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EMERGING
TECHNOLOGY
SERIES

Hydrogen Energy Technologies

UNITED NATIONS
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EMERGING TECHNOLOGY SERIES

Technology is now at the core of competitive strategies of successful industrial firms. The new and rapidly evolving generic technologies, such as biotechnology, new materials and information technologies, offer many opportunities and challenges for broad competitive strategies. They engender entirely new products, services, markets and businesses. Their impact is trans-sectoral, radically improving the competitiveness of products, processes and services of firms in a large number of traditional industrial sub-sectors. New materials improve product specifications and lower production costs in engineering and chemical industries; biotechnologies save energy and raw materials in chemicals, pharmaceuticals and food processing, while the pervasive applications of information technologies allow companies in all industrial sectors to re-engineer critical processes, improve overall efficiency and raise productivity across functional areas. Monitoring and access to information is now a key to competitiveness.

Experience in newly industrialized countries shows that access to reliable technical information can be instrumental in allowing manufacturers to leap whole periods of technological development and adopt state-of-the-art systems directly – without needing to undertake a painful and costly development phase. Up-to-date economic information and analysis of global economic trends and the prevailing industrial situation in other countries is likewise indispensable – and the gateway to identifying industrial needs, opportunities, constraints and priorities of the country and region concerned. Monitoring technological advances and economic analysis provide the basis for the formulation and effective implementation of appropriate industrial programmes and projects by both public and private entities. For developing countries, with their limited resources and often greater susceptibility to the negative aspects of technology-led change, such activities are doubly important. Yet many developing countries still lack the critical elements for technology monitoring of emerging technologies and their implications for national development strategies. If they are to maximise the benefits and minimize the negative effects of technology on social and economic development, developing countries must manage technology in an appropriate manner – and monitoring is an essential element of that management process.

One of the objectives of UNIDO is to carry out a set of coherent activities at the national, regional and international levels, to help developing countries at different stages of development to acquire, apply, develop and manage technologies against a global background of technological change. Investment and technology play a vital role in the industrial growth of developing countries, as well as their gradual integration into the international economy. Although most developing countries now have liberal regimes for investment and technology transfer, this is not a sufficient condition for industrial growth. There is a need for a wide-ranging investment and technology approach that will not only attract and retain the inflows of investment and technology, but also make the optimum use of them for the domestic economy. UNIDO's wealth of experience in industrialization, combined with its worldwide network of contacts makes the Organization an ideal partner to assist developing countries in building up their investment and technology partnerships. The Organization is a focal point of industrial technology; it is a global source of industrial information; and it is an honest broker for industrial cooperation.

Through this new series of publications on emerging technologies in developing countries, which supercedes the ***Industrial Technology Monitors*** and the ***Technology Trends Series***, UNIDO plans to sensitize industry and governments to the need for and requirements of technology monitoring and assessment in the areas of new and emerging technologies. These technologies play a catalytic role in the development process of the new global pattern of rapid and accelerating technological change, sweeping trade liberalization, far-reaching deregulation of markets – including the privatization of state-owned enterprises and commercialization of R&D – and the globalization of international business.

Investment and Technology Promotion Division

EMERGING
TECHNOLOGY
SERIES

Hydrogen Energy Technologies

Prepared for UNIDO
by
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UNITED NATIONS
INDUSTRIAL DEVELOPMENT
ORGANIZATION

Vienna, 1998

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HYDROGEN ENERGY TECHNOLOGIES

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Preface

Within the framework of the UNIDO programme on new technologies, hydrogen energy was one of the subject areas covered from the 1980s. In 1988, UNIDO carried out a study entitled "Hydrogen Energy Technology for Developing Countries". This study concluded that the necessary technologies existed for the near term application of hydrogen energy and that they were especially attractive for the developing countries. In 1991, UNIDO published a report on "Hydrogen Energy Initiation in Developing Countries", concentrating on the technologies suitable for developing countries. This study included a proposal to establish an International Centre for Hydrogen Energy Technologies. Following the recommendation of this study, UNIDO, in cooperation with other UN agencies, organized expert group meetings in Asia and Latin America to create awareness, to exchange views and to explore opportunities for developing countries to acquire the capability for hydrogen energy technologies.

As a result of this preparatory work, UNIDO undertook promotional activities towards the establishment of an International Centre for Hydrogen Energy Technologies with the financial support of the Government of Turkey. This included extensive consultations with experts and government officials in both developed and developing countries, after which a final report was prepared and presented to the Government of Turkey. A meeting of international experts was then held in Turkey in 1996 to review the concept of the Centre. The experts unanimously supported the idea of establishing the Centre to promote the introduction of hydrogen as a clean source of energy for the benefit of both developed and developing countries. At the end of the Meeting, the Government of Turkey indicated that they would allocate the required land, and provide the funds to build the Centre's premises and support its operation.

With the support of the Government of Turkey and based on the findings of the Expert Group Meeting, the proposal for the establishment of an International Centre for Hydrogen Energy Technologies under the auspices of UNIDO, was welcomed by the Industrial Development Board (IDB) of UNIDO.

The present report is a comprehensive review of the current status of hydrogen energy technology, which has been prepared by Professor T. N. Veziroglu and Dr. Frano Barbir. Professor Veziroglu has been a tireless champion of hydrogen energy technology and has been involved with UNIDO's efforts on the subject from the outset of this initiative. Professor Veziroglu is one of the world's leading experts on hydrogen energy and is currently the Director of the Clean Energy Research Institute of the University of Miami, and the President of International Association for Hydrogen Energy. Most importantly for UNIDO, he has been the major proponent for the establishment of the International Centre for Hydrogen Energy Technologies.

CHAPTER 1

INTRODUCTION - RATIONALE FOR HYDROGEN ENERGY

The economic growth of modern industrialized society has been based on the utilization of energy locked in fossil fuels. At the present time, about 80 per cent of the world energy demand is met by fossil fuels – coal, petroleum and natural gas [1,2]. These fuels are readily available in one form or another and convenient to use. Humankind has learned to exploit them relatively efficiently to produce the energy services that it needs [3].

However, consumption of fossil fuels has become a destructive force, locally because of emissions, spills and leaks, and strip mining, regionally because of pollutants' dispersion and acid rains, and even globally because of carbon dioxide accumulation and threatening consequences such as global warming, climate changes and sea level rise.

Energy technologies, particularly those related to fossil fuel extraction, transportation, processing and end-use (which is almost always combustion) have harmful impacts on the environment, which cause direct and indirect negative effects on the economy.

Excavation of coal devastates the land, which has to be reclaimed, and is out of commission for several years. During the extraction, transportation and storage of oil and gas, spills and leaks occur, which cause water and air pollution. Refining processes also have a negative environmental impact.

Most of the fossil fuel environmental impact occurs during the end use. The end-use for all fossil fuels is combustion, irrespective of the final purpose (i.e., heating, electricity production or motive power for transportation). The main constituents of fossil fuels are carbon and hydrogen, but also some other ingredients, which are originally in the fuel (e.g., sulphur), or are added during refining (e.g., lead, alcohols). Combustion of the fossil fuels produces various gases (CO_X, SO_X, NO_X, CH), soot and ash, droplets of tar, and other organic compounds, which are all released into the atmosphere and cause air pollution. Air pollution may be defined as the presence of some gases and particulates, which are not a natural constituent of the atmosphere, or even presence of the natural constituents but in an abnormal concentration. Air pollution causes damage to human health, animals, crops and structures, and reduces visibility.

Once in the atmosphere, triggered by sunlight or by mixing with water and other atmospheric compounds, the primary pollutants may undergo chemical reactions, change their form and become secondary pollutants, like ozone, aerosols, peroxyacyl nitrates, various acids, etc. Precipitation of sulphur and nitrogen oxides, which have dissolved in clouds and in rain droplets to form sulphuric and nitric acids is called acid rain; but also acid dew, acid fog and acid snow have been recorded. Carbon dioxide in equilibrium with water produces weak carbonic acid, but below pH 5, carbonic acid has no further acidifying effect. Acid deposition (wet or dry) causes soil and water acidification, resulting in damages to the aquatic and terrestrial ecosystems, affecting humans, animals, vegetation and structures.

The remaining products of combustion in the atmosphere, mainly carbon dioxide, together with other so-called greenhouse gases (methane, nitrogen oxides and chlorofluorcarbons), result in thermal changes by absorbing the infrared energy the Earth radiates back into the atmosphere, causing global temperature increase. The effects of the temperature increase are melting of the ice caps, sea level rise and climate changes, which include heat waves, droughts, floods, stronger storms, more and bigger wildfires, etc.

The cost of the above described negative effects are not included in the market price of fossil fuels. These costs are paid by the society, and/or will eventually be paid by society, directly or indirectly through taxes, health expenditures, insurance premiums, and through a reduced quality of living. In other words, fossil fuels are heavily subsidized. Using the scores of environmental scientists, the worldwide damage caused by fossil fuels has been estimated at approximately US$12 per GJ of fossil fuel consumption [4], acknowledging that this figure is somewhat higher for coal and somewhat lower for natural gas. On a global basis, this damage accounts for more than 10 per cent of the gross world product. This is, of course, not sustainable in the long run.

If environmental stress does not force a shift to other energy sources and other fuels, the finite supply of fossil fuels will mandate such a change eventually. Reserves of fossil fuels are finite, particularly those of oil and natural gas. Known reserves of oil and natural gas are about 8,000 EJ (1 EJ = 10^{18} J), which would be enough for the next 40 years at the current consumption rate [5]. The demand for energy continues to rise because of the continuing increase in world population and because of the growing demand by the developing countries in order to improve their living standards. If the population growth and the demand growth are taken into account, the remaining reserves of oil and natural gas would only last about 25 years. Even if the estimated additional undiscovered resources were added, that would satisfy the energy needs for fluid fuels for an additional 20 years or so. Coal reserves are much larger, known reserves are about 20,000 EJ, but estimated ultimately recoverable resources add up to 150,000 EJ [5]. These large amounts of coal could eventually be used to produce synthetic liquid fuels, allowing society to continue employing the present energy system, but also to continue with detrimental environmental effects, and at higher rates, which would ultimately lead to an environmental calamity with unforeseeable consequences.

Fortunately, our civilization is not running out of energy resources in an absolute sense, nor is it lacking technological options for transforming these resources into the particular forms that our patterns of energy use require [6]. However, we are running out of cheap oil and natural gas, out of environmental capacity to absorb the impacts of processing and burning fossil fuels, and out of public tolerance for the risks of nuclear energy. We seem as well to be lacking the commitment and money needed to develop long-term alternatives, the perceptiveness to embrace energy efficiency on the scale demanded, and the consensus needed to fashion any coherent strategy at all. These deficiencies suggest that civilization has entered a fundamental transition in the nature of the energy-society interaction. The transition is from convenient but ultimately scarce energy resources to less convenient but more abundant ones.

Energy sources which are and will be available include:

- direct solar radiation,
- indirect solar energy (hydropower, wind, currents, waves, ocean thermal energy, biomass),
- geothermal energy,
- tidal energy,
- nuclear energy (fission and fusion).

Nuclear energy requires a major engineering breakthrough in order to become publicly accepted as a viable option for the future (fission regarding safety, and handling and disposal of nuclear waste, and fusion regarding feasibility). Since the breakthrough is not in sight, the solution of the global energy problem must be found with the remaining energy sources from the list above. These sources are abundant, renewable and clean, but they are not as convenient as fossil fuels. They are only intermittently available and/or available away from consumption centres. They are not storable or transportable by themselves, and they cannot be used as a fuel for transportation. These shortcomings of the renewable energy sources point to the need for an energy carrier or an intermediary energy system to form the link between the new primary energy sources and the energy consuming sectors.

Electricity is an obvious choice as an energy carrier (or energy currency), since it is convenient and very efficient at the consumer end, and because it can be produced from any energy source, including renewable sources. Theoretically, electricity can be used for almost any application, e.g., heat generation and transportation. For some applications fuel would be more convenient, and for the others fuel is necessary, e.g., air transportation. In addition, electrical energy is not convenient for storage and for long distance transportation, which would be required since energy sources are available intermittently and/or far from consumption centres (e.g., solar, wind). It is therefore obvious that electricity cannot be the sole energy carrier of the future.

Hydrogen is another energy currency which supplements electricity very well and satisfies all other requirements which could be imposed on the energy carriers of the future. Hydrogen has some unique properties, which in conjunction with electricity make it an ideal energy carrier or fuel [7,8]:

- It can be produced from electricity and can be converted into electricity at relatively high efficiencies. Some processes for hydrogen production directly from solar energy are also being developed, such as photo-electro-chemical conversion or biological photo-production.
- Raw material for hydrogen production is water, which is available in abundance. Hydrogen is a completely renewable fuel, since the product

of hydrogen utilization (either through combustion or through chemico-electrical conversion) is pure water or water vapour.

- It can be stored in gaseous form (convenient for large-scale storage), in liquid form (convenient for air and space transportation) or in the form of metal hydrides (convenient for surface vehicles and other relatively small-scale storage requirements).
- It can be transported over large distances through pipelines or via tankers (in most of the cases more efficiently and economically than electricity).
- It can be converted into other forms of energy in more ways and more efficiently than any other fuel, e.g., through catalytic combustion, electro-chemical conversion and hydriding, as well as through flame combustion.
- Hydrogen as an energy currency is environmentally compatible, since its production from electricity (or directly from solar energy), its storage and transportation, and its end use do not produce any pollutants (except some NO_x if hydrogen is burned with air) or any other harmful effects on the environment. It also does not produce any greenhouse gases, particularly CO_2.

CHAPTER 2

PROPERTIES OF HYDROGEN

Hydrogen exists in three isotopes: protium, deuterium and tritium. A standard hydrogen atom (protium) is the simplest of all the elements and consists of one proton and one electron. Molecular hydrogen (H_2) exists in two forms: ortho- and para-hydrogen. Both forms have identical chemical properties, but due to different spin orientation have somewhat different physical properties. At room temperature hydrogen consists of approximately 75 per cent ortho- and 25 per cent para-hydrogen. Since para-hydrogen is more stable at lower temperatures its concentration increases at lower temperatures, reaching virtually 100 per cent in liquid hydrogen.

Hydrogen is an odourless, colourless gas. With a molecular weight of 2.016, hydrogen is the lightest element. Its density is about 14 times less than air (0.08376 kg/m^3 at standard temperature and pressure). Hydrogen is liquid at temperatures below 20.3 K (at atmospheric pressure). Hydrogen has the highest energy content per unit mass of all fuels. Its higher heating value is 141.9 MJ/kg, almost three times higher than that of gasoline. Some important properties of hydrogen are compiled in Table 2.1.

Table 2.1. Properties of hydrogen

Molecular weight	amu	2.016
Density	kg/m^3	0.0838
Higher heating value	MJ/kg	141.90
	MJ/m^3	11.89
Lower heating value	MJ/kg	119.90
	MJ/m^3	10.05
Boiling temperature	K	20.3
Density as liquid	kg/m^3	70.8
Critical point		
temperature	K	32.94
pressure	bar	12.84
density	kg/m^3	31.40
Self-ignition temperature	K	858
Ignition limits in air	(vol. %)	4-75
Stoichiometric mixture in air	(vol. %)	29.53
Flame temperature in air	K	2,318
Diffusion coefficient	cm^2/s	0.61
Specific heat (c_p)	kJ/(kg·K)	14.89

CHAPTER 3

HYDROGEN ENERGY SYSTEM

Hydrogen Energy System is a global energy system in which hydrogen is produced from available energy sources and used in every application where fossil fuels are being used today in transportation, residential, commercial and industrial sectors, and for electricity generation as shown in Figure 3.1.

In the Hydrogen Energy System, or Hydrogen Economy, hydrogen (and oxygen) is produced in large industrial plants where the primary energy source (solar, nuclear, and even fossil) and water, the raw material, are available. For large-scale storage, hydrogen can be stored underground in ex-mines, caverns and/or aquifers. Hydrogen is next transported, by means of pipelines or super tankers, to energy consumption centres. It is then used in electricity, transportation, industrial, residential and commercial sectors as a fuel and/or an energy carrier. The by-product is water or water vapour. Water and water vapour are recycled back, through rain, rivers, lakes and oceans, to make up for the water used in the first place to manufacture hydrogen.

The oxygen produced in the industrial plant making hydrogen could either be released into the atmosphere, or could be shipped or piped to industrial and city centres for use in fuel cells (instead of air) for electricity generation. This would have the advantage of increasing the utilization efficiency. The oxygen could also be used by industry for non-energy applications, and also for rejuvenating polluted rivers and lakes, or speeding up sewage treatment.

It should be noted that in the hydrogen energy system, hydrogen is not a primary source of energy. It is an intermediary or secondary form of energy or an energy carrier. Hydrogen complements the primary energy sources, and presents them to the consumer in a convenient form at the desired location and time. When combined with renewable energy sources hydrogen energy system results in a permanent energy system. Renewable energy sources are capable of providing all the energy needed by human civilization, and hydrogen will enable their widespread utilization.

Details of the hydrogen energy system, including production, storage, transportation, distribution, utilization, environmental impact and economics, are discussed in the subsequent chapters. More information can be found in the proceedings of the THEME and World Hydrogen Energy Conferences [9-20].

3.1 Historical development

The first vision of the energy system based on hydrogen was provided by science fiction writer and visionary Jules Verne in his novel *The Mysterious Island*:

> "... water decomposed into its primitive elements... and decomposed doubtless, by electricity ... will one day be employed as fuel, ... hydrogen and oxygen which constitute it, used singly or together, will furnish an inexhaustible source of heat and light, of an intensity of which coal is not capable, ... Water will be the coal of the future."

After investigating the electrochemical process first described by Sir William Grove in 1839, Ostwald in 1894 predicted that the 20th Century would become the Age of Electrochemical Combustion, with the replacement of the steam Rankine cycle heat engines by much more efficient, pollution free fuel cells. With emerging fuel cell technologies both in stationary and transportation applications his prediction is about to become true.

In 1923 Haldane predicted that hydrogen – derived from wind power via electrolysis, liquefied and stored – would be the fuel of the future [21]. This view was repeated in more technical detail, some 15 years later, by Sikorski [22], who realized hydrogen's potential as aviation fuel. He predicted that the introduction of hydrogen would bring about a profound transformation of aeronautics.

Lawaczek [23] in the early 1920s outlined the concepts for hydrogen powered cars, trains and engines, collaborated in developing an efficient pressurized electrolyzer, and was probably the first to suggest that energy could be transported via hydrogen-carrying pipelines, similar to natural gas.

One of the earliest and most fascinating efforts involving hydrogen was its use not only as a buoyancy medium, but also as a booster fuel for the huge German dirigibles that provided leisurely and elegant transatlantic air travel in the 1920s and 1930s [24]. During the same period, Erren and his team of engineers converted more than one thousand cars and trucks to multi-fuel systems using both hydrogen and gasoline as fuel [25]. In the early 1950's Bacon [26] developed the first practical hydrogen-air fuel cell, which was later modified for applications in the US space programme.

The concept of solar-originated hydrogen economy was first set down by Bockris (1962), developed and diagrammed by Justi (1965), named a Hydrogen Economy by Bockris and Triner (1970), formulated by Bockris (1971) and Bockris and Appleby (1972), and quantified by Gregory (1972) [27]. Marchetti (1972) proposed a nuclear hydrogen system, in which hydrogen would be produced using nuclear energy in isolated islands and shipped in liquid form to centres of consumption [28]. Bockris proposed a general plan for supplying American cities with solar-based energy via hydrogen. He suggested the use of floating platforms containing photovoltaic devices, producing hydrogen by the electrolysis of sea-water, and piping hydrogen to land [29]. A similar concept, but for Japan, called PORSHE (Planned Ocean Raft System for the Hydrogen Economy) was later proposed and elaborated by Escher and Ohta [30].

Justi [31] made the first diagram of the solar-hydrogen economy. He proposed the thermoelectric conversion of solar energy into hydrogen in the Mediterranean area, and transportation of hydrogen to Germany through a pipeline. He envisioned hydrogen as a fuel for households and industry, larg- scale and localized electricity generation, and transportation (in electric vehicles).

In 1974, Veziroglu organized the first international conference on hydrogen energy, The Hydrogen Economy Miami Energy Conference (THEME conference) and proposed the Hydrogen Energy System, in which hydrogen could be produced from any and all primary energy sources and used in every application where fossil fuels are being used – with the exception where carbon is specifically needed - as an answer to the interrelated problems of the depletion of fossil fuels and the global environmental problems caused by their use [9]. Veziroglu and Kakac [32,33], and Veziroglu and Ohta [34] discussed hydrogen production using various primary energy sources.

Bockris and Veziroglu outlined the solar hydrogen energy system and discussed the real economics of potentially competitive energy systems of the future [6]. They showed that if hydrogen utilization efficiency advantage and total fuel costs (i.e., cost of production plus the cost of environmental damage done in every step of the fuel cycle) are taken into account, the solar hydrogen energy system is the most economical energy system possible. Issues of real economics of hydrogen energy have been discussed thoroughly by Bockris [35], Veziroglu [36-38], and Veziroglu and Barbir [39-41].

Scott and Hafele addressed the issue of the global climatic disruption caused by excessive use of carbon fuels and concluded [42]:

> "There is a practical technological pathway that can mitigate and then reverse energy sector contributions to greenhouse gas climatic disruption. This pathway can bring economic growth and improvements to the quality life."

This technology is of course the Hydrogen Energy System. Scott and Hafele provided a vision of the transition to the Hydrogen Energy System as two sequential but overlapping waves: integrated energy systems (i.e., the mix of fossil fuel and hydrogen) and pure hydrogen technologies.

Winter feared that the point of transition to hydrogen and solar energy could be another "lost moment of history", [43]. Timely transition to these clean forms of energy would lead towards a new direction in the development of human civilization, qualitatively and quantitatively different than the path based on the utilization of fossil fuels.

Winter [44] envisaged the large-scale import of hydrogen to Germany and Europe from areas with highest insolation levels. He compared this enterprise with the import of natural gas from Siberia (which currently supplies about 30 per cent of the natural gas needs in Germany) and with the import of hydrogen from Canada (a project currently being developed by a Canadian-European consortium). Winter concluded that solar hydrogen is a viable alternative.

Rogner and Britton [45] analyzed the energy options for Europe and concluded that the energy currencies in the next century will be the complementary pair: hydrogen and electricity, though they did not discuss how and where hydrogen would be produced. They proposed a variety of long-term and near-term strategies and actions, which would eventually lead towards a hydrogen-electricity energy system.

3.2. National and international programmes

Several proposed or ongoing hydrogen projects seem to demonstrate that the transition has already begun:

The concept of a hydro-hydrogen clean energy system is being developed in a 100 MW_{el} international project between Canada and Germany [46]. The project is to demonstrate the provision of clean and renewable primary energy in the form of already available hydroelectricity from Quebec, converted via electrolysis into hydrogen, and shipped to Europe in liquid form where it would be 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.

A similar project has been proposed and investigated between Norway and Germany [47]. Hydrogen would be produced from surplus hydro energy in Norway, liquefied and shipped to Germany. It was found that this concept offers a comparatively cheap and fast-to-establish way to test and demonstrate the complete hydrogen production, transport, handling and distribution chain of supplying hydro-hydrogen to German end-users.

A "mini solar hydrogen energy system" has been established in Germany near Nürnberg, where the Solar-Wasserstoff-Bayern plant has been built as a test bed for the emerging hydrogen technologies [48]. This plant includes all the elements of the solar hydrogen energy system: photovoltaic arrays, electrolyzers, fuel cells, hydrogen storage, hydrogen appliances, hydrogen refueling station, and hydrogen powered vehicles.

ElJrushi proposed large-scale hydrogen production in the Libyan desert and export of hydrogen to Europe [49]. The German-Saudi Arabian project HYSOLAR demonstrates the feasibility of this concept and provides useful experience for design and operation of solar-hydrogen power plants in the future (Figure 3.2) [50].

The Japanese WE-NET Programme – sponsored by the Japanese Ministry of International Trade and Industry – is the most ambitious and most comprehensive hydrogen energy programme in the world [51]. Under this programme, Japan expects to spend about US$ 3 billion by the year 2020 in order to develop all the critical hydrogen energy technologies for conversion to the Hydrogen Energy System.

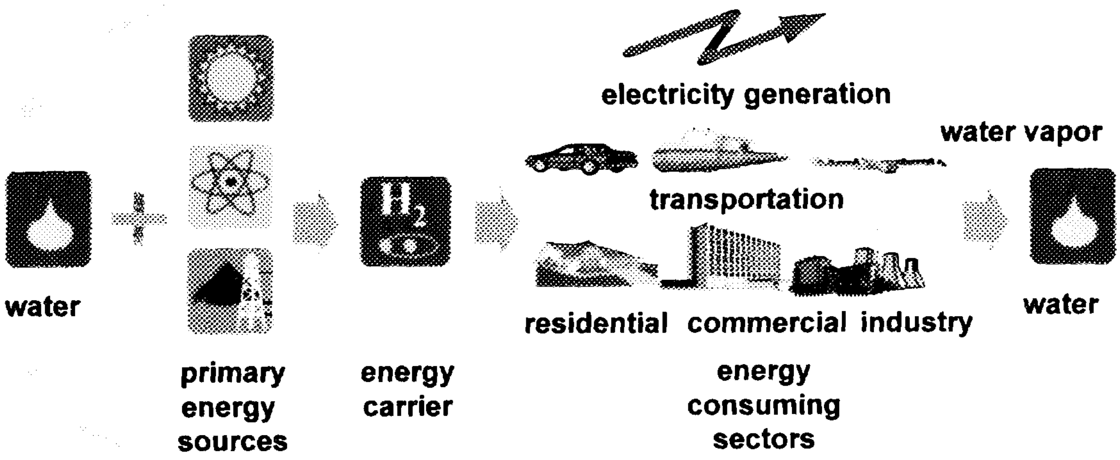

Figure 3.1 Hydrogen Energy System

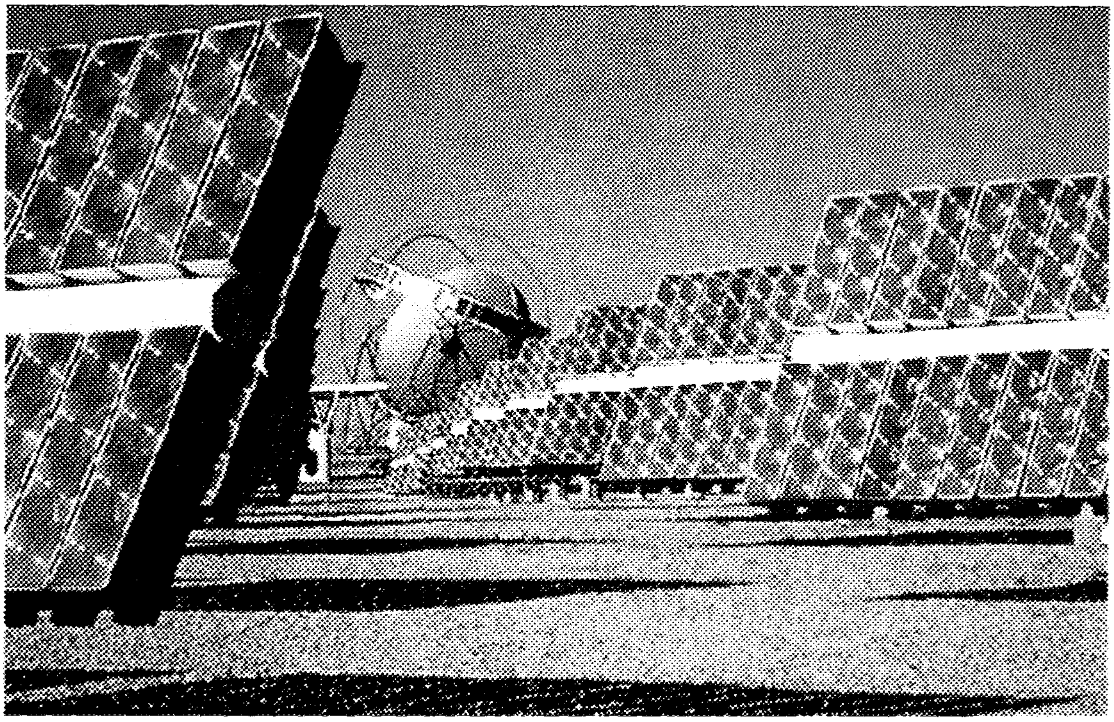

Figure 3.2 HYSOLAR project in Saudi Arabia

CHAPTER 4

HYDROGEN PRODUCTION

Hydrogen is the most plentiful element in the universe, making up about three quarters of all matter. All the stars and many of the planets essentially consist of hydrogen. However, on Earth free hydrogen is scarce. The atmosphere contains trace amounts of it (0.07 per cent), and it is usually found in small amounts mixed with natural gas in crustal reservoirs. A few wells, however, have been found to contain large amounts of hydrogen, such as some wells in Kansas that contain 40 per cent hydrogen, 60 per cent nitrogen and trace amounts of hydrocarbons [52]. The Earth's surface contain about 0.14 per cent hydrogen (tenth most abundant element), most of which resides in chemical combination with oxygen as water.

Hydrogen, therefore, must be produced. Logical sources of hydrogen are hydrocarbon (fossil) fuels (C_XH_Y) and water (H_2O). Presently, hydrogen is mostly being produced from fossil fuels (natural gas, oil and coal).

However, except for space programmes, hydrogen is not being used directly as a fuel or energy carrier. It is being used in refineries to upgrade crude oil (hydrotreating and hydrocracking), in the chemical industry to synthesize various chemical compounds (such as ammonia. methanol, etc.), and in metallurgical processes (as a reduction or protection gas). Presently, the total annual hydrogen production worldwide is about 40 million tonnes (5.6 EJ). Production of hydrogen as an energy carrier would require an increase in production rates by several orders of magnitude.

4.1. Hydrogen production from fossil fuels

4.1.1. Steam reforming of natural gas

Steam reforming of hydrocarbons (mainly natural gas) has been the most efficient, economical and widely used process for hydrogen production. A simplified basic flow diagram of a conventional steam reforming process is shown in Figure 4.1 [53]. The process basically consists of three main steps: (1) synthesis gas generation, (2) water-gas shift, and (3) gas purification. The feedstock, i.e. natural gas, is mixed with process steam and reacted over a nickel based catalyst contained inside a system of alloyed steel tubes. To protect the catalyst, natural gas has to be desulphurized before being fed to the reformer. The following reactions take place in the reformer:

$$CH_4 + H_2O \rightarrow CO + 3\,H_2 \tag{4.1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{4.2}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{4.3}$$

The reforming reaction is strongly endothermic and energy is supplied by combustion of natural gas or fuel oil. The metallurgy of the tubes usually limits the reaction temperature to 700-925°C. The synthesis gas leaving a catalytic reformer is typically a mixture of H_2, CO, CO_2 and CH_4. After the reformer the gas mixture passes through a heat recovery step cooling down to about 350°C and is fed into a water-gas shift reactor to produce additional hydrogen. The cold gas next passes through gas purification units to remove CO_2, the remaining CO and other impurities in order to deliver purified hydrogen. Several commercial processes can be used for removing CO_2 (and CO), such as wet scrubbing, pressure swing adsorption, and recently membrane processes.

The efficiency of the steam reforming process, expressed as the ratio of the heating value of produced hydrogen and energy input (feedstock, fuel and small amounts of electricity) is about 65 to 75 per cent. The cost of produced hydrogen is about US$ 6/GJ, but is strongly dependent upon the cost and availability of natural gas or other fuel feedstock.

4.1.2. Partial oxidation

Partial oxidation is used for converting hydrocarbons heavier than naphtha (for which steam reforming is not applicable). Most recently partial oxidation reformers are being developed for on-board reforming of natural gas, ethanol, and even gasoline, to be coupled with fuel cells for automobile propulsion. A simplified basic flow diagram of an industrial partial oxidation process is shown in Figure 4.2. There are three main steps: (1) synthesis gas generation, (2) water-gas shift reaction, and (3) gas purification. The partial oxidation reactions are typically as follows:

$$C_nH_m + n/2\,O_2 \rightarrow n\,CO + m/2\,H_2 + \text{heat} \qquad (4.4)$$

$$C_nH_m + n\,H_2O + \text{heat} \rightarrow n\,CO + (n+m/2)\,H_2 \qquad (4.5)$$

$$CO + H_2O \rightarrow CO_2 + H_2 + \text{heat} \qquad (4.6)$$

where $n=1$ and $m=1.3$ for residual fuel oils.

In the synthesis gas generation step, the hydrocarbon feedstock is partially oxidized with oxygen, and carbon monoxide is shifted with steam to produce CO_2 and H_2. Because of the difficulties of separating nitrogen to produce pure hydrogen, pure oxygen is typically used in this process. If hydrogen is to be used in fuel cells, air is an acceptable oxidant for partial oxidation since a relatively high nitrogen content does not significantly affect the fuel cell performance.

While the hydrocarbon-oxygen reaction is exothermic, additional energy required for the endothermic hydrocarbon-steam reaction, which is similar to steam reforming, is supplied by burning the additional fuel. Operating temperatures are rather high, 1,150°C to 1,315°C, but with novel catalysts it is possible to accomplish the partial oxidation process at lower temperatures. The product gas (a very hot mixture of hydrogen, oxygen, CO, CO_2, steam and a small amount of CH_4) is typically quenched with water as it exits the reactor to solidify the slag for downstream removal with cyclones, gas filtration or in a slurry. The sulphur contained in the feedstock is converted mainly to H_2S and only a small portion to COS. After sulphur removal, the gas is treated through the shift reaction and gas purification in the same way as the product gas from the steam reforming process.

The efficiency of partial oxidation is generally lower than for steam reforming, usually about 50 per cent. Hydrogen can be produced for approximately US$ 10/GJ if cheap oil (less than US$ 4/GJ) is available.

Recently, partial oxidation combined with steam reforming has started to be used for reforming lighter hydrocarbons and alcohols, such as gasoline, natural gas, propane, methanol and ethanol. Those reformers are being developed for small-scale reforming (50 kW and less) for both transportation and stationary power applications [54]. They typically use air instead of pure oxygen, which results in lower hydrogen content in the reformate gas. CO_2 removal process is not necessarily applied. With proper catalyst selection and thermal integration, these reformers can reach up to 80 per cent efficiency.

4.1.3. Thermal cracking of natural gas

The thermal decomposition of natural gas has been practiced for many years for the production of carbon black for rubber tyre vulcanization, for pigment and for the printing industry. A methane-air flame is used to heat-up firebrick to temperatures in the order of 1,400°C. The air is than turned off and the methane alone decomposes on the hot firebrick until the temperature drops to about 800°C. The micron size carbon particles are collected in the effluent gas stream in bag filters. The process is typically practised batchwise in tandem furnaces – while one furnace is producing carbon black, the other is being heated up. Attempts have also been made to thermally crack natural gas in a continuous fixed bed reactor [55]. With appropriate catalysts, it is possible to increase the rate of decomposition and accomplish an efficient continuous process. Another approach is to use high temperature plasma for thermal cracking of natural gas or even heavier hydrocarbons [56].

Because of a valuable by-product (carbon black), economics of this process for hydrogen production looks favourable. It should be noted that this is the only process of producing hydrogen from hydrocarbons that does not produce CO_2 (unless carbon black is later used as a fuel).

4.1.4. Coal gasification

In the coal gasification process (so called Koppers-Totzek process), the pulverized coal is rapidly partially oxidized with oxygen and steam at essentially atmospheric pressure. The raw gas is then cooled to recover waste heat, followed by quenching with water to remove entrained ash particles before going through the steps of compression, shift conversion and gas purification (again by conventional wet scrubbing or pressure swing adsorption processes). The product is hydrogen at about 2.8 MPa with purity higher than 97.5 per cent. The simplified block diagram is shown in Figure 4.3.

In order to avoid the expensive and highly energy consuming hydrogen compression step, Texaco has developed a coal gasification process at elevated pressure, around 5.5 MPa. By operating in a direct quench mode at this pressure, a high steam content in the synthesis gas is desirable for use in the shift reaction for additional hydrogen production. The raw gas is then desulphurized, shifted and purified. The product hydrogen is at about 4 MPa with a purity higher than 97 per cent.

The coal gasification process is complicated because of the necessity to handle solid fuel and to remove large amounts of ash. The solids handling problem has a significant impact on costs. Generally, the lower cost of coal does not compensate for the higher capital cost of coal gasification systems, compared to steam reforming, and the cost of produced hydrogen is about US$ 12 to US $14/GJ [53].

4.2. Hydrogen from biomass

Hydrogen can be obtained from biomass by a pyrolysis/gasification process [57]. The biomass preparation step involves heating of the biomass/water slurry to high temperature under pressure in a reactor. This process decomposes and partially oxidizes the biomass, producing a gas product consisting of hydrogen, methane, CO_2, CO and nitrogen. Mineral matter is removed from the bottom of the reactor. The gas stream goes to a high temperature shift reactor where hydrogen content is increased. A relatively high purity hydrogen is produced in the subsequent pressure swing adsorption unit. The whole system is very much similar to a coal gasification plant, with the exception of the unit for pretreatment of the biomass and the design of the reactor. Because of the lower calorific value per unit mass of biomass as compared to coal, the processing facility is larger than that of a comparably sized coal gasification plant.

4.3. Hydrogen production from water

A logical source for large-scale hydrogen production is water, which is abundant on Earth. Different methods of hydrogen production from water have been, or are being developed. They include:

- electrolysis,
- direct thermal decomposition or thermolysis,
- thermochemical processes,
- photolysis.

4.3.1. Electrolysis

Electrolysis appears to be the only method developed to-date which can be used for large-scale hydrogen production in a post-fossil fuel era. Production of hydrogen by water electrolysis is a more than 50-year old technology, based on a fundamentally simple process, is very efficient, and does not involve moving parts. Figure 4.4 shows a small-scale electrolysis plant.

The following reactions take place at the electrodes of an electrolysis cell filled with a suitable electrolyte (aqueous solution of KOH or NaOH or NaCl) upon the application of a potential:

$$\text{Cathode reaction: } 2\,H_2O\,(l) + 2e^- \rightarrow H_2\,(g) + 2\,OH^-\,(aq) \qquad (7)$$

Anode reaction: $2\,OH^-\,(aq) \rightarrow 1/2\,O_2\,(g) + H_2O\,(l)$ (8)

Overall cell reaction: $H_2O\,(l) \rightarrow H_2\,(g) + O_2\,(g)$ (9)

The reversible decomposition potential ($E_{rev} = \Delta G/nF$) of the above reaction is 1.229 V at standard conditions. The total theoretical water decomposition potential is 1.480 V corresponding to hydrogen's enthalpy (since $\Delta H = \Delta G + T\Delta S$). Due to irreversible processes occurring at the anode and cathode, including the electrical resistance of the cell, the actual potentials are always higher, typically between 1.75 and 2.05 V. This corresponds to the efficiencies of 72 to 82 per cent.

Several advanced electrolyzer technologies are being developed, such as:

- Advanced alkaline electrolysis, which employs new materials for membranes and electrodes that allow further improvement in efficiency – up to 90 per cent [58,59].
- Solid polymer electrolytic (SPE) process, which employs a proton-conducting ion exchange membrane as electrolyte and as membrane that separates the electrolysis cell. This type of electrolyzers can operate at very high current densities (up to 2 A/cm^2, which is about one order of magnitude higher than standard electrolyzers with alkaline liquid electrolyte). The water to be dissociated does not require dissolved electrolytes to increase its conductivity, and is added solely to the anode side [59,60].
- High temperature steam electrolysis, which operates between 700 and 1,000°C and employs oxygen ion-conducting ceramics as electrolyte. Electrical energy consumption is reduced since part of the energy required for water dissociation is supplied in the form of heat. The water to be dissociated is entered on the cathode side as steam which forms a steam-hydrogen mixture during electrolytic dissociation. The O_2-ions are transported through the ceramic material to the anode, where they are discharged as oxygen [61].

An electrolysis plant can operate over a wide range of capacity factors and is convenient for a wide range of operating capacities, which makes this process interesting for coupling with renewable energy sources, particularly with photovoltaics. Photovoltaics generate low voltage-direct current, exactly what is required for the electrolysis process.

The performance of photovoltaic-electrolyzer systems has been studied extensively both in theory and in practice [62-65]. Several experimental PV-electrolysis plants are currently operating all over the world, such as:

- Solar-Wasserstoff-Bayern pilot plant in Neunburg vorm Wald in Germany [48],
- HYSOLAR project in Saudi Arabia [66],
- Schatz Energy Center, Humboldt State University, Arcata, California [67],
- Helsinki University of Technology, Helsinki, Finland [68],

- INTA Energy Laboratory, Huelva, Spain, [69].

4.3.2. Direct thermal decomposition of water (thermolysis)

Water can be split thermally at temperatures above 2000 K. The overall thermal dissociation of water can be shown as [70]:

$$H_2O \rightarrow a\,H_2O + b\,OH + c\,H + d\,O + e\,H_2 + f\,O_2 \qquad (4.10)$$

The degree of dissociation is a function of temperature: only 1 per cent at 2000 K, 8.5 per cent at 2500 K and 34 per cent at 3000 K. The product is a mixture of gases at extremely high temperatures. The main problems in connection with this method are related to materials required for extremely high temperatures, recombination of the reaction products at high temperatures and separation of hydrogen from the mixture.

4.3.3 Thermochemical cycles

Thermochemical production of hydrogen involves the chemical splitting of water at temperatures lower than those needed for thermolysis, through a series of cyclical chemical reactions which ultimately release hydrogen. Since the mid-1960s, research has been carried out to investigate a number of potential thermochemical cycles for the production of hydrogen, and some 2,000 to 3,000 cycles have been invented. After examining their practicability in terms of reaction and process technology, only 20 to 30 remained applicable for large-scale hydrogen production. Some of the more thoroughly investigated thermochemical process cycles are listed below [60,71,72]:

- Sulphuric acid – iodine cycle,
- Hybrid sulphuric acid cycle,
- Hybrid sulphuric acid – hydrogen bromide cycle,
- Calcium bromide – iron oxide cycle (UT-3),
- Iron chlorine cycle (Mark 9).

Depending on the temperatures at which these processes are occurring, relatively high efficiencies are achievable (40 to 50 per cent). However the problems related to movement of a arge mass of materials in chemical reactions, toxicity of some of the chemicals involved, and corrosion at high temperatures remain to be solved in order for these methods to become practical.

4.3.4. Photolysis

Photolysis, or direct extraction of hydrogen from water using only sunlight as an energy source, can be accomplished by photobiological systems, photochemical assemblies or photoelectro-chemical cells [73,74]. The intensive research activities are opening new perspectives for photo-conversion, where new redox catalysts, colloidal semiconductors, immobilized enzymes and selected micro-organisms could provide means of large-scale solar energy harvesting and conversion into hydrogen.

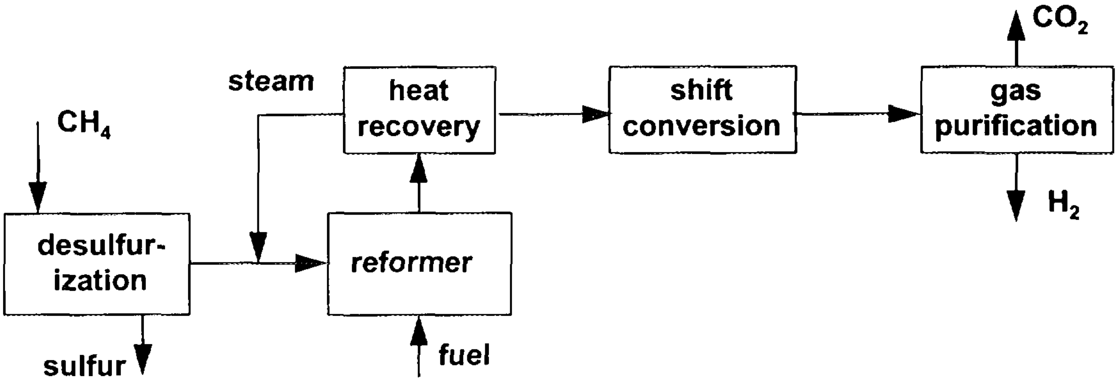

Figure 4.1 Block diagram of hydrogen production by steam reforming of natural gas

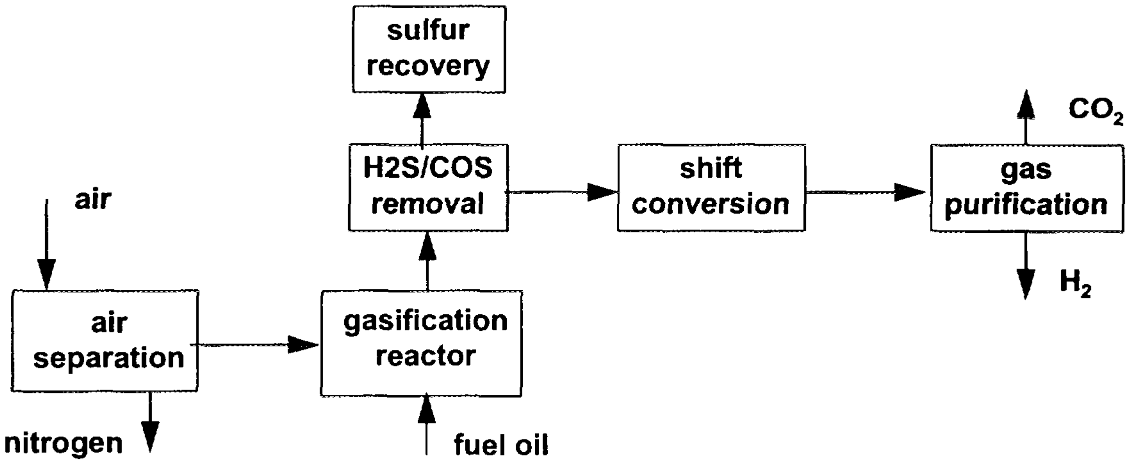

Figure 4.2 Block diagram of hydrogen production process by partial oxidation

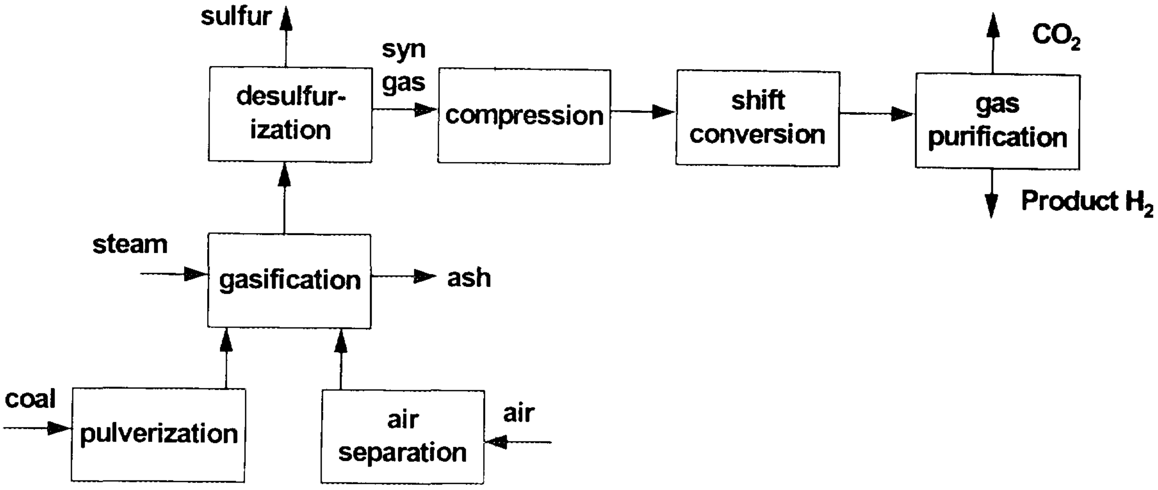

Figure 4.3 Block diagram of hydrogen production by coal gasification process

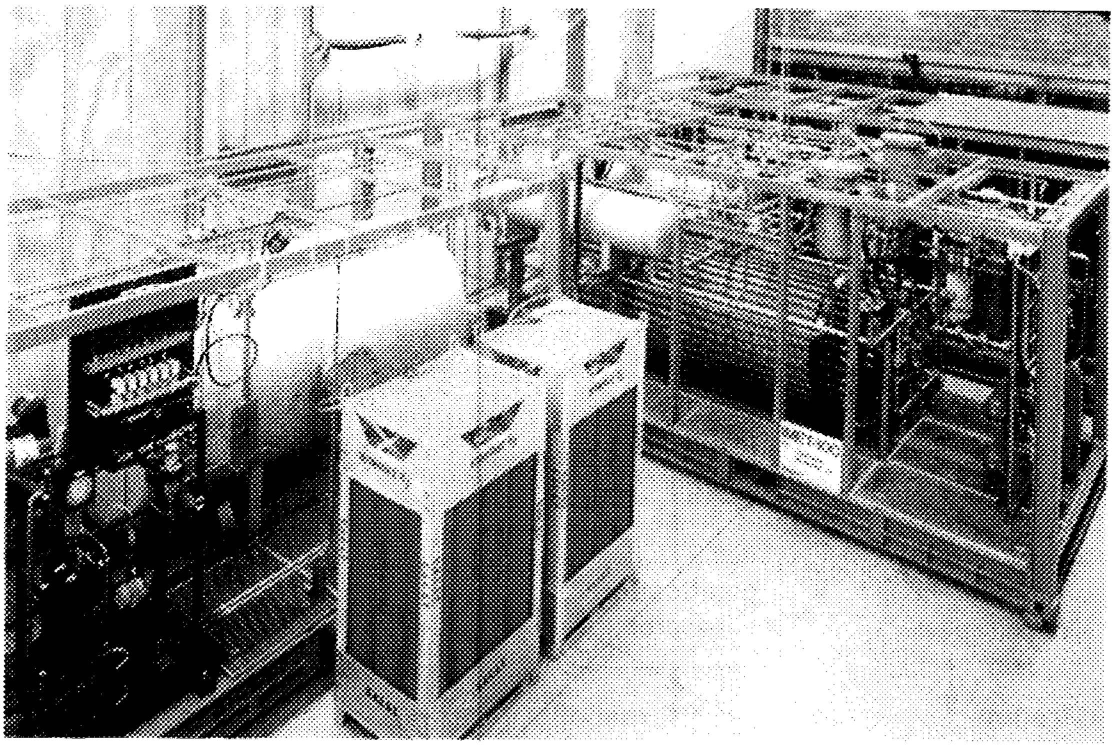

Figure 4.4 A small scale electrolysis plant

CHAPTER 5

HYDROGEN STORAGE AND DISTRIBUTION

Hydrogen as an energy carrier must be stored to overcome daily and seasonal discrepancies between energy source availability and demand. Also, to overcome geographical discrepancies between hydrogen production sites and hydrogen users, hydrogen has to be transported.

5.1. Hydrogen storage

Hydrogen can be stored either as a pressurized gas or as a liquid. It can also be stored in chemical or physical combination with other materials, such as metal hydrides, chemical hydrides, glass microspheres, and cryo-adsorbers. Depending on storage size and application, several types of hydrogen storage may be differentiated:

(1) Stationary large storage systems: These are typically storage devices at the production site or at the start or end of pipelines and other transportation pathways.

(2) Stationary small storage systems: These are used at the distribution or final user level, for example, a storage system to meet the demand of an industrial plant.

(3) Mobile storage systems for transport and distribution: These include both large-capacity devices, such as liquid hydrogen tankers – bulk carriers, and small systems, such as gaseous or liquid hydrogen truck trailers.

(4) Vehicle tanks: These are utilized to store hydrogen used as fuel for road vehicles.

Because of hydrogen's low density, its storage always requires relatively large volumes and is associated with either high pressures (thus requiring heavy vessels), or extremely low temperatures, and/or combination with other materials (much heavier than hydrogen itself). Table 5.1 shows achievable storage densities with different types of hydrogen storage. Some novel hydrogen storage methods may achieve even higher storage densities, but have yet to be proven in terms of practicality, cost and safety.

5.1.1. Large underground hydrogen storage

Future hydrogen supply systems will have a structure similar to today's natural gas supply systems. Underground storage of hydrogen in caverns, aquifers, depleted petroleum and natural gas fields, and man-made caverns resulting from mining and other activities is likely to be technologically and economically feasible [75]. Hydrogen storage systems of the same type and the same energy content will be more expensive by approximately a factor of three than natural gas storage systems, due to hydrogen's lower volumetric heating value. Technical problems, specifically for the underground storage of hydrogen other than expected losses of the working gas in the amount of 1 to 3per cent per year are not anticipated. The city of Kiel's public utility has been storing town gas with a hydrogen content of 60 to 65 per cent in a gas cavern with a geometric volume of about 32,000 m^3 and a pressure of 80 to 160 bar at a depth of 1,330 m since 1971 [76]. Gaz de France, the French National Gas Company, has stored hydrogen-rich refinery by-product gases in an aquifer structure near Beynes, France. Imperial Chemical Industries of the United Kingdom stores hydrogen in the salt mine caverns near Teeside, UK [77].

5.1.2. Above ground pressurized gas storage systems

Pressurized gas storage systems are used today in natural gas business in various sizes and pressure ranges from standard pressure cylinders (50 l, 200 bar) to stationary high-pressure containers (over 200 bar) or low pressure spherical containers (<30,000 m^3, 12 to 16 bar). This application range will be similar for hydrogen storage.

5.1.3. Vehicular pressurized hydrogen tanks

Development of ultra-light but strong new composite materials has enabled storage of hydrogen in automobiles. Pressure vessels that allow hydrogen storage at pressures 200 bar have been developed and used in automobiles (such as Daimler-Benz NECAR II). Storage density of higher than 0.05 kg of hydrogen per 1 kg of total weight is easily achievable [78].

5.1.4. Liquid hydrogen storage

Production of liquid hydrogen or liquefaction is an energy intensive process, typically requiring amounts of energy equal to about one third of the energy in liquefied hydrogen [79]. Novel liquefaction methods are being investigated in order to reduce energy requirements and costs. Magnetic liquefiers, for example, are expected to offer higher efficiency than conventional equipment, as well as reduced size and cost [80]. Hydrogen liquefaction and use of liquid hydrogen is usually practiced only where achieving high storage density is absolutely essential, such as in aerospace applications.

The storage of liquid hydrogen at a temperature of -253°C is practiced today on an industrial scale using vacuum-insulated spherical tanks (Figure 5.1). The largest facilities are those set up on rocket launch sites. The US National Aeronautics and Space Administration (NASA) uses a spherical tank with a geometrical capacity of 3,800 cubic meters. In future it will be possible to build larger capacity tanks, up to 12,000 m^3, corresponding to approximately 10 million m3 of hydrogen gas (at standard conditions). Evaporation losses from large stationary tanks are small, less than 0.1 per cent per day [76]. However, smaller and particularly mobile tanks have much higher evaporation (boil-off) losses (about 2 to 3 per cent daily). German car manufacturer BMW in cooperation with its suppliers, has developed a state-of-the-art liquid hydrogen tank and liquid hydrogen refueling station.

5.1.5. Metal hydride storage

Hydrogen can form metal hydrides with some metals and alloys. During the formation of the metal hydride, hydrogen molecules are split and hydrogen atoms are inserted in spaces inside the lattice of suitable metals and/or alloys. In this way an effective storage is created comparable to the density of liquid hydrogen. However, when the mass of the metal or alloy is taken into account then the metal hydride gravimetric storage density is comparable to storage of pressurized hydrogen. The best achievable gravimetric storage density is about 0.07 kg of H_2/kg of metal, for a high temperature hydride such as MgH_2 as shown in Table 5.2. It gives a comparison of some hydriding substances with liquid hydrogen, gaseous hydrogen and gasoline [81].

During the storage process (charging or absorption) heat is released which must be removed in order to achieve the continuity of the reaction. During the hydrogen release process (discharging or desorption) heat must be supplied to the storage tank.

An advantage of storing hydrogen in hydriding substances is the safety aspect. A serious damage to a hydride tank (such as one which could be caused by a collision) would not pose fire hazard since hydrogen would remain in the metal structure.

5.1.6. Novel hydrogen storage methods

Hydrogen can be physically adsorbed on activated carbon and be "packed" on the surface and inside the carbon structure more densely than if it has been just compressed. Amounts of up to 48 g H_2 per kg of carbon have been reported at 6.0 MPa and 87 K [82]. The adsorption capacity is a function of pressure and temperature, therefore at higher pressures and/or lower temperatures even larger amounts of hydrogen can be adsorbed. For any practical use, relatively low temperatures are needed (<100 K). Since the adsorption is a surface process, the adsorption capacity of hydrogen on activated carbon is largely due to the high surface area of the activated carbon, although there are some other carbon properties which affect the capability of activated carbon to adsorb hydrogen.

Researchers from Northeastern University in Boston, MA, have recently announced that they have developed a carbon storage material that can store as much as 75 per cent of hydrogen by weight [83]. This material, apparently some kind of carbon nanotubes or carbon whiskers, is currently being researched in several laboratories. The best results achieved with carbon nanotubes to date and confirmed by the National Renewable Energy Laboratory is hydrogen storage density corresponding to about 10 per cent of the nanotube weight [84].

Hydrogen can be stored in glass microspheres of approximately 50 µm diameter. The microspheres can be filled with hydrogen by heating them to increase the glass permeability to hydrogen. At room temperature, pressure of approximately 25 MPa is achieved resulting in storage density of 14 per cent mass fraction and 10 kg H_2/m^3 [85]. At 62 MPa a bed of glass microspheres can store 20 kg H2/m3. The release of hydrogen occurs by reheating the spheres to again increase the permeability.

Researchers at University of Hawaii are investigating hydrogen storage via polyhydride complexes. Complexes have been found which catalyze the reversible hydrogenation of unsaturated hydrocarbons. This catalytic reaction could be the basis for a low temperature hydrogen storage system with an available hydrogen density greater than 7 per cent [86].

5.2. Hydrogen transport and distribution

5.2.1. Interregional hydrogen transport

In the Hydrogen Energy System it is envisaged that from the production plants and/or storage, hydrogen will be transmitted to consumers by means of underground pipelines (gaseous hydrogen) and/or supertankers (liquid hydrogen).

Presently, hydrogen transportation through pipelines is used either in links between nearby production and utilization sites (up to 10 kilometres) or in more extensive networks (roughly 200 kms). Table 5.3 lists the principal existing hydrogen pipelines around the world [87]. Future developments will certainly entail greater flow rates and distances. It would be possible to use the existing natural gas pipelines, with some modifications however. For hydrogen pipelines, it is necessary to use steels less prone to embrittlement by hydrogen under pressure (particularly for very pure hydrogen (>99.5 per cent purity). Reciprocating compressors used for natural gas can be used for hydrogen without major design modifications. However, special attention must be given to sealing (to avoid hydrogen leaks) and to materials selection for the parts subject to fatigue stress. Use of centrifugal compressors for hydrogen creates more problems due to hydrogen's exceptional lightness.

As a rule, hydrogen transmission through pipelines requires larger diameter piping and more compression power than natural gas for the same energy throughput. However, due to lower pressure losses in the case of hydrogen, the recompression stations could be spaced twice as far apart. In economic terms, most of the studies found that the cost of large-scale transmission of hydrogen is about 1.5 to 1.8 times that of natural gas transmission. However, transportation of hydrogen over distances greater than 1,000 kms is more economical than transmission of electricity [88].

Sea transport of liquefied gas began with natural gas in the 1960s. Since that time, sea transport of liquefied natural gas (LNG) has increased to reach a volume of 60 million tons in 1993 (making 24 per cent of the volume of international trade). LNG tankers with a capacity of 130,000 m^3 are now common (Figure 5.2).

Liquid hydrogen may be transported in the same way as liquid natural gas. Transport of hydrogen by ship in a cryogenic tank was put into practice to supply the French space station in Kourou, Guiana. The Euro-Canadian project "Euro Quebec Hydro-Hydrogen Pilot Project" has produced a technical and economic study of a system including the overseas transport of a significant amount (100 MW) of liquid hydrogen. The hydrogen will be transported in a ship 180 m long, equipped with five 3,000 m^3 cryogenic tanks, for a total of 15,000 m^3 [89].

5.2.2. Regional hydrogen transport and distribution

To match the consumption demand, hydrogen can be regionally transported and distributed, both as a gas or as a liquid, by pipelines or in special cases in containers by road and rail transportation. Gaseous (and liquid) hydrogen carriage is subject to strict regulations ensuring public safety, which in some countries is very restrictive. The transportation of hydrogen in a discontinuous mode, whether in gaseous or liquid state, is currently used by occasional or low volume users. The cost of discontinuous transport is very high (it can be as high as two to five times the production cost). In the future energy system, discontinuous transportation of hydrogen would see little use, except for special users (mainly non-energy related).

Hydrogen in the gas phase is generally transported in pressurized cylindrical vessels (typically at 200 bar) arranged in frames adapted for road transport. The unit capacity of these frames or skids can be as great as 3,000 m^3. Hydrogen gas distribution companies also install such frames at the user site to serve as stationary storage.

Liquid hydrogen transportation is suitable for medium-scale utilization (few thousand cubic meters per day), for which delivery of gaseous hydrogen would not be practical. Liquid hydrogen is transported in double-skin vacuum tanks. The quality of the insulation of these tanks is such that hydrogen can be kept in them for several days. The tanks capacities up to 60 m^3 (5,000 m^3 of hydrogen gas) can be placed on semi-trailers (Figure 5.3) or railroad wagons. Liquid hydrogen is typically regasified at the delivery site, by controlled heating, avoiding use of discharge pumps.

Table 5.1. Hydrogen Storage Types and Densities

Storage Type	kg H_2 /kg	kg H_2/m^3
Large volume storage (10^2 to 10^4 m^3 geometric volume)		
Underground storage	-	5-10
Pressurized gas storage (above ground)	0.01-0.014	2-16
Metal hydride	0.013-0.015	50-55
Liquid hydrogen	~1	65-69
Stationary small storage (1 to 100 m^3 geometric volume)		
Pressurized gas cylinder	0.012	~15
Metal hydride	0.012-0.014	50-53
Liquid hydrogen tank	0.15-0.50	~65
Vehicle tanks(0.1 to 0.5 m^3 geometric volume)		
Pressurized gas cylinder	0.05	15
Metal hydride	0.02	55
Liquid hydrogen tank	0.09-0.13	50-60

Table 5.2. Hydriding Substances as Hydrogen Storage Media

Medium	Hydrogen Content kg/kg	Hydrogen storage capacity kg/l of vol.	Energy density kJ/kg	Energy density kJ/l of vol.
MgH_2	0.070	0.101	9,933	14,330
Mg_2NiH_4	0.0316	0.081	4,484	11,494
VH_2	0.0207	-	3,831	-
$FeTiH_{1.95}$	0.0175	0.096	2,483	13,620
$TiFe_{0.7}Mn_{0.2}H_{1.9}$	0.0172	0.090	2,440	12,770
$LaNi_5H_{7.0}$	0.0137	0.089	1,944	12,630
$R.E.Ni_5H_{6.5}$	0.0135	0.090	1,915	12,770
Liquid H_2	1.00	0.071	141,900	10,075
Gaseous H_2 (100 bar)	1.00	0.0083	141,900	1,170
Gaseous H_2 (200 bar)	1.00	0.0166	141,900	2,340
Gasoline	-	-	47,300	35,500

Table 5.3. Some Major Hydrogen Pipelines

Location	**Years of operation**	**Diameter mm**	**Length km**	**Pressure MPa**	**Purity**
AGEC, Alberta Canada	since 1987	273	3.7	3.79	99.9%
Air Liquide, France	since 1966	various	290	6.48-10	pure and raw
Air Products, Houston, TX	since 1969	114-324	100	0.35-5.5	pure
Air Products, Louisiana	since 1990	102-305	48	3.45	-
Chemische Werke Huls	since 1938	168-273	215	to 2.5	raw gas
Cominco, B.C., Canada	since 1964	5	0.6	30	62-100%
Gulf Petroleum Canada	-	168.3	16	-	93.5%
Hawkeye Chemical, Iowa	since 1987	152	3.2	2.75	-
ICI Bilingham, U.K.	-	-	15	30	pure
Philips Petroleum	since 1986	203	20.9	12	-

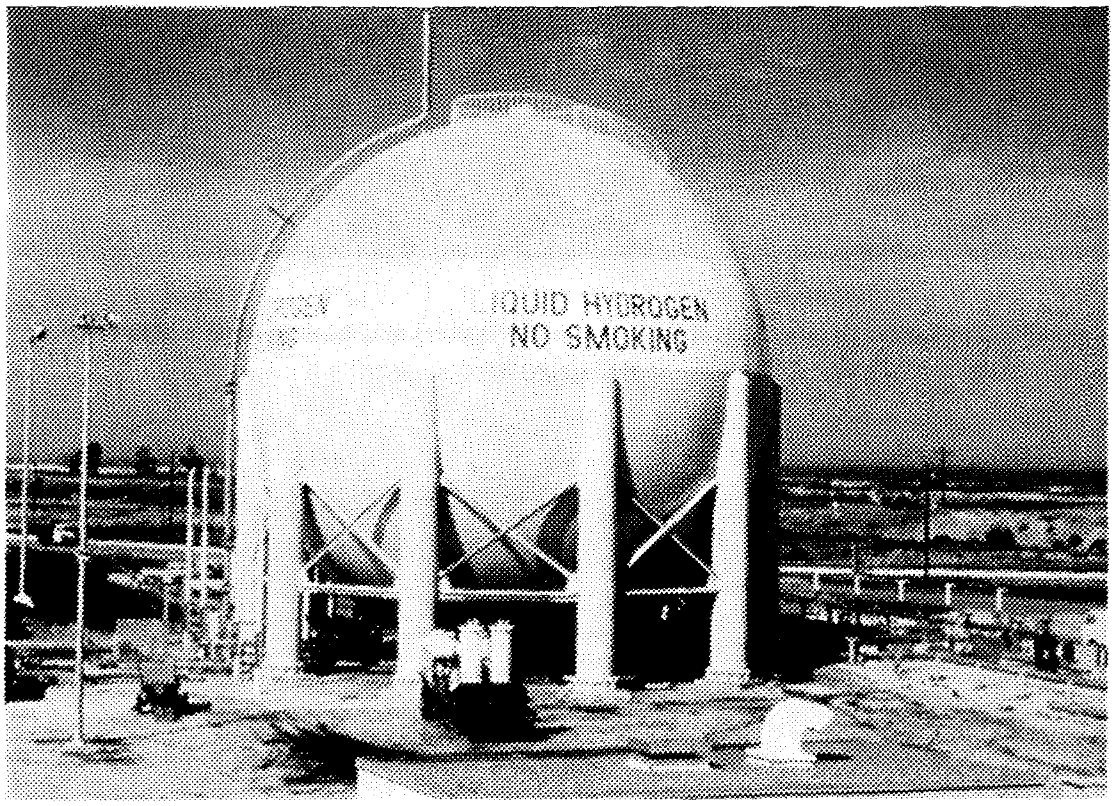

Figure 5.1 Liquid hydrogen storage

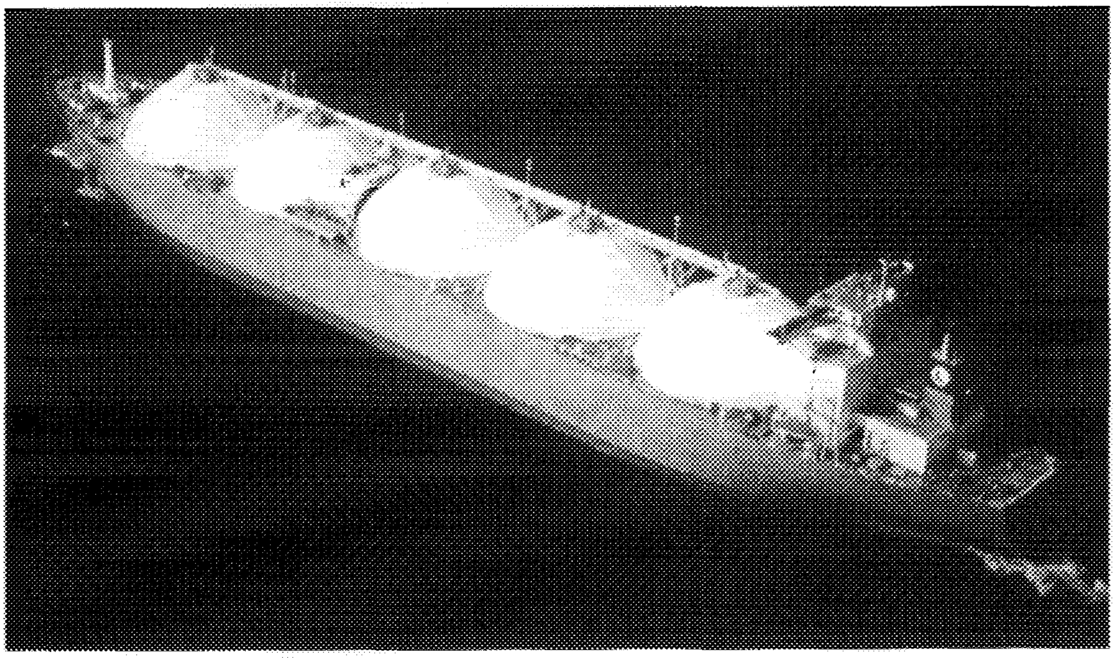

Figure 5.2 Tanker for liquified petroleum gas (similar tankers may be used for liquid hydrogen transport)

Figure 5.3 Truck for liquid hydrogen transport

CHAPTER 6

HYDROGEN CONVERSION TECHNOLOGIES

Hydrogen as an energy carrier can be converted to useful forms of energy in several ways, namely:

- combustion in internal combustion engines, jet and rocket engines
- combustion with pure oxygen to generate steam
- catalytic combustion to generate heat
- electrochemical conversion to electricity
- metal hydrides conversions.

6.1. Combustion in internal combustion, jet and rocket engines

Hydrogen is a very good fuel for internal combustion engines. Hydrogen powered internal combustion engines are on average about 20 per cent more efficient than comparable gasoline engines. The ideal thermal efficiency of an internal combustion engine is:

$$\eta = 1 - \left(\frac{1}{r}\right)^{k-1} \tag{6.1}$$

where:
r = compression ratio, and
k = ratio of specific heats (C_p/C_v).

This equation shows that the thermal efficiency can be improved by increasing either the compression ratio or the specific heat ratio. In hydrogen engines both ratios are higher than in a comparable gasoline engine due to hydrogen's lower self-ignition temperature and ability to burn in lean mixtures.

However, the use of hydrogen in internal combustion engines results in loss of power due to lower energy content in a stoichiometric mixture in the engine's cylinder. A stoichiometric mixture of gasoline and air, and gaseous hydrogen and air pre-mixed externally occupy ~2 per cent and 30 per cent of the cylinder volume, respectively. Under these conditions, the energy of the hydrogen mixture is only 85 per cent of the gasoline mixture, thus resulting in about 15 per cent reduction in power. Therefore, the same engine running on hydrogen will have ~15 per cent less power than when operated with gasoline. The power output of a hydrogen engine can be improved by using more advanced fuel injection techniques or liquid hydrogen. For example, if liquid hydrogen is premixed with air, the amount of hydrogen that can be introduced in the combustion cylinder can be increased by approximately one-third [90].

One of the most important advantages of hydrogen as a fuel for internal combustion engines is that hydrogen engines emit far fewer pollutants than comparable gasoline engines. Basically, the only products of hydrogen combustion in air are water vapor and small amounts of nitrogen oxides. Hydrogen has a wide flammability range in air (5 to 75 per cent vol.) and therefore high excess air can be utilized more effectively. The formation of nitrogen oxides in hydrogen/air combustion can be minimized with excess air. NO_x emissions can also be lowered by cooling the combustion environment using techniques such as water injection, exhaust gas recirculation, or using liquid hydrogen. The emissions of NO_x in hydrogen engines are typically one order of magnitude smaller than emissions from comparable gasoline engines. Small amounts of unburned hydrocarbons, CO_2, and CO have been detected in hydrogen engines due to lubrication oil [90].

The low ignition energy and fast flame propagation of hydrogen has led to problems of pre-ignition and backfire. These problems have been overcome by adding hydrogen to the air mixture at the point where and when the conditions for pre-ignition are less likely, such as delivering the fuel and air separately to the combustion chamber, and/or injecting hydrogen under pressure into the combustion chamber before the piston is at the top dead centre and after the intake air valve has been closed. Water injection and exhaust gas recirculation techniques are also used in hydrogen engines to help control premature ignition. It should be noted that most of the research on hydrogen combustion in internal combustion engines has been conducted with modifications of existing engines designed to burn gasoline. Redesign of the combustion chamber and coolant systems to accommodate hydrogen's unique combustion properties could be the most effective method of solving the problems of preignition and knocking [90].

Hydrogen use in turbines and jet engines is similar to the use of conventional jet fuel. The use of hydrogen avoids the problems of sediments and corrosion on turbine blades, which prolongs life and reduces maintenance. Gas inlet temperatures can be pushed beyond normal gas turbine temperatures of 800°C, thus increasing the overall efficiency. The only pollutants from the use of hydrogen in turbines and jet engines are again nitrogen oxides.

Hydrogen has traditionally been used in the space programme as fuel for the rocket engines of launch vehicles. The space programmes are currently the biggest consumer of liquid hydrogen. A tremendous body of experience in handling liquid hydrogen has been gained as a result of the development and use of liquid hydrogen/liquid oxygen fueled rocket engines in the space programme, including manufacture and liquefaction of hydrogen, as well as transportation, storage, pipelining, instrumentation, design practices, operational use and safety procedures. This experience may be a basis for development of other hydrogen technologies and their expansion in other energy markets.

6.2. Steam generation

Hydrogen combusted with pure oxygen results in pure steam, i.e.,:

$$2H_2 + O_2 \rightarrow 2H_2O \qquad (6.2)$$

The above reaction would develop temperatures in the flame zone above 3,000°C, therefore, additional water has to be injected so that the steam temperature can be regulated at a desired level. Both saturated and superheated vapour can be produced.

The German Aerospace Research Establishment (DLR) has developed a compact hydrogen/oxygen steam generator (Figure 6.1) [91]. The steam generator consists of the ignition, combustion and evaporation chambers. In the ignition chamber a combustible mixture of hydrogen and oxygen at a low oxidant/fuel ratio is ignited by means of a spark-plug. The rest of the oxygen is added in the combustion chamber to adjust the oxidant/fuel ratio exactly to the stoichiometric one. Water is also injected in the combustion chamber after it has passed through the double walls of the combustion chamber. The evaporation chamber serves to homogenize the steam. The steam's temperature is monitored and controlled. Such a device is close to 100 per cent efficient, since there are no emissions other than steam and little or no thermal losses.

The hydrogen steam generator can be used to generate steam for spinning reserve in power plants, for peak load electricity generation, in industrial steam supply networks and as a micro steam generator in medical technology and biotechnology [91].

6.3. Catalytic combustion

Hydrogen and oxygen in the presence of a suitable catalyst may be combined at temperatures significantly lower than flame combustion (from ambient to 500°C). This principle can be used to design catalytic burners and heaters. Catalytic burners require considerably more surface area than conventional flame burners. Therefore, the catalyst is typically dispersed in a porous structure. The reaction rate and resulting temperature are easily controlled by controlling the hydrogen flow rate. The reaction takes place in a reaction zone of the porous catalytic sintered metal cylinders or plates, in which hydrogen and oxygen are mixed by diffusion from opposite sides. A combustible mixture is formed only in the reaction zone and assisted with (platinum) catalyst to burn at low temperatures (Figure 6.2). The only product of catalytic combustion of hydrogen is water vapour. Due to low temperatures there are no nitrogen oxides formed. The reaction cannot migrate into the hydrogen supply, since there is no flame and hydrogen concentration is above the higher flammable limit (75 per cent).

Possible applications of catalytic burners are in household appliances, such as cooking ranges and space heaters. The same principle is also used in hydrogen sensors.

6.4. Electrochemical conversion (fuel cells)

Hydrogen can be combined with oxygen without combustion in an electrochemical reaction (reverse of electrolysis) to produce electricity (DC). The device where such a reaction takes place is called the electrochemical fuel cell or just fuel cell.

Depending on the type of the electrolyte used, there are several types of fuel cells:

- Alkaline fuel cells (AFC) use concentrated (85 wt%) KOH as the electrolyte for high temperature operation (250°C) and less concentrated (35-50 wt%) for lower temperature operation (<120°C). The electrolyte is retained in a matrix (usually asbestos), and a wide range of electrocatalysts can be used (such as Ni, Ag, metal oxides, and noble metals). This fuel cell is intolerant to CO_2 present in either fuel or oxidant [92].

- Polymer electrolyte membrane or proton exchange membrane fuel cells (PEMFC) use a thin polymer membrane (such as perfluorosulphonated acid polymer) as the electrolyte. The membranes as thin as 12-20 microns have been developed, which are excellent proton conductors. The catalyst is typically platinum with loadings about 0.3 mg/cm^2, or, if the hydrogen feed contains minute amounts of CO, Pt-Ru alloys are used. Operating temperature is usually below 100°C, more typically between 60 and 80°C.

- Phosphoric acid fuel cells (PAFC), use concentrated phosphoric acid (~100 per cent) as the electrolyte. The matrix used to retain the acid is usually SiC, and the electrocatalyst in both the anode and cathode is Platinum black. Operating temperature is typically between 150-220°C [92,93].

- Molten carbonate fuel cells (MCFC) have the electrolyte composed of a combination of alkali (Li, Na, K) carbonates, which is retained in a ceramic matrix of $LiAlO_2$. Operating temperatures are between 600-700°C where the carbonates form a highly conductive molten salt, with carbonate ions providing ionic conduction. At such high operating temperatures, noble metal catalysts are typically not required [92,93].

- Solid oxide fuel cells (SOFC) use a solid, non-porous metal oxide, usually Y_2O_3-stabilized ZrO_2 as the electrolyte. The cell operates at 900-1,000°C where ionic conduction by oxygen ions takes place [92,93].

A typical fuel cell consists of the electrolyte in contact with porous electrodes on both sides. A schematic representation of a fuel cell with reactant and product gases, and ions flow directions for the major types of fuel cells are shown in Figure 6.3. The electrochemical reactions occur at the three-phase interface – porous electrode/electrolyte/ reactants. The actual electrochemical reactions that occur in the above listed types of fuel cells are different (as shown in Table 6.1) although the overall reaction is the same, i.e., H_2

+ $\frac{1}{2}O_2 \rightarrow H_2O$. Low temperature fuel cells (AFC, PEMFC, PAFC) require noble electrocatalysts to achieve practical reaction rates at the anode and cathode. High temperature fuel cells (MCFC and SOFC) can also utilize CO and CH_4 as fuels. The operating temperature is high enough so that CO and CH_4 can be converted to hydrogen through the water-gas shift and steam reforming reactions respectively.

The electrolyte not only transports dissolved reactants to the electrode, but it also conducts ionic charge between the electrodes and thereby completes the cell electric circuit, as shown in Figure 6.3.

The reversible potential of the above electrochemical reactions is 1.229 V (at standard conditions, i.e., 25°C and atmospheric pressure), and it corresponds to the Gibbs free energy according to the following equation:

$$\Delta G^\circ = nFE^\circ \qquad (6.3)$$

where:
ΔG° = Gibbs free energy at 25°C and atmospheric pressure
n = number of electrons involved in the reaction
F = Faraday's constant
E° = reversible potential at 25°C and atmospheric pressure (V)

The reversible potential changes with temperature and pressure; in general it is lower at higher temperatures (reaching ~1.0 V at 1,000 K), and it is higher at higher pressures or higher concentrations of reactants. The actual voltage of an operational fuel cell is always lower than the reversible potential due to various irreversible losses, such as activation polarization, concentration polarization and ohmic resistance. While ohmic resistance is directly proportional to the current, activation polarization is a logarithmic function of current, and thus more pronounced at very low current densities, and concentration polarization is an exponential function of current and thus becomes a limiting factor at high current densities. Figure 6.4 shows a typical fuel cell polarization curve with pronounced regions of predominant irreversible losses. Figure 6.5 shows actual polarization curves of some representative fuel cells. The fuel cells are typically operated in a range between 0.6 and 0.8 V. The Space Shuttle fuel cell (alkaline) is designed to operate at 0.86 V and 410 mA/cm^2 [92]. PEM fuel cells have the highest achievable current densities, between 1 and 2 mA/cm^2 at 0.6 V with pressurized hydrogen and air.

The fuel cell efficiency is a function of cell voltage. The theoretical fuel cell efficiency is:

$$\eta_{FC} = \Delta G / \Delta H \qquad (6.4)$$

where ΔH is hydrogen's enthalpy or heating value (higher or lower). The theoretical fuel cell efficiency, defined as a ratio between produced electricity and higher heating value of hydrogen consumed is therefore 83 per cent. The lower heating value of hydrogen results in an efficiency of 98 per cent. Since the actual voltage of an operational fuel cell is lower than the reversible potential, the fuel cell efficiency is always lower than theoretical. Generally, the fuel cell efficiency is a product of several efficiencies:

$$\eta_{FC} = \eta_{Th} \cdot \eta_V \cdot \eta_F \cdot \eta_U \qquad (6.5)$$

where:

η_{Th} = thermal efficiency, i.e., ratio between Gibbs free energy of the reaction and heating value of the fuel, $\Delta G_f / \Delta H_{fuel}$ (similar to internal combustion engines, the fuel cell efficiency is often expressed in terms of lower heating value).

η_V = voltage efficiency, defined as a ratio between actual voltage (V) and thermodynamic voltage (E), i.e., V/E.

η_F = Faradaic efficiency, or ratio between the actual current and current corresponding to the rate at which the reactant species are consumed, I/nFm, where m is the rate (in moles/s) at which the reactants are consumed.

η_U = fuel utilization, or ratio between the amount of fuel actually consumed in the electrochemical reaction and fuel supplied to the fuel cell.

For a hydrogen/oxygen or hydrogen/air fuel cell operating with 100 per cent fuel utilization, the efficiency is a function of cell voltage only. For such a fuel cell the efficiency in an operating range between 0.6 V and 0.8 V is between 0.48 and 0.64.

In order to get useable voltages (i.e., tens or hundred Volts), the cells are combined in a stack. The cells are physically separated from each other and electrically connected in series by a bipolar separator plate. Figure 6.6 shows a schematic representation of a typical fuel cell stack.

Alkaline fuel cells have been used in the space programme (Apollo and Space Shuttle) since 1960's. Phosphoric acid fuel cells are already commercially available in container packages for stationary electricity generation. PEM fuel cells are a serious candidate for automotive applications, but also for small scale distributed stationary power generation. High temperature fuel cells, such as molten carbonate and solid oxide fuel cells, have been developed to a precommercial/demonstration stage for stationary power generation.

6.5. Metal hydrides

Hydrogen's property to form metal hydrides may be used not only for hydrogen storage (as described in Section 5.1.5) but also for various energy conversions. When a hydride is formed by the chemical combination of hydrogen with a metal, an element or an alloy, heat is generated, i.e., the process is exothermic. Conversely, in order to release hydrogen from a metal hydride heat must be supplied. These processes can be represented by the following chemical reactions:

Charging or absorption: $M + xH_2 \rightarrow MH_{2x} + \text{heat} \qquad (6.6)$

Discharging or desorption: $MH_{2x} + \text{heat} \rightarrow M + xH_2$ (6.7)

where M represents the hydriding substance, a metal, an element or an alloy. The rate of these reactions increase with increase in the surface area. Therefore, in general, the hydriding substances are used in powdered form to speed up the reactions.

Elements or metals with unfilled shells or subshells are suitable hydriding substances. Metal and hydrogen atoms form chemical compounds by sharing their electrons in the unfilled subshells of the metal atom and the K shells of the hydrogen atoms.

Ideally, for a given temperature, the charging or absorption process and the discharging or desorption process takes place at the same constant pressure. However, actually, there is a hysteresis effect and the pressure is not absolutely constant – for a given temperature charging pressures are higher than the discharging pressures. The heat generated during the charging process and the heat needed for discharging are functions of the hydriding substance, the hydrogen pressure and the temperature at which the heat is supplied or extracted. Using different metals and by forming different alloys, different hydriding characteristics can be obtained. In other words, it is possible to make or to find hydriding substances which are more suitable for a given application, such as waste heat storage, electricity generation, pumping, hydrogen purification and isotope separation.

6.5.1. Heat storage

Any heat, such as waste heat, solar heat and geothermal heat, can be stored as potential hydrogen hydriding energy by supplying the heat to a hydride as shown in the following relationship:

$$\text{Heat} + \text{Hydride} \longrightarrow \text{Hydriding substance} + \text{Hydrogen} \qquad (6.8)$$

Whenever heat is needed, hydrogen released can be supplied back to the hydride, releasing the hydriding reaction heat, viz.,:

$$\text{Hydrogen} + \text{Hydriding substance} \longrightarrow \text{Hydride} + \text{Heat} \qquad (6.9)$$

If hydrogen is supplied to the hydriding substance at the same pressure as it was released, then the heat released will be at the same temperature (or slightly lower due to the hysteresis effect) as that of the heat supplied. However, by increasing the pressure of the hydrogen supplied, the temperature of the heat released can be increased; and conversely, by reducing the hydrogen pressure, the temperature of the heat released can be reduced. This means that metal hydrides can be used as heat pumps.

6.5.2. Electricity storage

Hydriding substances can be used for electricity storage in two ways. In one of the methods, electricity (direct current) is used to electrolyze the water, and the hydrogen produced is stored in a hydriding substance. When electricity is needed, the hydrogen is released from the hydriding substance by adding heat and used in a fuel cell to produce direct current electricity. Heat from the fuel cell can be used to release hydrogen from the metal hydride.

In the second method, the cathode is covered with a hydriding substance (e.g., titanium nickel alloy). During the electrolysis of water, the hydrogen produced on the cathode surface is immediately absorbed by the hydriding substance covering the electrode. Then, when electricity is needed, the electrolyzer operates in a reverse mode as a fuel cell producing electricity using the hydrogen released from the metal hydride.

6.5.3. Heating/Cooling

Hydrogen, together with hydriding substances, can be used for heating or air-conditioning buildings. Figure 6.7 shows how one of the proposed systems works. The system consists of four hydride tanks, a solar collector (or a heat source) and a number of heat exchangers. Hydride Tank 1 is connected to hydride Tank 3 with a hydrogen pipe in order to allow the movement of hydrogen from one tank to the other. Similarly, hydride Tanks 2 and 4 are connected in the same fashion. Tanks 1 and 2 contain the same hydriding substance ($CaNi_5$), and Tanks 3 and 4 contain another hydriding material ($LaNi_5$). Heat exchangers and the hydride tanks are connected by water-carrying pipe circuits or loops, equipped with a set of switches and valves, so that a hydride tank in a given water loop can be replaced by another hydride tank.

When the system works as a heater, the heat from a heat source (e.g. solar collector) is carried to Tank 1 at about 100°C and drives the hydrogen from Tank 1 to Tank 3, where hydrogen is absorbed forming a hydride and heat is released at 40°C. The water loop carries this heat to the building heat exchangers and heats the air in the building. At the same time, water in the other loop absorbs heat from the ambient and carries it to Tank 4. This heat drives off the hydrogen from Tank 4 to Tank 2 where hydride is formed and heat is generated at 40°C. The whole operation of driving hydrogen from Tanks 1 and 4 to Tanks 3 and 2 takes about two minutes. At the end of this cycle, the hydride tanks are switched from one loop to the other in Cycle II (as shown in Figure 6.7). Now the solar heat and the ambient heat are used to drive off the hydrogen in Tanks 2 and 3 to Tanks 4 and 1, respectively. The heat produced during the absorption processes in Tanks 1 and 4 is used for heating the building. After this, the cycles are repeated.

When the system works as an air conditioner, the building heat exchangers are placed in the 8°C water loop, while the outside heat exchangers are placed in the 40°C water loops, and operation proceeds in two cycles as described above.

6.5.4. Electricity generation

If passed through a turbine or expansion engine, hydrogen moving from one hydride tank to the other could produce mechanical and electrical energy, as shown in Figure 6.8. The system is somewhat similar to the one proposed for heating and cooling. However, it consists of only three tanks containing the same kind of hydriding substance (in this case $LaNi_5$ alloy). During the first cycle, hydrogen driven off from the desorption tank (Tank 1) by means of solar heat (or heat from any other source) passes through the expansion turbine producing mechanical energy and electricity, and then at a lower pressure is absorbed by the hydriding substance in Tank 2 producing heat at 40°C. In this case, the heat is produced at a lower temperature than the temperature of the desorption since hydrogen is at a lower pressure after passing through the turbine. The heat produced in the absorption tank (Tank 2) is rejected to the environment through the water cooling system. The same water cooling system is also used to cool down the cooling tank (Tank 3) from 100°C to 40°C, since it has served as the desorption tank in the previous cycle. In the second cycle through a system of switches and valves, the tanks are displaced one step to the right in the diagram, i.e., the cooling tank becomes the absorption tank, the absorption tank becomes the desorption tank, and the desorption tank becomes the cooling tank. Then, the cycles are repeated. Using this method, low quality heat could be converted to electricity.

6.5.5. Pumping or pressurizing

The relationship between the hydrogen pressure (p) and the hydride temperature (T) in the absorption or desorption process is given by the following equation:

$$p = exp\left(\frac{\Delta H}{RT} + S\right) \tag{6.10}$$

where ΔH is the hydriding reaction enthalpy, R the gas constant, and S a constant depending on the hydriding substance. If the hysteresis is neglected, the above equation would hold for both the absorption and desorption processes. By using heat it would be possible to increase hydrogen pressure by a hundred or more times. The pressure ratio would be:

$$\frac{p_{Hi}}{p_{Lo}} = exp\left[\frac{\Delta H}{R}\left(\frac{1}{T_{Hi}} - \frac{1}{T_{Lo}}\right)\right] \tag{6.11}$$

where P_{Hi} is the hydrogen pressure corresponding to the hydride temperature T_{Hi} , and P_{Lo} is the hydrogen pressure corresponding to the hydride temperature T_{Lo}.

6.5.6. Hydrogen purification

In many applications, such as the hydrogenation of vegetable oils and some laboratory experiments, high purity hydrogen is needed. One property of the hydriding substances is that they absorb hydrogen but not the other elements or molecules which may be present as impurities. Using this property of the hydriding substances, it is possible to purify hydrogen simply and inexpensively. A hydride tank is first charged with impure hydrogen while heat is being removed. Only hydrogen forms hydride, which allows impurities to be flushed from the hydride tank. Once the impurities are flushed from the tank, heat may be applied and pure hydrogen is released from the hydride. For continuous operation, the system may be equipped with three tanks (absorption, flushing and desorption) and their roles can be switched in cycles.

6.5.7. Deuterium separation

The property of hydrides used for hydrogen purification, can also be used for deuterium separation. The system is similar to the hydrogen purification system. Deuterium is flushed from the hydriding tank, while hydrogen remains bonded in the metal hydride. Using titanium nickel alloy as the hydriding substance, it is possible to obtain 85 per cent pure deuterium after only two steps. With three and four steps, it is possible to obtain 99.9 per cent and 99.999 per cent pure deuterium respectively.

Table 6.1. Fuel cell reactions

Fuel Cell Type	Anode Reaction	Cathode Reaction
Alkaline	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$
Proton Exchange	$H_2 \rightarrow 2H^+ + 2e^-$	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Phosphoric Acid	$H_2 \rightarrow 2H^+ + 2e^-$	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Molten Carbonate	$H_2 + CO_3^= \rightarrow H_2O + CO_2 + 2e^-$	$\frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^=$
Solid Oxide	$H_2 + O^= \rightarrow H_2O + 2e^-$	$\frac{1}{2}O_2 + 2e^- \rightarrow O^=$

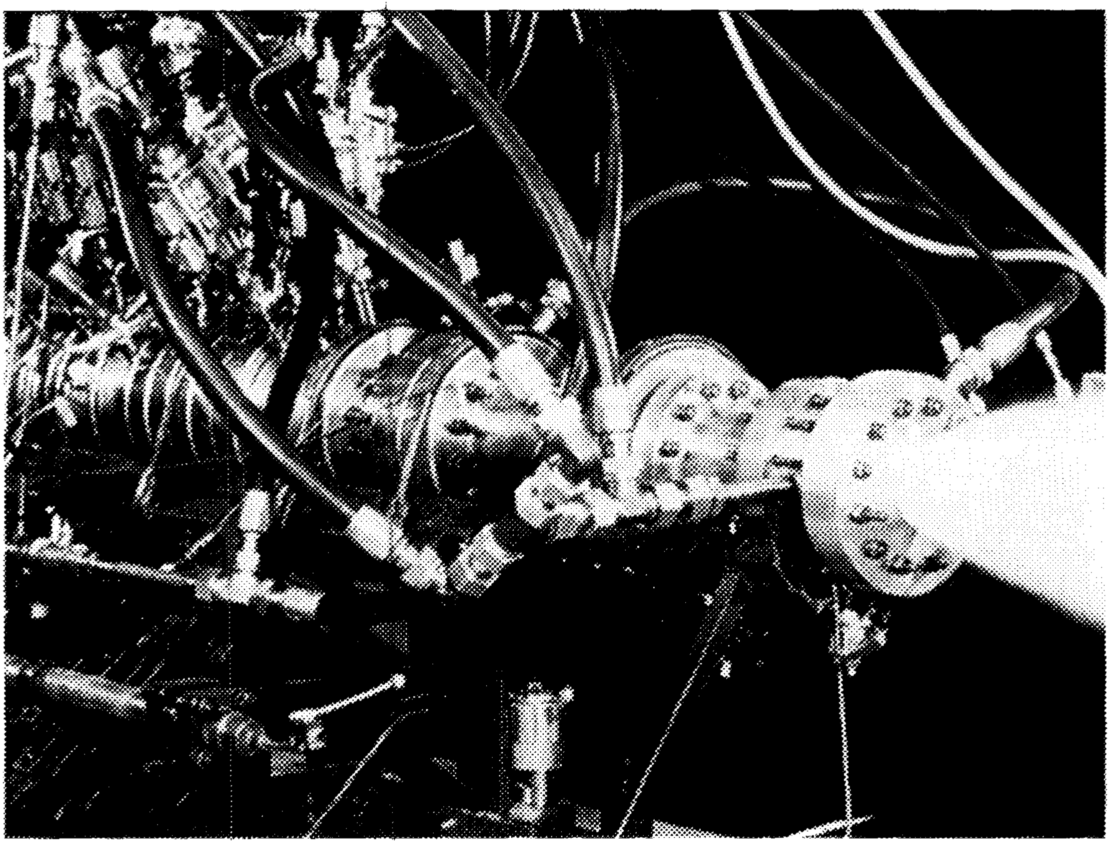

Figure 6.1 H_2/O_2 steam generator

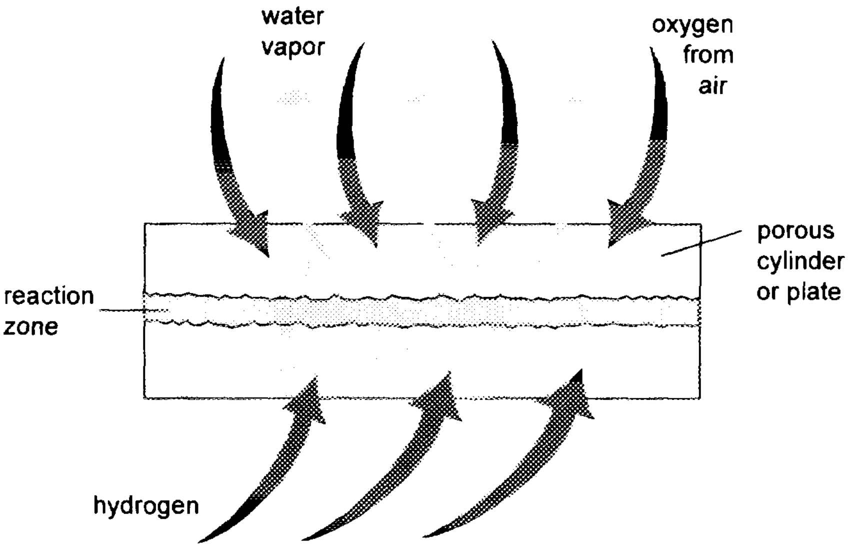

Figure 6.2 Schematic representation of catalytic burner

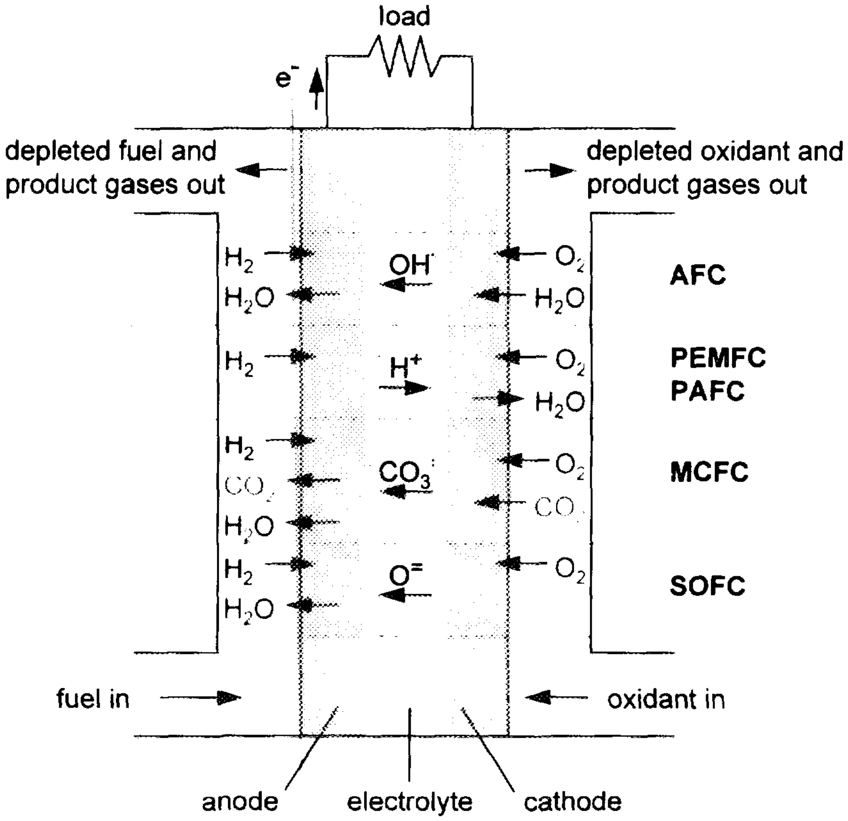

Figure 6.3 Operating principle of various types of fuel cells

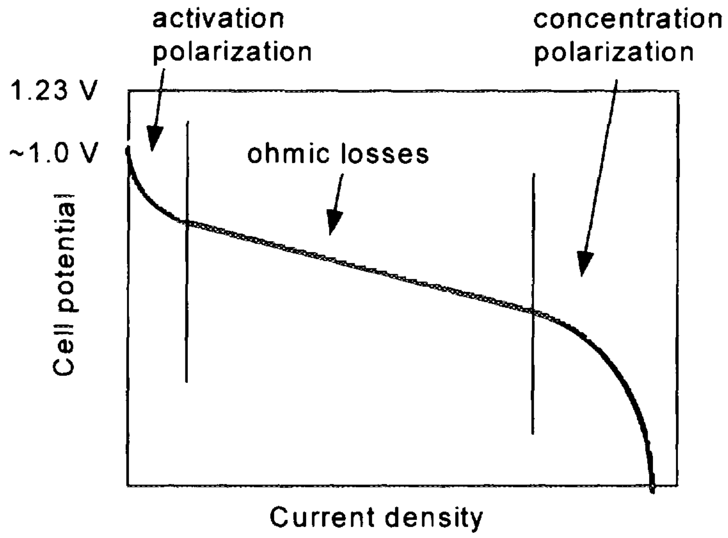

Figure 6.4 Typical fuel cell polarization curve

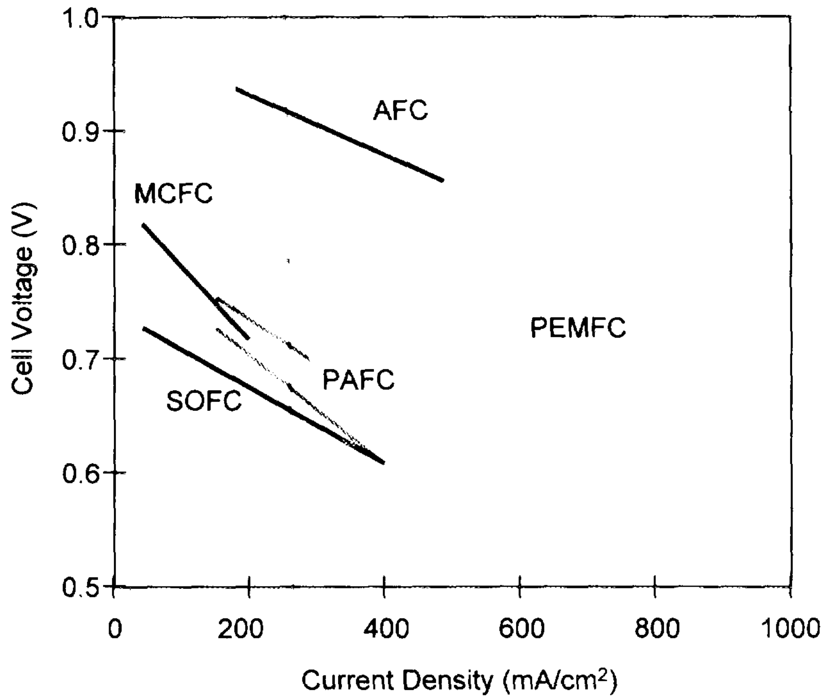

Figure 6.5 Polarization curves of some representative fuel cells

AFC – United Technologies' fuel cell operating in Space Shuttle, with H_2 and O_2 at 80-90°C, 410 kPa

PEMFC – Ballard's 25 kW fuel cell operating in Daimler-Benz vehicle (NECAR II) with H_2 and air (1996)

PAFC – IFC's fuel cell operating in ONSI PC25 200 kW power plant, operating on reformed natural gas and air at atmospheric pressure (1996) (dashed line is IFC's PC23 operating at 820 kPa)

MCFC – ERC's atmospheric pressure fuel cell operating with natural gas (1994)

SOFC – Westinghouse fuel cell operating at atmospheric pressure using natural gas (1991)

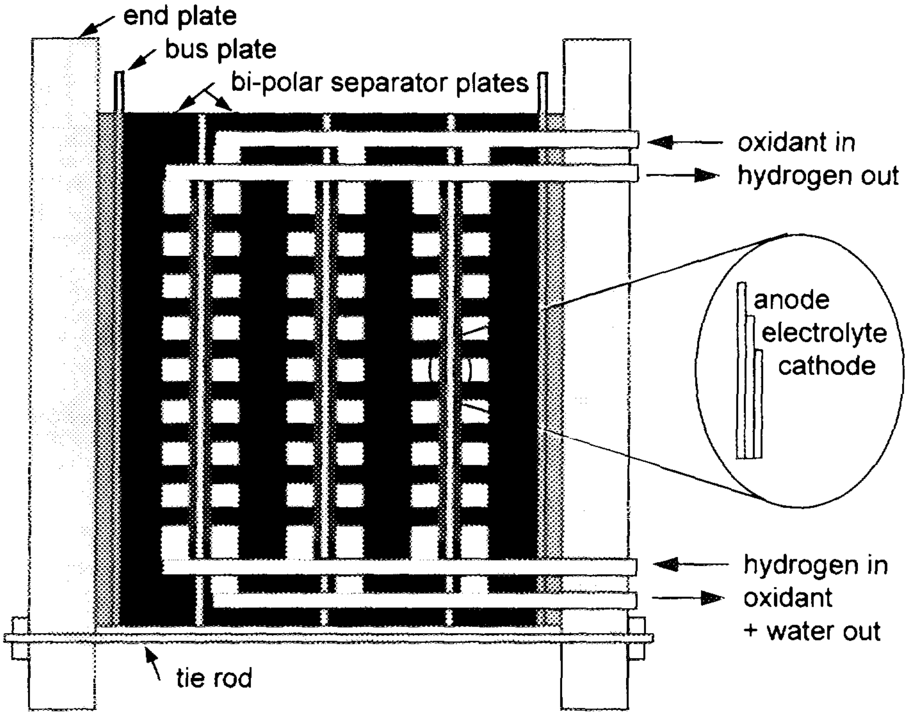

Figure 6.6 Schematic representation of a typical fuel cell stack

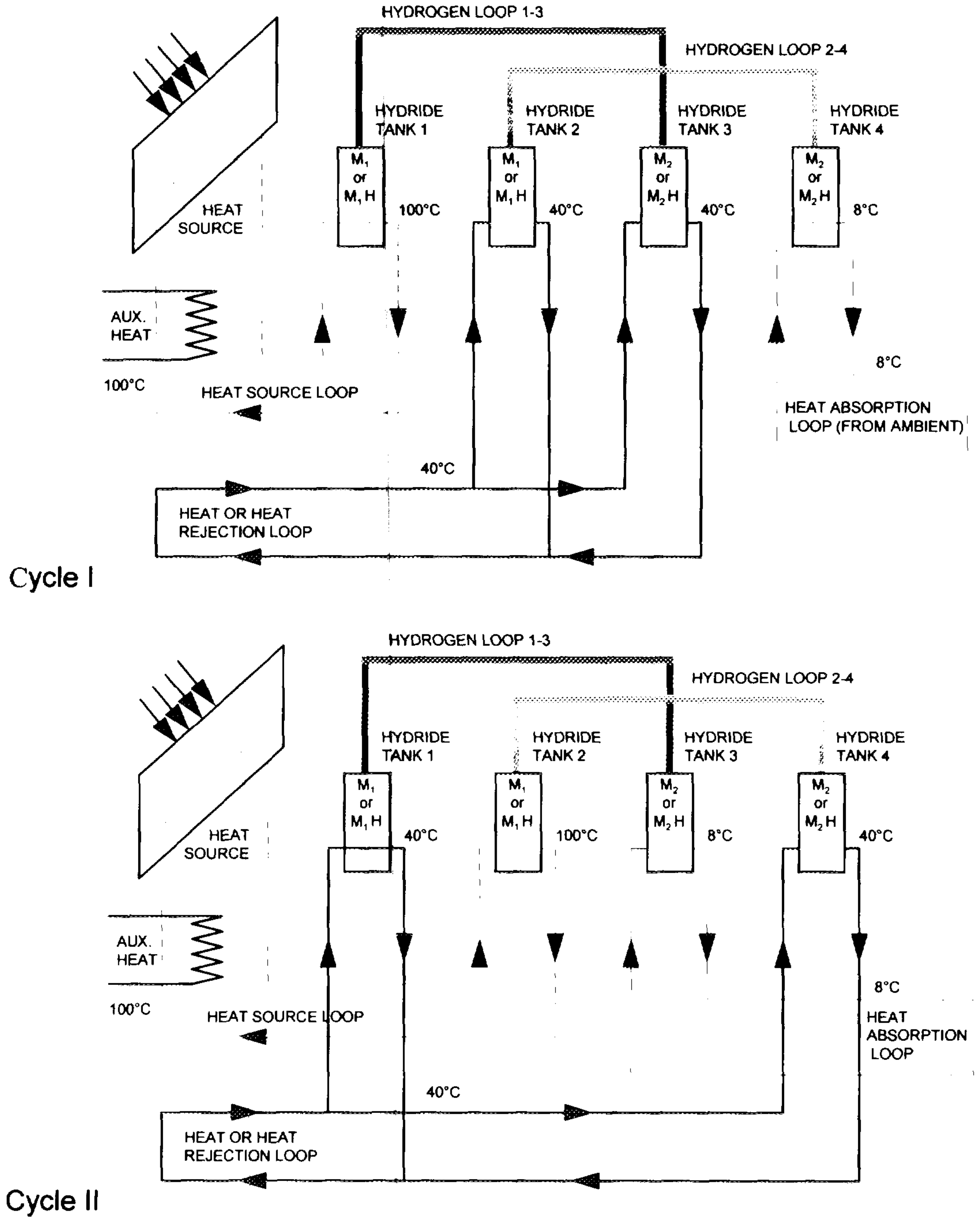

Figure 6.7 Hydrogen/hydride heating-cooling system

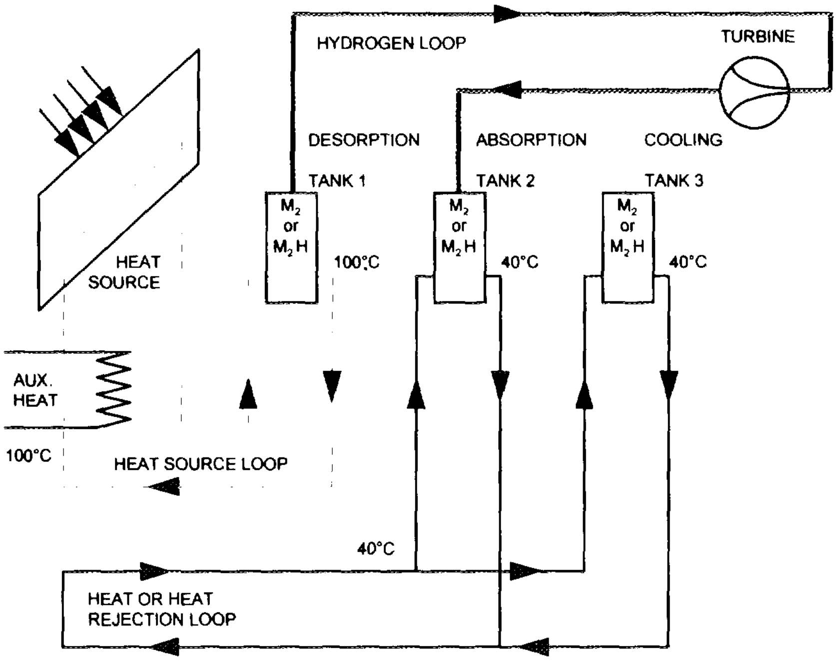

Figure 6.8 Electricity generation via hydrogen and hydrides

CHAPTER 7

HYDROGEN APPLICATIONS

Hydrogen as an energy carrier has many possible applications. it can be used instead of fossil fuels for virtually all purposes: as a fuel for surface and air transportation, as a fuel for heat production, and even as a fuel for production of electricity directly (in fuel cells) or indirectly (through gas and steam turbine driven generators).

7.1. Hydrogen powered automobiles

Efforts to convert vehicles to hydrogen operation began in the mid-1920s with the work of German engineer Rudolf Erren, who converted numerous engines to run on hydrogen for a variety of applications including trucks, buses and submarines [24]. Large amount of research work has been done on the use of hydrogen as a fuel for cars, trucks and buses starting in 1970s. This work has been mainly aimed towards conversion of the existing internal combustion engines to run on hydrogen (and solving problems related to hydrogen combustion characteristics) and studying the problem of hydrogen storage in vehicles. Three concepts, based on compressed hydrogen, liquid hydrogen and metal hydride storage have been developed, tested and successfully demonstrated.

Daimler-Benz has been studying the prospects of hydrogen as fuel for vehicles since 1973. The early work at Daimler-Benz culminated in a fleet test of hydrogen vehicles in Berlin, which began in 1984. Two types of vehicles were used for this test: (1) five model 280TE passenger cars which used mixed fuel gasoline/hydrogen, and (2) five model 310 delivery vans converted to pure hydrogen operation. Both types of vehicles were powered by hydrogen stored on-board in metal hydrides. The vehicles operated reliably and safely over the four-year test period, during which period valuable data were collected [94]. A more advanced Mercedes 230E was developed in 1989.

BMW has selected liquid hydrogen as a fuel of choice. Starting from 1979 several BMW vehicles have been retrofitted and modified to use hydrogen (Figure 7.1). In cooperation with DLR and Linde, the liquid hydrogen storage system has been constantly improving, and in the latest model was completely hidden between the back seat and the trunk. Concerns about difficulties in refueling liquid hydrogen have resulted in a completely automated refueling station where a robot performs all the operations necessary for refueling. BMW also made significant improvements on engines, such as the first direct injection of hydrogen into the cylinder [95].

Mazda introduced its first hydrogen fueled concept car, the HR-X, in 1991 [96]. The car had a compact rotary engine and a metal hydride tank. Since then Mazda has released an updated version of the HR-X, and a Miata also powered by a rotary engine and equipped with metal hydride storage [97].

Problems of on-board hydrogen storage can be reduced if engine efficiency is significantly improved. Fuel cells in combination with electric motors are more than two times as efficient as internal combustion engines in a driving cycle, and therefore offer potential for reducing on-board hydrogen storage requirements, as well as the fuel costs (in terms of $/mile).

Energy Partners, of West Palm Beach, Florida, built one of the first fuel cell powered passenger automobiles, completed in 1993 [98]. On an ultra-lightweight body of the Consulier vehicle, Energy Partners installed a hybrid fuel cell/battery electric propulsion system (Figure 7.2). The three fuel cell stacks, 5 kW each, provided power for normal driving and assisted in charging the battery bank. Equipped with a tank that holds 1 kg of hydrogen at 200 bar, the car had a range of 65 miles.

Daimler Benz in cooperation with Canadian fuel cell developer, Ballard, has built three generations of fuel cell vehicles. The first one, NECAR I, was a van, and the fuel cell power system, hydrogen storage and instrumentation occupied almost the entire inside space. With advancements made in fuel cell technology, the next vehicle – a mini-van called NECAR II – completed in 1996, had a much smaller fuel cell engine occupying only 150 litres [99]. The fuel cell propulsion system consisted of two fuel cell stacks, 25 kW each. Hydrogen was stored in lightweight pressure cylinders integrated into the roof of the vehicle. In 1997, Daimler Benz announcedthe development of the most advanced fuel cell vehicle to date – a class A sub-compact Mercedes car, called NECAR III, with basically the same engine as NECAR II, but with methanol as fuel using an on-board fuel reformer (Figure 7.3) [100].

Most of other car manufacturers are also involved in development of fuel cell powered vehicles:

- In 1996 Toyota revealed a fuel cell powered RAV-4 vehicle with metal hydride storage [101]. An updated version running on methanol was released in 1997 [102].
- Honda and Nissan signed a contract with Ballard in 1997 for delivery of fuel cell stacks [103].
- Volkswagen in a joint project with Volvo is currently working on a methanol fueled PEM fuel cell hybrid "Golf-type" vehicle which is expected to be up and running by 1999 [104]. The fuel cell stack was made by Ballard and the methanol reformer by Johnson-Matthey.
- Renault, a French car manufacturer has completed a station wagon called FEVER, powered by a 30 kW fuel cell system developed by De Nora, Italy [105]. The fuel of choice is liquid hydrogen. Another participant in this is Sweden's Volvo.
- At the Detroit Auto Show in early 1997, Chrysler displayed a wireframe mock-up of a mid-size sedan powered by a PEM fuel cell with an on-board gasoline reformer [106]. A working demonstration car is expected within two years, but the commercial vehicles are not expected to be in

operation so soon.

- General Motors was working with Ballard stacks in their Los Alamos National Laboratory, but is currently working on fuel cell stacks development and a methanol reformer in its laboratories. A conceptual design study of a fuel cell engine and a vehicle was released in 1994 [107], and a conceptual vehicle is expected to be completed by 1998.
- Ford has conducted a comprehensive study of hydrogen infrastructure and hydrogen safety in parallel with conceptual studies of fuel cell powered vehicles [108,109]. At least two prototypes are expected to be built by 1999 [110].

Most of the space related problems in fuel cell vehicles can be alleviated in buses. A Canadian fuel cell manufacturer demonstrated one of the first PEM fuel cell powered buses in 1993 [111]. The bus was driven over 2,000 kms in Vancouver, Los Angeles and Sacramento. Since then Ballard has built several more buses using more advanced fuel cell stacks, and is currently building several buses for the city of Chicago. Ballard plans to introduce a commercial fuel cell bus, which will have a range of 550 kms. Daimler-Benz introduced its first hydrogen fueled PEM cell city bus NEBUS (new electric bus) demonstrator (Figure 7.4). The engine consists of ten 25 kW fuel cell stacks by Ballard. Compressed hydrogen is carried in seven 150-litre, 300 bar roof-mounted cylinders. The range of the bus is 156 kms [112].

A possible niche market for the fuel cell vehicles may be small utility vehicles and golf carts. City of Palm Desert has launched a programme for introducing fuel cell golf carts developed by the Schatz Energy Center of the Humboldt State University, Arcata, California [113]. Several vehicles have been completed, and are running on the streets and golf courses of Palm Desert. Energy Partners, of West Palm Beach, Florida, has converted several John Deere Gator utility vehicles to fuel cell power [114], and two of them are currently in demonstration service at the Palm Springs airport in California (Figure 7.5).

7.2. Marine applications of hydrogen

Hydrogen/oxygen fuel cells (particularly low temperature fuel cells such as PEMFC) have characteristics which make them ideal for powering submarines:

- They do not need air – thus can operate underwater, provided that both fuel (hydrogen) and oxidant (oxygen) are stored on-board.
- They do not produce any emissions or waste products except water, and can therefore maintain zero buoyancy.
- They operate quietly since there are no moving parts – thus reducing sonar signature.
- They reject heat at low temperature – thus generating very low thermal signature.

- They are very efficient – thus providing longer cruising range and lower "indiscretion" time.

Figure 7.6 shows a conceptual design of a fuel cell powered submarine. Hydrogen and oxygen storage on-board may pose a problem due to weight and volume constraints. Liquid hydrogen and liquid oxygen seem to be the best option, although metal hydrides for hydrogen storage have been considered as well [115].

In 1989, Perry Technologies, Florida, completed a small submarine equipped with Ballard's fuel cell (Figure 7.7). The German Navy has decided to equip their next generation of submarines with hydrogen fuel cell power plants, and Siemens has developed reliable and efficient fuel cells exclusively for submarine applications [116]. Australian and Canadian navies are experimenting with hydrogen fuel cells for their submarines and naval vessels.

Fuel cell power plants (not necessarily PEMFC) may also be used for surface ships and boats, both as main propulsion engines (in conjunction with electric motors) and as auxiliary generators.

The Government of Iceland is considering production of hydrogen from geothermal energy (which is abundant in the country), and using it in their fishing boats instead of diesel oil (which they must import) [117]. This would also help the county to meet the proposed United Nations restrictions for CO_2 emissions.

7.3. Hydrogen powered airplanes

Liquid hydrogen has numerous advantages as a fuel for commercial subsonic and especially for supersonic aircraft [118]. The most important advantage of liquid hydrogen is its high energy content (142 MJ/kg), which is 2.8 times higher than the energy content of conventional jet fuel. A liquid hydrogen powered aircraft would therefore have to carry one third of the fuel mass of a conventional aircraft. This means more payload, smaller engines and higher fuel utilization. A subsonic hydrogen fueled passenger aircraft will need on average 16 per cent less fuel (in energy terms) to complete the same flight than a comparable conventional aircraft. This advantage will be even higher in a supersonic aircraft (28 per cent).

Hydrogen fueled aircraft will generally have a slightly lower lift-to-drag ratio (L/D) and a lower wing loading (gross weight/wing area) than conventional aircraft. These characteristics are due, at least in part, to the low density of the fuel. The lower L/D ratio results from the fact that despite requiring only about one third of the mass, liquid hydrogen requires a very large volume. It has been found advantageous to carry LH_2 fuel in the fuselage, rather than in wing tanks as is the case with jet fuel, in order to minimize the surface-to-volume ratio of the tanks. Consequently, LH_2 fueled aircraft tend to have larger fuselages. In addition, because of the low weight of its fuel, the LH_2 aircraft is much lighter at take-off and therefore needs less wing area. The combination of large fuselage and small wings naturally leads to a lower L/D ratio. Figure 7.8 shows a conceptual hydrogen powered Lockheed aircraft.

Liquid hydrogen can be used as a heat sink so that engine hot parts can be cooled effectively and efficiently. In addition, supersonic and hypersonic aircraft structures, which are subjected to intense aerodynamic heating can be cooled with the cryogenic hydrogen.

The fact that liquid hydrogen is clean and free of impurities has an effect on engine maintenance and life. Hydrogen also mixes faster with air, which results in rapid combustion, and therefore, provides a uniform temperature profile which minimizes thermal stresses in the combustion. The low emissivity of the hydrogen/air flame further reduces metal temperatures, so that combustor liners and turbine vanes and blades are subjected to less rigorous operating conditions.

Another advantage of hydrogen is its cleanliness. A hydrogen fueled engine will produce only water vapour and much smaller amounts of NO_x than a comparable jet fuel burning engine, which in addition to water vapour and NO_x produces CO, CO_2 and unburned hydrocarbons. Since most airports are now in or close to heavily populated urban areas, emissions from aircraft is gaining more and more attention.

In spite of the general opinion, hydrogen is actually a safer fuel for air transportation than presently used jet fuel. The occupants of the aircraft in the case of a survivable crash, and people and property in the immediate surroundings in any event, would be exposed to less hazard if a crashed aircraft were fueled with LH_2. This results from three fundamental considerations:

1. LH_2 tanks are less susceptible to damage because (i) they are mounted in the fuselage where they present a far smaller dimension to frontal impact; (ii) they are protected by a significant amount of structure, which must be crushed and penetrated before the tanks are exposed; and (iii) they are designed for higher pressure than the rest of the fuselage and therefore are less apt to the point of failure in the event of a survivable crash.

2. In the event that a tank is ruptured and there is a large spill of fuel, LH_2 will not spread as far as other fuels. It evaporates in a much shorter time, becomes buoyant almost immediately, and rises and dissipates into the atmosphere so rapidly that very little hazard is present to the surroundings outside the immediate area of the crash.

3. If the spilled fuel is ignited, which would be the case with any of the fuels in most occurrences, the duration of the LH_2 fire will be so brief that the fuselage will not be heated to the point of collapse, as would be the case with other fuels. The passengers and crew could be advised to simply stay in their seats until the fuel-fed fire burns itself out (a duration of about 15 seconds for an accident involving a 400-passenger aircraft). The surrounding area affected by the fuel-fed fire will be substantially smaller. In addition, hydrogen fire will not produce any toxic fumes (unlike other fuels).

However, hydrogen, like any other fuel, must be treated and handled with caution and respect, and certain procedures must be followed to ensure operator and aircraft safety. Experience of the commercial suppliers of LH_2, and the space programmes as its user over more than three decades has established procedures which have proved to be work-able and remarkably safe.

In April 1988, the flight of a commercial airliner (Tupolev 155) with one of the three turbofan engines fueled with liquid hydrogen was demonstrated in the USSR (Figure 7.9). On 19 June, 1988 an American pilot, William H. Conrad, became the first to fly an aircraft (Grumman-American "Cheetah") fueled solely by liquid hydrogen [118].

Since 1990, German and Russian companies, including Daimler-Benz Aerospace, and its divisions Airbus and Dornier, and Tupolev, have been jointly working on the development of hydrogen-powered propulsion technology for civilian aircraft (Figure 7.10). After a first phase of feasibility studies, project activities are currently being concentrated on the following topics [119]:

- development of technologies and components for the cryogenic fuel system and the engines of future series aircraft
- realization of a hydrogen demonstrator aircraft.

A Dornier 328 aircraft has been selected as a baseline for a hydrogen demonstrator, equipped with two Pratt & Whitney Canada PW 119 engines [119]. The first flight is anticipated for late 1999. Ultimately, the project is intended towards modification of an Airbus aircraft, wide-body, short/medium range A310.

7.4. Hydrogen application in buildings

Hydrogen can be used for space heating and cooling, and water heating in the same fashion as natural gas is being used today, with minor modifications to the burner and fuel supply. In addition, instead of flame combustion, hydrogen can be used in catalytic combustors directly heating and humidifying the air. Since no other emissions are generated, these heaters can safely be used indoors. Another option for space heating and cooling, as well as refrigeration, using hydrogen would be hydrogen/hydride refrigeration systems, as described in Chapter 6.

Either flame or catalytic burners can be used for cooking. It is important that the burner ports are designed in such a way that the hydrogen/air velocity is always higher than the velocity of flame propagation in hydrogen/air mixtures in order to prevent the flame back propagation.

Another way of providing heat in domestic applications would be to use the waste heat from residential/commercial fuel cell power systems. The fuel cells are very efficient in generating electricity, yet there is a significant amount of heat that may be recuperated and used for space and water heating. In this case the efficiency of fuel cells may be raised to the 70 to 80 per cent range.

In the 1970's Billings built a Hydrogen Homestead, which included several hydrogen powered appliances: a cooking range, oven, bar-b-que (Figure 7.11), and a booster-heater for an absorption-type heat pump for space heating. Hydrogen was stored in metal hydrides [120].

The Fraunhofer Institute for Solar Energy Systems, in Germany, has developed, designed and tested several appliances based on the principle of catalytic combustion of hydrogen, which are now deliverable to customers [121]. These appliances are: a catalytic hydrogen stove (Figure 7.12), an absorption refrigerator with catalytic H_2 burner, and a modular H_2 eliminator systems.

The Solar-Wasserstoff-Bayern [48] demonstration plant includes the following hydrogen appliances:

- Two gas-fired heating boilers for variable natural gas/hydrogen mixtures, 20 kW_{th} each, one using air and the other using oxygen as oxidants.
- Catalytic heater, 10 kW_{th} boiler output, fueled with natural gas and variable mixtures of natural gas/hydrogen and air as oxidant. The heater is integrated into the building heating system.
- Catalytically heated absorption-type refrigeration unit, with rated refrigeration capacity of 16.6 kW_{th}, with hydrogen as fuel and air as oxidant. This unit supports the existing chilled water circuit.

7.5. Hydrogen application in electricity generation

Hydrogen fuel cells are very efficient devices (up to 80 per cent combined electric and thermal efficiencies), which can produce both electricity and heat. Fuel cells can be used for both centralized (large-scale) or individual electricity generation. Several fuel cell concepts are currently being developed, and some, such as the phosphoric acid fuel cell plants, are already in the demonstration and commercialization phase.

Phosphoric Acid Fuel Cell (PAFC) is the most advanced type of fuel cell available to date and is closest to commercialization. Numerous demonstration plants have been constructed and are, or have been operating in the USA, Japan and Western Europe, ranging from several kilowatts to megawatts. ONSI, a division of International Fuel Cells (IFC), is selling 200 kW units, designated PC25 (Figure 7.13). These units are being powered by natural gas, mainly because hydrogen is not readily available. Japan is particularly active in fuel cell power systems development and demonstration. The world's largest fuel cell plant is the 11 MW Toshiba system at Goi, Chiba, which uses IFC stacks. Several other developers are active in Japan, such as Toshiba, Fuji and Mitsubishi [122].

Although PEM fuel cells are being considered primarily for automotive applications, they may have applications for small and medium sized electricity generation. Detroit Edison has formed a joint venture with MTI, a PEM fuel cell developer, to make a residential fuel cell power system powered by natural gas [123]. Ballard is developing a 250 kW PEM fuel cell stationary power plant. Figure 7.14 shows a 30 kW prototype installed at the consumer's site [124].

Energy Research Corporation (ERC), Danbury, Connecticut, has built molten carbonate fuel cell stacks for the 2 MW demonstration plant in Santa Clara, California. The plant was completed in 1996 and has been operational for almost a year. ERC is considering a new power plant rated at 1.4 MW. M-C Power is another developer of molten carbonate fuel cells, and has built and tested numerous stacks up to 20 kW power output. Major Japanese developers of this technology are IHI, Hitachi, Mitsubishi and Sanyo [122].

The solid oxide fuel cell (SOFC) is an all-solid-state power system, and as such is simpler in concept than both the phosphoric acid and molten carbonate fuel cells. Several concepts are currently being developed, including tubular, monolithic and planar stack configurations. To date the biggest solid oxide fuel cell is a 120 kW unit built by Westinghouse in 1997. Because of its high operating temperature (typically ~1,000°C) the system provides for internal reforming of methane and other hydrocarbons to produce CO and H_2. Efficiencies of about 50 per cent are achievable, and because of high-quality waste heat, may be further enhanced in co-generation applications or in bottoming cycles utilizing conventional steam turbines for additional power generation [122].

Fuel cells offer the ossibility of decentralized power generation, and may alleviate the need for establishing a massive grid infrastructure. This method of electricity generation and supply is very suitable for the biggest and fastest developing electricity markets, such as heavily populated urban areas in developed countries and scarcely populated developing countries. In the former case, decentralized, zero emission electricity generation may be the only option for expansion of energy services since building new power plants is physically impossible. In the latter case, developing countries do not have a developed electrical grid, and developing one for small power requirements but large distances would not be economical. Also, big central power plants would require a lot of capital investment, which may be a burden for underdeveloped and developing economies. Small-scale fuel cell power plants may be affordable.

Efficient hydrogen use in electricity generation will become very important in solar power plants, where hydrogen serves as an energy storage medium. During periods when solar energy availability is higher than energy demand, surplus energy can be used in electrolyzers to produce hydrogen, and during the periods when demand is higher than availability or sunlight is not available, electricity can be produced from hydrogen via fuel cells.

Another way to generate electricity from hydrogen is combustion of hydrogen in gas turbines or generation of steam, which can then be used in conventional steam turbines.

The German Aerospace Research Establishment (DLR) has developed a compact hydrogen/oxygen steam generator [91]. Such a device is close to 100 per cent efficient, since there are no emissions and little or no thermal losses. Rated at 40 MW, the generator consists of a heavy walled steel tube about 2 metres in length and 40 cms in diameter. The hydrogen/oxygen combustion would develop temperatures above 3,000°C, therefore additional water is injected so that the steam temperature can be regulated below 1,500°C. This steam generator has been developed for spinning reserve in power plants, but it can be used as well for peak load electricity generation, in industrial steam supply networks and as a micro steam generator in medical technology and biotechnology.

7.6. Hydrogen applications in industry

Hydrogen is currently being used as a reactant in the chemical and petroleum – but also in metallurgical – applications, electronics, glass manufacture, nuclear industry and electrical power generation systems. Among the major uses, ammonia production accounts for almost 50 per cent, petroleum processing about 37 per cent, and methanol production 8 per cent. The usage in petroleum processing is expected to increase rapidly due to various environmental regulations and due to the increased use of heavier crude oils [125].

7.6.1. Ammonia synthesis

Ammonia is the backbone of the fertilizer industry and is produced by reaction between nitrogen and hydrogen. With catalysts, the reaction takes place at 400°C at pressures between 150 and 300 bar in the so-called Haber-Bosch process. The production of one metric tonne of ammonia requires almost 2,000 m^3 of hydrogen. This industry consumes over 200 billion m^3 of hydrogen per year, or over 50 per cent of all the hydrogen produced in the world.

7.6.2. Petroleum processing

In the petroleum industry, hydrogen is catalytically reacted with hydrocarbons in many ways. This includes hydrocracking and hydroprocessing. In the hydrocracking process, cracking and hydrogenation of hydrocarbons takes place simultaneously to produce refined fuels with smaller molecules and higher H/C ratios. In the hydroprocessing, hydrogen is used to hydrogenate sulphur and nitrogen compounds, and to finally remove them as H_2S and NH_3. In modern refineries, hydrogen requirement is typically about 1 wt.per cent of crude processed.

7.6.3. Petrochemical production

Many petrochemicals are produced using hydrogen. In methanol production, which is one of the major users of hydrogen, hydrogen and carbon monoxide are reacted over a catalyst at high pressures and temperatures. Other uses of hydrogen include butyraldehyde from propylene by the oxo process, acetic acid from syn gas, butanediol and tetrahydrofuran from maleic anhydride, cyclohexane from benzene, etc. In the production of polypropylene, hydrogen is used to control the molecular weight of the polymer. One newer use for hydrogen is in plastic recycling. The recycled plastics are melted and then hydrogenated to produce lighter molecules which can be reused to produce polymers.

7.6.4. Oil and fat hydrogenation

Hydrogen has been used extensively to decrease the degree of unsaturation in fats and oils. During this process, several changes take place, such as an increase of the melting point and enhanced resistance to oxidation that enables preservation for a longer period of time.

7.6.5. Metallurgical applications

In the production of nickel, hydrogen is used in the reduction stage. Nickel present in solution as sulphate in the presence of ammonia is converted and precipitated as elemental nickel leaving ammonium sulphate.

Hydrogen is also used as a reducing gas for catalysts, such as nickel to convert it from oxide form to the active metal form.

Hydrogen offers energetic and environmental benefits when used in the production of iron. The direct reduction of iron ore to low-carbon sponge iron is achieved with hydrogen at 600 to 900°C or a mixture of hydrogen and carbon monoxide as reduction gas. This can be achieved in the batch, fluidized bed or shaft furnace processes [126].

In metallurgical processes, hydrogen mixed with N_2 is used for heat treating applications to remove O_2. This is used in annealing, furnace brazing, powdered metal sintering, etc.

Hydrogen can be used as an external agent and alloying element to treat materials (metals and intermetallics) in order to improve their structure and properties, with the purpose of creating new, advanced materials (127).

7.6.6. Electronics industry

In the electronics industry, in production of wafers and circuits, hydrogen is used to reduce silicon tetrachloride to silicon for epitaxial growth of polysilicon.

7.6.7. Glass and optical fibres manufacture

In float glass manufacture, a mixture of 4 per cent H_2 in N_2 is used to prevent oxidation of molten tin bath. In flame polishing of glass edges and in the manufacture of optical fibres via flame deposition, clean combustion is required, which requires the usage of hydrogen as fuel.

7.6.8. Nuclear reactors

In Boiling Water nuclear Reactors (BWR), and also in Pressure Water Reactors, trace amounts of oxygen present in the water is found to cause inte-granular stress corrosion cracking. Hydrogen is used to scavenge oxygen levels to below 100 ppb.

7.6.9. Electric power generation systems

Hydrogen has the lowest viscosity of all fluids, and hence is used to reduce friction in rotating armature in electrical power generation systems. Hydrogen also has the highest heat capacity, which makes it an ideal media for cooling. Hence, it is used for cooling power generators.

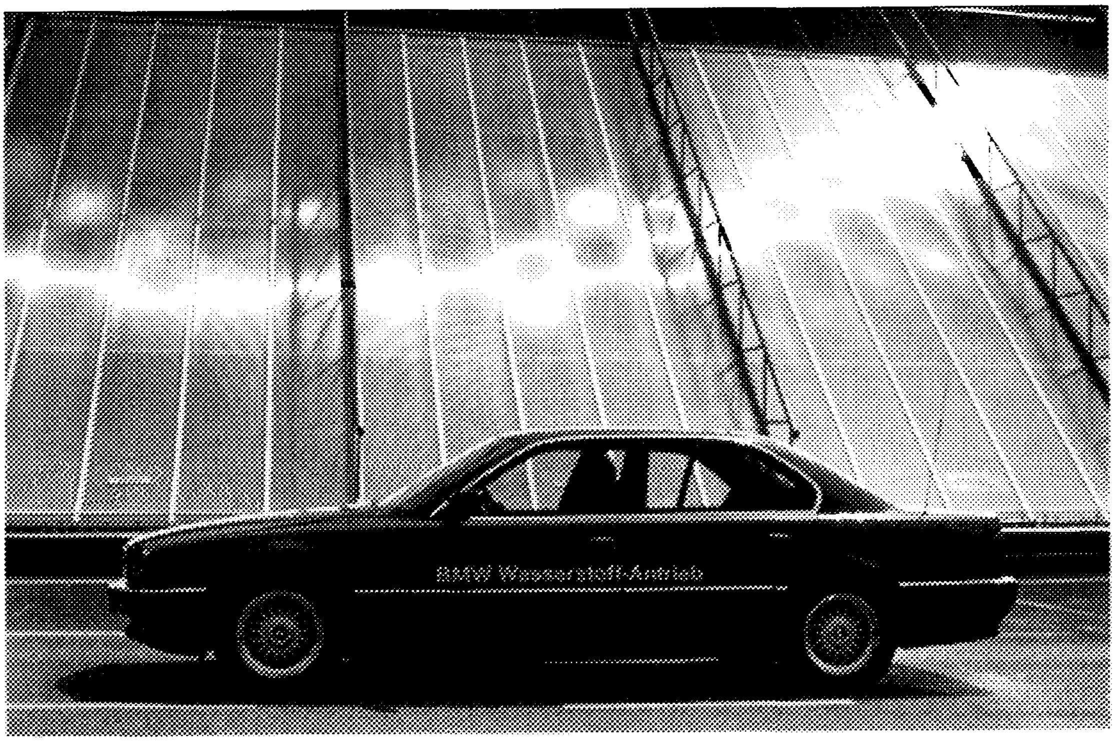

Figure 7.1: Hydrogen powered BMW automobile

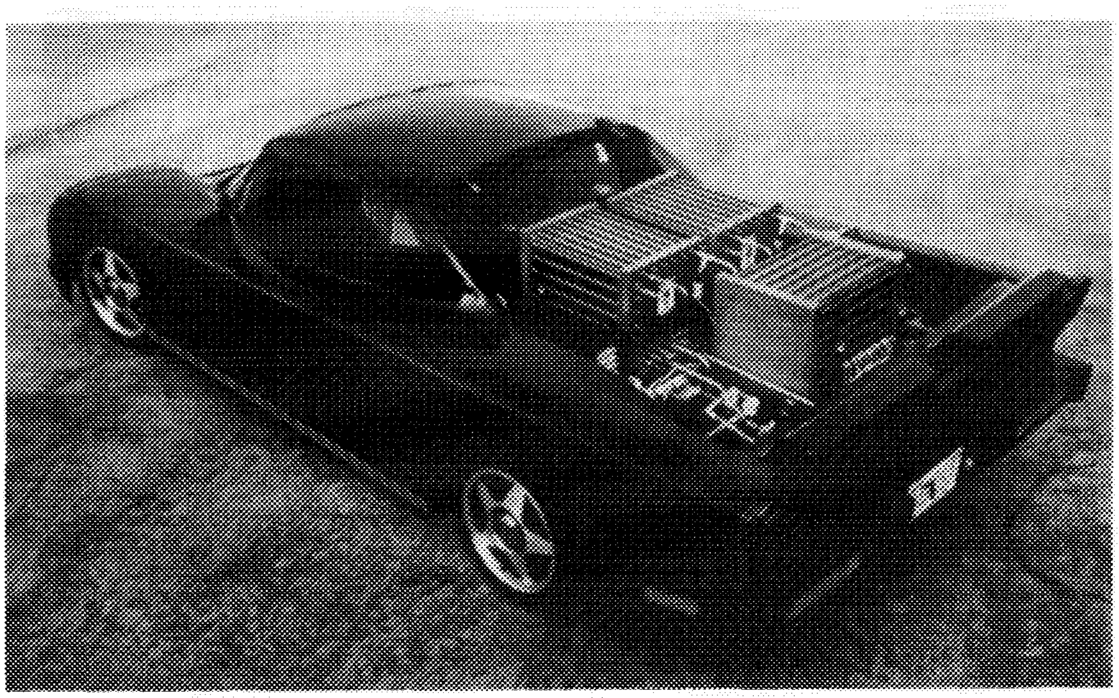

Figure 7.2: Energy Partners' fuel cell powered GreenCar

Figure 7.3: Daimler-Benz's fuel cell powered NECAR III prototype car

Figure 7.4: Daimler-Benz fuel cell bus (NEBUS) with compressed hydrogen storage

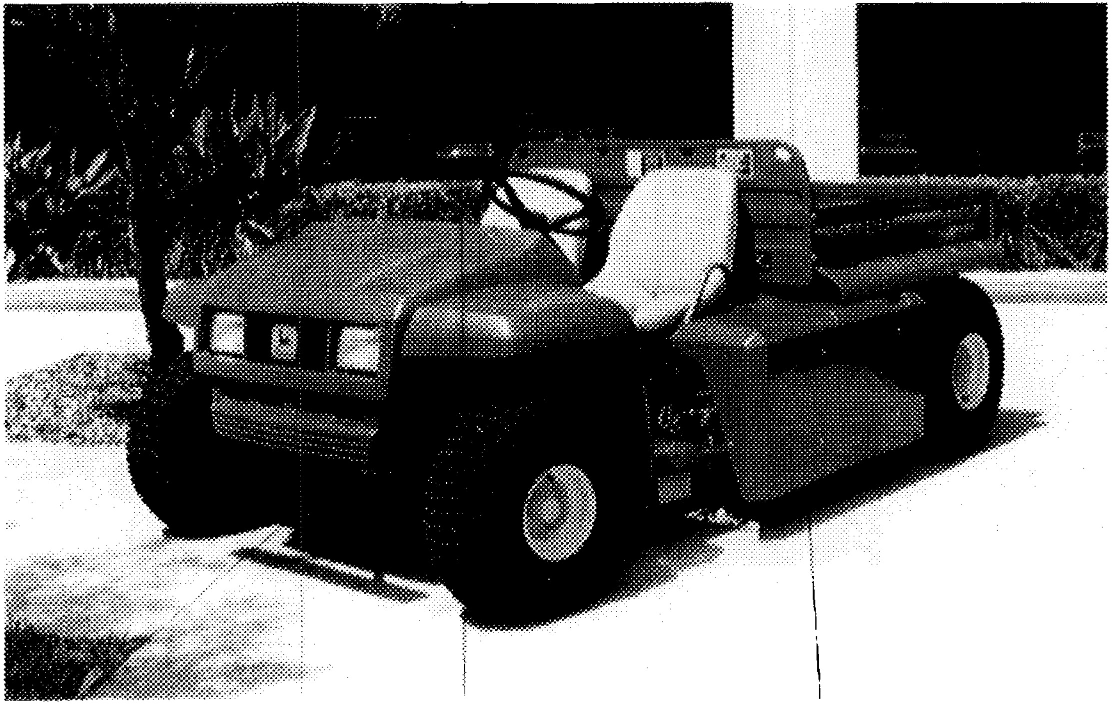

Figure 7.5: Fuel cell powered John Deere Gator (converted to fuel cells by Energy Partners)

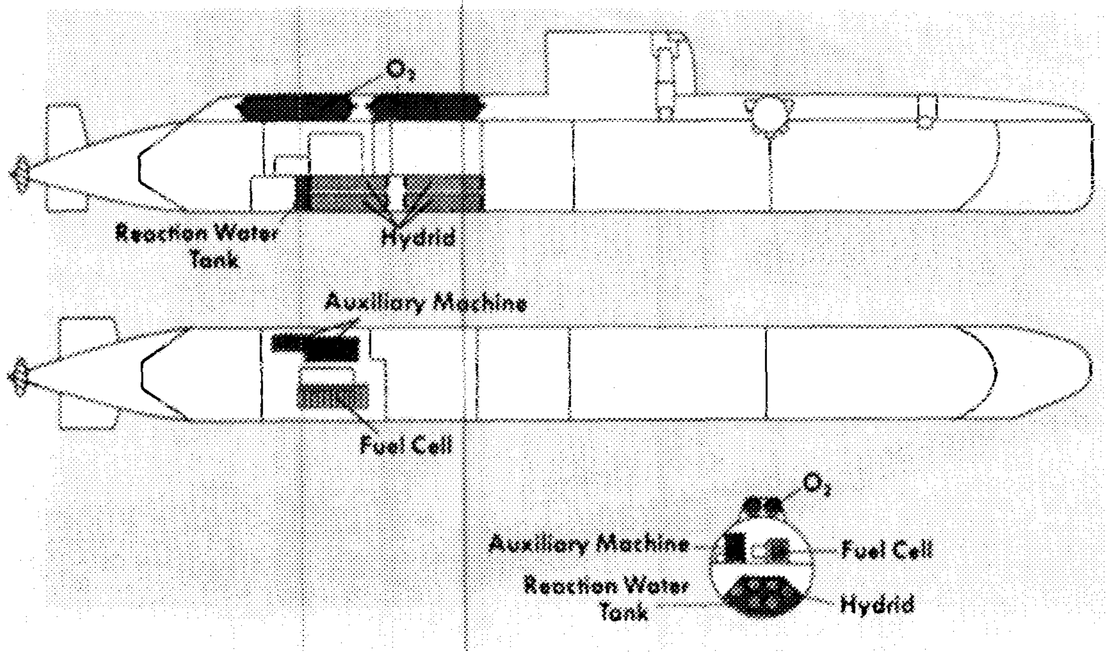

Figure 7.6: Conceptual design of a fuel cell powered submarine

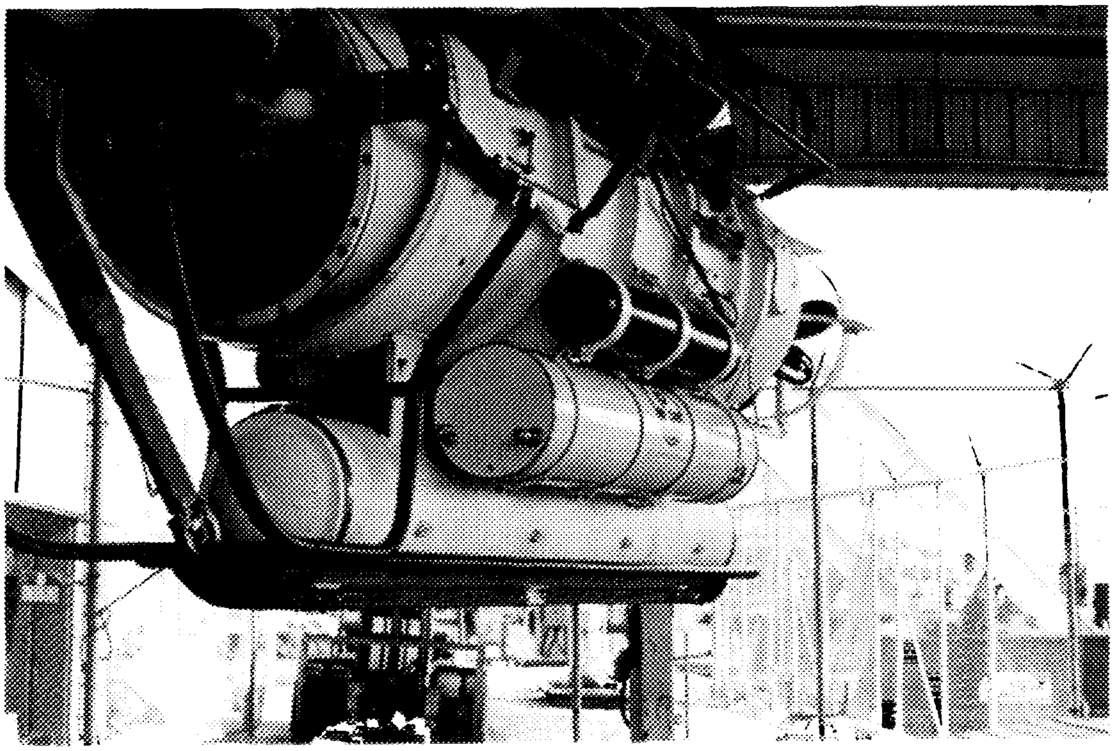

Figure 7.7: Fuel cell powered submarine built by Perry Technologies

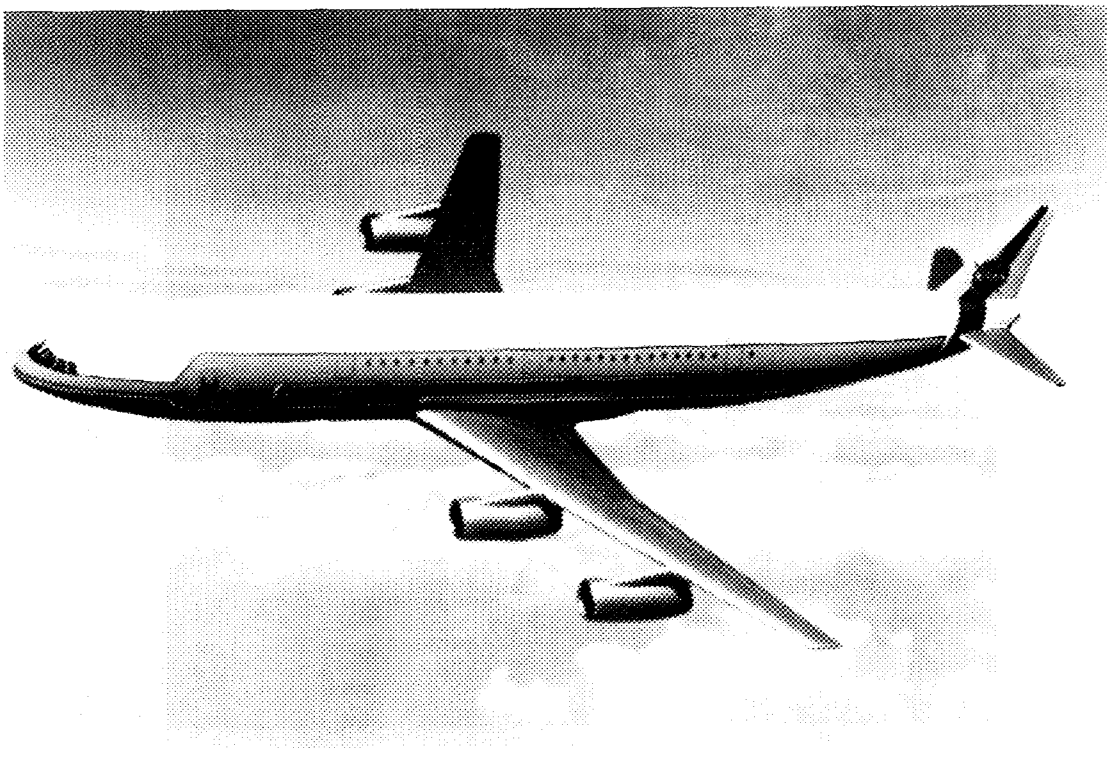

Figure 7.8: Liquid hydrogen powered concept airplane (Lockheed)

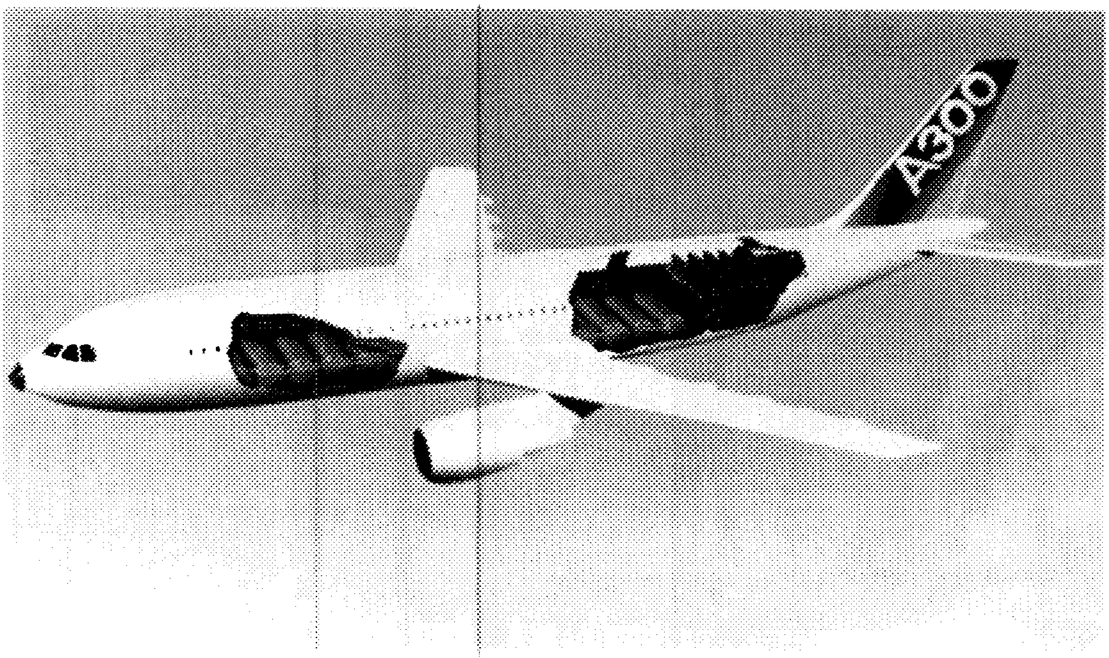

Figure 7.9: Liquid hydrogen powered concept airplane (Airbus)

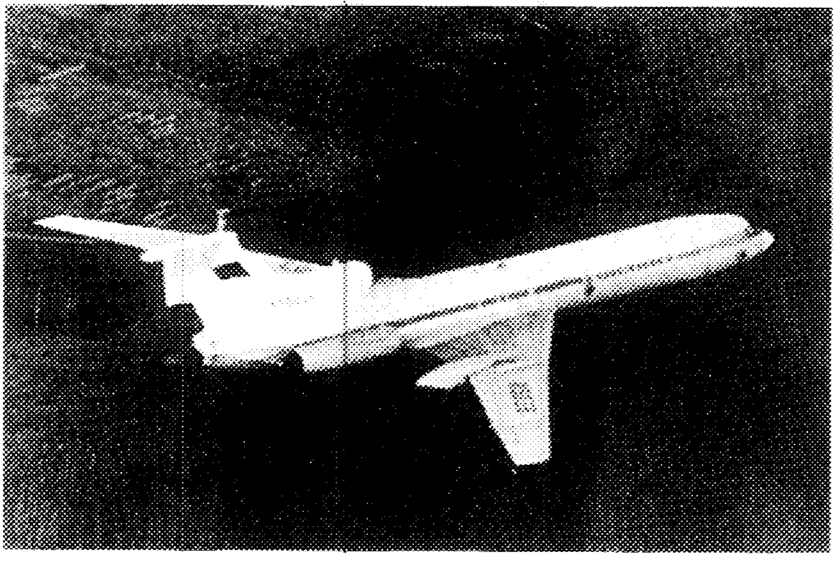

Figure 7.10 Tupolev 155 – first commercial aircraft flying on hydrogen fuel

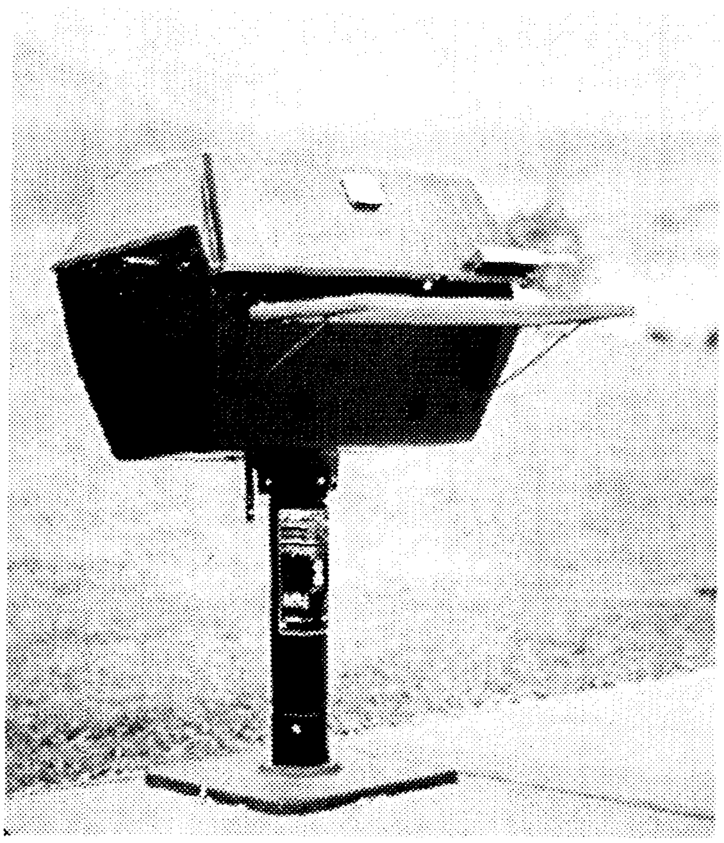

Figure 7.11: Hydrogen Bar-B-Que

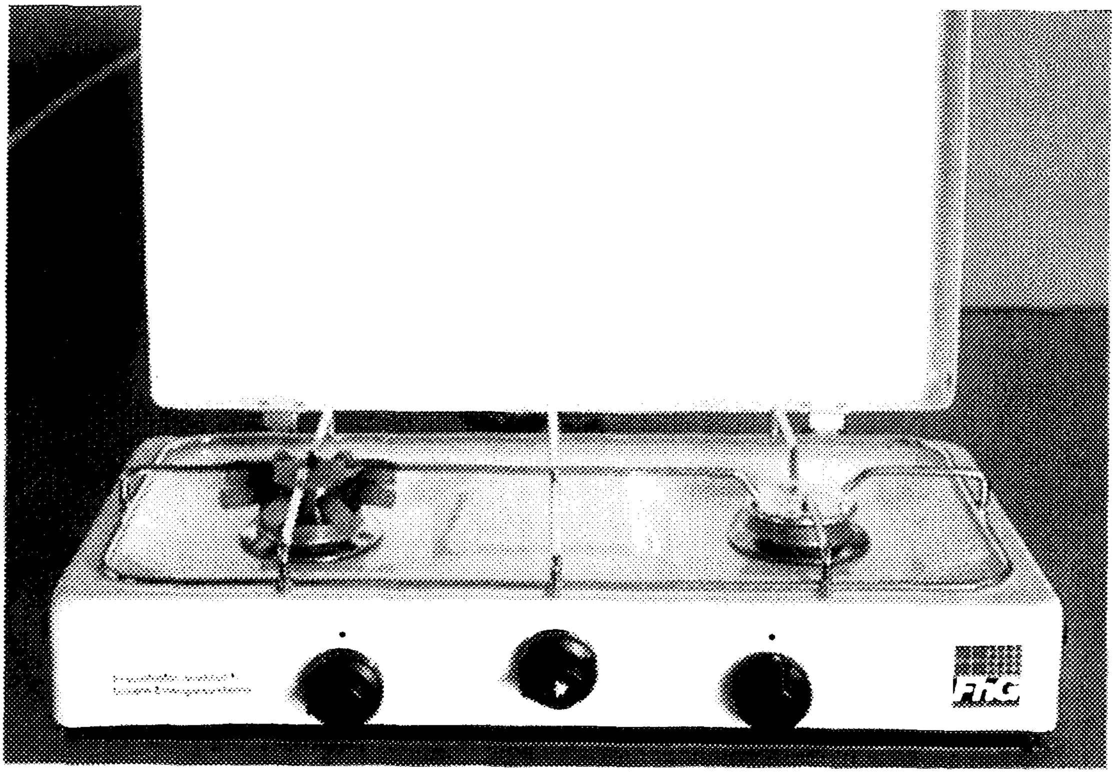

Figure 7.12: Cooking range with hydrogen catalytic heaters

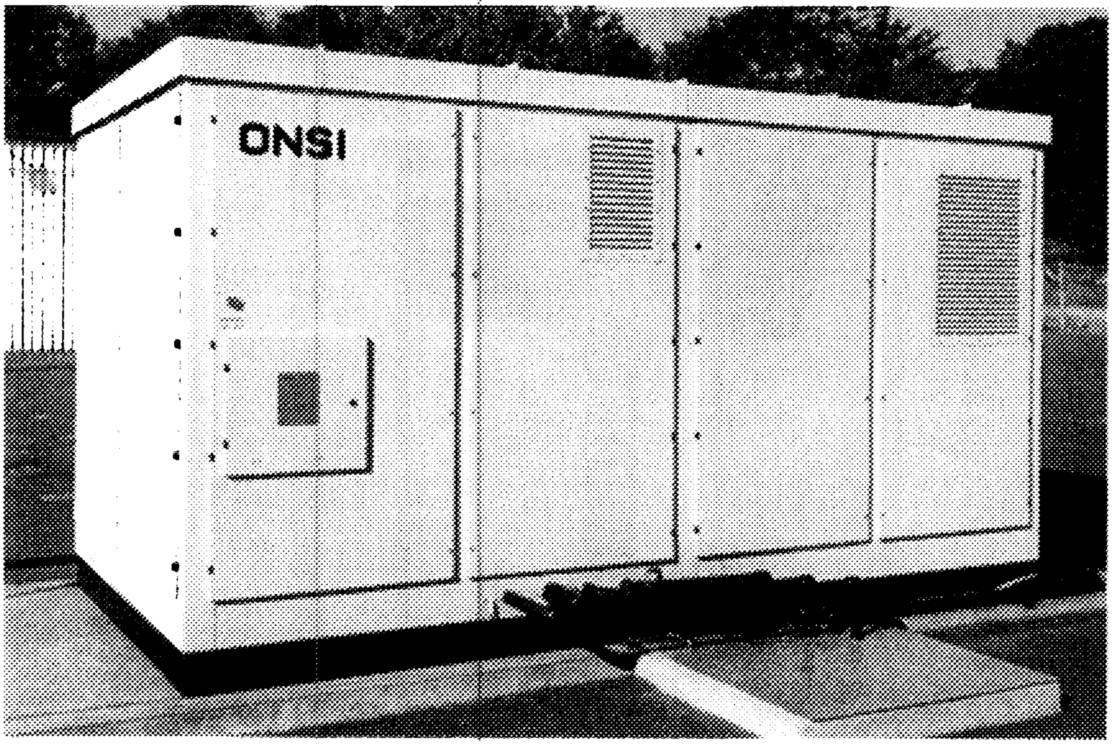

Figure 7.13: ONSI 25C 200 kW on-site PAFC power plant

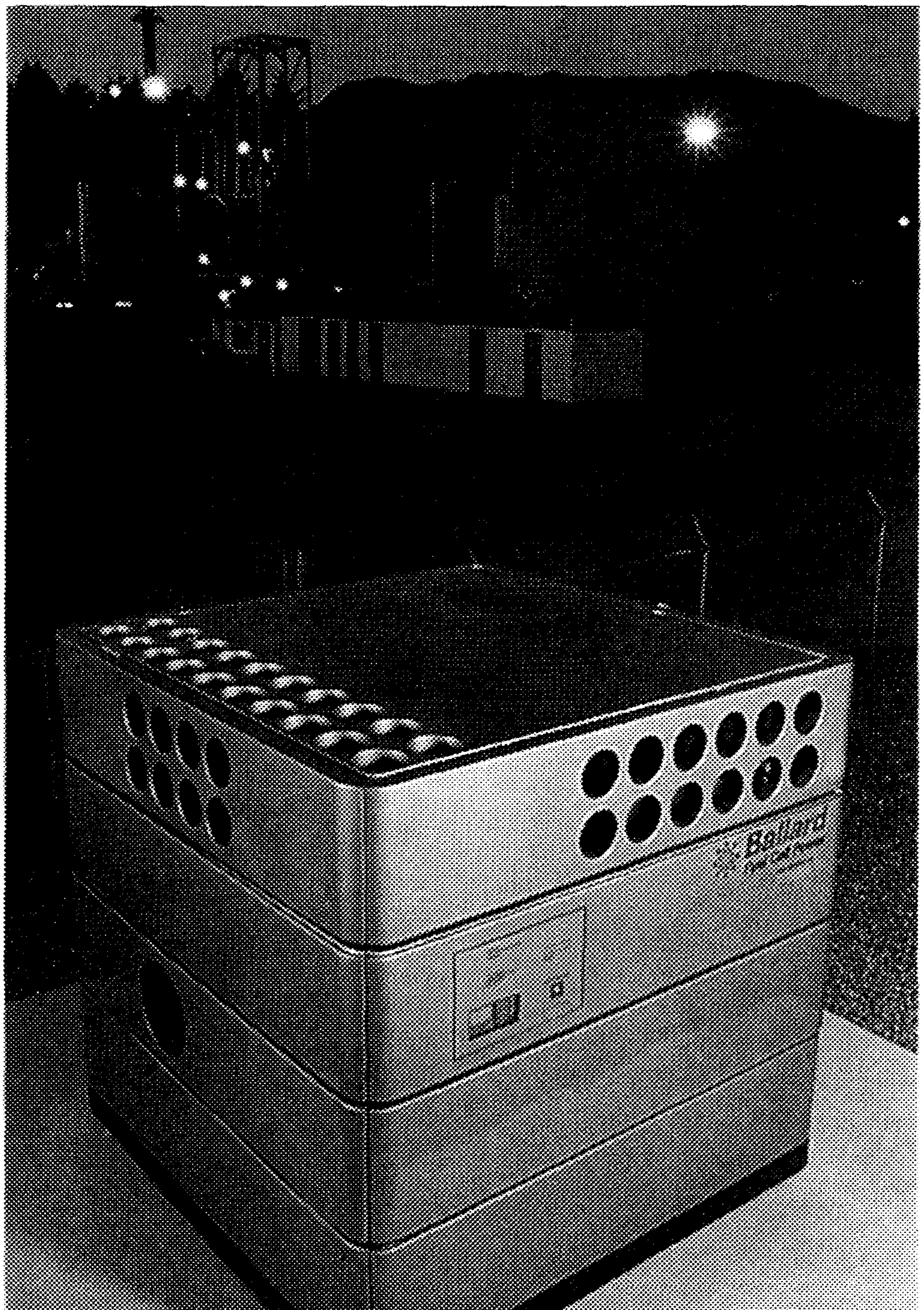

Figure 7.14: Ballard's 30 kW prototype stationary PEM fuel cell power plant

CHAPTER 8

SAFETY ASPECTS OF HYDROGEN USE

Like any other fuel or energy carrier, hydrogen poses risks if not properly handled or controlled. The risk of hydrogen, therefore, must be considered in relation to the common fuels such as gasoline, propane or natural gas. The specific physical characteristics of hydrogen are quite different from those common fuels. Some of those properties make hydrogen potentially less hazardous, while other hydrogen characteristics could theoretically make it more dangerous in certain situations.

Since hydrogen has the smallest molecule, it has a greater tendency to escape through small openings than do other liquid or gaseous fuels. Based on properties of hydrogen such as density, viscosity and diffusion coefficient in air, the propensity of hydrogen to leak through holes or joints of low pressure fuel lines may be only 1.26 to 2.8 times faster than a natural gas leak through the same hole (and not 3.8 times faster as is frequently assumed based solely on diffusion coefficients). Experiments have indicated that most leaks from residential natural gas lines are laminar [128]. Since natural gas has over three times the energy density per unit volume, the natural gas leak would result in more energy release than a hydrogen leak.

For very large leaks from high pressure storage tanks, the leak rate is limited by sonic velocity. Due to higher sonic velocity (1308 m/s), hydrogen would initially escape much faster than natural gas (sonic velocity of natural gas is 449 m/s). Again, since natural gas has more than three times the energy density than hydrogen, a natural gas leak will always contain more energy.

Some high strength steels are prone to hydrogen embrittlement. Prolonged exposure to hydrogen, particularly at high temperatures and pressures, can cause these steels to lose strength, eventually leading to failure. However, most other construction, tank and pipe materials are not prone to hydrogen embrittlement. Therefore, with proper a choice of materials, hydrogen embrittlement should not contribute to hydrogen safety risks.

If a leak should occur for whatever reason, hydrogen will disperse much faster than any other fuel, thus reducing the hazard levels. Hydrogen is both more buoyant and more diffusive than either gasoline, propane or natural gas. Table 8.1 compares some properties and leak rates for hydrogen and natural gas.

Hydrogen/air mixture can burn in relatively wide volume ratios, between 4 and 75 per cent of hydrogen in air. The other fuels have much lower flammability ranges, viz., natural gas 5.3 to 15 per cent, propane 2.1 to 10 per cent, and gasoline 1 to 7.8 per cent. However, the range has little practical value. In many actual leak situations the key parameter that determines if a leak would ignite is the lower flammability limit, and hydrogen's lower flammability limit is four times higher than that of gasoline, 1.9 times higher than that of propane, and slightly lower than that of natural gas.

Hydrogen has a very low ignition energy (0.02 mJ), about one order of magnitude lower than other fuels. The ignition energy is a function of fuel/air ratio, and for hydrogen it reaches a minimum at about 25 to 30 per cent. At the lower flammability limit hydrogen ignition energy is comparable to that of natural gas [109].

Hydrogen has a flame velocity seven times faster than that of natural gas or gasoline. A hydrogen flame would therefore be more likely to progress to a deflagration or even a detonation than other fuels. However, the likelihood of a detonation depends in a complex manner on the exact fuel/air ratio, the temperature and particularly the geometry of the confined space. Hydrogen detonation in the open atmosphere is highly unlikely.

The lower detonability fuel/air ratio for hydrogen is 13 to 18 per cent, which is two times higher than that of natural gas and 12 times higher than that of gasoline. Since the lower flammability limit is 4 per cent, an explosion is possible only under the most unusual scenarios, e.g., hydrogen would first have to accumulate and reach 13 per cent concentration in a closed space without ignition, and only then an ignition source would have to be triggered.

Should an explosion occur, hydrogen has the lowest explosive energy per unit stored energy in the fuel, and a given volume of hydrogen would have 22 times less explosive energy than the same volume filled with gasoline vapour.

Hydrogen flame is nearly invisible, which may be dangerous, because people in the vicinity of a hydrogen flame may not even know there is a fire. This may be remedied by adding some chemicals that will provide the necessary luminosity. The low emissivity of hydrogen flames means that near-by materials and people will be much less likely to ignite and/or be hurt by radiant heat transfer. The fumes and soot from a gasoline fire pose a risk to anyone inhaling the smoke, while hydrogen fires produce only water vapour (unless secondary materials begin to burn).

Liquid hydrogen presents another set of safety issues, such as risk of cold burns, and the increased duration of leaked cryogenic fuel. A large spill of liquid hydrogen has some characteristics of a gasoline spill, however it will dissipate much faster. Another potential danger is a violent explosion of a boiling liquid expanding vapour in case of a pressure relief valve failure.

In conclusion, hydrogen appears to poses risks of the same order of magnitude as other fuels. In spite of public perception, in many aspects hydrogen is actually a safer fuel than gasoline and natural gas. As a matter of fact, hydrogen has a very good safety record, as a constituent of the "town gas" widely used in Europe and USA in the 19th and early 20th centuries, as a commercially used industrial gas, and as a fuel in space programmes. There have been accidents, but nothing that would characterize hydrogen as more dangerous than other fuels.

One of the most remembered accident involving hydrogen is the Hindenburg dirigible disaster in 1937. However, hydrogen did not cause that accident and hydrogen fire did not directly cause any casualties. The accident appears to have been caused by static electricity discharge, and it was the balloon's lining that caught fire first [129]. Once the hydrogen with which the balloon was filled for buoyancy (instead of helium, as it was originally designed to be filled with) was ignited, it burned (as any fuel is supposed to). However, hydrogen fire went straight up and it did not radiate heat, so the people in the gondola underneath the balloon were not burned or suffocated. As a matter of fact, 56 survivors walked out of the gondola once it landed after all the hydrogen and balloon structure burned out. Therefore, even in a worst case scenario accident, hydrogen proved to be a safe fuel.

Table 8.1: Properties and leak rates of hydrogen and natural gas

	Hydrogen	Natural gas
Flow parameters		
Diffusion coef. (cm^2/s)	0.61	0.16
Viscosity (μ-poise)	87.5	100
Density (kg/m^3)	0.0838	0.651
Sonic velocity(m/s)	1308	449
Relative leak rates		
Diffusion	3.80	1
Laminar flow	1.23	1
Turbulent flow	2.83	1
Sonic flow	2.91	1

CHAPTER 9

HYDROGEN ENERGY STANDARDS

Development and particularly prospects, of hydrogen energy technologies have prompted the International Standards Organization (ISO) to begin working on international standards for hydrogen energy technologies [130]. International standards are needed to facilitate the economic and safe production, storage, transport and utilization of hydrogen as an environmentally compatible energy carrier and feedstock. To facilitate the implementation of internationally operable hydrogen distribution chains, storage infrastructure and fueling systems, the standardization of interfaces, safety requirements, product specifications, test procedures and measurement systems have to be created. In 1990, ISO formed a new technical committee, named TC-197 Hydrogen Energy. The work of this committee has been divided into subcommittees and working groups with the support of experts from industry, institutes and governments from around the world, and in liaison with the relevant organizations and other ISO Technical Committees.

ISO-TC 197 Committee presently has 28 member countries, with 12 countries having P (participating) status and 16 having O (observing) status. P status countries, which have voting rights, are Argentina, Canada, Egypt, France, Germany, Japan, Libya, Republic of Korea, Russian Federation, Sweden, Switzerland and the USA. The O status countries are Austria, Belgium, China, Czech Republic, Israel, Italy, Jamaica, Norway, Portugal, South Africa, Spain, Thailand, Turkey, Ukraine, United Kingdom and Yugoslavia. The Secretariat of the Committee is in Canada, with Professor Tapan K. Bose as Chairman and Ms. Danielle Allard as Secretary.

The Committee meets every year in order to prepare the international standards for hydrogen energy technologies. During the even years, the Committee meets in the same venue as the World Hydrogen Energy Conferences, either right before or right after the Conference. The Committee has already completed two standards for approval by ISO General Assembly. These are:

ISO/DIA 13984 Liquid Hydrogen – Land Vehicle Fueling System Interface

This international standard specifies the characteristics of liquid hydrogen refueling and dispensing systems on land vehicles of all types in order to provide a reasonable level of protection from loss of life and property resulting from fire and explosion.

This international standard is applicable to the design and installation of liquid hydrogen (LH_2) fueling and dispensing systems. It describes the system intended for the dispensing of liquid hydrogen to a vehicle, including that portion of it that handles the cold gaseous hydrogen coming from the vehicle tank, i.e., the system comprised between the tank container and the land vehicle.

ISO/DIS 14687 Hydrogen Fuel – Product Specification

This international standard specifies the quality characteristics of hydrogen fuel in order to assure uniformity in the final quality of the hydrogen product as produced and distributed for utilization in vehicular, appliance or other fueling applications.

This international standard applies to all modes of transportation and hydrogen fueling applications (ground, water, air and space).

CHAPTER 10

COMPARISON OF FUELS AND ENERGY SYSTEMS

10.1. Comparison of fuels

At the consumer end, about one-quarter of the primary energy is used as electricity and three-quarters as fuel. The primary energy sources must therefore be converted to these energy carriers needed by the consumer. In contrast with the fossil fuels, none of the new primary energy sources can directly be used as a fuel, e.g., for air transportation, land transportation. Consequently, they must be used to manufacture a fuel or fuels, as well as to generate electricity.

Since we need to manufacture a fuel for the post fossil fuel era, we are in a position to select the best possible fuel. There are many candidates, such as synthetic gasoline, synthetic natural gas (methane), methanol, ethanol and hydrogen. The fuel of choice must satisfy the following conditions:

- It must be convenient fuel for transportation
- It must be versatile or convert with ease to other energy forms at the user end
- It must have high utilization efficiency
- It must be safe to use.

In addition, the resulting energy system must be environmentally compatible and economical.

10.1.1. Transportation fuel

Surface vehicles and aircraft must carry their fuel for a certain distance before replenishing their fuel supplies. In the case of space transportation, the space vehicles must carry their fuel, as well as the oxidant, necessary for their scheduled range. Therefore, it is important that the transportation fuel be as light as possible and also take up as little space as possible. We can combine these requirements in a dimensionless number, termed the motivity factor [131]:

$$\phi_M = \frac{\left(\frac{E}{M}\right)\left(\frac{E}{V}\right)^{2/3}}{\left(\frac{E_h}{M_h}\right)\left(\frac{E_h}{V_h}\right)^{2/3}} \qquad (10.1)$$

where E is the energy generated by the fuel, M the mass of the fuel, V the volume of the fuel, and subscript h refers to hydrogen. The higher the motivity factor, the better the fuel for transportation. Table 10.1 lists the pertinent properties of some fuels, as well as the motivity factors calculated using Equation (1). It can be seen that among the liquid fuels LH_2 has the best motivity factor, while methanol has the lowest motivity factor. Among the gaseous fuels, GH_2 has the best motivity factor.

Consideration of the utilization efficiency advantage of hydrogen further improves hydrogen's standing as the best transportation fuel. Of course, this is one of the reasons why hydrogen is the fuel of choice for space programmes around the world, even though presently it is more expensive than fossil fuels.

10.1.2. Versatility

At the user end, all fuels must be converted through a process (such as combustion) to other forms of energy, e.g., thermal energy, mechanical energy and electrical energy. If a fuel can be converted through more than one process to various forms of energy at the user end, it becomes more versatile and more convenient to utilize. Table 10.2 lists various fuels and processes by which they can be converted to other forms of energy at the user end. It can be seen that all the fuels, except hydrogen, can be converted through one process only, that of combustion. Hydrogen, however, can be converted to other forms of energy in five different ways; i.e., in addition to flame combustion, it can be converted directly to steam, converted to heat through catalytic combustion, act as a heat source and/or heat sink through chemical reactions, and converted directly to electricity through electrochemical processes [81]. In other words, hydrogen is the most versatile fuel.

10.1.3. Utilization efficiency

In comparing the fuels, it is important to take into account the utilization efficiencies at the user end. For utilization by the user, fuels are converted to various energy forms, such as mechanical, electrical and thermal. Studies show that in almost every instance of utilization, hydrogen can be converted to the desired energy form more efficiently than other fuels [131].

Table 10.3 presents the utilization efficiency factors, defined as the fossil fuel utilization efficiency divided by the hydrogen utilization efficiency, for various applications. It can be seen that hydrogen is the most efficient fuel. This results in conservation of resources, in addition to conserving energy.

10.1.4. Safety

The safety aspects of fuels involve their toxicity on the one hand and the fire hazard properties on the other. In addition to the toxicity of their combustion products, the fuels themselves can be toxic. The toxicity increases as the carbon-to-hydrogen ratio increases. Hydrogen and its main combustion product, water or water vapour, are not toxic. However, No_x, which can be produced through the flame combustion of hydrogen (as well as through the combustion of fossil fuels) displays toxic effects.

Table 10.4 lists the characteristics of fuels related to fire hazards. Lower density makes a fuel safer, since it increases the buoyancy force for speedy dispersal of the fuel in case of a leak. For the same reason, higher diffusion coefficients are helpful. Higher specific heat causes a fuel to be safer, since it slows down the temperature increases for a given heat input. Wider ignition limits, lower ignition energies, and lower ignition temperatures make the fuels less safe, as they increase the limits in which a fire could commence. Higher flame temperature, higher explosion energy, and higher flame emissivity make a fuel less safe as well, since its fire would be more damaging.

Table 10.5 compares the safety of fuels. For each of the toxic element and fire hazard characteristics, it ranks the fuels from 1 to 3, 1 being the safest and 3 the least safe. These rankings have been summed up for each fuel in order to arrive at an overall ranking. The total rankings have been prorated to obtain the *safety factors*, defined as the ratio of the total ranking for hydrogen to that of a given fuel. It can be seen that hydrogen becomes the safest fuel, while gasoline is the least safe, methane being in between the two.

10.1.5. The best fuel

When we look at the fuel options critically under the criteria given above, it becomes clear that hydrogen is the best transportation fuel, the most versatile fuel, the most efficient fuel and the safest fuel. In summary, hydrogen is the best fuel.

As a result of the above discussion, it becomes clear that it would be expedient to manufacture hydrogen using any and all primary energy sources, in order to make up for their shortcomings. Such an energy system is then called the "Hydrogen Energy System."

10.2. Competing energy systems

Essentially, there are three contending energy systems: (1) the present fossil fuel system, (2) the coal/synthetic fossil fuel system, and (3) the solar hydrogen energy system, which is a special case of the hydrogen energy system.

10.2.1. Fossil fuel system

A simplified version of today's energy system is shown in Figure 10.1. Fossil fuels are used for transportation (mostly petroleum products), for heat generation in residential, commercial and industrial sectors, and for electric power generation. For transportation, mostly petroleum products are used (gasoline, diesel fuel, jet fuel, etc.). Heat generation includes space heating, domestic water heating, cooking, steam generation and direct heating and/or drying in various industrial processes. All three forms of fossil fuels are used for these purposes. In electric power generation, coal is used mainly for the base load generation, and natural gas and heating oil are used for peak load. Part of the electric power is produced by hydro and nuclear power.

In comparison to other energy systems, it can be assumed that 40 per cent of primary energy (in fossil fuel equivalent units) will be used for thermal energy generation, 30 per cent for electric power generation, and 30 per cent for transportation (two-thirds for surface transportation and one third for air transportation) [40]. Energy supplied by hydro and nuclear power plants (mostly in the form of electric power) and by other non-fossil fuel sources do not have to be taken into account, since it is assumed that it will be the same for all three considered systems. Actually, it is reasonable to expect that in future, even more electrical energy will be supplied by these sources.

When one considers the early 2000's, it can be expected that about one half of the thermal energy will be supplied by natural gas, and the rest by petroleum fuels (fuel oil and residual oil) and coal. Coal is assumed to be the main energy source for electricity generation, gasoline for surface transportation and jet fuel for air transportation. This is of course a simplified version of the fossil fuel energy system, but it is close enough to the present patterns of energy consumption, and can be used as the basis for comparisons.

10.2.2. Coal/synthetic fossil fuel system

Since coal reserves are much larger than the reserves of oil and natural gas, coal could eventually be used to produce synthetic liquid fuels, allowing society to continue employing the present energy system. Such a system is called the coal/synthetic fossil fuel system, since coal is to be used to manufacture synthetic fossil fuels, as well as to be directly used for electricity generation.

In this case, it can be assumed that the present fossil fuel system will be continued by substitution with synthetic fuels derived from coal wherever convenient and/or necessary. Patterns of energy consumption are also assumed to be unchanged (see Figure 10.2). Coal will be used extensively for thermal power generation and for electric power generation, because it is much cheaper than synthetic fuels. However, some end-uses require fluid fuels. Therefore, it has been assumed that synthetic natural gas (SNG) will be used for some thermal energy generation (primarily in the residential sector) and also as fuel for surface transportation, where it will share the market with synthetic gasoline. Synthetic jet fuel will be used in air transportation.

10.2.3. Solar hydrogen energy system

If solar energy, in its direct and/or indirect forms (e.g., hydro, wind, etc.), is used to manufacture hydrogen, then the resulting system is called a "solar hydrogen energy system". In this system, both the primary and secondary energy sources are renewable and environmentally compatible, resulting in a clean and permanent energy system. Figure 10.3 presents a schematic of the solar hydrogen energy system.

In this case, it is assumed that the conversion to hydrogen energy will take place, and one-third of hydrogen needed will be produced from hydro-power (and/or wind power) and two-thirds by direct and indirect (other than hydro-power) solar energy forms. The same percentage of energy demand sectors as the above systems will be assumed. It will further be assumed that one half of the thermal energy will be achieved by flame combustion, one quarter by steam generation with hydrogen/oxygen steam generators and the last quarter by catalytic combustion; electric power will be generated by fuel cells; one-half of the surface transportation will use gaseous hydrogen burning internal combustion engines and the other half will use fuel cells. In air transportation, both subsonic and supersonic, liquid hydrogen will be used.

10.3. Comparison of environmental effects

10.3.1. Pollution

Table 10.6 lists the pollutants for the three energy systems described. It can be seen that the coal/synthetic fossil system is the worst from the environmental point of view, while the solar-hydrogen energy system is the best. The solar-hydrogen system will not produce any CO_2, CO, SO_x, hydrocarbons or particulates, except some NO_x. However, the solar-hydrogen-produced NO_x is much less than those produced by the other energy systems. This is due to the fact that in the solar hydrogen energy system only the flame combustion of hydrogen in air will generate NO_x. The other utilization processes (such as direct steam generation, use of hydrogen in fuel cells, hydriding processes, etc.) will not produce any NO_x.

10.3.2. Vapour generation

There is a notion that the hydrogen energy system would produce more water vapour than the other energy systems, since the fuel is pure hydrogen. When one considers the problem in detail, this is not so.

Only the flame combustion of fuels in air or in oxygen will produce water vapour. In the case of hydrogen the other processes mentioned earlier (see Chapter 6) will not produce any water vapour. Consequently, and contrary to popular belief, the solar-hydrogen energy system will produce less water vapour than the other systems.

Global warming, which is caused by the utilization of fossil fuels, also causes an increase in water vapour generation. Assuming that the Earth's mean temperature has increased by 0.5°C since the beginning of the Industrial Revolution [132], this additional water vapour generation and that produced by the combustion of fuels have been calculated. The results are presented in Table 10.7. It can be seen that (1) the two fossil fuel systems generate much more additional (above natural) water vapour than the solar hydrogen energy system; (2) the additional water vapor generated by global warming is much greater than that produced by the combustion of fuels; (3) the amount of water vapour generated by fuels is minimal compared to that generated naturally; and (4) the solar hydrogen system causes the smallest increase in vapour generation. Again, when the additional vapour generation is considered, the solar hydrogen system becomes environmentally the most compatible system.

10.3.3. Environmental damage

Table 10.8 presents the environmental damage per GJ of the energy consumed for each of the three energy systems considered (derived from [4]), and also for their fuel components in 1998 US dollars, as well as environmental compatibility factors, defined as the ratio of the environmental damage due to the hydrogen-energy system to that due to a given energy system. The environmental damage for the solar-hydrogen energy system is due to the NO_x produced. It can be seen that the solar-hydrogen energy system is environmentally the most compatible system.

It should be mentioned that hydrogen also has the answer to the depletion of the ozone layer, mainly caused by chlorofluorocarbons. Refrigeration and air-conditioning systems based on the hydriding property of hydrogen do not need chlorofluorocarbons, but use hydrogen, and any hydrogen leak would not cause ozone layer depletion. Such refrigeration systems are also very quiet, since they do not have any moving machinery.

10. 4. Economic comparison of competing energy systems

The economical comparison between competing energy systems should be based on the effective costs of the services these fuels provide. The effective costs include the utilization efficiency, the cost of the fuel, and the costs associated with fuel consumption but which are not included in its price (so-called external costs). External costs include the costs of the physical damage done to humans, fauna, flora and the environment due to harmful emissions, oil spills and leaks, and coal strip mining, as well as governmental expenditures for pollution abatement and expenditures for military protection of oil supplies.

In economic considerations, it is also important to compare the future costs of hydrogen (which will be considerably lower than they are today because of the assumed market and technology development) with the future costs, both internal and external, of fossil fuels (which will unavoidably be higher than today's prices due to depletion, international conflicts, and environmental impact).

The effective cost of a fuel can be calculated using the following relationship:

$$C_r = (C_i + C_e)\,\frac{\eta_{fk}}{\eta_{sk}} \qquad (10.2)$$

where C_i is the internal cost or the conventional cost of the fuel, C_e the external cost including the environmental damage caused by the fuel, η_{fk} the fossil fuel utilization efficiency for application k, and η_{sk} the synthetic fuel (including hydrogen) utilization efficiency for the same application or the end use.

In order to evaluate the overall cost (C_0) to society, the three scenarios considered earlier will be used. This cost can be calculated from the relationship

$$C_0 = \sum_{n=1}^{n} \alpha_n C_m \qquad (10.3)$$

where α_n is the fraction of energy used by the energy sector n, such as electricity generating, heat producing, surface transportation, subsonic air transportation, and supersonic air transportation. Since α_n is a fraction, their sum is

$$\sum_{n=1}^{n} \alpha_n = 1 \qquad (10.4)$$

Substituting Eq. (2) into Eq. (3), one obtains

$$C_0 = \sum_{n=1}^{n} \alpha \left[\left(C_i + C_e\right) \frac{\eta_{fk}}{\eta_{sk}} \right]_n \qquad (10.5)$$

Using Eqs. (10.2)-(10.5), Tables 10.9-10.11 have been prepared for the three energy scenarios, i.e., the fossil fuel system, the coal/synthetic fossil fuel system, and the solar hydrogen energy system in 1998 US dollars. Comparing the results, it becomes clear that the solar hydrogen energy system is the most cost-effective energy system, and results in the lowest overall effective cost to the society.

Table 10.1. Energy densities (HHV) and motivity factors for liquid and gaseous fuels

Fuel	Chemical Formula	Energy per unit mass $\left(\frac{E}{M}\right)$ J/kg	Energy per unit volume $\left(\frac{E}{V}\right)$ J/m	Motivity Factor ϕ_M
Liquid Fuels				
Fuel oil	$C_{\leq 20}H_{\leq 42}$	45.5	38.65	0.78
Gasoline	$C_{5-10}H_{12-22}$	47.4	34.85	0.76
Jet fuel	$C_{10-15}H_{22-32}$	46.5	35.30	0.75
LPG	$C_{3-4}H_{8-10}$	48.8	24.40	0.62
LNG	$\sim CH_4$	50.0	23.00	0.61
Methanol	CH_3OH	22.3	18.10	0.23
Ethanol	C_2H_5OH	29.9	23.60	0.37
LH_2	H_2	141.9	10.10	1.00
Gaseous Fuels				
Natural gas	$\sim CH_4$	50.0	0.040	0.75
GH_2	H_2	141.9	0.013	1.00

Table 10.2. Versatility (convertibility) of fuels

Conversion Process	**Hydrogen**	**Fossil Fuels**
Flame Combustion	Yes	Yes
Direct Steam Production	Yes	No
Catalytic Combustion	Yes	Yes*/No
Chemical Conversion (Hydriding)	Yes	No
Electrochemical Conversion (Fuel Cells)	Yes	Yes*/No

*Natural gas only

Table 10.3. Utilization efficiency comparisons of fossil fuels and hydrogen

Application	Utilization Efficiency Factor $\phi_U = \eta_F/\eta_H$
Thermal Energy	
Flame Combustion	1.00
Catalytic Combustion	0.80
Steam Generation	0.80
Electric Power, Fuel Cells	0.54
Surface Transportation	
Internal Combustion Engines	0.82
Fuel Cells/Electric Motor	0.40
Subsonic Jet Transportation	0.84
Supersonic Jet Transportation	0.72
Weighted Average	0.72
Hydrogen Utilization Efficiency Factor	1.00
Fossil Fuel Utilization Efficiency Factor	0.72

Table 10.4. Characteristics related to fire hazard of fuels

Property	Gasoline	Methane	Hydrogen
Density[a] (kg/m^3)	4.40	0.65	0.084
Diffusion Coefficient in Air[a] (cm^2/sec)	0.05	0.16	0.610
Specific Heat at Constant Pressure[a] (J/g K)	1.20	2.22	14.89
Ignition Limits in Air (vol %)	1.0 - 7.6	5.3 - 15.0	4.0 - 75.0
Ignition Energy in Air (mJ)	0.24	0.29	0.02
Ignition Temperature (°C)	228 - 471	540	585
Flame Temperature in Air (°C)	2197	1875	2045
Explosion Energy[b] (g TNT/kJ)	0.25	0.19	0.17
Flame Emissivity (%)	34 - 43	25 - 33	17 - 25

[a] At normal temperature and pressure.

[b] Theoretical maximum; actual 10 per cent of theoretical.

Table 10.5. Safety ranking of fuels

Characteristic	Fuel Ranking[a]		
	Gasoline	Methane	Hydrogen
Toxicity of Fuel	3	2	1
Toxicity of Combustion (CO, SO_x, NO_x, HC, PM)	3	2	1
Density	3	2	1
Diffusion Coefficient	3	2	1
Specific Heat	3	2	1
Ignition Limit	1	2	3
Ignition Energy	2	1	3
Ignition Temperature	3	2	1
Flame Temperature	3	1	2
Explosion Energy	3	2	1
Flame Emissivity	3	2	1
TOTALS	30	20	16
Safety Factor ϕ_s	0.53	0.80	1.00

[a] 1, safest; 2, less safe; 3, least safe.

Table 10.6. Pollutants produced by three energy systems

Pollutant	Fossil Fuel System (kg/GJ)	Coal/Synthetic Fossil System (kg/GJ)	Solar-Hydrogen System (kg/GJ)
CO_2	72.40	100.00	0
CO	0.80	0.65	0
SO_2	0.38	0.50	0
NO_x	0.34	0.32	0.10
HC	0.20	0.12	0
PM*	0.09	0.14	0

* Particulate Matter.

Table 10.7. Comparison of vapour generation by three energy systems (for 1998 energy consumption)

Item	Unit	Fossil Fuel System	Coal/Synthetic Fossil System	Solar-Hydrogen System
Annual Vapor Generation by Energy System	10^{12} kg	8.9	9.3	6.0
Annual Vapor Generation due to Global Warming	10^{12} kg	3,900	3,900	0
Total Vapor Generation due to Energy System and Global Warming	10^{12} kg	3,909	3,909	6.0
Total Vapor Generation as Fraction of that Produced Naturally	%	0.782	0.782	0.001

Note: Annual vapor generation due to solar heating is 5 X 10^{17} kg.

Table 10.8. Environmental damage and environmental compatibility factors

Energy System and Fuel	Environmental Damage (1998 $/GJ)	Environmental Compatibility Factor, ϕ_E
Fossil Fuel System	12.47	0.055
Coal	14.51	
Oil	12.52	
Natural Gas	8.26	
Coal/Synthetic Fossil System	15.46	0.044
Syn-Gas	20.34	
SNG	13.49	
Solar-Hydrogen Energy System	0.68	1.000
Hydrogen	0.68	

Table 10.9. Effective cost off fossil fuel system

Application	Fuel	Energy Consumption Fraction	Effective Cost (1998 U.S. $/GJ)
Thermal Energy	Natural Gas Petroleum Fuels Coal	0.20 0.10 0.10	17.46 27.56* 17.75
Electric Power	Coal	0.30	17.25
Surface Transportation	Gasoline	0.20	31.61
Air Transportation	Jet Fuel	0.10	25.98
TOTAL OF FRACTIONS		1.00	
OVERALL EFFECTIVE COST			22.11

* Average for residential and industrial sector.

Table 10.10. Effective cost of coal/synthetic fuel system

Application	Fuel	Energy Consumption Factor	Effective Cost (1998 U.S.$/GJ)
Thermal Energy	Coal SNG	0.30 0.10	17.75 36.64
Electric Power	Coal	0.30	17.25
Surface Transportation	SNG Syn-gasoline	0.10 0.10	36.64 51.65
Air Transportation	Syn-jet	0.10	45.45
TOTAL OF FRACTIONS		1.00	
OVERALL EFFECTIVE COST			27.55

Table 10.11. Effective cost of solar-hydrogen energy system

Application	Fuel[a]	Energy Consumption Factor	Effective Cost (1998 US$/GJ)
Thermal Energy			
Flame Combustion	GH_2	0.20	26.04
Steam Generation	GH_2	0.10	20.83
Catalytic Combustion	GH_2	0.10	20.83
Electric Power			
Fuel Cells	GH_2	0.30	14.06
Surface Transportation			
IC Engines	GH_2	0.10	21.36
Fuel Cells	GH_2	0.10	10.41
Air Transportation			
Subsonic	LH_2	0.05	26.26
Supersonic	LH_2	0.05	22.51
TOTAL OF FRACTIONS		1.00	
OVERALL EFFECTIVE COST			19.23

[a] It has been assumed that one third of hydrogen will be produced from hydro-power and/or windpower, and tho thirds from solar.

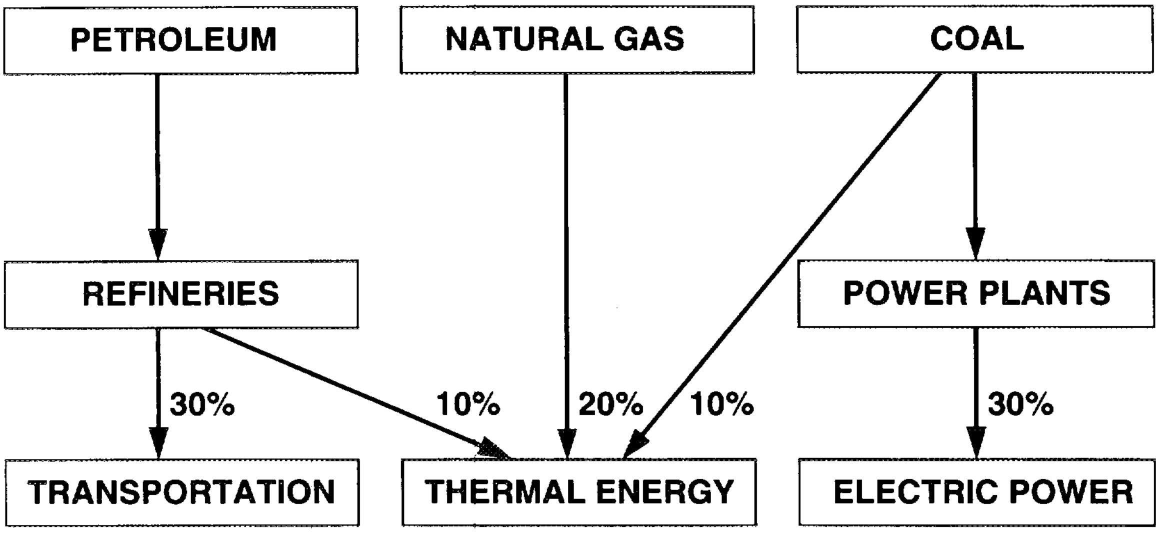

Figure 10.1. Fossil fuel system

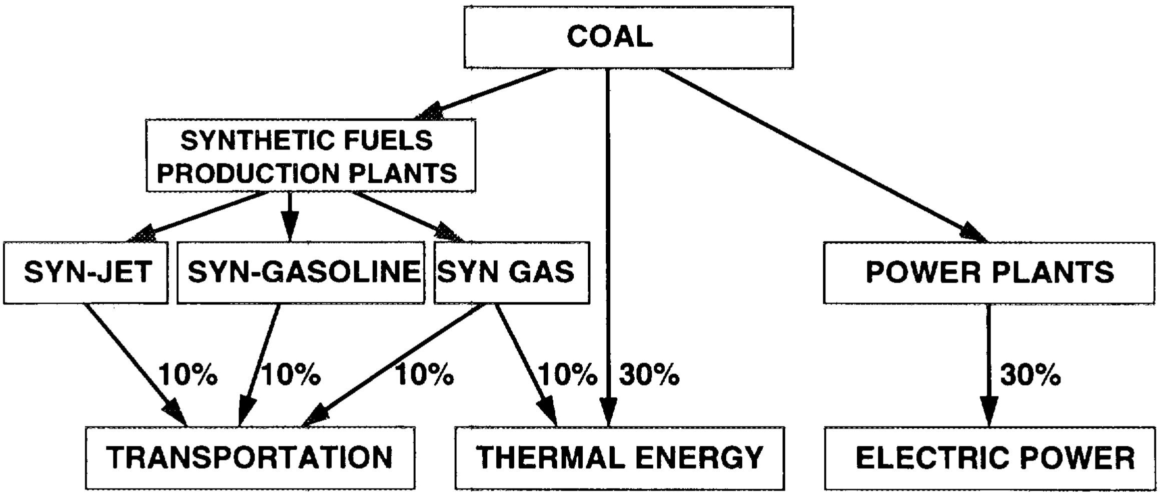

Figure 10.2. Coal/synthetic fossil fuel system

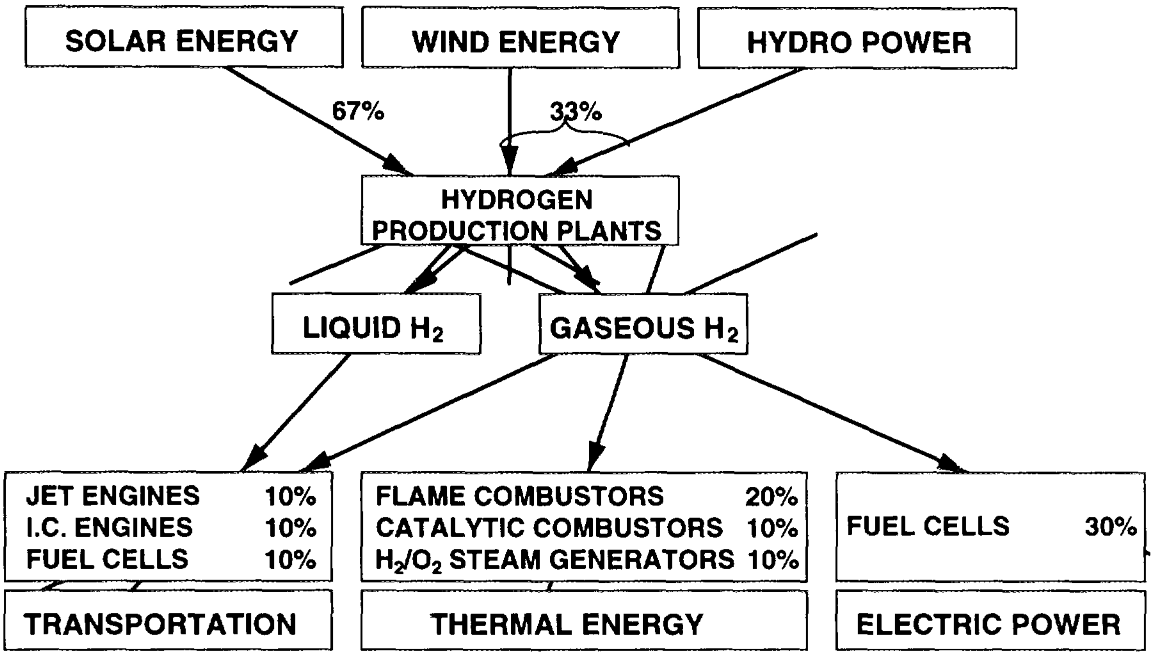

Figure 10.3. Solar-hydrogen energy system

CHAPTER 11

TRANSITION TO HYDROGEN ENERGY SYSTEM

As shown in the previous chapters, the hydrogen energy system has numerous advantages over the existing fossil fuel system. However, replacement of a global energy system will not and cannot happen overnight. There is an enormous capital tied in the existing energy system. Building another energy system that would compete with the existing one is out of the question. The new energy system must gradually replace the existing one. Since businesses are too often concerned with short-term profits, governments and international organizations must realize the long-term benefits of the hydrogen energy system and support the transition both legislatively and financially. Introduction of "real economics" and elimination of subsidies for the existing energy system would help in that transition. The term "real economics" refers to the economics that takes into account past, present and future environmental damage, depletion of environmental resources, military expenses for keeping energy sources accessible and other hidden external costs.

The most difficult would be the initial penetration of hydrogen energy technologies into the existing energy markets. As any new technology, hydrogen energy technologies are in most cases initially more expensive than the existing mature technologies, even when real economics is applied. Hydrogen and hydrogen energy technologies are expensive because neither hydrogen, nor equipment for hydrogen production and utilization are mass produced. They are not mass produced because there is no demand for them, and there is no demand because they are expensive. This is a vicious circle, and the only way for hydrogen energy technologies to penetrate into the major energy markets is to start with those technologies that may have niche markets, and penetrate them with or without governmental or international subsidies. Once developed, these technologies may help reduce the cost of other related hydrogen technologies and initiate and accelerate their market penetrations.

Another major difficulty is interrelation and interdependence between the hydrogen technologies. For example, it will be impossible to introduce hydrogen powered automobiles or hydrogen powered airplanes into the market without reliable and economically feasible technologies for hydrogen production, distribution, storage and refueling. On the other side, significant development of hydrogen production, distribution and storage technologies will never take place without a large demand for inexpensive hydrogen.

Ever growing energy related environmental problems and depletion of fluid fossil fuels (oil and natural gas) will eventually accelerate introduction of the new energy system. Various modelling studies, such as those conducted by a MIT team, presented in a popular book *Limits to Growth* in the early 1970s [133] and its sequel *Beyond the Limits* in the early 1990s [134], indicate that the global economy will peak some time in the first half of the next century, and after that continue to decline. The main reasons for that would be environmental stress and depletion of natural resources (including fluid fossil fuels). A modeling study conducted at University of Miami [135] has come up with similar results, although using a different method. Both studies, however, concluded that it would be possible to reverse the negative trends by timely introduction of clean, new technologies that will ease, and actually reverse the burden on the environment, and that will not depend on exhaustible natural resources. While the MIT study was not specific about those technologies, the University of Miami researchers have identified hydrogen energy technologies as a solution to global economic and environmental problems. The study indicated that the timing and the rate of introduction of the new energy system may be critical. As shown in Figures 11.1, 11.2 and 11.3, early introduction of the hydrogen energy system will have beneficial effects on both global economy and environment. If transition starts when economy begins to decline, it may be too late to reverse the trend, because economy would not be able to afford investing in such a long term project as establishing the new energy system. Winter intuitively feared that the point of transition to hydrogen and solar energy if missed or delayed could be another "lost moment in history" [43].

Historically, in the context of a longer time span, the fossil fuels era could be considered as a short interlude between the solar past and the solar future. In that short period (about three hundred years), the fossil fuels made possible a tremendous development of human civilization. However, if they are used to support the establishment of a permanent energy system, such as the solar hydrogen energy system, they could be considered as a spark which provided a transition from the low level solar energy past to the higher level solar energy future. Solar energy is steadily available in a quantity which exceeds human needs by several orders of magnitude.

Although all economic models are based on growth, it is clear that no system based on finite sources can continue to grow forever. A system based on the utilization of a constant flow of incoming energy (such as solar energy) will eventually reach a steady state. A steady state economy is defined as an economy with constant stocks of people and artifacts, maintained at some sufficient levels by the lowest feasible flows of matter and energy. If economic development means getting more services per unit of throughput, and economic growth is defined as the increase of services by increasing the size of stocks, then it is clear that the steady state economy would force an end to pure growth, but would not curtail, and in fact would stimulate development [136]. The steady-state level which the human civilization can obtain, depends on the rate of utilization of available solar energy and the effort required to convert solar energy into more useful forms of energy. Fortunately, our civilization is not running out of renewable energy resources in an absolute sense, nor is it lacking technological options for transforming these resources into particular forms that our patterns of energy use require. What is lacking is the commitment and money needed to develop long-term energy alternatives, the perceptiveness to embrace energy efficiency on the scale demanded, and the consensus needed to fashion any coherent strategy at all.

Hydrogen Energy System is a coherent, comprehensive and permanent solution to the global energy-economic-environmental problems, and as such deserves support from individual governments and industrial organizations. Hydrogen energy technologies are particularly interesting for those developing countries that do not have huge energy infrastructures in place. These countries do not have to follow the industrialization path of the developed countries by building huge power plants, power transmission lines, pipelines, transportation infrastructure, energy intensive industries, etc., and creating environmental problems associated with such development. Development of an energy infrastructure for an energy system that will not last long anyway, does not make much sense. Instead those countries may adopt a "softer" path by relying more on dispersed renewable energy sources and both traditional and advanced technologies for their utilization. Introduction of modular and portable fuel cell power systems seems to be a viable alternative. Although initially these new technologies may be more expensive, in the long run they are definitely beneficial to both the economy and the environment.

Consideration of individual hydrogen energy technologies outside the context of the complete hydrogen energy system creates an incomplete and most often skewed picture. It is often possible to find another technology that may be either better, or less expensive, or more efficient, or more convenient, but there is no other energy system (at least not based on presently known technologies) that can compare with the benefits that the Hydrogen Energy System offers.

The public in general is not aware of the solar hydrogen option and its benefits. It may be aware of some individual hydrogen energy technologies that draw the attention of the mass-media, such as a new hydrogen powered passenger vehicle or bus. However, more work is needed in educating the general public, as well as business leaders, politicians, legislators and decision makers, and making them aware of the energy related problems and the Hydrogen Energy System as a permanent solution.

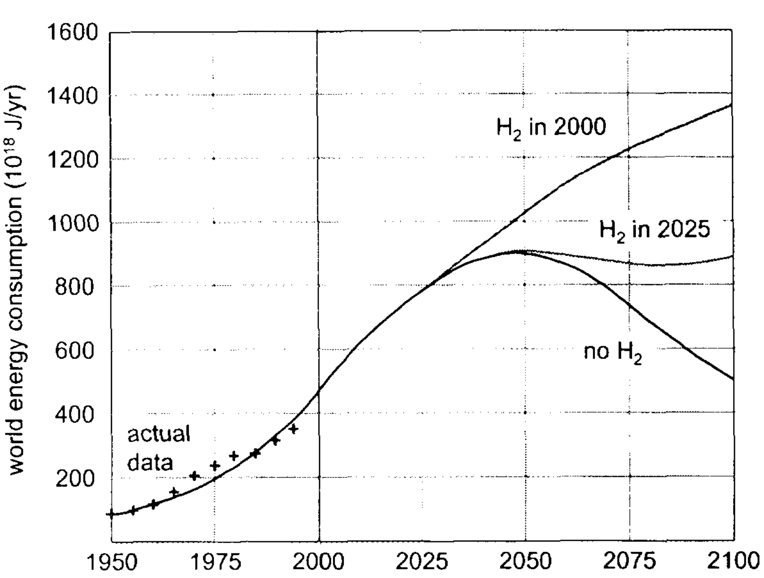

Figure 11.1 Projections of world energy consumption based on study conducted at University of Miami

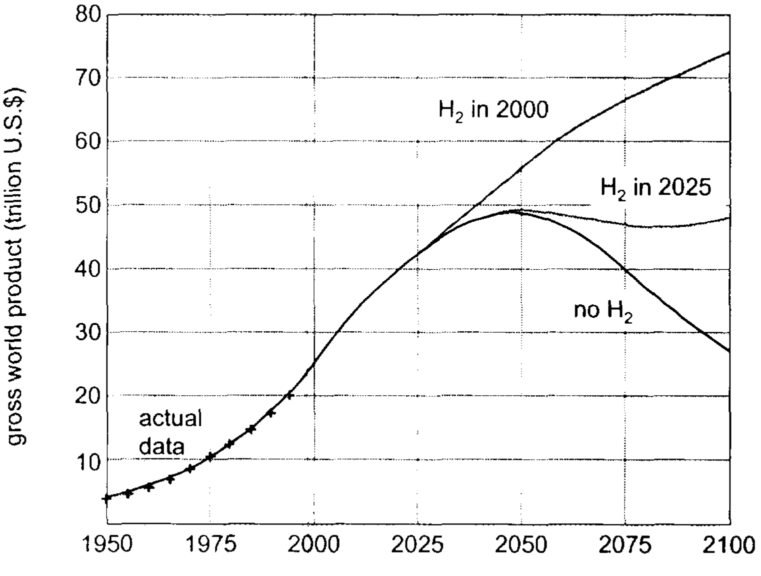

Figure 11.2 Projections of gross world product based on study conducted at University of Miami

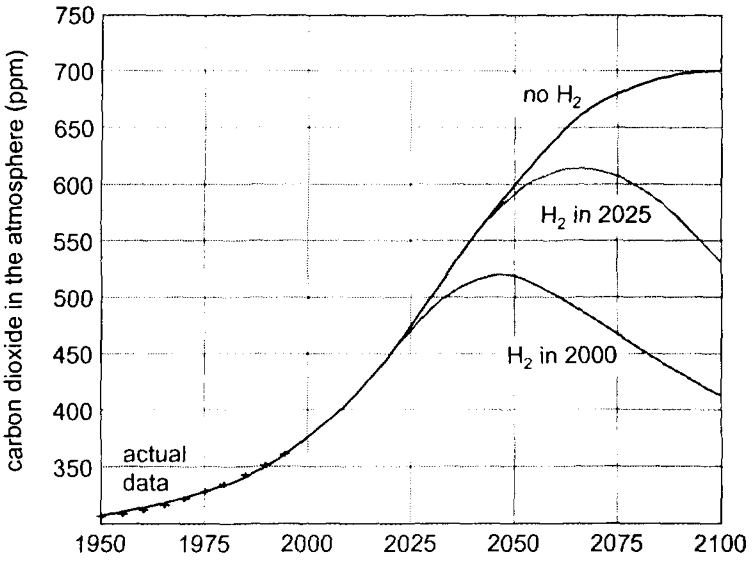

Figure 11.3 Projections of carbon dioxide concentration in the atmosphere based on study conducted at University of Miami

CHAPTER 12

INTERNATIONAL CENTRE FOR HYDROGEN ENERGY TECHNOLOGIES (ICHET)

Realizing the potential of emerging hydrogen energy technologies and Hydrogen Energy System as a universal and permanent energy system, the United Nations International Development Organization (UNIDO) has started an initiative to establish an International Centre for Hydrogen Energy Technologies (ICHET).

12.1. Objectives

The ICHET's mission is to act as a bridge between industrial and developing countries in spanning the gap between research and development organisations, innovative enterprises and the marketplace to stimulate appropriate applications of hydrogen energy technologies and hydrogen energy related industrial development throughout the world in general and in developing countries in particular.

The immediate objective of ICHET is to respond to demand from developing countries for energy services by promoting hydrogen energy technologies which are economically, technically and industrially appropriate.

The Centre will promote and facilitate the introduction of hydrogen energy technologies in participating countries through studies, applied research, training and education programmes, and advisory services. The Centre will also provide expert assistance in establishing, running and evaluation of pilot projects.

ICHET will be operating under the auspices of the United Nations Industrial Development Organisation and will have a specific application orientation in several broad areas, such as:

- Identifying opportunities in which hydrogen energy technologies may be cost-effectively deployed to improve living conditions within developing countries;
- Identifying proven hydrogen energy technologies appropriate to the requirements of developing countries;
- Identifying emerging hydrogen energy technologies with the potential to be responsive for the needs of developing countries;
- Promoting the application of hydrogen energy technologies in government, financial and commercial circles, and within the marketplace in particular;

- Promoting technology transfer to, and industrial development of, developing countries.

12.2. Benefits

The International Centre for Hydrogen Energy Technologies will provide a variety of benefits to its participants, both industrial and developing countries, by:

- Acting as a bridge for technology transfer, while encouraging international cooperation and eliminating of duplication of effort;
- Opening new opportunities for industries involved in hydrogen energy related areas;
- Encouraging the use of an energy system which will reduce atmospheric, marine and soil pollution, while providing access to renewable energy sources and ensuring sustainable economic development.

For developing countries the ICHET will offer the following additional advantages:

- Support the establishment of a clean and permanent energy system based on indigenous primary energy sources;
- Assist the developing world to attain greater levels of energy independence;
- Provide access to the technologies involved in the implementation of hydrogen energy systems, technologies which currently are almost exclusively being developed and deployed by the industrial countries;
- Help developing countries acquire the technical skills required for the changes due to take place in energy systems in the 21st century;
- Assist developing countries in preparation for the coming period of energy source conversion;
- Assist the current energy exporters in continuing to fill this role as the future exporters of hydrogen energy.

12.3. Functions

Amongst others, the International Centre for Hydrogen Energy Technologies will have the following functions:

- Promote and network on-going applied research and development work on hydrogen production, transport, storage, distribution and utilization. Databanks will be established and maintained for this purpose;
- Evaluate, develop and assist in the commercialization of hydrogen energy related inventions and ideas, especially those originating in developing countries;

- Conduct interdisciplinary research on the environmental impact of hydrogen production, storage, distribution and utilization systems;.

- Carry out pilot projects at the request of participating governments, institutions and agencies. These could include the supervision, implementation, operation and evaluation of projects to promote the implementation of the Hydrogen Energy System in developing countries;

- Provide advisory services, on request, in the selection of locations where a hydrogen energy system could be established with the best environmental and economic benefit to the community;

- Provide advisory services, on request, in the determination of the best and most economical implementation plans for establishing the Hydrogen Energy System;

- Undertake market research into the demand for energy services within developing countries, which may potentially be satisfied by hydrogen energy technologies;

- Organize marketing consulting services for enterprises in the business of supplying hydrogen energy products and services within developing countrie;.

- Promote appropriate system design and assist in the commercialisation of technologies and products for hydrogen production, storage, distribution and utilisation for use in developing countries in collaboration with research and commercial organisations in both industrial and developing countries;

- Adapt proven hydrogen energy technologies to the specific needs of the market in developing countries;

- Support the establishment of manufacturing infrastructure within developing countries to allow implementation of appropriate hydrogen energy technologies;

- Broker arrangements by which manufacturing technology may be transferred into developing countries; negotiate with financiers, aid agencies and donors to establish financial arrangements to support the application and commercialisation of hydrogen energy technologies within developing countries;

- Train and/or coordinate the training of engineers and technicians from developing countries in the design and operation of hydrogen energy systems;

- Organize short courses, workshops, seminars, symposia and conferences in order to educate the people in developing countries on hydrogen energy technologies and systems, as well as in pursuance of the aforementioned functions;

- Serve as a liaison between industrial and developing countries, promoting cooperation with other energy research institutes and the United Nations bodies in carrying out the above stated functions.

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APPENDIX II

List of companies and institutions involved in hydrogen energy technologies

Companies

AEG AG, Frankfurt, Germany

Air Liquide, Sassenage, France

Air Products, Allentown, Pennsylvania, USA

AlliedSignal Aerospace, Torrance, California, USA

Analytic Power Corp., Boston, Massachusetts, USA

Ansaldo Richerche, Genoa, Italy

Arthur D. Little, Cambridge, Massachusetts, USA

Asea Brown Boveri AG, Mannheim, Germany

Ballard Power Systems, Burnaby, British Columbia, Canada

Bayer AG, Leverkusen, Germany

BMW AG, Munich, Germany

BOC Gases. Murray Hill, New Jersey, USA

Chrysler Corporation, Madison Heights, Michigan, USA

Daimler-Benz AG, Stuttgart, Germany

Deutche Airbus GmbH, Hamburg, Germany

Delphi, Rochester, New York, USA

DeNora, Milan, Italy

Dornier GmbH, Friedrichshafen, Germany

Dupont, Wilmington, Delaware, USA

Electrolyser Corporation Ltd., Toronto, Ontario, Canada

Energy Partners Inc., West Palm Beach, Florida, USA

Energy Research Corp., Danbury, Connecticut, USA

EniRicherche, Rome, Italy

Ergenics, Ringwood, New Jersey, USA

Ford Motor Company, Dearborn, Michigan, USA

Fuji Electric, Yokosuka, Japan

Gaz de France, La Plainesaint, France

General Motors, Warren, Michigan, USA

GfE Metalle und Materialen GmbH, Nuernberg, Germany

W.L. Gore & Associates, Elkton, Maryland, USA

Hamburger Gaswerke GmbH, Hamburg, Germany

Hamilton Standard, Windsor Locks, Connecticut, USA

Hoechst AG, Frankfurt, Germany

H-Power Corporation, Belleville, New Jersey, USA

Hydro-Quebec, Montreal, Quebec, Canada

Hydrogen Appliances, Hamme, Belgium

Hydrogen Consultants, Inc., Littleton, Colorado, USA

International Fuel Cells, South Windsor, Connecticut, USA

Ishikawajima-Harima-Heavy Industries Co., Tokyo, Japan

Johnson Matthey, Reading, UK

Linde AG, Munich, Germany

Lockheed Corporation, Calabasas, California, USA

Ludwig-Bolkow-Systemtechnik GmbH, Ottobrun, Germany

Lurgi GmbH, Frankfurt, Germany

Lynntech, Inc., College Station, Texas, USA

Mazda Motor Corporation, Hiroshima, Japan

M-C Power, Burr Ridge, Illinois, USA

Metkon SA, Mendrisio, Switzerland

Messer Griesheim GmbH, Koeln, Germany

Mitsubishi Heavy Industries, Aichi-ken, Japan

Neste OY, Porvoo, Finland

Norsk Hydro a.s., Nottoden, Norway

Ovonics, Troy, Michigan, USA

Praxair, Danbury, Connecticut, USA

PlugPower, Latham, New York, USA

Rockwell International, Canoga Park, California, USA

Siemens AG, Erlangen, Germany

Sulzer, Switzerland

Teledyne Brown Engineering, Hunt Valley, Maryland, USA

Thiokol, Brigham City, Utah, USA

3M, St. Paul, Minnesota, USA

Toshiba, Japan

Toyota, Japan

Treadwell Corp., Thomaston, Connecticut, USA

Varta AG, Kelkheim, Germany

Research Organizations/Laboratories

Argonne National Laboratory, Argonne, Illinois, USA

Brookhaven National Laboratory, Upton, New York, USA

Centro Atomico Bariloche – C.N.E.A., Rio Negro, Argentina

Clean Energy Research Institute, University of Miami, Coral Gables, Florida, USA

Desert Research Institute, Reno, Nevada, USA

DLR, German Aerospace Research Establishment, Stuttgart, Germany

Florida Solar Energy Center, Cocoa, Florida, USA

Fraunhofer Institut für Solare Energiesysteme, Freiburg, Germany

Institute of Gas Technology, Des Plaines, Illinois, USA

Instituto Nacional de Tecnica Aerospacial, Spain

Jet Propulsion Laboratory, Pasadena, California, USA

Joint Research Centre of the Commission of the European Communities, Ispra, Italy KFA

Forschgszentrum Jülich GmbH, Jülich, Germany

Korea Institute of Energy Research, Taejon, Republic of Korea

Lawrence Livermore National Laboratory, Livermore, California, USA

Los Alamos National Laboratory, Los Alamos, New Mexico, USA

Max-Planck-Gessellschaft, Berlin, Mülheim/Ruhr, Germany

Materials & Energy Research Institute, Tokyo, Japan

National Aeronautics and Space Administration, USA

National Renewable Energy Laboratory, Golden, Colorado, USA

Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA

Osaka National Research Institute, AIST, Osaka, Japan

Pacific Northwest National Laboratory, Richland, Washington, USA

Paul Scherrer Institut, Villigen, Switzerland

Sandia National Laboratory, Albuquerque, New Mexico, USA

Solar-Wasserstoff-Bayern GmbH, Munich, Germany

Southeastern Technology Center, Augusta, Georgia, USA

Southwest Research Center, San Antonio, Texas, USA

Swiss Federal Institute of Technology, Zurich, Switzerland

Tianjin Institute of Power Sources, Tianjin, China

VITO, Mol, Belgium

ZSW Center for Solar Energy and Hydrogen Research, Stuttgart/Ulm, Germany

Universities

Case Western Reserve University, Cleveland, Ohio, USA

Ecole Polytechnique de Montreal, Montreal, Quebec, Canada

Humboldt State University, Arcata, California, USA

Loughborough University, UK

Massachusetts Institute of Technology, Cambridge, Massachusetts, USA

McGill University, Montreal, Quebec, Canada

Musashi Institute of Technology, Tokyo, Japan

Princeton University, Princeton, New Jersey, USA

Royal Military College of Canada, Kingston, Ontario, Canada

Stockholm University, Stockholm, Sweden

Technical University of Denmark, Lyngby, Denmark

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University of Melbourne, Victoria, Australia

University of Miami, Coral Gables, Florida, USA

University of Nevada, Reno, Nevada, USA

University of South Carolina, Columbia, South Carolina, USA

University of Victoria, BC, Canada

Vienna University of Technology, Vienna, Austria

Virginia Tech University, Blacksburg, VA, USA

Associations

International Association for Hydrogen Energy

Argentinean Hydrogen Association, Argentina

Clean Air Now, USA

German Hydrogen Association, Germany

Hydrogen Energy Systems Society, Japan

Italian Hydrogen Association, Italy

Korean Hydrogen Energy Association, Republic of Korea

National Hydrogen Association, USA

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Printed in Austria
V.97-29308–February 1998–500