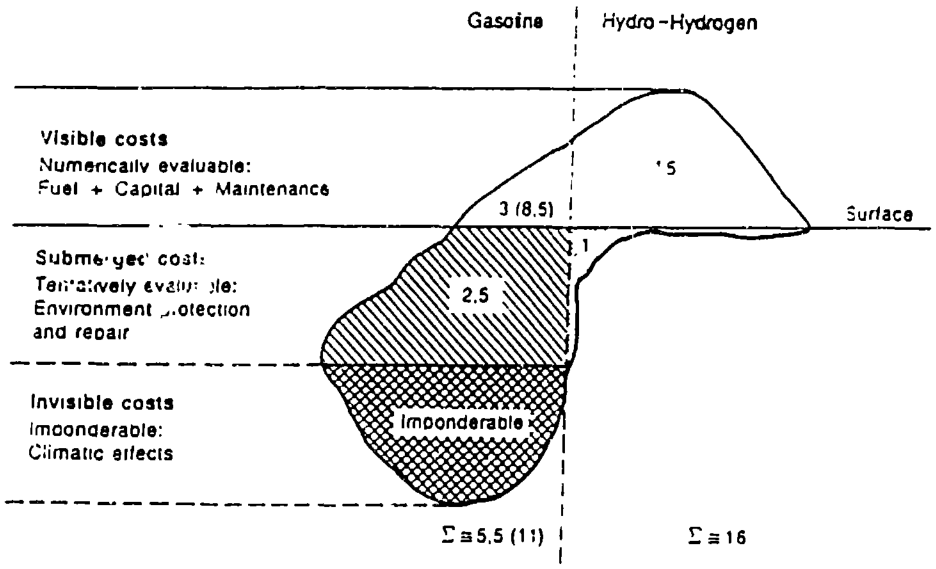
the decision was taken to retain LH_2 as vector for the realisation of the project.

Economics

The hydrogen cost of 14.8 ≈ 15 cents_{ECU}/kWh is depicted in Fig. 8.1.4 together with the cost of gasoline prices in Europe (average of the 12 EC countries, August 1990) of 8.5 cents_{ECU}/kWh which are made up of 3 cents_{ECU}/kWh for the crude oil itself, its transportation, refinement, manipulation and distribution, and of 5.5 cents_{ECU}/kWh for taxes.

With the above values and including the submerged costs of protection/repair of the damaged environment resulting from the use of fossil fuel of 2.5 cents_{ECU}/kWh, the "Fuel cost iceberg" would look as shown in Fig. 8.1.4, indicating the merits of clean technologies.

With internalization of external cost, hydrogen energy would be about 1.45 times higher than taxed and 2.9 times higher than non taxed hydrocarbon energy costs, not taking into account the imponderable costs of climate effects.



COST «ICEBERG»

(August 1990)

FUEL COST COMPARISON, $¢_{ECU}$/KWh (figures in ( ) are for taxed fuel)

Fig. 8.1.4 - Fuel cost "Iceberg".

Environmental aspects

As it is the case for any energy system, the construction of hydropower plants and the use/management of hydrogen has an impact on the local and the global ecosystem:

- hydropower: the usually quoted worldwide potential of 15-$20x10^3$ TWh/y is only 0.0057% of the hydrological cycle energy and is based on topological, technical and environmental concerns. In any case, careful site selection and adequate measures have to be undertaken in order to minimize the impacts;
- water vapour: the worldwide water evaporation from the oceans and rivers is - $5x10^{14}$ m^3 per year. If mankind's today's total energy consumption of sustained 11 TW would be effected by hydrogen, its yearly evaporation would be $2{,}5x10^{10}$ m^3 i.e. about 1/20000 of the natural evaporation. Once hydrogen will be massively used, local considerations are obligatory like it is the case for today's wet cooling towers;
- end use: whereas the combustion of hydrogen does not produce CO_2, CO, SO_2, VOC and particles, it entails emission of water vapor and NOx. Water vapour emissions from airplanes may be harmful since they generate depending on the cruising altitude and latitude - ice clouds with ensuing greenhouse effects. The problem is of utmost importance and actually under investigation; cruising altitude management is one answer. The formation of NOx from the atmospheric components N_2 and O_2 is a function of flame temperature and its duration. Considering the wide flammability range of hydrogen its combustion can be influenced by the design of the engine so that the NOx emission can be reduced. Hydrogen is an excellent fuel for fuel cells, its more or less cold combustion will reduce the NOx emissions even down to zero.

Phase III,0

A fund of 8 Mio ECU has been made available by the Commission of the European Communities in 1991 and 6.7 Mio ECU by European industry as well as 6.3 Mio ECU from the Government of Quebec and 2 Mio ECU from Canadian industry to undertake, in parallel to Phases III & IV demonstration projects on the utilisation of hydrogen in four fields where the use of hydrogen exhibits its attractiveness. In Europe, these projects are executed by industry on the basis of contracts following a tender action by the Commission with a cost sharing of at least 50% by the industrial partner:

- Vehicle propulsion: in Germany, for example, from the overall emissions those resulting from road traffic are: 52% NOx, 70% CO and 49% VOC. Public transport is predestinated for the introduction of clean and therewith expensive fuel since fuel costs are only a small fraction of the overall operating costs of buses. A typical diesel bus operation costbreakdown shows that fuel costs are only 7.3% of the total operation costs. Four public transport buses of different concepts will be built and operated: internal combustion engine, fuel cell, stirling engine.
- Aviation propulsion: the elimination of CO, CO_2, SO_2 and VOC by using hydrogen not only is beneficial for the atmosphere, but reduces considerably airport ground pollution. For example, the NOx emissions resulting from the daily average 1259 landing/take-off cycles at Los Angeles International Airport are equivalent to the operation of about I Mio passenger cars. A problem to be solved, however, is the increased water vapour emission. An Airbus combustion chamber designed for minimum NOx emission will be built and operated.
- Steel fabrication: with - 2 kg CO_2 emissions per kg steel fabricated with carbon as reductant, the world's steel fabrication contributes over 10% to the world's total anthropogenic CO_2 production. Hydrogen as excellent and clean reductant has a large potential to reduce CO_2 emissions.

  A demonstration component including iron ore reduction with hydrogen by plasma arc process will be designed, built and tested.
- Advanced techniques of liquid hydrogen storage.

Large scale model containers will be built and tested, including accident simulation and rupture tests.

In addition to the above, the following activities will be performed:

- economic studies related to social costs and the comparison and the use of conventional fuels and of hydrogen and define the advantages of hydrogen;
- investigations on the potential to lowering the costs related to the use of hydrogen and to demonstrate that it can be introduced as a clean and safe alternative fuel;
- detailed studies of safety codes and requirements and risk evaluation.

Funding

Up to now the EQHHPP has a total European funding for Phase II, Phase III,0 and a supplementary R & D programme of 35.7 Mio ECU from which 19.7 Mio ECU comes from the CEC, and 16 Mio ECU from industry. With 9,1 Mio ECU from Quebec - 6.1 Mio from Government, 3 Mio from industry the overall funding of the EQHHPP is in the order of 45 Mio ECU.

Outlook

An investigation is under way on the management and organisation structure for the realisation of the EQHHPP project. A EURO-QUEBEC HYDRO-HYDROGEN JOINT UNDERTAKING as an orderer, future owner and operator of the project and an EURO-QUEBEC HYDRO-HYDROGEN PROJECT MANAGEMENT, both being juridical bodies, are foreseen to be formed. Capital costs of the overall system of producing, transforming, storing, transporting and delivering hydrogen would be high and further developments have to be made to render them economically acceptable. Phase III,0 addresses this question of lowering the costs while it also addresses the question of showing the merits of hydrogen as a clean and dependable fuel.

Aknowledgement

The present report is largely based on the work undertaken by the representatives of the industrial and scientific partners of Phase II of the EQHHPP. The authors are grateful to all persons involved in this project for the quality of their work and their involvement in the project. The text of this paper has been presented at the 9th World Hydrogen Energy Conference, Paris, France, 22-25 June 1992.

8.2 - Activities and Programs in Germany

Hystorically, Germany has dedicated an impressive attention to hydrogen as an energy carrier. In more recent years, many studies have been conducted on solar hydrogen, mainly because of concerns about the environment. The most authoritative study on a possible solar hydrogen system has been performed under the sponsorshipness of German Parliament and it concluded that renewable energy sources and hydrogen can play an important role in a future environmentally sound economy. The attention on this theme permitted the organization of many programs, both in cooperation with other countries and with industries. In the above illustrated Euro-Quebec-Hydro-Hydrogen Pilot Project Germany covers an important role because hydrogen produced in Canada should be transported to Hamburg and utilized there for many applications. Important German industries, like Dasa, Aeg, Linde, Messer Griesheim, BMW and many other are involved in the project.

Particular attention is spent on solar photovoltaic hydrogen. On this field two main programs are carried on in Germany.

The first is a joint German-Saudi Arabian cooperation, the HYSOLAR project (HYdrogen from SOLAR energy), aiming at developing the technologies for solar hydrogen production and utilization. The project, started in 1986, is funded by the King Abdulaziz City for Science and Technology (KACST) of Kingdom of Saudi Arabia, the German Bundesministerium für Forschung und Technologie (BMFT) and the Ministerium für Wissenschaft und Kunst des Landes Baden-Württemberg. Partecipating institutions are: German Aerospace Research Establishment (DLR) and University of Stuttgart of Germany, King Abdulaziz City for Science and Technology, King Saud University, King Abdulaziz University (KAU) and King Fahd University of Petroleum and Minerals of Saudi Arabia. The first phase (1986-1992) of the project was organized in six tasks, three of which allowed the construction of three system facilities: the first, located in the Solar Vilage near Riyadh, is a 350 kW photovoltaic demonstration plant for hydrogen production via electrolysis. The plant is operated by KACST and comprises a photovoltaic array, based on monosilicon modules mounted on a structure able to perform two-axis tracking and to concentrate solar radiation by a factor 33. The photovoltaic array is in operation since 1981, and showed an overall efficiency over 8%, while the project for hydrogen production started in 1987. After some technical problems related to the electrolysis plant - that caused some delay in the start up of this section - operations restarted few months ago. In this configuration, the 350 kW system allows to investigate the possibility of exploiting solar energy in sunny countries through the use of hydrogen as an energy carrier. The second and third task concern a 10 kW and a 2 kW test and research facilities: the first is located at the University of Stuttgart and is operated by DLR; the second was built at Jeddah and is runned by KAU. These small plant are utilized to answer scientific and technical question in the field of advanced solar hydrogen technologies. They include all elements needed for hydrogen production and storage and should allow development of technologies, investigation of advanced concepts and operational experience. The other tasks cover: fundamental research programs on techniques like photoelectrochemistry and photocatalysis, advanced electrolysers and fuel cells; system studies and utilization program: within this frame steam generators, hydrogen fuelled motors, catalytic heater and other applications are investigated. Finally the educational and training program allows the dissemination of information. The expenses supported up to now amount to about 60 million DM. Last year a new bilateral agreement between Germany and Saudi Arabia, with a 1992-1995 budget of 28 millions of DM, allowed the starting of the second phase, in which activities should have a shift toward hydrogen utilization technologies.

The second German program aimed at investigation of solar photovoltaic hydrogen production, storage and use is the Solar Wasserstoff Bayern (SWB) project, operated by the society SWB GmbH. This society is owned by Bayernwerk (60%), Siemens, Linde, BMW and Dasa, each with a share of 10%. The project is funded by the Federal German State Government(35%) and by Bavarian Government (15%), being the other half supported by the shareholders. The project is organized in two phases, the first of which was concluded a few months ago. The first phase had a total cost of about 64 million DM and allowed the construction of a 280 kW photovoltaic plant at Neunburg warm Wald, including the sections for electrolytic hydrogen production, gaseous storage, utilization in many appliances. A station for liquid hydrogen storage was also built up, together with car refilling system: this latter is used to fill the reservoir of BMW hydrogen fuelled cars. The photovoltaic array is based on fixed flat plat panels, made of several technologies to allow the comparison of performances. Different ways to connect the array to the section of electrolys have been realized. Electrolysers are also made of different technologies; in particular membrane and advanced alkaline electrolysers are experimented. The storage of hydrogen and oxigen is obtained by compression up to 35 Bar in reservoirs able to contain 5000 Nm^3 and 500 Nm^3 respectively. Hydrogen is used to investigate fuel cells, heating boilers, catalytic heaters and other appliances. In general, the plant allows the testing of components at industrial scale. The second phase of the project has recently started with a budget of about 69 million DM. In this phase the plant will be implemented up to about 500 kW, by adding photovoltaic modules made by using new technologies, like amorphous silicon. Besides, the testing of new electrolysers, fuel cells and other appliances is foreseen. In general, SWB looks at a tight cooperation with the component suppliers, at the qualification of components and at the acquisition of better know-how on solar hydrogen systems.

A further initiative on solar photovoltaic hydrogen is managed by KFA. Togheter other partners, this company has started the construction and operation of a 40 kW photovoltaic-hydrogen-fuel cell demonstration plant, in order to investigate the way for achieving a decentralized, self supporting solar electric energy supply system. Photovoltaic modules will be mounted on the outer wall surfaces of the KFA central lybrary. Part of this building will be supplied by solar electricity. Hydrogen will be used as a medium to store summer surplus of electricity. In this task, KFA will use its well estabished on electrolysers and in particular on solar operated electrolysers.

Apart from these general-approach programs, in Germany there are many other activities on specific themes regarding hydrogen. It seems important to mention the engagement of BMW and Daimler-Benz on hydrogen fuelled vehicles and the researchs for the use of hydrogen in civil aviation. On their production cars, BMW and Daimler-Benz have been involved for many years on the experimentation of internal combustion engines fed by hydrogen and on the on-board storage. While BMW preferred liquid hydrogen, Daimler-Benz investigated different options. Both have acquired a great know-how arising from many years of on road experience. BMW has operated many vehicles fuelled by hydrogen, achieving operating ranges up to 300 km and a power output emulating conventional cars. Besided, together with MAN and Linde, it is now engaged in a project for the use of liquid hydrogen to fuel a city bus in Munich. Since 1984 Daimler-Benz has operated a fleet of 10 vehicles that have been drived for more than 750000 km and now it is also engaged in the experimentation of hydrogen for city buses, mainly whithin the framework of the EQHHPP project and in a joint German-Switzerland initiative. Deutsche Airbus is engaged on the activities aiming at modification of an existing aircraft, namely the A300, for liquid hydrogen fuelling. An in-depth study has been already conducted, including the design of the demonstrator, the evaluation of fuel consumption profiles, the estimation of operating costs.

It is quite difficult give a complete picture of all activities performed in Germany by a great number of operators, among which industries, municipal firms, research centers and universities. However, it seems important not to forget the engagement of the Fraunhofer Institute, that carries on many works on basic and applied research. Among the first, we should underline the efforts to develop electrochemical devices able to operate both as electrolyser, when supplied by electric energy, and as fuel cell, when fuelled by hydrogen. Recently the Fraunhofer Institute has completed the "self-sufficient solar house 2000", in which all energy needs are met by solar radiation. The system architecture foresees the hydrogen production via electrolysis in order both to feed catalytic heaters and to assure the seasonal storage of electric energy produced by photovoltaic modules. The conversion of hydrogen into electricity by a fuel cells, in fact, allows to satisfy electric demand also in low insolation periods.

In addition to experimental activites, many institutions are able to perform very in-depth ans reliable studies on hydrogen. For example, Dechema has conducted the study for the evaluation of technical and economical aspects related to the EQHHPP project.

A non complete list of other operators engaged on hydrogen is included in the EQHHPP description.

8.3 - Activities and Programs in Italy

The attention of this country to hydrogen is due to the generally accepted good characteristics of this element both as an energy carrier and as a fuel. The role of hydrogen as an energy carrier seems to be very important in view of a massive exploitation of solar energy field, particularly abundant in South of Italy: Italy, in fact, is dedicating a strong attention at solar photovoltaic technology. In this view, it is believed important to have available an energy carrier like hydrogen, that, being able to work also as an energy storage mean, can help to overcome the problem of intermittence of solar source. Hydrogen is also considered because, being environmentally sound, it can progressively penetrate in some applications like public road transport: that could also happen if it were produced from fossil fuels, in order to obtain local environmental benefits.

Some attention on hydrogen is given by ENEA, the Italian Agency for New Technology, Energy and the Environment. After an in-depth investigation of the activities undertaken in other countries and an evaluation of the state of the art of electrolytic hydrogen production, storage and applications, especially referring to transportation sector, ENEA has decided to operate a monitoring of all technological and systemic aspects and to experimentally investigate some important tasks: that in order to reach a reliable assessment of all technological and economic parameters needed to address further investigations on hydrogen related technologies.

A 5 kW photovoltaic-hydrogen experimental facility has been built: at present, operational tests on components are in progress. The plant comprises a photovoltaic generator, an alkaline electrolyser, metal hydrides and pressurized bottles for storage of hydrogen and a solid polimer electrolyte fuel cell. The plant will allow the comparison of different technologies and components at laboratory scale, the evaluation of matching among components and a preliminary assessment of safety and operation problems.

The public transportation sector is believed as a promising sector in which hydrogen can penetrate. In this view, the modification of a commercial vehicle - having a transportation capacity of ten people - is in progress. The main scopes are the demonstration of technical feasibility, to gain experience in operation, maintenance and safety aspects and to evaluate performances and economical parameters. For the future, the investigation of some new concepts, mainly in the direction of using hydrogen-methane mixtures, is foreseen.

An experimental program for the design and realization of light weight cylinders for gaseous hydrogen is being organized in cooperation with national and European partners. The program should allow the construction of some prototypes of vessels, made of composite materials, able to contain about 2 kWh of hydrogen per kg: the attainement of this goal would noticeably enwide the range of a hydrogen bus.

A cooperation agreement between ENEA and Solar Wasserstoff Bayern (SWB) has been signed in order to achieve a continous exchange of information on the respective activities.

Significant activities are carried on by Ansaldo Ricerche, involved at present in two projects concerning the realization of fuel cell busses fed by pure hydrogen, both based on the hybrid traction concepts. The first project, within the framework of the EUREKA program, is based on alkaline fuel cell as prime motor; the second, promoted by the EQHHPP, makes use of a SPE fuel cell for the same purpose. The partners for the first project are: Ansaldo Ricerche (Italy), Air Products (The Netherlands), Elenco N.V. (Belgium), Saft (France). City driving test of the bus are planned for 1994, first in Brussels and then in Amsterdam.

The partners of the second project are: Ansaldo Ricerche (Italy), Messer Griesheim (Germany), Azienda per i Servizi Municipalizzati di Brescia (Italy). The proton exchange membrane fuel cell will be supplied by the Italian firm De Nora, one of the most important company of the world on electrochemical technologies. A preliminary test on the road will be performed in Germany, while extensive city test will take place during 1994 in the city of Brescia, Italy.

Important activities are performed on fuel cells. ENEA has managed and financed, in cooperation with Ansaldo and Azienda Elettrica Milanese, the construction of a1MW phosforic acid fuel cell in Milan and a 200 kW plant in Bologna. Many other activities at laboratory scale are performed both by ENEA and De Nora and Ansaldo.

Excluding fuel cells, the expenses supported up to now from ENEA and Ansaldo amount to about 5 billions of Lit. The budget for 1993 is close to about 4 billions of Lit.

8.4 - Activities and programs in Japan

In Japan hydrogen technologies are mainly afforded within the framework of the Sunshine Project. In December 1992 Japan launched the idea of a World Energy Network (WE-NET), a general scheme of an international clean energy network using hydrogen conversion. The realization of this idea should happen by involving many operators of various countries for the investigation of all phases of hydrogen production from renewables, transport, storage and utilization. The long term goal is hydrogen import in Japan on the GW scale. Japan announced its intention to fund approximately $U.S. 2.5 billion over 27 years to develop the World Energy Networks (WE-NET) as part of its efforts to diversify its imported energy sources. At present, nearly 2.5 M$ per year are dedicated to research on hydrogen.

Activities started in 1974 and cover various kind of aspects, from production to transportation, storage and safe use of hydrogen. In the activities there are involved the Government Industrial Research Institutes of Osaka and Chugoku, the National Institute of Materials and Chemical Research and the Mechanical Engineering Laboratory. Besides, the use of hydrogen for road transport is studied by Nissan and Mazda.

Regarding production, two main technologies are being developed: solid polimer electrolysers operating at high efficiency and high current density and high temperature vapor electrolysers. On the former, research and development activities are directed toward achieving higher current densities than is possible today, in order to reduce the investment cost of such a kind of electrolysers. Since 1987, laboratory research has been performed on 50 cm^2 cells using advanced supports and membranes; results confirmed very good durability of the components. The subsequent step has been the construction of a filter press electrolyser module, in which 500 cm^2 electrodes are arranged in bipolar configuration. Operational tests are in progress: the aim is to determine problems in scale up, cell stacking, high temperature and pressure operation and so on. Up to now, a cell voltage of 1.8 V at 2 A/cm^2 was reached, with electrolyte temperature of 120 °C and a pressure of 3 atm.

On high temperature vapor electrolysers, the effort is devoted to individuate the best electrolytes in terms of conductivity, able to substitute conventionally studied electrolytes.

Metal hydrides are the most investigated technology for hydrogen storage. Many kind of alloys are investigated, among which the most promising are believed to be those based on magnesium and binary alloys like zirconium-nickel. Besides, basic research to understand the relation between crystal structure and hydrogen absorbtion are performed. Small scale experimental units of hydrogen tanks for road vehicles have been built and tested.

Particular attention is spent on Hydrogen oxigen stoichiometric combustion system, mainly in order to achieve the certainty to be able to control the system, and then to evaluate the applicability of the system to power generation. To this purpose a 23 kW gas turbine plant has been set up.

The investigation of the use of hydrogen as a fuel for cars started in the '70s. At present Nissan and Mazda are involved on the theme: both have already realized first prototypes of vehicles running on hydrogen.

In particular, Mazda Motor Corp. is affording the use of hydrogen in vehicles equipped with rotary engines, that give the chance to prevent the problems related with backfiring, preignition and abnormal combustion. A system to directly inject low pressure hydrogen in the early stage of compression stroke has been developed. Mazda claims that hydrogen powered vehicles are technically achievable quickly at a cost only 20% higher than conventional cars.

8.5 - Activities and Programs in Canada

Hydrogen is not an energy source in itself, but rather an energy medium or vector. Hydrogen can be produced from any energy source, either directly or through the generation of electricity followed by water electrolysis. Thus coal, natural gas, nuclear, hydro and solar power can all be used to produce hydrogen.

Like hydrogen, electricity is also an energy medium. Unlike hydrogen, however, it is difficult to store in any sizeable amount. Hydrogen and electricity are complementary and can be converted back and forth as required. Hydrogen has the added benefit of being a chemical feedstock.

Currently, hydrogen is an important chemical commodity and is indirectly used as a fuel through the upgrading of fossil fuels. Most hydrogen in Canada currently comes from steam methane reforming.

The current non-fossil hydrogen program of Energy, Mines and Resources Canada has several elements, totalling about $ 2.5 million per year.

a) *Hydrogen Production*

The objective is clean, efficient hydrogen production from renewable or sustainable energy sources.

The production of hydrogen through electrolysis is supported by:

- development of more efficient, novel membrane separators for electrolysis cells;
- testing and evaluation of electrocatalysts and separators; and
- development of an integrated photovoltaic hydrogen power plant.

b) *Hydrogen Storage, Transmission and Safety*

The objective is to develop the technologies and processes required for hydrogen to be a safe and effective energy carrier.

Work is supported on:

- development of a compact, load-following methanol reformer for integration with a fuel cell for transportation and mobile power applications;
- storage of hydrogen in chemical hydrides;
- basic hydrogen combustion studies;
- development of a more effective hydrogen sensor; and
- hydrogen-induced short fatigue crack propagation.

c) *Fuel Cells*

Fuel cells provide a clean and efficient means of using hydrogen as an energy carrier. When fuelled by pure hydrogen they are pollution-free, producing only electricity, heat and water.

Work is supported on:

- development of a fuel cell-powered transit bus;
- membrane development for solid polymer fuel cells;
- lightweight, portable alkaline fuel cell system;
- amorphous meatal catalysts for fuel cells; and
- development of a CO_2-tolerant alkaline fuel cell.

d) *EMR/Hydrogen Industry Council Program*

Support is provided to a joint government/industry cost-shared hydrogen R&D program addressing pre-commercial R&D of interest to industry. Project are evaluated and selected by a committee comprising governement and industry representative.

8.6 - Activities and programs in the United States

The U.S. Department of Energy (DoE) has recently set up a multiyear plan to provide overall guidance and leadership for federal investment in hydrogen research and development. It suggests critical research programs that can make significant contributions to the development of competitive hydrogen energy systems. It identifies areas where federal research is not timely - some of which may surprise some readers - because even successful results would not sufficiently improve hydrogen's attractiveness in large, national end-use markets.

The plan's principal evaluation tool for addressing hydrogen applications is energy pathway analysis, involving the consideration of all elements of an energy delivery system: required energy input, conversion, transmission, storage and utilization. Energy losses occur in each of these steps, and inefficiencies are compounded as the energy flow progresses. The final pathway efficiency is the ratio of end-use energy consumed to the input of primary energy. The pathway efficiencies are important because they may affect the required quantity of energy (or fuel), the total delivery system cost, and the level of environmental impact.

Pathway analysis is estimated particularly important for manufactured energy forms (or energy carriers) such as hydrogen and electricity, thus helping to focus investment on those steps where the potential for technology advancement is highest.

The analysis performed by DoE showd that some hydrogen pathways are clearly preferable to others when the combined factors of energy efficiency, capital cost, emissions, and domestic resource ownership are considered. Starting from solar energy, attractive pathways are believed photoconversion and bioconversion for both utility and transportation applications. Although they may be preferred approaches, these energy paths involve numerous processes or steps that require technical advancement. The following critical technologies were estimated to be developed if practical hydrogen pathways are to emerge in the mid and long term:

- Direct photoconversion production of hydrogen
- Biomass growth, harvesting, and conversion to hydrogen
- Anaerobic digestion of municipal solid wastes
- Fuel cell power plants suitable for vehicle propulsion
- Lightweight, compact storage for on-board vehicle use
- Efficient, low-cost storage for utility (stationary) use.
- Fuel cell systems for stationary applications
- Catalytic and heat engine conversions for transportation and industry applications.

Thus, a large spectrum of options are considered, in order to avoid dependence on a single scientific advancement or breakthrough. Many of the elements within the list are already receiving support under current DoE programs. Those critical technologies not already supported will receive first consideration for R&D investment using funds appropriated in response to the Spark M. Matsunaga Hydrogen Research, Development, and Demonstration Act of 1990, P.L. 101-566.

The recommended technology thrusts of the plan are steam reforming and thermochemical gasification of biomass, compact, lightweight storage systems for vehicles, internal combustion vehicles fuelled by hydrogen and fuel cells of several technologies. Besides, the plan recognizes that complementary studies are also required. These would include studies to refine pathway analysis and to identify new technical thrusts or displace prior ones, assessments to up-date comparative evaluations of hydrogen systems and other energy systems, and selected field evaluations of working models or prototypes.

Many activities are performed by several private and public institutions and universities, often under the co-ordination of National Renewable Energy Laboratories. At Humboldt State University Marine Laboratory a 9 kW photovoltaic-hydrogen fuel cell system is installed, in order to evaluate the feasibility of seasonal storage of electric energy by means of hydrogen. The system makes use of advanced components, such us a pressurized electrolyser and a proton exchange membrane fuel cell and is going to give first operational results.

Other activities are carried on by many states, like Hawaii, California, New York and Colorado. In the latter, an interesting activities is going on, concerning light duty vehicles with internal combustion engines fed by natural gas-hydrogen mixtures. First results were achieved y using natural gas with 15% (by volume) hydrogen content: a reduction by 50% of hydrocarbon emissions and by 50% of nitrogen oxide was achieved with respect to the vehicle fuelled on pure natural gas.

8.7 - Other programs

The reading of the preceeding paragraphs gives the chance to note that many other operators of different countries are working on hydrogen. For example Saudi Arabia is cooperating with Germany within the framework of HYSOLAR project. Belgium, The Netherlands, France, Switzerland operate on specific international programs. Sometimes, other activities are carried on in a national framework. This is the case, for example, of Switzerland: in this country an experimentation on the use of hydrogen to fuel heavy trucks has been conducted. A different approach to on board storage was given; in fact, a methylcyclohexane-toluene-hydrogen cycle has been experimented by the Swiss Federal Institute for Reactor Research, in cooperation with other Swiss operators. This cycle is based on the hydrogenation of toluene, by adding 1 unit of weight of hydrogen to 15 unit of weight of toluene: the final product is the methylcyclohexane: this compound is used as on board "fuel"; a proper catalytic dehydrogenator, located on the trucks, allows to obtain hydrogen. The transformation of toluene into methylcyclohexane has been already investigated in order to realize seasonal storage of energy. Apart from these experiences, other activities have been undertaken, among which the cited cooperation with Daimler-Benz. Some activities on photovoltaic electrolysers are conducted by Metkon. Electrowatt Engineering Services is going to built a 30 kW photovoltaic hydrogen pilot plant (Hydrosol pilot power plant). The project is sponsorized by the Swiss government. The operation will start in 1994. A two years campaign will be funded by the National Foundation for Energy Research.

The Belgian VITO, Flemish Institute for Technological Research, has launched a program to investigate many aspects related to hydrogen fuelled vehicles, including hydrogen storage, internal combustion engines, electric vehicles equipped with fuel cells. Besides economic, environmental and social implication are also analyzed.

In Spain, the National Institute for Aerospacial Technique (Inta) has undertaken a program for solar hydrogen production and utilization in the framework of solar energy activities. The program allowed the the construction of an experimental facility, made of a 8 kW photovoltaic array, alkaline electrolyser and gaseous hydrogen storage.

In Finland, the University of Technology of Helsinki is experimenting a 100% self-sufficient energy system for residential needs. The system consists of a small photovoltaic generator, storage based on battery and electrolytic hydrogen, fuel cell.

9. PLAN OF ACTION FOR THE DECADE 1995-2005

In developing a ten-year global plan of action for introduction of hydrogen as a carrier for renewable energy, it must be recognized that reasonable objectives should be set, given that the time frame for substantial penetration of renewable primary energy sources into the energy economy must necessarily be measured in decades.

Thus a ten year plan can be viewed as a first step. The work performed in Europe and North America in the past five years on integration of renewable energy technology and hydrogen technology provides a starting point or platform from which the next steps can be taken. Evolutionary and incremental improvements are necessary, through demonstration of state-of-the-art technology in parallel with continued advances in component parts.

It should be recognized that the system hydrogen production, hydrogen storage and hydrogen conversion or direct fuel use corresponds in function to the battery and the conventional fuel tank. Thus hydrogen role is to be complementary to that the battery technology (or other energy storage) technology. Where batteries and conventional fuels have limits, the effective exploitation of hydrogen technology can lead to the further development and market acceptance of renewable energy systems.

Hydrogen role as an energy carrier must be exploited as a value added to electricity from renewable sources. The role which hydrogen can play as part of a renewable energy economy is very dependent upon the needs of each region of the world and the local economics for harvesting renewable energy sources. Factors such as climate and weather patterns (which change themselves over time) are vital in assessing a region's needs and the potential benefit of hydrogen-related renewable energy systems.

Finally, a pathway following economic principles must be realised in achieving the growth of hydrogen-related renewable energy systems. All "environmentally friendly" benefits given to renewable technologies (which will grow in time as the external cost of conventional fossil-based energies becomes incorporated into their price) can be enjoyed by the hydrogen-related technologies. The key is to determine where hydrogen can add to the economics of renewables and thus increase their rate of market penetration.

If it is recognized that needs vary with each region, then a global strategy must be diverse and adaptable to each region's needs and the technologies must be available to meet those needs in the most effective manner.

A number of strategies and guiding principles can be stated:

a) *Regions Endowed With Renewable Energy Sources, Currently Depending on Imported Oil*:
Such countries are candidates to begin to take advantage of developments in hydrogen production, storage, transport and utilization. As hydrogen-based energy systems (central and local) are installed, the capital investment (made incrementally as demand requires) would enable substitution of imported fuel releasing foreign exchange for other developmental priorities. The substitution process would enable developing nations to evolve in both an economic and an environmentally sustainable manner. Such countries could become the leaders in clean energy and sustainable growth.

b) *Urban Regions With Very Poor Air Quality :*
Cities such as Mexico, Sao Paulo, Moscow, Dresden, Los Angeles, Santiago and many others have poor air quality due to the use of a fossil-based energy system. An evolutionary substitution of fossil-fuelled vehicles with mixed fossil and non-fossil fuels or pure hydrogen as the technologies become affordable will substantially clear the urban atmosphere and a major health problem.

c) *Independent Energy Systems for Remote Communities* :
Regions which are isolated, or where the building of transmission infrastructure is economically or technically difficult, will find local renewable energy an important

option. Hydrogen, as a more economic method than batteries to store large amounts of intermittent energy, can play a contributing role.

d) *Production of Cooking and Heating Fuel From Indigenous Renewables*:
Deforestation has stricken many countries causing soil erosion and loss of agricultural land as the collection of fire wood for cooking and heating becomes unsustainable. The situation is approaching a crisis, with the projected increase in developing nation's populations. Renewable energy systems which collect sunlight or wind have an important role to play in producing hydrogen (or electrolytic methanol) as a transportable and storable fuel.

e) *Intercontinental Transfer of Clean Energy from Countries with Surplus to Those in Need:*
For the past 100 years, our energy economy has mostly been based on coal, oil and natural gas. The transfer of oil and natural gas from regions of the world where it is in abundance to regions where it does not exist has been fundamental to our existence but also the cause of strategic global concerns, wars and environmental damage. Countries which possess abundant renewable energy sources which can be developed in an environmentally sound manner can now, through hydrogen, sell this energy to areas such as Europe and Japan which have dense populations, currently import fossil energy and seek to import clean energy as a substitute. Pipelines or shipment as liquid or by a hydrogen "carrier" material would be required that could be affordable in a future not so far particularly for hydropower, abundant and cheap in many countries.

f) *Grid Integrated Electrolysis:*
As electricity grids frequently have a high proportion of renewable or continuous primary energy sources, connection to the grid of variable energy consumers such as a water electrolysis plant can produce value-added products from incrementally available power; and at the same time support the utility planning process by lower risk, increased penetration of renewables and lower cost of power to all utility customers by full utilization of the investment in generating capacity.

The above roles for hydrogen in renewable energy systems will have different significances for various countries. Each country should evaluate their "solar" resources base to use hydrogen technology to best advantage.
Hydrogen strategies require the availability of all those component technologies necessary to make effective and complete systems at costs national markets can afford. Most components are, or are becoming, commercially available. Gaps exist and the development programs can be separated into system component development and overall system integration. The components include primary energy source technologies, hydrogen (and oxygen) production, hydrogen (and oxygen) storage, hydrogen transportation and hydrogen utilization. The scale of each part can be from a few kW or kWh to many GW or GWh, depending upon the application and the region.
Some lines of activity can be established in order to better use the resources in the short-mid term perspective of next ten years:
- *hydrogen cycle*: those initiatives aimed at demonstrating the technical feasibility of the overall hydrogen cycle from renewable energy sources must be supported. This is the case of Euro-Quebec-Hydro-Hydrogen Pilot Project, the Solar Wasserstoff Bayern and the Hysolar Projects. Many other programs should be undertaken, considering all possible path from the solar resources till end user. Within the framework of such general approach programs it is possible to examinate many hydrogen related technologies.
- *safety aspects*: in public opinion, safety is one the most important concerns related to hydrogen. Though the handling of hydrogen in chemical industry has reached high level of safety, one has to consider that the diffused hydrogen use in the energy system involves untrained personnel. Thus, research on safety in all phases of hydrogen cycle is of major

importance. The most correct approach is to develop both preventive safety measures and mitigation measures.

- *hydrogen production*: electric energy cost is major part of electrolytic hydrogen and, as a cosenquence, it is out of question that great attention must be paid to electric energy cost reduction from renewable sources. However, improvement of electrolyser efficiency has the same effect of electric energy cost reduction. Thus, research and development aimed at the realization of high efficiency, low cost electrolysers is indeed necessary. Besides, demonstration of technical feasibility, using today's available technology, must be encouraged: large scale (MW scale) pilot plant must be realized when sufficiently cheap and abundant solar resources are available, like hydropower; thus, the actual realization of the Euro-Quebec-Hydro-Hydrogen Pilot Project must be supported. Small-medium scale (tens or hundreds of kW) experimental plants must be built when less developed sources are considered (wind and solar photovoltaic). In this case, the plant must be also used to perform technical analysis, economic evaluations and to define the specifications of new, solar operated electrolysers.

The investigation of hydrogen production from biomass is strongly recommended because of resource large potential and the availability of many technologies. After hydrogen from hydropower, biomass could supply the next solar hydrogen.

- *hydrogen storage*: hydrogen storage is one of the most important barrier for large penetration of hydrogen (even non solar) in many applications, because present state of art technologies appear not adequate for large use of hydrogen. Then, th best political approach may be: to use present available storage techniques in those niche applications in which they give acceptable performances, like public road transportation; to investigate other promising technologies, like glass microencapsulation and activated carbons, for the future. In addition, the feasibility and the economic implications of using underground caverns for long term storage must be carefully evaluated. This would include: the inventory and the classification of existing caverns in the countries potentially interested to long term storage of hydrogen; small scale experience on the suitability of this solution.

-*hydrogen application*: this field must be largely developed, even using fossil derived hydrogen as a transition step toward solar hydrogen, in order to demonstrate that hydrogen is able to substitute fossil fuels in almost all applications. The cleaning of fossil fuels by using hydrogen will probably be the largest requirement of hydrogen in next years. Further important application is road transportation: that is significant from a double point of view: first, it demonstrates the adequacy of hydrogen in order to solve local environmental problems; secondly, successful demonstrations can push toward further applications and funding. The use of hydrogen-natural gas mixtures must be also considered because of easier acceptance of this solution and less technical and economical problems.

-*hydrogen transport*: the development and the actual realization of projects like the Euro-Quebec-Hydro-Hydrogen Pilot Project is of capital importance because they allow to investigate on significant scale the problems related to the transport of large quantities of liquid hydrogen. Gaseous hydrogen transport must be deeply examined too. This could happen starting from the analysis of the existing natural gas pipelines suitability for transport of hydrogen-natural gas mixtures. The small hydrogen pipelines operated in many countries can be a good starting point for the evaluation of technical and economical implications of building and operating large size pipelines for pure gaseous hydrogen transport.

It is probable that hydrogen-related renewable systems will follow a pathway of niches into the market system (similar to the experience with photovoltaics and wind turbines). Where hydrogen can provide an advantage, it should be exploited. Unique aspects of hydrogen technologies are their capability to be scaled down without unmanageable economic penalties. Small applications could be pathways for larger scale systems.

Like all technologies, hydrogen technologies will be constantly tested and improved by the entrepreneurial characteristics of our society. Focus on the nearer term commercial applications will provide justification for further development and adequate eventual markets.

Summary

Possible goals of a ten-year strategy include:

a) All countries which have committed to sustainable development will examine the role which hydrogen can play in their energy economy as a sustainable economic and environmentally energy contributor.

b) By the year 2005, 5% of new primary renewable energy supply will include a hydrogen-related component

c) Nations, participating through the UN or the International Energy Agency and other global bodies, will cooperate on development and demonstration of hydrogen-related renewable technologies which will assist sustainable development.

REFERENCES

References chap. 1

1) S. Ruben: "The Founders of Electrochemistry", Dorance & Company, Philadelphia, 1975

References chap. 2

2) DLR, ZSW, Ministry of Economics Affairs and Technology for the State of Baden-Wurttember: "Solar Hydrogen - Energy Carrier for the Future", Stuttgart 1989
3) C.-J. Winter, J. Nitsch (ed.): "Hydrogen as an Energy Carrier", Springer-Verlag, Berlin, 1988
4) L. Barra, D. Coiante: "Can Photovoltaics Become an Effective Energy Option?" Solar energy materials and solar cells, Vol. 27, N. 1 (1992) 79-89

References chap. 3

5) W. Barthknecht: Explosionen, Springer, 1978
6) J.H. Lee: Recent Results in the Study of Turbulent Deflagrations and Detonations, Int. Symp. on Control and Prevention of Gas Explosions, London, 1983
7) L.B. Thompson et al.: Nucl. Saf. 25, 3, 1984
8) M. Berman, J.C. Cummings: Reactors, Nucl. Saf. 25, 1, 1984
9) R.D. Witcofski, J.E. Chirivella: Experimental Results from Fast 1500 Gallon LH2 Spills, AIChE Cryogenic Properties, Process and Applications 82, 1986
10) H. Christner: Experimentelle Bestimmungen der Zündgrenzen von Mehrstoffgemischen in Abhängigkeit von Anfangstemperatur, -druck und Zündenergie, Dechema-Ausschuß Gas- und Flammenreaktionen, 1974
11) H.F. Coward, G.W. Jones: Limits of Flammability of Gases and Vapours, NBS Technical Note 503, 1952
12) B. Lewis, G. v. Elbe: Combustion, Flames and Explosions of Gases, Academic Press, 2nd edn. 1961
13) C. McKinley: Safe Handling of Hydrogen, American Chemical Society Symp. Ser. Vol. 116, 1980
14) Static Electricity 1972. National Fire Protection Assoc. Boston, NFPA 77, 1972
15) Dornier System GmbH: Sicherheitsaspekte einer künftigen europäischen Wasserstoff-Technologie, :bpublish.Abschlußbericht, 1979
16) J. Warnatz: Concentration, Pressure and Temperature Dependence of the Flame Velocity in Hydrogen-Oxygen-Nitrogen-Mixtures, Comb. Sci. Techn. 26, 1981
17) R.A. Strehlow, W.E. Baker: The Characterization and Evaluation of Accidental Explosions, NASA CR-134799, 1975
18) D. Burgess, J.N. Murphy, M.G. Zabetakis, H.E. Perlee: Volume of Flammable Mixture Resulting from the Atmospheric Dispersion of a Leak or Spill, Proc. 15th Symp. (Int.) on Comb., 1974
19) M. Fischer, H. Eichert: Hydrogen Safety in Energy Applications compared with Natural Gas, Proc. 5th WHEC, Toronto, Canada, 1984
20) J.H. Lee, I.O. Moen: The Mechanism of Transition from Deflagration to Detonation in Vapour Cloud Explosions, Prog. Energy Combust. Sci. 6, 1980
21) M. Fischer, R. Ewald: Sicherheit der Wasserstofftechnik, in: VDI-Berichte Nr. 602, 1987
22) K. Baumgärtner, R. Ewald: Sicherheitstechnik bei der Handhabung von Wasserstoff, Chem.Ing.Tech. 4, 1987
23) H. Eichert, M. Fischer: Sicherheit der Wasserstoff-Energietechnik - Eine notwendige Voraussetzung, VGB Kraftwerkstechnik, 1992 (im Druck)
24) F. Briscoe, P. Shaw: Spread and Evaporation of Liquid, Progr. Energy Comb. Sci. 6, 1980
25) H. Eichert: Zur Dynamik des Verbrennungsablaufs von Wasserstoff-Luft- und Wasserstoff-Methan-Luft-Gemischen, DLR-FB 89-39

26) J.H. Lee, R. Knystautas, A. Freiman: High-Speed Turbulent Deflagrations and Transition to Detonation in Hydrogen-Air-Mixtures, Comb. Flame 56, 1984
27) J.H. Lee, R. Knystautas, C. Guirao: The Link between Cell Size, Critical Tube Diameter, Initiation Energy and Detonability Limits, Fuel-Air Explosions, University of Waterloo Press, 1982
28) H. Eichert: Hydrogen-Air Deflagrations and Detonations: Numerical Calculations of 1-D Tube Combustion Processes, Int. J. Hydrogen Energy 12, 1987
29) J.A. Fay: Unusual Fire Hazard of LNG Tanker Spills, Comb. Sci. Techn. 7, 1973
30) N. Brehm: Ein Beitrag zum Phänomen des Übergangs Deflagration-Detonation, Dissertation, TU München, 1987
31) C.M. Guirao, R. Knystautas, J.H. Lee: A Summary of Hydrogen-Air Detonation Experiments, Nuclear Regulatory Commission Report NUREG/CR-4961, 1989
32) J.L. Hawksley: Unconfined Vapour Cloud Explosions Involving Hydrogen Rich Gases - Estimating the Blast Effects, Loss Prevention Bulletin 068, 1988

References chap. 4
33) McAuliffe, Charles A., Hydrogen and Energy, Gulf Publishing Company, Houston, Texas, USA, 1980
34) DLR, ZSW, Ministry of Economics Affairs and Technology for the State of Baden-Wurttember: "Solar Hydrogen - Energy Carrier for the Future", Stuttgart 1989
35) ZSW, DLR, LBST: "Technologies for Hydrogen Applications: Significance, End-Use Technologies and Technical and Economic Development Potentials", Stuttgart, March, 1992
36) L. Barra, D. Coiante: "Hydrogen-Photovoltaic Stand-Alone Power Stations: a Sizing Method", Int. Journal of Hydrogen Energy, Vol. 18, No. 4, PP. 337, 344, 1993
37) L. Barra, D. Coiante: "Energy Cost Analysis for Hydrogen-Photovoltaic Stand-Alone Power Stations", Accepted for pubblic. on Int. Journal of Hydrogen Energy, 1993

References chap.5
38) Pirani, S.N.; Stuart, A.T.B., Technical Status Report on Electrolyser's Photovoltaic Hydrogen Production & Storage Technology, paper presented at the 4th Annual Conference of the National Hydrogen Association, Washington DC, March 25, 1993.
39) Lehman, P.A.; Chamberlin, C.E., A Photovoltaic-Hydrogen-Fuel Cell Energy System: Preliminary Operational Results, paper presented at the 10th European Photovoltaic Solar Energy Conference and Exhibition, April 8 to 12, 1991, FIL Congress Centre, Lisbon, Portugal
40) H. Wendt (ed.): "Electrochemical Hydrogen Technologies", Elsevier, Amsterdam, 1990
41) C.-J. Winter, J. Nitsch (ed.): "Hydrogen as an Energy Carrier", Springer-Verlag, Berlin, 1988

References chap. 6
42) M.A.DeLuchi, University of California, " Hydrogen Vehicles: an Evaluation of Fuel Storage, Performance, Safety, Enviromental Impact, and Cost ", Int.J.Hydrogen Energy, no.2 1989
43) M.A. DeLuchi, Quanlu Wang, Daniel Sperling, Univerity of California, "Electric Vehicles: Performance, Lyfe-Cycle Cost, Emission, and Recharging Requirements ", Transpn Res.A., 1989
44) R.Gordon : " Composite Pressure Vessels for Gaseous Hydrogen Powered Vehicle ", Proc. 5th World Hydrogen Energy Conf. , Toronto, 1984
45) G.Pede, V.Sglavo, ENEA, "Applicazioni dell'idrogeno negli autoveicoli con motore a combustione interna", RTI-ENE(91)01
46) F. Scaramuzzi: "Criogenia", Enciclopedia delle Scienze Fisiche, Istituto dell'enciclopedia italiana, 1992

47) R. B. Scott: "Technology and uses of lyquid hydrogen", Pergamon Press, Oxford, 1964
48) G.K. White: "Experimental Techniques in low-temperature physics", Clarendon press, Oxford, 1968
49) R. F. Barron: "Cryogenic Systems", Oxford University Press, 1985
50) T. K. Nandi, S. Sarangi: "Performances and optimization of hydrogen liquefaction cycles", Int. J. of Hydrogen Energy, Vol. 18, N. 2, 1993
51) P.Parvopoassu : " Lezioni di Impianti Meccanici", Roma 1975
52) ASME : ASME B31.3 1990 Edition
53) Michel Pottier : "Hydrogen Production and Storage", Workshop held at Ispra, Italy,1981
54) Igoshin, Vainer, Kazarian, Smirnov : " The Utilization of Underground Caverns in Rock Salt Formation for Hydrogen Production and Storage "
Proc. 9th World Hydrogen Energy Conf. , Paris, 1992
55) T.H. Schucan : " Seasonal Sorage of Hydrogen and Use as a Fuel for Heavy Vehicles", 1987
56) M.Taube, D.Rippint, W.Knecht, B.Milisavljevic, N.Gruenenfelder : "A Prototype Truck Powered by Hydrogen from Organic Liquid Hydrides", Int.J.Hydrogen Energy, no.9 1985
57) K.L. Yan, B.G. Sellars, J.Lo, S.Johar, M.K. Murthy :" Storage of Hydrogen by High Pressure Microencapsulation in Glass", Int.J.Hydrogen Energy, no.10 1985
58) A.Akunets et al. : " Superhigh Strenght Microballons for Hydrogen Storage", Proc. 9th World Hydrogen Energy Conf. , Paris, 1992
59) B.Duret, A.Saudin : "Microspheres for on-board hydrogen storage", Proc. 9th World Hydrogen Energy Conf. , Paris, 1992
60) K.A.G. Amankwa, J.S. Noh, J.A. Schwarz : "Hydrogen Storage on Superactivated carbon at Refrigeration Temperatures", Int.J.Hydrogen Energy, no.14 1989
61) R.Chahine,T.K. Bose : " Low Pressure Adsorption Storage of Hydrogen ", 9th World Hydrogen Energy Conf. , Paris, 1992
62) AA.VV.: " Alternative Energy Sources for Road Transport, Hydrogen Drive Test ", Verlag TUV Rheinland 1990
63) Hans-Ulrich Huss, Daimler Benz AG, " Hydrogen Application in City Busses ", Ansaldo-CEC Symposium "Hydrogen within a Clean and Renewable Energy System", Genoa, October 28-29, 1991.
64) D.Reister e W. Strobl, BMW AG, " Current Development and Outlook for the Hydrogen Fuelled Car ", 1992
65) M.A.DeLuchi, University of California, " Hydrogen Vehicles: an Evaluation of Fuel Storage, Performance, Safety, Enviromental Impact, and Cost ", Int.J.Hydrogen Energy, no.2 1989
66) K.Collier, Clovis Linkous, Ali T-Raissi : "An overview of Hydrogen Research at the Florida Solar Energy Center"

References chap. 7

67) Bezin S. et Garat A.: "Etude des possibilités de conversion à l'hydrogène des resaux de transport de gaz"; Proc. of the Intern. CEC Seminar, Bruxelles 1980, D.Reidel Publ. Co.
68) Dutton R.: "Materials Degradation Problems in Hydrogen Energy Systems", Int. Journ. of Hydrogen Energy, Vol. 9, No. 1/2, pp. 147-155, 1984.
69) Kaske G. and Plenard F.J.: "High-purity hydrogen distribution network for industrial use in Western Europe", Int. Journ. of Hydrogen Energy, Vol. 10, No. 7/8, pp. 479-482, 1985.
70) Kaske G., Schmidt P. and Kanngiesser K.W: "Vergleich zwischen Hochspannungsgleichstromuebertragung und Wasserstofftransport" ("A Comparison between the Transport of Electricity and Hydrogen"), VDI Berichte No. 725, pp. 129-162, Duesseldorf 1989.

71) Louthan M.R. and Swanson R.E.: "Material Defects, Gas Purity and Hydrogen Embrittlement", Int. Journ. of Hydrogen Energy, Vol. 10, No. 7/8, pp. 551-554, 1985.

72) Penner S.S. and Iceman L.: "Energy", vol. II: Non-nuclear Energy Technologies, chapt. 11.3, Pergamon Press 1984.

73) Skelton L.W.: "The Solar-Hydrogen Energy Economy", chapt. 6, Van Nostrand Reinhold Co. 1983.

74) Socher M.: TA-Projekt: "Risiken bei einem verstaerkten Wasserstoffeinsatz" (report to the German Parliament: "Risks related to an increased use of Hydrogen"), Bonn, January 1993.

75) Winter C.J. and Nitsch J. (Eds.): "Hydrogen as an Energy Carrier; Technologies, Systems, Economy", chapt. 9, Springer Verlag, Berlin, 1988.

76) Zittel W., "Wasserstoffspeicherung, -transport und -verteilung" ("Hydrogen Storage, Transport and Distribution", report to the German Federal Ministry of Research and Technology), final draft, private communication, December 1992.

77) Nitsch, J. :" Aufbaustrategien fuer eine solare Wasserstoffwirtschaft", Bericht der VDI-Tagung "Wasserstoff-Energietechnik III, Enerbnisse und Optionen", Nuernberg, 1£-19 February 1992

78) ISI/PROGNOS, Verschiedene Autoren: "Konsistenzpruefung einer denkbaren zukuenftigen Wasserstoffwirtschaft", Untersuchung im Auftrag des Bundesministerium fuer Forschung und Technologie, Bonn 1992

79) J. Gretz, "Phase II and Phase III-0 of the 100 MW Euro-Quebec Hydro-Hydrogen Pilot Project". Proceedings of the 9th World Hydrogen Energy Conference, Vol. 3, Paris, June 22-25, 1992.

80) Germanischer Lloyd, Thyssen Nordseewerke, Rederei A. Bolten, "EQHHPP Phase II - Maritime Transport". Hamburg, September 5, 1990.

81) G. Giacomazzi, "Maritime Hydrogen Transportation".
Ansaldo-CEC Symposium "Hydrogen within a Clean and Renewable Energy System", Genoa, October 28-29, 1991.

References chap. 8

82) The 100 MW Euro-Quebec Hydro-Hydrogen Pilot Project, J. Gretz, J. Baselt, O. Uilmann, H. Wendt - International of Hydrogen Energy, Vol. 15, No. 6, pp 419-424, 1990.

83) EQHHPP - Phase II Final Report, Joint Management Group, 1991.

84) H. Steeb, W. Seeger, H. A. Oud: "Hysolar: an overview on the German-Saudi Arabian Program on Solar Hydrogen", Proceedings of the 9th World Hydrogen Energy Conference, Vol. 3, Paris, June 22-25, 1992

85) H. Blank, A. Szyska: "Solar-Hydrogen Demonstration Plant in Neunburg worm Wald", Proceedings of the 9th World Hydrogen Energy Conference, Vol. 3, Paris, June 22-25, 1992

86) Private Communications given at IEA Implementing Agreement on Hydrogen, Washington DC, March 1993

87) U.S. DoE: "Hydrogen Program Plan FY 1993-97", Office of Conservation and Renewable Energy

88) Lehman, P.A., Chamberlin, C.E.: "Operating Experience with a Photovoltaic-Hydrogen-Fuel Cell Energy System", Solar Hydrogen Energy Systems Symposium, ASME Winter Annual Meeting, Anaheim, California, November 1992

World Solar Summit
The Sun in the Service of Mankind
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REPORT ON "ENERGY AND HYDROGEN"

ABSTRACT

This report deals with the role of hydrogen in a future scenario in which solar energy in all its direct and indirect renewable forms (thermal, photovoltaic, wind, biomass, hydropower, etc.) would give a major contribution for a susteinable development.

A short review on the hystory of research on hydrogen shows that the attention on the use of this element as an energy carrier and as fuel is not so recent, because also in the past hydrogen was considered as suitable fuel for many applications and, as a consequence, some production technologies were investigated.

The strategic motivations that justifies an increasing penetration of hydrogen in the energy system are presented, pointing out the need of having at disposal, in addition to electricity, a further energy carrier like hydrogen, which presents environmentally sound characteristics. In fact, from the analysis of end user demands and of the technologies for exploitation of solar energy it results that electric energy and hydrogen present all requisites in order both to full utilize solar energy and to satisfy end users in the respect of the environment.

Special attention is paid to the safety performances of hydrogen, due to generally diffused concerns about this aspect. The characteristics of hydrogen with regard to this parameter are presented and discussed in comparison with some conventional fuels. A careful use of hydrogen and of proper technologies should allow acceptable safety in the phases of production, storage, transport and use of this element.

A description of hydrogen applications is presented, from which emerges that hydrogen is suitable to progressively substitute fossil fuels in most end uses. Some applications, like public road transports, that seem to be technically and economically effective for mid term, are discussed, presenting the advantages of hydrogen with respect to reduction of pollution.

A review of the technological options available for hydrogen production from renewables is presented, giving major emphasis at water electrolysis and production from biomasses, that seem to be the most promising and useful with regard to the technologies for the utilization of solar energy. Electrolysis, in fact, couples very well with all energy options that give electric energy, like hydropower, photovoltaic and wind; production from biomass appears attractive due to the large potential of biomass and to the good perspective in term of technical and economical effectiveness in the medium period. The state of art of the relative technologies is quite satisfying, but better performances are needed with regard to efficiency, investment costs and lifetime. Some other technics for hydrogen production from renewable energy sources, still at laboratory stage, are more briefly illustrated.

Hydrogen storage seems to be a key problem for large hydrogen penetration: this element, in fact, is the most light in nature and, as a consequence, is storable, at present, only paying a high price in term of weight and volume of the "reservoir" and, sometime, of energy expenditure. The state of today available technologies is presented, discussing the suitability of each of them for some applications. At present, some technics for hydrogen storage are satisfying for some specific applications, but the massive introduction of hydrogen needs significant improvement of these technics together with the development of some innovative concepts, at present under investigation, in order to obtain better performances with respect to the weight and volume of "reservoir". Special attention must be paid to the energy to spend for storing and extracting hydrogen and to losses.

The transport of hydrogen seems to be very important, mainly when large, centralized production plants are considered. In this case, the most appropriate ways to transport hydrogen should be pipelines (gaseous) and liquid in criogenic reservoir: in the report both technics are properly illustrated.

At present, many operators, both public and private, are involved on hydrogen activities. A strong effort is historically supported by Germany, which is involved in main important national and international programs. A growing attention on hydrogen is paid by other countries, like Japan, Canada and USA. Some other countries, among which Italy, are carrying on interesting programs on hydrogen. Though many significant applications are possible in the mid term, important penetration of hydrogen is expected in the long period: that favours cooperations among operators, that will result from the illustration of various activities and programs.

Finally, the strategic goals to attain on hydrogen-related technologies in order to facilitate the coming of a "solar age" are illustrated, and some proposal to meet these goals are presented.

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RAPPORT SUR "L'ENERGIE ET L'HYDROGENE"

RESUME

Ce rapport traite du rôle de l'hydrogène dans un panorama future dans lequel l'énergie solaire dans toutes ses formes directes et indirectes (thermique, photovoltaique, éolienne, hydraulique, de la biomasse, etc.) pourrait donner une contribution déterminante pour un développement soutenable.

Une exposition sur l'histoire de la recherche sur l'hydrogène révèle que l'attention à l'utilisation de cet élément en tant que vecteur d'énergie et combustible n'est pas si récente, puisque dans le passé aussi, l'hydrogène était considéré indiqué et même préférable à d'autres combustibles pour de différentes applications. Par conséquent, dans le passé, de différentes technologies de production ont été étudiées.

Dans la suite de ce rapport on expose les raisons stratégiques qui justifient la croissante pénétration de l'hydrogène dans le système de l'énergie, en faisant ressortir l'importance de pouvoir disposer, non seulement de l'électricité mais aussi d'un second vecteur d'énergie tel que l'hydrogène, à des caractéristiques de compatibilité ambiante très attrayantes.

De l'analyse de la demande des usagers derniers et des technologies d'exploitation de l'énergie solaire il ressort, en effet, que l'énergie électrique et l'hydrogène offrent toutes les qualités nécessaires pour un plan d'exploitation de l'énergie solaire et pour la satisfaction des usagers, dans le respect de l'environnement.

On réserve une attention considérable aux caractéristiques de l'hydrogène, à cause des préoccupations répandues concernant cet aspect. On illustre donc les principaux paramètres qui déterminent la sureté de l'hydrogène et l'on effectue une comparaison avec certains parmi les principaux combustibles conventionnels. Un usage propre de l'hydrogène, avec l'emploi de technologies convenables devraient garantir un niveau approprié de sureté dans toutes les stades de la production, stockage, transport et utilisation de l'hydrogène.

Ensuite on passe en revue les applications de l'hydrogène, à partir desquelles il ressort que l'hydrogène est indiqué en puissance pour remplacer les combustibles fossiles dans la plupart des usages derniers. On explique avec une attention particulière quelques applications - comme le transport routier publique - qui peuvent devenir compétitives dans le moyen délai, offrant les avantages de l'hydrogène pour la réduction de la pollution atmosphérique.

Dans la suite on passe à la description des options technologiques pour la production de l'hydrogène à partir des sources renouvelables, en donnant une attention spéciale à l'électrolyse de l'eau et à la production de biomasse: en effet, ces deux techniques se révèlent extrèmement prometteuses si l'on regarde aux principales technologies d'exploitation des sources renouvelables d'énergie. L'électrolyse, en effet, se rapproche très bien des options énergétiques qui transforment l'énergie renouvelable primaire en électricité, comme l'hydro-électricité, le photovoltaique et l'éolien. La production à partir de la biomasse est intéressante à cause du grand potentiel de cette source et des bonnes perspéctives en termes d'avantages techniques et économiques déjà dans le moyen délai. L'état de l'art des rélatives technologies de production de l'hydrogène paraît satisfaisant, mais il est nécessaire d'arriver à des progrès significatifs en termes d'efficacité, coûts d'investissement et vie moyenne. D'autres technologies de production de l'hydrogène par des sources renouvelables, qui sont encore au niveau de laboratoire, sont illustrées plus brièvement

Le stockage de l'hydrogène semble un problème de grande importance: en effet, cet élément est le plus léger à l'état naturel et, par conséquent, il ne peut être stocké aujourd'hui qu'en payant un prix élevé en termes de poids et volume du "récipient" et, dans quelques cas,

d'énergie dépensée pour le stockage. On décrit l'état des technologies qui sont disponibles aujourd'hui, en soulignant si elles sont indiquées pour certaines applications. Actuellement, quelques-unes de ces technologies ont déjà atteint un niveau satisfaisant dans certaines applications particulières, mais une pénetration massive de l'hydrogène dans le système de l'énergie suppose une amélioration significative de ces technologies, avec, en même temps, le développement de concepts innovatifs, qui sont en train d'être étudiés, pour réduire le poids et le volume du "récipient". En outre, il faudra s'engager à fond pour réduire l'énergie nécessaire pour stocker l'énergie et pour l'extraire du "récipient" et les pertes.

Le transport de l'hydrogène doit être considéré très important, surtout lorsque c'est le cas de grandes centrales de production éloigné des usagers derniers. Dans ces cas les techniques de transport qui se sont révélées les plus indiquées sont les "pipelines" pour l'hydrogène gazeux et les réservoirs cryogéniques pour l'hydrogène liquide: dans ce rapport on illustre les deux techniques.

En ce qui concerne les programmes de recherche et développement sur des sujets divers, on remarque l'engagement de nombreux opérateurs, publiques et privés. Un effort plus important est donné par l'Allemagne, impliquée dans des projets nationaux et internationaux très rélévants. On remarque une attention croissante dans d'autres pays, tels que le Japon, le Canada et les Etats Unis. D'autres pays, parmi lesquels l'Italie, ont tout récemment mis au point d'intéressants programmes sur ce sujet. Bien que l'hydrogène puisse être employé dans certaines applications déjà dans le moyen délai, on attend une pénetration significative dans les usages derniers dans la longue période, ce qui favorise la collaboration entre les différents pays qui résulte de quelques accords internationaux.

Enfin, on illustre les buts stratégiques qu'il faudra atteindre pour favoriser l'avènement de l'ère de l'énergie solaire, et l'on donne quelques indications utiles pour les atteindre.